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Short communication

Antimony and cerium co-doped tin oxide electrodes for pollutant degradation

Xueming Chen[a,*], Peidong Yao[a,*], Dahui Wang[a], Xingzheng Wu[b]

[a] Environmental Engineering Department, Zhejiang University, Zheda Road 38, Hangzhou 310027, China
[b] Materials Science Department, University of Fukui, Fukui, Japan

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ABSTRACT

The antimony and cerium co-doped tin oxide (SnO_2–Sb–Ce) films were successfully deposited on Ti substrates using ultrasonic spray pyrolysis (USP). The comparison of morphology and electrochemical properties between Ti/SnO_2–Sb–Ce and Ti/SnO_2–Sb electrodes was conducted. It was found that the Ti/SnO_2–Sb–Ce electrodes had smaller sizes of coating grains, higher overpotential for oxygen evolution, and better electrocatalytic activity than the Ti/SnO_2–Sb electrodes. The current efficiency was only 25% for degradation of 500 mg L^{-1} Orange II on the Ti/SnO_2–Sb electrode at a charge loading of 5.4 Ah L^{-1}, but increased to 47% on the Ti/SnO_2–Sb–Ce electrode under the same conditions.

1. Introduction

Electrocatalytic oxidation technology has promising application prospects owing to its high oxidation efficiency, fast reaction rate, easy operation and environmental benign in wastewater treatment [1–4]. The electrocatalytic oxidation efficiency depends strongly on the electrode materials [3,4]. Up to date, numerous types of electrodes have been investigated. Among them, the cost-effective Ti/SnO_2–Sb electrodes are particularly attractive. They have demonstrated higher degradation efficiency than conventional electrodes such as PbO_2, IrO_2, RuO_2 and Pt [5–7]. However, it should be noted that the electrocatalytic activity of the Ti/SnO_2–Sb electrodes is not sufficient yet, and therefore needs further improvement.

It is well known that the anodic oxygen-transfer reactions mainly occur on the sites of dopants for a semiconducting oxide mixture with high overpotential for oxygen evolution [8–10]. Therefore, the electrochemical activity of electrodes should be determined primarily by the properties of dopants. Actually, many researchers found that the incorporation of some foreign ions could considerably improve the electrocatalytic activity and stability of the electrodes [11–16]. It is worthy of mention that Ce is an attractive dopant due to its unique properties. When the Ce element with f-electron orbits is doped into the metal oxide coatings, additional energy bands can be induced in the structure of coatings. This may help to develop convenient channels for electrons transition and enhance the electrocatalytic characteristics of the anodes. It was reported that the electrocatalytic activity of PbO_2 electrodes for pollutants degradation could be enhanced significantly by doping Ce [15,16]. But little attention has been paid to Ti/SnO_2–Sb–Ce electrodes for pollutants degradation. The major objective of this paper is to demonstrate the good microstructure and high electrocatalytic activity of the Ti/SnO_2–Sb–Ce electrodes prepared for pollutant degradation. The Orange II, a typical toxic and non-biodegradable azo dye used in the textile industry, was selected as a model pollutant.

2. Experimental

Ti plates (20 mm × 24 mm × 1.6 mm) were used as substrates. Before deposition, the substrates were sandblasted first, then etched in boiling 37% hydrochloric acid for 2 min, and finally cleaned ultrasonically in deionized water for 10 min. After pretreatment, the SnO_2–Sb–Ce films were deposited on the Ti substrates using ultrasonic spray pyrolysis (USP) with the precursor that was prepared by dissolving $SnCl_4\cdot 5H_2O$, $CeCl_3\cdot 7H_2O$ and $SbCl_3$ into dilute hydrochloric acid solution. The concentration of $SnCl_4\cdot 5H_2O$ was 0.5 M and the molar ratio of Sn:Sb:Ce was 89:3:8. The USP deposition parameters were: substrate temperature 600 °C, atomizing rate 0.17 mL min^{-1}, N_2 flow rate 5 L min^{-1}, deposition time 0.5 h. The total oxide coating loading was about 20 g m^{-2}. More details about the USP deposition procedures can be found elsewhere [17].

