

Effect of Synthesis Temperature on Photocatalytic Activity of TiO₂ Nanoparticles Prepared via Solvothermal Method

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1- Introduction

The synthesis of photocatalysts has been the subject of numerous studies in the last two decades. TiO₂ nanoparticles have been employed in various fields including; solar cells, air purification, photocatalytic splitting of water for green-energy hydrogen production, removal of organic and inorganic pollutants, photokilling of pathogenic organisms and selective synthesis of organic compounds.

Different techniques have been presented for the synthesis of nano titania such as solvothermal method, precipitation method, sol-gel method, chemical vapor deposition and alkoxide pyrolysis. The sol-gel method is an easy technique but the obtained powders are amorphous and additional heat treatment is required for the crystallization of the anatase/rutile. The solvothermal method is another technique for one-step synthesis of nanostructured titania. The surface chemistry, crystalline phase and particle morphology of the solvothermal-derived titania can be easily controlled by modifying the reaction temperature and time, precursor composition, pressure, solvent property, aging temperature and aging time.

In this study, nano-crystallites of titania were synthesized via the solvothermal route at different temperatures (60-220 °C). The synthesis temperature, as one of the most important synthesis parameters, was investigated and its effects on the phase composition, crystal size and morphology were determined. The photocatalytic activity of the different titania samples were measured by photodegradation of aqueous methyl orange solution and correlated with the size, morphology, crystallization and composition of the particles.

2- Experimental procedure

For the synthesis of nano-TiO₂, two solutions were prepared separately. Solution A was prepared by dissolving 6 mL of tetrabutyl titanate (TBOT, 98%, MERCK) in 34 mL of anhydrous ethanol (C₂H₅OH, 99.7%, JATA Co., Iran). Solution B was made by combining 17 mL of anhydrous ethanol, 0.4 mL of concentrated nitric acid (HNO₃, 68%, MERCK), and 1.6 mL of distilled water. Solution A was added drop-wise to solution B under magnetic stirring at room temperature. The resultant mixture was agitated

at room temperature for 2 h until the transparent sol with precursor concentration of 0.3 M and pH of 1.5 was obtained. The sols were then transferred into a 100 mL teflon-liner stainless steel autoclave. The autoclave was kept at 60 to 180 °C for 8 h. Finally, the obtained precipitates were washed with distilled water and dried at 80 °C for 12 h. Microstructure analyses of the samples was performed using field emission scanning electron microscopy (FE-SEM, MIRA\TESCAN), transmission electron microscopy (TEM, FEG PHILIPS CN200) and atomic force microscopy (AFM, DME 95) techniques. XRD (Unisantix XMD400) analysis was used for structural characterization of the samples. The mean anatase crystallite diameter (d_{Scherrer}) was determined from the half-height width (β) of the (101) diffraction peak of anatase using the Scherrer equation ($d_{\text{Scherrer}} = 0.9\lambda / \beta \cos \theta$). The photocatalytic activity of the prepared TiO₂ powders was evaluated by degradation of methyl-orange under UV light in a prototype photocatalytic agitated reactor. Suspensions were prepared by adding 0.7 g of the synthesized titania powders to 300 mL of standard solution of methyl-orange with a concentration of 0.01 g/l. The methyl-orange photodegradation yield was determined during 120 minutes irradiation of the suspension. The photodegradation reactions were carried out in a transparent silica glass cylinder, while the suspension was agitated by a magnet stirrer rotating at 500 rpm. The glass cylinder along with the suspension within it was surrounded by 8 UV lamps as shown in Fig. 1.

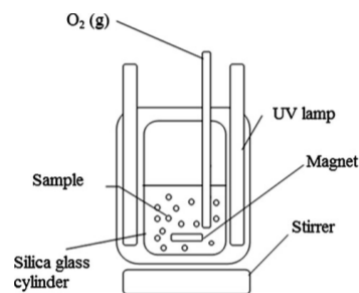


Fig. 1 A schematic of the slurry agitated photoreactor for methyl orange decomposition under UV irradiation

During irradiation, the suspension was bubbled with air. Samples were obtained at each 15 min time interval and their absorbency was measured using a PG UV-vis spectrophotometer (UV-T 80) at the maximum absorption wavelength of 465 nm, after separation of the suspended solids by centrifugation.

3- Results and discussion

The XRD patterns for the samples synthesized at different temperatures showed that an almost amorphous phase formed at 60 °C and anatase (Card No: 01- 071- 1167) was the dominant phase at higher synthesis temperatures. With increasing temperature, XRD patterns with sharper and higher peaks due to more crystallinity and crystallite growth of samples

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were obtained, as shown in Fig. 2.

