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Preparation and Photocatalytic Activities of Nano-Porous ZnO Thin Film

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A nano-porous ZnO film was prepared by using the porous anodic alumina template method. X-ray diffraction analysis and scanning electron microscopy were used to characterize the nano film. The photocatalytic properties of nano-porous ZnO films were investigated. The results show that the immersion time has great impact on the formation of the nano-porous ZnO film. The holes of porous anodic alumina template was gradually covered with ZnO nanomaterial and became smaller with increasing the immersion time. Finally, it was completely covered with ZnO. When exposed under UV radiation, the degradation rate of methyl orange increases with the increase of the amount of nano-porous ZnO film catalyst and with the exposure time. However, it decreases with increasing of the concentration of methyl orange.

Keywords: Nano-porous ZnO, Porous anodic alumina template, Photocatalytic, Degradation, Methyl orange.

INTRODUCTION

Nano-ZnO which possesses important characters both of nanomaterial and of oxide semiconductor has attracted greater attention of many researchers. After special forms of nano-ZnO crystal continuously reported, a lot of research work has been carried out on ZnO nanomaterial. The nano-ZnO as a semiconductor photocatalysis has also gradually emerged with in-depth study. While each kind of nano-ZnO photocatalyst has its individual synthesis methods, properties and photocatalytic properties [1-5].

Compare to the difficulties arose by the secondary pollution when recycling of the powder or granule form of nano ZnO photocatalyst. The film from nano-ZnO has the advantage on clean recycling process thus avoid secondary pollution, this give nano-ZnO film obvious practical application value [6,7]. In this study, by controlled immerse a porous anodic alumina (PAA) template into a ZnO colloidal solution under a ultrasonic vibration field, a nano-porous ZnO film which is also a kind of ZnO nanotubes was prepared. The photocatalytic properties of the nano-porous ZnO film were studied.

EXPERIMENTAL

Preparation: Zinc acetate dihydrate [$Zn(CH_3COO)_2{\cdot}2H_2O$] (1 g) and 10 mL glacial acetic acid were dissolved in 50 mL of isopropyl alcohol at room temperature in a beaker (denoted as solution A). Another 1 g zinc acetate dihydrate was dissolved in 50 mL of ethanolamine in another beaker (denoted as solution B). Then, solution B was dropwise added into solution A under continuous stirring. After that, the mixture was further stirred for 2 h in a water bath at 50 °C. Finally, the sol of ZnO precursor was obtained after aging the mixture for 48 h at room temperature.

The preparation process of ZnO nanotubes (*i.e.* nano-porous ZnO film) was shown in Fig. 1. First, a porous anodic alumina (PAA) template was immersed in the sol of ZnO precursor. During the immersion process, the sol will adsorbed on the surface of the anodic alumina template [process 1, Fig. 1(b)]. After that, the template was dried at 80 °C for 60 min [process 2, Fig. 1(c)]. Then, the template was annealed in furnace at 350 °C for 2 h [process 3, Fig. 1(d)].

The preparation of ZnO nanotubes used zinc acetate dihydrate as a precursor, isopropanol as solvent and ethanolamine as a stabilizer. The ZnO sol was prepared in the first step, then the ZnO sol transformed into porous ZnO films during the calcination process. The chemical equation is as follows:

$$4Zn(CH_3COO)_2 + H_2O \longrightarrow Zn_4O(CH_3COO)_6 + 2CH_3COOH$$

$$Zn_4O(CH_3COO)_6 \xrightarrow{\text{calcination}} 4ZnO + 3CH_3COCH_3 \uparrow + 3CO_2 \uparrow$$

Characterization: A SEM analysis of the samples was performed on a scanning electron microscope (Hitachi H-600), with accelerating voltage of 200 kV. A XRD analysis was

