

ELECTROCHEMICAL CHARACTERIZATION OF PbO₂-TiO₂ COMPOSITE PREPARED ON STAINLESS STEEL SUBSTRATE BY CYCLIC VOLTAMMETRY METHOD

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Abstract. In this study, PbO₂-TiO₂ composite was prepared on stainless steel (SS) substrate by cyclic voltammetry (CV) method from mixed solution containing TiO₂ sol-gel with size from 10 to 50 nm. In the electrochemical deposition, TiO₂ nanoparticle will disperse in the growing PbO₂ coating to create PbO₂-TiO₂ composite. These TiO₂ nanoparticles are delivered from the electrolyte bulk to the electrode surface by diffusion and migration. The electrochemical properties of SS/PbO₂-TiO₂ electrodes were investigated in 0.5 M H₂SO₄ solution by CV, PP (potentiodynamic polarization), and EIS (electrochemical impedance spectroscopy) methods with and without UV irradiation. The results showed that the exchange current density (i_0), the value of both the oxidation and reduction peaks ($i_{p,a}$ and $i_{p,c}$, respectively) depended on the TiO₂ concentration. With a solution containing 2 g/L TiO₂, the value of the redox peaks is the largest and the exchange current density obtained is close the maximum value, indicating that the SS/PbO₂-TiO₂ composite electrode exhibits the best electrochemical activity under this solution condition. Due to the presence of TiO₂ in the composite, the height of the redox peaks and the exchange current density increased sharply under UV light. This demonstrated that the photo-electrochemical activity of the composite is very good, which can be used to remove dyes in wastewater by electrocatalytic oxidation.

Keywords: SS/PbO₂-TiO₂, cyclic voltammetry, exchange current density, impedance spectroscopy

Classification numbers: 2.4.4, 2.5.2, 2.10.2.

1. INTRODUCTION

Lead dioxide (PbO₂) is a semiconductor material that is applied in many fields such as electrochemical sensors [1], treatment of toxic organic substances [2, 3], and power source materials [4]. To enhance the electrochemical activity of PbO₂, it was doped with some metal

oxides such as SnO₂ [5, 6], TiO₂ [7, 8], MnO₂ [9], and ZrO₂ [10], in which, TiO₂ was widely used to doping with PbO₂ to create composites with good electrochemical activity on different substrates such as Ti [11], Ti/SnO₂-Sb [12], and SS [13]. PbO₂-TiO₂ composites were synthesized by many different methods such as constant current [13 - 15] and constant potential [16]. However, the fabrication of PbO₂-TiO₂ coatings on SS substrates by CV method has not been completed yet.

In this paper, PbO₂-TiO₂ composites were deposited on SS substrates by using CV technique in a solution containing Pb(NO₃)₂ and additives. Then, their electrochemical properties were investigated in H₂SO₄ solution by electrochemical methods such as CV, PP- and EIS measurements under UV light and without UV irradiation.

2. MATERIALS AND METHODS

2.1. Materials

Nitric acid (65 - 68 %), copper (II) nitrate trihydrate (> 99 %), sodium hydroxide (> 99 %), ethylene glycol (> 99 %), and sulfuric acid (95 - 98 %) are provided by Xilong Scientific Co. Ltd (China). Lead nitrate (> 99 %) is provided by Merck (Germany) and TiO₂ nanoparticles are provided by a laboratory from the Institute for Applied Physics (Vietnam Academy of Science and Technology).

2.2. Preparation of samples

First, the substrates were polished on sandpaper from 400 to 2000. Next, they were dipped in a concentrated H₂SO₄ solution containing K₂Cr₂O₇ to dissolve impurities. Then, they were handled in 60 g/L NaOH solution by CV method at a scan rate of 100 mV/s to clean their surface. Finally, PbO₂-TiO₂ composite was deposited on SS substrates by CV method (scan rate of 50 mV/s, 300 cycles) in a solution containing 0.5 M Pb(NO₃)₂, 0.05 M Cu(NO₃)₂, 0.1 M HNO₃, 0.1 M C₂H₆O₂, and TiO₂ nanoparticles (varying from 0.5 to 3.0 g/L).

