Photochemical Anti-Fouling Approach for Electrochemical Pollutant Degradation on Facet-Tailored TiO₂ Single Crystals

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ABSTRACT: Electrochemical degradation of refractory pollutants at low bias before oxygen evolution exhibits high current efficiency and low energy consumption, but its severe electrode fouling largely limits practical applications. In this work, a new anti fouling strategy was developed and validated for electrochemical pollutant degradation by photochemical oxidation on facet-tailored {001}-exposed TiO₂ single crystals. Electrode fouling from anodic polymers at a low bias was greatly relieved by the free -OH-mediated photocatalysis under UV irradiation, thus efficient and stable degradation of bisphenol A, a typical environmental endocrine disrupter, and treatment of landfill leachate were accomplished without remarkable oxygen evolution in synergistic photoassisted electrochemical system. Electrochemical and spectroscopic measurements indicated a clean electrode surface during cyclic pollutant degradation. Such a photochemical antifouling strategy for low-bias anodic pollutants degradation was mainly attributed to the improved electric conductivity and excellent electrochemical and photochemical activities of tailored TiO₂ anodic material, whose unique properties originated from the favorable surface atomic and electronic structures of high-energy {001} polar facet and single-crystalline structure. Our work opens up a brand new approach to develop catalytic systems for efficient degradation of refractory contaminants in water and wastewater.

INTRODUCTION

The direct electrochemical oxidation (EC) at low bias before oxygen evolution has several merits for water treatment, such as high current efficiency and low energy consumption.¹ Pollutants are oxidized at a low rate after interfacial adsorption, without involvement of any substrate other than electron. One of its main bottlenecks is anode fouling and activity deterioration from intermediates surface deposition.¹ Photo-catalysis is an efficient and exhaustive technology for advanced water treatment,² and is demonstrated to be an effective strategy to remove anodic polymer.³⁻⁷ When PC and EC are combined into photoassisted electrochemical oxidation (PEC), the bias is sufficiently higher than anodic oxidation potentials of both pollutants and water.⁸⁻⁹ In this case, synergistic effects are anticipated: the improved PC activity due to anodic bias and oxygen evolution in EC and the enhanced EC activity owning to active oxygen species in PC. Compared to those combining indirect EC with indirect PC at high bias after oxygen evolution in literatures,⁸⁻¹⁶ the combination of direct EC with indirect PC at low bias before oxygen evolution is more attractive for water treatment due to its high current efficiency, low energy consumption and relieved electrode fouling. Thus, EC bias should be well controlled to be higher than pollutant oxidation potential but lower than water oxidation potential. However, no study is available.

In PEC, electrode material should have both high PC and EC activities. However, metal oxides usually lack either sufficient EC or PC activity due to their crystal and electronic structures,¹⁻² thus cannot be directly used in PEC. To resolve this problem, combining EC catalyst with PC catalyst onto one single side or two different sides of electrode is an effective way to prepare PEC anodic material. Thus, the photochemical properties of one substrate (e.g., TiO₂ and γ-Bi₂MoO₆) and the electrochemical properties of another substrate (e.g., boron-doped diamond, Pt, and transition metal oxides, such as RuO₂, SnO₂, PbO₂, IrO₂ and Ta₂O₅) are combined onto one single electrode.⁸⁻¹⁶ Up to now, most of PEC systems are constructed on these mixed electrodes by a complicated procedure, which might suffer from limited surface reactive sites due to the reduced interfacial domains.¹⁶ Recently, several single-component PEC electrodes, i.e., ZnWO₄, Bi₂WO₆, and γ-Bi₂MoO₆, have been developed¹⁹⁻²¹ and their pollutant degradation is
superior in synergistic PEC over the sum of PC and EC. To develop simple, efficient and stable anodic material is of considerable interest for PEC applications in water treatment.

TiO_2 is widely used as a good PC material for water treatment, but usually not recognized as an efficient EC material due to low conductivity and poor reactivity. However, with tailored structural modifications by self-and/or guest doping, the electrochemical properties of TiO_2 can be largely improved. Very recently, we improved the electrochemical capacity of TiO_2 by finely tuning the geometrical and electronic structures of surface localized constituent atoms. The shape-tailored TiO_2 single crystals (SCs) with dominant high-energy (001) facets (0.90 J m⁻²) has been demonstrated as an efficient anodic material, and exhibits a great activity for pollutants degradation via direct anodic pathway at low bias before oxygen evolution. In addition to the excellent PC activity of TiO_2 SCs, their emerging EC activity is even more important for practical treatment of wastewaters, which are often characterized of high concentration, heavy colority, and turbidity. Considering the dual functions of tailored TiO_2 SCs, it might be an excellent PEC anodic material to construct the photochemical antifouling model for water treatment.

