Research Article

Synthesis of Carbon Nanomaterials-CdSe Composites and Their Photocatalytic Activity for Degradation of Methylene Blue

Ming-Liang Chen, 1, 2 Ze-Da Meng, 1 Lei Zhu, 1 Chong-Yeon Park, 1 Jong-Geun Choi, 1 Trisha Ghosh, 1 Kwang-Youn Cho, 3 and Won-Chun Oh 1

1 Department of Advanced Materials Science & Engineering, Hanseo University, Daekogri 360, Haemimyun, Seosansi, Chungnam 356-706, Republic of Korea
2 School of Environmental Science and Engineering, Nanjing University of Information Science & Technology, Nanjing, Jiangsu 21004, China
3 Korea Institute of Ceramic Engineering and Technology, Seoul 153-801, Republic of Korea

Correspondence should be addressed to Won-Chun Oh, wc_oh@hanseo.ac.kr

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We use multi-walled carbon nanotube (MWCNT) and graphene as carbon nanomaterials to obtain carbon nanomaterials-CdSe composites using a facile hydrothermal method. The intrinsic characteristics of resulting composites were studied 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 spectrophotometer. The as-prepared carbon nanomaterials-CdSe composites possessed great adsorptivity of dyes, extended light absorption range, and efficient charge separation properties simultaneously. Hence, in the photodegradation of methylene blue, a significant enhancement in the reaction rate was observed with carbon nanomaterials-CdSe composites, compared to the CdSe compound.

1. Introduction

Carbon nanotube (CNT) was discovered in 1991 by Iijima [1] it has received considerable attention from many researchers [2–4] due to its interesting properties and wide applications. In addition to its outstanding mechanical characteristics, CNT exhibits excellent electrical, mechanical, magnetic, and thermal properties. These superior properties provide exciting opportunities to produce advanced materials for new applications [5–8]. A common use of CNT is to disperse it in other media as a reinforcement to enhance and modify their original characteristics. Graphene is considered a 2-dimensional carbon with a one-atom-thick planar sheet of sp² bonded carbon atoms that are densely packed in a honeycomb crystal lattice. Graphene is predicted to have remarkable properties, such as high thermal conductivity, superior mechanical properties, and excellent electronic transport properties [9–12]. These intrinsic properties of graphene have generated enormous interest for its possible implementation in a myriad of devices [13].

Recently, semiconductor nanoparticles such as TiO₂, ZnO, and CdSe quantum dot have been utilized to decorate CNT or graphene nanosheets to prepare carbon nanomaterials-based materials with remarkable optical and photovoltaic properties [14, 15]. Cadmium selenide (CdSe) is a kind of semiconductor with forbidden zone 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. In addition, CdSe is good photocatalyst because of the rapid generation of electron-hole pairs by photo-excitation and the highly negative reduction potentials of excited electrons [16, 17]. Functionalizing CNT and graphene nanosheets with CdSe not only can combine these advantages of CdSe and CNT and graphene nanosheets but also may result in new properties.
Hence, we used multiwalled carbon nanotube (MWCNT) and graphene as carbon nanomaterials for the synthesis of carbon-nanomaterials-CdSe composites. The intrinsic characteristics of resulting composites were studied 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 spectrophotometer. The photocatalytic activity of the as-synthesized samples was evaluated by degrading methylene blue (MB) under irradiation of visible light.

2. Experimental

2.1. Materials. Crystalline MWCNT powder (diameter: 20 nm, length: 5 μm) of 95.9 wt. % purity from Carbon Nano-material Technology Co., Ltd., Korea, was used as one of carbon nanomaterials. Graphene oxide which was prepared by a Hummers-Offeman method in our previous works [18–20] was used as another carbon nanomaterial. For the oxidation of MWCNT, m-chloroperbenzoic acid (MCPBA) chosen as the oxidizing agent was purchased from Acros Organics, New Jersey, USA. Benzene (99.5%) was used as the organic solvent which is purchased from the Samchun Pure Chemical Co., Ltd, Korea. Cadmium acetate dihydrate (Cd(CH3COO)2, 98%), selenium metal powder (Se), and all experiments were carried out using distilled water.

