Vietnam Journal of Chemistry, International Edition, **54**(6): 771-775, 2016
DOI: 10.15625/0866-7144.2016-00402

Preparation of Ti/TiO_2-PANi electrodes by combining method of thermal treatment with polymerization processing and their electrochemical property

Mai Thi Xuan[1], Nguyen The Duyen[2], Pham Thi Tot[1], Mai Thị Thanh Thuy[1], Nguyen Thi Van Anh[1], Phan Thi Binh[1*]

[1]*Institute of Chemistry, Vietnam Academy of Science and Technology*

[2]*Faculty of Chemistry, Hanoi Pedagogical University N^{o}2*

Received 8 August 2016; Accepted for publication 19 December 2016

Abstract

Ti/TiO_2-PANi-electrodes were synthesized by combining method of thermal treatment of titanium substrate with chemical polymerization processing of aniline on which. Their morphological structure was observed by scanning electron microscopy. The presence of PANi and TiO_2 were indicated by infrared spectra and X-ray diffraction, respectively. Their electrochemical properties were characterized by cyclic voltammetry and impedance spectroscopy. The results showed that their photoelectrochemical property with light on in 0.5 M H_2SO_4 indicating a n-conductor that depended on PANi thickness covered TiO_2-layer among them the best one obtained by oxidative temperature of 500 ^oC for 30 minutes during thermal treatment of titanium substrate connected with an immersing into acidic aniline solution for only 8 min during polymerization.

Keywords. TiO_2-PANi composite, cyclic voltammetry, impedance spectroscopy, combining method.

1. INTRODUCTION

Polyaniline (PANi) is a typical conductive polymer because of its optoelectrical, electrical and optical properties as well as energy storage and conversion [1-3]. It is widely applied to fabricate sensors [4], solar cell [5] and microbial fuel cell [6] due to its good environmental stability and easy synthesis. TiO_2 is a known semi-conductive oxide metal with chemical and physical stability, photo-catalytic and photoelectrochemical properties for application to dye solar cells [7], gas sensor [8] and environmental treatment [9]. These advantages are active reasons for researching hybrid of them to improve materials for some applications in case of power sources [10, 11] or electrochemical sensors [12]. However, some procedures resulting in the best one are opened.

In this paper the Ti/TiO_2-PANi electrode was prepared by thermal oxidation titanium substrate combined with chemical polymerization of aniline (Anil) under some conditions such as pretreatment of titanium substrate with different grits of sandpaper before it being tried at varied temperature. Characterization of the Ti/TiO_2-PANi electrodes under these conditions was considered.

2. EXPERIMENTAL

2.1. Materials and preparation

All chemicals used in this study were provided by Merck (Germany) except Anil (from Kato Chemical, Japan) which was fresh distilled under *vacuum* before use. The titanium electrodes were polished by sandpaper and then lubricant was removed from their surface by mixed solution of NaOH (5 g/L), Na_3PO_4 30 g/L, Na_2CO_3 40 g/L and Na_2SiO_3 (2 g/L) 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 oxidized for 30 min to form Ti/TiO_2 which were immersed then into acidic Anil solution under dropping ammonium persulfate as oxidation agent to form $Ti/PANi-TiO_2$ electrodes.

2.2. Detection method

The structure of material was carried out by infrared spectra on IMPACT 410-Nicolet unit. The morphology of material was examined by SEM on an equipment FE-SEM Hitachi S-4800 (Japan). The X-ray diffraction (XRD) of samples were obtained by X-ray diffractometer D8-Advance Bruker (Germany).

The electro- and photoelectrochemical characterizations were observed by photovoltammograms and electrochemical impedance spectroscopy (EIS) using the electrochemical workstation unit IM6 (Zahner-Elecktrik, Germany) with light on and off by UV-SUNBOX (75 W, Germany).

