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An Overview on Graphene based Semiconductor Photocatalysis: Advancement and Application

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Abstract: Since the discovery of graphene it has been considered one of the most beneficial materials to support numerous semiconductor materials in environmental applications. During the past few years this material has been used in photocatalysis science because of its unique optical, electrical and mechanical properties. Several approaches and synthesis method have been developed so for to fabricate graphene based materials. However the charge transfer mechanism between these hybrid/multi structure semiconductors is still debatable. This present review summarizes the advancement in fabrication techniques and new approach to explain the charge transfer mechanism and stability of these materials. The application of graphene based materials in catalytic degradation of various standard and industrial dyes are also highlighted.

Key words: Graphene; Semiconductor material; TEM; DRS; Raman spectroscopy

Introduction

Back in 2004 when two physicist Geim and Novoselov announced the discovery of two dimensional sheet of atoms (called graphene) as an allotropic form of carbon. Graphene a 2D sheet of carbon atoms packed in honeycomb network can be produced chemically by the exfoliation of graphite using different approaches, including thermal exfoliation, mechanical cleavage, chemical vapor deposition, and chemical functionalization [1-2].

Due to its planer structure, graphene can be used to wrap it in zero dimensional called fullerenes, by rolling along a given direction it can be transferred to 1 D carbon nanotubes or staked in three dimensional into graphite [3]. Therefore, graphene is recognized as the basic building block of all-dimensional carbon materials. Its unique structure imparts extraordinary and exceptional properties, such as a high mobility of charge carriers (>200000 $cm^2\ V^{-1}\ s^{-1}$), exceptional Young's modulus values, high spring constant, theoretically high specific surface area (2630 $m^2\ g^{-1}$), excellent thermal conductivity and optical transmittance which have spurred enormous interest in the scientific and industrial

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communities. The development of photocatalysis science has been the crucial point of significant attention in recent years, because of the wide range of research areas especially in environmental and energy related fields. The 21st century infuriating energy problems such as fossil fuel, environmental pollution and global warming are threatening human being life and society. Photocatalysis sciences are proved to be the main route in environmental purification and conversion of solar energy to useful chemical energy. This green technology has been widely applied to synthesize various materials for water splitting to produce hydrogen energy, electrochemical and photochemical processes to degrade various organic pollutants in both gaseous and liquid phases. 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. 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.

Construction and Designing of Binary Graphene based Materials

There has been numerous information underlining the rational design of graphene based materials with extraordinary 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 nanoparticles and graphene affect the catalytic properties of the desire graphene based catalyst. Therefore a rational design and a control synthesis process are very desirable to overcome these discrepancies.

Recently a facile and fast way for the synthesis of Pt/graphene via one pot microwave assisted method was reported in which graphene oxide was mixed with Pt precursor material and resulting solution were irradiated by microwave for 300 s. In this process simultaneous reduction of graphene oxide into graphene and attachment of noble metal attachment of noble metal nanoparticles are observed in ethylene glycol solution. The visible light photo catalytic activities of Pt/graphene nanocomposites were tested by rhodamine B (Rh.B) and methylene blue (MB) as a model contaminant [4]. Similarly the same method was followed to prepare Graphene/TiO_2, $PtSe_2$/graphene nanocomposites. The observation of these materials synthesis through microwave provides an idea of homogenous distribution of nanoparticles on graphene sheet by providing large number of reaction sites [5-6]. Figure 1 shows the $PtSe_2$ nanoparticles distribution on graphene sheet with different TEM resolution and XRD results for phase structure analysis. Similarly the same composite was prepare through ultrasonication method and compare the catalytic properties of these materials. The author reported enhanced catalytic behavior for the

