A comparative study on electrochemical oxidation of bisphenol A by boron-doped diamond anode and modified SnO$_2$-Sb anodes: Influencing parameters and reaction pathways

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ABSTRACT

In this study, electrochemical oxidation of bisphenol A (BPA) was investigated using BDD anode and two types of modified SnO$_2$-Sb anodes, TiO$_2$-NTs/SnO$_2$-Sb-PTFE and Ti/SnO$_2$-Sb/SnO$_2$-Sb-CNT. The influences of solution pH (3, 7 and 11) and the type of supporting electrolyte (0.05 M Na$_2$SO$_4$ and 0.1 M NaCl) on the electrocatalytic activity of the three anodes were investigated. The anodes exhibited remarkably different behavior for BPA oxidation, due to their different surface morphology, oxygen evolution potential and ability in the hydroxyl radical generation. Both BDD and the modified SnO$_2$-Sb anodes could degraded BPA effectively in 0.05 M Na$_2$SO$_4$ at pH 3 and 7. However, in 0.1 M NaCl, TiO$_2$-NTs/SnO$_2$-Sb-PTFE and Ti/SnO$_2$-Sb/SnO$_2$-Sb-CNT showed better electrocatalytic activity for BPA oxidation than BDD with less Cl loss and ClO$_3^-$ generation. On the contrary, a considerable amount of chlorinated intermediates and polymer byproducts were observed with BDD, resulting in its ineffective TOC removal (46.8%). It indicates that the modified SnO$_2$-Sb anodes are more environmentally benign for the treatment of wastewater containing chloride ion. LC–MS/MS and ion chromatography revealed the aromatic intermediates and aliphatic acids produced during BPA oxidation. Finally, the reaction pathways of BPA oxidation in Na$_2$SO$_4$ and NaCl supporting electrolytes are proposed.

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1. Introduction

Bisphenol A (BPA) serves as an important chemical in polymer industry and has been widely used as a monomer for the production of epoxy resins and polycarbonate resins. However, it is also known as an important endocrine disrupter which has been found in natural environment and treated effluents due to its extensive usage [1]. The exposure of BPA may affects the human health by its estrogenic activity even in very low concentration levels [2,3]. The byproducts of BPA generated during the treatment process may also exhibit high endocrine-disrupting effect [4]. Therefore, it is important to achieve completely degradation of BPA to final products such as CO$_2$, water or the environmentally benign products which are non-toxic and biodegradable [5].

To date, various techniques have been employed for the removal of aqueous BPA such as biological treatment [6], adsorption [7], wet oxidation [8] and advanced oxidation processes (AOPs) [9,10]. In recent years, electrochemical oxidation has emerged as a promising method for the removal or alleviation of aqueous BPA contaminants [11,12]. However, anode material is crucial to the success of this application [13]. Boron doped diamond (BDD) has been verified to be a very attractive anode material for the removal of organic pollutants through direct anodic oxidation due to its notably high oxygen evolution potential (OEP) [14–18]. Moreover, BDD has the advantage of high physical and electrochemical stability comparing with other electrodes [19–22], which is an important factor for its successful commercialization. Commercial BDD anodes have been reported for the total removal of various phenolic compounds, such as phenol [23], 4-nitrophenol [24], 4-chlorophenol [25] and bisphenol A [26,27]. However, the high fabrication cost of BDD material is prohibitive for its scale-up applications [28].

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Apart from BDD anode, antimony doped tin dioxide (SnO_2-Sb) is another type of anode material with high OEP. However, it has the problem of short service life which inhibits its commercial applications [29–31]. A lot of attempts have been made to overcome this problem. Two types of modified SnO_2-Sb electrodes (TiO_2-NTs/SnO_2-Sb-PTFE and Ti/SnO_2-Sb/SnO_2-Sb-CNT) have been fabricated in our recent studies, which exhibit enhanced electrocatalytic activity and improved service lifetime than the conventional Ti/SnO_2-Sb fabricated by thermochemical decomposition [32,33]. Thus, from the viewpoint of practical application, a comparative study on these novel SnO_2-Sb anodes with the commercial BDD anode would be meaningful to provide some insights into their electrocatalytic performance and potential as alternative anode materials to BDD in the treatment of recalcitrant organic pollutants.

In this work, BPA was used as the target pollutant for the comparative study on the electrocatalytic performance of commercial BDD anode and two types of modified SnO_2-Sb anodes (TiO_2-NTs/SnO_2-Sb-PTFE and Ti/SnO_2-Sb/SnO_2-Sb-CNT) fabricated in laboratory. Their surface morphology, oxygen evolution potential and ability for hydroxyl radical (HO$^\bullet$) generation of the anodes were characterized. The influences of operating parameters including the solution pH (3, 7 and 11) and the type of supporting electrolyte (0.05 M Na_2SO_4 and 0.1 M NaCl) on the electrocatalytic activity of the anodes were investigated. The aromatic intermediates and aliphatic acid intermediates of BPA oxidation were also analyzed to elucidate the reaction pathways and related mechanisms.

2. Experimental

2.1. Chemicals and materials

All of the chemicals are of or above analytical grade and used without further purification. Bishphenol A, Na_2SO_4, NaCl, dimethyl sulfoxide (DMSO) and 2,4-dintrophenylhydrazine were purchased from Sigma-Aldrich. Pure acetonitrile (LC–MS grade), NaOH pellet and HCl were purchased from Merck. All the solutions used in the experiments were prepared through Milli-Q water.

Nb/BDD anode with a coating thickness of 5 μm and boron doping concentration of 2500 ppm was purchased from NeoCoat Co., Switzerland. Two modified SnO_2-Sb electrodes, TiO_2-NTs/SnO_2-Sb-PTFE and Ti/SnO_2-Sb/SnO_2-Sb-CNT, were fabricated through pulse electrodeposition method. The fabrication processes of the modified SnO_2-Sb anodes are indicated in the Supplemental Information (Fig. S1). Both TiO_2-NTs/SnO_2-Sb-PTFE and Ti/SnO_2-Sb/SnO_2-Sb-CNT show polycrystalline SnO_2 with diffraction peaks at $2\theta = 26.8, 34.1°, 38.2°, 52.1°, 55.1°, 65.0°$ and $66.2°$ (Fig. S2). The presence of Ti substrate and TiO_2 is also observed with TiO_2-NTs/SnO_2-Sb-PTFE by EDS (Table S1) and XRD (Fig. S2).

