

# Graphene - Are they the Appropriate Materials for Pollutant degradation?

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15th July 2013

Graphene is composed of a single layer of carbon atoms arranged in a two dimensional (2D) honeycomb network of six membered rings.[1-20]. There are various properties of this material that make this material unique. In Table 1 some of these striking properties of these materials are assembled for ready reference. Related to these materials graphene oxide (GO) and reduced graphene oxide(rGO) are also considered to be relevant materials for various device applications. All these devices that are conceived on the basis of these three materials are essentially concerned exploiting its acceptor and donor characteristics for electrons. It may be appropriate to state that the possibility of graphene materials being exploited for a variety of device applications might have been over emphasized in the literature cited above. The derivative of graphene is graphene oxide (GO), which can be directly synthesized from graphite oxide. Typical GO is represented in Figure 1, which shows it contains functional oxygen groups (hydroxyl, epoxy, carbonyl and carboxyl) in  $sp^3$  carbons that vary the properties from pristine

Table 1: Some Typical Properties of Graphene Materials

S.No	Property	Value
1	Transparency	Above 90 percent
2	Surface area	2630 $m^2 g^{-1}$
3	Thermal conductivity	Greater than 3000 $W mK^{-1}$
4	Youngs Modulus	1Tpa
5	Ballistic transport	electrons behave as mass less relativistic particle
6	charge mobility	about 200,000 $cm^2 V^{-1}$
7	Electricalconductivity	(4.84 - 5.30) $10^3 W mK^{-1}$

graphene. Those components are usually the starting point of chemical reactions towards functionalization of graphene. These oxygen-containing groups can be expected to provide graphene with hydrophilic character and chemical reactivity. A typical configuration of graphene oxide is shown in Fig.1.

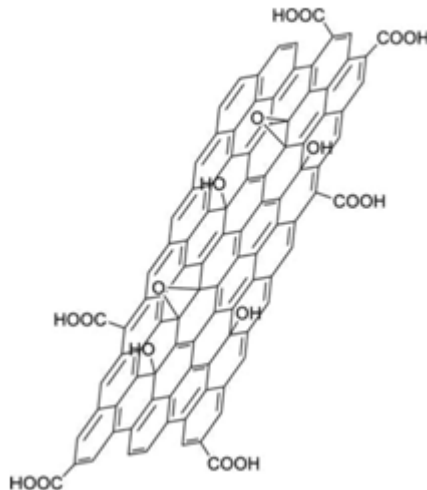


Figure 1: Representation of Graphene oxide structure. Reprinted from Ref.21

## Methods of Preparation

It is essential to understand the different preparation methods of graphene and its derivatives. The first demonstration was done by Novoselov et al. with the Scotch tape peel method, where bulk graphite was placed on the sticky side of regular tape and peeled away. Since then, many synthesis procedures to obtain graphene have been developed [22-26]. One example of graphene synthesis is the photolitho-graphically patterned trenches developed by Frank et al. that shear off graphite which is then rubbed on silicon dioxide to produce graphene [27]. Some other examples are molecular beam epitaxial growth on SiC by thermal decomposition [28,29]; solvothermal synthesis (a pyrolysis of an alcohol, usually nano-dispersed ethanol, and an alkali metal (Na) that gives fused monoatomic sheets of graphene) [30]; unzip of multi-walled carbon nanotubes (MWCNTs can be cut longitudinally if they are first suspended in  $\text{H}_2\text{SO}_4/\text{KMnO}_4$ ); electron beam irradiation of Poly(methyl methacrylate) (PMMA) nanofibres, arc discharge of graphite,

