

# Characterization and Physical Properties Investigation of Conducting Polypyrrole/TiO<sub>2</sub> Nanocomposites Prepared Through a One-Step “*In Situ*” Polymerization Method

Mirzaagha Babazadeh,<sup>1,2</sup> Faezeh Rezazad Gohari,<sup>1</sup> Ali Olad<sup>3</sup>

<sup>1</sup>Department of Chemistry, Tabriz Branch, Islamic Azad University, Tabriz, Iran

<sup>2</sup>Department of Chemistry, Bostanabad Branch, Islamic Azad University, Bostanabad, Iran

<sup>3</sup>Department of Applied Chemistry, Faculty of Chemistry, University of Tabriz, Tabriz, Iran

Received 16 September 2010; accepted 12 April 2011

DOI 10.1002/app.34689

Published online 22 August 2011 in Wiley Online Library (wileyonlinelibrary.com).

**ABSTRACT:** Nowadays, nanocomposites are a special class of materials having unique physical properties and wide application potential in diverse areas. The present research work describes an efficient method for synthesis of a series of polypyrrole/titanium dioxide (PPy/TiO<sub>2</sub>) nanocomposites with different TiO<sub>2</sub> ratios. These nanocomposites were prepared by one-step *in situ* deposition oxidative polymerization of pyrrole hydrochloride using ferric chloride (FeCl<sub>3</sub>) as an oxidant in the presence of ultra fine grade powder of anatase TiO<sub>2</sub> nanoparticles cooled in an ice bath. The obtained nanocomposites were characterized by Fourier-transform infrared (FTIR), thermogravimetric analysis (TGA), X-ray diffraction (XRD), and scanning electron microscope (SEM) techniques. The

obtained results showed that TiO<sub>2</sub> nanoparticles have been encapsulated by PPy with a strong effect on the morphology of PPy/TiO<sub>2</sub> nanocomposites. Also, the synthesized PPy/TiO<sub>2</sub> nanocomposites had higher thermal stability than that of pure PPy. The investigation of electrical conductivity of nanocomposites by four-point probe instrument showed that the conductivity of nanocomposite at low TiO<sub>2</sub> content is much higher than of neat PPy, while with the increasing contents of TiO<sub>2</sub>, the conductivity decreases. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 1922–1927, 2012

**Key words:** nanocomposite; conducting polymers; polypyrrole; titanium dioxide; *in situ* polymerization

## INTRODUCTION

Recently, the development of conducting polymers such as polyaniline, polypyrrole, and polythiophene have drawn the attention of scientists, because of the versatility of their applications, stability in air, high electrical conductivity, and easy synthesis and polymerization.<sup>1–4</sup>

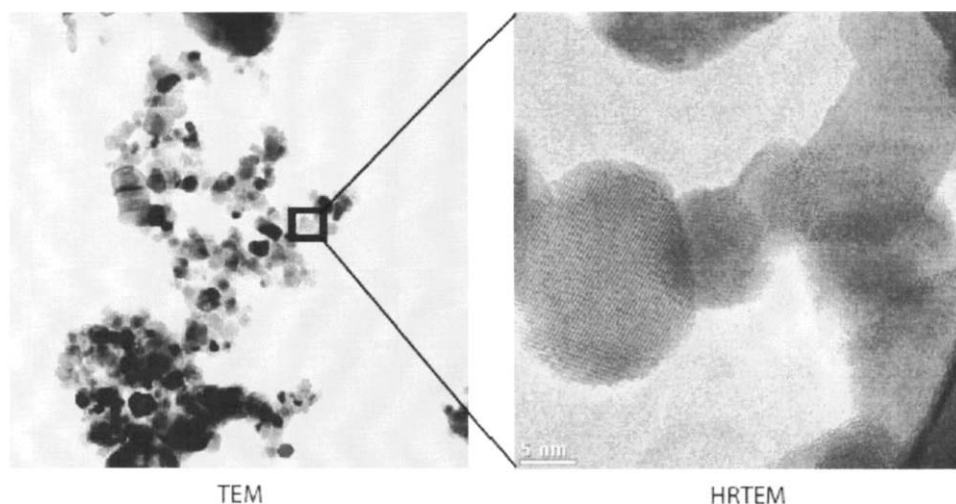
Conducting polymers can be prepared by chemical or electrochemical polymerization. In the chemical polymerization process, monomers are oxidized by oxidizing agents or catalysts to produce conducting polymers. The advantage of chemical synthesis is that it offers mass production at reasonable cost. On the other hand, the electrochemical method involves the direct formation of conducting polymers with better control of polymer film thickness and morphology, which makes them suitable for use in electronic devices.<sup>5,6</sup> Therefore, the physical and chemical properties of conducting polymers are considerably dependent upon the dopant and polymerization conditions.

