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Preparation and Properties of TiO_2 Microparticles and its Composites with Polypyrrole

HAITAO ZHAO[1,*], RUIPING LIU[1], SHAOHONG LIU[2] and RUITING MA[1]

[1]School of Materials Science and Engineering, Shenyang Ligong University, Shenyang 110168, P.R. China
[2]Key Laboratory for Anisotropy and Texture of Materials (Ministry of Education), School of Materials and Metallurgy, Northeastern University, Shenyang 110004, P.R. China

*Corresponding author: E-mail: zht95711@163.com

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Spherical anatase TiO_2 microparticles with good crystallinity were successfully synthesized by the homogeneous precipitation under mild conditions with ammonium fluorotitanate as the titanium source and urea as the precipitant. Then the TiO_2 microparticles were used as nucleus for the preparation of TiO_2/polypyrrole(TiO_2/PPy) composite. TiO_2/PPy composite was prepared by *in situ* polymerization of pyrrole on TiO_2 microparticles. The structural characteristics, morphology and dielectric properties of the composite powders were obtained by X-ray diffraction, scanning electron microscope and network analyzer. The results show that TiO_2 microspheres obtained in this work are anatase-type. The higher reaction temperature leads to smaller anatase microspheres. The morphologies of the final particles change into irregular with the increase of the reaction time. The ε′, ε″ and tande value for TiO_2/PPy composite are higher than polypyrrole in the frequency range of 8.2-12.4 GHz. The tande value for TiO_2/PPy has achieved a maximum of 0.57 at 11.9 GHz.

Keywords: TiO_2, Polypyrrole, Dielectric properties, Homogeneous precipitation.

INTRODUCTION

Conducting polymer-inorganic composite materials are receiving growing research interests in recent years, since they usually provide a new functional hybrid with synergetic or complementary activity between organic and inorganic materials, which are not available from their single components and can provide novel or enhanced properties for various applications[1-4]. The conducting polymer composites are attractive due to their various practical applications, such as rechargeable batteries, molecular electronics, corrosion protection coatings, electromagnetic interference shielding and microwave-absorbing materials[5-9], *etc*.

Polypyrrole is one of much interest due to its simple synthesis, unique properties and excellent environment stability. TiO_2 is one of the most promising photocatalysts and semiconductor because of its high photoactivity, low cost, nontoxicity, superior delivering ability, low density and chemical stability[10-13]. Moreover, TiO_2 is an excellent wave-transmitting material, which can widen the frequency bandwidth of microwave absorber[14]. Many ways have been explored for making TiO_2 particles of the small size[15]. However, monodispersed TiO_2 microspheres of good dispersion and stability by direct hydrolysis of titanium alkoxides are difficult to be prepared at temperatures below 100 °C[16,17]. Recently, the homogeneous precipitation method has been preferably used. The advantages of this method include processing at low temperatures, simpler synthetic process and the ease of morphology control. Therefore the homogeneous precipitation method is an economical way to synthesize TiO_2 powders.

Some work has been carried out to investigate the effect of operating conditions on the properties of TiO_2/PPy. Deng *et al.*[18] have successfully prepared conductive TiO_2/PPy nanocomposites by surface molecular imprinting technique using methyl orange as template molecule and the photocatalytic activity of the molecularly imprinted TiO_2/PPy nanocomposites were studied. Su and Huang[19] have synthesized resistive-type humidity sensors through *in situ* photopolymerization of TiO_2 nanoparticles/polypyrrole(TiO_2 NPs/PPy) composite thin films on an alumina substrate and the humidity sensing and electrical properties of the TiO_2 NPs/PPy composite thin films were investigated. Turac and Sahmetlioglu[20] investigated the effect of the molar ratio of TiO_2/PPy on the photocatalysis properties and microwave loss properties in the frequency band ranging from 30 MHz to 3000 MHz. However, to the best of our knowledge, the reports on preparation and dielectric properties of TiO_2/PPy composites in the frequency range of X-band frequencies (8.2-12.4 GHz) are scanty.

