

Author: Mustafa K. Bayazit

Title: Defect-Free Single-Layer Graphene by 10 s Microwave Solid Exfoliation and Its Application for Catalytic Water Splitting

DOI: 10.1021/acsami.1c03906

Year of publication: 2021

**Abstract:** Mass production of defect-free single-layer graphene flakes(SLGFs) by a cost-effective approach is still very challenging. Here, we report such single-layer graphene flakes (SLGFs) (>90%) prepared by a nondestructive, energy-efficient, and easy up-scalable physical approach. These high-quality graphene flakes are attributed to a novel 10 s microwave-modulated solid-state approach, which not only fast exfoliates graphite in air but also self-heals the surface of graphite to remove the impurities. The fabricated high-quality graphene films (~200 nm) exhibit a sheet resistance of ~280  $\Omega/\text{sq}$  without any chemical or physical posttreatment. Furthermore, graphene-incorporated Ni–Fe electrodes represent a remarkable ~140 mA/cm<sup>2</sup> current for the catalytic water oxidation reaction compared with the pristine Ni–Fe electrode (~10 mA/cm<sup>2</sup>) and a 120 mV cathodic shift in onset potential under identical experimental conditions, together with a faradic efficiency of >90% for an ideal ratio of H<sub>2</sub> and O<sub>2</sub> production from water. All these excellent performances are attributed to extremely high conductivity of the defect-free graphene flakes.

**Method of producing graphene:** Commercial graphite flakes (2 g) were added to a sealed vial containing Br<sub>2</sub>/solvent solution and then left for 2 h for intercalation at room temperature. Similarly, 1, 3, and 7 day treatment terms were also used to optimize the pretreatment process. Water, chloroform, and n-decane were selected as solvents. P-graphite flakes were filtered through filter paper and washed with fresh chloroform to remove the remaining Br<sub>2</sub> molecules and then was transferred into a clean vial and dried at room temperature in a fume cupboard. Dried samples were labeled as the P-graphite and stored at room temperature in a sealed glass vessel. 20?100 mg of the P-graphite was transferred into a sealed glass tube and irradiated by a microwave irradiation for about 10 s, using a CEM microwave fitted with an Infrared (IR) temperature sensor. The temperature of the solid reaction material was recorded as 360 ± 20°C. The reaction medium was cooled to 50 °C, and the glass tube was opened in a fume cupboard. Highly exfoliated solid graphitic material was obtained and labeled as EG. The EGs were further dispersed in organic solvents (DMF or NMP) or aqueous solution with a surfactant (sodium dodecylbenzenesulfonate (SDBS), cetyltrimethylammonium bromide (CTAB), or Triton X-100 (TX-100)) to produce a highly processable LDGFs, containing ?90% SLGFs.

No. of layers: Mono-layer

Author: Adel K.A. Aljarid

Title: Hometronics – Accessible production of graphene suspensions for health sensing applications using only household items

DOI: 10.48550/arXiv.2401.15418

Year of publication: 2024

Abstract: Nanoscience at times can seem out of reach to the developing world and the general public, with much of the equipment expensive and knowledge seemingly esoteric to nonexperts. Using only cheap, everyday household items, accessible research with real applications can be shown. Here, graphene suspensions were produced using pencil lead, tap water, kitchen appliances, soaps and coffee filters, with a children's glue-based graphene nanocomposite for highly sensitive pulse measurements demonstrated.

Method of producing graphene: A Graphite Pure 2900 9B pencil was initially crushed in a mortar and pestle, then ground in a SQ Professional Blitz Coffee Grinder - Spice Grinding Mill - One-Touch for ~60 s. A mass of 2.5 g of Fairy Max Power Washing Up Liquid was then mixed with 1 L of tap water. 300 mL of the soap mixture was then added to a Tefal BL420840 Blendforce II Blender (Plastic Jug, 600 W, 1.5 L) with 1 mL of Ecover Fabric Softener also added to the blender. 16 g of powdered pencil lead was then placed in the blender and stirred into the soap/softener/water mixture by hand. The blender was then turned on to the first (#1) setting for 1-minute on, 1 minute off intervals to reduce motor heating effects, until the total blending time reached 15 minutes. The solution was then transferred to a beaker and left to sit for 24 hrs. After which, the solution was passed through a Rombouts Italian No. 2 Coffee Filter. For the graphene sample preparation, 2 mL of Elmer's White PVA Glue, 1 mL of Elmer's Glue Slime Magical Liquid Solution, and 0.5 mL of graphene suspension were mixed by hand for approximately 5 to 7 minutes. To vary the graphene loading, different concentration suspensions, ranging from 1 mg/mL to 10 mg/mL, were used. For the pristine putty sample, in place of the graphene suspension, 0.5 mL of tap water was used. For all p-putty samples, they were left at room temperature for 40 minutes before testing.

No. of layers: Multi-layer

Author: Surajit Some

Title: High-quality reduced graphene oxide by a dual-function chemical reduction and healing process

DOI: 10.1038/srep01929

Year of publication: 2013

**Abstract:** A new chemical dual-functional reducing agent, thiophene, was used to produce high-quality reduced graphene oxide (rGO) as a result of a chemical reduction of graphene oxide (GO) and the healing of rGO. Thiophene reduced GO by donation of electrons with acceptance of oxygen while it was converted into an intermediate oxidised polymerised thiophene that was eventually transformed into polyhydrocarbon by loss of sulphur atoms. Surprisingly, the polyhydrocarbon template helped to produce good-quality rGOC (chemically reduced) and high-quality rGOCT after thermal treatment. The resulting rGOCT nanosheets did not contain any nitrogen or sulphur impurities, were highly deoxygenated and showed a healing effect. Thus the electrical properties of the as-prepared rGOCT were superior to those of conventional hydrazine-produced rGO that require harsh reaction conditions. Our novel dual reduction and healing method with thiophene could potentially save energy and facilitate the commercial mass production of high-quality graphene.

**Method of producing graphene:** GO was prepared from natural graphite powder (Bay Carbon, SP-1 graphite) by the modified Hummers and Offenman's method using sulphuric acid, potassium permanganate, and sodium nitrate. GO (10 mg) was dispersed in 10 mL of DI water by stirring at room temperature, followed by the addition of 2 mL of thiophene in round bottom flux. The resultant solution was heated with condenser under N<sub>2</sub> atmosphere at 80°C for 24 h. The formed solid material was then collected by filtration (glass frit funnel setup with membrane filter paper 0.45 mm) and washed several times with water, ethanol, dichloromethane and acetone before drying at 60°C for 24 h in a vacuum oven to yield rGO.

No. of layers: Mono-layer

Author: N. Reckinger

Title: Identifying and abating copper foil impurities to optimize graphene growth

DOI: 10.48550/arXiv.2309.14811

Year of publication: 2023

**Abstract:** Copper foil impurities are hampering scalable production of high-quality graphene by chemical vapor deposition (CVD). Here, we conduct a thorough study on the origin of these unavoidable contaminations at the surface of copper after the CVD process. We identify two distinct origins for the impurities. The first type is intrinsic impurities, originating from the manufacturing process of the copper foils, already present at the surface before any high-temperature treatment, or buried into the bulk of copper foils. The buried impurities diffuse towards the copper surface during high-temperature treatment and precipitate. The second source is external: silica contamination arising from the quartz tube that also precipitate on copper. The problem of the extrinsic silica contamination is readily solved upon using an adequate confinement the copper foil samples. The intrinsic impurities are much more difficult to remove since they appear spread in the whole foil. Nevertheless, electropolishing proves particularly efficient in drastically reducing the issue.

**Method of producing graphene:** The CVD reactor is a horizontal hot-wall split furnace (MTI corporation) fitted with a quartz tube (1.2 meter-long, 4-inch outer diameter). The copper sample is first put on the unpolished side of a sapphire wafer (C-plane (0001), 3-inch diameter, 600- $\mu\text{m}$ -thick, and single-side polished) to avoid Cu to be stuck on it, itself deposited on a quartz boat and inserted into the horizontal hot-wall split furnace's quartz tube at room temperature. After sealing the tube, it is pumped down to a pressure below  $2 \times 10^{-2}$  mbar. An argon flow is then fed into the tube until atmospheric pressure is restored. This preliminary purge ensures that the oxygen concentration in the tube is well controlled (equal to the residual oxygen in the argon canister, i.e. 1 ppm).<sup>50</sup> The CVD procedure is directly inspired and slightly adapted from our previous works performed in a different CVD equipment.<sup>4,36</sup> This testifies to the transferability and interoperability of our growth process.<sup>51</sup> The temperature-time profile is presented in Fig. S2. First, the temperature of the furnace is increased from room temperature to 1050 °C during 1 h under a 300 sccm flow of argon and kept at 1050 °C for an additional duration of 30 min. Next, 200 sccm of Ar/H<sub>2</sub> (10% H<sub>2</sub> in Ar) are introduced for 20 min. Just after, dilute methane (200 ppm in Ar) at a flow rate of 30-40 sccm is injected during 1 h for graphene growth. Finally, the power supply is shut down and the furnace is left to cool down naturally in the same gas mixture. Note that, in the text below, annealing designs the exact same process but without injecting methane in the tube.

No. of layers: Mono-layer

Author: Duy X. Luong

Title: Gram-scale bottom-up flash graphene synthesis

DOI: 10.1038/s41586-020-1938-0

Year of publication: 2019

**Abstract:** Most bulk-scale graphene is produced by a top-down approach, exfoliating graphite, which often requires large amounts of solvent with high-energy mixing, shearing, sonication or electrochemical treatment<sup>1–3</sup>. Although chemical oxidation of graphite to graphene oxide promotes exfoliation, it requires harsh oxidants and leaves the graphene with a defective perforated structure after the subsequent reduction step<sup>3,4</sup>. Bottom-up synthesis of high-quality graphene is often restricted to ultrasmall amounts if performed by chemical vapour deposition or advanced synthetic organic methods, or it provides a defect-ridden structure if carried out in bulk solution<sup>4–6</sup>. Here we show that flash Joule heating of inexpensive carbon sources—such as coal, petroleum coke, biochar, carbon black, discarded food, rubber tyres and mixed plastic waste—can afford gram-scale quantities of graphene in less than one second. The product, named flash graphene (FG) after the process used to produce it, shows turbostratic arrangement (that is, little order) between the stacked graphene layers. FG synthesis uses no furnace and no solvents or reactive gases. Yields depend on the carbon content of the source; when using a high-carbon source, such as carbon black, anthracitic coal or calcined coke, yields can range from 80 to 90 per cent with carbon purity greater than 99 per cent. No purification steps are necessary. Raman spectroscopy analysis shows a low-intensity or absent D band for FG, indicating that FG has among the lowest defect concentrations reported so far for graphene, and confirms the turbostratic stacking of FG, which is clearly distinguished from turbostratic graphite. The disordered orientation of FG layers facilitates its rapid exfoliation upon mixing during composite formation. The electric energy cost for FG synthesis is only about 7.2 kilojoules per gram, which could render FG suitable for use in bulk composites of plastic, metals, plywood, concrete and other building materials.

**Method of producing graphene:** Inside a quartz tube, two loosely fitting electrodes compress the carbon source using two copper-wool plugs or graphite spacers to contact the carbon sources to allow degassing of volatile materials. The compressing force is controllable by a modified small vice so as to minimize the sample resistance to 1–1,000 ?, and is key to obtaining a good flash reaction (0.004–4 S cm<sup>2</sup>)<sup>1</sup>. To control the discharge time, a mechanical relay with programmable millisecond-level delay time is used. The entire sample reaction chamber is placed inside a low-pressure container (plastic vacuum desiccator) for safety and to facilitate degassing. However, the FJH process works equally well at 1 atm. The capacitor bank consists of 20 capacitors with a total capacitance of 0.22 F. Each capacitor is connected to the main power cable (or bus) by a circuit breaker that is also used as a switch to enable/disable each capacitor. The capacitor bank is charged by a d.c. supply capable of reaching 400 V. The first prototype system is placed conveniently on one plastic mobile cart. Using a large 15-mm-diameter quartz tube, we achieve synthesis of 1 g of FG per batch using the FJH process. Safety notice: the capacitor bank is capable of generating fatal electric pulses. Therefore, the following steps are taken to protect the operator as well as the circuit, and we strongly suggest that these measures be followed. Darkened safety glasses should be worn to protect eyes from the bright light during the discharge flashing process. The voltage and current ratings for the circuit breaker are appropriate for the maximum voltage and the anticipated maximum current that will be supplied by each capacitor to the FJH discharge on the basis of a discharge time of 50–200 ms. We use the maximum charging and bleeding voltages at ~400 V with maximum currents of 0.7 A and 0.1 A, respectively. The pulse discharging voltage to the sample is ~400 V and current can reach up to 1,000 A in <100 ms. A 24-mH inductor is used to avoid current spikes while using the mechanical relay. Without the inductor, the mechanical relay could be prone to high-current arcing during the intermittent closing of the circuit. To protect the inductor from the spike voltage when shutting off the current, a diode and a low resistance resistor with appropriate ratings are connected parallel to the inductor. Additionally, to protect the capacitor from reverse polarity in case of oscillatory decay (which can occur in a fast discharge), an appropriate diode is placed parallel to the capacitor bank.

No. of layers: Multi-layer

Author: Benjamin Diby Ossonon

Title: Synthesis and characterization of sulfophenyl-functionalized reduced graphene oxide sheets

DOI: 10.1039/c6ra28311j

Year of publication: 2017

**Abstract:** We report the modification of graphene oxide (GO) by thermal reduction to obtain reduced graphene oxide (RGO) and subsequent modification by sulfophenyl groups as well as the characterization of these materials by thermogravimetric analysis coupled with mass spectroscopy (TGA-MS). The chemical modification of RGO was carried out by the spontaneous reaction of RGO with in situ generated sulfophenyl diazonium ions. The three different types of materials were also characterized by elemental analysis, Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy and X-ray photoelectron spectroscopy (XPS). The characteristic absorption band at 1034 and 1160 cm<sup>-1</sup> in the FTIR spectrum of the sulfophenyl-modified RGO (SRGO), as well as Raman spectroscopy and TGA-MS data indicated that sulfophenyl groups were successfully grafted on RGO. The presence of organic molecules at the SRGO surface was also demonstrated by elemental analysis, transmission electron microscopy, energy dispersive X-ray spectroscopy and XPS. TGA data and elemental analysis results showed that the loading of sulfophenyl groups was about 12 wt% and UV-visible-near IR spectroscopy confirms the slight increase of the optical band gap of RGO after covalent grafting of sulfophenyl groups on its surface.

**Method of producing graphene:** Graphene oxide was synthesized from natural graphite (<44 mm, 99.99%, supplied by Sigma-Aldrich) through the Hummers method which has been improved to be more environmentally friendly and produce graphene in good yield (95%). The graphite is first pre-oxidized by mixing graphite powder (5 g) with concentrated sulfuric acid (H<sub>2</sub>SO<sub>4</sub>, 12.5 mL), potassium persulfate (K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, 2.5 g) and phosphorus pentoxide (P<sub>2</sub>O<sub>5</sub>, 2.5g). The mixture was heated at 80 °C for 6 hours. After dilution with 500 mL of H<sub>2</sub>O, the mixture was stirred at room temperature overnight. After that, the product is recovered by centrifugation and washed thoroughly with Nanopure water until the filtrate has a pH close to 7 (neutral). The product obtained is then dried at room temperature for one day. Then, the preoxidized graphite is dispersed in H<sub>2</sub>SO<sub>4</sub> (0 °C, 115 mL). The temperature of the mixture is carefully controlled to not exceed 10 °C. Subsequently, potassium permanganate (KMnO<sub>4</sub>, 15 g) is gradually added with constant stirring for 1 hour. The dispersion is then incubated at 35 °C for 2 h and this is followed by the addition of Nanopure water (225 mL) in small portions (15 mL) to control the temperature of the mixture, which must remain below 50 °C. In order to completely dissolve the KMnO<sub>4</sub> remaining, hydrogen peroxide (H<sub>2</sub>O<sub>2</sub> 30%, 12.5 mL) was immediately added at the end of a second dilution (H<sub>2</sub>O, 700mL), and the mixture is stirred for 48 hours. Finally, the suspension is filtered, washed first with HCl (10%) to remove residual metal ions, and repeatedly with Nanopure water until the pH of filtrate becomes neutral. The filtrate is quickly tested by adding a few drops of 1 M NaOH to verify the presence of metal ions in GO. The product obtained (graphite oxide) is then dried in air. The resultant graphite oxide was dispersed in Nanopure water kept in the ultrasonic bath for 24 hours to maximize exfoliation. A homogeneous and stable colloidal suspension for several months is obtained (Fig. 1, GO). The reduced graphene oxide (RGO) is obtained by thermal reduction of GO in Ar/5% H<sub>2</sub> at various temperatures for 2 h. The resulting RGO can be dispersed in water and the dispersion stayed stable for few hours.

No. of layers: Mono-layer

Author: Tianzhu Zhou

Title: Super-tough MXene-functionalized graphene sheets

DOI: 10.1038/s41467-020-15991-6

Year of publication: 2020

**Abstract:** Flexible reduced graphene oxide (rGO) sheets are being considered for applications in portable electrical devices and flexible energy storage systems. However, the poor mechanical properties and electrical conductivities of rGO sheets are limiting factors for the development of such devices. Here we use MXene (M) nanosheets to functionalize graphene oxide platelets through Ti-O-C covalent bonding to obtain MrGO sheets. A MrGO sheet was crosslinked by a conjugated molecule (1-aminopyrene-disuccinimidyl suberate, AD). The incorporation of MXene nanosheets and AD molecules reduces the voids within the graphene sheet and improves the alignment of graphene platelets, resulting in much higher compactness and high toughness. *In situ* Raman spectroscopy and molecular dynamics simulations reveal the synergistic interfacial interaction mechanisms of Ti-O-C covalent bonding, sliding of MXene nanosheets, and  $\pi$ - $\pi$  bridging. Furthermore, a supercapacitor based on our super-tough MXene-functionalized graphene sheets provides a combination of energy and power densities that are high for flexible supercapacitors.

**Method of producing graphene:** Following Hummers' method, concentrated H<sub>2</sub>SO<sub>4</sub> (70 mL) was added to a mixture of graphite flakes (2.0 g) and NaNO<sub>3</sub> (1.2 g). Then the mixture was cooled to 0 °C with stirring for 1 h. Afterwards, KMnO<sub>4</sub> (6.0 g) was added slowly in portions, keeping the reaction temperature below 10 °C for 1 h. The reaction was stirred for another 4 hour in an ice bath (below 10 °C). When the reaction was finished, the mixed solution was warmed to 35 °C and stirred for 30 min. After water (300 mL) was added slowly, external heating was introduced to maintain the reaction temperature at 98 °C for 15 min. Then the hot solution was poured into 400 mL of water (60 °C). An additional 30% H<sub>2</sub>O<sub>2</sub> (3 mL) was added and the mixture stood for 2 days. After multiple washings, centrifugations, and ultrasonic dispersion, the suspension of GO platelets was obtained with the concentration of ~5.0 mg mL<sup>-1</sup>.

No. of layers: Mono-layer

Author: Panpan Zhang

Title: Vertically Aligned Graphene Sheets Membrane for Highly Efficient Solar Thermal Generation of Clean Water

DOI: 10.1021/acsnano.7b01965

Year of publication: 2017

Abstract: Efficient utilization of solar energy for clean water is an attractive, renewable, and environment friendly way to solve the long-standing water crisis. For this task, we prepared the long-range vertically aligned graphene sheets membrane (VAGSM) as the highly efficient solar thermal converter for generation of clean water. The VA-GSM was prepared by the antifreeze-assisted freezing technique we developed, which possessed the run-through channels facilitating the water transport, high light absorption capacity for excellent photothermal transduction, and the extraordinary stability in rigorous conditions. As a result, VA-GSM has achieved average water evaporation rates of 1.62 and 6.25 kg m<sup>-2</sup> h<sup>-1</sup> under 1 and 4 sun illumination with a superb solar thermal conversion efficiency of up to 86.5% and 94.2%, respectively, better than that of most carbon materials reported previously, which can efficiently produce the clean water from seawater, common wastewater, and even concentrated acid and/or alkali solutions.

Method of producing graphene: GO suspension (7 mg mL<sup>-1</sup>) was prepared from natural graphite powder according to a modified Hummers method as reported in our previous paper.<sup>49,50</sup> The GO sheets have lateral dimensions of 30–50 μm. Seven mL of GO (3 mg mL<sup>-1</sup>) suspension was deposited onto a cellulose membrane filter to form a GO film through vacuum filtration, annealed at 200 °C for 1 h, and then treated at 1000 °C for 2 h under nitrogen atmosphere. The samples used for solar steam generation in the experiments were treated with O<sub>2</sub>-plasma.

No. of layers: Multi-layer

Author: J.S. Gomez-Diaz

Title: Self-biased reconfigurable graphene stacks for terahertz plasmonics

DOI: 10.1038/ncomms7334

Year of publication: 2015

**Abstract:** The gate-controllable complex conductivity of graphene offers unprecedented opportunities for reconfigurable plasmonics at terahertz and mid-infrared frequencies. However, the requirement of a gating electrode close to graphene and the single ‘control knob’ that this approach offers limits the practical implementation and performance of these devices. Here we report on graphene stacks composed of two or more graphene monolayers separated by electrically thin dielectrics and present a simple and rigorous theoretical framework for their characterization. In a first implementation, two graphene layers gate each other, thereby behaving as a controllable single equivalent layer but without any additional gating structure. Second, we show that adding an additional gate allows independent control of the complex conductivity of each layer within the stack and provides enhanced control on the stack equivalent complex conductivity. These results are very promising for the development of THz and mid-infrared plasmonic devices with enhanced performance and reconfiguration capabilities.

**Method of producing graphene:** The samples were fabricated using CVD graphene grown on Cu foil and transferred onto the substrate using the standard wet transfer method. Supplementary Fig. 10 shows the flow of the fabrication process for the double-layer graphene stack. We deposit 72 nm of Al<sub>2</sub>O<sub>3</sub> by atomic layer deposition (ALD) on a an ultrahighresistivity (410 kO) p-type Si wafer. The ALD is performed at 200 °C using trimethylaluminum and distilled water as the reaction precursors. Before the dielectric deposition, the native oxide is removed from the Si wafer with a buffered oxide etch. The metal electrodes are patterned by optical lithography followed by a deposition of 5 nm of chromium, 50 nm of gold and a lift-off process. A graphene sheet is then transferred onto the top of one of the metal contacts. In the doublelayer graphene stack, the PMMA layer used as a support polymer during the transfer process is kept on top of the graphene to act as a dielectric between the two graphene sheets. The second graphene monolayer is subsequently transferred onto the top of the other predefined metal contact.

No. of layers: Multi-layer (stacked mono-layers)

Author: Yuan Huang

Title: Reliable Exfoliation of Large-Area High-Quality Flakes of Graphene and Other Two-Dimensional Materials

DOI: 10.1021/acsnano.5b04258

Year of publication: 2015

**Abstract:** Mechanical exfoliation has been a key enabler of the exploration of the properties of two-dimensional materials, such as graphene, by providing routine access to high-quality material. The original exfoliation method, which remained largely unchanged during the past decade, provides relatively small flakes with moderate yield. Here, we report a modified approach for exfoliating thin monolayer and few-layer flakes from layered crystals. Our method introduces two process steps that enhance and homogenize the adhesion force between the outermost sheet in contact with a substrate: Prior to exfoliation, ambient adsorbates are effectively removed from the substrate by oxygen plasma cleaning, and an additional heat treatment maximizes the uniform contact area at the interface between the source crystal and the substrate. For graphene exfoliation, these simple process steps increased the yield and the area of the transferred flakes by more than 50 times compared to the established exfoliation methods. Raman and AFM characterization shows that the graphene flakes are of similar high quality as those obtained in previous reports. Graphene field-effect devices were fabricated and measured with back-gating and solution top-gating, yielding mobilities of ~4000 and 12 000 cm<sup>2</sup>/(V s), respectively, and thus demonstrating excellent electrical properties. Experiments with other layered crystals, e.g., a bismuth strontium calcium copper oxide (BSCCO) superconductor, show enhancements in exfoliation yield and flake area similar to those for graphene, suggesting that our modified exfoliation method provides an effective way for producing large area, high-quality flakes of a wide range of 2D materials.

**Method of producing graphene:** We used SiO<sub>2</sub>/Si as the substrate and ordinary adhesive tape as the transfer medium. Contact with the tape transfers thick graphite flakes from a highly oriented pyrolytic graphite (HOPG) crystal (Figure 1a). Prior to exfoliating thin graphene from these flakes, the SiO<sub>2</sub>/Si substrate is ultrasonically cleaned in acetone, 2-propanol, and deionized (DI) water, and then subjected to oxygen plasma to remove ambient adsorbates from its surface (Figure 1b). Following the plasma cleaning step, the graphite-loaded tape is brought in contact with the substrate. Instead of immediately removing it to complete the exfoliation, the substrate with the attached tape is annealed for 2–5 min at 100 °C in air on a conventional laboratory hot plate (Figure 1c). After the sample is cooled to room temperature, the adhesive tape is removed (Figure 1d), which completes the exfoliation. Inspection by optical microscopy shows the successful transfer of few-layer graphene to the SiO<sub>2</sub>/Si substrate. The linear dimensions of areas with uniform thickness are routinely in the range from 20 μm to well above 100 μm, and the thin (few-layer) sections of the flakes are up to several 100 μm in size. We conclude that the yield (i.e., the total area of graphene obtained in a single exfoliation experiment) of our modified method is 20–60 times higher than that of the standard method. We performed additional experiments aimed at identifying the role of time and temperature of the annealing step. Within the probed parameter range, the exfoliation yield was generally high. Indeed, the total graphene area did not strongly depend on anneal time and temperature as we changed the annealing time from 2 to 30 min, and temperature from 80 to 140 °C. The highest yield, obtained for annealing at 100 °C for 2 min, was ~60% higher than the lowest yield observed (140 °C, 2 min), with all samples yielding substantially larger overall quantities of exfoliated graphene than the standard method, in line with the results shown above. From a practical perspective, increasing the annealing time and temperature has another negative effect, namely a substantially larger amount of glue residue distributed from the adhesive tape to the substrate surface (see Figure S4). Hence, we find that annealing at 100 °C for 2 min represents a good overall compromise of large graphene flakes, high exfoliation yield, and minimal amounts of residual glue.

No. of layers: 1–4 layers

Author: Sina Abdolhosseinzadeh

Title: Fast and fully-scalable synthesis of reduced graphene oxide

DOI: 10.1038/srep10160

Year of publication: 2015

**Abstract:** Exfoliation of graphite is a promising approach for large-scale production of graphene. Oxidation of graphite effectively facilitates the exfoliation process, yet necessitates several lengthy washing and reduction processes to convert the exfoliated graphite oxide (graphene oxide, GO) to reduced graphene oxide (RGO). Although filtration, centrifugation and dialysis have been frequently used in the washing stage, none of them is favorable for large-scale production. Here, we report the synthesis of RGO by sonication-assisted oxidation of graphite in a solution of potassium permanganate and concentrated sulfuric acid followed by reduction with ascorbic acid prior to any washing processes. GO loses its hydrophilicity during the reduction stage which facilitates the washing step and reduces the time required for production of RGO. Furthermore, simultaneous oxidation and exfoliation significantly enhance the yield of few-layer GO. We hope this one-pot and fully-scalable protocol paves the road toward out of lab applications of graphene.

**Method of producing graphene:** In a typical procedure, 1 g of graphite flakes (99%, Alfa Aesar) was added to 50 mL concentrated sulfuric acid (98%, Merck) while stirring in an ice-water bath. 3 g potassium permanganate (>99%, Sigma Aldrich) was gradually added by maintaining the temperature under 10 °C. Then, the suspension was stirred at room temperature for 25 min followed by 5 min sonication in an ultrasonic bath (SO-TEC, MUY-4). After repeating the stirring-sonication process for 12 times, the reaction was quenched by the addition of 200 mL distilled water. An extra 2h ultrasonic treatment was carried out before dividing the suspension into two equal parts; one washed to obtain AGO (described later) and the other was further processed for preparation of ARGO. After adjusting the pH at ~6 by the addition of 1M sodium hydroxide (>98%, Sigma Aldrich) solution, the suspension was further sonicated for 1 h. 10 g L-ascorbic acid (99%, Sigma Aldrich) was dissolved in 100 mL distilled water and then was slowly added to the exfoliated graphite oxide suspension at room temperature. The reduction was performed at 95 °C for 1 h. The resultant black precipitates were simply filtered by cellulose filter paper and further were washed with a 1M hydrochloric acid solution (37%, Merck) and distilled water to neutral pH. Finally, the filtrate was freeze-dried to obtain ARGO powder. The washing of AGO was adapted from a modified Hummers method. 20 mL hydrogen peroxide (30%, Merck) was added to the exfoliated graphite oxide suspension and stirred until gas evolution ceased. The AGO was washed with 1M hydrochloric acid solution and distilled water for several times each for 30 min by means of centrifugation (Eppendorf, 5810-R) at 10000 rpm. The final AGO precipitates were dried at room temperature.

No. of layers: Multi-layer (<5)

Author: Bocheng Qiu

Title: Facile synthesis of the Ti<sup>3+</sup> self-doped TiO<sub>2</sub>-graphene nanosheet composites with enhanced photocatalysis

DOI: 10.1038/srep08591

Year of publication: 2015

Abstract: This study developed a facile approach for preparing Ti<sub>31</sub> self-doped TiO<sub>2</sub>-graphene photocatalyst by a one-step vacuum activation technology involved a relative lower temperature, which could be activated by the visible light owing to the synergistic effect among Ti<sub>31</sub> doping, some new intersurface bonds generation and graphene oxide reduction. Compared with the traditional methods, the vacuum activation involves a low temperature and low-costing, which can achieve the reduction of GO, the self doping of Ti<sub>31</sub> in TiO<sub>2</sub> and the loading of TiO<sub>2</sub> nanoparticles on GR surface at the same time. These resulting TiO<sub>2</sub>-graphene composites show the high photodegradation rate of MO, high hydrogen evolution activity and excellent IPCE in the visible light irradiation. The facile vacuum activation method can provide an effective and practical approach to improve the performance of TiO<sub>2</sub>-graphene and other metal oxides-graphene towards their practical photocatalytic applications.

Method of producing graphene: Graphene oxide (GO) was synthesized from natural graphite powder using a modified Hummers methods. The detail experimental procedures were referring to the report published by Zhangpeng Li et al. 5 ml GO was dispersed into 20 ml double distilled water and ultraphonic for 1 hour, and then the solution was drying under 60uC for 12 h. Obtained brown flaky solid was heated at 300uC for 3 hours in the vacuum condition. The color of flaky solid was changing from brown to black. This black solid was dispersed into 20 ml double distilled water again and ultraphonic for 10 hours. The solid products were washed by the double distilled water for 5 times and dispersed into 5 ml double distilled water. Finally, it was transferred to a plastic bottle and denoted as GR.

No. of layers: Mono-layer

Author: Bing Deng

Title: Toward Mass Production of CVD Graphene Films

DOI: 10.1002/adma.201800996

Year of publication: 2018

**Abstract:** Chemical vapor deposition (CVD) is considered to be an efficient method for fabricating large-area and high-quality graphene films due to its excellent controllability and scalability. Great efforts have been made to control the growth of graphene to achieve large domain sizes, uniform layers, fast growth, and low synthesis temperatures. Some attempts have been made by both the scientific community and startup companies to mass produce graphene films; however, there is a large difference in the quality of graphene synthesized on a laboratory scale and an industrial scale. Here, recent progress toward the mass production of CVD graphene films is summarized, including the manufacturing process, equipment, and critical process parameters. Moreover, the large-scale homogeneity of graphene films and fast characterization methods are also discussed, which are crucial for quality control in mass production.

