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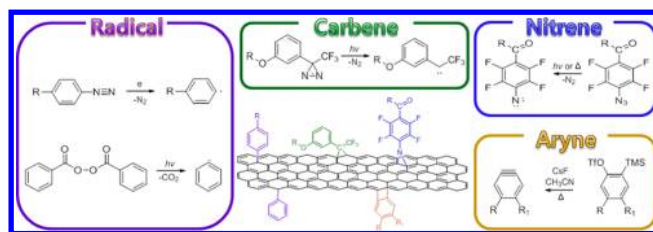
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CONSPECTUS

Graphene, a material made exclusively of sp^2 carbon atoms with its π electrons delocalized over the entire 2D network, is somewhat chemically inert. Covalent functionalization can enhance graphene's properties including opening its band gap, tuning conductivity, and improving solubility and stability. Covalent functionalization of pristine graphene typically requires reactive species that can form covalent adducts with the sp^2 carbon structures in graphene. In this Account, we describe graphene functionalization reactions using reactive intermediates of radicals, nitrenes, carbenes, and arynes. These reactive species covalently modify graphene through free radical addition, CH insertion, or cycloaddition reactions.



Free radical additions are among the most common reaction, and these radicals can be generated from diazonium salts and benzoyl peroxide. Electron transfer from graphene to aryl diazonium ion or photoactivation of benzoyl peroxide yields aryl radicals that subsequently add to graphene to form covalent adducts. Nitrenes, electron-deficient species generated by thermal or photochemical activation of organic azides, can functionalize graphene very efficiently. Because perfluorophenyl nitrenes show enhanced bimolecular reactions compared with alkyl or phenyl nitrenes, perfluorophenyl azides are especially effective. Carbenes are used less frequently than nitrenes, but they undergo CH insertion and $C=C$ cycloaddition reactions with graphene. In addition, arynes can serve as a dienophile in a Diels–Alder type reaction with graphene.

Further study is needed to understand and exploit the chemistry of graphene. The generation of highly reactive intermediates in these reactions leads to side products that complicate the product composition and analysis. Fundamental questions remain about the reactivity and regioselectivity of graphene. The differences in the basal plane and the undercoordinated edges of graphene and the zigzag versus arm-chair configurations warrant comprehensive studies. The availability of well-defined pristine graphene starting materials in large quantities remains a key obstacle to the advancement of synthetic graphene chemistry.

Introduction

The unique and superior properties of graphene make it the nanomaterial of choice for a broad range of applications including transistors, integrated circuits, displays, sensors, and nanocomposite materials. Despite its high potentials, major challenges still remain. These include poor solubility, intrinsic zero band gap energy, low reactivity and the availability of well-defined pristine graphene in large quantity, which have hampered the rapid development of graphene-based functional devices.

Many of these challenges can be potentially addressed through chemical functionalization of the material. Pristine graphene has limited solubility in most organic solvents except strongly interacting solvents such

as *N*-methylpyrrolidone and 1,2-dichlorobenzene. Functionalization of graphene by either physisorption of surfactants or polymers, or chemical derivatization with organic groups renders the material soluble in a wider range of organic solvents as well as in water.^{1,2} Individual graphene sheets can easily form agglomerates due to the van der Waals force induced by the π – π stacking interaction between graphene layers.^{3,4} Functionalization serves to stabilize graphene by lowering the surface energy of the material, for example, via polymeric stabilization by the addition of a polymer to graphene.^{1,5–7}

Opening a band gap in graphene is a prerequisite for the material to be used in electronic and photonic applications. Basal plane functionalization changes the local carrier

concentration and has shown to be an attractive way to open the band gap of graphene.^{8–11} In principle, one can prepare graphene materials with a tunable band gap from conducting to insulating simply by controlling the conjugation length of the delocalized carbon lattice through the extent of covalent functionalization.

