

## Preparation of Ce doped Ti-based $\text{SnO}_2/\text{Sb}$ electrode and its application in dyestuff wastewater degradation with improved treatment efficiency

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**Abstract.** In this study, a novel Ce doped Ti-based  $\text{SnO}_2/\text{Sb}$  electrode ( $\text{Ti}/\text{SnO}_2@\text{Sb}@\text{Ce}$ ) with high overpotential and high catalytic activity was prepared by two-step method. The nano-scale film was formed with the help of an additional step of hydrothermal synthesis process contributing to produce more OH radicals for dye degradation. The electrochemical performances of the  $\text{Ti}/\text{SnO}_2@\text{Sb}@\text{Ce}$  electrode were investigated by cyclic voltammetry (CV) and linear sweep voltammetry (LSV), and compared with the conventional electrode ( $\text{Ti}/\text{SnO}_2\text{-Sb-Ce}$ ) which was prepared by the direct thermal decomposition method. Degradation efficiency was tested by degrading methylene blue simulated wastewater. Results show that  $\text{Ti}/\text{SnO}_2@\text{Sb}@\text{Ce}$  not only has higher overpotential but possesses stronger electro-catalytic capability compared with  $\text{Ti}/\text{SnO}_2\text{-Sb-Ce}$ .

### Introduction

Wastewater treatment process is undergoing a profound transformation due to the fundamental changes in regulations governing the discharge and disposal of hazardous pollutants [1]. Traditional technologies, such as physical-chemical process, biological treatment, Fenton process, photocatalysis et al., are no longer able to meet the ever-increasing demand. Electrochemical oxidation can transform organic pollutants into  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and inorganic anions by hydroxyl radicals ( $\bullet\text{OH}$ ) [2], with high oxidation efficiency, easy operation and environmental compatibility[3], and it therefore has evoked great attention in recent years [4]. In this situation, the electrode materials become a decisive factor of the electrode performance. Dimensionally stable anodes (DSAs) with an awful lot of advantages, such as high stability, high activity and low cost, have been widely investigated for electrochemical applications over the past two decades [5]. Various metal oxides are used to prepare DSAs including  $\text{RuO}_2$ ,  $\text{MnO}_2$ ,  $\text{IrO}_2$ ,  $\text{PbO}_2$ , and  $\text{SnO}_2$ . Among of them,  $\text{SnO}_2$  has been regarded as an excellent anodic material in applications for electrochemical oxidation due to its good conductivity, low price, easy to prepare and high over-potential [6]. However, in the literature, much concern was paid on how to improve the electrodes' service lifetime, dope with different metal and change the load method, there are very few people focusing on the importance of mother liquor coating.

Based on the above conception, in this work, for the sake of obtaining a special surface and high overpotential electrode, Ce doped Ti-based  $\text{SnO}_2/\text{Sb}$  electrode ( $\text{Ti}/\text{SnO}_2@\text{Sb}@\text{Ce}$ ) was prepared using a combined facial hydrothermal synthesis following a high temperature decomposition method. To evaluate the electrochemical degradation efficiency of this electrode about dyestuff wastewater, methylene blue is chosen as the simulated target wastewater, since methylene blue is a typical azo dyestuff that can be used in various industrial productions including dye, medical, analysis and appraisal industry.

## Experimental

**Electrode preparation.** In order to prepare a metal oxide film material, the titanium substrate was pre-treated based on the following procedure. First, pure Ti sheets (99.9%, 30 mm × 20 mm × 1 mm) was mechanically polished with 600-mesh and 1200-mesh abrasive papers. Then, the titanium substrate was cleaned with deionized water and acetone was used to remove the solid particles and grease. It was then immersed in sodium hydroxide (20% m/m) at the temperature of 80°C for 60 min, and etched in boiling hydrochloric acid (30% v/v) for about 180 min to produce a gray surface with uniform roughness. Finally, the titanium substrate was washed by ultrasonic cleaning equipment and stored in deionized water.

The Ce doped Ti-based SnO<sub>2</sub>/Sb electrode (Ti/SnO<sub>2</sub>@Sb@Ce) was prepared by hydrothermal synthesis of 0.1 mol L<sup>-1</sup> SnCl<sub>4</sub> · 5H<sub>2</sub>O, 0.014 mol L<sup>-1</sup> SbCl<sub>3</sub>, 0.3 mol L<sup>-1</sup> C<sub>6</sub>H<sub>12</sub>O<sub>6</sub> · H<sub>2</sub>O and 0.001 mol L<sup>-1</sup> Ce(NO<sub>3</sub>)<sub>3</sub> · 6H<sub>2</sub>O in mixture solution consisted of deionized water and ethanol with volume ratio of 1:1 at 180°C for 24 hours, followed by thermal oxidation of the outer coating layer at 550°C for 2 hours. For a comparison, a conventional SnO<sub>2</sub> electrode (Ti/SnO<sub>2</sub>-Sb-Ce) was also prepared, which could just directly use the mixed solution to deposit on the Ti sheet and be calcinated.