**Method of producing graphene:** 30 in. Cu foil was wrapped onto an inner quartz tube with a diameter of ?7.5 in., which was then loaded inside an outer 8 in. quartz tube. Graphene growth was conducted at 1000 °C using LPCVD after annealing in a H<sub>2</sub> atmosphere. This process allowed the radial inhomogeneity in the reaction temperature and gas flow to be minimized. Very high-quality monolayer graphene was produced with a transmittance of 97.4% and sheet resistance as low as ?125 ??1.

No. of layers: Mono-layer

Author: Qingfeng Zhang

Title: Sulfur-assisted large-scale synthesis of graphene microspheres for superior potassium-ion batteries

DOI: 10.1039/d0ee03203d

Year of publication: 2021

**Abstract:** Large-scale low-cost preparation methods for high quality graphene are critical for advancing graphene-based applications in energy storage, and beyond. Here, we present a sulfur-assisted method that converts benzene rings of tetraphenyltin into high purity crystalline graphene. Specifically, three dimensional few layer graphene microspheres (FLGMs) were prepared which proved ideal for energy storage applications. For a potassium ion battery, the FLGM-based anodes exhibited a low discharge platform (average discharge platform about 0.1 V), a high initial capacity of 285 mA h g<sup>-1</sup> at 50 mA g<sup>-1</sup>, and a high rate performance (252 mA h g<sup>-1</sup> at 100 mA g<sup>-1</sup> and 95 mA h g<sup>-1</sup> at 1000 mA g<sup>-1</sup>). Additionally, the FLGM-based anodes exhibited excellent cycling stability with no capacity loss after 1000 cycles at 200 mA g<sup>-1</sup>. A process of this nature which does not require substrates, and is scalable for continuous or semi-continuous production of graphene, paves the way for graphene-based energy storage devices.

**Method of producing graphene:** Commercially, procured sulfur and tetraphenyltin powders (Shandong West Asia Chemical Industry Co., Ltd) are mixed in 50 : 50 wt%, and the mixture is then gradually polymerized into graphene by thermal annealing at 650 1C under an Ar atmosphere. Singlet S<sub>2</sub> released from sulfur gradually captures the H atoms in the benzene rings of tetraphenyltin and generates H<sub>2</sub>S, thereby yielding graphene, H<sub>2</sub>S and SnS<sub>2</sub>. Upon high temperature annealing at 2000 1C for 120 minutes, the structural defects in graphene are healed and SnS<sub>2</sub> is eliminated as a byproduct to yield an ensemble of FLGMs (Fig. 1c and d). Interestingly, such ensembles can be readily used as electrode materials, and manufactured on a large scale; for example, at the laboratory scale we obtained ~5 g of FLGMs in a single run. All chemicals were used directly without further purification. First, the desired amounts of elemental sulfur and tetraphenyltin (1 : 1 by mass) were mixed thoroughly via grinding. The mixed powders were first annealed at 650 1C for 2 h, and then heated to 2000 1C at a rate of 60 1C h<sup>-1</sup> and held at 2000 1C for 2 h under an Ar atmosphere to promote the growth of FLGMs.

No. of layers: Multi-layer (<5) (3D loosely stacked micro-structure)

Author: Zhe Ji

Title: High-yield production of highly conductive graphene via reversible covalent chemistry

DOI: 10.1039/C4CC09144B

Year of publication: 2012

**Abstract:** On the basis of the Diels-Alder reaction of graphite and tetracyanoethylene, graphite has been mechanically exfoliated into graphene adducts in a yield up to 38%. The graphene adduct can restore its conjugated structure via retro-Diels-Alder reaction under mild conditions, exhibiting a high conductivity of 1035 S m<sup>-1</sup>.

**Method of producing graphene:** Diels-Alder reaction was used to bond TCNE molecules onto the graphene layers of graphite to weaken the interlayer interactions and to improve the dispersibility of resulting graphene sheets. To increase the efficiency of Diels-Alder reaction, graphite was firstly treated with oleum into oleum-intercalated graphite (OIG) because of the following reasons: (1) oleum intercalation expands graphite basal spacing, opening the avenues for the penetration of TCNE molecules into the graphite crystals; (2) as a Lewis acid, oleum can function as a catalyst for Diels-Alder reaction; (3) mild oxidation caused by oleum<sup>11</sup> activates graphite to provide sufficient sp<sup>3</sup> carbons for Diels-Alder reaction, because computations predicted that the basal plane of pristine graphene is nearly inert to Diels-Alder reaction while defects and edges are much more active.<sup>12</sup> After Diels-Alder reaction, graphite-TCNE adduct was exfoliated by ultrasonication to form a stable dispersion of GA in NMP. The GA dispersion was then subjected to heating at 100 °C for 3 h to perform retro-Diels-Alder reaction. The cleavage and removal of TCNE addends from GA led to the formation of high-quality eGA sheets dispersible in NMP. The process of producing high-quality graphene was traced by comparing the interlayer distances of graphite, OIG, GA and eGA. With the assistances of expanded interlayer distances and improved solvent affinity, the graphite flakes treated by oleum and TCNE can be mechanically exfoliated into GA sheets to form a stable dispersion in NMP. To demonstrate the efficiency of our reversible covalent strategy, we compared this system to that without TCNE treatment or without oleum intercalation, or without both. A deep black dispersion of GA was obtained after sonication of TCNE graphite adducts for 1 h and successively purified by centrifugation. In the control systems, only light grey dispersions were obtained through the same preparation and purification processes. The concentration of GA dispersion was measured by UV-visible spectroscopy. The yield of GA was calculated to be 6.3 wt% (mass ratio of GA over feeding graphite) based on Lambert-Beer law. In comparison, the yields of the graphene produced in control systems were nearly 10 times lower. The yield of GA can be increased by the recycling use of the sediment obtained by centrifugation. After each cycle, newly generated defects and edge sites were exposed for Diels-Alder reaction in the successive cycle to guarantee the continuing exfoliation. After 10 cycles, an overall yield of 38 wt% was achieved. Accordingly, the yield of this reversible covalent strategy is comparable to that of conventional oxidation method.

No. of layers: Multi-layer (<5)

Author: Stefan Jaric

Title: Direct electrochemical reduction of graphene oxide thin film for aptamer-based selective and highly sensitive detection of Matrix metalloproteinase 2

DOI: 10.48550/arXiv.2311.04674

Year of publication: 2023

Abstract: Simple and low-cost biosensing solutions are suitable for point-of-care applications aiming to overcome the gap between scientific concepts and technological production. To compete with sensitivity and selectivity of golden standards, such as liquid chromatography, the functionalization of biosensors is continuously optimized to enhance the signal and improve their performance, often leading to complex chemical assay development. In this research, the efforts are made on optimizing the methodology for electrochemical reduction of graphene oxide to produce thin film-modified gold electrodes. Under the employed specific conditions, 20 cycles of cyclic voltammetry (CV) are shown to be optimal for superior electrical activation of graphene oxide into electrochemically reduced graphene oxide (ERGO). This platform is further used to develop a matrix metalloproteinase 2 (MMP-2) biosensor, where specific anti-MMP2 aptamers are utilized as a biorecognition element. MMP-2 is a protein which is typically overexpressed in tumor tissues, with important roles in tumor invasion, metastasis as well as in tumor angiogenesis. Based on impedimetric measurements, we were able to detect as low as 3.32 pg mL<sup>-1</sup> of MMP-2 in PBS with a dynamic range of 10 pg mL<sup>-1</sup> – 10 ng mL<sup>-1</sup>. Besides high specificity, ERGO-based aptasensor showed a potential of reuse due to demonstrated successful signal restoration after experimental detection of MMP-2.

Method of producing graphene: Prior to gold IDE modification, each electrode was washed in ethanol and DI water with ultrasonication for 5 minutes, and finally dried with pressurized air. Washed electrodes were pre-conditioned using CV between -0.5 and 1.0 V with a scan rate 0.5 V s<sup>-1</sup> in 0.05 M H<sub>2</sub>SO<sub>4</sub>. To modify the surface with positively charged amino groups, silanization of the glass surface with APTES was performed by incubation with 2% APTES in ethanol for 1 hour. After rinsing with pure ethanol, electrodes were dried and annealed at 120 °C for 1 hour. The gold surface was then modified with a 10 mM MEA aqueous solution by incubating for 1 hour. After rinsing with DI water, IDEs were dried and prepared for GO deposition. GO suspension was diluted with NMP to 0.2 mg mL<sup>-1</sup> and homogenized by sonication. To produce ultra-thin films of GO, 10 μL droplets were cast over working electrodes and left for 2 hours at RT, ensuring negligible solvent evaporation to produce the film as uniform as possible. After incubation, the GO droplet was removed, and electrodes were annealed in low-temperature conditions (100 °C) for 30 minutes to evaporate the excess of solvent. Thin-film GO was reduced electrochemically by running 20 cycles of CV in 1X PBS using voltage range between -1.2 and -0.4 V (0.05 V s<sup>-1</sup> scan rate).

No. of layers: 1 – 2 layers

Author: Satyaprakash Ahirwar

Title: Electrochemical Method To Prepare Graphene Quantum Dots and Graphene Oxide Quantum Dots

DOI: 10.1021/acsomega.7b01539

Year of publication: 2017

**Abstract:** In this study, we present the preparation of graphene quantum dots (GQDs) and graphene oxide quantum dots (GOQDs). GQDs/GOQDs are prepared by an easy electrochemical exfoliation method, in which two graphite rods are used as electrodes. The electrolyte used is a combination of citric acid and alkali hydroxide in water. Four types of quantum dots, GQD1–GQD4, are prepared by varying alkali hydroxide concentration in the electrolyte, while keeping the citric acid concentration fixed. Variation of alkali hydroxide concentration in the electrolyte results in the production of GOQDs. Balanced reaction of citric acid and alkali hydroxide results in the production of GQDs (GQD3). However, three variations in alkali hydroxide concentration result in GOQDs (GQD1, GQD2, and GQD4). GOQDs show tunable oxygen functional groups, which are confirmed by X-ray photoelectron spectroscopy. GQDs/GOQDs show absorption in the UV region and show excitation dependent photoluminescence behavior. The obtained average size is 2–3 nm, as revealed by transmission electron microscopy. X-ray diffraction peak at around 10° and broad D band peak at 1350 cm<sup>-1</sup> in Raman spectra confirm the presence of oxygen-rich functional groups on the surface of GOQDs. These GQDs and GOQDs show blue to green luminescence under 365 nm UV irradiation.

**Method of producing graphene:** Graphite rods (purity >99.9995%) are purchased from Alfa Aesar (CAS No. 7782-42-5). The graphite rods with a diameter of 3.05 mm and an approximate length of 60 mm are heated in a furnace (at 1050°C for 5 min) in the presence of air. After 5 min, the graphite rods are allowed to cool at room temperature. Thereafter, the graphite rods are washed with Milli-Q water to remove large particles from the surface of the graphite rods. The graphite rods are then used as anode and cathode, i.e., electrodes to be dipped in the electrolyte. Four types of GQDs are prepared i.e., GQD1?GQD4. For GQD1?GQD4, the electrolyte used is a mixture of citric acid monohydrate (0.1 M) and NaOH (0.15? 0.4 M) in Milli-Q water (50 mL). Thereafter, the electrochemical experiments are done with CHI660D Electrochemical Workstation. The separation between the graphite rods is ca. 25 mm. Cyclic voltammetry (CV) is performed prior to performing chronoamperometry. CV is performed with a voltage range of ?1 to +1 V, to wet the graphite electrodes. Thereafter, chronoamperometry is performed with a voltage of 10 V and a sensitivity (I/V) of 0.1 for 30 min. As a result, the color of the electrolyte solution changes from colorless to yellow, which confirms the exfoliation of graphite rod. After completion of this reaction, calcium chloride (0.15 M) is added to the prepared solution. This solution is slightly heated to precipitate calcium citrate. Centrifugation is performed for 15 min at 10 000 rpm twice to separate the calcium citrate precipitate. The supernatant is thereafter filtered through membrane filtration (HiMedia, Dialysis Membrane-150, LA401, pore size ca. 2.4nm) for 7 days to remove salt from the solution.

No. of layers: Multi-layer (3D dot structure)

Author: Andrea Capasso

Title: Ink-jet printing of graphene for flexible electronics: An environmentally friendly approach

DOI: 10.1016/j.ssc.2015.08.011

Year of publication: 2015

**Abstract:** Mechanical flexibility is considered an asset in consumer electronics and next-generation electronic systems. Printed and flexible electronic devices could be embedded into clothing or other surfaces at home or office or in many products such as low-cost sensors integrated in transparent and flexible surfaces. In this context the inks based on graphene and related two-dimensional materials (2DMs) are gaining increasing attention owing to graphene exceptional (opto)electronic, electrochemical and mechanical properties. The current limitation relies on the use of solvents, providing stable dispersions of graphene and 2DMs and fitting the proper fluidic requirements for printing, which are in general not environmentally benign, and with high boiling point. Non-toxic and low boiling point solvents do not possess the required rheological properties (i.e., surface tension, viscosity and density) for the solution processing of graphene and 2DMs. Such solvents (e.g., water, alcohols) require the addition of stabilizing agents like polymers or surfactants for the dispersion of graphene and 2DMs, which however unavoidably corrupt their properties, thus preventing their use for the target application. Here we demonstrate a viable strategy to tune the fluidic properties of water/ethanol mixtures (low-boiling point solvents) to first effectively exfoliate graphite and then disperse graphene flakes to formulate graphene-based inks. We demonstrate that such inks can be used to print conductive stripes (sheet resistance of ~13 KΩ/□) on flexible substrates (polyethylene terephthalate), moving a step forward towards the realization of graphene-based printed electronic devices.

**Method of producing graphene:** We exploited liquid phase exfoliation of graphite[56] to produce the graphene inks[16] in NMP and in the mixture EtOH/H<sub>2</sub>O. For the NMP-based ink, 1 g of graphite flakes (Sigma Aldrich) was dispersed in 100 mL of NMP and ultrasonicated (Branson ® 5800) for 6 hours. The obtained dispersion was then ultracentrifuged at ~16000 g (in a Beckman Coulter Optima™ XE-90 with a SW41Ti rotor) for 30 mins at 15 °C, exploiting sedimentation-based separation (SBS) to remove thick flakes and un-exfoliated graphite.[82, 83] After the ultracentrifugation process, we collected the supernatant by pipetting. The optimization of ink-jet printing ideally requires highly concentrated inks. In order to achieve such a target, the supernatant extracted after the first ultracentrifugation process was further ultracentrifuged at ~200000g for 60 mins at 15 °C. The high g force value promotes the sedimentation of the graphene flakes at the bottom of the ultracentrifuge tubes taking advantage of the higher density of the graphene flakes (~2.1g/cm<sup>3</sup>)[84] in comparison with the solvent (?NMP = 1.03 g/cm<sup>3</sup>).[85] The pellet (sedimented graphene flakes) is collected and the supernatant is discarded. The pellet was re-suspended in 3 mL of pure NMP using an ultrasonic bath for 10 min. This time was sufficient to re-disperse the graphene flakes, thus obtaining a stable (for more than 2 months) ink.

No. of layers: Multi-layer

Author: Ethan B. Secor

Title: Rapid and Versatile Photonic Annealing of Graphene Inks for Flexible Printed Electronics

DOI: 10.1002/adma.201502866

Year of publication: 2015

**Abstract:** The surging field of printed electronics offers a promising methodology for the fabrication of novel electronic devices, [ 1,2 ] which spans applications in energy conversion and storage, [ 3,4 ] flexible displays, [ 5 ] distributed sensor networks, [ 6 ] and intelligent and interactive packaging. [ 7 ] By integrating solution processed electronic materials in high-throughput, low-cost manufacturing platforms, printed electronics is poised to have a growing impact on many technologies. The vision of inexpensive, large-area electronics is enabled by rapid, solution-phase processing techniques, epitomized by roll-to-roll manufacturing. [ 8 ] Drop-on-demand inkjet printing is an important capability for this field, offering additive, noncontact, and digital patterning capabilities. As such, there is strong demand to develop inkjet-printable inks based on high-performance electronic materials to expand the scope of possible applications for printed electronics. To date, a wide range of materials have been adapted to inkjet printing, including organic molecules and polymers, metallic and ceramic nanoparticles, carbon and postcarbon nanomaterials, and sol-gel metal oxides. [ 9–12 ] Of these, graphene-based inks offer a desirable combination of electrical conductivity, chemical and environmental stability, and mechanical flexibility, and have been exploited for a range of applications in energy, [ 13,14 ] sensing, [ 15–17 ] and electronics. [ 18–20 ] While several strategies have been presented for inkjet printing of graphene, they are limited in one or more of several key qualities, namely, high electrical conductivity, rapid printing and post-processing, and broad substrate compatibility. [ 12 ] Here, we concurrently achieve these requirements by coupling inkjet printing with intense pulsed light (IPL) annealing to achieve rapid fabrication of high conductivity graphene patterns on myriad substrates.

**Method of producing graphene:** Graphene was exfoliated from graphite using a high shear mixer (Silverson L5M-A) with a square hole high shear screen. Ethyl cellulose (EC) (Sigma–Aldrich, 4 cP grade as measured at 5% in 80:20 toluene:ethanol, 48% ethoxy) was dissolved in ethanol (Koptec, 200 proof) at a concentration of 0.2–2% w/v (Supporting Information, Figure S2), and flake graphite (Asbury Graphite Mills, Grade 3061) was added at 10% w/v. This mixture was shear mixed for 2 h at 10 230 rpm in an ice bath, and then centrifuged at 4000 rpm (23000 g ) for 2 h to sediment out large graphite flakes (Beckman Coulter Avanti J-26 XPI centrifuge). The supernatant containing graphene, EC, and ethanol was harvested by pipette. For the flocculation step, this supernatant was mixed in a 16:9 wt. ratio with an aqueous NaCl solution (0.04 g mL  $^{-1}$  NaCl, Sigma–Aldrich, >99.5%) and centrifuged for 6 min at 7500 rpm (10 000 g ) to sediment the graphene/ EC composite. This sediment was washed with deionized water, collected by vacuum filtration (Millipore Nitrocellulose HAWP 0.45  $\mu$ m filter paper), and then dried to yield the graphene/EC powder, with a graphene content of 25–65 wt% depending on the starting EC loading.

No. of layers: 2-8 layers

Author: Arjunan Ariharan

Title: Heteroatom Doped Multi-Layered Graphene Material for Hydrogen Storage Application

DOI: 10.4236/graphene.2016.52005

Year of publication: 2016

**Abstract:** A variety of distinctive techniques have been developed to produce graphene sheets and their functionalized subsidiaries or composites. The production of graphene sheets by oxidative exfoliation of graphite can be a suitable route for the preparation of high volumes of graphene derivatives. P-substituted graphene material is developed for its application in hydrogen sorption in room temperature. Phosphorous doped graphene material with multi-layers of graphene shows a nearly ~2.2 wt% hydrogen sorption capacity at 298 K and 100 bar. This value is higher than that for reduced graphene oxide (RGO without phosphorous).

**Method of producing graphene:** Graphene Oxide (GO) was synthesized from graphite by a modified Hummers method. Briefly, graphite powder (2.0 g) was taken in a beaker, added 50 mL of concentrated sulfuric acid ( $H_2SO_4$ ) under vigorous agitation in an ice bath. Afterwards, sodium nitrate (2.0 g) and potassium permanganate (6.0 g) were slowly added in a sequence. Then, the mixture was transferred into a water bath and kept at 35°C for 2 hour. After that, 100 mL of distilled water was slowly added, causing a temperature rise to 98°C. Later, 140 mL of 4%  $H_2O_2$  was dropped into the reaction system. Finally, the product was washed with distilled water three times. The acquired solid was dried in vacuum at 50°C for 48 hours.

No. of layers: Multi-layer

Author: Sha Li

Title: Graphene-Quantum Dot Hybrid Photodetectors from 200 mm Wafer Scale Processing

DOI: 10.48550/arXiv.2303.00406

Year of publication: 2023

Abstract: A 200 mm processing platform for the large-scale production of graphene field-effect transistor-quantum dot (GFET-QD) hybrid photodetectors is demonstrated. Comprehensive statistical analysis of electric data shows a high yield (96%) and low variation of the 200 mm scale fabrication. The GFET-QD devices deliver responsivities of 105 - 106 V/W in a wavelength range from 400 to 1800 nm, at up to 100 frames per second. Spectral sensitivity compares well to that obtained using similar GFET-QD photodetectors. The device concept enables gate-tunable suppression or enhancement of the photovoltage, which may be exploited for electric shutter operation by toggling between the signal capture and shutter states. The devices show good stability at a wide operation range and external quantum efficiency of 20% in the short-wavelength infrared range. Furthermore, an integration solution with complementary metal-oxide-semiconductor technology is presented to realize image-sensor array chips and a proof-of-concept image system. This work demonstrates the potential for the volume manufacture of infrared photodetectors for a wide range of imaging applications.

Method of producing graphene: High-quality graphene was grown in a BM Pro 2×8" CVD furnace from Aixtron Ltd., using methane (CH<sub>4</sub>) as precursor and copper (Cu, 200 mm × 200 mm foil) as the catalyst. Semi-dry transfer was carried out using sacrificial polymeric support placed on the graphene surface and the Cu foil was etched away using ammonium persulfate (APS) etchant. After rinsing the bottom surface of the graphene with DI water, it was dried and stamped on the target substrate using uniaxial pressure. Finally, the polymer was removed using solvents.

No. of layers: Mono-layer

Author: Fatima Tuz Johra

Title: Facile and safe graphene preparation on solution based platform

DOI: 10.1016/j.jiec.2013.11.022

Year of publication: 2013

**Abstract:** Graphene has attracted increasing attention because of its interesting properties. In this study, graphene was prepared from graphite by a very simple and easy process. The two-step protocol involves conversion of graphite to graphene oxide (GO) by oxidation, and subsequent reduction of GO to graphene. The structures and properties of the obtained GO and graphene were characterized via X-ray diffraction, and Raman, NMR, UV-vis absorption, and X-ray photoelectron spectroscopic techniques. The morphologies of these products were observed via field emission scanning electron microscopy. The preparation protocol is simple, easy, environmental friendly, i.e., nontoxic, and the yield of graphene is high.

**Method of producing graphene:** High-purity graphite flakes (40 mm) were obtained from Taewon Scientific Co., and potassium permanganate (KMnO<sub>4</sub>), 95% sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), 85% phosphoric acid (H<sub>3</sub>PO<sub>4</sub>), 35–37% hydrochloric acid (HCl), 30% hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), 25–30% ammonia water (NH<sub>4</sub>OH), 99.9% ethanol (C<sub>2</sub>H<sub>5</sub>OH), and 99% ethyl ether [(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>O] were obtained from Duksan reagents and chemicals. A poly(tetrafluoroethylene) (PTFE) membrane filter was purchased from the Pall Corporation. Graphene oxide was prepared from graphite flakes via an improved Hummers' method [17]. A mixture of H<sub>2</sub>SO<sub>4</sub> and H<sub>3</sub>PO<sub>4</sub> (9:1 vol. equiv.) was added to a mixture of KMnO<sub>4</sub> and graphite flakes (3:1 wt. equiv.). Because of heat evolution from the exothermic process, a delay (15–20 min) was introduced to bring the temperature down to room temperature. The mixture was then placed on a heating mantle at 50 °C, with constant stirring for 12 h. After completion of the reaction, the mixture was cooled to room temperature and poured onto ice [400 mL of deionized (DI) water were used to make the ice] with 30% H<sub>2</sub>O<sub>2</sub> (~3 mL). The solution was then sieved using a testing sieve and the filtrate was centrifuged (4000 rpm, 4 h). The supernatant was then discarded, and the remaining solid was sequentially washed with water, 30% HCl, and ethanol (twice in each case); for each wash, the mixture was sifted through the sieve and the filtrate was then centrifuged (4000 rpm, 4 h) using a Mega 17R small, high-speed, refrigerated centrifuge machine, and the supernatant was decanted. After the multiple washing treatments, the remaining materials were coagulated using ethyl ether and then filtered through a PTFE membrane with a micropore size of 0.2 mm, followed by drying in vacuum. Graphene oxide was placed in a beaker and sonicated with DI water (0.1 mg mL<sup>-1</sup>) for 5 min, using an ultrasonicator. NH<sub>4</sub>OH (2–4 mL) were added to adjust the pH to ~11. The mixture was transferred to a Teflon-lined stainless-steel autoclave and placed in an oven at 180 °C for 6 h. After completion of the reaction, this solution was centrifuged (4000 rpm, 4 h), and the obtained materials were washed with DI water and ethanol (twice in each case) to remove impurities. Finally, the obtained material was collected by vacuum filtration and dried in vacuum.

No. of layers: 1-4 layers

Author: ZiZhao Xu

Title: Bulk-scale synthesis of randomly stacked graphene with high crystallinity

DOI: 10.1016/j.carbon.2021.09.034

Year of publication: 2021

**Abstract:** Since the strong interlayer interaction of AB-stacked graphene in bulk form degrades the superior property of single-layer graphene, formation of randomly stacked graphene is required to apply the high performances of graphene to macroscopic devices. However, conventional methods to obtain bulk-scale graphene suffer from a low crystallinity and/or the formation of a thermodynamically stable AB-stacked structure. This study develops a novel approach to produce bulk-scale graphene with a high crystallinity and high fractions of random stacking by utilizing the porous morphology of a graphene oxide sponge and an ultrahigh temperature treatment of 1500–1800 °C with ethanol vapor. Raman spectroscopy indicates that the obtained bulk-scale graphene sponge possesses a high crystallinity and a high fraction of random stacking of 80%. The large difference in the random-stacking ratio between the sponge and the aggregate samples confirms the importance of accessibility of ethanol-derived species into the internal area. By investigating the effect of treatment temperature, a higher random-stacking ratio is obtained at 1500 °C. Moreover, the AB-stacking fraction was reduced to less than 10% by introducing cellulose nanofiber as a spacer to prevent direct stacking of graphene. The proposed method is effective for large-scale production of high-performance bulk-scale graphene.

**Method of producing graphene:** GO was prepared from graphite by a modified Hummers' method[37]. The obtained GO dispersion was 1 wt% in water solvent, and the flake size of GO was about 10  $\mu\text{m}$  (observed by optical microscopy). The following freeze-drying process was carried out by a lab-made vacuum drying system to prepare a GO sponge. A GO dispersion was added into an ice tray and shaped into a 1-cm<sup>3</sup> cube. It was then frozen in a freezer at  $-10^\circ\text{C}$  overnight followed by pumping for 48 hours. Pumping sublimated the water in the frozen GO dispersion, leaving the GO network structure as a GO sponge. Then the GO sponge was thermally treated in ethanol/Ar gas under ultrahigh temperature conditions for repair and reduction. Instead of the solar furnace used in our previous study[22], the ultrahigh temperature process was performed at 1800 or 1650  $^\circ\text{C}$  using an infrared radiation furnace (SR1800G-S, THERMO RIKO Co.) or at 1500  $^\circ\text{C}$  using a tubular electric furnace (FT-01VAC-1650, FULL-TECH Co.). Both of the furnaces were connected to vacuum pumps to maintain a low pressure. We introduced 20 sccm of Ar under the total pressure of 26.6 Pa during temperature rise. After reaching the set temperature, the thermal treatment was conducted at ultrahigh temperature with flowing 100 sccm of Ar and 0.3 sccm of ethanol under the pressure of 106.6 Pa.

No. of layers: Mono-layer

Author: Anastasia Novikova

Title: Green-extraction of carbon thin films from natural mineral Shungite

DOI: 10.48550/arXiv.2110.12790

Year of publication: 2021

**Abstract:** Conventional fabrication methods to produce graphene are cumbersome, expensive and are not ecology friendly. This is due to the fact that a large volume of raw materials requires a large number of acids and alkalis, which in turn requires special disposal. Therefore, it is necessary to develop new technologies or refine existing technologies for the production of graphene and create new ecology-safe and effective methods to produce graphene. Here, we utilized the physical dispergation to extract graphene films from natural mineral shungite rock. We studied the structure of shungite via Raman spectrometry and X-ray phases analysis and found that shungite refers to graphite-like mineral structures. From spectral data, we learned that the main constituent of shungite is amorphous carbon in sp<sub>2</sub> and sp<sub>3</sub> forms. Transmission electron microscopy images of the processed material revealed that the obtained graphene films with well-developed surfaces are as small as 200 nanometers. Our green fabrication method of graphene can be widely used in a variety of fields from electronics (electrodes), optics, biotechnology (biosensors), ecology (sorbents for wastewater, air purification) to list a few.

**Method of producing graphene:** Prior to the production of graphene, shungite samples were crushed to pieces, cleaned of visible contaminants, and washed in distilled water for 5 minutes at room temperature of 25°C. Samples of graphene layers were prepared by the dispergation method using a digital ultrasonic cleaner R Technology under normal conditions (temperature 25°C). One gram of shungite was placed in a 50 ml plastic tube, then 25 ml of distilled water was added, closed and placed in a digital ultrasonic cleaner R Technology for 2 hours. We used the Transmission Electron Microscope (TEM) JEOL JEM 2100F to evaluate and characterize the samples obtained. The JEM-2100F, a Field Emission gun Transmission Electron Microscope, is a state-of-the-art ultra-high-resolution analytical TEM that is capable of providing high spatial resolution atomic imaging and microstructure analysis of material samples. To assess the structural features, we studied the Raman spectra using a LabRam HR Evolution Horiba Raman spectrometer with an excitation range of 325-785 nm with an ultra-low frequency (ULF) module, which allows one to determine the characteristics of the sample at very low frequencies (532 nm), and also measure anti-Stokes spectra. To study the composition of the elements, we used X-ray photoelectron spectroscopy (XPS). The studies were carried out using the ESCALAB 250, a multifunctional instrument that includes surface-sensitive XPS and Auger electron spectroscopy (AES) analysis methods. In this system, XPS high-speed routine analysis is optimized for large areas. The X-ray source, data acquisition system and sample movement are fully computer-controlled, providing the user with an automatic operation to analyze a large number of samples.

No. of layers: Mono-layer

Author: Xuebin Wang

Title: Three-dimensional struttured graphen egrown by substrate-free sugar blowing for high-power-density supercapacitors

DOI: 10.1038/ncomms3905

Year of publication: 2013

Abstract: Three-dimensional graphene architectures in the macroworld can in principle maintain all the extraordinary nanoscale properties of individual graphene flakes. However, current 3D graphene products suffer from poor electrical conductivity, low surface area and insufficient mechanical strength/elasticity; the interconnected self-supported reproducible 3D graphenes remain unavailable. Here we report a sugar-blowing approach based on a polymeric predecessor to synthesize a 3D graphene bubble network. The bubble network consists of mono- or few-layered graphitic membranes that are tightly glued, rigidly fixed and spatially scaffolded by micrometre-scale graphitic struts. Such a topological configuration provides intimate structural interconnectivities, freeway for electron/phonon transports, huge accessible surface area, as well as robust mechanical properties. The graphene network thus overcomes the drawbacks of presently available 3D graphene products and opens up a wide horizon for diverse practical usages, for example, high-power high-energy electrochemical capacitors, as highlighted in this work.

