Pristine graphene: functionalization, fabrication, and nanocomposite materials

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Abstract. Graphene has a wide range of unique properties including high carrier mobility, optical transparency, and exceptional electrical and thermal conductivity. The interest in graphene has been largely fueled by its potential to revolutionize a number of technologically important areas including materials science, biomedical science, and energy. 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. Covalent functionalization can enhance graphene's properties including opening its band gap, tuning conductivity, improving solubility, and enhancing the properties of graphene-based composite materials. This paper discusses our work on the chemical functionalization of pristine graphene, and synthesis of graphene-nanoparticle composite materials and three-dimensional graphene (3DG)-TiO$_2$ nanocomposite photocatalyst. In photocatalytic CO$_2$ reduction, the 3DG-TiO$_2$ nanocomposite demonstrated excellent activity, about 11 times higher than TiO$_2$ nanoparticles.

1. Covalent functionalization of pristine graphene
The potential of graphene to revolutionize electronics, photonics, sensing, imaging and nanomaterials has been hampered by the availability and processability of graphene materials. The ability to process graphene in solution is a critical step in making new graphene materials and integrating them into high-performance devices. Covalent chemistry offers an attractive means to modify graphene with well-defined chemical functionalities, modulate solubility and enable processability.

Covalent chemistry has the potential to open a substantial band gap on the otherwise zero-gap electronic band of pristine graphene. It has been suggested that a band gap can be created by breaking the equivalence between the A and B sublattices in graphene by introducing structural perturbations.$^{1,2}$ It is also known that in semiconductors, a band gap can be altered with an applied strain. This opens up enormous opportunities for the covalent chemistry to open and fine-tune the band gap, and to control the remarkable electronic properties of graphene materials.

Graphene contains exclusively conjugated sp$^2$ carbons delocalized in the entire plane. This large resonance stabilization makes graphene chemically inert and poses considerable challenge for the
chemical modification of pristine graphene. Limited methods have been reported for the covalent functionalization of pristine graphene. Most approaches involve reactive species, for example, nitrenes and free radicals (generated from diazonium ions, perfluorinated alkyl iodides, 2,2,6,6-tetramethylpiperidinylxox (TEMPO), or benzoyl peroxide. Nitrene adds to the double bonds on graphene to give a bivalent adduct. Addition of radicals to graphene, on the other hand, converts sp² carbons to sp³, and yields a single covalent bond as a result. Other reported covalent modification methods include the Diels−Alder reaction where graphene as a dienophile reacted reversibly with 2,3-dimethoxybutadiene or 9-methylanthracene. However, a later work revealed that the reaction enthalpies were highly unfavorable for the Diels–Alder reaction to occur on the basal plane of graphene. The authors concluded that the experimentally observed reaction was mostly on the graphene edges that have higher reactivity due to defects, or from physical absorption of the reagents on the basal plane of graphene.

2. Functionalization of pristine graphene with perfluorophenyl azides (PFPAs)

We have developed an efficient chemistry to covalently functionalize pristine graphene using PFPAs. Activation of PFPA by heat, microwave, or UV generates the highly reactive perfluorophenyl singlet nitrene, which reacts with graphene to give the covalent adduct. By changing the functional groups on PFPAs, we could make the graphene soluble in common organic solvents as well as in water. This coupling chemistry, which was highlighted by *Nature*, represents a powerful method for the covalent functionalization of graphene, especially on the basal planes which are much less reactive than the edges and are difficult to modify.

Several groups have conducted computational studies on the reaction of PFFA with graphene. DFT calculations concluded that the aziridine product from the (2+1) cycloaddition of perfluoroaryl nitrene with graphene (Figure 1A) would induce bond cleavage between adjacent carbons in the basal plane to give the azepine structure (Figure 1B). One study found that unlike the single covalent bond formed between a radical and graphene where the adduct acts as a strong scattering center, the divalent azepine adduct has a very small effect on the conductance near the Fermi level. This opens up the possibility of introducing chemical functionalities while at the same time preserving the conductance of graphene. In another work, the computation as well as experimental results showed that after functionalization with PFPA, the conductivity of the pristine graphene degraded only about 50%. The authors attributed this to the interaction of N with graphene’s π orbitals, i.e., σ–π interaction, which causes rehybridization of the C atoms from the sp² to sp²+η state (η is defined as the degree of additional hybridization).

![Figure 1](image-url). (A) Functionalization of graphene with PFPA to give the aziridine structure. (B) The azepine structure.

