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Article

Preparation of CuS-graphene oxide/TiO₂ composites designed for high photonic effect and photocatalytic activity under visible light

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ABSTRACT

CuS-graphene oxide/TiO₂ composites were prepared using a sol-gel method to improve the photocatalytic performance of the photocatalyst. The composites were characterized by X-ray diffraction, scanning electron microscopy, energy-dispersive X-ray analysis, and transmission electron microscopy. The photocatalytic activities were examined by the degradation of methylene blue (MB) under visible-light irradiation. The photodegradation of MB under visible-light irradiation reached 90.1% after 120 min. The kinetics of MB degradation was plotted alongside the values calculated from the Langmuir-Hinshelwood equation. The CuS-graphene oxide/TiO₂ sample prepared using 0.2 mol of TiO₂ showed the best photocatalytic activity. This was attributed to a cooperative reaction as a result of increased photoabsorption by graphene oxide and an increased photocatalytic effect by CuS.

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1. Introduction

Sulfides are important semiconductor materials and they have many applications as a result of their metal-like electrical conductivity [1,2], chemical-sensing capabilities [3], and ideal characteristics for solar-energy absorption [4]. In the past few years, various attempts have focused on the synthesis of CuS with different shapes, including nanoparticles [5], nanoflakes [6], nanotubes [7], microspheres [8], flower-like structures [9], nanowires [1], nanorods [10], sea-urchin-like structures [11], and nanoribbons [12]. Solution-phase approaches are appealing because of their low temperature, low cost, high efficiency, and potential for scale-up. Surfactants or templates are usually used in the reaction systems, and they play critical roles in the morphological control of CuS nanomaterials. However, the use of surfactants or templates inevitably increases the reaction complexity, results in impurities in the products, and is disad-

vantageous from the viewpoint of green chemistry. The development of facile, effective, and surfactant-free methods for the controlled synthesis of CuS nanomaterials is therefore highly desirable. Among the materials developed for photocatalytic applications (TiO₂, CuO, CdS, WO₃), TiO₂ (the anatase polymorph) is the most promising because of its high efficiency, low cost, chemical inertness, and photostability. The main drawback is its wide band-gap (3.2 eV), which requires ultraviolet (UV) irradiation for photocatalytic activation, so any shift in the optical response of TiO₂ from the UV to the visible spectral range will have a positive effect on its photocatalytic efficiency under solar irradiation, and on industrial up-scaling [13]. Copper sulfides have been extensively investigated in recent years because of their interesting optical and electrical properties, which result from variations in stoichiometry, composition, and morphology, and because of their potential applications in various fields, e.g., as absorbers for solid-state solar-cells [14], as

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room-temperature ammonia-gas sensors [15], and in photocatalytic reactions [16]. In addition, semiconductor composites such as MS/TiO₂ (M = Pb, Cu, Cd) also have good optical properties (absorption and photoluminescence) compared with the corresponding bulk ones, as a result of quantum confinement effects [17]. The micro-emulsion technique used in this study was selected because it maximized the homogeneity of the chemical composition at the nanoscale level [18]. The visible-light photocatalytic activity of CuS/TiO₂ was tested by measuring the degradation of an aqueous solution of parathion-methyl, which is an organophosphorus pesticide that is very stable under visible-light irradiation. Under the same conditions, the photocatalytic activities of a commercially available photocatalyst, i.e., pure anatase TiO₂ (Degussa P25), and cubic CuS nanoparticles were also examined.

Graphene, which was developed after the discovery of carbon nanotubes and C₆₀, is an excellent material for applications in fields such as non-condensed-matter physics and electronics [19]. Because it consists of a single-atom-thick sheet of sp²-bonded carbon atoms arranged in a hexagonal lattice, graphene shows outstanding mechanical, thermal, optical, and electrical properties. The interest in graphene-based materials has been extended to applications in such diverse fields as nanoelectronic devices, biomaterials, intercalation materials, drug delivery, and catalysis [20]. In another study, graphene/TiO₂ composites that exhibited high photocatalytic activities were synthesized, using graphene oxide and P25 as reactants, using a facile one-step hydrothermal method [21].

