Preparation of novel CdS-graphene/TiO₂ composites with high photocatalytic activity for methylene blue dye under visible light

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Abstract. In this study, CdS combined graphene/TiO₂ (CdS-graphene/TiO₂) composites were prepared by a sol-gel method to improve on the photocatalytic performance of TiO₂. These composites were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX) and transmission electron microscopy (TEM). The photocatalytic activities were examined by the degradation of methylene blue (MB) under visible light irradiation. The photodegradation rate of MB under visible light irradiation reached 90.1% during 150 min. The kinetics of MB degradation were plotted alongside the values calculated from the Langmuir–Hinshelwood equation. 0.1 CGT sample showed the best photocatalytic activity, which was attributed to a cooperative reaction between the increase of photo-absorption effect by graphene and photocatalytic effect by CdS.

Keywords. Graphene photocatalysts; TiO₂; CdS; methylene blue; visible light.

1. Introduction

Graphene is an excellent new material for applications in condensed-matter physics and electronics in the field of materials science since the discovery of carbon nanotubes and C₆₀ (Geim and Novoselov 2007). Graphene is a sheet of *sp*²-bonded carbon atoms arranged in a hexagonal lattice, of single-atom thickness, which shows outstanding mechanical, thermal, optical and electrical properties. Therefore, interesting graphene-based materials were extended to applications in diverse fields such as nanoelectronic devices, biomaterials, intercalation materials, drug delivery and catalysis (Gilje *et al* 2007; Akhavan *et al* 2011). Previous studies have reported that nanocarbon materials such as CNT and C₆₀ have some beneficial effects on the photocatalytic activity of homogeneous and heterogeneous semiconductors by effective electron transfer and interaction effects (Saleh *et al* 2010; Oh *et al* 2009). Among the various semiconductors, titanium dioxide (TiO₂) is known to be a good photocatalyst for the degradation of environmental contaminants due to its high photocatalytic activity (Meng *et al* 2007; Gaya and Abdullah 2008). These TiO₂-nanocarbon composites exhibited higher photocatalytic performance than that of bare TiO₂. However, some problems still hinder further promotion of the efficiency of TiO₂-nanocarbon composites, such as the weakening of light intensity arriving at the surface of catalysts due to the presence of nanocarbon and the lack of reproducibility due to variations in preparation and

treatment (Woan *et al* 2009). In comparison with CNT and C₆₀, graphene has a perfect *sp*²-hybridized two-dimensional carbon structure with better conductivity and a larger surface area, and so it seems reasonable to envision that the novel graphene–TiO₂ nanocomposite, which has high interfacial contact and potential, could be a much more promising composite to improve the photocatalytic performance of TiO₂. Furthermore, graphene is easy to produce from inexpensive natural graphite through the intermediate product ‘graphite oxide’ (GO) (Hummers and Offeman 1958; Marcano *et al* 2010). The presence of oxygen-containing functional groups in GO and reduced GO makes them excellent supporters to anchor TiO₂ nanocrystals during the synthesis of graphene–TiO₂ (Liang *et al* 2010). Recently, graphene/TiO₂ composites were successfully fabricated by various methods. Williams *et al* (2008) reported that a graphene/TiO₂ composite can be obtained via a UV-illuminated suspension of graphene oxide and TiO₂ under N₂ atmosphere, which inhibited the UV light from acting as a reducer. Liang *et al* (2010) reported that a hybrid of graphene and TiO₂ nanocrystals were prepared by directly growing TiO₂ nanocrystals on GO sheets. The direct growth of the nanocrystals on GO sheets was achieved by a two-step method, in which TiO₂ was first coated on GO sheets by hydrolysis and was then crystallized into anatase nanocrystals by hydrothermal treatment in the second step. Wang *et al* (2009) achieved self-assembly of TiO₂ with graphene composites through the stabilization of graphene in aqueous solution with the assistance of anionic sulfate surfactants. Chen *et al* (2010) prepared a visible-light responsive GO/TiO₂ composite with a *p/n* heterojunction by adding sodium dodecylsulfate to an

