Influence of polyaniline on photoelectrochemical characterization of TiO$_2$-PANI layers*

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Abstract
TiO$_2$-polyaniline (PANI) composites were prepared by thermal oxidation of titanium substrate combined with chemical polymerization of aniline. Their chemical structures were determined by infrared (IR) spectroscopy and x-ray analysis. Their morphological structures were characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Their electro- and photoelectrochemical properties were examined by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) analysis. The results showed that their photoelectrochemical behavior was better than that of TiO$_2$ electrode; among them the more PANI existed in composite the higher was the anodic photoelectrochemical current. It was also found that the composite has structure in the range of nanosize.

Keywords: TiO$_2$-PANI composite, cyclic voltammetry, impedance spectroscopy, nanostructure, photoelectrochemistry
Classification numbers: 4.10, 5.07, 5.08

1. Introduction
Polyaniline (PANI) is a low-cost and easily synthesized polymer that has shown good electrical conductivity when used as energy conversion material [1–3]. Conversely, Ti/ TiO$_2$ has shown to be an anodic stable electrode, but also an insulating material [4], however, its surface properties can be improved by doping PANI [5, 6] so that Ti/TiO$_2$-PANI composite can be used as anode material in power sources. A large number of studies on composite materials of TiO$_2$-PANI have been reported; most researches on these polymers are still focusing on the preparation of materials and characterization [4, 7], such as morphology and chemical structures as well as electrochemical properties [8, 9], such as electrochemical impedance and cyclic polarization. A few reports touched upon the photoelectrochemical properties of this composite when its PANI content varied.

In this paper the Ti/TiO$_2$-PANI electrode was prepared by thermal oxidation of titanium substrate combined with chemical polymerization of aniline. Characterization of composite under different conditions was considered. The incorporation of conducting PANI nanostructures into TiO$_2$ was found to enhance the photoelectrochemical response of composite.

2. Experimental
2.1. Materials and preparation
All chemicals used in this study were provided by Merck (Germany). Aniline was fresh distilled under vacuum before use. The titanium electrodes were polished by sandpaper with 400 grit and then lubricant was removed from their surface by
mixed solution of NaOH (5 g L\(^{-1}\)), Na\(_3\)PO\(_4\) 30 g L\(^{-1}\), Na\(_2\)CO\(_3\) 40 g L\(^{-1}\) and Na\(_2\)SiO\(_3\) (2 g L\(^{-1}\)) for 30 min before they were treated by HCl (20%) for 10 min. They were washed then by distilled water and ultrasonically in absolute alcohol. These pretreated electrodes were thermal oxidated at 500 °C for 30 min to form TiO\(_2\) which were then immersed into PANI solution to form TiO\(_2\)-PANI composites. The immersion time was varied from 30 to 120 min to consider the influence of PANI on electro- and photoelectrochemical properties of obtained composites compared with TiO\(_2\) electrode.

2.2. Detection method

The structure of materials was carried out by infrared spectra on IMPACT 410-Nicolet unit. The surface morphology of coatings was examined by SEM on equipment FE-SEM Hitachi S-4800 (Japan) and TEM on a Jeol 200CX (Japan). The x-ray diffraction (XRD) of samples was obtained by x-ray diffractometer D8-Advance Bruker (Germany). The electro- and photoelectrochemical characterizations were observed by photovoltammetry and electrochemical impedance spectroscopy (EIS) analysis on the electrochemical workstation unit IM6 (Zahner-Elecktrik, Germany) with light off and light on by UV-SUNBOX (Germany-75 W).

3. Results and discussion

3.1. SEM images

The SEM image of TiO\(_2\) electrode (figure 1) showed a non-uniform surface in comparison with those of TiO\(_2\)-PANI composites (figure 2). The longer the TiO\(_2\) electrode immersed in PANI solution the more PANI amount grew up on its surface so that a better morphological structure resulted (figure 2(d)).

3.2. TEM-images

The TEM images on figure 3 evidenced convincingly that among two clearly different colours, the light one belongs to PANI enclosing the dark one belongs to TiO\(_2\). Both of them had size in nanorange. The gained results from SEM and TEM analysis explained that nanostructural TiO\(_2\)-PANI composites were successfully prepared by combining chemical and thermal oxidation methods.

3.3. X-ray diffraction

An XRD spectrum used to determine structure of regarded materials was shown in figures 4(a) and (b). In both spectra a small peak at 2\(\theta\) degree near 36.2 belongs to
TiO$_2$ in rutile form and another peak at 2$\theta$ of 38.6 shows that TiO$_2$ in anatase was observed. Both of them were evidence for the existence of titanium dioxides in composite matrices.