Coating morphology was examined by field emission scanning electron microscopy (FE-SEM: Sirion-100, FEI, the Netherlands). Surface composition of the coating was analyzed using energy

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* Corresponding authors.
E-mail addresses: chenxm@zju.edu.cn (X. Chen), yyppdd@sina.com (P. Yao).

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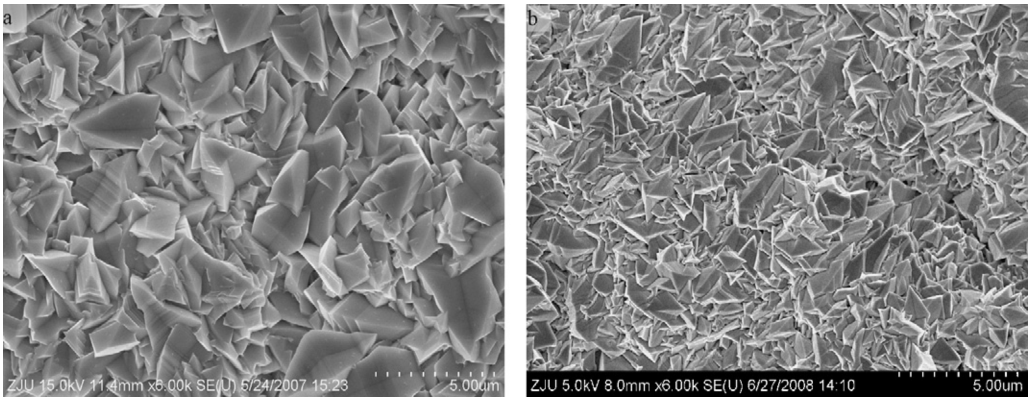

Fig. 1. FESEM images of Ti/SnO_2–Sb (a) and Ti/SnO_2–Sb–Ce (b) electrodes.

dispersion X-ray spectroscopy (EDX: S4800, Hitachi, Japan). The electrochemical behavior was investigated using a potentiostat/galvanostat (CHI600B, Chenhua, Shanghai, China). Ti plate was used as a counter-electrode, and the saturated calomel electrode (SCE: 0.241 vs NHE) was used as a reference electrode.

The electrochemical reactor had dimensions of 130 mm in height and 30 mm in diameter, and was operated in batch. A magnetic stirrer was used to enhance mass transport. Temperature was controlled at 30 °C with a water bath. More details about the electrochemical reactor can be found elsewhere [18]. Chemical oxygen demand (COD) was measured using a COD reactor and a direct reading spectrophotometer (DR/2500, Hach, USA). Current efficiency (CE) is defined as the ratio of current used in oxidizing pollutants to the total current supplied, and can be calculated by the following equation [7]:

$$\mathrm{CE} = \frac{\mathrm{COD}_t - \mathrm{COD}_{t+\Delta t}}{I \times \Delta t \times 8000} FV \times 100\% \qquad (1)$$

where t is the electrolysis time (s); COD_t and $\mathrm{COD}_{t+\Delta t}$ are the COD values at times t and $t + \Delta t$ ($\mathrm{mg\,L^{-1}}$), respectively; I is the electrolysis current (A); F is the Faraday's constant, 96,500 (C mol electrons^{-1}); and V is the volume of solution (L). Since the volume of the solution in the reactor decreased gradually due to sampling for the COD measurement, it was adjusted in calculating both the CE and the charge loading.

3. Results and discussion

Fig. 1 presents typical FESEM images of Ti/SnO_2–Sb and Ti/SnO_2–Sb–Ce electrodes. It was found that the Ti/SnO_2–Sb–Ce electrode was more compact. This indicates that doping Ce can improve the coating structure effectively. The average size of the SnO_2–Sb–Ce grains was about 1 μm, only half of the SnO_2–Sb grains. This is attributed to the formation of heterogeneous nuclei, CeO_2 [15,19].

Fig. 2 shows the EDX spectrum of the coating of the Ti/SnO_2–Sb–Ce electrode. The Sn, O, Ce and Sb peaks were clearly observed, indicating the formation of the oxide mixture of Sn, Sb and Ce. The molar ratio of Sn:Sb:Ce was 94.3:3.0:2.7.

