

Studies on the preparation and the photoelectrochemical properties of the nanoporous titania films attached with and without photosensitizer TCPP

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Abstract. Fabrication of TiO₂ nanoporous films was carried out by anodic oxidation using two-step voltage mode while the subsequent attaching of the photosensitizer 5,10,15,20-tetra(4-carboxyphenyl) porphyrin (TCPP) on the prepared TiO₂ nanoporous films was carried out by the electrochemical method. Photoelectrochemical properties of TiO₂ nanoporous films attached with and without photosensitizer TCPP were analysed by fluorescence spectroscopy and electrochemical test. Effects of process parameters on the photoelectrochemical properties of TiO₂ nanoporous films were also investigated. The optimized process parameters for the preparation of TiO₂ nanoporous films with the best photoelectrochemical property can be concluded as follows: oxidation potentials is 70–140 V, oxidation temperature is 25°C, H₂SO₄ electrolyte concentration is 0.5 mol l⁻¹ and oxidation time is 60 min. The results also show that attaching of the photosensitizer TCPP on the TiO₂ nanoporous films can indeed improve the properties of TiO₂ nanoporous films, and the optimized attaching temperature and attaching voltage are 25°C and 60 V, respectively.

Keywords. TiO₂; photosensitizer; nanoporous films; anodic oxidation; TCPP; electrochemical attaching method.

1. Introduction

In recent years, metal oxide TiO₂ has been widely studied for its rich source, low cost, environment friendly and chemical stability. Due to its high photocatalytic activity, TiO₂ thin film plays an important role in photovoltaic devices. However, TiO₂ is active only under ultraviolet light irradiation due to its wide band gap energy, which reduces its utilization ratio of solar energy and thus limits its application in solar cell. Since the spectral response of TiO₂ can move to visible region after with the reduction of dimensions or by sensitizing TiO₂ with proper photosensitizer which transition energy matches well with nano-structure TiO₂,^{1–3} the preparation of TiO₂ materials with nanometer size, such as TiO₂ nanoporous films, and TiO₂ materials sensitized with photosensitizer have attracted enormous attention.

In recent times, porphyrin has received much attention as a potential alternative photosensitizer owing to its high optical, thermal and chemical stability as well as its strong absorption spectra of characteristic electron in the visible region. In order to optimize porphyrin molecular properties and then improve the photovoltaic properties of the dye-sensitized solar cells (DSSCs) using porphyrin as the photosensitizer, porphyrin dyes are widely studied and designed by researchers at home and abroad. Results of the research works showed that carboxyl rather than other groups could well complete the electron transmission no matter whether it is connected on the meta position or the β -position of porphyrin.⁴

Although research works on the structure optimization of porphyrin have obtained considerable improvements,^{5,6} studies on the attaching technologies of the photosensitizer have not caused enough attentions, which lead to the limitation of further enhancing of the photoelectric conversion efficiencies of DSSC. At present, the sol–gel method and coating method are two normally used methods for the attaching of the photosensitizer.^{7–10} But these two methods have many disadvantages, for example, only physical bonding instead of chemical bonding can be established between the photosensitizer and TiO₂, which causes the electron transmission resistance from photosensitizer to TiO₂ increase. Furthermore, low binding force can lead to the break off of the coatings and further results in the shortening of the photosensitizer's service life.¹¹ Moreover, photosensitizer coated outside TiO₂ nano-grain will hinder the inner electron transmission to a certain extent.¹²

In general, high transmission resistance of electron from photosensitizer to TiO₂ is the bottleneck for the further enhancement of photoelectric conversion efficiencies. This problem can be solved if an unblocked transmission channel of electron from photosensitizer to TiO₂ can be established, and this is totally depended on the bonding mode between photosensitizer and TiO₂. Hence in the present research works, TiO₂ nanoporous films were firstly prepared by anodic oxidation. Based on which, attaching of the photosensitizer on the prepared TiO₂ nanoporous films were conducted using a new mode by the electrochemical method. The photoelectrochemical properties of TiO₂ nanoporous films attached with and without photosensitizer 5,10,15,20-tetra(4-carboxyphenyl) porphyrin (TCPP) were characterized and compared

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by fluorescence spectroscopy and electrochemical test. And effects of process parameters on the properties of TiO_2 nanoporous films were also investigated.

2. Experimental

2.1 Experimental chemicals and materials

All the chemicals were of analytical grade and used as-received. And all the solutions were prepared with redistilled water to ensure the stabilities of ions in the solution.

2.2 Pre-treatment of metal Ti

Before anodic oxidation, metal Ti needs to be pre-treated to remove the natural TiO_2 film and grease on the Ti sheet.¹³ The experimental details are given as follows.

Briefly, Ti sheet with purity of 99.9% was cut into pieces with the size of $20 \times 20 \times 0.1$ mm. Then a certain kind of resin was used to seal the Ti sheet between two sheet glasses with only the reaction region (15×15 mm) and the conductive part exposed outside (as shown in figure 1). Later, surface of the reaction region was cleaned by absorbent cotton immersed with acetone and rinsed with redistilled water. Then the sealed Ti specimen was immersed into 5% sodium hydroxide solution at 50°C for 5 min and 0.5% sulphuric acid solution and at room temperature for 10 s, successively, while rinsing of the specimen with redistilled water was conducted after each step. Finally, electrochemical degreasing of the Ti specimen was carried out at room temperature in the degreasing solution using Pt and Ti sheets as anode and cathode, respectively. After rinsing the Ti specimen with redistilled water for the last time, the whole pre-treatment of metal Ti was completed.

2.3 Preparation of TiO_2 nanoporous films by anodic oxidation

After pre-treatment, Ti specimen was anodic oxidized in the 0.5 mol l^{-1} sulphuric acid solution using a two-step voltage mode. Under this mode, a low potential (called as initial potential) was firstly applied on the electrode and leads to the rapid increase and sudden decline of the current density. When the current density decrease to the lowest value (a compact barrier layer was formed), a high potential (called as discharge potential) was applied immediately and the current

density will rapidly increase and suddenly decline again (nanoporous were formed), and finally become stable. The potentials mentioned here are the potential difference between the anode and cathode, and 'initial potential-discharge potential' was used to express the applied oxidation potential value in this paper.

