Effect of nanostructured graphene oxide on electrochemical activity of its composite with polyaniline titanium dioxide

Thi Binh Phan¹, Thi Thanh Luong², Thi Xuan Mai¹, Thi Thanh Thuy Mai¹ and Thi Tot Pham¹

¹Institute of Chemistry, Vietnam Academy of Science and Technology 18 Hoang Quoc Viet, Cau Giay, Hanoi, Vietnam
²Hanoi University of Industry, Minh Khai Ward, Bac Tu Liem District, Hanoi, Vietnam

E-mail: phanthibinh@ich.vast.vn

Received 29 December 2015
Accepted for publication 26 January 2016
Published 11 March 2016

Abstract
Graphene oxide (GO) significantly affects the electrochemical activity of its composite with polyaniline titanium dioxide (TiO₂). In this work various composites with different GO contents have been successfully synthesized by chemical method to compare not only their material properties but also electrochemical characteristics with each other. The results of an electrochemical impedance study showed that their electrochemical property has been improved due to the presence of GO in a composite matrix. The galvanodynamic polarization explained that among them the composite with GO/Ani ratio in the range of 1–14 exhibits a better performance compared to the other due to yielding a higher current density (280 μA cm⁻²). The TEM and SEM images which presented the fibres of a composite bundle with the presence of PANi and TiO₂ were examined by IR-spectra and x-ray diffraction, respectively.

Keywords: nanostructured graphene oxide composite, electrochemical impedance, dynamic current polarization

Classification numbers: 4.00, 5.00, 5.11, 5.15

1. Introduction

Currently, the function materials and their applications have attracted the most attention due to their outstanding properties concerning the bioelectrocatalytic degradation of organic molecules in organic wastes, especially in brewery wastewater. They are potential materials for fabricating fuel substrate for microbial fuel cell (MFC) due to the food-derived nature of the organic matter and the lack of high concentrations of inhibitory substances (for example, ammonia in animal wastewaters) [1]. The hybrid materials based on graphene oxide (GO) and polyaniline (PANI) are fabricated for different applications in a supercapacitor and biosensor because of their excellent electrochemical performances and biocompatibility [2, 3].

Graphene oxide is chemically oxidized graphene with advantageous characteristics such as thermal and chemical stability, high mechanical strength, large specific surface area, good electron conductivity and water solubility. Titanium dioxide (TiO₂) is one of the most studied semiconductors owing to excellent electronic properties, non-toxicity, low cost, physical and chemical stability and high reactivity, whose composites with GO [4] or PANi [5] are promising antibacterial materials.

In this work PANi-TiO₂-GO composites were prepared by chemical method and performed in paste form on titanium substrate. The effects of GO content in composites on their electrochemical properties were considered by electrochemical impedance measurement and dynamic current polarization one in brewery wastewater.
2. Experimental

2.1. Materials and methods

Most chemicals used in this study were provided by Merck (Germany). Aniline (Anil) was fresh distilled under vacuum before use. The titanium electrodes as electrode substrate were polished by sandpaper with 180 grits and then pretreated following the procedure in [6] before use. The PANI-TiO2-GO nanocomposites were prepared by chemical method using TiO2 in sol gel form (from the Institute of Applied Physics, VAST, Vietnam), GO in powder form (from the Institute of Chemistry, VAST, Vietnam) and ammoniumpersulfate (molar ratio to Anil was equal 1) as an oxidation agent under stirring at a temperature of about 0 °C–5 °C, GO content was varied from 0 to 10% compared with Anil, while the mass ratio of TiO2 to Anil was equal 1/6. The pastes of those composites using chitosan solution in acetic acid (1%) as a binder were performance on pretreated titanium substrate and dried at a temperature of 120 °C for 2 h. Brewery wastewater (chemical oxygen demand (COD) was 3555 mg l\(^{-1}\)) was chosen as a substrate electrolyte used for electrochemical measurements.

