

# Porous-ZnO-Nanobelt Film as Recyclable Photocatalysts with Enhanced Photocatalytic Activity

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**Abstract** In this article, the porous-ZnO-nanobelt film was synthesized by oxidizing the ZnSe-nanobelt film in air. The experiment results show that the porous-ZnO-nanobelt film possesses enhanced photocatalytic activity compared with the ZnO-nanobelt film, and can be used as recyclable photocatalysts. The enhanced photocatalytic activity of the porous-ZnO-nanobelt film is attributed to the increased surface area. Therefore, turning the 1D-nanostructure film into porous one may be a feasible approach to meet the demand of photocatalyst application.

**Keywords** Porous materials · ZnO · Nanobelt · Photocatalyst

## Introduction

In the past decade, some oxide semiconductors have been widely used as photocatalysts for the degradation of organic pollutants in water [1, 2]. Based on the viewpoint of application, high photocatalytic activity and recyclability are two major factors which should be regarded. Considering that photocatalytic reaction occurs at the surface of catalysts, great efforts have been focused on nanoparticles because high photocatalytic activity can be achieved owing to their large surface area in a relative small volume (high surface–volume ratio) [3–5]. Unfortunately, however, these

nanoparticle photocatalysts are generally suspended in solution, which limits the practical application due to the difficulty in their recycle [6]. In order to avoid this problem, some works have suggested that 1D-nanostructure film adhered to a rigid substrate as photocatalysts [6–9]. However, 1D-nanostructure photocatalysts have relatively low photocatalytic activity because of their lower surface-to-volume ratio compared to nanoparticles. In a word, it seems to be impossible to realize both high photocatalytic activity and recyclability for semiconductor photocatalysts.

The porous 1D nanostructures, namely, nanoparticle chains, in which nanoparticles connect each other and constitute 1D nanostructure, have the speciality of both nanoparticles and 1D nanostructures. Here, we propose that turning 1D-nanostructure film into porous one is a feasible approach to realize both high photocatalytic activity and recyclability and thus to meet the demand of photocatalyst application. Our results reveal that the as-synthesized porous-ZnO-nanobelt film (PZNF) by oxidizing the ZnSe-nanobelt film can be used as recyclable photocatalysts with enhanced photocatalytic activity compared to the ZnO-nanobelt film (ZNF).

## Experimental Details

ZnSe nanobelts were prepared on Si substrate using H<sub>2</sub>-assisted thermal evaporation method. They were synthesized at 950°C for 30 min with the carrier gas of high-purity Ar mixed with 5% H<sub>2</sub>. PZNF was obtained by oxidizing the ZnSe-nanobelt film on Si substrate in air at 1,000°C for 2 min. In order to make a comparison of photocatalytic activity, ZNF was prepared using the Au film as catalyst by vapor phase transport method, the growth process is similar to [5] The substrates before and

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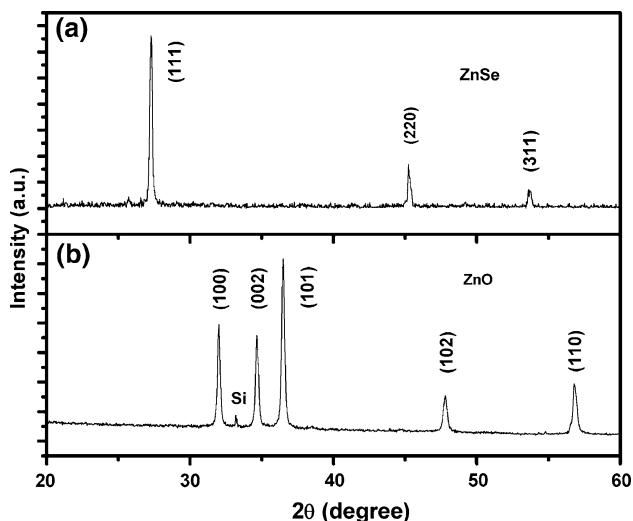
after deposition were weighed to obtain the weight of the as-prepared samples.

In order to examine the photocatalytic activity of samples, the methyl orange was chosen for photodecomposition study. Five milliliter methyl orange solution with a concentration of  $1.0 \times 10^{-5}$  M/L was added into two quartz cells. The PZNF and ZNF with identical mass (1.6 mg) on Si substrates were immersed into the solution. They were irradiated by light with a wavelength of 365 nm produced from a 125 W mercury lamp. The UV–vis absorption spectra of the solutions, before and after irradiation interval of 40 min, were recorded using a Cary 5E UV–Vis–NIR spectrophotometer.

