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Perspective

Construction of vesicle CdSe nano-semiconductors photocatalysts with improved photocatalytic activity: Enhanced photo induced carriers separation efficiency and mechanism insight

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ABSTRACT

Visible-light-driven photocatalysis as a green technology has attracted a lot of attention due to its potential applications in environmental remediation. Vesicle CdSe nano-semiconductor photocatalyst are successfully prepared by a gas template method and characterized by a variety of methods. The vesicle CdSe nano-semiconductors display enhanced photocatalytic performance for the degradation of tetracycline hydrochloride, the photodegradation rate of 78.824% was achieved by vesicle CdSe, which exhibited an increase of 31.779% compared to granular CdSe. Such an exceptional photocatalytic capability can be attributed to the unique structure of the vesicle CdSe nano-semiconductor with enhanced light absorption ability and excellent carrier transport capability. Meanwhile, the large surface area of the vesicle CdSe nano-semiconductor can increase the contact probability between catalyst and target and provide more surface-active centers. The photocatalytic mechanisms are analyzed by active species quenching. It indicates that h^+ and $.O_2^-$ are the main active species which play a major role in catalyzing environmental toxic pollutants. Simultaneously, the vesicle CdSe nano-semiconductor had high efficiency and stability.

Introduction

In the last few years, one of the major purposes of material researchers is to create routes of controlling the structure of materials on specific nanomorphologies. The structure and size of inorganic micro and nanomaterials are well known to have a significant impact on their widely varying electrical and optical applications. Owing to the special structure, vesicle inorganic micro and nanomaterials as novel materials have paid increasing attentions in various fields of modern science and technology (Nguyen et al., 2014; Liu et al., 2010; Wu and Crudden, 2012; Wu et al., 2013). Their regular vesicle

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structure shows an enhanced surface area and shortens transport distances for charge transport (Lai et al., 2012). So, they have been widely applied in photocatalysis (Dinh et al., 2014; Xue et al., 2013; Ye et al., 2014), solar cells (Dong et al., 2014), adsorption (El-Toni et al., 2014), and separation (Wei et al., 2014; Zhu et al., 2014). In the specific nanomorphologies, vesicle nano-semiconductor has caused widespread concern due to their specific structure and potential applications. Now, a large number of researchers have devoted themselves in exploring versatile methods to prepare vesicle materials (Cao et al., 2010; Fang et al., 2011).

Semiconductor nanocrystals have gained a lot of attention because of the ability to tune their photoresponse by size and surface treatment (Kongkanand et al., 2008). Recently, utilizing semiconductor nanomaterials for obtaining photocatalytic performance has attracted wide attentions in sewage system (Liu et al., 2013; Zhu et al., 2015; Dong et al., 2015).

The tailored structure of vesicle nano-semiconductor will have bright prospects in application in environment and chemistry. Responding to technology needs, a great deal of methods to synthesize versatile vesicle nano-semiconductor has been proposed (Niu et al., 2010). These methods could be roughly divided into two forms: soft template and hard template means. Hard template included silica, polystyrene, latex and resin sphere (Kang et al., 2014; Zhang et al., 2014), post-processing was necessary in hard template method, for example, heat treatment and acid or alkali dissolution, which might impair the morphology and structure of the vesicle nano-semiconductor. While soft template generally touched on vesicle, droplet, and gas bubble to form vesicle structure materials (Sanetuntikul et al., 2014; Wickramaratne and Jaroniec, 2015; Girija et al., 2015). Compared to the hard template method, the synthesis pathway of the soft template method was simplified and the post-processing was needless. Up to now, researchers have made great progress in synthesizing vesicle nano-semiconductor and plenty of proud achievements have been gained. However, it still is a daunting challenge about exploring effective and proportionate ways to prepare vesicle nano-semiconductor materials with appropriate size and good dispersion for promising applications.

