

Applications of Graphene Electrophoretic Deposition. A Review

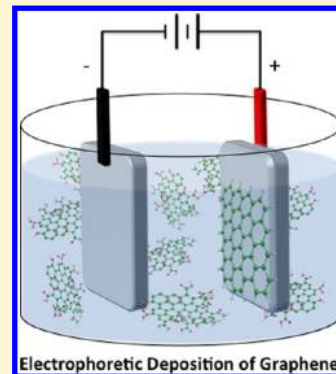
A. Chavez-Valdez,^{†,||} M. S. P. Shaffer,[‡] and A. R. Boccaccini^{*,†,§}

[†]Institute of Biomaterials, University of Erlangen-Nuremberg, 91058 Erlangen, Germany

[‡]Department of Chemistry, Imperial College London, South Kensington Campus, London SW7 2AZ, U.K.

[§]Department of Materials, Imperial College London, South Kensington Campus, London SW7 2AZ, U.K.

ABSTRACT: This Review summarizes research progress employing electrophoretic deposition (EPD) to fabricate graphene and graphene-based nanostructures for a wide range of applications, including energy storage materials, field emission devices, supports for fuel cells, dye-sensitized solar cells, supercapacitors and sensors, among others. These carbonaceous nanomaterials can be dispersed in organic solvents, or more commonly in water, using a variety of techniques compatible with EPD. Most deposits are produced under constant voltage conditions with deposition time also playing an important role in determining the morphology of the resulting graphene structures. In addition to simple planar substrates, it has been shown that uniform graphene-based layers can be deposited on three-dimensional, porous, and even flexible substrates. In general, electrophoretically deposited graphene layers show excellent properties, e.g., high electrical conductivity, large surface area, good thermal stability, high optical transparency, and robust mechanical strength. EPD also enables the fabrication of functional composite materials, e.g., graphene combined with metallic nanoparticles, with other carbonaceous materials (e.g., carbon nanotubes) or polymers, leading to novel nanomaterials with enhanced optical and electrical properties. In summary, the analysis of the available literature reveals that EPD is a simple and convenient processing method for graphene and graphene-based materials, which is easy to apply and versatile. EPD has, therefore, a promising future for applications in the field of advanced nanomaterials, which depend on the reliable manipulation of graphene and graphene-containing systems.



1. INTRODUCTION

Electrophoretic deposition (EPD) is a two-step process in which charged particles in suspension move toward an electrode of opposite charge due to the influence of an electric field and then deposit to form a compact film.¹ EPD is a versatile technique that can be applied to any powdered solid that forms a stable suspension;^{2–4} it operates successfully with a wide range of particle sizes, from micro- to nanometric particles (colloidal suspensions). EPD is also applicable to polymer molecules, as well as to diverse particulate geometries, including equiaxed particles, nanotubes, nanoplatelets, and nanorods. The versatility extends to almost any substrate morphology, from flat or cylindrical to porous, fibrous, or three-dimensional (3D), and to a wide range of (conductive) materials. In addition, EPD offers relatively short processing times and requires only simple, cost-effective equipment^{1–4} to produce uniform deposits with high microstructural homogeneity and adequate control of deposit thickness.³ Significantly, EPD offers the possibility of scaling up to large, application relevant dimensions.^{2,3}

EPD requires the use of a suitable medium for the stable dispersion of particles. Organic solvents such as alcohols and ketones are commonly used due to their relatively high density, good chemical stability, and low conductivity. The disadvantages are their toxicity, cost, and flammability.⁴ On the other hand, an aqueous medium has economical and environmental advantages over organic solvents and can be used for the deposition of sensitive materials.⁵ The main disadvantage of aqueous EPD is the tendency to electrolyze the water at low voltages; however,

this problem can be overcome by minimizing the ionic conductivity of the water or using alternating current (AC) EPD, as reviewed recently.⁶

Interest in EPD is increasing, especially in the field of nanotechnology, considering that nanoparticle suspensions can be manipulated by EPD to create advanced nanostructured coatings and nanoscale films with enhanced properties.⁷ The goal is usually the development of mechanically robust nanocomposite coatings, as well as functional nanostructured films for electronic, biomedical, optical, catalytic, and electrochemical applications.^{7,8} In the field of carbonaceous materials, EPD of carbon nanotubes (CNTs) was initiated a decade ago by Du et al.;⁹ since then, the field has continuously expanded due to the effective manipulation of CNTs (both single-walled (SWCNTs) and multiwalled (MWCNTs)) for applications such as field emission devices, fuel cells, supercapacitors, gas sensors, and biomedical scaffolds, among others.¹⁰ Nanodiamond suspensions have been used to prepare graphene layers via EPD and heat-treatment.¹¹ Recently, there has been an increasing number of investigations dealing with the EPD of graphene and graphene-based materials, reflecting the interest in finding processing routes that may help to exploit graphene's unique

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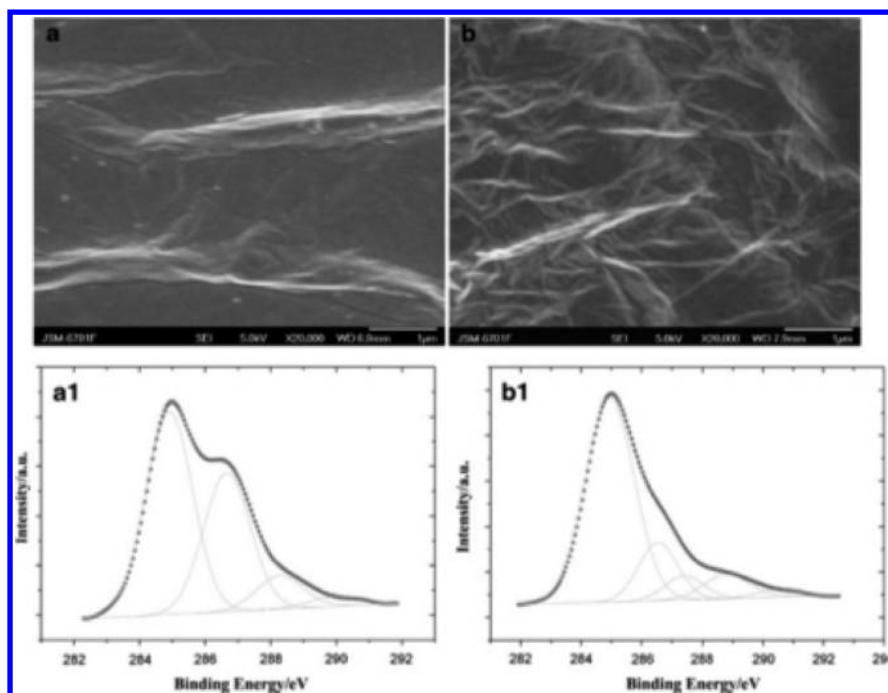


Figure 1. FE-SEM images of GO (a) and GS (b) films prepared by EPD and subsequent electrochemical reduction, respectively; C1s XPS spectra of GO (a1) and GS (b1) films (Reproduced with permission from ref 14. Copyright 2011 Springer).

physical properties, thus anticipating a promising future for applications of this material in high-technology sectors.

The increasing number of publications describing the EPD of graphene and graphene-based materials for a variety of applications demonstrates notable advances in the field and has motivated the preparation of this Review. This overview covers research in the field of electrophoretically deposited graphene-based layers focusing on the evaluation of the nanofilms obtained for the envisaged applications. Key studies in the literature are comprehensively discussed in the context of the specific application described in each case. The Review is, therefore, structured according to the end applications of electrophoretically produced graphene systems, and for each application presented, includes details about materials, suspension media, and EPD conditions.

2. APPLICATIONS OF ELECTROPHORETICALLY DEPOSITED GRAPHENE-BASED LAYERS

Graphene is a flat monolayer of carbon atoms in a two-dimensional (2D) honeycomb lattice.¹² It has excellent electric conductivity, optical transparency, large specific surface area, good thermal stability, electronic properties, and excellent mechanical strength. Applications include field-effect transistors, memory devices, photovoltaic devices, electron acceptors, light absorbers, sensing platforms (e.g., electrochemical sensors and fluorescence sensors), and matrices for mass spectrometry.¹³ EPD is increasingly considered as an attractive technique to process graphene and graphene-based structures, as discussed in this section.

2.1. Electrochemical Electrodes. EPD has been shown to be a useful technique to deposit graphene on conductive substrates for energy storage applications.^{14–20} The interest in graphene sheets (GSs) and other (graphitic) carbonaceous materials for electrical energy storage systems is well-known. Many carbonaceous materials are used as electrochemical electrodes in batteries, supercapacitors, and fuel cells; the high

conductivity and high surface area of graphenes makes them an attractive potential substitute or addition to conventional systems. One issue is the need to avoid restacking of the GSs on deposition or reduction, since the availability of the surface area to electrolyte (or reagents in the case of fuel cells) is key. In some cases, it has proven effective to combine graphene with other spacing components, but EPD has proven an effective means to create porous pure graphene electrodes. Electrochemical double layer capacitors are a simple example in which improved performance is directly related to the accessible surface area of the electrode, and have been a common target for graphene studies.^{21–24} It is worth noting that the flexibility and strength of GS are also attractive in this context, since the electrodes must be robust to handling and electrochemical cycling.²⁵ A number of variants of EPD have been used to form deposits suitable for electrodes, including graphene oxide (GO) deposition with postconversion to GS,¹⁴ direct deposition of GSs,¹⁵ GSs with different microstructures by tuning pH,¹⁶ exfoliated GO reduced before deposition,¹⁷ GO platelets^{18,19} reduced inherently by the EPD conditions, as well as GO layers modified with transition metal oxide interfaces.²⁰ As a typical example, Liu et al.,¹⁴ developed a two-step process, which involved EPD of GO and its subsequent transformation to GS by in situ electrochemical reduction. In this work,¹⁴ well dispersed aqueous suspensions of GO were prepared. GO acquired a negative charge with a zeta potential of -64.7 mV. The material was deposited on indium tin oxide (ITO) electrodes using a constant voltage of 150 V and a deposition time of 45 s. The prepared films were electrochemically reduced to obtain GSs by an explicit constant potential reduction step, in 0.1 M KCl aqueous solution. Figure 1 shows field-emission scanning electron microscopy (FE-SEM) images of GO after EPD and the unchanged morphology of the GS films after electrochemical reduction; X-ray photoelectron spectroscopy (XPS) spectra of the films confirm the oxidized nature of the GO film and the subsequent reduction. The films showed the typical behavior of

electric double-layer capacitors with a low contact resistance; the calculated specific capacitance of the GS film electrode was 156 F g^{-1} at 150 mA g^{-1} . The method thus provides GS films suitable for supercapacitor electrodes.

