Journal of the Taiwan Institute of Chemical Engineers 60 (2016) 643–650

Contents lists available at ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

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

# Ultrasound exfoliation of g-$C_3N_4$ with assistance of cadmium ions and synthesis of CdS/g-$C_3N_4$ ultrathin nanosheets with efficient photocatalytic activity

Lifang Zhang, Furong Huang, Changhui Liang, Liya Zhou, Xinguo Zhang, Qi Pang*

*College of Chemistry and Chemical Engineering of Guangxi University, Nanning 530005, China*

A R T I C L E  I N F O

*Article history:*
Received 29 July 2015
Revised 30 October 2015
Accepted 16 November 2015
Available online 3 December 2015

*Keywords:*
CdS/g-$C_3N_4$ ultrathin nanosheets
Ultrasound exfoliation
Synergic effects
Photocatalytic property

A B S T R A C T

Cadmium-assisted ultrasound exfoliation was used to synthesize CdS/g-$C_3N_4$ ultrathin nanosheet catalysts with visible-light photocatalytic activity. The samples showed enhanced photocatalytic performance. X-ray diffraction, transmission electron microscopy, ultraviolet–visible diffuse reflection spectroscopy, Fourier transform infrared spectroscopy, and photoluminescence spectroscopy confirmed the synthesized CdS/g-$C_3N_4$ ultrathin nanosheets. The photocurrent intensity and degradation of methyl orange (MO) of ultrathin CdS/g-$C_3N_4$ photocatalyst were 2 and 1.4 times higher than those of CdS/g-$C_3N_4$ nanocomposite obtained via ultrasound exfoliation without assistance of cadmium ion. These results were due to the well-matched band structure and close contact interfaces between the g-$C_3N_4$ nanosheets and CdS, which resulted in the effective transfer and separation of the photogenerated charge carriers. The mechanism for the photodegradation of MO by ultrathin CdS/g-$C_3N_4$ photocatalyst was also investigated.

## 1. Introduction

The development and utilization of sustainable alternative energy sources and environmental improvements are receiving considerable attention because of the depletion of fossil-fuel reserves [1]. Inorganic semiconductors have attracted much interest for photocatalytic water splitting to synthesize renewable fuels since the discovery of the phenomenon in the late 20th century [2,3]. CdS is a typical II–VI semiconductor with wide direct band gap and widely used in photocatalysis and electronic devices [4]. Despite the high photocatalytic activity and good chemical stability of CdS, the application of CdS semiconductor catalysts is limited because of its high recombination rate of electron–hole pairs and low absorption coefficient [5]. Das et al. [6] reported CdS-pillared zirconium–titanium phosphate exhibited enhanced photocatalytic activity for organic pollutants degradation. However, CdS is also unstable under photo-corrosion because photogenerated holes self-oxidize during photocatalysis [7]. Fabricating heterojunctions between two semiconductors can be used to overcome these barriers. Composites of organic polymers and inorganic semiconducting nanomaterials are based on excellent optoelectronic properties of polymers as well as on the size- and shape-dependent band gaps of inorganic semiconducting nanomaterials [8,9]. Moreover, polymer/inorganic semiconducting nanocomposites exhibit high carrier mobilities and increased light absorption [10].

Numerous studies have been conducted to investigate the stable and organic photocatalyst, namely, graphitic carbon nitride (g-$C_3N_4$). This compound exhibits sufficient hydrogen evolution, photochemical splitting of water, and mild and selective oxidation reactions under visible light [11,12]. For example, Parida et al. [13] recently reported their interesting research results about the layered g-$C_3N_4$ and NiFe-layered double hydroxide composites to enhanced photocatalytic activity. They also reported N,S-$TiO_2$/g-$C_3N_4$ nanocomposite with excellent activity for visible light induced water splitting [14]. Martha et al. reported a highly active g-$C_3N_4$ photocatalyst prepared from a mixture of urea and melamine with enhanced efficient hydrogen production [15]. Polymeric $C_3N_4$ is a typical semiconductor with a wide-band gap that ranges up to 5 eV upon structural variations or adatoms, as revealed by theoretical calculations [16]. CdS and g-$C_3N_4$ possess well-matched overlapping band structures that are suitable for constructing heterostructures that can effectively separate and transfer photogenerated charges. Therefore, combining $C_3N_4$ and CdS overcomes the disadvantages exist in $C_3N_4$ and CdS simultaneously [17]. Zhang et al. [18] prepared core/shell CdS/g-$C_3N_4$ nanowires through subsequent stirring of separately prepared CdS and ultrasonic g-$C_3N_4$. Jiang et al. [19] fabricated g-$C_3N_4$–CdS composite through precipitation method, in which the as-prepared bulk g-$C_3N_4$ was initially combined with Cd resource and then combined with S resource. Jie et al. [17] prepared CdS/g-$C_3N_4$ composites through chemical impregnation, in which the as-prepared CdS

