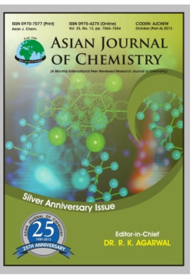
Asian Journal of Chemistry;   Vol. 25, No. 13 (2013), 7149-7152

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2013.14482



Study on the Preparation of ZnO/TiO_2 Composite Nanostructures and Its Properties

ZIQUAN LIU*, HONGMEI YANG, RUICUI LIU and FUYI JIANG*

School of Environmental and Material Engineering, Yantai University, Yantai 264005, P.R. China

*Corresponding authors: Tel/Fax: +86 535 6706038; E-mail: lzqytu@163.com; liuziquantom@163.com

(*Received*: 25 August 2012;   *Accepted*: 14 June 2013)   AJC-13660

The paper used the butyl titanate as the main resource to prepare TiO_2 nano-powder by dry hydrothermal method firstly. Then the TiO_2 samples were used as the main resources to adopt the hydro-thermal method to prepare TiO_2 nano-tube. After that $ZnCI_2$ and TiO_2 nano-tube were used as the main resources to prepare ZnO/TiO_2 composite nano-structure with the TiO_2 nano-tube as the base by the hydro-thermal method. X-ray diffraction, transmission electron microscope and other methods were used to study the phase, appearance characterization and performance analysis of the products. Also the paper used the photo-catalysis experiment for comparing the decomposing ability of the methyl orange of ZnO/TiO_2 composite nano-structure and pure TiO_2 nano-tube under the ultraviolet light. The results showed that the prepared TiO_2 nano-tubes are even in shape, ZnO in ZnO/TiO_2 composite nano-structure covers evenly on the nano-tube and ZnO/TiO_2 nano composite structure has a better photo-catalytic activity.

Key Words: TiO_2, ZnO/TiO_2, Nanotube, Composite nanostructures, Hydrothermal synthesis.

INTRODUCTION

Nanometer titanium dioxide is an important photo-catalysis material. Its characters include the high activity in photo-catalyzing organic matters, stability in chemical property, bearing the chemical and photochemical erosion and non-toxicity. It has great potential in disposing sewage, purifying air, *etc*. However, titanium dioxide is wide-gap material, it only absorbs the ultraviolet light part of the solar spectrum and the efficiency of using solar energy is low, so that its applications are limited. As sole photo-catalyst has its separate advantages and disadvantages, we perform nano-composition of titanium dioxide and nano-zinc oxide. Using the coupling between nano-particles can increase the efficiency of using solar energy to a great extent and increase the speed and efficiency of photo-catalyzing organic matters. Searching and developing an effective nano-composite photo-catalyst is significant in both theory and practice. The nano-composition and developing new techniques for it becomes a hot spot in this field[1-6].

Nano-ZnO and TiO_2 are important in the research of nanometer materials field. They have good performance and wide applications in optics and photo-electrochemistry. Documents show that nanometer ZnO/TiO_2 composite powder has great scattering power for visible light of 400-700 nm and has great abilities to absorb the ultraviolet radiation of 200-350 in the spectrum. So that it has great ability to prevent ultraviolet radiation and it improves a lot compared with sole-functioned nanometer ZnO and TiO_2 powder[3,7,8].

The purpose of this article is to look for simple ways and techniques to prepare nano-ZnO and the composite structure of nano-TiO_2 to provider a wider basis for the research of its performances in the future. We used X-ray diffraction, transmission electron microscope *etc*. to characterize the phase and appearance and analyze the performance of the products. We also use photo-catalysis experiment to compare the abilities to degrade methyl orange of ZnO/TiO_2 composite nanostructure and pure TiO_2 nano-tube under ultraviolet light.

