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Synthesis of CdS with Graphene by CBD(Chemical Bath Deposition) Method and Its Photocatalytic Acitiviy

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Abstract Synthesis of RGO (reduced graphene oxide)-CdS composite material was performed through CBD (chemical bath deposition) method in which graphene oxide served as the support and Cadmium Sulfate Hydrate as the starting material. Graphene-based semiconductor photocatalysts have attracted extensive attention due to their usefulness for environmental and energy applications. The band gap (2.4 eV) of CdS corresponds well with the spectrum of sunlight because the crystalline phase, size, morphology, specic surface area and defects, etc., of CdS can affect its photocatalytic activity. The specific surface structure (morphology) of the photocatalyst can be effective for the suppression of recombination between photogenerated electrons and holes. Graphene (GN) has unique properties such as a high value of Young's modulus, large theoretical specific surface area, excellent thermal conductivity, high mobility of charge carriers, and good optical transmittance. These excellent properties make GN an ideal building block in nanocomposites. It can act as an excellent electron-acceptor/transport material. Therefore, the morphology, structural characterization and crystal structure were observed using various analytical tools, such as X-ray diffraction, scanning electron microscopy, transmission electron microscopy, and Raman spectroscopy. From this analysis, it is shown that CdS particles were well dispersed uniformly in the RGO sheet. Furthermore, the photocatalytic property of the resulting RGO-CdS composite is also discussed in relation to environmental applications such as the photocatalytic degradation of pollutants. It was found that the prepared RGO-CdS nanocomposites exhibited enhanced photocatalytic activity as compared with that of CdS nanoparticles. Therefore, better efficiency of photodegradation was found for water purification applications using RGO-CdS composite.

Key words CdS-graphene, nanocomposites, photocatalysts, chemical bath deposition.

1. Introduction

Clean, renewable and green energy sources are significant challenges confronting in the new century. There is an increasing concern about its impact on climate change. Thus, the development of green, renewable energy sources is of central importance to address the future global demand of a carbon-neutral energy cycle. Among various renewable energy resources, solar energy represents the ultimate renewable source. Urgent breakthroughs are required in both fundamental science and applied technologies to enable a highly efficient and economic approach for harnessing solar energy. Some semiconductors can act as photocatalysts for light-induced chemical transformations.[1-6] The photogenerated holes and electrons play a very important role in pollutant degradation and photocatalytic disinfection. However, the photogenerated electrons and holes in the excited states are unstable and can easily recombine, dissipating the input energy as heat, which results in low efficiency of photocatalysis.

The band gap(2.4 eV) of CdS corresponds well with the spectrum of sunlight, and the conduction band edge is more negative than that of the redox potential. Its crystalline phase, size, morphology, specic surface area and defect, etc. can affect its photocatalytic activity. It has been suggested that the specic surface structure (morphology) of photocatalyst could be effective for the suppression of recombination between photogenerated electrons and holes. Graphene(GN) has unique properties such as high values of its Young's modulus(~1.0 TPa), large theoretical specific surface area(2630 m^2/g), excellent thermal conductivity(~5000 $Wm^{-1}K^{-1}$), high mobility of charge carriers(200,000 $cm^2V^{-1}s^{-1}$), and optical transmittance(~97.7%). These excellent properties support GN as ideal building blocks in nanocomposites.[7-11] It can act as an excellent electron-acceptor/transport material. Several attempts have been made to combine semiconductor oxide and graphene to obtain hybrid materials for superior photocatalytic performance.[12-17] However, the existing nano-composites exhibit low photocatalytic efficiency and methods used for fabriucation are high temeprature and cost. Hence, we would like prepare RGO/CdS nanocomposites using chemical bath deposition method.

In this paper, we have prepared RGO/CdS nanocomposites using chemical bath deposition method at 70°C.

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Further, the samples were used to test photocatalytic activity towards degradation of methylene blue dye using visible light.

2. Experimental Procedure

In a typical procedure, reduction of exfoliated GO with hydrazine hydrate, GO(100 mg) was loaded in a 250 ml round-bottom flask and DI water(100 ml) was then added. This dispersion was sonicated using a ultrasonic bath cleaner(150 W) for 1 h. Hydrazine hydrate(1.00 ml, 32.1 mmol) was then added and the solution heated in an oil bath at 100°C under a water-cooled condenser for 24 h over which the reduced GO gradually precipitated out as a black solid. This product was isolated by filtration and dried on the funnel under certain temperature.

