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Characterization of the hydrothermally synthesized nano-TiO_2 crystallite and the photocatalytic degradation of Rhodamine B

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Abstract

Pure anatase-TiO_2 nanoparticles with 8 nm average crystallite size was synthesized hydrothermally at 200 °C in 2 h. The structural and physico-chemical properties of nano-TiO_2 were determined by powder XRD, FT-IR, BET and SEM analyses. The behavior of anatase nano-TiO_2 in catalytic degradation of Rhodamine B (RB) dye in transparent nano-TiO_2 sol under UV-light was examined as a function of irradiation power of UV-light, irradiation time, amount of nano-TiO_2 and initial RB concentration in the sol. Rhodamine B was fully degraded with the catalysis of the nano-TiO_2 in a short time as low as 60 min. Photocatalytic activity of the nano-TiO_2 for degradation of RB was compared with Degussa P-25 at optimum catalysis conditions determined for the nano-TiO_2. It was found that, when compared to Degussa P-25, the nano-TiO_2 could be repeatedly used with increasing photocatalytic activity. It was found that the photodegradation obeys the pseudo first-order reaction kinetics with the rate constant of 0.0658 min^{-1}, and the half period $t_{1/2}$ was 10.53 min.

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Keywords: Nano-titania; Hydrothermal process; Photodegradation; Rhodamine B

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1. Introduction

One of the major sources of environmental contamination is dyestuff that mainly comes from the textile and photographic industries [1–3]. Within the overall category of dyestuffs, Rhodamine B dye (RB), one of the most common xanthene dyes, is famous for its good stability as dye laser materials [4]. It has become a common organic pollutant, so the photodegradation of RB is important with regard to the purification of dye effluents. Photocatalytic degradation of several organic contaminants using large band gap semiconductor particles (such as TiO_2, ZnO and WO_3) have been studied extensively [3,5,6]. These contaminants present in an aqueous suspension of TiO_2 can be degraded with ultraviolet and visible light [7–9]. As one of the most popular photocatalyst, TiO_2 particle has long been investigated in environmental purification, decomposition of dyes in wastewater [10–12]. Anatase, brookite and rutile are three crystalline forms of TiO_2 and anatase-TiO_2 has attracted more attention for its vital use as pigments [13], gas sensors [14], catalysts [15,16], photocatalysts [17–19] in response to its application in environmental related problems of pollution control and photovoltaics [20]. The catalytic and other properties of these materials strongly depend on the crystallinity, surface morphology, particle size 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 processes have been reported, such as sol–gel process [21], hydrolysis of inorganic salts [22], ultrasonic technique [23], microemulsion or reverse micelles and hydrothermal process [24–26]. Polar or non-polar different solvents have been used in this process. Except the

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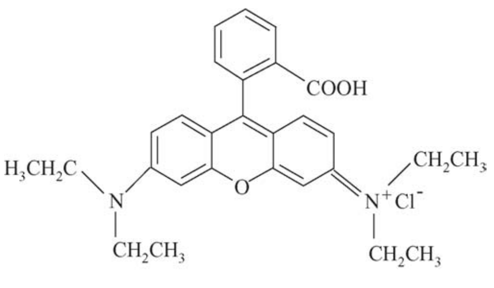
hydrothermal process, in these processes, high calcination temperature above 450 °C is usually required to form regular crystal structure. However, in the meantime, the high temperature treatment can decline the surface area and lose some surface hydroxyl or alkoxide groups on the surface of TiO_2, which prevents easy dispersion. Thus, in this work, the hydrothermal process was selected to synthesize nanosize crystallized TiO_2 at low temperatures, which has been attractive to further improve the photocatalytic activity of TiO_2 as catalysts. Compared with the other TiO_2 powders, these TiO_2 nanoparticles have several advantages, such as fully pure anatase crystalline form, fine particle size with more uniform distribution and high-dispersion either in polar or non-polar solvents, stronger interfacial adsorption and easy coating on different supporting material. Moreover, the hydrothermal process including aqueous solvents as reaction medium is environmentally friendly since the reactions are carried out in a closed system, and the contents can be recovered and reused after cooling down to room temperature.

