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# Synthesis and Characterization of $TiO_2$ Nanoparticles

ZIQUAN LIU*, RUMING WANG, FANGJUN KAN and FUYI JIANG*

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

*Corresponding authors: Tel/Fax: +86 53 56706038; E-mail: lzqytu@163.com; liuziquantom@163.com

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Nano titanium dioxide powder samples were separately prepared by sol-gel method, hydrolysis method, hydro-thermal method, co-precipitation method and sluggish precipitation method under experimental conditions. The prepared powders particles were characterized using XRD, TEM and thermal methods. Experimental statistics showed that the nano titanium dioxide powder prepare by the hydro-thermal method had the least grain size and its photo-catalytic performance was the best. It could completely decompose the prepared helianthine solution in about 2 h. At last this paper conducted DTA and TEM characterization of the nano titanium dioxide powder prepared by the hydro-thermal method and used the experiment to find its suitable heat treatment temperature.

**Keywords: $TiO_2$, Hydrothermal, Photocatalysis, Hydrolysis, Sol-gel.**

## INTRODUCTION

Nano titanium dioxide powder has many good functions and features, such as stable properties, non-toxic, high activity of photocatalysis, low cost and good at resisting chemical attack. It is also a nice photocatalyst, disinfector and antiseptic. Thus the preparation and features of nanometer titanium dioxide powder has naturally been a research hotspot for a long time[1-8]. There are many ways to prepare it, including some physical methods such as low-pressure gas evaporation method, sputtering method, plasma method, high energy ball milling and chemical methods such as settling method, hydrolysis, spraying method, oxidation-reduction method, laser synthesis, hydro-thermal method, sol-gel method, electro-spark method, *etc*[1,9,10]. More commonly-used methods are sol-gel method, hydrolysis, hydro-thermal method, coprecipitation method, sluggish precipitation, *etc*. However, up to now there haven't been relatively systematic experimental reports of these methods. We use these different methods to prepare nano powder of titanium dioxide and analyze XRD diffraction plus photocatalytic activity research of the samples made in turn. We use photocatalysis experiments to test the performance of the samples[11]. By comparing the photocatalytic activity of various samples, we can compare and analyze these preparing methods so that we can be sure of the more suitable methods under lab conditions. At last we will separately conduct differential thermal analysis and transmitting electrical microscope analysis of the best samples and discuss about the reasons of the good photocatalytic activity. By studying the suitability of various preparing methods, we find some references for the industrialized commodity production of nano titanium dioxide powder.

## EXPERIMENTAL

**Sol-gel method:** Add 7.21 mL dibutyl phthalate into 20 mL absolute ethyl alcohol, on magnetic stirrer to stir it for 0.5 h to make liquid A. After measuring and fully mixing 1.50 mL de-ionized water and 20 mL absolute ethyl alcohol, add three drops of concentrated hydrochloric acid to make liquid B. Add B into A, stir it intensely, after 0.5 h there will be gel which is a little bit milky white (there will be twice ultrasonic dispersions in-between), stop stirring and left for 12 h. Put the gel in the 80 °C constant-temperature drying box for 7 h. Porphyrize the product and put it to bake for 2 h in the 550 °C muffle and obtain the sample after cooling it.

**Coprecipitation method:** Prepare dilute solution of titanium tetrachloride. First add 10 mL hydrochloric acid in the beaker with 40 mL de-ionized water and put the beaker in the ice-water bath. Then placed it on the magnetic stirrer, add 6 mL pure solution of titanium tetrachloride drop by drop while stirring and prepare the expected solution. Keep the temperature of the solution of titanium tetrachloride under 10 °C, add excessive $H_2O_2$ into it, in the process the solution will turn dark red first, then it will get darker and finally it turn to black liquid. Under the effect of magnetic stirring, add ammonia gradually in the above-mentioned solution and adjust the pH to 10. When adding ammonia, a white sediment is obtained, but it dissolved with the stirring. A dense yellow particulate materials at pH is 8 is formed. With the increase of ammonia, the materials dissolve when pH is close to 10, the solution become bright milky yellow semi solid. Heat it to 50 °C and keep the temperature for 0.5 h and left for 18 h. Wash the sediment properly. After the seasoning, several layers are formed in the solution. The lower layer is light yellow cotton-shaped sediment. Inhale the clear solution from the upper part of the beaker by the straw. Pour the rest of the solution into the microburette to centrifugate it for 5 min. Pour out the solution from the microburette, add de-ionized water and use ultrasonic dispersion, centrifugate it again, repeat the action for three times. Put the sediment into the 60 °C drying box for 0.5 h and the white powder is formed. Heat it in the 500 °C muffle for 2 h and white anatase titanium dioxide will be produced.