In this work, we developed a new photochemical antifouling strategy for direct anodic oxidation of refractory pollutants at low bias before oxygen evolution, by using facet-tailored TiO_2 SCs in PEC and bisphenol A (BPA), a typical environmental endocrine disrupter, as target pollutant. PEC performance was comprehensively explored in terms of degradation efficiency, antifouling performance and energy consumption, with EC as reference. Furthermore, the application of such a PEC for treatment of landfills leachate, a complex and refractory wastewater, was also examined. In this way, the feasibilities of photochemical antifouling strategy and TiO_2-based PEC system for water treatment were demonstrated. The facet-tailored TiO_2 SCs exhibited high PC and EC activities, and were simple, abundant, cost-effective, safe and easy to be prepared compared to the reported PEC materials. Moreover, a unique EC-dominant PEC catalytic mechanism and pollutant degradation pathway occurred on the TiO_2 SCs electrode, in comparison with the PC-dominant catalytic process in other TiO_2-based PEC systems reported in literature.

**MATERIALS AND METHODS**

**Electrode Preparation and Characterization.** Facet-tailored TiO_2 SCs were prepared with a solvothermal method (Figures S1–S3, please see Supporting Information, SI, for details). Degussa P25, polycrystalline TiO_2 particles dominantly exposed by low-energy {010} facets (mean particle size of ~25 nm, anatase/rutile = 80:20, BET surface area of ~50 m²/g, exposed percentage of high-energy {001} facets less than 5%), were purchased for reference (Degussa Co, Germany) (SI Figures S4–S7). The well-defined Sb-SnO_2 and Ti_k−Ru_aO_x electrodes were also prepared by the high-temperature decomposition and oxidation of chloride precursors, TiCl_4, RuCl_3 and SnCl_2, respectively, onto the degreased and etched Ti substrate (SI Figures S8–S12).

TiO_2 SCs were characterized in terms of morphology and structure (SI Figures S1, S2, S5, and S6), their PC activity was evaluated by diffuse reflectance spectra (DRS) and transient photocurrent response, EC activity was characterized by cyclic voltammetry (CV) and differential pulse anodic stripping voltammetry (DPASV) in three-electrode system, PEC activity was examined by electrochemical impedance spectroscopy (EIS) and DPASV, either in dark or under UV irradiation (please see SI for details). The antifouling properties of electrodes were evaluated by DPASV, CV, DRS, Fourier transformation infrared spectroscopy (FTIR) and Raman analyses.

**BPA Degradation Test.** BPA degradation test was carried out in a cylindrical three-electrode single-compartment cell at ca. 20 °C (SI Scheme S1). The anode had an effective area of 6.0 cm² with a TiO_2 SCs loading of approximately 0.05 mg/cm² (totally 0.30 mg dosage), and a Ti sheet with the same area was used as the cathode. The gap between electrodes was 1.0 cm. A dosage of 80 mL 0.1 M Na_2SO_4 aqueous solution containing 5–100 mg L⁻¹ BPA was electrolyzed, and the applied bias (versus SCE) was controlled in a range of 0.5–2.0 V with an electrochemical workstation (CHI 760d, Chenhua Co., China). For UV illumination, a high-pressure 500 W Xe arc lamp (PLS-SXES00, Trusttech Co., China) equipped with a 10 cm IR filter was used. The UV light intensity was ~2.1 mW cm⁻² in a range of 300–400 nm, which was measured at 3 cm distance from the central lamp by a commercial radiometer (Model FZ-A, Photoelectric Instrument Plant of Beijing Normal University, China). No additional external resistance or iR compensation was used in the PEC system.

**Landfill Leachate Treatment Test.** The landfill leachate was collected from a local municipal landfill site of Hefei City in Anhui, China during a period from May 2016 to August 2016, and then stored in a refrigerator (4 °C). The raw leachate was initially treated on site by aerobic lagoon, denitrification and activated sludge process to remove the biodegradable organic compounds and ammonia. The physicochemical characteristics of the pretreated leachate are shown in SI Table S1. In UV–vis spectra of the raw leachate, no characteristics in 250–281 nm were observed. Thus, 300 nm was chosen to evaluate the color reduction.

