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Photoelectrocatalytic removal of bisphenol A using $[Ru(bpy)_2(tatp)]^{2+}$ modified TiO_2 electrode

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A novel photoelectrocatalytic method is applied to the oxidative removal of bisphenol A (BPA) that is regarded as a representative endocrine disrupting chemical. The result from electrocatalysis of $[Ru(bpy)_2(tatp)]^{2+}$ (bpy = 2,2′-bipyridine, tatp = 1,4,8,9-tetra-aza-triphenylene) present in solution or assembled electrochemically on the nano-TiO_2 electrode shows high removal efficiency for BPA by a Ru(III)-based coupled chemical reaction. The evidence from photocatalysis of $[Ru(bpy)_2(tatp)]^{2+}$ modified TiO_2 nanoparticles reveals a $[Ru(bpy)_2(tatp)]^{2+}$-controlled BPA removal sensitive to the irradiation of ultraviolet (UV) and visible light via an $^1O_2$ and •OH-based coupled chemical reaction, showing more than 97.3% removal efficiency within 30 min. The result from photoelectrocatalysis of $[Ru(bpy)_2(tatp)]^{2+}/TiO_2$ photoanode suggests a bifunctionalized BPA removal based on a BPA/H_2O_2 photoactivated fuel cell, showing more than 41.3% removal efficiency as well as good preliminary cell performance, which opens a way to search for diverse applications. It becomes evident that the photoelectrocatalytic removal of BPA depends on the coupled chemical reactions between BPA and intermediate species generating from excited states and electro-oxidation of Ru(II) complexes.

Keywords: Bisphenol A; Removal; Polypyridyl ruthenium(II) complex; TiO_2 nanoparticles; Photoelectrocatalysis

1. INTRODUCTION

Bisphenol A (BPA) has been widely used as a raw material in the manufacture of polycarbonate plastic and epoxy resin coating for various storage containers, baby bottles, tableware, white dental fillings and sealants [1,2]. Because of its wide usage and serious adverse impacts on human health and environment, BPA is regarded as one of the 114 hazardous pollutants listed by the U.S. Environmental Protection Agency. Therefore, it is necessary to find an efficient method for removing such a chemical to eliminate contaminations [3-5].

Various methods have been reported in the past three decades for persistent organic pollutants treatment, involving biochemical, electrochemical, sonochemical and photochemical reactions [6,7]. One of the most promising advanced oxidation technologies is that of photocatalysis due to its high removal efficiency and low energy consumption [8,9]. When a semiconductor catalyst is irradiated by UV light, the photogenerated holes (h^+) at the valence band react with water to produce hydroxyl free radicals (•OH), which have strong oxidizing ability to attack phenolic pollutants [10]. Titanium dioxide (TiO_2) is considered an effective semiconductor photocatalyst due to its good photocatalytic activity, physical and chemical stability, low cost and accessibility[11]. The TiO_2 photocatalyst is either dispersed into aqueous solutions and slurry reactors, or immobilized onto a solid substrate for the degradation of BPA, with the latter being more advantageous. However, TiO_2 can only absorb less than 5% of the solar energy because of its wide band gap, thus many researchers have attempted to expand its photoactivity to the visible light region for the development and improvement of solar energy utilization technologies [12-14].

Since polypyridyl Ru(II) complexes possess highly photosensitive and potentially electrochemical properties in the UV and visible light region, they have the potential to be developed into good photosensitizers and electrocatalysts used in the field of environmental protection and dye-sensitized solar cells [15-22]. In our previous study, an effective voltammetric method for BPA detection was proposed based on the electrocatalytic oxidation of $[Ru(bpy)_3]^{2+}$ [23]. In this work, we attempt to explore the photoelectrocatalytic removal of BPA by $[Ru(bpy)_2(tatp)]^{2+}$, which depends on the coupled chemical reactions between BPA and intermediate species generating from excited states and electro-oxidation of Ru(II) complexes. A $[Ru(bpy)_2(tatp)]^{2+}$ modified TiO_2 electrode prepared by multiple voltammetry is effectively used to fabricate a photoactivated BPA/H_2O_2 fuel cell for the BPA removal as well as photochemical conversion and storage of light energy. To the best of our knowledge, this is the first example of the oxidative removal of BPA based on a photo-sensitized fuel cell using polypyridyl Ru(II) complexes electrochemically assembled onto semiconductor nanoparticles as photoelectrocatalytic agents.