In the present work, ammonium fluorotitanate [$(NH_4)_2TiF_6$] is used for the preparation of TiO_2 microspheres by homo-

geneous precipitation method. Then the TiO_2 microspheres are used as nucleus to prepare the TiO_2/PPy composite in the emulsion polymerization system. The morphology, structure and properties for the TiO_2 microspheres and TiO_2/PPy composite are also studied in this work.

EXPERIMENTAL

Synthesis of TiO_2 microspheres: The titanium source for TiO_2 synthesis was ammonium fluorotitanate ($(NH_4)\backslash TiF_6$). Urea released ammonia *via* forced hydrolysis in water, was used to control the precipitation reaction. All the chemical reagents were analytical reagent and used as received without further purification. In a typical synthetic procedure, stoichiometric amounts of ammonium fluorotitanate and urea were dissolved in distilled water to make a solution, then the entire solution was stirred at 90 or 95 °C for 0.5 to 1.5 h. After cooling naturally to room temperature, the resultant solids were recovered *via* centrifugation, washed repeatedly with distilled water *via* ultrasonic dispersion and then dried at 60 °C for 5 h.

Synthesis of TiO_2/PPy composite: TiO_2/PPy composite was prepared by *in situ* polymerization in aqueous solution. In a typical procedure, pyrrole (analytical grade) and dodecylbenzene sulfonic acid (DBSA) were dissolved in 50 mL distilled water and stirred vigorously for 0.5 h until the system became transparent. An equivalent amount of TiO_2 was dispersed well in the mixture of aniline and stirred vigorously for 0.5 h. An aqueous solution of $(NH_4)_2S_2O_8$ (ammonium persulfate) as an oxidant was slowly added to the above reactant mixture. The polymerization was allowed to proceed for 8 h at about 0 °C under stirring. Finally, products were precipitated in an excess volume of acetone. The TiO_2/PPy composite was obtained by filtering and washing the suspension with distilled water and acetone and dried under vacuum at 60 °C for 24 h.

Characterization: Phase formation of the synthesized product was identified by X-ray diffraction (XRD, Ultima IV, Rigaku, Japan) by using CuK_α radiation (λ = 0.15418 nm) with a scanning rate 0.02° s^{-1} in the 2θ range of 15-90°. Morphology of the products was observed by scanning electron microscopy (SEM) on an S-3400N microscope operating at 25 kV. The complex permittivity ($\varepsilon' - j\varepsilon''$) of composite were measured using HP8510 network analyzer in the frequency range of X-band frequencies (8-12 GHz).

RESULTS AND DISCUSSION

Structure and morphology of TiO_2: X-ray diffraction patterns of TiO_2 are shown in Fig. 1. It can be observed that the XRD peaks of the powders in each case match well with anatase-type TiO_2 reported in the standard card (JCPDS CARD01-071-1166). No extra reflections in the XRD diffraction patterns representing any rutile or brookite impurity are found. This unambiguously confirms the formation of a pure anatase structure. The sharp diffraction peaks suggest good crystallinity of the powders. The method used in this work reduces the crystallization temperature to a very low one of 90-95 °C. This enhanced crystallization may be attributed to that the slow release of ammonia, which controls the rate of the precipitation reaction, by the forced hydrolysis of urea. Another reason may be that the moderately high reaction temperature (90-95 °C) enhances the mobility of the configurational ions, thus enabling these ions to arrive at the correct positions for TiO_2 crystallization. The direct crystallization of pure anatase, rather than brookite or rutile, suggests the importance of the synthetic conditions, especially the solution pH (7 in this work) and supporting anions (F-and NH^{4+} in this work) in the phase selection of TiO_2[21]. It is observed that the powders have better crystallinity with the increase of the reaction time from 0.5 to 1.5 h or the synthesis temperature from 90 to 95 °C.