As a material made of exclusive sp^2 carbon atoms, graphene benefits from the rich chemistries developed for its structurally related family members of fullerenes and carbon nanotubes. In fact, many graphene functionalization methods can find their roots in the literature of fullerene and carbon nanotubes. However, unlike fullerene and carbon nanotubes that have a curved structure and misaligned π -orbitals, graphene, on the other hand, has its π electrons delocalized over the entire 2D network. This makes graphene fairly inert chemically. It has been shown that the reactivity of graphene is lower than that of fullerenes and carbon nanotubes.^{12–14}

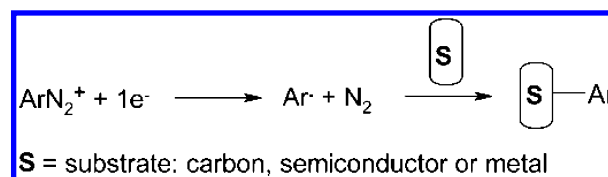
It is not surprising, therefore, that the covalent functionalization of pristine graphene involves mostly reactive species that can form covalent adducts with the sp^2 carbon structures in graphene. The topic of graphene chemistry has been reviewed extensively.^{1,6,8–11,15–19} For the comprehensive overview of graphene chemistry, readers are referred to these references as well as the relevant articles published in this special issue. In this Account, we limit the scope of the discussions to graphene functionalization reactions involving reactive intermediates of radicals, nitrenes, carbenes, and arynes.

Graphene Functionalization by Free Radicals

Diazonium Salts. Diazonium chemistry is one of the widely used methods to covalently functionalize conductive and semiconducting materials.²⁰ The functionalization reaction is thought to proceed through a free radical mechanism. The substrate acts as electron transfer agent that donates an electron to aryl diazonium ion to form an aryl radical after the elimination of nitrogen gas (Scheme 1). The high reactivity of diazonium salts coupled with the concerted N_2 cleavage is believed to be responsible for generating aryl radicals that are close to the substrate, which ensures a rapid reaction of the radical with the substrate rather than diffusion to the solution.²⁰ Because the diazonium compounds decompose rapidly, it is recommended that they should be freshly synthesized and used immediately after preparation.²¹

An early example applying the diazonium chemistry to graphene was introduced by the Haddon group.²² Epitaxial graphene grown on SiC substrate was treated with (*p*-nitrophenyl)diazonium tetrafluoroborate, resulting in the

SCHEME 1. Surface Functionalization via Diazonium Chemistry^a



^aAdapted with permission from ref 20. Copyright 2005 Royal Society of Chemistry.

covalent attachment of the aryl group to graphene. The reaction was attributed to the spontaneous electron transfer from the graphene layer and its substrate to the diazonium salt. The covalent bond formation was established by XPS. The surface coverage of the nitrophenyl group, measured by cyclic voltammetry, was estimated to be $\sim 1 \times 10^{15}$ molecules/cm² (vs the theoretical value of $\sim 8 \times 10^{15}$ molecules/cm² for a close-packed monolayer of vertically oriented nitrophenyl groups).

More detailed studies on the reactivity of (*p*-nitrophenyl)diazonium tetrafluoroborate with graphene and the electron transfer chemistry was conducted by Strano and co-workers.²³ Single-layer and multilayer graphene sheets, prepared by mechanical exfoliation of bulk graphite on silicon wafers followed by annealing, were treated with the diazonium salt allowing only the top layer and the edges of graphene sheets to react. Using the Raman D/G ratio as a measure of the degree of functionalization, the authors found that the single layer graphene was close to 10 times more reactive than bilayer or multilayer graphene. Because the intensity of the disorder D peak for graphene edges is polarization dependent, by examining the D peak intensity before and after diazonium functionalization, the contribution from the edges were determined. The authors thus observed at least 2 times higher reactivity of the edge than the bulk for single-layer graphene.

Functionalization with aryl diazonium salts alters the electronic properties of graphene. Tour et al. derives a simple kinetic model to describe the conductivity change of graphene upon functionalization with (*p*-nitrophenyl)diazonium tetrafluoroborate.²¹ After covalent modification, a portion of the sp^2 carbon on graphene is converted to sp^3 carbon. Assuming that the conversion of sp^2 to sp^3 carbon leads to a decrease in the conductivity of graphene, ~ 2 -fold decrease of current was derived within 5 min of reaction, indicating a relatively fast kinetics.