2.4 Synthesis of photosensitizer TCPP

A certain amount of 4-carboxybenzaldehyde, pyrrole, propionic acid were mixed and refluxed at 140°C for 4 h. After cooling to room temperature, the mixture was added with ethanol, magnetic stirred and stored under room temperature overnight for crystallization. The precipitated crystal was collected by filtration and washed with methanol. Then a mixture of chloroform and acetone was added into the product, while mixture of tetrahydrofuran (THF) and acetic acid was used to elute the product. The synthesized product was analysed by infrared spectroscopy and ultraviolet spectroscopy and the results are shown in figures 2 and 3, respectively. By comparison of figure 2a with the peak value in literature (figure 2b),¹⁴ it can be found that the peak value of the synthesized product matches well with the literature value, which means that the synthesized product is indeed TCPP. Results shown in figure 2 further confirmed this conclusion.

2.5 Attaching of photosensitizer TCPP on TiO_2 nanoporous films

Photosensitizer TCPP was attached on the prepared TiO_2 nanoporous films by the electrochemical method through constant voltage mode. The electrolyte used for the attachment was a mixture of H_2SO_4 solution and N,N-dimethylformamid (DMF) solution dissolved with TCPP. The electrolyte was prepared as follows: first, $1.6 \times 10^{-4} \text{ g ml}^{-1}$ TCPP DMF solution was prepared by dissolving 0.04 g TCPP in DMF and setting the volume to be 250 ml. Then the electrolyte could be obtained by mixing 100 ml of $1.6 \times 10^{-4} \text{ g ml}^{-1}$ TCPP DMF solution with 27.17 ml of 98% H_2SO_4 solution and setting the volume to be 1000 ml. During the attaching process, working electrode (prepared TiO_2 nanoporous films) and counter electrode (Ti mesh covered with a layer of electrodeposited Pt) were connected with the positive electrode and negative electrode of the electrical source, respectively.

2.6 Characterization of the TiO_2 thin films

Electrochemical measurements were performed at ambient temperature using CHI660E electrochemical working station (Huakeputian Instruments, Inc., Beijing). A standard three-electrode cell (shown in figure 4), which consists of a prepared TiO_2 film as the working electrode, a platinum plate as the auxiliary electrode, an aqueous KCl saturated calomel electrode (SCE) as the reference electrode and $0.25 \text{ mol l}^{-1} \text{Na}_2\text{SO}_4$

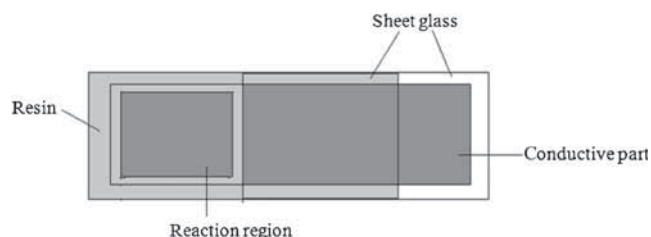


Figure 1. Schematic view of the metal Ti piece.

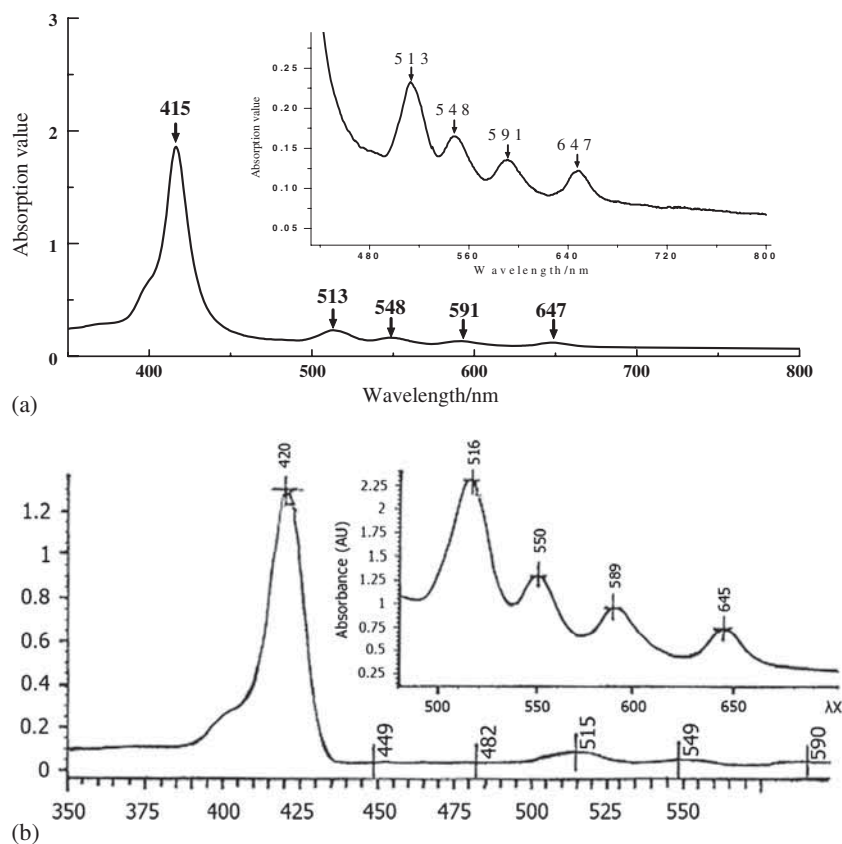


Figure 2. (a) UV-Vis absorption spectra of synthesized TCPP. (b) UV-Vis absorption spectra of TCPP in literature.

