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Letter

Plasma electrolytic oxidation preparation and characterization of SnO_2 film

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ABSTRACT

SnO_2 film is firstly prepared by plasma electrolytic oxidation technology in sodium stannate solution. The structure and photocatalytic property of the film are characterized by SEM, XRD and UV-Vis spectrophotometer. Rough and porous netlike film formed on the substrate. The XRD result showed the oxide was pure SnO_2. The absorption edge of the film was determined as 420 nm. Photocatalytic degradation of rhodamine indicated SnO_2 film was an effective photocatalyst.

1. Introduction

SnO_2 is used to photocatalytic decontamination treatment of polluted water and air purification due to its excellent chemical stability and unique catalytic property [1,2]. To date, most of the ongoing research on SnO_2 photocatalysis focuses on the use of nanocrystalline powder. However, the use of SnO_2 powder in photocatalysis is difficult due to that power is hard to separate, recycle and reuse. So, SnO_2 must be immobilized in films to be useful in any practical photocatalytic application.

Plasma electrolytic oxidation (PEO) has widely used to prepare oxide film on the Al, Mg and Ti [3,4]. The distinct properties of oxide film formed via PEO include high porosity, remarkable thickness and good adhesion to the metal substrates. Furthermore, the composition and structure of PEO film can be changed by adding different electrolyte ionic compositions. Our previous research [5] reveals that WO_3 can be generated when titanium is plasma electrolytic oxidized in electrolyte containing WO_4^{2-}. On this basis, we attempt to synthesis SnO_2 film by PEO technology in solution containing SnO_3^{2-}.

In this study, SnO_2 film is prepared by PEO in sodium stannate solution. The structure and photocatalytic property of film are investigated.

2. Experimental

The setup of plasma electrolytic oxidation consisted of ambipolar impulsing power source, electrolytic cell, mixing system, cooling system and exhaust system. The sketch map of setup is presented in Fig. 1.

A pure titanium (99.9%) sheet with dimensions 20 mm × 20 mm × 2 mm was selected as base material, polished with emery papers (#400–#1200 grit) and degreased using acetone followed by rinsing with distilled water. The electrolyte consisted of 10.7 g/L Na_2SnO_3, 2 g/L NaOH and 2 g/L NaF. A pure titanium sheet was used as an anode and a stainless steel plate was used as cathode. The positive voltage, negative voltage, frequency, duty cycle and treatment period were 300 V, −30 V, 700 Hz, 0.3 and 5 min, respectively. The temperature of electrolyte was kept at the range of 25–40 °C through circulating water cooling system during the complete PEO process. The prepared SnO_2 film was rinsed in distilled water, dried in hot air and then kept in a drying chamber. In order to compare the photocatalytic activity of SnO_2 film with TiO_2 film, we also prepared the TiO_2 film. The electrolyte for preparing TiO_2 film consisted of 10.7 g/L Na_3PO_4, 2 g/L NaOH and 2 g/L NaF, and the other parameters and processes were the same with SnO_2 film.

The morphologies of film were characterized by Quanta 200 scanning electron microscopy. The crystal structure was determined by X-ray diffractometer using Cu Kα. The UV–Vis absorption spectra of film were recorded on a Shimadzu UV-2550 spectrophotometer with an integrating sphere.

Photocatalytic activity of film was determined by photodegradation of rhodamine in aqueous solution. The film was pre-saturated in 10 ml of 10 mg/L rhodamine solution at dark for 30 min to reach adsorption/desorption equilibrium. A 365 nm ultraviolet germicidal lamp with 40 W was used as light source. The solution was constantly supplied with air during the reaction.

For the purpose of determining photocatalytic activity of film, the absorbance of rhodamine solution at 550 nm was tested by a Shimadzu UV-2550 spectrophotometer. Because the absorbance of dilute solution is linear with its concentration according to Lambert–Beer Law [6], degradation percentage of rhodamine η can be calculated according to the formula (1)

$$\eta = \frac{A_0 - A}{A_0} \times 100\% \quad (1)$$

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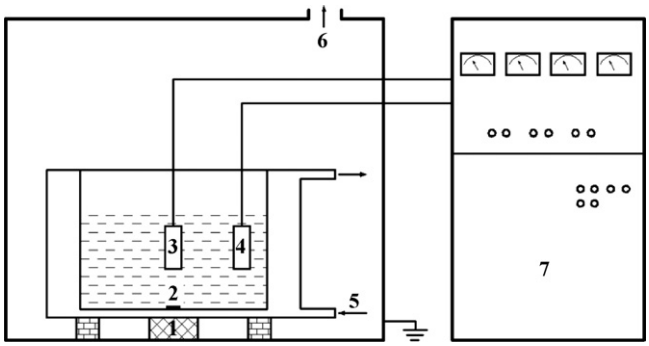

Fig. 1. Sketch map of plasma electrolytic oxidation setup: 1 magnetic stirrer; 2 rotor; 3 titanium sheet; 4 counter electrode; 5 circulating cooling system; 6 exhaust system; 7 power source.

where A_0 is the initial absorbance of rhodamine solution, A is the absorbance of rhodamine solution when photocatalytic reaction is finished.

