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Table of contents
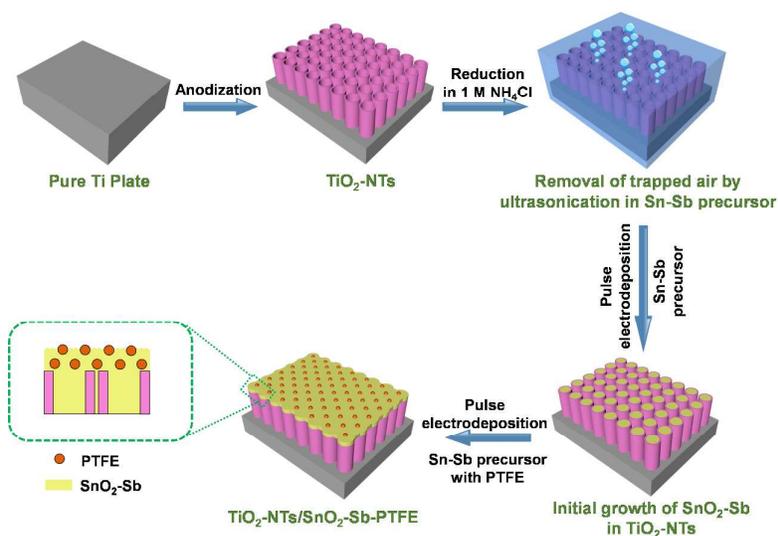
Novel TiO_2-NTs/SnO_2-Sb-PTFE electrodes were fabricated by pulse electrodeposition with higher oxygen evolution potential, improved surface hydrophobicity and enhanced electrocatalytic activity.

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ARTICLE

Enhanced electrochemical oxidation of phenol using hydrophobic TiO₂-NTs/SnO₂-Sb-PTFE electrode prepared by pulse electrodeposition

Weiyi Wu,[a, b] Zhao-Hong Huang[c] and Teik-Thye Lim[a, b]*

In this study, novel Sb-doped SnO₂ electrodes with polyetrafluoroethylene (PTFE) composite were fabricated by pulse electrodeposition. In this process, vertically aligned TiO₂ nanotubes (TiO₂-NTs) formed by anodization of Ti plate served as the substrate for SnO₂ eletrodeposition. Comparing with the conventional SnO₂-Sb electrodes, TiO₂-NTs/SnO₂-Sb-PTFE electrodes have higher oxygen evolution potential, improved surface hydrophobicity, superior hydroxyl radicals (HO•) generation and enhanced electrocatalytic activity by incorporation of PTFE nanoparticles. Field emission scanning electron microscopy (FESEM) shows that the surfaces of the PTFE composite electrodes exhibit microspherical structure. Energy-dispersive X-ray spectroscopy (EDS) confirms the uniform distribution of Sn, Sb, F and C on TiO₂-NTs/SnO₂-Sb-PTFE surfaces. More importantly, the electrodes exhibit a distinctive improvement of oxygen evolution potential (OEP) from 2.0 to 2.4 V (vs Ag/AgCl). The electrochemical impedance of TiO₂-NTs/SnO₂-Sb-PTFE also decreases significantly compared with Ti/SnO₂-Sb(conventional). The electrocatalytic performance of TiO₂-NTs/SnO₂-Sb-PTFE compared with Ti/SnO₂-Sb(conventional) and TiO₂-NTs/SnO₂-Sb were investigated using phenol as the model pollutant. The effects of initial solution pH and types of supporting electrolyte were investigated. The removal efficiency of total organic carbon (TOC), specific UV absorbance at 254 nm (SUVA₂₅₄) mineralization current efficiency (MCE) and energy consumption (Ec) with respect to different PTFE loadings on the electrodes were investigated. The anodic leaching of Sn ions was also studied in different conditions.

1. Introduction

For many years, the presence of biorefractory or recalcitrant compounds hinders the treatment of industrial wastewater. An alternative technology to conventional biological treatment methods is advanced oxidation processes (AOPs), which can remove or alleviate the refractory compounds by in situ generation of highly reactive oxygen species (ROS), mainly hydroxyl radicals (HO•). Among the AOPs, electrochemical oxidation has received special interest for the advantage of employing clean reagent electron for reaction, which has the environmental merit to minimize secondary pollutants.[1] From the viewpoint of environmental applications, it is critical to develop electrodes with good physical, chemical and electrochemical stability, high conductivity, high selectivity and satisfactory efficiency for organic oxidation.[2-4]

Recently, increasing efforts have been put forward to using mixed metal oxides (MMOs) as anode materials to remove various types of recalcitrant organic pollutants.[5-8] Among the MMOs, antimony doped SnO₂ (SnO₂-Sb) has been demonstrated to be a very promising material with several advantages such as relatively high oxygen evolution overpotential, easy preparation, low cost and superior performance for the electrochemical oxidation of organic

compounds. Pollutants such as phenol and phenolic compounds can be readily oxidized at SnO₂-Sb anode comparing with Pt and other MMO anodes, favoring complete oxidation of pollutants to CO₂ and H₂O.[9-11] However, the short service life of SnO₂-Sb electrode resulting from the weak adhesion between Ti substrate and SnO₂[12, 13] or the formation of nonstoichiometry SnO₍₂ ₋ ₓ₎[14] has represented an insurmountable barrier to its commercial applications.

Various attempts have been made to overcome this problem and improve the electrocatalytic performance of SnO₂-Sb electrodes. One approach is to develop doped SnO₂-Sb electrodes by including some noble or transition metal ions (Bi, Ir, Fe, Ni, Eu, La, Ce, Ru or Gd, etc.) into the precursor solutions or electrodeposition bath.[15-24] By introducing dopants, improvement of the electrocatalytic performances of SnO₂ electrodes would be obtained. However, there are still some remarkable limitations of this approach. For example, the presence of Ce did not lead to higher removal of pollutant although the service lifetime was enhanced.[22] The incorporation of Eu reduced the grain sizes of SnO₂-Sb but the increase of oxygen vacancies of SnO₂ was undesirable for its electrocatalytic performance.[18] Moreover, the introduction of Ir led to a lower oxygen evolution potential (OEP).[23] Therefore,

is important to develop highly stable SnO₂-Sb electrode without sacrificing its electrocatalytic activity.

Recently, SnO₂ electrodes with nanostructured and microstructured design have drawn much interest. One of the most important approaches is by employing highly ordered substrate.[10, 25, 26] Highly ordered vertically aligned TiO₂ nanotubes (TiO₂-NTs) can be prepared by anodization of Ti substrates, with mean pore diameters ranging from 100 to 220 nm. With the property of large surface area, TiO₂-NTs can serve as tubular template wherein SnO₂-Sb are implanted aiming to obtain improved loading capacity of Ti substrate.[27] TiO₂-NTs/SnO₂-Sb prepared by pulse electrodeposition has been verified to have distinctive oxygen evolution potential of about 2.4 V vs SCE and show remarkable better electrocatalytic activity compared with the SnO₂-Sb electrode prepared by sol-gel method.[28] Meanwhile, polymers are attractive materials to introduce specific properties of metal oxide anodes. Polypyrrole and polyetrafluoroethylene (PTFE) composites have been used to introduce the hydrophobicity of PbO₂ electrode and obtained improved OEP and electrocatalytic activity.[29, 30] In other work, TiN composite has also been incorporated on SnO₂-Sb electrode for improved electrocatalytic activity.[31]

In the present work, novel TiO₂-NTs/SnO₂-Sb-PTFE composite electrodes were fabricated by pulse electrodeposition for the first time to obtain the larger specific surface area and hydrophobic electrode surface. The surface morphology, crystalline structure and electrochemical properties of the novel electrodes were investigated. The capability of HO• generation on the electrodes were also evaluated. Phenol was selected as the model pollutant to investigate the performance of as-prepared electrodes. The effects of pH and supporting electrolytes (Na₂SO₄ and NaCl) on the process efficiency were investigated, with a proposed mechanism presented to depict the electrochemical oxidation processes in different electrolytes. Sn ions leaching of TiO₂-NTs/SnO₂-Sb-PTFE was also studied under different conditions of electrochemical oxidation to evaluate its feasibility for environmental application.