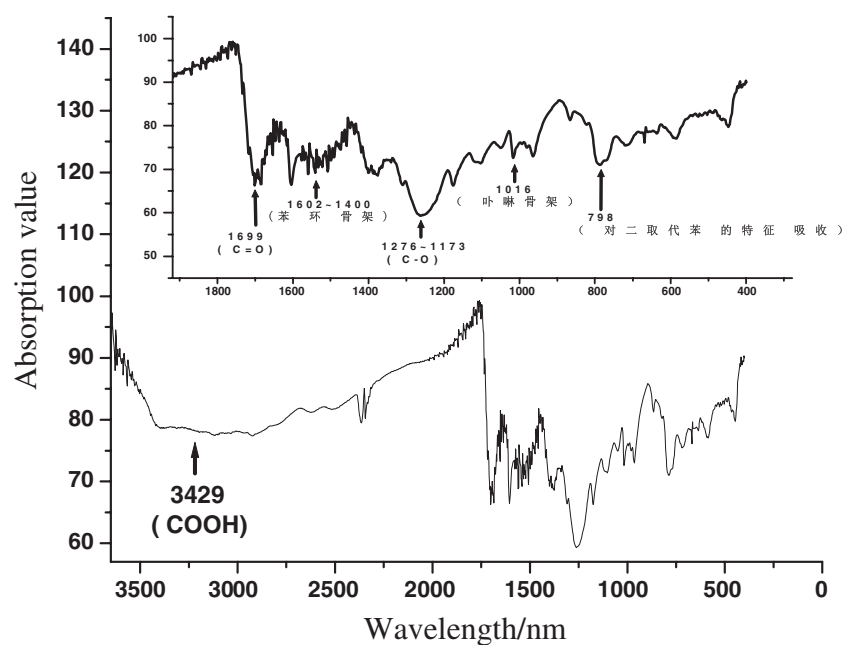


Figure 3. Infrared spectrum of synthesized TCPP.

solution as the electrolyte, was used for the electrochemical measurement. The working electrode was electrochemically degraded and rinsed with redistilled water in order to ensure

a clean surface before the measurements. Solution was not stirred during all the electrochemical measurements. The three-electrode cell was placed into a photochemical reaction

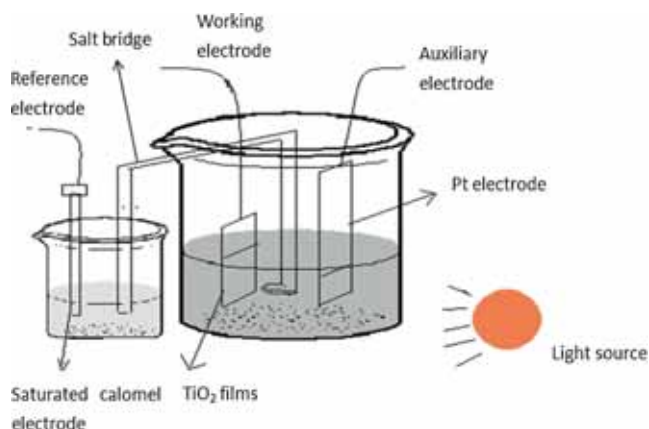


Figure 4. Schematic view of the three-electrode cell.

device (manufactured by Beijing NBET Technology Co., Ltd.) which contained a built-in Xenon lamp light source (Solar-500) simulating the solar light. The location of the three-electrode cell was adjusted to ensure that the light can vertically lay on the TiO_2 films. The photoelectrochemical properties of the prepared TiO_2 films were characterized by the open-circuit potential–time curves which were recorded alternately under the condition of lighting and darkness with the alternate time of 100 s and the total testing time of 600 s.

The fluorescence spectra of the TiO_2 films were obtained by fluorescence spectrophotometer (Jobin Yvon FL3-212-Tcspc) in the wavelength range of 300–800 nm with the excitation wavelength of 370 nm.

3. Results and discussions

3.1 Photoelectrochemical properties of TiO_2 nanoporous films

3.1a Effects of oxidation potential on the photoelectrochemical properties of TiO_2 nanoporous films: TiO_2 nanoporous films were prepared under different oxidation potentials at 25°C in 0.5 mol l^{-1} H_2SO_4 solution with the oxidation time of 60 min. The photoelectrochemical properties of the prepared TiO_2 nanoporous films were characterized by the open-circuit potential–time curves under the condition of lighting and darkness. And the results are shown in figure 5 and table 1.

It can be seen in figure 5 that the open-circuit potential changed obviously when the lighting condition alternates between lighting and darkness. Since lighting can promote the rapid separation of photogenerated electrons and holes which will successively diffuse to the interface between the electrode and solution, affect the electric double layer and further affect the open-circuit potential, change of the open-circuit potential under the condition of lighting and darkness can be used to evaluate the photoelectrochemical properties of the semiconductor materials. The more sensitive of the semiconductor materials to the light, the much bigger of ΔV can be observed.

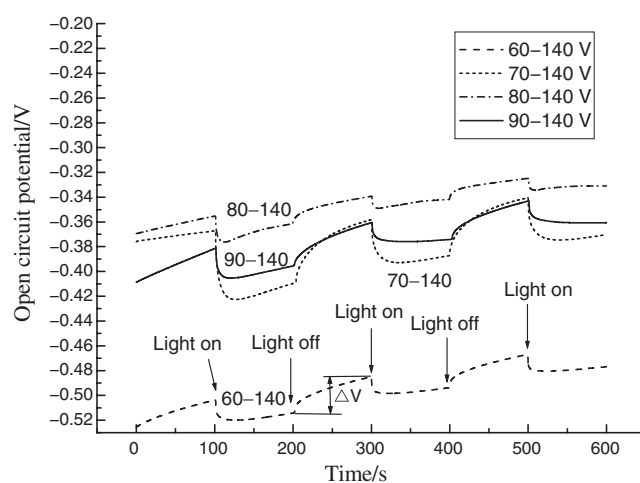


Figure 5. Open-circuit potential–time curves of TiO_2 nanoporous films prepared under different oxidation potentials.

Table 1. ΔV comparisons of TiO_2 nano-pore films prepared under different oxidation potentials.