Polypyrrole (PPy) is a conductive polymer with a conjugated-electron backbone that displays unusual electronic properties and uses in batteries, supercapacitors, electrochemical (bio) sensors, conductive textiles and fabrics, mechanical actuators, electromagnetic interference shielding, antistatic coating, and drug delivery systems.<sup>7–10</sup> However, the principal problems with the practical utilization of conducting polymers like PPy include its poor mechanical properties like brittleness and low processibility.

Nanocomposites are a special class of materials having unique physical properties and wide application potential in diverse areas. Novel properties of nanocomposites can be obtained by the successful combination of the characteristics of parent constituents into a single material. Encapsulation of inorganic nanoparticles inside the shell of conducting polymers is the most popular and interesting aspect of nanocomposites synthesis. These materials differ from both the pure polymers and the inorganic nanoparticles in some of the physical and chemical properties.<sup>11,12</sup>

Conducting polymer–inorganic oxide nanocomposites have recently attracted great attention owing to their unique microstructure, outstanding physicochemical and electro-optical properties, and wide

Correspondence to: M. Babazadeh (babazadeh@iaut.ac.ir).



**Figure 1** TEM image of TiO<sub>2</sub> nanoparticles.

range of potential uses as a battery cathode and also in constructing nanoscopic assemblies in sensors and microelectronics.<sup>13,14</sup>

Titanium dioxide (TiO<sub>2</sub>) is an important inorganic material in preparing conducting polymer composites because of its excellent physical and chemical properties, as well as extensive applications in diverse areas, such as coatings, solar cells, and photocatalysts.<sup>15,16</sup>

This present research work describes an efficient method to synthesize and characterization of PPy/TiO<sub>2</sub> nanocomposites by one-step *in situ* polymerization of pyrrole. TiO<sub>2</sub> nanoparticles with an average diameter about 15 nm were used as a dopant of PPy. The characteristics of the molecular structure, crystallinity, electrical properties, thermal stability, and morphology of the PPy/TiO<sub>2</sub> nanocomposites are also discussed.

## EXPERIMENTAL

### Materials

Pyrrole monomer, having molar mass of 67 g/mol and density of 0.97 g/cm<sup>3</sup>, was purchased from Merck and triply distilled until a colorless liquid was obtained. The distilled pyrrole was stored at lower than 5°C in the absence of light. TiO<sub>2</sub> nanoparticles (anatase) with an average particle size of 15 nm (Fig. 1) was obtained from Degussa and used as received. All other chemicals were reagent grade or purer.