3. Synthesis of nanoparticle-graphene nanocomposites

To covalently conjugate nanoparticles to pristine graphene, nanoparticles were first functionalized with PFPA, and were then covalently attached to graphene by UV irradiation (Figure 2a). We have successfully conjugated gold nanoparticles (AuNPs), silica nanoparticles (SNPs), iron oxide nanoparticles and quantum dots to CVD graphene, mechanically exfoliated graphene, and few layer
graphene (FLG) flakes. Figure 2b-d show that the covalently attached gold and silica nanoparticles on FLG.

![Synthesis of graphene-nanoparticle conjugates. TEM images of (b) AuNPs and (c, d) SNPs conjugated on FLG. Samples in c and d were prepared from FLG and PFPA-SNPs at 1:1 and 1:0.1 mass ratio, respectively.](image)

**Figure 2.** a) Synthesis of graphene-nanoparticle conjugates. TEM images of (b) AuNPs and (c, d) SNPs conjugated on FLG. Samples in c and d were prepared from FLG and PFPA-SNPs at 1:1 and 1:0.1 mass ratio, respectively.

4. TiO$_2$ nanoparticle-graphene composite
A heterogeneous photocatalyst is often a semiconductor that is capable of catalyzing photochemical reactions. There are various materials that show photocatalytic properties, among which, TiO$_2$ is one of the most widely used heterogeneous photocatalysts. It exhibits excellent physical and chemical stability, possesses desirable electronic and optical properties, and is inexpensive. When TiO$_2$ is irradiated with UV light, electrons are excited from the valence band to the conduction band. The excited electrons in the conduction band and holes in the valence band are responsible for the photocatalytic activity, carrying out reduction and oxidation with reagents at the surface of TiO$_2$. Albeit its many advantages, TiO$_2$ suffers from a large band gap (3.2 eV for anatase TiO$_2$) which requires activation by UV light, and a fast electron-hole recombination rate which reduces its photocatalytic efficiency.

Graphene-semiconductor composite nanomaterials have recently emerged, and have demonstrated high potential in enhancing the photocatalytic efficiency of semiconductor nanomaterials. In the composite nanomaterial, graphene acts as an electron acceptor to ensure fast charge transfer. Effective charge separation can therefore be achieved to slow down the electron-hole recombination, resulting in enhanced photocatalytic activity of TiO$_2$. Moreover, because graphene can absorb light in the visible region, the photo-excitation wavelength of graphene-TiO$_2$ hybrid nanomaterials can be extended to visible (400-700 nm). Consequently, the photocatalytic reactions can be carried out using the visible light instead of UV. The large surface area of graphene can additionally increase the concentration of adsorbed reagents as well as the surface interactions. Because the photocatalysis occurs at the surface of TiO$_2$, the increased adsorption and interactions with the adsorbed reagents lead to enhanced photocatalytic activities of graphene-TiO$_2$ hybrid nanomaterials.

Studies have shown that graphene-based composite materials exhibit better performance when the components are covalently linked, owing to the higher stability and stronger interactions between the
individual components than the non-covalent composites. Graphene is relatively inert and has limited dispersibility in solvents, which poses considerable challenges in graphene functionalization. The most common covalent functionalization uses graphene oxide (GO) owing to its abundant functional groups. However, the oxidation process produces various oxygen-containing species, and the structure and density of which are difficult to control. Even after reduction to reduced GO (rGO), the properties cannot be completely restored to those of the pristine graphene.

Graphene-TiO$_2$ composite nanomaterials are mostly prepared by hydrothermal, solvothermal and hydrolysis reactions. In these cases, GO instead of pristine graphene was used. The hybrid materials were prepared by reducing GO in the presence of a TiO$_2$ precursor (titanium(IV) isopropoxide, titanium(IV) fluoride, titanium(IV) butoxide), resulting in the deposition of TiO$_2$ particles on the surface of rGO. Because rGO was used, oxygen-containing species remained and could not be removed completely even after reduction. These defects disrupt the conjugated structure and the electron conduction of graphene.

We synthesized graphene-TiO$_2$ nanocomposite photocatalyst using pristine graphene and pre-made TiO$_2$ nanoparticles by conjugating PFPA-functionalized TiO$_2$ nanoparticles on few-layer graphene (FLG) flakes. Following the protocol shown in Figure 2a, TiO$_2$ nanoparticles were first functionalized with PFPA. The PFPA-functionalized TiO$_2$ nanoparticles were then treated with FLG under UV irradiation. When the FLG-TiO$_2$ samples were examined with TEM, agglomerated TiO$_2$ nanoparticles were observed (Figure 3). Agglomeration can reduce the catalytic activity of TiO$_2$ nanoparticles through recombination of excited electrons and holes in TiO$_2$.

