Applied Catalysis B: Environmental 222 (2018) 209–218

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

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

Dual templating fabrication of hierarchical porous three-dimensional ZnO/carbon nanocomposites for enhanced photocatalytic and photoelectrochemical activity

He Wang[a], Xuan Liu[b,*], Shulan Wang[a,*], Li Li[a,*]

[a] Department of Chemistry, School of Science, Northeastern University, Shenyang, 110819, China
[b] Department of Materials Science and Engineering, Carnegie Mellon University, Pittsburgh, PA, 15213, USA

ARTICLE INFO

Keywords:
ZnO
Dual template
Energy conversion
Hierarchical pores

ABSTRACT

Herein, a novel fabrication strategy to synthesize the ZnO/C nanocomposite with hierarchical porous structure was proposed with dual templating method that combines both ice and micelle templating. The composite material annealed at 900 °C showed the best photocatalytic reactivity for organic dye degradation compared with samples annealed at other temperatures, which is 2.2/7.0 times of the control ZnO + C sample under UV and visible light irradiation. The sample also showed superior photoelectrochemical performance while ultrasonic assisted photodegradation of methylene blue was also observed. This work demonstrates a novel and feasible approach for processing ZnO based photocatalysts with enhanced reactivity, which can be extended to the design of a broad series of functional metal oxide composites with high electrochemical performance for energy applications.

1. Introduction

Rapid economic development and population expansion serve as an efficient driving force to mitigate the environmental pollution and to alleviate the pressure arising from the energy crisis. Integration of energy materials and nanostructured devices is considered as an effective approach to solve the crisis [1,2]. Semiconductor photocatalysis and photoelectrochemical cell (PEC) have attracted significant attention as the potential sustainable and renewable technologies for solar energy harvesting and conversion to replace the conventional fossil fuel considering their applications in toxic organic pollutant degradation, CO_2 reduction, water splitting for hydrogen production, etc [3,4]. Among different metal oxide materials, ZnO is considered as one of the most important photocatalysts due to its physicochemical and functional advantages, such as non-toxicity, chemical stability, low expense, environmentally friendliness, etc. Meanwhile, ZnO has 10–100 times higher electron mobility than the commercial benchmark photocatalyst TiO_2, which extends its applications into a broad range including piezoelectric devices, solar cell, catalysis, gas sensoring, etc [5–8]. Use of both mechanical vibration and solar energy [9] can increase the energy output of nanostructured devices such as nanogenerators [10,11] to capture energy from multiple power sources considering unpredictable and unstable availability of renewable energy sources. The special piezoelectric output of ZnO with applied deformation also assists separation of photogenerated electrons and holes to different directions, resulting in decrease in their recombination rate, increase in photocatalytic efficiency and improvement in photocatalytic and photoelectrochemical performance [6–8].

As a multi-functional electronic semiconductor, ZnO has a wide band gap (3.37 eV). As a result, raw ZnO can only be activated under UV light irradiation with wavelength < 387 nm (4% of solar spectrum) [12]. To improve their photon absorption and to decrease the recombination rate of photo-generated charge carriers, different approaches have been attempted to increase their visible light response, such as metal and non-metal doping [13,14], dye sensitization [15,16] and oxide semiconductor coupling [17,18], etc. Recently, metal oxide/carbon mixture has attracted considerable attention to narrow down the band gap of metal oxide and to promote their quantum efficiency by intrinsic doping [13,19]. Furthermore, carbon can provide conductive channels for electrons to transfer after generation and also assist separation of photo-generated electron-hole pairs. For example, as one type of the high surface area carbon networks, graphene is widely used as the carbon source to couple with ZnO for the enhancement of its photo-activity [20–22]. ZnO in the small size (about 10 nm) dispersed on grapheme showed excellent photocatalytic performance under UV light irradiation [23].

