

Photoelectrocatalytic activity of two antimony doped SnO₂ films for oxidation of phenol pollutants

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Abstract: Two types of Sb-doped SnO₂ films on titanium substrate were prepared by the combination of electro-deposition and dip-coating (Ti/SnO₂-Sb₂O₄/SnO₂-Sb₂O₄) and single dip-coating (Ti/SnO₂-Sb₂O₄), respectively. The surface morphology and crystalline structure of both film electrodes were characterized using X-ray diffractometry(XRD) and scanning electron microscopy(SEM). XRD spectra indicate that the rutile SnO₂ forms in two films and a TiO₂ crystallite exists only in Ti/SnO₂-Sb₂O₄ electrode. SEM images show that the surface morphology of two films is typically cracked-mud structure. The photooxidation experiment was proceeded to further confirm the two electrode activity. The results show that the photoelectrocatalytic degradation efficiency of Ti/SnO₂-Sb₂O₄ electrode with sub-layer is higher than that of simple Ti/SnO₂-Sb₂O₄ electrode using phenol as a model organic pollutant. The Ti/SnO₂-Sb₂O₄/SnO₂-Sb₂O₄ photoanode has a better photoelectrochemical performance than Ti/SnO₂-Sb₂O₄ photoanode for the removal of organic pollutants from water.

Key words: Ti/SnO₂-Sb₂O₄; SnO₂ films; photoelectrocatalysis; phenol

1 Introduction

Photoelectrocatalytic process using semiconductor electrodes has been widely studied due to their inherent high catalytic activity for oxidation of organic pollutants in the past two decades[1–3]. Especially, metal/TiO₂ photoelectrode has received a lot of attention, because this technology can suppress the recombination of photogenerated electron-hole pairs by external bias[4–5], and solve the separation problem of TiO₂ particles from water solution. Unfortunately, applying external bias to Ti/TiO₂ electrode could improve the photocatalytic activity of Ti/TiO₂ electrode[6–8], but the improvement is very limited. The Ti/SnO₂ film electrode has attracted a lot of attention due to its high oxygen–evolution overpotential in electrochemical process[9–10]. Our study about Ti/SnO₂ film electrode allowed effective photooxidation of phenol under UV irradiation[11]. Thus we designed the Ti/SnO₂ as a novel photoanode in the

treatment of organics in water by photoelectrocatalysis. However, its poor conductivity limited its catalytic activity for oxidation of organics in water[12–14]. One of the methods to increase the electricity conductivity is to modify SnO₂ by doping various elements, such as F, P and Sb[15–17]. Among these elements, Sb-doped SnO₂ showed good electrical conductivity, high overpotential for oxygen–evolution and catalytic activity. On the other hand, Sb-doped SnO₂ is still a semiconductor ($E_g=3.5\text{--}3.8\text{ eV}$) and has the function of photoanode, although its application in the photoelectrocatalytic process has not been noted as TiO₂ thin film anode.

Besides, the preparation technology and method of electrode have much important effect on electrode function and performance as well as service life. Recently, many papers have reported the preparation and properties of SnO₂ film, such as sol-gel dip coating [18–19], spray pyrolysis[20–21], sputtering[22–23], chemical vapor deposition[24–25], and thermal evaporation[26]. Although various studies have demonstrated

the dependence of the properties of Sb-doped SnO_2 on preparation condition and method, there is little information about the performance of these modified SnO_2 as photoelectrocatalysts for the oxidation of organic pollutants.

