Synthesis of Graphene-CdSe Composite by a Simple Hydrothermal Method and Its Photocatalytic Degradation of Organic Dyes

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Abstract: A graphene-CdSe composite was synthesized by a facile hydrothermal method, and characterized by X-ray diffraction, scanning electron microscopy with energy dispersive X-ray analysis, transmission electron microscopy and UV-vis diffuse reflectance spectrophotometry. The graphene-CdSe composite efficiently catalyzed the photodegradation of methylene blue (MB), methyl orange (MO) and rhodamine B (Rh.B) in aqueous solution under UV or visible light irradiation. The graphene-CdSe composite exhibited a higher photocatalytic activity for the MB solution.

Key words: graphene; cadmium selenide; organic dye; photocatalytic activity

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Recently, it was found that carbon nanostructures (such as C₆₀ and carbon nanotubes), which are excellent electron acceptors and highly conductive scaffolds, are useful in photovoltaic conversion and photocatalysis [1–5]. Graphene, a flat monolayer of hexagonally arrayed *sp*²-bonded carbon atoms tightly packed into a two-dimensional (2D) honeycomb lattice, is a major focus of recent research due to its outstanding mechanical, electrical, thermal, and optical properties [6–9]. It has potential applications in many different areas [10–14]. The useful properties of graphene can be extended by integrating it with other nanomaterials to form unique hybrid materials. The fabrication of graphene materials decorated by metal nanoparticles is expected to give graphene nanocrystal hybrids with enhanced properties such as high catalytic activity and excellent electrochemical properties. Recently, semiconductor nanoparticles such as TiO₂, ZnO, and CdS have also been utilized to decorate graphene nanosheets to prepare graphene-based nanomaterials with remarkable optical and photovoltaic properties [15–17].

Cadmium selenide (CdSe) is an n-type semiconductor. Its band gap energy was reported to be from 1.65 to 1.8 eV [18–21]. It was found to be suitable for various optoelectronic applications in catalysis [22], solar cells [23], and biological labeling [24]. More recently, many groups have synthesized CdSe nanomaterials with high photocatalytic activity for the degradation of organic pollutants under UV light irradiation, such as CdSe-Pt nanorods and nanonets

[24], hybrid CdSe-Au nanodumbbells [25], and CdSe/ZnS-photosensitized nano-TiO₂ films [26]. However, few papers have discussed the preparation and properties of CdSe combined with graphene composites and their application in the degradation of organic dyes.

In this paper, we report the synthesis of graphene nanosheets coated with CdSe nanoparticles obtained directly by a hydrothermal preparation method. The composite was characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) with energy dispersive X-ray (EDX) analysis, transmission electron microscopy (TEM), and UV-Vis diffuse reflectance spectroscopy. The photocatalytic activity of the graphene-CdSe composite was evaluated by the degradation of different organic dyes, methylene blue (MB), methyl orange (MO), and rhodamine B (Rh.B), in aqueous solution under irradiation of UV or visible light.

1 Experimental

1.1 Synthesis of the graphene-CdSe composite

First, Na₂SO₃ (5 g, Duksan Pharmaceutical Co., Ltd, Korea) and selenium metal powder (0.5 g, DaeJung Chemicals & Metal Co., Ltd, Korea) were dissolved in 30 ml distilled water and refluxed for 1 h to form Na₂SeSO₃ solution. Cd(CH₃COO)₂ (0.5 g, DaeJung Chemicals & Metal Co., Ltd, Korea) was dissolved in 2 ml distilled water. NH₄OH (6 ml,

28%, DaeJung Chemicals & Metal Co., Ltd, Korea) was added to it and the mixture was stirred till it dissolved completely to form a $\text{Cd}(\text{NH}_3)_4^{2+}$ solution. Graphene oxide (0.5 g) prepared by the Hummers-Offeman method in our previous work [27] was added into the Na_2SeSO_3 solution and $\text{Cd}(\text{NH}_3)_4^{2+}$ solution under stirring to allow the formation of hydrogen bonds between the CdSe nanocrystals and graphene oxide. After hydrothermal reaction at 80 °C for 5 h, graphene oxide was reduced to graphene nanosheets and

CdSe compounds were grown on its surface to generate a graphene-CdSe composite. The preparation procedure is shown in Fig. 1. Finally, the temperature of the mixture was brought down to room temperature and the mixture was filtered through Whatman filter paper. The solid obtained was collected and washed with distilled water five times. After drying under vacuum at 100 °C for 8 h, the graphene-CdSe composite was obtained.

Fig. 1. Synthesis of graphene-CdSe composite by a simple hydrothermal method.