CdSe is an *n*-type semiconductor. Its band gap energy is reported to be in the range from 1.65 to 1.8 eV (Schierhorn et al., 2008), which makes it wide Applications in catalysis, sensor and solar cells. In the meantime, we report a moderate, simple and green liquid phase method to prepare vesicle CdSe nano-semiconductor with controlled diameters base on the soft template (H_2 vesicles) method. Vesicle CdSe nano-semiconductor was one-step prepared under open air condition in aqueous solution. The CdSe nanoparticles had a promise of aggregating around the liquid–liquid interface between H_2 vesicles and water, which resulted in the formation of vesicle structure. The outstanding features of the present work were as follows: (1) Se powder was used as Se source, which avoided an extra process to perpare the inappropriate Se precursor; (2) all reactions were completed under inert atmosphere protection; (3) the reactions proceeded in aqueous solution, so minimizing the pollution damage to the environment; (4) compared to granular CdSe, vesicle CdSe exhibits more superior photocatalytic performance; (5) the prepared vesicle CdSe nano-semiconductor has been implemented in remediation of residual antibiotics in water and displayed higher removal efficiency. In addition, the optical properties of the obtained nano-semiconductor were also evaluated.

1. Experimental section

1.1. Chemicals and materials

Cadmium chloride ($CdCl_2{\cdot}2.5H_2O$), sodium borohydride ($NaBH_4$), 3-mercaptopropionic acid ($C_3H_6O_2S$) and cetyltrimethyl ammonium chloride ($C_{15}H_{34}ClN$) were purchased from Shanghai Aladdin biochemical Technologies Inc., China. Selenium powder (Se) was purchased from Sinopharm Chemical Reagent Co., Ltd., China. All the chemicals were analytical grade and used as received without further purification.

1.2. Preparation of vesicle CdSe nano-semiconductor

In a typical procedure, 0.09134 g $CdCl_2{\cdot}2.5H_2O$ was added into a 100 mL flask dissolving with 30 mL deionized water. Then, 0.65 mmol of 3-mercaptopropionic acid (3-MP) and different qualities of cetyltrimethyl ammonium chloride (CTAC) as a cationic surfactant were added with stirring rate of 450 r/min and stirring time of 5 min. Meanwhile, 0.0592 g Se powders were mixed with 0.3783 g sodium borohydride in a 20 mL round bottom flask and then added with 5 mL deionized water stirring under nitrogen atmosphere until the transparent sol was obtained. When the solution turns clear with white precipitate appeared, the clear liquid was quickly injected into the above solution. Afterward, the solution was continuously stirred for 3 hr in 80°C water bath conditions. The final orange precipitates were collected, washed with distilled water and absolute ethanol, and then dried in vacuum at 40°C for 4 hr.

1.3. Characterizations

XRD patterns were obtained with a D/max-RA X-ray diffractometer (Rigaku, Japan) equipped with Ni-filtrated Cu $K\alpha$ radiation (40 kV, 200 mA). The 2θ scanning angle range was 10–80° at a scanning rate of 5°/min. The morphology, microstructure and size of vesicle CdSe nanomaterials were confirmed by high resolution transmission electron microscopy (HRTEM) (JEM-2100, HR, Electronic Co., Ltd., Japan). UV–vis diffuse reflectance spectra (UV–vis DRS, UV2450, Shimazduo, Japan) of catalyst powder was obtained for the dry-pressed disk samples using Specord 2450 spectrometer (Shimazu, Japan) equipped with the integrated sphere accessory for diffuse reflectance spectra, using $BaSO_4$ as the reflectance sample.). Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet Nexus 470 FT-IR (America thermo-electricity Company) with 2 cm^{-1} resolution in the range 400–4000 cm^{-1}, using KBr pellets. Thermogravimetric analysis (TGA) curve of catalyst powder was obtained with a comprehensive thermal analyzer (STA499C, Tolerance, Germany). X-ray photoelectron spectroscopy (XPS) data were collected on a PHI5300 analyzer (Perkin Elmer, USA) with aluminum $K\alpha$ radiation.

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