In this work, two electrodes were prepared: one was coated directly with catalyst layer ($\text{SnO}_2\text{-Sb}_2\text{O}_4$) to titanium substrate surface to form $\text{Ti/SnO}_2\text{-Sb}_2\text{O}_4$ electrode; the other included a $\text{SnO}_2\text{-Sb}_2\text{O}_4$ sub-layer to form $\text{Ti/SnO}_2\text{-Sb}_2\text{O}_4/\text{SnO}_2\text{-Sb}_2\text{O}_4$ electrode. Phenol was selected as model compound for study of catalytic performance of Sb-doped SnO_2 photoelectrocatalysis. Our goals are to evaluate the influences of Sb modifier and $\text{SnO}_2\text{-Sb}_2\text{O}_4$ sub-layer on electrode microstructure, electrochemical properties and photoelectrocatalytic activity for phenol oxidation.

2 Experimental

2.1 Preparation of Sb-doped SnO_2 electrode

2.1.1 Pre-treatment of Ti substrate

Ti plates with size of 70 mm×10 mm were polished using abrasive paper prior to etch in 40% NaOH solution at 95 °C for 4 h. Additional acid etching was carried out using 10% oxalic acid solution at the same condition. The etched Ti plate was then washed thoroughly using deionized water and dried.

2.1.2 Preparation of $\text{Ti/SnO}_2\text{-Sb}_2\text{O}_4/\text{SnO}_2\text{-Sb}_2\text{O}_4$ anode

The anode was prepared in two steps. First, $\text{SnO}_2\text{-Sb}_2\text{O}_4$ sub-layer was prepared using electrodeposition technique. In this process, the pretreated Ti plate was used as cathode and insoluble electrode as anode with 100 mL electrolyte solution containing 1.753 g $\text{SnCl}_4\cdot 4\text{H}_2\text{O}$, 0.114 g SbCl_3 , and 12 mL ethanol solution (analytical reagent) of tetrabutyl titanate (analytical reagent). A constant DC current of 0.12 A was applied for 30 min to electroplate the cathode, and then the Ti plate with electroplated sub-layer was dried in an oven at 450 °C for 2 h. Subsequent loading of the second layer of $\text{SnO}_2\text{-Sb}_2\text{O}_4$ was accomplished using dip-coating technique. The coating solution was made using 4 g $\text{SnCl}_4\cdot 5\text{H}_2\text{O}$, 0.156 g SbCl_3 and 1 mL concentrated HCl (37%) in 9 mL n-butanol (analytical reagent). After washing coating, the sample was dried at 100 °C for 5 min prior to calcination at 450 °C for 10 min. The dipping and thermal deposition process, washing coating and calcination process were repeated several times until reaching the loading times. The resulting electrode was annealed at 450 °C for 1 h to form $\text{Ti/SnO}_2\text{-Sb}_2\text{O}_4/\text{SnO}_2\text{-Sb}_2\text{O}_4$ electrode.

2.1.3 Preparation of $\text{Ti/SnO}_2\text{-Sb}_2\text{O}_4$ anode

The anode was prepared using dip-coating procedure as described above. The final electrode was also called $\text{Ti/SnO}_2\text{-Sb}_2\text{O}_4$ electrode without sub-layer.

2.2 Preparation of gas diffusion electrode

The gas diffusion electrode was prepared using coating and pressing method. Graphite, carbon black and nickel mesh were pressed to about 1 mm in thickness and annealed at 400 °C for 1 h. The resulting electrode was used as cathode for photoelectrocatalysis(PEC) process. Detailed preparing process can be found in Ref.[27].

2.3 Analytical methods

Scanning electron microscope(SEM) (LEO-438VP, Japan) equipped with an energy-disperse spectrometer (EDS) analyzer was used to study the surface morphology. X-ray diffraction (XRD) (D/max-2500, Japan) measurements were carried out to determine crystal phase structure of $\text{Ti/SnO}_2\text{-Sb}_2\text{O}_4$ electrode. UV-visible spectrophotometer (Model Cary50, USA) was used to measure phenol concentration. Total organic carbon(TOC) of phenol containing solutions was measured using a TOC analyzer (Multi N/C 3000, Germany).