1.2 Characterization of the graphene-CdSe composite

XRD (Shimadzu XD-D1) using monochromatic high intensity $\text{Cu } K_\alpha$ radiation ($\lambda = 0.15406 \text{ nm}$) was used to characterize the crystallinity. SEM (JSM-5600) was used to observe the surface state and structure. TEM (Jeol, JEM- 2010, Japan) was used to determine the state and particle size of the composite. TEM at an acceleration voltage of 200 kV was used to investigate the number and stacking state of the graphene layers of the various samples. TEM specimens were prepared by placing a few drops of sample solution on a carbon grid. The element mapping of regions of the composite was performed by EDX analysis (attached to the SEM). UV-Vis diffuse reflectance spectra were obtained using a UV-Vis spectrophotometer (Neosys-2000) by using BaSO_4 as a reference at room temperature. These were converted from reflection to absorbance by the Kubelka-Munk method.

1.3 Photocatalytic studies

The photocatalytic tests were performed at room temperature. MB (99.99+%), MO (99.99+%), and Rh.B (99.99+%) used as model pollutants were purchased from Duksan Pure Chemical Co., Ltd, Korea, Daejung Chemicals & Metals Co., Ltd, Korea, and Samchun Pure Chemical Co., Ltd, Korea, respectively. Table 1 shows the structure and properties of MB, MO, and Rh.B. Graphene-CdSe composite (0.03 g) was added into 50 ml of 10 $\mu\text{mol/L}$ (designated

as c_0) organic dye (MB, MO, or Rh.B) solution. This was maintained in the dark for 2 h to ensure the adsorption/desorption equilibrium of the organic dye. Then, the solution was irradiated with a UV or visible lamp. The first sample was taken at the end of the dark adsorption period (just before the light was turned on) to determine the MB concentration in the solution. This was treated as the starting point ($t = 0$) of the reaction when the concentration of

Table 1 Molecular structure and absorbance maximum (λ_{max}) of the organic dyes

Organic dye	Molecular structure	$\lambda_{\text{max}}/\text{nm}$
MB		665
MO		465
Rh.B		554

the organic dye was c_{ads} . Samples were withdrawn regularly from the reactor at 30, 60, 90, 120, 180, and 240 min and immediately centrifuged to separate any suspended solid before analysis. The concentration of organic dye (c) in the solution during the photocatalytic degradation reaction was monitored by measuring the absorbance of the solution samples with a UV-Vis spectrophotometer (Optizen POP) at $\lambda_{\text{max}} = 665, 465, \text{ and } 554 \text{ nm}$, respectively, for MB, MO, and Rh.B since no reaction products absorb at these wavelength and by using a calibration curve. The degradation efficiency ($\eta\%$) was calculated as

$$\eta(\%) = (1 - c/c_0) \times 100$$

where c is the concentration of organic dye at time t .

2 Results and discussion

2.1 Characterization results

Figure 2 shows the XRD patterns of graphene, CdSe, and the graphene-CdSe composite. The diffractogram of graphene exhibited the typical peaks at $2\theta = 25.9^\circ$ and 42.7° corresponding to the graphite (002) and (100) reflections (JCPDS 01-0646) [28], respectively. For the CdSe compound, the XRD diffraction peaks at 2θ of 25.4° , 42° , and 49.6° can be indexed to the characteristic peaks of the (111), (220), and (311) plane reflections of cubic crystal structure CdSe with lattice constants of 0.605 nm according to the standard powder diffraction data (JCPDS 65-2891 for CdSe, cubic) [29,30]. However, for the graphene-CdSe composite, only the peaks from CdSe were detected. The (002) and (100) reflection of graphene overlapped the cubic (111) and (200) reflection of CdSe. Therefore, the intensity of the peaks at $2\theta = 25.4^\circ$ and 42° from the graphene-CdSe composite was stronger than that from the CdSe compound, and

Fig. 2. XRD patterns of graphene (1), CdSe compound (2), and graphene-CdSe composite (3).

the micromorphology of graphene-CdSe was different from that of the mixture of graphene and CdSe. No peak for graphene oxide or impurities was detected, indicating that the hydrothermal method used in this study gave the formation of a graphene-CdSe composite and the graphene oxide was reduced completely after reaction with CdSe. This result agrees with previous works [31,32] which used graphene oxide as the support material to prepare graphene based nanomaterials.

Figure 3(a) and (b) shows the SEM microphotographs of the graphene-CdSe composite. Very uniform spherical-shaped CdSe particles and agglomerates were observed. Spherical-shaped agglomerated CdSe particles were coated on the surface of the graphene. More detailed information of the surface state and particle size were obtained by TEM (Fig. 3(c)). The 2D structure of the graphene sheet and the surface was very smooth. CdSe particles and agglomerates were coated on the surface of the graphene sheet.

