Facile synthesis of highly active Ti/Sb-SnO$_2$ electrode by sol-gel spinning technique for landfill leachate treatment

Shuchi Zhang, Xu Chen, Shuwen Du, Jingli Wang, Mengyu Tan, Jiayu Dong and Donglei Wu*

College of Environmental and Resource Science, Zhejiang University, Hangzhou 310058, China

*Corresponding author. E-mail: wudl@zju.edu.cn

ABSTRACT

Highly active Ti/Sb-SnO$_2$ electrodes were fabricated using sol-gel spin coating procedure, which exhibited a rough, uniform and multilayer coating structure. The effects of different Sb-SnO$_2$ film layers on the physiochemical, electrochemical properties and pollutant degradability of electrodes and the mechanism were evaluated on a systematic basis. The electrodes with more active layers exhibited higher electro-catalytic performance. Upon exceeding 8 layers, the promotion effect of the coating was reduced. Considering various factors, this paper recommends preparing Ti/Sb-SnO$_2$ electrodes coated with 8 layers to obtain higher electro-catalytic ability in landfill leachate treatment. The specific number of coating layers should be determined according to the electrode requirements. This work provided a theoretical basis and technical support for the preparation of Ti-SnO$_2$ electrodes with high electro-catalytic activity and stability, while it still remains a great challenge to achieve an excellent balance between performance and stability before Ti/Sb-SnO$_2$ electrodes can be implemented on a large scale in wastewater treatment.

Key words: coating layers, electro-catalytic ability, leachate treatment, oxygen evolution potential, Ti/Sb-SnO$_2$ electrodes

HIGHLIGHTS

- Sol-gel spin coating method could be used to exhibit a multilayer coating structure.
- Electrodes with more active layers had higher electro-catalytic performance.
- Upon exceeding 8 layers, the promotion effect of the coating was reduced.
- Ti/Sb-SnO$_2$ electrodes coated with 8 layers could obtain higher electro-catalytic ability during leachate treatment.

GRAPHICAL ABSTRACT

This is an Open Access article distributed under the terms of the Creative Commons Attribution Licence (CC BY 4.0), which permits copying, adaptation and redistribution, provided the original work is properly cited (http://creativecommons.org/licenses/by/4.0/).
INTRODUCTION

In recent years, nearly 80% of the world’s population is threatened by water security on a global scale (Vörösmarty et al. 2010). One of the most important reasons for water pollution is the massive discharge of refractory organic wastewater (Han et al. 2018), which is characterized by high organic load, complex characteristics and strong bio-inhibition (Sun et al. 2019). The most representative one is landfill leachate, which contains a large amount of pollutants such as biodegradable and refractory organics, inorganic salts (e.g., Na⁺, NH₄⁺) and heavy metals (Zhang et al. 2020a, 2020b). The generation of leachate is anticipated to increase as the amount of landfilled solid waste continues to grow globally (Feng et al. 2021). Electrochemical Advanced Oxidation Processes (EAOPs) emerge as a promising technology in the field of organic wastewater treatment (Seibert et al. 2020). Compared to traditional biological treatment methods, EAOPs has shown greater advantages like high efficiency, no requirement for chemicals and low-volume application (Ganiyu et al. 2018).

The key focus of EAOPs is to prepare electrodes with high electrochemical activity to promote the generation of hydroxyl radicals (indirect oxidation, E° = 2.8 V vs. SHE) and electron transfer (direct oxidation) (Chai et al. 2018). The OH radicals were electro-generated by the reaction as follows (Garcia-Segura et al. 2018; Fortunato et al. 2020):

\[ M + H_2O \rightarrow M(OH) + H^+ + e^- \]

where, M is referred as the electrode and M(OH) is the adsorbed hydroxyl radical. At the same time, the inevitable side reactions that consume the radical species leading to oxygen evolution would also happen (Garcia-Segura et al. 2018).

Nowadays, three kinds of electrodes, namely tin dioxide (SnO₂) (Mora-Gomez et al. 2019), lead dioxide (PbO₂) (Tan et al. 2011) and boron-doped diamond (BDD) (Olvera-Vargas et al. 2021) have attracted great attention from researchers because of high oxygen evolution potentials (OEP), which could favor the large production of reactive oxygen species to destroy organic matters (Skoumal et al. 2008; Moradi et al. 2020). BDD has proven to be the most potential material for anodic oxidation of organics (Olvera-Vargas et al. 2021). However, the high cost of BDD restricts its widespread commercial applications (Brillas et al. 2005; Ciriaco et al. 2009). PbO₂ electrode has shown excellent catalytic performance, long service lifetime and low cost as a non-active anode, but it also has some shortcomings such as secondary contamination due to Pb dissolution (Yao et al. 2019; Li et al. 2020a, 2020b). Generally speaking, SnO₂ cannot be directly used as an electrode coating material due to high resistance (Mora-Gomez et al. 2019). A number of researchers focused on the enhancement of OEP, service lifetime and current efficiency of SnO₂ electrodes (Chen et al. 2018). Doping is a powerful approach for modulating the electrical properties of metal oxides (Malviya et al. 2017). It was reported that Sb doped SnO₂ coating could not only greatly improve the conductivity of electrodes, but also led to higher electrochemical stability (Chen et al. 2020).