2.4 Photoelectrocatalytic reactor and experimental procedure

Fig.1 shows a schematic diagram of the batch scale experimental reactor system. The photoreactor system consists of a cylindrical quartz glass reactor with an effective vessel volume of 100 mL, an external UV light source and a two-electrode configuration. The two electrodes were placed in the reactor parallelly. $\text{Ti/SnO}_2\text{-Sb}_2\text{O}_4$ electrode faced to UV light was used as photocatalyst and electroanode. The gas diffusion electrode was used as cathode. The applied potential bias was obtained from a DC potentiostat (model 363, England). A 250 W high-pressure mercury lamp (main wavelength 365 nm, China) with a cooling water quartz jacket acted as a side light source. Air was supplied to

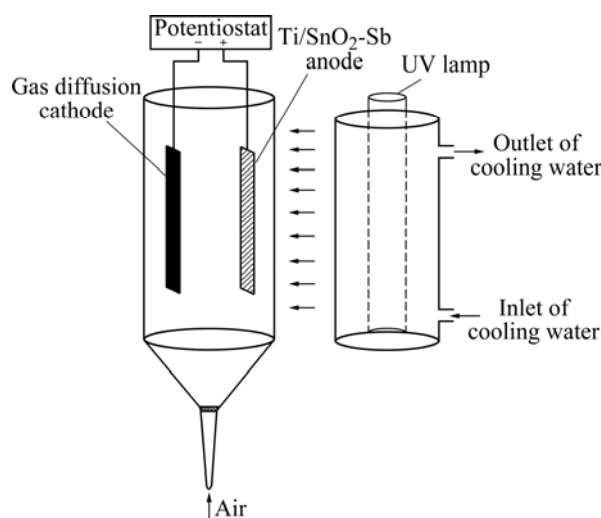


Fig.1 Schematic diagram of photoreaction systems

the reaction system from the bottom of reactor using a mini-type air pump.

During the reaction, phenol solution with the initial content of 20 mg/L was irradiated by UV light and aerated by air. Samples of phenol solution were taken periodically for measuring both phenol and TOC contents.

3 Results and discussion

3.1 XRD analysis

No apparent change was found in the XRD pattern of the Ti/SnO₂-Sb₂O₄/SnO₂-Sb₂O₄ electrode before and after use (Fig.2). In contrast, a TiO₂ peak is observed for Ti/SnO₂-Sb₂O₄ electrode without sub-layer of SnO₂-Sb₂O₄ after 30 h. This indicates the oxidation of Ti substrate during reaction process. Ti oxidation may further result in weak conductivity of Ti/SnO₂-Sb₂O₄ electrode[28]. Applying a sub-layer to Ti surface is proved to be useful in preventing Ti from oxidation and improving photoelectrocatalytic activity of Sb-doped SnO₂ electrode.

3.2 SEM analyses

The surface morphologies of the Sb-doped SnO₂ electrodes are shown in Fig.3. Fig.3(a) reveals a roughly porous surface of the Ti substrate after pretreatment. Roughness of the pretreated Ti surface is critical for generating desired catalysts layer on Ti surface. A flat and dense surface is formed after sub-layer of SnO₂-Sb₂O₄, which is applied by electro-deposition process

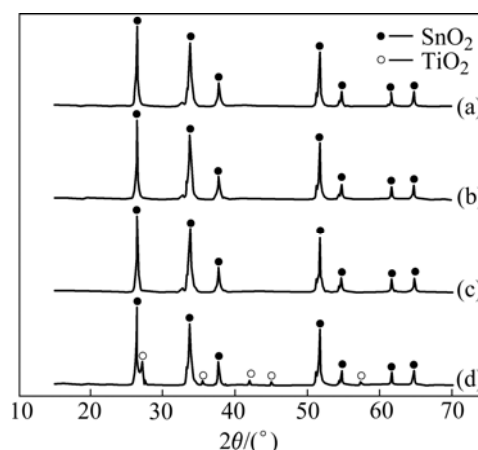


Fig.2 XRD patterns of Ti/SnO₂-Sb₂O₄ electrodes: (a) With sub-layer before use; (b) With sub-layer after use of 30 h; (c) Without sub-layer before use; (d) Without sub-layers after use of 30 h