Method of producing graphene: Typically, 10 g glucose was mixed with 10 g ammonium salts ( $\text{NH}_4\text{Cl}$ ), which was then heated under a desired heating rate (4  $\text{Cmin}^{-1}$  was recommended) and finally treated at 1,350  $^\circ\text{C}$  for 3 h under Ar atmosphere in a tube furnace (50 cm length by 5 cm diameter). A black foam-like product, that is, (struttured graphene) SG, was collected. White granulated sugar (a kitchen-use sugar from Nissin-Sugar Co.) was also used to replace glucose to grow SG.

No. of layers: Multi-layer (<5) (3D bubble network)

Author: Claudia Backes

Title: Spectroscopic metrics allow insitu measurement of mean size and thickness of liquid-exfoliated few-layer graphene nanosheets

DOI: 10.1039/c5nr08047a

Year of publication: 2016

**Abstract:** Liquid phase exfoliation is a powerful and scalable technique to produce defect-free mono- and few layer graphene. However, samples are typically polydisperse and control over size and thickness is challenging. Notably, high throughput techniques to measure size and thickness are lacking. In this work, we have measured the extinction, absorption, scattering and Raman spectra for liquid phase exfoliated graphene nanosheets of various lateral sizes ( $90 \leq \langle L \rangle \leq 810$  nm) and thicknesses ( $2.7 \leq \langle N \rangle \leq 10.4$ ). We found all spectra to show well-defined dependences on nanosheet dimensions. Measurements of extinction and absorption spectra of nanosheet dispersions showed both peak position and spectral shape to vary with nanosheet thickness in a manner consistent with theoretical calculations. This allows the development of empirical metrics to extract the mean thickness of liquid dispersed nanosheets from an extinction (or absorption) spectrum. While the scattering spectra depended on nanosheet length, poor signal to noise ratios made the resultant length metric unreliable. By analyzing Raman spectra measured on graphene nanosheet networks, we found both the D/G intensity ratio and the width of the G-band to scale with mean nanosheet length allowing us to establish quantitative relationships. In addition, we elucidate the variation of 2D/G band intensities and 2D-band shape with the mean nanosheet thickness, allowing us to establish quantitative metrics for mean nanosheet thickness from Raman spectra.

**Method of producing graphene:** Dispersions of graphene in aqueous surfactant solutions were prepared by shear mixing using a Silverson L5M rotor-stator mixer, as detailed previously.<sup>14</sup> A solution of sodium cholate in de-ionised water (1 g L<sup>-1</sup>) was prepared and then added to natural flake graphite (Sigma-Aldrich, 332461, or Asbury, grade 3763) at 100 g L<sup>-1</sup> with a typical volume of 1 L. Graphene was exfoliated using a 32 mm rotor at 4500 rpm for 60 min. In order to remove some low mass impurities (which we found to partly destabilize the dispersion and thus inhibit centrifugation-based size selection), the resulting dispersion was left to settle overnight, and the supernatant discarded. Fresh surfactant solution was then added and the exfoliation repeated as before. The dispersion was left to settle for several hours before subjecting the supernatant to the centrifugation-based size selection. To select nanosheets by size, we used controlled centrifugation with sequentially increasing rotation speeds as previously reported.<sup>14,27</sup> An initial centrifugation at 1.5 krpm (240g, 2 h) was performed to remove unexfoliated material. The supernatant was subjected to further centrifugation at 2 krpm (425g, 2 h). The sediment was collected in fresh water-SC (SC concentration 0.1 g L<sup>-1</sup> to facilitate imaging), while the supernatant was subjected to further centrifugation at 2.5 krpm (665g, 2 h). Again, the sediment was collected and the supernatant centrifuged at higher rpm. This procedure was repeated for 3 krpm (958g, 2 h), 5 krpm (2660g, 2 h), 10 krpm (10 170g, 2 h) and 18 krpm (32 600g, 2 h) to yield samples with decreasing sizes in the respective sediments. Compared with a method based on taking the supernatant from a single step centrifugation, this produces dispersions with lower polydispersity, as both smaller and larger nanosheets are removed from a given size selected dispersion. This greatly facilitates microscopic characterization required to accurately determine length and thickness. A Hettich Mikro 220R centrifuge equipped with a fixed angle rotor 1016 and sample aliquots of 10 mL was used for rotations up to 5 krpm. For the high speed centrifugations, 1.5 mL vials and a rotor 1195-A was used. In the case of the analysis of the stock-like dispersion, the sample of Asbury graphite exfoliated in SC was centrifuged at 1 krpm (104g, 2 h) and the sediment discarded. We note that the removal of non exfoliated graphite is required for the metrics to be applicable.

No. of layers: Multi-layer (<5)

Author: G. Rajendra Kumar

Title: Shear-force-dominated Dual-Drive Planetary Ball milling for Scalable Production of Graphene and Its Electrocatalytic Application with Pd nanostructures

DOI: 10.1039/C5RA24810H

Year of publication: 2016

**Abstract:** The exceptional properties of graphene-based derivatives have governed the numerous research fields in recent years. The scaled up, and reliable production of high-quality graphene is still a challenging task. This work elucidates the efficient and low-cost approach for mass production of high-quality graphene (50g scale batch) through dual-drive planetary ball milling of graphite with the dicarboxylic acid. The dimensional changes of graphite derived from the diffraction pattern of (002) plane at different milling hours and the unique signature of the graphene noticed in Raman spectroscopy. Transmission electron microscopy clearly envisioned the existence of single and bilayer graphene sheets. The non-destructive exfoliation evidenced by the surface binding states of C 1s core level spectra. The as-synthesized graphene utilized as the catalytic support for formic acid fuel cell applications. The graphene supported palladium nanocomposites prepared, and the electrocatalytic activity towards the formic acid oxidation explored. The cyclic voltammetry of graphene-palladium nanocomposite reveals the onset potential for formic acid oxidation at -0.1 V with prominent oxidation peak at 0.263 V.

**Method of producing graphene:** In a typical procedure, 50g of graphite flakes and 80g of oxalic acid (OA) were placed into stainless steel jar (2500 ml volume) containing 10 mm diameter of stainless steel balls used as grinding medium. The utilization of low diameter stainless steel balls are due to increase the impact and shear energy of the ball to powder and make a low dimensional interaction with graphite layers. Initially, the Dual-drive ball milling was executed at three different critical speeds (40%, 70%, and 98%). But the critical speed of 40% offers an efficient exfoliation with less defects than 70% and 98%. Accordingly, the optimized critical speed of 40% is adopted for the graphite exfoliation by shear force ball milling. The milling was carried out up to 20 h and rest time was one hour per cycle. Then, the milled graphite was treated with 1M Hydrochloric acid (HCl) to acidify the carboxylates and to remove the Iron impurities from milling jar in the milled graphite. Then, the mixture was washed with distilled water for several times until the pH becomes neutral. The mixture was filtered and subjected to the heat treatment at 600°C under an argon atmosphere for an appropriate time interval. Finally, as-prepared graphene was stored for prior use.

No. of layers: 1-2 layers

Author: Genhua Pan

Title: Transfer-free growth of graphene on SiO<sub>2</sub> insulator substrate from sputtered carbon and nickel films

DOI: 10.1016/j.carbon.2013.08.036

Year of publication: 2013

**Abstract:** Here we demonstrate the growth of transfer-free graphene on SiO<sub>2</sub> insulator substrates from sputtered carbon and metal layers with rapid thermal processing in the same evacuation. It was found that graphene always grows atop the stack and in close contact with the Ni. Raman spectra typical of high quality exfoliated monolayer graphene were obtained for samples under optimised conditions with monolayer surface coverage of up to 40% and overall graphene surface coverage of over 90%. Transfer-free graphene is produced on SiO<sub>2</sub> substrates with the removal of Ni in acid when Ni thickness is below 100 nm, which effectively eliminates the need to transfer graphene from metal to insulator substrates and paves the way to mass production of graphene directly on insulator substrates. The characteristics of Raman spectrum depend on the size of Ni grains, which in turn depend on the thickness of Ni, layer deposition sequence of the stack and RTP temperature. The mechanism of the transfer-free growth process was studied by AFM in combination with Raman. A model is proposed to depict the graphene growth process. Results also suggest a monolayer self-limiting growth for graphene on individual Ni grains.

**Method of producing graphene:** A carbon-containing film (SiC or amorphous carbon) and a metal film (Ni) were deposited by sputtering onto a Si substrate in the order of either substrate/SiC/Ni, or substrate/Ni/SiC. After deposition, the stacks were subjected to a rapid-thermal-process at temperatures ranging from 650 to 1000 °C. We find that graphene always grows atop the stack, irrespective of the deposition sequence of the two layers. After RTP, the Ni or Ni-silicide layer is etched away in HCl solution, Fig. 1d. This resulted in two possibilities: For thick Ni layers (>100 nm), after the Ni-silicide is dissolved in HCl, the graphene floats off the Si substrate and can be collected and transferred to a new substrate, which is an approach already employed by others [16,17,27]. However, if the Ni layer is sufficiently thin (<100 nm), graphene is retained on the original substrate.

No. of layers: Monolayer

Author: Lars Kotthoff

Title: Modeling and Optimizing Laser-Induced Graphene

DOI: 10.48550/arXiv.2107.14257

Year of publication: 2021

**Abstract:** A lot of technological advances depend on next-generation materials, such as graphene, which enables a raft of new applications, for example better electronics. Manufacturing such materials is often difficult; in particular, producing graphene at scale is an open problem. We provide a series of datasets that describe the optimization of the production of laser induced graphene, an established manufacturing method that has shown great promise. We pose three challenges based on the datasets we provide – modeling the behavior of laser-induced graphene production with respect to parameters of the production process, transferring models and knowledge between different precursor materials, and optimizing the outcome of the transformation over the space of possible production parameters. We present illustrative results, along with the code used to generate them, as a starting point for interested users. The data we provide represents an important real-world application of machine learning; to the best of our knowledge, no similar datasets are available.

**Method of producing graphene:** The graphene oxide samples used for the data we present here were prepared from graphite using the improved Hummers' method [Marcano et al., 2010]. Powdered samples, ground and sieved to 20 µm, were mixed in concentrated H<sub>2</sub>SO<sub>4</sub> and H<sub>3</sub>PO<sub>4</sub> and placed in an ice bath. KMnO<sub>4</sub> was added at a mixture temperature of 35°C and increased to 98°C before termination with ultrapure water (Millipore) and H<sub>2</sub>O<sub>2</sub>. The filtrate was then washed with HCl and subsequently with water repeatedly until a pH level of about 6.5 was obtained. The GO inks were produced using 25 mg of the freeze-dried GO powder, which was diluted in 100 ml deionized water and ultrasonicated with a cooling system. After the sample was centrifuged, the remaining supernatant was repeatedly diluted and ultrasonicated until a 200 ml dilution was obtained. The GO inks were spray-coated onto a 1 cm × 1 cm quartz or polyimide substrate (Kapton HN 125 µm, Dupont) in multiple passes until a thickness of 1 µm was achieved, verified with an optical profilometer. Laser-induced graphene (LIG) spots were patterned by reducing GO films deposited on quartz and polyimide, and by carbonization of polyimides directly. We denote GO on quartz, GO on polyimide, and polyimide as samples GOQ, GOPI, and PI, respectively. The patterning setup is shown in Figure 1. The deposited GO films were placed in a sample chamber which allows patterning in air, argon, or nitrogen environments with pressures up to 1000 psi. LIG patterns were irradiated using a 532 nm diode-pumped solid-state continuous-wave laser. The laser beam was focused with a 50x microscope lens to a spot size of 20 µm on the sample surface. Irradiated beam spots were positioned sufficiently far apart from each other to ensure pristine precursor material for each experiment. The sample area is about 1 cm<sup>2</sup>, allowing approximately 256, 25, and 25 patterns for samples GOQ, GOPI, and PI, respectively.

No. of layers: Mono-layer

Author: Libo Gao

Title: Face-to-face transfer of wafer-scale graphene films

DOI: 10.1038/nature12763

Year of publication: 2014

**Abstract:** Graphene has attracted worldwide interest since its experimental discovery<sup>1,2</sup>, but the preparation of large-area, continuous graphene film on SiO<sub>2</sub>/Si wafers, free from growth-related morphological defects or transfer-induced cracks and folds, remains a formidable challenge<sup>3</sup>. Growth of graphene by chemical vapour deposition on Cu foils<sup>4–7</sup> has emerged as a powerful technique owing to its compatibility with industrial-scale roll-to-roll technology<sup>6</sup>. However, the polycrystalline nature and microscopic roughness of Cu foils means that such roll-to-roll transferred films are not devoid of cracks and folds<sup>6,7</sup>. High-fidelity transfer or direct growth of high-quality graphene films on arbitrary substrates is needed to enable wide-ranging applications in photonics or electronics, which include devices such as optoelectronic modulators, transistors, on-chip biosensors and tunnelling barriers<sup>3,8,9</sup>. The direct growth of graphene film on an insulating substrate, such as a SiO<sub>2</sub>/Si wafer, would be useful for this purpose, but current research efforts remain grounded at the proof-of-concept stage, where only discontinuous, nanometre-sized islands can be obtained<sup>10</sup>. Here we develop a face-to-face transfer method for wafer-scale graphene films that is so far the only known way to accomplish both the growth and transfer steps on one wafer. This spontaneous transfer method relies on nascent gas bubbles and capillary bridges between the graphene film and the underlying substrate during etching of the metal catalyst, which is analogous to the method used by tree frogs to remain attached to submerged leaves<sup>11,12</sup>. In contrast to the previous wet<sup>4,5,13–15</sup> or dry<sup>6,7</sup> transfer results, the face-to-face transfer does not have to be done by hand and is compatible with any size and shape of substrate; this approach also enjoys the benefit of a much reduced density of transfer defects compared with the conventional transfer method. Most importantly, the direct growth and spontaneous attachment of graphene on the underlying substrate is amenable to batch processing in a semiconductor production line, and thus will speed up the technological application of graphene.

**Method of producing graphene:** The catalyst preparation and ICP-CVD growth are both performed in a customized sputter/electron-beam/ICP-CVD cluster. First, 8-inch or 4-inch SiO<sub>2</sub>/Si (or quartz) wafers are sputtered with Cu films at 100–200 uC. For face-to-face transfer, the wafers are pre-treated with N<sub>2</sub> plasma (1,000 W, 50 mtorr). The conditions for ICP-CVD growth are as follows: the wafer with a sputtered Cu film is treated with a H<sub>2</sub> plasma (150W) for 5 min with the substrate heated to 750 uC at 50 mtorr. A mixture of H<sub>2</sub> and CH<sub>4</sub> (H<sub>2</sub>:CH<sub>4</sub> 150:10) is introduced into the chamber for graphene growth (150W plasma power, 50 mtorr, 5 min). After growth, the graphene/Cu/wafer is spin-coated with PMMA (996,000 relative molecular mass, 4 wt% in ethyl lactate, 3,000 r.p.m. for 1 min) for protection. A 0.1M ammonium persulphate ((NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>) aqueous solution or 1M iron chloride (FeCl<sub>3</sub>) is used as the etchant. Baking at 150 uC for 10 min is needed to evaporate the water layer. Finally, face-to-face transferred graphene on the wafer is realized by removing the PMMA with acetone.

No. of layers: Mono-layer

Author: Ilke Uysal Unalan

Title: Polysaccharide-assisted rapid exfoliation of graphite platelets into high quality water dispersible graphene sheets

DOI: 10.1039/c4ra16947f

Year of publication: 2015

**Abstract:** Ultrasound exfoliation of graphite with the assistance of three polysaccharides (nonionic pullulan, cationic chitosan, and anionic alginate) was investigated in this work. The effects of polymer type, initial concentration of graphite, and ultrasonication period on the graphene yield and quality were compared. Under a sonotrode-type ultrasonication treatment for 30 min, graphene aqueous dispersions with concentrations of up to 2.3 mg ml<sup>-1</sup> in pullulan solutions and 5.5 mg ml<sup>-1</sup> in chitosan solutions were achieved. The obtained graphene nanosheets were characterized as low-defect mono-layer, bi-layer, and few-layer (<5), and formed stable dispersions in water for up to 6 months. The adsorption of pullulan and chitosan biopolymers on the graphene surface as determined by TGA technique was approximately 2.5 wt% and 8.5 wt%, respectively, which accounts for the dispersibility and stability of the graphene sheets in water. Findings arising from this work suggest that pullulan and chitosan are more effective in exfoliating graphite into graphene than alginate due to the different surface free energy and thermodynamic affinity. The polysaccharide-assisted aqueous-exfoliation approach enables the production of water-dispersible graphene with high quality and large quantity, thus providing an industrially scalable route for new potential applications of graphene-based nanocomposites, e.g. in the food packaging industry.

**Method of producing graphene:** Pullulan and alginate (1.0 g) were separately dissolved in 20 ml of distilled water (DI), whereas chitosan (0.4 g) was dissolved in 20 ml of DI with 1 wt% acetic acid. Graphite powder was dispersed in the aqueous biopolymer solutions and treated using an ultrasonic processor UP200S (maximum power ¼ 200W, frequency ¼ 24 kHz, Hielscher, Teltow, Germany) equipped with a cone frustum titanium sonotrode (model micro tip S3, tip diameter ¼ 3 mm, maximum amplitude ¼ 210 mm, acoustic power density or surface intensity ¼ 460 W cm<sup>-2</sup>) under the following conditions: 0.5 cycle and 50% amplitude, for a period of 10, 20, 30, and 60 min, respectively. Subsequently, mixtures were centrifuged at 1500 rpm for 60 min to remove unexfoliated graphite particles and then washed 5 times and again centrifuged at 5000 rpm for 20 min to remove excess biopolymers. The resultant dark-gray solutions were vacuum-dried at 40 °C until no mass-loss. The resulting polymer-graphene powders were redispersed in water (1 mg ml<sup>-1</sup> for pullulan and chitosan; 0.18 mg ml<sup>-1</sup> for alginate) for characterization. Graphene sheets obtained by pullulan-, alginate-, and chitosan-assisted ultrasonication were indicated as pull-G, alg-G, and chit-G, respectively.

No. of layers: Multi-layer (<5)

Author: Lei Cao

Title: Hydrophilic Graphene Preparation from Gallic Acid Modified Graphene Oxide in Magnesium Self Propagating High Temperature Synthesis Process

DOI: 10.1038/srep35184

Year of publication: 2016

**Abstract:** Hydrophilic graphene sheets were synthesized from a mixture of magnesium and gallic acid (GA) modified graphene oxide (GO) in a self-propagating high-temperature synthesis (SHS) process, and hydrophilic graphene sheets displayed the higher C/O ratio (16.36), outstanding conductivity (~88900 S/m) and excellent water-solubility. GO sheets were connected together by GA, and GA was captured to darn GO structure defects through the formation of hydrogen bonds and ester bonds. In SHS process, the most oxygen ions of GO reacted with magnesium to prevent the escape of carbon dioxide and carbon monoxide to from the structure defects associated with vacancies, and GA could take place the high-temperature carbonization, during which a large-area graphene sheets formed with a part of the structure defects being repaired. When only GO was reduced by magnesium in SHS process, and the reduced GO (rGO) exhibited the smaller sheets, the lower C/O ratio (15.26), the weaker conductivity (4200 S/m) and the poor water-solubility because rGO inevitably left behind carbon vacancies and topological defects. Therefore, the larger sheet, less edge defects and free structure defects associated with vacancies play a key role for graphene sheets good dispersion in water.

**Method of producing graphene:** Preparation of GO. GO was prepared by modified Hummers' method. 5.0 g graphite, 2.5 g NaNO<sub>3</sub>, and 125 ml H<sub>2</sub>SO<sub>4</sub> were loaded in a 1000 ml round-bottom flask with magnetic stirring. After being cooled with ice-water bath at 0 °C for 1 h, 17.5 g KMnO<sub>4</sub> was added into above reaction system. After reaction was kept at 0–5 °C for 1 h and then heated at 35 °C for 2 h, the mixture was diluted with 250 ml deionized water and reacted at 98 °C for 45 min. 200 ml deionized water and 50 ml H<sub>2</sub>O<sub>2</sub> (30%) were added into above suspension under the condition of magnetic stirring. After centrifugation and dry, GO was obtained. Preparation of GOGA. Exfoliation of GO was obtained by ultrasonication in water for 2 h. GOGA was prepared in three steps: (1) 1.5 g gallic acid was loaded into 500 ml GO (5 mg/ml) solution, and the mixture was dispersed by ultrasound for 40 min. (2) the mixed solution was allowed to stand at room temperature for 3 h. (3) The mixed solution was dried at 90 °C under air atmosphere for 24 h to obtain the mixture of gallic acid-modified GO (GOGA). As a control, different addition amount of gallic acid (1.0 g and 2.0 g) in equal mass of GO (were labeled as GOGA1 and GOGA2) were prepared with the same method. Preparation of rGOGA, rGOGA1, rGOGA2 and rGO. 3.0 g Magnesium powder and 1.5 g GOGA powder were mixed evenly. The mixture was put in a crucible, and mixture was covered with a thin layer of magnesium powder on the surface of mixture. Mixture was ignited by magnesium ribbon under air atmosphere condition. After the reaction is over, the mixed products were transferred to a beaker containing 250 ml of 3 M HCl. Products were transferred into the acid solution to remove MgO and residual Mg. The resulting rGOGA was collected with filtration, washed with deionized water until the filtrate turned out to be of neutral. Obtained rGOGA was dried at 60 °C under high vacuum conditions for 10 h. As a control, rGOGA1, rGOGA2 and rGO were prepared from GOGA1, GOGA2 and GO reduction by magnesium with the same methods.

No. of layers: Multi-layer (<5)

Author: Stevan Andric

Title: Ultrafast humidity sensor based on liquid phase exfoliated graphene

DOI: 10.1088/1361-6528/abb973

Year of publication: 2020

**Abstract:** Humidity sensing is important to a variety of technologies and industries, ranging from environmental and industrial monitoring to medical applications. Although humidity sensors abound, few available solutions are thin, transparent, compatible with large-area sensor production and flexible, and almost none are fast enough to perform human respiration monitoring through breath detection or real-time finger proximity monitoring via skin humidity sensing. This work describes chemiresistive graphene-based humidity sensors produced in few steps with facile liquid phase exfoliation (LPE) followed by Langmuir-Blodgett assembly that enables active areas of practically any size. The graphene sensors provide a unique mix of performance parameters, exhibiting resistance changes up to 10% with varying humidity, linear performance over relative humidity (RH) levels between 8% and 95%, weak response to other constituents of air, flexibility, transparency of nearly 80%, and response times of 30 ms. The fast response to humidity is shown to be useful for respiration monitoring and real-time finger proximity detection, with potential applications in flexible touchless interactive panels.

**Method of producing graphene:** The graphene dispersion was produced by dissolving graphite powder (Sigma Aldrich, product no. 332461) at a concentration of 18 mg ml<sup>-1</sup> in N-Methyl-2-pyrrolidone (NMP) (Sigma Aldrich, product no. 328634). The dispersion was sonicated in a low energy ultrasonic bath for 14 h. After sonication the dispersion was centrifuged at 3000 rpm for 60 min in order to separate non-exfoliated graphite flakes, which remain in the precipitate, and the exfoliated graphene flakes which are dispersed in the supernatant. A small volume of the supernatant is added to deionized water (18 MΩ cm<sup>-1</sup>) resulting in self-assembly of graphene nanoplatelets into a thin film on the water/air interface. The thin film is deposited on a pre-immersed substrate of choice following the Langmuir-Blodgett method.

No. of layers: Multi-layer (10)

Author: Shufen Wang

Title: Towards understanding the salt-intercalation exfoliation of graphite into graphene

DOI: 10.1039/c7ra07489a

Year of publication: 2017

**Abstract:** The preparation of graphene from graphite is critical for both theoretical studies and real-world applications. Herein, we present a systematic study to explore the fundamental factors that control the exfoliation of graphite into graphene in a salt-intercalation exfoliation system, using various inorganic salts as intercalators. The yields of the thin graphene sheets obtained, measured via UV-vis absorption spectrophotometry, suggest that both cations and anions significantly influence the exfoliation yields. X-ray photoelectron spectroscopy and energy dispersive spectroscopy analysis showed that both anions and cations become inserted into the space between conjugated graphite layers during the intercalation process. X-ray diffraction spectra revealed that the anion can enhance the salt-intercalation exfoliation by expanding the interlayer spacing. Compared to lithium chloride, both potassium chloride and lithium sulfate can significantly enhance the exfoliation yields of graphene. Optimizing the cation and anion species can improve the yield of graphene, because co-intercalation with both anions and cations occurs during the intercalation process in the solution of inorganic salts. Our work provides a guide for rationally designing the salt-intercalation exfoliation procedure to obtain higher yields of exfoliated 2D materials.

**Method of producing graphene:** 100 mg graphite, 2 g SDBS, 0.1 mol inorganic salt (LiCl, KCl or Li<sub>2</sub>SO<sub>4</sub>) and 100 mL deionized water were added into a threenecked flask. The mixture was stirred and kept boiling for 6 hours. Then, the residue was added into 100 mL ethanol for 2 hours of sonication. To remove the residual salts and surfactants, the residue was filtered through a vacuum funnel with a cellulose ester membrane (pore size of 0.025 mm) and washed three times with 100 mL deionized water. The solid residue was redispersed in deionized water or deposited on Si or Cu wafer for further characterization. Some samples were not sonicated for comparison, and the residual salts and surfactants were also removed by washing three times with deionized water.

No. of layers: Multi-layer (<5)

Author: Lu Zhang

Title: Preparation and characterization of graphene paper for electromagnetic interference shielding

DOI: 10.1016/j.carbon.2014.10.080

Year of publication: 2014

**Abstract:** Syntheses of multifunctional structures, both in two-dimensional and three-dimensional space, are essential for advanced graphene applications. A variety of graphene-based materials has been reported in recent years, but combining their excellent mechanical and electrical properties in a bulk form has not been entirely achieved. Here, we report the creation of novel graphene structures such as graphene pellet and graphene paper. Graphene pellet is synthesized by chemical vapor deposition (CVD), using inexpensive nickel powder as a catalyst. Graphene pellet can be further processed into a graphene paper by pressing. The latter possesses high electrical conductivity of up to  $1136 \pm 32 \text{ S cm}^{-1}$  and exhibits a breaking stress at  $22 \pm 1.4 \text{ MPa}$ . Further, this paper-like material with thickness of 50 lm revealed 60 dB electromagnetic interference (EMI) shielding effectiveness.

**Method of producing graphene:** Nickel powder (Alfa Aesar) of 2–3 lm average particle size and  $0.68\text{m}^2 \text{ g}^{-1}$  in specific surface area was pelletized into 6.4 cm diameter pellets using a compression machine (Carver, 973214A). The applied force was  $\leq 10 \text{ MPa}$ , and varied for different pellet thicknesses. The nickel pellet was placed on a quartz platform inside a quartz tube for growing of graphene by CVD. The nickel pellet was heated up to  $1000 \text{ }^\circ\text{C}$  in a tube furnace (FirstNano, ET1000) under Ar (1000 sccm). Hydrogen (325 sccm) was then introduced for 15 min, to reduce any metal catalyst oxide. Then, CH<sub>4</sub> was introduced for 5 min. Various hydrocarbon flow rates were tested (12, 15, 18, 25 and 28 sccm, corresponding to concentrations of 0.9, 1.1, 1.3, 1.9 and 2.1 vol%, respectively). The pellet was then cooled to room temperature with a rate of  $\leq 100 \text{ }^\circ\text{C min}^{-1}$  under Ar (1,000 sccm) and H<sub>2</sub> (325 sccm). The nickel pellet shrank  $\sim 30\%$  in all dimensions after CVD. The final 3D graphene structure in the form of pellet was produced by etching out nickel from the graphene/nickel pellet with HCl (3 M) at  $80 \text{ }^\circ\text{C}$  for 10 h. The obtained graphene pellet was washed with water to remove residual acid and dried at room temperature. Graphene paper was obtained by compressing the graphene pellet with a press between 2 flat steel plates. Different thicknesses of graphene paper can be fabricated by changing the compression load.

No. of layers: Multi-layer (<5)

Author: Rikson Siburian

Title: New Route to Synthesize of Graphene Nano Sheets

DOI: 10.13005/ojc/340120

Year of publication: 2017

**Abstract:** Synthesis of graphene nano sheets were carried out by using new route and ammonia as well as to produce gram scale graphene. Graphene nano sheets was characterized by using Fourier transform infrared spectroscopy (FTIR), X-ray powder diffraction (XRD), and Scanning Electron Microscopy-Energy Dispersive X-Ray (SEM-EDX). The results of XRD showed that the reemergence of diffraction lines C(002) at  $2\theta = 26.5^\circ$ , and the distance between the planes is 3.35 Å, which shows the typical structure of graphite and multiple layer of graphene. The results of SEM-EDX showed that the particle size and the graphene nano sheets has a smaller pore size and uniform and randomly arranged aggregates with a thin layer which is closely related to one another. Graphene nano sheets has small size or shape is small and thin also aggregate related with each other.

**Method of producing graphene:** 0.2 g of graphite powder was inserted into 250 mL erlenmeyer, then it was added 0.2 g NaNO<sub>3</sub> and 15 mL H<sub>2</sub>SO<sub>4</sub> 96%, respectively and stirred for 2 hours. After that, it was gradually added 1 g of KMnO<sub>4</sub> and stirred for 24 h to generate graphite solution. Subsequently, the solution was added 20 mL of H<sub>2</sub>SO<sub>4</sub> 5% and 1 mL of 30% H<sub>2</sub>O<sub>2</sub>, respectively and stirred for one hour. Then, the solution was centrifuged at a speed of 3000 Rotation per Minute (RPM) for 20 min. to separate the filtrate and supernatant. The filtrate was added 10 mL ammonia 10 M and stirred for 48 h and separate filtrate and precipitate. Finally, precipitate was dried at 80 oC for 24 h and characterized by using XRD and SEM-EDX, respectively.

No. of layers: Multi-layer

Author: Zhiyu Zou

Title: Operando atomic-scale study of graphene CVD growth at steps of polycrystalline nickel

DOI: 10.48550/arXiv.2001.07492

Year of publication: 2020

Abstract: An operando investigation of graphene growth on (100) grains of polycrystalline nickel (Ni) surfaces was performed by means of variable-temperature scanning tunneling microscopy complemented by density functional theory simulations. A clear description of the atomistic mechanisms ruling the graphene expansion process at the stepped regions of the substrate is provided, showing that different routes can be followed, depending on the height of the steps to be crossed. When a growing graphene flake reaches a monoatomic step, it extends jointly with the underlying Ni layer; for higher Ni edges, a different process, involving step retraction and graphene landing, becomes active. At step bunches, the latter mechanism leads to a peculiar 'staircase formation' behavior, where terraces of equal width form under the overgrowing graphene, driven by a balance in the energy cost between C-Ni bond formation and stress accumulation in the carbon layer. Our results represent a step towards bridging the material gap in searching new strategies and methods for the optimization of chemical vapor deposition graphene production on polycrystalline metal surfaces.

Method of producing graphene: Graphene was grown in a UHV chamber (base 5 pressure:  $1\times 10^{-10}$  mbar) by ethylene exposure ( $p = 5\times 10^{-8}-5\times 10^{-6}$  mbar) or via segregation from residual carbon at 400-500 oC.