2.2. Electrode characterization

The surface morphologies of the three electrodes were characterized through field emission scanning electron microscopy (FESEM, JEOL-7660F). Linear sweep voltammetry (LSV) experiments were conducted to measure the oxygen evolution potential of the electrodes using an electrochemical workstation (PGSTAT 302N, Autolab) equipped with a three-electrode cell in 0.5 M Na_2SO_4 electrolyte. The counter electrode and reference electrode were platinum and Ag/AgCl electrode, respectively. A scan range of 0 V–3.0 V and a scan rate of 50 mV s^{-1} were applied. The chlorine evolution potential of the electrodes were also examined through LSV in 3 M NaCl electrolyte and a scan range of 0 V–2.0 V, meanwhile other conditions were kept the same.

2.3. Bulk electrolysis of bisphenol A

The electrocatalytic activities of BDD, TiO_2-NTs/SnO_2-Sb-PTFE and Ti/SnO_2-Sb/SnO_2-Sb-CNT anodes were investigated through 6-h electrolysis of BPA synthetic wastewater in a 200 ml single-compartment cell. Synthetic wastewater containing 100 mg L^{-1} BPA was prepared in 0.05 M Na_2SO_4. The influence of pH on the electrocatalytic performance was investigated by adjusting the initial solution pH to 3, 7 and 11 using 0.5 M H_2SO_4 or 1 M NaOH. The influence of the type of supporting electrolyte was also investigated by comparing the electrochemical oxidation of 100 mg L^{-1} BPA in 0.1 M NaCl and 0.05 M Na_2SO_4 at pH 7. The current applied is 0.16 A and the nominal area of the electrodes is 8 cm^2. Platinum electrode with the same surface area was used as the cathode with 1-cm distance from the anode.

The aliquot solutions were drawn for analysis at 1-h interval. The elctrocatalytic performances of the electrodes were evaluated by determining the BPA concentration and total organic carbon (TOC) of the synthetic wastewater. TOC was measured using a TOC analyzer (TOC-L/CPH, Shimadzu). BPA concentrations were determined by high-performance liquid chromatography (HPLC, PerkinElmer Series 200) equipped with a reverse-phase C18 column (Hypersil Gold, Thermo Scientific). The mobile phase used was acetonitrile/water (40/60, v/v) with a flow rate of 1 ml L^{-1}, and the signal was acquired through a UV detector at 220 nm wavelength. Mineralization byproducts of formic acid, acetic acid, oxalic acid as well as chloride ion, chlorate ion and sulfate ion of the synthetic wastewater were quantified through ion chromatography (IC, Thermo Scientific Dionex ICS-2100). Other intermediates during electrochemical oxidation of BPA were verified by liquid chromatography tandem mass spectrometry (LC–MS/MS, Agilent 6460 Triple Quadrupole LC/MS System). The operation specifics of LC–MS/MS are described in the Supporting Information.
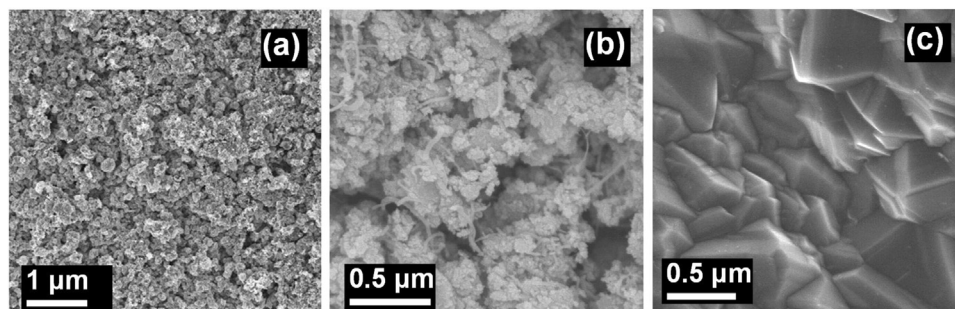

Fig. 1. FESEM images of (a) TiO_2-NTs/SnO_2-Sb-PTFE, (b) Ti/SnO_2-Sb/SnO_2-Sb-CNT and (c) BDD anodes.

3. Results and discussions

3.1. Characterization of the anodes

3.1.1. Surface morphology

Fig. 1 compares the FESEM images of TiO_2-NTs/SnO_2-Sb-PTFE, Ti/SnO_2-Sb/SnO_2-Sb-CNT and BDD electrodes. The surface morphologies of the modified SnO_2-Sb electrodes are significantly different from that of BDD. For TiO_2-NTs/SnO_2-Sb-PTFE and Ti/SnO_2-Sb/SnO_2-Sb-CNT, they both have rough surfaces with microshperical SnO_2 particles (Fig. 1a and b). Such surface morphology results in the larger specific surface area of the electrodes, which could provide more active sites for electrocatalytic reactions and contribute to their improved electrocatalytic activity than the conventional Ti/SnO_2-Sb fabricated by thermal chemical decomposition. In contrary, BDD electrode exhibits a rather different surface morphology with well-arranged crystals of different grain sizes. No cracks or voids could be observed on BDD electrode surface, leading to its good anticorrosion property.

3.1.2. Linear sweep voltammetry

Oxygen evolution potential (OEP) is an important indicator of anode materials in the application for electrocatalytic oxidation of recalcitrant organic compounds. Since the oxygen evolution reaction (OER) is a main competitive reaction for the degradation of organics by HO•, anodes with high OEP are expected to obtain better utilization efficiency of HO• for organic oxidation. LSV experiments were conducted in 0.5 M Na_2SO_4 to determine the OEP of TiO_2-NTs/SnO_2-Sb-PTFE, Ti/SnO_2-Sb/SnO_2-Sb-CNT and BDD anodes (Fig. 2). The highest OEP was obtained with BDD anode (2.5 V vs Ag/AgCl). However, the TiO_2-NTs/SnO_2-Sb-PTFE anode has an OEP (2.4 V vs Ag/AgCl) close to that of BDD. This is due to its hydrophobic surface which hinders the recombination of hydrophilic HO• and therefore the OER is inhibited. Ti/SnO_2-Sb/SnO_2-Sb-CNT has the smallest OEP of 2.2 V (vs Ag/AgCl), but still higher than that of the conventional Ti/SnO_2-Sb (2.0 V vs Ag/AgCl) [32].