In the present study, CuS-graphene oxide/TiO₂ composite nanoparticles were prepared using a sol-gel reaction, by the precipitation reaction of Cu(NO₃)₂ and Na₂S solutions and TiOSO₄·H₂O. The photocatalysts obtained by modification of TiO₂ and CuS combined graphene oxide nanoparticles were considered to be CuS-graphene oxide/TiO₂ composite materials. Their structural characteristics were determined using X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and energy-dispersive X-ray analysis (EDX). Methylene blue (MB) was selected as a typical dye for examining the photocatalytic activity of CuS-graphene oxide/TiO₂ under visible light. The kinetics and decomposition mechanism of the photocatalysis were also studied.

2. Experimental

2.1. Preparation

2.1.1. Synthesis of graphene oxide

Graphene oxide was prepared from graphite using a modification of the Hummers-Offeman method [22]. In brief, graphite powder (KS-6, 10 g) was dispersed in cold concentrated sulfuric acid (230 ml, 98 wt%, and dry-ice bath), and KMnO₄ (30 g) was gradually added with continuous vigorous stirring and cooling to prevent the temperature from exceeding 293 K. The ice bath was removed, replaced with a water bath, and the mixture was heated to 308 K for 0.5 h, with gas release under continuous stirring, followed by the slow addition of deionized water (460 ml). This produced a rapid increase in the solution

temperature up to a maximum of 371 K. The reaction was allowed to continue for 40 min to increase the degree of oxidation of the graphite oxide product, and then the reaction was terminated by the addition of more distilled water (140 ml), followed by H₂O₂ solution (30%, 30 ml), to yield a bright-yellow suspension. The solid product was separated by centrifugation at 3000 r/min and washed with 5% HCl, until sulfate ions were no longer detectable with barium chloride. The resultant solid product was then washed three times with acetone and dried in air 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 were placed in a cup, and 200 ml of deionized water were added. Ten minutes of magnetic stirring at 200 r/min yielded an inhomogeneous brown suspension. The resulting suspension was treated with a reducing agent, i.e., hydrazine solution (1:5, volume ratio of hydrazine to deionized water), under ultrasonication (0.5 h, 1.3 × 10⁵ J), and drying at 373 K gave graphene oxide. The preparation procedure is shown in Fig. 1.

2.1.2. Preparation of CuS-graphene oxide/TiO₂ composite photocatalysts

Cu(NO₃)₂·3H₂O (AR, Yakuri Pure Chemicals Co., Ltd, Japan, 0.1 mol) was dissolved in 30 ml of distilled water (30 ml), and Na₂S·H₂O (AR, Yakuri Pure Chemicals Co., Ltd, Japan, 0.1 mol) was dissolved in the resulting solution. Graphene oxide (0.5 g) powder was added and the mixture was stirred for 5 h at 343 K. The solution was filtered using a Millipore filter, washed three times with 5 ml of distilled water, and dried for 24 h at 373 K. TiO₂SO₄·H₂O (TOS, 0.1 or 0.2 mol, Aldrich) was added, and the mixture was stirred for 5 h at 343 K. The resulting CuS-modified TiO₂ was filtered using a Millipore filter, and washed three times with 5 ml of distilled water. Finally, it was

Fig. 1. Preparation of graphene oxide.

Table 1

Nomenclature of CuS-graphene oxide and CuS-graphene oxide/TiO₂ composites.