No. of layers: Mono-layer

Author: Eldad Grady

Title: Resist and Transfer Free Patterned CVD Graphene Growth on ALD Molybdenum Carbide Nano Layers

DOI: 10.48550/arXiv.1911.06490

Year of publication: 2019

**Abstract:** Multilayer graphene (MLG) films were grown by chemical vapour deposition (CVD) on molybdenum carbide (MoCx) substrates. We fabricated the catalytic MoCx films by plasma enhanced atomic layer deposition (PEALD). The mechanism of graphene growth is studied and analysed for amorphous and crystalline MoCx films. In addition, the unique advantages of catalytic substrate PEALD are demonstrated in two approaches to graphene device fabrication. First, we present a complete bottom up, resist-free patterned graphene growth (GG) on pre-patterned MoCx PEALD performed at 50°C. Selective CVD GG eliminates the need to pattern or transfer the graphene film to retain its pristine, as grown, qualities. Furthermore, we fabricated MLG directly on PEALD MoCx on 100 nm suspended SiN membrane. We characterise the MLG qualities using Raman spectroscopy, and analyse the samples by optical microscopy, scanning electron microscopy and X-ray diffraction measurements. The techniques of graphene device manufacturing demonstrated here pave the path for large scale production of graphene applications.

**Method of producing graphene:** MoCx thin films have been deposited by plasma-enhanced atomic layer deposition (PEALD) at various temperatures and plasma conditions, as described elsewhere [17]. Preprint Preprint PEALD was performed on 100mm Si (100) wafers coated with 450nm of thermally grown SiO<sub>2</sub>. The depositions were performed in an Oxford Instruments FlexAL2 ALD reactor, which is equipped with an inductively coupled remote RF plasma (ICP) source (13.56MHz) with alumina dielectric tube. MoCx thin films have been deposited by PEALD at various temperatures and plasma conditions, with MoCx films varying from 15μm to 30μm in thickness. MLG was grown by low-pressure CVD (LPCVD) in a quartz tube (d=50mm, l=60cm) furnace with 3 heat zones set to 1050°C. The typical base pressure when evacuated is 10<sup>-3</sup>mbar. The furnace is set on cartwheels, to allow samples to be rapid annealed, as furnace temperatures stabilise within 3.5 minutes after tube insertion. When moved away from the furnace, sample cooling down duration is typically 15 minutes. Carbon feedstock gas (CH<sub>4</sub>) is fed along with Argon through a quartz inner tube of 5mm in diameter to the sealed side of the outer tube. MoCx film have been saturated with carbon by annealing at temperatures between 500°C to 800°C with 100 sccm CH<sub>4</sub> gas flow at 4mbar pressure. Then, graphene films have been grown under similar conditions at 1100°C for 10 minutes. The samples were then promptly extracted from the furnace and allowed to cool down at ambient room temperature under Argas flow in the quartz tube. As shown in figure 3 a photoresist (PR) ma-N400 with 4.1μm thickness on 90nm SiO<sub>2</sub> on Si2" wafers were used for low temperature PEALD of MoCx film. After deposition, MoCx was patterned by lift-off process, and rinsed in isopropyl alcohol (IPA). 100nm and 50nm SiN membranes were supplied by Philips Innovation Services (PInS) foundry. MoCx were also deposited at 300°C on 100nm SiN membranes suspended on Si (5x5mm suspended rectangular area). MLG were then grown the MoCx films.

No. of layers: Multi-layer

Author: Andrea Capasso

Title: CVD-graphene/graphene flakes dual-films as advanced DSSC counter electrodes

DOI: 10.48550/arXiv.1910.14625

Year of publication: 2019

**Abstract:** The use of graphene-based electrodes is burgeoning in a wide range of applications, including solar cells, light emitting diodes, touch screens, field-effect transistors, photodetectors, sensors and energy storage systems. The success of such electrodes strongly depends on the implementation of effective production and processing methods for graphene. In this work, we take advantage of two different graphene production methods to design an advanced, conductive oxide- and platinum-free, graphene-based counter electrode for dye-sensitized solar cells (DSSCs). In particular, we exploit the combination of a graphene film, produced by chemical vapor deposition (CVD) (CVD-graphene), with few-layer graphene (FLG) flakes, produced by liquid phase exfoliation. The CVD-graphene is used as charge collector, while the FLG flakes, deposited atop by spray coating, act as catalyst for the reduction of the electrolyte redox couple (i.e., I<sub>3</sub>-I<sup>-</sup> and Co<sup>+2/+3</sup>). The as-produced counter electrodes are tested in both I<sub>3</sub>-I<sup>-</sup> and Co<sup>+2/+3</sup>-based semitransparent DSSCs, showing power conversion efficiencies of 2.1% and 5.09%, respectively, under 1 SUN illumination. At 0.1 SUN, Co<sup>+2/+3</sup>-based DSSCs achieve a power conversion efficiency as high as 6.87%. Our results demonstrate that the electrical, optical, chemical and catalytic properties of graphene-based dual films, designed by combining CVD-graphene and FLG flakes, are effective alternatives to FTO/Pt counter electrodes for DSSCs for both outdoor and indoor applications.

**Method of producing graphene:** Continuous films of graphene were synthesized on Cu foil (Sigma Aldrich, thickness 20  $\mu$ m, 99.999%) by CVD by using a cold-wall reactor with methane as a carbon precursor[200]. The Cu foil was loaded into the CVD reactor, which was then heated to 1060°C in Ar atmosphere to anneal the foil for 10 min. After this annealing step, the graphene growth was performed at 1060 °C for 10 min (pressure of 25 mbar) by flowing CH<sub>4</sub> (2 sccm), H<sub>2</sub> (20 sccm) and Ar (1000 sccm). The CVD reactor was then cooled down to 120 °C before removing the samples to prevent substrate oxidation. Samples of CVD-graphene of 1×1 cm<sup>2</sup> size were transferred to glass or SiO<sub>2</sub> substrates using wet transfer technique with poly(methyl methacrylate) (PMMA) as support medium[201]. Briefly, a thin layer of PMMA (2% solution in acetyl lactate, All resist GmbH) was deposited onto Cu/graphene by spin coating, and dried for 1 h at ambient conditions. The as-obtained samples were immersed in a 0.05 M solution of iron(III) chloride (FeCl<sub>3</sub>, Sigma-Aldrich) for 16 h to etch the Cu and release the graphene/PMMA film. Once the Cu was completely etched away, the graphene/PMMA membrane was removed from the FeCl<sub>3</sub> solution using a glass slide and transferred to deionized water several times to remove the etchant residue. Subsequently, the membrane was removed from the water using glass or SiO<sub>2</sub> substrates, and dried at ambient conditions. Finally, the PMMA support film was removed by immersing the sample in acetone (Sigma Aldrich) for 4 h and then rinsed in 2propanol (Sigma Aldrich). Graphene flakes production via LPE of graphite. The graphene flakes were produced by the LPE[114,147,148,192], followed by SBS[114,189,192] of pristine graphite (+100 mesh, ~75% min, Sigma Aldrich) in N-Methyl-2-pyrrolidone (NMP) (99.5% purity, Sigma Aldrich). Experimentally, 1 g of graphite was dispersed in 100 mL of NMP and ultrasonicated in a bath sonicator (Branson 5800 cleaner, Branson Ultrasonics) for 3 h. The resulting dispersion was then ultracentrifuged at 4300 g (in Beckman Coulter Optima XE?90 with a SW32Ti rotor) for 30 min at 15 °C, exploiting SBS to remove thick flakes and un-exfoliated graphite[202,203]. Subsequently, the supernatant (~80% of the dispersion) was collected by pipetting,

No. of layers: Few-layer flakes

Author: Tijana Tomasevic-Ilic

Title: Reducing sheet resistance of self-assembled transparent graphene films by defect patching and doping with UV/ozone treatment

DOI: 10.1016/j.apsusc.2018.07.111.

Year of publication: 2018

**Abstract:** Liquid phase exfoliation followed by Langmuir-Blodgett self-assembly (LBSA) is a promising method for scalable production of thin graphene films for transparent conductor applications. However, monolayer assembly into thin films often induces a high density of defects, resulting in a large sheet resistance that hinders practical use. We introduce UV/ozone as a novel photochemical treatment that reduces sheet resistance of LBSA graphene threefold, while preserving the high optical transparency. The effect of such treatment on our films is opposite to the effect it has on mechanically exfoliated or CVD films, where UV/ozone creates additional defects in the graphene plane, increasing sheet resistance. Raman scattering shows that exposure to UV/ozone reduces the defect density in LBSA graphene, where edges are the dominant defect type. FTIR spectroscopy indicates binding of oxygen to the graphene lattice during exposure to ozone. In addition, work function measurements reveal that the treatment dopes the LBSA film, making it more conductive. Such defect patching paired with doping leads to an accessible way of improving the transparent conductor performance of LBSA graphene, making solution-processed thin films a candidate for industrial use.

**Method of producing graphene:** A graphene dispersion was prepared from graphite powder (Sigma Aldrich, product no. 332461) from a concentration of 18 mg ml<sup>-1</sup> in N-Methyl-2-pyrrolidone (NMP, Sigma Aldrich, product no. 328634), exposed to 14 hours of sonication in a low-power sonic bath. The resulting dispersion was centrifuged for 60 min at 3000 rpm in order to reduce the concentration of unexfoliated graphite. The resulting dispersions were used to form films approximately 3 nm thick by LBSA, in the same way that we demonstrated in our previous work [12, 21]. A small amount of graphene dispersion is added to a water-air interface and after the film is formed, it is slowly scooped onto the target substrate (Figure 1a). Glass and SiO<sub>2</sub>/Si are used as substrates.

No. of layers: Multi-layer

Author: Ying Liu

Title: Dry transfer method for suspended graphene on lift-off-resist: simple ballistic devices with Fabry-P'erot interference

DOI: 10.48550/arXiv.1903.03780

Year of publication: 2018

**Abstract:** We demonstrate a fabrication scheme for clean suspended structures using chemical-vapor-deposition-grown graphene and a dry transfer method on liftoff-resist-coated substrates to facilitate suspended graphene nanoelectronic devices for technology applications. It encompasses the demands for scalable fabrication as well as for ultra-fast response due to weak coupling to environment. The fabricated devices exhibited initially a weak field-effect response with substantial positive (p) doping which transformed into weak negative (n) doping upon current annealing at the temperature of 4 Kelvin. With increased annealing current, n-doping gradually decreased while the Dirac peak position approached zero in gate voltage. An ultralow residual charge density of  $9 \times 10^8$  cm<sup>-2</sup> and a mobility of  $1.9 \times 10^5$  cm<sup>2</sup>/Vs were observed. Our samples display clear Fabry-P'erot (FP) conductance oscillation which indicates ballistic electron transport. The spacing of the FP oscillations are found to depend on the charge density in a manner that agrees with theoretical modeling based on Klein tunneling of Dirac particles. The ultra-low residual charge, the FP oscillations with density dependent period, and the high mobility prove excellent quality of our suspended graphene devices. Owing to its simplicity, scalability and robustness, this fabrication scheme enhances possibilities for production of suspended, high-quality, two-dimensional-material structures for novel electronic applications.

**Method of producing graphene:** First, a polydimethylsiloxane (PDMS) stamp was prepared and the graphene on copper foil was placed on the PDMS stamp with the graphene facedown. The copper foil was gently pressed onto the stamp in order to make graphene to adhere well to PDMS. The Cu/graphene/PDMS stamp was placed in Cu etchant (1M FeCl<sub>3</sub>) to remove the copper, followed by repeated rinsing in deionized water. To further remove etch residues from the graphene surface, the graphene-PDMS stamp was cleaned using the modified RCA method [20]. The substrate for graphene transfer was prepared by spin-coating two layers of LOR-3A resist (PMGI-based organic polymer from MicroChem) on p++ silicon substrate capped with 285-nm-thick SiO<sub>2</sub>. Each LOR layer resulted in a thickness of about 250nm. The cleaned Graphene-PDMS stamp and the LOR coated substrate were then mounted onto a home-made dry transfer setup. The stamp was next aligned and brought into contact with the substrate, after which the stamp was peeled off of the substrate. When the stamp was peeled off slowly, uninterrupted graphene transfer could be achieved leading to the graphene covering the entire substrate.

No. of layers: 1-2 layers

Author: Sheng Yang

Title: Organic Radical-Assisted Electrochemical Exfoliation for the Scalable Production of High-Quality Graphene

DOI: 10.1021/jacs.5b09000

Year of publication: 2015

**Abstract:** Despite the intensive research efforts devoted to graphene fabrication over the past decade, the production of high-quality graphene on a large scale, at an affordable cost, and in a reproducible manner still represents a great challenge. Here, we report a novel method based on the controlled electrochemical exfoliation of graphite in aqueous ammonium sulfate electrolyte to produce graphene in large quantities and with outstanding quality. Because the radicals (e.g., HO<sup>•</sup>) generated from water electrolysis are responsible for defect formation on graphene during electrochemical exfoliation, a series of reducing agents as additives (e.g., (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO), ascorbic acid, and sodium borohydride) have been investigated to eliminate these radicals and thus control the exfoliation process. Remarkably, TEMPO-assisted exfoliation results in large graphene sheets (5–10  $\mu\text{m}$  on average), which exhibit outstanding hole mobilities ( $\sim$ 405  $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ ), very low Raman ID/IG ratios (below 0.1), and extremely high carbon to oxygen (C/O) ratios ( $\sim$ 25.3). Moreover, the graphene ink prepared in dimethylformamide can exhibit concentrations as high as 6 mg mL<sup>-1</sup>, thus qualifying this material for intriguing applications such as transparent conductive films and flexible supercapacitors. In general, this robust method for electrochemical exfoliation of graphite offers great promise for the preparation of graphene that can be utilized in industrial applications to create integrated nanocomposites, conductive or mechanical additives, as well as energy storage and conversion devices.

**Method of producing graphene:** Graphite exfoliation was conducted in a home-built setup that used rolled graphite foils as working electrodes and platinum foils as counter electrodes (Figure 1a). An aqueous solution containing ammonium sulfate with a range of reducing agents (e.g., ascorbic acid, gallic acid, hydrazine monohydrate, sodium borohydride (NaBH<sub>4</sub>), hydrogen iodide, TEMPO; chemical structures shown in Figure S1) was tested as an electrolyte. Before exfoliation, the graphite foil was pretreated by alternately soaking it in liquid nitrogen and absolute ethanol. During this process, violent nitrogen evolution and ethanol solidification promoted the expansion of the graphite foils. The dilation was extremely rapid (within 10 s) and yielded a drastic volume increase at the graphite boundary ( $\sim$ 10 times), which facilitated the expansion of the graphite layers, as did the following anion intercalation steps. When the graphite anodes were immersed in the electrolyte, by applying a static bias of 10 V, they detached into small pieces in less than 10 s, spreading on top of the electrolyte and/or on the bottom of the electrochemical cell. After filtration and copious washing, these exfoliated graphene sheets were collected and then dispersed in DMF via mild sonication. A stable dispersion with a concentration of  $\sim$ 0.3 mg mL<sup>-1</sup> was obtained that was stable for 2 weeks without apparent aggregation. The total exfoliation yield was calculated using the mass ratio of dried graphene powder and the starting graphite precursor. Among the reductants, gallic acid and hydrogen iodide were not stable after turning on the electrical voltage. Hydrazine promoted exfoliation in very limited yield (less than 10 wt %). The addition of ascorbic acid, sodium borohydride, or TEMPO into conventional ammonium sulfate electrolyte does not change the efficiency of graphite exfoliation. Especially, a high yield of 75 wt % has been achieved with the use of TEMPO. It is worth noting that to maintain a constant concentration of sodium borohydride, it should be added successively because its hydrolysis occurs spontaneously during the exfoliation process. Moreover, depending on the size of the graphite foil and the volume of the electrolyte, the throughput can be easily scaled up to tens of grams. For instance, a midsized electrochemical cell was tested in continuous exfoliation with two graphite foils (A4 size,  $\sim$ 30 cm  $\times$  20 cm), which enabled the production of  $\sim$ 15.1 g of graphene per hour.

No. of layers: 1–3 layers

Author: Bipinchandra K. Salunke

Title: Facile synthesis of graphene using a biological method

DOI: 10.1039/c5ra25977k

Year of publication: 2016

**Abstract:** A new, facile, low cost, environmentally safe process is demonstrated for the production of few layer graphene by liquid phase exfoliation of graphite using extracts of medicinal plants in water. Plant extracts possibly function as bio-surfactants by creating a barrier in the aggregation by adsorbing on to the exposed surfaces of the graphite, weakening the attraction between the layers created by the van der Waals forces and allowing the graphite to slowly exfoliate in the form of undamaged flakes.

**Method of producing graphene:** The approach included low power sonication of expanded graphite (Samjung C & G, Korea, 1–10 g L<sup>-1</sup>) in plant extracts (50 g L<sup>-1</sup>) for 24 hours by maintaining the temperature lower than 30C with continuous flow of water in the ultrasonication bath (JACUltrasonic 4020P). After sonication, the dispersion was left to sit overnight to enable separation of large unstable graphite aggregates. The stably dispersed solution of graphene was collected and centrifuged at 1500 rpm for 90 min to get graphene solution which was used for further testing.

No. of layers: Multi-layer

Author: Nicolas Reckinger

Title: Restoring self-limited growth of single-layer graphene on copper foil via backside coating

DOI: 10.1039/C8NR09841G

Year of publication: 2019

**Abstract:** The growth of single-layer graphene (SLG) by chemical vapor deposition (CVD) on copper surfaces is very popular because of the self-limiting effect that prevents the growth of few-layer graphene (FLG). However, the reproducibility of the CVD growth of homogeneous SLG remains a major challenge, especially if one wants to avoid heavy surface treatments, monocrystalline substrates and expensive equipment to control the atmosphere inside the growth system. We demonstrate here that backside tungsten coating of copper foil allows the exclusive growth of SLG with full coverage by atmospheric pressure CVD implemented in a vacuum-free outfit. We show that the absence of FLG patches is related to the absence of decomposition of methane on the backside and consequently to the suppression of C diffusion through copper. In the perspective of large-scale production of graphene, this approach constitutes a significant improvement to the traditional CVD growth process since (1) a tight control of the hydrocarbon flow is no longer required to avoid FLG formation and, consequently, (2) the growth duration necessary to reach full coverage can be dramatically shortened.

**Method of producing graphene:** The samples are first laid on a flat fused silica boat and inserted into a tubular fused silica reactor at room temperature. An Ar flow of 2000 sccm is admitted for 15 min in the tube after sealing (purge step). Meanwhile, the hotwall furnace is pre-heated to 1050 °C. Next, the fused silica tube is introduced into the furnace and the Ar flow is reduced to 500 sccm. The sample is then exposed to Ar alone during 15 min and is oxidized at the surface due to residual oxidizing impurities. Thereafter, the Cu foil's surface is reduced for 45 min with the addition of 20 sccm of H<sub>2</sub>. Afterwards, dilute methane (CH<sub>4</sub>; 5% in 95% of Ar) is injected to grow graphene. For all the samples without W on the backside, the dilute CH<sub>4</sub> flow is set to 0.5 sccm, while it is variable otherwise (with a maximum of 3 sccm). The reactor is extracted 1 h later from the furnace after graphene growth and left to cool down naturally in the same gas mixture. The conditions corresponding to a dilute CH<sub>4</sub> flow of 0.5 sccm and a growth duration of 1 h are referred to as the “standard conditions” in the following. During the whole growth procedure, the reactor is maintained at atmospheric pressure (no pumping equipment connected to the system, which is called “vacuum-free”).

No. of layers: Mono-layer

Author: Woo Jin Hyun

Title: High-Resolution Patterning of Graphene by Screen Printing with a Silicon Stencil for Highly Flexible Printed Electronics

DOI: 10.1002/adma.201404133

Year of publication: 2015

**Abstract:** The integration of electronically functional materials using liquid-phase patterning technologies constitutes the core of the emergent field of printed electronics. [1] With applications spanning smart packaging, [2] distributed sensing, [3] flexible displays, [4] and energy management, [5] development of printed electronics offers the possibility of ubiquitous low-cost and flexible devices. [6] Central to this technology are high-performance functional inks and high-throughput printing methods such as inkjet, gravure, flexographic, and screen printing. [7] Graphene presents an attractive material for printed electronics due to its high conductivity, stability, and flexibility. Screen printing offers a particularly versatile strategy for the integration of graphene in a robust and practical printing process. In particular, high-resolution screen printing is desired to improve the device density and performance of electronic devices, but this requires advances in both ink design and printing methods. Here, we address these challenges with a novel strategy for high-resolution screen printing using a silicon stencil coupled with a high conductivity, flexible, pristine graphene ink.

**Method of producing graphene:** Natural graphite flake (20.0 g, Asbury Graphite Mills, 3061 Grade) was dispersed in a solution of ethyl cellulose (EC) in ethanol (0.1% w/v dispersion, 200 mL; EC: Aldrich, viscosity 4 cP, 5% in toluene/ethanol 80:20, 48% ethoxy; ethanol: Koptec, 200 proof) in a stainless steel beaker. A probe sonication system (Fisher Scientific Sonic Dismembrator Model 500, 13 mm Branson tip) was used to sonicate the dispersion for 105 min at 50 W in an ice water bath to exfoliate graphene sheets. The resulting dispersion was centrifuged (Beckman Coulter Avanti J-26 XPI) at 5000 rpm (?4500 g) for 15 min, and the supernatant was collected. This dispersion was further centrifuged at 7500 rpm (?10 000 g) for 15 min, and the sediment was collected. The wet sediment was redispersed with ethanol (25 mL ethanol per 1.0 g sediment) and EC (100 mg EC per 2.0 g sediment; EC: Aldrich, viscosity 22 cP, 5% in toluene/ethanol 80:20, 48% ethoxy) by bath sonication for 3 h. This dispersion was passed through a 3.1-?m-glass fiber filter membrane (Acrodisc). It was then mixed with an aqueous solution of NaCl (0.04 g mL ?1, Sigma-Aldrich, >99.5%) in a 16:9 weight ratio and centrifuged at 7500 rpm for 8 min, after which the supernatant was removed. To remove residual salt, the resulting graphene-EC solid was suspended in water, bath sonicated for 20 min, and collected by centrifugation at 7500 rpm for 10 min. This isolated graphene-EC composite was then dried to yield a powder. This process was repeated to produce enough material for

ink production. Thermogravimetric analysis of this powder revealed 78.3% mass retention at 400 °C, estimated to reflect the graphene solids content (temperature ramp at 10 °C min ?1 in air). AFM characterization was performed on samples dropcast on Si/SiO<sub>2</sub> wafers. Si/SiO<sub>2</sub> wafers were cleaned by sonication in acetone and isopropanol. They were then immersed in a solution of 2.5 × 10 ?3 M 3-aminopropyl triethoxysilane (Aldrich, 99%) in isopropanol for 30 min. A diluted dispersion of= graphene/EC in ethanol was dropcast onto the wafers and left for 10 min. After blowing the wafers dry with N<sub>2</sub> and rinsing with isopropanol, they were annealed in air at 400 °C in a tube furnace for 30 min to remove the EC.

No. of layers: Multi-layer

Author: Thomas H. Bointon

Title: High Quality Monolayer Graphene Synthesized by Resistive Heating Cold Wall Chemical Vapor Deposition

DOI: 10.1002/adma.201501600

Year of publication: 2015

Abstract: The growth of graphene using resistive-heating cold-wall chemical vapor deposition (CVD) is demonstrated. This technique is 100 times faster and 99% lower cost than standard CVD. A study of Raman spectroscopy, atomic force microscopy, scanning electron micro-scopy, and electrical magneto-transport measurements shows that cold-wall CVD graphene is of comparable quality to natural graphene. Finally, the first transparent flexible graphene capacitive touch-sensor is demonstrated.

Method of producing graphene: 25  $\mu$ m thick copper foils (Alfa Aesar 99.999%) were annealed for 10 minutes at 1035oC in a H<sub>2</sub> atmosphere to increase the Cu grain size. To understand the initial stages of graphene formation, the growth was carried out at temperatures ranging from 950oC to 1035oC and the growth time was varied from 10 seconds to 600 seconds. A constant flow rate of 0.4sccm of H<sub>2</sub> and 1.4sccm of CH<sub>4</sub> was used for all growths. A typical processing for the growth of continuous graphene films involves the following steps: (1) heating up the CVD system from room temperature to the growth temperature, (2) Cu foil annealing, (3) graphene nucleation and growth, (4) cooling down the system to room temperature (see Figure S5). During the heating up stage H<sub>2</sub> gas was flown at a rate of 0.4sccm with a chamber pressure of 0.01 Torr. The annealing step was performed for 10 minutes at 1035oC in a H<sub>2</sub> atmosphere, keeping the H<sub>2</sub> gas flow rate at 0.4sccm and the chamber pressure of 0.01 Torr. The temperature was then lowered at 1000oC for the growth of continuous graphene films. A constant flow rate of 0.4sccm of H<sub>2</sub> was kept throughout the nucleation and growth. For the nucleation stage, 1.4sccm of CH<sub>4</sub> was introduced for 40 seconds. This was followed by the growth stage where the CH<sub>4</sub> flow rate was increased to 7sccm for a 300 seconds. Finally, the system was cooled down at room temperature keeping the H<sub>2</sub> gas flow rate at 0.4sccm.

No. of layers: Mono-layer

Author: Mohammad Shafri Ismail

Title: Synthesis and characterization of graphene derived from rice husks

DOI: 10.11113/mjfas.v15n4.1228

Year of publication: 2018

**Abstract:** Graphene was successfully synthesized by activating rice husk ash (RHA) using potassium hydroxide (KOH) at 800 oC with 1:2 impregnation ratio. Raman spectroscopy analysis confirmed the presence of graphitic structure. The demonstrated methodology utilizes RHA as carbon source and used as sacrifice to prevent oxidation during synthesis process on the mixture of KOH and RHA against air at high temperature. The novelty of this synthesis methodology use environmentally-friendly biomass resource as a starting material, does not utilize catalysts, and prove that graphene can be synthesized at a relatively low synthesis temperature.

**Method of producing graphene:** The synthesis process of rice husk-derived graphene was performed in accordance with the process described by Muramatsu et al. (2014). As shown in Figure 4, 5 g of raw rice husk was grounded and treatment inside Carbolite furnace for 2 hours at 400 °C. The solid residue obtained were called as rice husk ash (RHA). Then, the RHA was chemically activated using KOH with impregnation ratio of 1:2 of KOH powder. The mixture was then compacted in a ceramic crucible. Next, the crucible was placed in the midpoint of a larger ceramic crucible. As shown in Figure 6, the empty space around ceramic crucible was fully covered by sufficiently pressing and packing the sacrificial RHA. The sacrificial RHA used to prevent oxidation on the mixture against air at high temperature. The crucibles were heated at 800 oC for 2 hours. Treatment was carried out as shown in Figure 7 where the chemically activated RHA was poured in 50 ml deionized water (DI water) and stirred for 30 minutes to remove potassium ions residue. The sample was centrifuged at 3200 round per minutes (RPM) for 30 minutes. Then, the sample was sonicated in 100 ml of DI water for 3 minutes with amplitude of 50%. After that, the sample was rinsed in 50 ml DI water using vacuum filtration over a PTFE membrane with 0.22 mm pore size. Next, the sample was dried in vacuum oven for 24 hours at 80 °C to remove moisture.

No. of layers: Multi-layer

Author: Leila Shahriary

Title: Synthesis of graphene using gamma radiations

DOI: 10.1007/s12034-015-0889-9

Year of publication: 2014

**Abstract:** Considering the advantages of radiolytic synthesis such as the absence of toxic chemical as a reducing agent, uniform distribution of reducing agent and high purity of product, the synthesis of graphene (rGO) from graphene oxide (GO) by the gamma irradiation technique using a relatively low dose rate of 0.24 kGy h<sup>-1</sup> has been described. Structural and physicochemical properties of GO and rGO were investigated with the help of various characterization techniques. The presence of peak at 271 nm in ultraviolet-visible spectrum, C=C aromatic stretching vibrations between 1450 and 1600 cm<sup>-1</sup> in the Fourier transform infrared spectrum and significant decrease in photoluminescence peak intensity at 470 and 567 nm wavelengths represent the reduction of GO to graphene by gamma irradiation. The decrease in stacking height from 7.71 nm in GO to 3.52 nm in rGO as observed from the X-ray powder diffraction analysis further confirms the same. Raman spectra show significantly lower D to G band ratio for rGO compared with GO. Also, the cyclic voltammograms obtained using GO- and rGO-modified electrodes (working electrode) in standard redox system show enhanced peak intensities together with decrease in potential difference between oxidation and reduction peaks in case of graphene.

**Method of producing graphene:** GO was synthesized from graphite powder using modified Hummer's method.<sup>31</sup> In brief, 1 g of graphite and 0.5 g of sodium nitrate were mixed together followed by the addition of 23 ml of conc. sulphuric acid under constant stirring. After 1 h, 3 g of KMnO<sub>4</sub> was added gradually to the above solution while keeping the temperature less than 20°C to prevent overheating and explosion. The mixture was stirred at 35°C for 1 h and the resulting solution was diluted by adding 500 ml of water under vigorous stirring. To ensure the completion of reaction with KMnO<sub>4</sub>, the suspension was further treated with 30% H<sub>2</sub>O<sub>2</sub> solution (5 ml). The resulting mixture was washed with HCl and H<sub>2</sub>O followed by filtration and drying, the GO sheets were thus obtained. GO (5 mg) was dispersed in 10 ml of ethanol-water (1 : 1) mixture using ultrasonic bath for 30 min. The dispersion was transferred into a glass bottle fitted with a septum. The dissolved oxygen was removed by bubbling nitrogen gas for 10 min. The samples were irradiated in a 60Co gamma-ray source at a dose rate of 0.24 kGy h<sup>-1</sup> for different doses (2.88– 14.40 kGy). The product so obtained was collected and washed with Milli-Q water and dried under vacuum. Similar procedure was adopted for other alcohols.

No. of layers: Multi-layer

Author: Uk Sim

Title: Double-Layer Graphene Outperforming Monolayer as Catalyst on Silicon Photocathode for Hydrogen Production

DOI: 10.1021/acsami.6b11750

Year of publication: 2017

**Abstract:** Photoelectrochemical cells are used to split hydrogen and oxygen from water molecules to generate chemical fuels to satisfy our ever-increasing energy demands. However, it is a major challenge to design efficient catalysts to use in the photoelectrochemical process. Recently, research has focused on carbon-based catalysts, as they are nonprecious and environmentally benign. Interesting advances have also been made in controlling nanostructure interfaces and in introducing new materials as catalysts in the photoelectrochemical cell. However, these catalysts have as yet unresolved issues involving kinetics and light-transmittance. In this work, we introduce high-transmittance graphene onto a planar p-Si photocathode to produce a hydrogen evolution reaction to dramatically enhance photon-to-current efficiency. Interestingly, double-layer graphene/Si exhibits noticeably improved photon-to-current efficiency and modifies the band structure of the graphene/Si photocathode. On the basis of in-depth electrochemical and electrical analyses, the band structure of graphene/Si was shown to result in a much lower work function than Si, accelerating the electron-to-hydrogen production potential. Specifically, plasma-treated double-layer graphene exhibited the best performance and the lowest work function. We electrochemically analyzed the mechanism at work in the graphene-assisted photoelectrode. Atomistic calculations based on the density functional theory were also carried out to more fully understand our experimental observations. We believe that investigation of the underlying mechanism in this high performance electrode is an important contribution to efforts to develop high-efficiency metal-free carbon-based catalysts for photoelectrochemical cell hydrogen production.

