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Carboxylic acid-functionalized cadmium sulfide/graphitic carbon nitride composite photocatalyst with well-combined interface for sulfamethazine degradation

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ABSTRACT

The carboxylic acid-functionalized cadmium sulfide/graphitic carbon nitride (CdS-TGA/g-C_3N_4) isotype heterojunction was prepared by thermal copolymerization of CdS-TGA/urea, which was formed via the interaction between $-COO^-$ groups on CdS-TGA NPs and -NH_2/-NH groups on urea. It was proposed that the well-developed combined interface between CdS-TGA and g-C_3N_4 was formed in CdS-TGA/g-C_3N_4 and consequently improved the stability and separation of the photo-generated charge carriers. As a result, the CdS-TGA/g-C_3N_4 exhibited significantly enhanced activity for the visible-light photocatalytic degradation of sulfamethazine (SM_2) as compared to CdS/g-C_3N_4. The $O_2\cdot^-$ was found to be the dominant active species for SM_2 decomposition and the possible photocatalytic degradation pathway of SM_2 over CdS-TGA/g-C_3N_4 was through sulfonate elimination. This work demonstrated rational design and preparation of CdS-based heterojunction composites via construction of well-combined interface, which could open up a new way for the development of efficient and stable visible-light photocatalysts.

1. Introduction

Widely used antibiotics as pharmaceuticals in the natural environment have a significant health risk for human beings [1,2]. As one of the most commonly used antibiotics, sulfamethazine (SM_2) has many toxic impacts on wildlife and humans even at very low concentrations [1,3]. Unfortunately, it is difficult to remove these antibiotics pollutants by conventional water treatment processes due to their high chemical stability [4,5]. Therefore, it is urgently essential to develop an economical and efficient technology for the decontamination of antibiotics.

As an environmental-friendly chemistry technology, photocatalysis has drawn much attention to the removal of antibiotics [6–8]. To date, various semiconductor photocatalysts have been reported for antibiotics decontamination under visible-light irradiation, including BiOBr [9], $BiVO_3$ [10], GaN [11] and graphitic carbon nitride (g-C_3N_4) [12–14]. Among them, CdS with a suitable energy band gap (2.4 eV) and high absorption coefficient has been widely used in water-splitting and pollutants decontamination [15,16]. However, the photocorrosion and limited photocatalytic activity largely restrict the practical application of CdS [17,18]. To enhance its photostability and activity, a variety of strategies have been employed, including fabrication of CdS with different morphologies, doping CdS with metal or coupling with magnetic materials, and integrating CdS with other semiconductors to form specific stack architectures [19–23].

In particular, combining CdS with other semiconductors to form heterostructures, such as CdS-TiO_2 [24], CdS-Ta_2O_5 [25] and CdS-WP [26], provides a feasible route to inhibit the recombination of photo-generated electron-hole pairs. It is well known that the migration rate of charge carrier and separation of the photo-generated electron-hole pairs are strongly dependent on the physical and chemical properties of heterostructures [27,28]. The construction of effective heterostructures between two semiconductors depends not only on the electronic structure of the semiconductors, but also largely on other properties, such as lattice match and electron affinity [29]. Recently, g-C_3N_4 has attracted much attention due to its low cost, visible-light response, simple synthesis and chemical stability [30–33]. Considering of the energy levels of g-C_3N_4 and CdS, it is found that their band-structures matched well, which is quite suitable to construct heterostructures [34–36].

Up to now, there have been several reports on the synthesis and

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application of CdS/g-C_3N_4 composites. For instance, Feng et al. [37] prepared CdS/g-C_3N_4 composites by chemical impregnation and subsequent calcination of the separately prepared CdS particles and g-C_3N_4 for photocatalytic hydrogen generation. Cao et al. [38] reported in-situ growth CdS/g-C_3N_4 composites by the solvothermal method for highly efficient photocatalytic hydrogen generation. Fu et al. [34] prepared CdS/g-C_3N_4 composites through an in situ precipitation-deposition method for the photocatalytic degradation of methyl orange (MO). In our previous report, g-C_3N_4/CdS composite was fabricated through a precipitation method for the degradation of methylene blue (MB) [39]. However, previous reports published are rarely focused on the effect of the interaction between CdS and g-C_3N_4 on the photocatalytic activity. Furthermore, there are limited studies available on photodegradation properties of g-C_3N_4/CdS composite towards antibiotic degradation. Since the well-developed combined interface between the materials also plays an important role in the photocatalytic activity of the heterostructure, it is urgent to synthesize CdS/g-C_3N_4 with well-developed combined interface heterostructure composites for efficient antibiotic decontamination.

In this work, the molecular composite precursors consisting of carboxylic acid-functionalized CdS NPs and urea (CdS-TGA NPs/urea) were operated by thermal treatment, in situ creating a novel organic–inorganic composite photocatalysts of CdS-TGA/g-C_3N_4 with closely contacted interfaces. The interaction between $-COO^-$ groups on CdS-TGA NPs and $-NH_2$/$-NH$ groups on urea led to the formation of a well-combined interface, which greatly promoted the transfer of electron-hole pairs and prolonged the lifetime of charge carriers. The obtained CdS-TGA/g-C_3N_4 photocatalysts had significantly enhanced photocatalytic activities for SM_2 degradation and the degradation pathways were also raised. Meanwhile, the effective photo-generated electrons transfer in CdS-TGA/g-C_3N_4 photocatalysts promoted the stability of CdS. The present work demonstrates an effective, facile and economic strategy for development of high-efficiency visible-light photocatalysts with well-combined interface, which provides a new chance for the practical application of CdS-based photocatalysts in antibiotics treatment.

