

Communication

Low Temperature Solvent Evaporation-induced Crystallization Synthesis of Nanocrystalline TiO₂ Photocatalyst

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A novel and efficient methodology for obtaining highly active photocatalyst of bi-phase TiO₂ with small particle size and high specific surface area was developed by solvent evaporation-induced crystallization (SEIC) method at low temperature. The prepared TiO₂ powder was characterized with X-ray diffraction (XRD), transmission electron microscopy (TEM) and BET surface areas. The photocatalytic activity was evaluated by the photocatalytic oxidation of acetone in air. The results showed that the photocatalytic activity of the TiO₂ powder prepared by this method approached that of Degussa P25. This may be attributed to the fact that the prepared TiO₂ powder had larger specific surface areas (265 m²·g⁻¹) and smaller crystallite size (about 5 nm), but relatively low crystallinity, as compared with Degussa P25.

Keywords solvent evaporation-induced crystallization method, titanium dioxide, nanocrystalline, photocatalyst

Introduction

A great deal of effort has been devoted in recent years to developing heterogeneous photocatalysts with high activities for environmental applications such as air purification, water disinfection, hazardous waste remediation, and water purification.¹⁻⁶ Among various oxide semiconductor photocatalysts, titanium dioxide has proved to be the most suitable because of widespread environmental applications for its biological and chemical inertness, strong oxidizing power, cost-effectiveness and long-term stability against photo-corrosion and chemical corrosion.^{1,2} Titanium dioxide can be used to catalyze many different reactions, such as alcohol dehydration, Photo-Kolbe oxidations of organic acids,⁷ oxidation of aromatic compounds,⁸ degradation of paint pigments,⁹ and nitrogen oxide reduction under UV illumination.¹⁰ However, the photocatalytic activity must be further improved from the point of view of practical use and commerce.¹¹ To achieve this, an anatase powder with good

crystallinity, small grain size and high specific surface area is desirable to improve the photocatalytic activity. Among the methods available for the synthesis of small TiO₂ nanoparticles, the sol-gel method has been widely employed due to the inexpensive equipment required, low temperatures and the homogeneous and highly pure product produced. Usually, the particles obtained by this method are amorphous in nature and calcination temperature higher than 350 °C are required to realize the transition from amorphous to anatase phase.¹² However, such high calcination temperatures will result in increased size of the nanoparticles and decreased specific surface area. To obtain small nanocrystalline TiO₂ powder with high specific surface area, larger than 250 m²·g⁻¹, a reasonable pathway would be to lower the temperature of the phase transition. In this study, a novel and efficient method for preparing highly photoactive nano-sized TiO₂ photocatalyst with small grain size and high specific surface area has been developed by hydrolysis of TTIP in pure water at room temperature, and evaporation of solvent at 100 °C. This is the first time to report the photocatalytic activity of nanocrystalline TiO₂ powder prepared by solvent evaporation-induced crystallization method at low temperature showing high photocatalytic activity, small particle size and high specific surface area.

To synthesize nano-sized TiO₂ particles, titanium tetrakisopropoxide (TTIP, Aldrich) was used as a titanium source. TTIP (0.063 mol) was added dropwise to 113.4 mL of pure water under vigorous stirring at room temperature. The molar ratio of H₂O to TTIP was 100. Sol samples formed by the hydrolysis process were aged in closed beaker at room temperature for 24 h in order to further hydrolyze the TTIP and form TiO₂ gel precipitates. After the aging, the samples were evaporated at 100 °C in an oven for about 24 h in air in order to remove water and alcohol

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in the gels, and then ground to fine powder to obtain TiO₂ xerogel. Some wet gel was also obtained by separating precipitates from the above mixtures, and then dried at room temperature for 48 h.

The X-ray diffraction (XRD) patterns obtained on a Philips MPD 18801 X-ray diffractometer using Cu K α radiation at a scan rate of $2\theta = 0.05$ ($^{\circ}$)/s were used to determine any phase present and their crystallite size. The phase content of a sample was calculated from the integrated intensities of anatase (101), rutile (110) and brookite (121) peaks according to literature.^{13,14} The average crystallite sizes of anatase, rutile, and brookite were determined according to the Scherrer equation using the fwhm data of each phase after correcting the instrumental broadening.^{13,14} The Brunauer-Emmett-Teller (BET) surface area (S_{BET}) of the powder was analyzed by nitrogen adsorption in a Micromeritics ASAP 2010 nitrogen adsorption apparatus. The samples measured were degassed at 100 $^{\circ}\text{C}$ before the actual measurements. The BET surface area was determined by the multipoint BET method using the adsorption data in the relative pressure (p/p_0) range, 0.05–0.3. The pore-size distribution, from the desorption branch of the isotherm, was calculated following the method developed by Barret, Joyner and Halender (BJH), assuming a cylindrical pore modal.¹⁵ For TEM observation, the powder samples were dispersed in ethanol via ultrasonic irradiation and then deposited onto carbon-coated copper grids. After solvent evaporation, the samples were observed with a TEM (Jcol Co., 1200EX, Japan).