Oxidation potential (V)	H_2SO_4 concentration (mol l^{-1})	Oxidation time (min)	Oxidation temperature (°C)	ΔV (V)
60–140	0.5	60	25	0.029
70–140	0.5	60	25	0.051
80–140	0.5	60	25	0.023
90–140	0.5	60	25	0.035

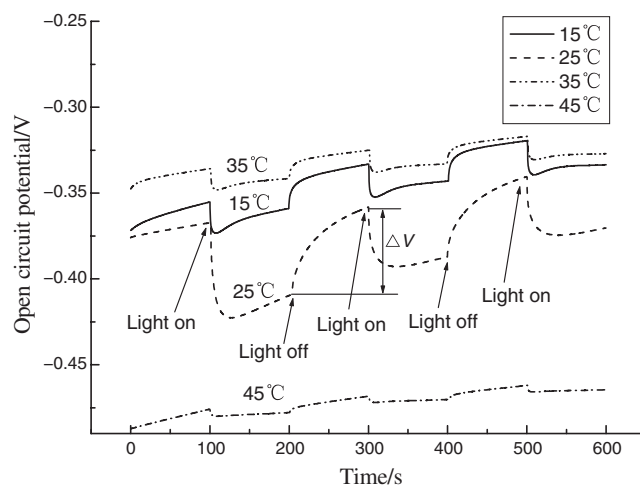


Figure 6. Open-circuit potential–time curves of TiO_2 nanoporous films prepared at different oxidation temperatures.

It can be seen from figure 5 and table 1 that TiO_2 nanoporous films prepared under 70–140 V show the highest ΔV value, which reveals that the TiO_2 nanoporous films prepared under 70–140 V possess the best photoelectrochemical property.

3.1b Effects of oxidation temperature on the photoelectrochemical properties of TiO₂ nanoporous films: TiO₂ nanoporous films were prepared at different oxidation temperatures under 70–140 V in 0.5 mol l⁻¹ H₂SO₄ solution with the oxidation time of 60 min. The photoelectrochemical properties of the prepared TiO₂ nanoporous films were characterized by the open-circuit potential–time curves under the condition of lighting and darkness. And the results are shown in figure 6 and table 2.

It can be seen from figure 6 and table 2 that TiO₂ nanoporous films prepared at 25°C show the highest ΔV value, which reveals that the TiO₂ nanoporous films prepared at 25°C possess the best photoelectrochemical property.

Table 2. ΔV comparisons of TiO₂ nano-pore films prepared at different oxidation temperatures.

Oxidation temperature (°C)	H ₂ SO ₄ concentration (mol l ⁻¹)	Oxidation potential (V)	Oxidation time (min)	ΔV (V)
15	0.5	70–140	60	0.026
25	0.5	70–140	60	0.051
35	0.5	70–140	60	0.017
45	0.5	70–140	60	0.010

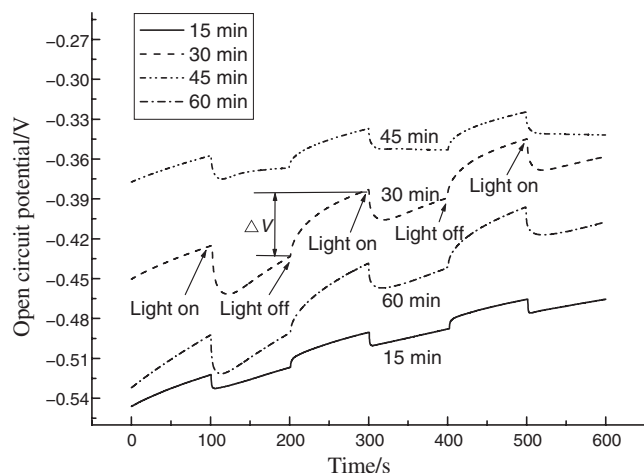


Figure 7. Open-circuit potential–time curves of TiO₂ nanoporous films prepared under different oxidation times.

Table 3. ΔV comparisons of TiO₂ nano-pore films prepared under different oxidation times.

Oxidation time (min)	Oxidation potential (V)	H ₂ SO ₄ concentration (mol l ⁻¹)	Oxidation temperature (°C)	ΔV (V)
15	70–140	0.5	25	0.026
30	70–140	0.5	25	0.051
45	70–140	0.5	25	0.028
60	70–140	0.5	25	0.053

3.1c Effects of oxidation time on the photoelectrochemical properties of TiO₂ nanoporous films: TiO₂ nanoporous films were prepared with different oxidation times under 70–140 V in 0.5 mol l⁻¹ H₂SO₄ solution at 25°C. The photoelectrochemical properties of the prepared TiO₂ nanoporous films were characterized by the open-circuit potential–time curves under the condition of lighting and darkness. And the results are shown in figure 7 and table 3.

It can be seen from figure 7 and table 3 that TiO₂ nanoporous films prepared with the oxidation time of 60 min show the highest ΔV value, which reveals that the TiO₂ nanoporous films prepared with the oxidation time of 60 min possess the best photoelectrochemical property.

Based on the above analysis, it can be concluded that the optimized process parameters for the preparation of TiO₂ nanoporous films with the best photoelectrochemical property are as follows: oxidation potentials is 70–140 V, oxidation temperature is 25°C, H₂SO₄ electrolyte concentration is 0.5 mol l⁻¹ and oxidation time is 60 min.

3.2 Photoelectrochemical properties of TCPP-attached TiO₂ nanoporous films

As mentioned above, attachment of photosensitizer TCPP can improve the photoelectrochemical properties of TiO₂ nanoporous films. But the traditional attaching methods have many disadvantages, such as poor physical bonding between the photosensitizer and TiO₂, which leads to the high electron transmission resistance from photosensitizer to TiO₂ and limits the improvement of the photoelectrochemical properties of TiO₂ nanoporous films. Hence in the present work a method which made the TCPP attachment realized through the electrochemical technique was proposed. Using this method, the attaching process was conducted on anode under an electric field environment in the electrolyte containing TCPP. Since TCPP possesses negative charge, it will move to the anode under the electric field and enrich

