TiO₂ Microflowers Assembled by 6-nm Single-Crystal Stranded Wires with Improved Photoelectrochemical Performances

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ABSTRACT

As the diffusion length of charge carriers in TiO₂ is around 10 nm, it would be an efficient way to increase the photocatalytic properties by controlling the size within 10 nm. Herein, TiO₂ microflowers assembled by 6-nm single-crystal stranded wires grown on Ti foam (TiO₂-SWs/TF) were synthesized which facilitated electron transfer rate with a photocurrent of 0.33 mA cm⁻² compared to that of the P25/TF (0.06 mA cm⁻²). A photoelectrochemical (PEC) system combining degradation of bisphenol A and H₂ production was constructed based on the as-obtained TiO₂-SWs/TF as photoanode and Pt wire as cathode. This PEC system exhibited excellent ability for simultaneous bisphenol A degradation and H₂ production, giving a 94% bisphenol A degradation efficiency within 60 min at 1.2 vs (Ag/AgCl) V with power consumption of only 0.02 kWh m⁻³. The excellent PEC degradation of bisphenol A by the TiO₂-SWs/TF could mainly be ascribed to the fast electron transfer via the 6-nm ultrathin wires and synergetic effect of photocatalysis and electrochemical process. Two pathways for PEC degradation of bisphenol A were proposed based on the intermediates identified by Ultra Performance liquid chromatography-quadrupole-time of flight-mass spectrometry (UPLC-Q-TOF-MS).

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1. Introduction

TiO₂-based nanomaterials have been extensively used in photocatalytic degradation of refractory organics in aquatic waters [1–3]. However, fast recombination of electrons and holes and slow charge carrier transfer cause bottlenecks in improving the photocatalytic activity of TiO₂ nanomaterials [4,5]. In the past decades, one-dimension TiO₂ nanostructures such as nanorods, nanowires, and nanotubes have been studied extensively as they might provide electron transport pathways during the photocatalytic process [6–8]. Nevertheless, it is not fast enough to inhibit recombination of photogenerated electron-hole pairs with these traditional one-dimension nanostructures, which might result in decreased photocatalytic activity [9–11]. Besides, larger diameters of some one-dimension nanostructures, multi-crystal phases, crystal boundaries as well as defects resulted in slow electron transport [12,13]. A number of reports have demonstrated the photocatalytic performances of one-dimension TiO₂

nanostructures could be significantly enhanced with ultrathin and long structure [14–17]. For example, TiO₂ nanotubes with an average wall thickness of 7 nm exhibited a higher photocurrent, which was almost twice that of ~40-nm wall thickness nanotubes, highlighting a better charge transport of thinner structure [18]. It was reported that the diffusion length of charge carriers in TiO₂ is around 10 nm [19]. Thus, controlling the size of TiO₂ within 10 nm would improve their photocatalytic performances. For example, Wu synthesized ultrathin anatase TiO₂ nanobelts about 2–4 nm in thickness which exhibited much improved photocatalytic activity in photodegradation of rhodamine B as its much reduced charge migration path and the enhanced charge transport [20]. However, most prepared well dispersed ultrathin TiO₂ nanostructures are easy to aggregate to decrease their high surface energy and keep stable [21,22]. Besides, those power samples of ultrathin TiO₂ would be deposited on some conductive substrates to prepare electrodes for further application, which would decrease their specific surface area and even generate poor conductivity as weak connection to the substrates. Therefore, a feasible strategy is to fabricate 3D architecture assembled by isolated ultrathin wires in thickness within 10 nm.

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Photoelectrochemical (PEC) method has been used as an effective route combining the advantages of photocatalysis and electrochemistry in pollutant treatment. The applied electric field can provide a bias potential to the anode and significantly facilitate the transfer of carriers and suppressed the recombination of photogenerated electrons and holes. The photogenerated electron-hole pairs are beneficial to the formation of reactive species such as $\cdot\text{OH}$, which will facilitate the degradation of organic components [23,24].

