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Low temperature preparation and characterization of nanospherical anatase TiO_2 and its photocatalytic activity on Congo red degradation under sunlight

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Abstract

Nanospherical titanium oxide with anatase structure was obtained at low temperature and normal pressure using a simple method of preparation. The dilute titanium (III) chloride solution was stirred at room temperature for several hours, and then ammonium hydroxide with hydrogen peroxide was added. A yellow gel $TiO_2{\cdot}xH_2O$ was obtained with nanodot shape and amorphous structure. Heated at 300 °C, it crystallized to pure anatase structure with nanospherical shape. The anatase particles prepared show good adsorption and photodegradation of Congo red solution under the sunlight. Materials were characterized by powder X-ray diffraction, thermal analysis, transmission electron microscope and UV spectroscopy.

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1. Introduction

Titanium oxide TiO_2 is now widely used in degradation of pollutant in many industrial areas. One important use is degradation of dyes usually left from textile industries [1–5], because the methods of preparation affect its photocatalytic efficiency. In the recent years, researches are carried out in order to improve its preparation methods [6–13]. Suitable preparation method will be simple, using low temperature and without expensive starting materials or complicated experimental steps to reach the final product. By using soft chemistry techniques that uses low temperature preparation, the product particles are obtained usually in the nanosize range, which shows higher activity. With such method, the particles size and their shape also can be controlled. This is important, because in a recent study it is shown that the particle's shape affect the photocatalytic activity of the catalyst; thus nanodot shape anatase was found to be more reactive than nanorod anatase [12]. Another experimental parameter which researchers want to improve is the radiation source [14–17]. Easy application and lower cost will be achieved if the prepared catalyst is active under sunlight/visible light. Photodegradation of dyes under sunlight has few reports, especially with pure undoped titanium oxide. Recently with a soft chemistry method, we show that nanorod rutile prepared at room temperature shows excellent photocatalytic degradation of Congo red solution under sunlight [17]. In the present paper with a simple and low temperature method, anatase phase was obtained with nanospherical shape that shows active photodegradation of Congo red solution under sunlight, interestingly in the same manner as nanorod rutile phase although the two phases have different crystalline structure.

2. Experimental

About 20 ml of $TiCl_3$ (DBH Chemical Ltd.) solution was diluted with 180 ml of distilled water in 500 ml beaker. Then about 40 ml of 10% NH_4OH was added during the stirring of the mixture at room temperature. After a few minutes of stirring, 3.5 ml of 30% H_2O_2 (DBH Chemical Ltd.) was added drop wise. The solution color changed from dark purple to

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yellow and formed a yellow gel after 16 h of stirring. The gel obtained was washed with distilled water several times in order to remove chlorine ions. The Congo red solution was prepared by dissolving Congo red powder ($C_{32}H_{24}N_6O_6S_2$ from BDH Chemical Ltd. Poole England) in distilled water to obtain a solution of 2.5×10^{-5} M concentration. The photocatalysis experiments were carried out in 100 ml beaker containing about 70 ml of Congo red aqueous solution (0.025 mM) and about 100 mg of TiO_2. The photodegradation experiments were carried out under sunlight. First the mixture was stirred for about 15 min in the dark, then the solution was exposed to the sunlight for about 45 min with continued stirring. These experiments were followed by different spectroscopic techniques as powder X-ray diffraction (Philips 1710, diffractometer), thermal analysis (TG and DTA, 2960 Universal TA Instruments, under nitrogen gas and with heating rate 10 °C min^{-1}), UV spectroscopy (UV spectrometer Cary 50 Conc) and transmission electron microscope (Jeol, 1234).

3. Results and discussion

Fig. 1 depicts X-ray diffraction pattern of the powder obtained after drying the titanium dioxide gel $TiO_2 \cdot xH_2O$ at room temperature. No diffraction peaks can be seen in the pattern which indicates an amorphous structure. Fig. 2 depicts its TEM micrograph. It shows agglomeration of very fine dot particles of average size 2 nm.

