

# TiO<sub>2</sub>-Graphene Nanocomposites. UV-Assisted Photocatalytic Reduction of Graphene Oxide

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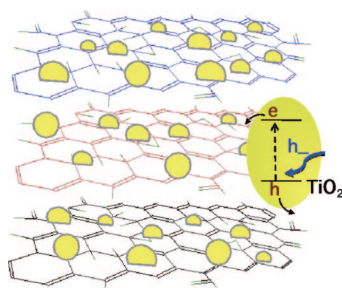
Carbon nanostructures such as carbon nanotubes and graphene offer new opportunities to develop nanocomposites with unusual electronic catalytic properties. Recent interest in understanding properties of graphene has led many theoretical and experimental efforts worldwide.<sup>1</sup> Of particular interest is the possibility to exfoliate graphene through a combination of oxidation and sonication procedures, followed by reduction through chemical methods. The strong van der Waals interactions among these reduced graphene sheets results in their tendency to aggregate in solution. Both electrostatic stabilization<sup>2</sup> and chemical functionalization<sup>3,4</sup> methods have proven to be useful to suppress aggregation of exfoliated graphene sheets. The requirement to obtain graphene as individual sheets and to maintain it in the reduced form introduces complexity in designing composite systems (e.g., semiconductor or metal nanoparticle and graphene composites). Recently, we reported the formation of a graphene–gold composite system that is suspendable in an aqueous medium using a chemical reduction method.<sup>5</sup>

Since graphene is readily processable from aqueous and polar solvents, it offers the convenience to cast thin films for various technological advances. For example, the dispersion of catalyst particles on carbon nanostructures can provide new ways to increase the surface area and improve the catalyst performance of energy conversion devices. Enhanced electrocatalytic activity of Pt particles dispersed on carbon nanotubes has already been reported in fuel cells.<sup>6,7</sup> Silver particles protected by graphite oxide sheets have been assembled as ultrathin films using a layer-by-layer self-assembly technique.<sup>8</sup> Graphene-based

**ABSTRACT** Graphene oxide suspended in ethanol undergoes reduction as it accepts electrons from UV-irradiated TiO<sub>2</sub> suspensions. The reduction is accompanied by changes in the absorption of the graphene oxide, as the color of the suspension shifts from brown to black. The direct interaction between TiO<sub>2</sub> particles and graphene sheets hinders the collapse of exfoliated sheets of graphene. Solid films cast on a borosilicate glass gap separated by gold-sputtered terminations show an order of magnitude decrease in lateral resistance following reduction with the TiO<sub>2</sub> photocatalyst. The photocatalytic methodology not only provides an on-demand UV-assisted reduction technique but also opens up new ways to obtain photoactive graphene-semiconductor composites.

**KEYWORDS:** graphene · TiO<sub>2</sub> · carbon nanostructures · photocatalysis · electron transfer · UV-assisted reduction · graphene-semiconductor composite

composite materials prepared *via* dispersion in polymers show significant improvement in the electronic and thermal conductivity.<sup>9,10</sup> Two dimensional carbon nanostructures such as graphene can also potentially serve as a support material with which to anchor semiconductor particles and improve the performance of optoelectronic and energy conversion devices. We have now designed an *on-demand* reduction strategy to obtain graphene-semiconductor composite nanostructures (Scheme 1). In our maiden effort, we have succeeded in carrying out UV-induced photocatalytic reduction of graphene oxide and maintaining well-separated graphene-semiconductor composite sheets.



**Scheme 1.** TiO<sub>2</sub>-graphene composite and its response under UV-excitation.

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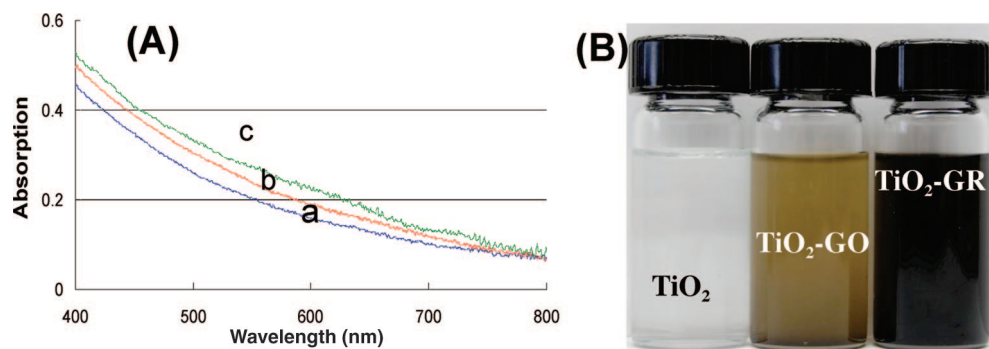