2. Experimental

2.1 Chemicals and materials

All the chemicals were of analytical grade and used without further purification. SnCl₂.2H₂O, SbCl₃, Na₂SO₄, NaCl, NaF, NH₄Cl, PTFE, glycerol, dimethyl sulfoxide (DMSO), 2,4-dintrophenylhydrazine and (3-aminopropyl)trimethoxysilane were obtained from Sigma-Aldrich. Merck's absolute acetone, NaOH pellet, HCl and phenol were used in the experiments. PTFE was in the form of emulsion with 60 wt % dispersion in water. Pure titanium plates (99.9%) with a thickness of 0.5 mm were purchased from Qixin Company (Baoji, China).

2.2 TiO₂-NTs preparation

Pure titanium plates (60mm × 20mm) were polished by mechanical polisher with 120, 320, 800 and 1200 grid sand papers in sequence. Then they were washed in acetone and Milli Q water with ultrasonic assistance for 15 min, respectively. After that the titanium plates were immersed in 18% hydrochloric acid at 85 °C for 20 min to remove titanium oxide. In order to fabricate TiO₂-NTs substrate, the clean Ti plate was anodized in a two-electrode cell (1 cm distance) at room

temperature, in which the clean Ti acted as anode and another titanium plate with same dimension as the cathode. The electrolyte is an aqueous solution containing a mixture of glycerol and Milli Q water (1.3:1 v/v), NaF (0.5 wt %) and Na₂SO₄ (0.2 M). Anodization experiments were carried out at a voltage of 30 V for 240 min with continuous magnetic stirring. Finally, the prepared substrates were annealed at 500 °C for 90 min at both a heating and cooling rate of 1 °C min⁻¹ to get vertically aligned TiO₂-NTs.

2.3 TiO₂-NTs/SnO₂-Sb-PTFE preparation

TiO₂-NTs/SnO₂-Sb-PTFE were prepared by pulse electrodeposition in a two-electrode cell (1 cm distance) using potentiostat (PGSTAT302N, Autolab) at 40 °C. Fig. 1 shows the schematic diagram for electrode design and preparation. Prior to pulse electrodeposition, TiO₂-NTs were pretreated by reduction in 1 M NH₄Cl at a potential of −1.5 V vs Ag/AgCl at 40 °C, aiming to improve the conductivity of TiO₂-NTs substrate. Then the TiO₂-NTs were vertically immersed into the electrolyte which was consisted of 0.1 M SnCl₂.2H₂O, 0.02 M SbCl₃ and a certain concentration hydrochloric acid, and they were degased in an ultrasonic bath for 10 min. This procedure was to remove the trapped air in the TiO₂-NTs. The impregnation of NTs with electrolyte is expected to favor the initial growth of SnO₂-Sb on the internal walls of the NTs. The nominal area of the electrode surface is 10 cm².
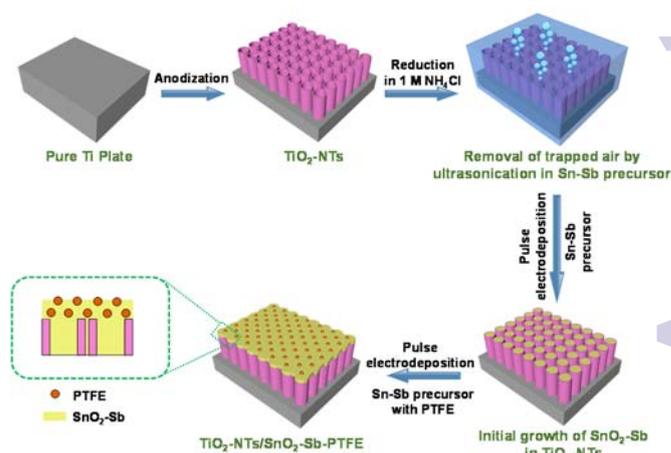
Fig. 1 Schematic illustration of TiO₂-NTs/SnO₂-Sb-PTFE electrode preparation

The initial deposition of SnO₂-Sb was conducted in the above electrolyte. A pulse current with an anodic pulse (5 mA cm⁻², 50 ms), a cathodic pulse (−5 mA cm⁻², 5 ms) and a relaxation time (0 mA cm⁻², 1 s) was applied at 40 °C for 15 min. After that, the electrode was put into electrolytes consisted of 0.1 M SnCl₂.2H₂O, 0.02 M SbCl₃, a certain concentration of hydrochloric acid and plural PTFE dispersions (0, 1.5, 4.5 and 13.5 mL L⁻¹) using the same pulse electrodeposition method for 2 h. A 0.05 wt % (3-aminopropyl)trimethoxysilane solution was added in the electrolyte to lower the surface tension. The resulting electrodes were marked TiO₂-NTs/SnO₂-Sb, TiO₂-NTS/SnO₂-Sb-PTFE(1.5), TiO₂-NTS/SnO₂-Sb-PTFE(4.5) and TiO₂-NTS/SnO₂-Sb-PTFE(13.5) with respect to the different concentrations of PTFE in the electrodeposition baths.

The conventional Ti/SnO$_2$-Sb electrode having the same nominal surface area was prepared by thermochemical decomposition according to the literature.[32]

2.4 Bulk electrolysis experiments

Bulk electrochemical oxidation of phenol was carried out in a 200 ml single-compartment electrochemical cell at room temperature for 6 h under continuous stirring. Conventional Ti/SnO$_2$-Sb electrode prepared by thermochemical decomposition, TiO$_2$-NTs/SnO$_2$-Sb and TiO$_2$-NTS/SnO$_2$-Sb-PTFE electrodes prepared by pulse electrodeposition were employed as the anodes, and a titanium plate with the same area served as the cathode. The distance between the two electrodes is 1 cm. The influencing factors that were investigated including the types of supporting electrolytes (Na$_2$SO$_4$ and NaCl) and the initial solution pH (pH = 3, 7 and 11). Either 0.05 M Na$_2$SO$_4$ or 0.1 M NaCl were used as the supporting electrolytes for synthetic wastewater solution containing 5 mM phenol. Initial pH of solutions were adjusted by adding drops of 1 M HCl, 0.5 M H$_2$SO$_4$ or 1M NaOH solutions. The current density was set as 20 mA cm^{-2}, and the samples were drawn for analysis with 1 h time interval. The accelerated life tests were conducted by anodic polarization at current density of 100 mA cm^{-2} in 0.1 M H$_2$SO$_4$ to evaluate the service lifetime of the electrodes. The accelerated life in hours was determined by the time when the cell potential increased 5 V from the initial value.[32]

The electrocatalytic performance of the electrodes were evaluated by measurement of total organic carbon (TOC) and specific ultra-violet absorbance at wavelength of 254 nm (SUVA$_{254}$). SUVA$_{254}$ is defined as the UV absorbance at wavelength of 254 nm normalized by dissolved organic carbon (DOC) concentration, which is equivalent to the determined TOC since the solutions were crystal clear. The TOC of the samples were measured by a TOC analyzer (TOC-L/CPH, Shimadzu). The UV absorbance of the samples at wavelength of 254 nm were determined by a UV-Vis spectrophotometer (UV 9000, Metash). HO$^{\bullet}$ was quantitatively determined by high-performance liquid chromatography (HPLC, Perkin Elmer Series 200) with DMSO trapping according to literature.[33] The organic acids intermediates of phenol oxidation were qualitatively determined by ion chromatography (IC, Thermo Scientific Dionex ICS-2100). Atomic absorption spectroscopy (AAS, Perkin Elmer AAnalyst 100) was used to analyze the leached Sn ions in the solutions after 6 h bulk electrolysis.

