

SELF-DECOMPOSITION EFFECT OF GRAPHENE BASED CdSe COMPOSITES FOR ORGANIC DYE IN DARK

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ABSTRACT

Herein we obtain CdSe-TiO₂ composite, graphene-CdSe composite and graphene-TiO₂ composite by using a facile hydrothermal method. The as-prepared composites are characterized by Brunauer emmett Teller (BET) surface area measurement, X-ray diffraction (XRD), scanning electron microscopy (SEM) with an energy dispersive X-ray (EDX) analysis, transmission electron microscopy (TEM), UV-vis diffuse reflectance spectra (DRS). According to the decomposition results of methylene blue (MB) solution in dark, it can be observed that the graphene-CdSe composites show a very interesting character, self-decomposition effect of MB in dark.

Keywords: Graphene, CdSe, Hydrothermal, UV-vis DRS, Self-decomposition

INTRODUCTION

In most of the industrial wastewater treatment works, adsorption by activated carbon, advanced chemical oxidation, enhanced coagulation and photochemical process are commonly employed technologies for removal of refractory pollutants from industrial wastes. Among of them, the advance of photochemical processes has made the decomposition of synthesized refractory organics sustainable, especially with the advent of semiconductor photocatalysts.^{1,2} Several semiconductors have been developed to exhibit photocatalytic behavior. One of the most commonly referenced semiconductors for waste degradation is TiO₂.¹ TiO₂ is of great interest mainly due to its unique properties, such as high photoactivity and size dependent optical properties.¹ However, TiO₂ is a wide band gap semiconductor (band gap around 3.2 eV), which adsorbs light only in the UV light with wavelength below near 400 nm, preventing efficient absorption of sunlight in the visible region. There are also many semiconductors display good photocatalytic activity under visible light ($\lambda > 420$ nm). One of them is cadmium selenide (CdSe), with band gap of 1.7 eV, and its valence electrons can be easily evoked to conduction band when the light wavelength of evoking light is less than or equal to 730 nm.^{3,4} However, all of them can display photocatalytic activity, the light source is indispensable.

Graphene, monolayer of carbon atoms arranged in a honeycomb network, has recently gained revolutionary aspirations⁵⁻⁸ because of its remarkable electronic,⁷ thermal,⁹ and mechanical properties.¹⁰ These unique properties make it a choice as inorganic fillers to improve electrical, thermal and mechanical properties of composite materials.¹¹ Graphene is extremely attractive for energy storage application due to its unique reported properties.¹² And the utilization of graphene oxide to store and shuttle electrons has been also reported recently.¹³

Therefore, the purpose of this study is that prepare the graphene based CdSe and examine its self-decomposition effect for decomposition of methylene blue solution in dark without light irradiation.

EXPERIMENTAL

The experimental work consists of preparation of graphene-CdSe composite, characterization of graphene-CdSe composite and self-decomposition effect of graphene-CdSe composite.

Preparation of graphene-CdSe composite

Preparation of graphene-CdSe composite: Firstly, 5 g sodium sulfite (Na₂SO₃, 95%, Duksan Pharmaceutical Co., Ltd, Korea) and 0.5 g selenium metal powder (Se, DaeJung Chemicals &Metal Co., Ltd, Korea) were dissolved in 30 mL distilled water and refluxed for 1 h to form Na₂SeSO₃ solution. And 0.5 g cadmium acetate dihydrate (Cd(CH₃COO)₂, 98%, DaeJung Chemicals &Metal Co., Ltd, Korea) was dissolved in 2 mL distilled water. 6 mL ammonium hydroxide (NH₄OH, 28%, DaeJung Chemicals &Metal Co., Ltd, Korea) was added to it and the mixture was stirred till it dissolved completely to form Cd(NH₃)₄²⁺ solution. 0.5 g graphene oxide which prepared

by a Hummers-Offeman method in our previous works¹⁴⁻¹⁶ was added into Na₂SeSO₃ solution and Cd(NH₃)₄²⁺ solution under stirring to allow formation of hydrogen bonds between CdSe nanocrystals and graphene oxide. After a hydrothermal reaction at 80 °C for 5 h, graphene oxide was reduced to graphene nanosheet and CdSe compounds naturally grew on its surface to generate a graphene-CdSe composite. The titanium(IV) oxide nanopowder (anatase, □25 nm, 99.7%, metals basis, Sigma-Aldrich, Co., USA) was used as TiO₂ source. The graphene-TiO₂ composite and CdSe-TiO₂ composite used as comparison samples were prepared by using the same method.