**Electrochemical testing.** All the electrochemical measurements of the Ti/SnO<sub>2</sub>@Sb@Ce and Ti/SnO<sub>2</sub>-Sb-Ce electrodes were tested on a CHI760D electrochemical workstation (Chenhua Instrument Shanghai Co. Ltd. China) with a conventional three-electrode cell. The as-prepared electrode was used as the working electrode with a test area of 2 × 3 cm<sup>2</sup>, a saturated calomel electrode (SCE) as the reference electrode and titanium plate as the counter electrode. All the solutions were prepared with deionized water and the reagents used in the experiments were of analytical grade. Before each measurement, the system was kept at open circuit potential for 20 min until the potential was stable. Linear sweep voltammetry (LSV) characterization was conducted in 0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> and 0.1 mol L<sup>-1</sup> Na<sub>2</sub>SO<sub>4</sub> aqueous solutions, at a scan rate between 10 and 100 mV s<sup>-1</sup>. Cyclic voltammetry (CV) curves were performed between 0.5 and 2.5 V (vs. SCE) with different sweep rates.

Methylene blue degradation was conducted in a 200 mL glass beaker. The prepared anode, and a Ti sheet cathode having the same area were placed in the beaker with a separation distance of 20-mm. A direct current power supply with a voltage range of 0–10V was employed. The current density was controlled at the constant 20, 40, 60 mA cm<sup>-2</sup>, respectively. The initial methylene blue solution (10mg L<sup>-1</sup>) was placed in the glass beaker with 0.1 mol L<sup>-1</sup> Na<sub>2</sub>SO<sub>4</sub> and 0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> electrolyte. During the experiments, the solution in the glass beaker was analyzed every 10 min for the color removal efficiency of methylene blue. A UV-VIS spectrophotometer was used to record the absorbance, with a maximum adsorption wavelength of methylene blue trihydrate at 662 nm.

## Results and Discussion

**Cyclic voltammetry.** Fig. 1(a) presents the typical CV curves performed with Ti/SnO<sub>2</sub>@Sb@Ce and Ti/SnO<sub>2</sub>-Sb-Ce electrodes in the case of 0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>, 0.1 mol L<sup>-1</sup> Na<sub>2</sub>SO<sub>4</sub> and 10 mg/L methylene blue aqueous solutions at a scan rate of 20 mV s<sup>-1</sup>. It can be seen that the onset potential of oxygen evolution reaction (OER) is located in the potential range 2.1 ~ 2.3 V on the Ti/SnO<sub>2</sub>@Sb@Ce electrode, and 1.8~2.0 V on the Ti/SnO<sub>2</sub>-Sb-Ce electrode. This suggests that SnO<sub>2</sub>@Sb@Ce as a novel material has a sufficient oxygen overvoltage before H<sub>2</sub> (cathode) and O<sub>2</sub> (anode) form, since weak interactions exist between the hydroxyl radical (•OH) and the electrode surface. No peaks are found on the CV curves when scan rate was 20 mVs<sup>-1</sup>, indicating that there was no direct electron transfer occurring on both the electrode surfaces. All these facts may suggest that a nano-scale film that was formed with the help of an additional step of hydrothermal synthesis process contributes to produce more •OH radicals for dye degradation, and remit the mechanical stress

generated between the Ti substrate and the coating.