**Analysis.** UV–visible absorption and fluorescence spectra were recorded on a spectrophotometer (UV-2401PC, Shimadzu Co., Japan) and spectrophotofluorophotometer (RF-5301PC, Shimadzu Co., Japan) respectively. BPA was determined by high-performance liquid chromatography (HPLC-1100, Agilent Inc.) with a Hypersil-ODS reversed-phase column and detected by a diode array detector (DAD). Intermediates were identified by gas chromatography mass spectrometry (GC/MS, GCMS-2010A, Shimadzu Co., Japan). COD was determined using the Standard Methods.

**RESULTS AND DISCUSSION**

**Morphology, Structure, and PEC Properties of TiO_2 SCs.** The prepared bipyrudal TiO_2 SCs exhibited sheet shape and were enclosed by eight equivalent {101} facets and two equivalent {001} facets (SI Figure S1a and b). The clear crystalline lattice fringes and the indexed {001} zone axis diffraction further confirm their single-crystalline structure (SI Figure S1c–e). The X-ray diffraction results highly matched anatase TiO_2 (JCPDS No. 21–1272), and the diffraction peak broadening was attributed to their small crystal size. Deposition of TiO_2 SCs onto carbon paper to fabricate the PEC electrode was performed using dip-coating technology,
and the TiO₂ SCs were spread uniformly and tightly with a loading of ca. 0.05 mg/cm² (SI Figure S1f), suggesting that the carbonaceous substrate interacted with the TiO₂ SCs through physical adsorption, electrostatic binding or charge transfer interaction.

An efficient PEC material should simultaneously possess excellent PC and EC activities on one single anode. Superior PC (Figure 1a and b), EC (Figure 1c and d) and PEC (Figure 1e-h) activities were observed for the TiO₂ SCs electrode in terms of optical absorption, electron transfer, photocurrent generation, electrochemical response, ·OH-mediated photoluminescence (PL) generation and pollutant degradation (SI Figures S14–S19), compared to typical P25 and Ti₀.₇Ru₀.₃O₂ electrodes under the identical conditions. The reduced ΔEp of the TiO₂ SCs electrode indicates its reduced kinetic barrier of electron transfer and/or improved active surface area for interfacial reaction (Figure 1c), both of which are essential for the enhanced EC activity from polar-facet engineering and single-crystalline structure. The high EC activity of the TiO₂ SCs electrode was further confirmed by its large peak current...
for the BPA anodic oxidation (Figure 1d).36 These electrochemical superiorities could be attributed mainly to the single crystal structure and exposed high-energy polar {001} facets.24−27 Moreover, by a combination of PC with EC, the electron transfer resistance was further decreased, and the BPA oxidation and ·OH yield were substantially improved for the PEC electrode (Figure 1e−h). All of these properties endowed the {001}-TiO2 SCs as an excellent PEC material for pollutant degradation.

**BPA Degradation Performance of PEC.** The greatest BPA degradation rate was obtained in the PEC (k = 26.92 × 10−3 min−1), which was much higher than the sum of the PC (k = 0.41 × 10−3 min−1) and EC (k = 19.10 × 10−3 min−1) (Figure 2a). BPA of 30 mg/L was completely degraded in 2.0 h in the PEC, rather than 4.0 h in EC. The substantially enhanced BPA degradation efficiency in the PEC indicates a possible synergistic effect when the EC and PC were combined on the TiO2 SCs electrode. It should be mentioned that the observed low BPA removal efficiency in the PC did not indicate a weak photodriven activity of the electrode, but should be ascribed to the excessive BPA solution (80 mL) and insufficient catalyst dosage (0.3 mg). The photocatalyst/solution weight/volume ratio, 0.00375 mg/mL, was only ca. 1/300 of the typical value, 1 mg/mL, widely used in previous PC-related studies. Also, although a small amount of water molecules could be oxidized at the selected +1.3 V/SCE on the TiO2 SCs, this side reaction was limited due to the large ohmic drop and overpotential, as indicated by the LSV results and the digital photos of the PEC cells with the TiO2 SCs electrode (SI Figures S20 and S21), in which no obvious gas bubbles were generated at the solution surface.