Characterization of graphene-CdSe composite

Characterization of graphene-CdSe composite: The Brunauer-Emmett-Teller (BET) surface area of CdSe-TiO₂ composite was evaluated from the N₂ adsorption isotherms at 77 K using a BEL Sorp Analyzer (BEL). X-ray diffraction (XRD, Shimadzu XD-D1) result was used to identify the crystallinity with monochromatic high-intensity CuK α radiation ($\lambda = 1.5406$ Å). Scanning electron microscopy (SEM, JSM-5600) was used to observe the surface state and structure of prepared composites using an electron microscope. Transmission electron microscopy (TEM, Jeol, JEM- 2010, Japan) was used to determine the state and particle size of prepared composite. TEM at an acceleration voltage of 200 kV was used to investigate the number and the stacking state of graphene layers on various samples. TEM specimens were prepared by placing a few drops of sample solution on a carbon grid. The element mapping over the desired region of prepared composite was detected by an energy dispersive X-ray (EDX) analysis attached to SEM. UV-vis diffuse reflectance spectra (DRS) were obtained using an UV-vis spectrophotometer (Neosys-2000) by using BaSO₄ as a reference at room temperature and were converted from reflection to absorbance by the Kubelka-Munk method.

Self-decomposition effect of graphene-CdSe composite

Self-decomposition effect of graphene-CdSe composite: The self-decomposition effect of graphene-CdSe composite was evaluated by using methylene blue (MB, C₁₆H₁₈N₃S-Cl, 99.99+%, Duksan Pure Chemical Co., Ltd, Korea) as the model substrate and the experiment was performed in the dark condition at room temperature. 0.03 g Graphene-CdSe composite was added to 50 mL of 5.0×10⁻⁵ mol/L MB solution which was hereafter considered as the initial concentration (c₀). Samples were then withdrawn regularly from the reactor by an order of time, and immediately centrifuged to separate any suspended solid. The clean transparent solutions were analyzed by using a UV-vis spectrophotometer (Optizen POP) at wavelength of 665 nm.¹⁷

RESULTS AND DISCUSSION

Table 1 shows the BET surface area of CdSe-TiO₂ composite, graphene-CdSe composite and graphene-TiO₂ composite. CdSe-TiO₂ composite and graphene-TiO₂ composite have similar value of BET surface area, which is 112.73 m²/g and 101.38 m²/g, respectively. However, the graphene-CdSe

composite has much smaller BET surface area, only is 10.46 m²/g. These results can consider that CdSe-TiO₂ composite has highest adsorption effect for MB solution, graphene-TiO₂ composite is next, and graphene-CdSe composite has lowest adsorption effect for MB solution.

To confirm the structures, the powder XRD patterns of CdSe-TiO₂ composite, graphene-CdSe composite and graphene-TiO₂ composite were recorded, as shown in Fig. 1. The peak appearing at around 25.9° corresponds to the (002) diffraction peak of graphite from the graphene (JCPDS 01-0646).¹⁸ The strong diffraction peaks appearing at about 25.3, 37.9°, 47.8°, 54.3°, 55° and 62.7° can be assigned to the (101), (004), (200), (105), (211) and (204) crystal planes of anatase TiO₂ (JCPDS No. 21-1272).^{19,20} Some peaks around 2θ of 42° and 49.6° which can be indexed to the characteristic peaks (220), and (311) plane reflections of cubic crystal structure CdSe with lattice constants of 6.05 Å (JCPDS No. 65-2891)^{21,22} can be also observed. No peaks for impurities are detected, indicating that the hydrothermal method used in this study is responsible for the formation of the graphene-CdSe composite.

