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.

The purpose of this article is to look for simple ways and techniques to prepare nano-ZnO and the composite structure of nano-TiO₂ 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/TiO₂ composite nanostructure and pure TiO₂ 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 TiO₂ nanopowder: 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 °C hydro-thermal treatment for 90 min; dried and grinded the sediments to get the TiO2 nano-powder.

**Hydro-thermal method to prepare TiO2 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 °C. 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 plate until all of them appear flocculent. Then centrifuged it and dry it in the drying box. Grind it to obtain the TiO2 nano-tube samples.

**Hydro-thermal synthesis to prepare ZnO/TiO2 nano-tubes:** Measure correctly 0.8 g TiO2 nano-tube, put it into three 500 mL beakers with 200 mL de-ionized water, use supersonic dispersion for 30 min. Then add adequate ZnCl2 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 °C. Then bake them for 2 h in the drying box at 150 °C. Grind the solid and the solid becomes ZnO/TiO2 composite structure with 10 wt % of ZnO.

**Comparison of the absorbency of ZnO/TiO2 and TiO2:** Measure correctly 4 mL glycerol, 4 mL de-ionized water and pour them into the beaker. Add adequate TiO2 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/TiO2 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 TiO2 nano-tubes and ZnO/TiO2 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.

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**RESULTS AND DISCUSSION**

**XRD analysis of TiO2 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 75°, in correspondence with the characteristic diffraction peak of the anatase TiO2. There are also diffraction peaks at 53.82° and 55.04°, in correspondence with the characteristic diffraction peak of rutile TiO2. 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 TiO2 nano powder](image1)

![Fig. 2. XRD picture of TiO2 nanotube](image2)
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](image1)

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 is 31.76, 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](image2)

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](image3)

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.
Conclusion

TiO₂ nano-powder samples prepared by drying hydrothermal method has anatase as the main crystal phase with little rutile. The granularity of the powder is small. TiO₂ nanotube prepared by hydro-thermal method has good tubular structure. We used hydro-thermal method to prepare ZnO/TiO₂ nano-composite structure with TiO₂ nano-tube as the base. ZnO covers TiO₂ nano-tube evenly. Compared with pure TiO₂ nanotube, ZnO/TiO₂ nano-composite structure has better ability to absorb ultraviolet light. ZnO/TiO₂ nano-composite structure has a higher photo-catalytic activity than pure TiO₂.

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