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Figure 2. BPA removal behaviors in the PC, EC and PEC with the bifunctional TiO2 SCs, Degussa P25 and typical Ti0.7Ru0.3O2 electrodes: degradation (a−e) and mineralization (f). Reaction conditions: solution volume (80 mL), BPA concentration (30 mg L−1), Na2SO4 concentration (0.1 M), anode size (6.0 cm2), catalyst dosage (0.05 mg/cm2 × 6.0 cm2 = 0.3 mg), cathode size (6.0 cm2, Ti sheet), electrode gap (1.0 cm), bias (+1.3 V/SCE), UV (500 W Xe arc lamp, λ < 420 nm), pH (~5.0), temperature (~20 °C), stirring rate (500 rpm), and reaction time (6.0 h).
exposed polar \{001\} facet.\textsuperscript{24} By virtue of both high EC and PC activities on one single TiO\textsubscript{2} SCs electrode, a novel EC-dominant PEC system was effectively established for efficient pollutant degradation at a low potential bias (Figure 2), in comparison with the widely reported PC-dominant PEC systems on other TiO\textsubscript{2}-based electrodes.\textsuperscript{32−34} In addition, the bifunctional TiO\textsubscript{2} SCs electrode also exhibited a much higher activity than the carbon and Sb-doped SnO\textsubscript{2}/Ti electrodes in both EC and PEC systems (SI Figure S25).

Various intermediates, such as 4-isopropenylphenol (SI Figure S26a), hydroquinone (SI Figure S26b), benzoquinone (SI Figure S26c), citric acid (SI Figure S26d), maleic acid (SI Figure S26e) and acetic acid (SI Figure S26f), were detected in BPA degradation. The maximum accumulation concentrations of hydroquinone and maleic acid were higher and the time to peak was shorter in the PEC than those in the EC (SI Figure S26b and e), indicating a faster BPA degradation rate in the PEC. Furthermore, the maximum accumulation concentrations of the other four intermediates were higher and the time to peak was longer in the EC than in the PEC (SI Figure S26a, c, d, and f), suggesting a slower BPA mineralization rate in the EC. These results are highly consistent with the superior BPA degradation performance in PEC with TiO\textsubscript{2} SCs electrode (Figure 2a).

In the PEC, the BPA removal efficiency was drastically improved, and the current efficiency was much higher than that in the EC (SI Table S2). It should be noted that the energy consumption in UV irradiation was not taken into account (SI Table S2). The electro-assisted adsorption also contributed to the BPA removal by establishing the synergistic adsorption-promoted degradation on the TiO\textsubscript{2} SCs electrode (SI Figure S28).\textsuperscript{37} The BPA degradation and mineralization decreased slightly after 20 cycles in the PEC, indicating their good stability for long-term applications (Figure 3a, c, and d). In the EC, it began to continuously decrease after the seventh run, demonstrating the progressive surface fouling on the TiO\textsubscript{2} electrode by the increased accumulation of the polymeric products at a low bias (Figure 3b).

**Anti-Fouling Properties of PEC Electrode.** The well-defined oxidation peak toward BPA at ca. 0.60 V in the first cycle was substantially reduced and even completely disappeared in subsequent cycles in EC (Figure 4a), suggesting the formation and progressive accumulation of anodic polymeric film, which deactivated TiO\textsubscript{2} electrode.\textsuperscript{1,31} In comparison, such a deactivation was considerably decreased in PEC due to its enhanced catalytic capacity and antifouling properties (Figure 4b).

Both FTIR and DRS were used to characterize the samples extracted from the used electrodes with methanol as solvent. Compared to BPA monomer, in the characteristic spectra of polymerized BPA from EC (Figure 4c), the broad band of O−H stretch in hydroxyl groups, C = C ring stretch, and out-of-plane C−H bend, at 3220-, 1600-, and 830- cm\textsuperscript{-1}, disappeared, but two strong and sharp bands at 2924- and 2854 cm\textsuperscript{-1}, which are the characteristic of sp\textsubscript{3} C−H stretching modes, and the band for typically nonconjugated C = O bonds at 1750 cm\textsuperscript{-1}, were observed.\textsuperscript{31} In DRS spectra, B band at 270 nm associated with π−π electronic transition of phenol disappeared and only E\textsubscript{2} band was observed at 227 nm (Figure 4d). These results indicate that the polymeric film on EC electrode was mainly composed of aliphatic hydrocarbons including carbonyl...
groups. In comparison, no obvious characteristic spectra of both FTIR and DRS were measured for samples extracted from PEC, implying the complete degradation of polymeric film and full regeneration of active sites on TiO2 SCs electrode. Thus, a much higher electrochemical activity and stability were obtained.