There are four main methods that can help to prepare antimony-doped tin oxide (Ti/Sb-SnO₂): dip-coating (Zhou et al. 2019), electrolyte deposition (Sun et al. 2020a, 2020b, 2020c), spin coating (Sivakumar et al. 2021) and pyrolysis spray (Elangovan et al. 2005). Based on the above-mentioned preparation method, Ti/Sb-SnO₂ electrodes have been widely used in various kinds of wastewater treatment (Maharana et al. 2015; Zhang et al. 2020a, 2020b). Researchers usually used co-doped SnO₂–Sb–x (x-element) (Endoh & Kurihara 1998; Duan et al. 2014), interlayer insertion (Li et al. 2020a, 2020b, 2020c) and Ti substrate modification (Hodges et al. 2018) to further enhance the service life and electro-catalytic property of Ti/Sb–SnO₂ electrode (Aguilar et al. 2018).

Most of the previous studies have focused on the parameter adjustment of electrode preparation such as solvent type (Sun et al. 2020a, 2020b), metal element ratio (Elangovan et al. 2005) etc, while a few were devoted to the effects of different Sb-SnO₂ coating layers and practical application of landfill leachate treatment. The objectives of this paper were to: (1) to provide a sol-gel spin coating method to fabricate Ti/Sb–SnO₂ electrodes that could exhibit a rough, uniform and multilayer coating structure; (2) to systematically assess the effects of different Sb-SnO₂ film layers on physiochemical, electrochemical properties and pollutant degradability of Ti/Sb–SnO₂ electrodes; and (3) to reveal the mechanism of electrochemical activity of electrodes with different coating layers, further providing theoretical guidance and technical support to prepare the electrodes with high electro-catalytic activity and stability in the field of wastewater treatment.
**METHODOLOGY**

**Electrode preparation**

A four-step procedure involving titanium substrate pretreatment, precursor reagent preparation, sol-gel spin coating and subsequent calcination process was used to form an Sb-SnO$_2$ coating on Ti substrates to prepare Ti/Sb-SnO$_2$ electrodes (Figure 1) (Comninellis & Vercesi 1991). Ti substrates (3 cm × 3 cm × 1 mm) were initially polished by 100-grits, 500-grits and 1000-grits sandpapers and then successively washed with acetone and deionized water. Then, clean Ti plates were soaked in 35 wt% oxalic acid solution, which was heated at 100 °C for 2 h until TiO$_2$ was thoroughly dissolved. The resulting Ti substrates were preserved in acetone for further use (Jin et al. 2020).

The Sb-SnO$_2$ coating was prepared on Ti substrates by employing the sol-gel spin coating method. For the preparation of precursor reagent, a mixture of SnCl$_4$ 5H$_2$O and SbCl$_3$ at molar ratio of 10:1 was dissolved in water at a low pH. When completely dissolved, a certain amount of citric acid was added and polyethylene glycol was also added into the solution. After ultrasonic treatment, agitation and aging treatments, the resulting reagent was sealed for further use. The reagent was spin-coated on the cleaned Ti substrates at the speed of 1,000 rpm for 10 s and 3,000 rpm for 15 s, followed by an evaporation treatment at 120 °C for 10 min and a calcination process at 500 °C for 10 min. The procedures (spin coating, drying, and sintering) were repeated 2, 4, 8, 12, and 16 times, respectively, and finally, the electrodes were annealed in a muffle furnace at 500 °C for 2 h.

**Physicochemical characterization**

Scanning electron microscopy (SEM, SU8010, Japan), X-ray diffraction (XRD, Bruker D8 Advance, Germany) study and X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha +, USA) techniques were applied to characterize the surface morphology of Ti/Sb–SnO$_2$ electrodes. The XPS data were corrected with reference to the C 1s peak at 284.8 eV.

**Electrochemical characterization**

The electrochemical characterization involved techniques like linear scanning voltammetry (LSV), cyclic voltammetry (CV) and tafel tests performed in 0.5 M H$_2$SO$_4$ solution on an electrochemical workstation (CHI1100C, Shanghai) with a platinum plate and saturated calomel electrode (SCE) as counter and reference electrode, respectively. LSV tests were run in the range of 0–3 V at a scan rate of 50 mV s$^{-1}$. CV tests were performed over the voltage range of –1.0 to 0 V versus SCE at scan rate of 50 mV s$^{-1}$. Tafel curves were obtained at 50 mV/s to explore the kinetics of oxygen evolution reaction.
The working life of the anodes was evaluated by ASL, which was conducted in 0.5 M H₂SO₄ solution. A constant anodic current density of 100 mA cm⁻² was provided by a DC power supply (Yuanfang, WY605, China). The cellular voltage was recorded using a data acquisition system (Agilent, 34970A). The time when the cell voltage was increased to 10 V informed about the anode deactivation due to coating failure (Sun et al. 2020a, 2020b, 2020c). The service life was calculated by the following formula: \( T_{\text{actual}} = T_{\text{test}} \left( \frac{i_{\text{test}}}{i_{\text{actual}}} \right)^2 \) (1).