Figure 1. (A) The absorption spectra of graphene oxide and  $\text{TiO}_2$  suspension in ethanol (a) before UV-irradiation, (b) after 5 min, and (c) after 15 min of UV irradiation; (B) The change in color of a 10 mM solution of  $\text{TiO}_2$  nanoparticles with 0.5 mg/mL GO before and after UV irradiation for 2 h. A suspension of 10 mM  $\text{TiO}_2$  nanoparticles is also shown for comparison.

## RESULTS AND DISCUSSION

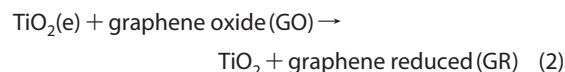
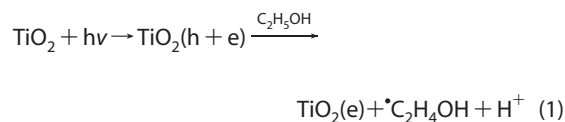
### UV-Assisted Reduction of Graphene Oxide in $\text{TiO}_2$ Suspensions.

The graphene oxide upon exfoliation carries sufficient functional groups (*e.g.*, epoxides, hydroxyls, carboxylic acids) to render itself suspendable in polar solvents. It has been shown that removal of coexisting metal ions and/or functionalization with amines keeps these graphene sheets from collapsing upon chemical reduction with hydrazine.<sup>2,3</sup> In the present study we prepared a mixture of graphene oxide and colloidal  $\text{TiO}_2$  in ethanol and subjected it to steady state UV-irradiation. The change in the absorption spectrum following the UV-irradiation over a 15 min period is shown in Figure 1A. The samples were placed in a 0.5 cm optically transparent cell and illuminated under white light while nitrogen was bubbled through the solution. The samples were periodically examined for changes in absorption.

The change in color from light brown to dark brown to black can be seen as the reduction of GO proceeds (Figure 1B). This color change has previously been suggested as partial restoration of the  $\pi$  network within the carbon structure and has been witnessed through chemical reduction of the GO sheets.<sup>11,12</sup> No significant changes in the absorption could be seen during UV-irradiation when  $\text{TiO}_2$  was excluded from the suspension. This observation establishes the mediating role of  $\text{TiO}_2$  in the reduction of GO. Since  $\text{TiO}_2$  particles carry surface charge in suspensions, they can be readily suspended in polar solvents. Thus, the  $\text{TiO}_2$ -graphene composite becomes readily soluble in polar solvents. The suspension after UV-irradiation remains stable for about an hour. Slow settling of the composite can be seen after this period. Stirring or mild sonication of the  $\text{TiO}_2$ -graphene sample facilitated its resuspension.

The photocatalytic properties of semiconducting  $\text{TiO}_2$  particles are well-researched.<sup>13</sup> Upon UV-irradiation of a deaerated suspension of  $\text{TiO}_2$  colloids, one observes charge separation. In the presence of eth-

anol the holes are scavenged to produce ethoxy radicals, thus leaving the electrons to accumulate within  $\text{TiO}_2$  particles (reaction 1). The accumulated electrons serve to interact with the graphene oxide sheets in order to reduce certain functional groups.



