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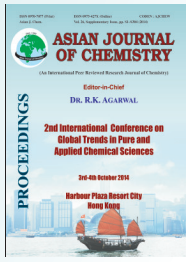

REVIEW

Progress in Design and Fabrication of Novel Graphene-Based Semiconductor Photocatalysts

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Graphene, a 2D material with extraordinary mechanical, optical and electrical properties has recently attracted enormous interest in photocatalysis science. It has been considered one of the most useful entities for the fabrication of various composite materials in environmental and energy applications. This review summarizes the recent progress in the design and fabrication of graphene-based semiconductor photocatalysts through various strategies including hydrothermal, microwave techniques, ultrasonication and sol gel methods. In addition, the photocatalytic properties of the prepared graphene-based composite systems and their application in photocatalytic degradation of organic pollutants are also discussed.

Keywords: Graphene, Photocatalyst, Microwave, TEM, Nanocomposites.

INTRODUCTION

The improvement of photocatalysis science has been the focal point of considerable attention in recent years, because of the wide range of research areas especially in environmental and energy related fields. So far the catalytic properties of large number of materials have been used to transform solar energy into chemical energy to perform oxidation/reduction reactions for obtaining useful products like hydrogen energy, hydrocarbons and radical species to degrade pollutants. Among them TiO_2 has been used extensively in many application because of its chemical stability, oxidizing abilities, long durability, nontoxicity and low cost. The interaction of light energy comparable with the band gap of semiconductors generates electrons and holes in the conduction and valence bands, respectively. These charge carriers either recombine or transfer to the surface of the photocatalyst to contribute to a series of photocatalytic reactions. For a proficient semiconductor photocatalyst, slow recombination rate, fewer charge trapping centers, proper energy level offsets and stability against light are highly desirable for improving the photocatalytic activity. In the previous studies, various strategies, including crystal and textural modification, band gap adjustment, heterostructuring, surface improvement of semiconductor photocatalysts, have been developed for the advancement of the photocatalytic performance. Recently graphene based semiconductor materials attract increasing attention in photocatalyst science. Graphene has attracted a strong interest due to its higher thermal, mechanical and optical properties. It is a promising material for energy-storage, electronic and optical devices, interfacing to biological materials and other numerous applications. In catalysis in sensing application the hybrid graphene materials is used because of promising capabilities. Several approaches have been reported for the production of graphene sheets supporting semiconductor nanocrystals.

Fabrication and designing of graphene based materials: There have been several reports highlighting the rational design of graphene based photocatalysts with high photocatalytic activity. Graphene has been considered to provide excellent support materials because of two dimensional structures by providing a large surface area and attractive potential to efficiently control their redox properties. In general when semiconductor nanoparticles are attached on the graphene sheet very small amount of nanoparticles is in a direct contact with graphene surface. Such a small interaction between nanopar-ticles and graphene affect the catalytic properties of the desire graphene based catalyst. Therefore a rational design and a control synthesis process are highly desirable to overcome these discrepancies.

Recently modified microwave techniques have been developed to synthesize Pt/graphene and Pt/graphene-TiO_2 as an enhanced photocatalyst material. The synthesis process was

considered to be fast and facile for the fabrication of these materials. The visible light photocatalytic activities of the as prepared samples were tested by methylene blue and rhodamine-B decomposition. High photocatalytic activity was observed for Pt/G3 nanocomposite. Enhanced activity is attributed to homogeneous distribution of Pt nanoparticles on graphene sheet. The DRS also confirms the large absorption in the visible range which further confirms that visible light can be used as incident radiation to study the photocatalytic properties of the Pt/graphene nanocomposites[1]. The TEM and XRD images of the Pt/graphene nanocomposites are depicted in Fig. 1(a-b). To further study the enhanced photocatalytic properties TiO_2 is considered to attach on Pt/graphene composites *via* microwave techniques. The propose mechanism and synthesis process are given in Fig. 2. It is clearly observe that the Pt-graphene/TiO_2 nanocomposite can be used as efficient photocatalyst under UV-visible light irradiation. This high activity is attributed to the synergetic effect of high charge mobility and the observed red shift in the absorption edge of the Pt-graphene/TiO_2 nanocomposites.