Nomenclature	Preparation method
0.1 CG	0.5 g graphene oxide + 0.1 mol Cu(NO ₃) ₂ ·3H ₂ O + 0.1 mol Na ₂ S·H ₂ O
0.1 CGT	0.5 g graphene oxide + 0.1 mol Cu(NO ₃) ₂ ·3H ₂ O + 0.1 mol Na ₂ S·H ₂ O + 0.1 mol TOS
0.2 CGT	0.5 g graphene oxide + 0.1 mol Cu(NO ₃) ₂ ·3H ₂ O + 0.1 mol Na ₂ S·H ₂ O + 0.2 mol TOS

dried for 3 h at 373 K. The CuS-graphene oxide/TiO₂ composites were obtained by heat-treatment at 773 K. The preparation conditions and sample codes are listed in Table 1.

2.2. Characterization

The crystal phases of the composite photocatalysts were obtained using XRD (Shimadzu XD-D1, Japan) with Cu K α radiation ($\lambda = 0.154$ nm) in the range $2\theta = 10^\circ$ – 80° at a scan speed of $1.2^\circ/\text{min}$. The morphologies of the photocatalysts were analyzed using SEM (JSM-5200 JOEL, Japan) at 3.0 keV; the SEM instrument was equipped with an EDX system. TEM (JEOL, JEM-2010, Japan) was used to observe the surface states and structures of the CuS-graphene oxide/TiO₂ composites. TEM at an accelerating voltage of 200 kV was used to investigate the sizes and distributions of the Ti and Cu particles deposited on the fullerene surfaces of the samples. The TEM specimens were prepared by placing a few drops of the sample solution on a carbon grid. The Brunauer-Emmett-Teller (BET) surface areas, pore volumes, and pore sizes of the photocatalysts were obtained using N₂ adsorption-desorption measurements at 77.4 K using a BET specific surface area analyzer (Monosorb, USA).

2.3. Photocatalytic degradation of MB

The photocatalytic activities of the CuS-graphene oxide/TiO₂ composite photocatalysts were evaluated by monitoring the photodegradation of an aqueous solution of MB under visible light (KLD-08L/P/N, 8 W). The CuS-graphene oxide/TiO₂ was placed in 100 ml of a 50 mg/L MB (AR, > 99.99%, Duksan Pure Chemical Co., Ltd., Korea) aqueous solution. Under magnetic stirring, the mixed solution was irradiated with visible light. Samples were taken every 30 min after centrifugal separation, and the MB concentration in the supernatant was analyzed using a spectrophotometer (OPTIZEN POP, Mecasys, Korea) at 664 nm. Visible light was used as the light source. The reactor was placed for 30 min in a dark box so that the photocatalyst composite particles adsorbed the maximum possible amount of MB molecules. After the adsorption state was reached, visible-light irradiation was restarted to cause the degradation reaction. In the MB degradation process, a glass reactor (diameter 4 cm, height 6 cm) was used and the reactor was placed on a magnetic churn dasher. The suspension was then irradiated with visible light for a set irradiation time. Visible-light irradiation of the reactor was performed for 30, 60, 90, or 120 min. Samples were withdrawn regularly from the reac-

tor and dispersed powders were removed using a centrifuge. The clean transparent solution was analyzed using UV-Vis spectroscopy. The MB concentration in the solution was determined as a function of the irradiation time.

3. Results and discussion

3.1. XRD patterns

Figure 2 shows the XRD patterns of CuS-graphene oxide/TiO₂. The XRD patterns of the composites show that the CuS-treated graphene oxide/TiO₂ composites contained a mixture of anatase and rutile, formed below 773 K. The crystal structure of TiO₂ depended mainly on the heat-treatment temperature. Based on the results reported by Maldonado-Hodar et al. [23], the XRD patterns of the TiO₂/carbon composites showed the formation of anatase crystallites at low temperatures. Mixtures of anatase structures were observed with increasing pyrolysis temperature. This means that an increase in the heat-treatment temperature induced a phase transition from pure anatase to a mixture of anatase. Therefore, the TiO₂ structure in the CuS-graphene oxide/TiO₂ composites is a mixture of anatase. In the XRD patterns in Fig. 2, the diffraction peaks at $2\theta = 34.3^\circ$ and 46.8° were assigned to 0.1 CG, and the diffraction peaks at $2\theta = 26.4^\circ$, 38.1° , and 48.5° were assigned to 0.1 CGT. In the pattern of 0.2 CGT, additional peaks at $2\theta = 26.4^\circ$, 38.1° , and 48.5° were observed, and these were assigned to the CuS cubic phase. In addition, for 0.2 CGT, the peak intensities were lower and the peak shapes were wider. This might be caused by the small amount of CuS in the CuS/TiO₂ composite, and the low preparation temperature of CuS in the sol-gel method. The CuS in CuS/TiO₂ was therefore mainly amorphous [24].