thermal fusion of PAHs. Large area films of graphene are obtained by chemical vapour deposition (CVD) from the reaction of carbon-based gases on a metal catalyst. A metal substrate is placed into a furnace and heated at low vacuum at high temperatures to increase its domain size by annelation. Then, methane and hydrogen gases are inserted into the furnace. Carbon atoms are deposited on the surface of the substrate through chemical adsorption with hydrogen. When the furnace is cooled, it crystallizes into single layer graphene (SLG). This method has been successful with other metal substrates like Pt, Ni, Fe, Pd and Co. Possibly, only graphene grown by CVD on different metals and their modifications are, currently, scalable processes. Roll-to-roll technique is a promising technique that can allow sample transfers, produce good quality graphene and can be scaled-up. Other relevant production methods are based on the obtained from reduced Graphene Oxide. The most important methods of GO synthesis are mainly based on three graphite oxidation procedures. In the first one,  $\text{KClO}_3$  reacts with graphite in fuming  $\text{HNO}_3$ . The second method is a modification replacing  $\text{KClO}_3$  with  $\text{H}_2\text{SO}_4$ . Third process generally known as Hummers method, a mixture of  $\text{KMnO}_4$  and  $\text{H}_2\text{SO}_4$  reacts with graphite to form oxide graphite. These three methods of wet chemical synthesis are the basis of GO production. Probably, the most commonly used techniques are variations of Hummers method. Raw graphite is oxidized using  $\text{KMnO}_4:\text{H}_2\text{SO}_4$  and  $\text{NaNO}_3$  producing positively charged carbon layers with negative hydrogen-sulphate ions. The two layers increase their distance by hydrolyzing the compounds between the carbon layers. Then, by removing the extra ions produced by the oxidants, the layers tend to separate automatically and thin-film particles in aqueous solution are obtained. After several treatments, uniform-thin graphene oxide films are produced.

Moreover, there are other methods of producing GO; namely, sonication of graphite oxide and RF Plasma functionalization (produces GO by etching the graphite surface and selectively oxidize SLG and the top later of multilayer samples. The scalability of GO production techniques is concerned, they have been proved to be efficient in graphene-based semiconductors production. By definite conditions of the Hummers method, (no  $\text{Na}_3\text{NO}_3$ , increased amount of  $\text{KMnO}_4$  and  $\text{H}_2\text{SO}_4:\text{H}_3\text{PO}_4$  in a 9:1 mixture) fewer defects, higher yield, equivalent conductivity and no production of toxic gases is achieved. Therefore, this is considered to be the suitable method to prepare graphene oxide in large quantities. From GO, reduced graphene oxide can be obtained by means of reducing agents. There are two main reaction groups, chemical and non-chemical reductions. The former group is based on liquid-phase exfoliation, an intermediate process between exfoliation and chemical growth where GO obtaining methods are applied with a following chemical reduc-

tion. The reducing agents are varied: hydrazine hydrate,  $\text{NaBH}_4$ , sodium hydrosulfite, iron/HCl and other metals like aluminium, acetic acid/HCl. A variation of liquid-phase exfoliation is electro-chemical exfoliation, a green mass-production technique to obtain exfoliated graphene flakes. By using a mixture of solvents with narrow electro-chemical window (e.g., water) and a liquid with large electro-chemical window [e.g., room temperature ionic liquid (RTIL)], hydroxyl and oxygen radicals can be produced by the electrolysis of water. Then, the oxygen radicals corrode the graphite anode on defect sites, grain boundaries and edge sites. This induces the separation of the edge sheets and the intercalation of RTIL anions within the sheets. The electrode is expanded and provokes the precipitation, which makes the sheets precipitate, generating a graphene solution. This is a relevant technique since it can produce rGO with reduced sheet resistance (0.0150.21 K Ohm/sq in comparison to 1100 K Ohm/sq obtainable by chemical reduction) and greater transparency (96 percent versus the 80 percent achievable by means of chemical reduction). This would greatly affect the final photoelectrochemical performance of the material. The reduction and exfoliation level and the size of rGO sheets are controlled by tuning the applied potential and varying the RTIL. Some other methods are microwave-induced reduction, flash reduction and solvent-assisted thermal reduction, but, as in the case of GO, many other production methods are being continuously developed. The objective is to achieve large-scale production methods of quality graphene. As far as the interaction between semiconductors and rGO is concerned, the remaining oxygen-containing groups interact with the semiconductor to attach it. The problem is that Hummers method produces a large number of defects. Hence, they reduce the recombination probability, so alternative methods are being developed to reduce the quantity of defects produced. Examples of this are solvent-exfoliated graphene and non-oxidative preparation of graphene with a mixture of water and ethylene glycol by an ultrasonic reaction. These methods would be upscalable and are the leading edge towards mass production of quality graphene.