However, Gao et al. reported that the conductivity could be enhanced by covalently attaching aryl groups to the basal plane of graphene (Figure 1a).²⁴ The authors attributed

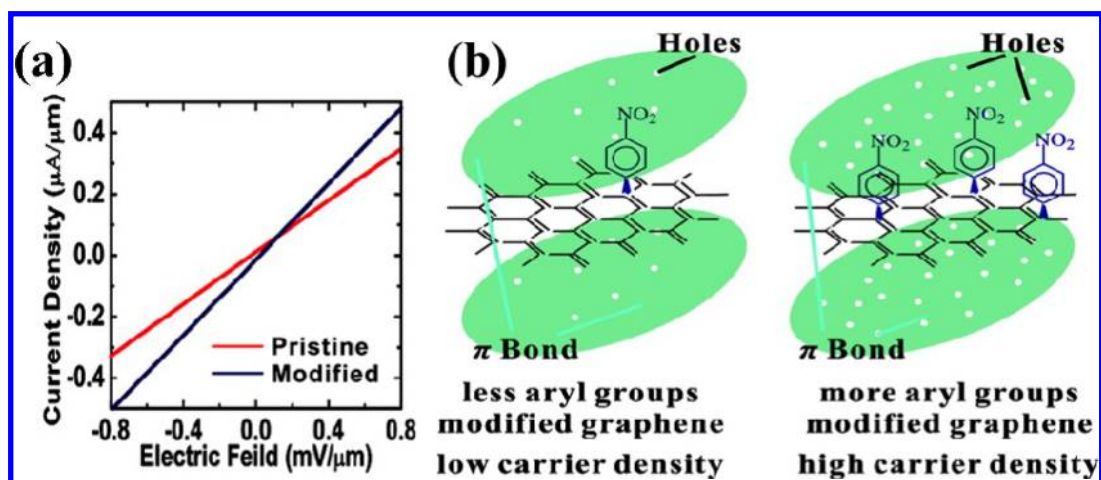


FIGURE 1. (a) I – V curves of pristine and modified graphene. (b) Proposed charge transfer effects introduced by p -nitrophenyl group covalently bonded to the basal plane of graphene. Adapted with permission from ref 24. Copyright 2011 American Chemical Society.

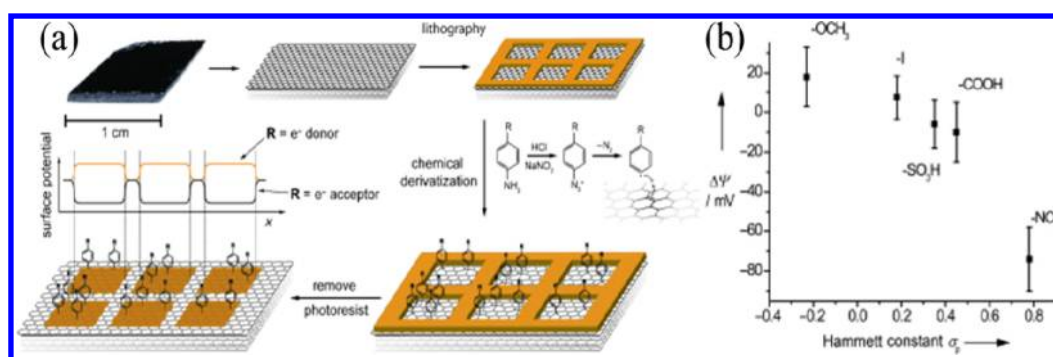


FIGURE 2. (a) Selective functionalization of HOPG surface via the diazonium chemistry. (b) Change in surface potential vs Hammett constant on the graphene stack. Adapted with permission from ref 25. Copyright 2009 WILEY-VCH Verlag GmbH & Co. KGaA.