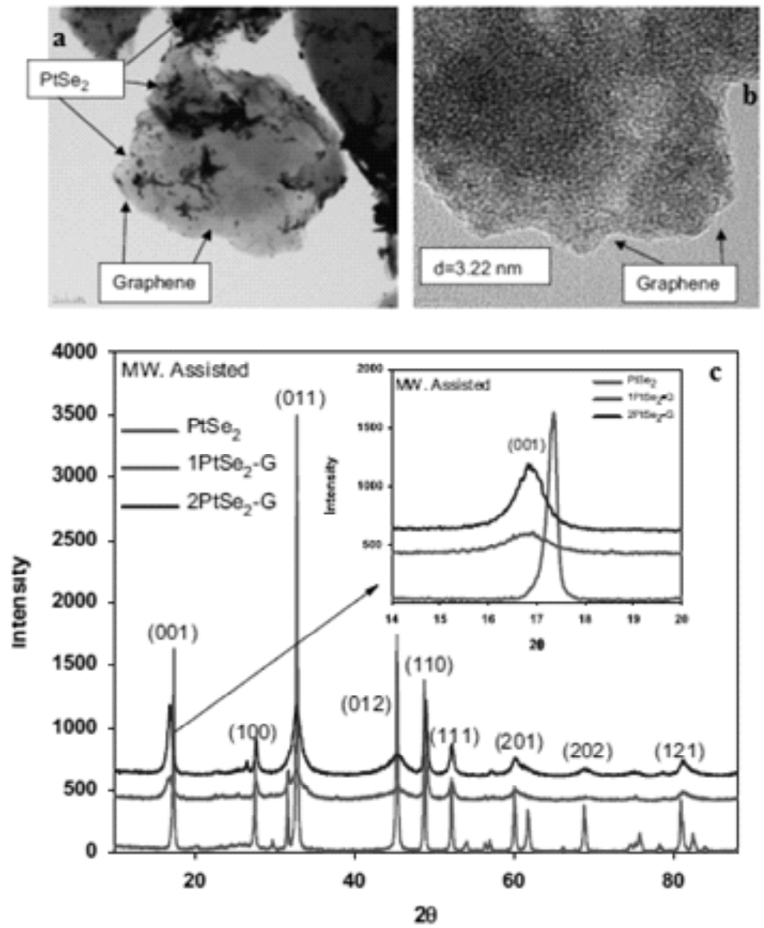

Figure 1: (a-b) TEM images of $PtSe_2$/graphene composites (c) XRD pattern of PtSe2/graphene nanocomposites [ref: 6].

composites synthesis via microwave techniques [7]. Lead selenide graphene based photocatalyst materials were also prepared through ultrasonic techniques and enhanced visible light catalytic activity was observed as depicted in figure 2, [8]. Cadmium selenide (CdSe)-graphene composite materials were synthesized via a facile hydrothermal method and the intriguing catalytic activity of the composites was investigated using organic dyes in complete absence of irradiation source (UV or visible light). The catalytic activity of CdSe-graphene composites was measured using methyl orange (MO) and rhodamine B (Rh.B) dye solutions [9]. The degradation of the organic dyes in absence of any irradiation was illustrated by the degradation property of CdSe and charge mobility. The catalytic activity after repeated use of the composites was also tested in order to investigate the stability of CdSe-graphene composites. The antimicrobial effect was also investigated under visible light using CdSe/graphene as photocatalyst material and some promising bactericidal effect was observed as shown in figure 3, [10]. The reusability and catalytic studies of graphene based zinc selenide was also observed and quiet stable catalytic