EXPERIMENTAL

XRD-7000 X-ray diffraction, 722 visible spectrophotometer, 20 w straight tube-ultraviolet germicidal lamp (this experiment uses self-made photo-reactor, the center of the reaction tube is 10 cm, 20 w ultraviolet germicidal light is used as the light source), filtrating equipment, T8-1B magnetic heating stirring apparatus, KQ2200B supersonic cleaner, LDZ4-2 auto-balancing centrifuge, high-pressure autoclave, DGL-2000 drying oven, muffle furnace.

Titanyl sulfate (AR), ferric nitrate (AR), butyl titanate (AR), urea (AR), hydrochloric acid (AR), sodium hydroxide (AR), methyl orange (AR), zinc chloride (AR) and glycerol used as received.

Drying hydro-thermal method to prepare TiO_2 nano-powder: After mixing 12 mL butyl titanate with 50 mL absolute ethyl alcohol, we used ultrasonic dispersion to disperse it for about 25 min; after adding 0.28 g de-ionized water into the mixture, continue the ultrasonic dispersion for 5 min; we transferred the thoroughly-mixed solution into the autoclave, centrifuged it quickly after 106 ºC hydro-thermal treatment for 90 min; dried and grinded the sediments to get the TiO_2 nano-powder.

Hydro-thermal method to prepare TiO_2 nano-tube: Measure 30 g NaOH powder and 0.5 g titanium dioxide nano-powder separately and put them into autoclave. Measure 90 mL de-ionized water and add it into the autoclave. Put the autoclave into the muffle furnace after screwing down it, baking it for 4 days at 170-175 ºC. Take it out after 4 days, open it after cooling it completely, introduced the flakes at the bottom of the autoclave into the beaker, add de-ionized water and use supersonic to clean the platet until all of them appear flocculent. Then centrifuged it and dry it in the drying box. Grind it to obtain the TiO_2 nano-tube samples.

Hydro-thermal synthesis to prepare ZnO/TiO_2 nano-tubes: Measure correctly 0.8 g TiO_2 nano-tube, put it into three 500 mL beakers with 200 mL de-ionized water, use supersonic dispersion for 30 min. Then add adequate $ZnCl_2$ under constant use magnetic stirring for 10 min to mix it completely. According to the stoichiometric ratio of the compound, add separately 0.1 mol/L NaOH solution, use magnetic stirring for 10 h. Subside, leach the solution and wash it for many times. Put the sediments into the oven for 12 h at 80 ºC. Then bake them for 2 h in the drying box at 150 ºC. Grind the solid and the solid becomes ZnO/TiO_2 composite structure with 10 wt % of ZnO.

Comparison of the absorbency of ZnO/TiO_2 and TiO_2:

correctly 4 mL glycerol, 4 mL de-ionized water and pour them into the beaker. Add adequate TiO_2 nano-tube, mix it thoroughly and use the supersonic dispersion. Switch on the electric source, turn on the instruments, open the lid of the sample room and preheat it for 10 min. Adjust the power switch of sensitivity to 1. Rotate the wavelength-choosing button according to the required wavelength. Pour blank solution and test solution separately into the 3/4 of cuvette, use lens wiping paper to clean its outer wall, put them in the sample room and make the blank tube face directly the light path. Adjust the zero adjuster to T=0 when the lid of the camera is open. Cover the lid, adjust 100 adjuster, making T of blank tube equals 100. After the pointer is still, pull out the sample litter gradually, read out A and T of the blank tube and record them. Measure A and T of ZnO/TiO_2 of different wavelengths by the same procedures and record them. Completing the colour comparison, turn down the electric source, take out the cuvette and wash it. Use soft cloth or wadding to wipe up the sample room.

Experiment of photo-catalysis: Measure 2 mg of methyl orange, dissolve it in 200 mL de-ionized water and make the methyl orange solution with the concentration of 10 mg/L. Measure 3 shares of 25 mL to pour into the beaker with the number of 1, 2 and 3. Measure separately 0.15 g of TiO_2 nano-tubes and ZnO/TiO_2 composite nano-structure and pour them into number 2 and number 3 solution. Operate the magnetic stirring for 5 min and put the beaker under the ultraviolet germicidal lamp with a distance of 10 cm. After radiating for 0.5 h, take out a certain amount of solution from the beaker and filter it, then use visible light photometric analyzer to measure its absorbency and transmission. Repeat this procedure for many times and record the statistics.