3. RESULTS AND DISCUSSION

3.1. Material characterization

3.1.1. Morphology study

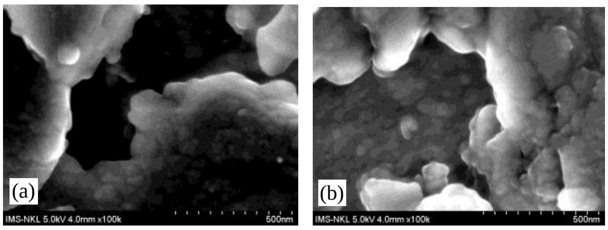

Figure 1: SEM images of Ti/TiO_2 electrode before (a) and after (b) immersion into acidic Anil solution (dry temperature: 500 ^oC for 30 min, sand paper: 180 grit, immersion time into Anil solution: 8 min)

The SEM images indicated that the pure Ti/TiO_2 electrode (a) obtained by temperature oxidative process had else large uncovered place by TiO_2 on the surface which was then fully coated by chemical polymerization during immersion into acidic Anil solution using $(NH_4)_2S_2O_8$ as oxidative agent. It explained that PANi was formed on the both of titanium substrate and TiO_2 layer resulting in a new Ti/TiO_2-PANi electrode.

3.1.2. IR analysis

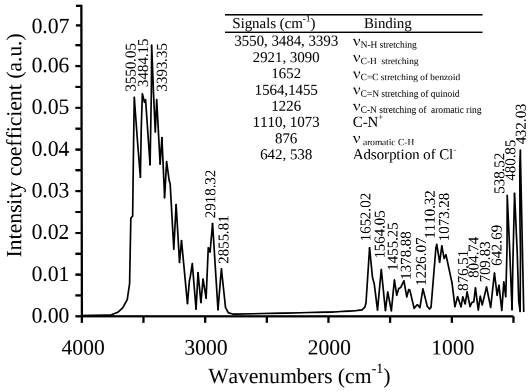

Figure 2: IR-spectrum of Ti/TiO_2-PANi electrode (dry temperature: 500 ^oC for 30 min, sandpaper: 180 grit, immersion time into Anil solution: 8 min)

The data from figure 2 showed that some typical function groups belonging to PANi [13] such as stretching bands of aromatic benzene and quinoid rings at 1652 cm^{-1} and 1564-455 cm^{-1}, respectively, from 3550 to 3393 cm^{-1} (N-H stretching), 3090 and 2921 cm^{-1} (C-H stretching). It indicated the existence of PANi in composite electrode.

3.1.3. X-ray diffraction

The figure 3 demonstrated the existence of both modifications of TiO_2 by 2θ-scale, among them the rutile form was indicated at 27.5 ^{o} while anatase one was evidenced at positions of 25.2, 38.5, 48 and 54 degree.

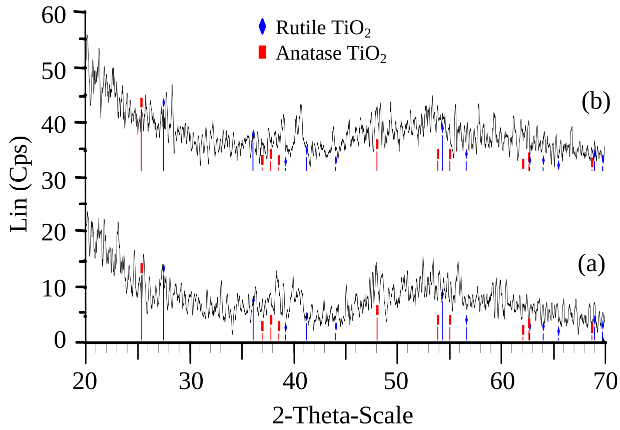

Figure 3: X-ray spectra of Ti/TiO_2 electrode (a) and Ti/TiO_2-PANi electrode (dry temperature: 500 ^oC for 30 min, sand paper: 180 grit, immersion time into Anil solution: 8 min)

3.2. Electrochemical and photoelectrochemical characterization of materials

3.2.1. The influence of immersion time of Ti/TiO_2 electrode into acidic Anil solution during polymerization process

The figure 4 illustrated CV diagrams of Ti/TiO_2-PANi electrode in 0.5 M H_2SO_4 with light on and off for comparison with each other. It showed that the anodic photoelectrochemical current indicating n-semiconductor under light on (b) was improved if immersion time until 12 min, among them the highest one obtained by 8 min. It was bad if immersion time increased over 12 min due to the thicker PANi film coated on TiO_2. Under light off (a) we can observe more clearly the redoxidation peaks of PANi [14] in the case of immersion time for 14 min in comparison with the rest ones. Additionally, the higher current peak demonstrated the thicker PANi film on Ti/TiO_2 electrode resulting in a decrease of anodic photoelectro-chemical current.