2. EXPERIMENTAL

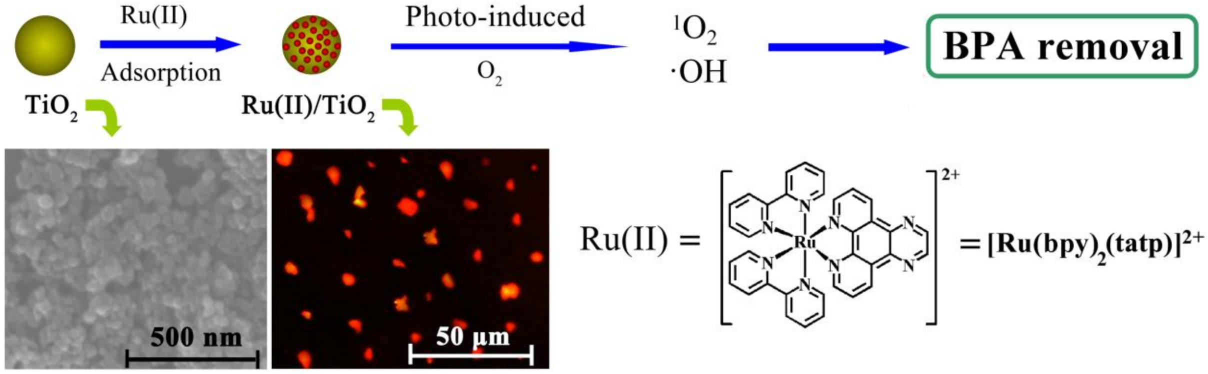

Figure 1. Schematic diagram for illustrating the photocatalytic removal principle of bisphenol A (BPA) by $[Ru(bpy)_2(tatp)]^{2+}$ modified TiO_2 nanoparticles.

Bisphenol A (BPA) was purchased from Sigma Company. TiO_2 (Degussa P25, approximately 80% anatase and 20% rutile) was used as received. $[Ru(bpy)_2(tatp)](ClO_4)_2$ and $[Cu(phen)_2Cl]Cl$ were synthesized by reported procedures in the literature [24,25]. The structure of $[Ru(bpy)_2(tatp)]^{2+}$ is shown in Figure 1. A TiO_2 suspension was spread onto the indium tin oxide (ITO) surface to form a TiO_2 thin film, which was subsequently dried in a dryer at 100 °C for 20 min and 450 °C for 30 min to make the TiO_2 film firmly adhere to the ITO surface. By 21 cycles of repetitive differential pulse voltammograms (DPVs), the sensitizer $[Ru(bpy)_2(tatp)]^{2+}$ was electrochemically assembled onto the TiO_2/ITO electrode.

DPVs measurements were performed on a CHI620d electrochemical system (Shanghai, China), with ITO as the working electrode, platinum as the auxiliary electrode and Ag-AgCl (0.1 M NaCl) as the reference electrode. The detection of BPA was carried out by DPVs, with a pulse width of 0.2 s, step potential of 10 mV and amplitude of 50 mV. The surface morphology of the TiO_2/ITO electrode was analyzed by SEM (Zeiss Ultra55, Germany). The fluorescent images of the $[Ru(bpy)_2(tatp)]^{2+}/TiO_2$/ITO electrode were captured by Nikon Eclipse TS100 inverted fluorescence microscope (Tokyo, Japan), with a Nikon E4500 camera under the excitation of blue light. The performance of the photoactivated fuel cell was measured in a two-compartment cell. UV lamp of 8 W or visible light of 10 W were used as the light source. The anodic and cathodic compartments were filled with 0.1 mM BPA and 1.0 mM H_2O_2, respectively. All solutions were prepared with supporting electrolyte of 0.1 M NaCl (pH 10.0) unless otherwise noted. All experiments were carried out at room temperature (23−25 °C).