**Pollutant degradation experiment**

The pollutant degradation tests were conducted in a stirred cell containing 100 mL landfill leachate (3,938.75 mg/L COD, 279.45 mg/L TN, EC = 11.92 mS/cm) that included 3,078 mg/L Cl⁻ as a supporting electrolyte at room temperature. The basic physical-chemical characterization of the effluent is represented in Table 1. All the tests were carried out with the applied voltage of 4 V over a reaction time of 120 min. The prepared electrode was used as anode and titanium plate was used as cathode with a distance of 1 cm. Chemical oxygen demand (COD) analyses were carried out by rapid digestion spectrophotometric method with potassium dichromate using a benchtop VIS spectrophotometer (DR3900, Hach Company, USA). Total nitrogen (TN) analyses were conducted by Alkaline potassium persulfate digestion-UV spectrophotometric method. LSV tests were run before and after the electrode degradation.

**RESULTS AND DISCUSSION**

**Physicochemical characterization**

More detailed information on morphology can be obtained from the SEM images taken about the different coating layers of electrodes. Images having magnification of 1.0 K and 5.0 K are illustrated in Figure 2. The surface of the pre-treated Ti substrate presented a honeycomb structure having many cracks and holes (Figure 2(a)). After coating with Sb-SnO₂ precursor solution, the electrodes presented a smooth and compact surface with fewer cracks on the catalyst layer, proving that a uniform oxide layer in firm contact with the Ti substrate had formed (Huang et al. 2020). An obvious porous structure was observed due to the evaporation of solvent during the heating process (Xiao et al. 2020). The electrode surface became denser and more compact as the layers increased within 8 layers, and the number of holes decreased, which was beneficial to increase the specific surface area and to enhance the bonding ability between the substrate and the coated layer. However, the electrodes coated with 12 and 16 layers presented a flat surface, indicating lower conductivity. The cracks on the surface of 16-coated electrodes increased compared with 12-coated electrodes. The phenomenon of crack production was attributable to the differences in the shrinkage or expansion properties between the Sn-Sb active layer and titanium substrate during calcination and the evaporation of solvent in the dry rubbing process (Bi et al. 2019a). The penetration of electrolyte into the substrate through these cracks would reduce the binding force between the coating and the substrate, which would seriously affect the electrochemical activity and stability (Li et al. 2020a, 2020b, 2020c).

To better elucidate the catalytic mechanism, the crystal structure of coating was analyzed by XRD pattern (Figure 3). The peak XRD positions of electrodes with different coating layers were basically similar, which were consistent with the data of JCPDS card 44-1294 on titanium matrix. Ti had a higher diffraction peak intensity due to X-ray penetration through the oxide coating during the test. The diffraction peaks of SnO₂ were observed at 53.143°, 63.298° (JCPDS card 50-1429) and 26.495°, 33.727° (JCPDS card 46-1088). Doping of Sb ions in SnO₂ coating could not be clearly discerned through the XRD spectrum (Yang et al. 2017), the reasons might be: 1. The Sb content was too low to be detected by XRD; 2. The element Sb might have

| COD (mg/L)   | TN (mg/L)  | TP (mg/L) | NH₃-N (mg/L) |
|--------------|------------|-----------|--------------|
| 3,938.75 ± 2.75 | 279.45 ± 2.92 | 38.08 ± 0.95 | 152.03 ± 0.95 |
| NO₃-N (mg/L) | pH         | EC (mS/cm) | Cl⁻ (mg/L)   |
| 20.10 ± 0.07 | 4.74 ± 0.01 | 11.92 ± 0.23 | 3,078 ± 4.92  |
entered into the lattice of SnO$_2$ crystal by substitution. The diffraction peak width was inversely proportional to the grain size. The wider the peak width, the smaller the grain size. It could be deduced from the decreased grain size that the catalytic active sites of the electrode increased (Chen et al. 2018).

X-ray photoelectron spectroscopy (XPS) was performed to quantify O, Sn, and Sb on the electrodes, as well as to study their chemical states and stoichiometry. The core level 3d spectra of Sn are shown in Figure 4(a) and 4(b), the Sn 5d$_{5/2}$ peak at 487 eV and the Sn 5d$_{3/2}$ peak at 496 eV were observed for Ti/Sb-SnO$_2$ electrodes, indicating a successful coating of SnO$_2$ layer on Ti substrate (Wang et al. 2020), which was similar to the XPS peaks as reported by Choi et al. (1996). Due to

Figure 2 | SEM images of Ti/Sb-SnO$_2$ electrodes (a) Ti substrate, (b) 2 layers, (c) 4 layers, (d) 8 layers, (e) 12 layers, (f) 16 layers.