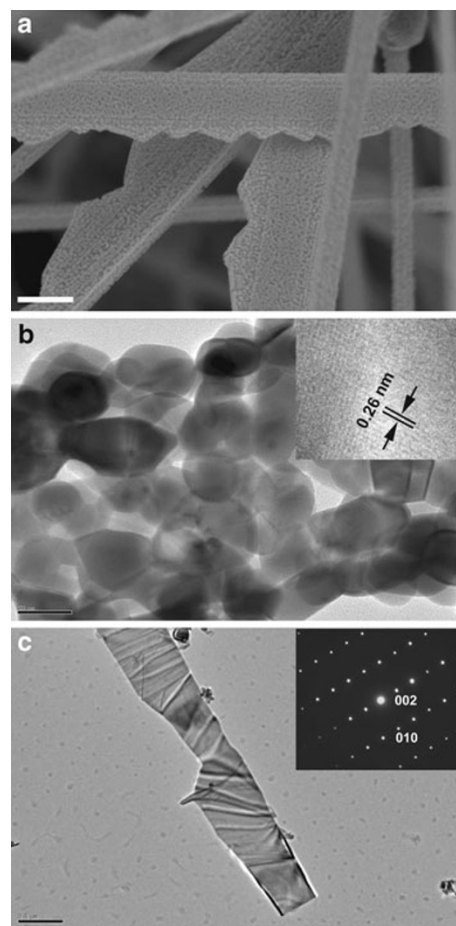
Samples collected from the silicon substrates were characterized by a field-emission scanning electron microscopy (FE-SEM, Sirion 200), high-resolution transmission electron microscopy (HRTEM, JEOL-2010), and X-ray diffraction (XRD, Philips X'pert PRO).

## Results and Discussion

The X-ray diffraction (XRD) pattern of the as-synthesized ZnSe nanobelts is shown in Fig. 1a. It can be seen that ZnSe nanobelts are of zinc blende structure (JCPDS 80-0021). After annealing in air at 1,000°C for 2 min, they are oxidized, and ZnO can be obtained corresponding to the reaction equation  $\text{ZnSe} + \text{O}_2 \rightarrow \text{ZnO} + \text{SeO}_2$ , where  $\text{SeO}_2$  vaporizes [10]. The XRD pattern of the annealed sample in Fig. 1b is consistent with wurtzite structured ZnO (JCPDS 80-0075). There exists no peak of other purity, except that from Si substrate. It indicates that ZnSe is oxidized into ZnO.



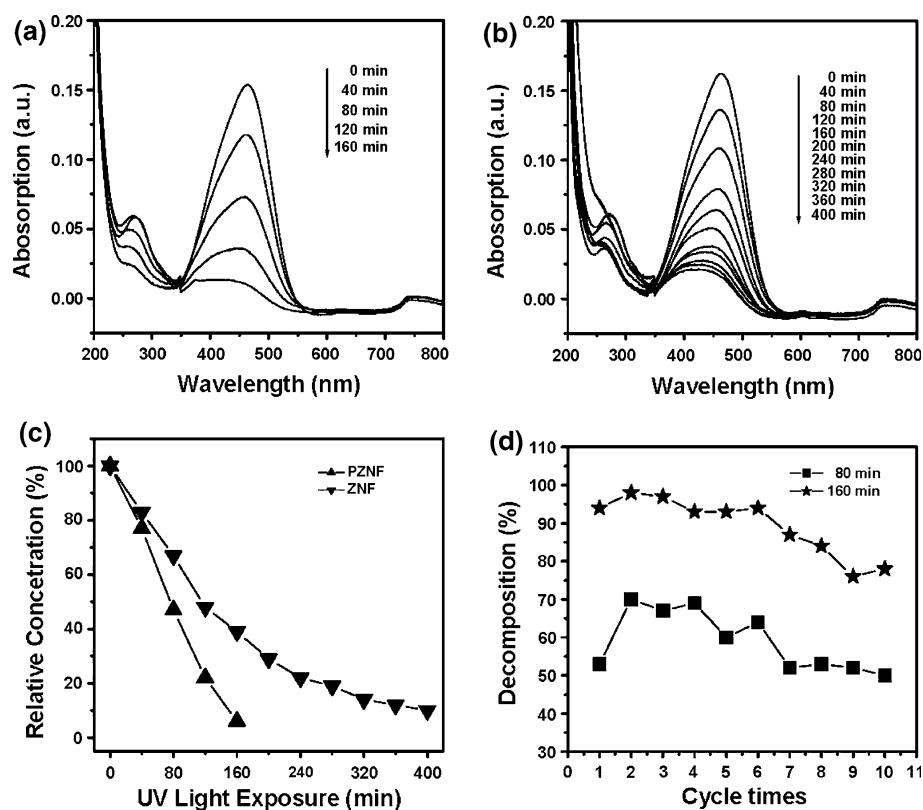
**Fig. 1** XRD patterns of **a** and **b** correspond the as-synthesized ZnSe nanobelts and porous-ZnO nanobelts, respectively