Fig. 3. SEM (a and b) and TEM (c) images of the graphene-CdSe composite.

To get information on the elements and element mass, the graphene-CdSe composite was examined by EDX. Figure 4 shows the EDX microanalysis and element mass of the graphene-CdSe composite. The main elements such as C, Cd, and Se were present. The strong C signal mainly originated from the graphene nanosheets. The Cd and Se peak came

from the precursor materials $\text{Cd}(\text{CH}_3\text{COO})_2$ and selenium metal powder.

Figure 5 shows the UV-Vis diffuse reflectance spectra of CdSe and the graphene-CdSe composite. The reflectance characteristics of the CdSe compound were quite similar to that of the graphene-CdSe composite except that the CdSe

Fig. 4. EDX microanalysis (a) and element mass (b) of the graphene-CdSe composite.

Fig. 5. UV-Vis diffuse reflectance spectra of CdSe and the graphene-CdSe composite.

compound has an absorption edge at 830 nm. We calculate the band gap energy of CdSe by $ah\nu = A(h\nu - E_g)^{1/2}$, where α , ν , E_g , and A are the absorption coefficient, light frequency, band gap, and a constant, respectively. Therefore, the band gap energy (E_g) of the CdSe-TiO₂ composite can be estimated from a plot of $(ah\nu)^{1/2}$ versus photon energy ($h\nu$). The band gap energy of CdSe was 1.74 eV, which was close to the literature value of 1.65 to 1.8 eV (CdSe) [18–21].

Moreover, the two composites both exhibited strong absorption in the UV light region at wavelengths less than 400 nm and the visible light region at wavelengths at 400–800

nm, which were assigned to CdSe. The absorption of the graphene-CdSe composite was higher than that of the CdSe compound in both UV light and visible light regions, indicating the graphene-CdSe composite would exhibit better photoactivity than the CdSe compound.

2.2 Degradation of organic dyes solution

The degradation of organic dye can be divided to two parts: adsorption in the dark for 120 min and photocatalysis under light irradiation for 240 min [33,34]. The effects of reaction variables such as organic dye, initial concentration, catalyst amount, light source, etc. on the degradation efficiency were studied. The results are given below.

2.2.1 Effect of different organic dyes

The effect of different organic dyes on degradation efficiency was investigated by using the concentration of 10 $\mu\text{mol/L}$ under 240 min UV irradiation with a catalyst amount of 0.03 g. The results are shown in Fig. 6. The graphene-CdSe composite achieved almost 100% MB removal after adsorption for 120 min in the dark, while MO and Rh.B were removed by only 6% and 19%, respectively. From Table 1, it is clear that the molecule size of MB is much smaller than that of MO and Rh.B, which explained why the graphene-CdSe composite showed the best adsorption effect for the MB solution over the MO and Rh.B solutions. For the photocatalytic effect, the MO in the solution was decreased 40% after 240 min while Rh.B in the solution was decreased by only 20% for the same irradiation time. The result indicates that the graphene-CdSe composite gave the best degradation for the MB solution. So, we chose the MB solution with which to perform further experiments.

Fig. 6. Degradation efficiency of different organic dyes by the graphene-CdSe composite under UV irradiation. The concentration of organic dye was 10 $\mu\text{mol/L}$. The amount of graphene-CdSe composite was 0.03 g.

2.2.2 Effect of catalyst amount

Experiments were performed to study the rate of degradation with different catalyst amounts ranging from 0.01 to 0.03 g for a MB solution with a concentration of 10 $\mu\text{mol/L}$. The results are shown in Fig. 7. The degradation efficiency of the MB solution increased sharply with catalyst amount. This was due to an increased number of adsorption and catalytic sites on the surface of the graphene-CdSe composite. The result indicated that the optimum catalyst amount for the degradation of MB solution was 0.03 g.

Fig. 7. Degradation efficiency of MB solution by the graphene-CdSe composite under UV irradiation with different amounts of graphene-CdSe composite. The concentration of MB was 10 $\mu\text{mol/L}$.

2.2.3 Effect of MB concentration

The effect of MB concentration on degradation efficiency was investigated by varying the concentration from 100 to 10 $\mu\text{mol/L}$ under 240 min UV irradiation with a catalyst amount of 0.03 g. The results are shown in Fig. 8. The de-

Fig. 8. Degradation efficiency of MB solution with different concentrations by the graphene-CdSe composite under UV irradiation. The amount of graphene-CdSe composite was 0.03 g.

gradation efficiency decreased with an increase in concentration of MB from 100 to 10 $\mu\text{mol/L}$. After UV irradiation for 240 min, the MB solution with a concentration of 50 $\mu\text{mol/L}$ had 20% dye removed while the MB solution with a concentration of 100 $\mu\text{mol/L}$ had only 5.6% dye removed. One possible reason is that at a high MB concentration, some UV light is absorbed by MB molecules in the aqueous solution rather than by the catalyst particles, which reduced the efficiency for the catalytic reaction. Another possible reason is that the intermediate products formed upon the photocatalytic degradation of MB compete with MB molecules for the limited adsorption and catalytic sites on the surface of the catalyst particles, and thus inhibited the degradation of MB to some extent. This result indicated that the optimum MB concentration was 50 $\mu\text{mol/L}$.