In this work, we have synthesized TiO_2 microflowers assembled by 6-nm single-crystal stranded wires grown on Ti foam (TiO_2 -SWs/TF) by a facile hydrothermal method. These single-crystal 6-nm stranded wires without grain boundaries greatly facilitated electron transfer rate and provided more active sites for organic molecules absorption with large specific surface area. Moreover, a high-efficient PEC system combined bisphenol A (a representative of endocrine disrupting chemicals) degradation with H_2 evolution was constructed successfully based on the fabricated TiO_2 -SWs/TF as the photoanode and Pt wire as the cathode. This PEC system using the obtained TiO_2 -SWs/TF could provide an effective route to refractory pollutants removal as well as H_2 production with the assistance of sunlight for energy conversation.

2. Experimental

2.1. Preparation of the TiO_2 -SWs/TF

Commercial Ti foam (purity 99.5%) pieces were used as Ti substrates to grow TiO_2 with size of $2\text{ cm} \times 4\text{ cm} \times 1\text{ mm}$ (width $\times$ length $\times$ thickness). These pieces were ultrasonically cleaned in the mixture of ultrapure water, acetone and ethanol (volume ratio of 1:1:1) for 1 h and then dried for further use. In a typical synthesis, 0.5 mL of titanium (IV) butoxide was added into 27 mL of HCl solution (24 mL of ultrapure water and 3 mL of concentrated HCl) (35–37%) and stirred for 30 min. Then the solution was poured into a Teflon-lined stainless steel autoclave with capacity of 50 mL. One piece of dried Ti foam was placed against the inner wall and most was immersed in the mixture. The sealed autoclave was kept in an oven at 150°C for 2–8 h and cooled down to room temperature naturally. The precursor was then rinsed with ultrapure water ($18.2\text{ M}\Omega\text{ cm}^{-1}$ from a Milli-Q Plus system, Millipore) several times, dried at 80°C , and then transferred into a furnace with heat treatment at 450°C for 1 h at a ramping rate of $10^\circ\text{C min}^{-1}$ in air. The mass per unit for TiO_2 on the obtained TiO_2 -SWs/TF was measured and calculated to be $\sim 8.3\text{ mg cm}^{-2}$.

2.2. Preparation of the P25/TF for comparison

The P25 nanoparticles (Degussa) were sonicated in ultrapure water for 30 min, forming uniform suspension. The suspension was then spin-coated on one side of the Ti foam. The as-prepared electrode of the P25/TF was dried at 80°C and its mass per unit was $\sim 8.3\text{ mg cm}^{-2}$ and treated at 450°C for 1 h. The P25/TF was used as the working electrode in the PEC system for comparison.

2.3. Characterizations

The X-ray diffraction spectrum (XRD) was obtained by X'Pert PRO MPD with $\text{Cu K}\alpha$ radiation over the 2θ range of 20 – 80° . The morphology and structure of the prepared sample were characterized by field-emission scanning electron microscopy (FE-SEM, SU8020, HITACHI), transmission electron microscopy (TEM), and high-resolution TEM (HRTEM, JEM-2100, JEOL, Japan).

2.4. Photoelectrochemical measurements

All the measurements were carried out with an electrochemical workstation (Gamry, Interface1000, USA) in a standard three-electrode quartz cell (Fig. S1). The as-prepared electrode, an Ag/AgCl electrode, and platinum wire were used as photoanode (the working electrode), reference electrode, and counter electrode, respectively. The gap between the working electrode and counter electrode was set to be 1.5 cm. The solution containing 0.5 mol L^{-1} Na_2SO_4 was used as the supporting electrolyte. A Xeon lamp (CEL-HXF300, 20A) was used as the simulated sunlight source. The irradiation distance from the light source to the photoanode was set as 8 cm. The electrochemical impedance spectroscopy (EIS) was carried out at 0 vs. (Ag/AgCl) V in the frequency range of 0.01 Hz–100 kHz with AC potential of 10 mV under the simulated sunlight. The Mott-Schottky plots were performed at an AC frequency of 1 kHz in the dark. The used area of the TiO_2 photoanode was 6 cm^2 . The transient response of photocurrent was collected as switching the light on and off every 30 seconds at the potential of 0.5 vs. (Ag/AgCl) V under simulated sunlight irradiation.