As shown in our earlier studies, the electrons stored in  $\text{TiO}_2$  nanoparticles are readily scavenged by carbon nanostructures such as fullerenes and carbon nanotubes.<sup>14,15</sup> In the present experiments graphene oxide, with its extended epoxy and carboxylate groups, readily interacts with  $\text{TiO}_2$  particles and undergoes reduction under UV irradiation. The affinity of surface hydroxyl groups of  $\text{TiO}_2$  surface to undergo charge transfer interaction with carboxylic acid functional groups has been well established.<sup>16</sup> Thus, the direct interaction between  $\text{TiO}_2$  and graphene provides the basis to obtain  $\text{TiO}_2$ -graphene composites. In addition, it enables us to explore a photocatalytic reduction procedure to obtain reduced graphene sheets in solution.

The photocatalytic method differs from the chemical reduction method (*e.g.*, reduction with hydrazine) that is usually employed to obtain graphene sheets from graphene oxide.<sup>2,17,18</sup> The advantage of photocatalytic reduction is that it can be triggered on demand by tuning the UV-irradiation. Following the photocatalysis procedure, the solvent can be dried and the  $\text{TiO}_2$ -graphene can be recovered in the powder form and redispersed in polar solvents. Figure 2 shows the dried samples (297 K, in air) of  $\text{TiO}_2$ -GO and  $\text{TiO}_2$ -GR obtained from the ethanol suspensions of  $\text{TiO}_2$  and GO before and after UV irradiation.



Figure 2.  $\text{TiO}_2$ -graphene oxide ( $\text{TiO}_2$ -GO) and  $\text{TiO}_2$ -reduced graphene ( $\text{TiO}_2$ -GR) powders obtained after solvent evaporation and drying the samples at room temperature.

**Stepwise Electron Transfer to Graphene Oxide.** To confirm the ability of graphene oxide to accept electrons from  $\text{TiO}_2$  in a quantitative fashion, we introduced GO in small increments to previously irradiated  $\text{TiO}_2$  colloids in ethanol. This procedure not only excludes UV during the reduction process but also allows us to estimate the number of electrons involved in the reduction process.

As established earlier,<sup>19,14</sup>  $\text{Ti}^{4+}$  centers serve as trapping sites for photogenerated electrons.  $\text{TiO}_2$  suspensions turn blue during UV irradiation as the electrons accumulate within the  $\text{TiO}_2$  particles (reaction 1). Spectrum a in Figure 3A represents trapped electrons in UV-irradiated  $\text{TiO}_2$  suspension with a broad absorption maximum around 650 nm. (Note that spectrum  $a_0$  corresponds to the  $\text{TiO}_2$  nanoparticles prior to irradiation.) For a 10 mM solution, this band maximized over a 1-h period of UV exposure. These trapped electrons remain stable in deaerated solution, thus enabling quantitative extraction by the controlled addition of graphene oxide. Figure 3A shows the decrease in absorbance with incremental addition of deaerated graphene oxide suspension. It is important that the addition of the suspension with a microsyringe is done in the presence of nitrogen. Any trace contamination of air results in the scavenging of electrons by oxygen. Figure 3A also gives specific experimental conditions required to generate enough electrons to reduce GO. For example, 1 h of irradiation of 3.7 mL of 10 mM  $\text{TiO}_2$  nanoparticles was required for the reduction of 300  $\mu\text{g}$  of GO.

It had been established earlier that the molar absorbance of trapped electrons in  $\text{TiO}_2$  is  $760 \text{ M}^{-1} \text{ cm}^{-1}$  at 650 nm.<sup>15</sup> Thus, we can estimate the number of moles of electrons transferred from  $\text{TiO}_2$  to graphene oxide by monitoring the decrease in the absorbance. Figure 3B shows the dependence of extracted electrons on the amount of graphene oxide added. From the slope of the linear part of the plot in Figure 3B we obtain a value of 0.01 moles of electrons per gram of graphene oxide. Using the carbon-to-oxygen ratio of 2.25 as reported in the original preparation of graphitic oxide,<sup>20</sup> a gram of GO corresponds to 0.02 moles of oxygen. In this case, this implies that approximately 50% of the oxygen sites are able to accept electrons from  $\text{TiO}_2$  and undergo re-