### Instrumental measurements

X-ray diffraction (XRD) patterns of neat TiO<sub>2</sub>, PPy, and PPy/TiO<sub>2</sub> nanocomposites were measured in the range of  $2\theta = 10\text{--}80^\circ$  by step scanning on the Simens X-ray diffraction D5000 with Cu K<sub>α</sub> radiation ( $\lambda = 0.154$  nm). Fourier-transform infrared (FTIR)

spectra of pristine TiO<sub>2</sub>, PPy, and PPy/TiO<sub>2</sub> nanocomposites were recorded on a Bruker Spectrometer Tensor 27 FTIR with KBr pellets. The size of TiO<sub>2</sub> particles was investigated with a Hitachi 600 transmission electron microscope (TEM). The morphology of neat TiO<sub>2</sub>, PPy, and PPy/TiO<sub>2</sub> nanocomposites was investigated by scanning electron microscopy (SEM, LEO-440i). Thermal stability of pure PPy and nanocomposites was investigated by thermal gravimetric analyzer (Perkin-Elmer, TGA-7) under a nitrogen flow (35 mL/min) and heating rate of 10 °C/min. The electrical conductivity of the samples was measured at room temperature on compressed pellets of the powder by conventional four-point probe technique using the following equations:

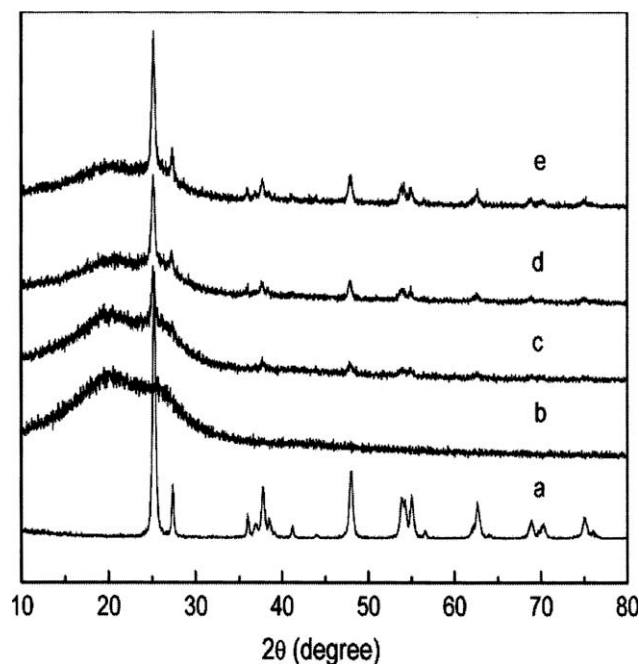
$$\text{Resistivity}(\rho) = \pi t / \ln 2(V/I) = 4.53 \times t \times (\text{resistance})$$

$$\text{Conductivity}(\sigma, \text{S/cm}) = 1/\rho$$

where,  $t$  is the thickness of the sample,  $V$  is the measured voltage, and  $I$  is the source current.

### Preparation of PPy

The distilled pyrrole (4.0 g, 60 mmol) was dissolved in 50 mL of 1.5M HCl aqueous solution. Ferric chloride (FeCl<sub>3</sub>, 1.0 g, 6 mmol) was dissolved in 20 mL of 1.5M HCl and added dropwise to the solution of pyrrole at 0°C. The polymerization was immediately initiated and the reaction was allowed to continue for 3 h at mentioned temperature with continuous stirring. The obtained black polymer was collected via filtration, washed several times with HCl solution and large amount of distilled water to remove excess FeCl<sub>3</sub>. The synthesized polymer was then dried under vacuum at 60°C for 24 h. Finally, 1.68 g of PPy as a black powder was collected with a yield of 42%.



**Figure 2** XRD curve of (a) pure  $\text{TiO}_2$ , (b) Pure PPy, (c)  $\text{PPy}/\text{TiO}_2$  (0.025), (d)  $\text{PPy}/\text{TiO}_2$  (0.05), and (e)  $\text{PPy}/\text{TiO}_2$  (0.1) nanocomposites.