2.2. Detection method

The structure of materials was carried out by infrared spectra on IMPACT 410-Nicolet unit. The morphology of the material was examined by scanning electron microscopy (SEM) on an equipment FE-SEM Hitachi S-4800 (Japan) and transmission electron microscopy (TEM) on a Jeol 200CX (Japan). The x-ray diffraction of the samples was obtained by an x-ray diffractometer D8-Advance Bruker (Germany). The electrical conductivity measurement by cyclic voltammetry (CV) and electrochemical impedance spectroscopy analysis as well as dynamic current polarization measurement were carried out on the electrochemical workstation unit IM6 (Zahnner-Elektrik, Germany).

3. Results and discussion

3.1. Electrical conductivity measurement

The conductivity of composites was determined through CV diagrams in figure 1 and table 1. The higher slope has the CV line, the higher electrical conductivity obtains the material [7]. The conductivity was calculated by the following equation

\[ \delta = d \frac{\Delta I}{\Delta E}, \]

where \(\delta\) is electrical conductivity (mS cm\(^{-1}\)), \(\Delta E\) is the potential difference (mV), \(\Delta I\) is the responsive current difference (mA) and \(d\) is the thickness of the sample (cm).

The results showed an increase of electrical conductivity when GO was used for fabricating composite, among them the highest value reached in the case of GO/Anil ratio of 1/12 (127.02 mS cm\(^{-1}\)).

3.2. Electrochemical impedance study

Figure 2(a) illustrates Nyquist plots simulated following electrical equivalent circuits on figures 2(b) and (c) where the symbols are measured points and the solid lines are fitting ones. Two schemas were found where the first one with six elements belonged to composites with the presence of GO (figure 2(b)) and the other one with seven elements belonged to those without GO (figure 2(c)). The obtained data given in table 2 showed an important effect of GO not only on both capacitance (\(C_1\)) and resistance (\(R_1\)) of the layer but also on the electrochemical process due to an appearance of adsorption capacitance (\(C_{ad}\)) and Warburg diffusion (W). In fact, GO-composites have very small values of \(R_1\) and \(C_1\) in comparison with that non-containing GO at which the electrochemical reactions may be prevented owing to the appearance of \(R_{ad}\) and very small constant phase element (CPE) (0.3 nF). However, it was found the highest \(R_f\) (326.1 \(\Omega\)) and W (118.5 \(\Omega\ s^{1/2}\)) values for composite with GO/Anil ratio of 1 to 12.

The diffusion coefficient \(D\) can be calculated by the following equation [8]

\[ D = \frac{\nu R^2T^2}{n^4 F^2 \Lambda^2 C^2 \sigma^2}, \]

where \(\nu\) is the reaction order, \(R\) is the Boltzman gas constant, \(T\) is the absolute temperature, \(n\) is the exchange electron number in the charge transfer process, \(F\) is the Faraday constant, \(\Lambda\) is the electrode surface area, \(C\) is the oxidant/ reductant concentration on the electrode material (\(C = 1\)); \(\sigma\) is the Warburg constant obtained by fitting.

It suggests that both reaction order (\(\nu\)) and exchange electron number (\(n\)) equal 1 because bacteria in brewery wastewater as a substrate in MFC are reactants taking part in
Figure 2. (a) Effect of GO on Nyquist plots of composites measured in brewery wastewater; electrical equivalent circuits belong to (b) PANi-TiO$_2$-GO and (c) PANi-TiO$_2$. Measurement parameters: frequency 100 kHz–10 MHz, amplitude 5 mV, COD 3555 mg l$^{-1}$.