3.2. Bulk electrolysis of BPA

3.2.1. Influence of anode materials

Table 1 shows the rate of BPA degradation and TOC removal with TiO_2-NTs/SnO_2-Sb-PTFE, Ti/SnO_2-Sb/SnO_2-Sb-CNT and BDD anodes at different solution pH (3, 7 and 11) in 0.05 M Na_2SO_4. The results are well fitted with pseudo-first-order reaction model and the apparent rate constants (k) and R-Square (R^2) for fitting are given in Table 1. It is obvious that the type of anode material has a remarkable influence on their electrocatalytic performances of BPA oxidation. In general, BDD anode exhibits the best electrocatalytic activity for BPA oxidation at various pH, which is probably due to its high OEP. TiO_2-NTs/SnO_2-Sb-PTFE and Ti/SnO_2-Sb/SnO_2-Sb-CNT show similar performance for BPA degradation. All of the three electrodes could achieve very high BPA degradation rate (>95%) in pH 3 and pH 7 solutions. However, a greater difference in TOC removal rates of the three anodes was observed. The superior TOC removal by BDD anode indicates that more BPA molecules are completely mineralized to CO_2 and H_2O, demonstrating its higher electrocatalytic activity. In other work, BDD anode is reported to effectively remove the TOC of aqueous BPA at high current density without reducing its anode stability [13].

The HO• generated on the anode surfaces was quantified by DMSO trapping to help to understand the differences of their electrocatalytic behavior (Fig. 3). HO• production capabilities of the three anodes follow the descending order: TiO_2-NTs/SnO_2-Sb-PTFE (36.3 μM) > BDD (34.2 μM) > Ti/SnO_2-Sb/SnO_2-Sb-CNT (28.3 μM). It is worth noting that the highest OEP of BDD does not result in the highest HO• generation. Similar findings were also reported in other studies [14,34]. It suggests that the high electrocataltyic activity of BDD for BPA degradation does not rely on the generation of large amount of HO•, but the higher utilization rate of HO•.

3.2.2. Influence of solution pH

The effect of solution pH on the electrocatalytic performance of the electrodes was investigated in 0.05 M Na_2SO_4. As can be seen in Table 1, all of the three electrodes show better BPA removal

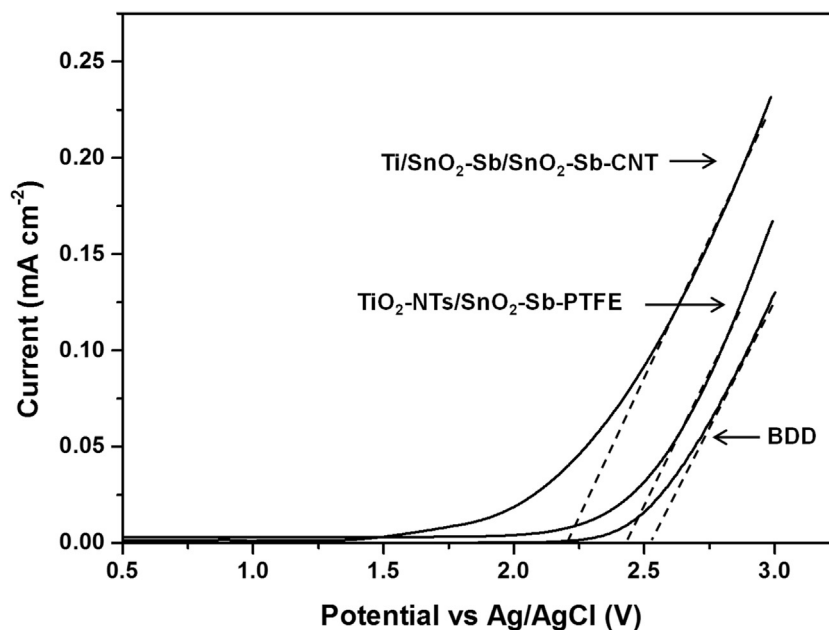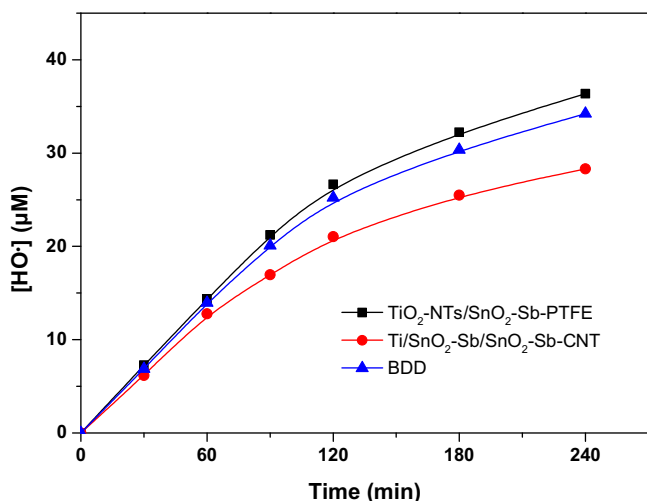**Fig. 2.** Linear sweep voltammetric curves of TiO_2-NTs/SnO_2-Sb-PTFE, Ti/SnO_2-Sb/SnO_2-Sb-CNT and BDD anodes in 0.5 M Na_2SO_4 at a scan rate of 50 mV s^{-1}.

Table 1
Performance of BPA degradation and TOC removal during bulk electrolysis of 100 mg L^{-1} BPA with the modified SnO$_2$ electrodes and BDD at pH 3, 7 and 11 in 0.05 M Na$_2$SO$_4$.