Figure 3 | XRD images of Ti/Sb-SnO$_2$ electrodes with 2, 4, 8, 12, 16 coating layers.
low concentration, 3d Sb could not be clearly detected in the full spectrum, while the Sb 3d$_{5/2}$ peak at 532 eV and the Sb 3d$_{3/2}$ peak at 541 eV were observed in fine spectra, indicating that the antimony was bound with oxygen. As shown in Figure 4(c), the XPS peak of Sb 3d$_{3/2}$ was weaker than Sb 3d$_{5/2}$. The peak heights of Sn and Sb elements obviously increased with the increasing coating layers. The shift of peaks position to lower binding energy indicated a change in oxygen environment (Bjelajac et al. 2020). Sn 3d binding energies of 12 and 16 coating layers were lower than others, which might be owing to high average electron cloud density. Higher electron cloud density means less lattice oxygen and more oxygen vacancies,
thus promoting the generation of hydroxyl radicals, which was basically consistent with the information reflected in the LSV curve. The O 1s spectrum of Sb–SnO₂ coating was fitted by several peaks located at about 531 eV (Figure 4(d)), which was ascribed to lattice O (530 eV), surface adsorption oxygen (531 eV), and organic oxygen (533 eV), respectively (Kundu et al. 2008; Sun et al. 2020a, 2020b, 2020c). The peak in the figure is the result of the overlap of the above oxygen. As presented in Table 2, the oxygen peak tended to be 531 eV, indicating that the surface adsorption oxygen (Oads) was dominant while the lattice oxygen (Olat) was relatively fewer. Surface adsorption oxygen was directly related to the electrochemical oxidation process because it could participate in the direct oxidation or promote the generation of -OH in the indirect oxidation. The Oads content of Ti/Sb–SnO₂ electrodes coated with more layers was obviously larger, indicating stronger electro-catalytic ability was obtained.

Based on the above analyses, it was inferred that the substitution of Sn⁴⁺ by Sb⁵⁺ would increase the conductivities of the anodes due to excess electrons. Besides, permeating in Sn vacancies of SnO₂, Sb as cationic doping could accelerate the charge transfer of the electronic conductor (Cobley et al. 2015).

**Electrochemical characterization**

The OEP value is a key parameter to evaluate the electro-catalytic ability of an electrode materials, and the higher OEP usually represents higher current efficiency for electrochemical degradation owing to fewer side reactions and lesser energy loss (Li et al. 2020a, 2020b, 2020c). As shown in Figure 5(a), the polarization curves of the electrodes were divided into two regions. The curve remained constant in the first region, while the current sharply increased in another region with increasing voltage. In the second region, a tangent was drawn where the curve abruptly arose, and the potential of the intersection of the tangent and the horizontal axis was the OEP of the electrode (Bi et al. 2019b). A comparison of the OEP of electrodes with different coating layers demonstrated the fact that the OEP slightly increased with the increasing coating layers (Figure 5(a)). The OEPs of electrodes coated with 8, 12 and 16 surface layers were around 1.8 V, while the 2 and 4 surface layers had 1.3 V and 1.4 V, respectively. Besides, the steady-state current under 2.1 V was basically linear with the coating layers. The main reasons could be: oxygen vacancies in the electrode surface had a great influence on OEP. SnO₂, as an n-type semiconducting metal oxide, strongly depends on its non-stoichiometric composition (Feng et al. 2010). Higher electron cloud density could be obtained by applying more layers on the surface, which meant more oxygen vacancies were formed to promote the generation of hydroxyl radicals. While exceeding 8 layers, the effect of increasing the number of coating layers on improving OEP was not significant.

CV test was performed to measure the electro-catalytic activity of the electrodes. Generally, CV shows a series of anodic and cathodic peaks, representing the double-layer charging and the solid-state redox transition of the active oxides (Elgrishi et al. 2018; Liu et al. 2019). Voltammetric charge (q*) was also measured to compare the number of active sites of the electrodes. q* is closely related to the conductive material, oxide content, surface morphology, dispersion, scanning speed, temperature and electrolyte, which was also an effective indicator of the dispersion degree of the catalyst in the coating (Wang et al. 2019). As presented in Figure 5(b), the degradation reaction of electrodes was mainly based on the quasi-reversible reaction. The voltammetric charge (q*) initially increased and then decreased with increasing coating layers. The reason was that as the amount of effective substances in the metal oxide coated on the electrode surface kept increasing, the active coating layer was tightly and uniformly bound to the etched titanium matrix with good continuity; thereby, the electrode had a larger electrochemical active area (Voiry et al. 2018). Besides, the peak current density of the 8-active layer was higher under similar conditions in comparison to other electrodes, which showed that the electrodes with 8 active

| Electrode layers | Binding energy (eV) | O1s (Olat) | O1s (Oads) | Oads content (%) | Content – Oads/(Oads + Olat) x 100% |
|------------------|--------------------|-----------|-----------|----------------|----------------------------------|
| 2                | 530.13             | 531.61    |           |                | 95.78%                           |
| 4                | 530.18             | 531.96    |           |                | 97.03%                           |
| 8                | 530.33             | 531.83    |           |                | 96.61%                           |
| 12               | 530.98             | 532.02    |           |                | 96.57%                           |
| 16               | 530.16             | 531.33    |           |                | 99.19%                           |
layers had a faster electron transfer rate (Bi et al. 2020). Electrodes with 12 and 16 active layers had higher OEP at the cost of conductivity. Therefore, the electro-catalytic performance of the electrode could be remarkably improved by coating the proper number of layers of the active substance.

The kinetics of oxygen evolution reaction is often studied in terms of semi-logarithmically plotted current-potential curve known as a Tafel plot (Kapalka et al. 2008), as described by the Butler-Volmer equation:

\[ i = i_0 \exp(\alpha_a n F \eta / RT) + \exp(\alpha_c n F \eta / RT) \]  

(2)

where \( i \) (A cm\(^{-2}\)) is the current density, \( \eta \) is the overpotential of the electrode, \( \alpha_a \) and \( \alpha_c \) are the charge transfer coefficients of the anode and cathode, \( n \) is the number of electrons participating in the reaction, \( F \) represents the Faraday constant, \( R \) is the gas constant and \( T \) is the thermodynamic temperature. The formula can be simplified as: \( \log(i) = \log(i_0) + \eta / b \), where \( b = 2.303 \times \frac{RT}{\alpha F} \) (Li et al. 2020a, 2020b, 2020c).