3. Results and discussion

3.1. Surface and cross-sectional morphologies of film

The SEM micrographs of SnO_2 film are presented in Fig. 2. Rough and porous netlike film forms on the titanium substrate. The formation of such highly branched structures is caused by gas generation during the film process. All the pores are well separated and homogeneously distribute over the surface. Cross-sectional views of SnO_2 film reveal a dense morphology. The thickness of film is estimated to be 80 μm. There is no obvious discontinuity between the film and the underlying substrate. It appears that the SnO_2 film is well adhered to the substrate.

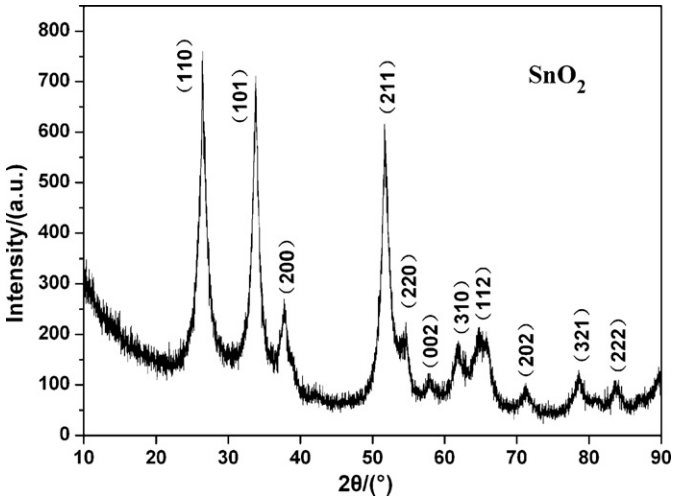

Fig. 3. XRD patterns of SnO_2 film.

3.2. XRD analysis of film

Fig. 3 shows XRD patterns of SnO_2 film. All peaks are assigned to SnO_2. The peaks of SnO_2 are wide, which means the grain of SnO_2 is rather small. The grain size of SnO_2 is calculated by Scherrer formula and determined as 60 nm. The experimental diffraction peaks and that of JCPDS data are tabulated in Table 1 [7].

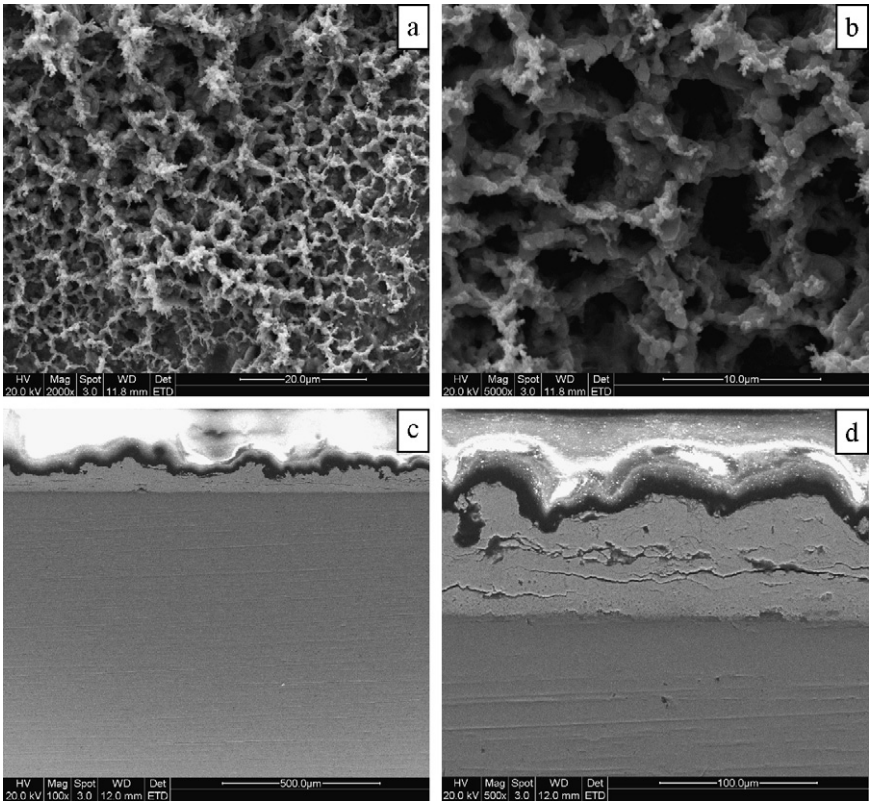

Fig. 2. Morphologies of SnO_2 film: (a and b) surface; (c and d) cross-section.

Table 1
Experimental and JCPDS data diffraction peak positions of SnO_2 phase.