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aqueous solution of TiCl_3 and GO, in which TiO_2 could be excited by visible light with wavelengths longer than 510 nm. Other researchers synthesized graphene/ TiO_2 composites using graphene oxide and P25 as reactants by a simple one-step hydrothermal method and obtained higher photocatalytic activity than that of bare TiO_2 (Zhang *et al* 2010). In the present study, CdS-graphene/ TiO_2 composite nanoparticles were prepared by a sol-gel reaction of $\text{Cd}(\text{NO}_3)_2$ solutions, the other was a precipitation reaction of $\text{Cd}(\text{NO}_3)_2$ and Na_2S solutions and titanium oxysulfate. In terms of the modification of TiO_2 and CdS combined graphene nanoparticles, the new photocatalysts were considered to be CdS-graphene/ TiO_2 composite materials. Their structural characteristics were characterized by XRD, SEM, TEM and EDS. MB was selected as a typical dye to examine the photocatalytic activity of CdS-graphene/ TiO_2 under visible light. The decomposition kinetics and mechanism of the photocatalysts were also studied.

2. Experimental

2.1 Synthesis of graphene

For the synthesis of graphene, oxide (GO) was prepared first, and then graphene oxide was prepared from graphite according to a modification of the Hummers–Offeman method (Inagaki *et al* 2003). In brief, graphite powder (10 g) was dispersed in cold concentrated sulphuric acid (230 mL and 98 wt%, in a dry ice bath) and potassium permanganate (KMnO_4 , 30 g) was gradually added with continuous vigorous stirring and cooling to prevent the temperature from exceeding 293 K. The dry ice bath was removed and replaced by a water bath and the mixture was heated to 308 K for 0.5 h with gas release under continuous stirring, followed by slow addition of deionized water (460 mL), which produced a rapid increase in the solution temperature up to a maximum of 371 K. The reaction was maintained for 40 min in order to increase the oxidation degree of the graphite oxide product and then the resultant bright-yellow suspension was terminated by the addition of more distilled water (140 mL) followed by hydrogen peroxide solution (H_2O_2 , 30%, 30 mL). The solid product was separated by centrifugation at 3000 rpm and washed initially with 5% HCl until sulphate ions were no longer detectable with barium chloride. The solid product was then washed three times with acetone and air dried overnight at 338 K. After sonication for 30 min, the graphite oxide was transformed into graphene oxide. The reduction of graphene oxide was performed as follows: twenty-five milligrams of graphene oxide powder was placed in a cup and 200 mL de-ionized water was then added. Ten min of magnetic stirring at 200 rpm yielded an inhomogeneous brown suspension. The resulting suspensions were further treated with a reduction agent, hydrazine solution (the volume ratio of hydrazine to de-ionized water was 1:5), under ultrasonication (for 0.5 h at 1.3×10^5 J). After drying at 373 K, the sample was reduced

Figure 1. Preparation procedure of graphene oxide.

from graphene oxide to pure graphene. The preparation procedure is shown in figure 1.

2.2 Materials

As a supporting material, graphene oxide powder was used as received. Titanium oxysulfate ($\text{TiOSO}_4 \cdot \text{H}_2\text{O}$, Aldrich Chemical Co. Ltd., USA) was used as a titanium dioxide source. The MB (analytical grade, $\gg 99.99\%$) was purchased from Duksan Pure Chemical Co. Ltd., Korea. The analytical reagents, $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Na}_2\text{S} \cdot \text{H}_2\text{O}$ were purchased from Yakuri Pure Chemicals Co. Ltd., Japan. The water used for solutions and experimental preparations was ultra-pure.

2.3 Preparation of CdS-graphene/ TiO_2 composite photocatalysts

Firstly, 0.1 mol of $\text{CdCl}_2 \cdot \text{H}_2\text{O}$ was dissolved in 30 mL distilled water and 0.1 mol $\text{Na}_2\text{S} \cdot \text{H}_2\text{O}$ was dissolved in the resulting solution. Graphene oxide powder (0.2 g) was added and then the solution was stirred for 5 h at 343 K. Next, it was filtered using a Millipore filter and washed three times with 5 mL of distilled water and dried for 24 h at 373 K. CdS-graphene composites were produced through heat treatment at 773 K. Secondly, 0.1 or 0.3 mol of $\text{TiO}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ were added and stirred for 5 h at 343 K. CdS modified TiO_2 was filtered using a Millipore filter and washed three times with 5 mL of distilled water. Finally, it was dried for 3 h at 373 K. CdS-graphene/ TiO_2 composites were produced through heat treatment at 773 K. Table 1 lists preparation conditions and sample codes.

2.4 Characterization

The crystal phases of the composite photocatalysts were obtained by XRD (Shimata XD-D1, Japan) with $\text{CuK}\alpha$ radiation ($\lambda = 0.154$ nm) in the 2θ range of $10\text{--}80^\circ$

Table 1. Nomenclatures of CdS combined graphene and CdS combined graphene/TiO₂ composites.