Electrodes	pH	BPA degradation (%)	k_{BPA} (1×10^{-3} min^{-1})	R_1^2	TOC removal (%)	k_{TOC} (1×10^{-3} min^{-1})	R_2^2
TiO$_2$-NTs/SnO$_2$-Sb-PTFE	3	98.9	11.7	0.949	81.4	4.8	0.989
	7	96.9	9.5	0.991	80.4	4.7	0.978
	11	84.7	5.4	0.989	75.8	4.0	0.999
Ti/SnO$_2$-Sb/SnO$_2$-Sb-CNT	3	95.7	8.9	0.996	81.8	4.8	0.998
	7	96.3	9.4	0.983	78.6	4.3	0.993
	11	87.7	5.8	0.997	73.7	3.6	0.996
BDD	3	100.0	15.1	0.947	87.1	5.9	0.992
	7	98.1	10.1	0.976	91.7	7.0	0.999
	11	92.2	6.9	0.996	88.9	6.0	0.997

Fig. 3. Concentration evolution of hydroxyl radicals on the electrodes in 0.05 M Na$_2$SO$_4$.

efficiency at acidic solution pH. Complete degradation of BPA could be achieved with TiO$_2$-NTs/SnO$_2$-Sb-PTFE and BDD anodes at 6 h and 5 h. Meanwhile, 96% BPA was degraded with Ti/SnO$_2$-Sb/SnO$_2$-Sb-CNT in pH 3 solution. On the contrary, the electrocatalytic oxidation of BPA seems to be less effective in pH 11 solutions wherein only 84–91% BPA degradation could be achieved. The solution pH could influence the electrocatalytic activity of the anodes in several aspects. First, the solution pH affects the oxidative power the HO$^\bullet$ radical generated on the anode surfaces:

$$H_2O \rightarrow HO^\bullet + H^+ + e^- \tag{1}$$

when solution pH is 0, the redox potential of HO$^\bullet_{aq}$/H$_2$O is 2.59 V at the standard condition. According to Nernest equation, the redox potential of HO$^\bullet_{aq}$/H$_2$O at other pH can be calculated by:

$$E^0(HO^\bullet_{aq}/H_2O) = 2.59 - 0.059 \, pH \tag{2}$$

Therefore, in acidic pH range, HO$^\bullet$ exhibits a higher oxidative potential and thus complete degradation of BPA is favorable. Second, CO$_2$, as a main product of electrochemical oxidation, could be dissolved in alkaline solution and exists as HCO$_3^-$ and CO$_3^{2-}$ ions. Both anions are strong HO$^\bullet$ scavengers and therefore inhibit BPA oxidation by HO$^\bullet$.

However, it is interesting that a similar TOC removal efficiency for BPA oxidation in pH 11(88%) and pH 3 (87%) solutions was observed with BDD anode. It can be related to the ionization of BPA.
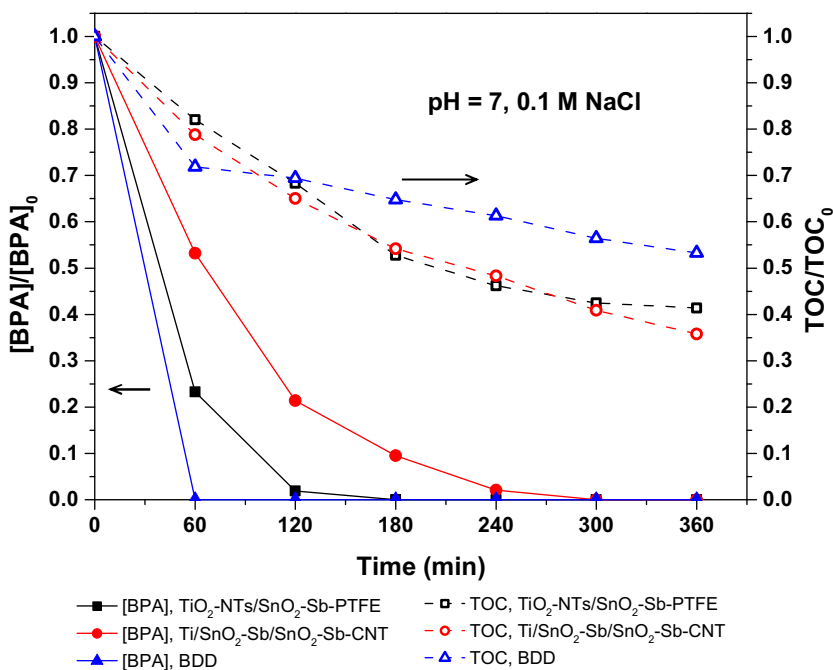
Fig. 4. Performance of BPA degradation and TOC removal during bulk electrolysis of 100 mg L^{-1} BPA with the modified SnO$_2$ electrodes and BDD at pH 7 in 0.1 M NaCl.
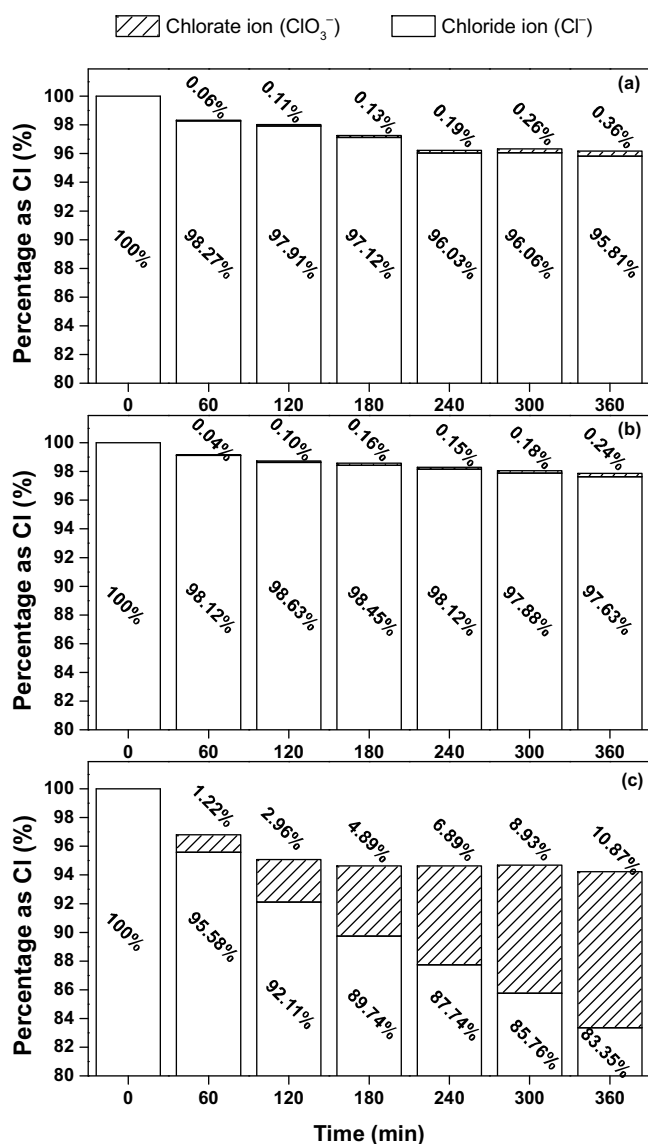
Fig. 5. Evolution of percentages of Cl existing as Cl^- and ClO_3^- during bulk electrolysis of $100\,mg\,L^{-1}$ BPA in 0.1 M NaCl at pH 7 with (a) TiO_2-NTs/SnO_2-Sb-PTFE, (b) Ti/SnO_2-Sb/SnO_2-Sb-CNT and (c) BDD.
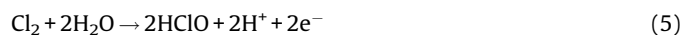
At low pH, some pollutants cannot be dissociated and the electromigration mass transfer is weakened [35,36]. The dissociation constant (pK_a) of BPA is ranging from 9.6 to 10.2. Thus, in pH 11 solution, deprotonation reaction occurs and BPA will present as bisphenolate anions. The bisphenolate anions could be drawn towards the positively charged anode surface by electric potential as well as being attacked by the electrophilic $HO^\bullet$. Such effect gives rise to the improved mass transfer which offsets the effect of lower oxidative power of $HO^\bullet$ at alkaline condition. Thus, the TOC removal rate did not decrease with pH.