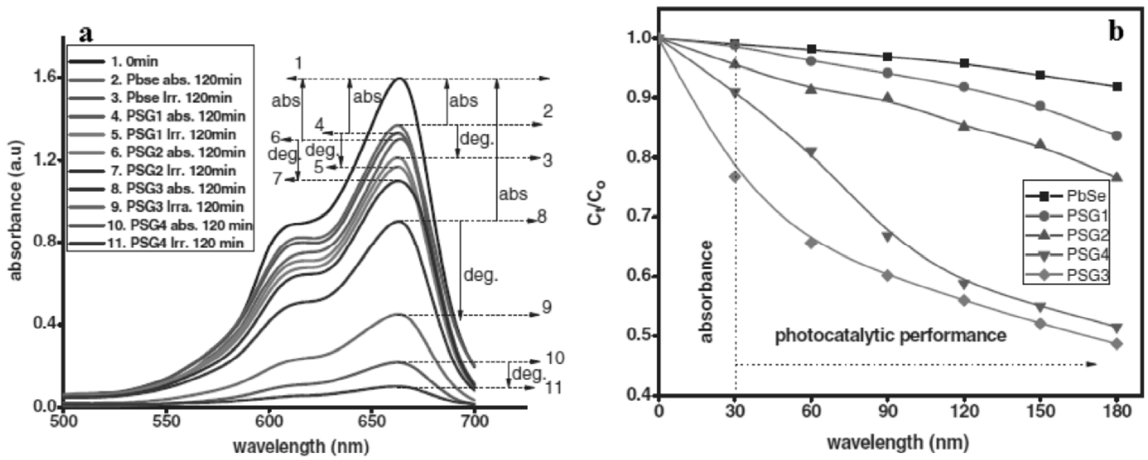

Figure 2: Degradation efficiencies of PbSe/graphene (a) MB dye (b) Concentration plot vs /irradiation time [ref: 8].

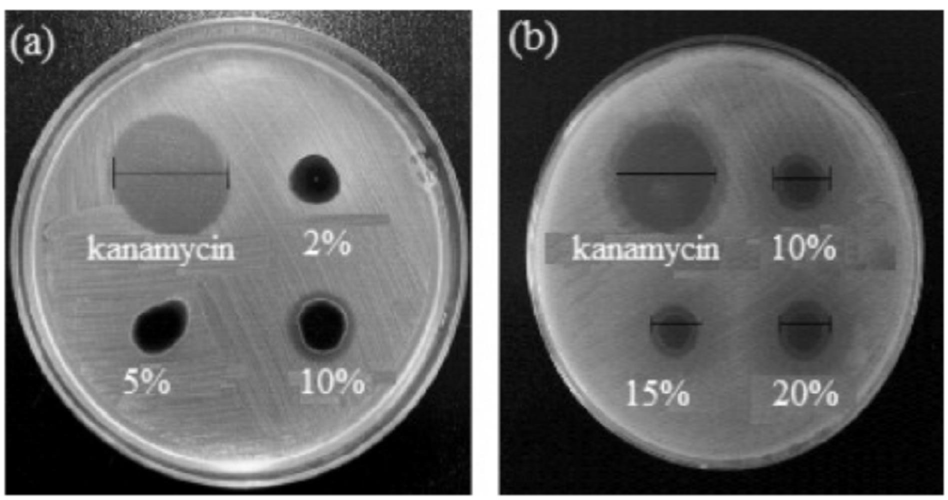

Figure 3: (a-b) Photograph of bactericidal effect observed by halo test for bacterium Streptococcus aureus with standard antibiotic Kanamycin and (a) 2%, 5% and 10% of CdSe-graphene composite solutions (b) 10%, 15% and 20% of CdSe-graphene composite solutions[ref 10].

behavior was observed synthesized via hydrothermal techniques [11]. The MO degradation activity was also achieved and enhancement in the catalytic behavior was observed through platinum selenide based graphene nanocomposites [12].

The photocatalysis of binary composites was studied via various techniques a few of them were highlighted in the above discussion. The ultimate goal to achieve a better photocatalyst having some remarkable properties i.e., short synthesis time, nontoxic, environmental friendly, low price etc, are debatable points. The quests for the desire properties scientist extends the compositional and structural design of catalyst materials and tries to obtain ternary and quaternary material's to explore new way of charge transfer mechanism and catalytic effect for graphene based materials.