2.3. Research methods

Electrochemical measurements of SS/PbO₂-TiO₂ electrodes were performed by a three-electrode system consisting of a Pt sheet as counter electrode, SS/PbO₂-TiO₂ electrode as working electrode, and Ag/AgCl, sat.KCl electrode as reference electrode. The electrochemical properties of the electrodes were investigated in 0.5 M H₂SO₄ solution by CV (scan rate of 100 mV/s, potential region from 0.8 to 1.8 V), PP (scan rate of 5 mV/s, potential from -200 to +200 mV compared to open circuit potential (OCP)), and EIS (frequency from 10 mHz to 100 kHz, amplitude of 5 mV) methods under UV light and without UV irradiation.

3. RESULTS AND DISCUSSION

3.1. Cyclic voltammetry

Figure 1 shows the CV curves at the 30th cycle of SS/PbO₂-TiO₂ composite electrodes in 0.5 M H₂SO₄ solution at a scan rate of 100 mV/s. There are two oxidation peaks at about 1.60 and 1.75 V indicating that PbO₂ is formed in the α and β structural forms. However, there is only one reduction peak that appears at about 1.21 V reflecting β -PbO₂ being reduced to PbSO₄.

These redox peaks all appear at potential positions on the CV spectra similar to those reported in previous studies [17, 18]. As the TiO₂ concentration increases from 0.5 to 2.0 g/L, the values of the oxidation and reduction peaks both increase (from -163 mA/cm² to -209 mA/cm² and from 94.7 mA/cm² to 123 mA/cm², respectively). But continuing to increase from 2.0 to 3.0 g/L, their values decrease (-197 mA/cm² and 114 mA/cm², respectively). The height of the peak characterizes the electrical conductivity and the electrode catalyst. The higher the height of the peak, the better the conductivity and electrochemical activity of the electrode [18]. Therefore, an electrolytic solution containing TiO₂ with a concentration of 2 g/L is the most suitable.

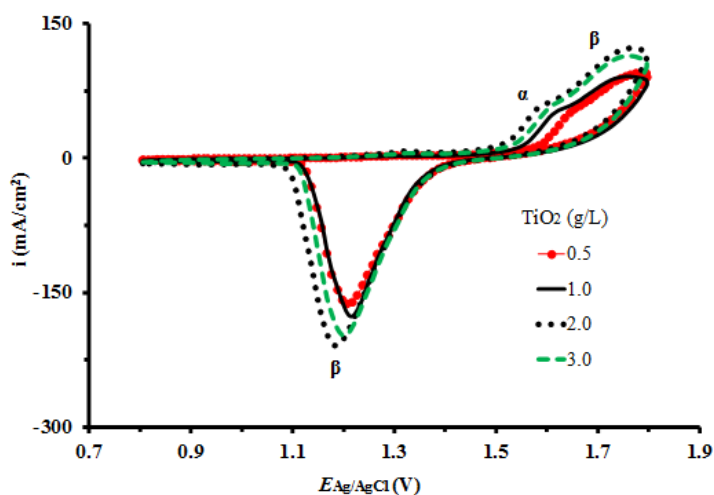


Figure 1. Influence of TiO₂ concentration during sample preparation on the CV spectra (the 30th cycle) of SS/PbO₂-TiO₂ electrodes measured in 0.5 M H₂SO₄ solution (scan rate of 100 mV/s, potential range of 0.8 - 1.8 V).

Figure 2 shows the CV curves of SS/PbO₂ compared to those of SS/PbO₂-TiO₂ composite electrodes in 0.5 M H₂SO₄ solution at a scan rate of 100 mV/s under UV light. In the 1st cycle, there was no oxidation peak appearing, but two reduction peaks were observed at about 1.18 and 1.26 V indicating the reduction of α and β -PbO₂ to lead sulfate, respectively [18]. From the 2nd cycle, there was only one reduced peak reflecting β form and it increased following the number of cycles, however, the position of this peak potential was shifted slightly to the left side. From the 5th cycle, there were two oxidation peaks at about 1.60 and 1.75 - 1.77 V.

Table 1. Kinetic parameters of SS/PbO₂ electrode from Figure 2a (samples prepared with 300 cycles at 50 mV/s).

Number of CV cycle	Oxidation peak				Reduction peak			
	into α -PbO ₂		into β -PbO ₂		from α -PbO ₂		from β -PbO ₂	
	E _p (V)	i _p (mA/cm ²)	E _p (V)	i _p (mA/cm ²)	E _p (V)	i _p (mA/cm ²)	E _p (V)	i _p (mA/cm ²)
1	-	-	-	-	1.16	-49.5	1.27	-38.9
2	-	-	-	-	-	-	1.27	-36.4
5	1.61	9.4	1.78	35.2	-	-	1.25	-61.8
10	1.61	29.9	1.79	57.4	-	-	1.23	-112.0
20	1.61	36.8	1.78	77.1	-	-	1.21	-140.0
30	1.61	43.8	1.78	87.9	-	-	1.20	-153.0

The data of peak potential and the value of peak current density for the SS/PbO₂ and SS/PbO₂-TiO₂ electrodes are given in Tables 1 and 2, respectively. The results show that under UV light the redox peaks of the SS/PbO₂-TiO₂ electrode are 1.5 times higher than those of the SS/PbO₂ electrode due to the presence of TiO₂.