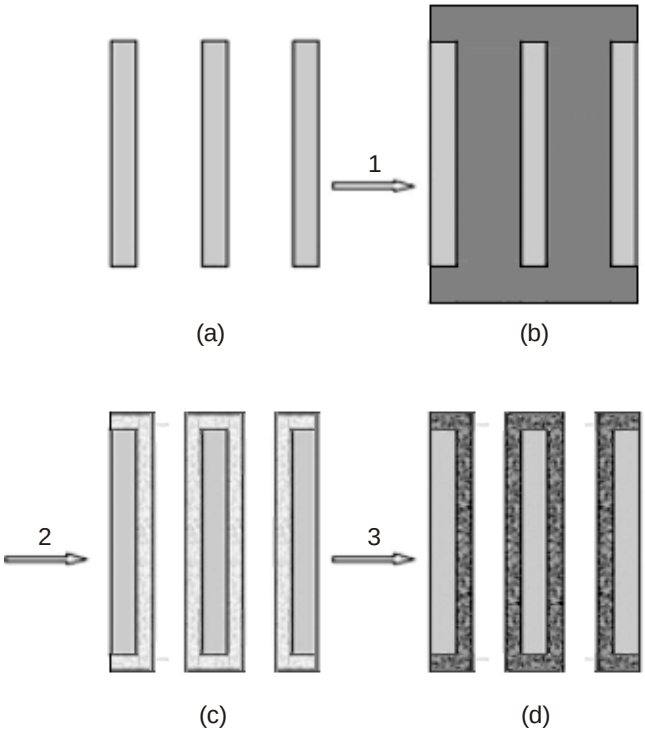

Fig. 1. Preparation of ZnO nano-tube; (a) the porous anodic alumina template; (b) the porous anodic alumina template immerse in a ZnO sol; (c) the ZnO absorbed on the wall of anodic alumina template after drying; (d) after high-temperature calcined there was formed a nano-porous ZnO thin films with nanotube structure (*i.e.* the catalyst) inside the nanopores of the anodic aluminum template

performed on a X-ray diffractometer (D8 ADVANCE, Bruker-AXS, German) with CuK_α radiation, tube voltage of 40 kV, tube current of 40 mA, scan speed of 1° min^{-1}, step width of 0.03° and scan range of 10-80°.

Photocatalytic activity: The catalyst was added into a 40 g/L methyl orange solution with concentration of 0.2 %, 0.4 %, 0.6 % (by weight) respectively. Then each of the solution was exposed under a UV lamp (Xiguang, China) with wavelength of 253.7 nm and 30 W. The distance between the lamp and the methyl orange solution is 10 cm. The solution was continuously stirred at 20 °C. Each solution was sampled in every 0.5 h. The absorbance at 464 nm was measured using a UV-visible spectrophotometer (New Century-T6, China). The activity of the catalyst was characterized by the degradation rate of the sample. And the degradation rate should be calculated as follows:

$$X = \left(1 - \frac{A_t}{A_0}\right) \times 100\ \%$$

where A_0 is the absorbance before the degradation process and A_t is the absorbance after the degradation process.

RESULTS AND DISCUSSION

SEM analysis: Fig. 2(a) is a SEM photograph of the surface of a blank porous anodic alumina template. The image shows that the template is densely constituted of many pores with uniform size and the average diameter of the pore on the template is 100 nm. Fig. 2(b) and (c) are a SEM image of porous anodic alumina template sample which immersed in the sol for 6 or 8 min respectively. As Fig. 2(b) and (c) shows, with the immersion time increased, the diameter of the hole on the porous anodic alumina template becomes smaller and the holes were completely covered when the time is long enough. Fig. 2(d) is a SEM picture of a longitudinal section of the porous anodic alumina template that immersed in the colloidal solution for 6 min. And the thickness of the ZnO film is about 1 μm in the picture. In general the porous anodic alumina template method should include the following steps. First, a porous anodic alumina material should be immersed into a solution of the precursor material of the target material. Then, with the porous anodic alumina material wetted by the solution, the precursor material of the target material should comprehensively contact with the porous anodic alumina material. After the solvent molecules are removed by evaporation process, the precursors molecules of target material will penetrate into the surface of the porous anodic alumina material. Finally the target material will be made after a calcination process.