3. RESULTS AND DISCUSSION

3.1. Electrocatalytic removal of BPA

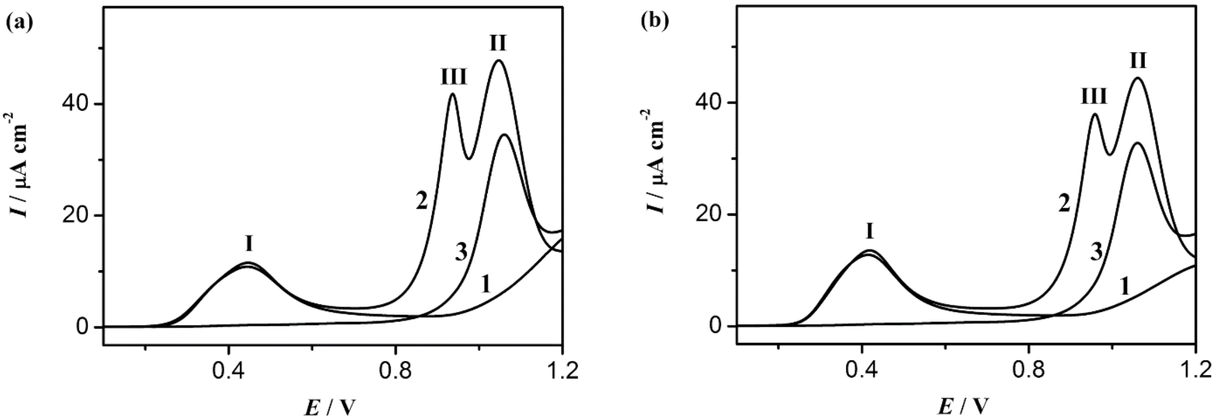

Figure 2. Differential pulse voltammograms (DPVs) of 0.1 mM BPA (a) or 0.1 mM BPA/0.5 g L^{-1} TiO_2 (b) in the absence (line 1) and presence of 0.1 mM $[Ru(bpy)_2(tatp)]^{2+}$ (line 2) on the ITO electrode in 0.1 M NaCl solutions. Line 3 corresponds to DPVs of 0.1 mM $[Ru(bpy)_2(tatp)]^{2+}$ (a) or 0.1 mM $[Ru(bpy)_2(tatp)]^{2+}$/0.5 g L^{-1} TiO_2 (b).

As depicted by curve 1 of Figure 2a, differential pulse voltammograms (DPVs) of 0.1 mM bisphenol A (BPA) in alkaline solution show an oxidative wave (peak I) at 0.445 V, assigned to the direct oxidation of BPA on the ITO electrode. Two new oxidative waves (peaks II and III) appear at 0.94 V and 1.05 V when 0.1 mM $[Ru(bpy)_2(tatp)]^{2+}$ is added to the BPA solution (curve 2 of Figure 2a). Obviously, peak II at 1.05 V corresponds to the oxidation of Ru(II) to Ru(III) (curve 3 of Figure 2a). Consequently, peak III at 0.94 V can be ascribed to the electrocatalytic oxidation of BPA by $[Ru(bpy)_2(tatp)]^{2+}$, which implies the formation of $[Ru(bpy)_2(tatp)]^{2+}$-BPA complex, as reported in our previous study [23]. The electrocatalytic mechanism is shown in equations 1-3 (BPA_{Ox} represents the oxidized product of BPA). When 0.5 g L^{-1} TiO_2 is added to the $[Ru(bpy)_2(tatp)]^{2+}$/BPA solution (Figure 2b), the direct or electrocatalytic peak currents of BPA by $[Ru(bpy)_2(tatp)]^{2+}$ are hardly affected by TiO_2, suggesting that TiO_2 has no electrochemical activity in the applied potential range.