(Fig.3(b)). It is believed that this dense surface provides barrier for oxygen diffusion and reaction with Ti as evidence by XRD study above. Both the surfaces of the Ti/SnO₂-Sb₂O₄ electrode prepared by dip-coating procedure (Fig.3(c)) and the double layered Ti/SnO₂-Sb₂O₄/SnO₂-Sb₂O₄ electrode by a procedure of electro-deposition and subsequent dip-coating (Fig.3(d)) look rather rough with a mixed mud-flat cracking and agglomerates. The factor leading to the formation of such a complex morphology may be the difference in thermal expansion coefficients of substrates or layer materials

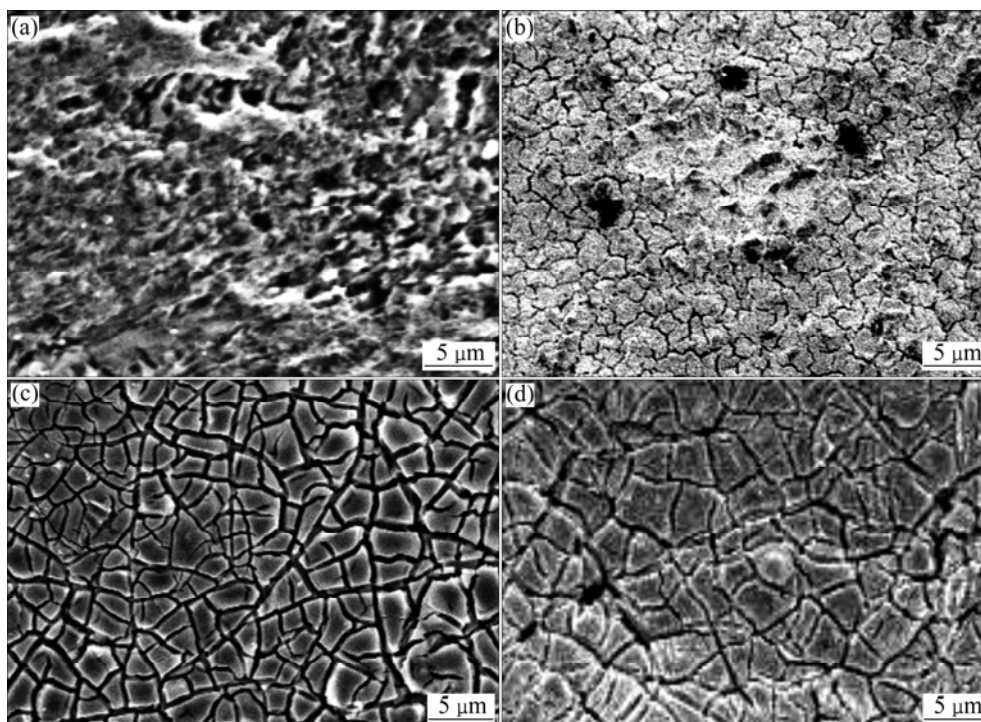


Fig.3 SEM images of Ti/SnO₂-Sb₂O₄ electrodes

[29]. The surface morphology significantly influences the activity of the electrode for the oxidation of phenol in aqueous solution. Lower activity of $\text{Ti/SnO}_2\text{-Sb}_2\text{O}_4$ electrode without sub-layer is apparently related to cracks which may provide convenience for oxygenous infiltration and diffusion, resulting in the decrease of electrode performance. Thus, adding sub-layer is an appropriate measure for the preparation of $\text{Ti/SnO}_2\text{-Sb}_2\text{O}_4$ electrode.