Smaller was the slope of Tafel curve, the lower was the over-potential required to reach the specified current density, thus a higher electro-catalytic activity (Chen et al. 2018). As shown in Figure 5(c), there were obvious linear regions in each curve, which indicated that the oxygen evolution reaction was mainly controlled by electrochemical polarization (Mann & Thurgood 2011). As presented in Table 3, the Tafel slopes for the electrodes with 2, 4, 8, 12 and 16 coating layers were 0.208 dec\(^{-1}\), 0.199 dec\(^{-1}\), 0.080 dec\(^{-1}\), 0.062 dec\(^{-1}\) and 0.057 dec\(^{-1}\) respectively. It could be deduced that electrodes with more
coating layers possessed higher oxygen evolution activity, which accelerated the electrochemical transfer step. When exceeding 8 layers, the promotion effect of the coating was reduced.

As presented in Figure 5(d), the service life of the electrodes was calculated with 2, 4, 8, 12 and 16 coating layers, which were 0.5 min, 0.5 min, 10.3 min, 33.0 min and 58.7 min respectively. Obviously, the service span of the electrodes was proportional to the number of coating layers on the electrode surface. The industrial application of EAOPs is hindered by the short life service of Ti/Sb-SnO₂ electrodes due to the low adhesion between the coating and the substrate.

Table 3 | The kinetic parameters of Tafel curves of electrodes with 2, 4, 8, 12, 16 coating layers

| Layers | E_corr (V vs. SCE) | Cat SLP (V) | Ano SLP (V) | Cat Int (log i) | Ano Int (log i) |
|--------|-------------------|-------------|-------------|-----------------|-----------------|
| 2      | 0.241             | 0.197       | 0.208       | −4.844          | −4.830          |
| 4      | −0.049            | 0.074       | 0.199       | −5.661          | −4.786          |
| 8      | −0.167            | 0.057       | 0.080       | −4.293          | −4.547          |
| 12     | −0.253            | 0.025       | 0.062       | −4.821          | −4.354          |
| 16     | −0.253            | 0.308       | 0.057       | −4.856          | −4.546          |

Figure 6 | (a) COD concentration, (b) COD removal efficiency and (c) TN removal efficiency obtained by different Sn-Sb layers.
In practical engineering application, the number of coating layers should be determined by considering both the service life and economic cost. It still remains a great challenge to achieve an excellent balance between performance, cost, and stability before Ti/Sb-SnO2 electrodes can be implemented on an industrial scale (Shao et al. 2017; Li et al. 2020a, 2020b, 2020c).

Pollutant degradation experiment

Shown in Figure 6 are the results of the removal efficiency of COD and TN with different Sn-Sb layers. Obviously, electrodes with 8 layers exhibited the highest COD removal efficiency (32.30%) and the highest TN removal efficiency (60.38%). As presented in Figure 7, although electrodes with 12 and 16 layers showed higher current densities before electrode invalidation, they had worse stability and lower current densities after electrode invalidation compared to the electrodes with 8 layers. With the increase of the number of coating layers, the increase of current density could be ascribed to the increased amount of active material, which enhanced the number of electro-excited carriers. However, once the Sb-SnO2 film thickness reached a certain threshold, charge carrier recombination became increasingly important, since the very short carrier diffusion length effectively limited the ability to remove charges from the electrode (Wang et al. 2011). Besides, electrodes with excess layers appeared to have larger particle size and lower coating adhesion that would also influence the electrode catalytic activity and pollutant degradation effect, which was consistent with the information reflected in the above electrochemical characterization. It was detected that Cl− concentration decreased from 3,078 mg/L to 1,998 mg/L before and after the electrolysis, indicating the formation of active chlorine species during the catalysis process. The organics degradation path, active species degradation mechanism, carbon and nitrogen balance were under way in our lab.

CONCLUSION

Ti/Sb–SnO2 electrodes with different active layers were fabricated using the sol-gel spin coating method. Various tests like LSV, CV, Tafel and ASL demonstrated that electrodes with more active layers had higher electro-catalytic performance, indicating a uniform, rough and highly active electrode surface was developed. When exceeding 8 layers, the promotion effect of the coating was reduced. Considering various factors, this paper recommends preparing Ti/Sb–SnO2 electrodes coated with 8 layers to get higher electro-catalytic ability and stability in wastewater treatment. The specific number of coating layers should be determined according to the electrode’s requirements. It still remains a great challenge to achieve higher stability by increasing the binding energy before Ti/Sb-SnO2 electrodes could be implemented on full-scale in wastewater treatment.

ACKNOWLEDGEMENTS

This work was financially supported by the National Key Research and Development Program of China(Grant No. 2020YFD1100401).
DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

REFERENCES

Aguilar, Z. G., Coreño, O., Salazar, M., Sirés, I., Brillas, E. & Nava, J. L. 2018 TiIr–Sn–Sb oxide anode: service life and role of the acid sites content during water oxidation to hydroxyl radicals. J. Electroanal. Chem. 820, 82–88.