2.2.4 Effect of light source

The photocatalytic activity of the graphene-CdSe composite was performed by the degradation of MB solution (50 $\mu\text{mol/L}$) under 240 min of UV light (6 W, $\lambda = 365 \text{ nm}$) and visible light (8 W, $\lambda \geq 420 \text{ nm}$) irradiation with a catalyst amount of 0.03 g. The results are shown in Fig. 9. The results clearly showed that the MB degradation efficiency under UV irradiation for 240 min was 18% while under visible light irradiation for the same time it was 35%. This is due to that the power of the visible light (8 W) was higher than that of the UV light (6W). It also indicated that the graphene-CdSe composite showed photocatalytic activity not only under UV light but also under visible light. Photocatalytic reactions on the graphene-CdSe composite surface can be expressed by the Langmuir-Hinshelwood model [35]. The photocatalytic degradation of MB by the graphene-CdSe composite under UV and visible light obeyed

Fig. 9. Degradation efficiency of MB solution by the graphene-CdSe composite under irradiation of UV light and visible light. The concentration of organic dye was 50 $\mu\text{mol/L}$. The amount of graphene-CdSe composite was 0.03 g.

pseudo-first order kinetics with respect to the concentration of MB:

$$-dc/dt = k_{app}c$$

Integration of the equation (with $c = c_{ads}$ at $t = 0$, with c_{ads} being the initial concentration in the bulk solution after dark adsorption and t the reaction time) lead to

$$-\ln(c/c_{ads}) = k_{app}t$$

where c and c_{ads} are the reactant concentration at time $t = t$ and $t = 0$, respectively, k_{app} and t are the apparent reaction rate constant and time, respectively. Accordingly, a plot of $-\ln(c/c_{ads})$ versus t will yield a slope of k_{app} . The results are displayed in Fig. 10. The linearity of the plot suggested that the photodegradation reaction approximately followed pseudo-first order kinetics with k_{app} of 0.002 min^{-1} and 0.0034 min^{-1} for degradation under UV light and visible light, respectively.

Fig. 10. Apparent first order kinetics, $-\ln(c/c_{ads})$ vs t , for MB degradation on graphene-CdSe composite under UV light (1) and visible light (2) irradiation. The concentration of MB solution was $50 \mu\text{mol/L}$. The amount of catalyst was 0.03 g .

The scheme for the excitation and charge transfer process between CdSe particles and graphene nanosheets under light irradiation is shown in Fig. 11. Under irradiation by visible lamp, the graphene nanosheets act as good electron acceptors [15,36–38] and accept the electrons produced by light irradiation. Meanwhile, the CdSe can be also excited to produce electrons and holes in the conduction band (CB) and valence band (VB) of CdSe. Then the electrons accepted by the graphene nanosheets from light excitation can transfer into the CB of CdSe, thereby increasing the number of electrons as well as the rate of electron-induced redox reactions. The generated electrons (e^-) react with dissolved oxygen molecules and produce oxygen peroxide radicals $\text{O}_2^{\cdot-}$. The positive charged hole (h^+) can react with the OH^- derived from H_2O to form hydroxyl radicals $\text{OH}^\cdot$. The MB molecules then can be photocatalytically degraded by the oxygen peroxide radicals $\text{O}_2^{\cdot-}$ and hydroxyl radicals $\text{OH}^\cdot$ to CO_2 , H_2O , and other mineralization products.

Fig. 11. Graphene acting as a 2D conducting support for CdSe particles.

3 Conclusions

A graphene-CdSe composite was successfully synthesized by a simple hydrothermal method. Only the cubic crystal structure of CdSe was present on the graphene-CdSe composite. The surface of the graphene was coated with CdSe particles. C, Cd, and Se present with high contents in the composite. The graphene-CdSe composite had strong photoabsorption in the UV light and visible light range. The photocatalytic activity of the graphene-CdSe composite was investigated by the degradation of MB, MO, and Rh.B in aqueous solution under UV or visible light irradiation. The graphene-CdSe composite exhibited excellent photocatalytic activity for the degradation of MB solution under visible light irradiation.

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