3.2. Surface morphology and EDX analysis

The SEM images of the CuS-graphene oxide/TiO₂ catalysts are shown in Fig. 3. It can be seen from Fig. 3 that the TiO₂ particles are fine and agglomerated on the graphene oxide surface, but are not uniform. In particular, the development of pores on the graphene oxide surface can be observed, which is con-

Fig. 2. XRD patterns of CuS-graphene oxide/TiO₂.

Fig. 3. SEM images of graphene oxide (a), CuS-graphene oxide (b), and CuS-graphene oxide/TiO₂ (c).

sistent with the N₂ adsorption-desorption results. Generally, it is considered that good particle dispersion produces high photocatalytic activity. In previous studies, the treatment of CuS-graphene oxide/TiO₂ composites with nitric acid produced a more homogeneous and uniform distribution of the TiO₂ particles [23]. More detailed information on the surface states can be obtained using TEM. Zhang et al. [25] reported that a good dispersion of small particles provides larger numbers of sites for reactants than are provided by aggregated particles.

Figure 4 shows the elemental contents of the CuS-graphene oxide and CuS-graphene oxide/TiO₂ composite photocatalysts. EDX showed that the elemental content of CuS-graphene oxide/TiO₂ consisted mainly of Ti and O, and small quantities of Cu and S. The spectra showed higher amounts of C and Ti in the samples treated with acid than in the non-treated samples. One possible explanation for this is that the formation of surface complexes through the acid treatment includes carbon ions, producing TiO₂ complexes at the carbon active sites. As shown in Table 2, the amount of Ti increases with increasing amounts of TOS precursor [24].

TEM images of CuS-graphene oxide/TiO₂ are shown in Fig. 5. The TEM images show graphene oxide sheets and CuS nanoparticles [26]. CuS-graphene oxide shows the two-dimensional structure of the graphene oxide sheets, and indicates that the

Fig. 5. TEM images of CuS-graphene oxide/TiO₂ composites.

surface is very smooth. The morphology of graphene oxide consists of thinly stacked flakes of shapes with well-defined multilayered structures at the edges. The size of the CuS nanoparticles is about 20 nm for all the CuS-graphene oxide/TiO₂ samples.

The BET surface area of the graphene oxide was 1083 m²/g, and this greatly decreased to about 3.57 and 13.29 m²/g for the 0.1 CG and 0.1 CGT composites, respectively. The BET surface areas are summarized in Table 2. It is evident that there was a large change in the micropore size distribution for the CuS-graphene oxide/TiO₂ composites compared with that of graphene oxide. This indicates that although the total surface area decreased after the formation of TiO₂ particles by the TOS treatment, the TOS could penetrate into the micropores and mesopores of graphene oxide and become adsorbed in the pores as TOS molecules. The adsorbed TOS would be converted into TiO₂ by heat-treatment. Reducing the recombination of holes and electrons by doping TiO₂ with transition metals has been proposed as another means of improving the photocata-

Fig. 4. EDX elemental microanalysis spectra of 0.1 CG (a) and 0.1 CGT (b).

Table 2

BET surface areas and EDX elemental microanalysis results of graphene oxide and CuS-graphene oxide/TiO₂.