In this work, photocatalytic activity of a nano-TiO_2, which was hydrothermally synthesized at 200 °C within 2 h, was examined for degradation of RB in aqueous solutions and the results were compared with commercially available Degussa P-25 TiO_2 at optimum catalysis conditions determined previously for the nano-TiO_2.

2. Experimental

2.1. Materials

Titanium-iso-propoxide ($Ti(OPr^i)_4$, 97%) purchased from Alpha was used as titanium source for the preparation of TiO_2 photocatalyst. 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%) stored over molecular sieve (Fluka, 3 ÅXL8) was used as solvent. Rhodamine B dye purchased from a local textile factory was of analytical reagent grade and used without further purification, which its chemical formula is presented as,



Degussa P-25 (Germany) TiO_2 with the BET surface area of $50\,m^2\,g^{-1}$ and anatase to rutile ratio of 80:20 was used as received. 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 hydrothermally synthesized TiO_2 nanoparticles was analyzed by X-ray powder diffraction (XRD) pattern obtained from Rigaku Geigerflex D Max/B diffractometer with Cu Kα radiation ($\lambda = 0.15418$ nm) in the region $2\theta = 10–90°$ with a step size of 0.04°. The crystallite size of the anatase particle was calculated from the X-ray diffraction peak according to the Scherrer's equation. The surface morphology of TiO_2 was examined by a LEO EVO 40 Model scanning electron microscope (SEM). The BET surface area, average pore diameter and micropore volume of the nano-TiO_2 particle was calculated from the N_2 adsorption isotherm at liquid N_2 temperature using ASAP 2000 model BET analyzer. The sample was degassed at 130 °C for 4 h before N_2 adsorption. Pore size distribution of nano-TiO_2 was computed by DFT plus method.

Dye concentration in the solutions and mixtures before, during and after UV-irradiation was measured by a Schimadzu 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 change the irradiation time and power input from 390 to $1100\,W\,m^{-2}$.

2.2. Preparation of nanocrystalline TiO_2 and photodegradation experiments

$Ti(OPr^i)_4$ 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 $1\,ml\,min^{-1}$. 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 mole ratio of $H_2O/Ti(OPr^i)_4$ and $HCl/Ti(OPr^i)_4$ were 2 and 0.2, respectively. The as-obtained powders were separated through centrifugation and dried in a vacuum sterilizer at 30 °C for 4 h. Thus, nanosized TiO_2 crystallite powder was obtained.

Before examining the photocatalytic activity for aqueous degradation of RB, TiO_2 sol was prepared. For this purpose, certain amount of TiO_2 was just mixed with deionized water without addition of any reagent, such as dispersants and the mixture was ultrasonicaly treated for 10–15 min. Meanwhile, self-dispersed and transparent 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 power ınput for 15 min, the nano-TiO_2/RB dye sol was poured into the glass reaction cell which has 12 separate sample compartments and one cover and the cell was immediately located in the Solar Box ready for UV-irradiation inducing the photochemical reaction to proceed. The nano-TiO_2 sol/RB solution was also transparent before and after the degradation procedure. The decomposition of RB was monitored by measuring the absorbency at 548 nm (λ_{max}) and degradation was quantified by detecting RB concentration (C) directly in the sol before, during and after UV-irradiation. No filtration or centrifuging was needed for the nano-TiO_2 sol/RB system after photocatalysis procedure and before UV–vis spectrophotometric analysis, since it was already self-dispersed and transparent, i.e. it does not contain any visible solid particles.

Photocatalytic activity of the nano-TiO_2 was compared with Degussa P-25 for degradation of RB at optimum catalysis conditions determined for the nano-TiO_2, except that Degussa P-25

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