The completely electrochemical oxidation of phenol can be expressed as:

$$C_6H_6O + 11H_2O \rightarrow 6CO_2 + 28H^+ + 28e^- \quad (1)$$
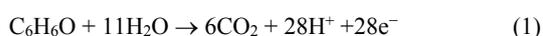
At given time t, the mineralization current efficiency (MCE) of the electrochemical oxidation process can be calculated by the following equation:[34]

$$MCE (\%) = \frac{100.\Delta[TOC]_{exp}}{\Delta[TOC]_{theory}} \quad (2)$$

where $\Delta[TOC]_{exp}$ and $\Delta[TOC]_{theory}$ (mg dm^{-3}) are the experimental TOC change and theoretical TOC change at given time t, respectively. The value of $\Delta(TOC)_{theory}$ can be calculated by:

$$\Delta[TOC]_{theory} = \frac{1000.n_c ItM}{n_e FV} \quad (3)$$

where n_C is the number of organic carbon, I is the applied current (A), t is the electrolysis time (s), M is the atomic weight of carbon (M = 12 g mol^{-1}), n_e is the number of electron transfers, F is the Faradic constant (96485 C mol^{-1}) and V is the volume of solution (dm^3). For phenol oxidation, n_C and n_e are 28 and 6 respectively.

The specific energy consumption (E$_c$, kWh kgTOC^{-1}) can be calculated as follows:

$$E_C = \frac{1000.E_{cell}It}{\Delta[TOC]_{exp}V} \quad (4)$$

where E$_{cell}$ is the average cell potential (V), I is the applied current (A), t is the electrolysis time (h), $\Delta[TOC]_{exp}$ is the experimental TOC change (mg dm^{-3}) and V is the volume of solution (dm^3).

2.5 Analytical techniques

The surface morphology and element composition of the electrodes were characterized using field emission scanning electron microscopy (FESEM, JEOL-7660F) and energy dispersive X-ray spectroscopy (EDS, Oxford Xmax80 LN2 Free). The crystal structure of the fabricated electrodes were characterized by X-ray diffraction (XRD, Bruker D8 Advance) with Cu-Ka (λ=1.5418 Å) operating at 40 kV and 40 mA, with corresponding 2θ range of 10-80°. The contact angle of water on the electrode surface was determined by a contact angle meter (DSA100). Electrochemical properties of the electrodes were investigated in a conventional three-electrode system using electrochemical workstation (PGSTAT 302N, Autolab). Pt served as the counter electrode and Ag/AgCl served as the reference electrode, and the electrolyte was 0.5 M Na$_2$SO$_4$. Cyclic voltammetry (CV) was performed to determine the OEP of the electrode with the scan range of 0.3-3.0 V and scan rate of 50 mV s^{-1}. Anodic polarization experiments were studied using chronoamporometric method at a potential of 1.4 V and 3.0 V vs Ag/AgCl respectively for 10 s with/without 5 mM phenol. Electrochemical impedance spectroscopy (EIS) was carried out at 1.0 V to measure the impendence of the electrodes. The frequency ranges from 100 kHz to 5 mHz with an amplitude of 10 mV, and equivalent circuit simulation was applied to determine the values of electrochemical parameters.

3. Results and discussion

3.1 Characteristics of TiO$_2$-NTS/SnO$_2$-Sb-PTFE

3.1.1 Surface structure and wetting property. The surface morphology of the TiO$_2$-NTs substrate and the fabricated electrodes are examined by FESEM. As can be seen in Fig. 2a, highly ordered TiO$_2$-NTs were uniformly grown on Ti plate with an average pore diameter of 100 nm, and the thickness of the wall ranges from 10 to 20 nm. The surface of the conventional SnO$_2$-Sb electrodes shows "mud-cracked" structure (Fig. 2b), which is a typical structure in MMO anodes prepared by thermochemical decomposition. The cracks is undesirable because it would give rise to the weak adhesion between SnO$_2$ and Ti substrate. In addition, such cracks may lead to the permeation of electrolyte into the Ti substrate, and finally the formation of a passivating layer between SnO$_2$-Sb and Ti substrate. It was also confirmed by the accelerated life test that the conventional Ti/SnO$_2$-Sb electrode has a lowest service lifetime of only 6.4 h (Table 1). In Fig. 2c, improvement of the surface morphology is observed in TiO$_2$

NTs/SnO₂-Sb fabricated by pulse electrodeposition. The SnO₂-Sb nanoparticles show microspherical shape with diameters ranging from 100 to 200 nm, and no crack is observed on the electrode surface comparing with the conventional Ti/SnO₂-Sb. The service lifetime of TiO₂-NTs/SnO₂-Sb was also improved up to 28h, which is 4.3 times that of the conventional Ti/SnO₂-Sb. After the incorporation of PTFE nano particles, a layer of PTFE can be observed on the surfaces of all the three electrodes with different PTFE loadings (Fig. 2d-f). Compared with TiO₂-NTs/SnO₂-Sb without PTFE, the electrode surfaces with PTFE loading become rough in morphology. Such morphology leads to increased specific surface area which can provide more active sites for the electrocatalytic oxidation reactions to take place. It is also notable that a reduced SnO₂-Sb particle grain size is observed at TiO₂-NTs/SnO₂-Sb-PTFE(4.5), indicating grain refining effect for SnO₂-Sb deposition. The accelerated service lifetime of TiO₂-NTs/SnO₂-Sb-PTFE(4.5) and TiO₂-NTs/SnO₂-Sb-PTFE(13.5) were further improved up to 98h and 103 h, corresponding to 15.3 and 16 times that of the conventional SnO₂-Sb, respectively.
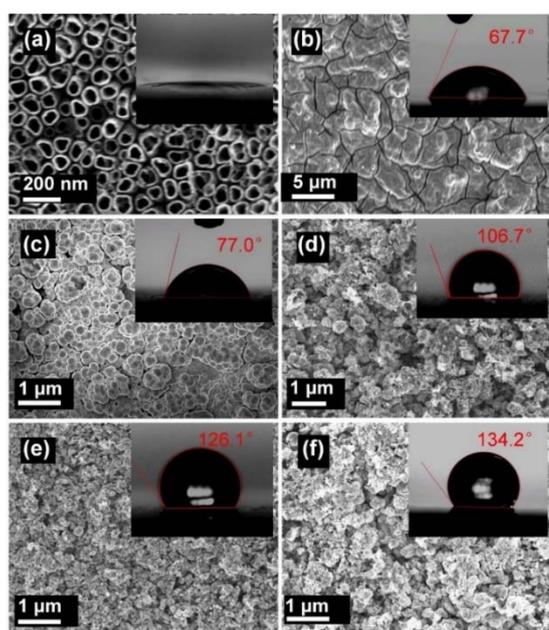
Fig. 2 FESEM images and contact angles (inset) of (a) TiO₂-NTs, (b) conventional TiO₂ /SnO₂-Sb, (c) TiO₂-NTs/SnO₂-Sb, (d) TiO₂-NTs/SnO₂-Sb-PTFE(1.5), (e) TiO₂-NTs/SnO₂-Sb-PTFE(4.5) and (f) TiO₂-NTs/SnO₂-Sb-PTFE(13.5)