2.2. Synthesis of CdSe and Carbon-Nanomaterials-CdSe Composites

2.2.1. Synthesis of CdSe. For the synthesis of CdSe compound, the sodium selenosulfite (Na2SeSO3) solution and Cd(NH3)42+ solution were prepared at first. Na2SO3 (5 g) and selenium metal powder (0.5 g) were dissolved in 30 mL distilled water and refluxed for 1 h to form Na2SeSO3 solution. Meanwhile, Cd(CH3COO)2 (0.5 g) was dissolved in 2 mL distilled water. NH4OH (6 mL) was added to it, and the mixture was stirred till it dissolved completely to form Cd(NH3)42+ solution. Finally, Cd(NH3)42+ solution and Na2SeSO3 solution were mixed together, and the mixture was stirred and refluxed for at least 5 h. After the temperature of the mixture was brought down to room temperature and the mixture was filtered through Whatman filter paper, the solids obtained were collected and washed with distilled water for 5 times. After being dried in vacuum at 353 K for 8 h, the graphene-CdSe composite and CNT-CdSe composite were obtained.

2.2.2. Synthesis of Carbon-Nanomaterials-CdSe Composite. MWCNT had to functionalize by MCPBA to introduce active function groups as it was very stable. 1 g MCPBA was melted in 60 mL benzene. And then 0.5 g MWCNT was put into the oxidizing agent. The mixture was stirred with a magnet for 6 h at 343 K. Then the MWCNT was dried at 373 K and spared.

The same amounts of graphene oxide and functionalized MWCNT were mixed with Cd(NH3)42+ solution and Na2SeSO3 solution which were prepared as above mentioned, and the mixtures were stirred and refluxed for at least 5 h, respectively. After the temperature of the mixtures was brought down to room temperature and the mixtures were filtered through Whatman filter paper, the solids obtained were collected and washed with distilled water for 5 times.

2.3. Characterization. X-ray diffraction (XRD, Shimadzu XD-D1) result was used to identify the crystallinity with monocromatic high-intensity CuKa radiation (λ = 1.5406 Å). Scanning electron microscopy (SEM, JSM-5600) was used to observe the surface state and structure of prepared composite using an electron microscope. Transmission electron microscopy (TEM, Jeol, JEM-1010, 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.

2.4. Photocatalytic Activity Measurements. The photocatalytic activity under visible light (KLD-08L, 220 V, 50–60 Hz, 8W, pure white, λ > 420 nm, Fawoo Tech) irradiation of the carbon-nanomaterials-CdSe composites was evaluated by using MB as the model substrate. In an ordinary photocatalytic test performed at room temperature, 0.05 g graphene-CdSe composite and CNT-CdSe composite were added to 50 mL of 5.0 × 10−5 mol/L MB solution, respectively. Before turning on the visible lamp, the solution mixed with composite was kept in the dark for at least 2 h, allowing the adsorption/desorption equilibrium to be reached. Then, the solutions were irradiated with visible lamp. The first sample was taken out at the end of the dark adsorption period (just before the light was turned on), in order to determine the MB concentration in solution after dark adsorption, which was hereafter considered as the initial concentration (c0). Samples were then withdrawn regularly from the reactor by an order of 30 min, 60 min, 90 min, 120 min, 180 min, and 240 min, 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 [21].
3. Results and Discussions

3.1. Characterization. Figure 1 shows X-ray patterns of CdSe compound, graphene-CdSe composite, and CNT-CdSe composite. For CdSe compound, the XRD diffraction peaks around 2θ of 25.4°, 42°, and 49.6°, which can be indexed to the characteristic peaks (111), (200), and (311) plane reflections of cubic crystal structure CdSe with lattice constants of 6.05 Å according to the standard powder diffraction data (ICPDS No. 65–2891 for CdSe, cubic) [22, 23]. However, for graphene-CdSe composite and CNT-CdSe composite, only the typical peaks arising from CdSe were detected. The (002) and (100) reflection around 2θ of 25.9° and 42.7° due to graphene overlaps the cubic (111) and (200) reflection around 2θ of 25.4° and 42° of CdSe. Therefore, the intensity of peaks at 25.4° and 42° in both of graphene-CdSe composite and CNT-CdSe composite is stronger than that in CdSe compound and the micromorphology of graphene-CdSe composite and CNT-CdSe composite is different from that of the mixture of Graphene or MWCNT and CdSe.

Figure 2 shows the SEM microphotographs of CdSe compound, graphene-CdSe composite, and CNT-CdSe composite. From Figures 2(a) and 2(b), very uniform spherical-shaped CdSe particles with agglomerate can together be observed. For graphene-CdSe composite (Figures 2(c) and 2(d)), spherical-shaped agglomerated CdSe particles are coated on the surface of graphene. For CNT-CdSe composite, as shown in Figures 2(e) and 2(f), spherical-shaped agglomerated CdSe particles are mixed with MWCNT. More detailed information of the surface state can be confirmed by the TEM. Figure 3 shows the TEM image of graphene-CdSe composite and CNT-CdSe composite, from which it can be clearly observed that the CdSe particles are homogeneously coated on the surface of 2D structure graphene for graphene-CdSe composite. For CNT-CdSe composite, the surface of MWCNTs has been coated with CdSe layers uniformly with particle size of about 10 nm.