RESULTS AND DISCUSSION

XRD analysis of TiO_2 nano-powder: Fig. 1 shows that the XRD analysis of the samples have relatively pronounced diffraction peaks when 2θ is 25.12, 37.72, 47.88, 62.52, 70.32 and 75º, in correspondence with the characteristic diffraction peak of the anatase TiO_2. There are also diffraction peaks at 53.82º and 55.04º, in correspondence with the characteristic diffraction peak of rutile TiO_2. It indicates that this sample has anatase as the main crystal phase with little rutile. Analysis from XRD peak broadening method shows that the granularity of the nano-titanium dioxide powder prepared by the drying hydro-thermal method is small.

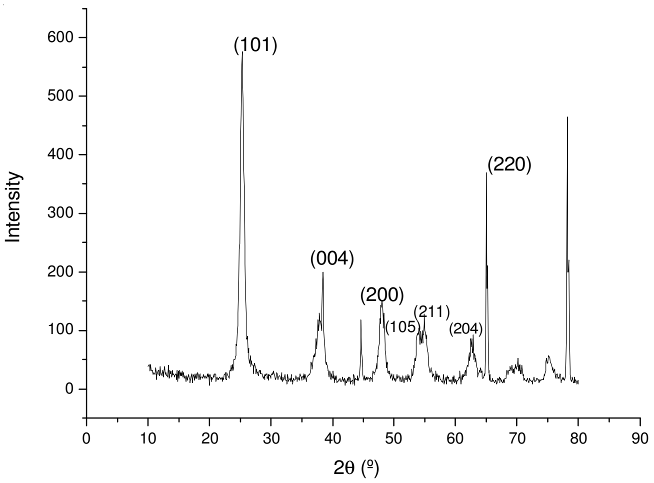


Fig. 1. XRD picture of TiO_2 nano powder

XRD diffraction pattern (Fig. 2) shows that the TiO_2 nano-tube samples have comparatively pronounced diffraction peaks when 2θ is 25.12, 37.72,47.88, 62.52, 70.32 and 75º, in correspondence with the characteristic diffraction peak of anatase TiO_2. There are also diffraction peaks at 53.82º and 55.04º, in correspondence with the characteristic diffraction peaks of rutile TiO_2. From the analysis we see that the TiO_2 nano-tube samples have the anatase as the main crystal phases with little rutile phases.

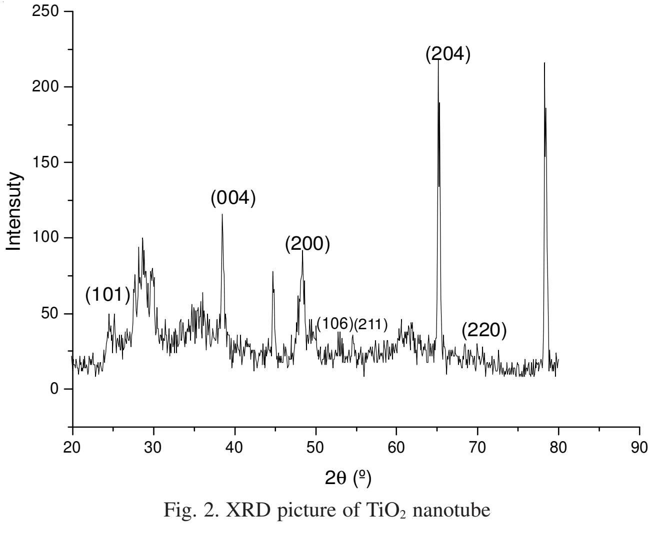


Fig. 2. XRD picture of TiO_2 nanotube

TEM analysis: From TEM picture (Fig. 3) it is clear that the TiO$_2$ nano-tube sample prepared by the hydro-thermal method has good tubular structures.