The electrochemical stability of the TiO2 SCs electrode was also evaluated by examining the CV response of ferrocyanide ion (10 mM) as a redox marker (Figure 4e). The oxidative current on the used EC electrode (3.92 mA, scanning rate of 10 mV/s) was substantially lower than that of the raw one (7.11 mA), suggesting the anodic deactivation by the nonexhaustive incineration of polymerized BPA due to the limited EC activity. In contrast, a much less decrease in oxidative current was observed for the PEC electrode after the BPA degradation (6.14 mA), implying that no massive organics remained because of the sufficiently high PEC activity. These results agree well with the FTIR and DRS results. In addition, Raman analysis was used to explore the changes in crystal structure and electrode stability after cyclic operation. Raman peaks at around 142, 394, 512, and 634 cm\(^{-1}\) could be identified (Figure 4f), neither broadening nor shift occurred after 5 cyclic degradation in both EC and PEC, excluding the possible structural destruction of the tailored TiO2 SCs.

Therefore, the TiO2 SCs electrode deactivation in the EC should be attributed mainly to the residual polymerized BPA film adsorbed onto the active and inactive sites because of the limited electrochemical capacity at 1.3 V, rather than the structural and crystal destruction of the anodic material. This was further validated by DRS and FTIR measurements. In comparison, no any deactivation and structural destruction occurred in PEC because of the synergistic effects between the EC and PC on the bifunctional TiO2 SCs anode.

**PEC Mechanism and BPA Degradation Pathway on the TiO2 SCs Electrode.** The bifunctional TiO2 SCs could be simultaneously activated by potential and UV via the nonband-gap and band gap excitation mechanisms respectively (Scheme 1). At a bias of +1.3 V/SCE (\(E < E_g \approx 3.2 \text{ eV}\)), electrons were excited from conductance band (CB) to cathode to generate remaining holes in CB (Reaction 1), while electrons were excited from valence band (VB) to CB to form reactive electron–hole pairs under UV irradiation (\(\lambda = 300\sim400 \text{ nm}\)) (Reaction 2). Then, carriers were spatially separated by anodic bias, which provided a potential gradient within electrode to

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**Figure 4.** Antifouling properties of the TiO2 SCs electrode in the EC and PEC: cyclic DPV curves (a, b), FTIR spectra (c), DRS spectra (d), CV curves (e) and Raman spectra (f). Measurement conditions: DPV (solution = 0.1 M Na2SO4 + 30 mg L\(^{-1}\) BPA, potential range = −0.3−1.0 V, scan rate = 0.1 V/s, UV = 500 W Xe arc lamp, \(\lambda < 420 \text{ nm}\) and effective anode area = 6.0 cm\(^2\)) and CV (solution = 0.1 M Na2SO4 + 5.0 mM [Fe(CN)6]\(^{3-}\)/[Fe(CN)6]\(^{4-}\), pH = 5.5, potential range = −0.4−0.6 V, scan rate = 0.1 V/s and effective anode area = 6.0 cm\(^2\)).
drive electrons to counter electrode along conductive substrate (Reactions 3 and 4). Both electro- and photogenerated holes on TiO2 SCs could respectively form surface-bound and free ·OH from water oxidation (Reactions 5−8). The electro-generated holes and surface-bound ·OH under potential bias could oxidize pollutants (≡C−OH) without exhaustive mineralization to generate various polymeric products (Reactions 9 and 10), which could be effectively degraded and mineralized by the photogenerated holes and free ·OH under UV irradiation (Reactions 11 and 12). When the potential bias was further increased, oxygen evolution from water oxidation with surface-bound and free ·OH as the main intermediates would largely occur (Reactions 13 and 14).