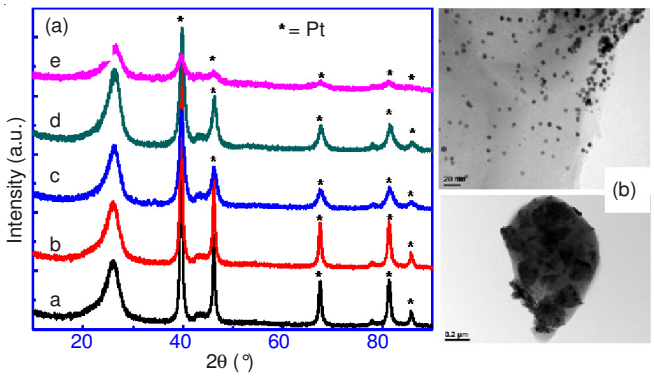

Fig. 1. (a) XRD pattern of Pt/graphene nanocomposites (b) TEM images of Pt/graphene composite presenting graphene sheet decorated with Pt particles [Ref. 1]

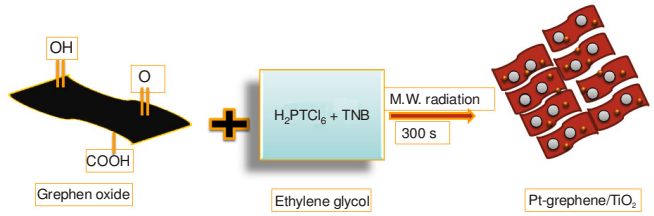

Fig. 2. Schematic diagram of graphene anchoring Pt and TiO_2 nanoparticles [Ref. 2]

The absorption spectra and the corresponding observed band gap are expressed[2] in Fig. 3(a-b). Similarly $PtSe_2$-graphene nanocomposites were synthesized through microwave techniques. Attachment of $PtSe_2$ on graphene sheet increases the absorption towards visible range. The visible light catalytic response was studied and enhanced photocatalytic performance was observed. Fig. 4 (a) depicts the TEM images and the distribution of $PtSe_2$ nanoparticles on graphene sheet. $PtSe_2$-graphene nanocomposite was also synthesized *via* ultrasonic techniques. In comparison to microwave techniques the distribution of the particles were found to be partially agglomerated[3,4] as shown in Fig. 4 (b). PbS/graphen-TiO_2 nanocomposites were synthesized *via* sol gel method.

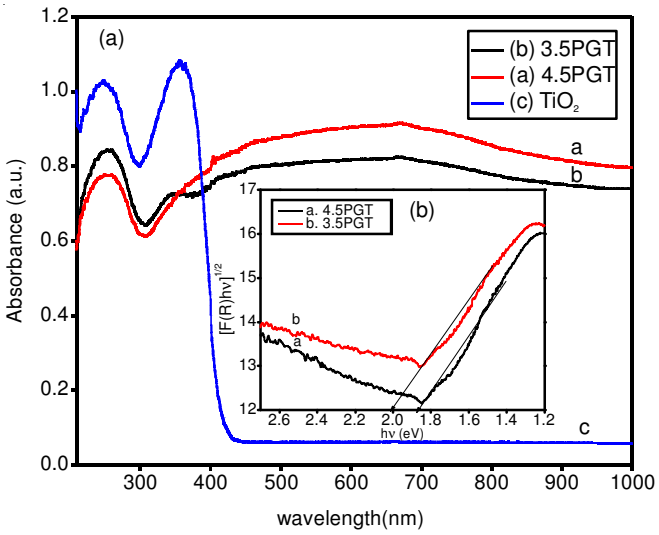

Fig. 3. (a) UV-visible diffuses absorbance spectra (b) Corresponding band energy calculation using KM function [Ref. 2]

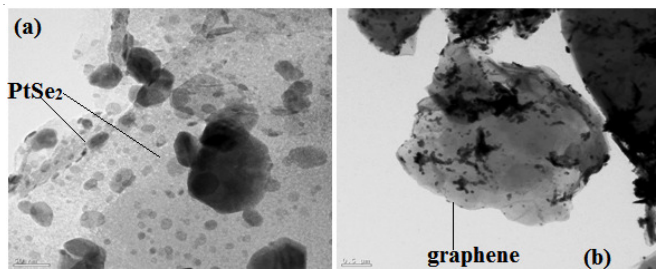

Fig. 4. TEM images of $PtSe_2$/graphene nanocomposite (a) Microwave assisted (b) Ultrasonic assisted [Ref. 3-4]