**Method of producing graphene:** Monolayer graphene was synthesized using thermal CVD. First, a copper (Cu) foil ( $10 \times 10 \text{ cm}^2$ ) was placed in a quartz tube and heated to  $1000^\circ\text{C}$  for 60 min with flowing H<sub>2</sub> at 10 sccm. Then, a gas mixture of 45 sccm CH<sub>4</sub> and 10 sccm H<sub>2</sub> flowed for 30 min under 10 Torr. After 30 min, the heater was turned off and removed from the Cu foil. Next, to handle the monolayer graphene on the front side of the Cu foil, a protective layer of poly(methyl methacrylate) (PMMA) was spin-coated on the graphene on the front side of the Cu foil, and the graphene on the back was removed using oxygen plasma (100 W RF power, 12 s). Then, the PMMA film on the graphene was removed using acetone, and the remaining Cu was etched away using a 0.1 M ammonium persulfate solution. Finally, the monolayer graphene was rinsed in deionized water and transferred onto a p-type silicon substrate without a silicon oxide layer. For the various stacked graphene layers, graphene with PMMA was floated on deionized water and transferred onto another graphene layer on Cu and etched/rinsed again. The transfer and etching/rinsing procedure was repeated for up to 4 layers of graphene. To synthesize graphene with defects, the monolayer graphene on the back side of the copper was removed using oxygen plasma, and the graphene on the front side of the Cu was treated with argon plasma (10 W RF power, 4 s). The PMMA layer was coated onto this graphene, and the Cu foil was removed. Then, the treated graphene was transferred onto silicon or used in the stacking process.

No. of layers: Mono-layer

Author: Adam J. Cooper

Title: Single stage electrochemical exfoliation method for the production of few-layer graphene via intercalation of tetraalkylammonium cations

DOI: 10.1016/j.carbon.2013.09.009

Year of publication: 2013

Abstract: We present a non-oxidative production route to few layer graphene via the electrochemical intercalation of tetraalkylammonium cations into pristine graphite. Two forms of graphite have been studied as the source material with each yielding a slightly different result. Highly orientated pyrolytic graphite (HOPG) offers greater advantages in terms of the exfoliate size but the source electrode set up introduces difficulties to the procedure and requires the use of sonication. Using a graphite rod electrode, few layer graphene flakes (2 nm thickness) are formed directly although the flake diameters from this source are typically small (ca. 100–200 nm). Significantly, for a solvent based route, the graphite rod does not require ultrasonication or any secondary physical processing of the resulting dispersion. Flakes have been characterized using Raman spectroscopy, atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS).

Method of producing graphene: Two types of working electrode (HOPG and a graphite rod) were employed in the 3-electrode system, which also consisted of a platinum wire counter electrode and silver wire (with glass frit) or platinum wire as the pseudo-reference electrode. However, to facilitate comparison with other work, all potentials are quoted with respect to a Ag/AgClO<sub>4</sub> reference electrode, constructed by placing a silver wire in a solution of 0.01 M AgClO<sub>4</sub> and 0.1 M TBAClO<sub>4</sub> in NMP. The reference solution is separated from the bulk electrolyte by a glass frit (Vycor®, Scientific and Medical Products Ltd., Cheadle, UK) and sealed via heat shrink. For reference, the potential of the ferrocene couple (FeCp<sub>2</sub>=FeCp<sub>2</sub><sup>+</sup>) in NMP was found to be 0.428 Vvs. Ag/AgClO<sub>4</sub>.

Tetraalkylammoniumcationswere chosen as the intercalating species. Tetramethylammonium perchlorate (TMA ClO<sub>4</sub>), tetraethylammonium tetrafluoroborate (TEA BF<sub>4</sub>), and tetrabutylammonium tetrafluoroborate (TBA BF<sub>4</sub>), were employed as electrolytes. The electrolyte (0.1 M) was dissolved in NMP (10 mL) in a 3-neck round bottom flask. All potentials were controlled by a PGSTAT100 potentiostat (Autolab, Utrecht, The Netherlands) using Autolab GPES software.

No. of layers: 2-5 layers

Author: Muhammad Ashraf Saiful Badri

Title: Green synthesis of few-layered graphene from aqueous processed graphite exfoliation for graphene thin film preparation

DOI: 10.1016/j.matchemphys.2017.02.029

Year of publication: 2017

**Abstract:** The development of an approach for producing a very low defect graphene with simple and green technique is essential for highly conductive graphene thin film preparation. This paper describes the preparation of graphene thin film from aqueous processed graphene dispersion using alkaline lignin (AL) as surfactant, a low cost route to produce high yield ( $0.72 \pm 0.05$  mg/mL) with free structural defect of graphene sheets. In this work, the cationic properties of AL adsorbed on the exfoliated graphene sheet surfaces are easily removed via centrifugation, thermal and annealing treatments so that prepared graphene thin films exhibit good electrical conductivity and defect ratio reduction. Using optimum AL solution with concentration of 0.5 mg/mL, the precursor graphite is successfully being exfoliated into few layer graphene sheets (<4 layers) without significant basal plane defects as verified by XRD and Raman spectroscopy with the ratio of D band and G band intensities (ID/IG) value as low as 0.17. The mechanism of graphene dispersion formation are elucidated and thin layer of conductive graphene films are deposited onto cleaned substrates via dip coating technique. Untreated graphene thin film exhibited an electrical conductivity around 615.8 S/m at room temperature, surprisingly, the improvement of electrical conductivity as high as 5376.3 S/m is obtain after thermal and annealing treatments. The prepared graphene thin film also demonstrated a very high transparency in visible region at 550 nm ( $\square 90\%$ ).

**Method of producing graphene:** 2.2. Preparation of graphene dispersion Graphene dispersion was synthesized following to Liu and his group [17] method with modification. In our method, the chosen amounts of AL (0.4 mg/mL) were added to 20 mL scintillation vials and the AL solutions were bath sonicated for 15 min 40 mg/mL of graphite was added to each AL solution and all the mixtures were stirred for 15 min at room temperature. The mixtures were then ice bath sonicated for another 5 h maintaining the temperature of the bath below 35 C. The resulting dispersions were left undisturbed overnight and then centrifuged for 90 min at 600 rpm. After centrifugation, the supernatant was carefully removed by micropipette and stable graphene dispersion was obtained. This dispersion was then transferred to a 50 mL Teflon-lined autoclave and maintained at 200 C for 2 h for thermal treatment. After that, graphene dispersion was added with 5 mL of deionized water and centrifuged at 600 rpm for 90 min to remove free AL from uniform graphene dispersion. 2.3. Preparation of graphene thin films The acquired graphene dispersion was vacuum-filtered onto a mixed cellulose membrane (mixtures of cellulose acetate and cellulose nitrate, 0.025 mm pore size, 47 mm diameter). The filter cake was washed with excess deionized water for three times and then re-dispersed in n-butyl acetate by bath sonication for 30 min. Then, graphene thin films were prepared through dip coating onto suitable substrates (PET, quartz and glass) using dip coater instrument. The annealing of prepared graphene thin film was carried out at 200 C for 5 h in argon atmosphere to increase the conductivity of graphene film. 2.4. Procedure for dip coating system All deposition parameters such as substrate immersion and removal speed, substrate immersion time, drying time and dipping cycle can be controlled by dip coater instrument. Deposition of graphene dispersion onto cleaned substrates (PET, glass and quartz) were started by filling the number of dipping cycles (either 1, 2 or 3 cycles) in the setting. The immersion and removal speed used were 0.57 cm/min and 0.27 cm/min respectively. The immersion time and drying time for the substrates in each cycles were 1 min for all samples.

No. of layers: Multi-layered graphene (>5 layers)

Author: Teresa Campo

Title: Graphene Synthesis by Plasma-Enhanced CVD Growth with Ethanol

DOI: 10.3844/ajeassp.2016.574.583

Year of publication: 2016

**Abstract:** A modified route to synthesize graphene flakes is proposed using the Chemical Vapor Deposition (CVD) technique, by using copper substrates as supports. The carbon source used was ethanol, the synthesis temperature was 950°C and the pressure was controlled along the whole process. In this CVD synthesis process the incorporation of the carbon source was produced at low pressure and 950°C inducing the appearance of a plasma blue flash inside the quartz tube. Apparently, the presence of this plasma blue flash is required for obtaining graphene flakes. The synthesized graphene was characterized by different techniques, showing the presence of non-oxidized graphene with high purity.

**Method of producing graphene:** After cleaning, copper substrates were placed into a quartz boat and introduced in a cylindrical quartz reactor (inner diameter of 25 mm and 1 m-length) within a tube furnace. The quartz reactor was maintained at an initial vacuum of 10–2 Torr using a mechanical pump. Figure 1 shows the scheme of the synthesis procedure. The temperature was risen to 950°C, at a rate of 30°C/min (Guermoune et al., 2011). Samples were maintained at this temperature for 26 min, using an H<sub>2</sub> constant flow of 10 sccm to remove possible organic impurities. After the first 20 min of this step, a flow mixture of N<sub>2</sub> gas and ethanol vapor (30 sccm), previously generated by an overpressure of N<sub>2</sub>, was introduced into the reactor. In this moment, a blue plasma discharge was generated. At the same time, the reactor pressure increases to 102 Torr during a few seconds until the pressure stabilizes at 1 Torr. Once the growth time finishes, a cooling process takes place. During the first 30 min of the cooling step, a constant flow of H<sub>2</sub> 10 sccm is maintained and, after that, an Ar flow of 300 sccm is introduced into the reactor.

No. of layers: Few-layered graphene ( <5 layers)

Author: Feng Chen

Title: Facile synthesis of few-layer graphene from biomass waste and its application in lithium ion batteries

DOI: 10.1016/j.jelechem.2016.02.035

Year of publication: 2016

**Abstract:** Graphene is an appealing two-dimensional material with superior mechanical, electrical, and thermal properties. Mass production of high-quality graphene is attracting more and more researchers' attention in recent years. Most of the current methods for synthesizing graphene use purified chemical reagents that could be expensive for large-scale production. In this study, we have developed a less expensive method to synthesize high-quality graphene sheets from wheat straw via a combined hydrothermal and graphitization approach. The resulting graphene sheets show favorable features such as ultrathin nanosheet frameworks (2–10 atomic layers), high graphitization (up to 90.7%), graphite-like interlayer spacing (0.3362 nm), and the mesoporous structure. When used as an anode material for lithium ion batteries, the few-layer graphene delivers high reversible capacity (502 mAh g<sup>-1</sup> at 0.1 C), superior rate capability (463.5, 431.4, and 306.8 mAh g<sup>-1</sup> at 1, 2, and 5 C, respectively), and good cycling performance (392.8 mAh g<sup>-1</sup> at 1 C after 300 cycles). The wheat straw-derived graphene sheets also display the relatively flat voltage profiles with a negligible charge/discharge voltage hysteresis. Moreover, this low-cost, highly efficient, and catalyst-free technique is a significant milestone towards environmentally-sustainable, commercially feasible fabrication of carbon nanomaterials from renewable natural resources.

**Method of producing graphene:** Wheat straw was used as the starting material to obtain few-layer graphene by carbonization and graphitization of its hydrothermal product. Detailed steps are as follows: the raw material was first cut into small pieces (approximately 3 cm in length) and washed with distilled water, and then dried at 60 °C for 12 h before use. Within the subsequent hydrothermal treatment, 4 g of the washed wheat straw was immersed in a 400 mL Teflon-lined stainless steel autoclave wherein 280 mL of homogeneous 3 M KOH solution was contained, and then the autoclave was heated at a temperature of 150 °C for 6 h. When cooled down to room temperature naturally, the resulting samples were fetched out, collected by vacuum filtration with quantitative filter paper, washed by ultrasonication in 120 mL deionized water for 30 min and dried in an oven at 80 °C. The following high temperature pyrolysis and chemically activation was carried out at 800 °C for 3 h under the protection of N<sub>2</sub> atmosphere at a heating rate of 5 °C min<sup>-1</sup> and a N<sub>2</sub> flow rate of 150 cm<sup>3</sup> min<sup>-1</sup>. After that, the carbonaceous product was thoroughly washed with 0.5 M HCl solution to remove the residual KOH and dried in a vacuum oven at 80 °C for 12 h. Finally, the as prepared product was thermally treated at 2600 °C for 5 min using a graphite furnace in an argon atmosphere. The typical yield of few layer graphene by using wheat straw as starting material was found to be ca. 11.3 wt.%.

No. of layers: Few-layered graphene (<5 layers)

Author: Dandan Hou

Title: Facile synthesis of graphene via reduction of graphene oxide by artemisinin in ethanol

DOI: 10.1016/j.jmat.2018.01.002

Year of publication: 2018

**Abstract:** The preparation of reduced graphene oxide (RGO) by chemical reduction of graphene oxide (GO) usually involves highly toxic reducing agents which are harmful to the environment and human health. In this paper, a mediated facile and relative green approach for the preparation of RGO in ethanol using artemisinin as a reducing agent is reported for the first time. The morphology and de-oxidation efficiency of the obtained RGO were characterized by transmission electron microscope (TEM), atomic force microscope (AFM), and X-ray photoelectron spectroscopy (XPS). The results showed that artemisinin can effectively reduce GO into few-layered RGO with a high carbon to oxygen ratio (11.7). The mechanism for elimination of oxygen-containing functional groups decorated on GO nanosheets by artemisinin was proposed. The important features of relatively environmentally friendly and facile operation procedures endow this approach with great promise in the mass production of RGO and various graphene-based materials, especially for biomaterials.

**Method of producing graphene:** GO dispersions with concentration of 1 mg/mL were prepared by dispersing 100 mg GO in 100 mL ethanol with sonication for 1 h. Then 10 artemisinin was added into 100 mL GO dispersion, respectively. The mixtures were further sonicated for 60 min and placed into an electric-heated thermostatic waterbath for 24 h at 95 C. In order to clarify whether the reduction caused by artemisinin or just by ethanol, it is necessary to conduct a reduction experiment in ethanol without adding any artemisinin. Specifically, 0.1 g GO was placed in 100 mL ethanol and sonicated for 60 min followed by heating in water bath at 95 C for 24 h. It is noteworthy that because ethanol is more volatile than water, it needs to add 100 mL ethanol into the glass bottles every 6 h and screw down the lid fairly tightly. After reduction, the obtained RGO was washed three times with ethanol and DI-water, respectively, to remove the impurities.

No. of layers: Few layer graphene (3 layer)

Author: Dapeng Wei

Title: Laser direct synthesis of graphene on quartz

DOI: 10.1016/j.carbon.2012.11.026

Year of publication: 2012

**Abstract:** We demonstrate a laser-based technique to directly synthesize few layer graphene on quartz substrates without using any metal catalyst. In our approach, a photoresist S-1805 (from Shipley Comp.) film coated on quartz wafers was heated, and then decomposed, by irradiation of a continuous-wave laser. The carbon atoms from the photoresist were dissolved in the molten quartz, and then extracted to form graphene when the temperature of the quartz was decreased. Raman spectroscopy shows the as-produced graphene is two to three layers thick. This laser-based method will provide a new approach and platform for applications of graphene-based devices.

**Method of producing graphene:** Two 1 · 2 cm quartz wafers were used as substrate to grow graphene. The quartz wafers were first cleaned by ultrasonication in methanol, acetone, and DI water, and were dried by high purity N<sub>2</sub> gas. Photoresist S-1805 (from Shipley Comp.) was diluted with a volume ratio of 1:6 in Thinner-P (from MicroChem Corp.), and was then spin-coated on the quartz wafer at 10,000 rpm. The thickness of the coated film is about 30 nm. The photoresist-coated quartz wafers were then baked for 5 min at 120 C. One coated quartz wafer was covered by another piece of quartz wafer, and then mounted on a sample stage in a vacuum chamber. Before growing graphene, the chamber was pumped and purged by high-purity N<sub>2</sub> gas, and maintained at a pressure below 0.1 Torr. A continuous wave (CW) Nd:YAG laser with a wavelength of 532 nm was focused on the S-1805 film through the transparent quartz substrate using a lens of 150 mm focal length. The carbon atoms were decomposed from the laser heated photoresist, then dissolved in the molten quartz, and extracted to form graphene when the temperature of quartz was decreased. With our optical setup, the graphene was produced with a laser power of 2.8 W, irradiated for 3 min.

No. of layers: 2-3 layer

Author: Noha A. El Essawy

Title: Green synthesis of graphene from recycled PET bottle wastes for use in the adsorption of dyes in aqueous solution

DOI: 10.1016/j.ecoenv.2017.07.014

Year of publication: 2017

**Abstract:** Polyethyleneterephthalate (PET) is an important component of post-consumer plastic waste. This study focuses on the potential of utilizing "waste-treats-waste" by synthesis of graphene using PET bottle waste as a source material. The synthesized graphene is characterized by SEM, TEM, BET, Raman, TGA, and FT-IR. The adsorption of methylene blue (MB) and acid blue 25 (AB25) by graphene is studied and parameters such as contact time, adsorbent dosage were optimized. The Response Surface Methodology (RSM) is applied to investigate the effect of three variables (dye concentration, time and temperature) and their interaction on the removal efficiency. Adsorption kinetics and isotherm are followed a pseudo-second-order model and Langmuir and Freundlich isotherm models, respectively. Thermodynamic parameters demonstrated that adsorption of dye is spontaneous and endothermic in nature. The plastic waste can be used after transformation into valuable carbon-based nanomaterials for use in the adsorption of organic contaminants from aqueous solution.

**Method of producing graphene:** First, waste PET bottles were crushed and sieved to obtain the desired size fractions (1–3 mm) using a conventional sieve-shaker. Then 2 g of raw PET waste was introduced into an enclosed 50 mL stainless steel autoclave reactor (SS316). The closed stainless steel reactor was placed inside the center of an electric furnace and heated to 800 °C with a rate of 8 °C min<sup>-1</sup> and maintained at this temperature for 1 h. After that the system was left to cool overnight. The resulted dark products were collected and crushed. As it was illustrated in Fig. 1, the bottle wastes were used as a precursor for the synthesis of graphene.

No. of layers: Few layer graphene

Author: G. Deokar

Title: Towards high quality CVD graphene growth and transfer

DOI: 10.1016/j.carbon.2015.03.017

Year of publication: 2015

**Abstract:** We report on a facile, simple, and green graphene oxide (GO) reduction method based on a supercritical alcohol approach. The influence over the chemical, thermal, morphological, and textural properties of reduced graphene oxides (RGOs) of five different alcohols in their supercritical conditions – methanol, ethanol, 1-propanol, 2-propanol, and 1-butanol – was investigated in detail. Although the thermal stabilities and Fourier-transform infrared spectra of RGOs produced using the different alcohols are very similar, a substantial difference in the carbon-to-oxygen ratios measured by X-ray photoelectron spectroscopy and Brunauer–Emmett–Teller surface areas are observed. The RGO produced using supercritical ethanol exhibited a much higher carbon-to-oxygen ratio of 14.4 and a much larger surface area of 203m<sup>2</sup>/g compared with that produced using the other supercritical alcohols. Raman spectra showed that the RGOs produced using supercritical ethanol and supercritical 2-propanol retained more of the graphitic structure. X-ray diffraction analysis revealed that RGOs produced using supercritical 1-propanol and supercritical 1-butanol retained at least two different interlayer spacings. The deoxygenation mechanism of GO in supercritical ethanol is proposed based on gas and liquid product analysis.

**Method of producing graphene:** Graphene was synthesized on polycrystalline Cu foils (50 lm thick Alfa-Aesar, purity 99.9999%) in a rapid thermal processing CVD chamber, fitted with a pressure regulation device and temperature control by an optical pyrometer. The typical sample size was a few cm<sup>2</sup>. Cu foils were pre-cleaned in acetic acid at 35 °C for 10 min in order to remove the surface oxide [6]. The samples were immediately loaded in the CVD growth reactor and pumped to the base vacuum pressure (105 mbar). Then, the Cu foil was heated to 1060 °C and held for 5 min under Ar/H<sub>2</sub>:100/5 sccm (standard cubic centimeter per minute at standard temperature and pressure) with 10 Torr chamber pressure. Afterwards, the gaseous carbon source, CH<sub>4</sub> (20 sccm), was introduced for 5 min to carry out the graphene growth. Finally, the sample was fast cooled (30 °C/s) below 700 °C and further slowly to room temperature under H<sub>2</sub> and Ar ambient. A typical graphene growth process is shown schematically in Fig. 1. It should be noted that its total duration is only 30 min, which is much less than the process time in standard hot-wall furnaces [8].

No. of layers: Mono-layer

Author: G.G. Gebreegziabher

Title: One-step synthesis and characterization of reduced graphene oxide using chemical exfoliation method

DOI: 10.1016/j.mtchem.2019.02.003

Year of publication: 2019

**Abstract:** Graphene has many potential applications. Currently, its synthesis starts with the oxidation of graphite to graphene oxide followed by a separate reduction step. But, this leads to extra cost, prolonged time, and contamination. Here, we report the preparation of reduced graphene oxide (rGO) directly from graphite in a solution of potassium permanganate and concentrated sulfuric acid assisted by ultrasonication. The morphology, optical, chemical, thermal, microstructural, and electrical properties of prepared samples were studied using scanning transmission electron microscopy, selected area electron diffraction, ultraviolet-visible spectroscopy, Fourier-transform infrared spectroscopy, thermogravimetric analysis, Raman spectroscopy, X-ray powder diffraction, and cyclic voltammeter, respectively. The analysis confirms that quality of rGO with thickness (~0.36 nm) that can be dispersed in water with the desired properties was obtained. We can use this method to prepare rGO directly from graphite for energy storage.

**Method of producing graphene:** Synthesis of GO and rGO from graphite powder was achieved using H<sub>2</sub>SO<sub>4</sub>/KMnO<sub>4</sub> as oxidant upon heating on a hot plate with continuous stirring (900 rpm) for 24 h. Specifically, the 4 g of graphite and 400 mL of 98% H<sub>2</sub>SO<sub>4</sub> were placed in separate 1000 mL elementary flasks. The mixtures were then heated for 2 h at temperatures of 60C for one mixture and 120C for the other, under constant stirring using magnetic stirrer followed by the gradual addition of 10 g of KMnO<sub>4</sub> to each reaction mixture and heating these mixtures for the next 22 h under similar conditions. After the reaction mixture was cooled, 13 mL of 30% H<sub>2</sub>O<sub>2</sub> was added to complete the oxidation process followed by the addition of cold deionized water. Caution: Every preparation procedure must be done in a fume hood. Upon leaving the mixtures overnight, a yellow solution supernatant with brown precipitate was obtained from the sample prepared at 60C, while a clear supernatant solution with black precipitate was obtained from the sample heated at 120C. The obtained samples were purified by washing with deionized water in repeated ultracentrifugation (10,000 rpm) and vacuum filtration until the solutions become neutral and free of impurity. Acetone was added to remove water residual from the samples and ensure easy drying at room temperature. Finally, the solid samples were ultrasonicated for 40 min and made ready for characterization.

No. of layers: Few-layered graphene ( 5 layers)

Author: Ferial Ghaemi

Title: Synthesis of Different Layers of Graphene on Stainless Steel Using the CVD Method

DOI: 10.1186/s11671-016-1709-x

Year of publication: 2016

**Abstract:** In this study, different types of graphene, including single-, few-, and multi-layer graphene, were grown on a stainless steel (SS) mesh coated with Cu catalyst by using the chemical vapor deposition (CVD) method. Even though the SS mesh consisted of different types of metals, such as Fe, Ni, and Cr, which can also be used as catalysts, the reason for coating Cu catalyst on the SS surface had been related to the nature of the Cu, which promotes the growth of graphene with high quality and quantity at low temperature and time. The reaction temperature and run time, as the most important parameters of the CVD method, were varied, and thus led to the synthesis of different layers of graphene. Moreover, the presence of single-, few-, and multi-layer graphene was confirmed by employing two techniques, namely transmission electron microscopy (TEM) and Raman spectroscopy. On top of that, electron dispersive X-ray (EDX) was further applied to establish the influence of the CVD parameters on the growth of graphene.

**Method of producing graphene:** In this work, stainless steel (150 meshes, NE Scientific Co., Malaysia) that comprised of 50- $\mu\text{m}$  diameter fibers was purchased and applied as a substrate to synthesize the graphitic structures on its surface. The composition of the SS mesh was obtained by using EDX and is given in the following: C 0 wt%, Si 0.53 wt%, Cr 19.10 wt%, Ni 8.6 wt%, and Fe 70.3 wt%, while the rest had been related to other components. The pristine SS mesh was cut into a circle shape with 2-cm diameter and immersed into 9 M sulfuric acid solution for a few minutes to pretreat the SS surface. After that, the SS mesh was immersed into 50 mM Cu(NO<sub>3</sub>)<sub>2</sub>.3H<sub>2</sub>O solution and sonicated for 2 h to coat the surface of SS with Cu particles. The EDX results of SS mesh coated with Cu are as follows: C 0%, O 5.3%, Si 0.21%, Cr 10.2%, Ni 5.2%, Fe 46.2%, and Cu 32.2%, while the remaining weight was related to other components. The presence of oxygen was associated with the elemental composition of Cu nitrate trihydrate. Besides, when the SS mesh was placed into the CVD reactor and the temperature was increased to 300 °C, the nitrate compound was removed. In order to synthesize the graphene, pure acetylene (C<sub>2</sub>H<sub>2</sub>) was used as the hydrocarbon source, while nitrogen (N<sub>2</sub>) and hydrogen (H<sub>2</sub>) were utilized as the carrier gases. Next, the reaction temperature and the time in the CVD technique were altered to grow the graphene with different layers. First, the SS mesh was located in the CVD chamber, and then, the temperature was increased (950°C) under the flow of N<sub>2</sub> gas. When the system reached the required temperature, the acetylene gas as a carbon source was inserted into the system at 50 sccm with the presence of H<sub>2</sub>/N<sub>2</sub> flow (10 ssm/50 sccm), for different run times from 10 to 50 min. Finally, the C<sub>2</sub>H<sub>2</sub> flow rate was stopped, and the furnace was turned off under the presence of N<sub>2</sub> flow.

No. of layers: Multi-layered (Carbon nanotube)

Author: Abdeladim Guermoune

Title: Chemical vapor deposition synthesis of graphene on copper with methanol, ethanol, and propanol precursors

DOI: 10.1016/j.carbon.2011.05.054

Year of publication: 2011

**Abstract:** Large area, high quality graphene was synthesized from different liquid alcohols by chemical vapor deposition on copper foils in a tube furnace. The quality of the synthesized graphene was systematically investigated with various growth conditions. Alcohol vapor exposure times of 5 min and an average growth temperature of 850 °C yield continuous graphene monolayer films, as inferred from Raman spectroscopy. X-ray photoelectron spectroscopy shows that the oxygen moieties found in the source molecules have no measurable doping or oxidation effect in the synthesized graphene. Raman spectroscopy indicates that graphene films transferred to insulating substrates are of high quality. The field effect mobility of large area graphene transistors was measured at room temperature to be in the range 1800–2100 cm<sup>2</sup>/V s at carrier densities between 10<sup>11</sup>/cm<sup>2</sup> and 10<sup>12</sup>/cm<sup>2</sup>.

**Method of producing graphene:** In this paper, we report CVD growth of large-area, high quality graphene on Cu foils using aliphatic alcohols as carbon sources. Copper is the transition metal of choice in our work because the low solubility of carbon leads to easier control of graphene growth by surface adsorption, rather than dissolution, segregation and precipitation as in nickel [2]. Alcohols such as methanol, ethanol and 1-propanol are comparatively cheaper, easier to use, and less flammable than high purity methane and thus advantageous as liquid precursors for graphene growth. A detailed analysis of the CVD grown graphene layers was performed, including Raman spectroscopy, Raman mapping, electrical characterization of micrometer-scaled devices, scanning electron microscopy (SEM), optical imaging, atomic force microscopy (AFM), X-ray photoemission spectroscopy (XPS) and a comparison to graphene produced by mechanical exfoliation of graphite and by methane decomposition. The experimental procedure for graphene growth begins with cleaning the Cu catalysts. Twenty-five micrometer thick, Cu foils (Alfa Aesar, N# 13382) were immersed in 1 M acetic acid at 60 °C for 10 min followed by immersion in acetone and 2-propanol for 10 min in each solvent. The Cu foils were then loaded into a quartz tube and exposed to a 10 sccm H<sub>2</sub>, 10 mTorr environment while the temperature was raised to the growth temperature, 850 °C. The quartz tube was held at this temperature for 20 min to remove any generated oxide or oxide layer on the Cu. Alcohols were outgassed to 10–6 Torr using 3–5 freeze–pump–thaw cycles. Upon introduction of the alcohol vapor to the system, the tube pressure increases to 1 Torr, a pressure below the vapor pressure of all three alcohols at room temperature, thus allowing alcohol vapors to be drawn into the chamber (see Supplementary material Fig. 1S). The Cu films were exposed to the alcohol vapor for approximately 5 min at 1 Torr. Next, the alcohol vapor was cut off and the system was rapidly cooled to room temperature with rates varying from 300 °C/min to 30 °C/min while maintaining H<sub>2</sub> pressure at 10 mTorr. After growth, poly(methyl methacrylate) (PMMA, 950 kDa, 4% solution in anisole) was spin coated onto the surface of the graphene coated Cu. A hard bake at 120 °C for 1 min was used to stiffen the PMMA handle. The sample was then immersed in a room temperature ammonium persulfate (0.1 M) bath to etch the Cu foil. The remaining PMMA-supported graphene was then carefully transferred to a de-ionized water bath to remove residual etchant. The target substrate was used to lift the PMMA-supported graphene from the water bath. Heavily doped Si (ndoped, 8–20 mX-cm) with 300 nm of dry, chlorinated thermal oxide, was chosen as the substrate for back-gated electrical transport measurements. The sample was then dried at ambient temperature for 48 h in a clean environment. Liquid PMMA is drop cast on the stiffened PMMA handle to release tension and promote conformal adhesion to the substrate. The PMMA was then dissolved in a warm acetone bath to produce a pristine graphene layer on the target substrate (supplementary material, Figs. 3S and 4S).

No. of layers: Mono-layer

Author: Guoxiu Wang

Title: Highly efficient and large-scale synthesis of graphene by electrolytic exfoliation

DOI: 10.1016/j.carbon.2009.07.040

Year of publication: 2009

**Abstract:** Highly efficient and large-scale synthesis of graphene from graphite was produced by electrolytic exfoliation using poly(sodium-4-styrenesulfonate) as an effective electrolyte. Scanning and transmission electron microscopy, and atomic force microscopy confirmed the existence of monolayer graphene sheets and stacks containing a few graphene sheets. Raman spectroscopy demonstrated that the as-prepared graphene sheets have low defect content. Based on the measurement of FTIR spectra, the edge-to-face interaction (p–p interaction) between the graphene surface and aromatic rings of poly(sodium-4-styrenesulfonate) could be primarily responsible for producing exfoliation of the graphite electrode to graphene during electrolysis. In contrast to micromechanical exfoliation, electrolytic exfoliation can be scaled up for large-scale and continuous graphene production.