## Photodegradation of Organic Pollutants

Li and his coworkers [19] were the first to report the photodegradation of organic compounds (methylene blue (MB)) using  $\text{TiO}_2$  (commercial P25, Degussa)graphene (P25GR) nanocomposites. P25graphene (P25GR) nanocomposites were obtained via a facile, one-step hydrothermal method using P25 and GO as the starting materials. Compared to the bare P25 catalyst, the P25 GR composite exhibited three advantages. First, the pipi stacking be-

tween MB and the aromatic regions of graphene enhanced the adsorptivity of the dyes on the surface of the catalysts (Fig. 2(A)), leading to a synergetic effect between adsorptivity and photoreactivity. Second, the introduction of graphene extended the light responding range of P25 by 30 40 nm (Fig. 2(B)), facilitating a more efficient visible light driven photocatalysis. The red shift could be attributed to the formation of the TiOC bonds during the preparation. Last P25graphene showed a decrease in the solid state interface layer resistance and the charge transfer resistance on the surface compared to bare P25, according to the electrochemical impedance spectra (EIS) (Fig. 2(C)). It is possible all these four factors can be cumulatively account for the photoactivity of the composite system. Thus, P25GR nanocomposites demonstrated significant advancement over bare P25 in the photodegradation of MB dye under both UV and visible light irradiation (Fig. 2(D) and (E)). In view of the high efficiency achieved in the P25graphene catalyst, many efforts have been devoted to the growth of TiO<sub>2</sub> nanostructures on graphene through in situ or one-pot routes. In most studies, TiO<sub>2</sub> nanostructures were fabricated on graphene via: the hydrolysis of various Ti precursors including TiF<sub>4</sub> titanium(IV) ammonium oxalate and TiCl<sub>4</sub> on graphene; the solvothermal process; or the two step method (hydrolysis of a Ti precursor, e.g. Ti(BuO)<sub>4</sub>, in the presence of GO, followed by the solvothermal reaction. Moreover, Kamat et al.[31]and Ng et al.[32] developed the fabrication of TiO<sub>2</sub>graphene composites by carrying out UV-assisted photocatalytic reduction of graphite oxide using TiO<sub>2</sub> nanoparticles. In addition, other methods,such as the microwave-assisted synthesis and the redox reaction between Ti<sup>3+</sup> and GO, can be also adopted to form the TiO<sub>2</sub>graphene composites. All of the obtained TiO<sub>2</sub>graphene nanocomposites exhibited superior (does this claim is justified?) performance in the photodegradation compared to pure TiO<sub>2</sub>. The improvement in the photocatalytic activities can be attributed to the enhanced adsorptivity of dyes, extended photo-response range, and enhanced charge separation and transportation properties, as mentioned above.However the relative contribution of these four factors have not been resolved in the available literature. It is possible the enhanced adsorption may facilitate the charge transfer due to proximity of the species to the charge carrier generation site. Despite the success with the TiO<sub>2</sub>graphene photocatalysts, there still remain several challenges, such as the exploration of a decent visible light photocatalytic activity, and a further suppression of the charge recombination. To circumvent these, several strategies including tuning the crystal facets of TiO<sub>2</sub>, morphology control of the composites, as well as coupling of TiO<sub>2</sub>graphene with other materials have been attempted. There have been many studies, with different efficiencies, that degrade compounds such as malachite green, methyl