### Preparation of $\text{PPy}/\text{TiO}_2$ nanocomposites

The  $\text{PPy}/\text{TiO}_2$  nanocomposites were synthesized according to the following method. Different amounts of  $\text{TiO}_2$  nanoparticles (0.025, 0.035, 0.05, 0.075, and 0.1 g) were separately suspended into 50 mL of 1.5M HCl aqueous solution and sonicated in an ultrasound bath for 20 min to get well dispersed. Then, pyrrole (4.0 g, 60 mmol) was added into the suspension at  $0^\circ\text{C}$  with constant stirring. After that,  $\text{FeCl}_3$  (1.0 g, 6 mmol) was dissolved in 20 mL of 1.5M HCl and added dropwise into the above cooled mixture. The *in situ* polymerization was carried out with the stirring speed of 600 rpm at  $0^\circ\text{C}$  for 3 h. The resulting precipitate was filtered off, washed several times with HCl solution and large amount of distilled water to remove excess  $\text{FeCl}_3$ . Finally, the samples were collected and dried under vacuum at  $60^\circ\text{C}$  for 24 h to obtain black  $\text{PPy}/\text{TiO}_2$  nanocomposites.

## RESULTS AND DISCUSSION

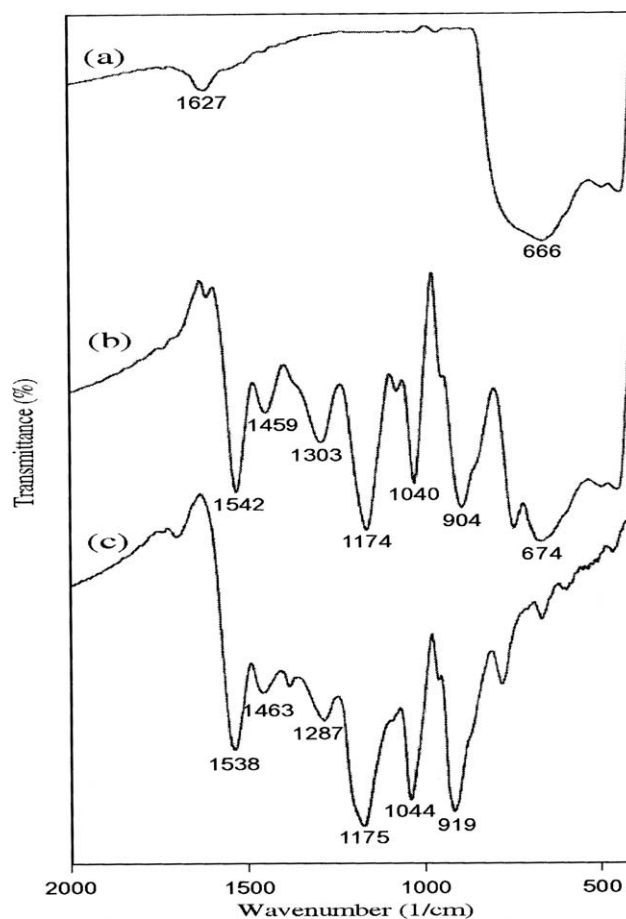
### XRD patterns study of nanocomposites

XRD patterns of pure  $\text{TiO}_2$ , PPy, and the synthesized  $\text{PPy}/\text{TiO}_2$  nanocomposites are presented in Figure 2. The broad peak in the region of  $2\theta = 10\text{--}30^\circ$  in XRD pattern of pure PPy (curve b) shows that the synthesized PPy in the absence of  $\text{TiO}_2$  nanoparticles is amorphous. Also, the main diffraction peaks of pure anatase  $\text{TiO}_2$  nanoparticles are appeared at  $25^\circ$ ,  $38^\circ$ , and  $48^\circ$  (curve a). It can be seen from curves (c–e)

that the main peaks of  $\text{PPy}/\text{TiO}_2$  nanocomposites are similar to those of neat  $\text{TiO}_2$  nanoparticles. XRD patterns of  $\text{PPy}/\text{TiO}_2$  nanocomposites show that the broad weak diffraction peak of PPy still exists, but its intensity has been decreased. It implies that when pyrrole is polymerized on  $\text{TiO}_2$ , each phase maintains his initial structure. The mean size of  $\text{TiO}_2$  nanoparticles and  $\text{PPy}/\text{TiO}_2$  nanocomposites, calculated by Scherrer's formula, are about 19 nm and 30 nm, respectively. The result is in good agreement with the TEM image of  $\text{TiO}_2$  nanoparticles.