Elements of Ti, Sn, Sb, F, C and O were detected by EDS on TiO₂-NTs/SnO₂-Sb-PTFE electrodes. Fig. 3 shows the uniform distribution of elements Sn, Sb, F and C on TiO₂-NTs/SnO₂-Sb-PTFE(4.5) by elemental mapping. The atomic percentages of the elements are investigated and listed in Table 2. There is still a small portion of Ti detected on the electrode surfaces. However, more amount of Ti was detected on the conventional Ti/SnO₂-Sb (1.15%), which is possibly due to the cracks of the electrode leading to the exposure of Ti substrate. Sb/Sn ratios of TiO₂-NTs/SnO₂-Sb-PTFE electrodes are around 4%, while the value is 2.6% on the conventional Ti/SnO₂-Sb. It should be noted that when the PTFE loading in the electrodepositon bath increases 3 times from 4.5 ml L^{-1} to 13.5 ml L^{-1}, the real atomic percentage of F in the electrode surface only increases by a factor of 1.8 (from 0.58% to 1.08%). It indicates that PTFE loading of TiO₂-NTs/SnO₂-Sb-PTFE(13.5) has reached a saturation level and further increase of PTFE in the electrodepositon bath would not result in higher PTFE content in the electrode surface.
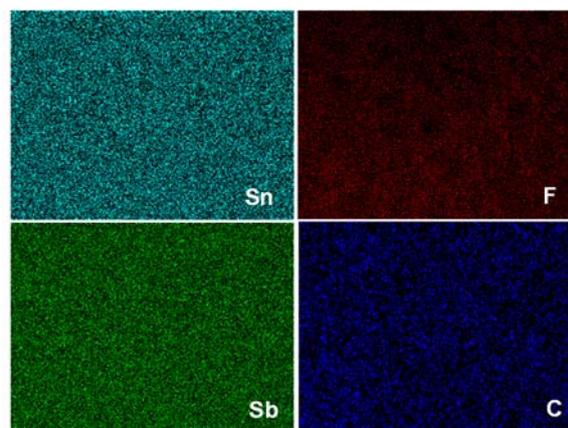
Fig. 3 Elemental mappings of Sn, Sb, F and C on the surface of TiO₂-NTs/SnO₂-Sb-PTFE(4.5)

The contact angle of TiO₂-NTs (Fig. 2a) is very low (below 10°) and shows its super hydrophilic property. Both the conventional Ti/SnO₂-Sb and TiO₂-NTs/SnO₂-Sb have hydrophilic surface (contact angles 67.7° and 77° respectively). For TiO₂-NTs/SnO₂-Sb-PTFE, because of the strong hydrophobicity of PTFE, its surface wetting property prominently changes and the contact angles are 106.7°, 126.7° and 134.2° respectively with the increasing PTFE loading.

Fig. 4 compares the XRD patterns of various electrodes. TiO₂ is indexed to anatase phase with diffraction peaks at 2θ = 25.6°, 38.1° and 48.3°. The diffraction peaks at 2θ = 26.8°, 34.1° and 52.0° are indexed to the (110), (101) and (211) planes of SnO₂. No obvious peaks of Sb are detected due to the incorporation of Sb into the SnO₂ crystals. The intensities of (101) and (211) peaks for SnO₂ of conventional Ti/SnO₂-Sb

Table 1 Parameters of the Ti/SnO₂-Sb(conventional), TiO₂-NTs/SnO₂-Sb and TiO₂-NTs/SnO₂-Sb-PTFE electrodes

Electrode	OEP (V vs Ag/AgCl)	Service lifetime (h)	Current density without phenol[a] (mA cm⁻²)	Current density with phenol[a] (mA cm⁻²)	ΔCurrent density (mA cm⁻²)	Contact angle (°)
Conventional Ti/SnO₂-Sb	2.0	6.4	8.32	10.54	2.22	67.7
TiO₂-NTs/SnO₂-Sb	2.1	28	8.47	11.60	3.13	77.0
TiO₂-NTs/SnO₂-Sb-PTFE(1.5)	2.2	51	10.29	14.71	4.42	106.7
TiO₂-NTs/SnO₂-Sb-PTFE(4.5)	2.4	98	10.21	16.55	6.34	126.1
TiO₂-NTs/SnO₂-Sb-PTFE(13.5)	2.4	103	9.36	12.41	3.05	134.2

[a] Current densities were measured at the potential of 3.0 V vs Ag/AgCl.

Table 2 Elemental compositions of Ti/SnO₂-Sb(conventional), TiO₂-NTs/SnO₂-Sb and TiO₂-NTs/SnO₂-Sb-PTFE electrode surfaces

Electrode	Surface elemental composition (Atomic %)					
	Ti	Sn	Sb	C	F	O
Conventional Ti/SnO₂-Sb	1.15	32.3	0.84	-	-	66.7
TiO₂-NTs/SnO₂-Sb	0.76	32.1	1.33	-	-	65.8
TiO₂-NTs/SnO₂-Sb-PTFE(1.5)	0.61	33.3	1.28	0.12	0.22	64.5
TiO₂-NTs/SnO₂-Sb-PTFE(4.5)	0.52	32.3	1.41	0.30	0.58	64.9
TiO₂-NTs/SnO₂-Sb-PTFE(13.5)	0.48	32.4	1.22	0.57	1.08	64.3

and TiO₂-NTs/SnO₂-Sb are similar. However, the intensity of (110) peak is much stronger in the conventional TiO₂-NTs/SnO₂-Sb, indicating a preferred orientation of SnO₂ along (110) direction. The diffraction peak at 2θ = 18.2° suggests that PTFE has been successfully incorporated in the electrode surface coating. The higher PTFE loading, the stronger the peak intensity.
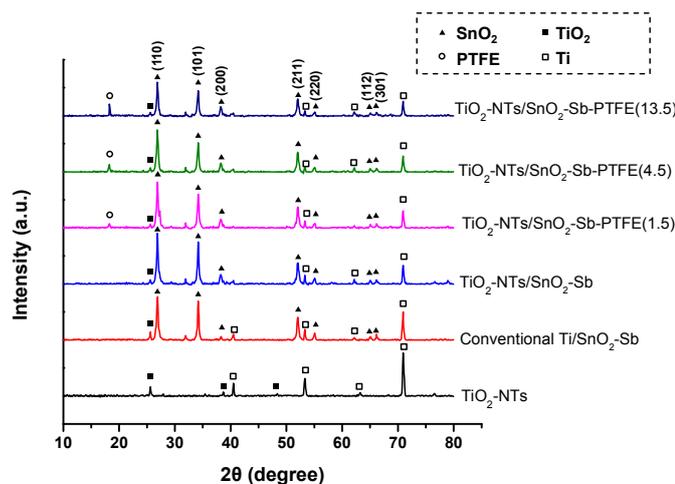
Fig. 4 XRD patterns of the electrodes

3.1.2 Electrochemical properties. In environmental application of anodes, OEP is an important indicator of electrocatalytic activities for organics oxidation. Fig. 5 shows the CV curves of the conventional Ti/SnO₂-Sb, TiO₂-NTs/SnO₂-Sb and TiO₂-NTs/SnO₂-Sb-PTFE electrodes in 0.5 M Na₂SO₄, and the corresponding values of OEP are given in Table 1. The conventional Ti/SnO₂-Sb has a lowest OEP of 2.0 V, and the value increases slightly to 2.1 V in TiO₂-NTs/SnO₂-Sb fabricated by pulse electrodeposition. However, after introducing PTFE the OEP of the anodes are further increased, with the highest OEP of 2.4 V observed in TiO₂-NTs/SnO₂-Sb-PTFE(4.5) and TiO₂-NTs/SnO₂-Sb-PTFE(13.5). First, the enhancement of OEP is attributed to the change of surface wetting property from hydrophilic to hydrophobic, which inhibits the surface adsorption of hydrophilic HO•. Second, PTFE hinders the movement of HO• into the electrode interior. Thus, the oxygen evolution reaction (OER) is inhibited.[30]

