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Enhanced visible-light-driven photocatalytic activities of 0D/1D heterojunction carbon quantum dot modified CdS nanowires

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ABSTRACT

Zero-dimensional carbon dots (0D C-dots) and one-dimensional sulfide cadmium nanowires (1D CdS NWs) were prepared by microwave and solvothermal methods, respectively. A series of heterogeneous photocatalysts that consisted of 1D CdS NWs that were modified with 0D C-dots (C-dots/CdS NWs) were synthesized using chemical deposition methods. The mass fraction of C-dots to CdS NWs in these photocatalysts was varied. The photocatalysts were characterized using X-ray diffraction, scanning electron microscopy, transmission electron microscopy, X-ray photoelectron spectroscopy, and ultraviolet-visible spectroscopy. Their photocatalytic performance for the spitting of water and the degradation of rhodamine B (RhB) under visible light irradiation were investigated. The photocatalytic performance of the C-dots/CdS NWs was enhanced when compared with that of the pure CdS NWs, with the 0.4% C-dots/CdS NWs exhibiting the highest photocatalytic activity for the splitting of water and the degradation of RhB. The enhanced photocatalytic activity was attributed to a higher carrier density because of the heterojunction between the C-dots and CdS NWs. This heterojunction improved the electronic transmission capacity and promoted efficient separation of photogenerated electrons and holes.

1. Introduction

Energy production and environmental pollution have become increasingly important issues for social and economic development. Photocatalytic technologies show great promise to help solve these problems as they can convert solar energy into chemical energy efficiently [1,2]. Since the discovery of water splitting using TiO_2 by Fujishima et al. [3] in 1972, photocatalytic technology has attracted significant attention [4–6]. However, TiO_2 is a wide bandgap semiconductor (~3.2 eV) and as such can only be excited by ultraviolet light. As ultraviolet energy only accounts for 4%–5% of the solar spectrum, while visible light accounts for the majority of total solar radiation energy, the use of TiO_2 in these applications is limited. Therefore, the development of semiconductor materials that allow photocatalysis when irradiated with visible light is of great importance.

Cadmium sulfide (CdS) is of particular interest as it is a nar-

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row bandgap semiconductor (~2.4 eV) that responds to visible light, has a relatively simple chemical structure and exhibits high photocatalytic performance [7–10]. However, the photogenerated electrons and holes undergo fast recombination, which limits the practical use of CdS. Improving the separation efficiency of photogenerated electron-hole pairs is key to enhancing the photocatalytic activity of CdS. This problem can be solved by controlling morphology [11] and by surface modification of CdS [12,13]. The large specific surface area of 1D CdS NWs and their unique topographic structure favors the transfer of the electrons from the bulk to the surface, which is advantageous for photocatalytic reactions [14]. Surface modification primarily relies on the fabrication of a heterojunction structure using CdS with other materials, such as TiO_2 [15,16], ZnO [17,18], MoS_2 [19] and precious metals (Au [20], Ag [21]). This method improves the photocatalytic performance of CdS. However, these materials require complex and costly preparation methods. Therefore, developing new materials using simple preparation methods for low cost is critical.

Carbonaceous materials, including graphene, carbon nanotubes and carbon quantum dots (CQDs) have proven effective when coupled with photocatalysts at inhibiting the recombination of photogenerated electron-hole pairs because of their unique physical and optical properties [22–25]. Among these carbon-based materials, 0D C-dots are a relatively new carbon nanomaterial with a size below 10 nm, and were first obtained by electrostripping carbon nanotubes in 2004 [26]. As this material is low cost and non-toxic, it has been used for biological imaging, devices, photoelectric chemistry, supercapacitors and photocatalysis [27,28].

