



## Preparation and Characterization Polyaniline/TiO<sub>2</sub> Composites

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This work presents the synthesis and characterization of polyaniline/TiO<sub>2</sub> composites (PTC). Polyaniline/TiO<sub>2</sub> composites was prepared by chemical oxidation of aniline and TiO<sub>2</sub> by ammonium peroxydisulfate [(NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>] as an oxidant in sulfuric acid medium. The polyaniline/TiO<sub>2</sub> composite was characterized in terms of particle size, morphology and chemical structure. The chemical structure of product were studied by fourier transform infrared spectroscopy, scanning electron microscopy and X-ray diffraction.

**Key Words:** Polyaniline, Titanium oxid (TiO<sub>2</sub>), Composite, Morphology.

### INTRODUCTION

Polymer and metal oxides have been studied for many years for their independent electrical, optical and mechanical properties. Recently, the combination of semiconducting and mechanical properties of conjugated polymers with the properties of metals or semiconducting inorganic particles has brought new prospects for applications<sup>1</sup>. One widely studied metal oxide is titanium dioxide due to its unique optical, electrical, chemical, high photocatalytic activity and photoelectric conversion efficiency properties<sup>2-4</sup>.

Titanium dioxide is one of the typical of *n*-type semiconductor, while polyaniline is one of the typical conductive polymers, which is usually considered as *p*-type materials. It has good mechanical flexibility and environmental stability and its conductivity could be controlled with acid/base (doping/undoping), it has potential application in many fields, such as lightweight battery electrode, electromagnetic shielding device, anticorrosion coatings and sensors<sup>5,6</sup>. Additionally, in the fields of sensors, the conductive polymer is one kind of sensitive materials at or near room temperature operating and has a convenient operating and attractive prospect of development<sup>7,9</sup>.

Among all the conducting polymers, polyaniline is generally recognized to be one of the most important conducting polymers and has the great potential for commercial application because of its unique electrical, optical and optoelectrical properties, as well as its ease of preparation and excellent environment stability<sup>10-12</sup>. Nano-TiO<sub>2</sub> also has excellent physical and chemical properties and it has been used in coating, sensor, solar cell and photocatalyst<sup>13-16</sup>. Although a large number of studies on composite materials of polyaniline/TiO<sub>2</sub> have been

reported, most of researches on these polymers are still focusing on the preparation of materials and morphology characterization<sup>17,18</sup>.

In this study, characteristics of polyaniline/TiO<sub>2</sub> composite such as morphology, chemical structure and particle size were studied.

### EXPERIMENTAL

A magnetic mixer model MK20, digital scale model FR 200, scanning electron microscope (SEM) model XL30, fourier transform infrared (FTIR) spectrometer model shimadzu 4100 and X-ray diffraction (XRD) model PW3040/60 were employed.

Materials used in this work were aniline (extra pure > 99 %,  $d = 1.02 \text{ g/cm}^3$ ), ammonium peroxydisulfate and sulfuric acid from Merck. TiO<sub>2</sub> (anatase) nanoparticles with an average 250 nm. All reagents were used as received without further purification, unless stated otherwise. Distilled deionized water was used throughout this work. Aniline monomer was purified by simple distillation.

**Preparation of polyaniline/TiO<sub>2</sub>:** For preparation of polyaniline/TiO<sub>2</sub> nanocomposite, 2.5 g [(NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>] was added to 100 mL of sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) 1.0 M and then a uniform solution was resulted by using magnetic mixer. Then 2 g of TiO<sub>2</sub> was added to the solution and 1 mL fresh distilled aniline monomer was injected to stirred solution. The reaction was carried out for 5 h at room temperature. Consequently, the product was filtered to separate the impurities. Product was washed several times with deionized water and dried at temperature about 40 °C.

**Preparation of polyaniline/TiO<sub>2</sub> with PVP as surfactant:** For preparation of polyaniline/TiO<sub>2</sub> nanocomposite with PVP, 2.5 g ((NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>) was added to 50 mL of sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) 1.0 M and then a uniform solution was resulted by using magnetic mixer. A 2 g of TiO<sub>2</sub> was added to the 50 mL solution containing 0.6 g of poly(vinyl pyrrolidone) (PVP). Then two solutions mixed and 1.0 mL fresh distilled aniline monomer was injected to stirred solution. The reaction was carried out for 5 h at room temperature. Consequently, the product was filtered to separate the impurities. Product was washed several times with deionized water and dried at temperature about 40 °C in oven for 18 h.