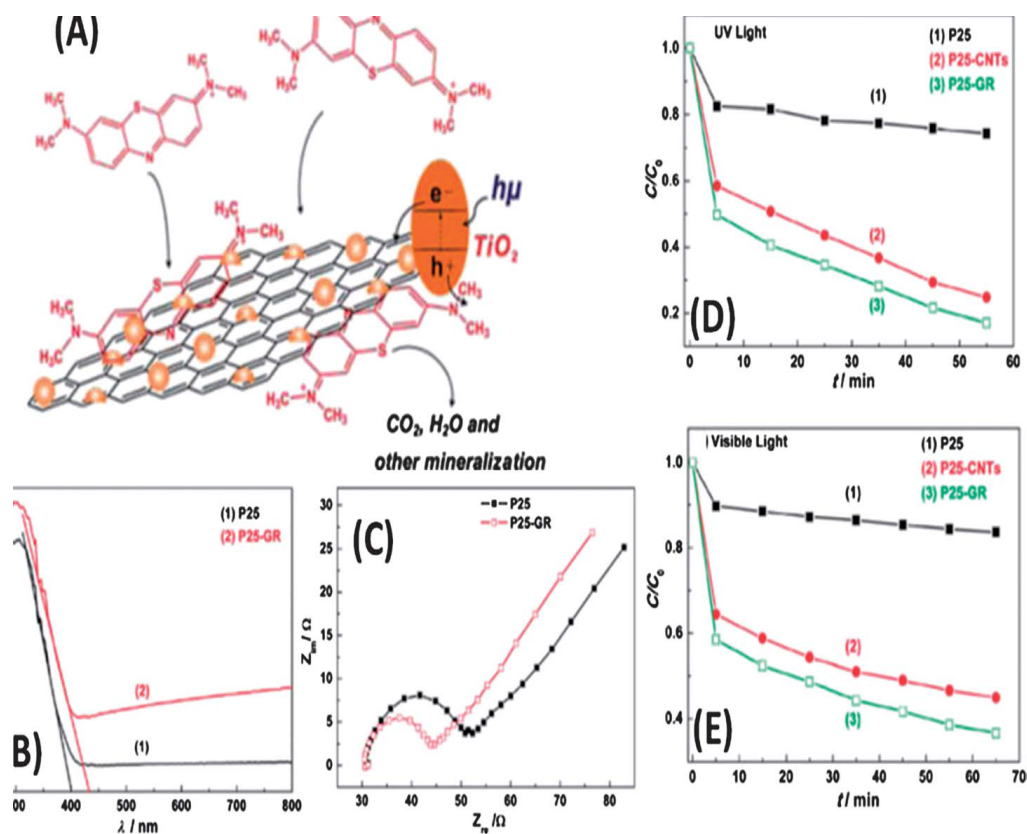


Figure 2: A) Schematic structure of the P25-graphene composite and tentative processes of the photodegradation of MB, illustrating adsorption of MB on graphene sheets, and the role of graphene. (B) Diffuse reflectance absorption spectra and (C) electrochemical impedance of (1) P25 and (2) P25GR, respectively. Comparison of photocatalytic activity in the degradation of MB under (D) UV light and (E) visible light over (1) P25, (2) P25CNTs, and (3) P25GR photocatalysts. Representation of Graphene oxide structure. Reprinted from Ref. H. Zhang, X. J. Lv, Y. M. Li, Y. Wang and J. H. Li, ACS Nano, 2010, 4, 380386.

orange MO, Rhodamine B (Rh. B), methylene blue (MB) and Acid Orange 7 (AO7). The mechanism behind the degradation, depicted in Figure 3, is similar in all of them. Electrons cannot flow directly from MB to  $\text{TiO}_2$  since their energy levels do not match. A photoexcited electron from MB flows into  $\text{TiO}_2$  CB via graphene (Path 1), where radical species are generated. Pollutants are usually aromatic compounds that create pi-pi stacking with rGO, raising the concentration of those molecules near the catalytic semiconductor nanocrystals. The production of oxidants and the reduction of radicals facilitate the reaction when the pollutant is closer. Therefore, the photodegradation is enhanced by pi-pi interactions. Moreover, as with previous pollutants, large surface area, extended light absorption range, high electron mobility and increased efficiency in charge separation improve the photocatalytic activity. There is an alternative electron mechanism that consists in an electron from the VB of  $\text{TiO}_2$  flowing to the conduction band of the semiconductor. This mechanism is possible by the band gap narrowing produced by graphene sheets. Reactive species that will degrade the pollutant are then produced (Path 2). Some of the pollutants studied are dyes,