The photocatalytic activities of the samples were evaluated. As prepared PbS-grephene/TiO_2 composite exhibit much higher photocatalytic activity towards the degradation of methylene blue than PbS-grephene. This higher activity is attributed to the coupled semiconductor with TiO_2 which provides a maximum interfacial contact with grephene surface without aggregation which is necessary factor for increasing the photocatalytic performance. The couplings of PbS with TiO_2 extend the photoresponse to visible region. And enhanced photocatalytic response was observed[5] as shown in Fig. 5. CdSe/graphene-TiO_2 heterogeneous catalysts were prepared by calcinations of CdSe-graphene composites with titanium(IV) *n*-butoxide as the source of TiO_2 at 873 K. The UV spectrophotometric study indicated the photo derivative ability of the CdSe/graphene-TiO_2 composites in visible light is significant and the sample dyes methyl orange degraded 71 % whereas methyl orange degraded around 85 % by the end of just 180 min of exposure to visible light. CdSe/graphene-TiO_2 composites have excellent photocatalytic activity in cyclic experiment which emphasizes the brilliant stability of the catalyst and the photochemical stability. The proposed mechanism for the CdSe/graphene-TiO_2 catalyst[6] was given in Fig. 6. In this context several heterogeneous photocatalyst materials were synthesized and the influence of graphene has been observed by performing numerous experiments for the degradation of organic pollutants[7-10]. Ag_2Se-graphene/TiO_2 nanocomposites were synthesized *via* sonochemical methods and observed the dye adsorption experiments to show the catalytic activity using

