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Characterization and photocatalytic properties of TiO_2-nanosols synthesized by hydrothermal process at low temperature

Funda Sayılkan [a], Meltem Asiltürk [b], Sema Erdemoğlu [b], Murat Akarsu [c], Hikmet Sayılkan [a,*], Murat Erdemoğlu [d], Ertuğrul Arpaç [e]

[a] *Inönü University, Faculty of Education, Department of Science, 44280 Malatya, Turkey*
[b] *Inönü University, Faculty of Arts and Science, Department of Chemistry, 44280 Malatya, Turkey*
[c] *Institute für Neue Materialien, D-66123 Saarbrücken, Germany*
[d] *Inönü University, Department of Mining Engineering, 44280 Malatya, Turkey*
[e] *Akdeniz University, Faculty of Arts and Science, Department of Chemistry, 07100, Antalya, Turkey*

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Abstract

Transparent nanocrystalline pure anatase titania (nano-TiO_2) was synthesized by hydrothermal process at 200 °C. Photocatalytic activity of the nano-TiO_2 as in the form of sol was tested for degradation of Methylene Blue (MB) and Reactive Red 120 (RR-120) in aqueous solutions. Structural and physico-chemical properties of the nano-TiO_2 were characterized using powder XRD, SEM, BET, FT-IR and elemental analyses. Complete photodegradation of RR-120 was successfully achieved by aid of the nano-TiO_2 whereas MB was not degraded, maybe because of reversible color change in nano-TiO_2 sol/MB mixture after the UV irradiation was stopped. Potocatalytic activity of the synthesized the nano-TiO_2 for degradation of RR-120 was compared with Degussa P-25 at optimum conditions determined for RR-120. It was found that the nano-TiO_2 can be repeatedly used with higher photocatalytic activity than Degussa P-25.

Keywords: Nano-titania; Hydrothermal process; Photodegradation; Dye; Transparent sol

1. Introduction

Nanocrystalline TiO_2, one of the most popular photocatalyst, have long been investigated in environmental purification, decomposition of dyes in wastewater [1–3]. Anatase, brookite and rutile are three crystalline forms of titania. Among these crytalline forms anatase-TiO_2 is attracting more attention for its vital use as pigments [4], gas sensors [5], catalysts [6,7], photocatalysts [8–10] in response to its application in environmental related problems of pollution control and photovoltaics [11]. The catalytic and other properties of these materials strongly depend on the crystallinity, surface morphology, the particle sizes and preparation methods. The increased surface area of nanosized titania particles may prove beneficial for the decomposition of dyes in aqueous media. TiO_2 nanoparticles in powder have real advantages in relation to photocatalytic activity. In order to do this, different preparation process have been reported, such as sol–gel process [12], hydrolysis of inorganic salts [13], ultrasonic technique [7], microemulsion or reverse miscelles and hydrothermal process [14–17]. In this work, the hydrothermal process was used to synthesize pure anatase titania particles at low temperature. The photocatalytic activity of hydrothermally synthesized TiO_2 was examined for aqueous degradation of MB and RR-120.

* Corresponding author. Fax: +90 422 341 0042.
E-mail address: hsayilkan@inonu.edu.tr (H. Sayılkan).

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2. Experimental

2.1. Chemicals and apparatus

Titanium-*iso*-propoxide ($Ti(OPr^i)_4$, 97%) purchased from Alpha was used as titanium source for TiO_2 photocatalyst preparation. Degussa P-25 titanium dioxide (Germany) was used as received (BET surface area 50 m^2/g and anatase:rutile ratio 80:20). Hydrochloride acid from Merck (HCl, 37%) was used as catalyst for alkoxide hydrolysis. $Ti(OPr^i)_4$ and HCl were used without further purification. *n*-Propanol (Riedel de Haen, 99%) was used as solvent and stored over molecular sieve (Fluka, 3ÅXL8) before use. Methylene Blue (MB) and Reactive Red 120 (RR-120) purchased from a local textile factory was of analytical reagent grade and used without further purification. Deionized water was used for the hydrolysis of Ti $(OPr^i)_4$ and for preparation of all sols and solutions.