$$[Ru(bpy)_2(tatp)]^{2+} + BPA \Leftrightarrow \{[Ru(bpy)_2(tatp)]^{2+} - BPA\} \tag{1}$$

$$\{[Ru(bpy)_2(tatp)]^{2+} - BPA\} - e^- \overset{ITO}{\Leftrightarrow} \{[Ru(bpy)_2(tatp)]^{3+} - BPA\}/ITO \tag{2}$$

$$\{[Ru(bpy)_2(tatp)]^{3+} - BPA\}/ITO \Leftrightarrow \{[Ru(bpy)_2(tatp)]^{2+} - BPA_{Ox}\}/ITO \tag{3}$$

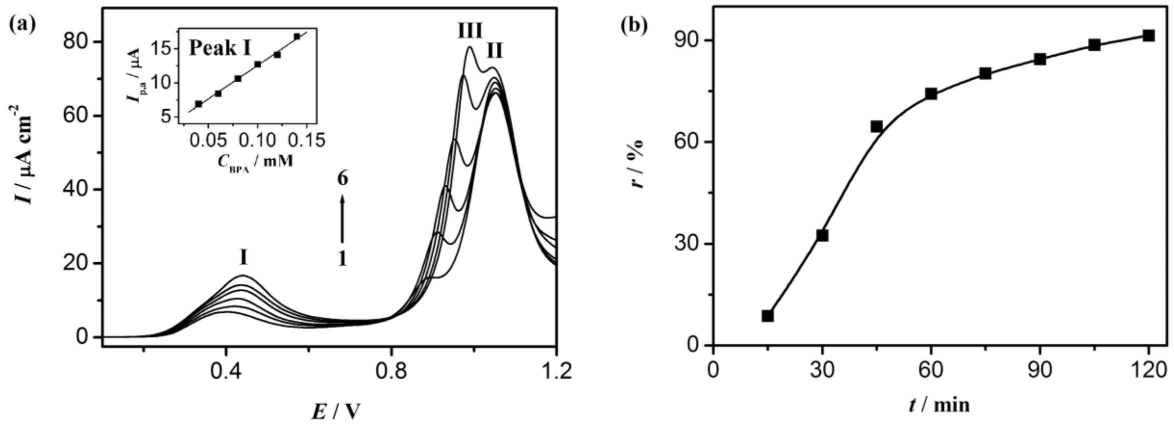

Figure 3. (a) DPVs of 0.1 mM $[Ru(bpy)_2(tatp)]^{2+}$ upon increasing BPA concentrations (mM): (1) 0.04,(2) 0.06, (3) 0.08, (4) 0.10, (5) 0.12, (6) 0.14. The inset shows peak I current as a function of BPA concentrations. (b) Electrocatalytic removal efficiency of 0.1 mM BPA by 0.1 mM $[Ru(bpy)_2(tatp)]^{2+}$ at an anodic potential of 1.1 V for different electrocatalytic times.

While BPA concentrations are changed from 0.04 to 0.14 mM, the direct or electrocatalytic peak currents (peak I or III) increase with the rising BPA concentrations (Figure 3a). By monitoring peak I current (inset of Figure 3a) as a function of BPA concentrations, the electrochemical voltammetric detection of BPA can be carried out, with a sensitivity of 89.8 μA/mM and a detection limit of 0.67 μM ($S/N = 3$). In the following studies, the BPA concentration in solution is monitored by peak I current, thus the BPA removal efficiency $r\%$ is obtained by equation 4 (where C_0 represents the initial BPA concentration, and C_t represents BPA concentration after electrocatalysis or photocatalysis for a time). When an anodic potential of 1.1 V is applied to the $[Ru(bpy)_2(tatp)]^{2+}$/BPA system for a time, BPA can be electrocatalytically removed by oxidizing Ru(III) that is generated in the applied potential, with a BPA removal efficiency of 91.4% in 120 min (Figure 3b). It is obvious that $[Ru(bpy)_2(tatp)]^{2+}$ is effective in the electrocatalytic removal of BPA by a Ru(III)-based coupled chemical reaction [26].