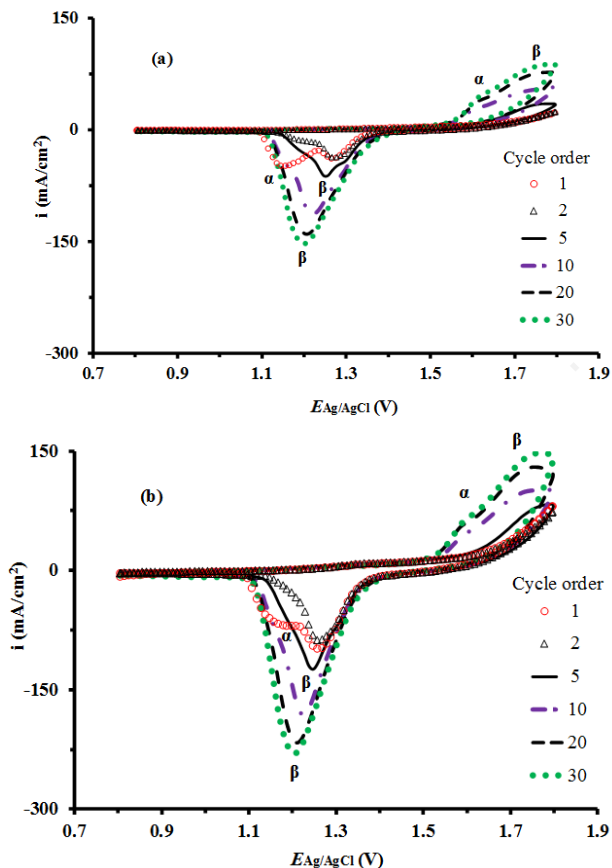


Figure 2. CV spectra of (a) SS/PbO₂ and (b) SS/PbO₂-TiO₂ electrodes measured in 0.5 M H₂SO₄ under UV irradiation (scan rate of 100 mV/s; potential range of 0.8 - 1.8 V) (samples prepared with 300 cycles at scan rate of 50 mV/s).

Table 2. Kinetic parameters of SS/PbO₂-TiO₂ electrode from Figure 2b (samples prepared with 300 cycles at 50 mV/s).

Number Of CV cycle	Oxidation peak				Reduction peak			
	into α -PbO ₂		into β -PbO ₂		from α -PbO ₂		from β -PbO ₂	
	E _p (V)	i _p (mA/cm ²)	E _p (V)	i _p (mA/cm ²)	E _p (V)	i _p (mA/cm ²)	E _p (V)	i _p (mA/cm ²)
1	-	-	-	-	1.18	-69.2	1.26	-98.7
2	-	-	-	-	-	-	1.26	-87.8
5	1.60	21.6	1.77	81.7	-	-	1.25	-124
10	1.60	48.9	1.75	101	-	-	1.23	-182
20	1.60	61.4	1.75	130	-	-	1.22	-214
30	1.60	67.4	1.76	148	-	-	1.21	-230