**Hydrolysis:** Prepare the dilute solution of titanium tetrachloride. The method is most similar to the above-mentioned experiment, we can produce liquid A. Dissolve 14.74 g ammonium sulphate in the 60 mL de-ionized water and add 6 mL hydrochloric acid into it, which produce liquid B. Pour B into A (keep the temperature under 15 °C), B appears to be oily and gradually dissolves in A. The solution becomes clear and is heated to be 95 °C. In the process when the temperature is about 60 °C, the color gradually gets darken, it turns turbid at 95 °C. Add ammonia until pH is 6, the solution turns milky white and become pure white sediment after seasoning it for 12 h. After pouring out the clear solution in the upper part, add a certain amount of de-ionized water into it. Then pour it into a microburette to centrifugate for 5 min. Then pour out the water in the microburette, add de-ionized water again. Put it in ultrasonic washer, centrifugate it after mixing thoroughly, repeat the action for three times. Put the white sediment which has been washed in the 80 °C drying box, dry it for 24 h and the sample becomes a dark solid mass. Place the sample in the 550 °C muffle to bake for 2 h to get nano powder of titanium dioxide.

**Hydro-thermal method:** Add 1 g pollen into the beaker with 25 mL absolute ethyl alcohol, use ultrasonic dispersion and the solution is straw yellow. Add 4 mol dibutyl phthalate into the solution and use ultrasonic dispersion for 20 min until the solution becomes tawny. Then add three drops of de-ionized water into it and continue ultrasonic dispersion for 3 minutes. Transfer the solution to the high-pressure autoclave, conduct the hydro-thermal treatment for 1.5 h under 105 °C in the drying box and then centrifugate it quickly. Pour out the solution, dry the solid for 17 h under 40 °C and get soil-like products which is a little bit red. Place the sample in the crucible for 1 h, keep the temperature for 2 h after the temperature rises from room temperature to 400 °C. Continue rising the temperature to 550 °C in 1 h, for 2 h. Then cool it and get the white titanium dioxide powder.

**Sluggish precipitation:** Measure and take 7.21 g titanyl sulfate and 1.8 g carbamide separately and dissolve in adequate de-ionized water. Then mix the two solutions. Keep the temperature for 2 h after heating the mixed solution to 98 °C, the solution becomes translucent when the temperature reaches 50 °C. With the temperature rising, about 70 °C, the solution becomes cloudy, bubble and sediment begins to appear. After seasoning the solution for 12 h, pour out the upper solution, centrifugate the sediment after washing it for three times by the de-ionized water. Place the white sediment in the 60 °C drying box for 12 h, white powders will be produced. Put them to bake in the 550 °C muffle for 2 h, to obtain the nano titanium dioxide powder.

**Detection of photocatalytic activity:** This experiment uses self-made photoreactor, the center of the reaction tube is 10 cm, use 20 w ultraviolet germicidal lamp as the light source. The reagent of the experiment is helianthine (analytically pure). Prepare 10 mg/L helianthine solution, measure separately nano titanium dioxide powder prepared by the five methods and pour them separately into the five solutions that have been prepared. Use magnetic stirring for 5 min. Put the beaker under the ultraviolet germicidal lamp with a distance of 10 cm. After irradiating for 1.5 h take a certain amount of solution from the beaker to filter and then use visible light photometric analyzer to detect its absorbency and transmission. Repeat the irradiating experiment and get a complete data.

## RESULTS AND DISCUSSION

**XRD analysis of titanium dioxide:** XRD (Figs. 1-5) of the samples prepared by the five different methods have relatively pronounced diffraction peaks when 2θ is 25.12°, 37.72°, 47.88°, 67.52° 70.32° and 75°, in accordance with the characteristic peaks of anatase titanium dioxide. There are also diffraction peaks when 2θ is 53.82° and 55.04° in accordance with the characteristic peak of rutile titanium dioxide. It shows that anatase is the main crystal phase of this sample while there are also some rutile crystals. But by XRD diffraction peak broadening method, the wider the diffraction maximum is, the smaller the grain of the powder is, we can roughly decide that the granularity of nanometer titanium dioxide powder prepared by drying box hydro-thermal method is smaller than that by other methods.