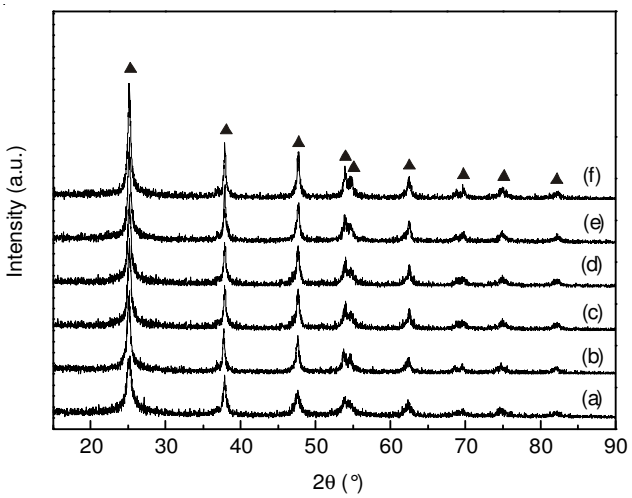

Fig. 1. XRD patterns of TiO_2 powders synthesized under various conditions: (a) 90 °C 0.5 h; (b) 90 °C 1 h; (c) 90 °C 1.5 h; (d) 95 °C 0.5 h; (e) 95 °C 1 h; (f) 95 °C 1.5 h

Fig. 2 shows the particle morphologies of the powders synthesized under various conditions. It is observed that the resultant particles obtained after 0.5 h are microspheres in each case, irrespective of the reaction temperature at 90 °C (sample A, Fig. 2, a) or 95 °C (sample D, Fig. 2, d). Furthermore, these microspheres show good dispersion. The average diameter of the microspheres is approximately 600 nm for sample A. It can be observed that a higher reaction temperature leads to smaller anatase microspheres, with average sizes for sample D (Fig. 2, d) of about 500 nm. The morphologies of the final particles change into irregular shape and bad dispersion with the increase of the reaction time from 0.5 to 1.5 h, suggesting the reaction time is a decisive factor affecting the morphology of the final particles.

Structure and morphology of TiO_2/PPy: X-ray diffraction patterns of polypyrrole, TiO_2 and TiO_2/PPy composite are shown in Fig. 3. It can be observed that there is a wide peak at about 2θ = 23.4° in the X-ray diffraction pattern of polypyrrole (Fig. 3a). The results imply that the polypyrrole chains have ordered arrangement to some extent. It is observed that the diffraction pattern for TiO_2/PPy (Fig. 3b) composite contains both the characteristic peaks of TiO_2 and the wide peak of polypyrrole. In addition, the intensities of peaks for TiO_2/PPy composite become weaker than that of the pure TiO_2, which suggests that the polypyrrole coating layer has an effect on the crystallinity of TiO_2. The morphology of TiO_2/PPy composite containing 30 wt. % TiO_2 particles are shown in Fig. 4. SEM image reveals that TiO_2/PPy composite particles are similar to spheres and there is some reunite phenomenon.