Preparation method	Nomenclatures
0.2 g Graphene oxide + 0.1 M cadmium sulfide	0.1 CG
(0.2 g Graphene oxide + 0.1 M cadmium sulfide) + 0.1 M TOS	0.1 CGT
(0.2 g Graphene oxide + 0.1 M cadmium sulfide) + 0.3 M TOS	0.3 CGT

at a scan speed of 1.2°/min. The decomposition kinetics for photocatalytic activity were measured between 600 and 700 nm using a UV-Vis spectrophotometer (OPTIZEN POP, Meacasy, Korea) equipped with an absorbance sphere. The morphologies of photocatalysts were analysed by SEM (JSM-5200 JOEL, Japan) at 3.0 keV, which was equipped with an energy dispersive X-ray analysis system (EDS). Transmission electron microscopy (TEM, JEOL, JEM-2010, Japan) was used to observe the surface state and structure of the CdS-graphene/TiO₂ composites. At an acceleration voltage of 200 kV, TEM was used to investigate the size and distribution of the titanium and iron particles deposited on the fullerene surfaces of various samples. TEM specimens were prepared by placing a few drops of sample solution onto a carbon grid. BET surface area, pore volume and pore size of the photocatalysts were obtained by measuring N₂ adsorption at 77.4 K using a BET specific surface area analyser (Monosorb, USA).

2.5 Measurement of photocatalytic activities

The photocatalytic activities of CdS-graphene/TiO₂ composite photocatalysts were evaluated by monitoring the photodegradation of MB aqueous solution under visible light. A piece of CdS-graphene/TiO₂ of 75 × 50 mm in size, was placed into 100 mL of a 50 mg/L MB aqueous solution. Under magnetic stirring, the mixed solution was irradiated with visible light. Samples were then taken every 30 min, after centrifugal separation, and the MB concentration in the supernatant was analysed using a spectrophotometer (OPTIZEN POP, Mecasys, Korea) at 664 nm. Then, the solution was irradiated with a visible light using an LED lamp. The suspension was irradiated with visible light for a set of irradiation time. The whole system was enclosed in a closed chamber in such a way that only visible light from (Fawoo 50–60 Hz 8 W pure white light, Lumidas-H) LED lamp could fall directly on the solution mixture via a hollow tube and the experimental system could not be influenced by any other external sources.

3. Results and discussion

3.1 XRD patterns

Figure 2 shows XRD patterns of the catalysts. The diffraction peaks corresponding to CdS and TiO₂ are marked as

Figure 2. XRD patterns of CdS-graphene/TiO₂ for (a) 0.1 CG, (b) 0.1 CGT and (c) 0.3 CGT.

‘D’ and ‘T’, respectively. XRD patterns of the composites showed that the cadmium sulfide treated graphene/TiO₂ composite contained a mixture of anatase and rutile formed below 773 K. The crystal structure of titanium dioxide was determined mainly by the heat treatment temperature. In the results reported by XRD patterns of TiO₂/carbon composites formation of anatase crystallites at low temperatures was revealed. On the other hand, mixtures of anatase and rutile structures were observed with increasing pyrolysis temperature. This means that an increase in the heat treatment temperature induces a phase transition from pure anatase to a mixture of anatase and rutile, or to rutile. Therefore, TiO₂ structure in the CdS-graphene/TiO₂ composite is a mixture of anatase and rutile. Figure 2 shows XRD patterns of CdS-graphene composites and CdS-graphene/TiO₂ composites. In the pattern of CdS-graphene/TiO₂ (figure 2), the diffraction peaks at $2\theta = 25.3^\circ$, 27.8° , 28.5° and 43.0° were assigned to 0.1 CdS-graphene (figure 2a), while the diffraction peaks at $2\theta = 25.4^\circ$, 27.1° , 28.5° and 43.4° were assigned to 0.3 CdS-graphene (figure 2b). In the pattern of 0.1 CdS-graphene/TiO₂ (figure 2c), additional peaks at 25.5° , 27.1° and 28.1° were also observed, which were assigned to the CdS cubic phase. In addition, the peak intensity was lower and the peak shape was wider. This might be due to the small amount of CdS in the CdS/TiO₂ composites, and for the sol-gel method, the preparation temperature of CdS was relatively low. Hence, CdS in CdS/TiO₂ was

mainly amorphous (Subrahmanyam *et al* 2010; Liu *et al* 2011).

