Preparation of CdS/graphene Hybrid Aerogels with Effective Photocatalytic Activity

Peng-chao HOU¹, Guang-jian XING¹,*, Sai WANG¹, Chang ZHAO² and Chun-na YU²

¹College of Materials Science & Engineering, Beijing Institute of Petrochemical Technology, Beijing, 102617, China
²Department of Mathematics and Physics, Beijing Institute of Petrochemical Technology, Beijing, 102617, China
*Corresponding author

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Abstract. In this study, we report a facile and one-step method to synthesize CdS/graphene hybrid aerogels (CdS/GA). XRD, FTIR, Raman, XPS spectroscopy, and FESEM technique were applied to characterize the structure and morphology of the aerogels, and the results confirmed that the CdS/GA exhibited a 3D interconnected macroporous framework of graphene sheets with uniform dispersion of CdS nanoparticles. Due to the good absorption property and the reduction of electron-hole pair recombination in CdS, the CdS/GA composites have an excellent photocatalytic activity for MO and RhB under UV irradiation.

Introduction

In recent years, photocatalysts have become a research hotspot because of their rapid oxidation, high oxidation effect, and low or no formation of byproducts [1,2]. CdS is an important semiconductor photocatalyst, and it can potentially be applied in pollutant photodegradation due to its suitable band gap (about 2.4 eV) and high absorption coefficient (>10⁴) [3]. While, the low specific surface area, severe photocorrosion, and high electron-hole recombination of CdS lead to a low photocatalytic activity [4]. Therefore, an attractive strategy is to combine CdS particles with large specific surface area substrate materials to improve the photocatalytic activity, stability and dispersion of CdS.

Compared with two-dimensional (2D) graphene sheets, three-dimensional (3D) graphene aerogels (GAs) could be considered ideal high-performance carrier materials for CdS particles resulting from their high porosity, high specific surface area, excellent electron mobility, high chemical stability and fast mass transport kinetics [5,6]. Therefore, CdS/graphene hybrid aerogels could be considered promising photocatalytic materials and may possess a significant improvement in photocatalytic activity because that the hybrid aerogels integrate the intriguing properties of graphene sheets and CdS, and unique characteristics of aerogels.

In our work, we develop a facile and one-step method to synthesize CdS/graphene aerogels (CdS/GA). Cadmium chloride and thiacetamide were used as cadmium and sulfur sources, respectively, and EDA was used as a reducing agent for GO. The mixture was under hydrothermal conditions to prepare CdS/graphene hydrogels (CdS/GH), then the CdS/GH was freeze-dried to obtain CdS/GA for further structural characterization and photocatalysts activity investigation.

Experimental Section

Materials

Natural graphite powder (purity ≥99.95%), thiacetamide (TAA), cadmium chloride (CdCl₂·5/2H₂O), ethylene diamine (EDA), methyl orange (MO), and Rhodamine B (RhB) were purchased from Shanghai Aladdin Industrial Co., Ltd., Shanghai. All reagents and chemicals were reagent grade and used as received without further purification.
Synthesis of CdS/GA

Graphite oxide (GO) was obtained from natural graphite powder through a modified Hummers method [7]. Then the GO was dispersed in deionized water via an ultrasonic to obtain brown GO solution (5.0 mg mL\(^{-1}\)). A mixed solvent containing 10 mL deionized water, 10 mL as-prepared aqueous GO solution, 0.18 g TAA, and 0.46 g cadmium chloride in a 25 mL Teflon-lined autoclave, then 60 μL EDA was added into the mixture and stirred for approximately 20 min at room temperature, and then heated to 150 °C and kept for 8 h to form CdS/GH. After the reactor cooled down naturally in room temperature, the CdS/GH was subsequently taken out, washed with deionized water several times. Finally, the CdS/GH was freeze-dried to obtain CdS/GA for further characterizations.

Materials Characterization

The structure of the CdS/GA was characterized by X-ray diffraction (XRD, Shimadzu XRD-7000) and LabRAM HR800 spectrometer for Raman spectra. The morphology of CdS/GA was observed using field emission (FE)-SEM (S-4800, Hitachi, Japan). FTIR spectra were recorded on a Nexus 670 (Nicolet, USA) from 400 to 4000 cm\(^{-1}\). X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi) was used to determine the elemental compositions of the as-prepared CdS/GA samples.

Measurement of the Photocatalytic Degradation of MO and RhB

MO and RhB dyes were used to explore the photocatalytic activity of the obtained CdS/GA. In the experiments, 10 mg of CdS/GA was added into aqueous dye solution (10 mL, 10 mg L\(^{-1}\)), then the solution was exposed under the UV irradiation. The concentration of dye was measured by UV-vis spectrometer (Unico 2100, USA) at the maximum absorbance of each dye (465 and 554 nm for MO and RhB, respectively).