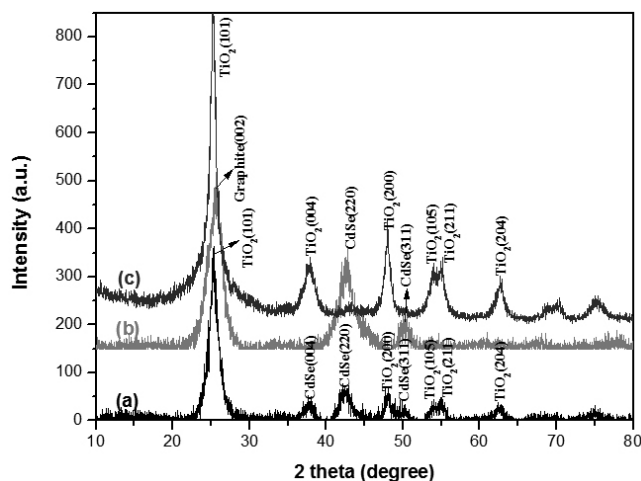


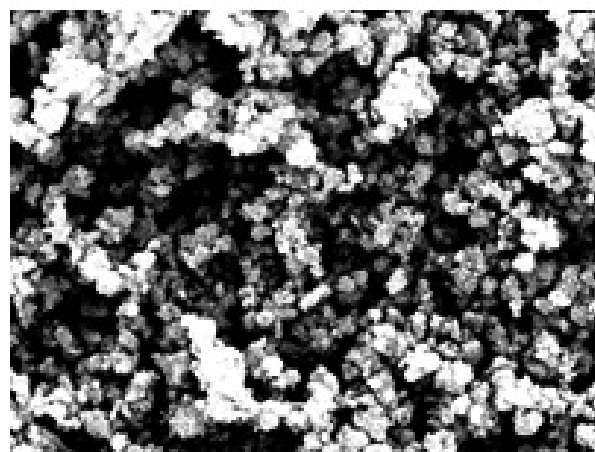
Figure 1. XRD patterns of CdSe-TiO₂ composite (a), Graphene-CdSe composite (b) and Graphene-TiO₂ composite (c).

Fig. 2 shows the SEM microphotographs of CdSe-TiO₂ composite, graphene-CdSe composite and graphene-TiO₂ composite. For CdSe-TiO₂ composite, TiO₂ particles homogenously coated on the spherical-shaped CdSe particles with particle size of 100 nm, as shown in Fig. 2 (a). For graphene-CdSe composite, spherical-shaped CdSe particles are coated on the surface of graphene can be observed from Fig. 2 (b). For graphene-TiO₂ composite, shown in Fig. 2 (c), TiO₂ particles are also coated on the surface of graphene. More detailed information of the surface state and particle size of graphene-CdSe composite can be confirmed by the TEM. Fig. 3 shows the TEM images of graphene nanosheet and graphene-CdSe composite. The 2D structure of graphene sheets can be observed from the Fig. 3 (a), indicates the surface is very smooth. Comparison with it, for graphene-CdSe composite, the CdSe particles are homogenously coated on the surface of 2D structure graphene can be clearly observed from Fig 3. (b).

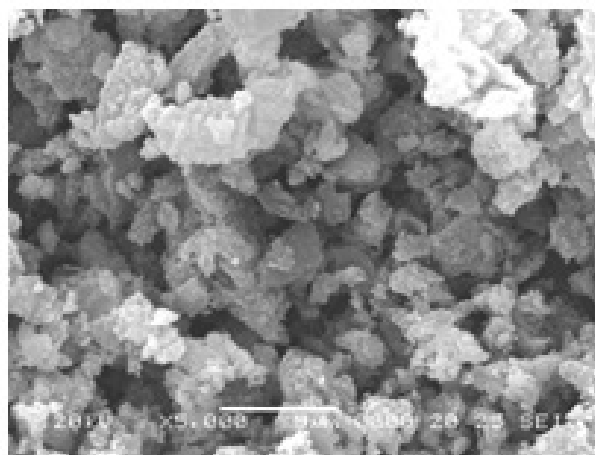
To get information about change in elements, the prepared graphene-CdSe composite was examined by EDX. Fig. 4 and Table 1 show the EDX microanalysis of CdSe-TiO₂ composite, graphene-CdSe composite and graphene-TiO₂ composite. For graphene-CdSe composite, main elements such as C, Cd, Se, O, Na and S are existed. The strong C signal should mainly originate from graphene nanosheets. The Cd, Se, O, Na and S peak comes from the precursor materials Cd(CH₃COO)₂ and Selenium metal powder. No impurity elements can be observed in Fig. 4 (b), indicated high purity graphene-CdSe composite was prepared.