Furthermore, both the $\text{Ti/SnO}_2\text{-Sb}_2\text{O}_4$ and $\text{Ti/SnO}_2\text{-Sb}_2\text{O}_4/\text{SnO}_2\text{-Sb}_2\text{O}_4$ electrodes were analyzed by means of EDS, and the results about the molar ratios of Sn and Sb are shown in Table 1. In this study, the theoretical composition ratio of Sn to Sb atoms is 100:6. From the results of Table 1, it can be found that the molar ratios of the final coatings are not consistent with the theoretical composition. There are two reasons: one is element volatilization during heat treatment, and the other is instrument error by itself.

Table 1 Composition of $\text{Ti/SnO}_2\text{-Sb}$ electrode (molar fraction, %)

Electrode	x(Sn)/%	x(Sb)/%	x(O)/%	x(Sb)/x(Sn)
With sub-layer	77.64	4.57	17.79	5.9
Without sub-layer	77.03	5.03	17.94	6.5

3.3 Performance of phenol degradation

Complete phenol oxidation was achieved using the $\text{Ti/SnO}_2\text{-Sb}_2\text{O}_4/\text{SnO}_2\text{-Sb}_2\text{O}_4$ electrode after 2 h reaction, while only about 86% phenol conversion was achieved under the same conditions using $\text{Ti/SnO}_2\text{-Sb}_2\text{O}_4$ electrode (Fig.4). The phenol mineralization rates after 3 h were determined to be 85% and 73% for $\text{Ti/SnO}_2\text{-Sb}_2\text{O}_4/\text{SnO}_2\text{-Sb}_2\text{O}_4$ electrode and $\text{Ti/SnO}_2\text{-Sb}_2\text{O}_4$, respectively. These results indicate that the sub-layer of

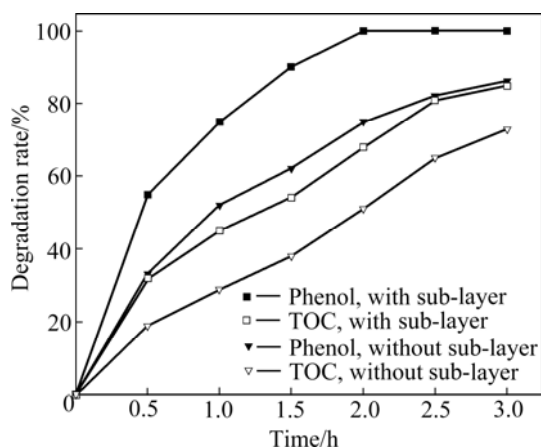


Fig.4 Effect of sub-layer on photoelectrocatalytic degradation of phenol

$\text{SnO}_2\text{-Sb}_2\text{O}_4$ on Ti substance improves the activity of the catalysts for phenol oxidation.

3.4 Linear voltammogram

The current properties of the $\text{Ti/SnO}_2\text{-Sb}_2\text{O}_4/\text{SnO}_2\text{-Sb}_2\text{O}_4$ and $\text{Ti/SnO}_2\text{-Sb}_2\text{O}_4$ electrodes were investigated in phenol solution without electrolyte, and the linear voltammograms of two electrodes are shown in Fig.5. In dark, the anode current of the $\text{Ti/SnO}_2\text{-Sb}_2\text{O}_4/\text{SnO}_2\text{-Sb}_2\text{O}_4$ electrode is higher than that of the $\text{Ti/SnO}_2\text{-Sb}_2\text{O}_4$ on the condition of only anodic bias, which is similar to the result of the combination of the same anodic bias and UV illumination. Under UV illumination, the current efficiency of the two electrodes is better than that in dark, and the $\text{Ti/SnO}_2\text{-Sb}_2\text{O}_4$ electrode with sub-layer can acquire a higher photocurrent[30] than $\text{Ti/SnO}_2\text{-Sb}_2\text{O}_4$ electrode without sub-layer at the same anode bias, which indicates that the $\text{Ti/SnO}_2\text{-Sb}_2\text{O}_4/\text{SnO}_2\text{-Sb}_2\text{O}_4$ electrode can promote the separation of photoelectrocatalytic electron-hole pair due to improved anode conductivity. Moreover, the probability of electrons that can get away from hole recombination increases with increasing the voltage. As a result, it is necessary to employ an anodic bias in photocatalytic process.