**Analysis of photocatalytic activity:** This experiment uses self-made photoreacctor, the center of the reaction tube is 10 cm and uses 20 w ultraviolet germicidal lamp as the light source. The reagent of the experiment is helianthine (analytically pure) $C_{14}H_{14}N_3NaO_3S$.

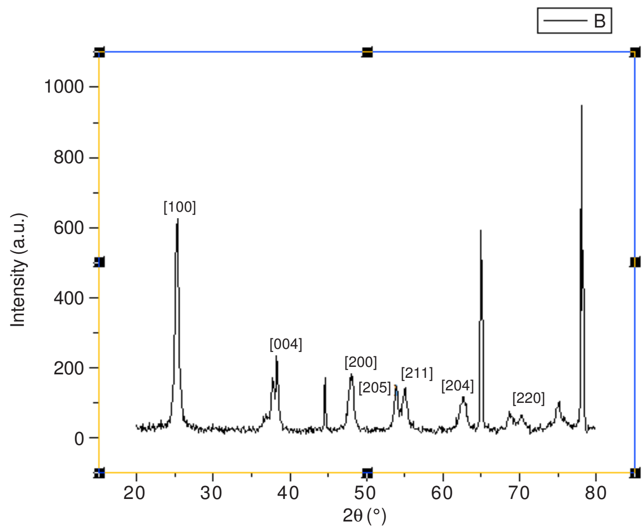


Fig. 1. XRD pattern of $TiO_2$ sample prepared by sol-gel method

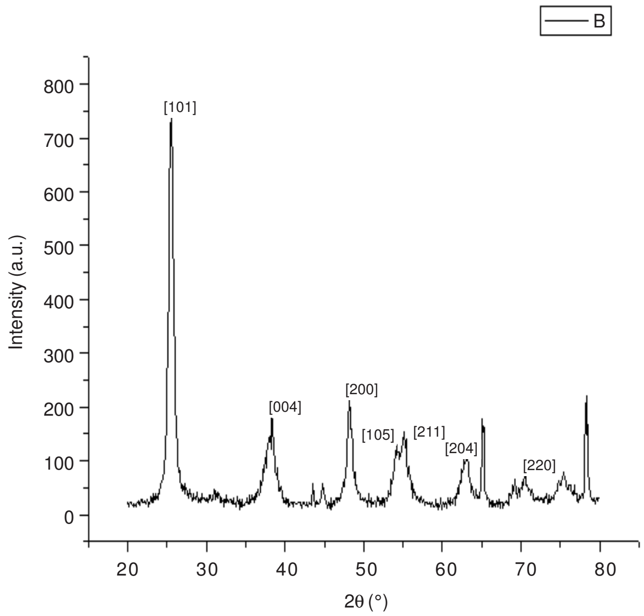


Fig. 2. XRD pattern of $TiO_2$ sample prepared by coprecipitation

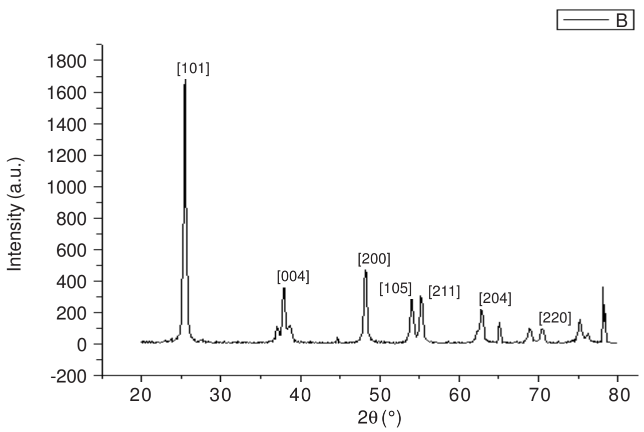


Fig. 3. XRD pattern of $TiO_2$ sample prepared by hydrolysis

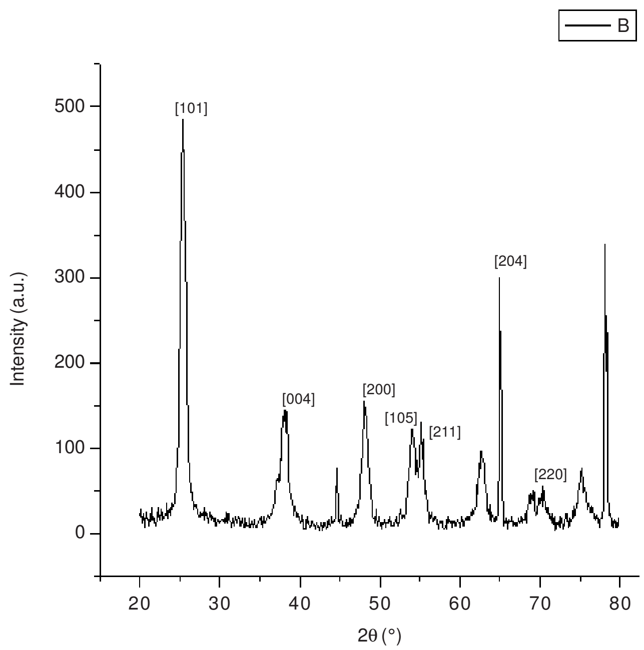


Fig. 4. XRD pattern of $TiO_2$ sample prepared by hydrothermal method