Results and Discussion

![Figure 1. XRD (a), Raman (b), and FTIR spectra of the CdS/GA.](image)

Fig.1(a) presents the XRD patterns of the CdS/GA and pristine GA. As is known to all, the typical diffraction peak of GO is about 10.8°, corresponding to the (001) reflection [8]. The GA and CdS/GA instead exhibited relatively broad peaks at 24.3°, corresponding to the (002) plane of graphite. This change indicates the reduction of GO and the restoration of graphitic structures after hydrothermal reaction. The other peaks of CdS/GA were indexed to 25.1°, 28.3°, 36.8°, 44°, 48°, 52.2°, indexed to the diffractions of (100), (101), (102), (110), (103) and (112) planes, matched well with the previous reported XRD pattern of CdS [9], which is confirming that the formation of CdS in the microstructure of graphene aerogels. As shown in Fig. 1(b), two prominent peaks appear at about 1340 and 1593 cm\(^{-1}\), which are assigned to the well-defined D band and G band, respectively. The intensity ratio of the D band to G band (I\(_D\)/I\(_G\)) diagnostically indicates the degree of disorder and defects of carbon materials [10]. The I\(_D\)/I\(_G\) values increased from 0.94 for GA to 1.38 for the CdS/GA, indicating that the defects arose due to the CdS crystals growing onto the graphene sheets.

Fig. 1(c) shows the FTIR spectra of the CdS/GA and GA. The peaks at 3420, 1620, 1380, 1070 cm\(^{-1}\)
can be attributed to -OH, C=O, C-OH, and C-O stretching vibrations, which are related to the hydroxyl and carboxyl. These oxygen-related bands mainly derived from GO, and the peak become weak after reduction, indicating that most of the oxygen-containing groups of GO sheets were eliminated.

Fig. 2 shows the FESEM images of the CdS/GA. As shown in Fig. 2(a), it can be seen that the hybrid aerogel was composed of randomly oriented graphene sheets and exhibited a hierarchical and interconnected porous structure with micropores ranging from several to dozens of micrometers. Fig. 2(b) shows that large quantities of monodisperse particles were grown uniformly on the graphene sheets. The high-resolution FESEM image shown in Fig. 2(c) clearly demonstrates that the CdS nanoparticles possessed a size of nearly 100 nm.

Fig. 3(a) shows the wide scan spectra of GA and CdS/GA, which showed a predominant narrow graphitic C 1s peak at 284.8 eV and an O 1s peak at ca. 532.9 eV. An additional N 1s peak centered at 401 eV can be attributed to the doping of N atoms within aerogels caused by using the ethylenediamine as reducing agent. Besides, the CdS/GA showed more peaks than GA, including Cd 3d peak at ca. 405.8 eV and S 2p peak at ca. 164.2 eV. Fig. 3(b) shows the high-resolution C 1s spectra of the CdS/GA, which can be deconvoluted into three subpeaks: C-C group at ca. 284.8 eV, C-O group at ca. 285.8 eV, and C=O group at ca. 287.4 eV. Fig. 3(c) and 3(d) show the Cd 3d and S 2p peaks of the CdS/GA, respectively. The peaks at 405.8 and 412.3 eV corresponded to the Cd 3d5/2 and Cd 3d3/2, the peak at 164.2 eV corresponded to the S 2p, which further verified the existence of CdS in CdS/GA.

Figure 2. FESEM images of the CdS/GA.

Figure 3. (a) XPS wide scan spectra, and high spectra of (b) C1s, (c) Cd 3d, and (d) S 2p of the CdS/GA.
Figure 4. Photocatalytic of the CdS/GA for MO (a) and RhB (b), C/C_0 versus time plots for the MO(c) and RhB (d).

Fig. 4(a) and 4(b) reveal the temporal evolution of the absorption spectra of MO and RhB aqueous solutions under UV irradiation adsorbed by the CdS/GA, respectively. The MO and RhB absorption peaks decreased gradually with contact time and completely disappeared after about 12 min, indicating the full removal of the dyes from water. Fig. 4(c) and 4(d) shows the C/C_0 versus time plots for the adsorption of MO and RhB solution with the CdS/GA. The insets of Fig. 4(c) and 4(d) illustrate the color of MO and RhB aqueous solution changed over time, until to approximately colorless after photodegradation. The excellent photodegradation ability is due to the higher crystallinity, higher surface-to-volume ratio of the CdS particles, and lower carrier recombination rate, which is the result of the CdS particles tightly distribution onto the graphene sheets.

Conclusions

In summary, the CdS/GA composites were prepared successfully by a facile and one-step method. The CdS/GA possessed prominent interconnected 3D networks decorated with CdS nanoparticles. Owing to the unique integrated properties of CdS and GA, the CdS/GA demonstrated much better photocatalytic performance towards the photocatalytic degradation of organic dye pollutants, such as anionic MO and cationic RhB under UV irradiation. This work provides a new insight into the synthesis of CdS/GA composites, and the composites could be used as an effective photocatalytic degradation material.

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