3.2.3. Influence of the type supporting electrolyte

The type of supporting electrolyte plays an important role in the electrocatalytic oxidation of organic pollutants, since it can result in the generation of different secondary oxidants which are involved in the electrocatalytic reactions. Apart from SO_4^{2-}, Cl^- is another type of most common anions in natural water system or wastewaters. Fig. 4 shows the time course of BPA degradation and TOC removal with the three electrodes in 0.1 M NaCl of pH 7. It is surprising that significantly different trends were observed for BPA

degradation and TOC removal when using NaCl as the supporting electrolyte. BPA concentration seems to decrease rather rapidly, especially for BDD anode. In fact, the BPA compound could not be detected by HPLC after 1-h bulk electrolysis with BDD anode. For TiO_2-NTs/SnO_2-Sb-PTFE and Ti/SnO_2-Sb/SnO_2-Sb-CNT, the BPA degrades at a slower rate and the periods for its total degradation are 3 h and 5 h, respectively. However, their BPA degradation rates are still much faster than those in 0.05 M Na_2SO_4, where complete degradation of BPA could not be achieved in pH 7 solution.

On the contrary, the rates of TOC removal are much slower under the same experimental condition. It indicates that that BPA is not effectively mineralized to CO_2 despite the rapid decrease of BPA concentration. Among the three electrodes investigated, the best TOC removal is obtained with Ti/SnO_2-Sb/SnO_2-Sb-CNT (64%), while that achieved with BDD is only 47%. They are much less than those achieved in 0.05 M Na_2SO_4 (79% and 92%). Murugananthan et al. [27] reported that in the electrocatalytic oxidation of BPA with BDD anode, TOC removal could be inhibited by employing NaCl as supporting electrolyte, but no significant difference were observed with Na_2SO_4 or $NaNO_3$ supporting electrolyte. However, it is interesting that the TOC degraded at a much faster rate with BDD anode than TiO_2-NTs/SnO_2-Sb-PTFE and Ti/SnO_2-Sb/SnO_2-Sb-CNT during the first hour. It could be attributed to the production of reactive chlorine in the presence of Cl^-:

$$Cl^- \rightarrow Cl^\bullet + e^- \tag{3}$$

$$2Cl^\bullet \rightarrow Cl_2 \tag{4}$$

$$Cl_2 + 2H_2O \rightarrow 2HClO + 2H^+ + 2e^- \tag{5}$$

$$HClO \rightarrow ClO^- + H^+ \tag{6}$$

In LSV experiments of the three electrodes in 3 M NaCl, the dramatic increase of current in the potential range of 1.1–1.5 V (vs Ag/AgCl) shows that the reactive chlorine is produced before the OER (Fig. S3). Massive production of reactive chlorine is responsible for the fast TOC removal during the initial stage of bulk electrolysis of BPA. On the other hand, BPA may undergo dramatic chlorination reactions to produce organochlorine intermediates, which are more recalcitrant for subsequent degradation and more toxic. In fact, accumulation of pale yellow foam was observed during bulk electrolysis of BPA in 0.1 M NaCl with BDD anode, which may be an evidence of the polymerization of the organochlorine intermediates. However, such effect was not observed in the experiments using the modified SnO_2-Sb anodes, demonstrating that $HO^\bullet$ is generated and participates in the electrocatalytic oxidation of BPA in 0.1 M NaCl. In other work using graphite anode which has smaller OEP, the presence of NaCl could improve the electrocatalytic performance for BPA oxidation [37]. The slower BPA degradation rate but higher TOC removal with Ti/SnO_2-Sb/SnO_2-Sb-CNT anode indicates that less chlorinated byproducts is generated, which is an important advantage over BDD for electrocatalytic oxidation of BPA in wastewater consisting of Cl^-.

3.2.4. Concentration change of chlorine species

Since reactive chlorine species are expected to play an important role in the electrochemical oxidation of BPA in 0.1 M NaCl, more detailed information could be provided by examining the production of chlorine species. Apart from Cl^- which has been originally presented in the synthetic wastewater, considerable amount of chlorate (ClO_3^-) could also been detected by IC for the

Table 2
Compounds detected through LC–MS/MS.