Fig. 3 shows the cyclic voltammograms (CVs) obtained on a Ti/SnO_2–Sb–Ce electrode and on a Ti/SnO_2–Sb electrode in 0.5 M H_2SO_4 solution. It can be seen that the onset potential for O_2 evolution on the Ti/SnO_2–Sb–Ce electrode is about 2.2 V vs NHE, higher than that on the Ti/SnO_2–Sb electrode. This reveals that doping Ce can improve the current efficiency because O_2 evolution is the main secondary reaction. Fig. 4 compares CVs in 0.5 M H_2SO_4 + 500 $\mathrm{mg\,L^{-1}}$ Orange II solution. Addition of Orange II to the electrolyte resulted in a well-defined Orange II oxidation peak on the Ti/SnO_2–Sb–Ce electrode, but no corresponding peak was observed on the Ti/SnO_2–Sb electrode. This indicates that the Ti/SnO_2–Sb–Ce electrode should have higher electrocatalytic activity for Orange II degradation than the Ti/SnO_2–Sb electrode.

In order to investigate the influence of Ce on the electrocatalytic activity further, degradation experiments using Orange II as a model pollutant were carried out on different electrodes. Fig. 5 shows the variations of COD with charge loading. At a charge

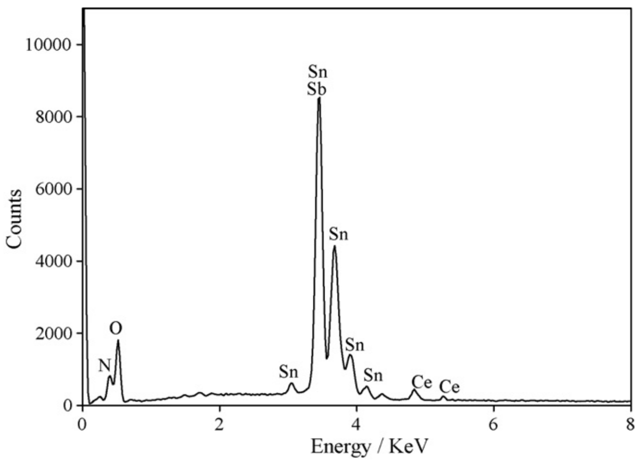

Fig. 2. EDX of Ti/SnO_2–Sb–Ce electrodes.

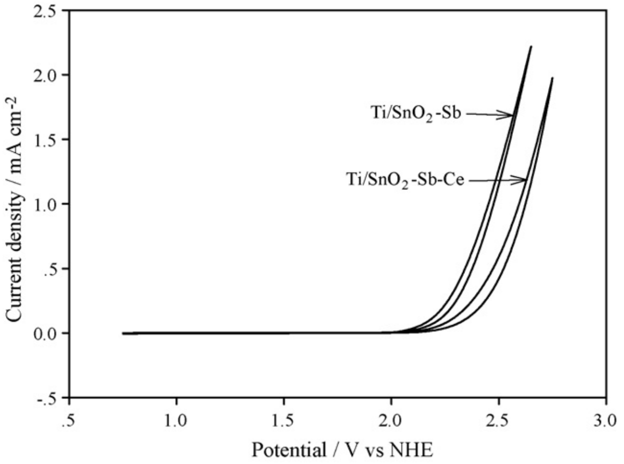

Fig. 3. CVs in 0.5 M H_2SO_4 solution at 25 °C and a scan rate of 100 mV s^{-1} on different electrodes.

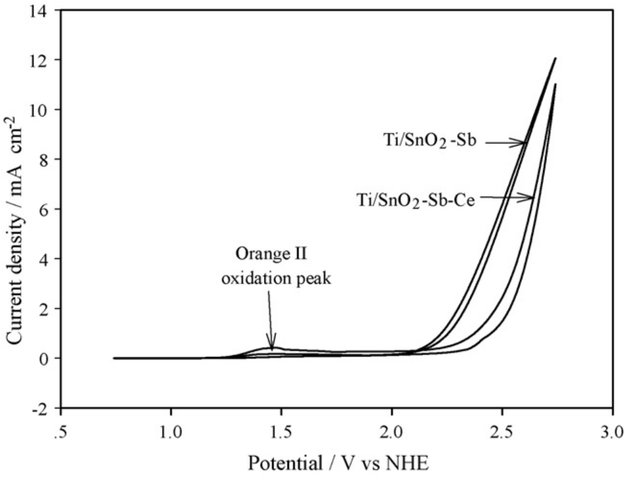

Fig. 4. CVs in 0.5 M H_2SO_4 + 500 mg L^{-1} Orange II solution at 25 °C and a scan rate of 100 mV s^{-1} on different electrodes.