According to thermal analysis, TG curve (Fig. 3a) shows a weight loss starting from room temperature until about 380 °C. This loss corresponds to about 50% in mass of the sample. Two endothermic peaks can be seen on DTA curve (Fig. 3b); the first one is centered at 100 °C (about 39% mass lost on TG curve) and corresponds to the loss of adsorbed water. The second peak is centered at 252 °C (about 7% mass lost on TG curve) and correspond to the loss of chemically bonded water with probably hydrogen peroxide. The endothermic peak is followed by an exothermic peak centered at 290 °C. Another smaller weight loss can be seen in the TG curve (about 4% mass lost) starting at about 285 °C and ending at 385 °C, probably corresponds to the loss of hydroxide groups present within the sample structure. DTA curve shows a second exothermic peak centered at about 370 °C. The

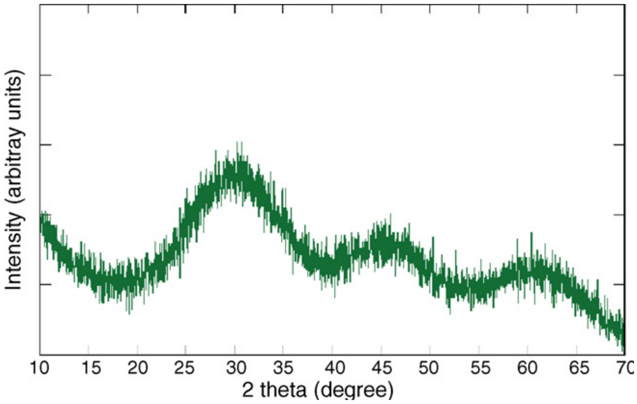

Fig. 1. X-ray diffraction pattern of powder obtained from drying the yellow gel at room temperature.

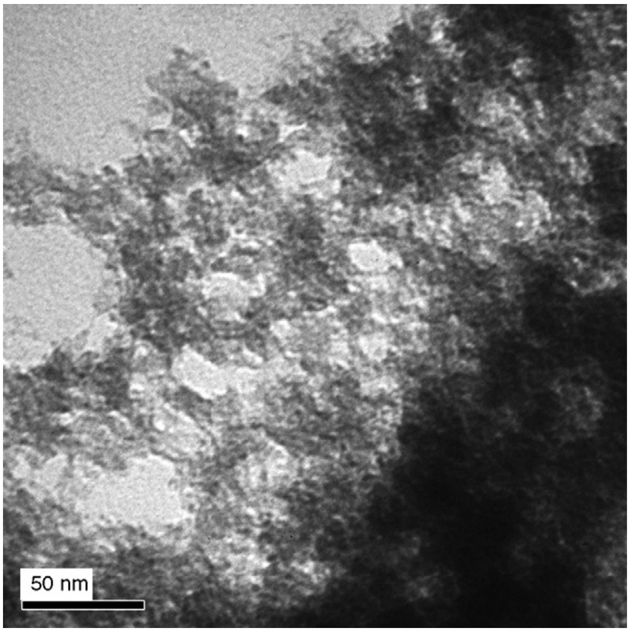

Fig. 2. TEM micrograph of as-prepared wet titanium dioxide yellow gel.