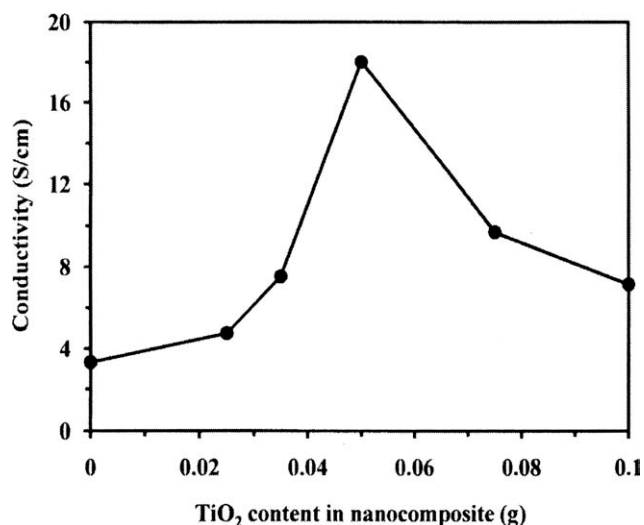
### FTIR spectra investigation

The FTIR spectra of pure  $\text{TiO}_2$ , PPy, and  $\text{PPy}/\text{TiO}_2$  nanocomposites are shown in Figure 3. The spectrum of pristine  $\text{TiO}_2$  [Fig. 3(a)] shows one major band at  $666\text{ cm}^{-1}$  and a weak peak at  $1627\text{ cm}^{-1}$  in the  $400\text{--}2000\text{ cm}^{-1}$  range. The FTIR spectrum of pure PPy powder prepared with the  $\text{FeCl}_3$  oxidant [Fig. 3(c)] shows that characteristic bands around  $1538$  and  $1463\text{ cm}^{-1}$  correspond to the  $\text{C}=\text{C}$  and  $\text{C}-\text{N}$  stretching modes, respectively. The bands at  $1287$  and  $1044\text{ cm}^{-1}$  are related to the in-plane



**Figure 3** FTIR spectra of (a) pristine  $\text{TiO}_2$ , (b)  $\text{PPy}/\text{TiO}_2$  nanocomposites, and (c) pure PPy.





**Figure 4** Electrical conductivity versus the contents of TiO<sub>2</sub> in PPy/TiO<sub>2</sub> nanocomposites.

vibrations of C—H, and strong bands near 1175 and 919 cm<sup>-1</sup> indicate the doping state of PPy.<sup>17</sup> The FTIR spectrum of PPy/TiO<sub>2</sub> nanocomposite [Fig. 3(b)] is similar of the PPy spectrum, which shows that PPy chains have been formed in the nanocomposites. However, the incorporation of TiO<sub>2</sub> leads to the obvious shift of some FTIR bands of PPy.

#### Electrical conductivity measurement

The electrical conductivity was measured by four-point probe technique. The obtained conductivity results showed that with increasing TiO<sub>2</sub> content in nanocomposite structure, the conductivity increases slightly, but excess TiO<sub>2</sub> content causes decreasing of conductivity (Fig. 4). As shown in Figure 4, the conductivity of pure PPy is 3.3 S/cm, and dramatically increases to 18.02 S/cm when the TiO<sub>2</sub> content increases to 0.05 g at PPy/TiO<sub>2</sub> nanocomposites. This phenomenon is quite inconsistent with the results of most conducting composites combined with inorganic particles. The doping by TiO<sub>2</sub> nanoparticles may be induce the formation of more efficient network for charge transport in the polypyrrole chains, leading to higher conductivity.<sup>18</sup> Similar results have also been reported for polyaniline/TiO<sub>2</sub> composites.<sup>19,20</sup> Also, it was found that when content of TiO<sub>2</sub> in nanocomposites increases from 0.05 g to 0.075 g and 0.1 g, the conductivity gradually decreases. This decreasing conductivity showed that with introducing excess TiO<sub>2</sub> nanoparticles in nanocomposite structures, the transport of carriers between different molecular chains of PPy is hindered and the conductivity decreases. On the other hand, the interaction at the interface of PPy and