Heterogeneous Graphene based Materials

Heterogeneous photocatalyst PbS-graphene/TiO_2 was syntheses via sol gel method and enhanced decomposition of standard dye was observed. This higher catalytic effect was attributed to the coupled semiconductor materials with positive synergistic effect between PbS and graphene. The couplings of PbS with TiO_2 extend the photoresponse to visible region. And enhanced photocatalytic effect was observed [13]. In this context a heterogeneous catalyst $PtSe_2$/graphene-TiO_2 was synthesized via ultrasonication techniques. The catalytic behavior was investigated through the decomposition of rhodamine B (Rh.B) as a standard dye. Enhanced photocatalytic activities were observed by increasing the weight% of graphene in the $PtSe_2$–graphene/TiO_2 nanocomposites. The coupling of TiO_2 with $PtSe_2$–graphene alters the optical properties by observing a precise band gap in the visible range was also reported [14]. The schematic can be seen in figure 4.

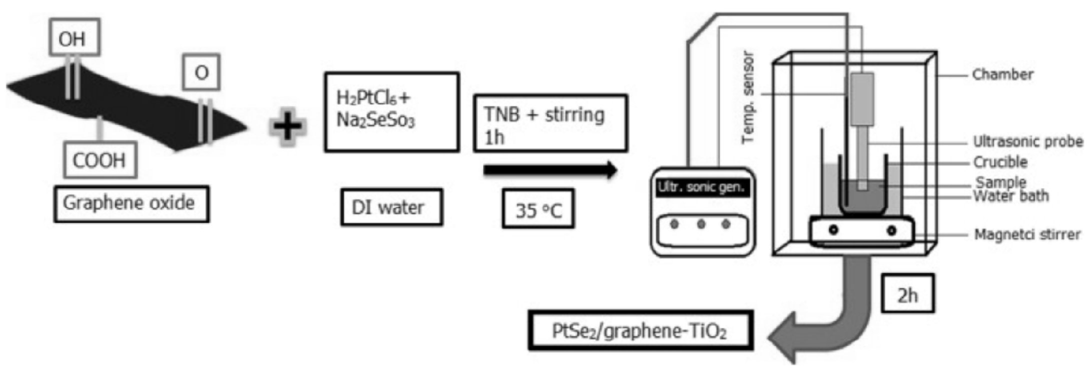

Figure 4: Schematic for the preparation of $PtSe_2$/graphene-TiO_2 nanocomposites [ref 14].

To further study the enhanced photocatalytic properties TiO_2 is considered to attach on $PtSe_2$/graphene composites via microwave techniques. It is clearly observe that the $PtSe_2$-graphene/TiO_2 nanocomposites 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 $PtSe_2$-graphene/TiO_2 nanocomposites. The absorption spectra and the corresponding observed band gap are expressed in figure 5(a-b) [15].

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 that the sample dyes MO degraded 71% whereas MO degraded around 85% by the end of just 180 min of exposure to visible light.

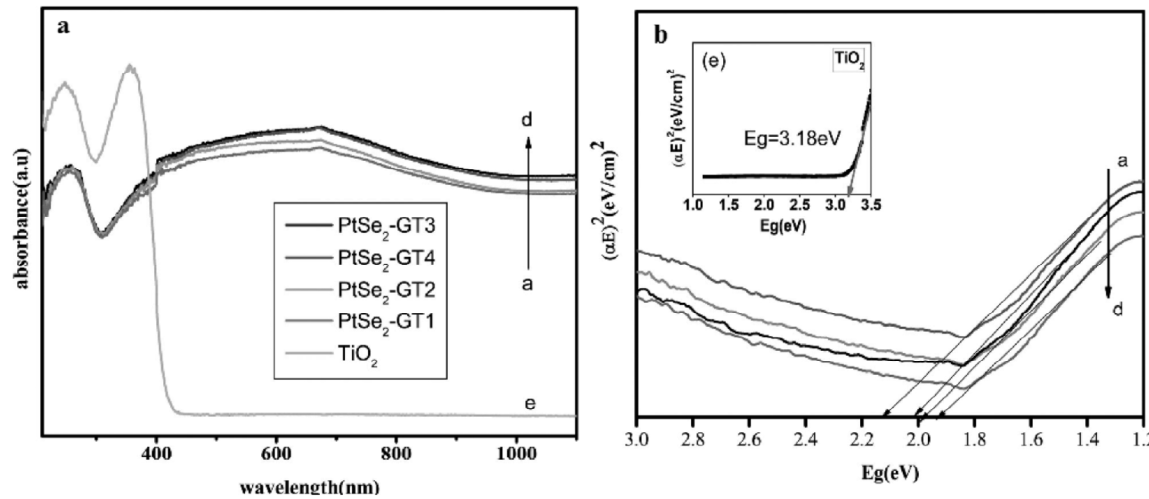

Figure 5: DRS results (a) Absorption spectrum (b) Transform K.M function plot to obtain E_g [ref 15]