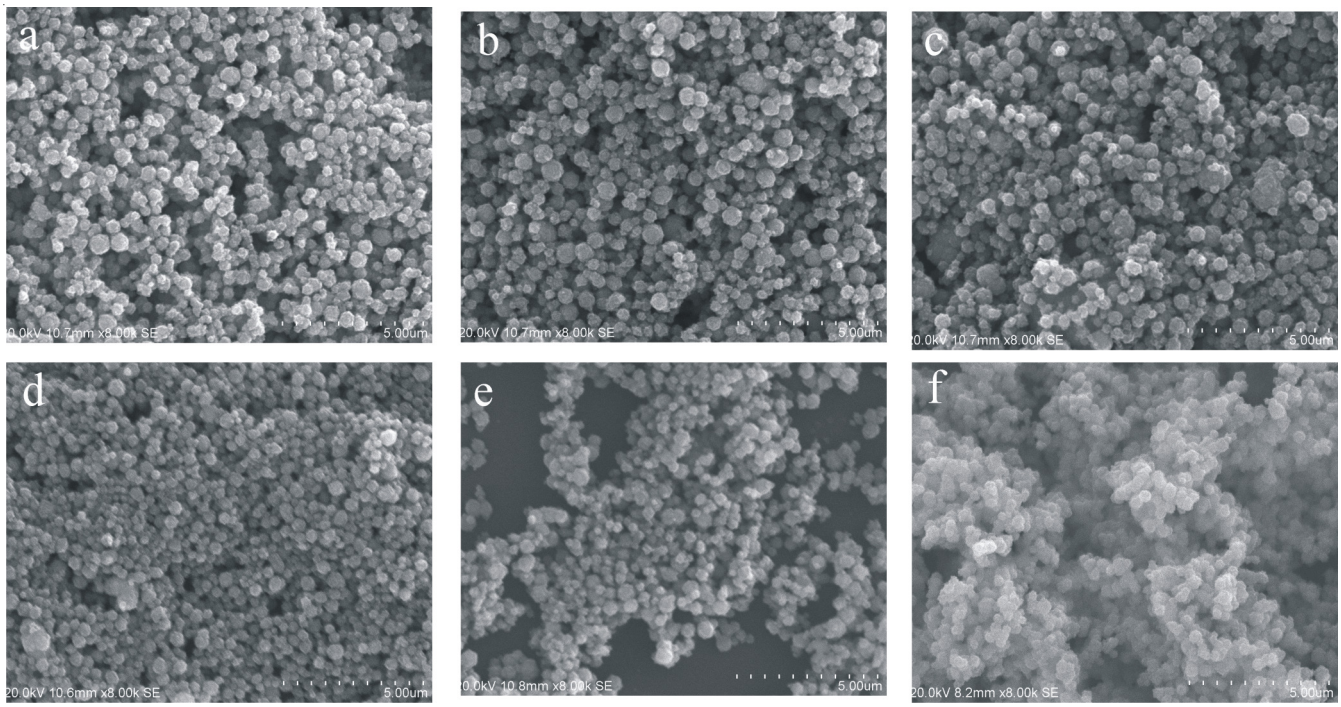

Fig. 2. SEM micrographs of TiO_2 powders synthesized under various conditions: (a) 90 °C 0.5 h; (b) 90 °C 1 h; (c) 90 °C 1.5 h; (d) 95 °C 0.5 h; (e) 95 °C 1 h; (f) 95 °C 1.5 h