Name of compound	Retention time (min)	m/z	Structure
isopropenylphenol	1.64	133	
4-hydroxyacetophenone	1.65	135	
4-[2-(3,4-dihydroxyphenyl)propan-2-yl]-quinone	4.22	257	
BPA dicatechol	4.23	259	
BPA 3,4-quinone	5.22	243	
BPA catechol	5.55	241	
BPA	6.15	227	

treated water (Fig. S4). However, other chorine species such as hypochlorite (ClO^-), chlorite (ClO_2^-) and perchlorate (ClO_4^-) could not be detected. The absence of ClO^- and ClO_2^- may due to their nature of high reactivity and weak stability in water, which could result in their decomposition to more stable chlorine species or reaction with BPA. ClO^- and ClO_2^- have been reported to decompose spontaneously through the following reactions [38]:

$$3ClO^- \rightarrow ClO_3^- + 2Cl^- \tag{7}$$

$$ClO^- + ClO_2^- \rightarrow ClO_3^- + Cl^- \tag{8}$$

$$2ClO^- \rightarrow 2Cl^- + O_2 \tag{9}$$

Moreover, the generation of ClO_4^- is not favorable since it requires excessive oxidation potential. As a result, Cl^- and ClO_3^- are the dominant chlorine species in treated water.

Fig. 5 shows the evolution of the percentages of ClO_3^- and residual Cl^- in synthetic wastewater during the electrochemical oxidation of BPA in 0.1 M NaCl at pH 7. There are Cl losses in the wastewater with all of the three anodes. For BDD anode, only 94.2% of initial Cl is detected as Cl^- and ClO_3^- after 6-h bulk electrolysis, while the values are 96.2% and 97.9% for TiO_2-NTs/SnO_2-Sb-PTFE and Ti/SnO_2-Sb/SnO_2-Sb-CNT anodes. Cl_2 is produced and they could be released from the synthetic wastewater as gas Cl_2, contributing to the loss of initial Cl. Among the three electrodes, BDD has a relatively high chorine evolution potential of 1.3 V (vs Ag/AgCl) and the smallest peak current (Fig. S3), indicating its less drastic Cl_2 generation. However, the highest level of Cl loss is observed with BDD, demonstrating that more Cl^- has been involved in the generation of organochlorine compounds during BPA oxidation. This is in agreement with its rapid BPA degradation

but slow TOC removal (Fig. 4). Apart from the Cl loss, BDD and the modified SnO_2 anodes also exhibit significantly different performances for the amount of ClO_3^- produced. For TiO_2-NTs/SnO_2-Sb-PTFE and Ti/SnO_2-Sb/SnO_2-Sb-CNT, the final ClO_3^- only corresponds to 0.36% and 0.24% of the initial Cl in treated water after 6-h bulk electrolysis. Nevertheless, the value is 10.87% for BDD, which increases by a factor greater than 30 comparing with those of the modified SnO_2-Sb anodes. In BDD, steady accumulation of ClO_3^- is observed throughout the bulk electrolysis, but the Cl loss slows down after 2 h. This is probably due to the dramatic formation of organochlorine compounds during the first 2 h, which consumed a large amount of Cl^-. After that, the reactive chlorine species are not effective enough for further degradation of organochlorine byproducts. Least Cl loss was detected with Ti/SnO_2-Sb/SnO_2-Sb-CNT anode, which also exhibits the best performance for BPA oxidation. Negligible change of SO_4^- concentration was detected during bulk electrolysis of BPA in 0.05 M Na_2SO_4, demonstrating that SO_4^- was quite stable and did not involve in the electro-catalytic oxidation of BPA.

3.3. Intermediate products and reaction pathways

3.3.1. Aromatic intermediates

Since both BDD and modified SnO_2 anodes are non-active anodes [19], the non-selective oxidation of BPA by surface-generated HO$^\bullet$ could lead to the generation of various intermediate products via different pathways, including electron transfer, hydrogen abstraction and radical addition [39]. Among them, aromatic intermediates of BPA are of great concern due to the potential endocrine-disrupting activity and other toxicity. Thus, identification of the aromatic intermediates helps to understand the reaction pathways of BPA degradation as well as the environmental benignity of the electrochemical oxidation process.
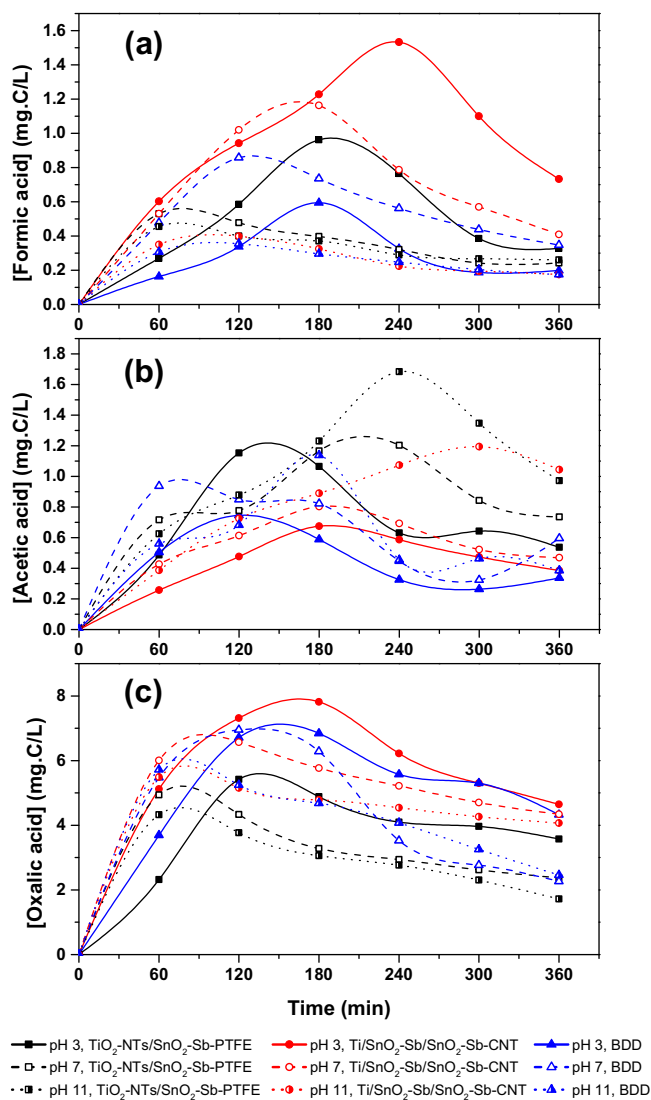
Fig. 6. Evolution of (a) formic acid, (b) acetic acid and (c) oxalic acid during the bulk electrolysis of $100\,mg\,L^{-1}$ BPA in 0.05 M Na_2SO_4 at pH of 3, 7 and 11.