3.4. Infrared spectrum analysis

The given data in figure 5 illustrates the main groups belonging to PANI structure like that reported in [6, 10]. It explains that PANI existed in our composite material.

3.5. Photoelectrochemical characterization

3.5.1. Photovoltammetry. The photovoltammetry can be used to evaluate both the electrochemical behavior with light off (figure 6(a)) and the photoelectrochemical behavior with light on (figure 6(b)) of materials prepared by variation of immersion time of TiO$_2$ into PANI solution. The longer the TiO$_2$ electrode immersed in PANI solution, the higher photoelectrochemical current the electrode got because the more PANI amount grew up on its surface structure. However, this photoelectrochemical behavior seems not to be rising when immersion time is larger than 120 min due to so much PANI on the TiO$_2$ surface forming.

The photoelectrochemical current response versus cycle number is shown in figure 7 with light off (a) and light on (b). It is concluded that this response reduced by increasing cycle number, but it received nearly constant value after 5 cycles.

3.5.2. Electrochemical impedance spectroscopy (EIS). From above results given by photovoltammograms we have chosen the composite prepared by immersing TiO$_2$ into PANI solution for 90 min for EIS studying the photoelectrochemical properties of materials including TiO$_2$ and TiO$_2$-PANI composite. The solid lines are fitting data following equivalent circuit shown in figure 8(c) and the symbols are measuring data (figures 8(a) and (b)). Table 1 lists the best fitting values calculated from the above schema. It was found that 6 elements took part in the electrochemical process, where $R_s$ represents the electrolyte resistance, $W$ represents the Warburg diffusion element, $R_t$ and $C_t$ represent the resistance and capacitance of material film, $R_a$ and $C_{CPE}$ represent the charge transfer resistance and constant phase element, respectively. The results explained that the $R_a$ reduced about 25 times for TiO$_2$ and 50 times for TiO$_2$-PANI composite under light on in comparison with light off.
Figure 6. The influence of immersion time of TiO$_2$ into PANI solution on CV-diagrams of materials. The measurements were taken (a) without UV and (b) under UV illumination in 0.5 M H$_2$SO$_4$.

Figure 7. Current response following cycle number of TiO$_2$-PANI composite (TiO$_2$ immersed 90 min in PANI solution). The measurements were taken (a) without UV and (b) under UV illumination in 0.5 M H$_2$SO$_4$.

Figure 8. The influence of immersion time of TiO$_2$ into PANI solution on Nyquist plot of materials. The measurements were taken (a) without UV, (b) under UV illumination in 0.5 M H$_2$SO$_4$ and (c) electrical equivalent schema. Sample prepared by immersing TiO$_2$ into PANI solution for 90 min.
respectively. This means that due to the presence of PANI in composite matrix, nearly half of $R_{ct}$ is reduced under light on.

4. Conclusion

From the above results we conclude that nanostructured TiO$_2$-PANI composite was prepared by combining chemical and thermal oxidation methods. The immersion time of about 90 min is enough to achieve optimal photoelectrochemical characterization. The presence of PANI can contribute to raising photoelectrochemical response of that composite in comparison with TiO$_2$ because nearly half of the charge transfer resistance is reduced.

The use of this composite as anode material for fuel cells is the subject of a subsequent experimental work.

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Table 1. Electrochemical parameters corresponding to figure 8 estimated from fitting of experimental data to schema shown in figure 8(c).

| UV light | Obtained materials | $R_s$ (Ω) | $C_T$ (µF) | $R_T$ (kΩ) | $C_{CPE}$ (µF) | $n$ | W (KDW) | $R_{ct}$ (MΩ) |
|----------|--------------------|-----------|-----------|-----------|----------------|-----|---------|-----------|
| Turn off | TiO$_2$            | 3.52      | 100.10    | 27.00     | 2.15           | 0.89 | 647.70  | 5.87      |
| Turn on  | TiO$_2$-PANI       | 3.29      | 74.62     | 38.56     | 1.71           | 0.87 | 236.80  | 6.06      |
| Turn on  | TiO$_2$            | 3.68      | 23.93     | 11.79     | 5.57           | 0.88 | 176.90  | 0.23      |
| Turn on  | TiO$_2$-PANI       | 2.89      | 19.62     | 17.16     | 3.33           | 0.80 | 68.10   | 0.12      |

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