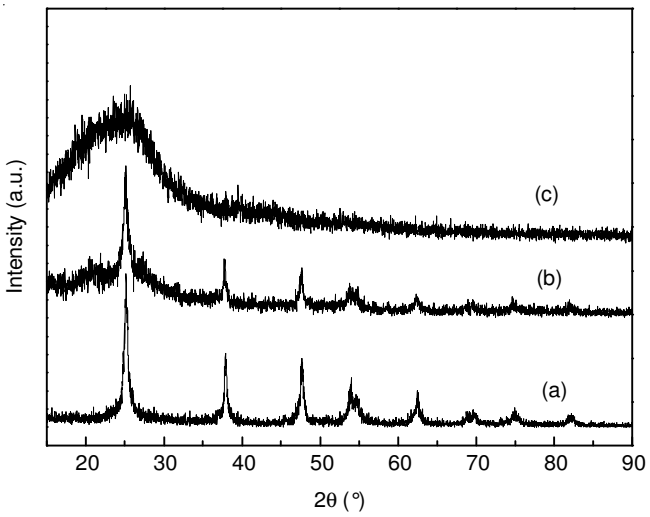

Fig. 3. XRD patterns of (a) TiO_2, (b) TiO_2/PPy and (c) polypyrrole

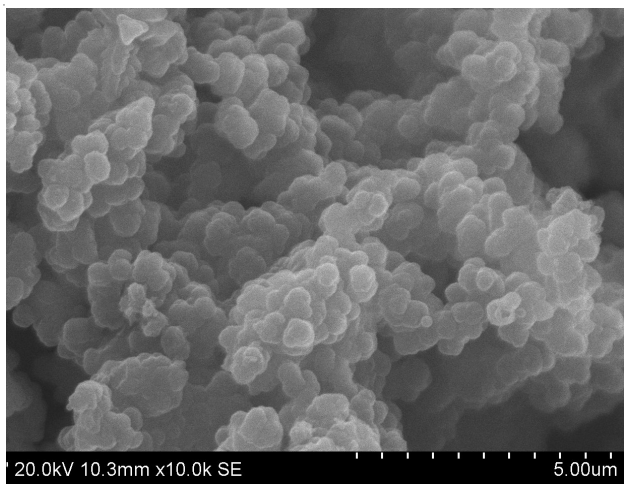

Fig. 4. SEM micrograph of TiO_2/PPy composite

Dielectric properties of the samples: Fig. 5 shows the real ε′ and imaginary ε″ parts of complex permittivity spectra in the frequency range of 8.2-12.4 GHz for polypyrrole and TiO_2/PPy composite, respectively. As seen in Fig. 5, the ε′ spectra for polypyrrole show lower values from 6.0 at 8.2 GHz to 5.1 at 12.4 GHz. However, ε′ for TiO_2/PPy is higher and values lie from 8.0 at 8.2 GHz to 6.1 at 12.4 GHz. The values of ε″ of polypyrrole range from 2.4 to 2.7, while for TiO_2/PPy between 2.6 and 3.8.

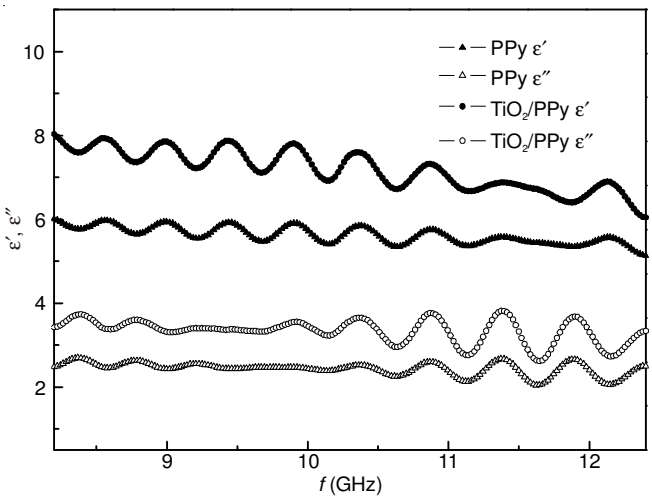

Fig. 5. Complex permittivity spectra of polypyrrole and TiO_2/PPy composite in 8.2-12.4 GHz

Materials with higher tan δ_e (tan $\delta_e = \varepsilon''/\varepsilon'$) are considered as lossy materials that indicate strong absorption. So, the value of the loss tangent could predict the microwave absorption property of the materials. Fig. 6 shows the dielectric loss tangent for PPy and TiO_2/PPy composite in the frequency range of 8.2-12.4 GHz, respectively. It is observed that the average tan δ_e

value is 0.43 for polypyrrole. The tan δ_e value for TiO_2/PPy is higher than polypyrrole in the X band. It has achieved a maximum tan δ_e of 0.57 at 11.9 GHz. The TiO_2/PPy composite will give rise to better microwave absorption property in the frequency range of 8.2-12.4 GHz compared with polypyrrole because it possess higher tan δ_e value. In general, the dielectric constants of polymers are not high. Addition of high dielectric constant material can significantly enhance the dielectric constant of polymeric systems because the larger dielectric constant can be achieved near the percolation threshold of the composite. The interface across polypyrrole and TiO_2 that possessing different permittivity may lead to the larger dielectric constant for TiO_2/ PPy composite.

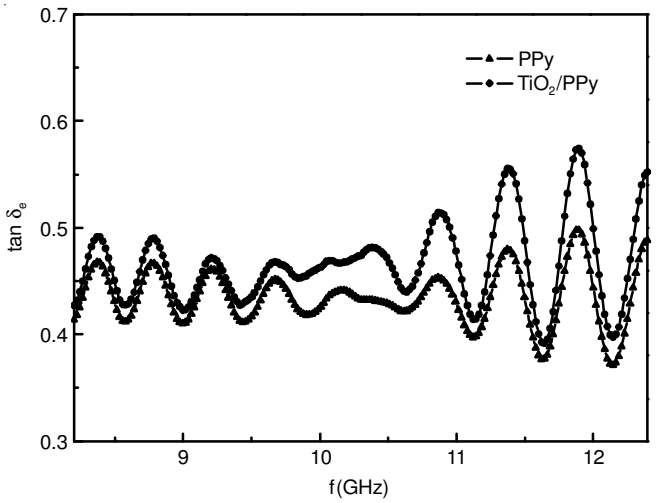

Fig. 6. Dielectric loss spectra of polypyrrole and TiO_2/PPy composite in 8.2-12.4 GHz