The design of a RGO-CdS hybrid is a work described by Fig. 1. In a typical process, about 25 mg of RGO was dispersed in 80 ml of water. 0.5 mM of $CdSO_4$ and Thiourea were added into each 40 ml amount of water. After stirring for 15 min, 20 ml of NH_3 solution was then added and stirred for another 15 min. The suspension

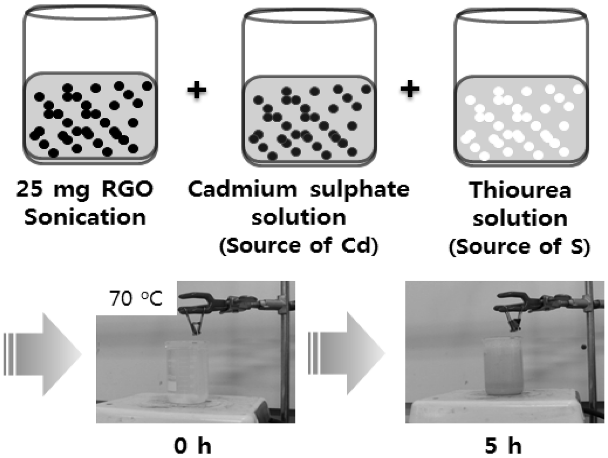

Fig. 1. CBD(Chemical Bath Deposition) to synthesize the CdS-RGO powders.

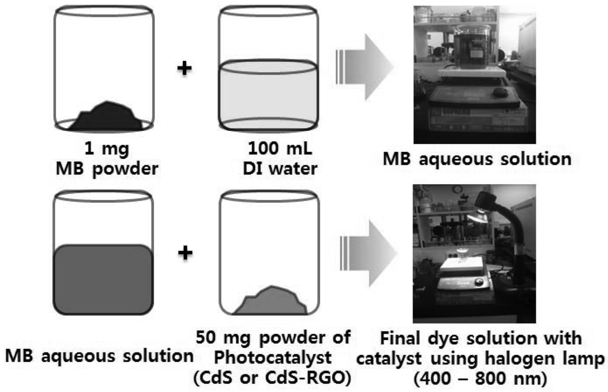

Fig. 2. Process of visible photocatalytic measurment.

was transferred onto heater and kept at 70°C for 5 h. After cooling to room temperature, the green precipitate in the bottom of beaker was collected, filtered, thoroughly washed with water to remove any unreacted chemicals, and dried under vacuum for 4 h.

The photocatalytic performance of the CdS-RGO powders was evaluated by photocatalytic degradation of MB under visible light irradiation. The powders(0.5 g/l) were dispersed in the 100 ml MB aqueous solution(0.1 mg/l). The mixed suspensions were magnetically stirred for 1 h in the dark to reach an adsorption-desorption equilibrium. Under ambient conditions and stirring, the mixed suspensions were exposed to visible irradiation. At certain time intervals, 3 ml of the mixed suspesions were extracted and centrifugated to remove the photocatalyst. The degradation process was monitored by measuring the absorption of MB in filtrate at 663 nm using UV-vis absorption spectrometer. Fig. 2 shows the process of visible photocatalytic measurement.

3. Results and Discussion

There are several analysis to confirm the systhesis of CdS-RGO. For example, SEM and Raman spectroscopy

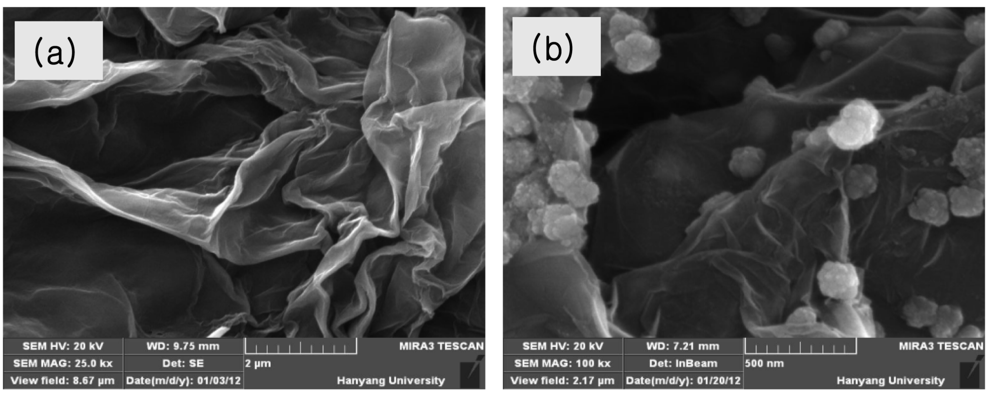

Fig. 3. SEM image of (a) GO(Graphene Oxide) and (b) CdS-RGO(Graphene nanosheet with CdS nanoparticles).

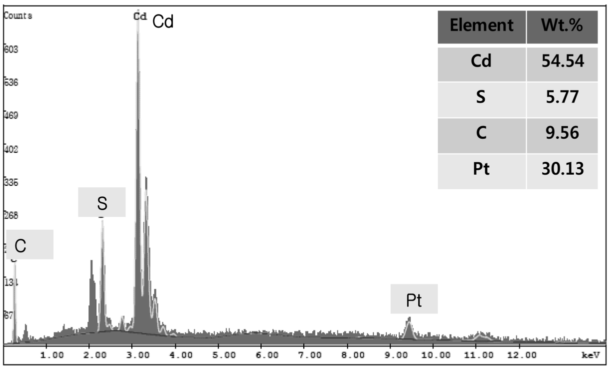

Fig. 4. EDS analysis of CdS-RGO nanocomposites.