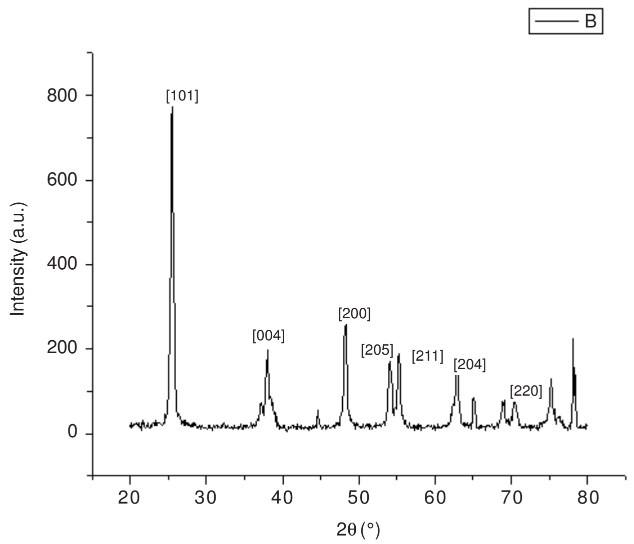


Fig. 5. XRD pattern of $TiO_2$ sample prepared by homogeneous precipitation method

Figs. 6 and 7 showed that nano titanium dioxide prepared by hydro-thermal method has the best photocatalytic activity. After 2 h of being irradiated by the ultraviolet germicidal lamp, the absorbency can reach 0.035, the transmission can be 92.3, almost of all the helianthine is catalyzed to decompose. Secondly, sol-gel method and coprecipitation method have relatively good photocatalytic activity, while nano titanium dioxide powder prepared by homogenous precipitation and hydrolysis doesn't have good photocatalytic activity.