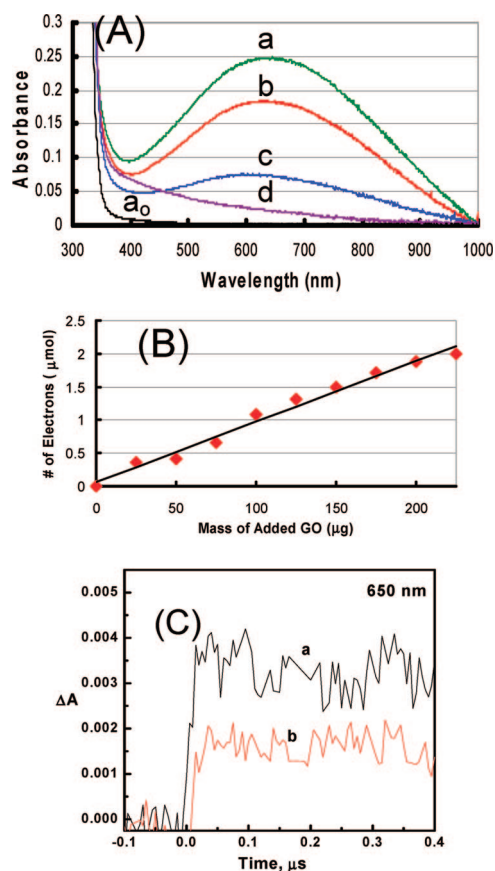
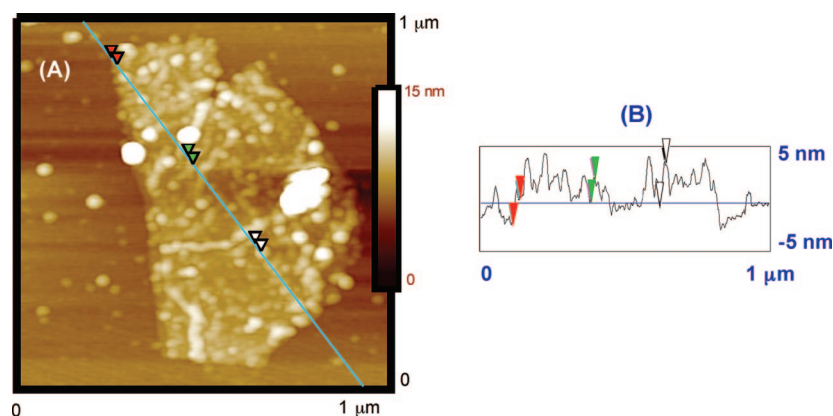


Figure 3. (A) Absorption spectra of UV-irradiated 10 mM  $\text{TiO}_2$  suspension in ethanol (spectrum a) and after the addition of graphene oxide suspension (deaerated): (a) 0, (b) 50, (c) 150, (d) 300  $\mu\text{g}$  GO ( $a_0$  corresponds to  $\text{TiO}_2$  suspension prior to UV irradiation). (B) The dependence of electrons extracted from  $\text{TiO}_2$  on the amount of GO added to the suspension. (C) Transient decay of trapped electrons in  $\text{TiO}_2$  recorded following 308 nm laser pulse excitation (a) without and (b) with 200  $\mu\text{g}$  GO.

duction. This estimate gives a quantitative value of sites that are potentially reducible through the  $\text{TiO}_2$  electrons. It is likely that a small fraction of the electrons may also get stored in graphene sheets, similar to the storage phenomenon seen for carbon nanotubes.<sup>15,21</sup> Furthermore, based on earlier observations, the carboxylic acid groups on the graphene oxide sheets are likely to evade the mild reduction conditions.<sup>2</sup>

To probe the electron transfer between excited  $\text{TiO}_2$  and GO we carried out nanosecond laser flash photolysis using 308 nm laser pulse excitation. The absorption of the trapped electron was monitored at 650 nm (Figure 3C). The appearance of the absorption was prompt, indicating the completion of the trapping process within the pulse duration. In the presence of GO the magnitude of the absorption decreased by  $\sim 50\%$  indicating the transfer of electrons to GO within the pulse duration. These results further confirm the role of  $\text{TiO}_2$  in transferring the electrons to GO in the sub-microsecond time scale.