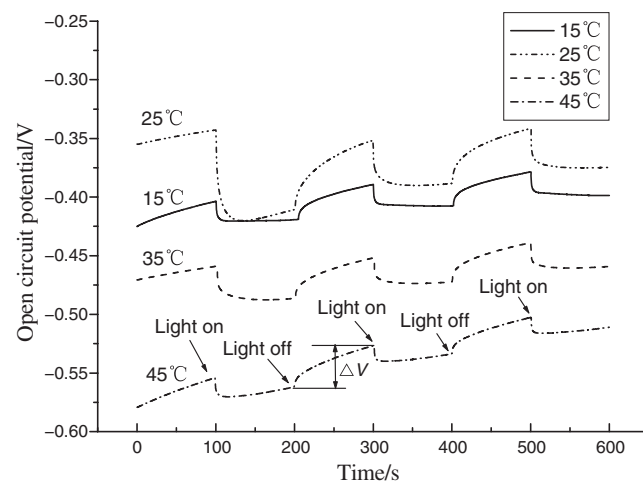


Figure 8. Open-circuit potential–time curves of TCPP-attached TiO₂ nanoporous films prepared at different attaching temperatures.

near the anode. Furthermore, the previous research¹⁵ indicated that the TiO₂ nanoporous films prepared by electrochemical oxidation showed anatase crystals which contained large amount of hydroxyl on its surface. Hence when TCPP with negative charge transfers to the anode region, chemical bonding will occur between the carboxyl on TCPP and the hydroxyl on TiO₂ nanoporous films to form ester bond. This bonding is much more stable and beneficial to establish an unblocked transmission channel of electron from photosensitizer to TiO₂. All of these can reduce the electron transmission resistance from photosensitizer to TiO₂ and

finally bring the obvious improvement of the photoelectrochemical properties of TiO₂ nanoporous films.

In order to certify the effects of our method, attaching of the photosensitizer TCPP on the prepared TiO₂ nanoporous films was performed using the electrochemical technique and the effects of the attaching process parameters on the properties of TCPP-attached TiO₂ nanoporous films were also investigated.

Table 4. ΔV comparisons of TCPP-attached TiO₂ nano-pore films prepared at different attaching temperatures.

Attaching temperature (°C)	Oxidation potential (V)	Attaching time (min)	Attaching voltage (V)	ΔV (V)
15	70–140	60	40	0.0299
25	70–140	60	40	0.0591
35	70–140	60	40	0.0345
45	70–140	60	40	0.0346

3.2a Effects of attaching temperature on the photoelectrochemical properties of TCPP-attached TiO₂ nanoporous films: TiO₂ nanoporous films were firstly prepared under 70–140 V in 0.5 mol l⁻¹ H₂SO₄ solution at 25°C with the oxidation time of 60 min, which are the optimized process parameters for the preparation of TiO₂ nanoporous films according to the above research. And then attaching of TCPP on the prepared TiO₂ nanoporous films were conducted under 40 V for 60 min at different temperatures. The obtained TCPP-attached TiO₂ nanoporous films were characterized by the open-circuit potential–time curves under the condition of lighting and darkness. And the results are shown in figure 8 and table 4.