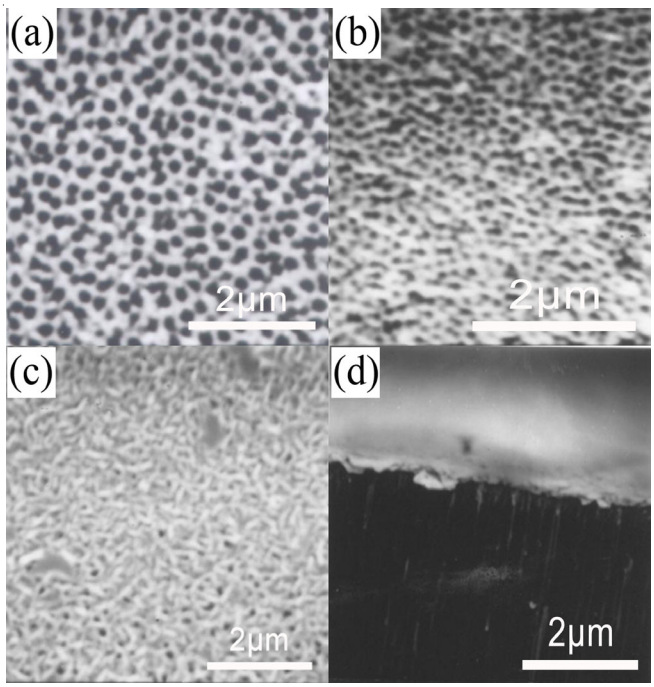

Fig. 2. SEM photograph of the surface of the template after different immersion time: (a) 0 min; (b) 6min; (c) 8 min; (d) side view of (b)

XRD analysis: The XRD spectrum analysis of nano-porous ZnO films is shown in Fig. 3. In this XRD analysis result, the seven major diffraction peak (100), (002), (101), (102), (110), (103) and (112) of zinc oxide were observed at the 2θ = 31.7º, 34.4º, 36.2º, 47.5º, 56.6º, 62.8º and 69.1º respectively. This diffraction data is in good agreement with the PDF card value of hexagonal ZnO (card number 5-0664), which indicating the ZnO nanotubes sample belongs to the hexagonal crystal system.

Photocatalytic properties: The different content (10, 20, 30, 40 and 50 g/L) of catalysts were added into 40 mg/L aqueous solution of methyl orange and the effect of different content of catalyst on the ability of photocatalytic had been studied. Fig. 4 shows the relation between catalyst content and the degradation rate of methyl orange, under UV irradiation

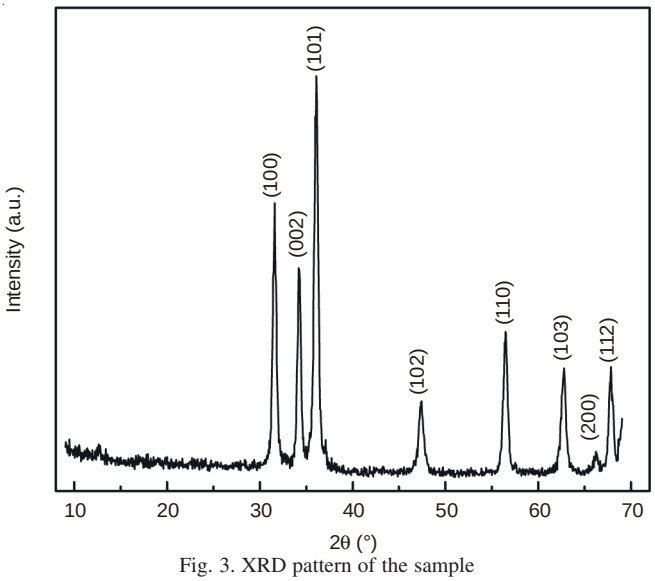

Fig. 3. XRD pattern of the sample

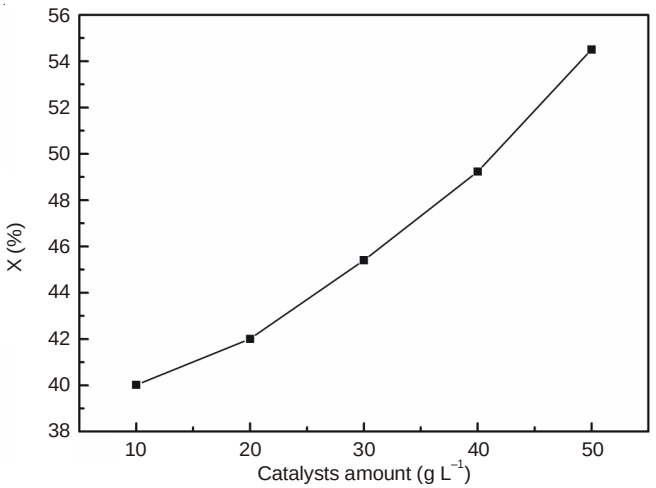

Fig. 4. Relation between catalyst amount and degradation rate of methyl orange under UV irradiation of 0.5 h

of 0.5 h. As the curve shows, with the increase of the amount of catalyst, there is a corresponding increase in the degradation rate of methyl orange, which is because of the increase of the amount of the catalyst in favour of the adsorption and reaction of methyl orange molecule on the catalyst surface [8].