$$r\% = \frac{(C_0 - C_t)}{C_0} \times 100\% \qquad (4)$$

3.2. Photocatalytic removal of BPA

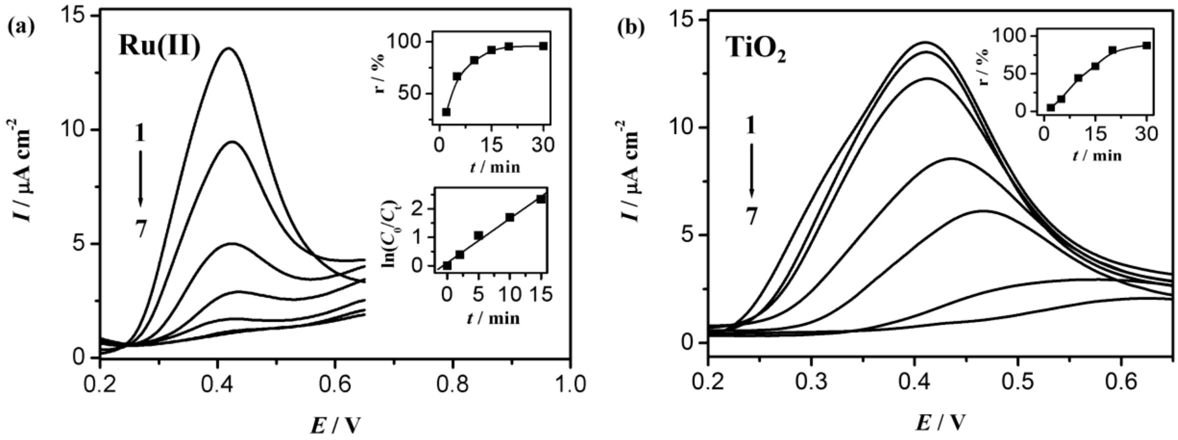

Figure 4. DPVs of 0.1 mM BPA photocatalytic by 0.1 mM $[Ru(bpy)_2(tatp)]^{2+}$ (a) or 0.5 g L^{-1} TiO_2 (b) in 0.1 M NaCl solutions under UV irradiation for different times (min): (1) 0, (2) 2, (3) 5, (4) 10, (5) 15, (6) 20, (7) 30. The inset shows the removal efficiency or $\ln(C_0/C_t)$ as a function of time.

Figure 4a is DPVs of 0.1 mM $[Ru(bpy)_2(tatp)]^{2+}$/0.1 mM BPA under UV irradiation of 365 nm for different times in the condition of oxygen saturation. The oxidative peak current of BPA is decreased obviously as UV irradiation time increased, indicating that $[Ru(bpy)_2(tatp)]^{2+}$ can induce the oxidative removal of BPA by the generation of excited states of Ru(II) complexes [27]. By monitoring the peak current of BPA in solution, the BPA removal efficiency can be obtained (Figure 4a inset). The BPA removal efficiency is 66.5% in 5 min. A high removal efficiency of 95.9% is yielded when UV irradiation time is 30 min. According to the first-order and second-order kinetic models, plotting $\ln(C_0/C_t)$ or $(1/C_t - 1/C_0)$ as a function of time, the kinetic reaction model for the removal of BPA by $[Ru(bpy)_2(tatp)]^{2+}$ is investigated [28]. As seen from the fitting results of Figure 4a inset, the removal of BPA by $[Ru(bpy)_2(tatp)]^{2+}$ under UV irradiation conforms to the first-order reaction kinetic model with a removal rate constant of 0.155 min^{-1} (R^2=0.985). Additionally, when 0.5 g L^{-1} TiO_2 is used as photocatalyst (Figure 4b), the BPA removal efficiency is 16.2% in 5 min and 87.7% in 30 min, respectively, which is lower than that of $[Ru(bpy)_2(tatp)]^{2+}$, revealing that $[Ru(bpy)_2(tatp)]^{2+}$ as photocatalyst is fast and efficient for the UV light-induced oxidative removal of BPA.

