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Effect of ultraviolet irradiation on crystallization behavior and surface microstructure of titania in the sol–gel process

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Abstract

Nanosized titania was prepared at various hydrolysis ratios ($r = H_2O/Ti$) by photo-assisted and conventional sol–gel methods. It was found that hydrolysis ratio and ultraviolet irradiation greatly affect the titania crystallization behavior. The introduction of photo-irradiation benefits anatase formation throughout a wide range of hydrolysis ratio. XPS results show that hydrolysis reaction was promoted by ultraviolet irradiation. In addition, photo-irradiation was also verified to be in favor of the generation of large specific surface area and high crystallinity, which resulted in relative high photocatalytic activity of TiO_2 prepared by a photo-assisted sol–gel method.

Keywords: Titanium dioxide; Sol–gel process; Photo-irradiation; Crystallization; Photocatalysis; Surface microstructure; Anatase; Rutile; Hydrolysis; Condensation

1. Introduction

Titanium dioxide is a material of great importance due to useful electrochemical, dielectric, electroconductive, and optical properties. It is widely used as cosmetics, pigments, photocatalysts, adsorbents, catalytic supports, and sensors [1–3]. For these applications, the morphology, average particle size and particle size distribution, porosity, phase composition, and crystallinity of titania are important factors to be controlled. Among the various methods developed to prepare TiO_2 [4–10], sol–gel method is the most used since the sol–gel processing has a prominent advantage of the facile control of structures and properties of the product through simple alteration of processing parameters. Recently, many modified sol–gel processes have been applied in the preparation of nanosized TiO_2. Hydrothermal treatment has been demonstrated favorable for preparing ultrafine nanocrystalline TiO_2 without particle agglomeration [11] and anatase with a high thermal stability [12]. Yu et al. [13] synthesized highly photocatalytic active nanosized TiO_2 particles by hydrolysis of titanium tetraisopropoxide via ultrasonic irradiation.

Extensively applied in the photoreduced preparation of noble metal nanocrystals [14,15] and narrowing the size distribution of semiconductor nanoparticles [16,17], ultraviolet irradiation has also been used to densify and crystallize the sol–gel derived precursor films such as SiO_2, TiO_2, ZrO_2 and ZnO films [18–21] as an alternative method to calcination. In addition to thermal effect, ultraviolet laser has also been believed to induce electronic excitations during such post-treatment [19,21]. More recently, we developed a photo-assisted sol–gel method [22–24] in which titanium alkoxide was hydrolyzed in acidic medium under ultraviolet irradiation to prepare nanosized TiO_2 with high crystallinity and small crystallite size at relatively low calcination temperature. We found that the phase transitions from amorphous to anatase and anatase to rutile were promoted by ultraviolet light irradiation, and the photocatalytic activity of titania film prepared with photo-irradiation was much higher than that of the sample prepared without irradiation. However, the

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general effects and mechanism of ultraviolet irradiation in the hydrolysis and condensation reactions are still not very clear. It is well known that the hydrolysis ratio ($r = H_2O$/metal), catalyst and complexing ligands are the main factors controlling the growth of transition metal oxides in the sol–gel process. So as to better understand the general effect of ultraviolet irradiation, we prepared nanosized TiO_2 at various hydrolysis ratios by photo-assisted and conventional sol–gel methods in this work. We found that ultraviolet irradiation has great effect on crystallization behavior and surface microstructure of TiO_2 in a wide range of hydrolysis ratio.

2. Experimental section

2.1. Materials preparation

All chemicals used in this study were of analytical grade and used without further purification. Titanium (IV) isopropoxide was supplied from Aldrich. The others were from Beijing Chemical Company. Millipore water (18.2 MΩ) was used in all experiments.