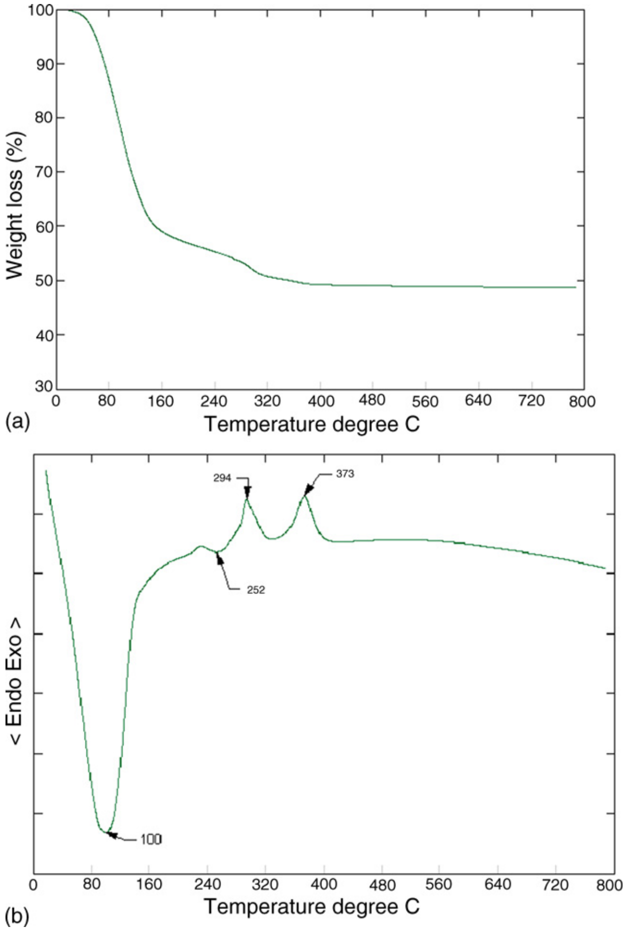

Fig. 3. (a) TG and (b) DTA curves of as-prepared sample dried at room temperature.

sample heated at 300 °C or above this temperature for 4 h shows only pure crystalline phase anatase. Thus, probably the first exothermic peak corresponds to the decomposition of hydrogen peroxide present with the sample and the second exothermic peak corresponds to transformation of the sample from amorphous phase to crystalline phase.

The X-ray diffraction pattern of the sample heated at 300 °C is shown in Fig. 4a. All diffraction peaks correspond to anatase phase without any other impurity phase.

With more heating the particles size becomes bigger which is reflected in the X-ray diffraction pattern with sharper diffraction peaks. Anatase phase in the present work has higher temperature range of stability; even at 800 °C for 5 h (Fig. 4b), anatase remains almost as pure phase; only the highest intensity peak of rutile is present with a very low intensity. At 900 °C, the X-ray diffraction pattern is essentially the stable phase rutile (Fig. 4c).

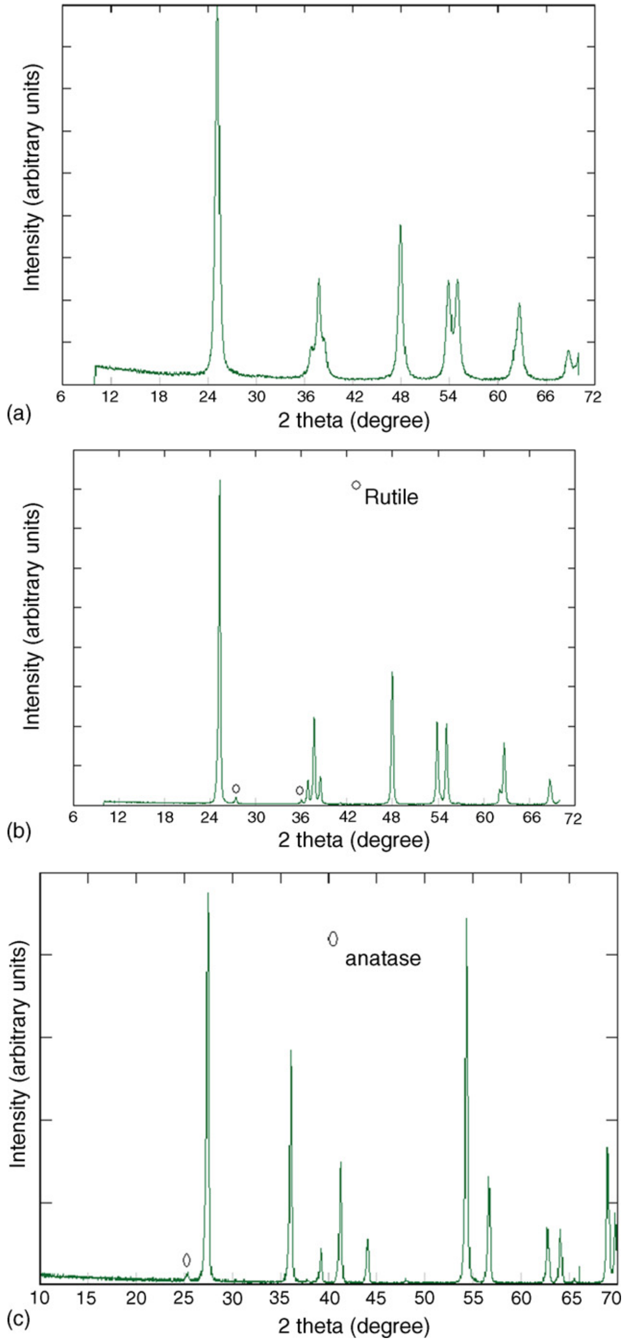

Fig. 4. X-ray diffraction patterns of powder heated at: (a) 300 °C (4 h), (b) 800 °C (5 h) and (c) 900 °C (5 h).