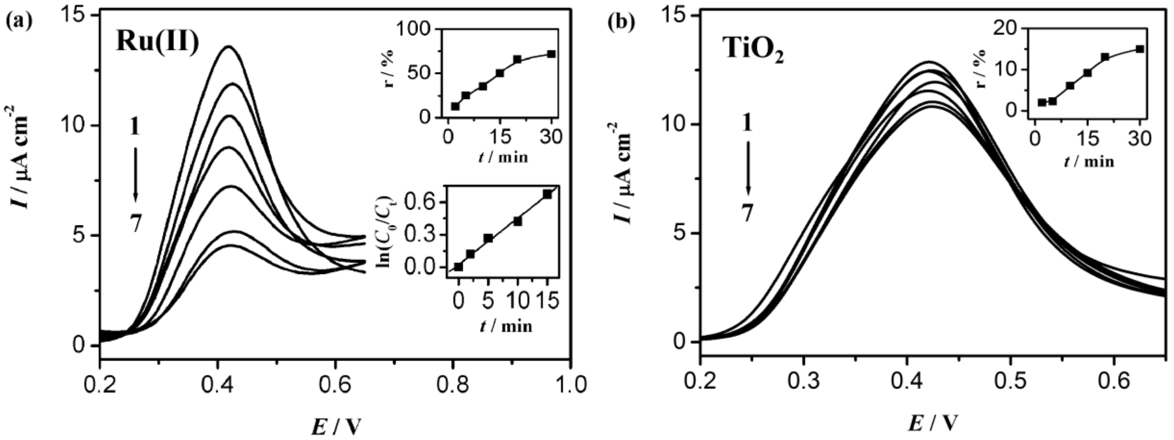

Figure 5. DPVs of 0.1 mM BPA photocatalytic by 0.1 mM $[Ru(bpy)_2(tatp)]^{2+}$ (a) or 0.5 g L^{-1} TiO_2 (b) in 0.1 M NaCl solutions under visible irradiation for different times (min): (1) 0, (2) 2, (3) 5, (4) 10, (5) 15, (6) 20, (7) 30. The inset shows the removal efficiency or $\ln(C_0/C_t)$ as a function of time.

When visible light is substituted as the excitation light source, $[Ru(bpy)_2(tatp)]^{2+}$ can also degrade BPA, with a removal efficiency of 71.5% when visible irradiation time is 30 min (Figure 5a). The removal reaction under visible light also conforms to the first-order reaction kinetic model (Figure 5a inset), with a removal rate constant of 0.043 min^{-1} (R^2=0.991). However, when TiO_2 is used as photocatalyst, the oxidation peak current of BPA only shows a slight decrease in 30 min (Figure 5b), which implies that TiO_2 can barely degrade BPA under visible irradiation due to it large band gaps [29].

The results above demonstrate that $[Ru(bpy)_2(tatp)]^{2+}$ as a photocatalyst can be highly efficient in the light induced oxidative removal of BPA under both UV and visible light irradiation, which provides a possibility for the effective use of solar energy.

Table 1. Removal efficiency of 0.1 mM BPA under UV irradiation for 30 min in the absence and presence of 200 mM mannitol (•OH scavenger) or 20 mM histidine ($^1O_2$ scavenger).