Table 2. Calculation of electrochemical parameters corresponding to figure 2.

| Mass ratio of GO/Anil | $R_s$ (Ω) | $C_1$ (nF) | $R_f$ (Ω) | CPE (nF) | $C_{ad}$ (μF) | $R_{ad}$ (kΩ) | $R_{ct}$ (Ω) | $\sigma$ (Ω$^{-1}$ s$^{-1}$) | D (cm$^2$ s$^{-1}$) | L (TH) |
|-----------------------|-----------|------------|-----------|-----------|--------------|--------------|------------|------------------|----------------------|--------|
| 0                     | 0.298     | 50.840     | 3701      | 0.3       | —            | 0.459        | 19.98      | —                | —                    | 901    |
| 1/14                  | 319.1     | 3.333      | 156.3     | —         | 58.12        | 2.238        | —          | 30.73            | $9.37 \times 10^{-16}$ | —      |
| 1/12                  | 613.8     | 3.277      | 326.1     | —         | 51.36        | 2.234        | —          | 118.5            | $0.63 \times 10^{-16}$ | —      |
| 1/10                  | 336.7     | 4.290      | 167.9     | —         | 51.42        | 2.952        | —          | 51.72            | $3.31 \times 10^{-16}$ | —      |

Table 3. Vibration signals of IR-spectra from figures 4 and 5.

| Wavenumber $\nu$ (cm$^{-1}$) | Binding | GO | PANi-TiO$_2$-GO |
|-------------------------------|---------|----|-----------------|
| 3500; 3362                    | $\nu_{\text{OH}}$ | 3580 | $\nu_{\text{OH}}$ |
| 3542                          | $\nu_{\text{N-H}}$ | 3542 | $\nu_{\text{N-H}}$ |
| 2919                          | $\nu_{\text{C-H aromatic}}$ | 2919 | $\nu_{\text{C-H aromatic}}$ |
| 3057                          | $\nu_{\text{C-H}}$ | 2883 | $\nu_{\text{C-H}}$ |
| 1718; 1654                    | $\nu_{\text{C-O}}$ | 1654 | $\nu_{\text{C-O}}$ |
| 1558; 1517                    | benzoid | 1560 | benzoid |
| 1485                          | quinoid | 1485 | quinoid |
| 1438                          | $-\text{N=quinoid=N}$ | 1438 | $-\text{N=quinoid=N}$ |
| 1127                          | $\nu_{\text{C=O}}$ | 1294 | $\nu_{\text{C=O}}$ |
| 1127                          | C–N$^+$ group | 1127 | C–N$^+$ group |

Figure 3. Effect of GO contents on dynamic current polarization in brewery wastewater (current scan rate of 5 $\mu$A s$^{-1}$, COD = 3555 mg l$^{-1}$).
the charge transfer process. The values of the calculated diffusion coefficient are ranged \(10^{-16}\) cm\(^2\) s\(^{-1}\), among them the diffusion process in the case of GO/Anil equal 1 to 14 used for the fabricating composite was faster than the other owing to the biggest one \((9.37 \times 10^{-16} \text{ cm}^2 \text{ s}^{-1})\) caused by the smallest \(R_f\) \((156.3 \Omega)\).

3.3. Current dynamic polarization

According to [9], the current dynamic polarization can be used for the evaluation of the performance and electrocatalytic activity with microbial fermentation products. In figure 3 the galvanodynamically recorded polarization curves of composites are shown and compared in terms of their current density at 0.4 V versus Ag/AgCl. As can be seen, the composite with GO/Anil ratio of 1 to 14 exhibits a significantly better performance, yielding a current density of 280 \(\mu\)A cm\(^{-2}\), compared to only 170–200 \(\mu\)A cm\(^{-2}\) observed with other rest composites.

3.4. Infrared analysis

The results given in figure 4 and table 3 explained that GO existed in composite due to –OH stretching mode at 3500 and 3362 cm\(^{-1}\), 3057 cm\(^{-1}\) (C–H), 1718 and 1654 cm\(^{-1}\) (C=O), 1558 and 1517 cm\(^{-1}\) (C=C), 1227 cm\(^{-1}\) (C–O) [10–12]. Figure 5 shows some signals belonging to GO such as at 3500 cm\(^{-1}\) (–OH), 1560 cm\(^{-1}\) (C=C) and 1294 cm\(^{-1}\) (C–O). It was also found that PANi existed in composite owing to vibration signals of benzoid and quinoid rings at 1560 and 1485 cm\(^{-1}\), respectively [13]. Some other signals were found at 3542 cm\(^{-1}\) assigning N–H stretching mode, 2833 cm\(^{-1}\) (C-H), 1438 cm\(^{-1}\) (–N=quinoid=N–), 1127 cm\(^{-1}\) (C–N\(^+\))