The photocatalytic activity experiments on TiO₂ particles for the oxidation of acetone in air were performed at ambient temperature using a reactor of 7000 mL. The detailed experimental process can be found in reference.¹¹ The photocatalytic oxidation of acetone is a pseudo-first-order reaction and its kinetics may be expressed as follows: $\ln(c_0/c) = kt$, where k is the apparent reaction rate constant, c_0 and c are the initial concentration and the reaction concentration of acetone, respectively.

Fig. 1 shows the XRD patterns of the TiO₂ wet gel and xerogel powder. It can be seen that the TiO₂ wet gel directly obtained by hydrolysis of TTIP is amorphous. However, the TiO₂ xerogel powder shows distinctive peaks at the d (nm) value of [101](0.352), [004](0.2382), [200](0.1896), [105] and [211](0.1698) of anatase [JPCDS Pattern No. 21-1272 (TiO₂)], and [120] (0.351), [111] (0.3465) and [121] (0.2911) of brookite [JPCDS Pattern No. 29-1360(TiO₂)], indicating that anatase and brookite are formed at 100 $^{\circ}\text{C}$. For brookite, the lines 120 (100%) and 111 (80%) are not visible because they are coincident with the anatase one 101. Usually, The transformation temperature of amorphous to anatase phase of TiO₂ is about 400 $^{\circ}\text{C}$.¹² Also, if an amorphous wet gel is directly heated to 100 $^{\circ}\text{C}$, XRD results indicate that no phase transformations occur (not shown here). Therefore, the above results suggest that solvent evaporation at 100 $^{\circ}\text{C}$ promotes the phase transition and crystallization of amorphous TiO₂ wet gel. Why solvent

evaporation can induce or promote crystallization of TiO₂ at low temperature. This is probably due to the fact that the residual un-hydrolytic alkyls and organic solvent can suppress rapid crystallization of the TiO₂ particles by chemisorbing on the surface of TiO₂ particles.⁴ Usually, with increasing hydrolysis temperature, a stronger nucleophilic substituent reaction between H₂O and alkoxide molecules will occur and more alkoxy groups in the alkoxide will be substituted by hydroxyl groups of H₂O.^{4,16} Therefore, the decrease of the quantity of unhydrolysed alkyls in precursors results in reduction in steric hindrance by the residual alkyls preventing crystallization to crystalline anatase.⁴ Moreover, the evaporation of organic solvent during drying is also beneficial to the crystallization of TiO₂ sol. It was determined by using the Scherrer equation that the grain sizes of anatase and brookite are 5.2 and 3.3 nm, respectively. The mass percentages of anatase and brookite are 65% and 35%, respectively.

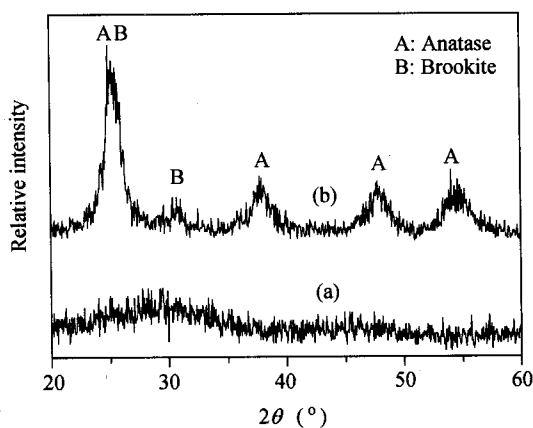


Fig. 1 XRD patterns of the TiO₂ wet (a) gel and xerogel powder (b) prepared by solvent evaporation-induced crystallization method at 100 $^{\circ}\text{C}$ for 24 h.