Chen et al.¹⁵ used EPD to directly deposit graphene nanosheets on nickel foams to form an electrode structure. First, graphene colloids were prepared using *p*-phenylene diamine (PPD) in ethanol. EPD on 3D nickel foam acting as a negative working electrode was carried out at 50 V, followed by annealing at 400°C for 3 h. The nanosheets can be observed by SEM (Figure 2) at high magnification with some corrugation due

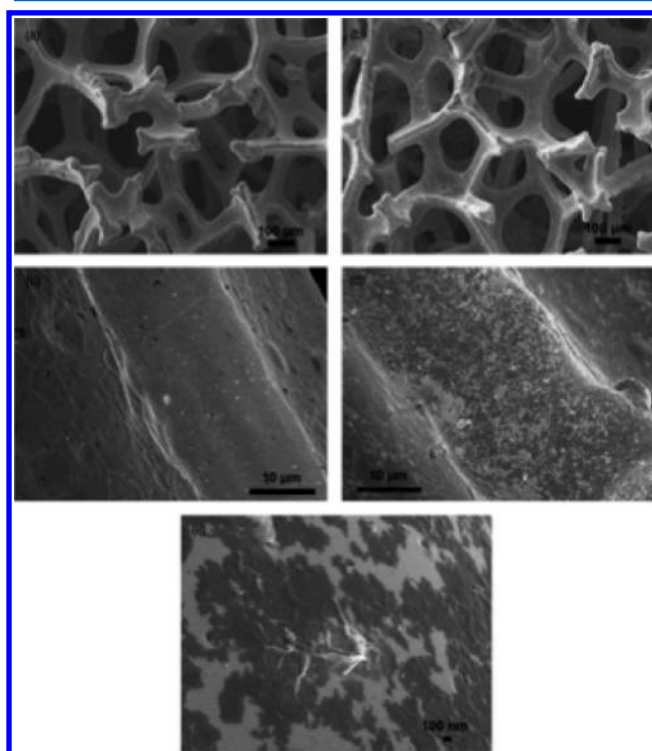


Figure 2. FE-SEM images of (a,c) bare nickel foam and (b,d,e) graphene nanosheets deposited on nickel foam by EPD. (Reproduced with permission from ref 15. Copyright 2010 Elsevier.)

to aggregation and shrinkage. Again, the high capacitance results obtained with graphene nanosheets, that is, their ability to store energy, suggests their potential application as electrochemical capacitors. The study also demonstrated that EPD can be successfully applied to the deposition of GS on 3D conducting porous structures, which is of wide technological relevance to other applications, particularly, but not only, as electrochemical electrodes. It should be noted that the addition of PPD has been also considered by other authors,²⁶ allowing the fabrication of reduced graphene from GO suspensions without any other treatments. Interestingly, the reduced graphene becomes positively charged due to the absorption of the oxidation product of PPD (OPPD) on its surface, showing high stability even for long times; the PPD thus acts both as reductant and, as OPPD, a stabilizer for the reduced GS. A comparison of ethanol, glycol, dimethylformamide (DMF) and *N*-methyl-2-pyrrolidone (NMP) showed ethanol suspensions to be most suitable for EPD and on ITO-coated glass substrates.²⁶

In related studies, Hasan et al.¹⁶ tuned the pH of graphene suspensions to obtain deposition on the positive ("smooth rug" microstructure) or negative ("porous brick" microstructure)

electrode. Aqueous suspensions of exfoliated GO flakes were prepared with individual thickness of 0.7 nm and a negative charge at a range of pH values. Figure 3a–c shows the films obtained at pH 11.5 using 3 V and 3 min as EPD conditions. The material deposited homogeneously on the stainless steel electrode with some overlapping of the sheets. Figure 3d–f shows the images of the film deposited at pH 2.8 using 15 V for 10 min. The particular microstructure (porous brick) was formed by stacking sheets of different heights. The static contact angles of both types of graphene films are also shown in this figure, indicating a more hydrophobic behavior for the brick microstructure. It was also shown that it is possible to detach the layers from the substrate to obtain free-standing pure graphene constructs.

Lee and co-workers¹⁷ developed two processing approaches involving EPD of graphene. In the first case, GO obtained from graphite oxidation and exfoliation was suspended in aqueous solution for EPD, and then the films were reduced via dip coating in aqueous hydrazine solution. In the second case, GO was reduced to graphene nanosheets in alkali solution and then deposited by EPD. The alignment of the films was evaluated by soft X-ray absorption, and it was shown that films reduced with hydrazine after deposition were smoother and better aligned. EPD proved to be a technique suitable for the production of graphene films with better packing and alignment compared to spray coating techniques, while avoiding the addition of cross-linking molecules or binders.

Lake et al.²⁰ reported the preparation of hybrid capacitor electrodes, combining redox-active pseudocapacitive oxides with the graphene framework. The electrodes were based on deposition of a nanostructured transition metal oxide (Co_3O_4 and MnO_2) by a hydrothermal method, followed by EPD of GO and its chemical reduction. The substrates used for deposition of metal oxides were aluminum, copper, titanium, and stainless steel. Co_3O_4 nanowires were first deposited followed by deposition of MnO_2 nanostructures to increase the capacitance of the material. The GO layer deposited on top of the metal oxides was uniform. The films were annealed at 100°C and then chemically reduced in situ with sodium borohydride. After the reduction process, films exhibited an increase in density, which should increase the charge mobility, in addition to the direct chemical effect. The reduced GO layer was porous, exhibiting high surface area. Cyclic voltammetry measurements in KOH electrolyte showed values of specific capacitance for the films up to 117 F/g . The film provided good electrical contact, a high concentration of electroactive sites, as well as shorter transport and diffusion path lengths leading to relatively high specific capacitances. The low-cost two-step process developed, which does not require the addition of binders, thus leads to reduced GO layers coupled to metal oxide layers to enhance the energy density of the electrode.

Other types of graphene containing nanocomposites such as graphene-NiO,^{27,28} graphene-TiO₂,²⁹ and graphene-CdSe quantum dots³⁰ have been obtained by EPD. In the work of Xia et al.²⁷ for example, the addition of NiO to the carbon material, which can be used as capacitor, improved the power and energy densities increasing the capacitance. For EPD, a GO suspension in isopropyl alcohol was used in which GO exhibited a positive surface charge in the presence of magnesium nitrate. The EPD conditions were 100 V and 20 s, and graphene was deposited on nickel-foam substrates. The GS was well adhered to the substrate due to the formation of a hydroxide layer at the interface. Porous NiO was then added by chemical bath deposition showing a

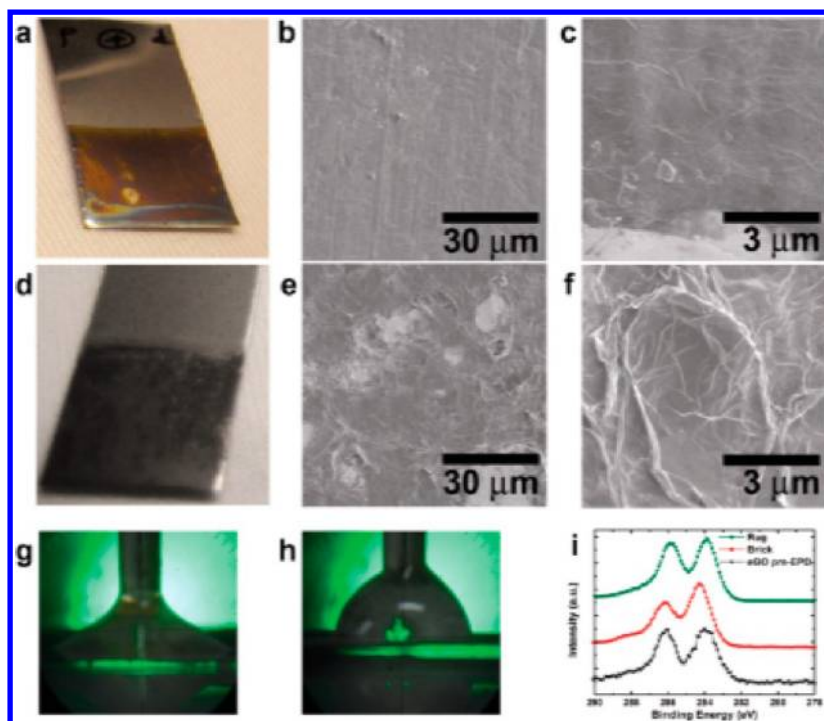


Figure 3. Characterization of electrophoretically deposited GO films obtained by Hasan et al.¹⁶ Films with rug microstructure shown in a photograph (a) and in SEM images (b,c). Films with brick microstructure shown in a photograph (d) and in SEM images (e,f). Static water static contact angles for the rug (g) and brick (h) films, 41° and 79°, respectively. (i) XPS measurements of the C1s spectra for the rug and brick GO films and the GO sheets prior to EPD. Since the C1s spectra remain largely unchanged after EPD, the associated higher contact angle of the brick films is attributed to the presence of microscale voids, such as air pockets, and not to the film chemistry. (Reproduced with permission from ref 16. Copyright 2010 American Chemical Society).

netlike structure with interconnected nanoflakes and pore size of 30–300 nm in diameter and thickness of 10–20 nm. The composite exhibited excellent pseudocapacitive behavior with values of 400 and 324 F/g at 2 and 40 A/g, respectively, and retained 94% of the initial capacitance over 2000 cycles. The enhancement of the pseudocapacitive properties was related to the reinforcement of the electrochemical activity of the graphene film. It was demonstrated that a two-step process involving EPD and chemical bath deposition is a feasible technique to obtain graphene-based composites with enhanced capacitance. For the same type of graphene–NiO composites, Wu et al.²⁸ used only EPD instead of a two-step process. GO nanosheets were exfoliated from natural graphite flakes. The material was then dispersed in isopropyl alcohol, and nickel nitrate was added, allowing a degree of coordination to the GO surface groups. The originally negatively charged GSs were thus charged by the nickel ions, to produce a good dispersion of mixed Ni–GS precursor. After deposition on stainless steel, the films were dried at 300 °C for 1 h. During EPD, the nickel ions were electrochemically reduced to nickel particles and then converted to NiO nanoparticles after annealing, producing a good final dispersion in the hybrid deposit. The specific capacitance of the NiO-attached GO films reached 569 F/g, which is 40 times higher than that of bare GO electrode (13 F/g). The increase in specific capacitance in the composite was attributed to the presence of the nanoparticles that increased the distance between the GSs and acted as nanospacers to avoid face-to-face aggregation, as well as provided the pseudocapacitance of the oxide. EPD is thus a convenient technique to obtain, in a single step, layers of graphene modified with NiO exhibiting high capacitance. This

process can be applied to combinations of graphene with other materials for a variety of applications.