To get information about change in elements and element weight%, the prepared CdSe compound, graphene-CdSe composite, and CNT-CdSe composite were examined by EDX. The weight % of main elements in CdSe compound, graphene-CdSe composite, and CNT-CdSe composite is shown in Table 1. Main elements, Cd and Se, were detected in all of CdSe compound, graphene-CdSe composite, and CNT-CdSe composite. Beside these two kinds of elements, Cd and Se, main element carbon was also exited in graphene-CdSe composite and CNT-CdSe composite. Some impurities such as Na, S, and O were also found in composites. The EDX results reveal the presence of CdSe and carbon with high content in prepared samples.

Figure 4 shows the UV-vis diffuse reflectance spectra of CdSe compound, graphene-CdSe composite, and CNT-CdSe composite at wavelength from 400 nm to 1100 nm. The reflectance characteristics of the CdSe compound were quite similar to those of the graphene-CdSe composite and CNT-CdSe composite except that the CdSe compound has an absorption edge at 830 nm. Substituting the critical wavelength of CdSe = 830 nm into the Planck equation (E = hv), the band gap energy of CdSe is 1.74 eV, which is fairly close to literature value of 1.65 to 1.8 eV (CdSe) [16, 17]. Moreover, the prepared samples exhibit strong absorption in the visible light region with wavelength at 400–800 nm, assigned to the band adsorption of CdSe. And the absorption of graphene-CdSe composite and CNT-CdSe composite is higher than that of CdSe compound in visible light region, indicating the graphene-CdSe composite and CNT-CdSe composite would exhibit more excellent photoactivity than CdSe compound.

3.2. Photodegradation of MB Solution. The photocatalytic activities of the prepared samples were evaluated by the photodegradation of MB aqueous solution under visible light irradiation. The decreasing concentration of MB in the photocatalytic reaction was used to evaluate the activity of the composite. Figure 5 represents the degradation of MB over CdSe compound, graphene-CdSe composite, and CNT-CdSe composite under visible light irradiation, from which we can clearly see that the concentration of the MB solution gradually diminishes with increasing irradiation time for all of samples. After irradiation for 240 min, the CdSe compound has almost no photocatalytic activity toward the
photodegradation of MB solution. The presumed reason is that a mass of visible light may be absorbed by the MB molecules in aqueous solution rather than the CdSe particles for high MB concentration, which can reduce the efficiency of the catalytic reaction. However, for graphene-CdSe composite and CNT-CdSe composite, a much excellent photocatalytic activity toward the photodegradation of MB solution can be observed and the MB concentration is removed 55% after irradiation under visible light for 240 min. The high activity can be attributed to the synergetic effects of high electron absorptivity and high charge mobility of carbon nanomaterials.

The scheme of excitation and charge transfer process between CdSe particles and graphene nanosheets or CNT under light irradiation is shown in Figure 6. Under irradiation by visible lamp, the graphene nanosheets and CNT
acting as good electron acceptors [14, 24–26] can accept the electrons by light irradiation. Meanwhile, the CdSe can be also excited to produce the electrons and holes in the conduction band (CB) and valence band (VB) of CdSe. Then the electrons accepted by graphene nanosheets and CNT from light 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\(^-\)) probably react with dissolved oxygen molecules and produce oxygen peroxide radical O\(_2^{•-}\), and the positively charged hole (h\(^+\)) may react with the OH\(^-\) derived from H\(_2\)O to form hydroxyl radical OH\(^•\). The MB molecule then can be photocatalytically degraded by oxygen peroxide radical O\(_2^{•-}\) and hydroxyl radical OH\(^•\) to CO\(_2\), H\(_2\)O, and other mineralization.

### 4. Conclusions

High-purity carbon nanomaterials-CdSe composites were prepared by a simple hydrothermal method. Typical cubic CdSe structure can be observed in XRD patterns of all of carbon nanomaterials-CdSe composites. From the SEM and TEM results, for graphene-CdSe composite, spherical-shaped agglomerated CdSe particles are homogenously coated on the surface of 2D structure graphene for graphene-CdSe composite. For CNT-CdSe composite, the surface of MWCNTs has been coated with CdSe layers uniformly with particle size of about 10 nm. The carbon nanomaterials-CdSe composites show a higher absorption under visible light region compared with CdSe compound. The MB degradation results suggest the carbon-nanomaterials-CdSe composites are much more effective photocatalyst than CdSe.
compound. The high activity can be attributed to the synergetic effects of high electron absorptivity and high charge mobility of carbon nanomaterials.

References


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