Journal of Environmental Chemical Engineering xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

Journal of Environmental Chemical Engineering

journal homepage: www.elsevier.com/locate/jece

Improved visible-light photocatalytic activity and anti-photocorrosion of CdS nanoparticles surface-modified by conjugated derivatives from polyvinyl chloride

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ARTICLE INFO

Article history:
Received 3 March 2015
Accepted 17 May 2015

Keywords:
Photocatalyst
CdS
Polyvinyl chloride
Conjugated polymer
Photodegradation
Photocorrosion

ABSTRACT

Cadmium sulfide (CdS) nanoparticles were surface-modified by conjugated polymer (CPVC) derived from conventional polyvinyl chloride (PVC) via heat-treatment at 150 °C. The as-prepared CPVC/CdS nanocomposites were characterized by Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), transmission electron microscopy (TEM), UV–vis diffuse reflection spectroscopy (UV–vis DRS), photoluminescence spectroscopy (PL), electrochemical impedance spectroscopy (EIS), and photocurrent (I_{ph}). The visible-light photocatalytic activity and stability of the nanocomposites were investigated by evaluating photodegradation of methyl orange (MO) and phenol, and their anti-photocorrosion performance was investigated by determining the concentrations of Cd^{2+} in the photodegrading systems under visible light irradiation. The results show that a small amount of CPVC on the surface of CdS nanoparticles hardly changes their crystallinity and sizes, while significantly improves their absorption in visible light range and separation efficiency of photogenerated electrons and holes. The CPVC/CdS nanocomposites exhibit much higher visible-light photocatalytic activity and anti-photocorrosion performance than pure CdS, and show good visible-light photocatalytic stability. The visible-light photocatalytic mechanism has been discussed.

Introduction

Cadmium sulfide (CdS), a well known semiconductor with a narrow band gap of 2.5 eV, can be easily excited by visible light to form photogenerated electrons and holes, so it has been widely investigated for degrading organic pollutants or producing hydrogen and oxygen via water splitting under visible light irradiation [1–3]. Unfortunately, pure CdS exhibits two main drawbacks as an efficient photocatalyst. The first is that the photogenerated electron/hole pairs in CdS can easily recombine, leading to low visible-light photocatalytic activity. The second is high photocorrosion of CdS in aqueous media, which restricts its practical applications in a large scale [4–6]. Therefore, several techniques have been developed to overcome the above-mentioned problems, including combination of CdS with another semiconductor (TiO_2, ZnO, MoS_2, etc.) [7–15], graphene [16–19], g-C_3N_4 [20–23], and conjugated polymers [24–28].

Among these modification techniques, the combination of CdS with conjugated polymers has attracted much attention because both visible-light photocatalytic activity and anti-photocorrosion property of the CdS-based composite photocatalysts are obviously improved. Zhang and Zhu [24] prepared a CdS-based composite photocatalyst by immersing CdS powders into tetrahydrofuran solution of polyaniline (PANI), and Duan et al. [25] prepared the similar composite photocatalyst by immersing CdS powders into chloroform solution of poly(3-hexylthiophene) (P3HT). The two groups investigated the visible-light photocatalytic activity by evaluating dye degradation and anti-photocorrosion performance. The results showed that both PANI and P3HT modified CdS photocatalysts exhibited drastically improved visible-light photocatalytic activity and anti-photocorrosion performance. Additionally, Zhang et al. [26] synthesized a series of polypyrrole (PPy)/CdS photocatalysts, and found that much more hydrogen evolution can be produced via water splitting in the presence of these composite photocatalysts than pure CdS. However, the drawbacks of PANI,

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http://dx.doi.org/10.1016/j.jece.2015.05.013
2213-3437/

P3HT and PPy lie in their expensiveness, difficult preparation and uncontrollability for their molecular weight; thus, it is necessary to look for new kinds of conjugated polymers derived from ordinary polymer products.

Polyvinyl chloride (PVC), a commercial polymer, is extensively used in many fields such as buildings, industries and home furniture. It is well known that a partly conjugated polymer (CPVC) can be obtained from PVC via dehydrochlorination reaction when PVC is heated at high temperatures such as 150 °C [29–31]. The schematic reaction process is shown in Scheme 1. We prepared TiO_2-based and g-C_3N_4-based composite photocatalysts by compounding TiO_2 or g-C_3N_4 and PVC derivative with conjugated structure, and found that this conjugated polymer obviously enhanced the visible-light photocatalytic activity of TiO_2 and g-C_3N_4 [32,33]. On the basis of the conjugated structure of PVC derivative and our previous investigations, it is reasonable to infer that the visible-light photocatalytic activity of CdS can be improved by the modification of the conjugated polymer derived from PVC.

Experimental

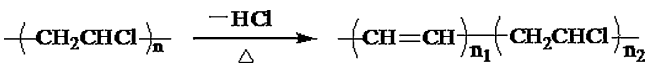
Materials

Cadmium acetate dihydrate, dimethyl sulfoxide (DMSO) and ethylene diamine tetraacetic acid (EDTA) were purchased from Tianjin Guangfu Fine Chemical Research Institute, China. Sodium sulfide nonahydrate, tetrahydrofuran, methyl orange and phenol were purchased from Beijing Chemical Reagents Company, China. All the above reagents were of AR grade and used without further purification. PVC (R-1069, Tianjin Botian Chemical Co., Tianjin, China) was purified by reprecipitation from tetrahydrofuran solution into methanol for 2 times. The precipitate was dried at room temperature under reduced pressure for more than 2 days. Deionized water was used throughout the experiment process.