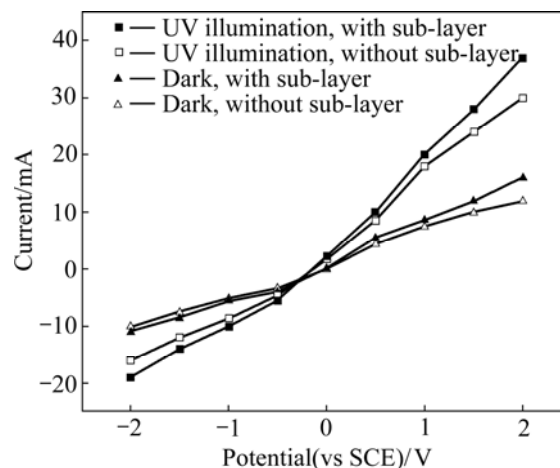


Fig.5 Linear voltammograms of $\text{Ti/SnO}_2\text{-Sb}_2\text{O}_4$ electrode with sub-layer and without sub-layer (scanning speed: 100 mV/s, scanning range: $-2.0\text{--}2.0\text{ V (vs SCE)}$)

3.5 Comparison of different degradation processes

The efficiencies of phenol degradation and TOC degradation from phenol solution were measured at four different processes, which were adsorption, photocatalytic, electrocatalytic and photoelectrocatalytic processes, and the results are presented in Fig.6. During all the experiments, the $\text{Ti/SnO}_2\text{-Sb}_2\text{O}_4/\text{SnO}_2\text{-Sb}_2\text{O}_4$ electrode and a gas diffusion electrode were immersed in the phenol solution, and air was supplied to the reaction system from the bottom of reactor.

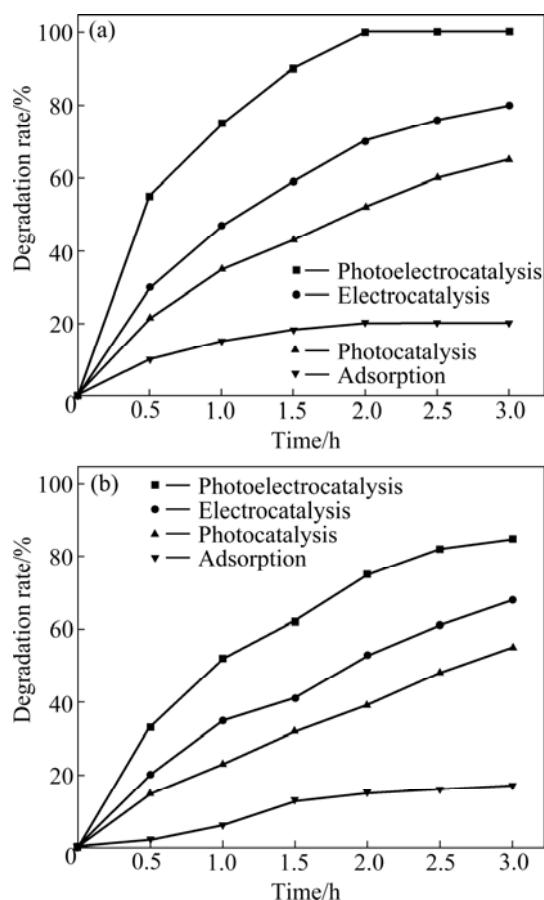


Fig.6 Comparison of removal rate of different degradation processes: (a) Phenol removal; (b) TOC removal