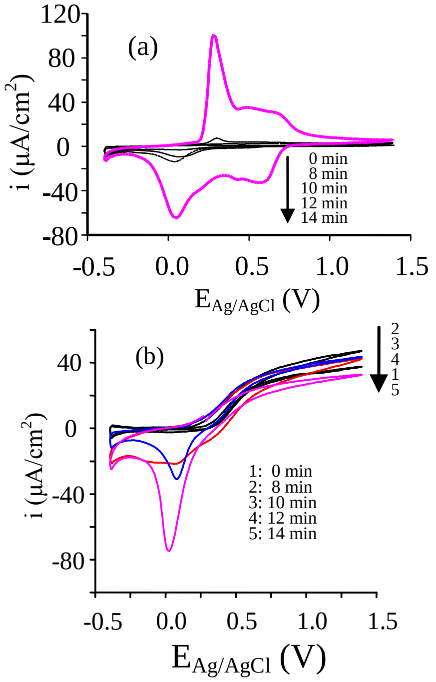

Figure 4: The influence of immersion time of TiO_2 electrode into Anil solution on their CV-diagrams in 0.5 M H_2SO_4 with light off (a) and light on (b) (oxidative temperature: 500 ^oC for 30 min, sand paper: 180 grit)

3.2.2. The influence of oxidative temperature of titanium substrate

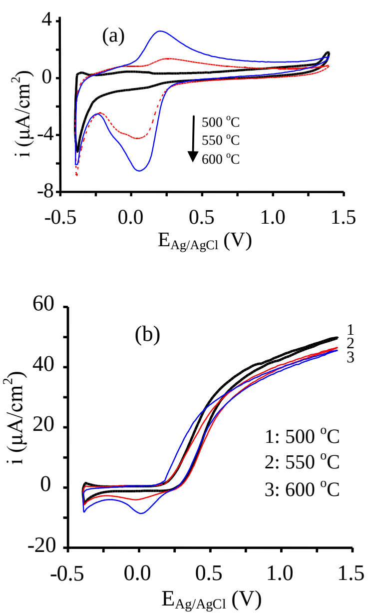

Figure 5: The influence of oxidized temperature of titanium substrate on CV-diagrams of Ti/TiO_2-PANi in 0.5 M H_2SO_4 light off (a) and light on (b) (immersion time: 8 min, sand paper: 180 grit)

The oxidized temperature played an important role in preparing Ti/TiO_2 as substrate for polymerization process to get Ti/TiO_2-PANi composite electrode. The anodic photoelectron-chemical current decreased if oxidative temperature increased (b) because the thicker PANi film through higher reoxidation peak was observed (a) when Ti/TiO_2 was prepared at higher temperature.

3.2.3. The influence of grit of sandpaper

The grit of sandpaper which used for pre-treatment of titanium substrate contributed to the thickness of PANi film on the composite electrode during polymerization. In fact, the higher grit the sandpaper got, the thicker PANi film was obtained because its higher redoxidation peaks on CV-diagram was shown (a). A decrease of anodic photo electrochemical was found by increasing sandpaper grit. It was explained that this photoelectro-chemical current depended on the thickness of PANi film on Ti/TiO_2 electrode. It means that the thicker formed PANi film, the less photo electrochemical current considered the Ti/TiO_2-PANi electrode.

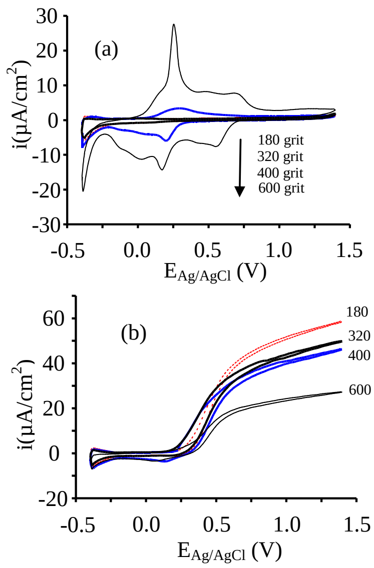

Figure 6: The influence of grit of sandpaper using for polishing titanium substrate on CV-diagrams of Ti/TiO_2-PANi in 0.5 M H_2SO_4 with light off (a) and light on (b) (immersion time: 8 min, oxidative temperature: 500 ^oC)

3.3. Electrochemical characterization in brewery wastewater

From above results given by photovoltammo-grams we have chosen the composite electrode prepared by optimal conditions: immersing TiO_2 into acidic Anil solution for 8 min, the oxidized temperature at 500 °C and sandpaper of 180 grit for electrochemical measurements.