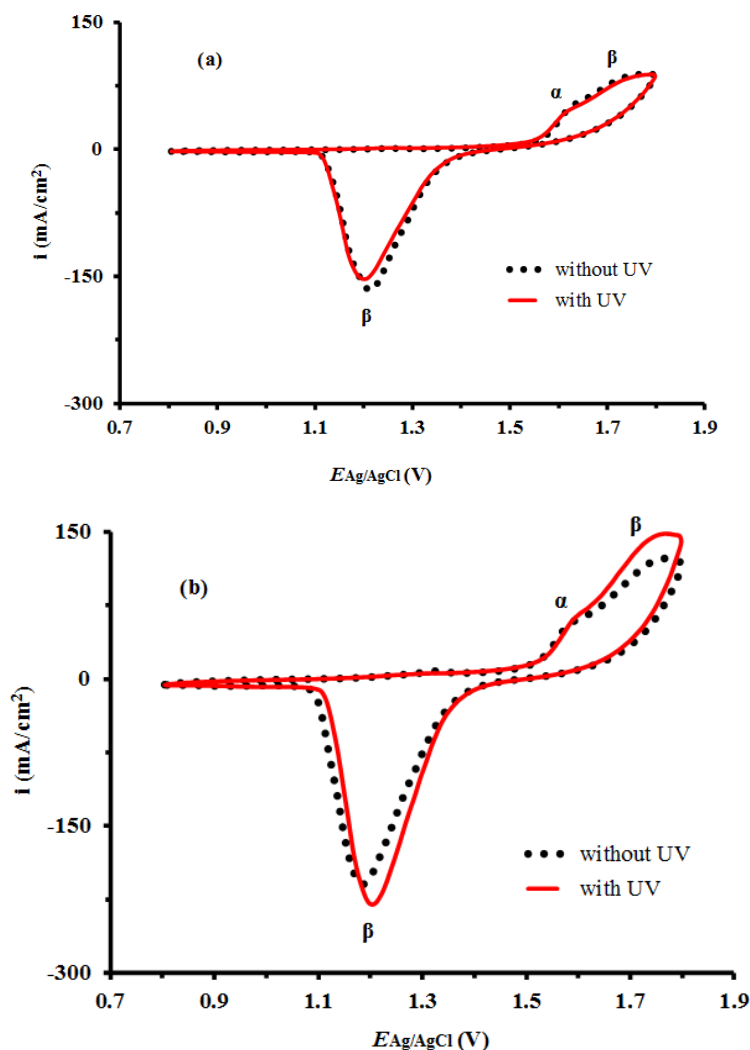


Figure 3. CV curve at the 30th cycle of (a) SS/PbO₂ and (b) SS/PbO₂-TiO₂ electrodes measured in 0.5M H₂SO₄ under UV and without UV irradiation (scan rate of 100 mV/s; potential range of 0.8 - 1.8 V).

The CV spectrum at the 30th cycle of SS/PbO₂ compared to that of SS/PbO₂-TiO₂ electrode measured in 0.5M H₂SO₄ under UV light and without UV irradiation is displayed in Figure 3. For the SS/PbO₂ electrode (Figure 3a), the value of redox peaks was almost unchanged under UV light and without UV irradiation. In contrast, it increased clearly when the SS/PbO₂-TiO₂ electrode (Figure 3b) was worked under UV light, suggesting a role of TiO₂ in the coating due to its photo-electrochemical property [19]. TiO₂ is a material that has good photocatalytic and photo-electrocatalytic abilities, in which TiO₂ nanoparticles exhibit higher photocurrent than TiO₂ microparticles because of their higher specific surface area [20]. Furthermore, in order to have a uniform composite structure and for TiO₂ to easily go deep into the structure of PbO₂ during the electrodeposition process, the use of TiO₂ nanoparticles is more suitable than TiO₂ microparticles for intercalation. The height of the peak reflects the redox capacity of the material. Therefore, the higher the peak, the greater the redox rate.

3.2. Determination of exchange current density

In essence, PbO_2 and $\text{PbO}_2\text{-TiO}_2$ are metal oxide coatings with good electrical conductivity, often used as electrochemical catalyst materials for the oxidation of some organic compounds present in wastewater [2, 7, 12]. According to a previously published work [21], the higher the exchange current density (ECD) of the electrode, the better its electrocatalytic ability. Therefore, the PP curves were measured in 0.5 M H_2SO_4 containing TiO_2 at concentrations varying from 0.5 to 3.0 g/L for detecting ECD of the samples. They are set in logarithmic form (Figure 4) to determine the ECD (i_0) by extrapolating the Tafel straight line. The results given in Table 3 show that i_0 increases sharply with TiO_2 concentrations in the range of 0.5 - 2.0 g/L, and then slightly increases.