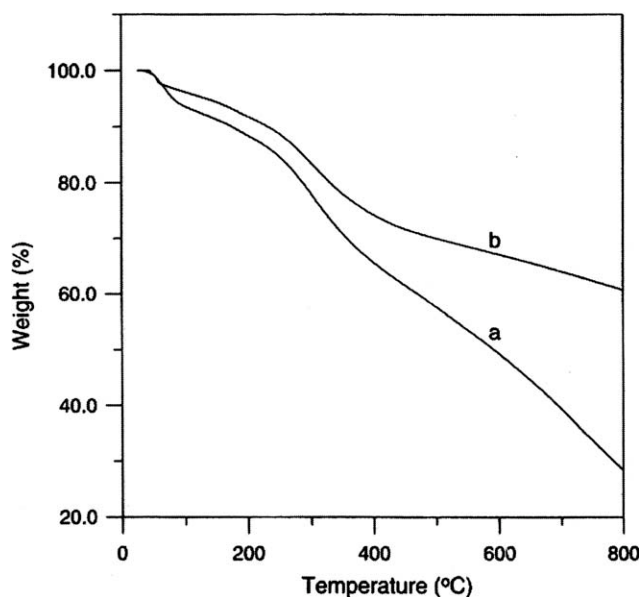
TiO<sub>2</sub> probably led to the reduction of the conjugation length of PPy in nanocomposites.