Combinations of graphene with conducting polymers of the type polypyrrole or porphyrin have been also reported for developing devices with relatively high (pseudo)capacitance.^{31,32} EPD of the graphene material was carried out followed by electropolymerization. First, commercially available graphene was deposited on titanium substrates by EPD. After EPD, pyrrole was deposited by means of electropolymerization. The nanocomposite with a highly porous structure assisted the interaction of the electrode with the electrolyte. Cyclic voltammetry tests showed high capacitance (1510 F/g) due to the porous morphology of the nanocomposite. This type of nanocomposite electrode is particularly suited to supercapacitors, although it may also have relevance to photovoltaic cells and other energy storage devices. In addition, other conducting polymers can also be considered for suitable combinations with graphene. Karousis et al.³² for example, reported the preparation and characterization of graphene-oxide-(4-aminophenyl)-10,15,20-triphenyl-21,23H-porphyrin (H₂P) composites and used EPD for the preparation of electrodes to evaluate the photoelectrochemical properties of the composite. The starting material was graphite, which was oxidized and then converted to GO with addition of different reactants. Then, the material was reacted with H₂P to obtain the composite. The composite formed a stable suspension in DMF. GO–H₂P films were deposited by EPD on nanostructured SnO₂ films cast onto an optically transparent electrode (OTE/SnO₂) to be used in photoelectrochemical cells. During photoluminescence spectroscopy measurements, the composite electrode absorbed incident light in the visible region with a broader absorption than the composite before

EPD. This effect was the result of cluster formation of porphyrin moieties or electronic interaction between GO and H_2P . These graphene-polymer composites made by EPD have potential use in novel optoelectronic devices.

Another significant application of GO layers is in fuel cells as electrocatalyst supports. Several publications have reported the deposition of composites formed by graphene and metallic nanoparticles such as Pt,^{33–35} and Au.³⁶ For example, graphene-platinum nanocomposites have been prepared with the aim to produce electrocatalyst supports for fuel cells and to reduce the use of precious metals. In the investigation of Seger et al.,³³ GO was obtained from chemical oxidation of graphite powder. The preparation of the composite was achieved by mixing H_2PtCl_6 with GO in aqueous solution during a process called borohydride reduction to obtain metallic Pt attached to the GSs. Then, the GO–Pt material was added to tetrahydrofuran solution, and it was deposited by EPD (or drop cast) on carbon (Toray) paper substrates. For EPD, an electric field of 75 V/cm and a concentration of Pt of 10 $\mu\text{g}/\text{cm}^2$ were used. The graphene-Pt composites were treated with hydrazine for reduction and reestablishment of the sp^2 network of GO. The films were subsequently annealed at 300 °C for 8 h to remove the hydrazine. The composites were tested by electrochemically active surface area (ECSA) measurements for assessing the catalyst surface available for charge transfer and the conduction of electrons using hydrogen adsorption/desorption. An enhancement of 77% in the ECSA was obtained (related to the electrode annealed for 2 h), proving that graphene–Pt composite layers deposited by EPD are attractive materials for electrocatalyst support applications.

A related investigation reported the production of similar graphene–Pt nanoparticle composites by EPD from colloidal suspensions.³⁴ Nanocomposites were developed by two approaches: alternating layers of graphene and Pt nanoparticles and suspensions containing the composite material. GO was obtained from exfoliation of graphite oxide, and subsequent reduction of the material in hydrazine was employed to obtain graphene. The mixture of graphene and platinum nanoparticles was prepared in DMF, and the particles were deposited on ITO-coated glass substrates. Graphene showed a negative surface charge in water with zeta potential of -35.9 mV, and it was deposited at 4 V for 30 s. In the case of Pt nanoparticles, a zeta potential of -18.3 mV was acquired in acetone, and the particles were deposited at 5 V for 180, 300, and 600 s. When using a two-layer deposition, the first layer of graphene covered well the ITO substrate after a deposition time of 30 s and had a thickness of approximately 80 nm. Then, Pt nanoparticles were deposited on top of this layer but were not homogeneously distributed and formed clusters. For EPD of graphene–Pt composites, a deposition time of 60 s resulted in substrates completely covered with graphene and Pt nanoparticles of smaller size. The results showed better electrocatalytic performance, measured by cyclic voltammetry, of the composite layers obtained by a single step than in those obtained by layer-by-layer deposition. It is expected that these composites can be used for dye-sensitized solar cells and hydrogen generation devices. Moreover, Pt/graphene nanocomposites with high catalytic activity and good stability for the oxidation of methanol have been prepared by EPD combined with in situ electrochemical reduction.³⁵ Expandable graphene oxide (EGO) was obtained from expandable graphite powder and deposited by EPD on ITO substrates, by applying 150 V for 45 s. The voltage applied was 150 V for 45 s. After EPD, the film was electrochemically reduced in situ to obtain GSs

(EGSs), and Pt nanoparticles were electrochemically deposited to obtain a composite material. Typical morphologies of the GO sheets and composites are shown in Figure 4. The as-deposited

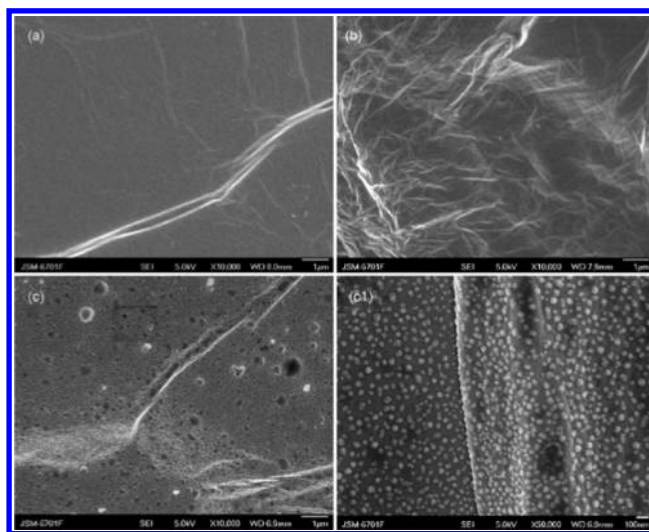


Figure 4. FE-SEM images of EGO (a), EGS (b), and Pt/EGS (c,c1) layer obtained by EPD at increasing magnifications. (Reproduced with permission from ref 35. Copyright 2010 Elsevier).

GO film was formed of many graphene layers with a total thickness of 1 μm when using a deposition time of 45 s. In the composite, Pt nanoparticles were evenly distributed and dispersed on the GSs. According to cyclic voltammetry results, dispersed Pt nanoparticles on the surface of GSs had an electrocatalytic effect for methanol oxidation. The high surface area and electrical conductivity of graphene and the synergistic electrocatalytic effect with Pt nanoparticles make the composites suitable as support structures in fuel cells.

In related investigations, Zhu et al.³⁶ prepared reduced graphene–Au nanoparticle composites by EPD. The composite material was obtained by microwave-assisted reduction of HAuCl_4 in alkaline graphite oxide dispersion. The composite was dispersed in acetone-ethanol solution with $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ as charging agent. The substrate material was conductive graphite paper. EPD tests were carried out at 30 V for 30 min. The composite morphology showed reduced nanosheets in a 3D porous structure with dispersed Au nanoparticles. The thickness of the film was approximately 20 μm . The electrical conductivity of the composite was improved by the addition of Au nanoparticles. Electrochemical impedance spectroscopy results showed higher catalytic activity and electrical conductivity in the composite. The energy conversion efficiency value for this type of electrode was 1.36%, and the incident photon-to-current conversion efficiency was 48%, which is higher than the values for Pt or Au counter electrodes used in quantum dot solar cells. These favorable results are due to the suitable combination of a conductive graphene network structure and highly catalytic Au nanoparticles. The results indicate that when applying EPD, the low-cost production of flexible counter electrodes with higher performance for solar cells is possible. These electrodes are candidates to substitute the current higher-cost Pt-, Au-, CoS-, and Cu_2S -based electrodes.

2.2. Field Emission Devices. The stability, conductivity, and sharp “edge” of GSs are cited as reasons to consider application as field emission electrodes. Careful control of the morphology is required, to maximize roughness and GS individualization, since

a high effective aspect ratio improves the field enhancement (and lowers the effective turn on voltage). Due to difficulties in isolating single GSs for field emission measurements and the need for large area emitters for flat panel displays and lighting cathodes, EPD has been explored as a potential electrode fabrication method.^{26,37–39} In the investigation of Wu et al.,³⁷ GO was obtained from artificial graphite and suspended in isopropyl alcohol. The suspension was stabilized with magnesium nitrate, a positive “charger” for the naturally negatively charged material; a similar technique was originally developed for CNTs. For EPD tests, voltages in the range 100–160 V were applied for 1 min. The results showed graphene layers with homogeneous and macroscopically planar structure but a random GS orientation, leading to locally sharp edges suitable for emission; the study claims 80% single nanographenes with a thickness of 1.1 nm, based on dilute depositions, but it is not clear what level of restacking may occur in thicker deposits. The individual GSs exhibited a high electric conductivity ($\sim 10^3$ S cm^{-1}) after processing, with the ensemble films offering adequate conductivity for measurement. Varying the deposition time, voltage, and the relative concentration of additive and graphene led to changes in the thickness of the electrophoretically deposited sheets. The deposited graphene films exhibited field emission properties comparable to those of CNTs due to their excellent electrical conductivity and high aspect ratio of the emitting edges. The graphene films showed high emission stability without degradation at low current densities. The stability of these electrophoretic graphene films was attributed to their homogeneous surface morphology and the presence of at least some edges oriented nearly normal to the substrate for emission uniformity. Therefore, this type of film can be used as conductive coatings in electronic devices and high-performance field emitters. On the other hand, Chen et al.³⁸ reported a hysteresis phenomenon during the measurements of field emission properties of graphene films obtained by EPD. As a further development, Maiti et al.³⁹ reported the preparation of flexible field emission arrays by depositing graphene films reduced with hydrazine in aqueous suspension onto 3D carbon fabric substrates. In this case, EPD was carried out at constant current condition of 2.4 mA/cm for 5 s to 10 min. Graphene was seen to be uniformly distributed on single carbon fibers within the woven geometry of the fabric. Short deposition times resulted in flat layers, while higher deposition times resulted in thicker coatings exhibiting wrinkles and agglomeration. After EPD, plasma etching was applied to the deposited films, which generated a hierarchical structure of isolated graphene nanocones supported on the carbon fibres. This structure maximized the apparent field enhancement, leading to a low threshold field of $0.81 \text{ V } \mu\text{m}^{-1}$, as the carbon fiber support created a flexible field emission device, as well as providing a high degree of electrical and thermal conductivity.