Fig. 5 shows the UV-vis diffuse reflectance spectra of CdSe-TiO₂ composite, graphene-CdSe composite and graphene-TiO₂ composite. It can be seen from figure that CdSe/TiO₂ composite and graphene-TiO₂ composite have absorption edge at 740 nm and 430 nm, indicate that the CdSe/TiO₂ composite and graphene-TiO₂ composite absorb light at wavelength less than 740 nm and 430 nm, respectively. However, for graphene-CdSe composite, no absorption edge can be observed and high absorption intensity can be also observed from 400 nm to 1100 nm. As we know, the pristine TiO₂ materials can only absorb

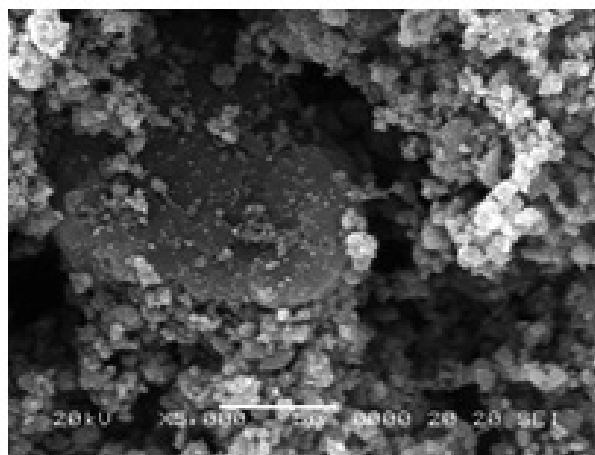
the light at wavelength less than 400 nm, which belong to ultraviolet ray range. So, it can be indicated that introduction of grapheme, the graphene-CdSe composite have excellent activity under visible light region.



(a)

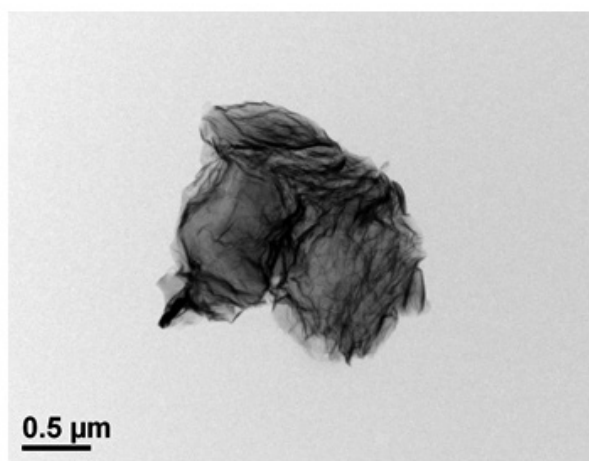


(b)



(c)

Figure 2. SEM microscopes of CdSe-TiO₂ composite (a), Graphene-CdSe composite (b) and Graphene-TiO₂ composite (c).



(a)