2. Experiment

2.1. Materials

Thioglycollic acid (TGA), NaOH, Na_2S and urea were purchased from Sinopharm chemical reagent Co. Ltd. $Cd(NO_3)_2{\cdot}4H_2O$, ethanol and sulfamethazine (SM_2) were received from Aladdin industrial Inc. All of the chemicals were of analytical grade and used without further purification.

2.2. Preparation of carboxylic acid-functionalized CdS NPs

To modify the surface of CdS with carboxylic acid ($-COOH$), TGA was selected to couple with CdS to form rod-like micelles on the surface of CdS in aqueous phase. Briefly, 0.4 mL TGA were added drop-by-drop, into 80 mM $Cd(NO_3)_2{\cdot}4H_2O$ solution and stirred for 20 min. Then 100 mM Na_2S was added slowly into the resultant mixture after the solution pH was adjusted to 10.5 by 1 M NaOH solution. Next, the mixture was stirred for 30 min and aged for 90 min without stirring at 65 °C. Finally, the orange CdS-TGA nanoparticles (NPs) were obtained and collected by centrifugation, washed with distilled water and ethanol for several times, and dried in oven at 60 °C overnight.

2.3. Preparation of CdS-TGA/g-C_3N_4

The CdS-TGA/g-C_3N_4 photocatalysts were prepared by a typical procedure. Specifically, a certain amount of as-prepared CdS-TGA NPs and 20 g urea were mixed thoroughly in 50 mL distilled water and then the suspension was dispersed by ultrasonication for 20 min. Then the mixture was stirred at 75 °C to remove excess water under stirring and the molecular CdS-TGA NPs/urea composite precursors were obtained. After that, the composite precursors were transferred into an alumina crucible with cover, heated to 450 °C with a heating rate of 2 °C/min and maintained for 120 min in air atmosphere. After cooling down to room temperature, the as-constructed CdS-TGA/g-C_3N_4 was collected by centrifugation, washed with distilled water and dried in oven at 60 °C overnight. The obtained samples were denoted as x CdS-TGA/ y g-C_3N_4, where x and y refer to the mass ratio of CdS and C_3N_4, respectively. For comparison, CdS-TGA NPs were replaced by CdS NPs to prepare CdS/g-C_3N_4 under the same preparation conditions of CdS-TGA/g-C_3N_4.

2.4. Characterization

The X-ray diffraction (XRD) patterns were acquired from a Bruker D8 Advanced diffraction-meter. The transmission electron microscopy (TEM) observations were acquired using a JEM-2100 electron microscope. The Fourier transform infrared (FT-IR) experiment was carried out on a Nexus 870 spectrometer. The X-ray photoelectron spectra (XPS) measurements were carried out on an RBD upgraded PHI-5000C ESCA system (Perkin Elmer) with Mg Kα radiation ($h\nu = 1253.6$ eV). The Schottky curve was obtained on CHI 660E electrochemical workstation equipped with a standard three-electrode system (a platinum foil electrode as the counter electrode and an Ag/AgCl electrode as the reference electrode). The photoluminescence (PL) spectra were recorded by jobinYvon SPEX Fluorolog-3-P spectroscope. The time-resolved fluorescence decay spectra were performed on an Edinburgh FLSP920 spectrophotometer with an excitation wavelength at 338 nm. The UV–vis diffuse reflectance spectra (DRS) were performed on a Hitachi U-3010 UV–vis spectrometer. The photocurrent transient response and electrochemical impedance spectroscopy were carried out on a CHI 660B electrochemical workstation in a standard three-electrode system. The electron paramagnetic resonance (EPR) spectra were obtained on a JEOL JES-FA200 spectrometer. The intermediate products were identified by a high-performance liquid chromatograph equipped with mass spectrometer.

2.5. Photocatalytic degradation of sulfamethazine

The obtained photocatalysts were used in photocatalytic degradation of SM_2 in a quartz tube at the XPA-7 photochemical reactor. Briefly, 0.02 g photocatalysts were suspended in 50 ml SM_2 solution (30 mg L^{-1}). The suspension was kept stirring in the dark for 30 min to reach the adsorption-desorption equilibrium before a 500 W Xe lamp was turned on. At given irradiation time intervals, 1 mL of the suspension was withdrawn and then filtered to remove all photocatalyst particles. The concentration of the residual SM_2 was detected by a high performance liquid chromatography (e2685, Waters) which configured with a Waters 2489 UV–vis detector. For photocatalyst stability test, the used catalysts were washed with distilled water, dried at 60 °C and then used again.

3. Results and discussion

3.1. Physicochemical properties of CdS-TGA/g-C_3N_4

The formation procedure of the CdS-TGA/g-C_3N_4 photocatalyst is illustrated in Fig. 1. TGA is a strong chelating reagent, which can couple with CdS to form carboxylic acid-functionalized CdS NPs (CdS-TGA NPs) in aqueous phase [40,41]. The post-grafting incorporation of CdS-TGA NPs into the networks of g-C_3N_4 was using a Schiff base chemistry reaction accompanied by the thermal polymerization of the CdS-TGA/urea composite precursors [12,42]. In detail, CdS-TGA NPs were added into urea solution, then the molecular CdS-TGA NPs/urea composite precursors were formed through the interaction between $-COO^-$