Preparation of surface-modified CdS nanoparticles

The CdS nanoparticles were prepared using a simple ion-exchange method. The aqueous solution of sodium sulfide (50 g, $Na_2S{\cdot}9H_2O$ 9.61 g 0.04 mol) was added dropwise into the solution of cadmium acetate (50 g, $Cd(CH_3COO)_2{\cdot}2H_2O$ 5.33 g 0.02 mol) under magnetic stirring for 1 h to produce CdS nanoparticles. After that, the obtained suspension containing CdS nanoparticles was filtered, washed with a large amount of water for three times, and dried at 70 °C in an oven for 12 h. The as-prepared CdS powders were grinded carefully for further use.

The preparation of CPVC/CdS photocatalysts was described as follows. Firstly, a small amount of purified PVC was dissolved in 10 mL of tetrahydrofuran. Then, 1.0 g of CdS nanoparticles was added into the above PVC solutions with different mass ratios of PVC and CdS (1:10, 1:20, 1:50, 1:100 and 1:200), and was ultrasonicated to obtain PVC/CdS nanocomposites via solvent volatilization. Finally, the PVC/CdS nanocomposites were heated at 150 °C for 2 h to obtain CPVC/CdS nanocomposite photocatalysts. The as-prepared photocatalysts were labeled as CPVC/CdS (1:*x*), where 1:*x* is the mass ratio of PVC and CdS in the PVC/CdS nanocomposites. The idealized preparation process is described as Scheme 1.



Scheme 1. Dehydrochlorination reaction of PVC heat-treated at high temperatures.

Characterizations

The chemical compositions of photocatalysts were investigated by Fourier-transform infrared spectroscopy (FTIR, Prestige-21, Shimadzu Co., Japan) in the range of 400–4000 cm^{-1}, and KBr was chosen as the reference sample.

X-ray photoelectron spectroscopy (XPS) measurements were recorded on a PHI 5000C ESCA system with a monochromatic Al Kα source ($h\nu$ = 1486.6 eV). The X-ray anode was run at 250 W, and the high voltage was kept at 15 kV with a detection angle of 54°. Spectra were recorded with constant pass energy of 100 eV for the survey and high resolution spectra. The binding energies were referenced to C1s core level (Eb = 284.6 eV). The fitting of high resolution spectrum was provided through the CasaXPS software.

The crystal structure of the CPVC/CdS nanocomposite and pure CdS was investigated by X-ray diffraction (XRD) (Rigaku D/MAX-2500 diffractometer) in the range of 2θ = 10–90° using Cu Kα radiation (λ = 0.15406 nm) with a Nickel filter as X-ray source. The accelerating voltage and applied current were 40 kV and 100 mA, respectively. The crystallite-size was calculated using the Scherrer's formula.

Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were recorded with a field emission transmission electron microscope (JEM-2100, Co., Japan) operated at an accelerating voltage of 200 kV.

UV–vis diffuse reflectance spectroscopy (UV–vis DRS) was performed on a Shimadzu-2550 Scan UV–vis system equipped with an integrating sphere attachment (Shimadzu Co., Japan) with $BaSO_4$ as the background. The spectra were recorded in the range of the wavelength 200–800 nm.

The Brunauer–Emmett–Teller (BET) specific surface areas of the investigated samples were determined by a Micromeritics TriStar II 3020 surface area and porosity system at 77 K using nitrogen as adsorption gas.

The photoluminescence (PL) emission spectra of samples were investigated at room temperature using a Fluorescence spectrophotometer (F-4600 FL Spectrophotometer, Hitachi, Japan) with excitation wavelength of 350 nm.

Electrochemical impedance spectra (EIS) were performed on an electrochemical system (Solartron 1255B Frequency response analyzer and Solartron SI-1287 Electrochemical interface) with 0.1 M KCl solution as the electrolyte and FTO/CPVC/CdS or FTO/CdS electrode as the working electrode. Both CPVC/CdS and CdS films were coated on the FTO substrates (fluorine-doped SnO_2, 15 Ω/sq) using a doctor-blade method. The counter electrode was platinum electrode, and the reference electrode was saturated calomel electrode (SCE).

Photocatalytic activity measurement

The photodegradation of MO or phenol was used to evaluate the visible-light photocatalytic activity of the CPVC/CdS nanocomposites and pure CdS. The investigated photocatalysts (0.10 g) were added into a cylindrical glass vessel containing an aqueous MO or phenol solution (100 mL, 10 mg L^{-1} for MO solution and 20 mg L^{-1} for phenol solution), and the obtained suspension was continuously stirred in the dark for 1 h in order to reach an adsorption–desorption equilibrium. After that, the suspension was irradiated under the visible light emitted from a 300 W iodine tungsten lamp (Philips Co.) with a 400 nm optical filter. The distance between the surface of the suspension and the light source was about 45 cm. During irradiation, the samples were taken out every 20 min from the reactor, and were centrifuged to separate the solid photocatalysts. The clarified solution was analyzed by a 723 UV–vis spectrometer (Shanghai Spectrum Instruments Co., Ltd., China), and the absorbance of MO was measured at a wavelength of