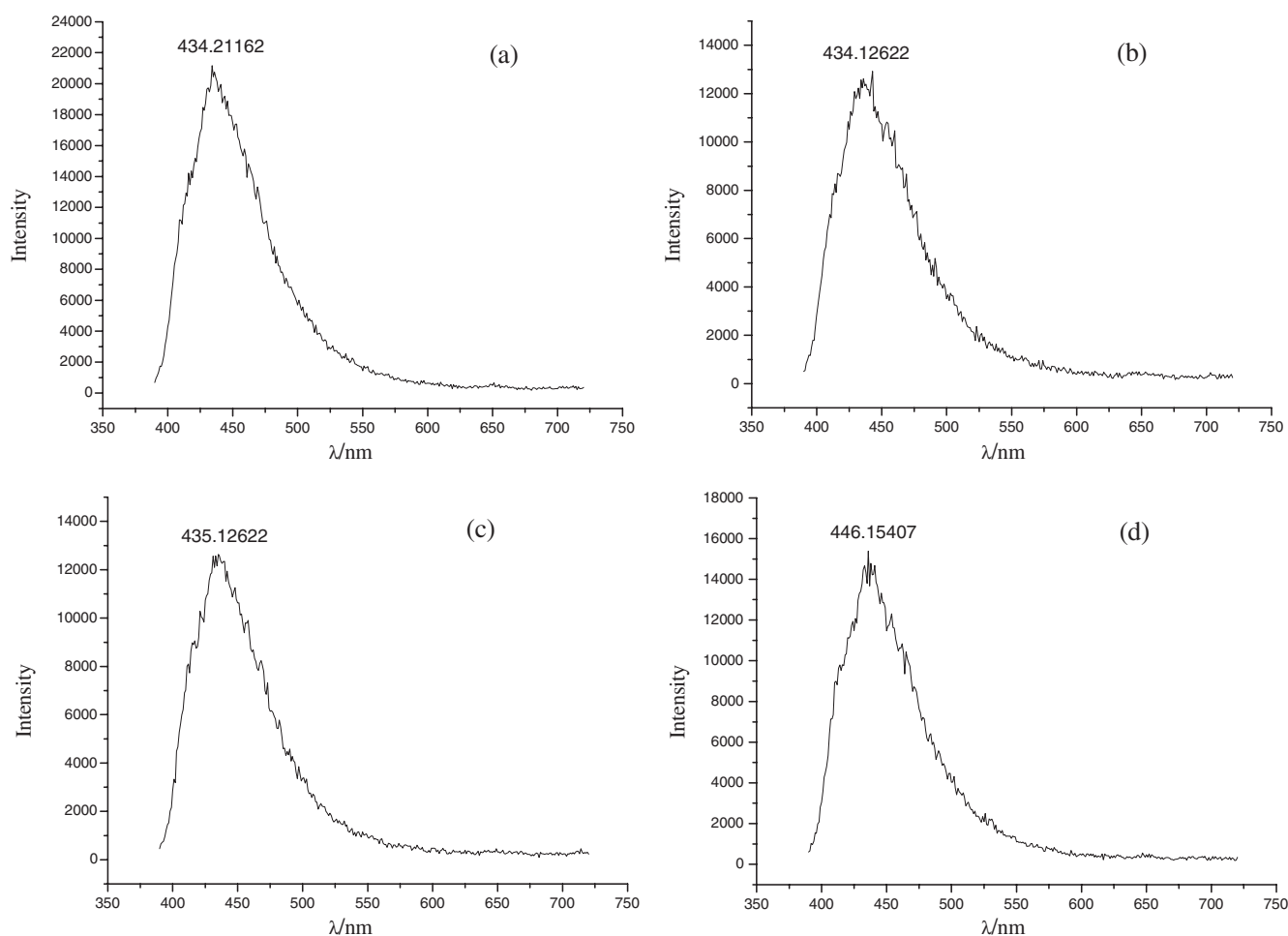


Figure 9. Fluorescence spectroscopy of TCPP-attached TiO₂ nanoporous films prepared at different attaching temperatures: (a) 15°C, (b) 25°C, (c) 35°C and (d) 45°C.

Table 5. Peak intensity and location of the fluorescence spectroscopy in figure 9.

Attaching electrolyte temperature (°C)	Peak location (nm)	Peak intensity
15	434	12,622
25	434	21,162
35	436	15,407
45	435	12,622

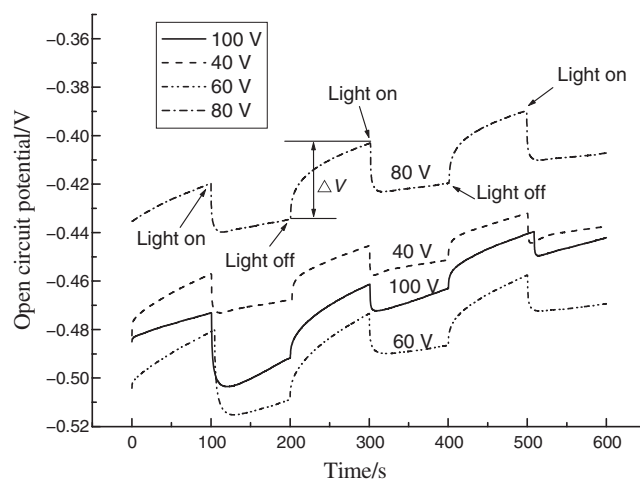
It can be seen from figure 8 and table 4 that TCPP-attached TiO₂ nanoporous films prepared in the electrolyte at 25°C show the highest ΔV value, which reveals that the TCPP-attached TiO₂ nanoporous films obtained in the electrolyte at 25°C possess the best photoelectrochemical property.

The obtained TCPP-attached TiO₂ nanoporous films were also characterized by fluorescence spectroscopy. And the corresponding results are shown in figure 9 and table 5. According to the fluorescence emission principle, free electron will transit from the ground state or the low-energy state to the excited state or the high-energy state and then transits back and send out radiation with the same or different wavelength to the original radiation after it absorbs radiation with characteristic wavelength. The peak intensity in the fluorescence spectroscopy can be used to evaluate the attaching effect of photosensitizer TCPP, i.e., photoelectrochemical properties of the TCPP-attached TiO₂ nanoporous films. The more amount of TCPP attached on the TiO₂ nanoporous films, the more sensitive of the semiconductor materials to the light and certainly the much higher of the peak intensity can be observed.

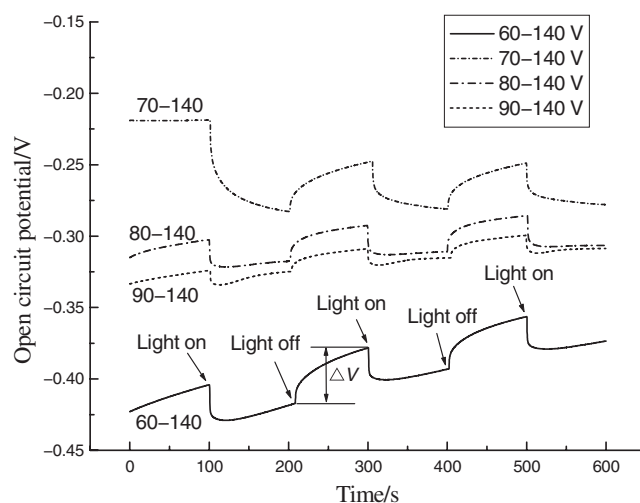
It can be seen from figure 9 and table 5 that TCPP-attached TiO₂ nanoporous films prepared in the attaching electrolyte at 25°C show the highest peak intensity value, which reveals that the TCPP-attached TiO₂ nanoporous films obtained at 25°C possess the best photoelectrochemical property. This conclusion matched well with that obtained by open-circuit potential–time curves in figure 8 and table 4.

3.2b Effects of attaching voltage on the photoelectrochemical properties of TCPP-attached TiO₂ nanoporous films: TiO₂ nanoporous films were prepared under 70–140 V in 0.5 mol l⁻¹ H₂SO₄ solution at 25°C with the oxidation time of 60 min. And then attaching of TCPP on the prepared TiO₂ nanoporous films were conducted in the attaching electrolyte for 60 min at 25°C but under different attaching voltages. The obtained TCPP-attached TiO₂ nanoporous films were characterized by the open-circuit potential–time curves under the condition of lighting and darkness. And the results are shown in figure 10 and table 6.

It can be seen from figure 10 and table 6 that TCPP-attached TiO₂ nanoporous films prepared under the attaching voltage of 60 V show the highest ΔV value, which reveals that the TCPP-attached TiO₂ nanoporous films obtained at this voltage possess the best photoelectrochemical property.

**Figure 10.** Open-circuit potential–time curves of TCPP-attached TiO₂ nanoporous films prepared under different attaching voltages.**Table 6.** ΔV comparisons of TCPP-attached TiO₂ nano-pore films prepared under different attaching voltages.

Attaching voltage (V)	Attaching time (min)	Attaching electrolyte temperature (°C)	Oxidation potential (V)	ΔV (V)
40	60	25	70–140	0.0222
60	60	25	70–140	0.0353
80	60	25	70–140	0.0314
100	60	25	70–140	0.0302

**Figure 11.** Open-circuit potential–time curves of TCPP-attached TiO₂ nanoporous films prepared under different oxidation potentials.