---

* Corresponding author. Tel.: +86 7713233718.
*E-mail address:* 185693445@qq.com (Q. Pang).

http://dx.doi.org/10.1016/j.jtice.2015.11.013
1876-1070/

particles and bulk g-$C_3N_4$ were mixed by stirring. However, g-$C_3N_4$ is usually obtained via polycondensation at elevated temperatures and forms a bulk-layered material. Many studies have focused on separating bulk-layered materials to monolayers with unique electronic and optical properties [20]. The structure of g-$C_3N_4$ is similar to that of graphene. Pristine graphene is a material with zero band gap and does not show photocatalytic activity. This material only serves as an electron acceptor or transport intermediate in a photocatalytic reaction, but the 2D materials of graphene exhibit excellent properties, such as high carrier mobility, large specific surface area, and quantum hall effect [21,22]. Thus, 2D materials are widely investigated. Yi et al. [23] prepared ultrathin g-$C_3N_4$ nanosheets by liquid exfoliation of as-prepared bulk g-$C_3N_4$ in water route, and the as-obtained ultrathin g-$C_3N_4$ nanosheets exhibited enhanced intrinsic photoabsorption and photoresponse. Štengl et al. [24] applied ultrasound-assisted exfoliation to mono- and bilayered materials in hydrophobic and hydrophilic environments for large-scale preparation of monolayers.

In this study, we report a novel and simple synthetic approach toward ultrathin CdS/g-$C_3N_4$ nanosheets on the basis of the synergistic effect of ion-assisted ultrasound exfoliation to obtain ultrathin g-$C_3N_4$/CdS nanosheets. Moreover, CdS/g-$C_3N_4$ nanocomposites were synthesized using low-cost melamine as precursor to obtain bulk g-$C_3N_4$. The suspensions of bulk g-$C_3N_4$ and $Cd(CH_3COO)_2{\bullet}2H_2O$ were ultrasonically treated for a certain time and then combined with S. This method is different from the synthesis of as-prepared ultrathin g-$C_3N_4$ nanosheet-CdS nanocomposite [25].

The highlights of ultrathin CdS/g-$C_3N_4$ nanosheet composites system are based on the following conditions. Dimethyl sulfoxide (DMSO) can be used as a solvent and a source of S. Synergistic effect of physical cadmium-assisted ultrasound exfoliation and chemical hydrothermal is highly beneficial for producing composites. Quantum dot-doped g-$C_3N_4$ nanocomposition shows remarkably enhanced photocurrent because of the anticipated change in the electronic structure of g-$C_3N_4$ [26]. The heterostructure of CdS/g-$C_3N_4$ leads to the effective transfer and separation of photogenerated charge carriers and enhances photocatalytic performance. Thus, we confirm that visible-light photodegradation of methyl orange (MO) and transient photocurrent response with high efficiency can be designed using this hybrid nanomaterial.

## 2. Experimental

### 2.1. Chemicals

All reagents were of analytical grade and not further purified before the experiment.

### 2.2. Synthesis of g-$C_3N_4$ compounds

The g-$C_3N_4$ compounds were initially synthesized using a high-temperature thermal polymerization method. Melamine (2 g) was heated at 550 °C in a covered crucible under nitrogen atmosphere for 4 h and then naturally cooled to room temperature under nitrogen gas. Finally, the yellow bulk product was grounded, collected, and stored as the precursor.