3.5. X-ray diffraction

The data given in figure 6 provided separately the spectra of PANi (curve (a)) and TiO\(_2\) (curve (b)) with which the spectrum belonging to the composite could be compared. It was found on the spectrum of curve (c) the peak at 2\(\theta\) degree of about 27 presented for amorphous PANi and the other peaks belonging to anatase TiO\(_2\) at those of 38°, 48°, 55° and 63°.

3.6. SEM images

The SEM images on figure 7 show that TiO\(_2\), which was provided in sol-gel form \((50 \text{ g l}^{-1})\), existed in grain with a size approximately smaller than 20 nm and GO in the typical layered wrinkle structure. Compared with those images, the GO-composite existed in a layered structure of GO on which PANi was deposited to form the fibre bundles.

3.7. TEM images

The TEM images in figure 8 evidenced convincingly that among three clearly different colours, the light one belongs to PANi enclosing the big dark one which belongs to graphene oxide and the other small dark one belongs to TiO\(_2\). All of them had a size in the nanorange. The gained results from SEM and TEM analysis explained that nanostructured PANi-TiO\(_2\)-GO composites were successfully prepared by chemical method.

4. Conclusion

The GO composite was successfully synthesized by chemical method, which existed in a layered structure combined with fibre bundles in nano size resulting in very small electrochemical impedance in comparison with that without GO. It explained that the presence of GO improved the electrochemical property of the composite on which the adsorption
process and Warburg diffusion were found by simulating the best performance, yielding a current density of 280 \( \mu \text{A cm}^{-2} \).

**Acknowledgments**

This study was financially supported by the **NAFOSTED** of Vietnam under code number 104.99-2013.44. The authors would like to thank the Humboldt Fellowship for the support of the IM6 equipment.

**References**

[1] Pant D, Van Bogaert G, Diels L and Vanbroekhoven K 2010 *Bioresource Technol.* **101** 1533

[2] Mitchell E, Candler J, De Souza F, Gupta R K, Gupta B K and Dong L F 2015 *Synthetic Met.* **199** 214

[3] Zheng J, Ma X, He X, Gao M and Li G 2012 *Procedia Eng.* **27** 1478

[4] Chang Y-N, Ou X-M, Zeng G-M, Gong J-L, Deng C-H, Jiang Y, Liang J, Yuan G-Q, Liu H-Y and He X 2015 *Appl. Surf. Sci.* **343** 1

[5] Hu Z, Huang Y, Sun S, Guan W, Yao Y, Tang P and Li C 2012 *Carbon* **50** 994

[6] Pham T T, Nguyen T D, Mai T X, Mai T T T, Tran H Y and Phan T B 2015 *Adv. Nat. Sci.: Nanosci. Nanotechnol.* **6** 025008

[7] Phan T B 2007 *Macromol. Symp.* **249–250** 228

[8] Zahnner Messsysteme 2007 Thales Software Package for Electrochemical Workstations IM6/sex user manual, Zahner-Elektrik Company

[9] Rosenbaum M, Zhao F, Quaas M, Wulff H, Schröder U and Scholz F 2007 *Appl. Catal. B: Environ* **74** 262

[10] Nethravathi C and Rajamathi M 2008 *Carbon* **46** 1994

[11] Zhu P, Shen M, Xiao S and Zhang D 2011 *Physica B: Condensed Matter* **406** 498

[12] Pham V H, Cuong T V, Huy S H, Oh E, Kim E J, Shin E W and Chung J S 2011 *J. Mater. Chem.* **21** 3371

[13] Razak S I A, Ahmad A L and Zein S H S 2009 *J. Phys. Sci.* **20** 27

**Figure 7.** SEM images of composite compared with GO and TiO2.

**Figure 8.** TEM images of PANi-TiO2-GO composite.