Sample	$A_{\text{BET}}/(\text{m}^2/\text{g})$	Element content (wt%)				
		C	O	Cu	S	Ti
GO	1083.00	100.00	0.00	0.00	0.00	0.00
0.1 CG	3.57	64.77	17.35	13.99	3.16	0.00
0.1 CGT	13.29	41.74	32.38	4.73	3.11	20.29

Fig. 6. FT-IR spectra of 0.1 CG, 0.1 CGT, and 0.2 CGT.

lytic activity. Generally, the BET surface area is thought to decrease, as a result of blocking of the surface micropores [27].

The FT-IR spectrum of fullerene was rather simple and suggested extensive oxidation. The spectrum of the crystalline material showed well-distinguished and sharp bands, whereas the spectra of the amorphous materials were less resolved. The hydration results established the importance of defining the FT-IR conditions (Fig. 6). They also suggested that this type of study can be performed on CuS-graphene composites. Figure 6 shows the FT-IR spectra of 0.1 CG, 0.1 CGT, and 0.2 CGT. The FT-IR spectrum of 0.1 CGT was similar to that of 0.2 CGT. In the spectrum of 0.1 CG, the peak at 1043 cm^{-1} was assigned to the carboxylic acid bending vibration, which occurs between 1000 and 1300 cm^{-1} , and the peak at 1394 cm^{-1} was assigned to amine symmetric stretching modes, which occur in the range $1080\text{--}1360\text{ cm}^{-1}$. Variable C=C bands at approximately 1620 and 1680 cm^{-1} and a variable C=C band at 1540 cm^{-1} were observed. This confirms that artificial ageing is occurring on the surface, and that the types of structural changes inferred from the spectra are consistent with the mechanism proposed in the literature: the formation of C–O bonds resulting from oxidation of the hydrocarbon triterpenic molecules by the direct binding of C and C–O radicals, followed by further oxidation to carbonyl functional groups. In the spectrum of 0.1 CGT, the weak peaks at 1070 cm^{-1} and 1216 cm^{-1} were assigned to C–O bonds. In the spectrum of 0.2 CGT, the weak peaks at 1022 , 1147 , and 1220 cm^{-1} were assigned to C–O bonds and the peak at 1430 cm^{-1} was assigned to C=C bonds. Comparing spectra of 0.1 CG and 0.1 CGT, the peak intensity of the functional group on the oxidized fullerene was weak and decreased. This is because some of the functional groups had combined with TiO_2 particles. The CuS-graphene particles were bound to TiO_2 by different functional groups.

3.3. Photocatalytic activities and photodegradation mechanism

Figure 7(a) shows the degradation curves of a 50-mg/L MB aqueous solution irradiated with visible light. The MB photodegradation rate with the 0.1 CGT was obviously higher than that with the 0.1 CG. When irradiated for 120 min under visible

Fig. 7. Photodegradation behavior of MB with 0.1 CG, 0.1 CGT, and 0.2 CGT under visible-light irradiation (a) and corresponding $-\ln(C/C_0)$ versus time plots (b).

light, the degradation rate of MB with 0.1 CGT was approximately 16%–30% higher than that with the 0.1 CG. This could be attributed to the effects on the porous carbon materials with the introduction of TiO_2 samples; dispersion was improved, and the degradation efficiency was also enhanced, as a result of photogenerated electrons, which were easily transferred to the TiO_2 conduction band. Similar results were observed by Oh et al. [28]. Figure 7(b) shows the $-\ln(C/C_0)$ versus t plots at 0–120 min irradiation time. The photodegradation followed first-order kinetics, which can be expressed as follows: $-\ln(C/C_0) = K_{\text{app}}t$, where K_{app} is the apparent reaction rate constant, and C_0 and C are the initial and reaction concentrations, respectively, of MB. Table 3 lists the K_{app} values for 0.1 CG, 0.1 TiO_2 , 0.1 CGT, and 0.2 CGT composites for the degradation of MB solutions. The K_{app} value of the 0.2 CGT sample was the largest, which is in accordance with the photocatalytic activity. After visible-light irradiation for 120 min, the MB solution was photodegraded by only 10% with CuS-graphene oxide. However, when the CuS-graphene oxide/ TiO_2 composite was used as the photocatalyst, the MB solution was photodegraded by 33%, i.e., 2.3 times more than by CuS-graphene oxide. This indicates that the prepared CuS-graphene oxide/ TiO_2 composites have excellent photocatalytic activities in the visible-light region [29]. As shown in Fig. 7, during the photodegradation process, an appropriate adsorption capacity is crucial for achieving high photocatalytic activity. Adsorption of the react-