#### TGA diagrams investigation

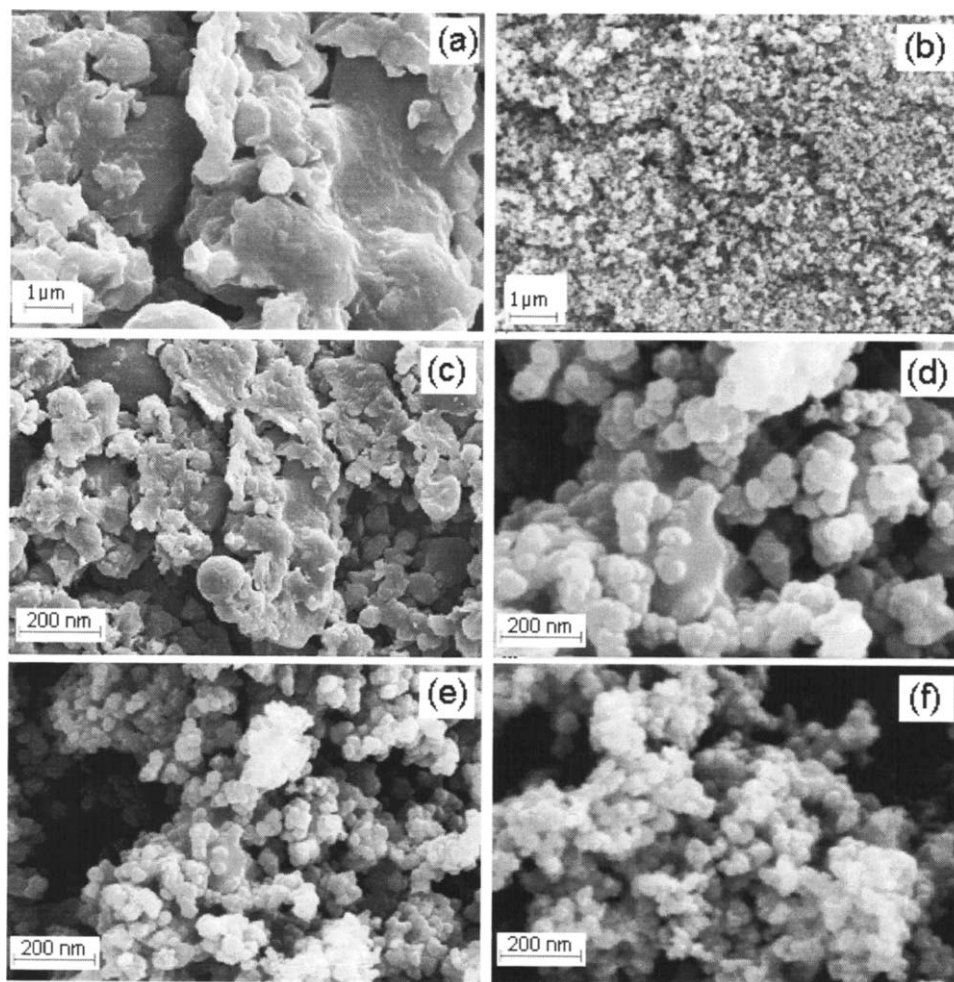
TGA diagrams for pure PPy and the PPy matrix in the PPy/TiO<sub>2</sub> nanocomposites are shown in Figure 5. Due to the thermal stability of the TiO<sub>2</sub>, and to allow a better comparison between the analyses of PPy and PPy-TiO<sub>2</sub> nanocomposites, curve (b) in this figure demonstrates the weight change of the PPy matrix in the PPy-TiO<sub>2</sub> nanocomposites. As shown in Figure 5, a serious degradation observes at ~ 100°C which can be caused by the presence of a little residual water in the synthesized samples. In the PPy/TiO<sub>2</sub> nanocomposites, the obvious degradation begins at ~ 250°C and the degradation is depressed at ~ 450°C. At the ending temperature of 800°C, the weight loss of the PPy in the pure PPy and the PPy/TiO<sub>2</sub> nanocomposites are 72 and 39%, respectively. Also, the temperature at the 10% weight loss for the pure PPy and the PPy/TiO<sub>2</sub> nanocomposites are 175 and 233°C, respectively. Therefore, the obtained TGA results suggest that the PPy/TiO<sub>2</sub> nanocomposites have higher thermal stability than pure PPy in this study.

#### SEM images study

The morphology and shape of pure TiO<sub>2</sub> nanoparticles, neat PPy, and PPy/TiO<sub>2</sub> nanocomposites were characterized by SEM instrument and the obtained pictures are presented in Figure 6. As shown in Figure 6(a), TiO<sub>2</sub> nanoparticles were aggregated due to their high surface energy. Figure 6(c) shows that the morphology of composite at low content of TiO<sub>2</sub>



**Figure 5** TGA diagrams of (a) PPy and (b) PPy/TiO<sub>2</sub> nanocomposites.



**Figure 6** SEM images of (a) pure PPy, (b) pure  $\text{TiO}_2$ , (c) PPy/ $\text{TiO}_2$  (0.025), PPy/ $\text{TiO}_2$  (0.05), PPy/ $\text{TiO}_2$  (0.075), and PPy/ $\text{TiO}_2$  (0.1) nanocomposites.

(0.025 g  $\text{TiO}_2$ ) is much similar to that of neat PPy [Fig. 6(b)], and with increasing contents of  $\text{TiO}_2$ , the morphology of composites appears as nanoparticles [Fig. 6(d,e)]. It indicates that the  $\text{TiO}_2$  nanoparticles have a nucleus effect on the pyrrole polymerization and caused a homogeneous PPy shell around them. The SEM images help us draw a conclusion that the doping of  $\text{TiO}_2$  has a strong effect on PPy's morphology and with the increase of  $\text{TiO}_2$  contents, the composites show a transformation in morphology from typical PPy to nanoparticles.