* Corresponding authors.
E-mail addresses: xuanliucmu@gmail.com (X. Liu), slwang@mail.neu.edu.cn (S. Wang), lilicmu@gmail.com, lilicmu@alumni.cmu.edu (L. Li).

http://dx.doi.org/10.1016/j.apcatb.2017.10.012
Received 9 July 2017; Received in revised form 3 October 2017; Accepted 6 October 2017
Available online 07 October 2017
0926-3373/

A hierarchical pore structure is important for practical applications of metal oxide and carbon materials in many fields, such as catalyst, gas adsorbent, energy storage, etc, considering the interconnected network between macropores and mesopores that can efficiently transport external species to the intrinsic active sites of component materials [24,25]. Particularly in photocatalytic applications, the macroporous channels can provide the light transfer path and extend the photon energy to reach the intrinsic surface of mesopores with enhancement in solar energy utilization efficiency and thus to increase photocatalytic activity [26,27]. Meanwhile, the macropores also can decrease the back-pressure during transportation of fluid and gas, and increase the flow rates of guest species within the hierarchical network.

Herein, we demonstrate a novel and simple strategy to synthesize a hierarchical ZnO/C porous structure by the dual templating method, combining ice templating alongside micelle-templating with citric acid-based zinc complexes as precursors. Different annealing temperatures on formation of pore structures as well as their photocatalytic activity for organic dye degradation were discussed in detail. Meanwhile, the ultrasonic-wave-generated piezo-phototronic effect of the synthesized ZnO for assisting photocatalytic reactivity and corresponding photoelectrochemical performance were also analyzed to further explore the use of materials for solar energy conversion. The advantage of current method is to provide a simple and feasible route for the fabrication of ZnO/carbon with micro-, meso-, and macro-porous structures together into the nanocomposites. Meanwhile, this method is also broadly applicable to the fabrication of other metal oxide/carbon materials, such as TiO_2, SnO_2, et al., which significantly extends its use to a wide range of energy and electronic related applications. To the best of our knowledge, this is the first report about dual templating method to fabricate hierarchical porous 3D ZnO/carbon nanocomposites at three different length scales for enhanced photocatalytic and photoelectrochemical activity.

2. Experimental

2.1. Sample preparation

$Zn(CH_3COO)_2{\cdot}2H_2O$ (AR 99%, Aladdin, Shanghai) was used as the zinc precursor while pluronic F127 ($EO_{106}PO_{70}EO_{106}$) copolymer (Sigma, St. Louis, MO, USA) served as the soft template for mesoporous structure and carbon sources. In the synthesis of ZnO/C composite materials, 70 mg F127 and 437.3 mg $Zn(CH_3COO)_2{\cdot}2H_2O$ were dissolved in a mixture of deionized water (5 mL) and ethanol (5 mL) by ultrasonic followed with addition of 144 mg of citric acid (AR 99%, TianJin, Yongda). The solution was then under continuous ultrasonic to form milky suspension. The solution was transferred to a 25 mL plastic tube and plunged into liquid nitrogen bath for 30 min to fully freeze the samples, followed with freeze drying for 24 h to remove the ice template by sublimation. The white powders were calcined for 1 h at 250 °C and then heated to different temperatures in the range from 400 °C to 1000 °C with a heating rate of 10 °C/min for 30 min to form the hierarchical ZnO/C framework. In addition, commercial ZnO was mechanically mixed with sucrose and annealed at 900 °C (noted ZnO + C(900 °C)) as the control sample, while the mixture without annealing was used as another reference.

