Full Length Article

Fabrication and enhanced H_2O_2-sensing properties of the uniform porous FTO glasses with tunable pore sizes and densities

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ABSTRACT

The pores with tunable sizes and densities have been prepared in the conductive layer of FTO glasses while keeping the conductivity and transparency almost unvaried, by immersing the FTO glasses coated with Zn powder in the mixed aqueous solution of HCl and ethanol. The average pore size and density can be continuously tuned in the ranges of 22–120 nm and 9–120/μm^2, respectively, by simply adjusting the Zn concentration and/or ethanol volume ratio. The etching mechanism based on the oxidation of Zn by SnO_2 (competing with HCl) has been revealed. Compared with FTO, the porous FTOs made here can greatly increases the detection sensitivity of H_2O_2 up to 3.7 times, when they work as the host substrate of NiO.

1. Introduction

Due to the high electrical conductivity, transparency, and thermal stability, transparent conducting glasses (TCG) including FTO (fluorine-doped SnO_2) and ITO (tin-doped In_2O_3) glasses have been intensively used in information displays (liquid crystal displays, plasma displays, touch panels etc.) [1], electroluminescent devices [2], electrochromic devices [3], bioanalytical devices [4,5], solar cells [6–9], sensors [10,11], etc. To increase the performance of TCG in these applications, a lot of efforts have been made to produce pores in the conductive layer to greatly increase the surface area while keeping the high electrical conductivity and transparency. In general, the reported methods for preparing porous TCG can be divided into three classes. The first class is the mesopore arising from the 3D close packing of FTO or ITO nanoparticles. The typical methods for 3D packing nanoparticles to form pores are doctor-blade technique [6,7], spin coating [12], screen-printing [13], pulse laser deposition [8,14], and magnetron sputtering deposition [15]. The pore size and density can be modified by changing the size and packing density of nanoparticles. However, the pore size is very small, and usually limited within 30 nm (estimated using hexagonal close packing of 100 nm nanospheres). The second class is using organic molecules or solid particles as the template to produce the mesopores. The typical method is sol-gel technique [5,16–18]. The pore size and density can be tuned by changing the size and concentration of the template molecules or particles, respectively. Unfortunately, the preparation procedure is too complicated [17] or the pore induced by

the template is still small, and usually below 50 nm [18]. The final class is etching the conductive layer to form nanopore or submicropores. The typical method is the electrochemical etching route [9–11]. By optimizing the reacting species, the electric potential and current, the pores with size ranging from several tens to a couple of hundred nanometers can be obtained. However, the electrochemical etching obviously decreases both the electrical conductivity and transparency of FTO glasses.

The mixture of Zn powder and aqueous HCl is usually used to etch FTO glasses. However, the study of the etching mechanism has been scarce. Here we reveal that Zn can reduce SnO_2 to $SnCl_2$ in HCl solution, thus leading to the etching, although Zn and SnO_2 is nonreactive at room temperature. This etching method has been used firstly to prepare the uniform porous FTO glasses (PFTO). Furthermore, ethanol has been used to enhance the reaction of Zn and SnO_2 by depressing the competing reaction of Zn and HCl, thus optimizing the etching. This method has three advantages. First, it is simple, fast, and cheap. Second, the pores are not only uniform, but also tunable in sizes and densities in large range. Finally, the conductivity and transparency of FTO glasses are almost kept, which should greatly improve the performance of FTO glasses. As expected, using PFTOs made here instead of FTO as the host substrate of NiO, greatly increases the detection sensitivity of H_2O_2 up to 3.7 folds.