LC–MS/MS was used to analyze the aromatic intermediates of treated water with initial solution pH of 7. Table 2 summarizes the seven main compounds that were detected by LC–MS/MS. Their corresponding peaks of the total ions chromatography could not be observed during the bulk electrolysis of BPA and disappeared after 6 h, suggesting their effectively mineralization (Fig. S5). The product ions at m/z of 133, 135, 241, 243, 257 and 259 are attributed to the $[M-H]^-$ ions of aromatic intermediates (Figs. S6 and S7). The $[M-H]^-$ ion of BPA was also detected at m/z 227. When the bulk electrolysis of BPA was conducted in NaCl supporting electrolyte, none of the peaks associated with the above-mentioned intermediates were detected. However, various peaks with high signal intensity were observed in m/z range of 400–1200, which could be probably due to the polymerization of organochlorine byproducts (Fig. S8).

3.3.2. Aliphatic acid intermediates

Aliphatic acids could be generated after ring-opening reactions of BPA molecules or aromatic intermediates. Various aliphatic acid intermediates for electrocatalytic oxidation of BPA have been

reported in literature [13]. In this study, several acids including formic acid, acetic acid and oxalate acid were quantified through IC. Fig. 6 shows the concentration evolution of the detected aliphatic acids in 0.05 M Na_2SO_4 at different pH. The concentrations of the aliphatic acids are expressed as carbon content $(mg\,C\,L^{-1})$ for ease comparing their contribution to the TOC of wastewater. It is clear that the formation and accumulation of aliphatic acids are influenced by both the anode material and solution pH. Formic acid and oxalic acid are found to be produced in larger amount in pH 3 solution, while the production of acetic acid is favorable at pH 11. Among them, oxalic acid contributes most to the TOC with all the three anodes. The concentrations of oxalic acid increase rather fast in the first hour, and start to decay after 1–2 h in pH 7 and pH 11 solutions and 3 h in pH 3 solution. Although the completely removal of the aliphatic acids is not obtained within the period of bulk electrolysis, they are environmentally benign compounds which would not cause secondary pollution.

In 0.1 M NaCl, the behavior of aliphatic acid production could be quite different during the bulk electrolysis of BPA (Fig. 7). Continuous accumulation of formic acid and acetic acid was observed throughout the bulk electrolysis process, resulting in their much higher concentrations after 6 h. It indicates that the reactive chlorine species are not effective enough to completely degrade them CO_2 and H_2O. However, oxalic acid accumulates very fast during the first hour, and then degrades steadily after reaching the maximum concentration. The oxidation of oxalic acid may lead to the formation of formic acid and CO_2, thus contributes to the reduction of TOC and continuous accumulation of formic acid:

$$C_2H_2O_4 \rightarrow CH_2O_2 + CO_2 \qquad (10)$$

In order to understand the nature of the treated water in NaCl, the percentage contributions of the detected aliphatic acids to the solution TOC are calculated and shown in Fig. 8. The detected aliphatic acids account for 8% to 10% of solution TOC after 1-h bulk electrolysis of BPA with the modified SnO_2 anode, smaller than that of BDD (11%). However, after 6-h bulk electrolysis, the values for TiO_2-NTs/SnO_2-Sb-PTFE and Ti/SnO_2-Sb/SnO_2-Sb-CNT are 41% and 44% respectively, which are much larger than that of BDD (19%). Since BPA molecules have been totally removed with BDD anodes after 1 h (Fig. 4), the rest of TOC must be originated from the aromatic intermediates, organochlorine intermediates and aliphatic acids. When using BDD anode, the less contribution of aliphatic acids to TOC of the treated water indicates that the aromatic and organochlorine intermediates are not effectively degraded. Since those byproducts are likely to exhibit higher toxicity than aliphatic acids, the use of BDD anode for the treatment of wastewater which contains a large amount of Cl^- must be executed with great caution.

3.3.3. Reaction pathway

The possible reaction pathways for electrocatalytic oxidation of BPA are proposed and shown in Fig. 9. The attack of $HO^\bullet$ to the aromatic ring has been reported to be a favorable process during BPA degradation by different AOPs [13,40,41]. In Na_2SO_4 supporting electrolyte, $HO^\bullet$ seems to firstly attack the aromatic ring of BPA and generate hydroxylated products such as BPA catechol ($m/z = 241$) and BPA dicatechol ($m/z = 259$) through radical addition. Then the hydroxylated products are subsequently oxidized by $HO^\bullet$ through dehydrogenation reaction and form byproducts of 4-[2-(3,4-dihydroxyphenyl)propan-2-yl]-quinone ($m/z = 257$) and BPA 3,4-quinone ($m/z = 241$). Kitamura et al. [42] investigated the estrogenic activity of BPA derivatives and their findings suggested that the estrogenic activity of BPA could be reduced by additional hydroxyl groups on the aromatic ring. Therefore, BPA catechol and
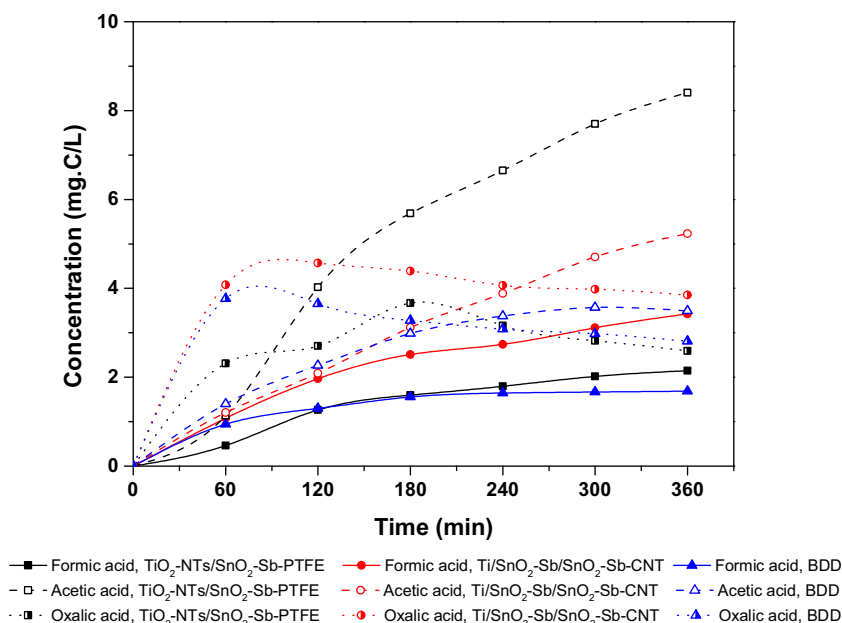
Fig. 7. Evolution of (a) formic acid, (b) acetic acid and (c) oxalic acid during the bulk electrolysis of 100 mg L^{-1} BPA in 0.1 M NaCl at pH 7.