The anodic polarization of the electrodes was studied at a constant potential of 1.4 V and 3.0 V vs Ag/AgCl to investigate their electrocatalytic activities towards phenol. At 1.4 V which is below the OEP, no background current was observed either in the presence or absence of phenol, suggesting phenol cannot be oxidized at this potential. When the potential was set as 3.0 V, the current densities of the five electrodes ranged from 8.32 mA cm⁻² to 10.29 mA cm⁻² in 0.5 M Na₂SO₄ (Table 1). However, after the addition of 5 mM

phenol, there were drastic increases of the current densities. The increment of current density of TiO₂-NTs/SnO₂-Sb-PTFE(4.5) (6.34 mA cm⁻²) was significantly greater than that of conventional Ti/SnO₂-Sb (2.22 mA cm⁻²) and TiO₂-NTs/SnO₂-Sb (3.13 mA cm⁻²) revealing its superior electrocatalytic activity towards phenol. Nevertheless, the value was much smaller in TiO₂-NTs/SnO₂-Sb-PTFE(13.5) (3.05 mA cm⁻²) compared with TiO₂-NTs/SnO₂-Sb-PTFE(4.5). Such phenomenon is attributed to their differences of surface morphology. The particle size of SnO₂-Sb on TiO₂-NTs/SnO₂-Sb-PTFE(4.5) is much smaller, indicating more active sites for the oxidation of phenol to take place, so that the electrocatalytic activity is improved.
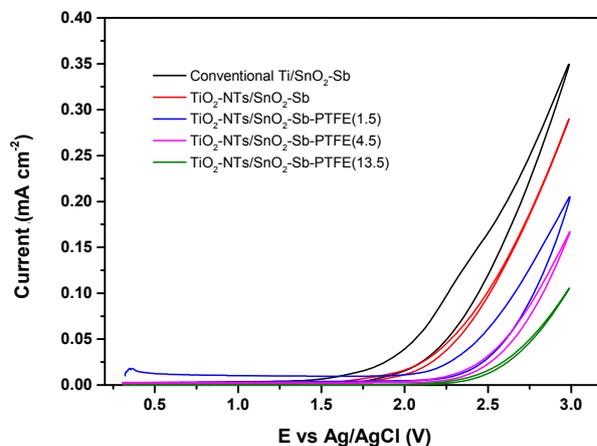
Fig. 5 Cyclic voltammetric curves of the electrodes in 0.5 M Na₂SO₄ with potential range of 0.3-3.0 V vs Ag/AgCl and scan rate of 50 mV s⁻¹

EIS studies were carried out to further investigate the electrochemical impedance of the novel electrodes. Fig. 6a shows the Nyquist plots of the electrodes. As shown in the figure, well developed semicircle patterns are observed, which suggested that mass diffusion control is negligible.[21] TiO₂-NTs substrate is non-conductive with an electrochemical impedance larger than 20000 Ω. After partial reduction of TiO₂-NTs substrate and pulse electrodeposition of SnO₂-Sb, the electrochemical impedance decreased significantly. Equivalent circuit module Rs(RctQ) was employed to better interpret the EIS results (Fig. 6b). The simulation values of the electrochemical parameters are given in Table 3. In this circuit model, Rs represents the uncompensated ohmic resistance between the working electrode and referrence electrode, Rct is the charge transfer resistance, and Q is the constant phase element (CPE) of double layer. The values of n are all in the range of 0.75-1 representing the performance of the electrodes are close to pure capacitors. Comparing with the conventional Ti/SnO₂-Sb, Rs of TiO₂-NTs/SnO₂-Sb decreases by the

employment of TiO₂-NTs substrate, suggesting better conductivity. Slight increases of R_s are observed at TiO₂-NTs/SnO₂-Sb-PTFE electrodes. This is probably due to the property of PTFE which is non-conductive. Despite the slight increases of R_s, it should be noted that the charge transfer resistances decrease significantly at TiO₂-NTs/SnO₂-Sb-PTFE electrodes. TiO₂-NTs/SnO₂-Sb-PTFE(4.5) has a lowest R_{ct} of only 54.13 Ω cm^{-2}, which is only 38% and 53% that of conventional Ti/SnO₂-Sb and TiO₂-NTs/SnO₂-Sb by pulse electrodeposition. Lower R_{ct} results in the faster electron transfer on electrode surface, indicating an improvement of electrocatalytic activity by incorporation of PTFE nanoparticles. Meanwhile, the R_s of TiO₂-NTs/SnO₂-Sb-PTFE(4.5) (5.30 Ω cm^{-2}) is also smaller than that of the conventional Ti/SnO₂-Sb (5.89Ω cm^{-2}). Thus, TiO₂-NTs/SnO₂-Sb-PTFE(4.5) is expected to exhibits much better electrocatalytic activity. Moreover, the TiO₂-NTs/SnO₂-Sb-PTFE electrodes showed higher capacitance, which can result from electrochemically active surface area of the coatings.[35]
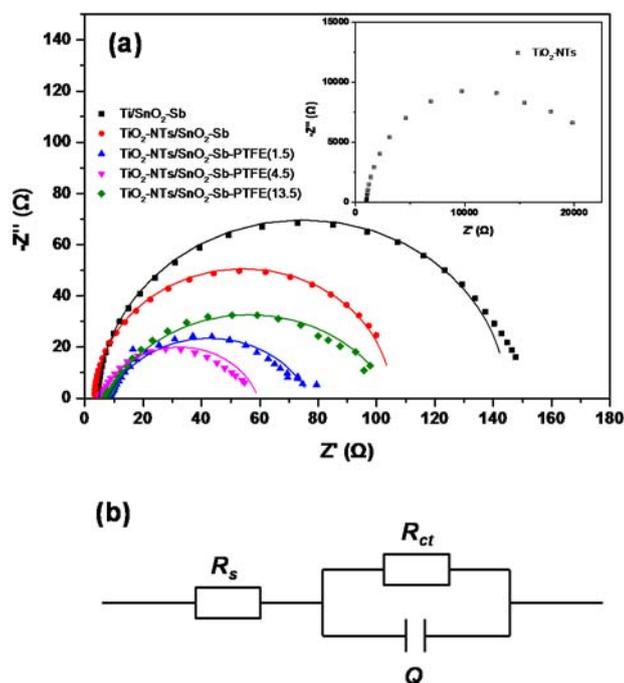
Fig. 6 (a) Nyquist plots of the electrodes and simulation curves of the EIS results (inset is the Nyquist plot of TiO₂-NTs) and (b) equivalent circuit model $R_s(R_{ct}Q)$

3.2 Electrochemical oxidation of phenol

3.2.1 Influence of PTFE loadings. Fig. 7 shows the removal of TOC during electrochemical oxidation of phenol in 0.05 M Na₂SO₄.

When using the conventional Ti/SnO₂-Sb, the removal of TOC of phenol is only 69% after 6 h electrochemical oxidation at pH 7. An improvement of TOC removal (73%) is observed at TiO₂-NTs/SnO₂-Sb fabricated by pulse electrodeposition. As mentioned above, such enhancement is probably attributed to the reduced electrochemical impedance and the improved surface morphology of the 3-dimensional TiO₂-NTs. Moreover, the TOC removal efficiency was greatly enhanced in TiO₂-NTs/SnO₂-Sb-PTFE electrodes (up to 93%), indicating the improved electrocatalytic activity of phenol oxidation by incorporation of PTFE in the electrode surfaces. The enhancement of TOC removal can be attributed to several reasons. First, the high OEP of TiO₂-NTs/SnO₂-Sb-PTFE favors the HO˙ generation. Second, the surfaces of TiO₂-NTs/SnO₂-Sb-PTFE electrodes are hydrophobic, so that the HO˙ generated would be released as free HO˙ rather than combining together for oxygen evolution. Hence, the removal efficiency is enhanced. The above results were verified by the HO˙ concentration in solution (Fig. 8). The TiO₂-NTs/SnO₂-Sb-PTFE electrodes showed superior ability of HO˙ generation (up to 36 μM) than Ti/SnO₂-Sb(conventional) (26 μM) and TiO₂-NTs/SnO₂-Sb (28 μM) after 240 min bulk electrolysis. The best TOC removal was obtained in TiO₂-NTs/SnO₂-Sb-PTFE(4.5) which has the highest HO˙ generation (Fig. 7b). In addition, the TiO₂-NTs/SnO₂-Sb-PTFE(4.5) has notably smaller SnO₂-Sb particles, which also give more active sites for phenol degradation.