Several investigations have focused on the enhancement of the field emission properties of graphene films obtained by EPD by coating with CsI,⁴⁰ combining with SnO_2 ,⁴¹ doping with nitrogen or boron,⁴² and/or adding a Ti interface layer.⁴³ In the case of CsI,⁴⁰ the salt was added by drop-coating onto annealed GS films (500 °C, 2 h), prepared by EPD as reported in ref 37. For comparison purposes, MWCNTs were also deposited by EPD and coated with CsI. The obtained graphene films were smooth with uniform morphology and a thickness below 1 nm. After coating, CsI dispersed well on the surface showing a uniform particle distribution on the GS. The field emission properties of the GSs were improved after coating with CsI, showing a turn-on

field that decreased from $4.4 \text{ V}/\mu\text{m}$ to $2.5 \text{ V}/\mu\text{m}$ while the threshold field decreased from $9 \text{ V}/\mu\text{m}$ to $5.8 \text{ V}/\mu\text{m}$, respectively; this improvement was attributed to the low electron affinity of CsI. Surprisingly, the field emission characteristics were better for the graphene than for the MWCNT control, possibly due to the distinct morphology, edges, and corrugation in the GSs that acted as sharper emitters than the relatively larger MWCNTs. In a related investigation, Ding et al.⁴¹ reported the development of graphene– SnO_2 composites. For the preparation of the composite, graphene was deposited by EPD on Si substrates. Graphene was dispersed in isopropyl alcohol with the addition of a zinc nitrate hexahydrate “charger”. A voltage of 300 V was applied for 3 min to obtain graphene layers. Then, Sn nanoparticles were deposited on the graphene surface by sputtering. After preparing the composite, it was heated at 400 °C in O_2 atmosphere to obtain graphene– SnO_2 nanostructures. The field emission properties and photoluminescence of the composites were evaluated. The field emission-current density measurements showed that the turn-on field of the graphene layer was $4.14 \text{ V}/\mu\text{m}$ and $5.39 \text{ V}/\mu\text{m}$ (10 min sputtering) and $3.86 \text{ V}/\mu\text{m}$ (5 min sputtering) for the composite. The threshold field was $9.4 \text{ V}/\mu\text{m}$ and $10.2 \text{ V}/\mu\text{m}$ (10 min) and $8.6 \text{ V}/\mu\text{m}$ (5 min) for the graphene layer and the composite, respectively. These results indicated that field emission characteristics of the composite were improved by adding the graphene layer and by decreasing the sputtering time. The photoluminescence results also indicated an increase after deposition of graphene. Therefore, it was concluded that the graphene layer could improve both the field emission and photoluminescence properties of SnO_2 nanostructures. Palnitkar et al.³³ reported the preparation of nitrogen and boron doped graphene materials, via arc discharge in hydrogen. The doping was done by arc discharge in hydrogen. The materials (doped and undoped) were deposited by EPD, onto silicon wafers, following the process reported by Wu et al.,³⁷ using isopropyl alcohol as the dispersing medium and voltage and deposition time of 100 V and 1 min, respectively. The lowest turn-on field was obtained with nitrogen-doped graphene ($0.6 \text{ V}/\mu\text{m}$). It was claimed⁴² that values for all samples were lower than values reported in literature. Furthermore, the addition of a Ti layer at the interface between the chemically reduced GO and the silicon substrate, followed by an annealing process, was shown to improve the field emission properties.⁴³ The method involved deposition of a 100 nm Ti layer by ion-beam sputtering before the GO EPD. The films were annealed at different temperatures from 600 to 900 °C in argon atmosphere for 1 h. The surface morphology of the films changed after the annealing treatment, decreasing the surface roughness and increasing densification. The best field emission performance was obtained with annealed GO–Ti layers. The role of the Ti transition layer was to improve the adhesion between graphene and the substrate and therefore the contact between the substrate and emitter, as well as field emission. The cathode materials prepared by EPD may have practical relevance to the fabrication of low cost, large-area field emitters in the future.

2.3. Transparent Conductors. An et al.¹⁸ and Ishikawa et al.¹⁹ studied the fabrication of transparent, conductive (reduced) GO films by EPD; transparent conductors are required for flat displays and light emitting diodes, among many other applications, but requires deposition over large areas. In this research,¹⁸ reduced GS was obtained without the addition of chemical agents or high-temperature treatments, instead relying on the intrinsic EPD process. GO synthesized from natural graphite was dispersed in water and deposited on stainless steel

meshes and other conductive substrates such as Cu, Ni, Al, and p-type Si. The stacked layers formed were homogeneous and smooth (Figure 5) with a thickness of 4 μm after deposition for 2

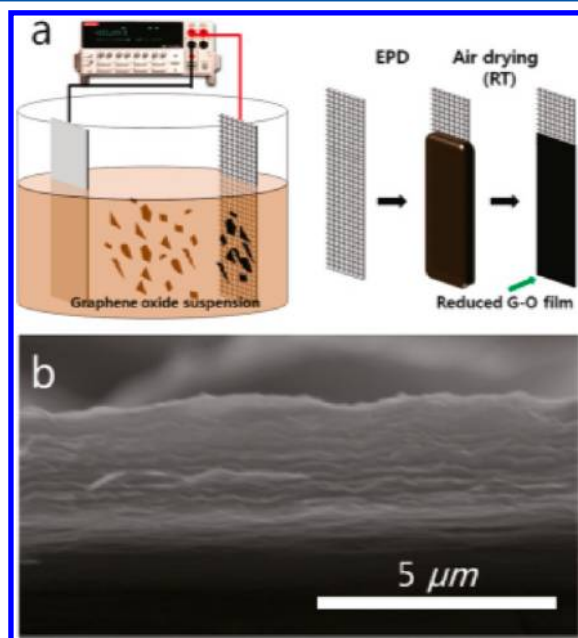


Figure 5. (a) Schematic diagram of the EPD process used to obtain conductive GO films according to An et al.¹⁸ and (b) cross-sectional SEM image of EPD-GO film. (Reproduced with permission from ref 18. Copyright 2010 American Chemical Society.)

min. The deposition times in this investigation allowed the formation of layers from hundreds of nanometers to tens of micrometers in thickness. The conductivity values of the obtained films ($1.43 \times 10^4 \text{ S m}^{-1}$) were higher than the values for GO paper obtained by the filtration method ($0.53 \times 10^{-3} \text{ S m}^{-1}$).⁴⁴ In general, the oxygen-containing functional groups of GO were substantially removed during the EPD process with the result that the film showed improved conductivity and low adhesion to the substrate for easy detachment. Alternatively, monolayer GO flakes were obtained from exfoliation of graphite oxide¹⁹ and deposited on SiO_2/Si substrates. The optimal conditions to obtain graphene films with high uniformity were a voltage of 10 V and EPD time of 5 min. These conditions allowed a few layers of reduced graphene to be obtained with no wrinkles. The optical transmittance of the films was 83.7%. The films showed lower sheet resistance than chemically or thermally reduced GO films, and they have potential for applications requiring transparent conductive materials. XPS spectra showed EPD-graphene films to be significantly reduced after deposition, which indicates that the films were electrochemically reduced, the mechanism of reduction was not further investigated, however, and this remains an interesting area for future research as it can have interesting implications for the broader application of graphene EPD.

2.4. Electrodes for Solar Cells. There is increasing interest in the fabrication of carbon-based electrodes for dye-sensitized solar cells to substitute current Pt electrodes; the preparation by EPD of pure graphene counter electrodes is attractive, given their chemical stability, conductivity, and robustness; their transparency may have given more flexibility in cell design.^{45–47} Choi et al.^{45,46} evaluated the electrochemical properties (conversion efficiencies) and transparency of graphene electrodes. For EPD,

suspensions were prepared using deionized water with a concentration of graphene of 0.25 wt %. Then, magnesium nitrate, ethanol, and the graphene solution were mixed together to obtain a stable suspension. Fluorine-doped SnO_2 (FTO) glass was used as working electrode. The EPD conditions explored were 10–30 V, times of 5–30 s, and annealing at 200–600 $^\circ\text{C}$ for 1 min. The optical properties measured by UV visible spectrometer showed 5, 7, 11, and 16 graphene layers deposited by using different deposition times. An optical transmittance over 80% was obtained at low deposition times, which was seen to decrease with increasing deposition time. High-energy conversion efficiency of 2.3% and current density of 5.5 mA/cm^2 were achieved with this type of graphene counter electrode. In a more recent study,⁴⁶ the thickness of the graphene layer was 5 nm and 5.69% conversion efficiency was achieved after annealing at 600 $^\circ\text{C}$ due to removal of magnesium ions and oxygen attached to the GS. Similar research by Sima et al.⁴⁷ used GSs obtained by electrochemical oxidation of graphite followed by reduction with hydrazine and exfoliation. The GSs obtained were transparent but a multilayer material was formed. The material was dispersed in water acquiring a negative surface charge for EPD without a separate “charger”. In these investigations, EPDed graphene again proved to be a suitable material for counter electrodes in dye-sensitized solar cells.