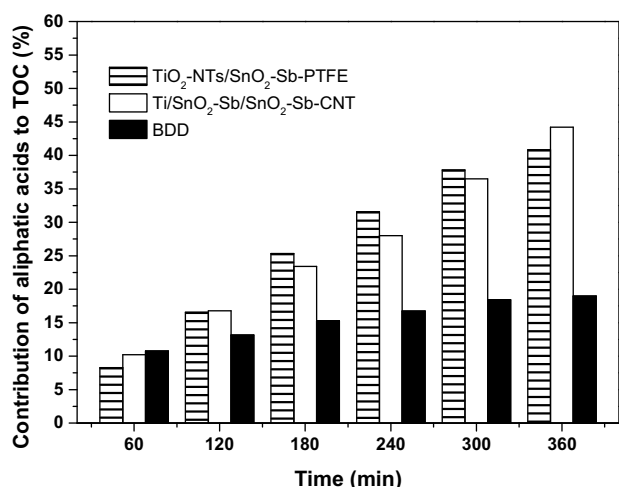**Fig. 8.** Evolution of the contribution of the aliphatic acids to the TOC during bulk electrolysis of 100 mg L^{-1} BPA in 0.1 M NaCl at pH 7.

BPA dicatechol are supposed to exhibit less endocrine-disrupting activity. However, BPA 3,4-quinone has been reported to cause the oxidative DNA damage of liver and thus it has to be completely removed [43]. LC–MS/MS results indicate that BPA 3,4-quinone has been totally degraded after 4 h, 5 h and 5 h with TiO$_2$-NTs/SnO$_2$-Sb-PTFE, Ti/SnO$_2$-Sb/SnO$_2$-Sb-CNT and BDD anodes, respectively.

One-ring aromatic compounds, such as isopropenylphenol ($m/z = 133$) and 4-hydroxyacetophenone ($m/z = 135$), are produced after the cleavage of the isopropylidene bride. The formation of phenoxyl BPA radical followed by β-scission to produce isopropenylphenol and phenoxyl radicals were probably responsible for this pathway [40]. The formation of aliphatic acids demonstrates that the ring-opening reactions of BPA and its aromatic byproducts occurred. Finally, they are completely mineralized to CO$_2$ and H$_2$O and the TOC is decreased.

In NaCl supporting electrolyte, the generation of reactive chlorine lead to the formation of organochlorine byproducts by chlorination reactions. They can further undergo polymerization
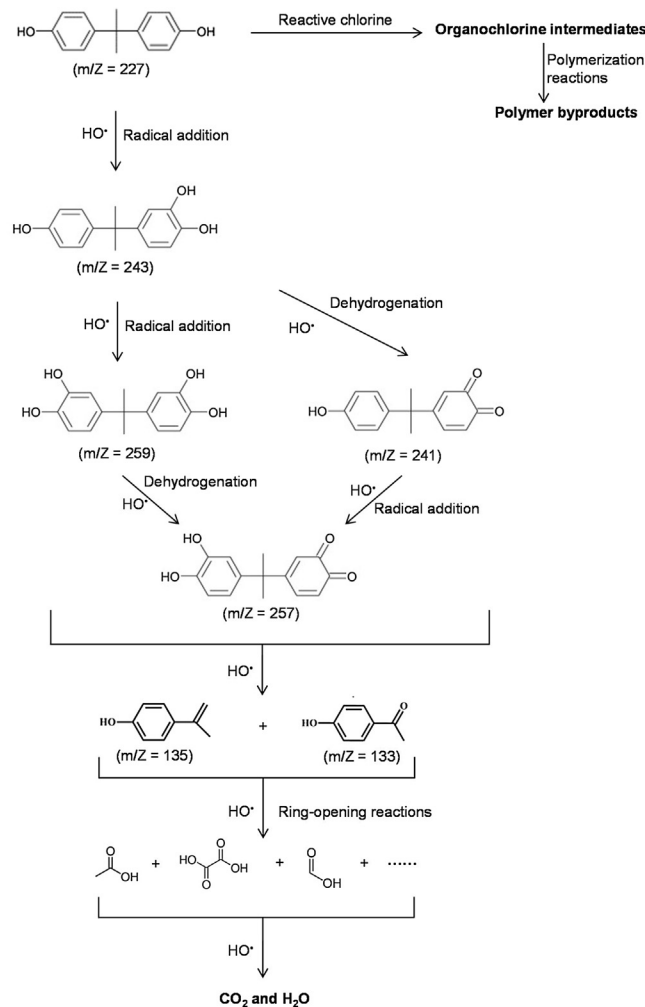

Fig. 9. Proposed reaction pathways of electrocatalytic oxidation of BPA by the anodes.

reactions to produce the polymer byproducts, which are more resistant for oxidation.

4. Conclusion

A comparative study on the eletrochemical oxidation of BPA by TiO$_2$-NTs/SnO$_2$-Sb-PTFE, Ti/SnO$_2$-Sb/SnO$_2$-Sb-CNT and the commercial BDD anode was conducted. BDD anode exhibits the most superior electrocatalytic activity for BPA oxidation in 0.05 M Na$_2$SO$_4$, due to its high OEP and effective utilization of HO$^\bullet$. However, Ti/SnO$_2$-Sb/SnO$_2$-Sb-CNT shows the best electrocatalytic activity for BPA oxidation in 0.1 M NaCl with the least Cl loss and ClO$_3^-$ generation. While using BDD anode may lead to the dramatic formation of organochlorine intermediates and their resulting polymer byproducts, which may cause toxicity in the treated water. The degradation of BPA occurs through a reaction pathway with six main aromatic intermediates identified by LC–MS/MS and three aliphatic intermediates quantified by IC. Hydroxylation, dehydrogenation and ring-opening reactions are involved in the reaction pathways.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jece.2016.05.034.

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