Catalyst with concentration of 30 g/L was added into 40 mg/L aqueous solution of methyl orange. The relationship between the time exposed to UV irradiation and the degradation rate of methyl orange are showed in Fig. 5. As the curve shows, with the increase of irradiation time, there is a corresponding increase in the degradation rate of methyl orange, which exhibited quasi-first-order reaction kinetics. This is because in the photocatalytic reaction, the photocatalytic activity of the catalyst will enhance by the increase of light-induced charge (including electrons and holes) [9], while the prolonging of the exposure time will lead to an increase of the light-induced charge.

Catalyst (30 g/L) was added into aqueous solution of methyl orange of different concentrations (10, 20, 30, 40 and 50 g/L) respectively, with exposure under irradiation of 0.5 h and the result of methyl orange degradation rate of the sample

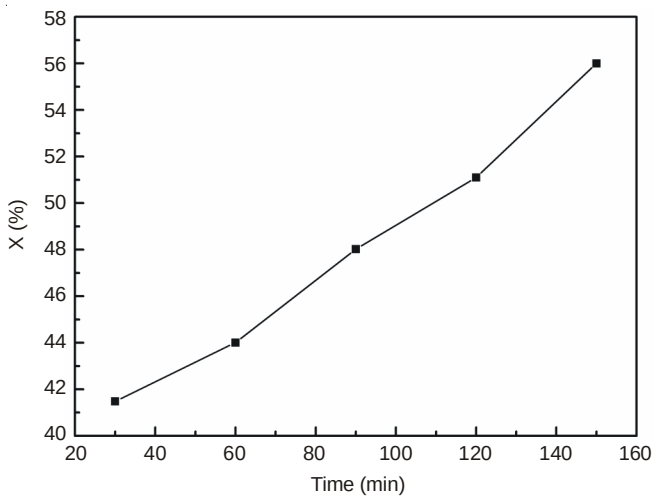

Fig. 5. Relationship between UV irradiation time and the degradation rate of methyl orange by catalysis

is shown in Fig. 6. As the curve shows, the degradation rate of the methyl orange decreases with the increase of the concentration of methyl orange, that is because an excessive initial concentration of methyl orange can affect the transmittance of the solution, thereby reduces the opportunity that photons reach to the surface of the catalyst.

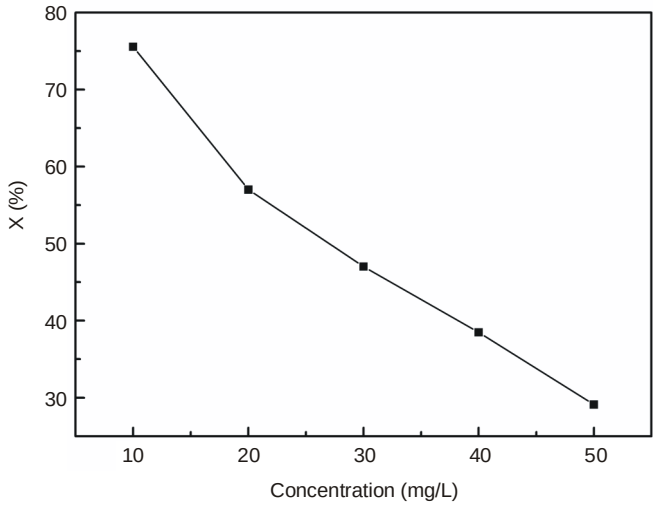

Fig. 6. Relation between different concentrations of catalyst and the degradation rate of methyl orange under UV irradiation of 0.5 h

Conclusion

Porous anodic alumina (PAA) template method are used in the preparation of nano-porous ZnO thin films, in which immersion time have a greater impact on the formation of ZnO nanotubes. With the immersion time increase, the holes of porous anodic alumina template covered with ZnO nanomaterial becomes smaller, finally the holes of porous anodic alumina template are completely covered. The 6 min is the best immersion time. The degradation rate of methyl orange will be increased as the amount of catalyst increasing, as well as the UV irradiation time prolonging. But the increase of the concentration of the methyl orange will reduce the degradation rate of the methyl orange.

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