## RESULTS AND DISCUSSION

### Characterization of PAN/TiO<sub>2</sub> composite

The scanning electron micrographs of TiO<sub>2</sub>, Polyaniline (PAN) and PAN/TiO<sub>2</sub> composite was analyzed using Hitachi (model S3000 H) instrument. The pigment was spread over a copper block over, which gold was sputtered. The FTIR spectra of TiO<sub>2</sub>, PAN FTIR spectrometer in wave number range 2000-500 cm<sup>-1</sup>. The powder X-ray diffraction of the TiO<sub>2</sub>, PAN was analyzed using PHILIPS (model PW3040/60) X-ray diffractometer using Cu K-radiation in the 2θ range 5-90° at the scan range of 0.0170° 2θ with continuous scan type with scan step time of 15.5056 s.

**Morphology of polymer:** The scanning electron micrographs of PAN, TiO<sub>2</sub>, PAN/TiO<sub>2</sub> and PAN/TiO<sub>2</sub> with PVP composite are shown in Figs. 1-5, respectively. It can be seen that large sized crystals of TiO<sub>2</sub> is fully covered by polyaniline in the case of PAN/TiO<sub>2</sub> composite. The effect of amount of surfactant on the particle size of PAN/TiO<sub>2</sub> composite are shown in Table-1.

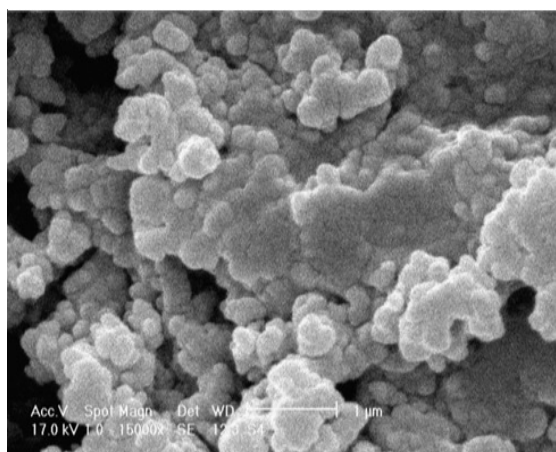


Fig. 1. Scanning electron micrograph of PAN generated in aqueous media. Reaction conditions: ((NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> = 25 g/L, aniline monomer 10.75 × 10<sup>-2</sup> mol/L, reaction time 5 h at room temperature)

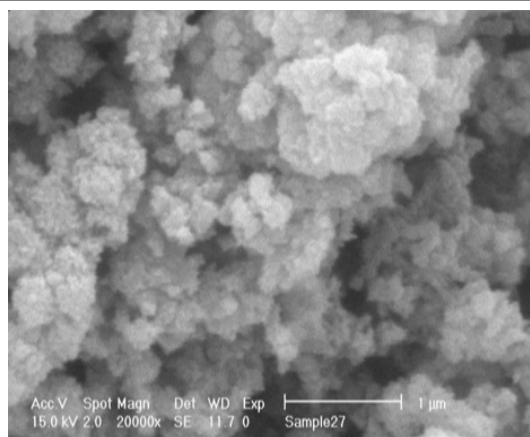


Fig. 2. Scanning electron micrograph of PAN/PVP in aqueous media. Reaction conditions: ((NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> = 25 g/L, aniline monomer 10.75 × 10<sup>-2</sup> mol/L, PVP = 6 g/L, Reaction time 5 h at room temperature)

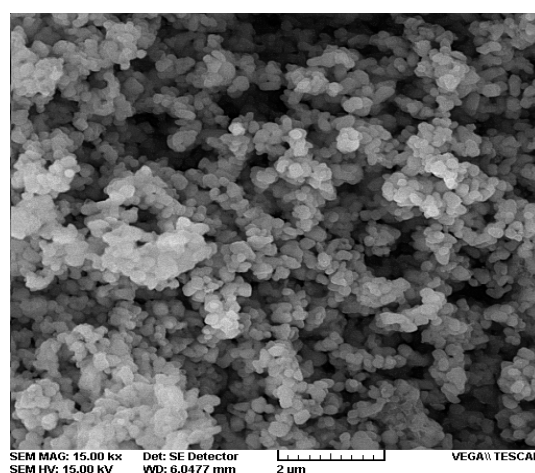


Fig. 3. Scanning electron micrograph of the pure TiO<sub>2</sub> particles showing the average particle size of approximately 250 nm