As well as the counter electrode, EPD has also been used to prepare graphene-enhanced TiO_2 nanostructured coatings as the active electron-collecting electrode in dye sensitized solar cells.²⁹ Graphene was used as reinforcement to improve the mechanical, thermal and electrical properties of TiO_2 . The schematic representation of the process used to obtain this type of composites is presented in Figure 6. GSs were prepared from chemical reduction of graphite oxide and hydrazine. Then, the GS were dispersed in anhydrous ethanol, and titanium alkoxide precursor was added to form the composite via a hydrolysis reaction. An ethanol suspension of positively charged GS- TiO_2 particles was used for EPD. A voltage of 30 V for 3 min was

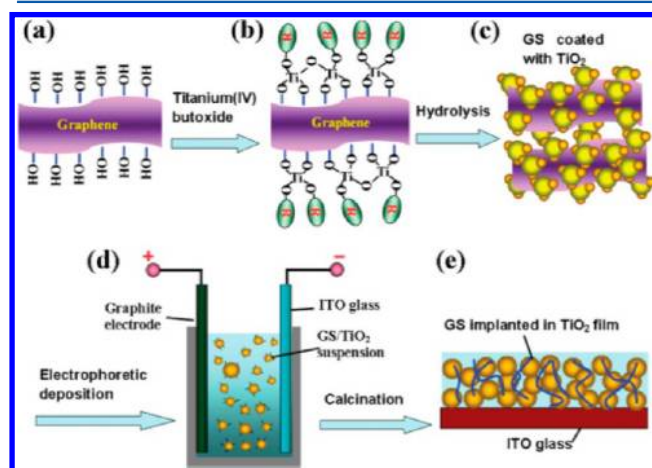


Figure 6. Schematic flowchart of in situ incorporation of GS in nanostructured TiO_2 films by EPD, according to Tang et al.²⁹ (a) GS prepared by chemical exfoliation with residual oxygen-containing functional groups, such as hydroxyl, (b) schematic diagram showing titanium(IV) butoxide grafted on reduced GS surfaces by chemisorptions, (c) schematic diagram of GS coated with TiO_2 colloids after hydrolysis, (d) illustration of the EPD process used to prepare GS/ TiO_2 composite films, (e) schematic representation of the structure of the GS/ TiO_2 composite film after calcination. (Reproduced with permission from ref 29. Copyright 2010 American Chemical Society.)

applied to obtain a film thickness of 460 nm. The films were uniform with large areas covered. It was observed that the incorporation of GS up to a certain amount improved the conductivity of the composite. The photovoltaic performance of the films was also tested. The power conversion efficiency was increased significantly by the presence of GS. This result was due to a decreased charge-transfer resistance in the composite films as result of GS addition.

An approach to economically harvest solar energy has been reported that is based on the preparation of composite quantum dot solar cells.³⁰ Graphene is a promising electron acceptor in photovoltaic devices and was used with CdS quantum dots to fabricate a photovoltaic device composed of a layered nanofilm. Graphene in aqueous suspension obtained from natural graphite was deposited by EPD on ITO glass. EPD was carried out under constant current density for 75s. Then a layer of CdS quantum dots was deposited by chemical bath deposition. These two processes, i.e., EPD and chemical bath deposition, were repeated several times to obtain a layered material. CdS quantum dots were seen to be uniformly distributed on graphene nanosheets with diameter of 5 nm, which can favor the performance of a photovoltaic device. The different graphene and CdS layers deposited had thicknesses of 30 and 120 nm, respectively. A maximum value of 16% in incident photon-to-charge-carrier conversion efficiency was achieved from eight graphene–CdS bilayers. It was confirmed that the performance of CdS quantum dots solar cells can be improved by the addition of graphene and by forming a nanoscale layered structure, which can collect and transport photogenerated charges. This type of devices obtained by a simple two-step process involving EPD and chemical bath deposition has potential for applications in the next generation of solar cells.

2.5. Electrochemical Sensors and Biosensors. Graphene films obtained by EPD have been used as electrochemical sensors⁴⁸ and biosensors.⁴⁹ For example, Tang et al.⁴⁸ reported the preparation of GS for the detection of explosive compounds such as TNT. Nanostructures as electrodes provide the surface area, catalytic activity and chemical stability for electrochemical reduction of explosive compounds and can be incorporated into sensing platforms. Aromatic explosives can be strongly adsorbed on graphene surfaces due to π – π interactions. In the study of Tang et al.,⁴⁸ GO nanosheets of 1.2 nm in thickness were synthesized from graphite and dispersed in DMF for EPD. The suspension showed high stability with negatively charged GSs. The deposition electrode used was glassy carbon substrates, and an optimum voltage of 120 V was applied for 3 min. The graphene film was subjected to hydrazine vapor for reduction to eliminate the oxygen functional groups and to restore conductivity. The results showed fast electron-transfer ability in reduced films and lower electron transfer resistance improving the conductivity of the film. The graphene sensor showed excellent sensitivity and selectivity to nitroaromatic compounds. This study showing the possibility of EPD fabrication of novel graphene-based sensors can be expanded to consider applications in trace detection, environmental monitoring, or laboratory analysis. In many applications, it may be important to consider whether the electrode has resistance to fouling. Akhavan et al.⁴⁹ tested the toxicity of graphene nanosheets in the form of nanowalls obtained by EPD. First, a suspension containing Mg^{2+} –GO nanosheets synthesized by a chemical exfoliation method was used to obtain graphene nanowalls. For EPD, GO was dispersed as described by Wu et al.³⁷ After EPD, the nanowalls were reduced with hydrazine vapor or used without

reduction. Both materials deposited, namely, graphene oxide nanowalls (GONWs) and reduced nanowalls (RGNWs), were tested for bacterial toxicity. The deposited material on a stainless steel substrate showed multilayer GSs with some sheets in perpendicular orientation providing sharp edges. Bacteria *Escherichia coli* and *Staphylococcus aureus* were used for bactericidal tests in contact with the graphene films. A better antibacterial activity (Figures 7 and 8) was found with RGNWs

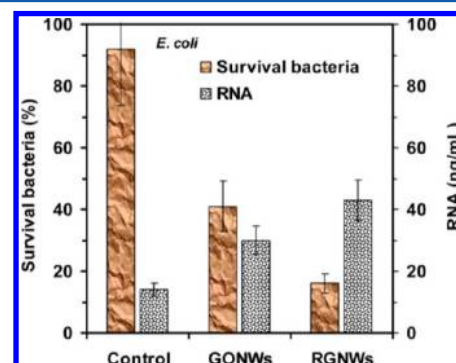


Figure 7. Cytotoxicity of GONWs and RGNWs deposited by EPD to *E. coli*, and concentrations of RNA in the PBS of the *E. coli* bacteria exposed to the nanowalls, according to Akhavan et al.⁴⁹ (Reproduced with permission from ref 49. Copyright 2010 American Chemical Society).

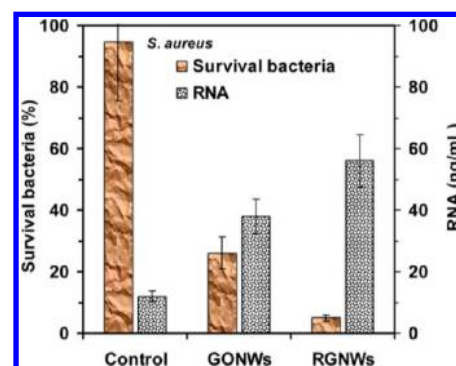


Figure 8. Cytotoxicity of GONWs and RGNWs deposited by EPD to *S. aureus*, and concentrations of RNA in the PBS of the *S. aureus* bacteria exposed to the nanowalls, according to Akhavan et al.⁴⁹ (Reproduced with permission from ref 49. Copyright 2010 American Chemical Society.)

due to better charge transfer between the bacteria and the sharper edges for the reduced material. Although the reduced nanowalls showed toxicity against both bacteria, the effect was stronger for *S. aureus*. This study has thus demonstrated the versatility of EPD for development of this type of graphene nanowalls, which provide potentially useful biosensing and bioelectronics platforms.

2.6. Graphene-Containing Functional Carbonaceous Nanocomposites: Various Applications. This section covers the EPD of graphene in combination with other carbonaceous (nano)materials to obtain nanocomposites for various applications. In particular, the combination of graphene and CNTs attracts increasing attention given their chemical similarity and complementary morphology, which can be conveniently exploited in functional devices in areas ranging from optoelectronics⁵⁰ to solar cells,^{51,52} and supercapacitors.^{53–55} There is increasing interest in producing carbon nanostructured films on flexible conductive substrates for applications in the field of

optoelectronics through low-cost fabrication methods.^{56,57} Bittolo Bon et al.,⁵⁰ for example, deposited carbon based composites on polymeric substrates in order to modify the substrate's electrical and optical properties. GS and carboxy-functionalized carbon nanotubes (C-SWCNTs) were used as starting materials. Different concentrations of GSs and C-SWCNTs were dispersed in anhydrous 1-ethyl-2-pyrrolidinone and sonicated to obtain a stable suspension. For comparison purposes, the drop cast method was also used, but it showed agglomerated powder in some areas of the substrate, also leaving undesired uncovered areas. The GS film obtained by EPD was uniform with a flake-like morphology, the C-SWCNTs film showed a rough surface of CNT bundles, while the hybrid material C-SWCNT-GS showed a decrease in surface roughness. The thickness of the EPD films was in the range of 1 to 2 nm. These films exhibited the best optical and electrical properties according to transmittance and conductivity measurements. The addition of CNTs increased the thickness of the films as well as the absorbance and conductivity. The role of CNTs in the film was to act to connect and space the GS. EPD can be thus considered to be a cost-effective and robust technique to produce carbonaceous nanocomposites of GS-SWCNTs on flexible substrates with improved optical and electrical properties. Zhu et al.⁵¹ and Kim et al.⁵² reported the preparation of reduced graphene-CNT composites on graphite substrates for dye-sensitized solar cells due to their excellent electronic, conductive, and mechanical properties, superior chemical stability, and high specific surface area. In this work,⁵¹ the conversion of graphite oxide to GS was achieved by the microwave-assisted oxidation and reduction process. The added CNTs were reported to act as connectors between GS in order to improve the electric, optic, catalytic, and mechanical properties.^{58,59} For EPD, suspensions were prepared by mixing MWCNTs in an acetone-ethanol mixture with the addition of reduced graphene. A voltage of 30 V for 30 min was used to obtain composite films with different concentrations of CNTs. FE-SEM images of the composites with different concentrations of CNTs showed that the addition of CNTs resulted in a network structure bridging gaps between reduced GS and acting as "wires" that connected the sheets. This configuration favors electron transfer between CNTs and graphene. Using too high a concentration of CNTs completely covered the GSs. The thickness of the composites was approximately 20 μm . Conductivity measurements showed an increase in the electric conductivity with CNTs content and the counter electrodes obtained by EPD had efficiency comparable to that of (expensive) Pt electrodes. The current density showed higher values than for Pt electrodes due to the large surface area for catalysis especially for composites incorporating 60 wt % of CNTs. EPD represents thus a promising technique for the production of carbonaceous composite electrodes for dye sensitized solar cells with improved current density and conductivity. In the study of Kim et al.,⁵² suspensions for EPD were prepared in ethanol with addition of magnesium nitrate. The graphene electrodes obtained by EPD showed wrinkles due to overlapping. The optical transmittance of the electrodes was 62, 70, and 67% for graphene, SWNTs and graphene-SWNT composites, respectively. In the evaluation for solar cells, the best results were obtained with graphene electrodes with values of conversion efficiency of 5.87%. Future work in this area should focus on improving the efficiency of the carbon-based electrodes, which can be achieved with optimization of the EPD processing method.