Because brewery wastewater is potential substrate electrolyte using for microbial fuel cell (MFC) [15], the reached composite electrode was measured in that electrolyte to consider its electrochemical property through CV and EIS demonstrations.

3.3.1. CV-diagram study

The electrochemical Responded current versus cycle number are shown in figure 7. It is concluded that this response was insignificantly changed during cycling indicating that the Ti/TiO_2-PANi electrode active stably in brewery wastewater.

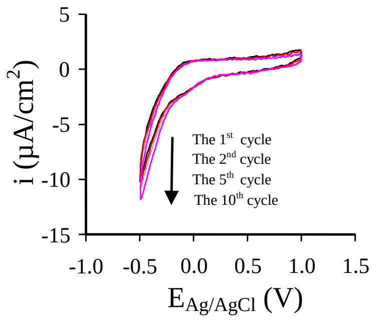

Figure 7: Responded current following cycle number of Ti/TiO_2-PANi electrode (TiO_2 immersed 8 min in Ani solution, the oxidized temperature at 500 °C, 180 grit paper) measured in brewery wastewater

3.3.2. EIS study

The EIS measurements were carried out under condition of frequency from 100 kHz to 10 MHz, amplitude of 5 mV and COD of 2100 mg/L (sandpaper of 180 grit, the oxidized temperature at 500 °C for 30 min, Ti/TiO_2 electrode immersed into Anil solution for 8 min.

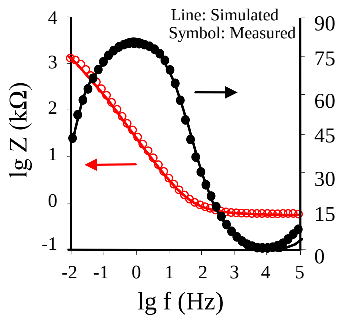

Figure 8: The Bode plots of Ti/TiO_2-PANi electrode were measured in brewery wastewater

Similarly, the composite electrode prepared at the same above conditions was characterized by EIS plots where the solid lines are fitting data following equivalent circuit shown in figure 10 and the symbols are measuring ones (figures 8 and 9). The results showed that the simulated lines fitted well into measured points indicating that the electrical equivalent circuit was suitable. It included 6 elements where R_s (549.7Ω) represents the electrolyte resistance, W (6.744 KΩ$s^{-1/2}$) represents the Warburg diffusion element, R_f (93.85 kΩ) and C_f (19.52 μF) represent the resistance and capacitance of material film, R_{ct} (1.984 MΩ) and C_{ad} (8.497 μF) represent the charge transfer resistance and adsorption capacitance, respectively.

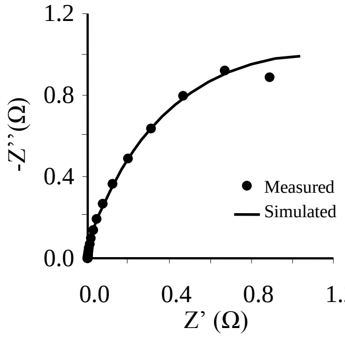

Figure 9: The Nyquist plot of Ti/ TiO_2-PANi electrode in brewery wastewater

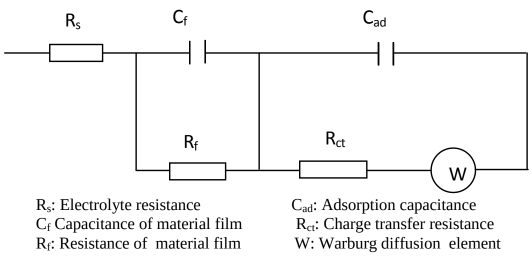

Figure 10: Electrical equivalent circuit belongs to Ti/TiO_2-PANi electrode simulated from figure 9

4. CONCLUSION

From above results it could be concluded that Ti/TiO_2-PANi electrode by combining thermal oxidation method with polymerization processing under optimal conditions (immersion time of about 8 min for Ti/TiO_2 electrode into acidic Anil solution, the oxidized temperature at 500 °C, sandpaper of 180 grit) achieved the best photo electrochemical characterization in 0.5 M H_2SO_4. The stability of this composite electrode was obtained also in brewery wastewater. Using this composite as anode material for microbial fuel cell or dye-sensitized solar cell a range of deeper experimental has to be carried out continuously, which is being published by us in the future.