The adsorption effect of phenol plays an important role in the phenol removal, because the adsorption of organic pollutants on the catalysts is the key step in the catalytic reaction[31]. Thus, the adsorption effect of the two electrodes must be considered at first. Adsorption process was performed in the absence of the UV light and potentiostat for 3 h, and only 20% of phenol was removed. For the photocatalytic degradation process alone, the phenol degradation rate can reach 65% after 3 h reaction. When 2.0 V cell voltage was applied for 3 h in the absence of UV illumination, the phenol degradation rate was 80%. However, both in the presence of 2.0 V cell voltages and UV illumination, the phenol concentrations were decreased rapidly with increasing reaction time, and the degradation rate can reach 100% after 2 h. It can be seen that the phenol removal increases with the increase of reaction time in all four processes, but the photoelectrocatalytic degradation rate was obviously higher than that of other processes. Thus, it can be concluded that phenol can be removed from the water more efficiently by photoelectrocatalytic process.

A similar conclusion can be drawn by comparison of the TOC reduction efficiency, which is shown in

Fig.6(b). TOC removal efficiencies are 17%, 68% and 55% in the presence of adsorption, photocatalytic and electrocatalytic processes, respectively, while the phenol mineralization rate of photoelectrocatalytic process can reach 85%. The TOC removal rate in the photoelectrocatalytic process is the highest. This should be attributed to the synergetic effect between photocatalysis and electrocatalysis in this photoreactor, and the adsorption also plays an important role in the degradation process.

4 Conclusions

1) Two electrodes of $\text{Ti/SnO}_2\text{-Sb}_2\text{O}_4/\text{SnO}_2\text{-Sb}_2\text{O}_4$ and $\text{Ti/SnO}_2\text{-Sb}_2\text{O}_4$ were obtained. The $\text{Ti/SnO}_2\text{-Sb}_2\text{O}_4$ was prepared by the simple procedure of dip-coating method and the $\text{Ti/SnO}_2\text{-Sb}_2\text{O}_4/\text{SnO}_2\text{-Sb}_2\text{O}_4$, i.e. the Sb-doped SnO_2 film electrode with Sb-doped SnO_2 film sub-layer, was prepared by the procedure of electrodeposition technique and subsequent dip-coating method.

2) The XRD spectra of two film electrodes ($\text{Ti/SnO}_2\text{-Sb}_2\text{O}_4/\text{SnO}_2\text{-Sb}_2\text{O}_4$ and $\text{Ti/SnO}_2\text{-Sb}_2\text{O}_4$), which were annealed at 450 °C, correspond to rutile SnO_2 , and an anatase TiO_2 crystallite is found only in the thin film of $\text{Ti/SnO}_2\text{-Sb}_2\text{O}_4$ electrode. SEM measurement shows that $\text{Ti/SnO}_2\text{-Sb}_2\text{O}_4/\text{SnO}_2\text{-Sb}_2\text{O}_4$ electrode looks rougher with a mixed mud-flat cracking and agglomerates.

3) The $\text{Ti/SnO}_2\text{-Sb}_2\text{O}_4/\text{SnO}_2\text{-Sb}_2\text{O}_4$ electrode can acquire a higher photocurrent than $\text{Ti/SnO}_2\text{-Sb}_2\text{O}_4$ electrode.

4) The degradation experiments show that the Sb-doped SnO_2 film electrode with sub-layer has a higher phenol and TOC removal rate than $\text{Ti/SnO}_2\text{-Sb}_2\text{O}_4$ electrode in electrocatalytic process and photoelectrocatalytic process. Therefore, $\text{Ti/SnO}_2\text{-Sb}_2\text{O}_4/\text{SnO}_2\text{-Sb}_2\text{O}_4$ is not only a good electrochemical anode in treating organic pollutants but also a good photoanode in electro-assisted photocatalytic process for complete oxidation of organic pollutants.

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