2.2. Structural characterization

X-Ray diffraction (XRD) patterns were obtained on a UItima IV (Rigaku, Japan) with CuKα radiation (λ = 0.1542 nm) at the working voltage of 40 kV and current of 40 mA. Surface morphology and elemental analysis was investigated by field-emission scanning electron microscope (SEM) (Ultra Plus, Carl Zeiss, Germany) equipped with energy dispersive spectroscopy (EDS). X-ray photoelectron spectroscopy (XPS) measurement was conducted to examine chemical bonding between ZnO and carbon on ESCALAB 250Xi (Thermo Fisher Scientific) analyzer with Al Ka ($h\nu$ = 1486.6 eV) as the excitation source. Room-temperature Raman spectroscopy was measured by Finder Vista at 532 nm with 10% filter. High resolution transmission electron microscopy (TEM) was conducted using a Tecnai G2 F20 S-TWIN at an acceleration voltage of 200 kV. Nitrogen adsorption/desorption isotherms (American Micromeritics ASAP 2020 sorptometer) were obtained at 77 K to determine the specific surface area of the samples using the Brunauer-Emmett-Teller (BET) analysis method while pore size distribution was obtained by the Barret-Joyner-Halenda (BJH) model based on the desorption data and pore volume measured at P/P_0 = 0.99 point. Thermogravimetric and differential thermal analyses (TG/DTA) (METTLER TOLEDO-3) were used to analyze the ZnO precursor at 25–1100 °C with a heating rate of 10 °C/min under nitrogen atmosphere with a flow rate of 100 mL/min.

2.3. Photocatalytic dye degradation setup

The photocatalytic methylene blue (MB, Shenyang Chemical Reagent Co. Ltd., P.R. China.) degradation with ZnO/C was measured under UV and visible light produced from 125 W high-pressure mercury lamp and 300 W high-pressure xenon lamp with a 420 nm cutoff filter (PLS-SXE 300), respectively. The light intensities used for the photocatalytic experiments are 250 mW/cm^2 (visible) and 310 mW/cm^2 (UV). 15 mg ZnO/C photocatalyst was added into 80 mL 4×10^{-5} M MB solution under magnetic stirring for 60 min in dark to reach the adsorption-desorption equilibrium before photocatalytic reaction. 6 mL solution was taken out in certain duration intervals during illumination and centrifuged to remove the catalyst for further analysis. Degradation of MB was then evaluated with a UV–vis spectrophotometer by comparing the intensity of the maximum absorbance peak (λ = 664 nm) (denoted as C) and the initial intensity (denoted as C_0) before irradiation. To investigate the ultrasonic-wave-generated piezo-phototronic effect of the ZnO/C nanocomposites, an ultrasonic probe with the frequency of 50 kHz was placed into the suspensions to provide mechanical vibration.

2.4. Photoelectrochemical (PEC) measurements

2 × 1 cm FTO glass was cleaned by acetone, ethyl alcohol and water successively before photoelectrochemical measurement. ZnO/C (900 °C) powder was then mixed with *N*-methyl pyrrolidone solution to form the slurry which was then uniformly coated onto the surface of FTO substrate and dried at 80 °C. The electrochemical measurements were then carried out with a three-electrode photoelectrochemical cell in 1 M Na_2SO_4 aqueous electrolyte with ZnO/C coated FTO glass as the working electrode, Pt as the counter electrode and a saturated calomel electrode (SCE) as the reference. Linear sweep voltammetry was swept linearly from 0 to 1.2 V vs SCE at a scan rate of 50 mV s^{-1}. The photocurrent measurement was performed in the visible range by using a 300 W high-pressure xenon lamp with the 420 nm cutoff filter. Detailed experimental setup for material synthesis and photocatalytic/photoelectrochemical performance evaluation is shown in Scheme 1.

3. Results and discussion

The phase composition of ZnO/C samples was investigated with XRD and the results are shown in Fig. 1a and b. The samples annealed at 600–900 °C exhibit the characteristic peaks corresponding to the (100), (002), (101), (102), (110), (103), (200), (112) and (201) planes, which are consistent with the reference peaks from hexagonal wurtzite ZnO (JCPDS-36-1451). No other phases relating to impurities are observed in the patterns. With increase in the annealing temperatures over 600 °C, the sharp narrow peaks with high diffraction intensity are formed, confirming the improvement of crystallization for samples. The corresponding crystallite size was also calculated by Scherrer's equation and shown in Table 1. Based on the results, it can be observed that the