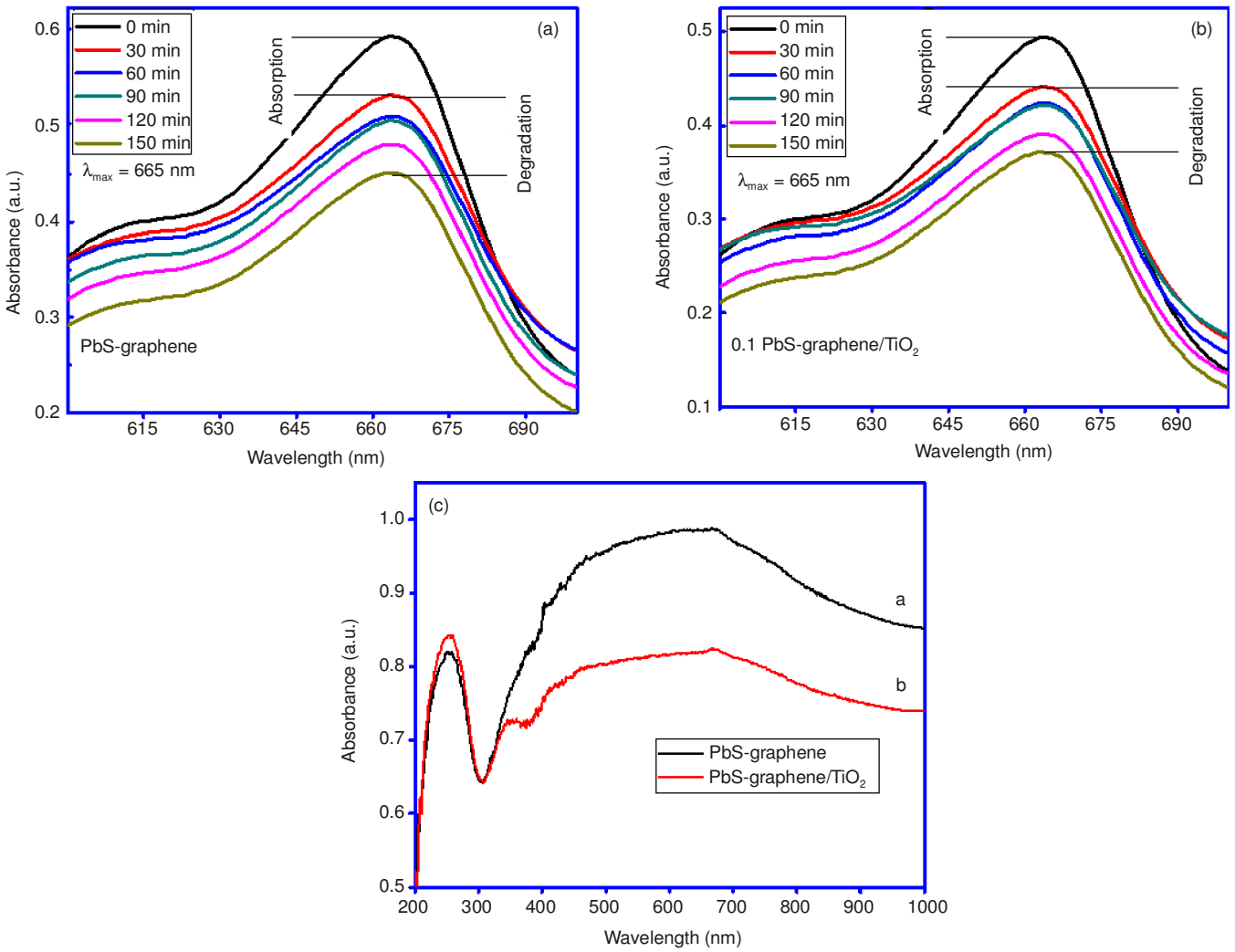

Fig. 5. Photocatalytic degradation efficiency of (a) PbS-graphene (b) PbS-graphene/TiO_2 nanocomposites (c) DRS absorption spectra of PbS-graphene and PbS-graphene/TiO_2 [Ref. 5]

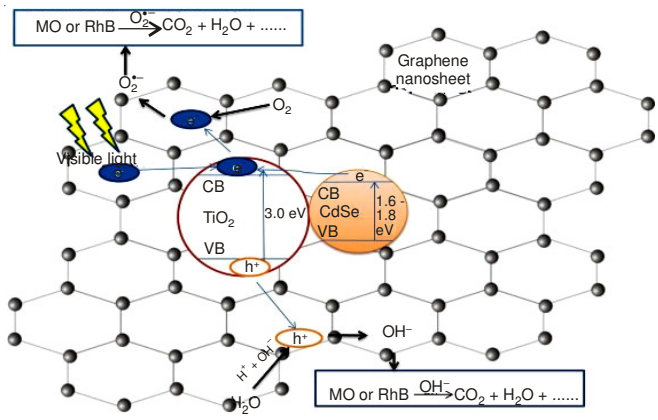

Fig. 6. Proposed mechanism for CdSe-graphene/TiO_2 nanocomposites [Ref. 6]

organic dyes[11]. Graphene/TiO_2 photocatalyst has been synthesized *via* sonochemical method and the catalytic activities of the materials were investigated using rhodamine-B as an organic dye[12]. Hydrothermally synthesized CdSe-graphene nanocom-posite was used as a catalyst for the degradation of methyl orange and rhodamine-B as organic dyes. Interesting results were found by observing the catalytic effect under dark ambience. At the end of 150 min of ultrasonication in dark state, rhodamine-B went through the highest degradation efficiency of 98 and 90 % of methyl orange was degraded. The degradation reaction kinetics of rhodamine-B with sono-catalyst was found to be greater than methyl orange following first order reaction. Reused CdSe-graphene sonocatalyst showed very minute change in degradation efficiency which indicates admirable stability of the catalysts. As all the sono-catalytic degradation occurs in dark conditions, that proves the degradation of azo dyes (methyl orange and rhodamine-B) requires no special conditions such as additional irradiation with visible light or UV light. The proposed mechanism and the corresponding degradation efficiency[13] is given in Fig. 7(a-b).