**Fig. 2** **a** SEM image of the porous ZnO nanobelts on Si substrate. The scale bar is 500 nm. **b** TEM image of a single porous ZnO nanobelt. The inset is HRTEM of several ZnO nanoparticles. The scale bar is 50 nm. **c** TEM image of a single solid ZnO nanobelt. The inset is SAED. The scale bar is 500 nm

The scanning electron microscopy (SEM) image in Fig. 2a shows that micron-scale interspace exists among the ZnO nanobelts by oxidizing ZnSe nanobelts. It would make the organic pollutants easily enter and adsorbed by the inner nanobelts, and thus the high photocatalysis efficiency may be expected. Furthermore, each porous-ZnO nanobelt is made up of a large number of pores and nanoparticles, which connect each other and constitute a nanoparticle chain. The transmission electron microscopy (TEM) image in Fig. 2b reveals that each ZnO nanoparticle has the diameter of about 50 nm. The high-resolution TEM image (inset in Fig. 2b) indicates that each ZnO nanoparticle is single crystal. This phenomenon originates from that the outward diffusion flux of ZnSe is more than inward one of  $\text{O}_2$  and the net flow of ZnSe is balanced by inward flow of vacancies, namely, the Kirkendall effect [11–13]. Due to the quick oxidation reaction, the flaking and spallation occur in pre-formed ZnO surface layer (Fig. 2b) [14]. As a result,  $\text{O}_2$  enters through the cracks and oxidizes inner

**Fig. 3** The time-dependent UV–vis spectra in **a** and **b** are recorded for the methyl orange solution containing PZNF and ZNF, respectively. **c** The variation of relative concentration of remaining methyl orange molecules with respect to irradiation time. **d** Degradation changes as a function of irradiation time (80 and 160 min) over 10 cycles. The beginning concentration  $C_0$  is taken as that in **a**