The SUVA₂₅₄ degradation of the 5 electrodes is represented in the inset of Fig. 7. SUVA₂₅₄ is strongly correlated with the aromatic extent of pollutants. The higher the SUVA₂₅₄, the higher degree of aromaticity of the dissolved organic compounds.[36] Increase of SUVA₂₅₄ in the first hour using Ti/SnO₂-Sb(conventional), TiO₂-NTs/SnO₂-Sb and TiO₂-NTs/SnO₂-Sb-PTFE(13.5) as anodes shows that the cleavage reaction of aromatic ring is not favored despite the TOC decreases. The main aromatic intermediates of phenol involves catechol, hydroquinone and benzoquinone.[37] When using TiO₂-NTs/SnO₂-Sb-PTFE(4.5) and TiO₂-NTs/SnO₂-Sb-PTFE(1.5) as anodes, the SUVA₂₅₄ decreased readily during the 6 h electrochemical oxidation, indicating phenol and aromatic intermediates undergo ring cleavage reactions. IC measurements showed that they were subsequently oxidized to aliphatic acid including maleic acid, oxalic acid, acetic acid and formic acid. Finally, they can be completely degraded to CO₂ and H₂O. The final SUVA₂₅₄ after 6 h electrochemical oxidation is 0.098 SUVA₂₅₄,₀ on TiO₂-NTs/SnO₂-Sb-PTFE(4.5), which is only 29% and 46% that of Ti/SnO₂-Sb(conventional) and TiO₂-NTs/SnO₂-Sb. This result suggests that TiO₂-NTs/SnO₂-Sb-PTFE(4.5) has the merit of fully alleviating the aromatic intermediates into mineral acids, which are biodegradable and environmentally more benign.

Fig. 9a shows the MCE of different electrodes for electrocatalytic oxidation of phenol. The highest MCE was obtained on TiO₂-NTs/SnO₂-Sb-PTFE(4.5) (17.8 % at 1 h and 11.6 % at 6 h). Therefore, TiO₂-NTs/SnO₂-Sb-PTFE(4.5) exhibits the highest efficiency for electrocatalytic oxidation of

Table 3 EIS simulating parameters of Ti/SnO₂-Sb(conventional), TiO₂-NTs/SnO₂-Sb and TiO₂-NTs/SnO₂-Sb-PTFE electrodes

Electrodes	R_s (error%) (Ω cm^{-2})	R_{ct} (error%) (Ω cm^{-2})	n	CPE (error%) (mF cm^{-2})
Conventional Ti/SnO₂-Sb	5.89 (0.48)	139.57 (0.74)	0.923	0.54 (0.59)
TiO₂-NTs/SnO₂-Sb	4.32 (1.26)	101.45 (0.633)	0.941	0.52 (1.12)
TiO₂-NTs/SnO₂-Sb-PTFE(1.5)	7.71 (3.41)	69.64 (6.44)	0.757	1.96 (16.47)
TiO₂-NTs/SnO₂-Sb-PTFE(4.5)	5.30 (2.31)	54.13 (3.77)	0.814	1.04 (11.90)
TiO₂-NTs/SnO₂-Sb-PTFE(13.5)	6.97 (2.32)	98.62 (5.49)	0.746	2.14 (9.74)

phenol. As shown in Fig. 9b, TiO$_2$-NTs/SnO$_2$-Sb-PTFE(4.5) has the lowest E_c among the 5 electrodes. The E_c of TiO$_2$-NTs/SnO$_2$-Sb-PTFE(4.5) to reach 60 % TOC removal is 49 kWh kgTOC^{-1}, which is only 0.68 time that of Ti/SnO$_2$-Sb(conventional) and 0.78 time that of TiO$_2$-NTs/SnO$_2$-Sb. On the basis of above analysis, TiO$_2$-NTs/SnO$_2$-Sb-PTFE(4.5) appears to be the most optimal electrode with the most TOC removal and SUVA$_{254}$ decrease, highest MCE and lowest energy consumption.

Fig. 8 Concentration evolution of hydroxyl radicals on the electrodes in 0.05 M Na$_2$SO$_4$

Fig. 7 TOC concentration and SUVA$_{254}$ as a function of time during phenol degradation at: (a) pH 3; (b) pH 7; (c) pH 11
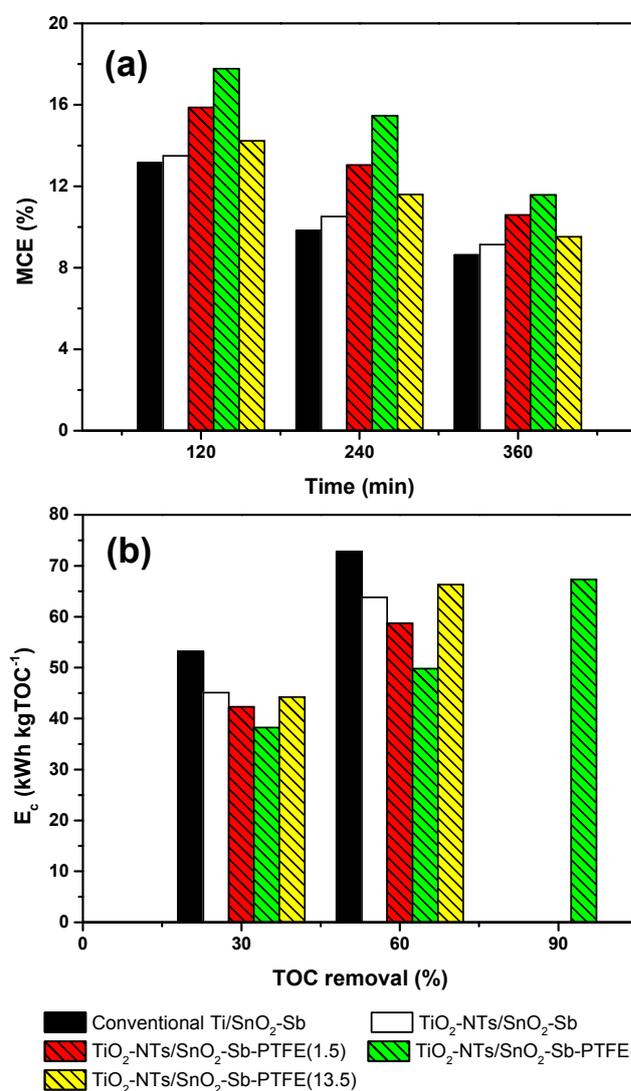
Fig. 9 (a) MCE changes with time and (b) specific energy consumption with TOC removal rate at pH 7 in 0.05 M Na$_2$SO$_4$