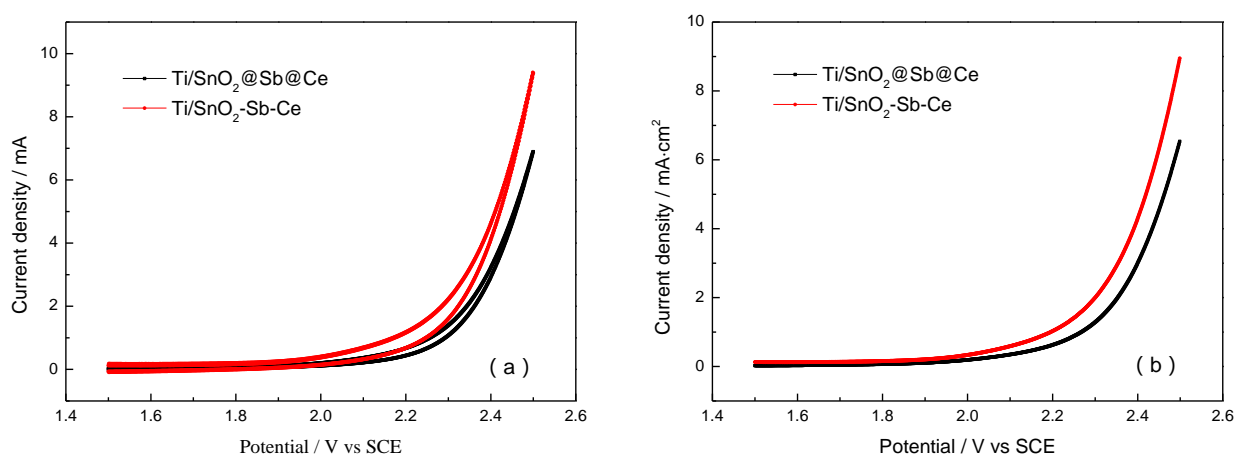


Fig. 1 (a) The CV curves of Ti/SnO<sub>2</sub>@Sb@Ce electrode (black line), Ti/SnO<sub>2</sub>-Sb-Ce electrode (red line), which were measured in 0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>, 0.1 mol L<sup>-1</sup> Na<sub>2</sub>SO<sub>4</sub> and 10mg/L methylene blue aqueous solutions at a scan rate of 20 mV s<sup>-1</sup>. (b) The LSV curves of Ti/SnO<sub>2</sub>@Sb@Ce electrode (black line), Ti/SnO<sub>2</sub>-Sb-Ce electrode (red line), which were measured in 0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> and 0.1 mol L<sup>-1</sup> Na<sub>2</sub>SO<sub>4</sub>, at a scan rate of 20 mV s<sup>-1</sup>.

**Linear sweep voltammetry.** In order to further compare the electrochemical properties of the two electrodes, LSV curves were recorded in the aqueous solution of 0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> and 0.1 mol L<sup>-1</sup> Na<sub>2</sub>SO<sub>4</sub>, at a scan rate of 20 mV s<sup>-1</sup> as illustrated in Fig. 1(b). Higher overpotential for oxygen evolution reaction of the electrodes can bring higher electrochemical activity for the oxidation of organic pollutants, since the OER is a competing reaction that lowers the current efficiency of organic oxidation. At Ti/SnO<sub>2</sub>@Sb@Ce anode, for example, the OER is 2.25V when the current density of 1 mA cm<sup>-2</sup> produced, while at Ti/SnO<sub>2</sub>-Sb-Ce electrode, the OER is 2.1V. This suggests that the former OER is 150 mV more positive than the latter OER. In addition, the smaller size of the catalyst on the electrode surface may lead to more quantity and higher reactivity of hydroxyl radicals.

**Decolorization test.** The decolourization shown in Fig. 2(a) allowed us to observe that colour removal efficiency of methylene blue enhances with the increase of current density in the range 20~60 mA cm<sup>-2</sup>. As can be observed in Fig. 2, the 40-min removal efficiency is 85.41% when 20 mA cm<sup>-2</sup> of current density was applied on the Ti/SnO<sub>2</sub>@Sb@Ce electrode. When the current density was increased to 40 mA cm<sup>-2</sup>, the removal efficiency was significantly improved reaching to 94.26% after the same time electro-oxidation treatment. However, further increasing the current density from 40 to 60 mA cm<sup>-2</sup>, the colour removal efficiency is only slightly increased and tends to level off. After a comparison of the three different current densities, it is suggested that increasing the current density of the electrochemical system has a positive influence on the electrocatalytic oxidation process, because a growing number of current density results in a higher production of hydroxyl radicals generated from water oxidation. Further from Fig. 2, it can be noted that the colour removal efficiency was greatly improved on the Ti/SnO<sub>2</sub>@Sb@Ce electrode (where the catalyst was synthesized with the addition of hydrothermal process). For Ti/SnO<sub>2</sub>-Sb-Ce electrode (where the catalyst was prepared with the direct thermal decomposition method), the removal efficiency was no more than 90 % after 60-min electrolysis at the applied current density at 20 mA cm<sup>-2</sup>. It rose obviously to 100 % after 60-min when the applied current density ascended to 60 mA cm<sup>-2</sup> using Ti/SnO<sub>2</sub>@Sb@Ce electrode. From decolourization results it can be concluded that under the condition of same current density, the colour removal efficiency by using Ti/SnO<sub>2</sub>@Sb@Ce electrode is always better than Ti/SnO<sub>2</sub>-Sb-Ce electrode. This may be due to the fact that the catalyst made by hydrothermal synthesis process can

provide more active sites, which can enhance the electro-catalytic capability of electrode as-prepared.