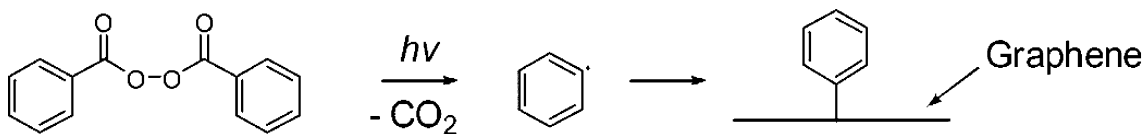
the difference in conductivity to the higher concentration of reagents and longer reaction time, which yielded graphene with higher degree of functionalization than previously described. The authors argued that, at lower extent of modification, the p -nitrophenyl groups act as defects lowering the carrier mobility by decreasing the mean free path and/or opening a band gap (Figure 1b, left). At higher degree of modification, the density of holes on graphene, created by the electron transfer process to the p -nitrophenyl group, increased (Figure 1b, right). This effect overshadows that of decreasing carrier mobility, leading to an increase in conductivity (Figure 1a).

Stark et al. employed the diazonium chemistry to control the surface potential of graphene.²⁵ The authors used photoresist to create a patterned surface on highly oriented pyrolytic graphite (HOPG), and then selectively functionalized the top layer by exposing the diazonium reagent to the unmasked areas (Figure 2a). Functionalization with p -nitrophenyl group induced a change in the surface potential, measured by Kelvin force microscopy, of $\Delta\psi = -74 \pm 16$ mV relative to HOPG. The

authors then studied the effect of the substituent on the phenyl group by functionalizing HOPG top layer using various aryl diazonium salts. A qualitative correlation between the change in surface potential ($\Delta\psi$) and the Hammett substitution constant (σ_p) was observed (Figure 2b).

The band gap in graphene can be opened by diazonium functionalization. Haddon et al. introduced a band gap in epitaxial graphene using (p -nitrophenyl)diazonium tetrafluoroborate.²⁶ Covalent attachment of the aryl group on the basal plane of graphene converted sp^2 carbon to sp^3 and modified the conjugation length of delocalized carbon lattice. A band gap of approximately 0.36 eV, measured by angle-resolved photoemission spectroscopy, was observed for the functionalized epitaxial graphene.

Diazonium functionalization improves the solubility of pristine graphene without using an external stabilizer.^{27,28} If no surfactant is added, pristine graphene can easily precipitate and aggregate. After functionalization with aryl diazonium salts, graphene showed a solubility of 0.01–0.02 mg/mL in DMF,^{27,28} which is similar to the solubility

SCHEME 2. Graphene Functionalization with Benzoyl Peroxide^a^aAdapted with permission from ref 31. Copyright 2009 American Chemical Society.

of graphene when using excess tetrabutylammonium hydroxide.²⁹ In work of Hirsch et al., synthesis of graphene from graphite powder followed by in situ functionalization with *p*-*t*-butylphenyldiazonium tetrafluoroborate or *p*-sulfonylphenyldiazonium chloride yielded functionalized graphene with a solubility in chloroform of up to 27 $\mu\text{g/mL}$.³⁰

Benzoyl Peroxide. In addition to diazonium salts, benzoyl peroxide can also generate phenyl radicals. Brus et al. reported a functionalization reaction on graphene using benzoyl peroxide.³¹ Single- and few-layer graphene flakes, prepared on silicon wafer by mechanical exfoliation of bulk graphite, were immersed in a solution of benzoyl peroxide and treated under intense laser irradiation. The reaction led to a significant decrease in the electrical conductivity of graphene and an increase in the hole-doping level.

The electron transfer from photoexcited graphene to benzoyl peroxide was suggested to be the key step in this reaction. The surface-adsorbed benzoyl peroxide accepts a hot electron from photoexcited graphene, decomposes to benzoate and benzoyloxy radicals which is then converted to a phenyl radical by the elimination of CO_2 (Scheme 2). The authors reported ~ 14 times higher reactivity for single-layer than double-layer graphene, and attributed the enhanced reactivity of single-layer graphene to the surface induced corrugation, the lack of interlayer π stacking, or direct contact with the substrate.