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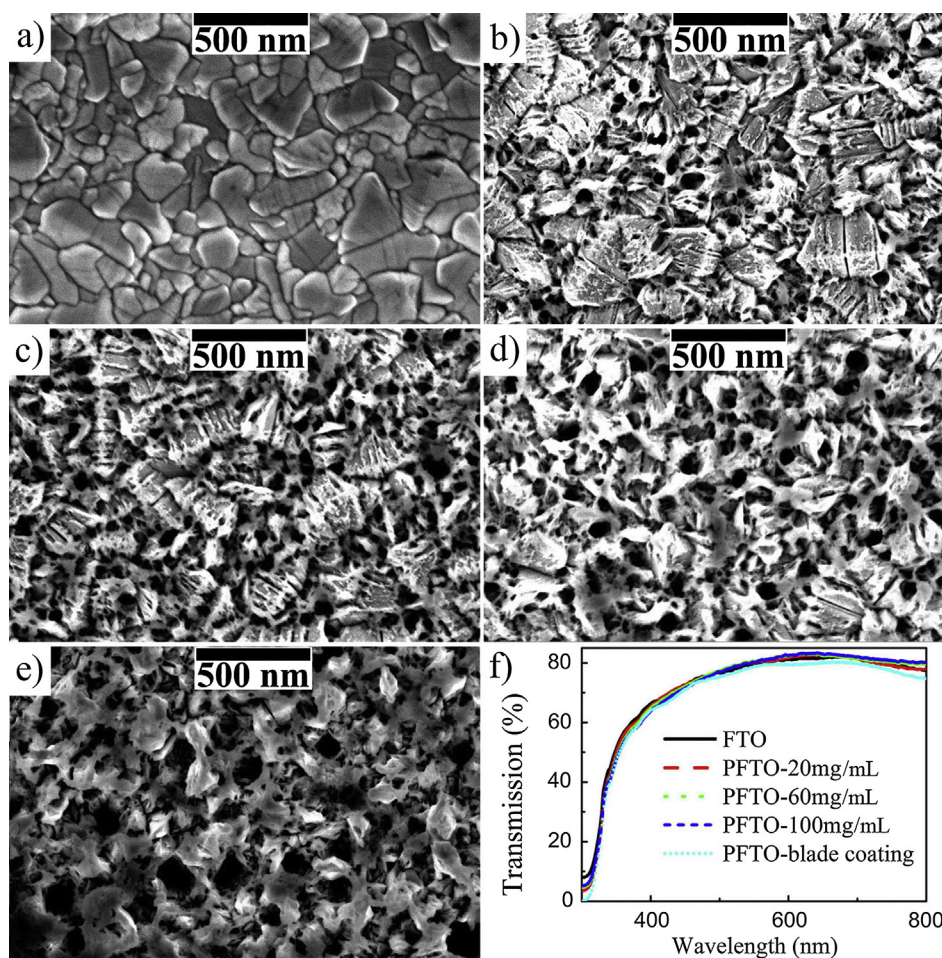 *E-mail addresses:* zhangjh@nju.edu.cn (J. Zhang), mgu@nju.edu.cn (M. Gu).

Fig. 1. SEM images of FTO (a) and PFTOs etched using spin coating of 20 (b), 60 (c), and 100 mg/mL (d) of Zn powder dispersion, and blade coating of Zn powder (e). The black scale bar is 500 nm. (f) Corresponding transmission spectra of the five samples.

2. Experimental

The commercial FTO glasses (7 Ωsq^{-1}, 2.2 mm × 15 mm × 15 mm) were cleaned by sequential ultrasonication for 30 min in aqueous detergent, acetone, ethanol, and deionized water, followed by drying in an oven at 50 °C for 5 h. All the AR grade reagents were used as received. The morphology of samples was examined using a scanning electron microscope (SEM, Helios600i, FEI). The transmission and absorption spectra were recorded using a UV–Vis spectrophotometer and quartz cells (for the liquid samples only) with ~1-cm path length. The oxidation state of Sn was characterized by a x-ray photoelectron spectrometer (XPS, PHI 5000 VersaProbe, UlVAC-PHI).

3. Results and discussion

3.1. Fabrication of PFTOs

As shown in Fig. 1a, the commercial FTO has smooth surface composed of dense particles. In a typical etching, the commercial Zn powder was well dispersed in ethanol using stirring and ultrasonication, then spin coated onto the precleaned FTO at 1500 rpm for 30 s, followed by immersing in the mixed aqueous solution of HCl (0.04 M) and ethanol (with volume ratio of 0.5) for 2 h. The etched FTOs were washed with deionized water 3 times and dried in an oven at 50 °C for 5 h. As seen in Fig. 1b, when 20 mg/mL of Zn dispersion was used, a lot of pores were successfully produced in the FTO layer. Most of the pores are around 22 nm, and distribute randomly with average pore density of 26/μm^2. Upon increasing the Zn concentration to 60 mg/mL, the

average pore size and density greatly increase to 44 nm and 120/μm^2, respectively. Significantly, both the pore size and distribution become uniform (Fig. 1c). It can be ascribed to the better Zn coating coverage induced by the higher Zn concentration. Further increasing the Zn concentration to 100 mg/mL, the pores increase in average size to 82 nm but decrease in density to 70/μm^2, and remain uniform in distribution (Fig. 1d). To obtain larger pores, Zn powder was blade coated onto FTO to form a dense Zn coating coverage. As expected, the average pore size was greatly increased to 120 nm, meanwhile, the average pore density decreased to around 30/μm^2 (Fig. 1e) due to the increase of the pore size. In all of the above PFTO samples, the coherence and integrality of the FTO layer are well kept after the pore formation, and both the high conductivity and transparency of FTO are almost unvaried. The sheet resistance of these PFTO is around 9 Ωsq^{-1}, which is close to that of FTO. As shown in Fig. 1f, compared with FTO, the uniform pore structures of the PFTO only slightly reduce the transmittance due to the light scattering of pores [9–11].

3.2. The etching mechanism

In order to control the pore structures, the following experiments were designed to reveal the etching mechanism. (1) FTOs were immersed in aqueous solution of HCl (2.4 M), ZnCl$_2$ (1 M), and HCl (0.1 M) mixed with ZnCl$_2$ (1 M) at room temperature for 24 h, respectively; (2) the similar experiments were carried out at 80 °C for 6 h. No pores were formed in all these experiments, confirming the following conclusions. (1) FTO can't be dissolved by aqueous HCl, it is the characteristic of FTO; (2) both the product (ZnCl$_2$) and heat release of