In this work, the BPA degradation in PEC was initiated primarily by EC and also by PC with the TiO2 SCs anode (Scheme 1). BPA was mainly degraded under potential bias via electrochemical direct oxidation, which was initiated by electro-generated holes through direct electron transfer at anode surface (Pathway 1, SI Scheme S2). The given anodic potential (+1.3 V/SCE) was markedly higher than \( E_0(\text{BPA/\text{BPA}^-}) \) (∼ +0.7 V/SCE, Figure 1d and 1f), but substantially lower than \( E_0(\text{H}_2\text{O}/\cdot\text{OH}) \) (∼ +2.3 V/SCE). Both the high catalytic activity (\( k_{\text{EC}}/k_{\text{PEC}} \) ratio in BPA degradation) and the low PL signal (\( k_{\text{EC}}/k_{\text{PEC}} \) ratio in ·OH generation) in EC system indicate a EC-dominant synergistic mechanism in PEC system with the main electro-generated hole-mediated BPA degradation pathway, while other three oxidation pathways played minor roles.

\[
\text{TiO}_2(\text{h}^+)_{\text{CB}} + \cdot\text{OH} \rightarrow \text{CO}_2 + \text{H}_2\text{O}
\]

(1)

\[
\text{TiO}_2(\text{h}^+)_{\text{VB}} + \text{TiO}_2(\text{e}^-)_{\text{CB}} \rightarrow \text{TiO}_2(\text{h}^+)_{\text{VB}} + \text{current}
\]

(2)

\[
\text{TiO}_2(\text{h}^+)_{\text{CB}} + \text{OH}^- \rightarrow \text{TiO}_2(\cdot\text{OH})_{\text{bound}}
\]

(3)

\[
\text{TiO}_2(\text{h}^+)_{\text{CB}} + \text{H}_2\text{O} \rightarrow \text{TiO}_2(\cdot\text{OH})_{\text{bound}} + \text{H}^+ + \text{e}^-
\]

(4)

\[
\text{TiO}_2(\text{h}^+)_{\text{VB}} + \cdot\text{OH} \rightarrow \text{TiO}_2(\cdot\text{OH})_{\text{free}}
\]

(5)

\[
\text{TiO}_2(\text{h}^+)_{\text{VB}} + \text{H}_2\text{O} \rightarrow \text{TiO}_2(\cdot\text{OH})_{\text{free}} + \text{H}^+ + \text{e}^-
\]

(6)

\[
\text{TiO}_2(\cdot\text{OH})_{\text{bound}} + \cdot\text{OH} \rightarrow \text{CO}_2 + \text{H}_2\text{O}
\]

(7)

\[
\text{TiO}_2(\cdot\text{OH})_{\text{free}} + \cdot\text{OH} \rightarrow \text{CO}_2 + \text{H}_2\text{O}
\]

(8)

\[
\text{TiO}_2(\cdot\text{OH})_{\text{bound}} \rightarrow 1/2\text{O}_2 \uparrow +\text{H}^+ + \text{e}^-
\]

(9)

\[
\text{TiO}_2(\cdot\text{OH})_{\text{free}} \rightarrow 1/2\text{O}_2 \uparrow +\text{H}^+ + \text{e}^-
\]

(10)
only (Figure 2a, SI Figure S29 and Scheme 1). Such an EC-dominant PEC mechanism on the facet-tailored TiO2 SCs electrode was substantially different from the widely reported PC-dominant PEC mechanism on other TiO2-based electrodes (SI Scheme S3).24 At +1.3 V/SCE, although electro-generated holes were unable to oxidize adsorbed H2O and OH− to generate free ⋅OH, the electrochemical surface-bound ⋅OH-mediated indirect oxidation pathway could not be ruled out in this case, as this potential bias is sufficient for water oxidation initiated with surface-bound ⋅OH (SI Figures S13–S17).3 In electrochemical direct oxidation (Pathway 1, SI Scheme S2), the adsorbed BPA was initially transformed to 4-isopropenylphenol (m/z = 133) and phenol respectively by electro-generated holes. Then, the two aromatic intermediates were partially oxidized to some aliphatic acids via aromatic ring cleavage in the most direct and simple pathway. Finally, the formed aliphatic acids were completely mineralized to CO2 and H2O.24 However, it is well-known that some polymeric compounds, which are highly resistant to further oxidation via direct anodic mechanism.31 Furthermore, these polymeric products can be strongly adsorbed onto anode surface and firmly block active sites from further reactions, leading to severe electrode deactivation (Figure 4a and SI Scheme S2).31,33 Thus, only a partial, selective and unstable BPA oxidation (i.e., conversion) occurred in EC (Figures 2 and 3 and SI Figure S26).