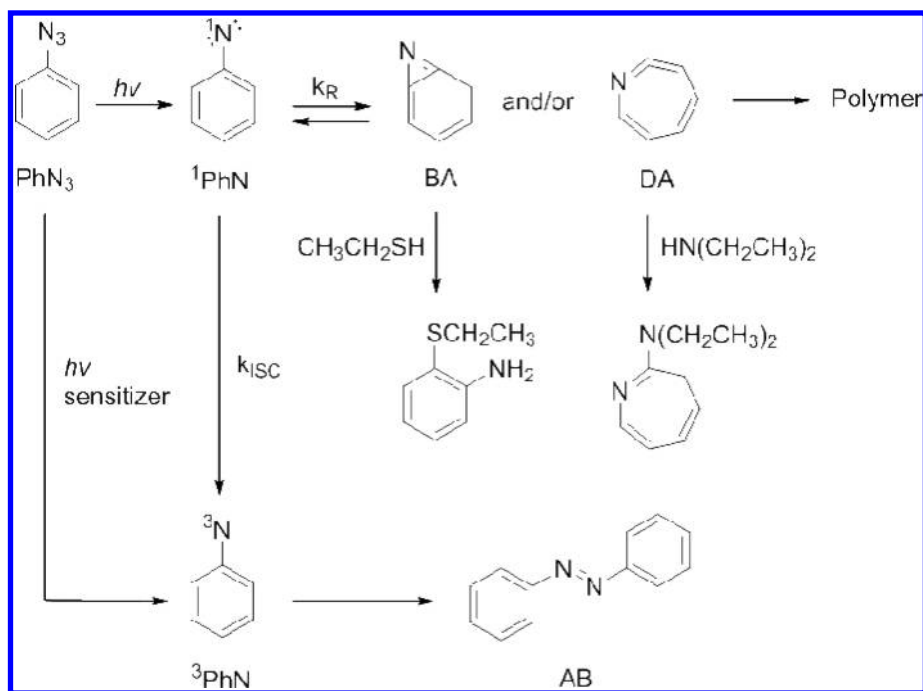
Styrene. Suslick and Xu reported an interesting radical chemistry on graphene by irradiating graphite powder in styrene with high intensity ultrasound.³² The reaction condition, 2 h sonication at 0 $^\circ\text{C}$ under Ar, allowed graphite to exfoliate as well as styrene to polymerize onto the graphene flakes. The reaction was proposed to involve radicals generated during sonication of styrene, which reacted with the graphene to form polystyrene functionalized graphene. The covalent bond formation was supported by the appearance of the Raman D band that is indicative of the conversion of sp^2 to sp^3 carbon, and the high stability of the polystyrene-functionalized graphene that could be dispersed in organic solvents without precipitation.

Graphene Functionalization with Nitrenes

Upon light or thermal activation, the azide functionality dissociates into molecular nitrogen and a highly reactive singlet nitrene species.^{33–37} The fate of the singlet nitrene, and especially aromatic nitrenes such as phenyl nitrene, has been explored over several decades.^{33–37} Singlet phenyl nitrene does not react with alkenes or alkanes to form bimolecular adducts. In solution at ambient temperature, it isomerizes to benzazirine and then to cyclic ketenimine, which can be intercepted with ethanethiol and diethylamine, respectively (Scheme 3).³⁵ In the absence of an amine, the cyclic ketenimine reacts with phenyl azide to form macromolecular structures in the form of a tar. Intersystem crossing (ISC), occurring at cryogenic temperature and is promoted with a photosensitizer, can also take place, leading to the triplet state which is called a 1,3-diradical (Scheme 3).³⁵

The nitrene chemistry has become a powerful method for the chemical modification of carbon nanotubes and fullerenes^{38–43} and subsequently has been successfully adapted to graphene. A variety of azides have been tested to functionalize graphene. Kim et al. used azidotrimethylsilane to thermally dope epitaxial graphene in vacuum, and acquired 0.66 eV band gap for the functionalized graphene.⁴⁴ The degree of functionalization was relatively small, as shown by the intensity ratio of $\text{N/C} \approx 1/53$ from the N 1s and C 1s core-level XPS spectra. The functionalized graphene was stable toward thermal treatment at 250 $^\circ\text{C}$ for 5 min. Further annealing at 850 $^\circ\text{C}$ for 5 min resulted in the band gap closure and restoration of the metallic behavior of graphene.

