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Hierarchical heterostructure of CdS nanoparticles sensitized electrospun TiO_2 nanofibers with enhanced photocatalytic activity

Zhendong Wei [a,1], Yue Li [a,1], Shenglian Luo [a,b,*], Chengbin Liu [a], Deshui Meng [a], Mingyue Ding [a], Guisheng Zeng [a,*]

[a] State Key Laboroator of Chemo/Biosensing and Chemometrics, College of Chemistry and Chemical Engineering, Hunan University, Changsha 410082, People's Republic of China
[b] Key Laboratory of Jiangxi Province for Ecological Diagnosis-Remediation and Pollution Control, Nanchang Hangkong University, Nanchang 330063, People's Republic of China

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ABSTRACT

CdS nanoparticles coated on one-dimensional (1-D) TiO_2 nanofibers with high photocatalytic activity, hierarchical heterostructure were successfully synthesized by a simple and practical electrospinning-assisted route. The CdS nanoparticles were dispersed within the entire surface of the as-electrospun TiO_2 nanofibers, forming the hierarchical heterostructure. And, the composited nanofibers possessed extended light absorption region and lowest recombination rate of the electron–hole pairs. The removal efficiency of methyl blue (MB) over CdS/TiO_2 nanofibers, CdS modified P25, TiO_2 nanofibers and P25 was 80.8%, 73.4%, 72.4% and 51.2%, respectively. The highest photocatalytic activities over CdS/TiO_2 nanofibers might arise from the increased surface area and the favorable electrons-transfer properties. Furthermore, the removal efficiency of MB in the present of Na_2S–Na_2SO_3 as sacrificial agents can be improved by 120% compared to photocatalytic degradation in pure water due to the special redox capacity of suppressing photocorrosion of CdS. It is expected that the present work is notable for understanding the unique properties of the 1-D coupled nanocomposites and applying their practical application in the environmental protection issues.

1. Introduction

During recent decades, the photodegradation of organic pollutants has received extensive attention due to the harmful to human health [1–6]. Considering to utilize the solar energy more effectively, many efforts have been made to develop efficient visible-light photocatalysts. Until now, many visible-light photocatalysts have been developed, such as AgX (X = Cl, Br) [7–9], C_3N_4 [10], graphite oxide [11], Ag_3PO_4 [12], TiO_2-based materials [13–15], and so on. Among these, TiO_2-based photocatalysts still have been recognized as the most promising photocatalyst because it is environmentally friendly, high efficiency, low cost, and high photostability [16–18].

CdS with the narrow band gap of 2.4 eV used to sensitize TiO_2 is an efficient way to fabricate TiO_2-based catalysts with extended absorption in the visible light and higher photocatalytic activity, resulting from a type II heterostructures formed. Several techniques have been developed for the fabrication of CdS–TiO_2 composited nanostructures such as hydrothermal synthesis [19], template growth [20], and sol–gel [21]. To obtain significantly improved photoelectrochemical properties, the architecture of the composite material is critical. Recently, one-dimensional (1-D) TiO_2 nanostructures have attracted increased attention because of their enlarged surface areas and reduced diffusion lengths compared to conventional TiO_2 materials [22,23]. Kamat and co-workers reported that the responses of the photoelectrochemical cell in the visible light performed on CdS modified 1-D TiO_2 was superior to that of CdS modified TiO_2 nanoparticles, because the 1-D structure is useful for separating and directing electrons to the collecting electrode surface [24].

Electrospinning, as one of the technique that fabricate 1-D nanostructure, offering advantages of simplicity, process controllability, low cost and scalability, has been employed in many applications [25–27]. Furthermore, it could build the new platform for fabricating 1-D fibers from mm to nm size ranges in diameter and the as-electrospun nanofibers possess high photocatalytic activity and favorable recycling characteristics due to their 1-D nanostructure and large length to diameter ratio [28].

* Corresponding authors. Address: State Key Laboroator of Chemo/Biosensing and Chemometrics, College of Chemistry and Chemical Engineering, Hunan University, Changsha 410082, People's Republic of China (S. Luo). Tel./fax: +86 731 88823805.
E-mail addresses: sllou@hnu.edu.cn (S. Luo), zengguisheng@hotmail.com (G. Zeng).
[1] These authors contributed equally to this work.

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Herein, we reported a facile method to prepare CdS/TiO_2 heterostructures photocatalyst with efficient electrons-holes separation ability via a simple and practical electrospinning-assisted technique. The formation of CdS nanoparticles on the 1-D TiO_2 nanofibers was carried out by successive ionic layer adsorption and reaction (SILAR) method. Since the nanoparticles provide high surface area to facilitate the MB adsorption and the 1-D TiO_2 nanostructures enhance photo-generated electrons transport due to their enhanced surface-to-volume ratio, the CdS nanoparticles/1-D TiO_2 composite nanofibers could be an ideal structure for photocatalysis application. And, the composited nanofibers simultaneously covered the advantages of extended light absorption range and increased charge separation rate because of the unique properties of hierarchical heterostructure. In the photocatalytic degradation of MB, CdS/TiO_2 nanofibers showed excellent photocatalytic activity superior to the electrospun pure TiO_2 nanofibers, P25 and CdS modified P25. Moreover, we found a small amount of Na_2S–Na_2SO_3 as sacrificial agent was added to the MB solution could effective suppress the photocorrosion of CdS, thus improving the stability of the photocatalyzer and the removal efficiency of MB. This indicating the as-electrospun nanofibers could be reclaimed easily with the help of sacrificial agent without a decrease of the photocatalytic activity. To the best of our knowledge, this was the first report to employ electrospun CdS/TiO_2 for efficient photodegradation of organic pollutions, and we found the sacrificial agent could accelerate the degradation.

