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Surfactant-free solvothermal synthesis of ZnO nanorods for effective sunlight degradation of 2,4-dichlorophenol

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ABSTRACT

ZnO nanorods (ZNRs) were successfully synthesized via a facile and surfactant-free solvothermal method. The detailed characteristics of ZNRs revealed that the synthesized nanorods were wurtzite hexagonal phase pure ZnO and exhibited well-crystalline with good optical properties. A possible formation mechanism of the nanorod structure was interpreted in terms of the crystal nucleation and crystal growth direction. By utilizing the as-synthesized ZNRs as photocatalysts, significant photodegradation was observed towards endocrine disrupting chemical 2,4-dichlorophenol under natural sunlight irradiation. The considerable photodegradation of 2,4-dichlorophenol was attributed to the unique higher length-to-width ratio of synthesized ZNRs with good crystallinity and optical properties which might enhance the electron–hole pairs separation and might lead to the generation of a large amount of reactive radicals.

1. Introduction

Disruption of the endocrine system in wildlife and humans by anthropogenic chemicals has become an issue of worldwide concern due to the recognition of that the environment is contaminated with various endocrine disrupting chemicals (EDCs) that exert hormonal imbalance activity [1]. 2,4-Dichlorophenol (2,4-DCP) is one of the EDCs, which is widely used as a biocide, wood treatment agent and as a by-product of bleaching in paper mills. Widespread occurrences of 2,4-DCP in surface waters have been reported in several countries at concentrations ranging from <1 to 20 $\mu g\,L^{-1}$ [2]. Numerous in vitro and in vivo tests have demonstrated that 2,4-DCP can modulate transcription of steroidogenetic genes in both human and fish and disrupt steroidogenesis, and thus, impairing reproduction [2]. Among the various techniques, the semiconductor mediated photocatalysis has become a desirable method to transform the organic pollutants into nontoxic molecules to eliminate the environmental pollution. ZnO is a promising semiconductor because of its wide band gap ($\sim$3.3 eV), catalytic and photochemical properties along with its low cost [3]. Nanostructured materials often exhibited chemical and physical properties quite different from their bulk counterparts. Specifically, ZnO rod-structured nanomaterials have unusual features of higher length-to-width ratio and larger surface areas, which enable their wide uses in many aspects such as photocatalysts, chemical and biosensors, solar cell, optoelectronic and spintronic [1,3,4]. Consequently, the synthesis of ZnO rod-structured nanomaterials has recently garnered significant attention. Hitherto, most of rod-structured nanomaterials were developed via the surfactants or structure-directing reagents assisted routes, which were hard to achieve mass production at a low cost.

On the basis of the above consideration, this work reported the synthesis of ZnO nanorods (ZNRs) by a facile and surfactant-free solvothermal method, which was used as effective photocatalysts for the degradation of 2,4-DCP under sunlight irradiation. Furthermore, a possible explanation of the formation of nanorod structure was also presented. To the best of our knowledge, there are no reports about ZNRs as photocatalysts for the degradation of 2,4-DCP at present.

2. Experimental

In a typical experiment, 4.0 mmol $Zn(CH_3COO)_2 \cdot 2H_2O$ was dissolved into 60 mL of ethanol under vigorous stirring for 3 h. At the same time, 60 mmol NaOH was dissolved into 100 mL of ethanol and a homogeneous solution was obtained after constant stirring for 3 h. Then, the solution containing $Zn(CH_3COO)_2 \cdot 2H_2O$ was added drop-wise into the alkaline solution under stirring. After being stirred for 1 h, the resulting solution was transferred to a Teflon-lined autoclave and maintained at 150 °C for 20 h. The as-formed products were filtrated, washed with deionized water and

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ethanol for several times, dried at 60 °C for 12 h and finally calcined at 450 °C for 2 h.

The obtained products were characterized by X-ray diffraction (XRD, Philips PW1820 diffractometer), UV–vis diffuse reflectance spectroscopy (UV–vis DRS, Perkin Elmer Lambda 35), Raman spectroscopy (Renishaw), field-emission scanning electron microscopy with energy dispersion X-ray (FESEM-EDX, Quanta FEG 450), transmission electron microscopy (TEM, Philips CM 12) and high-resolution transmission electron microscopy (HRTEM, Tecnai 20).

The photocatalytic experiments were performed on sunny days between 11:00 and 14:00 in the month of January 2014. A 100 mL of 50 ppm 2,4-DCP in the presence of catalysts (100 mg) was exposed to the sunlight with intensity of 90,000 lx after the mixture was magnetically stirred for 1 h in the dark to get the adsorption–desorption equilibrium. The concentration of 2,4-DCP was determined using a HPLC (Perkin Elmer Series 200) at given time intervals after the ZNRs were centrifuged. Meanwhile, the comparison studies with commercial anatase TiO_2 were also conducted.