Barron et al. refluxed solvent-exfoliated graphene flakes together with Boc-protected azidophenylalanine in *o*-dichlorobenzene for 4 days.⁴⁵ XPS data showed a ratio of 13:1 for C (graphene)/Phe in the product. In addition, the final product showed a high density of phenylalanine determined by TGA (69 wt % mass loss). To exclude the possibility of peptide formation, azidophenylalanine was protected at both carboxyl and amino ends (Boc-Phe-OMe) and the experiment was repeated. The TGA result, 78 wt %

SCHEME 3. Chemistry of Phenyl Nitrene^a

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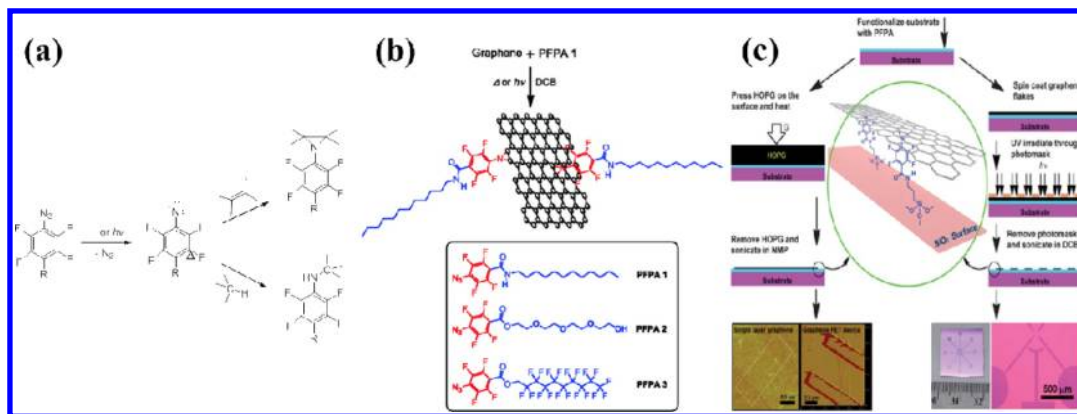
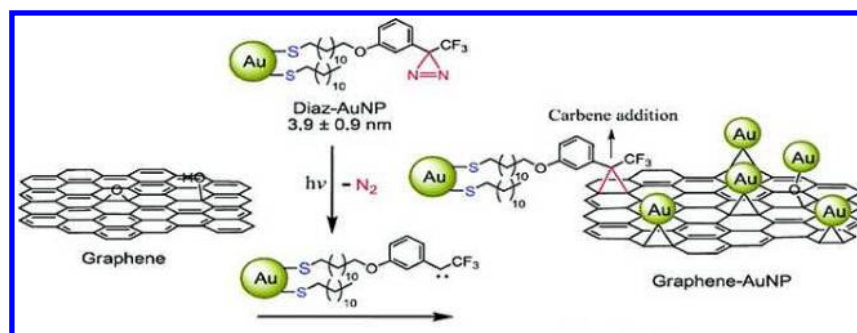


FIGURE 3. (a) Insertion and addition reaction of singlet perfluorophenyl nitrene. (b) Functionalization of pristine graphene with PFPAs. (c) Fabrication of covalently bound graphene films and patterned structures on silicon wafer. Adapted with permission from refs 74 (Copyright 2010 American Chemical Society) and 75 (Copyright 2011 Royal Society of Chemistry).

mass loss, again showed a high extent of functionalization. Singlet phenyl nitrene mostly isomerizes to cyclic ketenimine, which then reacts with the phenyl azide itself to form a polymeric tar (Scheme 3).³⁵ It is therefore highly likely that multilayers, rather than a single layer of phenyl azide, was deposited on graphene resulting in an apparent high degree of functionalization.

We have developed a graphene functionalization chemistry using perfluorophenyl azides (PFPAs). Polyfluorinated aryl nitrenes were developed to overcome the lack of biomolecular chemistry of alkyl and phenyl nitrenes,^{46–52} and

have become a class of popular and highly efficient photoaffinity labeling agents.⁵³ The fluorine substituents ortho to the azido group increase the lifetime of the singlet phenyl nitrene, and raise the activation energy of its isomerization to the cyclic ketenimine by a combined steric effect and high electronegativity of the fluorine atom.^{34,54} The result is a greater lifetime of the singlet nitrene and a significantly increased C–H insertion and/or C=C addition reaction products in comparison to nonfluorinated phenyl azide (Figure 3a).^{34,54–58} We have demonstrated that PFPAs are highly efficient in the covalent functionalization

