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Article

Visible-light photocatalytic efficiencies and anti-photocorrosion behavior of CdS/graphene nanocomposites: Evaluation using methylene blue degradation

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A series of CdS nanocrystals/graphene (CdS/GR) nanocomposites with various graphene contents were prepared. Their photocatalytic efficiencies and anti-photocorrosion behavior were studied using methylene blue degradation under visible-light irradiation. The results showed that the introduction of graphene improved the migration efficiency of photogenerated carriers and inhibited charge carrier recombination. The photocatalytic efficiencies of the as-prepared CdS/GR nanocomposites were influenced by the graphene content, achieving a maximum at a graphene content of 4.6 wt% (denoted by CdS/GR-4.6%). The anti-photocorrosion behavior of the CdS/GR-4.6% nanocomposite was further investigated using a photoelectrochemical method and X-ray diffraction analysis. The photocorrosion of CdS nanocrystals was effectively suppressed after the introduction of graphene sheets. Compared with bare CdS nanocrystals, the photocurrent of the CdS/GR-4.6% nanocomposites increased 2.3-fold.

1. Introduction

In recent years, graphene has been recognized as an ideal high-performance photocatalyst carrier or promoter because of its unique atom-thick two-dimensional structure, excellent transparency, high specific surface area, excellent electron mobility, and high chemical stability [1,2]. Various graphene-based semiconductor nanocomposites coupled with suitable semiconductor nanocrystals (NCs) have been designed and prepared, and used in photocatalysis applications, including non-selective processes for the degradation of pollutants [3], selective transformations in organic synthesis [4], and water splitting to provide clean hydrogen energy [5]. Many previous studies have proven that the photocatalytic efficiencies of various graphene-based semiconductor nanocomposites were significantly improved by the introduction of graphene sheets [6,7]. As is generally known, good stability after catalytic reactions is an important index in evaluating catalytic performance because of the stringent ecological and economic demands for sustainability [8]. The rapid deactivation of photocatalysts is an unavoidable issue in most cases, and this seriously limits the applications of photocatalysts. However, a literature survey showed that previous research on graphene-based photocatalysts focused on enhancing photocatalytic activity and selectivity, and catalyst recovery and anti-photocorrosion behavior were not seriously investigated. It is therefore still necessary to investigate the photostabilities of graphene-based nanocomposites to enable their use in practical applications.

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CdS is an important semiconductor photocatalyst, and it can potentially be applied in pollutant photodegradation [9] and water splitting to produce clean hydrogen energy [10]. The band gap of CdS (2.42 eV) is narrower than that of TiO_2 (3.2 eV), which facilitates the use of visible light, and this makes CdS a competitive candidate as a photocatalyst. Unfortunately, previous studies [9,10] have proven that CdS has a low separation efficiency of photogenerated electron-hole pairs and is particularly prone to photocorrosion, which is an inherent disadvantage of CdS photocatalysts and is fatal for its cyclic operation and in environmental applications. To improve the photoactivities and photostabilities of semiconductor photocatalysts, some efforts have been devoted to producing CdS-based nanocomposites by coupling with another semiconductor, a polymer matrix, or carbon nanotubes [9,11–13]. In the resulting CdS/TiO_2 [11], CdS/Bi_2S_3 [12], CdS/polyaniline [9], or CdS/carbon nanotube nanocomposites [13], the coupled materials acted as acceptors for photogenerated electrons, promoting charge separation and leaving too few holes on CdS to cause photocorrosion, leading to enhancement of photoreaction efficiency and significant inhibition of photocorrosion. The photoexcited charges were effectively separated and recombination was delayed as a result of the increased photocatalytic activity and suppression of photocorrosion.