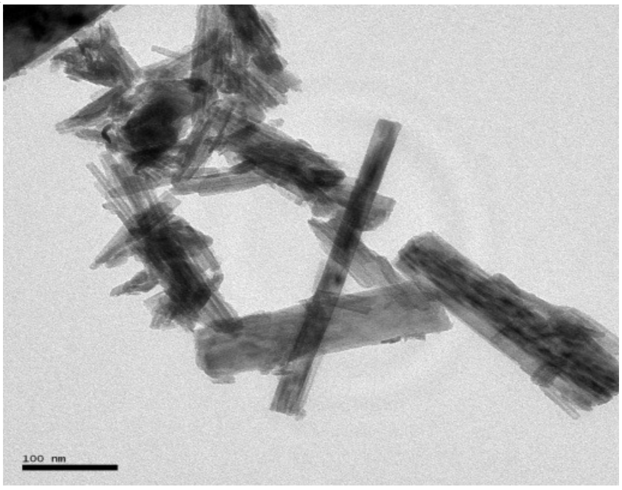


Fig. 3. TEM images of TiO$_2$ nanotube

XRD analysis: We know from Fig. 4 XRD diffraction analysis that the samples have relatively pronounced diffraction peaks when 2θ is 25.12, 37.72, 47.88, 62.52, 70.32 and 75º, in correspondence with the characteristic diffraction peaks of anatase TiO$_2$; there are also diffraction peaks at 53.82º and 55.04º, in correspondence with the characteristic diffraction peaks of rutile TiO$_2$. The peaks of the samples when 2θ is31.76, 34.42, 36.22, 47.50, 56.64, 62.86, 67.94 and 69.06º are in correspondence with the diffraction peaks of ZnO.

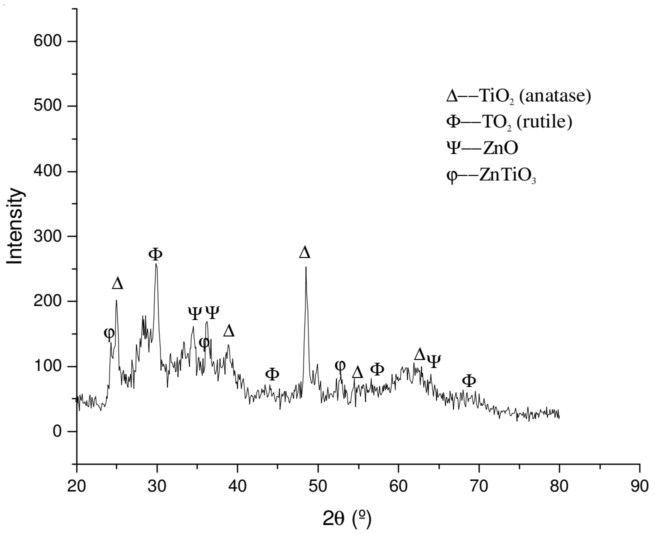


Fig. 4. XRD picture of ZnO/TiO$_2$ composite

TEM analysis: From Fig. 5 TEM picture, we observed that after adding ZnO, the structure of the nano-tube is not damaged, it still has good tubular structure, only that the colour is darker. It indicates that ZnO has covered the nano-tube evenly.