2.5. Photoelectrochemical degradation of bisphenol A

PEC degradation of bisphenol A experiments by the TiO_2 -SWs/TF (P25/TF for comparison) were carried out at room temperature in a three-electrode single-compartment quartz cell as described in PEC measurement. 1 g of Na_2SO_4 and 70 mL of bisphenol A solution was put into the reaction cell under the simulated sunlight. The bisphenol A concentrations were determined using a high performance liquid chromatography (HPLC, 1260, Agilent Technology) equipped with a C-18 column (Agilent Technology) and two detectors connected in series, namely a diode array detector (Waters 996) and a fluorescence detector (Waters 474). The mobile phase consists of H_2O and methanol (30:70 v/v) with flow rate of 1 mL min^{-1} . The injection volume of bisphenol A solution was $10\text{ }\mu\text{L}$ and the retention time was 8 min. The detection wavelength was set as 274 nm. The degradation experiments last 180 min and 1 mL of solution is taken out for analysis every half an hour. The removal ratio of bisphenol A was calculated according to the equation of $R = (C_0 - C_t)/C_0 \times 100\%$, where R is the removal ratio of bisphenol A, C_0 was the initial concentration of bisphenol A (obtained by HPLC test), and C_t was the concentration of bisphenol A in the solution over a period of time. The intermediates of bisphenol A degradation were directly identified and analysed by Ultra-high Performance Liquid Chromatography-Quadrupole-Time of Flight-Mass Spectrometry.

3. Results and discussion

3.1. A probable growth mechanism of the TiO_2 -SWs/TF electrode

A probable growth mechanism was proposed in Fig. 1a based on the growth process shown in Fig. S2. Firstly, titanium (IV) butoxide hydrolyzed into the precursor of tiny grains grown on the surface of Ti foam by the role of hydrolysis inhibition of HCl. Then, these precursor seeds formed, inducing the formation of one-dimensional columns with continuous hydrolysis. As the uneven surfaces of Ti foam, those columns grew into flower-like microstructures. By further characterization, it was observed the single-crystal columns were assembled by parallel ultrathin stranded nanowires. As reported single-crystalline rutile TiO_2 nanorods with exposed (110) facets with vertical growth along [001] direction [25], these one-dimensional columns also showed exposed (110) facets and grew along the direction of [001]. Interestingly, the assembled structures seem like multi-strand wires as shown in the red rectangle, which might benefit for electron transfer.

Fig. 1. (a) A probable growth schematic illustration of the TiO_2 microflowers assembled by 6-nm single-crystal stranded wires on Ti foam, (b) SEM image of the microflower particles, (c) magnified SEM image of one particle, containing lots of one-dimensional square column rods. (d) TEM image of several particles, (e) TEM image (scale bar: 10 nm) taken from the marked tip in Fig. 1d with corresponding SAED pattern inserted, (f) HRTEM image corresponding to the marked tip in Fig. 1e, (g) XRD pattern of the prepared TiO_2 -SWs/TF.

The morphology, the structure, and the component of the as-prepared TiO_2 were then characterized in Fig. 1b–1g. Fig. 1b showed the overview morphology of microflower particles $\sim 5 \mu\text{m}$ in diameter grown on Ti foam. The magnified SEM image in Fig. 1c showed the microflower particle was composed of square columns with an average diameter of 500 nm. From TEM images of Fig. 1d and 1e, it was obvious the columns were assembled by many ultrathin nanowires with an average diameter of $\sim 6 \text{ nm}$. The inset of Fig. 1e showed the corresponding SAED pattern of dozens of nanowires, revealing the single-crystal structure of the column. A single nanowire about 6 nm in thickness with spacings of 0.325 nm corresponding to the (110) planes in Fig. 1f. The diffraction peaks of the TiO_2 -SWs/TF could be indexed to rutile TiO_2 (JCPDS. 21-1276) and the intensity of (110) facet was stronger than other facets, which might be ascribed to the exposed facets of (110) planes. The other peaks indexed as (101), (200), (111), (210), (211), (220), (002), (310), (301), and (112) are well agreed with rutile TiO_2 .