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 degradation of MO and Rh.B by CdSe/graphene-TiO_2 catalyst is depicted given in figure 6 [16].

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 MB as an organic test dye.

TEM images of CdS-graphene and CdS-graphene/TiO_2 with scales of 0·2 µm–100 nm are shown in figure 7 [17]. Titanium dioxide mediated semiconductor, nickel sulfide (NiS_2) doped graphene photocatalysts were prepared by simple hydrothermal method for the treatment of dye contaminated aqueous solutions. This ternary composite shows markedly high photocatalytic properties as shown in figure 8 with corresponding TEM image [18]. CdS combined graphene/TiO_2 (CdS-graphene/TiO2) composites were prepared by a sol–gel method to improve on the photocatalytic performance of TiO_2. The photocatalytic activities were examined by the degradation of methylene blue (MB) under visible light irradiation. The photo degradation rate of MB under visible light irradiation was found high and it is attributed to cooperative reaction between the increase of photo-absorption effect by graphene and photocatalytic effect by CdS [19]. Ag_2S graphene/TiO_2 composites were synthesized by a facile sonochemical method. During the synthesis reaction, the reduction of graphene oxide and loading of Ag_2S and TiO_2 particles were achieved. The Ag_2S graphene/TiO_2 composites possessed a large adsorption capacity for dyes, an extended light absorption range, and efficient charge separation properties. 1,5 diphenyl carbazone. The high activity was attributed to the synergetic effects of high charge mobility and the red shift in the absorption edge of the Ag_2S graphene/TiO_2 composites [20]. Similarly Ag_2Se graphene/TiO_2 was synthesized through ultrasonication and enhanced