Photocatalyst	No scavenger	Scavenger	
		Mannitol	Histidine
0.1 mM $[Ru(bpy)_2(tatp)]^{2+}$	95.9%	94.6%	0
0.1 mM $[Ru(bpy)_2(tatp)]^{2+}$/0.5 g $L^{-1}TiO_2$	97.3%	70.6%	20.3%

In order to study the photocatalytic mechanism for BPA removal, Table 1 shows the removal efficiency of BPA by $[Ru(bpy)_2(tatp)]^{2+}$ or $[Ru(bpy)_2(tatp)]^{2+}/TiO_2$ in the absence and presence of mannitol or histidine under the excitation of UV light, when mannitol is a hydroxyl radical (•OH) scavenger and histidine is a singlet oxygen ($^1O_2$) scavenger [30,31]. When 0.1 mM $[Ru(bpy)_2(tatp)]^{2+}$ is used as a photocatalyst, the removal efficiency of BPA is 95.9% in 30 min. In the presence of histidine, the BPA removal efficiency is almost 0, while mannitol can hardly affect the removal efficiency of BPA, indicating that $[Ru(bpy)_2(tatp)]^{2+}$ as a photocatalyst is mainly based on the generation of $^1O_2$, which acts as an oxidizing reagent for BPA removal [32].

With 0.1 mM $[Ru(bpy)_2(tatp)]^{2+}$/0.5 g $L^{-1}$$TiO_2$ as the photocatalyst, the removal efficiency of BPA is 97.3% in 30 min. In the presence of mannitol or histidine, the BPA removal efficiency is 70.6% and 20.3%, respectively, suggesting that $[Ru(bpy)_2(tatp)]^{2+}$ modified TiO_2 nanoparticles as photocatalyst for BPA removal is an $^1O_2$ and •OH-based coupled chemical reaction.

3.3. Photoanode-induced removal of BPA

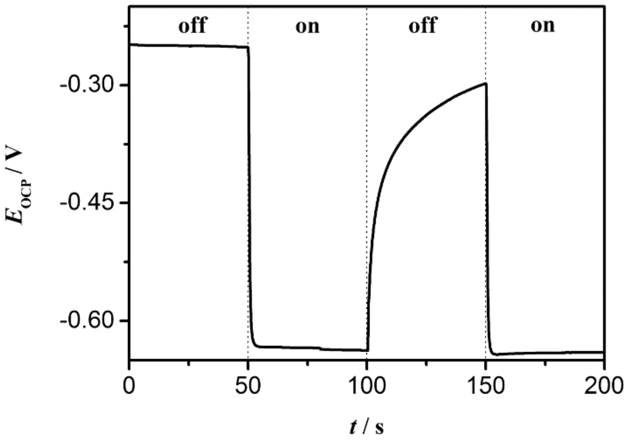

Figure 6. Effects of UV light (off and on) on cell voltage of 0.1 mM BPA fuel cells employing $[Ru(bpy)_2(tatp)]^{2+}/TiO_2$/ITO anodes.

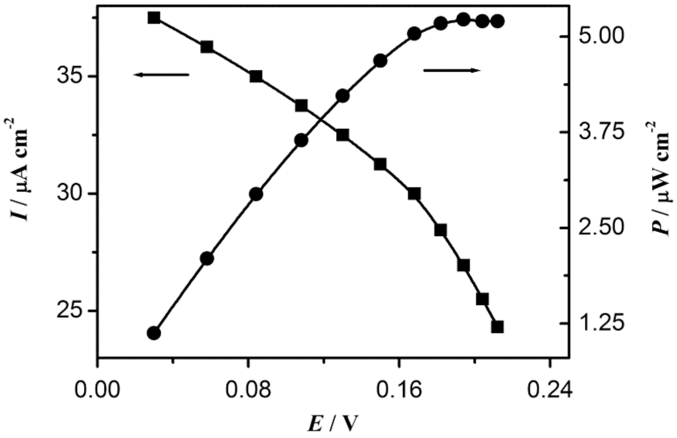

Figure 7. Cell current and power output of 0.1 mM BPA fuel cells under the excitation of UV light by altering the external load from 2000 Ω to 22000 Ω.