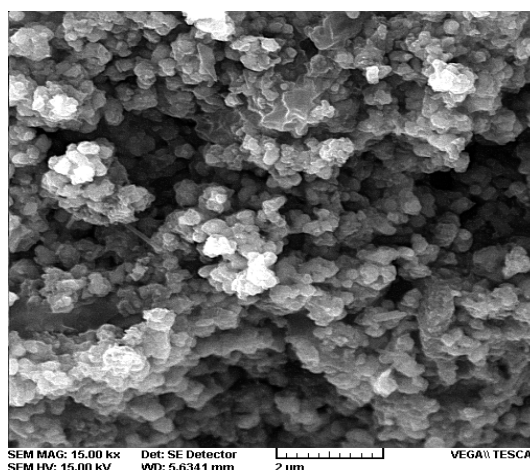


Fig. 4. Scanning electron micrograph of PAN/TiO<sub>2</sub> in aqueous media. Reaction conditions: ((NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> = 25 g/L, aniline monomer 10.75 × 10<sup>-2</sup> mol/L, TiO<sub>2</sub> = 20 g/L, Reaction time 5h at room temperature)

TABLE-1  
PREPARATION CONDITIONS AND EFFECT OF SURFACTANT ON THE PARTICLE SIZE

Type of product	Type of oxidant	Concentration of surfactant (g/L)	Average particle size (mm)
Polyaniline	(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	---	350
Polyaniline with Poly (vinyl pyrrolidone)	(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	0.6	100
Polyaniline /TiO <sub>2</sub>	(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	---	350
Polyaniline /TiO <sub>2</sub> with Poly (vinyl pyrrolidone)	(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	0.6	300

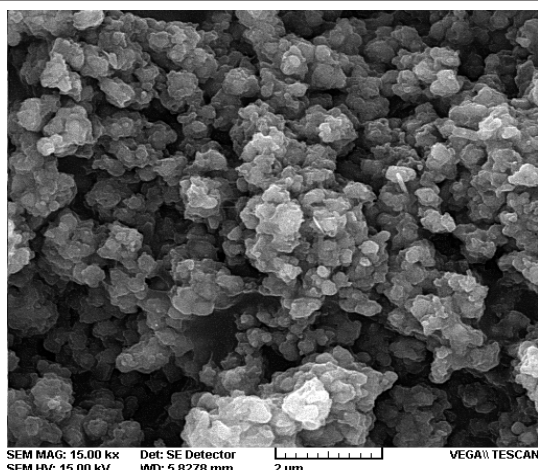


Fig. 5. Scanning electron micrograph of PAN/TiO<sub>2</sub> in aqueous media. Reaction conditions: ((NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> = 25 g/L, aniline monomer 10.75 × 10<sup>-2</sup> mol/L, TiO<sub>2</sub> = 20 g/L and PVP = 6 g/L, Reaction time 5 h at room temperature)

Figs. 6 and 7 showed the FTIR spectra of PAN and PAN-TiO<sub>2</sub> composite, respectively. The main characteristics of bands of polyaniline are found at 1609 and 1303 cm<sup>-1</sup> which are the stretching mode of C=N and C=C, respectively. The band at 1222 cm<sup>-1</sup> is due to C-N stretching mode of benzenoid ring and the band at 1124 cm<sup>-1</sup> is assigned to a plane bending vibration of C-H mode. These peaks when compared to that of pure polyaniline<sup>19</sup> are found to be shifted slightly due to strong interaction of TiO<sub>2</sub> particle with polyaniline. Similar observation has been reported by Lee *et al.*<sup>20</sup>. In the case of TiO<sub>2</sub>, strong absorption around 670 cm<sup>-1</sup>. due to Ti-O stretching<sup>21</sup> is observed while this band is found to be weak in PAN/TiO<sub>2</sub> composite due to the presence of PAN.

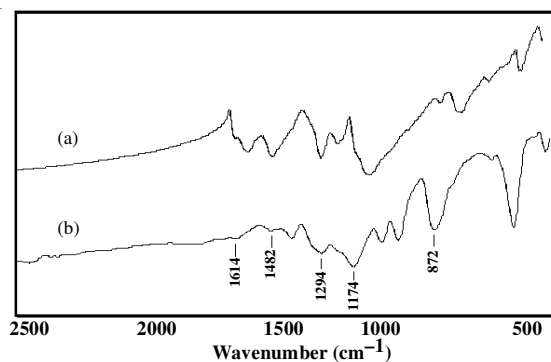


Fig. 6. FTIR spectra of a) PAN and b) PAN with PVP

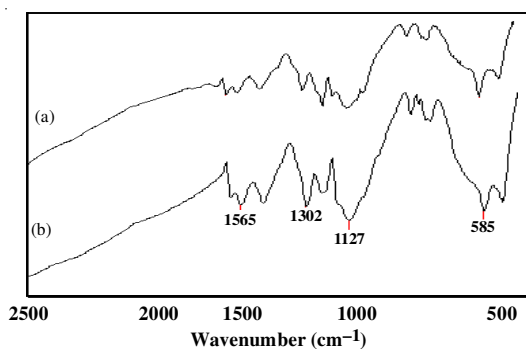


Fig. 7. FTIR spectra of a) PAN/TiO<sub>2</sub> composite and b) PAN/TiO<sub>2</sub> composite with PVP