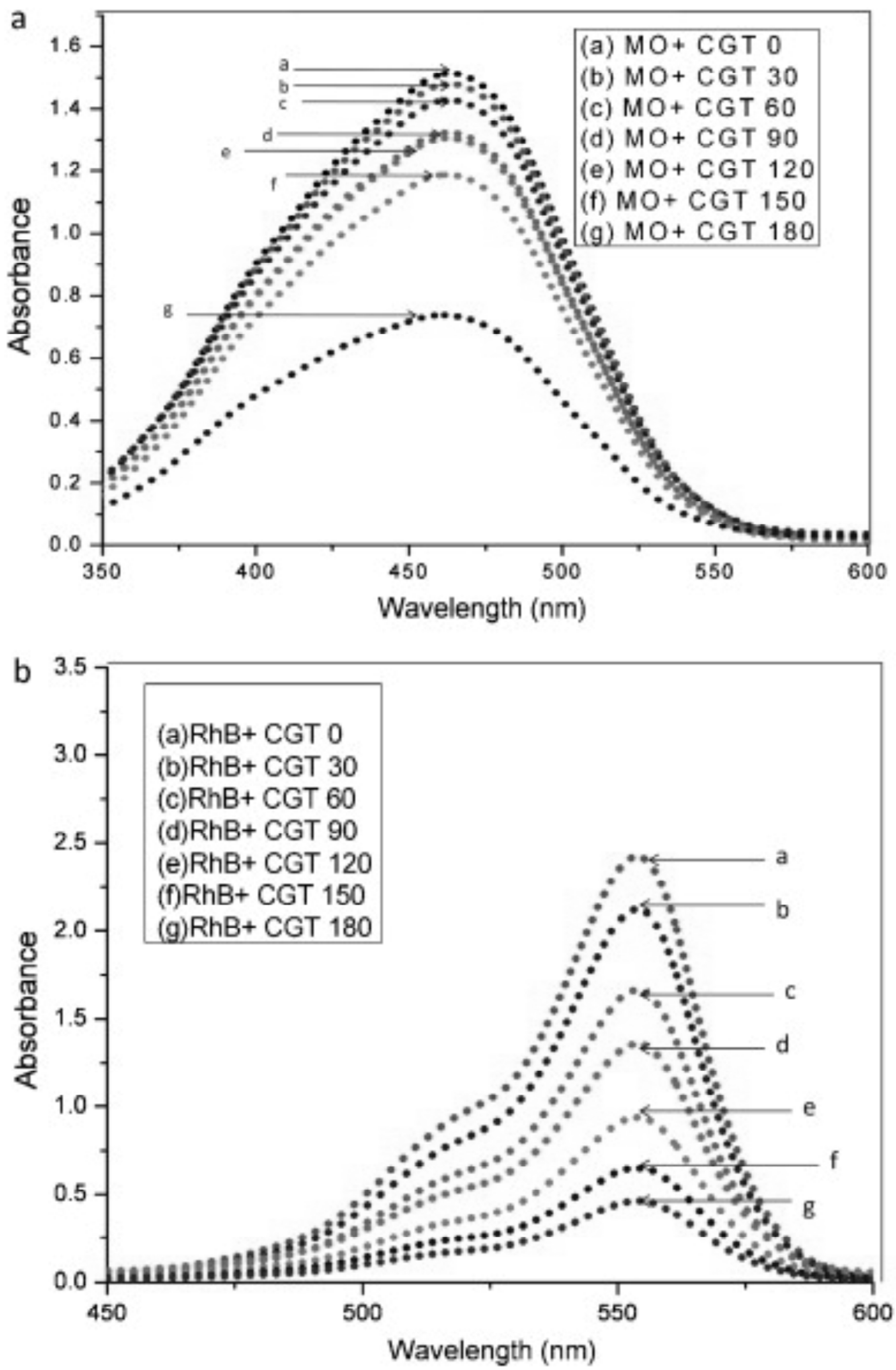

Figure 6: Degradation of MO and Rh.B for CdSe-graphene/TiO_2 nanocomposites [ref: 16]

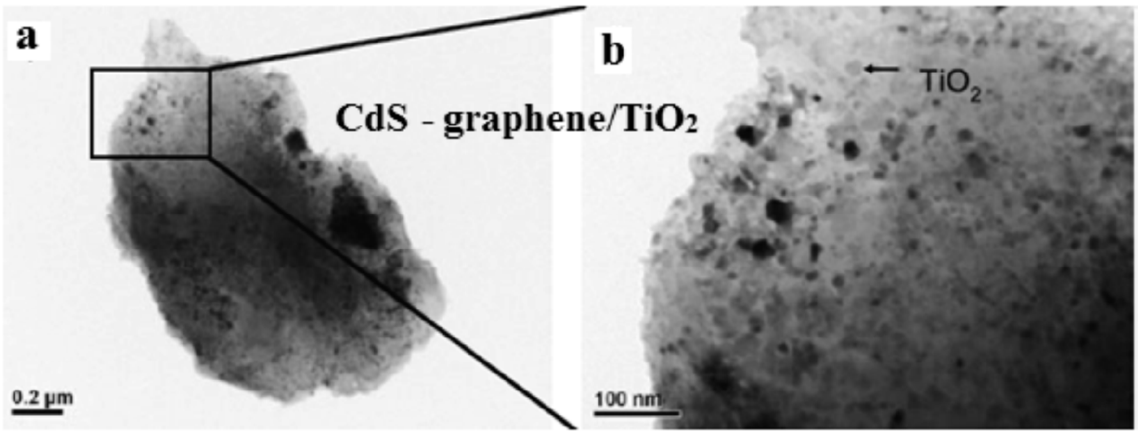

Figure 7: (a-b) CdS-graphene/TiO_2 with different magnification [ref 17]

catalytic effect was observed as compared to other reports. The improved catalytic effect was attributed to the synergistic effect between Ag_2Se and graphene supported by TiO_2 as co catalyst material [21].