Bi, Q., Guan, W., Gao, Y., Cui, Y., Ma, S. & Xue, J. 2019a Study of the mechanisms underlying the effects of composite intermediate layers on the performance of Ti/SnO2–Sb-La electrodes. Electrochim. Acta 306, 667–679.

Bi, Q., Guan, W., Gao, Y., Cui, Y., Ma, S. & Xue, J. 2019b Study of the mechanisms underlying the effects of composite intermediate layers on the performance of Ti/SnO2–Sb-La electrodes. Electrochim. Acta 306, 667–679.

Bi, Q., Wang, Z., Dang, C., Zhang, Z., Wu, G., Cheng. W. & Xue, J. 2020 A study on the effect of introducing S-doped GO into the active layer on the performance of wire mesh Ti/Co-Mn/SnO2-Sb-La electrodes. J. Alloys. Compd. 862, 158033.

Bjelajac, A., Petrović, R., Vujanec, V., Veltruska, K., Matolin, V., Siketic, Z., Provatas, G., Jaksic, M., Stan, G. E., Socol, G., Mihailescu, I. N. & Janackovic, D. 2020 Sn-doped TiO2 nanotubular thin film for photocatalytic degradation of methyl orange dye. J. Phys. Chem. Solids 147, 109609.

Brillas, E., Sirés, I., Arias, C., Cabot, P. L., Centellas, F., Rodríguez, R. M. & Garrido, J. A. 2005 Mineralization of paracetamol in aqueous medium by anodic oxidation with a boron-doped diamond electrode. Chemosphere 58 (4), 399–406.

Chai, S., Wang, Y., Zhang, Y., Zhao, H., Liu, M. & Zhao, G. 2018 Construction of a bifunctional electrode interface for efficient electrochemical mineralization of recalcitrant pollutants. Appl. Catal., B 237, 473–481.

Chen, A., Xia, S., Pan, H., Xi, J., Qin, H., Lu, H. & Ji, Z. 2018 A promising Ti/SnO2 anodes modified by Nb/Sb co-doping. J. Electroanal. Chem. 824, 169–174.

Chen, Z., Xie, Q., Ding, J., Yang, Z., Zhang, W. & Cheng, H. 2020 Instant postsynthesis aqueous dispersion of Sb-doped SnO2 nanocrystals: the synergy between small-molecule amine and Sb dopant ratio. ACS Appl. Mater. Interfaces 12, 29937–29945.

Choi, W. K., Jung, H. J. & Koh, S. K. 1996 Chemical shifts and optical properties of tin oxide films grown by a reactive ion assisted deposition. J. Vac. Sci. Technol., A: Vac., Surf. Films 14 (2), 359–366.

Ciríaco, L., Anjo, C., Correia, J., Pacheco, M. J. & Lopes, A. 2009 Electrochemical degradation of Ibuprofen on Ti/Pt/PbO2 and Si/BDD electrodes. Electrochim. Acta 54 (5), 1464–1472.

Coble, A. J., Tudela, I., Abbas, B. & Mkhlef, B. 2015 Low-frequency ‘delay time’ ultrasound and its effect on electroless Cu metallisation of a Pd activated dielectric material. Thin Solid Films 597, 226–230.

Comninellis, C. & Vercesi, G. P. 1991 Characterization of DSA*-type oxygen evolving electrodes: choice of a coating. J. Appl. Electrochem. 21 (4), 335–345.

Duan, T., Wen, Q., Chen, Y., Zhou, Y. & Duan, Y. 2014 Enhancing electrocatalytic performance of Sn-doped SnO2 electrode by compositing nitrogen-doped graphene nanosheets. J. Hazard. Mater. 280, 304–314.

Elangovan, E., Shivashankar, S. A. & Ramamurthi, K. 2005 Studies on structural and electrical properties of sprayed SnO2:Sb films. J. Cryst. Growth 276 (1), 215–221.

Elgrishi, N., Rountree, K. J., McCarthy, B. D., Rountree, E. S., Eisenhart, T. T. & Dempsey, J. L. 2018 A practical beginner’s guide to cyclic voltammetry. J. Chem. Educ. 95 (2), 197–206.

Endoh, T. & Kurihara, Y. 1998 Influence of Pb impurity on melting point and metallography of Sn-5wt%Sb alloy. Electron. Commun. Jpn. (Part II: Electronics) 81 (1), 1–12.

Feng, Y., Cui, Y., Liu, J. & Logan, B. E. 2010 Factors affecting the electro-catalytic characteristics of Eu doped SnO2/Sb electrode. J. Hazard. Mater. 178 (1), 29–34.

Feng, D., Song, C. & Mo, W. 2021 Environmental, human health, and economic implications of landfill leachate treatment for perchloroethylene and polychloroalkyl substance removal. J. Environ. Manage. 289, 112558.

Fortunato, G. V., Kronka, M. S., Dos Santos, A. J., Ledendecker, M. & Lanza, M. R. V. 2020 Low Pd loadings onto Printex L6: synthesis, characterization and performance towards H2O2 generation for electrochemical water treatment technologies. Chemosphere 259, 127523.

Ganjuv, S. O., Vieira Dos Santos, E., Tossi De Araújo Costa, E. C. & Martínez-Huitte, C. A. 2018 Electrochemical advanced oxidation processes (EAOPs) as alternative treatment techniques for carwash wastewater reclamation. Chemosphere 211, 998–1006.