A series of graphene-CNT composite systems have been investigated for supercapacitor applications; e.g., Lu et al.⁵³ deposited reduced GO-CNT composites, Ata et al.⁵⁴ deposited graphene, CNTs, TiO_2 , and their composites by EPD, and Seo et al.⁵⁵ investigated the EPD of GS-MWCNTs composites. Microwave-assisted reduction was used to obtain the reduced GO by Lu et al.⁵³ Purified CNTs were mixed with reduced GO in acetone-ethanol solution with addition of aluminum nitrate to increase the surface charge. The electrodes prepared with different concentrations of CNTs were compared to pure reduced GO and CNTs. According to AFM results, a large area of reduced GO was formed with a thickness of 3 nm and composed of 3–4 layers. Deposition of reduced GO was possible with corrugated sheets covering the complete substrate forming an open pore structure. CNTs formed a network structure for electrolyte ions to flow. During composite formation, CNTs deposited on top of the graphene layer therefore connecting the sheets. The network structures can serve as fast electronic and ionic conducting channels, providing ideal electrodes for energy storage devices (see also section 2.1). The best results in terms of electrochemical capacitance and electric conductivity were obtained on composites containing 40% CNTs. A higher concentration of CNTs made the network structure dominate the behavior of the composite. Therefore, it is important to tune the relative concentration of graphene and CNTs to obtain the optimal microstructure that can enhance the effective conductivity of the composites. In the research by Ata et al.,⁵⁴ aurintricarboxylic acid ammonium salt (aluminon) was used as a charging agent, which was shown also to provide attractive film forming properties. For EPD, suspensions of the different materials in water with addition of aluminon were prepared, and voltages in the range of 7–10 V were applied. The adsorption of aluminon resulted in well-dispersed suspensions and negatively charged particles. The deposition mechanism was explained with a pH decrease at the anode surface, protonation, and charge neutralization of anionic COO^- groups of aluminon. The film surfaces were crack-free and homogeneous with some residual porosity. CNT- TiO_2 composites were also prepared with addition of aluminon. The composites were homogeneous and were composed of TiO_2 nanoparticles and CNTs evenly distributed. The results thus demonstrated EPD as a versatile preparation method for advanced composite films containing carbonaceous materials and oxide particles for various applications. Recently, Seo et al.⁵⁵ deposited GS-MWCNT composites on Ni substrates. In this work,⁵⁵ GSs were prepared by the electrochemical exfoliation method.⁶⁰ Then, different concentrations of GSs were mixed with MWCNTs in isopropyl alcohol, and nickel nitrate was added to the suspension. The surface morphology of the deposited composites showed MWCNTs uniformly attached to the GSs without agglomeration. The composites with a 60/40 graphene/MWCNTs ratio showed the highest capacitance values. This result was due to a relatively high porosity in a configuration where CNTs act as spacers between GSs providing an efficient pathway for electrolyte ions. These high-capacitance composite electrodes may also be attractive for applications in Li-ion batteries.

Finally, it has been reported that EPD is a suitable technique to obtain nanodiamond particle deposits, which can then be converted to nanographene sheets.^{11,61} It was reported^{11,61} that nanodiamond suspensions were prepared in isopropyl alcohol with additions of iodine, acetone, and water to positively charge the diamond particles. The EPD conditions to obtain isolated particles on highly oriented pyrolytic graphite (HOPG)

Table 1. Overview of Graphene EPD Showing Materials and EPD Conditions Investigated

materials			EPD conditions		application	ref.
coating	substrate	suspension medium	voltage	time		
nanodiamond	pyrolytic graphite (HOPG)	isopropyl alcohol	10 V	30 s	electronic applications	11
GO and graphene nanosheets	ITO coated glass	water	0.1 to 1 mA for 1 to 5 min	1–5 min	electronic devices	17
nanodiamond	pyrolytic graphite (HOPG)	isopropyl alcohol with additions of acetone, water and iodine	–6.67 V/cm	30 s	electronic devices	61
GO	ITO	water	150 V	45 s	supercapacitors	14
graphene modified with p-phenylene diamine (OPPD) with $-N^+$	nickel foams	ethanol	50 V		electrochemical capacitors	15
graphene	stainless steel, meshes, Cu, Ni, Al, and p-type Si	water	10 V	1–10 min	paper-like conductive materials	18
GO flakes	Si coated with SiO_2	water	1–30 V	1–30 min	transparent conductive materials: flat displays	19
GO	stainless steel coated with Co_3O_4 and MnO_2	anhydrous alcohol	1–40 V	6–12 h	supercapacitors	20
reduced graphene–CNTs		acetone–ethanol	30 V–5 min	5 min	supercapacitors	53
graphene, CNTs, TiO_2	stainless steel, Pt foils and platinized silicon wafers	water	7–10 V		energy storage	54
GO–NiO	nickel foams	isopropyl alcohol	100 V	20 s	supercapacitors	27
graphene–NiO	stainless steel	isopropyl alcohol	60 V		supercapacitors	28
graphene–polypyrrole	Ti	isopropanol	20 V	30 min	supercapacitors	31
graphene–SWCNTs	ITO coated polyethylene terephthalate	1-ethyl-2-pyrrolidinone anhydrous	1 and 5 V	30 s	optoelectronics	50
graphene oxide	stainless steel	water (HCl and KOH)	3 and 15 V	≤ 10 min	display screens and energy storage devices.	16
graphene	ITO coated glass	isopropyl alcohol	160 V	1 min	field emitters	37
graphene	Si coated with Ti	isopropyl alcohol	300 V	3 min	field emitters	38
graphene	3D carbon fabric	water	2.4 mA/cm	5 s to 10 min	field emitters	39
graphene	ITO	ethanol, glycol, DMF and NMP	50 V	3 h	field emitters	26
graphene	Ti plates	isopropyl alcohol	150 V	10 min	field emitters	40
graphene– SnO_2	Si	isopropyl alcohol	300 V	3 min	field emitters	41
nitrogen, boron doped graphene	Si	isopropyl alcohol	160 V	1 min	field emitters	42
graphene–Ti	Si wafers	isopropyl alcohol	300 V	5 min	field emitters	43
graphene	fluorine-doped SnO_2 (FTO) glass	water	30 V	5, 10, 15, and 30 s	dye sensitized solar cells	45
graphene	fluorine doped SnO_2 (FTO) glass	distilled water	10 V	10 s	dye sensitized solar cells	46
graphene	FTO	water	3 V	60 s	dye sensitized solar cells	47
graphene–Platinum	carbon Toray paper	tetrahydrofuran	75 V/cm		electrocatalysts supports for fuel cells	33
graphene–Pt	ITO coated glass	DMF	5 V	<3 min	dye-sensitized solar cells (DSSC) and hydrogen generation	34
GS–Pt nanoparticles	ITO	water	150 V	45 s	supports for fuel cells	35
graphene–Au nanoparticles	graphite paper	acetone–ethanol	30 V	30 min	counter electrodes for quantum dot-sensitized solar cells	36
graphene–CNTs	graphite paper	ethanol–acetone	30 V	30 min	dye-sensitized solar cells	51
graphene, SWNTs, Graphene-SWNTs	FTO	ethanol with additions of magnesium nitrate	30 V		counter electrodes in dye-sensitized solar cells	52
GS–MWCNTs	Ni foils	isopropyl alcohol	100 V	10 min	Li-ion batteries	55
GS– TiO_2	ITO coated glass	ethanol	30 V	3 min	photovoltaic devices	29
graphene–CdS. ITO glass	ITO coated glass	water	0.5 mA/cm	75 s	solar cells	30
graphene–porphyrin	OTE/ SnO_2	DMF	100 V		photovoltaic devices	32
graphene	glassy carbon	(DMF)	120 V	3 min	sensors for explosive compounds	48
graphene nanowalls	stainless steel	isopropyl alcohol	150 V	2 min	biocompatible materials	49

substrates were 10 V and 30 s^{11} and electric fields ranging from -0.07 to -67 V/cm .⁶¹ The nanodiamond film deposited was heat treated at $1600\text{ }^\circ\text{C}$ to obtain a single nanographene sheet exhibiting $10\text{--}15\text{ nm}$ in size and interlayer distances of 0.35 to 0.37 nm . Usually, heat treatment transforms nanodiamond particles to graphite, but, due to the size of the material deposited or the presence of oxygen during the thermal treatment,

individual flat nanographene sheets containing approximately 3000 carbon atoms were produced on the HOPG substrate.

3. DISCUSSION

Graphene is an important material being considered for numerous applications such as power energy storage materials, supercapacitors, photoelectrochemical devices, sensors, biomedical substrates, field emitters, and counter electrodes for dye-

sensitized solar cells. EPD is being increasingly applied to manipulate graphene for a broad variety of applications as discussed in Section 2. For EPD processing, it is particularly important to obtain stable dispersions in convenient media, such as water, ethanol, isopropyl alcohol, and acetone. Table 1 presents a summary of the studies reviewed in the previous section collating the available relevant information on the EPD parameters used, mainly voltage and deposition time. A variety of graphenes, suspension media, and electrode substrates have been investigated. The graphene precursor material used for EPD is almost always GO, which can be easily dispersed in water and is composed of one or few layers. This material is typically reduced to GS by removing the oxygen-containing groups, either intrinsically by the voltage applied during the EPD process, or by deliberate further thermal/chemical/electrochemical steps. The reduced GO is also known as functionalized, chemically modified, or converted graphene; it is important to note that such material never fully recovers the intrinsic properties of true crystalline graphene due to retained oxygen and the etched carbon framework.⁶² Further, GO is not necessarily one single phase, but rather a mixture of less oxidized GS and polyaromatic oxidation debris;⁶³ the implications of this heterogeneity for EPD are yet to be explored but may be significant. Proof of deposition of single-layer nanographene can be challenging, and, in any case, evidence collected for dilute depositions is unlikely to accurately reflect the structure of thicker films. Nevertheless, GO routes are convenient, and the resulting recovered GSs are sufficient for many applications.