### CONCLUSIONS

Conducting PPy/ $\text{TiO}_2$  nanocomposites in HCl solution were successfully prepared by one-step *in situ* chemical oxidative polymerization of pyrrole using  $\text{FeCl}_3$  as oxidant in the presence of ultra fine grade powder of anatase nano- $\text{TiO}_2$  particles cooled in an ice bath. The obtained results from XRD, FT-IR, TGA, and SEM data confirmed that  $\text{TiO}_2$  nanoparticles are encapsulated by PPy. Electrical conductiv-

ity measurements indicate that the conductivity of nanocomposites at low  $\text{TiO}_2$  content is much higher than that of neat PPy, while with the increasing contents of  $\text{TiO}_2$ , the conductivity shows an orderly decrease. TGA investigation shows that thermal stability of PPy/ $\text{TiO}_2$  nanocomposites is higher in comparison with pure PPy. SEM study shows that  $\text{TiO}_2$  nanoparticles have a strong effect on the morphology of PPy/ $\text{TiO}_2$  nanocomposites. This employed method is very simple and inexpensive, and it can be easily applied industrially.

### References

1. Skotheim, T. A.; Elsenbaumer, R.; Reynolds, J. R. *Handbook of Conducting Polymers*; Marcel Dekker: New York, 1998.
2. Su, P. G.; Chang, Y. P. *Sens Actuators B Chem* 2008, 129, 915.
3. Hatechett, D. W.; Josowicz, M. *Chem Rev* 2008, 108, 746.
4. Lange, U.; Roznyatovskaya, N. V.; Mirsky, V. M. *Anal Chim Acta* 2008, 614, 1.
5. Ram, M. K.; Adami, M.; Faraci, P.; Nicolini, C. *Polymer* 2000, 41, 7499.
6. Oh, E. J.; Jang, K. S. *Synth Met* 2001, 119, 109.
7. Kuwabata, S.; Tomiyori, M. *J Electrochem Soc* 2002, 149, A988.

8. An, K. H.; Jeon, K. K.; Heo, J. K.; Lim, S. C.; Bae, D. J.; Lee, Y. H. *J Electrochem Soc* 2002, 149, A1058.
9. Jurewicz, K.; Delpeux, S.; Bertagna, V.; Beguin, F.; Frackowiak, E. *Chem Phys Lett* 2001, 347, 36.
10. Ruangchuay, L.; Sirivat, A.; Schwank, J. *Synth Met* 2004, 140, 15.
11. He, Y. *Powder Tech* 2004, 147, 59.
12. Liu, Y. C.; Huang, J. M.; Tsai, C. E.; Chuang, T. C.; Wang, C. C. *Chem Phys Lett* 2004, 387, 155.
13. Rupali, G.; Amitabha, D. *Sens Actuators B: Chem* 2001, 77, 326.
14. Yuvaraj, H.; Park, E. J.; Gal, Y. S.; Taek, L. K. *Colloids Surf A* 2008, 313/314, 300.
15. Zhang, L.; Liu, P.; Su, Z. *Polym Degrad Stab* 2006, 91, 2213.
16. Bian, C.; Yu, Y.; Xue, G. *J Appl Polym Sci* 2007, 104, 21.
17. Liu, J.; Wan, M. *J Mater Chem* 2001, 11, 404.
18. Armes, S. P.; Gottesfeld, S.; Beery, J. G.; Garzon, F.; Agnew, S. F. *Polymer* 1991, 32, 2325.
19. Su, S. J.; Kuramoto, N. *Synth Met* 2000, 114, 147.
20. Mo, T. C.; Wang, H. W.; Chen, S. Y.; Yeh, Y. C. *Ceram Int* 2008, 34, 1767.