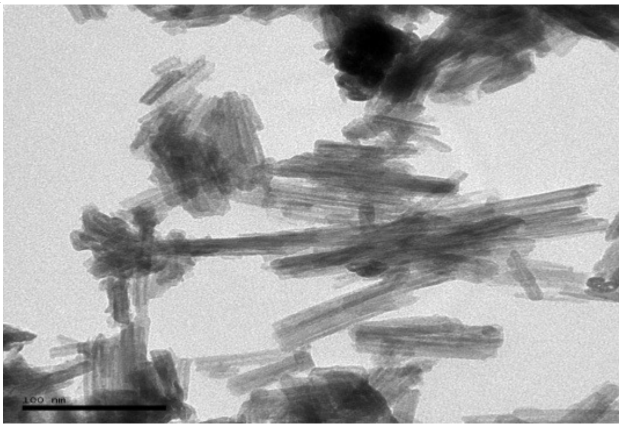


Fig. 5. TEM picture of ZnO/TiO$_2$ composite

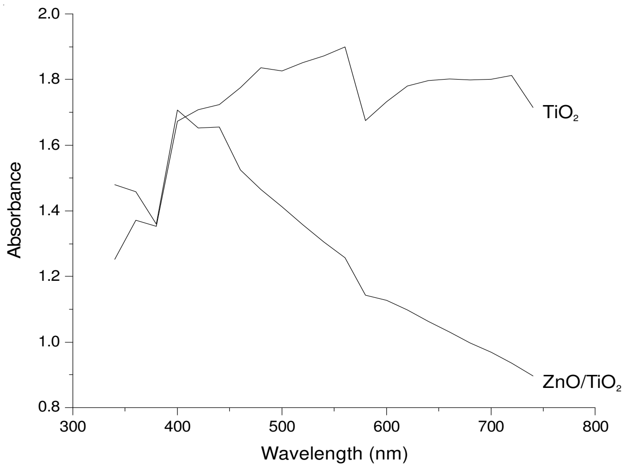


Fig. 6. Visible absorption degrees comparison picture of ZnO/TiO$_2$ and TiO$_2$

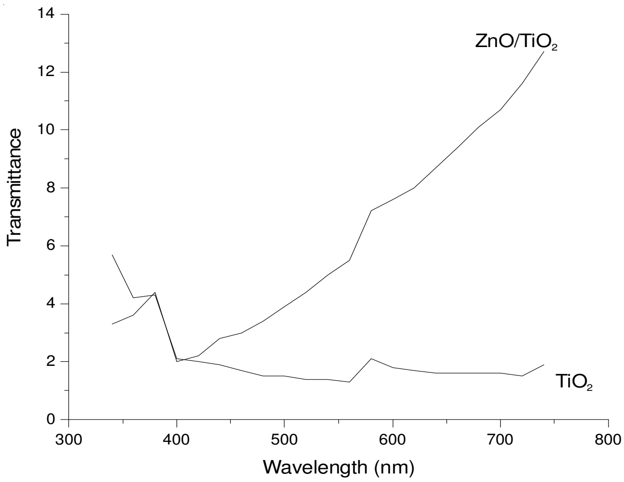


Fig. 7. Transmission ratio comparison pictures of ZnO/TiO$_2$ and TiO$_2$

Comparison of the absorbency of ZnO/TiO$_2$ and TiO$_2$: From Figs. 6 and 7 of the absorbency experiment, suggest that compared with pure TiO$_2$ nano-tube, ZnO/TiO$_2$ nano-composite structure has a better ability to absorb the ultraviolet light and a lower transmittance. So that ZnO/TiO$_2$ nano-composite structure will hopefully degrade some toxic organic pollutants under the sunlight.

Effect of ZnO composition on the catalytic activity of TiO$_2$ nano-tube: Figs. 8 and 9 of the photo-catalysis experiment show that compared with methyl orange and pure TiO$_2$ nano-tube, ZnO/TiO$_2$ nano-composite structure has a higher photo-catalytic activity.