Comparing the EPD conditions and parameters used in the reviewed papers, most of them report the application of constant voltage conditions with voltage ranges encompassing low voltages, e.g., 5 V, to relatively high voltages of 300 V. Deposition times for graphene layer formation during EPD varied greatly from seconds to hours depending on the EPD conditions, solvent used, and intended application. Short deposition times can produce flat thin films, while long deposition times lead to thick coatings (tens of micrometers), which usually exhibit agglomerated and wrinkled architectures. For the preparation of graphene suspensions, water and isopropanol are the predominant media used. The suspensions developed in the different studies all have in common a relatively high stability in some cases, even without addition of organic stabilizers. In general terms, the polar groups of the GO provide the necessary solution stabilization, which can be enhanced by additional stabilizers, adsorbed polymers, or ionic charging agents. Surprisingly, only a few papers report the formation of gas bubbles during deposition from aqueous medium, even in cases where high voltages were applied. In other studies, high voltages lead to water electrolysis and void formation in the resulting EPD film; such effects may be suppressed by using low ionic strength or reducing the applied voltage.⁴ Another interesting aspect is that only a few studies consider constant current conditions during EPD, possibly due to the simpler experimental setting required for constant voltage EPD.¹ However investigation of EPD under constant current conditions could lead to enhanced homogeneity of deposits. In comparison to other solution-based deposition techniques available for graphene deposition, such as spin coating, layer by layer, dip coating, and spray coating, EPD appears to offer better control of thickness, uniformity,⁶⁴ and adhesion to the substrate.¹⁴ The reviewed papers have shown that EPD can be manipulated to produce single isolated and stacked layers of graphene, in a variety of orientations and densities. Single GSs are very attractive for novel nanotechnology applications because

they offer the most unusual and generally beneficial intrinsic properties; on the other hand, stacked layers of graphene usually show a decrease in the physical properties, but are easier to produce. Both types of configurations have promising applications.

EPD is also attractive in that, in principle, it can be used for large-scale manufacturing, on a variety of substrate materials and morphologies. The examples discussed above show that graphene can be successfully deposited on planar and 3D structures as well as porous, fibrous, and even flexible substrates. Graphene can be combined with other components to create functional composites. Metal oxide, conducting polymer, and metallic nanoparticle combinations have all been demonstrated, leading to a great variety of functional films with enhanced optical and electrical properties, enabling the use of graphene in novel applications. EPD can also be conveniently combined with other compatible processes, such as chemical bath deposition or electropolymerization. Many of the techniques and applications considered for graphene film EPD are closely related to earlier ideas for CNTs. This mapping has helped the field to blossom rapidly. Perhaps some of the most interesting studies have combined CNT and graphene materials to great effect. The complementary geometry addresses limitations of each system alone. For example, the nanotube network forming ability helps to connect graphene flakes while maintaining a high active surface area open structure that might otherwise be lost to restacking.

Some of the most promising composite graphene electrode applications are in supercapacitors and dye-sensitized solar cell electrodes. For example, pure graphene has shown specific capacitance values of 156 F/g,¹⁴ but in combination with NiO, values of 569 F/g²⁸ have been measured, while combination with polymers has led to reports of impressive supercapacitive behaviour, with values³¹ reaching 1510 F/g.

Graphene deposits obtained by EPD have shown great potential as substitutes of Pt in counter electrodes of dye-sensitized solar cells. The lower price of graphene in comparison to Pt and graphene's attractive properties such as high electrical conductivity, corrosion resistance, and electrocatalytic activity, make graphene a very attractive material in applications where it can replace Pt, Au, or Ni advantageously. Conversion efficiencies of 6.17% were reported for graphene–CNT composites, which is comparable to current Pt electrodes.⁵¹ Again, the combination of CNTs with graphene, which can be conveniently achieved by suitable EPD-based processing, is seen to be particularly promising. It is also worth noting that the high electrical conductivity and optical transparency of graphene, not to mention its flexibility, neutral color, and strength, are attractive features that suggest potential applications as transparent conducting electrodes in liquid crystal displays, light emitting diodes, or indeed solar cells. While the need to EPD on a conductive substrate is not ideal, films can be detached and transferred to other substrates.

Nanoelectronics is an obvious field of application for graphene given the nanoscale dimensions of GS. One of the main challenges for the production of graphene-based electronic materials, e.g., transistors, is the preparation of single GSs. While this Review has revealed that EPD is a feasible technique to deposit such individual GSs in a reproducible manner, the intrinsic quality provided by the GO route may be limiting; improvements in GO or other graphene solubilizing strategies may help to resolve the issues in the future. In many applications, the higher electron mobility of graphene is attractive, yet the lack

of band gap is problematic. However, there is intense effort currently applied to a wide range of methods to tune the band gap and hence the conductivity of the material; codeposition using EPD and doping, as discussed above, are interesting possibilities. Other new applications of graphene may yet emerge, for example, in polymer composites, where toughness and mechanical strength may be complemented by wear resistance or barrier properties. Finally, GO has been shown to be an antibacterial material and detached graphene layers, easily produced by EPD, can be used as antibacterial paper for the food industry or in clinical applications. It is worth noting that human and environmental safety must still be considered in this context and others.

4. CONCLUSIONS

EPD is a materials processing technique that has its traditional application in ceramics and colloidal processing. It is being increasingly applied for the manipulation of graphene, which expands the extraordinary progress made in the past few years in the EPD of other nanomaterials, notably CNTs, rendering EPD a significant nanotechnology processing tool. EPD is enabling the development of a great variety of devices based on the ordered arrangement of graphene (and in some cases the combination of graphene with CNTs and with other nanoparticles) intended for numerous applications in high-technology areas, which include power energy storage materials, supercapacitors, photoelectrochemical devices, photovoltaic devices, biomedical substrates and scaffolds, field emitters, structural and functional composites, (counter) electrodes for dye-sensitized solar cells, supports for fuel cells, sensors, and transparent conductive films for applications such as display screens. The simplicity of the EPD approach coupled with the modest equipment requirement, low cost, rapid deposition times, versatility in terms of shape and dimensions of substrates and easy dispersion of graphene represent significant advantages of the technique for applications where large areas of uniform graphene layers are needed. Graphene layers and combinations of graphene with other materials obtained by EPD exhibit attractive properties, including high electrical conductivity, good thermal stability, optical transparency and mechanical strength. Therefore, further developments and increased research efforts, based on the knowledge and experience gained so far, as reviewed here, can be predicted. As an alternative to regular EPD, which is based on direct current (DC) conditions, it is anticipated that also AC-EPD will be considered for graphene layer preparation. This technique is especially useful in water-based suspensions and with high voltages in order to avoid water electrolysis. In this context, AC-EPD might be an attractive technique for graphene processing due to the high stability of graphene in water, coupled with the advantage of considerably reducing deposition time and increasing deposition voltage. For AC-EPD to be successful, however, some important considerations must be taken into account when establishing the AC-EPD process parameters, such as electrode configuration, voltage, and frequency. At high frequencies, for example, the use of large AC voltages will require the optimization of the electrode separation to effectively achieve deposition. More basic research in the field of AC-EPD (and pulsed EPD) is thus expected. As discussed elsewhere for EPD of nanomaterials,⁸ also in the case of graphene EPD, modeling and “design of experiment” approaches are required to establish clear links between the process parameters and the physical characteristics and properties of the films obtained. “Trial-and-error” approaches, which are time-consuming and poorly

predictive, still dominate the field of EPD and further understanding of the basic kinetics of deposition of graphene will depend on establishing a deeper knowledge of the GO electrophoresis and deposition processes. It is expected that the numerous applications of graphene films obtained by EPD which have been reviewed in this paper will continue to expand; EPD, as has been the case for CNTs,¹⁰ is likely to become one of the techniques of choice to manipulate and process graphene enabling further applications of this material exploiting its outstanding properties and potentially low cost.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: aldo.boccaccini@ww.uni-erlangen.de.

Present Address

^{||}Katcon Institute for Innovation and Technology (KIIT), 66629, Apodaca, Mexico. E-mail: alejandra.chavez@katcon.com.

Notes

The authors declare no competing financial interest.

Biographies



Alejandra Chavez received her Ph.D. in Metallurgical and Ceramic Engineering from Cinvestav (Mexico, 2010). During 2011 she was a Post-Doctoral Research Associate at the Institute of Biomaterials of the University of Erlangen-Nuremberg (Germany). Currently, she is a Research Scientist at the Katcon Institute for Innovation and Technology (KIIT) in Mexico. Her research interests include functional ceramics, and their composites and coatings, for thermal and biomedical applications.



Milo Shaffer is a Professor of Materials Chemistry at Imperial College, London, and Co-director of the London Centre for Nanotechnology. He has extensive experience in carbon and inorganic nanomaterials synthesis, modification, characterization, and application. He has

developed and studied a wide variety of nanocomposite systems, including both structural matrices and conducting polymers for electrochemical and photovoltaic applications.



Aldo R. Boccaccini is a Professor of Biomaterials and Head of the Institute of Biomaterials at the Department of Materials Science and Engineering, University of Erlangen-Nuremberg, Germany. Previously, he was a Professor of Materials Science and Engineering at Imperial College, London, where he is currently a Visiting Professor. His research activities are in the broad area of glasses, ceramics, composites and porous materials for biomedical, functional, and/or structural applications. He has developed the electrophoretic deposition (EPD) technique for production of nanostructured materials, composites, and functional coatings.