**Figure 4.** (A) AFM image of  $\text{TiO}_2$ -GO. (B) Depth profile of the line of interest on the graphene sheet. The red marker corresponds to a bilayer graphene sheet with a height of 2.2 nm, whereas the green and white markers correspond to nanoparticle sizes ranging from 2.6 to 4 nm, respectively. Additional cross-sections exhibited individual particle heights as great as 7 nm.

$\text{TiO}_2$  is a relatively mild reductant with conduction band around  $-0.5$  V versus NHE at neutral pH. Under UV-irradiation, it is capable of transferring electrons to fullerenes and carbon nanotubes. In the present experiments, the oxygen sites that are susceptible for reduction at this redox potential can undergo transformation, leaving reduction-resistant sites undisturbed. It is not clear at this stage whether the photocatalytic reduction can fully restore the conjugated  $\text{sp}^2$  network. It is likely that the reduction process will result in the creation of turbostratic graphene,<sup>4</sup> which is known to exhibit limited conductivity compared to bulk graphite.

**Morphology of  $\text{TiO}_2$ -Graphene Nanocomposites.** A dilute suspension of  $\text{TiO}_2$ -graphene was dropcast onto a heated mica substrate and analyzed through atomic force microscopy (AFM). Figure 4 shows the AFM image of the  $\text{TiO}_2$ -graphene composite. It is evident that the individual graphene sheets are coupled to  $\text{TiO}_2$  nanoparticles. Nanoparticles such as  $\text{TiO}_2$  can interact with the graphene oxide sheets through physisorption, electrostatic binding, or through charge transfer interactions. For example, gold nanoparticles are deposited on graphene sheets through physisorption.<sup>5</sup> AFM images of  $\text{TiO}_2$ -graphene composite samples before and after UV-irradiation exhibited similar particle density. This observation indicated that the binding of the  $\text{TiO}_2$  particles to graphene is unaffected by the UV-assisted reduction. The initial binding of the  $\text{TiO}_2$  particle through the carboxylate linkage remains unaffected and thus likely to keep them intact in the composite.

The cross section analysis indicates a height of  $\sim 2$  nm for the graphene sheet and a particle diameter for  $\text{TiO}_2$  of 2–7 nm. It is widely accepted that graphene sheet thickness increases as a result of the bulky carbonyl, epoxy, and carboxyl groups on graphene oxide sheets.<sup>22</sup> “Dry” values of graphene oxide sheet thicknesses have been calculated to be as low as 0.6 nm by XRD; however, single-sheet GO is typically found to be

on the order of 0.9–1.3 nm when analyzed by AFM.<sup>17,18</sup> On the basis of this estimate, we can quantify the thickness of graphene sheets obtained through photocatalytic reduction to be mono- or bilayer graphene.

**Resistivity Measurements.** Decrease in the resistivity of graphene oxide sheets is an effective measure to follow the reduction process. Complete reduction of various oxygenated sites and reconstruction of the  $\text{sp}^2$  network is important in attaining maximum conductivity in these 2-D carbon nanostructures. In the present experiments 40 nm gold-sputtered films were cast on 1 cm wide borosilicate glass slides except for a gap of 1 mm at the center. Samples (500  $\mu\text{g}$ ) of  $\text{TiO}_2$ -graphene suspension in etha-

no (before and after UV-irradiation) were dropcast onto this gap and allowed to dry at slightly elevated temperatures ( $\sim 80$  to  $100$  °C). The lateral resistances of the films prior- and post-UV irradiation were measured to provide an estimate of the impact of reduction on the resistivity of the samples. A similar measurement approach has been previously used to quantify conductivity changes in oxidized and reduced graphite oxide through both chemical and electrochemical means.<sup>12</sup>

The films cast with graphene oxide- $\text{TiO}_2$  suspension prior to UV irradiation showed a measured resistance of 233  $\text{K}\Omega$ . Two hours of irradiation of the suspension resulted in an order of magnitude decrease in the resistance, to an average value of 30.5  $\text{K}\Omega$ . The measurements done previously on chemically reduced graphite oxide using this method achieved lateral unreduced resistances of 32  $\text{M}\Omega$  and reduced resistance values 12  $\text{K}\Omega$  across a 2 mm gap with 3 mm thickness.<sup>12</sup> The smaller resistance values in our unreduced graphite oxide sample may be attributed to contributions in conductivity of the  $\text{TiO}_2$  nanoparticles and thicker film thicknesses. (Since both samples (before and after UV-reduction) contained same concentration of  $\text{TiO}_2$ , the contribution of  $\text{TiO}_2$  to decreased resistivity is expected to be constant.)