3.2.2 Influence of pH. The effect of pH on phenol oxidation by the different electrodes was investigated in 0.05 M Na_2SO_4. Fig. 7 shows that all of the 3 electrodes achieve better TOC removals in acidic solutions than that in neutral and basic solutions. The TOC removals at pH 3 are 74%, 79% and 94% respectively using Ti/SnO_2-Sb, TiO_2-NTs/SnO_2-Sb and $TiO_2-NTs/SnO_2-Sb-PTFE(4.5)$ as anodes. The $SUVA_{254}$ also decreases more rapidly, indicating a faster ring cleavage of the aromatic intermediates. On the contrary, TOC removals are not favorable at pH 11. The results can be explained from the viewpoint of thermodynamics, because the oxidative power of $HO^\bullet$ varies with pH. $HO^\bullet$ radicals are generated from the oxidation of water:

$$H_2O \rightarrow HO^\bullet + H^+ + e^- \qquad (5)$$
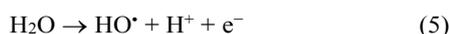
Given that the redox potential of $HO^\bullet_{aq}/H_2O$ is 2.59 V at pH 0 at the standard condition, the relationship between solution pH and redox potential of $HO^\bullet_{aq}/H_2O$ can be calculated by Nernst equation:

$$E^o(HO^\bullet_{aq}/H_2O) = 2.59 - 0.059 \text{ pH} \qquad (6)$$

Thus, the values of $E^o(HO^\bullet_{aq}/H_2O)$ are 2.41, 2.18 and 1.94 at pH 3, 7 and 11. Therefore, higher TOC removal can be achieved in low pH range. However, in the basic solution with pH 11, the decrease of TOC removal is at a greater extent using $TiO_2-NTs/SnO_2-Sb-PTFE(4.5)$ (82%) as anode than those using conventional Ti/SnO_2-Sb (64%) and TiO_2-NTs/SnO_2-Sb (73%). This is probably because the electrocatalytic oxidation of phenol with $TiO_2-NTs/SnO_2-Sb-PTFE(4.5)$ relies more on $HO^\bullet$ generation. Hence, the phenol oxidation is greatly influenced when the oxidative power of $HO^\bullet$ reduces in the basic solution.

3.2.3 Influence of supporting electrolytes. The types of supporting electrolytes may influence the types of oxidative species generated, and hence the process efficiency of electrochemical oxidation. Fig. 10 shows the TOC removals and the corresponding $SUVA_{254}$ of phenol using different anodes in 0.05 M Na_2SO_4 and 0.1 M NaCl at pH 7. TOC removals in the presence of 0.1 M NaCl are slightly higher than those in the presence of 0.05 M Na_2SO_4 with Ti/SnO_2-Sb(conventional) and TiO_2-NTs/SnO_2-Sb. However, a decrease of TOC removal efficiency is observed with $TiO_2-NTs/SnO_2-Sb-PTFE(4.5)$. The reactive chlorine will be generated in the presence of Cl^- through the following reactions:

$$Cl^- \rightarrow Cl^\bullet + e^- \qquad (7)$$

$$2Cl^\bullet \rightarrow Cl_2 \qquad (8)$$

$$Cl_2 + 2H_2O \rightarrow 2HClO + 2H^+ + 2e^- \qquad (9)$$

$$HClO \rightarrow ClO^- + H^+ \qquad (10)$$
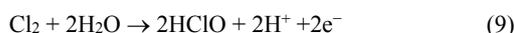
Fig. 11 shows the schematic illustration of electrochemical oxidation of phenol using $TiO_2-NTs/SnO_2-Sb-PTFE(4.5)$ and the conventional Ti/SnO_2-Sb as anodes in 0.05 M Na_2SO_4 and 0.1 M NaCl. Since Cl_2 can only present in the solution in very low pH (usually < 1), the main reactive chlorine species for phenol oxidation are $Cl^\bullet$, HClO and ClO^-. Although the oxidative power of $Cl^\bullet$ (2.2 V), HClO (1.63 V) and ClO^- (0.90 V) are lower than that of $HO^\bullet$ (2.59 V), their advantages of massive production and longer lifetime over $HO^\bullet$ make them degrade phenol more effectively. However, for $TiO_2-NTs/SnO_2-Sb-PTFE(4.5)$ electrode which has superior generation of free $HO^\bullet$ due to its hydrophobic surface, the TOC removal of phenol is inhibited by the following competing reactions:[38]

$$Cl^- + HO^\bullet \rightarrow Cl^\bullet + OH^- \qquad (11)$$

$$Cl_2 + HO^\bullet \rightarrow HClO + Cl^- \qquad (12)$$
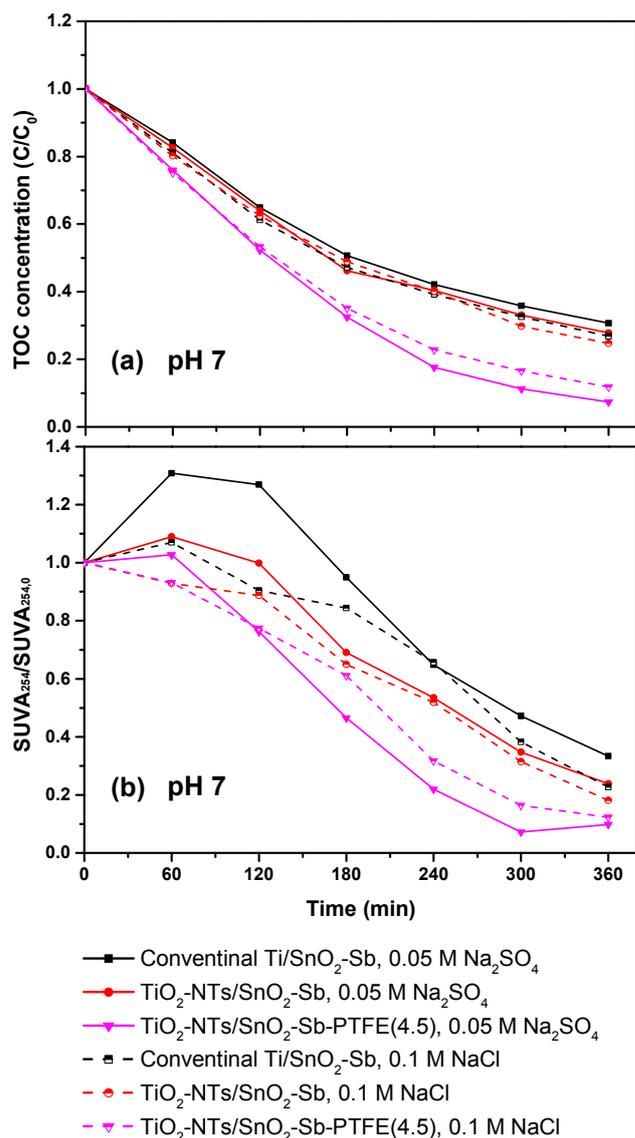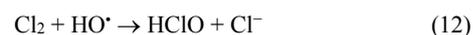
Fig. 10 TOC concentration and $SUVA_{254}$ as a function of time during phenol degradation at: (a) pH 7; (b) pH 3; (c) pH 11