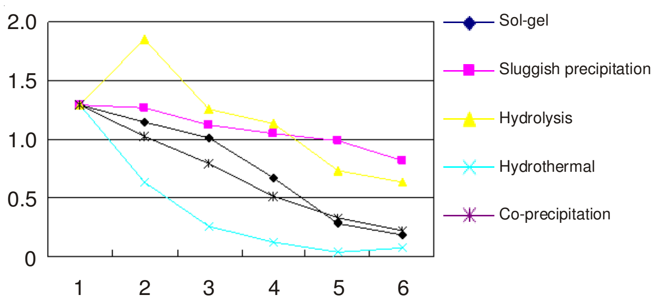


Fig. 6. Relation of absorbency and degradation time

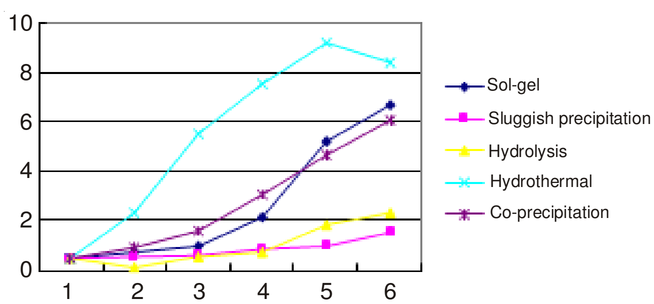


Fig. 7. Relation of transmission and degradation time

**Thermal gravimetric analysis:** From the TG curve of the pollen sample, it is clear that the pollen has relatively pronounced weightless sag in three intervals which are 40-345, 300-540 and 570-650 °C. The overall weightlessness of the three intervals is separately 50, 90 and 92 % (Fig. 8). The first interval is comparatively wide and steep, showing many elements dissipate in this area. Firstly the evaporation of water, secondly the organic elements which evaporate at low temperature. The curve of the second interval slows down as water plus those elements disappear and the speed of weight-losing decreases. As for the third interval, there only remains the decomposition of the rest, the speed of weight-losing decreases more, so that the corresponding curve slows down more. In accordance, in the three intervals of the TG curve of the pollen sample, there is separately a radiation peak at 330, 510 and 645 °C, so there are overall three radiation peaks (Fig. 9). As elements in the pollen kernel that tend to evaporate and decompose at low temperature, the shape of the first radiation peak is sharp and steep. At 320 °C, a little organic element burn and make the second radiation peak. We speculate that at 520 °C, as some high-ignition temperature organic elements burn, they make the third radiation peak. As these elements are small in number, so the peak that is made is comparatively low.

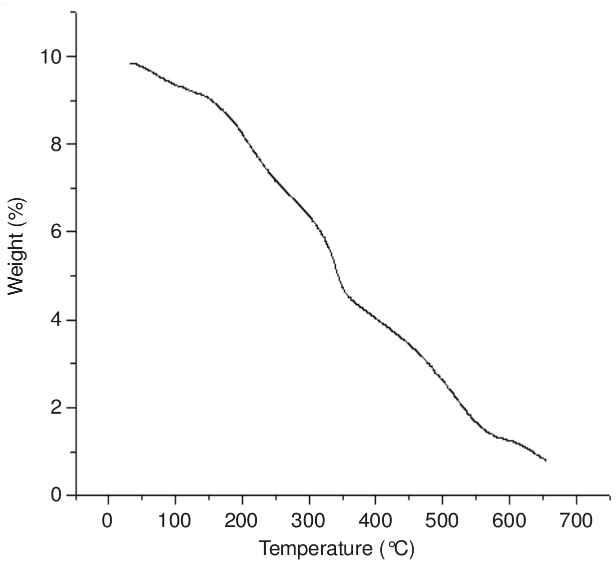

Fig. 8. TG curve of pollen sample

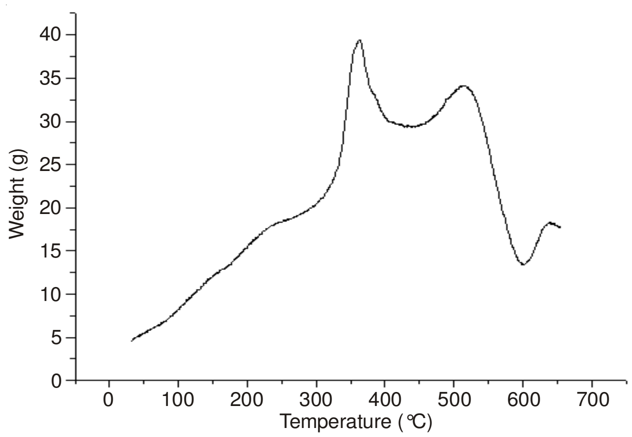

Fig. 9. DTA curve of pollen sample

In TG curve of titanium dioxide sample that there are also obvious weightlessness in 180-255, 300-400 and 450-550 °C, the rate of weight loss is separately 70, 52, 63 % (Fig. 10). And in the DTA, there are three radiation peaks at 260, 335 and 510 °C (Fig. 11) The first radiation peak is a little earlier than that of the pollen. It is because of the burning of the precursor of titanium dioxide. We can imply from the picture that baking between 500-550°C can strip down the pollen crust and get the high performance shell-like nano titanium dioxide.