Heterogeneous CdS-graphene and CdS-graphene/TiO_2 composites were synthesized by a simple sol-gel method. The photocatalytic studies were carried out by using methylene blue as an organic test dye. The corresponding TEM image of the nano-composites was given in Fig. 8. TEM images of CdS-graphene and CdS-graphene/TiO_2 with scales of 0·2 μm-100 nm are shown in Fig. 9. TEM image of CdS-graphene shows 2D structure of the graphene sheets and indicates that the surface is very smooth as depicted in Fig. 8 (a-b). The morphology of graphene oxide is thin stacked flakes with well-defined

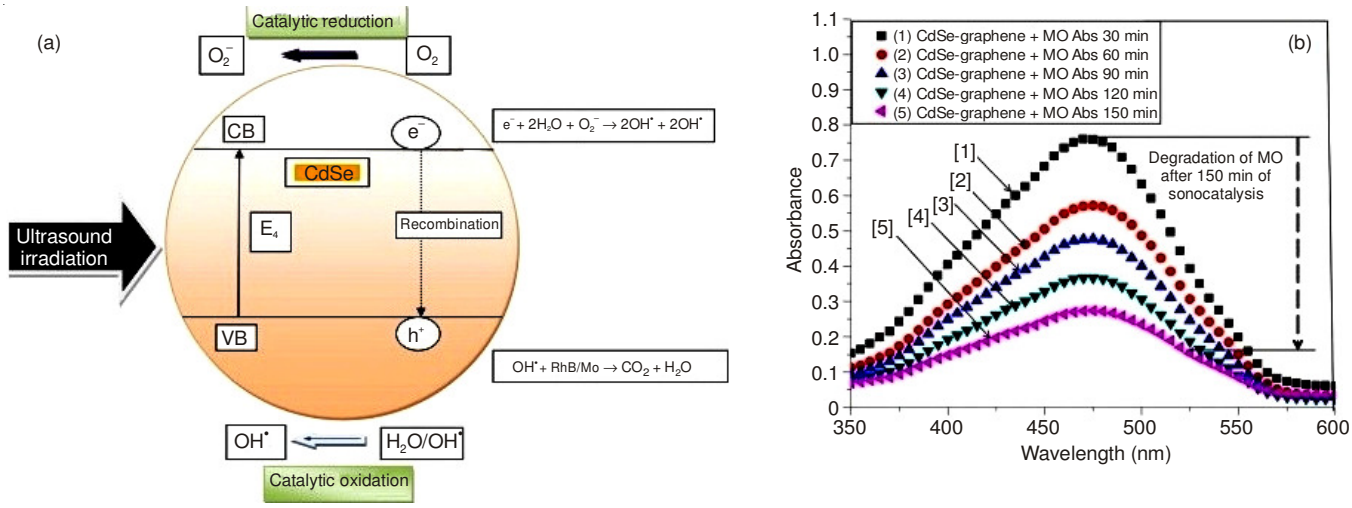

Fig. 7. (a) Transfer of charges in CdSe/graphene nanocomposite under ultrasonic irradiation; (b) Sonocatalytic degradation efficiency over methyl orange by CdSe/graphene [Ref. 13]

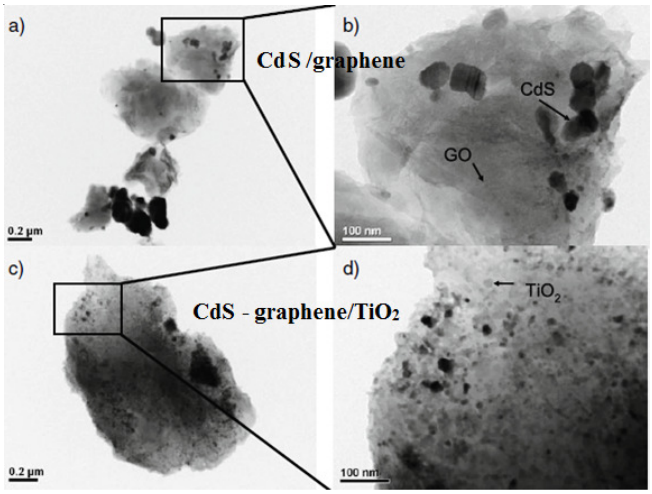

Fig. 8. (a-b) TEM images of CdS/graphene (c-d) CdS-graphene/TiO_2 [Ref. 14]