In a typical preparation of titania colloid, anhydrous 2-propanol solution (29 mL) containing 9 mL titanium (IV) isopropoxide was slowly added into 46.8 mL alcohol solution containing 3 mL hydrochloric acid and different amount of deionized water under vigorous stirring at room temperature. The hydrolysis ratio ($r = H_2O/Ti$) varied from 4 to 20. After mixing, the sol was stirred and illuminated for 15 h by a 375 W high-pressure mercury lamp. A Pyrex reactor was used to cut off light of wavelength shorter than 290 nm and a circulating water cuvette was used to avoid the heating effect of the lamp. The distance between the lamp and reactor was 15 cm and the intensity of the UV radiation reaching the reactor was about 4 mW cm^{-2}. Under the otherwise identical conditions, TiO_2 colloid was also prepared by a sol–gel method in the dark for comparison. Titania powders were prepared by evaporating solvent from the colloid at room temperature and then annealing the gel at different temperatures for 4 h. The samples prepared by a photo-assisted sol–gel method were denoted as R4-P, R7-P, R10-P and R20-P (the number labels the hydrolysis ratio and P represents photo-irradiation). The samples prepared in the dark were marked as R4-N, R7-N, R10-N and R20-N (the number labels the hydrolysis ratio and N represents non-irradiation).

2.2. Photocatalytic experiments

Rhodamine B (RB) was from Tokyo Kasei Kogyo Co. Ltd. and used as received. An aqueous suspension of RB (1.0×10^{-5} mol L^{-1}, 50 mL) and TiO_2 (2.5 mg) contained in a 80 mL Pyrex vessel was stirred for about 30 min in the dark to reach the adsorption/desorption equilibrium. Subsequently the dispersion was irradiated with ultraviolet light provided by a 375 W high-pressure mercury lamp. A 1.0 cm thick circulating water cuvette was used to remove the heat of the lamp. Variations in the concentration of the dye in the degraded solution were monitored by UV-Vis spectroscopy (Shimadzu UV-1601 PC).

2.3. Samples characterization

The XRD patterns were acquired on a Rigaku D/max 2500 X-ray diffraction spectrometer (Cu$K\alpha$, $\lambda = 1.54056$ Å) at a scan rate of 0.02° 2θ S^{-1}. The average crystallite size was calculated according to the Scherrer formula ($D = k\lambda/B\cos\theta$). The BET surface areas of the samples were determined by nitrogen adsorption–desorption isotherm measurement at 77 K. The samples annealed at 373 K were degassed at 100 °C prior to actual measurements. However, for the samples calcined at higher temperature, the degassing temperature was 180 °C. The average pore size was calculated from the desorption branch of the nitrogen isotherm by the BJH method. TEM samples were prepared by dispersing the powders in ethanol and then depositing onto carbon-coated copper grids. These samples were then observed with a JEOL-2010 electron microscope at an accelerating voltage of 200 KV. XPS measurements were carried out with an SECA Lab 220i-XL spectrometer by using an unmonochromated Al $K\alpha$ (1486.6 eV) X-ray source. All the spectra were calibrated to the binding energy of the adventitious C1 s peak at 284.6 eV. Thermogravimetric analyses (TGA) were carried out in a Perkin-Elmer thermoanalyze under dry air, using platinum crucibles and a constant heating rate of 10 °C min^{-1} up to 700 °C.

3. Results and discussion

Fig. 1 shows XRD patterns of TiO_2 powders prepared with and without UV irradiation followed by drying at 373 K. It can be seen that the crystallization behavior greatly depends on the hydrolysis ratios and photo-irradiation. Anatase is the main phase in most of the samples except for R7-N and R20-P. A small shoulder frequently occurring on the higher angle side of the anatase (1 0 1) peak indicates the presence of small amounts of brookite [25]. In the conventional sol–gel process, at low hydrolysis ratio ($r = 4$), only a trace amount of rutile is observed, while a large amount of rutile (about 87% of weight fraction according to the calculation method reported in Ref. [26]) is detected at $r = 7$. When the content of H_2O is increased further, anatase becomes the dominant crystalline phase again although amorphous phase is evidently present in the sample prepared at $r = 10$. In contrast, nearly pure anatase is acquired when the sols were irradiated by UV light except for the sample prepared at $r = 20$. It can be also observed from Fig. 1 that the diffraction peaks of the samples prepared with photo-irradiation are sharper than those of the samples prepared without irradiation in most cases, indicating the higher degree of crystallinity of these photo-irradiated samples. Table 1 gives the crystallite sizes of TiO_2 calculated by