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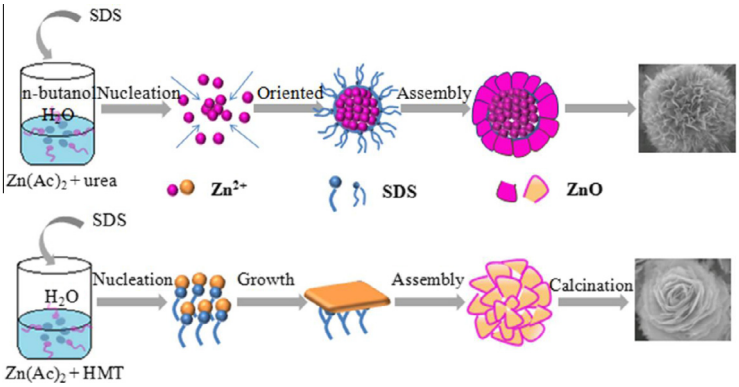
Preparation of flower-like ZnO architectures assembled with nanosheets for enhanced photocatalytic activity

Yu Miao [a], Haijiao Zhang [a,*], Shuai Yuan [c], Zheng Jiao [a], Xuedong Zhu [b,*]

[a] Institute of Nanochemistry and Nanobiology, School of Environmental and Chemical Engineering, Shanghai University, Shanghai 200444, PR China
[b] State Key Laboratory of Chemical Engineering, East China University of Science & Technology, Shanghai 200237, PR China
[c] Research Center of Nanoscience and Nanotechnology, Shanghai University, Shanghai 200444, PR China

GRAPHICAL ABSTRACT



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ABSTRACT

As an important semiconductor metal oxide, various methods have been developed for preparation of ZnO architectures owing to their excellent properties and extensive applications. In this paper, two kinds of 3D flower-like ZnO architectures assembled with numerous nanosheets were successfully synthesized by a simple hydrothermal route assisted by sodium dodecyl sulfate (SDS), origining from the different alkali environment created by urea and hexamine (HMT). SEM and TEM results revealed that the two products had hydrangea-like and rose-like nanostructures with uniform particle sizes, respectively. XRD results confirmed that the growth process of ZnO involved a phase transformation from intermediate compound basic zinc carbonate to ZnO. Base on the experimental results, the formation mechanisms of two kinds of flower-like ZnO undergoing nucleation, oriented growth and self-assembly processes were discussed. The photocatalytic results indicated that both samples exhibited high photocatalytic activities and good cycling stability for the degradation of rhodamine B (RhB), which was almost completely degraded within 25 min, in comparison to those milled samples (above 45 min). The excellent performances were mainly ascribed to their unique nanostructure, good stability, and uniform particle size.

* Corresponding authors.
E-mail addresses: hjzhang128@shu.edu.cn (H. Zhang), xdzhu@ecust.edu.cn (X. Zhu).

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1. Introduction

In recent years, self-assembly of nanoscale building blocks into fancy architecture has been a hotspot for the synthesis of micro- and nanostructures multifunctional materials. Three-dimensional (3D) hierarchical nanostructures, assembled by 1D and 2D nanoscale building blocks including nanowires [1], nanorods [2] and nanosheets [3], have received special attention due to their unique optical [4,5] and electrical properties [6,7]. Up to now, many functional materials with novel architectures such as TiO_2, ZnO, SnO_2 and other metal oxides have been reported [8–11]. Among them, ZnO has been considered as a promising semiconductor material by virtue of its unique advantages regarding direct wide band gap of 3.37 eV, large exciton binding energy of 60 meV and low cost. As a result, ZnO is extensively applied in various fields such as gas sensors [12], solar cells [13], light-emitting diodes [14] and photocatalysts [15,16] .

Many approaches have been developed to fabricate ZnO materials with different morphologies including Ostwald ripening process, chemical vapor deposition (CVD), self-assembly [17], and template techniques [18–20]. In particular, the template method is proved to an effective way for synthesis of nanomaterials with either hard or soft templates because of its controllability and flexibility [21]. Very recently, there has been a growing interest for the soft-templating synthesis method based on a self-assembly process because of its simple, facile, low cost and high yields. That can effectively avoid the multiple experiment processes, and unfriendly to the environment, coming from the disadvantages of hard template method [22]. Generally speaking, soft templates used are some micelles, vesicles formed by surfactants including cationic, anionic and nonionic surfactants [23]. Zhang et al. [24] prepared the mesoporous ZnO microspheres consisting of plate-like nanoparticles *via* a cetyltrimethylammonium bromide (CTAB)-assisted hydrothermal method. A facile surfactant SDBS-directed solvothermal synthesis was been demonstrated for fabricating of ZnO with diverse morphologies by Zhang et al. [25]. Wei et al. [26] synthesized ZnO rods through a wet chemical method in the presence of polyvinylpyrrolidone (PVP). In our previous work, a 3D flower-like ZnO hierarchical nanostructure was also prepared *via* a self-assembly process by using a copolymer F127-directed method for the first time [27].