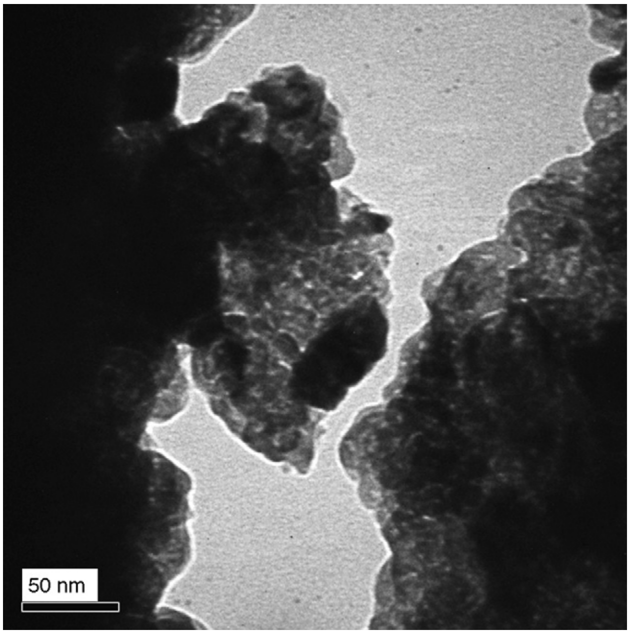

Fig. 5. TEM micrograph of TiO_2 anatase heated at 300 °C.

Fig. 5 shows TEM micrograph of anatase powder TiO_2, obtained by heating the yellow gel at 300 °C. It shows agglomeration of spherical particles of average size 13 nm. Although the size has increased after heating, but the particles remain smaller. The crystallite size measurements were also calculated using the Scherrer equation, $d = k\lambda/\beta(2\theta)\cos\theta$, where d is the crystallite size, k a constant (=0.89 assuming that the particles are spherical), λ the wavelength of the X-ray radiation, β the width of the XRD peak at half peak-height in radian, and θ is the angle of diffraction. The particle size obtained from the two high intensity peaks at $2\theta = 25.20^\circ$ and 47.92° were respectively 15.1 nm and 14.4 nm which are very near to the value estimated from TEM picture.

Photodegradation of Congo red solution was carried out at room temperature by using the as-prepared anatase phase as catalyst and sunlight as light source. First, this mixture was stirred for 15 min in the dark, which leads to a total adsorption of Congo red on anatase particles, the red solution become colorless and the titanium oxide powder, previously white, is now reddish. This is also confirmed by UV spectrum. Fig. 6a shows disappearance of Congo red highest intensity peak. Then, this mixture was stirred for 45 min under the sunlight. The experiment was conducted between 11:00 and 12:00 a.m. The temperature under sunlight was 30 °C. With reaction time running, the red color intensity of anatase particles decreases until disappearance. This indicates decomposition of Congo red on titanium oxide particles surface. As it can be seen in (Fig. 6b) there is no difference between the UV curves before

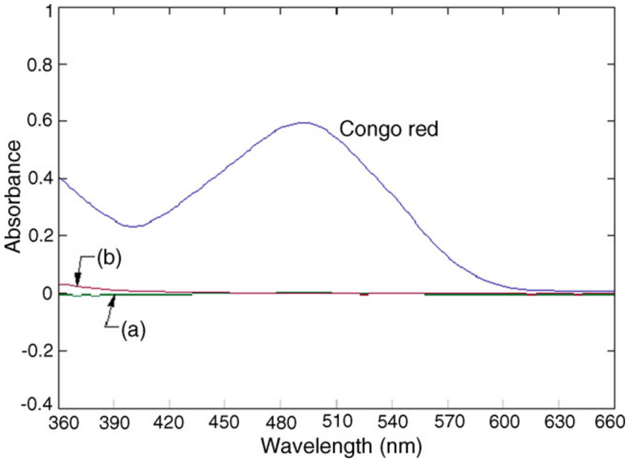

Fig. 6. UV spectra: (a) Congo red solution with anatase under sunlight for 45 min and (b) Congo red solution with anatase in the dark for 15 min.