3.2. Bisphenol A degradation by the TiO_2 -SWs/TF electrode

PEC process has been considered as a high-efficient way to remove organic pollutants, which can be driven by light

irradiation, thus it will reduce electrical energy consumption with the aid of solar light. The degradation tests in a three-electrode system were applied at different potentials by the TiO_2 -SWs/TF electrode using PEC method. At the concentration of 10 mg dm^{-3} , the bisphenol A removal efficiency reached 96% (red line), 54% (blue line), and 39% (black line) after 3 hrs at the applied potential of 1.2, 0.9, and 0.6 V, respectively (Fig. S3). Results suggested the optimum applied potential was 1.2 V. To verify the high-efficient degradation by TiO_2 -SWs/TF electrode using PEC method, the control experiments by photocatalysis only using TiO_2 -SWs/TF under the simulated sunlight and electrochemistry method same as PEC system without light irradiation were also carried out (Fig. 2a, experimental section, SI). The results showed the removal efficiency was only $\sim 2\%$ by photocatalytic method and $\sim 30\%$ by electrochemical method after 3 hrs. Even using the P25/TF as electrode by PEC method, the removal efficiency could be $\sim 70\%$, lower than the degradation efficiency ($\sim 100\%$) using the TiO_2 -SWs/TF electrode. SEM images of the P25/TF were shown in Fig. S4 with nanoparticles of P25 $\sim 30\text{--}40 \text{ nm}$ in diameter on the substrate. It was clearly shown the concentration change of bisphenol A by HPLC during PEC process (Fig. S5). The synergetic effect of photocatalysis and electrochemical method as well as the prepared

Fig. 2. (a) PC, EC, and PEC degradation of 10 mg dm^{-3} bisphenol A by TiO_2 -SWs/TF electrode as well as PEC degradation by P25/TF at 1.2 vs. (Ag/AgCl) V with pH = 6 (original solution without adjusting); (b) PEC degradation of bisphenol A at 1.2 vs. (Ag/AgCl) V with different pH values (pH = 0, 3.5, 6, and 9).

TiO₂-SWs/TF electrode played an important role in improving the degradation of bisphenol A. Besides, the degradation of bisphenol A by PEC was sensitive to pH values as shown in Fig. 2b. Without adjusting, the pH of the original bisphenol A solution was ~6, and the degradation efficiency was 96% after 3 hrs. But the removal efficiency of bisphenol A was decreased to 75% when the pH value was increased to 9.0. If we decreased the pH values, the degradation efficiency was increased even up to 94% in 60 min at pH = 0, indicating a high and fast removal of bisphenol A in acid solution.

Notably, during the removal of bisphenol A at pH = 0 by PEC, we could observe hydrogen evolution reaction at the opposite Pt electrode, which might be useful for hydrogen energy and fuel cell. Besides the applied potential, the photogenerated electrons quickly transferred to the Pt cathode also promote the occurrence of H₂. Meanwhile, the oxidation of bisphenol A at the photo-electrode provided higher photocurrent. Fig. 3a showed liner scanning potentials of the TiO₂-SWs/TF in 0.5 mol L⁻¹ of H₂SO₄ under simulated sunlight. It was obvious the added light could increase the current density with potential ranged from 0.4 to 2.0 V (red line vs black line). Besides, there was a slight increase of current with bisphenol A added in the electrolyte (blue line vs red line). The inset of Fig. 3a showed a direct observation of H₂ bubbles at the opposite electrode and no O₂ at the anode in our PEC system. In Fig. 3b, the transient current response at potentials of 0.6, 0.9, and 1.2 V showed a better observation on the small increases of current density after bisphenol A added in. Results showed there was no obvious difference at 0.6 and 0.9 V when bisphenol A was added or not. Actually, the increase of current density between 0.4 and 1.15 V (take 0.6 and 0.9 V for example) could be attributable to the photocurrent of the TiO₂-SWs/TF irradiated by sunlight because it is hard for water splitting under the condition [26,27]. When the applied potential increased from 1.15 to 2 V (take 1.2 V for example), the current density increases quickly while H₂ bubbles on the Pt wire due to the electrochemical water splitting. At the applied potential of 1.2 V, the current density of TiO₂-SWs/TF with bisphenol A (blue solid line) was higher than that without bisphenol A (red solid line), revealing the oxidation of bisphenol A increased the water splitting. Clearly, the bisphenol A oxidation takes precedence over oxygen evolution reaction (OER) on the anode at 1.2 V as the theoretical potential of water splitting is 1.427 vs. (Ag/AgCl) V [28]. To be mentioned, TiO₂ is poorly active for OER, which might benefit for the bisphenol A degradation [29].