3.2c Effects of oxidation potential on the photoelectrochemical properties of TCPP-attached TiO₂ nanoporous films: TiO₂ nanoporous films were prepared under different oxidation potentials at 25°C in 0.5 mol l⁻¹ H₂SO₄ solution with the oxidation time of 60 min. And then attaching

of TCPP on the prepared TiO₂ nanoporous films were conducted in the attaching electrolyte for 60 min at 25°C and under the voltage of 60 V. The photoelectrochemical properties of the prepared TCPP-attached TiO₂ nanoporous films were characterized by the open-circuit potential–time curves under the condition of lighting and darkness. And the results are shown in figure 11 and table 7.

It can be seen from figure 11 and table 7 that TCPP-attached TiO₂ nanoporous films prepared under the oxidation

potentials of 70–140 V show the highest ΔV value, which reveals that the TCPP-attached TiO₂ nanoporous films obtained under this oxidation potential possess the best photoelectrochemical property.

The obtained TiO₂ nanoporous films attached with or without TCPP were also characterized by fluorescence spectroscopy. And the corresponding results are shown in figures 12, 13 and table 8.

It can be seen from figures 12, 13 and table 8 that the peak intensity of TiO₂ nanoporous films attached without TCPP are in the range of 7000–10000 while those of the TiO₂ nanoporous films attached with TCPP are in the range of 15,000–24,000. Enhancement of the peak intensity can be observed in the fluorescence spectroscopy of all the samples prepared under different oxidation potentials after the TiO₂ nanoporous films were sensitized with TCPP. This indicates that attaching of the photosensitizer TCPP indeed improves the properties of the TiO₂ nanoporous films. It can also be found that TCPP-attached TiO₂ nanoporous films prepared under the oxidation potentials of 70–140 V show the highest peak intensity value, which reveals that the TCPP-attached

Table 7. ΔV comparisons of TCPP-attached TiO₂ nano-pore films prepared under different oxidation potentials.

Oxidation potential (V)	Attaching voltage (V)	Attaching electrolyte temperature (°C)	Attaching time (min)	ΔV (V)
60–140	60	25	60	0.040
70–140	60	25	60	0.064
80–140	60	25	60	0.025
90–140	60	25	60	0.016

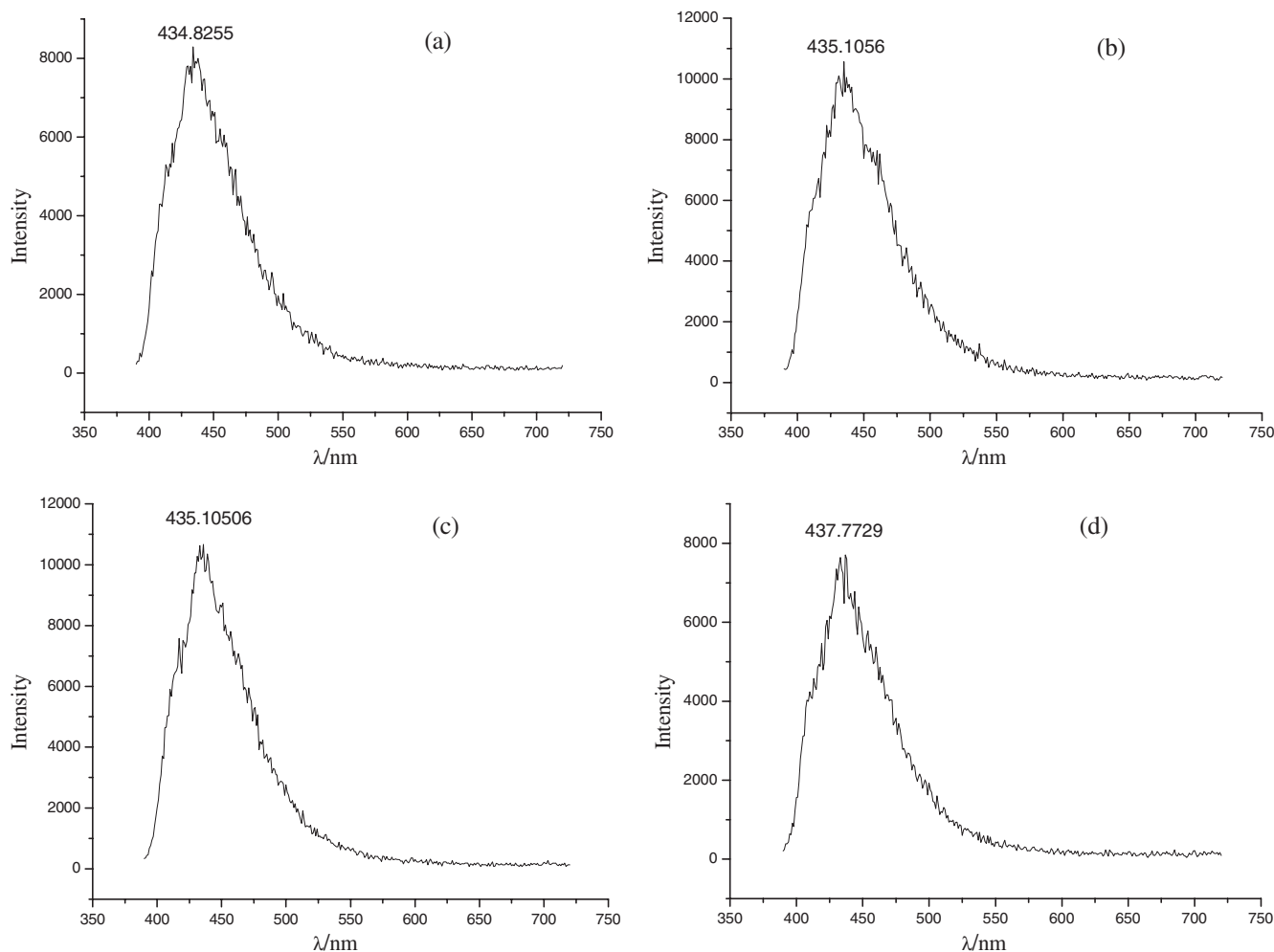


Figure 12. Fluorescence spectroscopy of TiO₂ nanoporous films prepared under different oxidation potentials: (a) 60–140 V, (b) 70–140 V, (c) 80–140 V and (d) 90–140 V.