In recent years, CdS/graphene (CdS/GR) nanocomposites have been prepared and used as photocatalysts in various applications, including photodegradation of pollutants [6], water splitting to produce clean hydrogen energy [5,14], and selective organic transformations [15], and the high photocatalytic activities of CdS/GR nanocomposites have been seriously investigated in these previous studies. To the best of our knowledge, the anti-photocorrosion and photostability behavior of CdS/GR nanocomposites have not yet been explored. In this study, we prepared a series of CdS/GR nanocomposites with different graphene contents and investigated their photocatalytic efficiencies and anti-photocorrosion behavior under visible-light irradiation. In the photocatalysis reaction system, methylene blue (MB) was selected as the model dye; MB is an important thiazine and is extensively used as a colorant for paper, cotton, silk, and leather [16]. Ultraviolet-visible (UV-vis) diffuse reflectance absorbance spectra (DRS) and electrochemical impedance spectra (EIS) studies clarified the enhanced photocatalytic efficiencies of CdS/GR nanocomposites. X-ray diffraction (XRD) analysis and photoelectrochemical curves both proved that the nanocomposites could suppress the photocorrosion of CdS NCs in the presence of graphene sheets.

2. Experimental

2.1. Preparation of the CdS/GR nanocomposites

A series of CdS/GR nanocomposites with various graphene contents were synthesized as in our previous work [17–19]. Briefly, 17 mg grapheme oxide (GO) sheets (prepared by the modified Hummers' method) were dispersed in 10 mL twice-distilled water by sonication for 30 min to give a brown solution, and 50 mL 0.035 mol/L $Cd(NO_3)_2$ solution was added drop-by-drop into the as-prepared solution under stirring for 3 h. Then H_2S gas was bubbled through this dispersion for 1 h to form a green CdS/GR precipitation in situ. The resulting solids were centrifuged and washed three times with distilled water and acetone, and dried in vacuum at 45 °C for 24 h. In addition, CdS/GR nanocomposite doped with different graphene amounts were prepared by the above procedure with various amounts of GO sheets and free CdS NCs was obtained in the absence of GO sheets.

2.2. Characterization of the CdS/GR nanocomposites

Transmission electron microscopy (TEM) image was obtained with a JEOL 2100 transmission electron microscope (JEOL, Japan) operated at 200 kV. The UV-vis DRS of the samples were measured using a Perkin-Elmer Lambda 18 UV-vis-NIR spectrometer. XRD analysis was conducted using a Bruker D8 diffractometer with high-intensity Cu K_α (λ = 1.54 Å) radiation. The visible-light source was a 250-W Xe lamp (Beijing Trusttech Co., Ltd.) with an intensity (passing through a 400-nm UV-cut filter) of 100 mW/cm^2. All electrochemical and photoelectrochemical measurements were conducted using a CHI660 B electrochemical analyzer (Chen Hua Instruments, Shanghai, China) with a conventional three-electrode system, in which a glassy carbon electrode (GCE, 3 mm in diameter) was used as the working electrode, Ag/AgCl was used as the reference electrode, and platinum wire was used as the counter electrode. The photoelectrochemical curves were obtained in 0.1 mol/L Na_2SO_4 at 0 V with a scan rate of 100 mV/s. EIS (presented as Nyquist plots) was performed in a 0.1 mol/L KCl solution containing 5 mmol/L $Fe(CN)_6^{3-/4-}$, across a frequency range from 100 kHz to 0.05 Hz at 0.24 V, and the amplitude of the applied sine wave potential in each case was 5 mV.

2.3. Fabrication of modified electrodes

Prior to modification, the GCE was polished with sand paper and then with 1.0, 0.3, and 0.05 μm alumina slurries, and sonicated in a water bath to remove any residues. CdS/GR nanocomposite (1 mg) with 4.6 wt% graphene sheets (denoted by CdS/GR-4.6%) was dispersed in 1 mL of twice-distilled water to produce a CdS/GR-4.6% homogeneous suspension, and then 6 μL of the suspension were cast on the pretreated GCE surface and dried in air at room temperature to form a GCE modified with CdS/GR-4.6% nanocomposite (denoted by CdS/GR-4.6%/GCE). As a comparison, CdS/GCE and blend/GCE (a physical mixture of graphene sheets and CdS NCs with a graphene sheet content of 4.6 wt%) were prepared using similar procedures.

2.4. Photocatalytic measurements

The photocatalytic activities of the as-prepared CdS/GR nanocomposites were investigated using the photodegradation of MB under visible-light irradiation. A 250-W Xe lamp was used as the visible-light source. A UV-cut filter, which can filter out UV light with wavelengths below 400 nm, was placed between the glass tube and the lamp. The CdS NCs and the blend