![Figure 3. TEM image of TiO$_2$ nanoparticles conjugated on FLG flakes.](image)

5. 3-Dimensional graphene-TiO$_2$ photocatalyst composite

5.1. 3-Dimensional graphene

The recent development of three-dimensional graphene (3DG) represents a significant advance in the availability of pristine graphene materials. Pristine 3DG can be prepared by chemical vapor deposition (CVD) using a macroporous Ni or Cu foam during graphene synthesis. Ni or Cu foam serves two purposes: (1) to catalyze the dissolution/deposition of graphene during pyrolysis of carbon precursors; (2) to serve as a physical template onto which graphene is deposited. When the template is removed by acid etching, a free-standing three-dimensional network of pristine graphene is obtained (Figure 4a). The macroporous structure of the template is maintained (Figure 4b). Because 3DG is fabricated on a continuous interconnected structure, it has minimal edge defects and more uniform surface (Figure 4c). Depending on the substrate, the 3DG produced can range from single to several layers.
3DG possesses many unique properties in addition to those of the typical graphene nano-sheets.\textsuperscript{43-45} It has high specific surface area resulting from the interconnected graphene network. While 2D graphene sheets have conducting pathways restricted to the planar direction, 3DG provides multiple channels for fast electron transport. Its excellent electrical conductivity is also due to the absence of inter-sheet contact resistance. Moreover, 3DG reduces the agglomeration of 2D graphene sheets caused by the strong inter-sheet π-π stacking. While 2D graphene sheets are fragile and difficult to handle, 3DG is a freestanding material (\textbf{Figure 4a}). Practically, 3DG can be made into different sizes and shapes. The surface area and porosity can be controlled by the template. High purity Ni and Cu foams are commercially available and can be purchased as large pieces, e.g., 1 m$^2$, or cut into desired size and shape.

5.2. 3-Dimensional graphene-TiO$_2$ photocatalyst composite
We covalently conjugated TiO$_2$ nanoparticles on a pristine 3D graphene.\textsuperscript{47} The 3D graphene was prepared by CVD on a macroporous Ni foam substrate.\textsuperscript{46} Because the microporous structures of the Ni foam template are interconnected, the 3D graphene synthesized on this template would consist of a continuous piece of pristine graphene free of edge defects (\textbf{Figure 4}). To conjugate TiO$_2$ nanoparticles, 3D graphene was first functionalized with PFPA-COOH (\textbf{Figure 5}). The TiO$_2$ nanoparticles were conjugated by a solvothermal treatment through binding with the carboxyl groups on the graphene surface.

Densely packed and uniformly distributed TiO$_2$ particles were observed on 3D graphene (\textbf{Figure 6A}).\textsuperscript{47} This is in sharp contrast with the product prepared on FLG, where the conjugated TiO$_2$ nanoparticles were sparse and were substantially agglomerated (\textbf{Figure 3}). To test the photocatalytic performance of the composite catalyst, CO$_2$ reduction was carried out in the presence of TiO$_2$-3D graphene by irradiating the sample with a 200 W mercury lamp. As a control, TiO$_2$ nanoparticles of TiO$_2$-3D graphene for comparison. The result shows that the amount of CO produced by TiO$_2$-3D graphene after 4 h was 11-fold higher than that by bare TiO$_2$ (\textbf{Figure 6B}). This result can be attributed to a combination of 3D graphene substrate, high density of TiO$_2$ nanoparticles and excellent particle dispersity.
Figure 6. (A) SEM image of TiO$_2$ nanoparticles conjugated on 3D graphene. (B) The production of CO in photocatalytic CO$_2$ reduction on 3D graphene-TiO$_2$. CO was observed as the only gaseous product under this condition (triethylamine as the sacrificial electron donor, irradiated with a 200 W mercury lamp (140 mW/cm$^2$)).

Conclusions

Despite its high potential, the utility of graphene in practical applications has been hindered by the availability of high quality pristine graphene, and the integration with other technologically important materials. The ability to covalently functionalize graphene can enhance graphene's properties as well as produce high-performance composite materials. We have developed an efficient method to covalently functionalize pristine graphene. Covalently conjugated nanoparticle-graphene composite materials showed high density of nanoparticles on graphene basal planes. Finally, a 3D graphene-TiO$_2$ nanocomposite demonstrated excellent photocatalytic activity, about 11 times higher than TiO$_2$ nanoparticles in reducing CO$_2$.

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