The Cl^- and Cl_2 played the role of $HO^\bullet$ scavengers so that TOC removal by free $HO^\bullet$ is not favorable. Therefore, the TOC removal efficiency decreases in 0.1 M NaCl. All of the 3 electrodes obtain faster $SUVA_{254}$ decrease in the presence of NaCl in the first 2 h (Fig. 10). This is because reactive chlorine tends to react with electron rich moieties such as of aromatic intermediates,[39] hence, the aromatic rings open more easily. However, after 2 h the decrease of $SUVA_{254}$ of phenol with $TiO_2-NTs/SnO_2-Sb-PTFE(4.5)$ is slower in 0.1 M NaCl than that in 0.05 M Na_2SO_4, indicating the inhibition of phenol degradation by less amount of $HO^\bullet$.
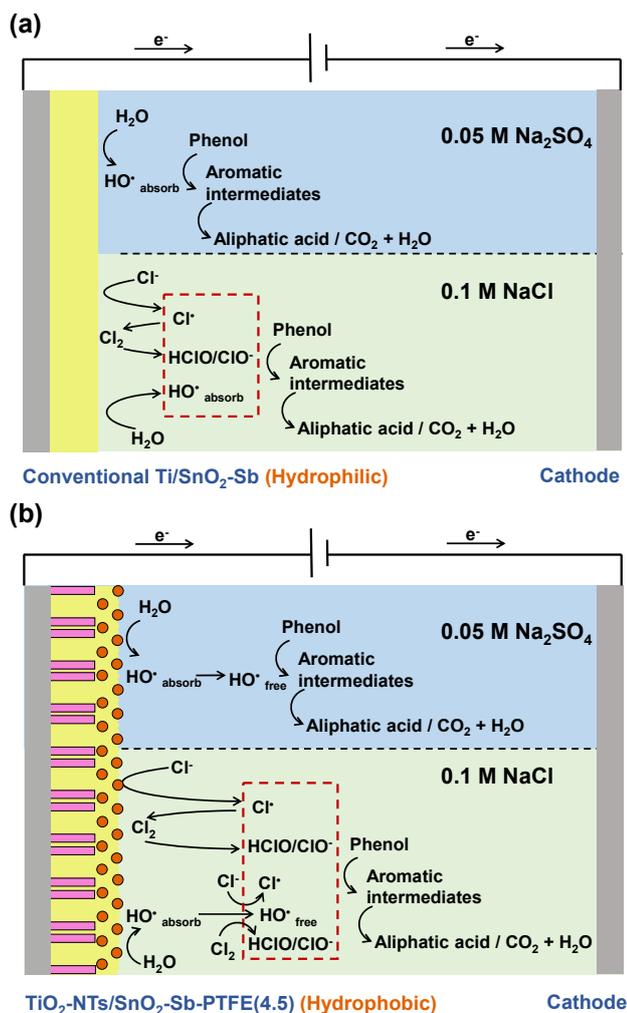
Fig. 11 Schematic illustration of electrochemical oxidation of phenol in 0.05 M Na_2SO_4 and 0.1 M NaCl using (a) conventional Ti/SnO_2-Sb and (b) TiO_2-NTs/SnO_2-Sb-PTFE(4.5)

3.3 Leaching of Sn ions

In industrial application using SnO_2 electrodes for removing organic compounds, the leaching of Sn ions has become an issue of concern which may cause the secondary pollution. Fig. 12a shows the concentration of Sn ions released from the electrodes after 6 h electrochemical oxidation at different initial solution pH in 0.05 M Na_2SO_4. Sn concentrations detected at Ti/SnO_2-Sb(conventional) were larger than those of TiO_2-NTs/SnO_2-Sb and TiO_2-NTs/SnO_2-Sb-PTFE electrodes at all solution pH. At pH 3, Sn dissolved concentration was 1.1×10^{-4} M using the conventional Ti/SnO_2-Sb as anode, while those released from TiO_2-NTs/SnO_2-Sb-PTFE electrodes were 7.1×10^{-5} M to 8.0×10^{-5} M. With the increase of initial solution pH from 3 to 7, Sn leaching further decreased but not significantly. However, at initial solution pH 11, only trace amount of Sn ions was detected with the lowest value of 3.6×10^{-6} M at TiO_2-NTs/SnO_2-Sb-PTFE(13.5). The concentration of the leached Sn ions was greatly influenced by the final solution pH. During OER at anodes, the simultaneously generation of H^+ gives rise to a dramatic decrease of solution pH. The high OEP of TiO_2-NTs/SnO_2-Sb-PTFE electrodes could inhibit the OER, thus less H^+ is generated and Sn leaching is not favorable. Final solution pH was low at initial

solution pH 3 and 7. However, the final solution pH was near neutral at initial solution pH 11, where the dissolution of Sn ions is inhibited. On the other hand, PTFE could also present a barrier for SnO_2 and electrolytes to contact, which inhibits the anodic dissolution of SnO_2.
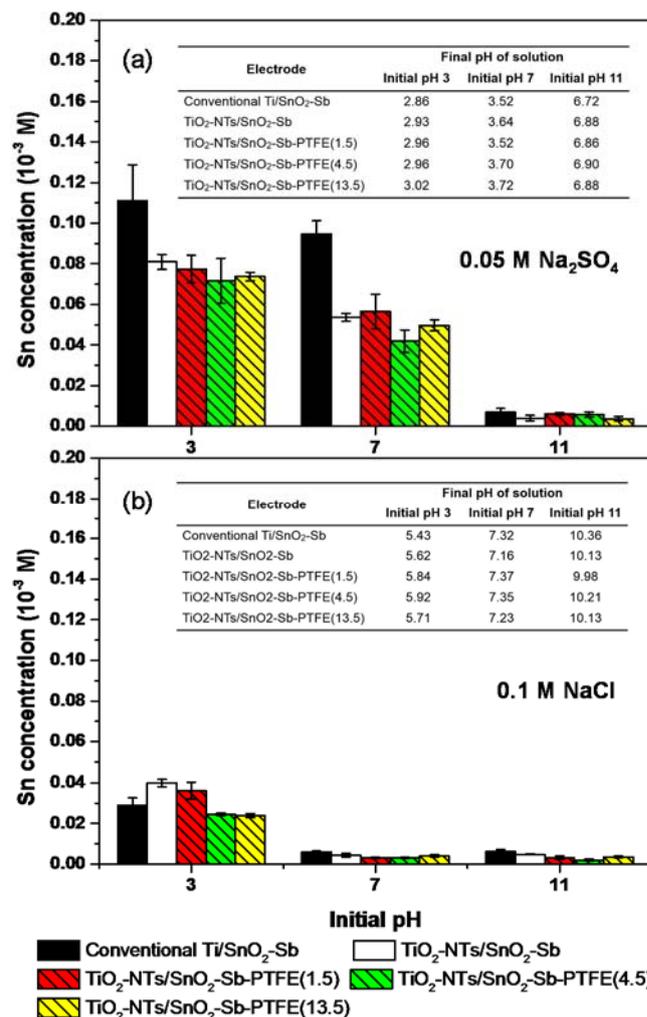
Fig. 12 Leached Sn ions concentration (± S.D) after 6 h electrochemical oxidation in (a) 0.05 M Na_2SO_4 and (b) 0.1 M NaCl (insets are the final pH of solutions after 6 h electrochemical oxidation)

The Sn ions leaching can be further inhibited using 0.1 M NaCl as supporting electrolyte (Fig. 12b). Cl_2 can be generated at anode surface without H^+ generation, but the solution H^+ is consumed at the cathode to form H_2. Thus, there is an increase of solution pH after 6 h of electrochemical oxidation. Therefore, Sn ions are not likely to be leached out. Lowest Sn ions concentration was detected to be only 2×10^{-6} M at basic solution with initial pH 11 using TiO_2-NTs/SnO_2-Sb-PTFE(4.5). In general, the TiO_2-NTs/SnO_2-Sb-PTFE can effectively inhibit the leaching of Sn ions through the presence of PTFE layer.

Conclusions

TiO_2-NTs/SnO_2-Sb-PTFE composite electrode with high hydrophobic surface, high oxygen evolution potential (2.4 V vs Ag/AgCl), small electrochemical resistance and good stability

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was successfully prepared by pulse electrodeposition method. The TiO$_2$-NTs/SnO$_2$-Sb-PTFE exhibited remarkably better electrocatalytic performance for phenol degradation than the conventional Ti/SnO$_2$-Sb prepared by thermochemical decomposition and TiO$_2$-NTs/SnO$_2$-Sb without PTFE. The TOC removal and SUVA$_{254}$ degradation of phenol confirmed 4.5 mL L^{-1} to be the optimal PTFE loading for TiO$_2$-NTs/SnO$_2$-Sb-PTFE electrodes. The pH and types of supporting electrolytes (Na$_2$SO$_4$ and NaCl) had more significant influence on phenol oxidation efficiency with TiO$_2$-NTs/SnO$_2$-Sb-PTFE(4.5) electrode, which had the superior ability of HO$^•$ generation because of its hydrophobic surface. The TiO$_2$-NTs/SnO$_2$-Sb-PTFE also showed leaching-resistant for the leaching of Sn ion, making it have the environmental merit for the degradation of recalcitrant organic pollutants in aquatic systems.

Acknowledgements

Notes and references

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