Fig. 8 showed the XRD pattern of TiO<sub>2</sub>, PAN/TiO<sub>2</sub> and PAN/TiO<sub>2</sub> composite (PTC) with PVP. It can be seen that the XRD pattern of PTC is more or less similar to that of TiO<sub>2</sub>. Further the broad diffraction peak of PAN at 2θ = 27.6° is absent in the polyaniline/TiO<sub>2</sub> composite which indicates that the presence of TiO<sub>2</sub> in the polymerization system strongly affects the crystalline behaviour of formed PAN and the interaction of PAN and TiO<sub>2</sub> restrict the crystallization of PAN. When polyaniline absorbed on the surface of TiO<sub>2</sub> particles, the molecular chain of absorbed PAN is confined and the degree of crystallinity decreases. But in the case of PAN-MnO<sub>2</sub> composites, it is reported that the crystallographic phase of MnO<sub>2</sub> is distorted due to polymerization reaction<sup>22</sup>. It also confirms that the polyaniline deposited on the surface of TiO<sub>2</sub> particles has no effect on the crystallization behaviour of TiO<sub>2</sub> particles. Lee *et al.*<sup>20</sup> and Xu *et al.*<sup>23</sup> have reported similar observation on the XRD pattern of polyaniline/nano-TiO<sub>2</sub> composites.

The main peaks of the PAN/TiO<sub>2</sub> composite 2 = 27.6°, 36.25°, 41.4°, 54.45°, 56.75°, 69.15° respectively. According to Scherrer's equation<sup>24</sup>:

$$\beta = k\lambda / D\cos\theta$$

where  $\lambda$  is the X-ray wavelength,  $k$ , the shape factor,  $D$ , the average diameter of the crystals in angstroms,  $\theta$ , the bragg angle in degree and  $\beta$  is the line broadening measured by half-height in radians. The value of  $k$  depends on several factors, including the miller index of the reflection plane and the shape of the crystal. If the shape is unknown  $k$  is often assigned a value of 0.89. When the reflecting peak at 2θ = 27.6° are chosen to calculate the average diameter. The average diameter of the crystals of the pure TiO<sub>2</sub>, PAN/TiO<sub>2</sub> composite and PAN/TiO<sub>2</sub> composite with PVP are 52, 52 and 44 nm, respectively.

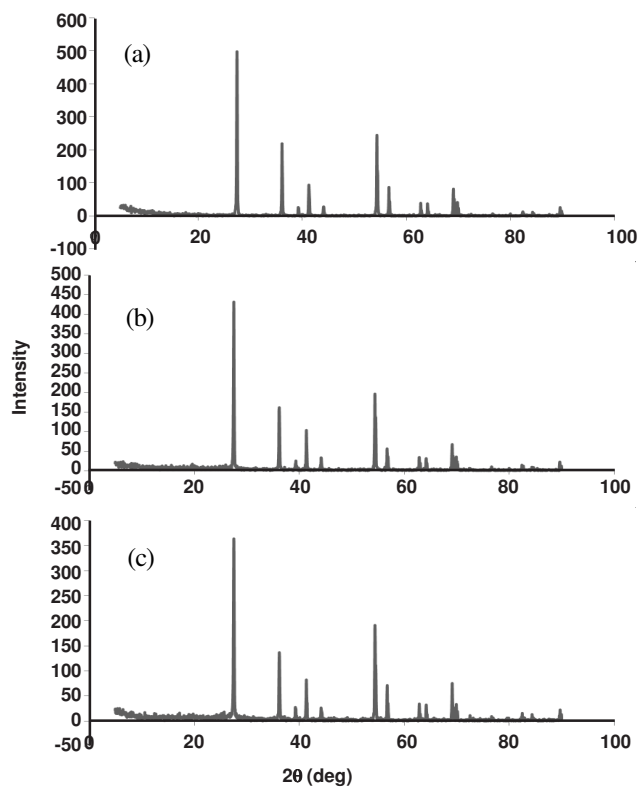


Fig. 8. XRD pattern of a) TiO<sub>2</sub>, b) PAN/TiO<sub>2</sub> composite and c) PAN/TiO<sub>2</sub> composite with PVP