SCHEME 4. Carbene Chemistry for the Covalent Attachment of Au Nanoparticles to Reduced Graphene Oxide^a

^aAdapted with permission from ref 79. Copyright 2011 American Chemical Society.

of polymers,^{59–66} carbohydrates,^{67–69} small molecules,^{70,71} C₆₀,⁷² and graphene.^{73–75} The coupling reaction can be initiated by light, heat, or electrons, taking place under ambient conditions in either solution or solid state.⁷⁶ Furthermore, PFPAs can be readily synthesized from commercially available pentafluorobenzene derivatives, and the compounds are stable as long as they are protected from direct light exposure.

Treating graphene with PFPAs introduces well-defined functional groups to pristine graphene by thermal or photochemical activation.⁷⁴ This was accomplished in one step by heating the solution of *o*-dichlorobenzene-exfoliated graphene flakes and PFPAs at 90 °C for 3 days (Figure 3b). The reaction can also be carried out photochemically by irradiating the solution with a 450-W medium pressure Hg lamp. The functional group on PFPAs (R, Figure 3a) introduces various functionalities on pristine graphene. For example, the hydrocarbon or oligo(ethylene oxide) spacer renders graphene soluble in common organic solvents or water. Further derivatization of the surface functional groups introduces additional molecules or materials to tune the properties of graphene materials.

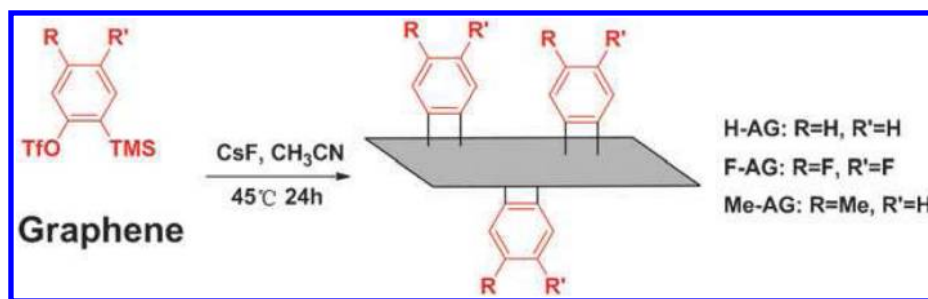
The PFPAs chemistry offers a convenient way to fabricate stable graphene films, ribbons, and patterned structure on various substrates. This can be accomplished by first introducing PFPAs to the substrate followed by covalently immobilizing graphene by photoactivation. In one example, silicon wafers were functionalized with PFPAs by silanization (Figure 3c). HOPG was then pressed onto the PFPAs-surface and was heated to covalently attach the bottom layer of the HOPG on the wafer. After sonication, single- and few-layer graphene films and ribbons were obtained.⁷³ This is a simple and efficient method for the fabrication of stable graphene on technologically significant substrates such as silicon wafers. Additionally, because the PFPAs reaction can be triggered by photons and electrons, lithography techniques

can be applied where the location and spatial features of the attached graphene can be controlled.⁷⁵ To demonstrate the feasibility, we placed a photomask on graphene flakes that were deposited on PFPAs-functionalized wafers and irradiated the sample with UV. Patterned graphene structures were obtained and the feature size was controlled by the configuration of the photomask.⁷⁷

Graphene Functionalization with Carbenes

Chloroform⁷⁸ and diazirines⁷⁹ are two carbene precursors that have been successfully used to functionalize reduced graphene oxide. Chloroform, upon treating with a base, forms dichlorocarbene that can be transferred to organic layer by a phase transfer catalyst.⁸⁰