The heterojunction formed when C-dots are loaded onto the surface of a semiconductor material can greatly improve its photocatalytic performance and stability [25]. In addition to the up-conversion function of the carbon-based material in these heterojunction systems, C-dots can also replace precious metals as the center of photo-induced electron, which effectively separates the photoinduced carrier [29–32] and results in improved photocatalytic performance. Xia et al. [33] successfully prepared carbon quantum dots/BiOX (X = Br, Cl) hybrid nanosheets to investigate their photocatalytic performance under visible light irradiation. These systems exhibited highly efficient separation of the photogenerated electron-holes pairs and only a small resistance induced by the CQDs was observed using electrochemical impedance spectroscopy (EIS). Huang et al. [34] prepared environmentally friendly CQDs/$ZnFe_2O_4$ photocatalysts and they reported that the CQDs acted as an electron reservoir and transporter as well as a powerful energy-transfer component in the photocatalysis of CQDs/$ZnFe_2O_4$.

In this work, 0D C-dots and 1D CdS NWs were synthesized using microwave and solvothermal methods, respectively. C-dots/CdS NWs heterojunction photocatalysts were then prepared using a simple chemical deposition method. The C-dots/CdS NWs exhibited improved photocatalytic degradation of RhB and hydrogen production during the splitting of water when compared with pure CdS NWs. The mechanisms that caused this enhanced photocatalytic performance were examined.

2. Experimental

2.1. Preparation of 0D C-dots solution and 1D CdS NWs

0D C-dots were prepared using a simple microwave method. In a typical synthesis, glucose (0.2 g) was dispersed in distilled water (10 mL) and subsequently treated in a microwave oven for 10 min.

In a typical synthesis of 1D CdS NWs, $Cd(NO_3)_2{\cdot}4H_2O$ (12.5 mmol) and thiourea (37.5 mmol) were dispersed in ethylenediamine (60 mL). After mixing thoroughly using ultrasound, the mixture was transferred into a Teflon-lined autoclave (100 mL) and heated at 160 °C for 20 h. After centrifugation, the centrifugate was washed three times with deionized water and ethanol and then dried at 60 °C overnight.

2.2. Preparation of 0D/1D C-dots/CdS NWs

C-dots/CdS NWs were prepared using a simple chemical deposition method. In a typical synthesis, a measured amount of 1D CdS NWs was dispersed in distilled water (50 mL) and treated using ultrasonication for 10 min. Subsequently, the C-dot solution was added dropwise into the CdS solution and stirred for 4 h. The amount of solution added was varied to give weight ratios of 0.2%, 0.4%, 0.6%, and 0.8% of the 0D C-dots solution. The mixtures were centrifuged at 8000 r/min, and the resulting products were dried in an oven at 60 °C for 12h. The final products are referred to as 0.2% C-dots/CdS NWs, 0.4% C-dots/CdS NWs, 0.6% C-dots/CdS NWs, and 0.8% C-dots/CdS NWs.

2.3. Characterization

X-ray diffraction (XRD; D/MAX-2500/PC; Rigaku Co., Tokyo, Japan) was used to identify the crystalline structures of the samples. The micro-morphology of as-prepared pure CdS NWs and C-dots/CdS NWs were observed using field emission scanning electron microscopy (FE-SEM, Ultra 55, Zeiss, Germany). The surface microstructure and interfaces of the C-dots/CdS NWs were observed using high-resolution transmission electron microscopy (HRTEM; Tecnai G2 F20, FEI Company, USA). The elementary composition and bonding information of the materials were analyzed using X-ray photoelectron spectroscopy (XPS; Axis Ultra, Kratos Analytical Ltd., England). A UV-visible diffuse reflectance spectrophotometer (UV-vis DRS; U-41000, HITACHI, Tokyo, Japan) was used to determine the optical absorption properties of the samples. The photoluminescence of the as prepared materials were characterized using a fluorescence spectrometer (PL; Fluoro Max-4, HORIBA Jobin Yvon, France).

2.4. Photocatalytic performance and free radical capture testing

Testing the degradation of the dye involved adding the photocatalyst (0.05 g) into a solution of rhodamine B (RhB; 100 mL, 10 mg/L). Before illumination, the mixture was stirred for