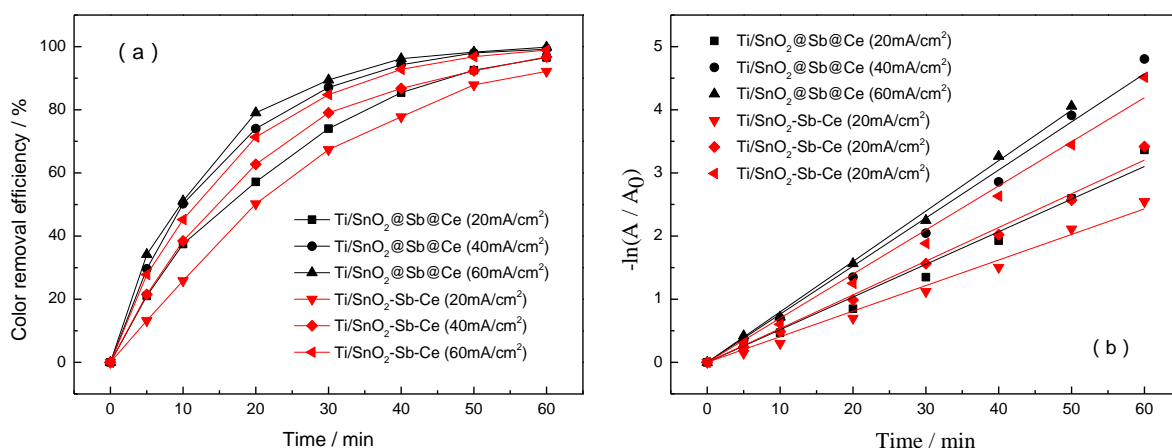


Fig. 2(a) Color removal efficiency of methylene blue on Ti/SnO<sub>2</sub>@Sb@Ce electrode and Ti/SnO<sub>2</sub>-Sb-Ce electrode at different current densities; (b) Linear relationship between  $-\ln(A/A_0)$  and time on Ti/SnO<sub>2</sub>@Sb@Ce electrode and Ti/SnO<sub>2</sub>-Sb-Ce electrode at different current densities.

The relationship between time and colour removal was shown in Fig. 2(b). We can observe that  $-\ln(A/A_0)$  is linear with time. From Table 1 it is found that rate constant (K) for electrochemical degradation reaction improves with increasing current density. When the current density increased from 20 to 40 mA cm<sup>-2</sup> on the Ti/SnO<sub>2</sub>@Sb@Ce electrode, the value of K increased from 0.051 to 0.076 and further to 0.080 when the current density continued to rise to 60 mA cm<sup>-2</sup>. At the same time, the removal rates of Ti/SnO<sub>2</sub>@Sb@Ce electrode were obviously constantly faster than Ti/SnO<sub>2</sub>-Sb-Ce electrode. All the above results reveal that increasing the current density of the electrochemical system is propitious to accelerate electrocatalytic oxidation process, owing to the formation rate of hydroxyl radicals on anode promoted with the increase of current density. On the other hand, the Ti/SnO<sub>2</sub>@Sb@Ce electrode synthesized by the modification of hydrothermal process can promote this effect due to its more efficient active sites, which can cause the concentration of hydroxyl radicals to raise.

Table 1 Pseudo-first order rate constants of the two electrodes

Electrode	Current density (mA cm <sup>-2</sup> )	K	R <sup>2</sup>
Ti/SnO <sub>2</sub> @Sb@Ce	20	0.051	0.9922
	40	0.076	0.9958
	60	0.080	0.9987
Ti/SnO <sub>2</sub> -Sb-Ce	20	0.041	0.9946
	40	0.053	0.9965
	60	0.070	0.9946

## Conclusions

In short, the electrochemical performance of electrode has been significantly improved by combining hydrothermal synthesis and high temperature decomposition method. Electrochemical oxidation

degradation process of pollutants is remarkably affected by the preparation methods of anode materials and current density. The Ti/SnO<sub>2</sub>@Sb@Ce electrode can give a higher catalytic activity than that of Ti/SnO<sub>2</sub>-Sb-Ce electrode due to more efficient active sites provide by Ti/SnO<sub>2</sub>@Sb@Ce electrode, suggesting that the addition of hydrothermal synthesis process can enhance the treatment efficiency of the electrode if it is applied in industry.

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