The PEC degradation of bisphenol A follows the pseudo first-order reaction kinetics with the first-order reaction kinetic constant (k_{app}) calculated in Fig. S6. Results showed that k_{app}

values were 0.053, 0.027, 0.018, and 0.0077 min⁻¹ at pH = 0, 3.5, 6, and 9, respectively, revealing the TiO₂-SWs/TF showed the best activity at pH = 0. Furthermore, the electrical energy consumption (E_c) was calculated as 0.02 kWh m⁻³ (pH = 0) in our system using the TiO₂-SWs/TF as electrode. Compared to 0.88 kWh m⁻³ by P25/Ti foam (this work), 0.13 kWh m⁻³ by TiO₂/BDD, 0.11 kWh m⁻³ by Au-TiO₂/ITO, and 0.38 kWh m⁻³ by TiO₂ NTA/Ti foil reported by others (Table S1), [30–32] our energy consumption was much lower. Though the E_c using TiO₂/Ti foil was 0.01 kWh m⁻³, its bisphenol A concentration (0.03 mg dm⁻³) was much lower than ours (10 mg dm⁻³) [33]. The above results demonstrated that our PEC system achieved 94% bisphenol A degradation (10 mg dm⁻³) within 60 min at 1.2 V and pH = 0 when using the TiO₂-SWs/TF as the photoanode. The fabricated TiO₂-SWs/TF assembled by 6 nm-thick ultrathin single-crystal nanowires provided channels for electron transport, which would support the bisphenol A degradation. Meanwhile, the improved bisphenol A degradation also increased H₂ production, finally providing higher current density. Besides, the Ti foam substrate and TiO₂ arrays had a wide range of pH due to its strong resistance to acid and alkali. In the light of energy conservation, the PEC system made contribution to electric power saving with the aid of simulated sunlight by PEC method during bisphenol A degradation.

3.3. PEC properties of the TiO₂-SWs/TF

To disclose the improved properties of the TiO₂-SWs/TF electrode for PEC degradation of bisphenol A, transient photocurrent response, Nyquist plots, and Mott-Schottky curve were characterized in Fig. 4. As shown in Fig. 4a, the photocurrent density of the TiO₂-SWs/TF reached 0.33 mA cm⁻², which was 5.5 times higher than that of the P25/TF (0.06 mA cm⁻²), indicating the 6 nm-thick ultrathin nanowires provided faster electron transport and therefore exhibited an better photoactivity than P25. It was the 6-nm stranded wires (particles for P25) have a greater impact on electron transfer compared to the contact interface between TiO₂-SWs/TF (P25/TF) and Ti foam substrate. SEM images showed both the TiO₂-SWs and P25 have a good contact interface on the Ti foam before and after degradation, serving a good pathway for the electron transfer. Notably, magnification of SEM images demonstrated clearly the P25 particles which dispersed on the uneven surfaces still had a good contact interface with the Ti foam substrate after bisphenol A degradation, indicating the electrons could be transferred safely and quickly in the PEC process. (Fig. S7, S8, S9) To further elucidate the interfacial properties between the electrode and the electrolyte, the charge transfer characteristics of

Fig. 3. (a) Linear scanning voltage of the TiO₂-SWs/TF in 0.5 mol L⁻¹ of H₂SO₄. The inset showed digital image of H₂ bubbles at the Pt wire electrode. (b) Transient current response of TiO₂-SWs/TF at different applied potentials of 0.6, 0.9, and 1.2 V.