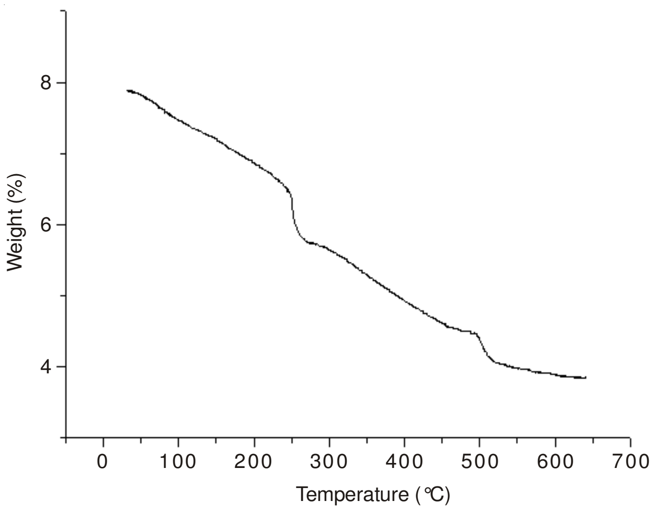

Fig.10. TG curve of $TiO_2$ sample

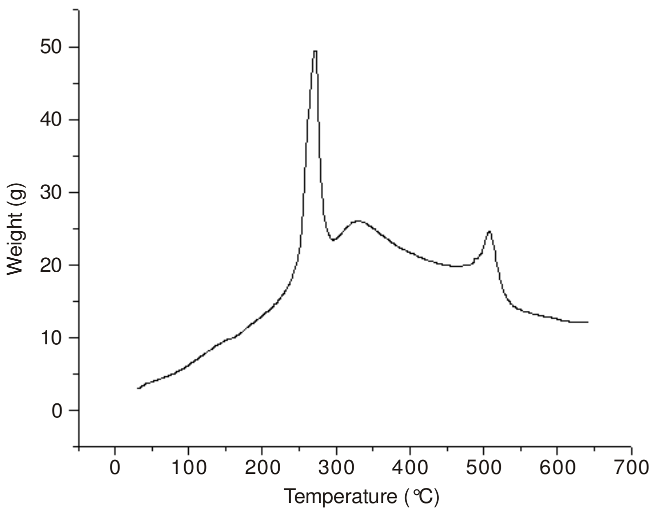

Fig.11. DTA curve of $TiO_2$ sample

**Transmission electron microscope analysis:** Fig. 12 showed that the grain diameter of the nano titanium dioxide powder prepared by hydro-thermal method is about 10 nm and it is pretty well-distributed. This should be the reason why hydro-thermal method has the best photocatalytic effect.

## Conclusion

Nano titanium dioxide powder was prepared with five different methods separately. By conducting XRD detection of these five titanium dioxide samples, test showed that the grain diameter of nano particle prepared by hydro-thermal method was the smallest. Transmission electron micro scope picture displayed that the actual grain was about 10 nm and was relatively well-distributed. Detection of the photocatalytic activity of the five samples suggested that samples prepared by the hydro-thermal method had the best property in these test, it could completely decompose the prepared helianthine

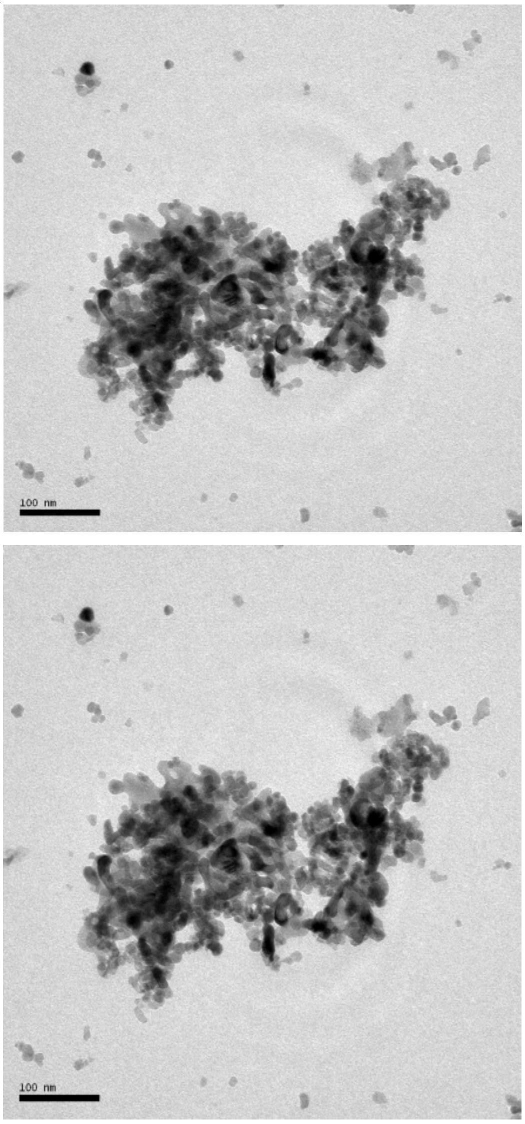


Fig. 12. TEM images of $TiO_2$ nanopowders

solution in about 2 h. Through the experiment, the test datum showed that the best sintering temperature scope of hydrothermal method was between 500 to 550 °C.

## ACKNOWLEDGEMENTS

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