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■ REFERENCES

- (1) Sarkar, P.; Nicholson, P. S. *J. Am. Ceram. Soc.* **1996**, *79* (8), 1987–2002.
- (2) Van de Biest, O.; Vandeperre, L. *J. Annu. Rev. Mater. Sci.* **1999**, *29*, 327–353.
- (3) Boccaccini, A. R.; Zhitomirsky, I. *Curr. Opin. Solid State Mater. Sci.* **2002**, *6*, 251–260.
- (4) Besra, L.; Liu, M. *Prog. Mater. Sci.* **2007**, *52*, 1–61.
- (5) Boccaccini, A. R.; Keim, S.; Ma, R.; Li, Y.; Zhitomirsky, I. *J. R. Soc. Interface* **2010**, *7* (Suppl 5), S581–S613.
- (6) Chavez Valdez, A.; Boccaccini, A. R. *Electrochim. Acta* **2012**, *65*, 70–89.
- (7) Dickerson, J. H.; Boccaccini, A. R. *Electrophoretic Deposition of Nanomaterials*; Springer: New York, 2012.
- (8) Corni, I.; Ryan, M. P.; Boccaccini, A. R. *J. Europ. Ceram. Soc.* **2008**, *28*, 1353–1367.
- (9) Du, C. S.; Heldbrant, D.; Pan, N. *Mater. Lett.* **2002**, *57*, 434–438.
- (10) Boccaccini, A. R.; Cho, J.; Roether, J. A.; Thomas, B. J. C.; Minay, E. J.; Shaffer, M. S. P. *Carbon* **2006**, *44*, 3149–3160.
- (11) Affoune, A. M.; Prasad, B. L. V.; Sato, H.; Enoki, T.; Kaburagi, Y.; Hishiyama, Y. *Chem. Phys. Lett.* **2001**, *348*, 17–20.
- (12) Geim, A. K.; Novoselov, K. S. *Nat. Mater.* **2007**, *6*, 183–191.
- (13) Huang, X.; Yin, Z.; Wu, S.; Qi, X.; He, Q.; Zhang, Q.; Yan, Q.; Boey, F.; Zhang, H. *Small* **2011**, *7* (14), 1876–1902.
- (14) Liu, S.; Ou, J.; Wang, J.; Liu, X.; Yang, S. *J. Appl. Electrochem.* **2011**, *41*, 881–884.
- (15) Chen, Y.; Zhang, X.; Yu, P.; Ma, Y. *J. Power Sources* **2010**, *195*, 3031–3035.
- (16) Hasan, S. A.; Rigueur, J. L.; Harl, R. R.; Krejci, A. J.; Gonzalo-Juan, I.; Rogers, B. R.; Dickerson, J. H. *ACS Nano* **2010**, *4* (12), 7367–7372.
- (17) Lee, V.; Whittaker, L.; Jaye, C.; Baroudi, K. M.; Fischer, D. A.; Banerjee, S. *Chem. Mater.* **2009**, *21*, 3905–3916.
- (18) An, S. J.; Zhu, Y.; Lee, S. H.; Stoller, M. D.; Emilsson, T.; Park, S.; Velamakanni, A.; An, J.; Ruoff, R. S. *J. Phys. Chem. Lett.* **2010**, *1*, 1259–1263.
- (19) Ishikawa, R.; Ko, P. J.; Kurokawa, Y.; Konagai, M.; Sandhu, A. *J. Phys.: Conf. Ser.* **2012**, *352*, 012003.
- (20) Lake, J. R.; Cheng, A.; Selverston, S.; Tanaka, Z.; Koehne, J.; Meyyappan, M.; Chen, B. *J. Vac. Sci. Technol. B* **2012**, *30* (3), 03D118.
- (21) An, K. H.; Kim, W. S.; Park, Y. S.; Moon, J. M.; Bae, D. J.; Lim, S. C.; Lee, Y. S.; Lee, Y. H. *Adv. Funct. Mater.* **2001**, *11*, 387–392.
- (22) Jiang, F. T.; Fang, Y. Z.; Chen, L.; Xue, Q. S.; Lu, Y. *Mater. Lett.* **2010**, *64*, 199–202.
- (23) Kim, C. *J. Power Sources* **2005**, *142*, 382–388.
- (24) Merino, C.; Soto, P.; Vilaplana-Ortego, E.; Gomez de Salazar, J. M.; Pico, F.; Rojo, J. M. *Carbon* **2005**, *43*, 551–557.
- (25) Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Zhang, Y.; Dubonos, S. V.; Grigorieva, I. V.; Firsov, A. A. *Science* **2004**, *306*, 666–669.
- (26) Chen, Y.; Zhang, X.; Yu, P.; Ma, Y. *Chem. Commun.* **2009**, *30*, 4527–4529.
- (27) Xia, X.; Tu, J.; Mai, Y.; Chen, R.; Wang, X.; Gu, C.; Zhao, X. *Chem.—Eur. J.* **2011**, *17*, 10898–10905.
- (28) Wu, M. S.; Lin, Y. P.; Lin, C.; Lee, J. T. *J. Mater. Chem.* **2012**, *22*, 2442–2448.
- (29) Tang, Y.; Lee, C. S.; Xu, J.; Liu, Z. T.; Chen, Z. H.; He, Z.; Cao, Y. L.; Yuan, G. D.; Song, H. S.; Chen, L. M.; et al. *ACS Nano* **2010**, *4*, 3482–3488.
- (30) Guo, C. X.; Yang, H. B.; Sheng, Z. M.; Lu, Z. S.; Song, Q. L.; Chang, M. L. *Angew. Chem., Int. Ed.* **2010**, *49*, 3014–3017.
- (31) Mini, P. A.; Balakrishnan, A.; Nair, S. V.; Subramanian, K. R. V. *Chem. Commun.* **2011**, *47*, 5753–5755.
- (32) Karousis, N.; Sandanayaka, A. S. D.; Hasobe, T.; Economopoulos, S. P.; Sarantopoulou, E.; Tagmatarchis, N. *J. Mater. Chem.* **2011**, *21*, 109–117.
- (33) Seger, B.; Kamat, P. V. *J. Phys. Chem. C* **2009**, *113*, 7990–7995.
- (34) Chartarrayawadee, W.; Moulton, S. E.; Li, D.; Too, C. O.; Wallace, G. O. *Electrochim. Acta* **2012**, *60*, 213–223.
- (35) Liu, S.; Wang, J.; Zeng, J.; Ou, J.; Li, Z.; Liu, X.; Yang, S. *J. Power Sources* **2010**, *195*, 4628–4633.
- (36) Zhu, G.; Pan, L.; Sun, H.; Liu, X.; Lv, T.; Lu, T.; Yang, J.; Sun, Z. *Chem. Phys. Chem.* **2012**, *13*, 769–773.
- (37) Wu, Z. S.; Pei, S.; Ren, W.; Tang, D.; Gao, L.; Liu, B.; Li, F.; Liu, C.; Cheng, H. M. *Adv. Mater.* **2009**, *21*, 1756–1760.
- (38) Chen, J.; Li, J.; Yang, J.; Yan, X.; Tay, B. K.; Xue, Q. *Appl. Phys. Lett.* **2011**, *99*, 173104.
- (39) Maiti, U. N.; Maiti, S.; Das, N. S.; Chattopadhyay, K. K. *Nanoscale* **2011**, *3*, 4135–4141.
- (40) Liu, J.; Zeng, B.; Wu, Z.; Sun, H. *ACS Appl. Mater. Interfaces* **2012**, *4*, 1219–1224.
- (41) Ding, J.; Yan, X.; Li, J.; Shen, B.; Yang, J.; Chen, J.; Xue, Q. *ACS Appl. Mater. Interfaces* **2011**, *3*, 4299–4305.
- (42) Palnitkar, U. A.; Kashid, R. V.; More, M. A.; Joag, D. S.; Panchakarla, L. S.; Rao, C. N. R. *Appl. Phys. Lett.* **2010**, *97*, 063102.
- (43) Jun, Li, J.; Chen, J.; Luo, B.; Yan, X.; Xue, Q. *AIP Adv.* **2012**, *2*, 022101.
- (44) Park, S.; An, J.; Piner, R. D.; Jung, I.; Yang, D.; Velamakanni, A.; Nguyen, S. B. T.; Ruoff, R. S. *Chem. Mater.* **2008**, *20*, 6592–6594.
- (45) Choi, H.; Hwang, S.; Bae, H.; Kim, S.; Kim, H.; Jeon, M. *Electron. Lett.* **2011**, *47*, 281–283.
- (46) Choi, H.; Kim, H.; Hwang, S.; Han, Y.; Jeon, M. *J. Mater. Chem.* **2011**, *21*, 7548–7551.
- (47) Sima, M.; Enculescu, I.; Sima, A. *Optoelectron. Adv. Mater., Rapid Commun.* **2011**, *5*, 414–418.
- (48) Tang, L.; Feng, H.; Cheng, J.; Li, J. *Chem. Commun.* **2010**, *46*, 5882–5884.
- (49) Akhavan, O.; Ghaderi, E. *ACS Nano* **2010**, *4*, 5731–5736.
- (50) Bittolo Bon, S.; Valentini, L.; Kenny, J. M.; Peponi, L.; Verdejo, R.; Lopez-Manchado, M. A. *Phys. Status Solidi A* **2010**, *207*, 2461–2466.
- (51) Zhu, G.; Pan, L.; Lu, T.; Xu, T.; Sun, Z. *J. Mater. Chem.* **2011**, *21*, 14869–14875.

- (52) Kim, H.; Choi, H.; Hwang, S.; Kim, Y.; Jeon, M. *Nanoscale Res. Lett.* **2012**, *7*, 53.
- (53) Lu, T.; Pan, L.; Li, H.; Nie, C.; Zhu, M.; Sun, Z. *J. Electroanal. Chem.* **2011**, *661*, 270–273.
- (54) Ata, M. S.; Sun, Y.; Li, X.; Zhitomirsky, I. *Colloid Surf. A* **2012**, DOI: 10.1016/j.colsurfa.2012.02.001.
- (55) Seo, S. D.; Hwang, I. S.; Lee, S. H.; Shim, H. W.; Kim, D. W. *Ceram. Int.* **2012**, *38*, 3017–3021.
- (56) Moore, V. C.; Strano, M. S.; Haroz, E. H.; Hauge, R. H.; Smalley, R. E.; Schmidt, J.; Talmon, Y. *Nano Lett.* **2003**, *3*, 1379–1382.
- (57) Bekyarova, E.; Itkis, M. E.; Cabrera, N.; Zhao, B.; Yu, A.; Gao, J.; Haddon, R. C. *J. Am. Chem. Soc.* **2005**, *127*, 5990–5995.
- (58) Li, C.; Li, Z.; Zhu, H.; Wang, K.; Wei, J.; Li, X.; Sun, P.; Zhang, H.; Wu, D. *J. Phys. Chem. C* **2010**, *114*, 14008–14012.
- (59) Jeong, H. Y.; Lee, D. S.; Choi, H. K.; Lee, D. H.; Kim, J. E.; Lee, J. Y.; Lee, W. J.; Kim, S. O.; Choi, S. Y. *Appl. Phys. Lett.* **2010**, *96*, 213105.
- (60) Lee, S. H.; Seo, S. D.; Park, K. S.; Shim, H.-W.; Kim, D. W. *Mater. Chem. Phys.* **2012**, *135*, 309–316.
- (61) Enoki, T. *Phys. Solid State* **2004**, *46*, 651–656.
- (62) Pei, S.; Cheng, H. M. *Carbon* **2012**, *50*, 3210–3228.
- (63) Rourke, J. P.; Pandey, P. A.; Moore, J. J.; Bates, M.; Kinloch, I. A.; Young, R. J.; Wilson, N. R. *Ang. Chem. Int. Ed.* **2011**, *50*, 3173–3177.
- (64) Vozar, S.; Poh, Y.; Serbowicz, T.; Bachner, M.; Podsiadlo, P.; Qin, M.; Verploegen, E.; Kotov, N.; Hart, A. *Rev. Sci. Instrum.* **2009**, *80*, 023903.