**Method of producing graphene:** High purity graphite rods (/ 6 mm, 99.999%, Aldrich) were used as electrodes. Poly(sodium-4-styrenesulfonate) (PSS, Mw = 70,000, Aldrich) was dissolved in de-ionized (DI) water to form the electrolyte (0.001 M). In a typical synthesis, two graphite rods were placed in an electrolysis cell filled with the electrolyte. A constant potential of 5 V (DC voltage) was applied to the two electrodes (CHI 660 C Electrochemical Workstation). A diagram of the synthesis apparatus is shown in Fig. 1. After 20 min electrolysis, black product gradually appeared at the positive electrode (anode). The exfoliation continued for 4 h. Then the product (a dispersion) was taken from the electrolysis cell. The dispersion was centrifuged at low speed (1000 rpm) to remove large agglomerates. The top of the dispersion was then decanted. This graphene–PSS suspension is very stable in nature. After 6 months storage, there is no any precipitation. To obtain dry graphene powders, the dispersion was washed with DI water and ethanol, and then dried in a vacuum oven at 80 °C. The yield of graphene was estimated by weighting the dried graphene powders and the dried sediment. Our electrolytic exfoliation method results in producing graphene at a yield at about 15 wt.%. Graphene paper was also made by vacuum filtration through an anodized aluminum oxide (AAO) membrane (/ 47 mm, 200 nm pore size, Whatman).

No. of layers: Mono-layer

Author: Mahbub Hassan

Title: High-yield aqueous phase exfoliation of graphene for facile nanocomposite synthesis via emulsion polymerization

DOI: 10.1016/j.jcis.2013.08.006

Year of publication: 2013

**Abstract:** Aqueous phase exfoliation was developed for producing high-yield graphene nanosheets from expanded graphite (EG). The process included ultrasonication with sodium dodecyl sulfate (SDS) emulsion in aqueous phase. The high throughput exfoliation process was characterized by UV-vis spectroscopy, transmission electron microscopy (TEM) and electrical impedance spectroscopy (EIS). Controlled sonication experiments revealed that optimum exfoliation corresponds to maxima in UV-vis spectra. TEM results showed that the exfoliated graphene comprised nanoflakes having 65 layers ( $\approx$ 60%) and 610 layers for 90% of the product. The potential use of this highly dispersed graphene was demonstrated by onepot synthesis of graphene/polymer composite via in situ emulsion polymerization with styrene. The integrated role of SDS included adsorption and exfoliation of graphite, dispersion of graphene produced and assisting with micelle formation in emulsion. The high surface area graphene nanosheets as dispersed phase in polymeric nanocomposites showed significant improvement in thermal stability and electrical conductivity.

**Method of producing graphene:** 2.2. Synthesis of thermally expanded graphite About 50 mg of GIC was placed on a small ceramic boat and loaded into a moving-bed tubular furnace (OTF-1200X, MTI Corporation), preheated to 900 C. The boat was placed at one end of the 0.4 m axial path of the furnace and moved gently during a 10 s period till it reached the oven exit. The thermally expanded exfoliated graphite was cooled to room temperature and removed from the boat for further processing. 2.3. Synthesis of graphene sheets The EG obtained is held by weak van der Waals forces. Thus, to obtain the desired GNS, the EG was subjected to a final exfoliation stage. A dispersion was prepared in 20 mL distilled water by mixing 0.1 wt% EG with 0.3 wt% of SDS powder. The resulting mixture was sonicated for 60 at room temperature. All sonication processes were carried out with a tip horn sonicator (Branson 450D) with a cylindrical tip (10 mm end cap diameter). The output power was fixed at 30 W to deliver energy at the 1650–1800 J/min level. The vial was placed in an ice bath during sonication in order to prevent any significant rise in temperature. The dispersion produced was preserved for further processing and characterization.

No. of layers: 60%  $\leq$  5 layer and 905  $\leq$  10 layer

Author: Ranjit Hawaldar

Title: Large-area high-throughput synthesis of monolayer graphene sheet by Hot Filament Thermal Chemical Vapor Deposition

DOI: 10.1038/srep00682

Year of publication: 2012

Abstract: We report hot filament thermal CVD (HFTCVD) as a new hybrid of hot filament and thermal CVD and demonstrate its feasibility by producing high quality large area strictly monolayer graphene films on Cu substrates. Gradient in gas composition and flow rate that arises due to smart placement of the substrate inside the Ta filament wound alumina tube accompanied by radical formation on Ta due to precracking coupled with substrate mediated physicochemical processes like diffusion, polymerization etc., led to graphene growth. We further confirmed our mechanistic hypothesis by depositing graphene on Ni and SiO<sub>2</sub>/Si substrates. HFTCVD can be further extended to dope graphene with various heteroatoms (H, N, and B, etc.,), combine with functional materials (diamond, carbon nanotubes etc.,) and can be extended to all other materials (Si, SiO<sub>2</sub>, SiC etc.,) and processes (initiator polymerization, TFT processing) possible by HFCVD and thermal CVD.

Method of producing graphene: Preparation of monolayer graphene sheet by HFTCVD. A homemade HFTCVD system (Fig. 1a) was used to grow graphene on Cu (GoodFellow, thickness 0.025 mm, purity 99.9%), Ni (GoodFellow, thickness 0.025 mm, purity 99.9%) and SiO<sub>2</sub> (300 nm)/Si (p-type, Crystal GmbH). The substrates were cleaned by sonication in organic solvents (acetone and isopropanol) prior to the loading in the CVD chamber. In our HFTCVD system, Ta filament was used (Advent Research Materials, diameter ,0.40 mm, purity ,99.9%), and substrates were placed in the middle of alumina tube (Frialit-Degussit Technical Ceramics, diameter ,2 cm, length ,8 cm). All precursors gases (CH<sub>4</sub>, H<sub>2</sub> and Ar) with purity ,99.99% from Praxair and Air Liquide were used for graphene deposition.

No. of layers: Mono-layer

Author: L. Huang

Title: Synthesis of high-quality graphene films on nickel foils by rapid thermal chemical vapor deposition

DOI: 10.1016/j.carbon.2011.09.012

Year of publication: 2011

**Abstract:** We report the synthesis of high-quality graphene films on Ni foils using a cold-wall reactor by rapid thermal chemical vapor deposition (CVD). The graphene films were produced by shortening the growth time to 10 s, suggesting that a direct growth mechanism may play a larger role rather than a precipitation mechanism. A lower H<sub>2</sub> flow rate is favorable for the growth of high-quality graphene films. The graphene film prepared without the presence of H<sub>2</sub> has a sheet resistance as low as 367 ohm/sq coupled with 97.3% optical transmittance at 550 nm wavelength, which is much better than for those grown by hot-wall CVD systems. These data suggest that the structural and electrical characteristics of these graphene films are comparable to those prepared by CVD on Cu.

**Method of producing graphene:** The CVD-grown graphene was carried out at home-made cold-wall reactor apparatus consisting of a RTP system (RTP1000, Ecopia) and a modified gas supply unit to meet the requirement of growing graphene films in a short time (e.g. 10 s), as shown in Fig. 1. Prior to CVD, the Ni foil (thickness: 25 lm, purity: 99.99%, Alfa Aesar) was placed in a reaction ion etching system (RIE-200NL, Samco) for the following etching parameters (etch time 30 min, RF power 100 W, Ar gas flow 100 sccm, gas pressure 2 Pa) to create a fresh Ni surface. The Ar plasma treated Ni foils was immediately loaded onto the PG (Pyrolytic Graphite)/PBN (Pyrolytic Boron Nitride) heater stage. The temperature was monitored by a shielded thermocouple measured on top of the heater and thus truly represented the catalyst Ni foil temperature. Additionally, cooling water was circulated through the walls of the reactor. The reaction chamber was pumped down to 3 mTorr using a rotary vacuum pump. The Ni foil was heated up to 1000 °C at a 100 °C/min heating rate, and maintained for 30 min in the N<sub>2</sub>/H<sub>2</sub> atmosphere (N<sub>2</sub>:H<sub>2</sub> = 700:100 sccm, total pressure 4.5 Torr) to activate Ni grain growth. Subsequently, the CVD growth of graphene was triggered by the addition of CH<sub>4</sub> (8 sccm) along with N<sub>2</sub> (700 sccm) and H<sub>2</sub> (100 sccm) (All gases supplied by Cheng Gong Gas, 99.999%) to maintain 20 Torr of the chamber pressure by adjusting a throttle valve. In order to optimize the growth of graphene, we investigated the effect of growth time and H<sub>2</sub> concentration on the quality of graphene. After CVD growth, the samples were cooled down from 1000 to 500 °C with a consistent cooling rate of 200 °C/min, under a flow of N<sub>2</sub> (700 sccm). After CVD growth, the as-grown graphene films were transferred to different target substrates using the following method [19]. First, a thin layer of poly(methyl methacrylate) (PMMA) (Sigma–Aldrich product No. 182265, dissolved in chlorobenzene with a concentration of 46 mg/ml) was spin-coated onto the as-grown graphene at 500 rpm for 5 s first, then 2500 rpm for 20 s. The PMMA/graphene/Ni foil was cured at 180 °C for 1 min, and subsequently, the rear side of the Ni foil was polished to remove the coatings. The graphene/PMMA film was released from the Ni foil by chemical etching of Ni with a FeCl<sub>3</sub> (1 M) solution over a period of 24 h, followed by rinsing with de-ionized water. The floating PMMA supported-graphene was transferred onto arbitrary substrates such as a SiO<sub>2</sub>/Si substrate and a flexible transparent PET substrate (Autotype, 0.125 mm thick film). Finally, PMMA was dissolved by acetone, leaving graphene on a target substrate.

No. of layers: Mono-layer

Author: Hyosub An

Title: Graphene synthesis on Fe foil using thermal CVD

DOI: 10.1016/j.cap.2011.03.077

Year of publication: 2011

**Abstract:** Graphene synthesis was performed on Fe foil at low temperature. A 100 mm-thick Fe foil as a catalyst and acetylene as a hydrocarbon source were used for graphene growth. With a low acetylene flow rate (5 sccm) and short exposure time (5 min), single- to few-layer graphene sheets partially covering the Fe substrate were obtained. With sufficient exposure times (15e30 min), and acetylene flow rates (25e50 sccm), continuous graphene layers were obtained at temperatures ranging from 600 °C to 800 °C. The measured Raman spectra showed that defects decreased with an increasing synthesis temperature. Even though the 2D and G peak intensities of the Raman spectrum appeared to be similar, the thickness of the graphene layers synthesized at 700 °C and 750 °C was measured to be as thick as w15 nm and w29 nm, respectively. Considering that the estimated number of graphene layers should be less than 2e3 without creating stacking disorder between the interlayers, it appears that an ordered stacking, (i.e., ABAB stacking) and therefore electronic coupling between layers, may not occur in the synthesized graphene layers on Fe foil under those process conditions.

**Method of producing graphene:** Fe foils (100 mm-thick, 99.5% metal basis) were purchased from Nilaco as the growth substrate. Samples with various sizes ranging from 1x1 cm to 3x3 cm were prepared. The samples were ultrasonically cleaned in acetone, methanol and deionized water. These samples were loaded into a CVD quartz chamber. The chamber was vacuumed under 1-3 mTorr by a mechanical pump, and hydrogen (H<sub>2</sub>) (99.999% purity) diluted in Ar (99.999% purity) gas was injected into a reactor to prevent oxidation of the Fe. In this experiment, samples were heated at a rate of 1 C/s by a rapid thermal CVD system with halogen lamps. The samples were pre-annealed at 600-800 °C in an Ar and H<sub>2</sub> atmosphere. Then C<sub>2</sub>H<sub>2</sub> (99.96% purity) was flowed. The process pressure was set to 350-450 mTorr during growth. growth times (15-30 min) and the amount of C<sub>2</sub>H<sub>2</sub> flow rates (5-50 sccm) to investigate characteristics of the graphene layers under different synthesis conditions. After the soaking step, the halogen lamps were turned off and the reactor started to cool down to room temperature with very high cooling rates. Process gas injection was maintained through room temperature during the cooling step. The synthesized graphene layers on the Fe foil were inspected by optical microscope, scanning electron microscopy (SEM), transmission electron microscopy (TEM), and Raman spectroscopy

No. of layers: Multi-layered graphene (>5 layers)

Author: Izabela Janowska

Title: Microwave Synthesis of Large Few-Layer Graphene Sheets in Aqueous Solution of Ammonia

DOI: 10.1007/s12274-010-1017-1

Year of publication: 2010

**Abstract:** Few-layer graphene (FLG) sheets with sizes exceeding several micrometers have been synthesized by exfoliation of expanded graphite in aqueous solution of ammonia under microwave irradiation, with an overall yield approaching 8 wt.%. Transmission electron microscopy (in bright-field and dark-field modes) together with electron diffraction patterns and atomic force microscopy confirmed that this graphene material consisted mostly of mono-, bi- or few-layer graphene (less than ten layers). The high degree of surface reduction was confirmed by X-ray photoelectron and infrared spectroscopies. In addition, the high stability of the FLG in the liquid medium facilitates the deposition of the graphene material onto several substrates via low-cost solution-phase processing techniques, opening the way to subsequent applications of the material.

**Method of producing graphene:** The expanded graphite (EG) with different concentrations (1.0 mg/mL) was dispersed in the liquid phase, i.e. distilled water and aqueous solution of ammonia (33 wt.%). The dispersion was homogenized by sonication in a low-power sonic bath for 30 min. The sediment was separated by filtration and dried before further processing. The microwave experiments were carried out on a Mars (CEM Corp.) microwave oven with the following characteristics: adjustable power between 300 and 1200 W and maximum temperature of 250 °C. The microwave irradiation was set at 300 W, keeping the temperature between 120 and 200 °C for 60–120 min. The FLG sheets were formed as a suspension in the aqueous phase above the solid residual EG. In order to extract as much as possible of the FLG from the starting EG, the mixture was sonicated for 30 min followed by a decantation step. In the case of pure water as a solvent, the colourless suspension of the graphene sheets was separated from the starting EG by decantation or extraction with a toluene–ammonia (aq.) system, due to the low concentration of the FLG material in the solution.

No. of layers: Few-layered graphene (<10 layers)

Author: Jianguo Zhao

Title: An approach for synthesizing graphene with calcium carbonate and magnesium

DOI: 10.1016/j.carbon.2012.06.024

Year of publication: 2012

**Abstract:** Graphene sheets were prepared by the calcination of calcium carbonate with magnesium powder under the protection of argon gas flow. CaO, MgO and graphene sheets were achieved by the reaction of CaCO<sub>3</sub> with Mg, which is an environmentally friendly way for producing graphene. The graphene sheets were characterized by transmission and scanning electron microscopy, X-ray diffraction, atomic force microscopy and Raman spectroscopy. Few-layer graphene was prepared, with the number of layers ranging from 4 to 10.

**Method of producing graphene:** The apparatus for the experiment was an electrical furnace equipped with a horizontal quartz tube 50 mm in diameter, 1000 mm in length, and a 150 mm long reaction zone in the middle. Magnesium powder and calcium carbonate powder were mixed and pulverized. The mixture was then put on a porcelain boat, which was moved into the middle part of the electrical furnace, and heated up to 850 C within 5 h under the protection of argon gas. The entire calcination process was conducted at ambient pressure. The reaction took 30 min at the temperature of 850 C. The power was turned off to let the furnace cool down to room temperature under the protection of argon gas. After the reaction was completed, the grey products were collected and transferred to a beaker containing 200 ml of 3 M HCl. The product was stirred in the acid solution at room temperature overnight to remove MgO, CaO, and any remaining Mg metal. Mg, MgO and CaO react with hydrochloric acid to form MgCl<sub>2</sub> and CaCl<sub>2</sub>, which are soluble in water. So, it is easy to get a pure carbon material as the final product. The mixture was then filtered, washed with deionized water several times until the filtrate turned out to be of neutral pH. Finally, the isolated solid carbon product was dried under high vacuum overnight at 25 C.

No. of layers: Few-layered graphene ( 4 < x < 10 layers)

Author: Zhen-Yu Juang

Title: Graphene synthesis by chemical vapor deposition and transfer by a roll-to-roll process

DOI: 10.1016/j.carbon.2010.05.001

Year of publication: 2010

**Abstract:** We synthesized centimeter-scale single- to few-layer graphene (FLG) films via chemical vapor deposition (CVD) on Ni foils. We demonstrate that the precipitation mechanism may not be the only important mechanism in the formation of graphene by CVD in Ni system, and that controlling the cooling rate in the CVD process may not be the appropriate way to control the thickness of graphene films. In addition, we are the first to demonstrate the transfer of centimeter-scale FLG from Ni foil to transparent flexible polyethylene terephthalate substrates via an efficient roll-to-roll process.

Comparing to rigid substrates, synthesis of graphene on flexible Ni foil has necessity for the use of a roll-to-roll transfer process.

**Method of producing graphene:** In this paper, we present the development of CVD synthesis and a roll-to-roll transfer process of graphene. The CVD synthesis method, using transition metals as substrates, is a promising technique for the synthesis of large-scaled graphene films. Before the roll-to-roll transferring process, SLG and FLG were synthesized using Ni foil (30 lm in thickness, The Nilaco Corp.) as the substrate. After the Ni substrates were loaded into a quartz tubular furnace, the samples were heated to the process temperature of 900 C and maintained for 10 min under a H<sub>2</sub>/Ar (10 and 400 sccm, respectively) atmosphere. A CH<sub>4</sub>/H<sub>2</sub>/Ar gas mixture (10, 10 and 400 sccm, respectively) was then introduced into the quartz tube for 10 min, and the furnace was cooled to room temperature with fast (3 C/s) and slow (0.3 C/s) cooling rates. The gas mixture during cooling is the same as heating stage. The pressure was maintained at 750 Torr during whole process using advanced pressure control system (APC, MKS Instruments).

No. of layers: Mono-layer and few-layer

Author: Tommi Kaplas

Title: Few-layer graphene synthesis on a dielectric substrate

DOI: 10.1016/j.carbon.2011.11.020

Year of publication: 2011

**Abstract:** We report on few-layer graphene synthesis on fused silica, with the help of pre-deposited copper films with thickness of few hundred nanometers, by using chemical vapor deposition technique. Depending on the copper film thickness, the deposited graphene samples on copper/silica interface were either micron sized graphene flakes or uniform graphene films of a sub-millimeter width. The quality of graphene grown beneath the pre-deposited copper film was found to be comparable with that of graphene grown on bulk copper. The developed technique opens new route towards the space-selective CVD graphene growth on dielectric substrates.

**Method of producing graphene:** In experiment, we employed the thermal evaporator to deposit 200 nm thick Cu films on a 2 inch quartz substrate. The Cu coated quartz sample was placed in the tube furnace (Carbolite CTF 12/75/700). The chamber was pumped into a vacuum and purged twice with nitrogen and once with hydrogen to ensure all remaining moisture and air to be removed. After the cleaning the chamber was pumped down to vacuum and injected with hydrogen up to 5.5 mBar pressure at room temperature. In the next stage, the temperature was risen up to 700 °C at the rate of 10 °C/min. Then the chamber was pumped down and the graphitization gas (1:1 H<sub>2</sub>:CH<sub>4</sub>) mixture was let into the chamber rising the pressure up to 10 mBar. At the next step, the temperature was risen up to 950 °C with rate of 10 °C/min. The maximum temperature was kept for one minute followed the cooling at the rate about 5-10 °C/min (see Fig. S1) in H<sub>2</sub>:CH<sub>4</sub> atmosphere. At 700 °C the methane-hydrogen gas mixture was pumped out from the chamber and replaced with hydrogen at the pressure of 10 mBar. Then the chamber cooled down in overnight to room temperature.

No. of layers: Few layer graphene

Author: Karthikeyan Krishnamoorthy

Title: Graphene nanosheets: Ultrasound assisted synthesis and characterization

DOI: 10.1016/j.ulsonch.2012.09.007

Year of publication: 2012

**Abstract:** A facile sonochemical route for the synthesis of graphene nanosheets via reduction of graphene oxide (GO) has been reported. The synthesized graphene sheets are characterized using UV-vis spectra, Fourier transform infra-red (FT-IR) spectra, transmission electron microscope, X-ray photoelectron spectra (XPS) and Raman spectroscopic techniques. The UV-vis spectroscopy results showed that the absorption peak was red shifted due to the reduction of GO into graphene. FT-IR and XPS spectra revealed the removal of oxygenated functional groups in graphene after the reduction process. Raman spectra confirmed the restoration of new sp<sub>2</sub> carbon domains in graphene sheets after the reduction. The sonochemical approach for the synthesis of graphene nanosheets is relatively fast, cost-effective and efficient as compared to other methods.

**Method of producing graphene:** 2.2. Synthesis of graphene oxide The graphene oxide was synthesized according to the modified Hummer's method using graphite powder as the starting material [6,21]. Briefly, graphite powder (2 g) was stirred in 98% H<sub>2</sub>SO<sub>4</sub> (35 mL) for 2 h. KMnO<sub>4</sub> (6 g) was gradually added to the above solution while keeping the temperature less than 20 C. The mixture was then stirred at 35–40 C for 30 min. The resulting solution was diluted by adding 90 mL of water under vigorous stirring and a dark brown color suspension was obtained. The reaction was terminated by the addition of 150 mL of distilled water and 30% H<sub>2</sub>O<sub>2</sub> solution (10 mL). After continuously stirred for 2 h, the mixture was washed by repeated centrifugation and filtration using 5% HCl aqueous solution in order to remove the residual metal ions. Further, the centrifugation process was repeated with distilled water until the pH of the solution becomes neutral. Finally, a brown colored precipitate of graphitic oxide was obtained by filtration and was allowed to dry under vacuum. The exfoliation of graphitic oxide into graphene oxide was achieved by ultrasound irradiation. Briefly, 0.2 g of as-synthesized graphitic oxide was redispersed in 200 mL of distilled water and allowed to sonication for 30 min which results in exfoliation of graphitic oxide into monolayers of graphene oxide (GO) and is further used for the synthesis of graphene. 2.3. Sonochemical reduction of graphene oxide into graphene nanosheets The as-synthesized GO nanosheets were used as the starting precursor for the synthesis of graphene via sonochemical method. Briefly, the pH of the as exfoliated GO solution (0.2 g in 200 mL) was adjusted to reach 10 by NaOH solution followed by the addition of 2 mL of hydrazine and the entire reaction is subjected to ultrasound irradiation for 2 h. The sonication reaction was conducted without any cooling, so that a temperature of about 60 ± 5 C was reached at the end of the reaction. The experiment is performed under atmospheric conditions. The obtained graphene nanosheets was washed thoroughly with distilled water and centrifuged at 12000 rpm for 10 min in order to remove the residuals. The procedure was repeated for several times until the synthesized product becomes free from trace amount of impurities. Further, the synthesized graphene nanosheets were dried in a hot air oven and were used for further characterization. The graphene or reduced graphene oxide nanosheet synthesized by ultrasonic method is named as US-rGO. In order to confirm the reduction reaction and the rate kinetics were enhanced in the presence of ultrasound, we also examined the same reduction reaction in the absence of ultrasound. The experiments were performed with the same concentration in the absence of ultrasound irradiation. The detailed procedure for the control experiment is given in supporting document.

No. of layers: Mono-layer

Author: A. Kumar

Title: Rapid synthesis of few-layer graphene over Cu foil

DOI: 10.1016/j.carbon.2011.11.033

Year of publication: 2011

**Abstract:** We report a unique process for rapid synthesis of few-layer graphene films on Cu foil by microwave plasma chemical vapor deposition (MPCVD). We show that the plasma/metal interaction can be advantageous for a rapid synthesis of such thin films. The process can produce films of controllable quality from amorphous to highly crystalline by adjusting plasma conditions during growth processes of  $\leq 100$  s duration and with no supplemental substrate heating. Films have been characterized using Raman spectroscopy, scanning electron microscopy, transmission electron microscopy and X-ray photoelectron spectroscopy. The results help to identify the stages involved in the MPCVD deposition of thin carbon films on Cu foil, and the findings open new pathways for a rapid growth of few-layer graphene films.

**Method of producing graphene:** Graphene film synthesis was performed in a SEKI AX5200S MPCVD system with H<sub>2</sub> (50 sccm) and CH<sub>4</sub> (5 sccm) as the feed gases. A 25 lm thick copper foil (Alfa Aesar, 99.8% purity) was used as the substrate. The foil was cut in 2 · 2 cm<sup>2</sup> pieces and placed into the MPCVD chamber, which was evacuated to a base pressure of 2 Torr and then filled with high-purity hydrogen at a pressure of 10 Torr. The Cu foil was supported by a ceramic stand that elevated it from the Mo puck by about 15 mm (see Fig. 1(a)). The elevation of the Cu foil above Mo puck was found to be critical for the growth of the films because it ensures a strong coupling between the plasma and the Cu foil, thus enabling rapid self-heating of the foil by the microwave plasma. No additional heater was used. The thermocouple attached to the substrate table indicated a maximum reading of approximately 65 C during the process. A dual-wavelength infrared pyrometer indicated a maximum temperature of  $700 \pm 25$  C. However, as the copper foil is coated with graphene, the surface emissivity changes, making reliable IR measurements difficult. The entire growth is accomplished in less than 5 min and generally involves two stages. First, in a plasma cleaning and annealing step, the foil is kept in 400 W hydrogen plasma for 3 min. A H<sub>2</sub> flow rate of 50 sccm was used with downstream pressure control to maintain 10 Torr chamber pressure throughout the process. This process leads to rapid self-heating and removal of copper oxide from the foil surface. The second stage involves introduction of CH<sub>4</sub> (while maintaining the hydrogen plasma) at a flow of 5 sccm for a short duration (between 30 s and 2 min), providing approximately 10% CH<sub>4</sub> concentration in hydrogen. Depending on the growth duration and whether or not annealing is used, different forms of carbon can be deposited

No. of layers: Few-layered graphene ( 4 < x < 8 layers)

Author: Alexander Malesevic

Title: Synthesis of few-layer graphene via microwave plasma-enhanced chemical vapour deposition

DOI: 10.1088/0957-4484/19/30/305604

Year of publication: 2008

**Abstract:** If graphene is ever going to live up to the promises of future nanoelectronic devices, an easy and cheap route for mass production is an essential requirement. A way to extend the capabilities of plasma-enhanced chemical vapour deposition to the synthesis of freestanding few-layer graphene is presented. Micrometre-wide flakes consisting of four to six atomic layers of stacked graphene sheets have been synthesized by controlled recombination of carbon radicals in a microwave plasma. A simple and highly reproducible technique is essential, since the resulting flakes can be synthesized without the need for a catalyst on the surface of any substrate that withstands elevated temperatures up to 700 °C. A thorough structural analysis of the flakes is performed with electron microscopy, x-ray diffraction, Raman spectroscopy and scanning tunnelling microscopy. The resulting graphene flakes are aligned vertically to the substrate surface and grow according to a three-step process, as revealed by the combined analysis of electron microscopy and x-ray photoelectron spectroscopy.

**Method of producing graphene:** FLG was synthesized in a MW PECVD set-up composed of an Iplas Cyrannus MW plasma source mounted on top of a stainless steel vessel. The plasma source consists of a 6 kW, 2.45 GHz cylindrical MW resonator, which couples the MW power through five annular slots in a quartz tube and enables operation either in the TM012 or in the surface wave plasma mode. For all the experiments, the plasma was operated in the TM012 mode. A flexible substrate holder allows free positioning of substrates along the axis of the quartz tube. A broad range of materials was used as substrates, including quartz, silicon, nickel, platinum, germanium, titanium, tungsten, stainless steel, tantalum and molybdenum. Prior to growth, the substrates are heated for 20 min in a 2 kW MW plasma at 40 Torr, using a H<sub>2</sub> flow of 200 sccm. This plasma is sufficiently powerful to heat the samples from room temperature up to 700 °C, as measured by a thermocouple embedded in the substrate holder. Immediately after the heating step, CH<sub>4</sub> mixed with H<sub>2</sub> is introduced into the growth chamber with a CH<sub>4</sub>/H<sub>2</sub> ratio of 1/8 at a total flow rate of 200 sccm. Keeping the plasma power and pressure at 2 kW and 40 Torr, respectively, FLG was grown with this gas mixture for various growth times ranging from 1 to 3000 s.

No. of layers: Few-layered graphene ( 4 < x < 6 layers)

Author: Meihua Jin

Title: Synthesis and systematic characterization of functionalized graphene sheets generated by thermal exfoliation at low temperature

DOI: 10.1088/0022-3727/43/27/275402

Year of publication: 2010

Abstract: We describe the low-temperature thermal exfoliation of graphite oxide to obtain functionalized graphene sheets (FGSs). Graphite oxide, which is highly oxidized graphite produced by a modified Brodie method, is further exfoliated by a simple heat treatment at 270–275 °C under ambient Ar. The FGSs that are generated have fewer defects and less oxygen content than in commercial graphene sheets (GSs) prepared at high temperatures (>900 °C). X-ray photoelectron spectroscopy demonstrates a clear  $\pi$ -plasmon peak in the FGSs of the type that is seen in precursor graphite, but not in commercial GSs. Thus, our FGSs exhibit high 2D crystallinity and minimal defects.

Method of producing graphene: In this work, the process of preparing FGSs consists of two steps, as shown in figure 1: (i) room-temperature oxidation to generate GO and (ii) low-temperature exfoliation to obtain FGSs. The GO was produced by a modified Brodie method using precursor graphite as a starting material. One gram of precursor graphite (99.999%, 200 mesh, Alfar Aesar, USA) was mixed with 8.5 g sodium chlorate and 20 ml fuming nitric acid at room temperature and stirred for 24 h. The mixed solution was then neutralized with deionized water and dried at 80 °C for 12 h. The completely dried GO was transferred to a chamber with a temperature-programmed furnace. Ar gas was pumped into the chamber at a flow rate of 3000 ml min<sup>-1</sup> and the temperature was increased at a ramping rate of 9.0 °C min<sup>-1</sup> from room temperature to 300 °C. Exfoliation took place in a temperature range 270–295 °C. Various structural properties of the obtained FGS were compared with those of commercially available GSs prepared by the conventional high-temperature exfoliation with sulfuric acid (N-BARO TECH, Korea).

No. of layers: Mono-layer

Author: V Miseikis

Title: Rapid CVD growth of millimetre-sized single crystal graphene using a cold-wall reactor

DOI: 10.1088/2053-1583/2/1/014006

Year of publication: 2014

**Abstract:** In this work we present a simple pathway to obtain large single-crystal graphene on copper (Cu) foils with high growth rates using a commercially available cold-wall chemical vapour deposition (CVD) reactor. We show that graphene nucleation density is drastically reduced and crystal growth is accelerated when: (i) using ex situ oxidized foils; (ii) performing annealing in an inert atmosphere prior to growth; (iii) enclosing the foils to lower the precursor impingement flux during growth. Growth rates as high as 14.7 and 17.5  $\mu\text{m min}^{-1}$  are obtained on flat and folded foils, respectively. Thus, single crystal grains with lateral size of about 1 mm can be obtained in just 1 h. The samples are characterized by optical microscopy, scanning electron microscopy, x-ray photoelectron spectroscopy, Raman spectroscopy as well as selected area electron diffraction and low-energy electron diffraction, which confirm the high quality and homogeneity of the films. The development of a process for the quick production of large grain graphene in a commonly used commercial CVD reactor is a significant step towards an increased accessibility to millimetre-sized graphene crystals.