3.2 Surface morphology and EDX analysis

SEM images of CdS-graphene/TiO₂ catalysts are shown in figure 3. According to figure 3, we can observe that the TiO₂ particles are fine and agglomerated on the surface of graphene, but are not uniform. In particular, development of the pores on the graphene surface can be observed, which is consistent with the N₂ adsorption experiment. Generally, it is considered that good particle dispersions can produce high photocatalytic activity. In previous studies, a nitric acid treatment on CdS-graphene/TiO₂ composites enhanced the homogeneity and uniformity of the distribution of TiO₂ particles. Figure 4 shows elemental contents of CdS-graphene/TiO₂ composite photocatalysts (Subrahmanyam *et al* 2010). EDX showed that the elemental contents of CdS-graphene/TiO₂ were composed mainly of Ti and O elements along with small quantities of Cd and S. These spectra showed that there are higher amounts of carbon and

titanium in the samples treated with acid than the non-treated samples. One possible explanation is that the acid treatment leads to the formation of surface complexes including carbon ions which produce titanium oxide complexes for the carbon active sites. As shown in table 2, the amount of Ti increases as the amount of TOS precursor is increased (Liu *et al* 2011). TEM images of CdS-graphene and CdS-graphene/TiO₂ with scales of 0.2 μm –100 nm are shown in figure 5. CdS particle colour shows black and TiO₂ particle colour shows gray. TEM image of CdS-graphene (figure 5a–b) shows 2D structure of the graphene sheets and indicates that the surface is very smooth. The morphology of GO is one of thin stacked flakes of shapes with well-defined multilayered structures at the edge. The TEM images of CdS-graphene/TiO₂ show the graphene sheets and CdS nanoparticles. A uniform dispersion of CdS particles on the graphene sheet can be observed in figure 5(c–d). The size of nanoparticles is about 20 nm for all of the CdS-graphene/TiO₂ samples (Baby *et al* 2010; Zhu *et al* 2010). The CdS-graphene/TiO₂ catalysts were denoted as 0.1 CG and 0.1 CGT. BET surface area of the graphene oxide was 1083 m²/g, which decreased greatly to about 3.570 m²/g for 0.1 CG and 13.288 m²/g for 0.1

Figure 3. SEM images of (a–b) GO, (c–d). CdS-graphene and (e–f) CdS-graphene/TiO₂.

Figure 4. EDX elemental micro-analysis spectra of CdS-graphene and CdS-graphene/TiO₂: (a) 0.1 CG and (b) 0.1 CGT.

Table 2. BET surface area and EDX elemental microanalysis (wt%) of graphene and CdS-graphene/TiO₂.

Samples	S_{bet} (m ² /g)	Elements (wt%)				
		C	O	Cd	S	Ti
Graphene	1083	100	0	0	0	0
0.1 CG	3.570	32.18	5.16	43.67	8.03	0
0.1 CGT	13.288	37.54	25.00	14.48	4.10	15.41

CGT composites. These BET surface areas are summarized in table 2. It is evident that there was a large change in the micropore size distribution for CdS-graphene/TiO₂ composites compared with that of graphene. This result indicated that although the total surface area decreased after formation of TiO₂ particles by TOS treatment, it is considered that the TOS could penetrate into micropore and mesopore structures of graphene and become adsorbed in pores as TOS molecules, which would be converted to TiO₂ through heat treatment. As another means of improving photocatalytic activity, reducing the recombination of holes and electrons by doping TiO₂ with transition metals was proposed. Generally, BET surface area is thought to decrease due to the blocking of micropores on the surface (Oh and Chen 2007).

3.3 Photocatalytic activities and photodegradation mechanism

Figure 6 shows degradation curves of a 50 mg/L MB aqueous solution under visible light. The photodegradation rate of MB with 0.1 M CdS-graphene/TiO₂ composites was obviously higher than that of 0.1 M CdS-graphene composites. When irradiated for 150 min under visible light, the degradation rate of MB with 0.1 M CdS-graphene/TiO₂ was ~16–30% higher than that of 0.1 M CdS-graphene composites. According to a previous study, electrons in the conduction band are generated on the surface of TiO₂ when it is irradiated with light of energy equal to or exceeding its bandgap. Theoretically, pure TiO₂ cannot be excited by visible light irradiation. On the other hand, the photocatalytic