## Conclusion

PAn/TiO<sub>2</sub> composite can be successfully prepared by chemical polymerization of aniline and TiO<sub>2</sub> in the presence of sulfuric acid using ammonium peroxydisulfate as an oxidant. The FTIR spectra of PAn/TiO<sub>2</sub> composite is similar to that of PAn. XRD pattern of PAn/TiO<sub>2</sub> composite indicates that the crystallinity of TiO<sub>2</sub> is not altered by polyaniline coating. The XRD pattern shown that the polyaniline has no effect on the crystalline behaviour of TiO<sub>2</sub>. The SEM studying of PAn/TiO<sub>2</sub> composite have shown that the TiO<sub>2</sub> particles are fully covered with polyaniline. Also by addition of the surfactant PVP to the solution particles size decreases, because surfactant influence the physical and chemical properties of solution. As shown in the figures, the surfactant has a considerable effect on the size and homogeneity of particles.

## REFERENCES

1. Q.T. Vu, M. Pavlik, N. Hebestreit, J. Pflieger, U. Rammelt and W. Plieth, *Electrochim. Acta*, **51**, 1117 (2005).
2. Q.T. Vu, M. Pavlik, N. Hebestreit and U. Rammelt, *React. Funct. Polym.*, **65**, 69 (2005).
3. J.J.M. Halls, K. Pichler, R.H. Friend, S.C. Moratti and A.B. Holmes, *Appl. Phys. Lett.*, **68**, 3120 (1996).
4. K. Takahashi, Y. Takano, T. Yamaguchi, J.I. Nakamura, C. Yokoe and K. Murata, *Synth. Met.*, **155**, 51 (2005).
5. J. Huang and R.B. Kaner, *J. Am. Chem. Soc.*, **126**, 851 (2004).
6. X. Zhang, W.J. Goux and S.K. Manohar, *J. Am. Chem. Soc.*, **126**, 4502 (2004).
7. M. Matsuguchi, J. Io, G. Sugiyama and Y. Sakai, *Synth. Met.*, **128**, 15 (2002).
8. A. Riul Jr., A.M. Gallardo Soto, S.V. Mello, S. Bone, D.M. Taylor and L.H.C. Mattoso, *Synth. Met.*, **132**, 109 (2003).
9. V.V. Chabukwar, S. Pethkar and A.A. Athawale, *Sens. Actuators B.*, **77**, 657 (2001).
10. G. Gustafsson, Y. Cao, G.M. Treacy, F. Klavetter, N. Colaneri and A.J. Heeger, *Nature*, **357**, 477 (1992).
11. A.G. MacDiarmid, *Synth. Met.*, **84**, 27 (1997).
12. N. Gospodinova and L. Terlemezyan, *Prog. Polym. Sci.*, **23**, 1443 (1998).
13. X. Wang, Y. Zu and X. Li, *Adv. Chem. Technol.*, **1**, 67 (2000).
14. W. Zhou, C.W. Sun and Z.Z. Yang, *Acta Inorg. Mater.*, **13**, 275 (1998).
15. B. O'Regan and M. Gratzel, *Nature*, **353**, 737 (1991).
16. M. Machida, K. Norimoto, T. Watanabe, K. Hashimoto and A. Fujishima, *J. Mater. Sci.*, **34**, 2569 (1999).
17. D.C. Schnitzler, M.S. Meruvia, I.A. Hummelgen and A.J.G. Zarbin, *Chem. Mater.*, **15**, 4658 (2003).
18. M. Baibarac, I. Baltog, S. Lefrant, J.Y. Mevellec and O. Chauvet, *Chem. Mater.*, **15**, 4149 (2003).
19. S. Sathiyarayanan, S. Muthukrishnan and G. Venkatachari, *Electrochim. Acta*, **51**, 6313 (2006).
20. I.S. Lee, J.Y. Lee, J.H. Sung and H.J. Choi, *Synth. Met.*, **152**, 173 (2005).
21. K. Gurunathan, D.P. Amalnerker and D.C. Trivedi, *Mater. Lett.*, **57**, 1642 (2003).
22. A.H. Gemeay, J.A. Mansour, R.G. El-Sharkaway and A.B. Zaki, *Eur. Polym. J.*, **41**, 2575 (2005).
23. J.C. Xu, W.M. Liu and H.L. Li, *Mater. Sci. Eng.*, **25**, 444 (2005).
24. H.P. Klong and L.E. Alexander, *X-ray Diffraction procedures for Crystalline and Amorphous Materials*, Wiley, New York, pp. 491-539 (1959).