multilayered structures at the edge. The TEM images of CdS-graphene/TiO_2 show the graphene sheets and CdS nanoparticles. A uniform dispersion of CdS particles on the graphene sheet can be observed in Fig. 8 (c-d)[14]. It is clear from the above discussion that many factors can exert a considerable influence on the catalytic properties of the graphene based materials. These properties include size and shape, surface area, pore structure and homogenous distribution of nanoparticles on the surface of graphene sheet. Thus for the development and enhancement of photocatalytic properties of these materials the above mentioned problems should address carefully in synthesizing and fabricating process. A generalized photocatalytic mechanism is discussed under the light of above studies on graphene based materials. The photocatalytic performance of the graphene based nanocomposites in terms of photo degradation of organic dyes molecules under UV/visible light irradiation is investigated. Three steps are mainly required for photocatalytic mechanism. The adsorption of the pollutants, light absorption by the catalytic material used and charges transport. This transfer of charges will responsible for the creation of radical species which further decompose the pollutants. Carbon materials have astonishing absorption properties therefore mainly used in various environmental applications. Most of the industrial dyes are aromatic in nature and they create π-π stacking interaction with the graphene aromatic domains[15-17]. The concentration of the organic molecule increases at the surface of the photocatalytic materials due to adsorption process. By the irradiation of light electron are excited from the valance band of photocatalyst to conduction band creating hole in the valence band. The photo excited electron and holes will react with water molecule to create a radical oxygen species which further decompose the pollutants. The intrinsic electron hole pair recombination is normally 10^{-9} second which results in emission and low photocatalytic activity a very less electron-hole pair are trapped and participate in the catalytic reaction. In order to increase the photocatalytic activity cocatalysts are attached on the graphene sheet. Therefore the trapped electron will transfer to cocatalysts and separate the excite molecules and greatly retained the recombination process. Light irradiation (UV-visible) produces electrons (e^-) in the conduction band (CB) and holes (h^+) in the valence band (VB) of the photcatalyst in the nanocomposite. Thus a number of electrons (e^-) and holes (h^+) were generated. Meanwhile graphene nanosheets transfer electrons (e^-) to the conduction band of catalyst, thereby increasing the number of electrons as well as the rate of electron-induced redox reactions. The graphene coupled with semiconductor photocatalyst system shows enhanced catalytic activity due to high charge seperation induced by the synergetic effects of graphene and semiconductor photocatalyst. It is known that the fractional reduction of graphene oxide only partially restores the sp^2 networks therefore the remaining oxygen sites still able to to accept electron and undergo reductoion[18]. The generated electrons (e^-) react with dissolved oxygen molecules and produce oxygen peroxide radicals $O_2^{\bullet-}$. The positive charge hole (h^+) can react with OH^- derived from H_2O to form hydroxyl radicals $OH^\bullet$. The organic dyes may degraded by oxygen peroxide radicals $O_2^{\bullet-}$ and hydroxyl radicals $OH^\bullet$ to CO_2, H_2O and other mineralization products[19,20]. In future some more complex systrem are needed *i.e.* ternary or multicomponent for the

devlopment and enhancement of graphene based semiconductor materials. Recently a multicomponenet graphene based materials has been fabricated and enhanced catalytic properties were reported[21]. The tuning of band gap of the one component in ternary system can facilitate the charge separation ability at different levels. Also, through the proper choice of size, shape and composition of the multi component graphene-based photocatalysts, momentous improvements can be attained in the photocatalysis. In addition, the step up of more efficient synthesis methods or strategies is highly desirable to improve the interfacial contact between graphene and photocatalyst components in graphene-based photocatalysts system in order to improve the catalytic efficiency.

Conclusion

In summary, well-designed graphene can be introduced into various semiconductor photocatalysts to form graphene-based semiconductor composites. The introduction of graphene in these semiconductor materials can improve their properties enormously. These properties include high dye adsorption abilities, extension of light absorption to visible region, enhanced charge separation, which increases the photocatalytic efficiencies of these systems. A variety of methods has been developed for the synthesis of graphene based semiconductor materials. These composite photocatalysts have been widely used for the degradation of pollutants and other environmental applications.

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