### 2.3. Synthesis of CdS/g-$C_3N_4$ hybrid materials

CdS/g-$C_3N_4$ nanocomposites were prepared using the synergistic method of intercalation-exfoliation similar to the Joensen method with minor modifications [27] and hydrothermal process. DMSO (75 mL) was added to 0.212 g of $Cd(CH_3COO)_2{\bullet}2H_2O$ and a measured amount of g-$C_3N_4$. Subsequently, the suspension was sonicated for 1 h to assist the exfoliation process. The mixture was transferred into a Teflon-lined stainless autoclave (100 mL), maintained at 180 °C for 12 h, and then naturally cooled at room temperature. The precipitation was washed several times with acetone and ethanol by ultrasonic treatment for 30 min and centrifuged to remove residual reactants. The product was dried in a vacuum oven at 80 °C for 2 h. The sample was the ultrasonically obtained CdS/g-$C_3N_4$, and pure CdS was also obtained by the same conditions without the g-$C_3N_4$ powder. CdS/g-$C_3N_4$ was prepared by the same conditions without ultrasonication.

### 2.4. Characterization

The structures and compositions of the products were analyzed using X-ray diffraction (XRD) on a BRUKER D8 ADVANCE X-ray powder diffractometer with Cu K$\alpha_1$ radiation ($\lambda$ = 1.5406 Å) within the 2$\theta$ range of 10°–80°. The accelerating voltage and emission current were 40 kV and 40 mA, respectively. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were taken on FEI Tecnai G2 (F30 S-TWIN/X-MAX80) at 200 kV. The ultraviolet–visible (UV–vis) diffuse reflection spectra were recorded for the dry-pressed disk samples using a Scan UV–vis spectrophotometer (UV–vis diffuse reflectance spectroscopy (DRS), UV-2501 PC, Shimadzu, Japan) equipped with an integrating sphere assembly using 100% $BaSO_4$ as the reflectance sample. A Hitachi F-2500 spectroscope recorded the products of the photoluminescence (PL) spectra and was equipped with an integrated sphere attachment. Fourier transform infrared (FTIR) spectra were recorded using Spectrum100 (PerkinElmer, USA). FTIR spectrometry within the wavenumber range of 400–4000 $cm^{-1}$ was applied using the KBr-pellet technique. Electrochemical measurements were performed on a CHI 660E electrochemical workstation (Chenhua Instrument, Shanghai, China). Visible irradiation was conducted using a 500 W Xe lamp (CHF-MX, Beijing).

### 2.5. Photoelectrochemical measurements

The device for electrochemical measurements was constructed by assembling the expected CEs ($CuS_2$) and CdS/g-$C_3N_4$-sensitized titanium dioxide ($TiO_2$) photoanodes using a 60-$\mu$m thick Scotch spacer with a binder clip and then filling with a droplet (10 $\mu$L) of polysulfide electrolyte. The polysulfide electrolyte aqueous solution consisted of 0.5 M $Na_2S$, 0.125 M S, and 0.2 M KCl. At least three cells were prepared under each condition, and the cells were tested in parallel.

Preparation of photoanodes: $TiO_2$ sol–gel was prepared according to the literature [28]. $TiO_2$ sol–gel films were prepared on fluorine-doped tin oxides (FTOs) by using the spin coating method. After coating, the films were naturally dried at room temperature. The $P_{25}$ slurry was covered by the doctor-blade method and finally sintered at 450 °C for 30 min. The films were subsequently placed in 40 mM $TiCl_4$ aqueous solution at 70 °C for 40 min and then sintered at 450 °C for 30 min according to the typical procedure for dye cells. CdS/g-$C_3N_4$–$TiO_2$ photoanodes were prepared via electrophoretic deposition. The electrophoretic deposition was performed by combining acetone (30 mL) and CdS/g-$C_3N_4$ powder (30 mg) in a 100 mL beaker and sonicating it as directed. Pure g-$C_3N_4$ sample was electrophoretically deposited using the same procedure. The mixture was sonicated for 15 min to disperse the powder photocatalysts well in the iodine solution [29]. Two parallel FTO electrodes, 10–15 mm apart, were immersed in the solution, and a 50 V bias was applied using a DC power supply for 3 min. With the applied voltage, the positively charged particles were deposited on the cathodic side. The coated area was fixed at 0.8 cm × 0.8 cm and then dried.

Fabrication of counter electrodes: The brass sheet was initially placed in 12 M HCl at 70 °C for 30 min, washed with water, and dried. The sheet was dipped into the polysulfide electrolyte aqueous solution for 10 min and then naturally dried. This sheet was then formed as the counter electrode.