**Method of producing graphene:** The 25  $\mu\text{m}$  thick Cu foil used in this work (if not differently mentioned) was supplied by Alfa Aesar (purity 99.8%, lot no. 13382). Such foil is also referred to a slow-purity in the text. The foil was electropolished in an electrochemical cell made using a commercially available Coplin staining jar as the vessel and an electrolyte solution described previously [12]. The grooves of the staining jar ensured that the foil was kept flat and parallel to the counter electrode (a thicker Cu plate), which helped achieve homogeneous polishing of the surface. More detailed information on the electropolishing setup and process as well as its effects can be found in the supplementary information (SI). Graphene films were synthesized at a pressure of 25 mbar inside a 4 inch cold-wall CVD system (Aixtron BM). To achieve more reproducible atmospheric and thermal conditions and to reduce the effective gas flow, the sample was contained in a custom-made enclosure, comprising a quartz disk suspended 6 mm above the sample using graphite spacers (figure 1(a)). A typical temperature profile of a CVD growth process is shown in panel (c) of figure 1, indicating the four distinct parts: temperature ramp-up (I), annealing (II), growth (III) and cool-down (IV). The annealing as well as the growth was performed at approximately 1060 °C, which was calibrated according to the melting point of Cu. The annealing time was kept at 10 min in all cases. The gas flow during the temperature rampup and the annealing stages (panel (c), I and II) was 1000 sccm. The samples which had the largest grains were annealed in argon atmosphere (mentioned as Ar annealing process in the text); other samples were annealed in hydrogen (mentioned as hydrogen annealing in the text). The gas flow rates during growth (panel (c), III) were typically set to 1 sccm of methane, 20 sccm of hydrogen and 900 sccm of argon. The growth time was one hour. After the growth, the chamber was cooled in argon/hydrogen atmosphere to a temperature of 120 °C before introducing the samples to air (figure 1(c), IV).

No. of layers: Mono-layer

Author: Myoungdo Seo

Title: Supercritical alcohols as solvents and reducing agents for the synthesis of reduced graphene oxide

DOI: 10.1016/j.carbon.2013.07.053

Year of publication: 2013

Abstract: We report on a facile, simple, and green graphene oxide (GO) reduction method based on a supercritical alcohol approach. The influence over the chemical, thermal, morphological, and textural properties of reduced graphene oxides (RGOs) of five different alcohols in their supercritical conditions – methanol, ethanol, 1-propanol, 2-propanol, and 1-butanol – was investigated in detail. Although the thermal stabilities and Fourier-transform infrared spectra of RGOs produced using the different alcohols are very similar, a substantial difference in the carbon-to-oxygen ratios measured by X-ray photoelectron spectroscopy and Brunauer–Emmett–Teller surface areas are observed. The RGO produced using supercritical ethanol exhibited a much higher carbon-to-oxygen ratio of 14.4 and a much larger surface area of 203m<sup>2</sup>/g compared with that produced using the other supercritical alcohols. Raman spectra showed that the RGOs produced using supercritical ethanol and supercritical 2-propanol retained more of the graphitic structure. X-ray diffraction analysis revealed that RGOs produced using supercritical 1-propanol and supercritical 1-butanol retained at least two different interlayer spacings. The deoxygenation mechanism of GO in supercritical ethanol is proposed based on gas and liquid product analysis.

Method of producing graphene: GO was prepared using the modified Hummers method [48,49]. A detailed description of the experimental procedure for GO synthesis is given in the Supplementary data. The current experimental setup can produce ca. 17 g of GO using 12 g of natural flake graphite in each batch reaction. For the GO reduction in supercritical alcohols, 1 g of GO was dispersed in 8 ml of each alcohol using a vortex mixer. The mixed suspension was sonicated for 1 h in a 20-mL glass vial. Then, 3.5 mL of the mixed suspension was introduced into a SUS 316 reactor with an inner volume of 11 ml. After being tightly sealed, the reactor was immersed into a molten salt bath (salt weight ratio of KNO<sub>3</sub>:NaNO<sub>3</sub>:Ca(NO<sub>3</sub>)<sub>2</sub> = 46:24:30) and reacted for 2 h at 400 C. At this condition, approximately 3 wt.% of ethanol was decomposed to gas product. After the reaction, the reactor was taken out from the salt bath and quenched in a cold water bath. After the cooling, the produced RGO suspension was rinsed and filtered through a FP Vericel<sup>□</sup> poly(vinylidene fluoride) membrane filter. Wet RGO powder was dried in a vacuum oven at 70 C overnight, and sieved using a mesh size of 75 lm. The RGOs synthesized using the different supercritical alcohols were designated as RGOscMeOH, RGO-scEtOH, RGO-scPrOH, RGO-scBuOH, and RGOscIPA.

No. of layers: nil

Author: Lam Van Nang

Title: Controllable Synthesis of High-Quality Graphene Using Inductively-Coupled Plasma Chemical Vapor Deposition

DOI: 10.1149/2.082204jes

Year of publication: 2012

Abstract: High-quality graphene was synthesized on Cu foil using inductively-coupled plasma chemical vapor deposition (ICPCVD). ICP is very effective, such that a few-layer graphene could be formed within a few seconds. However, the graphene thickness was gradually decreased by increasing the growth time and plasma power, finally being saturated at a single layer. The graphene quality was also significantly enhanced by the preferential etching of the structurally-disordered C structures, followed by the newly synthesized graphene layer. Understanding ICPCVD growth kinetics, governed by the graphene formation by C atoms and C etching by H atoms, is useful for the controllable synthesis of high-quality graphene for various applications.

Method of producing graphene: To investigate the rf plasma effect, graphene growth was carried out with a diluted CH<sub>4</sub> gas, in which graphene was not formed without applying plasma. The CH<sub>4</sub> gas of 1 SCCM (denoting cubic centimeter per minute at STP) and the mixed gases of 10% H<sub>2</sub> and 90% Ar (forming gas) of 100 SCCM were introduced in a hot-wall tubular reaction chamber (Fig. 1). The Cu foil (Alfa Aesar) was pre-treated with an acetic acid solution at 60°C for 10 min, followed by washing with de-ionized water. The foil was heated to a graphene synthesis temperature (950°C) and annealed for 10 min with forming gas flow (100 SCCM) to remove native oxides from the Cu foil and to enlarge its grains. The synthesis pressure was fixed at 1 Torr. The synthesis time and rf plasma power varied in the ranges of 5min and 200 W, respectively. The synthesized graphene on Cu was transferred on SiO<sub>2</sub>/Si or glass substrate for various characterizations. First, a 500 nm layer of poly-methyl methacrylate (PMMA) was spincoated on the surface of the graphene film to serve as support. The graphene layer at the back side of the Cu foil was then etched off using oxygen plasma. After the etching of the Cu foil with FeCl<sub>3</sub> z E-mail: etkim@cnu.ac.kr aqueous solution at 40°C, the PMMA/graphene was transferred to a target substrate. The graphene on the SiO<sub>2</sub>/Si or glass substrate was achieved by dissolving the PMMA film using acetone

No. of layers: 1 – 2 layers

Author: Van Tu Nguyen

Title: Synthesis of multi-layer graphene films on copper tape by atmospheric pressure chemical vapor deposition method

DOI: 10.1088/2043-6262/4/3/035012

Year of publication: 2013

Abstract: Graphene films were successfully synthesized by atmospheric pressure chemical vapor deposition (APCVD) method. Methane ( $\text{CH}_4$ ) gas and copper (Cu) tapes were used as a carbon source and a catalyst, respectively. The CVD temperature and time were in the range of 800–1000 °C and 10 s to 45 min, respectively. The role of the CVD temperature and time on the growth of graphene films was investigated in detail via scanning electron microscopy (SEM) and Raman spectroscopy techniques. The results of SEM images and Raman spectra show that the quality of the graphene films was improved with increasing of CVD temperature due to the increase of catalytic activity.

Method of producing graphene: The graphene films were synthesized by thermal CVD method under high temperature (1000 °C) in argon (Ar) environment (1000 sccm). The Cu tapes with a thickness of 35 $\mu\text{m}$  and a size of 0.5 cm  $\times$  0.5 cm were used as substrates for graphene-films synthesis process. To reduce the native copper oxide and to facilitate Cu grain growth on the Cu tape surface, the samples were annealed at CVD temperature for 30 min in a flow of Ar and hydrogen (H<sub>2</sub>, 300 sccm). After 30 min, a flow of methane ( $\text{CH}_4$ , 30 sccm) was introduced for growth process (figure 1). The time for the CVD process ranged from 30 min. After a preset graphene growth time, the samples were cooled rapidly under a flow of Ar (1000 sccm)

No. of layers: Multi-layered graphene (>5 layers)

Author: K. S. Novoselov

Title: Two-dimensional atomic crystals

DOI: 10.1073/pnas.0502848102

Year of publication: 2005

**Abstract:** We report free-standing atomic crystals that are strictly 2D and can be viewed as individual atomic planes pulled out of bulk crystals or as unrolled single-wall nanotubes. By using micromechanical cleavage, we have prepared and studied a variety of 2D crystals including single layers of boron nitride, graphite, several dichalcogenides, and complex oxides. These atomically thin sheets (essentially gigantic 2D molecules unprotected from the immediate environment) are stable under ambient conditions, exhibit high crystal quality, and are continuous on a macroscopic scale.

**Method of producing graphene:** Fig. 1 shows several examples of cleaved samples and illustrates that they are only one atomic layer thick but nearly macroscopic laterally. To extract such 2D crystallites, we used a simple but effective procedure. A fresh surface of a layered crystal was rubbed against another surface (virtually any solid surface is suitable), which left a variety of flakes attached to it (the rubbing process can be described as similar to “drawing by chalk on a blackboard”). Unexpectedly, among the resulting flakes we always found single layers. Their preliminary identification amid thicker flakes and other residue was done in an optical microscope. 2D crystallites become visible on top of an oxidized Si wafer (Fig. 1d), because even a monolayer adds up sufficiently to the optical path of reflected light so that the interference color changes with respect to the one of an empty substrate (phase contrast). The whole procedure takes literally half an hour to implement and identify probable 2D crystallites. Their further analysis was done by atomic force microscopy (AFM), for which single-layer crystals were selected as those exhibiting an apparent (12) thickness of approximately the interlayer distance in the corresponding 3D crystals.

No. of layers: Mono-layer

Author: Panbo Liu

Title: A facile synthesis of reduced graphene oxide with Zn powder under acidic condition

DOI: 10.1016/j.matlet.2012.09.085

Year of publication: 2012

**Abstract:** The traditional synthesis of reduced graphene oxide (RGO) from graphene oxide (GO) involves harmful chemical reducing agents and is undesirable for practical applications. Here, we have demonstrated a green and facile approach to synthesize RGO with Zn powder under acidic conditions at room temperature, which results in a substantial removal of oxygen functionalities, and yields a C/O ratio as high as 8.2. The conductivity of RGO is  $6.5 \times 10^2$  S/m, which is about 14 times higher than that of NaBH<sub>4</sub>-reduced-GO. Furthermore, the approach offers a potential for cost-effective, environmentally friendly, and large-scale production of RGO.

**Method of producing graphene:** Graphite oxide was synthesized using graphite flakes by the Hummers method [15]. GO was achieved by ultrasonication of graphite oxide in water for 2 h. In a typical experiment, 0.8 g Zn powder and 10 mL HCl (35 wt%) were added into 40 mL GO (1 mg/mL) solution. The mixture was stirred for 30 min. After that, 10 mL HCl (35 wt%) was added into the above solution and then maintained for a period of time to remove excess Zn powder. Finally, the resulting RGO was collected with filtration, washed with pure water and ethanol several times, and dried at 90 °C for 12 h in a vacuum oven.

No. of layers: Multi-layered graphene (>5 layers)

Author: Xu-Yuan Peng

Title: Synthesis of electrochemically-reduced graphene oxide film with controllable size and thickness and its use in supercapacitor

DOI: 10.1016/j.carbon.2011.04.047

Year of publication: 2011

Abstract: An electrochemical synthesis method of reducing graphene oxide (GO) under constant potential is reported. Electrochemical technique offers control over reaction parameters such as the applied voltage, electrical current and reduction time; whereas the desired size and thickness of the film can be pre-determined by controlling the amount of precursor GO deposited on the electrode with defined shape and surface area. This synthesis technique produces high quality electrochemically reduced GO (ERGO) film with controllable size and thickness. Electrochemical symmetrical supercapacitors based on ERGO films achieved a specific capacitance of 128 F/g with an energy density of 17.8 Wh/kg operating within a potential window of 1.0 V in 1.0 M NaNO<sub>3</sub>. The supercapacitor was shown to be stable, retaining ca. 86% of the original specific capacitance after 3500 charge–discharge cycles. The results indicate that this simple synthesis technique for providing graphene-like materials has great potential in various applications such as energy storage.

Method of producing graphene: 2.1. Preparation of GO Graphene oxide (GO) was prepared from graphite flakes (GF) (Aldrich, Product No. 332461) based on Hummers method followed by exfoliation using sonication (details see S1, Supplementary material) [6]. 2.2. Preparation of Au-PET substrate and Fabrication of GO film on Au-PET substrate Gold coated polyethylene terephthalate sheet (Au-PET) was prepared as the electrode substrate for GO film fabrication. The PET was sputter coated with gold using a Polaron SC7640 sputter coater for 10 min (voltage: 2 kV; plasma current: 25 mA) at a fixed rate of 10 nm min<sup>-1</sup>. Therefore the final thickness of the gold film deposited on the PET substrate was ca. 100 nm. GO thin film was prepared as following: 10 mL of GO suspension (20 mg/mL) in MilliporeTM water was casted on one end of the gold electrode to cover an area of 4 · 5 mm<sup>2</sup>. The GO film was formed after drying in an oven at 70 °C for 2 h, with an estimated thickness of around 10 nm, assuming that the density of GO was close to unity. Hence, the thickness of the GO film produced was controlled by the concentration and volume of the GO suspension used to cover electrode of fixed surface area. 2.3. Electrochemical reduction of GO Electrochemical reduction of solid GO film was performed at 1.1 V (vs. Ag/AgCl) in 0.5 M NaNO<sub>3</sub> for 4.5 h by using a CHI 630 electrochemical analyzer system. A platinum disk electrode and a Ag/AgCl electrode were used as the counter and reference electrode, respectively. Electrochemical reduction of GO in suspension was carried out at 1.7 V (vs. Ag/AgCl) with constant mechanical stirring. A gold disk was used as working electrode (D = 2 mm), with a platinum wire and a Ag/AgCl electrode as counter and reference electrodes, respectively. To investigate the weight loss from GO after electrochemical reduction, the Au-PET substrate was dried in oven under dynamic vacuum at 70 °C for 24 h and then measured by analytical balance. 2.0 mL aliquots of 2.05 mg/mL GO solutions were used to prepare GO films (4.1 mg) on Au-PET substrate. After reduction, the ERGO film was dried in oven under dynamic vacuum at 70 °C for 24 h and then measured by analytical balance. Only 2.9 mg ERGO was obtained after electrochemical reduction, indicating 29.3% weight loss after reduction due to the removal of oxygen from the film. 2.4. Chemical reduction of GO For comparison, GO in aqueous suspension and as solid film were also reduced chemically using hydrazine according to Stankovich's method (details see S2, Supplementary material) [7].

No. of layers: Multi-layered graphene (~10 layers)

Author: Dong Han Seo

Title: Single-step ambient-air synthesis of graphene from renewable precursors as electrochemical genosensor

DOI: 10.1038/ncomms14217

Year of publication: 2016

**Abstract:** Thermal chemical vapour deposition techniques for graphene fabrication, while promising, are thus far limited by resource-consuming and energy-intensive principles. In particular, purified gases and extensive vacuum processing are necessary for creating a highly controlled environment, isolated from ambient air, to enable the growth of graphene films. Here we exploit the ambient-air environment to enable the growth of graphene films, without the need for compressed gases. A renewable natural precursor, soybean oil, is transformed into continuous graphene films, composed of single-to-few layers, in a single step. The enabling parameters for controlled synthesis and tailored properties of the graphene film are discussed, and a mechanism for the ambient-air growth is proposed. Furthermore, the functionality of the graphene is demonstrated through direct utilization as an electrode to realize an effective electrochemical genosensor. Our method is applicable to other types of renewable precursors and may open a new avenue for low-cost synthesis of graphene films.

**Method of producing graphene:** Ambient-air thermal synthesis of grapheme. The growth of graphene was carried out in a thermal CVD furnace (OTF-1200X-UL, MTI Corp) with a quartz tube (100 cm in length, 5 cm in diameter). Polycrystalline Ni foils (25 mm, 99.5%, Alfa Aesar) were used as the growth substrate. The experimental schematic is shown in Fig. 1. Briefly, two alumina plates were placed in the heating zone of the furnace. One alumina plate was loaded with 0.14 ml of soybean oil precursor and the other was loaded with the Ni foil growth substrate. The openings of the quartz tube were then sealed. The growth of graphene proceeds with a gradual heating and fast quenching temperature profile. First, the furnace temperature was raised to 800 °C at a rate of 30 °C min<sup>-1</sup>. This was followed by holding at 800 °C for 3 min. After the growth step, the sample was immediately removed from the heating zone to enable a rapid cooling (at approximately 25 °C min<sup>-1</sup>) to segregate the homogeneous and continuous graphene films. Owing to the evaporation and thermal expansion of the precursor material, a small build-up in pressure within the tube was observed. Throughout the heating stage (200 to 800 °C), atmospheric pressure was maintained in the quartz tube by allowing this build-up of gases to exit via the exhaust of the tube. A controlled gas environment was created in the tube through enabling the circulation of gases produced by precursor evaporation. Following the heating stage, pressure within the quartz tube was observed to be stabilized at atmospheric pressure. No additional gases were introduced into the quartz tube throughout the entire growth process.

No. of layers: Single to few layered graphene

Author: Emre O. Polat

Title: Synthesis of Large Area Graphene for High Performance in Flexible Optoelectronic Devices

DOI: 10.1038/srep16744

Year of publication: 2015

Abstract: This work demonstrates an attractive low-cost route to obtain large area and high-quality graphene films by using the ultra-smooth copper foils which are typically used as the negative electrodes in lithium-ion batteries. We first compared the electronic transport properties of our new graphene film with the one synthesized by using commonly used standard copper foils in chemical vapor deposition (CVD). We observed a stark improvement in the electrical performance of the transistors realized on our graphene films. To study the optical properties on large area, we transferred CVD based graphene to transparent flexible substrates using hot lamination method and performed large area optical scanning. We demonstrate the promise of our high quality graphene films for large areas with ~400 cm<sup>2</sup> flexible optical modulators. We obtained a profound light modulation over a broad spectrum by using the fabricated large area transparent graphene supercapacitors and we compared the performance of our devices with the one based on graphene from standard copper. We propose that the copper foils used in the lithium-ion batteries could be used to obtain high-quality graphene at much lower-cost, with the improved performance of electrical transport and optical properties in the devices made from them.

Method of producing graphene: CVD Synthesis of Graphene. For single layer graphene, at 1035 °C methane was sent into growth chamber in company with hydrogen (Partial pressures of CH<sub>4</sub> and H<sub>2</sub> gases are 285mTorr and 40mTorr and corresponding rate of flows are 25 sccm and 4 sccm respectively). We annealed the Cu substrates for half an hour at 1035 °C before the growth. Hydrogen flow was kept constant during the heating, annealing, growth and cooling. After 10minutes of growth, samples were left for fast cooling to room temperature. The growth took place in a 8 inch diameter quartz chamber. We used both the commercially available 20μm thick smooth Cu foils (Mitsui mining and smelting co., LTD, B1-SBS) and the standard 25μm Alfa Aesar Cu foil (item #13382) as growth substrates in the same CVD chamber.

No. of layers: Mono-layer

Author: Qiqi Zhuo

Title: Large-scale synthesis of graphene by the reduction of graphene oxide at room temperature using metal nanoparticles as catalyst

DOI: 10.1016/j.carbon.2012.10.014

Year of publication: 2012

Abstract: A simple chemical approach has been developed for the synthesis of graphene through a mild reduction of graphene oxide (GO) using metal nanoparticles as the catalyst for the hydrolysis reaction of NaBH<sub>4</sub> at room temperature. The morphology and structure of the graphene were characterized with atomic force microscopy and transmission electron microscopy. The reduction process and quality of graphene were followed and examined by UV-vis absorption spectroscopy, X-ray photoelectron spectroscopy, Raman spectroscopy and X-ray diffraction. By this method, graphene can be prepared in large quantity without using toxic reducing agents such as hydrazine or its derivatives, making it environmentally benign. The reaction is conducted under mild conditions (room temperature), resulting in the formation of fewer defects. The method can be easily scaled up and the metal catalyst can be recycled.

Method of producing graphene: In a typical experiment, firstly, 5 mg of the as-prepared GO were dispersed into 50 mL DI water under mild ultrasonic treatment to obtain a uniform GO aqueous solution (0.1 mg/mL). Then, 10 mL GO solution (1 mg GO) was taken out to join a 20-mL vial, and 100 μL of 1 mM metal salts and 10 mg NaBH<sub>4</sub> were added into the solution. After 1 h reaction, a suspension solution was obtained. The product was collected by centrifugation and washed by 3% HCl and DI water for three times, respectively. After washing, the metal solution can be concentrated and then be used as the catalyst again to the reduction of GO. In a typical scale-up experiment, 1 L GO solution (100 mg GO) was reduced by the same method to obtain 72 mg r-GO

No. of layers: nil

Author: S. Saqib Shams

Title: Synthesis of graphene from biomass: A green chemistry approach

DOI: 10.1016/j.matlet.2015.09.022

Year of publication: 2015

**Abstract:** A simple, eco-friendly and scalable method of obtaining graphene from dead camphor leaves (*Cinnamomum Camphora*) using one-step pyrolysis is reported here. Under flowing nitrogen atmosphere, dead camphor leaves were heated to 1200 °C at 10°C/min and then cooled down to room temperature without external disturbances. With the help of π–π interaction with D-Tyrosine and centrifugation, we were able to separate few-layer graphene (FLG) from the final pyrolytic components. TGA is adopted to track the degradation process of camphor leaves under 800 °C and the formation mechanism of FLG is properly discussed. BET, Raman, SEM, AFM, and TEM tests were carried out to characterize the property of graphene, which prove an average of 7 layers of graphene (FLG).

**Method of producing graphene:** Camphor leaves were collected and washed using acetone to clean dirt off the samples, and then they were dried for 4 h at 60 °C in a vacuum oven to remove any traces of solvent. The sample leaves were cut into smaller pieces so as to remove any persistent stalks and veins and to collect the leafy portion with relatively consistent thickness. The dried samples were put in a ceramic boat with a lid, and they were then placed inside a vacuum oven. The air was pumped out and then a constant flow of N<sub>2</sub> was introduced for the rest of the experiment. The oven was firstly heated up to 1200 °C at 10 °C/min and then the temperature was maintained at 1200 °C for 4 min. At last, the sample was cooled to room temperature without controlling the temperature decreasing rate (Scheme 1). After the high temperature pyrolysis of the leaves, the sample was taken out and mixed with D-Tyrosine and trichloromethane. 0.1 g of the sample along with 0.02 g of D-Tyrosine was dissolved in 50 ml of trichloromethane, and the mixture was treated with sonication for 15 min in an ice bath. High speed centrifugation (5000 rpm, 5 min) was applied to the mixture to precipitate amorphous carbons. After these procedures, FLG was suspended in the solvent while other forms of carbon stayed at the bottom of the tube as sediment. With filtering, FLG suspension was extracted and can be used for characterization. The π–π interaction between graphene and D-Tyrosine stabilized the FLG solution. (See Scheme 1). Since D-Tyrosine is soluble in both strong acids and bases, it can easily be removed from the suspension by washing with either a strong acid or a base, as long as its further presence is not required.

No. of layers: Few-layered graphene (~7 layers)

Author: Hareema Saleem

Title: Synthesis route of reduced graphene oxide via thermal reduction of chemically exfoliated graphene oxide

DOI: 10.1016/j.matchemphys.2017.10.020

Year of publication: 2017

Abstract: Graphene, a two-dimensional material, is now considered as a rewarding contestant for nanodevices due to its morphology and novel properties. The chemical exfoliation and thermal annealing methods are appraised as an inventive route towards the production of graphene at prodigious scale. This method is utilized for the oxidation of graphite flakes having an oxidizing specialist and thermally reduced the graphene oxide into reduced graphene oxide. We have examined the samples through different characterization techniques. X-ray diffraction displayed the peaks of graphene oxide at 11.8° and reduced graphene oxide at 25.5°. Scanning electron microscopy images revealed the single and multilayers morphology. The optical microscopy examined the number of layers of graphene oxide through the various contrasts of light. UV-Vis spectroscopy showed the hills of graphene oxide and reduced graphene oxide at 215 nm and 267 nm. Fourier transform infrared spectroscopy has been utilized to examine the resonating modes.

Method of producing graphene: 2.1. Chemical exfoliation method Oxidized the graphite flakes by chemical exfoliation method. Mixed 3 g of graphite flakes with 9:1 mixture of concentrated H<sub>2</sub>SO<sub>4</sub>/H<sub>3</sub>PO<sub>4</sub> (360:40 ml) and 18 g of KMnO<sub>4</sub>. Stirred the mixture mechanically at 35-40 C for 4e5 h to produce the slightly exothermic reaction. Heated and stirred it at 50 C for 12 h. Then cooled it to room temperature and poured 400 ml ice of distilled water and 5 ml hydrogen peroxide H<sub>2</sub>O<sub>2</sub> in a mixture to complete the reaction. The dark pink color was converted into mustard color. Washed the mixture with 1 M HCl and distilled water till the pH of supernatant liquid reached 7 2.2. Exfoliation of graphene oxide (GO) To exfoliate the GO, sonicated the GO dispersion under normal condition for 30 min. The homogeneous brown dispersion was produced which was utilized for reduction. Dried the solution in the vacuum oven at 40 C for 24 h 2.3. Thermal reduction of graphene oxide The GO was annealed in a Nabertherm GmbH N17/HR-400V Muffle heating furnace at 500 C at a heating rate of 2 C min 1 for 2 h and allowed to cool in furnace till the temperature decreased till 50 ± 5 C. The GO was completely converted into reduced graphene oxide (rGO)

No. of layers: Multi-layered

Author: Kaveri Satheesh

Title: Synthesis and electrochemical properties of reduced graphene oxide via chemical reduction using thiourea as a reducing agent

DOI: 10.1016/j.matlet.2013.09.044

Year of publication: 2013

**Abstract:** Synthesis of reduced graphene oxide sheets from graphene oxide using thiourea as a reducing agent through chemical reduction has been explored. Fourier transform infrared spectroscopy, Raman spectroscopy, Transmission electron microscopy and X-ray diffraction analysis confirm the formation of graphene sheets. Thermogravimetric analysis reveals the thermal stability of graphene. Electrochemical performance of the graphene electrode was analyzed by cyclic voltammetry, which showed an increase in capacitive behavior compared to graphene oxide. This investigation highlights the importance of the preparation of reduced graphene oxide sheets using thiourea as a reducing agent and its energy storage applications in supercapacitors.

**Method of producing graphene:** Synthesis of GO: Graphite Oxide (GO) was synthesized from graphite powder by using Hummers method [17]. 2 g of graphite powder was added to a mixture of 46 ml of concentrated H<sub>2</sub>SO<sub>4</sub> and 1 g of NaNO<sub>3</sub> in an ice bath. Then 6 g of KMnO<sub>4</sub> was added slowly to the suspension under stirring to avoid any violent or explosive reactions and the temperature of the mixture was kept below 10 °C by cooling. After adding the KMnO<sub>4</sub> to the mixture, the dark green suspension was removed from the ice bath and the temperature was raised to 35 °C and maintained 1 h, which resulted in a thick paste. Then the mixture was diluted by 92 ml of water. Because of the addition of water in concentrated sulfuric acid medium a large amount of heat was released. Then the temperature was raised to 98 °C and maintained for 2 h. The reaction was terminated by the addition of 280 ml of water and 30% H<sub>2</sub>O<sub>2</sub>, resulting in brown mixture. Then the mixture was filtered and washed with 10% HCl, ethanol and water. The resulting solid was dried in a vacuum oven at 60 °C for 12 h. Then GO was obtained in the form of dry brown powder. Synthesis of graphene sheets: Typically, 100 mg of GO was dispersed in 100 ml of water through ultrasonication for 1 h to yield GO dispersion. 0.5 mol of thiourea was added to the dispersion under stirring at 95 °C for 12 h. With the reduction process, the brown color of GO dispersion turns into black color. Finally the black color product (rGO) was washed with water and ethanol. The filtered product was dried in a vacuum oven at 60 °C for 12 h.

No. of layers: Few layer graphene (4 layer)

Author: Montree Sawangphruk

Title: Synthesis and antifungal activity of reduced graphene oxide nanosheets

DOI: 10.1016/j.carbon.2012.06.056

Year of publication: 2012

**Abstract:** Reduced graphene oxide (rGO) nanosheets were produced using a modified Hummers method. Antifungal activity of rGO nanosheets was tested against three fungi i.e., *Aspergillus niger* (*A. niger*), *Aspergillus oryzae* (*A. oryzae*) and *Fusarium oxysporum* (*F. oxysporum*). The rGO inhibits the mycelial growth of the fungi and it is believed that this is due to its sharp edges. The half maximal inhibitory concentration (IC<sub>50</sub>), a measure of the effectiveness of the rGO in inhibiting the fungi, was investigated. IC<sub>50</sub> values of the rGO against *F. oxysporum*, *A. niger*, and *A. oryzae* are 50, 100, and 100  $\mu\text{g}/\text{ml}$ , respectively.

**Method of producing graphene:** 2.2. Preparation of graphene oxide GO was synthesized by using a Hummers method [9] with our modification as follows. Graphite powder (3.0 g) and NaNO<sub>3</sub> (1.5 g) were put to a concentrated H<sub>2</sub>SO<sub>4</sub> (150 ml) while stirring at 100 rpm in an ice bath for 1 h. KMnO<sub>4</sub> (8.0 g) was slowly added to the mixture at 25 °C for 2 h without stirring. Milli-Q water (90 ml) was added to the suspension and kept stirring (100 rpm) at 95 °C for 12 h. Then, 30% H<sub>2</sub>O<sub>2</sub> (30 ml) was slowly added to the diluted suspension. For the purification, the mixture was filtered through polyester fiber (Carpenter Co.). The filtrate was centrifuged at 6000 rpm for 15 min and the remaining solid material (GO) was then washed in succession with 200 ml of water, 100 ml of 30% HCl, and 100 ml of ethanol. This process was repeated for 3 times. The final product GO was collected by filtration and vacuum dried. 2.3. Reduction of graphene oxide GO powder (100 mg) was sonicated in Milli-Q water (30 ml) for 30 min. Hydrazine hydrate (3 ml) was added to the as-dispersed suspension. After that, the mixture was refluxed at 98 °C for 24 h. For workup, the product (rGO) was harvested using the same purification method mentioned above. The final product rGO was collected by filtration and vacuum dried.