($h\,k\,l$)	Experimental (2θ)	Literature (2θ)
(1 1 0)	26.462	26.589
(1 0 1)	33.823	33.877
(2 0 0)	37.804	37.956
(2 1 1)	51.656	51.777
(2 2 0)	54.634	54.762
(0 0 2)	57.876	57.828
(3 1 0)	61.861	61.887
(1 1 2)	64.772	64.741
(2 0 2)	71.230	71.279
(3 2 1)	78.591	78.714
(2 2 2)	83.676	83.717

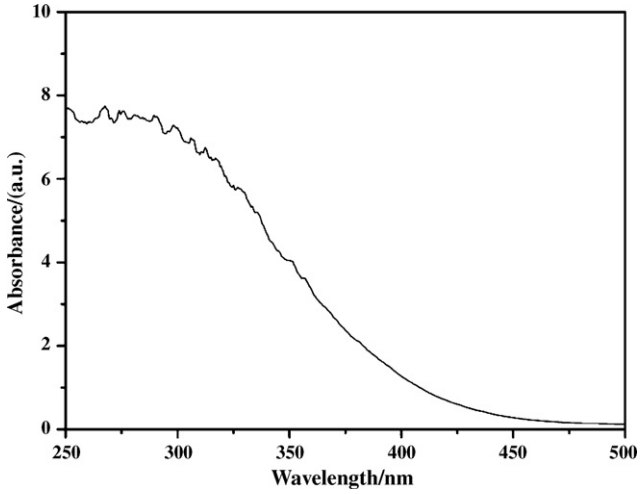

Fig. 4. UV–Vis absorption spectrum of SnO_2 film.

The forming reason of SnO_2 film can be interpreted as follows. SnO_3^{2-} could be uniformly absorbed at the surface of anode under electric field, and decomposed into SnO_2 under the elevated temperature generated by micro-plasma discharge. As-deposited SnO_2 forms film at the surface of anode.

3.3. UV–Vis diffuse reflectance spectra of film

Fig. 4 shows the UV–Vis diffuse reflectance spectra of SnO_2 film. The oxide film reveals excellent absorption of UV light. The absorption edge of SnO_2 film occurs at 420 nm, and the band gap E_g is calculated according to the formula (2)

$$E_g = \frac{hc}{\lambda} = \frac{1243.1}{\lambda} \quad (2)$$

where E_g is the band gap (eV) of the film, h is the Planck's constant (4.135667×10^{-15} eV s), c is the velocity of light (3×10^8 m/s), λ is the cut-off wavelength of the spectra (nm), and the unit of 1243.1 is eV nm. The band gap energy of SnO_2 film is calculated to be 2.95 eV, which is considerably less than the well-known SnO_2 band gap of 3.5–3.6 eV. The reason of this discrepancy is not very clear and being investigated now.

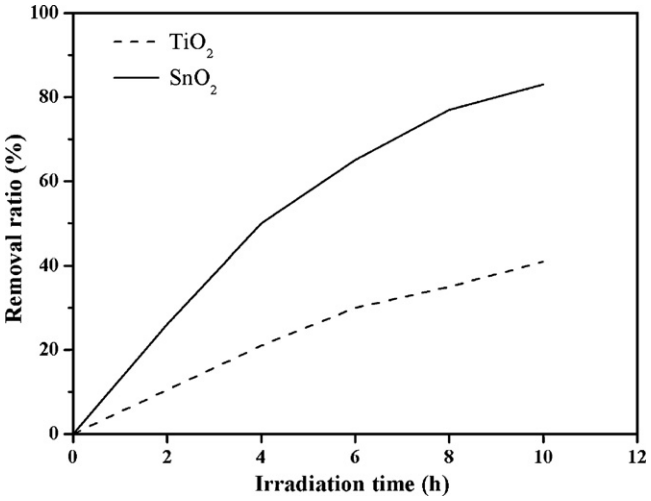

Fig. 5. Removal ratio of rhodamine as a function of irradiation time.

3.4. Photo-degradation of rhodamine

No detectable degradation of rhodamine occurs without SnO_2 film and TiO_2 film. The removal ratio of rhodamine is presented in Fig. 5. The result indicates that about 83% of rhodamine is degraded by SnO_2 film within 10 h of UV irradiation whereas about 41% of rhodamine is degraded by TiO_2 film within 10 h of UV irradiation, so photocatalytic activity of SnO_2 film is higher than that of TiO_2 film.

The porous surface structure should be responsible for providing more surface sites, in which holes could react with adsorbed molecules. Excellent absorption ensures many photos absorbed to generate holes, which has very strong oxidizing power due to the valence band of SnO_2 lying more positive than TiO_2. Both contribute to photocatalytic degradation of rhodamine.

4. Conclusions

SnO_2 film was successfully produced by the plasma electrolytic oxidation technique in stannate electrolyte. SnO_2 film presented porous netlike surface and high absorption in UV region, which were responsible for its high photocatalytic activity. Future works will focus on the further improvement of photocatalytic activity of SnO_2 film by adjusting process parameters, such as power voltage, reaction time, electrolyte composition, etc.

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