It is evident from the above discussion that there are many concern points that can affect the photocatalytic properties of graphene based materials. These may be shape, size and distribution of nanoparticles on graphene surface, less agglomeration, strong interfacial contact, high surface area and pore structure. For the advancement of photocatalytic system the above mention problems should be address carefully in the process of fabrication.

For the investigation of UV/vis light catalytic properties of graphene based materials there are some basic important step i.e., the pollutant adsorption catalytic surface, light absorption and transfer of charges. 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 ð-ð stacking interaction with the graphene aromatic domains [22-23]. Thus due to adsorption process the concentration of the molecule on the surface of the catalyst materials increases. Light irradiation excites electron form the valance band of the semiconductor material to conduction band and creates a hole in the valance 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/Vis-) 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 CB 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 GO only partially restores the sp^2 networks therefore the remaining oxygen sites still able to to accept electron and undergo reductoion [24]. 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. We propsed the above general mechanism for the photocatalyst system and the schematic is shown in figure 9.

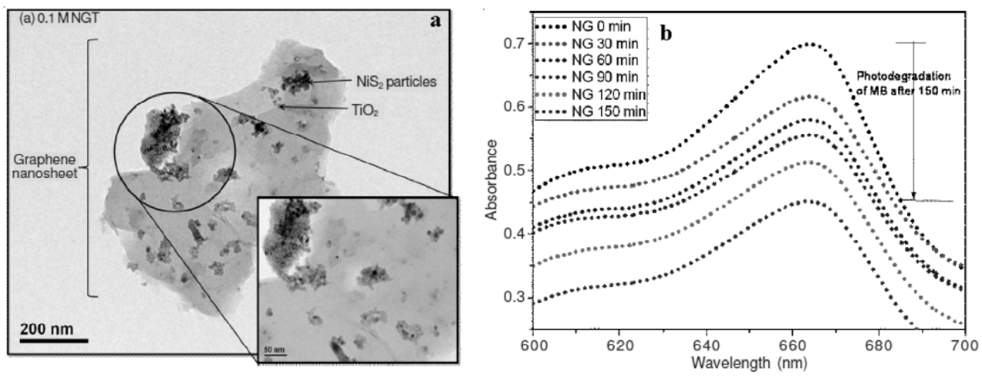

Figure 8: (a) TEM image CdS-graphene/TiO_2 (b) MB dye decomposition results [ref 18].

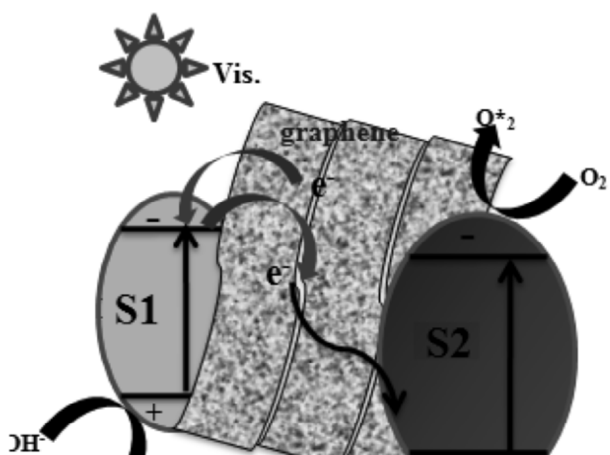

Figure 9: Proposed mechanism for the ternary graphene based materials.

Conclusion

In summary, for the synthesis of graphene based semiconductor materials in photocatalysis science one need to introduce a well-designed stable low price semiconductor. The semiconductor needs to be active in wide range of electromagnetic spectrum especially in visible range. The introduction of graphene in these semiconductor materials can improve their optical and mechanical properties enormously. There is no doubt graphene based materials have a great potential for being robust materials to address various environmental and energy-related issues.

By the introduction of reasonable design for graphene based materials its application in conversion technology may be significantly improved in more sensible way.

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