No. of layers: Few layer graphene

Author: Soo Min Kim

Title: The effect of copper pre-cleaning on graphene synthesis

DOI: 10.1088/0957-4484/24/36/365602

Year of publication: 2013

**Abstract:** Copper foil is the most common substrate to synthesize monolayer graphene by chemical vapor deposition (CVD). The surface morphology and conditions of the copper foil can be very different depending on the various suppliers or different batches. These surface properties of copper strongly affect the growth behavior of graphene, thus rendering the growth conditions irreproducible when different batches of Cu foil are used. Furthermore, the quality of the graphene is severely affected as well. In this work, we report a facile method of copper pre-cleaning to improve the graphene quality and the reproducibility of the growth process. We found that the commercial Ni etchant (based on nitric acid) or nitric acid is the most effective cleaning agent among various acidic or basic solutions. The graphene grown on thus-treated copper surfaces is very clean and mostly monolayer when observed under scanning electron microscopy (SEM) and optical imaging, as compared to the graphene grown on untreated copper foil. Different batches (but with the same catalog number) of copper foil from Alfa Aesar Company were examined to explore the effect of copper pre-cleaning; consistent growth results were obtained when pre-cleaning was used. This method overcomes a commonly encountered problem in graphene growth and could become one of the standard protocols for preparing the copper foil substrate for growing graphene or other 2D materials.

**Method of producing graphene:** Pre-cleaning step: As mentioned previously, our hypothesis is that most of the impurity particles were on the Cu surface. To remove these impurities, the foil was briefly dipped in Ni etchant solution for 30–90 s depending on the amount of impurities observed (see figure S2 available at [stacks.iop.org/Nano/24/365602/mmedia](https://stacks.iop.org/Nano/24/365602/mmedia)). (Note: we have observed that Cu foil having more impurities requires a longer surface cleaning time. However, if the cleaning time is more than 2 min, the copper foil becomes severely damaged and is not useful for growth of graphene.) The main component of the Ni etchant is nitric acid, which reacts with Cu according to  $\text{Cu(s)} + 4\text{HNO}_3\text{(aq)} \rightarrow \text{Cu(NO}_3)_2\text{(aq)} + 2\text{NO}_2\text{(g)} + 2\text{H}_2\text{O}$ . (1) During this reaction, the Cu on the surface is being oxidized and dissolved in the solution; at the same time  $\text{NO}_2$  gas is violently generated, helping to push the impurity particles away. In this way, the original surface of the Cu foil, together with the impurities, is scraped off and a new, clean but very rough surface is obtained. After cleaning, the copper foil is dipped in DI water for further washing. This washing process is carried out three times, each time with fresh DI water. It should be noted that this step is very important. To remove the DI water from the copper completely, the copper foil is briefly washed with acetone and isopropanol and dried by blowing with  $\text{N}_2$ . 2.1. Graphene growth procedure Graphene was synthesized by low pressure chemical vapor deposition using a copper foil (25  $\mu\text{m}$ , 99.8%, Alfa Aesar) as a catalytic metal substrate. After the pre-cleaning process, the copper foil was annealed at 1000 °C for 30 min under a 10 sccm hydrogen atmosphere (~330 mTorr) to increase the grain size and to obtain a smooth surface, followed by graphene synthesis under 5 and 10 sccm of methane and hydrogen atmospheres for 40 min (~450 mTorr) while maintaining the same temperature. During the cooling of the chamber, 10 sccm of hydrogen was flowed until the furnace was cooled to room temperature.

No. of layers: Mono-layer

Author: Sasha Stankovich

Title: Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide

DOI: 10.1016/j.carbon.2007.02.034

Year of publication: 2007

Abstract: Reduction of a colloidal suspension of exfoliated graphene oxide sheets in water with hydrazine hydrate results in their aggregation and subsequent formation of a high-surface-area carbon material which consists of thin graphene-based sheets. The reduced material was characterized by elemental analysis, thermo-gravimetric analysis, scanning electron microscopy, X-ray photoelectron spectroscopy, NMR spectroscopy, Raman spectroscopy, and by electrical conductivity measurements.

Method of producing graphene: GO was prepared from purified natural graphite (SP-1, 30-lm nominal particle size, Bay Carbon, Bay City, MI) by the Hummers method 2.2. Reduction of exfoliated GO with hydrazine hydrate In a typical procedure, GO (100 mg) was loaded in a 250-mL roundbottom flask and water (100 mL) was then added, yielding an inhomogeneous yellow-brown dispersion. This dispersion was sonicated using a Fisher Scientific FS60 ultrasonic bath cleaner (150 W) until it became clear with no visible particulate matter. Hydrazine hydrate (1.00 mL, 32.1 mmol) was then added and the solution heated in an oil bath at 100 C under a water-cooled condenser for 24 h over which the reduced GO gradually precipitated out as a black solid. This product was isolated by filtration over a medium fritted glass funnel, washed copiously with water (5 · 100 mL) and methanol (5 · 100 mL), and dried on the funnel under a continuous air flow through the solid product cake.

No. of layers: Mono-layer

Author: Tanveer A. Tabish

Title: A facile synthesis of porous graphene for efficient water and wastewater treatment

DOI: 10.1038/s41598-018-19978-8

Year of publication: 2018

**Abstract:** The use of two-dimensional graphene-based materials in water treatment has recently gained significant attention due to their unique electronic and thermal mobility, high surface area, high mechanical strength, excellent corrosion resistance and tunable surface chemistry. However, the relatively expensive, poor hydrophobicity, low adsorption capacity and recyclability, and complex post-treatment of the most pristine graphene frameworks limit their practical application. Here, we report a facile scalable method to produce highly porous graphene from reduced graphene oxide via thermal treatment without addition of any catalyst or use of any template. Comparing to conventional graphene counterparts, as-prepared porous graphene nanosheets showed evident improvement in hydrophobicity, adsorption capacity, and recyclability, making them ideal candidate materials for water treatment. Superhydrophobic and superoleophilic porous graphene prepared in this work has been demonstrated as effective absorbents for a broad range of ions, oils and organic solvents, exhibiting high selectivity, good recyclability, and excellent absorption capacities > 90%. The synthesis method of porous graphene reported in this paper is easy to implement, low cost and scalable. These attributes could contribute towards efficient and cost-effective water purification and pollution reduction.

**Method of producing graphene:** Exfoliated graphite oxide flakes, with ~0.5–20 µm lateral size and ~1.5nm thickness, were prepared following the modified Hummers method previously reported by us<sup>36</sup>. Graphite was initially oxidized to form graphite oxide, which was further exfoliated and chemically reduced to graphene sheets. The thickness of GO sheets varied between 0.8–1 nm. Before the reduction, 500 ml aqueous solution of graphite oxide with concentration of 1 mg/ml was synthesized, and further exfoliated for 2 h in an ultrasonic bath (Bandelin Sonorex RK-100H). The pH values were found to be in the range 9–11. 150ml GO (1mg/ml) was combined with 1.5ml of hydrazine (35wt%) under magnetic stirring in a fask which was heated to 100 °C. After 12h reaction, hydrazine (1.5ml) was again added to perform the reaction for additional 2h to ensure full reduction of the GO. The rGO was allowed to settle, washed with distilled water and filtered until the supernatant became clear. To obtain porous nanosheets, the filtered product was oven-dried in vacuum overnight and then thermally treated at 200 °C in Ar for 12 h under a slow ramp rate of 3 °C min<sup>-1</sup>. The preparation scheme is schematically shown in Fig. S1 of supporting information (SI).

No. of layers: Few layer graphene

Author: Xin Tong

Title: Controllable synthesis of graphene sheets with different numbers of layers and effect of the number of graphene layers on the specific capacity of anode material in lithium-ion batteries

DOI: 10.1016/j.jssc.2011.03.004

Year of publication: 2011

**Abstract:** High quality graphene sheets are synthesized through efficient oxidation process followed by rapid thermal expansion and reduction by H<sub>2</sub>. The number of graphene layers is controlled by tuning the oxidation degree of GOs. The higher the oxidation degree of GOs is getting, the fewer the numbers of graphene layers can be obtained. The material is characterized by elemental analysis, thermogravimetric analysis, scanning electron microscopy, atomic force microscopy, transmission electron microscopy and Fourier transform infrared spectroscopies. The obtained graphene sheets with single, triple and quintuplicate layers as anode materials exhibit a high reversible capacity of 1175, 1007, and 842 mA h g<sup>-1</sup>, respectively, which show that the graphene sheets with fewer layers have higher reversible capacity.

**Method of producing graphene:** The typical synthesis process is as follows: (i) to produce Graphite Oxide(GO)by a modified Hummers method [25], (ii) to synthesize Expanded Graphite (EG) using a so-called explosion-expansion method and (iii) to obtain graphene sheets (GS) through chemical vapor reduction [26]. 2.1.1. Oxidation of graphite The general method is: firstly, 1 g graphite powders (the mean diameter of 18 mm provided by Mei Ge Electrical Carbon Co., Ltd. China) were poured into the mixture of 92 mL concentrated sulfuric acid (95–98%) and 24 mL nitric acid (65%) in a 500 mL flask(under ice bath). After the suspended solution was strongly stirred at 0 1C for 15 min. Then 6 g KMnO<sub>4</sub> (AR) was gradually added in the above mixture solution. (The mass ratio of graphite and KMnO<sub>4</sub> in GO1, GO2 and GO3 (the oxidation degrees of GO1–GO3 are relatively higher) are 1:3, 1:4, and 1:6, respectively). The suspended solution was stirred continuously for 1 h. We called this process low temperature oxidation. Subsequently, in order to increase the oxidation degree of the graphite, the mixture was heated to 80 1C for 30 min, and then 92 mL of deionized water was slowly added in. The suspension was stirred at 80 1C for 30 min again. After that, 5 mL H<sub>2</sub>O<sub>2</sub> (30%) was added into the solution to reduce the residual permanganate. On completion of the reaction, the mixture was washed with 5% solution of HCl and water until sulfate could not be detected with BaCl<sub>2</sub>. Finally, the GO powders were dried at 80 1C for 24 h. The dosage of oxidizer was controlled to produce oxidized graphite of different degrees. 2.1.2. Expansion of GO In this step, the obtained GO powders (400 mg) were loaded in a quartz boat. The quartz boat was placed into a 25-mm internal diameter; 1-m long quartz tube. After the sample was flushed with argon for 30 min (the velocity of argon is 100 mL min<sup>-1</sup> ), the quartz tube was heated to 300 1C for 1 h (at heating rates of 15 1C min<sup>-1</sup> ) in tube furnace under argon flow. 2.1.3. Reduction of EG Graphene sheets obtained from thermal expansion contain residual H and OH groups. Therefore, to remove H and OH groups, the as-prepared EG were reduced in a tube furnace by H<sub>2</sub> (the gas flow is consisted of H<sub>2</sub> (40 mL min<sup>-1</sup> ) and argon (60 mL min<sup>-1</sup> )) for 2 h at 500 1C. After the GS was dispersed into ethanol, to remove a small amount of precipitate, post-treatment of sonication and centrifugation is used and then the desired graphene sheets are collected for further characterizations.

No. of layers: 1 – 4 layers

Author: Pierre Trinsoutrot

Title: Three dimensional graphene synthesis on nickel foam by chemical vapor deposition from ethylene

DOI: 10.1016/j.mseb.2013.09.018

Year of publication: 2013

Abstract: 3D multi-layers graphene networks were synthesized on nickel foam from ethylene between 700 and 1000 °C by chemical vapor deposition. Large nickel foam substrates were used allowing the accurate measurement of graphene masses. The weight of graphene increased with run duration and when decreasing temperature. Graphene was also present inside the hollow branches of the foam. We demonstrated that the weights of graphene formed largely exceed the masses corresponding to carbon solubility into nickel. Indeed weight percentages of graphene as high as 15% were obtained, corresponding to graphene layers of 500 nm to 1 μm thick. This means that graphene formation could not be due only to carbon dissolution into nickel and then precipitation during the cooling step. Another mechanism probably coexists, involving continuous graphene formation in presence of ethylene either by segregation from the dissolved carbon into nickel or by surface CVD growth.

Method of producing graphene: The CVD synthesis of graphene was carried out in a 100 mm quartz tube of 1400 mm in length. A three zones furnace of 760 mm length surrounds the reactor. The 1.8 mm-thick nickel foam samples (99.9% Alantum, 40 mm × 60 mm) were placed in the central isothermal zone of the reactor, using a substrate holder which maintains them vertically during the process. They were heated 750 °C in a H<sub>2</sub> and Ar flow and annealed for 40 min. Then 15 sccm of ethylene were introduced into the reactor during 40 min with the same Ar and H<sub>2</sub> flow rates. The samples were then cooled to room temperature under the same Ar/H<sub>2</sub> flow rates without carbon precursor. All experiments were performed at 700 Torr. The samples were systematically weighed before and after graphene synthesis on a Mettler Toledo (AX105 Delta Range) balance (accuracy of ±0.0003 g)

No. of layers: Multi-layered graphene (>3 layers)

Author: Wei-Jhih Lin

Title: Graphene modified basal and edge plane pyrolytic graphite electrodes for electrocatalytic oxidation of hydrogen peroxide and b-nicotinamide adenine dinucleotide

DOI: 10.1016/j.elecom.2009.09.018

Year of publication: 2009

Abstract: Graphene was cast on basal and edge plane pyrolytic graphite electrodes for electrochemical applications. The morphology of the resulting graphene modified electrode was investigated by atomic force microscopy. In cyclic voltammetric responses, both anodic and cathodic peak currents varied linearly with the square root of scan rates over the range of 25–600 mV in 0.1 M KCl containing 5 mM  $\text{Fe}(\text{CN})_6^{4-}$  at graphene modified basal and edge plane pyrolytic graphite electrodes, which suggests a diffusion-controlled process. The graphene modified basal and edge plane pyrolytic graphite electrodes exhibited the abilities to lower the electrooxidation potentials of b-nicotinamide adenine dinucleotide and hydrogen peroxide in comparison with bare basal and edge plane pyrolytic graphite electrodes. The electrocatalytic behavior obtained at the graphene modified basal and edge plane pyrolytic graphite electrodes may lead to new applications in electroanalysis.

Method of producing graphene: Graphene was prepared by reduction of graphene oxide by hydrazine. Graphene oxide was synthesized from graphite powder by a modified Hummers method [21,22]. A 2.5 g of KMnO<sub>4</sub> was slowly added into a mixture of 5 g of graphite, 3.75 g of NaNO<sub>3</sub>, and 375 mL of concentrated H<sub>2</sub>SO<sub>4</sub> with stirring for 2 h at 0 C. After 5 days of vigorous stirring at room temperature, a 700 mL of 5 wt.% H<sub>2</sub>SO<sub>4</sub> solution was slowly added and stirred for 2 h at 98 C. Then, a 15 mL of 30 wt.% hydrogen peroxide solution was added in the cooled mixture and stirred for 2 h at room temperature. Repeating cycles of centrifugation and redispersing in a mixed solution of 3 wt.% of H<sub>2</sub>SO<sub>4</sub> and 0.5 wt.% of hydrogen peroxide were employed to purify the precipitate. Further washing used 3 wt.% HCl and water and passed through a weak basic ion-exchange resin to remove the remaining acid. The resultant solution was filtrated and dried to obtain the graphene oxide. The stable suspension of chemically reduced graphene oxide in N,N-dimethylformamide (DMF) was prepared according to the Ruoff procedure [23]. First, 30 mg of graphene oxide was dispersed in 1 mL of water by sonication for 1 h. Then, 9 mL of DMF was added in 1 mL of water containing 30 mg of graphene. Finally, 10 mL of hydrazine was added in the prepared 10 mL mixed solution with vigorous stirring for 12 h at 80 C and a black suspension of graphene was obtained. The product was characterized using transmission electron microscopy and AFM (not shown). The graphene samples contained 4–6 layers on average which is similar to other work [24].

No. of layers: 4-6 layers

Author: Baolin Xing

Title: Facile synthesis of graphene nanosheets from humic acid for supercapacitors

DOI: 10.1016/j.fuproc.2017.05.021

Year of publication: 2017

**Abstract:** A simple, cost-effective, and environmentally friendly route was developed to synthesize graphene nanosheets from humic acid via preliminary carbonization coupled with oxidation-exfoliation-thermal reduction. Such graphene nanosheets have a high specific surface area (495 m<sup>2</sup>·g<sup>-1</sup>) with large pore volume (2.987 cm<sup>3</sup>·g<sup>-1</sup>), unique interconnected mesoporous structure and uniform oxygen-containing functional groups in layered graphene framework, which offer a favorable and efficient pathway for the electrolyte propagation and transportation. The electrodes of supercapacitors made from these graphene nanosheets exhibit a maximum specific capacitance of 272 F·g<sup>-1</sup> at the current density of 50 mA·g<sup>-1</sup> in aqueous electrolyte, and possess excellent rate capability, low resistance, superior cycling performance with over 96.5% initial capacitance retention after 8000 cycles. The corresponding supercapacitors deliver a desirable energy density of 6.47 Wh·kg<sup>-1</sup> at a powder density of 2250 W·kg<sup>-1</sup>. This study demonstrates a promising synthesis route for large-scale production of graphene nanosheets from renewable and green humic acid for high performance supercapacitors.

**Method of producing graphene:** 2.2. Synthesis of graphene nanosheets The carbonized powder from humic acid was used as starting materials to synthesize graphene oxide by using a modified Hummers method. Briefly, 5 g carbonized powder, 30 g KMnO<sub>4</sub> and 5 g NaNO<sub>3</sub> were slowly added into 220 ml concentrated H<sub>2</sub>SO<sub>4</sub> in sequence and vigorously stirred in an ice bath for 10 h. The mixture was then heated to 35 °C and maintained for 3 h with continuous stirring. The mixture was then diluted by 440 ml distilled water, and the temperature of mixture was controlled to be under 85 °C during the dilution process. After that, H<sub>2</sub>O<sub>2</sub> (30 wt%) was added into the mixture drop by drop until the color of solution became bright yellow. The mixture was finally centrifuged (8000 rpm, 6 min) and the supernatant was discarded. The remaining solid was then successively washed with 1 M HCl solution and deionized water several times by centrifugation until the pH of the solution was neutral. The obtained solid was ultrasonicated in deionized water for 8 h, and the resultant suspension was then dried by freeze drying to obtain graphene oxide. For the thermal exfoliation-reduction of graphene oxide process, 1 g of obtained graphene oxide was placed in a quartz crucible (with a lid) and heated at 900 °C for 5 min in a muffle furnace under nitrogen atmosphere. The graphene nanosheets were collected after a natural cooling. The synthesis procedure for graphene nanosheets is illustrated in Fig. 1.

No. of layers: few layer graphene (< 10 layers)

Author: Xinmeng Zhang

Title: Graphene nanosheets synthesis via chemical reduction of graphene oxide using sodium acetate trihydrate solution

DOI: 10.1016/j.synthmet.2014.04.007

Year of publication: 2014

**Abstract:** The synthesis of chemically reduced graphene oxide nanosheets (RGO) from graphite oxide commonly involves some harmful chemical reductants that are undesirable for most practical applications of graphene. An easy and environment friendly approach has been developed to reduce graphene oxide(GO) by using sodium acetate trihydrate as a reductant. The as-prepared RGO was characterized by X-raydiffraction (XRD), Raman spectroscopy, Fourier transform infrared spectroscopy (FT-IR), X-ray photo-electron spectroscopy (XPS), field emission transmission electron microscopy (FETEM), atomic force microscopy (AFM) and thermogravimetric analysis (TGA). Results show that GO was reduced to few-layers level with poor dispersion in water. A mechanism for removing of epoxy and hydroxyl groups from GO with sodium acetate trihydrate has been proposed. Considering that all the raw materials used are low cost, nontoxic and widely available, this approach may open up the new possibility for cost-effective,environment friendly and large-scale production of graphene.

**Method of producing graphene:** 2.2. Preparation of GO GO was prepared from graphite powder through a modified Hummers method [22]. In brief, graphite powder (0.5 g) was dispersed in 23 ml of concentrated H<sub>2</sub>SO<sub>4</sub>. After magnetic stirring for 0.5 h, KMnO<sub>4</sub> (3 g) and NaNO<sub>3</sub> (0.5 g) were slowly added into the above solution with stirring and the temperature of the mixture was kept below 20 °C by cooling. After oxidizing for 2 h, the reaction mixture was transferred to 35 °C water bath and stirred for 32 h. Then, the temperature of mixture was raised to 95 °C after adding 140 ml of DI water. The mixture was maintained at as mentioned temperature and continued stirring for another 2 h. The color of solution changed from dark brown to bright yellow during the drop-wise addition of 3 ml of 30% H<sub>2</sub>O<sub>2</sub>. The synthetic mixture was repeatedly washed and settled with DI water until the PH of solution was 7. After drying at 60 °C under vacuum, graphite oxide sample was obtained as grey powder. Graphite oxide powder was dispersed in DI water to create 1 mg/ml of dispersion. Exfoliated graphite oxide to form GO was achieved through ultrasonication (100W, 40 kHz) for 3 h, in which the bulk graphite oxide powder was transformed into GO. 2.3. Reduction of GO using sodium acetate trihydrate solution Graphene was synthesized via the chemical reduction of GO by sodium acetate trihydrate. A typical procedure was as follows, 1.10 g CH<sub>3</sub>COONa·3H<sub>2</sub>O was dispersed into 55 ml of GO dispersion (1 mg/ml). After being stirred for 0.5 h, the solution was stirred for 24 h at 95 °C. During reduction, the yellow-brown solution gradually changed into a black “fluffy” precipitate. The as-obtained RGO were settled and it was washed with DI water several times to remove the impurities

No. of layers: Few layer graphene

Author: Y H Ding

Title: A green approach to the synthesis of reduced graphene oxide nanosheets under UV irradiation

DOI: 10.1088/0957-4484/22/21/215601

Year of publication: 2011

Abstract: We present a totally green approach towards the synthesis and stabilization of aqueous graphene dispersions through UV-irradiated reduction of exfoliated graphene oxide (GO). Polyvinyl pyrrolidone (PVP) is used to enhance the dispersibility of reduced graphene oxide (RGO) by one-step functionalization. The proposed method is low cost and easy without using any photocatalysts or reducing agents, which can open up a new possibility for green preparation of stable RGO dispersions in large-scale production.

Method of producing graphene: 2.1. Materials and methods GO was prepared by chemical oxidation of natural graphite according to the modified Hummers' method. While maintaining vigorous agitation, natural graphite powder (carbon content >98 wt%, 1.5 g) and sodium nitrate (1.5 g) were mixed with sulfuric acid (70 ml, 98 wt%) in an ice bath. Then potassium permanganate (9 g) was added to the suspension under stirring conditions and the temperature of the system was maintained at 283 K. (Notice: the reaction will get out of control if potassium permanganate was added quickly.) Later the ice bath was removed and the mixture was heated at 303 K for 10 h. Next 100 ml deionized water was carefully added dropwise to the container. The reaction was allowed to proceed for 2 h at 363 K, then the resultant bright-yellow suspension was diluted and further treated with 30 ml 30% hydrogen peroxide. The mixture was followed by centrifugation and careful washing by hydrochloric acid and deionized water until near pH 7. The obtained product was dried under vacuum to remove the water (323 K). Colloidal dispersions of individual GO nanosheets ( $2 \text{ mg ml}^{-1}$ ) were prepared with the aid of ultrasound (KQ-300GVDV, 40 kHz, 100 W). Then the as-prepared GO dispersions were treated with UV irradiation (365 nm, 125 W, height ~5 cm). As a comparison PVP was added to the GO solution to stabilize the RGO nanosheets ( $0.2 \text{ mg ml}^{-1}$ ).

No. of layers: single and multilayer

Author: Takatoshi Yamada

Title: Low-temperature graphene synthesis using microwave plasma CVD

DOI: 10.1088/0022-3727/46/6/063001

Year of publication: 2013

**Abstract:** The graphene chemical vapour deposition (CVD) technique at substrate temperatures around 300 °C by a microwave plasma sustained by surface waves (surface wave plasma chemical vapour deposition, SWP-CVD) is discussed. A low-temperature, large-area and high-deposition-rate CVD process for graphene films was developed. It was found from Raman spectra that the deposited films on copper (Cu) substrates consisted of high-quality graphene flakes. The fabricated graphene transparent conductive electrode showed uniform optical transmittance and sheet resistance, which suggests the possibility of graphene for practical electrical and optoelectronic applications. It is intriguing that graphene was successfully deposited on aluminium (Al) substrates, for which we did not expect the catalytic effect to decompose hydrocarbon and hydrogen molecules. We developed a roll-to-roll SWP-CVD system for continuous graphene film deposition towards industrial mass production. A pair of winder and unwinder systems of Cu film was installed in the plasma CVD apparatus. Uniform Raman spectra were confirmed over the whole width of 297mm of Cu films. We successfully transferred the deposited graphene onto PET films, and confirmed a transmittance of about 95% and a sheet resistance of less than  $7 \times 10^5 \Omega/\text{sq}$ .

**Method of producing graphene:** Our CVD apparatus is equipped with four parallel microwave launchers having five slot antennas in each launcher. It has a substrate holder (400 mm × 600 mm), which enables the reciprocating motion of the substrate in order to deposit graphene on a large area with high uniformity [18]. Graphene depositions were carried out by a two-step process. The first step was the plasma cleaning of the substrate surface, and the second step was graphene deposition. The substrates were mounted on the sample holder. The CVD chamber was evacuated using a turbo molecular pump. For plasma cleaning of the substrate a gas mixture of Ar and H<sub>2</sub> was used (CH<sub>4</sub>/Ar/H<sub>2</sub> flow rate (sccm) 0/50/10), and the duration of the cleaning process was 20 min, Pressure (Pa) 3–5, Microwave power (kW) 12–18. After that, the chamber was evacuated once, and the graphene deposition process was performed using a CH<sub>4</sub>/H<sub>2</sub>/Ar plasma. Typical plasma conditions of the cleaning and deposition processes are listed in table 1 (CH<sub>4</sub>/Ar/H<sub>2</sub> flow rate (sccm) 30/20/10)(Pressure (Pa) 3–5) (Microwave power (kW) 12–18) (Time (min) 0.5–3). The substrates used in this study were rolled Cu foils (33μm in thickness) and rolled aluminium (Al) foils (12μm in thickness). The average surface roughness of the Cu substrate measured by AFM was about 1 nm and typical domain sizes of the Cu substrate area were in the range between 100 and 400μm. For graphene deposition by thermal CVD, a high-temperature heat treatment at around 1000 °C before graphene deposition was important to deposit high-quality graphene since the heat treatment leads to a highly (1 1 1) oriented Cu surface and enlarges the grain size

No. of layers: Bi-layer

Author: Yingpeng Wu

Title: Efficient and large-scale synthesis of few-layered graphene using an arc-discharge method and conductivity studies of the resulting films

DOI: 10.1007/s12274-010-0027-3

Year of publication: 2010

Abstract: An arc-discharge method using a buffer gas containing carbon dioxide has been developed for the efficient and large-scale synthesis of few-layered graphene. The resulting samples of few-layered graphene, well-dispersed in organic solvents such as N,N-dimethylformamide (DMF) and 1,2-dichlorobenzene (o-DCB), were examined by transmission electron microscopy (TEM), X-ray diffraction (XRD), Raman spectroscopy, atomic force microscopy (AFM), and thermal gravimetric analysis (TGA). The electrical conductivity and transparency of flexible films prepared using a direct solution process have also been studied.

Method of producing graphene: Briefly, a direct current (DC) arc-discharge was carried out in a home-made water-cooled stainless steel chamber filled with a mixture of carbon dioxide and helium. Different buffer gas compositions, ranging from 5 vol% to 40 vol% CO<sub>2</sub>, and direct currents of 100 to 200 A were employed for the purposes of comparison. The discharge voltage was kept around 30 V by controlling the distance between the two electrodes. Both electrodes were normal graphite rods obtained commercially, with an anode diameter of 13 mm and a cathode diameter of 40 mm. After discharge, the cotton-like deposition product that formed on the inner wall of the chamber was collected and examined. The optimized conditions for the production of fewlayered graphene were found to be as follows: a low voltage (<35v), a high buffer gas pressure (>1270 Torr), high current (about 150 A) and 25%–40% (v/v) CO<sub>2</sub> in the total buffer gas.

No. of layers: 4-5 layers

Author: C Zhang

Title: Facile synthesis of graphene on dielectric surfaces using a two-temperature reactor CVD system

DOI: 10.1088/0957-4484/24/39/395603

Year of publication: 2013

Abstract: Direct deposition of graphene on a dielectric substrate is demonstrated using a chemical vapor deposition system with a two-temperature reactor. The two-temperature reactor is utilized to offer sufficient, well-proportioned floating Cu atoms and to provide a temperature gradient for facile synthesis of graphene on dielectric surfaces. The evaporated Cu atoms catalyze the reaction in the presented method. C atoms and Cu atoms respectively act as the nuclei for forming graphene film in the low-temperature zone and the zones close to the high-temperature zones. A uniform and high-quality graphene film is formed in an atmosphere of sufficient and well-proportioned floating Cu atoms. Raman spectroscopy, scanning electron microscopy and atomic force microscopy confirm the presence of uniform and high-quality graphene.

Method of producing graphene: Figure 1 illustrates the CVD reactor used in this work. The first high-temperature zone (the upstream one) was heated to 1050 °C and the second high-temperature zone (the downstream one) was heated to 1000 °C, while the temperature of the low-temperature zone (the middle region between the high-temperature zones) is ~800 °C. In order to get a stable reaction atmosphere, a vacuum pump was used to remove the air inside the tube. As depicted in figure 1, two 8 × 12 cm<sup>2</sup> strips of commercially available Cu foil of thickness 25 µm (99.8% purity) were respectively placed in the high-temperature zones and a SiO<sub>2</sub> substrate (2 cm × 2 cm × 0.05 cm, with both sides polished) was spaced in the middle region of the low-temperature zone. Then the furnace was heated and pumped down to 1.0×10<sup>-6</sup> Torr. The Cu foils surrounding the quartz tube were simultaneously annealed to 1000 °C in a 100 sccm H<sub>2</sub> flow for 20 min to remove the remaining copper oxide. Subsequently, H<sub>2</sub> (100 sccm) and CH<sub>4</sub> (200 sccm) were supplied for 30 min growth. After growth, the furnace was cooled down to room temperature quickly by simply opening the furnace

No. of layers: Mono-layer

Author: Zhiyong Wang

Title: Low-cost and large-scale synthesis of graphene nanosheets by arc discharge in air

DOI: 10.1088/0957-4484/21/17/175602

Year of publication: 2010

**Abstract:** Large scale production of graphene nanosheets was achieved by arc evaporation of a graphite rod in air. The graphene nanosheets are ~100–200 nm wide and the number of layers is mainly in the range of 2–10. Several tens of grams of product were obtained per day. The yield of graphene nanosheets was found to be dependent on the pressure of the air, i.e. high pressure facilitates the formation of graphene nanosheets, but low pressure favors the growth of other carbon nanostructures including carbon nanohorns and nanospheres. Based on this result, a pressure-induced mechanism of formation of graphene nanosheets is proposed. The impurities in the products could be eliminated by oxidation in air.

**Method of producing graphene:** The electric arc oven for synthesis of graphene mainly comprises two electrodes and a steel chamber cooled by water. The cathode and anode were graphite rods (purity: 99.99%) with diameters of 8 and 6 mm, respectively. The current in the discharge process was maintained at 100 A. Initial air pressures from 400 to 1000 Torr were employed to investigate the influence of gas pressure. The pressure in the oven was increased to a certain level during the discharge process because of the heating effect. A 10 cm long anode graphite rod was consumed in a period of ~10 min. After the consumption of the anode, flue products deposited on the inner wall of the chamber were collected. Several tens of grams of products were obtained per day. Heat treatment in air was performed to purify the products. The sample was heated in air from room temperature to 600 °C for 2 h and then was cooled down to room temperature.

No. of layers: few layer graphene (< 10 layers)