Conclusion

Crystalline microspheres with anatase structures have been directly obtained *via* homogeneous precipitation under mild conditions with ammonium fluorotitanate as the titanium source and urea as the precipitant. The higher reaction temperature leads to smaller anatase microspheres with average sizes about 500 nm. The morphologies of the final particles change into irregular with the increase of the reaction time. Theε′, ε″ and tan δ_e value for TiO_2/PPy composite are higher than polypyrrole in the frequency range of 8.2-12.4 GHz. The tan δ_e value for TiO_2/PPy has achieved a maximum tan δ_e of 0.57 at 11.9 GHz.

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REFERENCES

1. J. Jiang, L. Ai and L. Liu, *Mater. Lett*., **64**, 888 (2010).
2. J. Stejskal, M. Trchová, J. Brodinová, P. Kalenda, S.V. Fedorova, J. Prokeš and J. Zemek, *J. Colloid Interf. Sci*., **298**, 87 (2006).
3. S.M. Abbas, A.K. Dixit, R. Chatterjee and T.C. Goel, *J. Magn. Magn. Mater*., **309**, 20 (2007).
4. S. Kumar, V. Singh, S. Aggarwal, U.K. Mandal and R.K. Kotnala, *Compos. Sci. Technol*., **70**, 249 (2010).
5. S.A. Joshi, S.A. Gangal and S.K. Gupta, *Sens. Actuators B*, **156**, 938 (2011).
6. M. Ferenets and A. Harlin, *Thin Solid Films*, **515**, 5324 (2007).
7. C. Yang, P. Liu, J. Guo and Y. Wang, *Synth. Met*., **160**, 592 (2010).
8. B.K. Sharma, N. Khare, R. Sharma, S.K. Dhawan, V.D. Vankar and H.C. Gupta, *Compos. Sci. Technol*., **69**, 1932 (2009).
9. C. Yang, Y. Gung, W. Hung, T.H. Ting and K.H. Wu, *Compos. Sci. Technol*., **70**, 466 (2010).
10. X. Zhang, L. Song, X. Zeng and M. Li, *Energy Procedia*, **17**, 422 (2012).
11. M. Afuyoni, G. Nashed and I.S.S.M. Nasser, *Energy Procedia*., **6**, 11 (2011).
12. H. Song, M. Dai, Y. Guo and Y.-J. Zhang, *Fuel Process. Technol*., **96**, 228 (2012).
13. J. Zhou, Y. Cheng and J. Yu, *J. Photochem. Photobiol. Chem*., **223**, 82 (2011).
14. Q. Li, C. Zhang and J. Li, *J. Alloys Comp*., **509**, 1953 (2011).
15. J. Du, W. Chen, C. Zhang, Y. Liu, C. Zhao and Y. Dai, *Chem. Eng. J*., **170**, 53 (2011).
16. Y.X. Zhang, G.H. Li, Y.X. Jin, Y. Zhang, J. Zhang and L.D. Zhang, *Chem. Phys. Lett*., **365**, 300 (2002).
17. J.G. Li, T. Ishigaki and X. Sun, *J. Phys. Chem. C*, **111**, 4969 (2007).
18. F. Deng, Y. Li, X. Luo, L. Yang and X. Tu, *Colloids Surf. A*, **395**, 183 (2012).
19. P. Su and L. Huang, *Sens. Actuators B*, **123**, 501 (2007).
20. E. Turac and E. Sahmetlioglu, *Synth. Met*., **160**, 169 (2010).
21. S. Liu, X. Sun, J. Li, X. Li, Z. Xiu and D. Huo, *Eur. J. Inorg. Chem*., 1214 (2009).