Diazirines are three-membered heterocyclic rings that have a sp³ carbon atom bonded to an azo group. Analogous to azides, diazirines decompose upon heating or irradiation to release molecular nitrogen and give the electron-deficient carbene species. The highly reactive carbene is capable of undergoing insertion reaction to C–H bonds and [1 + 2] cycloaddition reaction to C=C bonds in high yield, if there is no competing reaction paths.⁸¹ 3-Aryl-3(trifluoromethyl)diazirine becomes one of the mostly used diazirine compounds due to the lack of intramolecular rearrangement of the corresponding carbene.⁸¹ Initially developed as photoaffinity labels for proteins,⁸² diazirines have found applications in surface modification and the synthesis of functional materials. Not surprisingly, diazirines are also used to functionalize of carbon nanotubes,^{83,84} diamond,⁸⁵ fullerene^{86–88} and more recently, reduced graphene oxide.⁷⁹ Similar to azides, diazirines are stable in the absence of light and can rapidly form carbene upon light activation.⁸¹ Compared with phenyl azides, however, diazirines can be time-consuming to synthesize and less efficient as some carbenes require a second photon to generate.⁸⁹

SCHEME 5. Graphene Functionalization via Aryne Cycloaddition^a

^aAdapted with permission from ref 94. Copyright 2010 Royal Society of Chemistry.

Workentin and co-workers immobilized Au nanoparticles on reduced graphene oxide using 3-aryl-3(trifluoromethyl)-diazirine.⁷⁹ Au nanoparticles were functionalized with mixed thiols of 1-decanethiol and a thiol-derivatized diazirine, and were UV irradiated in the presence of reduced graphene oxide in THF to give Au nanoparticles–graphene conjugate (Scheme 4). The product was characterized by the presence of Au peak in XRD and the change in the absorbance of the Au nanoparticle-functionalized graphene.

Graphene Functionalization via Aryne Cycloaddition

Arynes are an uncharged reactive intermediate generated by the abstraction of two *ortho* substituents on arenes. A common reaction of arynes is the Diels–Alder reaction with dienes. A few studies can be found on aryne cycloaddition to fullerene derivatives where the fullerenes act as dienes.^{90–93}

Ma et al. reported graphene functionalization via aryne cycloaddition by treating graphene sheets with 1,2-(trimethylsilyl)phenyl triate and CsF (Scheme 5).⁹⁴ The degree of functionalization was determined as 1 per 17 carbons from the 36.5% weight loss measured by TGA, or 1 per 16 carbons from the integration of the F1s and C1s peaks by XPS.

Conclusion

In this Account, we summarize the functionalization reactions of graphene with reactive intermediates of free radicals, nitrenes, carbenes, and arynes. Covalent modification breaks the extended conjugation of π -electrons in graphene, resulting in band gap opening and change in conductivity. Also introduced are functional groups that control chemical properties and allow further conjugation of additional molecules and materials to graphene. Covalent modification further improves the solubility and processability of graphene materials.

Synthetic chemistry offers a powerful means to tune material properties, for example, by the degree of functionalization on graphene. Practically, however, the precise

control over reactivity, regioselectivity and grafting density can be a challenging task. The reactivity and regioselectivity of the basal plane vs the under-coordinated edges, the zigzag vs armchair configuration are fundamental questions that warrant comprehensive studies. The high reactivity of the reactive intermediates makes it difficult to control the reaction kinetics. Side reactions often occur, making it challenging to control the composition of the surface coating and the grafting density. For instance, radicals can combine or react with species other than the substrate. Nitrenes and carbenes often react with solvents or among themselves. At high concentrations, polymeric products can form and deposit on graphene, which further complicate the composition of the surface coating. Also challenging is the analysis of the grafting products. Structural analysis methods such as NMR often require milligrams of materials. The availability of well-defined pristine graphene starting materials in large quantity will be essential in the progress of chemical functionalization of graphene.

BIOGRAPHICAL INFORMATION

Jaehyeung Park is pursuing a Ph.D. degree in the Department of Chemistry at the University of Massachusetts Lowell under the direction of Prof. Mingdi Yan. He received his B.S. (2008) and M.S. (2010) from Kyungpook National University (Korea).

Mingdi Yan is a Chemistry Professor at the University of Massachusetts Lowell where she leads a research group in the synthesis of functional nanomaterials for nanoelectronic and biomedical applications. She obtained a B.S. from the University of Science and Technology of China (USTC) (1988) and a Ph.D. from the University of Oregon (1994).

FOOTNOTES

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The authors declare no competing financial interest.

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