2. Experimental section

2.1. Chemicals

Poly (vinylpyrrolidone) (PVP; Mw = 1,300,000) was purchased from Alfa Aesar. TiO_2 (P25, 20% rutile and 80% anatase) was purchased from Degussa. All other reagents and materials involved were obtained commercially from the Beijing Chemical Reagent Plant (Beijing, China) and were used as received without further purification. The water used was ultrapure. The experiments were carried out at room temperature and humidity.

2.2. Characterization

The morphology of the sample was studied using a field-emission scanning electron microscope (FE-SEM; Hitachi S-4800, 5 kV) and high-resolution transmission electron microscopy (HRTEM; JEOL JEM-2100F). Energy dispersive spectroscopy (EDS) attached to the TEM was employed to analyze the composition of the structure. The X-ray diffraction (XRD) patterns of the products were recorded by a Rigaku Dmax 2200 X-ray diffractometer equipped with Cu Kα radiation (λ). Diffuse reflectance absorption spectra (DRS) were obtained on using a Hitachi U-3010 spectroscopy with $BaSO_4$ as a reference. Specific surface areas were measured by Brunauer–Emmett–Teller (BET) nitrogen adsorption–desorption (NOVA 2200e, Quanthachrome, USA.).

2.3. Sample preparation

Typically, 0.45 g of PVP was added to 3 mL ethanol with vigorous stirring for 1 h, obtaining PVP polymer. 1.5 g of titanium tetraisopropoxide ($Ti(O^iPr)_4$) was dissolved in a mixture of 3 mL ethanol and 3 mL acetic acid by stirring for 1 h to obtain the TiO_2 sol. Then the PVP polymer was added to the TiO_2 sol solution, followed by vigorous stirring for 3 h. After that the prepared precursor solution was put into a syringe for electrospinning. An electrical potential of 10 kV was applied at an electrode distance of 15 cm. The as-collected nanofibers were calcined at 450 °C for 3 h.

CdS nanoparticles were deposited on TiO_2 nanofibers using previously reported SILAR method [19]. In a typical procedure, the TiO_2 nanofibers were immersed in a solution containing 0.2 M $Cd(NO_3)_2$ for 2 min, rinsed with deionized water, and then immersed in 0.2 M Na_2S solution for 2 min followed by another rinsing with deionized water. Such a SILAR process was repeated 15 times to get a suitable CdS coating on the TiO_2 electrode. Then, the as-prepared CdS/TiO_2 nanofibers were calcined at 300 °C for 1 h to get the crystal CdS.

2.4. Photoelectrochemical measurements

The photoelectrochemical responses of the samples were carried out with a CHI 660C electrochemical analyzer (CHI Inc., USA) in a three-electrode configuration. All the samples were analyzed under room temperature without bias potential. The as-prepared CdS nanoparticles sensitized TiO_2 electrode was used as the working electrode, a platinum wire as the counter electrode, and an Ag/AgCl (KCl saturated) electrode as the reference electrode. 0.43 M/0.5 M Na_2S–Na_2SO_3 aqueous solution was used as the electrolyte. A 500 W Xe lamp (Beijing Changtuo) was used as UV–visible and visible light source by applying a cutoff filter. The incident light intensity was 100 mW/cm^2 measured by a radiometer (FZ-A, Photoelectric Instrument Factory of Beijing Normal University, China). Electrochemical impedance spectroscopy (EIS) measurements of the samples in 0.1 M KCl solution with 5 mM $[Fe(CN)_6]^{3-/4-}$ electroactive probes were tested to understand the charge transport properties of the heterojuncntion electrode. The amplitude of the sinusoidal wave was 5 mV and the frequency range examined varying from 1 MHz to 100 MHz.

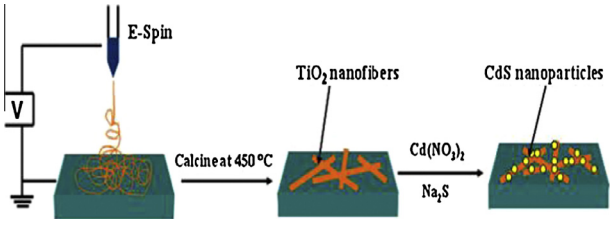
2.5. Photocatalytic experiments

Photocatalytic reaction for the degradation of MB was carried out in a quartz cell under UV–visible light and visible light irradiation of a 500 W Xe lamp with a cutoff filter. The average light intensity was 100 mW/cm^2. The initial concentration of the MB aqueous solution was 5 mg/L^{-1}. All the experiments were performed with magnetic stirring, using 0.43 mM/0.5 mM Na_2S/Na_2SO_3 as sacrificial reagent for the comparison. The photocatalysis process was monitored with a UV–visible spectrophotometer by recording variations of the absorption band maximum (660 nm) in the UV–visible spectrum of MB.

3. Results and discussion

3.1. Photocatalyst characterization

The synthesis route is schematically shown in Scheme 1. The electrospun TiO_2 nanofibers were prepared by electrospinning a $Ti(O^iPr)_4$/PVP solution in ethanol onto the aluminum foil collector followed by annealing at 450 °C. CdS nanoparticles were deposited on the TiO_2 nanofibers through a sequential SILAR method. The



Scheme 1. Schematic illustration of the formation mechanism of CdS modified TiO_2 nanofibers.