Table 3 K_{app} values of photocatalysts for the degradation of MB solutions

Sample	K_{app}
0.1 CG	3.3×10^{-3}
0.1 TiO ₂	2.7×10^{-3}
0.1 CGT	2.3×10^{-3}
0.2 CGT	1.7×10^{-3}

ing substances on the surface of the catalyst is an important step in the photocatalytic process [30].

A simple schematic diagram of the mechanism of the photocatalytic activity of the CuS-graphene oxide/TiO₂ composite is shown in Fig. 8. CuS has a small band-gap (1.74 eV) and shows photocatalytic activity under visible-light irradiation. It becomes excited and generates hole-electron pairs. Subsequently, the holes react with adsorbed hydroxyl ions to generate hydroxyl radicals, and the electrons react with adsorbed oxygen to generate superoxide ions. In a graphene-oxide-modified CuS system, the graphene oxide acts as a photosensitizer. Graphene oxide could use its own photoabsorptive characteristics to absorb electrons from photoinduced irradiation and transfer them to CuS, increasing its electron density. In this way, CuS-graphene oxide compounds could generate more holes and electrons, and generate more hydroxyl radicals and superoxide ions. As a result of the production of hydroxyl radicals and superoxide ions, dyes are fragmented to CO₂ and H₂O [31]. In addition, with the substitution of oxygen atoms by graphenes and CuS in the anatase crystal structure of TiO₂, new levels are introduced between the conduction and valence bands of TiO₂. The electrons generated by TiO₂ can be promoted from the valence band to the graphene level introduced by CuS, or from the lower to the higher graphene levels, which can increase the quantity of electrons. The CuS-graphene oxide/TiO₂ composites have a narrower band-gap, and can increase the level of absorption in the visible-light region. The departed holes can migrate to the surface of the CuS particles, thereby enhancing the rate of photodecomposition under visible-light irradiation. This in turn generates much larger amounts of ·O₂⁻ and ·OH, and enhances the photodegradation

Fig. 8. Reaction mechanism of CuS-graphene oxide/TiO₂ composite under visible-light irradiation.

activity. In the photodecomposition reaction, graphenes can generate electrons, as well as capture and transfer the electrons photogenerated by CuS and TiO₂ under visible-light irradiation, and this can reduce the recombination rate of photoelectron-hole pairs [32].

4. Conclusions

CuS-graphene oxide and CuS-graphene oxide/TiO₂ composites were successfully synthesized using a simple sol-gel method. In the XRD patterns, the cubic crystal structure of CuS can be observed. The TEM images show that the TiO₂ surface is uniformly coated with graphene oxide and CuS layers, and that the graphene oxide particle size is about 20 nm. The photocatalytic activity suggests that the composites show strong photoabsorption under visible light and that the presence of graphene oxide enhances this photoabsorption in the visible-light range. The photocatalytic activities of the CuS-graphene oxide/TiO₂ composites were investigated by degradation of MB in aqueous solution under visible-light irradiation.

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Graphical Abstract

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CuS-graphene oxide/TiO₂ composite nanoparticles were prepared using a sol-gel reaction by the precipitation reaction of Cu(NO₃)₂ and Na₂S solutions and TiOSO₄·H₂O on graphene oxide. The photocatalytic activity of CuS-graphene oxide/TiO₂ under visible light was examined.

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