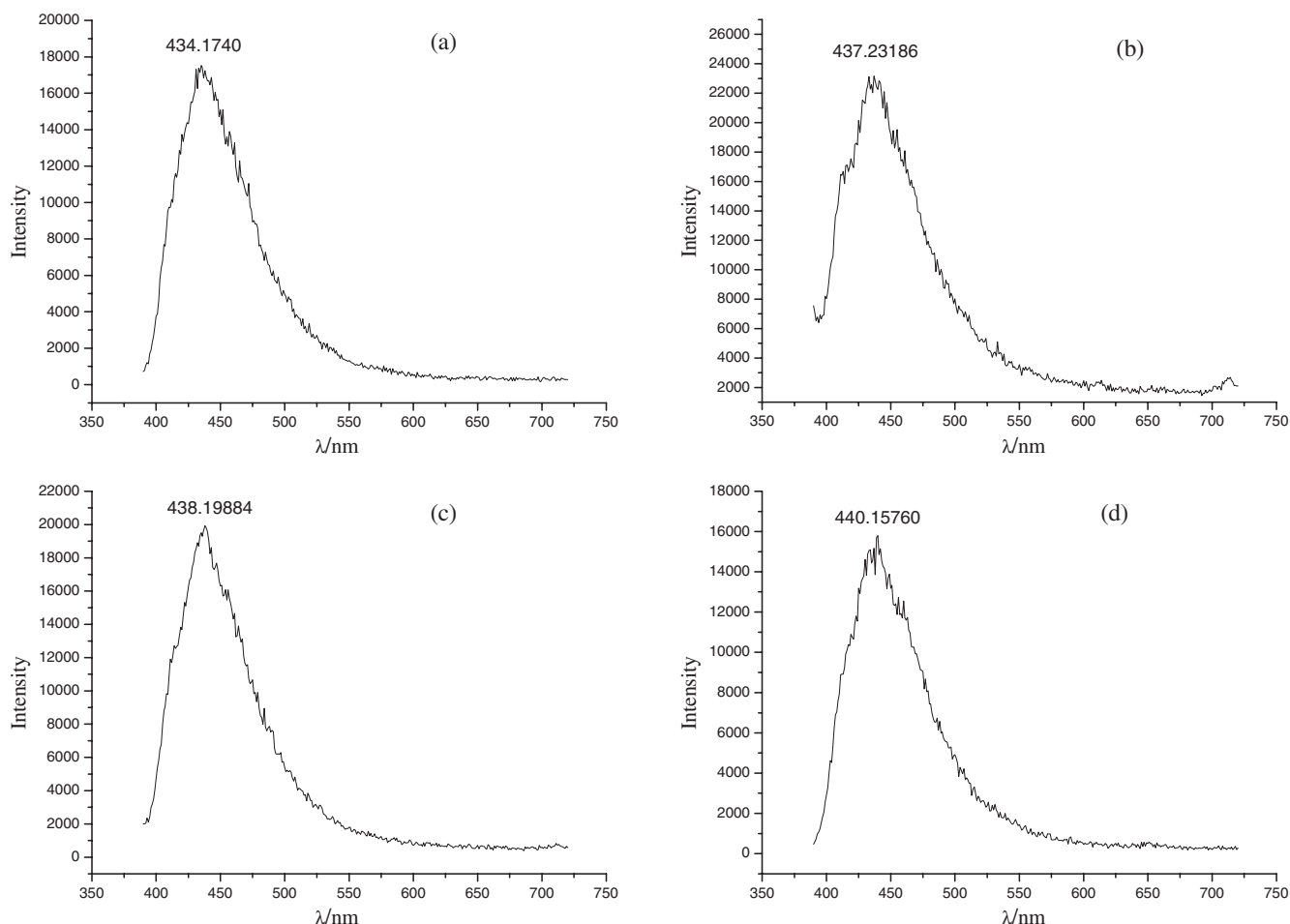


Figure 13. Fluorescence spectroscopy of TCPP-attached TiO₂ nanoporous films prepared under different oxidation potentials: (a) 60–140 V, (b) 70–140 V, (c) 80–140 V and (d) 90–140 V.

Table 8. Peak intensity and location of the fluorescence spectroscopies in figures 12 and 13.

Oxidation potential (V)	TiO ₂ nano-pore films		TCPP-attached TiO ₂ nano-pore films	
	Peak location (nm)	Peak intensity	Peak location (nm)	Peak intensity
60–140	434	8225	434	17,409
70–140	435	10,564	437	23,186
80–140	435	10,506	438	19,884
90–140	437	7729	440	15,760

TiO₂ nanoporous films obtained under this oxidation potential possess the best photoelectrochemical property. And this conclusion matches well with that obtained by open-circuit potential–time curves in figure 11 and table 7.

4. Conclusions

In this paper, TiO₂ nanoporous films were prepared by anodic oxidation using two-step voltage mode while the constant voltage electrochemical method was used to attach of photosensitizer TCPP on the prepared TiO₂ nanoporous films. Properties of TiO₂ nanoporous films attached with and without

photosensitizer TCPP were analysed by electrochemical test and fluorescence spectroscopy and the effects of process parameters on the properties of TiO₂ nanoporous films were also investigated. The results show that the optimized process parameters for the preparation of TiO₂ nanoporous films with the best photoelectrochemical property are as follows: oxidation potential is 70–140 V, oxidation temperature is 25°C, H₂SO₄ electrolyte concentration is 0.5 mol l⁻¹ and oxidation time is 60 min. Attaching of TCPP on the TiO₂ nanoporous films can indeed improve the properties of TiO₂ nanoporous films, and the optimized attaching electrolyte temperature and attaching voltage are 25°C and 60 V, respectively.

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