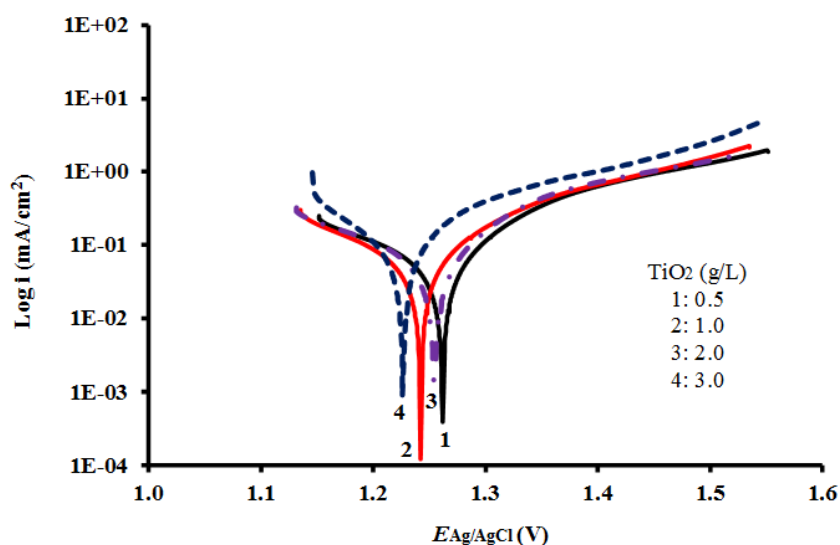


Figure 4. Influence of TiO_2 concentration during sample preparation on PP curves in logarithmic form measured in 0.5 M H_2SO_4 (scan rate of 5 mV/s).

Table 3. Effect of TiO_2 concentration when synthesized with 300 cycles, at 50 mV/s on kinetic parameters obtained from Figure 4.

TiO_2 concentration (g/L)	i_0 ($\mu\text{A}/\text{cm}^2$)	E_0 (V)
0.5	39.6	1.263
1.0	44.2	1.243
2.0	53.4	1.254
3.0	56.6	1.225

The PP curves in logarithmic form of $\text{SS}/\text{PbO}_2\text{-TiO}_2$ electrode measured in 0.5 M H_2SO_4 under UV light and without UV irradiation are shown in Figure 5. When the electrode worked under UV light, i_0 reached $79.3 \mu\text{A}/\text{cm}^2$, higher than without UV irradiation ($53.4 \mu\text{A}/\text{cm}^2$). This suggests a useful role of TiO_2 in the coating due to its photoelectrochemical properties under UV light. The improved i_0 will increase the electrocatalytic ability of the $\text{SS}/\text{PbO}_2\text{-TiO}_2$ electrode. This result is in good agreement with the CV result mentioned above.

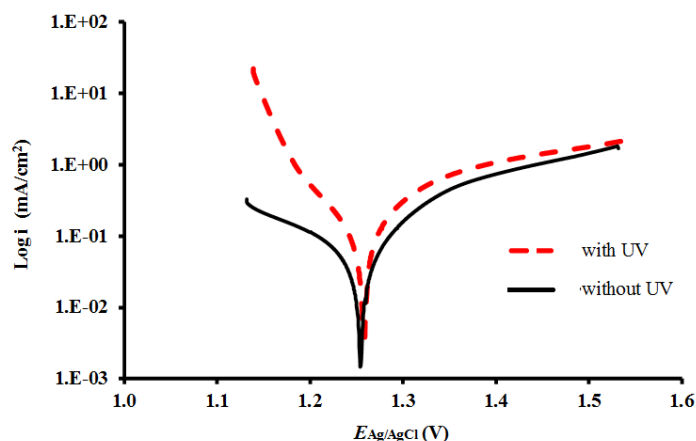


Figure 5 The PP curves (scan rate of 5 mV/s) in logarithmic form of SS/PbO₂-TiO₂ electrode measured in 0.5 M H₂SO₄ under UV and without UV irradiations (sample prepared under condition of 2 g/L TiO₂).

3.3. EIS study

Figure 6a shows the EIS of SS/PbO₂-TiO₂ composite electrode in Nyquist plot where the symbols are measured points and the solid lines are simulated ones under UV light and without UV irradiation. Through the simulation process, we know how the electrochemical process occurred.