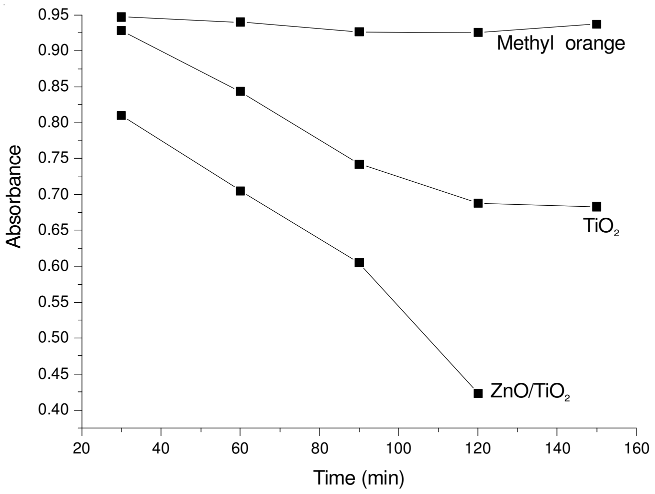


Fig. 8. Visible absorption degrees comparison picture of ZnO/TiO_2, TiO_2 and methyl orange

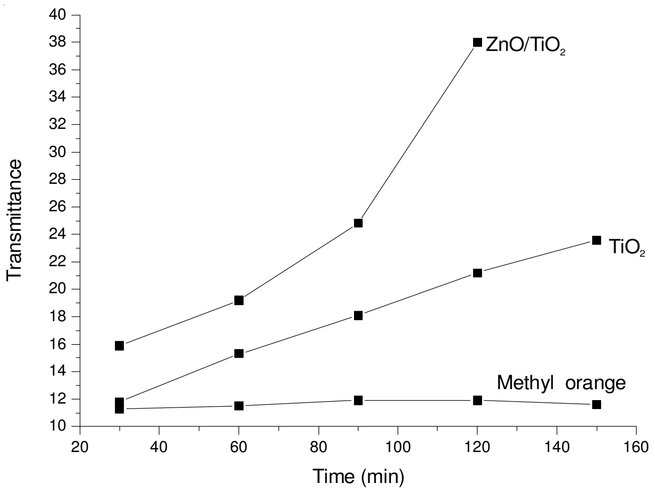


Fig. 9. Transmission ratio comparison picture of ZnO/TiO_2, TiO_2 and methyl orange

Conclusion

TiO_2 nano-powder samples prepared by drying hydro-thermal method has anatase as the main crystal phase with little rutile. The granularity of the powder is small. TiO_2 nano-tube prepared by hydro-thermal method has good tubular structure. We used hydro-thermal method to prepare ZnO/TiO_2 nano-composite structure with TiO_2 nano-tube as the base. ZnO covers TiO_2 nano-tube evenly. Compared with pure TiO_2 nano-tube, ZnO/TiO_2 nano-composite structure has better ability to absorb ultraviolet light. ZnO/TiO_2 nano-composite structure has a higher photo-catalytic activity than pure TiO_2.

ACKNOWLEDGEMENTS

This work was supported by The National Natural Science Foundation of China (50972123) and The National Natural Science Foundation of China (51272223). The Natural Science Foundation of Shandong Province (ZR2012EML06).

REFERENCES

1. L. Lhomme, S. Brosillon, D. Wolbert and J. Dussaud, *Appl. Catal. B*, **61**, 227 (2005).
2. T. Aungpradit, P. Sutthivaiyakit, D. Martens, S. Sutthivaiyakit and A.A.F. Kettrup, *J. Hazard. Mater.*, **146**, 204 (2007).
3. X.B. Chen and S.S. Mao, *Chem. Rev.,* **107**, 2891 (2007).
4. C.S. Lim, *Asian J. Chem.*, **23**, 4862 (2011).
5. K. Ohshima, K. Tsuto, K. Okuyama and N. Tohge, *Aerosol Sci. Technol.*, **19**, 468 (1993).
6. G. Marcì, V. Augugliaro, M.J. López-Munoz, C. Martin, L. Palmisano, V. Rives, M. Schiavello, R.J.D. Tilley and A.M. Venezia, *J. Phys. Chem.*, **105**, 1026 (2001).
7. Z.C. Liu, D.X. Zhou, S.P. Gong and H. Li, *J. Alloys Comp.*, **475**, 840 (2009).
8. M.R.Hoffman, S.T.Martin, W. Choi and D.W. Bahnemann, *Chem. Rev.*, **95**, 69 (1995).