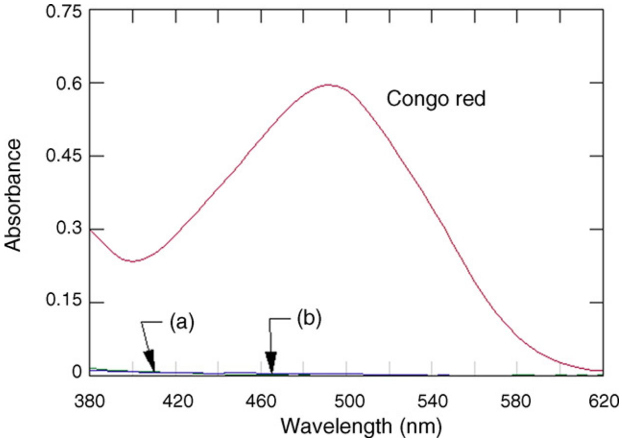

Fig. 8. UV spectra: (a) Congo red solution with nanorod rutile under sunlight for 45 min and (b) Congo red solution with nanospherical anatse under sunlight for 45 min.

and after exposition to the sunlight, because the Congo red is completely removed from the solution just by adsorption. The experiment shows that without sunlight Congo red adsorbed was not decomposed.

The photodegradation of Congo red by anatase was compared with nanorod rutile phase powder recently prepared [17]. First, the two powder samples (nanospherical anatase and nanorod rutile) were tested for Congo red adsorption in the dark for 15 min. The two samples were found to show similar adsorption (Fig. 7). Although anatase shows slightly better adsorption, the difference is very small. The experiment under the sunlight for 45 min shows that the red color of sample particles decreases with time until disappearance (Fig. 8). These two forms of titanium oxide showed similar activity for Congo red photodegradation under the sunlight. Both forms have the same chemical composition TiO_2 but different crystalline structure, they differ by the distortion of each octahedral and by assembly patterns of the octahedral chains which leads to different surface structure. Because the two phases have different crystalline structure, their interaction between the surface and the species present in the solution should be different; it will be expected that the two samples will not be active with the same shape and size. Thus, it is possible that the nanorod shape for rutile and spherical shape for anatase are the most favorable shape for photodegradation of Congo red under the sunlight.

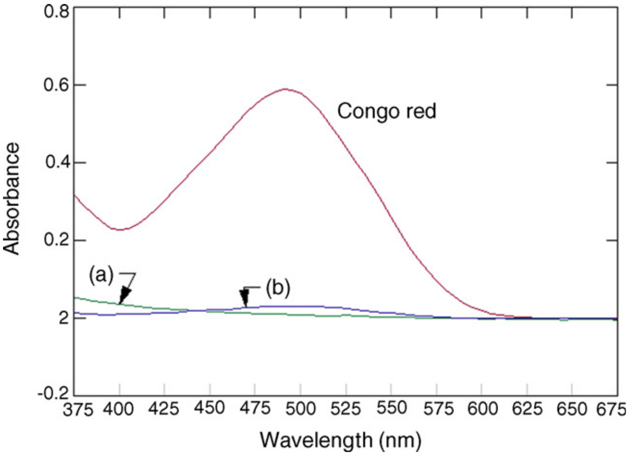

Fig. 7. UV spectra: (a) Congo red solution with anatase nanospherical particles in the dark (15 min) and (b) Congo red solution with rutile nanorod particles in the dark (15 min).

4. Conclusion

By using a simple soft chemistry method of preparation, pure anatase phase was obtained with nanospherical shape and a wide range of stability before converting to rutile. The high purity of the product with possible size and shape control are not possible using the classical solid state technique that uses higher temperature. It is important that the present material shows good activity under sunlight for degradation of dye sample (Congo red) which will be beneficial for both application cost and environment.

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