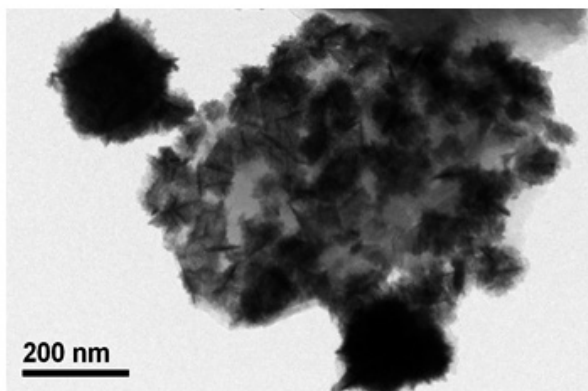
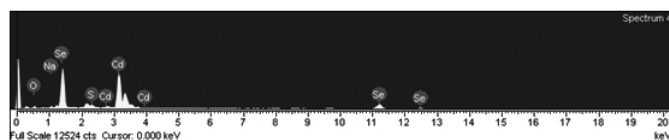
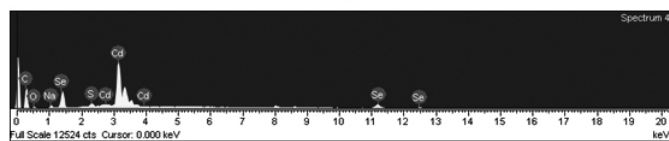


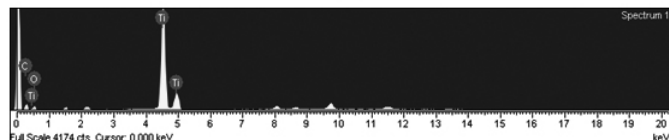
Figure 3. TEM image of graphene (a) and graphene-CdSe composite (b).



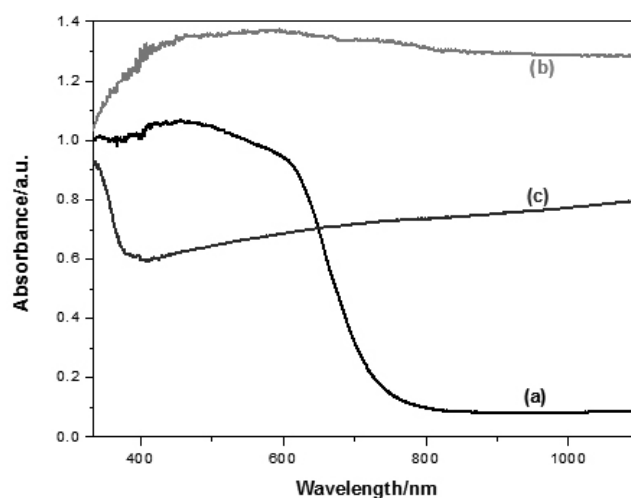
(a)



(b)



(c)

Figure 4. EDX microanalysis of CdSe-TiO₂ composite (a), Graphene-CdSe composite (b) and Graphene-TiO₂ composite (c).Figure 5. UV-vis diffuse reflectance spectra of CdSe-TiO₂ composite (a), Graphene-CdSe composite (b) and Graphene-TiO₂ composite (c).

The self-decomposition effect of graphene-CdSe composite is performed in dark condition by decomposition of MB solution. Fig. 6 represents the decomposition of MB solution over CdSe-TiO₂ composite, Graphene-CdSe composite and CNT-TiO₂ composite by varying the time in dark condition. It has been known that the MB solution containing prepared composite maintained continuously in the dark for 2 h and establishment of adsorption/desorption equilibrium of MB solution could be reached. And this adsorption effect is mainly subjected to BET surface area of prepared composite. From the results of BET surface area of prepared composite, the CdSe-TiO₂ composite has largest BET surface area, graphene-TiO₂ is next, graphene-CdSe composite has smallest BET surface area. However, from the Fig. 7, after maintaining continuously in the dark for 2 h, the graphene-CdSe composite displays best decomposition effect for MB solution, which decomposed 40%. The graphene-TiO₂ composite decomposes 8% of MB solution, and the CdSe-TiO₂ composite shows lowest decomposition effect for MB solution, which decomposed only 2%. More interestingly, when we extend the time of the MB solution containing prepared composite in dark continuously, the CdSe-TiO₂ composite and graphene-TiO₂ composite have no decomposition for MB solution. However, the graphene-CdSe composite decomposes the MB solution continuously and the MB solution has been decomposed 94% when the time extended to 20 h. This phenomenon can be only explained by the self-decomposition effect of the graphene-CdSe composite.