Garcia-Segura, S., Ocon, J. D. & Chong, M. N. 2018 Electrochemical oxidation remediation of real wastewater effluents – a review. Process Saf. Environ. 113, 48–67.

Han, J., Xia, X., Haider, M. R., Jiang, W., Tao, Y., Liu, M., Wang, H., Ding, Y., Hou, Y., Cheng, H. & Wang, A. 2018 Functional graphene oxide membrane preparation for organics/inorganic salts mixture separation aiming at advanced treatment of refractory wastewater. Sci. Total Environ. 628–629, 261–270.

Hodges, B. C., Cates, E. L. & Kim, J. 2018 Challenges and prospects of advanced oxidation water treatment processes using catalytic nanomaterials. Nat. Nanotechnol. 13 (8), 642–650.

Huang, L., Li, D., Liu, J., Yang, L., Dai, C., Ren, N. & Feng, Y. 2020 Construction of TiO2 nanotube clusters on Ti mesh for immobilizing Sn–SnO2 to boost electrocatalytic phenol degradation. J. Hazard. Mater. 393, 122329.
Jin, Y., Lv, Y., Yang, C., Cai, W., Zhang, Z., Tong, H. & Zhou, X. 2020 Fabrication of superhydrophobic Ti/SnO2-Sb/α-PbO2/Fe-β-PbO2-PTFE electrode and application in wastewater treatment. J. Electron. Mater. 49 (4), 2411–2418.

Kapalka, A., Föti, G. & Comminellis, C. 2008 Determination of the Tafel slope for oxygen evolution on boron-doped diamond electrodes. Electrochem. Commun. 10 (4), 607–610.

Kundu, S., Wang, Y., Xia, W. & Muhler, M. 2008 Thermal stability and reducibility of oxygen-containing functional groups on multilayered carbon nanotube surfaces: a quantitative high-resolution xps and TPD/TPR study. J. Phys. Chem. C 112 (43), 16869–16878.

Li, D., Liu, H. & Feng, L. 2020a A review on advanced FeNi-based catalysts for water splitting reaction. Energ. Fuel. 34 (11), 13491–13522.

Li, J., Li, M., Li, D., Wen, Q. & Chen, Z. 2020b Electrochemical pretreatment of coal gasification wastewater with Bi-doped PbO2 electrode: preparation of anode, efficiency and mechanism. Chemosphere 248, 126021.

Li, X., Yan, J. & Zhu, K. 2020c Effects of IrO2 interlayer on the electrochemical performance of Ti/Sb-SnO2 electrodes. J. Electroanal. Chem. 878, 114477.

Liu, B., Wang, C., Chen, Y. & Ma, B. 2019 Electrochemical behavior and corrosion mechanism of Ti/IrO2-RuO2 anodes in sulphuric acid solution. J. Electroanal. Chem. 837, 175–183.

Maharana, D., Niu, J., Gao, D., Xu, Z. & Shi, J. 2015 Electrochemical degradation of Rhodamine B over Ti/SnO2-Sb electrode. Water Environ. Res. 87 (4), 304–311.

Malviya, K. D., Klotz, D., Dotan, H., Shlenkevich, D., Tyganuk, A., Mor, H. & Rothschild, A. 2017 Influence of Ti doping levels on the photoelectrochemical properties of thin-film hematite (α-Fe2O3) photoanodes. J. Phys. Chem. C 121 (8), 4206–4215.

Mann, R. F. & Thurgood, C. P. 2011 Evaluation of Tafel–Volmer kinetic parameters for the hydrogen oxidation reaction on Pt(110) electrodes. J. Power Sources 196 (10), 4705–4713.

Moradi, M., Vasseghian, Y., Khataee, A., Kobya, M., Arabzade, H. & Dragoi, E. 2020 Service life and stability of electrodes applied in electrochemical advanced oxidation processes: a comprehensive review. J. Ind. Eng. Chem. 87, 18–39.

Mora-Gomez, J., Ortega, E., Mestre, S., Pérez-Herranz, V. & García-Gabaldón, M. 2019 Electrochemical degradation of norfloxacin using BDD and new Sb-doped SnO2 ceramic anodes in an electrochemical reactor in the presence and absence of a cation-exchange membrane. Sep. Purif. Technol. 208, 68–75.

Olvera-Vargas, H., Goren-Datar, N., García-Rodríguez, O., Mutnuri, S. & Lefebvre, O. 2021 Electro-Fenton treatment of real pharmaceutical wastewater paired with a BDD anode: reaction mechanisms and respective contribution of homogeneous and heterogeneous OH. Chem. Eng. J. 404, 126524.

Seibert, D., Zorzo, C. F., Borba, F. H., de Souza, R. M., Quesada, H. B., Bergamasco, R., Baptista, A. T. & Inticher, J. J. 2020 Occurrence, statutory guideline values and removal of contaminants of emerging concern by electrochemical advanced oxidation processes: a review. Sci. Total Environ. 748, 141527.

Shao, C., Yu, J., Li, X., Wang, X. & Zhu, K. 2017 Influence of the Pt nanoscale interlayer on stability and electrical property of Ti/Pt/Sb-SnO2 electrode: a synergistic experimental and computational study. J. Electroanal. Chem. 804, 140–147.