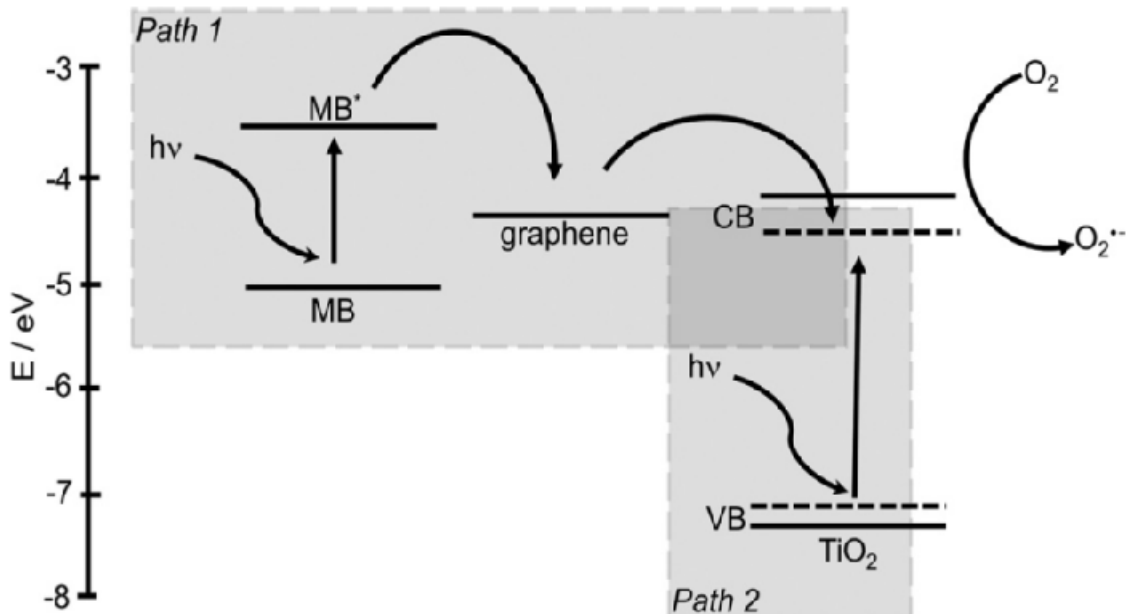


Figure 3: Proposed mechanism for the photodegradation of methylene blue (MB) by graphene-wrapped anatase nanoparticles under visible-light irradiation. Reprinted Lee, J.S.; You, K.H.; Park, C.B., *Adv. Mater.* 2012, 24, 10841088.

which are degraded by the use of quantum dot/TitaniaG/GO/rGO systems. In these cases, the photoabsorption can be produced by light excitation in the quantum dot (QD) or in Titania. That is what Zhang and his work-team [33] reported in a rGO/TiO<sub>2</sub> composite with PbS QDs. Both PbS and TiO<sub>2</sub> can get excited by different wavelengths, as a consequence the photocurrent efficiency was increased. The mechanism is analogous to the previous example. Ghosh et al. [34] worked with CdSe-rGO-TiO<sub>2</sub> particles. CdSe, with a band gap of 1.61.8 eV can accept visible light. The electrons generated in CdSe are transferred to the conduction band of TiO<sub>2</sub>, whose band gap is 3.0 eV. Besides, rGO can also capture electrons, which are transferred to the CB of the CdSe and, in the same way, to TiO<sub>2</sub>. This is one case in which, by coupling semiconductor quantum dots and rGO better photocatalytic results can be achieved. Bi<sub>2</sub>O<sub>3</sub> is another example of sensitized quantum dot that decorates (001) TiO<sub>2</sub> facets on rGO. Hous group proposed a photocatalytic mechanism. TiO<sub>2</sub> has a higher reduction potential than H<sup>+</sup>/H<sub>2</sub> and therefore more active CB edge potential than Bi<sub>2</sub>O<sub>3</sub>. Photoinduced electrons on TiO<sub>2</sub> are transferred to Bi<sub>2</sub>O<sub>3</sub> compound and the holes to Titania. An interesting study was conducted by Lin et al. and other groups that are researching other types of ternary composites based on rGO-TiO<sub>2</sub> and Fe<sub>3</sub>O<sub>4</sub>. This photocatalyst can degrade many different organic dyes (RhB, Orange Pure and Acid Blue 92), has enhanced photocatalytic activity, and can be recollected with a magnet. Besides, photodissolution of Fe<sub>3</sub>O<sub>4</sub> is inhibited, thus, it has a high stability and can be reused many times. However, its catalytic activity is not as good as pure rGO/TiO<sub>2</sub> and GO/TiO<sub>2</sub> composites. To conclude, some of the developed systems could be useful in self-cleaning coating. Under UV irradiation for TiO<sub>2</sub> systems, the photocatalytic oxidation reactions can degrade organic contaminants.