Acknowledgement. *This study was financially supported by the NAFOSTED of Vietnam under code number 104.99-2013.44.*

REFERENCES

1. K. Gurunathan, A Vadivel Murugan, R. Marimuthu, U. P. Mulik, D. F. Amalnerkar. *Electrochemically synthesized conducting polymeric materials for applications towards technology in electronics, optoelectronics and energy storage devices.* Materials Chemistry and Physics, **61**, 173-194 (1999).
2. Y. S. Negi and P. V. Adhyapak. *Development in Polyaniline Conducting Polymers,* J. Macromol. Sci. Polymer reviews, **42(1)**, 35-53 (2002).
3. H. Karami, M. F. Mousavi, M. Shamsipur. *A novel dry bipolar rechargeable battery based on polyaniline,* J. Power Sources, **124**, 303-308 (2003).
4. YunYano, Katunori Terayama, and Sumi Yamasaki. *White polyaniline as a time display: reaction of polyaniline with gaseous oxygen*, Synthetic Metals, **85**, 1381-1382 (1997).
5. S. X. Tan, J. Zhai, M. X. Wan, L. Jiang, D. B. Zhu. *Polyaniline as a hole transport material to prepare solid solar cells,* Synth. Met., **137**, 1511-1512 (2003).
6. Ali Mehdinia, Minodokht Dejaloud, Ali Jabbari. *Nanostructured polyaniline-coated anode for improving microbial fuel cell power output*, Chemical Paper, **67(8)**, 1096-1102 (2013).
7. Chi-Hwan Han, Hak-Soo Lee, Sang-Do Han. *Synthesis of nanocrystaline TiO_2 by sol-gel combustion hybrid method and application to dye solar cell*, Bull. Korean Chem. Soc., **29(8)**, 1495-1498 (2008).
8. B. Karunagaran, Periyayya Uthirakumar, S. J. Chung, S. Velumani, E.-K. Suh. *TiO_2 thin film gas sensor for Monitoring ammonia*, Materials Characterization, **58**, 80-684 (2007).
9. A. Bozzi, T. Yuranova, J. Kiwi. *Self-Cleaning of Wool-Polyamide and Polyester Textiles by TiO_2-Rutile Modification under Daylight Irradiation at Ambient Temperature*, Journal of Photochemistry and Photobiology A: Chemistry, **172**, 27-34 (2005).
10. K. S. Patil, P. H. Zope. *Review on polyaniline: TiO_2 nanocomposite for energy storage application.* International Journal of Engineering Sciences & Research technology, **4(9)**, 494-498 (2015).
11. Xochitl D. Benetton, S. G. Navarro-Ávila, C. Carrera-Figueiras. *Electrochemical evaluation of Ti/TiO_2-polyaniline anodes for microbial fuel cells using hypersaline microbial consortia for synthetic-wastewater treatment*, Journal of New Materials for Electrochemical Systems, **13**, 1-6 (2010).
12. Duong Ngoc Huyen, Nguyen Trong Tung, Nguyen Duc Thien, and Le Hai Thanh. *Effect of TiO_2 on gas sensing features of TiO_2/PANi nanocomposite,* Sensors (Basel), **11(2)**, 1924-1931 (2011).
13. J. Vivekanandan, V. Ponnusamy, A. Mahudeswaran and P. S. Vijayanand. *Synthesis, characterization and conductivity study of polyaniline prepared by chemical oxidative and electrochemical methods*, Archives of Applied Science Research, **3(6)**, 147-153 (2011).
14. N. Gospodinova, L. Terlemezyan. *Conducting polymers prepared by oxidative polymerisation: Polyaniline,* Prog. Polym. Sci., **23**, 1443-1484 (1998).
15. Ahmed ElMekawy, Sandipam Srikanth, Suman Bajracharya, Hanaa M. Hegab, Poonam Singh Nigam, Anoop Singh, S. Venkata Mohan, Deepak Pant. *Food and agricultural wastes as substrates for bioelectrochemical system (BES): The synchronized recovery of sustainable energy and waste treatment.* Food Research International, **73**, 213-225 (2015).

Corresponding author: **Phan Thi Binh**
Institute of Chemistry
Vietnam Academy of Science and Technology
18, Hoang Quoc Viet, Cau Giay, Hanoi
E-mail: phanthibinh@ich.vast.vn.