By 21 cycles of repetitive DPVs, the sensitizer $[Ru(bpy)_2(tatp)]^{2+}$ can be electrochemically assembled onto the TiO_2/ITO electrode [24]. The SEM and fluorescence images in Figure 1 show that TiO_2 is spherically aggregated on the ITO surface and $[Ru(bpy)_2(tatp)]^{2+}$ is uniformly distributed on the TiO_2/ITO surface [23,33,34]. Consequently, we attempted to assemble a photoactivated fuel cell, with $[Ru(bpy)_2(tatp)]^{2+}$/TiO_2/ITO as the photoanode, $[Cu(phen)_2Cl]^+$/SWCNTs/C as the cathode [25], and BPA/H_2O_2 as the oxidized/reduced fuels. As shown in Figure 6, the open-circuit photovoltages (OCP) obtained by using $[Ru(bpy)_2(tatp)]^{2+}$/TiO_2/ITO anode are −0.251 V (light off) and −0.637 V (light on), with a negative shift of 0.386 V, revealing that the excited state of Ru (II) complex produced by UV irradiation can inject electrons onto the ITO electrode through the TiO_2 layer [24]. The cell performance of the BPA fuel cells is illustrated in Figure 7, with a short-circuit photocurrent (I_{sc}) of 37.50 $\mu A\ cm^{-2}$ and a maximum power density (P_{max}) of 5.20 $\mu W\ cm^{-2}$. It is noted that photoactivated fuel cell is an ideal clean energy device that consumes "fuel" (such as organic pollutants BPA) while generating electricity, thus it provides a basis for the photo-induced oxidative removal of BPA [35]. When the UV irradiation time is 30 min, the removal efficiency of BPA is 41.3%. Comparison of BPA degradation with other published works is shown in Table 2. This is the first example for the oxidative removal of BPA based on a photo-sensitized fuel cell using polypyridyl Ru(II) complexes electrochemically assembled to TiO_2 nanoparticles as photoelectrocatalytic agents, which opens a way to search for diverse applications.

Table 2. Comparison of BPA degradation with other published works.

Catalyst	BPA concentration	Source of irradiation	Performance	Reference
CdS/TiO_2/ITO	1.0 mmol L^{-1}	visible light	48.5% in 120 min	28
Ag–BiOI/ITO	20 mg L^{-1}	visible light	88.6% in 120 min	35
Fe_3O_4/β-CD	20 mg L^{-1}	Solar	82.55% in 5 h	36
Au/TiO_2/Ti	11.2 mg L^{-1}	UV light	22.9% in 180 min	37
Zr doped TiO_2	15 mg L^{-1}	UV light	100% in 80 min	38
Ce-doped ZnO	50 mg L^{-1}	UV light	100% in 24 h	39
0.1 mM Ru(II)	0.1 mmol L^{-1}	visible light	71.5% in 30 min	this work
0.1 mM Ru(II)	0.1 mmol L^{-1}	UV light	95.9% in 30 min	this work
Ru(II)/TiO_2/ITO	0.1 mmol L^{-1}	UV light	41.3% in 30 min	this work

4. CONCLUSIONS

A photoelectrocatalytic method is successfully applied to the oxidative removal of bisphenol A (BPA). The following conclusions are derived from this study:

(1) Under the irradiation of UV light, both $[Ru(bpy)_2(tatp)]^{2+}$ and TiO_2 can induce the oxidative removal of BPA. As visible light is substituted, $[Ru(bpy)_2(tatp)]^{2+}$ can also effectively induce the oxidative removal of BPA, while TiO_2 can hardly degrade BPA.

(2) On the basis of the photoelectrocatalytic oxidation of BPA induced by $[Ru(bpy)_2(tatp)]^{2+}$-sensitized TiO_2 anodes, a photoactivated fuel cell is fabricated with UV light as the excitation light source. Based on the BPA/H_2O_2 photoactivated fuel cell, a removal efficiency of 41.3% is obtained in 30 min.

(3) The removal mechanism experiments indicate that $[Ru(bpy)_2(tatp)]^{2+}$ as a photocatalyst for BPA removal is mainly based on the generation of singlet oxygen ($^1O_2$), and $[Ru(bpy)_2(tatp)]^{2+}$ modified TiO_2 nanoparticles is an $^1O_2$ and •OH-based coupled chemical reaction.

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