Fig. 4. (a) Transient photocurrent response of the TiO₂-SWs/TF and the P25/TF at 0.5 vs. (Ag/AgCl) V. (b) Nyquist plots of the TiO₂-SWs/TF and the P25/TF were carried out at 0 vs. (Ag/AgCl) V. in the frequency range of 0.01 Hz–100 kHz with AC potential of 10 mV under simulated sunlight. The inset showed the SEM images and the electron transfer routes of the TiO₂-SWs and the P25. (c) Mott-Schottky curve of the TiO₂-SWs/TF and P25/TF in the dark. (d) Schematic illustration for bisphenol A degradation with PEC method by TiO₂-SWs/TF photoanode and Pt cathode.

the TiO₂-SWs/TF and the P25/TF were studied by EIS in Fig. 4b. It is clear that the size of the arc radius is obviously reduced by TiO₂-SWs/TF, indicating that electron transport is much easier and faster on the TiO₂-SWs/TF than that on the P25/TF [34]. It might be the faster electrons transport along (001) to the Ti foam with reduced recombination of photoinduced electron-hole pairs, while the P25/TF was poorer for electron transport as it was composed of aggregated NPs with contact resistance, as shown in the inset of Fig. 4b. In addition, charge carrier density could be calculated from the Mott-Schottky plot of the TiO₂-SWs/TF in Fig. 4c. It showed a typical plot of n-type semiconductor and there was a good linear relationship between C⁻² and the potential in the range of -0.55 to -0.3 V for the TiO₂-SWs/TF. From the positive slope of the straight line according to the Mott-Schottky Eq. (1) [35],

$$N_d = \frac{2}{e_0 \varepsilon \varepsilon_0} \times \left[\frac{d(1/c^2)}{dE} \right]^{-1} \quad (1)$$

where N_d is the donor density, e_0 is the electron charge ($e_0 = 1.6 \times 10^{-19}$ C), ε is the dielectric constant of rutile TiO₂

($\varepsilon = 170$) [36], ε_0 is the permittivity of vacuum ($\varepsilon_0 = 8.85 \times 10^{-14}$ F cm⁻¹), and E is the applied bias. The carrier density (N_d) of the TiO₂-SWs/TF and the P25/TF was estimated to be 2.75×10^{21} and 1.20×10^{21} cm⁻³. The V_{fb} was calculated to be -0.62 V and -0.55 V by extrapolating the x axis intercept of the linear region in the M-S plots. Compared to the reported N_d values of various electrodes with different morphologies (Table 1, $1.20 \times 10^{16} \sim 3.80 \times 10^{20}$), the TiO₂-SWs/TF was one order of magnitude higher, indicating that the TiO₂ microflowers assembled by 6-nm single-crystal stranded wires facilitated the electron transport.

Fig. 4d illustrated electron transport (including the electrons provided by the applied electric field and the photocatalysis) through the PEC system during the process of bisphenol A degradation with the TiO₂-SWs/TF photoanode and Pt cathode. As for the synthesized TiO₂ stranded wires on the anode, the electrons generated by the simulated sunlight irradiation jumped from the valence band (VB) to the conduction band (CB), while the holes left on the VB migrated to the surface and reacted directly with absorbed hydroxyl groups to generate reactive hydroxyl radicals (such as ·OH). The radicals and the holes would oxidize

Table 1
Carrier density compared to other reported results.

Electrode	Morphology	Carrier density (cm ⁻³)	Reference
Rutile TiO ₂	6 nm-thick ultrathin single-crystal nanowires	2.75×10^{21}	this work
Anatase TiO ₂	nanosponges	3.60×10^{19}	[37]
Ag-TiO ₂	nanobelts	6.90×10^{19}	[38]
Ag ₂ S-TiO ₂	nanotubes	1.60×10^{19}	[39]
N doping-TiO ₂	nanotubes	1.20×10^{16}	[40]
S doping-TiO ₂	nanorods	3.80×10^{20}	[41]

Fig. 5. Concentration change of three intermediates of bisphenol A degradation by the TiO₂-SWs/TF in PEC process.

bisphenol A to intermediates, which would later be verified in Figs. 5 and 6. The electrons then transferred from the CB to the outer of the nanowires. These single-crystal 6 nm-thick ultrathin nanowires could provide fast electrons transfer routes to the Ti foam substrate, which would remarkably increase the current density (about 5.5 times of P25). On the other electrode, the electrons provided by the applied potential and oxidation of bisphenol A quickly transferred to the Pt cathode where H⁺ ions were reduced to H₂. In this way, high-efficient degradation of bisphenol A as well as H₂ production occurred at 1.2 V with pH = 0 simultaneously. It was noted that our PEC system had a very low energy consumption of 0.02 kWh m⁻³ (pH = 0), which was the original aim of the research to use sunlight to reduce electric power consumption.