loading of 5.4 Ah L^{-1}, the Ti/SnO_2–Sb electrode could only reduce COD from initial 760 to 360 mg L^{-1} with a current efficiency of 25%. In contrast, nearly 100% COD reduction was achieved on the Ti/SnO_2–Sb–Ce electrode at the same charge loading, with a current efficiency of 47% being obtained. In addition, as shown in Fig. 6, the eventual solution after degradation still had brown color for the Ti/SnO_2–Sb electrode, whereas the solution became colorless for the Ti/SnO_2–Sb–Ce electrode. Obviously, the Ti/SnO_2–Sb–Ce electrode is much more active than the Ti/SnO_2–Sb electrode. The Ti/SnO_2–Sb–Ce electrode is also much more active than many other electrodes, such as Ti/SnO_2, Ti/IrO_2, graphite and Ebonex, which have current efficiencies of 4–14% only in degrading Orange II under similar conditions [20,21]. The mechanisms of Ce in enhancing the electrocatalytic activity are complicated. It is generally believed that pollutants are degraded by the active oxygen on anodes [7,22]. The Ce element has unique outer electronic structure. The electrons at the 4f orbital, which are not fully occupied, can occupy the 5d orbital and become valence electrons [23]. When Ce is doped into the metal oxide coatings, additional energy bands can be induced in the structure of coatings. This probably improves the electrochemical properties of the coating, resulting in a significant increase in electrocatalytic activity. In addition, CeO_2 is known to have a good oxygen storage capacity [24,25]. This favors the accumulation of the active oxygen on the anode surface, leading to a further improvement in electrocatalytic activity. Moreover, as demonstrated in Fig. 1, doping Ce caused a decrease in the average grains size of the coating film. Such a decrease in the average grains size can increase the specific surface area of the Ti/SnO_2–Sb–Ce electrode. This is also beneficial to the electrocatalytic degradation.

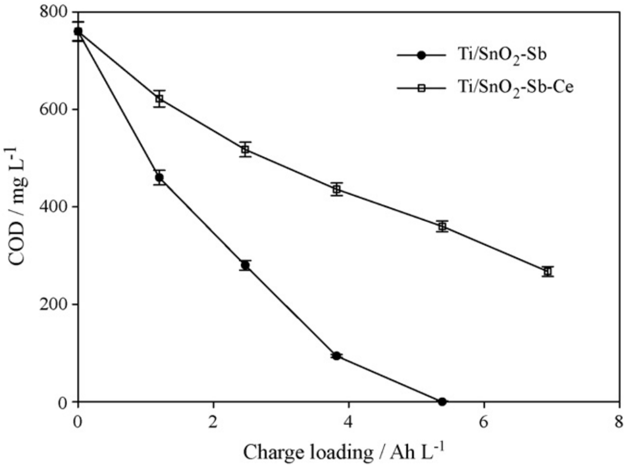

Fig. 5. COD variations with charge loading on different electrodes under conditions of 100 A m^{-2}, 30 °C, pH 11.3, 500 mg L^{-1} Orange II and 1500 mg L^{-1} Na_2SO_4.

Fig. 6. Color changes of solutions: (a) original 500 mg L^{-1} Orange II solution; (b) solution after degraded on a Ti/SnO_2–Sb electrode; and (c) solution after degraded on a Ti/SnO_2–Sb–Ce electrode.

4. Conclusion

The Ti/SnO_2–Sb–Ce electrodes were successfully fabricated using USP. The comparison of morphology and electrochemical properties between Ti/SnO_2–Sb–Ce and Ti/SnO_2–Sb electrodes indicated that the former ones have better electrocatalytic activity. The current efficiency for degradation of 500 mg L^{-1} Orange II on the Ti/SnO_2–Sb–Ce electrode was 22% higher than that on the Ti/SnO_2–Sb electrode under the same conditions.

Acknowledgements

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