Motived by above studies, we present a facile hydrothermal method for preparing the flower-like ZnO hierarchical nanostructures with uniform morphologies, which was directed by sodium dodecyl sulfate (SDS). The morphology of the products constructed by numerous ZnO nanosheets can be controlled by simply adjusting the reaction conditions. To insight into the growth process of the products, some reaction parameters such as the dosage of surfactant, the gel compositions and the time evolution were also systematically investigated. Consequently, the different transformation mechanisms based on template-assisted self-assembly process were suggested to introduce the structure formation, respectively. Meanwhile, the photocatalytic tests were also evaluated by degradation of organic dye rhodamine B (RhB).

2. Experimental section

2.1. Materials

Zinc acetate dehydrate ($Zn(Ac)_2{\cdot}2H_2O$), sodium dodecyl sulfate (SDS), hexamine (HMT), urea, and n-butanol were purchased from Shanghai Chemical Industrial Co. Ltd. (Shanghai, China). All chemicals used were analytical grade without further purification. Absolute ethanol and distilled water were used throughout the experiment.

2.2. Synthesis of flower-like ZnO architectures with different morphologies

Synthesis of hydrangea-like ZnO (H-ZnO): typically, 0.25 g SDS was dissolved in 40 mL mixed solvent containing H_2O and n-butanol with a volume ratio of 3 under magnetic stirring to form a clear solution. Meanwhile, 5 mmol $Zn(Ac)_2{\cdot}2H_2O$ and 40 mmol urea were dissolved in 50 mL distilled water under magnetic stirring for 30 min. Then, the SDS solution was added into the solution dropwise and stirred continuously for 2 h at room temperature. The resulting mixture was transferred into a Teflon-lined stainless steel autoclave and kept at 100 °C for 12 h. After the autoclave was cooled to room temperature, the white precipitation was centrifuged and washed with ethanol and distilled water in sequence several times, and dried at 60 °C overnight. Finally, the ZnO products were obtained by calcining the precipitates at 500 °C for 2 h under air atmosphere.

Rose-like ZnO (R-ZnO) was prepared as follows: 10 mmol $Zn(Ac)_2{\cdot}2H_2O$, 10 mmol HMT and 5 mmol SDS were dissolved in 20 mL distilled water. After 30 min vigorous stirring, the solution was transferred into Teflon-lined autoclave and maintained at 160 °C for 12 h, following the remaining similar procedure to obtain the rose-like ZnO.

For comparison, two kinds of ZnO samples were prepared by the similar methods only without the addition of SDS, and named HN-ZnO and RN-ZnO, respectively.

2.3. Characterizations

The samples were determined using X-ray powder diffraction (XRD, $\lambda = 0.154$ nm, D/Max-2550, 40 kV, 250 mA), scanning electron microscopy (SEM, JEOL JSM-6700F), electron energy disperse spectroscopy (EDS, OXFORD INCA), transmission electron microscopy (TEM, JEOL 200CX). UV–Vis diffuse reflectance spectra were analyzed by Hitachi U-3010 spectrophotometer. Photoluminescence (PL) spectra were recorded using a Hitachi F-7000 fluorescence spectrophotometer at room temperature. FT-IR spectrum was recorded on a Nicolet AVATAR 370 Fourier transform infrared spectrometer at a wavenumber of 500–4000 cm^{-1} using KBr pellets. N_2 adsorption–desorption isotherms were recorded on a QUADRASORB SI apparatus at 77 K, after the product were annealed at 150 °C for 6 h. The Brunauer–Emmett–Teller (BET) specific surface area was calculated by using the desorption data. Thermogravimetric (TG) analysis was carried out with a Metter Toledo TGA/SDTA 851^e system at a heating rate of 10 °C min^{-1} in a flow of air.

2.4. Photodegradation

The photocatalytic activities of ZnO products were evaluated by the degradation of rhodamine B (RhB) aqueous solution at ambient temperature using a 300 W mercury lamp as light source. Typically, 20 mg of photocatalyst was added to 50 mL RhB aqueous solution (10 mg/L) in a quartz glass container. The solution was continuously stirred in the dark for 30 min to ensure the establishment of an adsorption–desorption equilibrium between the photocatalyst and RhB before irradiation. A certain volume of the suspension solution was withdrawn at a sequence of time intervals. After disposal of the photocatalyst by a centrifugation, the concentration of residual aqueous solution was measured by the UV–Vis spectrophotometer at 552 nm to calculate the degradation of the RhB based on the Beer–Lambert law.