3. Results and discussion

Fig. 1(a) shows the XRD pattern of as-synthesized products. All the diffraction peaks were labeled and can be readily indexed to hexagonal wurtzite ZnO (JCPDS Card no. 36-1451). The sharp and narrow peaks showed that the products obtained were in a well crystallized form. No other crystalline impurities were detected in the pattern, indicating the phase purity of the ZNRs. Further evidence of the formation of ZnO came from the EDX analysis. The Zn and O peaks can be easily observed (Fig. 1(b)). According to the estimation of the peak areas, the atomic ratio of Zn/O was approximated to 1:1. The weak C peak was also detected, which originated from the supporting carbon tape.

Fig. 1(c) shows the UV–vis DRS spectrum of as-synthesized products. A steep absorption edge which lay between 370 and 380 nm without any other absorption peak was observed. The band gap energy (E_g) of the ZNRs can be calculated according to the equation E_g (eV)$=1240/\lambda$ (nm), where λ is the wavelength of absorption onset [1]. The E_g was measured to be 3.27 eV (inset of Fig. 1(c)) which was consistent with that reported for bulk ZnO [5]. The Raman spectrum of the products in Fig. 1(d) shows a strong peak at 438 cm^{-1} of E_{2H} mode, which was one of the characteristic peaks of wurtzite ZnO and further confirmed the synthesized ZNRs were pure ZnO. The peaks located at 336, 380 and 575 cm^{-1} were corresponded to the $E_{2H}-E_{2L}$, A_1 (TO) and E_{1L} modes of ZnO, respectively [6]. Therefore, the high intensity at E_{2H} mode suggested the excellent optical and crystalline properties of the synthesized ZNRs.

Fig. 2(a) and (b) shows the low and high magnification FESEM images of as-synthesized products. It was clear that the products were rod shaped and grown in large quantity. The nanorods were 58–139 nm in diameter and 1–3 μm long. TEM observation of the products further confirmed the FESEM results (Fig. 2(c)). The HRTEM image in Fig. 2(d) shows very clear and well-defined lattice fringes of ZnO. Moreover, the interplanar spacing of the nanorod was 0.26 nm corresponding to the *d*-spacing of the (002) plane of wurtzite structured ZnO, which indicated that the nanorod grew along the [0001] direction. From the HRTEM results, it can be verified that the synthesized products have highly crystalline structure, which was essential for excellent photocatalytic materials. In particular, the obtained ZnO products are also promising materials for spintronics, since they can possess the ferromagnetic properties. The ferromagnetic behavior depends on the structure of ZnO grain boundaries [7,8]. Herein, the micrographs (Fig. 2) witnessed that the obtained ZnO products were nanograined and contained the very developed grain boundaries and free surfaces, which can show ferromagnetic behavior.

On the basis of studies mentioned above, the growth of ZNRs could be proposed based on the chemical reactions involved and crystal growth habits of ZnO. The reaction process can be

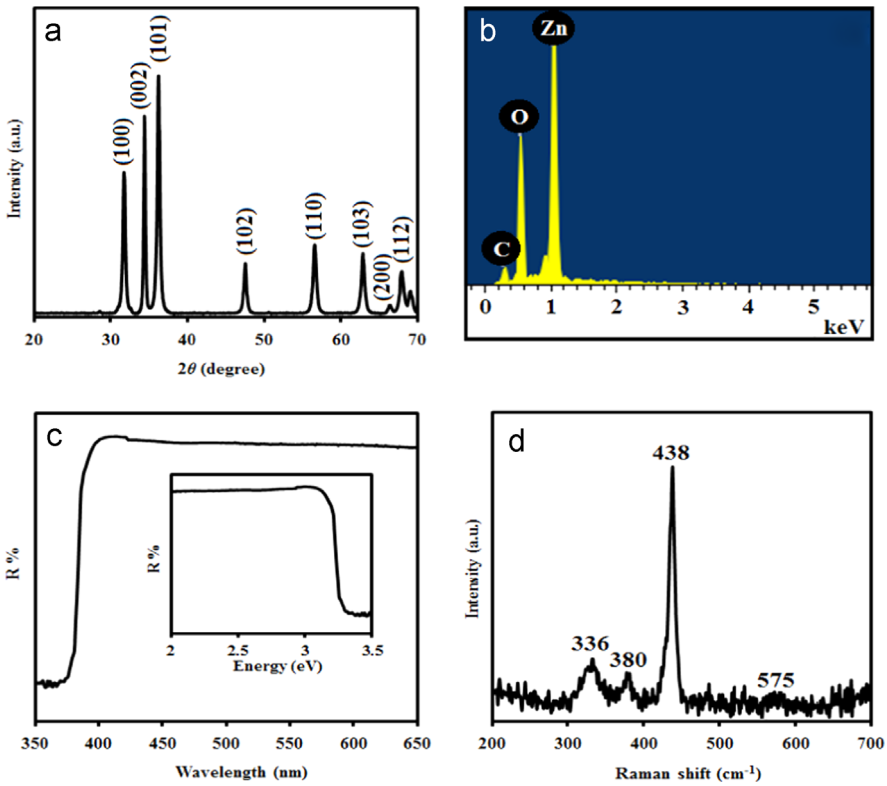

Fig. 1. (a) XRD pattern, (b) EDX spectrum, (c) UV–vis DRS spectrum and (d) Raman spectrum of ZNRs. Inset of (c) is the plot of *R*% versus photon energy.