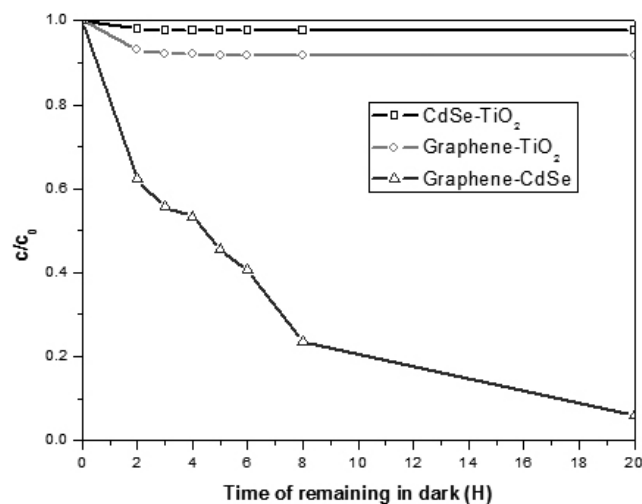
Figure 6. Decomposition efficiency of MB solution by CdSe-TiO₂ composite, graphene-CdSe composite and graphene-TiO₂ composite in dark condition. The concentration of MB is 5×10^{-5} M; the amount of composite is 0.03 g.

Table 1. BET surface area, element microanalysis of CdSe-TiO₂ composite, graphene-CdSe composite and graphene-TiO₂ composite.

Samples	BET (m ² /g)	Elements					
		C (%)	Ti (%)	O (%)	Cd (%)	Se (%)	Na and S (%)
CdSe-TiO ₂ composite	112.73	-	31.98	31.06	18.34	11.36	7.26
Graphene-CdSe composite	10.46	34.49	-	5.45	45.47	11.8	2.79
Graphene-TiO ₂ composite	101.38	29.13	30.48	40.39	-	-	-

The electrons storage and transfer effect of graphene nanosheet can be explained as following. When the graphene-CdSe composite has been prepared, it was kept in a clear bottle and irradiated by the fluorescent lamp in the lab. The fluorescent lamp (32 W, 32SSEX-D, Osram, Korea) has wavelength of 400~1000 nm with main wavelength of 750~1000 nm. According to the UV-vis diffuse reflectance spectra, we can know that the graphene-CdSe composite has high absorption intensity of light at wavelength between 400 nm to 1100 nm. So the graphene nanosheets can absorb many electrons (e⁻) from the fluorescent light and store these electrons. After mixing with MB solution in dark, these electrons (e⁻) can sequential transfer into the conduction band (CB) of CdSe. As described in our recent work²³ which we had confirmed the band gap of CdSe was 1.74 eV. So the electrons (e⁻) can easily shift from the lowest-energy state in CB to the highest-energy state in the valence band (VB). When the electrons collected enough, an electron can be excited from VB to CB. Meanwhile, the hole (h⁺) can be performed in the VB of CdSe. This process can be carried out sequentially due to a larger amount of electrons stored on the surface of graphene sheet. The excited electrons (e⁻) probably react with dissolved oxygen molecules and produce oxygen peroxide radical O₂^{-•}, the performed hole (h⁺) may react with the OH⁻ derived from H₂O to form hydroxyl radical OH[•]. The MB molecule absorbed on the surface of graphene-CdSe composite then can be degraded by oxygen peroxide radical O₂^{-•} and hydroxyl radical OH[•] to CO₂, H₂O and other mineralization.

CONCLUSIONS

Graphene-CdSe composite have been successfully prepared by a simple hydrothermal method. The prepared Graphene-CdSe composite has very small BET surface area. The diffraction peak of graphite and cubic crystal structure CdSe can be observed from XRD pattern. SEM and TEM results show the CdSe particles are homogenously coated on the surface of 2D structure graphene. Some main elements such as C, Cd, Se and Na are existed in Graphene-CdSe composite from EDX element microanalysis. From UV-vis diffuse reflectance spectra, no absorption edge can be observed and high absorption intensity can be also observed from 400 nm to 1100 nm. As the results of decomposition of MB solution in dark, it can be indicated that the graphene-CdSe composite has self-decompose effect due to the storage and transfer electrons effect of graphene nanosheet.

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