are the such analysis to check if there are CdS nanoparticles attached on the graphene nanosheets. As shown in Fig. 3, SEM images for graphene nanosheet and CdS nanoparticles with an average diamter of 150 nm, are uniformly distributed over entire graphene sheet. In case of pure graphene sample, the sheet with its thickness of few nanometer is formed while its size is in micrometers. To find out component of the nanocomposites, EDS analysis was carried out, which is shown in Fig. 4. EDS spectrum clearly shows the peak corresponding to CdS and graphene. This results confirms the formation of nanocomposites. For the more accurate observation, Raman spectroscopy was implemented for CdS-RGO nanocomposites as shown in Fig. 5. The existence of two significant peaks in RGO at about 1334 cm^{-1}(D band) and 1902 cm^{-1}(G band) are attributed to disordered sp^2 bonded carbon and breathing vibrations of six-membered sp^2 carbon rings of E2g and A1g modes in reduced graphene.[18] Moreover one additional peak at 596 cm^{-1} revealed the presence of CdS nanoparticles over graphene nanosheets in the sample. Hence, the CdS-RGO nanocomposites have been successfully fabricated using low temperature chemical bath deposition method.

To check photocatalytic efficiency of the CdS-RGO nanocomposites, photodegradation of methylene blue pollutant measurement has been carried out under visible light. Then, relevant absorbance of samples were measured by UV-visible spectroscopy and relative absorbance plotted in the Fig. 6. It was found that the absorption peak for the MB decreases gradually with increasing irradiation time due to degradation of MB(methelyene blue) molecules. The dye was completely degraded within 80 min. of irradiation for RGO/CdS sample, indicating rapid degradation. However, the dye molecules remained the same after 80 min. of irradiation for pure CdS sample. The change in absorbance of the MB solution with time in the presence of two catalysts, under visible light, is compared as shown in Fig. 6. It was found that there is

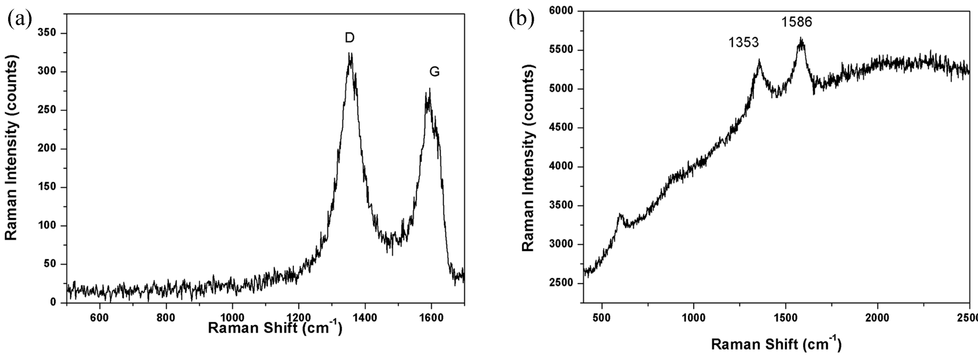

Fig. 5. Raman spectroscopy of (a) RGO and (b) CdS-RGO nano composites.

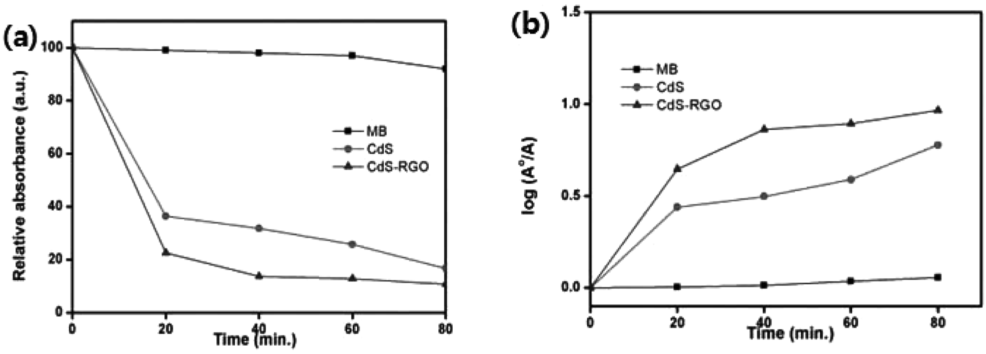

Fig. 6. Photodegradation efficiencies of CdS and RGO-CdS samples towards MB dye degradation under UV light irradiation (a) Relative absorbance for CdS vs. CdS-RGO, (b) log plot for CdS vs. CdS-RGO.

50% increase in photodegradation of pollutant MB for RGO/CdS nanocomposite sample compared with that for pure CdS nanoparticles. The improved catalytic efficiency for RGO/CdS sample is the result of reduction recombination loss due to graphene sheet. Furthermore, the graphene helps effective separation and transportation of photo-electrons.[19-21)]

4. Conclusion

Successful synthesis of RGO-CdS nanocomposites using chemical bath depostion method at low temeprature. FESEM images clearly shows the well dispersion of CdS nanoparticles over graphene nanosheet. The prepared nanocomposites exhibited enhanced photocatalytic activity of as compared with CdS nanoparticles. Therefore, better efficiency of photodegradation was performed for water purification application using RGO-CdS composite.

Acknowledgments

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