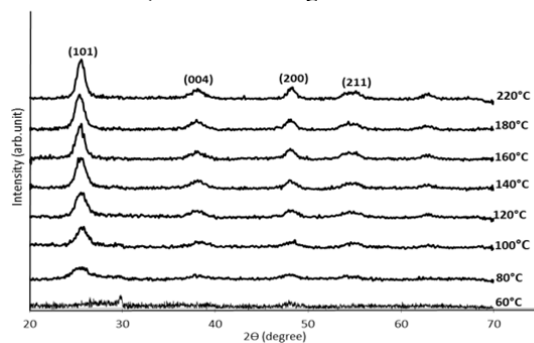


Fig. 2 X-ray diffraction patterns for TiO₂ powders

SEM micrographs of the powders synthesized at different temperatures are shown in Fig. 3a to d. As shown, samples prepared at low temperatures consist of a thin gel layer; the nucleation and growth of anatase crystals occurred in this thin gel layer. By increasing the temperature up to 220 °C, the formation of anatase was enhanced and the gel layer disappeared. Furthermore, another usual mechanism is nucleation and growth of anatase in the solution and the precipitation of the products at the bottom of the autoclave.

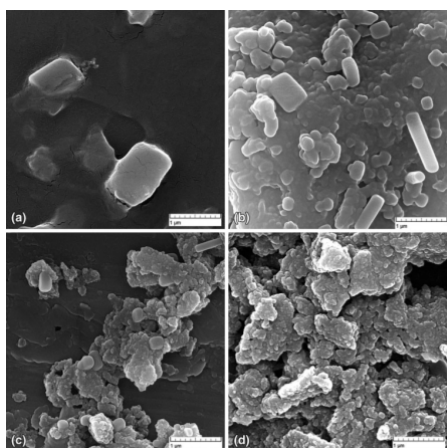


Fig. 3 SEM micrographs of the powders synthesized at (a) 100 °C; (b) 120 °C; (c) 180 °C; (d) 220 °C

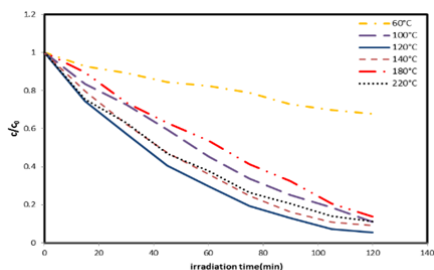


Fig. 4 The concentration changes of methyl orange versus illumination time for the powders synthesized for 8 h at different temperatures

Fig. 4 shows the concentration changes of methyl orange as a function of the illumination time under UV irradiation for the powders synthesized at different temperatures. To obtain high photocatalytic

activity, the catalyst should contain lots of surface reactive points. With increasing synthesis temperature, two competitive mechanisms can occur: 1) the thin gel layer concentration is decreased and the transformation to anatase leads to an increase in reactive points; 2) crystallite growth and particle agglomeration happens and consequently, reactive points decrease. So, the sample synthesized at a moderate temperature of 120 °C showed the highest photocatalytic activity.

The apparent activation energy of the formation of anatase was calculated to be 67.26 kJ/mol. The TEM micrograph of the powder synthesized at 120 °C for 8 h with the highest photocatalytic activity is shown in Fig. 5. As shown, agglomerated nano powders smaller than 10 nm were obtained, which is in agreement with the value calculated using the Scherrer equation.

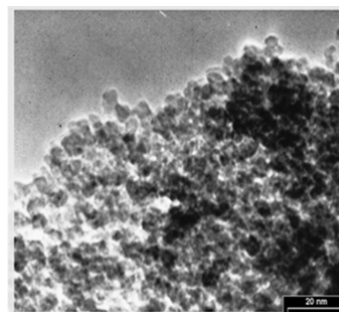


Fig. 5 TEM micrograph of the powder synthesized at 120°C

To derive kinetic information, the absorption decay due to the decomposition of methyl orange was considered. Since the initial concentration of methyl orange is low, the reaction rate can be represented with a first order equation:

$$\text{Rate} = -\frac{d[C]}{dt} = k_{\alpha} [C] \quad (1)$$

Where k_{α} is the constant apparent rate and $[C]$ the concentration of methyl orange. To determine the reaction rate constant, the curve of the variation of methyl orange concentration versus illumination time was fitted into Eq. (1). The value of the reaction rate constant was estimated to be equal to 0.24 min^{-1} .

4- Conclusions

This study investigated the solvothermal synthesis of nanocrystallite titania as powder at different synthesis temperatures. A maximum 94% degradation yield of methyl orange was obtained for the sample synthesized at 120 °C. Microstructure analysis of the TiO₂ powder showed that with increasing the synthesis temperature to 120 °C, the nucleation and growth of individual anatase crystallite in the amorphous phase significantly increased. This phenomenon led to subjecting more active catalytic points to photocatalytic reactions. However, further temperature increase caused the agglomeration of the nanoparticles and consequently diminishing the photocatalytic activity of the titania powders.