Sivakumar, P., Akker, H. S., Kumar Reddy, T. R., Bitha, Y., Ganesh, V., Kumar, P. M., Reddy, G. S. & Poloju, M. 2021 Effect of Ti doping on structural, optical and electrical properties of SnO2 transparent conducting thin films deposited by sol-gel spin coating. Opt. Mater. 113, 110845.

Skoumal, M., Arias, C., Cabot, P. L., Centellas, F., Garrido, J. A., Rodríguez, R. M. & Brillas, E. 2008 Mineralization of the biocidal chloroxylenol by electrochemical advanced oxidation processes. Chemosphere 71 (9), 1718–1729.

Sun, G., Wan, J., Sun, Y., Li, H., Chang, C. & Wang, Y. 2019 Enhanced removal of nitrate and refractory organic pollutants from bio-treated coking wastewater using corncobs as carbon sources and biofilm carriers. Chemosphere 237, 124520.

Sun, Y., Cheng, S., Li, L., Yu, Z., Mao, Z. & Huang, H. 2020a Facile sealing treatment with stannous citrate complex to enhance performance of electrodeposited Ti/SnO2–Sb electrode. Chemosphere 255, 126973.

Sun, Y., Cheng, S., Mao, Z., Lin, Z., Ren, X. & Yu, Z. 2020b High electrochemical activity of a Ti/SnO2–Sb electrode electrodeposited using deep eutectic solvent. Chemosphere 239, 124715.

Sun, Y., Cheng, S., Yu, Z., Li, L., Li, C. & Yang, J. 2020c Elucidating deactivation mechanisms of Pd-doped and undoped Ti/SnO2–Sb electrodes. J. Alloys Compd 834, 155184.

Tan, C., Xiang, B., Li, Y., Fang, J. & Huang, M. 2011 Preparation and characteristics of a nano-PbO2 anode for organic wastewater treatment. Chem. Eng. J. 166 (1), 15–21.

Voiry, D., Chhowalla, M., Gogotsi, Y., Kotov, N. A., Li, Y., Penner, R. M., Schaak, R. E. & Weiss, P. S. 2018 Best practices for reporting electrocatalytic performance of nanomaterials. ACS Nano 12 (10), 9635–9638.

Vörösmarty, C. J., McIntyre, P. B., Gessner, M. O., Dudgeon, D., Proussevitch, A. A., Green, P., Glibidden, S., Bunn, S. E., Sullivan, C., Liermann, C. R. & Davies, P. M. 2010 Global threats to human water security and river biodiversity. Nature 467 (7315), 555–561.

Wang, G., Ling, Y., Wheeler, D. A., George, K. E. N., Horsley, K., Heske, C., Zhang, J. Z. & Li, Y. 2011 Facile synthesis of highly photoactive α-Fe2O3-based films for water oxidation. Nano Lett. 11 (8), 3503–3509.

Wang, Y., Duan, H., Pei, Z. & Xu, L. 2019 Hydrothermal synthesis of 3D hierarchically flower-like structure Ti/SnO2–Sb electrode with long service life and high electrocatalytic performance. J. Electroanal. Chem. 855, 113655.

Wang, J., Wang, S., Zhang, Z. & Wang, C. 2020 Preparation of Cu/GO/Ti electrode by electrodeposition and its enhanced electrochemical reduction for aqueous nitrate. J. Environ. Manage. 276, 113557.

Xiao, Y., Wang, Y., Xiao, M., Liu, C., Hou, S., Ge, J. & Xing, W. 2020 Regulating the pore structure and oxygen vacancies of cobaltic oxide hollow dodecahedra for an enhanced oxygen evolution reaction. Npg Asia Mater. 12 (1), 75.
Yang, B., Wang, J., Jiang, C., Li, J., Yu, G., Deng, S., Lu, S., Zhang, P., Zhu, C. & Zhuo, Q. 2017 Electrochemical mineralization of perfluorooctane sulfonate by novel F and Sb co-doped Ti/SnO$_2$ electrode containing Sn-Sb interlayer. Chem. Eng. J. 316, 296–304.

Yao, Y., Ren, B., Yang, Y., Huang, C. & Li, M. 2019 Preparation and electrochemical treatment application of Ce-PbO$_2$/ZrO$_2$ composite electrode in the degradation of acridine orange by electrochemical advanced oxidation process. J. Hazard. Mater. 361, 141–151.

Zhang, C., Ding, W., Zeng, X. & Xu, X. 2020a Recovery of ammonia nitrogen from landfill leachate using a biopolar membrane equipped electrodialysis system. Water Sci. Technol. 82 (9), 1758–1770.

Zhang, N., Bu, J., Meng, Y., Wan, J., Yuan, L. & Peng, X. 2020b Degradation of p-aminophenol wastewater using Ti-Si-Sn-Sb/GAC particle electrodes in a three-dimensional electrochemical oxidation reactor. Appl. Organomet. Chem. 34 (6), e5612.

Zhou, C., Wang, Y., Chen, J., Xu, L., Huang, H. & Niu, J. 2019 High-efficiency electrochemical degradation of antiviral drug abacavir using a penetration flux porous Ti/SnO$_2$–Sb anode. Chemosphere 225, 304–310.

First received 14 June 2021; accepted in revised form 13 August 2021. Available online 26 August 2021