The crystalline phase of the nano-TiO_2 particles was analyzed by X-ray powder diffraction (XRD) pattern obtained from Rigaku Geigerflex D Max/B diffractometer with CuK_α radiation ($\lambda=0.15418$ nm) in the region $2\theta=10-90°$ with a step size of 0.04°. The crystallite size of the nano-TiO_2 was calculated from the X-ray diffraction peak according to the Scherrer's Equation $d_{hkl}=k\lambda/(\beta\ \cos\ (2\theta))$, where d_{hkl} is the average crystallite size (nm), λ is the wavelength of the CuK_α radiation applied ($\lambda=0.154056$ nm), θ is the Bragg's angle of diffraction, β is the full-width at half maximum intensity of the peak observed at $2\theta=25.3°$ (converted to radian) and k is a constant usually applied as ~0.94. A digital instrument SEM (LEO EVO 40) was used to examine the surface morphology. BET surface area and average pore diameter were determined by using ASAP 2000 model BET analyzer. The BET surface area, average pore diameter and micropore volume of the nano-TiO_2 was calculated from the N_2 adsorption isotherm at liquid N_2 temperature. The sample was degassed at 130 °C for 4 h before N_2 adsorption. Pore size distribution of the nano-TiO_2 was computed by DFT plus method. Dye concentration in the solutions and mixtures was determined using a Shimadzu 1601 model UV/VIS spectrophotometer. C and H elements in the nano-titania particle were analyzed by using element analyzer. UV-irradiation was carried out by a Solar Box 1500 model radiation unit with Xe-lamp and a controller to vary the irradiation time and power input from 390 to 1100 W/m^2.

2.2. Preparation of nanocrystalline TiO_2

$Ti(OPr^i)_4$ was dissolved in *n*-propanol. After stirring for 5 min at ambient temperature, a *n*-propanol-hydrochloride acid mixture was dropwise added into alkoxide solution by burette at the rate of 1 ml/min. After stirring for 5 min, the mixture of water-*n*-propanol was added into the last solution dropwise by burette at the same rate. The mixture was stirred at ambient temperature for 10 min. Sol-solution was then transferred into a stainless steel Teflon-lined autoclave and heated at 200 °C for 2 h. The molar ratio of $H_2O/Ti(OPr^i)_4$ and $HCl/Ti(OPr^i)_4$ were 2 and 0.2, respectively. As-obtained powders were separated through centrifuging and dried in a vacuum sterilizer at 30 °C for 4 h. Thus, the nano-TiO_2 powder was obtained.

2.3. Photocatalytic tests

Before examining the photocatalytic activity for aqueous degradation of MB and RR-120, TiO_2 sol was prepared. For this purpose, required amount of TiO_2 was dispersed ultrasonically in deionized water, without addition of any reagent to disperse the particles. After the ultrasonic treatment, the nano-TiO_2 sol was obtained. For photodegradation experiments required volume of dye solution was added into the nano-TiO_2 sol. After the temperature-constant sample preparation procedure and stabilizing the UV light at the necessary powers for 15 min, the nano-TiO_2/dye sol was poured into the glass reaction cell and the cell was immediately located in the Solar Box ready for UV-irradiation inducing the photochemical reaction to proceed. The decomposition of the dyes was monitored by measuring the maximum absorbency (λ_{max}) at 656.6 nm for MB and 548.5 nm for RR-120 and degradation was quantified by detecting final dye concentration (C) directly in the sol before, during and after UV-irradiation. It must be noted here that no filtration and centrifuging were needed for the nano-TiO_2 sol, since it was a self-dispersed suspension and therefore it was transparent. But, the suspensions of Degussa P-25 TiO_2 needed to remove from its suspension by filtration after photocatalysis procedure and before UV/VIS spectrophotometric analysis.

Since non-removability of the nano-TiO_2 seems like a disadvantage, reuse of the same sol which was used before for photodegradation was also investigated. For this purpose, dye was again and again added to the nano-TiO_2 sol and Degussa P-25 suspension, after complete mineralization of the dye was attained.

3. Results and discussion

3.1. Characterization of the nano-TiO_2

The crystalline phase of hydrothermally synthesized TiO_2 sample was analyzed by XRD, and its XRD pattern is shown in Fig. 1. All the sharp peaks observed in the XRD pattern belong to anatase phase of TiO_2. Briefly, a complete anatase TiO_2 crystalline phase was obtained. The average crystallite size of the nano-TiO_2 was estimated to be 8 nm. According to the results of elemental analysis, the nano-TiO_2 powder contains