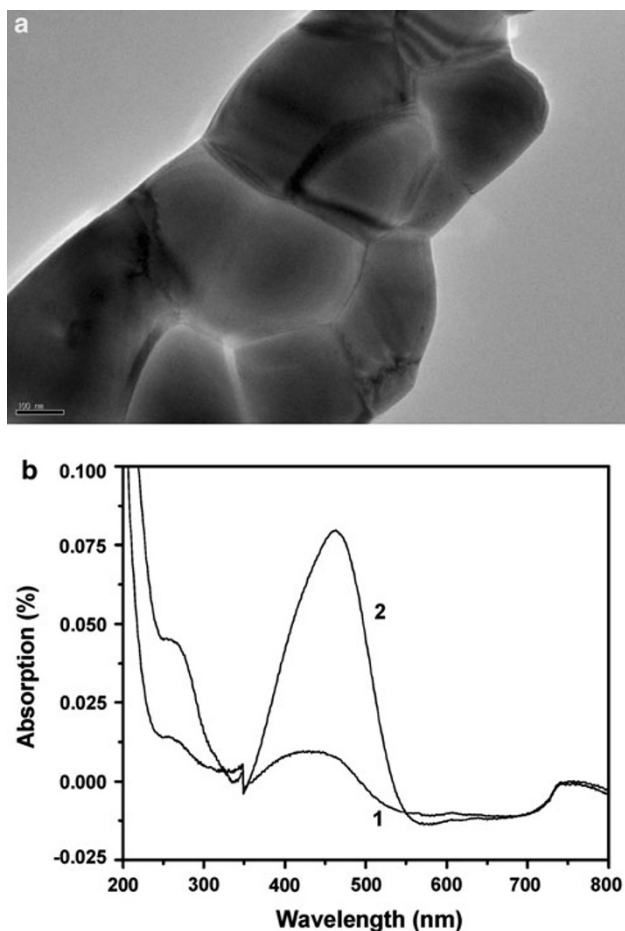


ZnSe, and porous-ZnO nanobelts are obtained. In order to make a comparison of photocatalytic activity, ZnO nanobelts were also synthesized on Si substrate by vapor phase transport method. Figure 2c is the TEM image of a single solid ZnO nanobelt. Obviously, the porous ZnO nanobelt has much higher surface-to-volume ratio than solid one, so PZNF possesses higher surface area than ZNF with the identical mass.

The photocatalytic activity of PZMF and ZMF with the same mass (1.6 mg) of ZnO on Si substrates was investigated using methyl orange molecules. The samples were immersed in the solutions and irradiated with light from a mercury lamp. The time-dependent UV–vis spectra of methyl orange solution containing PZNF and ZNF, before and after irradiation interval of 40 min, are illustrated in Fig. 3a, b, respectively. It can be seen that the intensity of absorption peak corresponding to the methyl orange molecules at 464 nm decreases with increasing the exposure time. The variation of relative concentration of remaining molecules with respect to irradiation time is given in Fig. 3c. Nearly complete degradation of methyl orange costs 160 and 400 min for PZNF and ZNF, respectively. Obviously, PZNF has much higher photocatalysis efficiency for the degradation of methyl orange than ZNF. Because photocatalytic reaction occurs at the surface of catalysts, we attribute this result to the higher surface area

in PZNF than that in ZNF with equal mass, which is further confirmed below. The recyclability of PZNF is also studied. After recording the absorbance spectra of the solution with irradiation for 80 and 160 min, PZNF was immersed into fresh solutions of the same concentrations again for another cycle of the photocatalysis experiment, and this experiment was repeated for 10 times. The results are shown in Fig. 3d. After 10 cycles, a little decrease in the degradation rate was observed. This decrease may be due to the unavoidable loss of the porous ZnO nanobelts into solution during the experiment and the photocorrosion of ZnO, because photocorrosion is a major obstacle for photocatalysts such as ZnO and CdS [15, 16]. This result reveals another very important point that the PZNF obtained in this work can be effectively used as recyclable photocatalysts. That is, PZNF obtained in our work possesses both high photocatalytic activity and recyclability.

After annealing PZNF in air at 1,000°C for 1 h, the porous ZnO nanobelts (Fig. 2a, b) turn into solid one because of the agglomeration of small ZnO grains, as shown in Fig. 4a. It can be seen that grain boundary instead of pore exists in the solid ZnO nanobelt. Thus, the surface area decreases rapidly after annealing PZNF for 1 h. The photocatalysis performance of PZMF before and after annealing for 1 h, with an irradiation of 2 h, was revealed in Fig. 4b. UV–vis spectra of 1 and 2 in Fig. 4b correspond



**Fig. 4** **a** TEM image of a single ZnO nanobelt obtained by annealing the porous ZnO nanobelt in air at 1,000°C for 1 h. The scale bar is 100 nm. **b** UV-vis spectra of 1 and 2 correspond the methyl orange solution, after 2 h irradiation, containing PZNF before and after annealing for 1 h, respectively

PZNF before and after annealing for 1 h, respectively. The contrast experiment result shows that the photocatalysts efficiency of PZNF decreases severely due to the agglomeration of ZnO grains after annealing for 1 h, and confirms definitely that the enhanced photocatalytic activity of PZNF is attributed to the increased surface area.

## Conclusions

In summary, we propose that oxidizing 1D-nanostructure film into porous one is a feasible approach to realize both

high photocatalytic activity and recyclability. Our results reveal that the as-synthesized porous-ZnO-nanobelt film by oxidizing the ZnSe-nanobelt film can be used as recyclable photocatalysts with enhanced photocatalytic activity compared to the ZnO-nanobelt film. Furthermore, the method may be applied to obtain other porous materials.

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