Another example is the decomposition of Rhodamine B reported by wang et al [35]. Their results are shown pictorially in Fig.4. It is seen that the QD supported system showed better photoactivity.

## Perception

There are a few issues which need to be stated explicitly since they are not found in the literature reports. Some of them may be trivial and some of the can require further extensive investigation. It is listed as follows:

1. Graphene based systems are multicomponent possibly multilayer systems and as such construction of these types of systems and sustaining them may be an issue of concern.



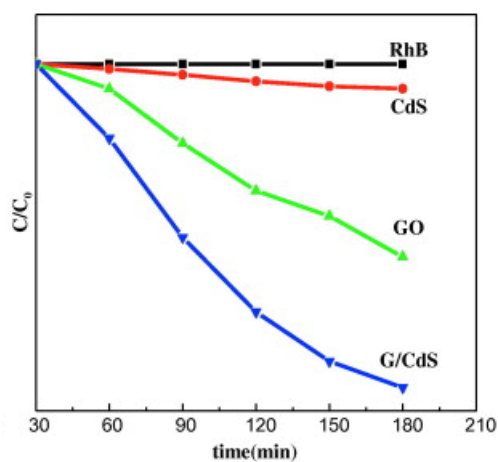


Figure 4: Degradation of Rh. B as a function of catalysis and irradiation time. Data from Ref 35.

A typical model representative configuration) is shown in Fig.5.

2.The exciton path has to be vectorial and this can not be driven in only

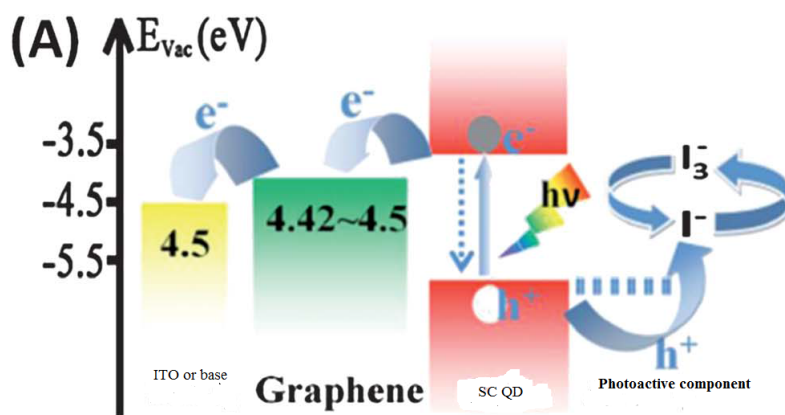


Figure 5: Typical but representation of graphene based photo-active system. Data adopted from Ref 20.

one path and hence the net efficiency may be considerably reduced.

3.Though energetics consideration favour the routes suggested, there can be many other trap states in the system which could reduce the net efficiency that can be achieved.

4.It is not clear which of the properties of graphene is essentially responsible

for the enhanced photoactivity observed.

5. It is necessary to establish if the recombination is considerably reduced or the energetics play major role for the observed photoactivity.

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