Although these initial measurements provide a relative measure of overall decrease in resistance following the UV-exposure, further reduction in resistance is desirable if one is interested in the design of electronic devices. The present method offers a new and soft method of reduction as compared to the conventional approach of using elevated temperatures or strong reducing agents for reducing graphene oxides. In addition the binding of the oxide particles keeps the exfoliated graphene sheets from the collapse after the reduction step. Further studies with different semiconductor nanoparticles and refinement of methodology are likely to offer even greater conductivity improvements.

## EXPERIMENTAL SECTION

**Materials and Methods.** Reagent grade chemicals were purchased from Aldrich unless otherwise stated. Ethanol (200-proof) was purchased from Decon Laboratories Inc; 98% titanium isopropoxide was purchased from Acros Organics. Conducting grade, -325 mesh, 99.9995% graphitic powder was purchased from Alfa Aesar.

TiO<sub>2</sub> colloidal suspension (10 mM) in ethanol was prepared by hydrolysis of titanium isopropoxide, through the dropwise addition of titanium isopropoxide to a vigorously stirred solution of ethanol. The colloidal suspension was continuously stirred prior to its use to prevent agglomeration of the particles. Nanoparticles made through this method have a broad size distribution of 2–7 nm, as confirmed by AFM, and can be stored for several days while stirred.

Graphite oxide (GO) was prepared through Hummers' method,<sup>20</sup> by reacting commercially obtained graphite powder in a mixture of H<sub>2</sub>SO<sub>4</sub>, NaNO<sub>3</sub>, and KMnO<sub>4</sub>. After completion of the reaction, H<sub>2</sub>O<sub>2</sub> was added to the reaction vessel. The GO was filtered and washed twice with 1 M HCl and twice with DI water. The GO separated in the form of a dry, brown powder. The final product was then added to the TiO<sub>2</sub> colloidal suspension and sonicated for 30 min to produce dispersion of graphene oxide sheets coated with the TiO<sub>2</sub> nanoparticles.

UV-irradiation of the TiO<sub>2</sub> and TiO<sub>2</sub>-graphene oxide (TiO<sub>2</sub>-GO) samples was performed using an Oriol 450 W xenon arc lamp. Typical concentrations were 10 mM TiO<sub>2</sub> and 1 mg/mL GO. A water filter, which was used to cutoff IR, assisted in maintaining the temperature of the ethanol sample (300 K) during irradiation with minimum variation in the experimental results. The suspensions were kept agitated during UV irradiation through bubbling of the solution with nitrogen gas. The agitation of the samples ensured uniform irradiation of the TiO<sub>2</sub>-GO suspension during the reduction process.

**Measurements.** Absorption measurements were made with a Cary 50 Bio UV-vis spectrometer. Samples were placed in optically transparent 0.5 or 1 cm quartz cells and deaerated by bubbling nitrogen. Samples for resistance measurements were made using gold-sputtered borosilicate glass slides with a 1-mm gap; 0.5 mL of 1 mg/mL graphene/graphene-oxide solutions were deposited in 50 μL portions onto the gap at elevated temperatures (~100 °C) to ensure immediate evaporation of the solvent for complete and reproducible coverage. The gold terminations of the coupons were connected via alligator clips to a Keithley digital multimeter, where resistance measurements were made. Atomic force microscopy (AFM) was carried out using a Digital Nanoscope III in the tapping mode. An etched silicon tip was used as a probe for imaging the samples, which were dropcast on freshly cleaved mica. Nanosecond laser flash photolysis experiments were carried out using laser 308-nm laser pulses from Lambda Physik excimer laser system. (Laser pulse width was 10 ns; intensity was ~10 mJ/pulse.) Unless otherwise specified, all the experiments were performed under N<sub>2</sub> purging condition.

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