3.4. Proposed degradation pathways based on intermediates

To further explore the degradation process of bisphenol A with PEC method, the intermediates were monitored with liquid chromatography-quadrupole-time of flight-mass spectrometry.

Fig. 6. Proposed PEC degradation pathways of bisphenol A by the TiO₂-SWs/TF.

The photocatalytic degradation of bisphenol A by TiO₂ has been reported by many researchers with intermediates at m/z 133, 135, 173, 207, 245 and so on [42,43]. In our system, three relatively large peaks at m/z 243, m/z 215, and m/z 135 were identified separately from the mass spectra (MS) derived from bisphenol A degradation (Fig. S10) except the peak of bisphenol A at 227. In Fig. 5, the intermediate at m/z 243 was detected earlier and its concentration increased quickly to the maximum at 60 min than the other two intermediates. Later, the intermediate at m/z 215 increased quickly and reached the maximum at 150 min while the intermediate at m/z 135 was increasing slowly during the 150 min. Other intermediates were not detected as they were not formed or their concentrations were very low. Bisphenol A was mainly degraded through demethylation and hydroxylation, producing hydroxylated and multihydroxylated intermediates, which were also observed in the previous studies [44,45]. Based on the relative abundances of the three detected intermediates and their changes with reaction time, two main pathways for PEC degradation of bisphenol A under the simulated sunlight were proposed in Fig. 6. The first pathway is hydroxylation, by which one hydroxyl group was added to the adjacent position of the phenolic hydroxyl group of bisphenol A molecule, resulting in the formation of m/z 243. Then it decomposed into the formation of m/z 215 after dealkylation and further oxidation as ring opening. The second pathway was subsequent bisphenol A cleavage and the intermediate of m/z 243, resulting in the formation of m/z 135, and m/z 151 after further hydroxylation. It was noted that the two degradation pathways were not isolated from each other. Besides, the intermediates, which were produced by the first pathway could also be degraded in the second pathway. Both of these intermediates from the two pathways were presumably oxidized further through ring-opening reactions into aliphatic compounds and then degraded to small amounts followed by mineralization.

4. Conclusions

In summary, TiO₂ microflowlers assembled by 6-nm single-crystal stranded wires (TiO₂-SWs/TF) were synthesized by a facile hydrothermal method. The fabricated TiO₂-SWs/TF had a photocurrent of 0.33 mA cm⁻² (5.5 times higher than the P25/TF of 0.06 mA cm⁻²) and a carrier density of 2.75 × 10²¹ cm⁻³ (higher in the order of magnitude compared to other reported values), showing a remarkable improvement in electron transport. In the constructed PEC system using the TiO₂-SWs/TF as photoanode exhibited an excellent activity of 94% bisphenol A degradation efficiency within 60 min at 1.2 V. The enhanced PEC degradation of bisphenol A could mainly be ascribed to the fast electron transport through the single-crystal 6 nm-thick ultrathin nanowires. The synergetic effect of photocatalytic and electrocatalytic also enhanced the electron transport and made the electrons provided by the applied potential and oxidation of bisphenol A quickly transfer to the Pt wire cathode where H⁺ ions were reduced to H₂. Moreover, the calculated electrical energy consumption in our system by the TiO₂-SWs/TF electrode was only 0.02 kWh m⁻³ (pH = 0), indicating a lower energy consumption with the aid of simulated sunlight. Additionally, three main intermediates were identified and two pathways were proposed in the PEC degradation of bisphenol A. The as-fabricated TiO₂-SWs/TF electrode showed high-efficient bisphenol A degradation with lower energy consumption using PEC method through the ultrafast electron transfer channels of 6-nm single-crystal stranded wires, which would provide a probable structure to improve PEC performance.

Competing interest

The authors declare no competing financial interest.

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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.electacta.2017.08.033>.

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