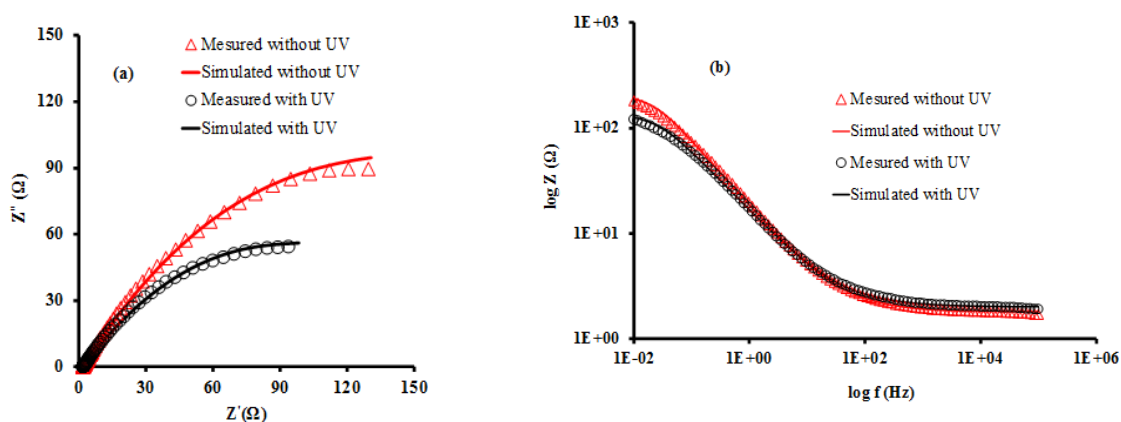


Figure 6. Comparison of EIS curves of SS/PbO₂-TiO₂ composite electrode measured in 0.5 M H₂SO₄ under UV and without UV irradiation (amplitude of 5 mV; frequency range of 10 mHz-100 kHz).

The results given in Figure 7 and Table 4 show an electrical equivalent circuit (EES) from Figure 6, including R_s , R_{ct1} , C_{CPE1} , R_{ct2} , C_{CPE2} , and C_{CPE3} . Fitting errors were 3.31 and 4.45 % for the case under UV light and without UV irradiation, respectively. The appearance of constant phase components (C_{CPE1} , C_{CPE3}) is due to the coatings having a porous solid structure and rough surface, while the C_{CPE2} formed may be due to the solution containing traces of impurities that lead to the pseudo-capacitive process illustrating CPE behavior [22]. In the absence of UV irradiation, the values of R_{ct1} and R_{ct2} are 148.7 and 82.53 Ω , respectively, indicating that the

charge transfer place on the electrode surface is more difficult than in the pore. In contrast, under UV light, they receive smaller values (95.17 and 51.32 Ω), decreasing by about 36-38 %. Besides, the value of electrochemical impedance Z at 10 mHz found at the electrode under UV light is 120.3 Ω , smaller than that found in the absence of UV light (181.1 Ω). This explains that the photo-electrochemical capacity of composite electrode has increased [19].

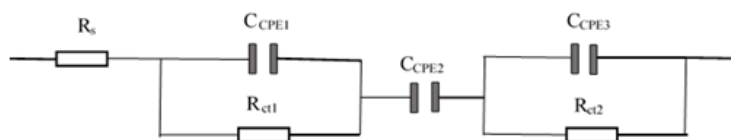


Figure 7. Electrical equivalent circuit for EIS curves in Figure 6.

R_s : Solution resistance
 R_{ct1} : Charge transfer resistance of the processes occurring on the electrode surface
 C_{CPE1} : Constant phase element of the electrode film
 C_{CPE2} : Pseudo constant phase element
 R_{ct2} : Charge transfer resistance of the processes occurring in the pore
 C_{CPE3} : Constant phase element of the processes occurring in the pore

Table 4. EIS simulation parameters of SS/PbO₂-TiO₂ composite electrode under UV light and without UV irradiation obtained from Fig. 6 and Fig. 7.

State of electrodes	R_s	C_{CPE1}		R_{ct1}	C_{CPE2}		R_{ct2}	C_{CPE3}	
	Ω	μF	α	Ω	μF	α	Ω	μF	α
Without UV	1.80	759.4	0.632	148.7	8.55	1.282	82.53	55.41	0.980
Under UV	2.00	712.4	0.610	95.2	9.51	1.254	51.32	56.31	0.951

4. CONCLUSIONS

The SS/PbO₂-TiO₂ composite electrode can be obtained by cyclic voltammetry method. The electrochemical properties of the composite were studied through the CV, PP, and EIS methods. The results showed that the solution containing 2 g/L TiO₂ has the best electrochemical properties. When irradiated with UV light, the electrochemical activity of the SS/PbO₂-TiO₂ composite electrode increased greatly. This demonstrated the photo-electrochemical properties of the composite due to the presence of TiO₂.

CRedit authorship contribution statement. Pham Thi Tot: Experiment, Investigation, Writing – original draft. Mai Thi Thanh Thuy: Data analysis, Resources. Phan Thi Binh: Data analysis, Writing–review and editing, Supervision.

Declaration of competing interest. The authors state no conflict of interest.

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