BPA was also degraded under UV irradiation via photochemical direct oxidation initiated by photogenerated holes (Pathway 1, SI Scheme S2) and photochemical indirect oxidation initiated by free ⋅OH (Pathway 2, SI Scheme S2) because of the sufficiently high potential of photogenerated holes in band gap excitation (EVB = ~2.8 eV/NHE).2 The ⋅OH-mediated oxidation has three representative steps (Pathway 2, SI Scheme S2). First, some hydroxylated derivatives from BPA were rapidly generated due to the selective attack of the free ⋅OH on different carbon atoms of BPA molecules, while these aromatic derivatives were unstable and readily decomposed into one-ring aromatic compounds through isopropylidene bridge cleavage; second, these aromatic compounds underwent further ring cleavage, leading to the formation of short-chain aliphatic acids; last, further oxidation of these organic acids to CO2 and H2O was undertook, accomplishing the mineralization of BPA.30

The progressive accumulation of the polymeric intermediates from the electrochemical direct oxidation of BPA through electron transfer in Pathway 1 led to the electrode fouling and thus a continuous deteriorator in EC performance (Figure 3 and SI Figure S26).31,33 When such an incomplete EC was combined with PC to construct a synergistic PEC on the bifunctional TiO2 SCs, a complete, nonselective and stable BPA degradation could readily occur (Figure 3 and SI Figure S26). The main reason was that these highly resistant and strongly adsorbed polymeric products formed in electrochemical direct oxidation in Pathway 1 could also be oxidized to aliphatic acids and finally mineralized to CO2 via photochemical indirect oxidation initiated by free ⋅OH (Pathway 3, SI Scheme S2).3,17,7

The well-known EC-assisted PC and their PC-EC synergism could favor such a photochemical anti fouling capacity in the PEC (SI Figures S15–S17).32–34 although the single PC exhibited a weak activity (Figure 2a). Thus, the spatially occupied active sites on TiO2 SCs were rapidly released, and the EC deactivated anodic material was promptly regenerated by ⋅OHfree formed in PC (Figure 4 and Scheme 1). In turn, these two processes could accelerate the overall degradation, which was responsible for the excellent and stable BPA removal in PEC (SI Table S2 and SI Figure S26).

Treatment of Landfill Leachate by PEC. To further examine the feasibility of such a PEC for pollution control, it was also applied to treat landfill leachate, a typical toxic and mixed wastewater (see SI for details).31 In 7 h treatment, although slight difference was found for the discoloration efficiency between EC and PEC (ca. 70% and 80%, respectively) (Figure 5a), a significant superiority was observed for the COD removal in PEC (more than 75%) over EC (less than 40%) (Figure 5b). This result indicated that the PEC with facet-tailored TiO2 SCs could be used as an efficient technology for real complex wastewater treatment.

Environmental Implications. Oxygen evolution is usually an inevitable side reaction to raise energy consumption in electrochemical water treatment. The direct anodic oxidation pathway at low bias before oxygen evolution is a potential strategy to this problem. However, how to overcome the serious electrode fouling and continuous activity decrease still remains a great challenge. In this study, by virtue of the excellent ⋅OHfree-mediated photochemical oxidation capacity of the bifunctional TiO2 SCs with dominant high-energy {001} polar facets, electrochemical degradation of refractory pollutants could be sustainably carried out at low bias with high
energy efficiency. The developed and validated photochemical antifouling strategy might be of considerable interest for practical applications of anodic oxidation at low bias in cost-effective removal of refractory pollutants in water and wastewater. Also, our findings provide a promising catalytic material with good photochemical and electrochemical activities, and opens up a brand new approach to develop more practical transition metal-oxide-based catalysts for efficient water treatment. However, considering the high energy consumption in UV irradiation, solar-light-driven photochemical antifouling warrants further investigations for practical applications.

■ ASSOCIATED CONTENT

S Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.7b04105. Characteristics of TiO$_2$ SCs and P25 (Figures S–S), Sb-doped SnO$_2$/Ti (Figures S1–S7) and Ti$_{83}$Ru$_{17}$/Ti electrodes (Figures S8–S10), additional PC, EC and PEC characterizations and BPA degradation tests (Figures S11–S13), evolution of main BPA degradation intermediates (Figures S26), light spectrum of the utilized Xe lamp (Figure S27), BPA adsorption tests (Figures S28), EC and PEC kinetic constant ratios (Figure S29), diagram of the PEC cell (Scheme S1), BPA degradation pathway (Scheme S2), the general PEC mechanism (Scheme S3), characteristics of landfill leachate (Table S1) and BPA removal behaviors under various conditions (Table S2) (PDF)

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