Figure 5. TEM images of (a), (b) CdS-graphene and (c), (d) CdS-graphene/TiO₂ composites.

activity of TiO₂ under visible light was improved by introducing CdS. The photocatalytic degradation of MB solution under visible light was used to examine the photocatalytic activity of 0.1 M CdS-graphene and 0.1 M CdS-graphene/TiO₂ composites. Figure 5 shows adsorption and photodegradation capabilities of different samples irradiated with visible light. We chose the methylene blue solution to determine the photocatalytic activity of CdS-graphene/TiO₂ composite under irradiation of visible light because the CdS-graphene/TiO₂ composite shows most photocatalytic activity for the degradation of this solution under UV light. As shown in figure 5, after visible light irradiation for 150 min, the methylene blue solution is photodegraded by only 10% by CdS-graphene. However, when the prepared CdS-graphene/TiO₂ composite is used as a photocatalyst, the methylene blue solution is photodegraded by 33%, which is 2.3 times more than by CdS-graphene. This indicates that the prepared CdS-graphene/TiO₂ composite also has excellent photocatalytic activity in the visible light region. As shown in the figure, during the photodegradation process, suitable adsorption capacity is crucial for achieving high photocatalytic activity. An important step in photocatalytic process is the adsorption of the reacting substances onto the surface of the catalyst (Oh and Chen 2007). A simple schematic mechanism of the photocatalytic activity of CdS-graphene/TiO₂ composites is shown in figure 6. As shown in the figure, during the photodegradation process, a suitable adsorption capacity is crucial for high photocatalytic activity. An important step in the photocatalytic process is the adsorption of reacting substances onto the surface of the catalyst (Zhu *et al* 2010). The narrow bandgap allows CdS-graphene/TiO₂ to absorb more photons, which will

enhance the photocatalytic efficiency of TiO₂ under visible light. Because of the inconsistent and overlapping conduction bands (CB), valence bands (VB) and bandgaps of the two semiconductors, when CdS/TiO₂ nanocomposites are irradiated under visible light, the photogenerated electrons can be excited from the VB of CdS into the CB of TiO₂, whereas photogenerated holes will be left in the VB of CdS. The electrons can react with O₂ to generate $\cdot\text{O}_2^-$, and the holes theoretically migrate to the surface and react with OH⁻ or H₂O to generate $\cdot\text{OH}$ radicals. These radicals can react with adsorbed pollutants. The reactions can be expressed as follows:

In addition, with the substitution of oxygen atoms by graphene and CdS in the anatase crystal structure of TiO₂, new levels are introduced between conduction and valence bands of TiO₂. The electrons generated by TiO₂ can be pro-

Figure 6. (a) Photodegradation behaviour of MB with 0.1 CdS-graphene oxide and 0.1, 0.2 CdS-graphene oxide/TiO₂ under visible light irradiation and (b) degradation of MB under visible light for CuS-graphene oxide/TiO₂.

moted from the valence band to the graphene level introduced by CdS, or from the lower to the higher graphene levels, which can increase the quantity of electrons level. Therefore, the CdS-graphene/TiO₂ composites have a narrower bandgap and an increased level of absorption in the visible-light region. The departed holes can migrate to the surface of the CdS particles. Therefore, the rate of photodecomposition under visible light irradiation is enhanced. Figure 7 presents the reaction mechanism of the CdS-graphene/TiO₂ composite under visible light irradiation. This in turn generates much larger amounts of $\cdot O_2^-$ and $\cdot OH$, which enhance the photo-degradation activity. In the photodecomposition reaction, graphene can generate electrons as well as capture and transfer the photogenerated electrons of CdS and TiO₂ under visible light irradiation, which can reduce the recombination rate of photo-electron-hole pairs (Zhu *et al* 2010).

4. Conclusions

CdS-graphene and CdS-graphene/TiO₂ composites were successfully synthesized by a simple sol-gel method. From the XRD patterns, cubic crystal structure of CdS can be observed. A TEM image shows that the surface of TiO₂ was coated with graphene and CdS layers uniformly with a particle size of graphene of about 20 nm. The photocatalytic activity suggests that the composites show strong photo-absorption of UV light and of light in the visible range, and the presence of graphene enhances the photoabsorption in the visible range. The photocatalytic activity of the CdS-graphene/TiO₂ composite is investigated by measuring the degradation of MB in aqueous solution under visible light irradiation.

Figure 7. Reaction mechanism of CdS-graphene/TiO₂ composite under visible light irradiation.

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