The structure of TiO₂ xerogel samples was further studied by TEM. Fig. 2 shows TEM image of TiO₂ xerogel powder prepared by solvent evaporation-induced crystallization method at 100 $^{\circ}\text{C}$ for 24 h. The size of the primary particle is very small and about (5 \pm 1) nm, which is in

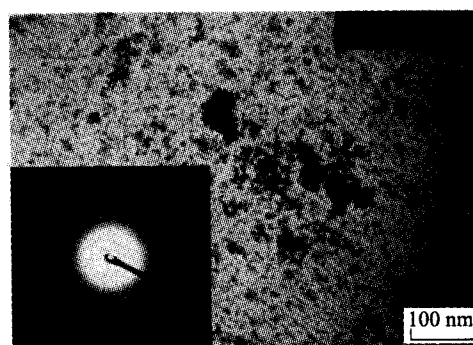


Fig. 2 TEM photographs of TiO₂ xerogel powder prepared by solvent evaporation-induced crystallization method at 100 $^{\circ}\text{C}$ for 24 h.

agreement with the value determined by XRD. The related electron diffraction pattern also indicates the formation of crystalline TiO₂ at 100 °C.

Fig. 3 shows pore size distribution curve calculated from desorption branch of the nitrogen isotherm by the BJH method and the corresponding nitrogen adsorption-desorption isotherms (Inset) of TiO₂ xerogel sample. The sharp decline in desorption curve is indicative of mesoporosity, while the hysteresis between the two curves demonstrates that there is a diffusion bottleneck, possibly caused by non-uniform pore size. The pore size distribution calculated from desorption branch of the nitrogen isotherm by the BJH (Barrett-Joyner-Halenda) method shows a narrow range of 2.5–6.9 nm with an average pore diameter of ca. 4.9 nm. The mesoporous structure of TiO₂ powder is attributed to pores formed between TiO₂ particles.¹⁶ It is these mesoporous pores that allow rapid diffusion of various reactants and products during photocatalytic reaction and enhance the speed of photocatalytic reaction. It can also be determined from the isotherms that the S_{BET} value of xerogel powder is 265 m²·g⁻¹.

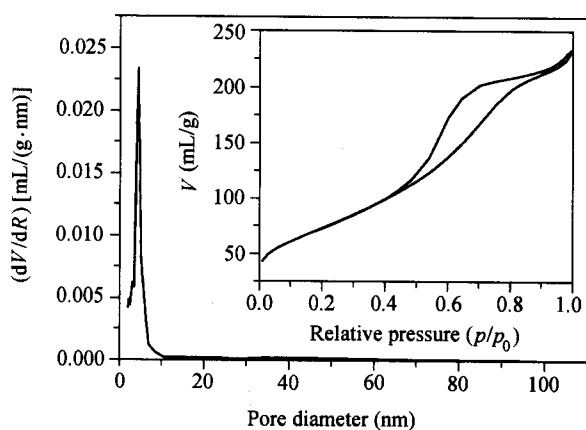


Fig. 3 Pore size distribution curve calculated from desorption branch of the nitrogen isotherm by the BJH method. Inset: the corresponding nitrogen adsorption-desorption isotherms of as-prepared TiO₂ xerogel sample by solvent evaporation-induced crystallization method.

Fig. 4 shows the comparison of the apparent rate constants (min⁻¹) of wet gel, xerogel and Degussa P-25 (P25). It can be seen that TiO₂ wet gel shows almost no photocatalytic activity (negligible). This is due to TiO₂ being in amorphous status. However, for xerogel, it shows decent photocatalytic activity with a rate constant of 3.8 × 10⁻³ min⁻¹. Its photocatalytic activity approaches that of P25 (4.2 × 10⁻³ min⁻¹), which is well known to have a high photocatalytic activity.^{1,2} This may be attributed to the fact that the former has larger specific surface areas, smaller crystallite size. Usually, the specific surface areas and crystallite size of P25 are about 50 m²·g⁻¹ and 30 nm, respectively.^{17,18} P25 shows better crystallization due to high temperature chloride processes, therefore, it exhibits higher photocatalytic activity.¹¹

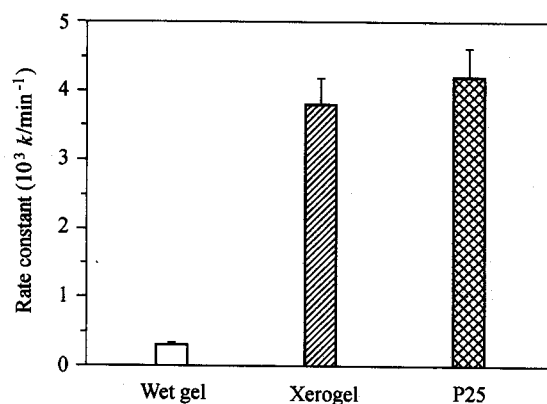


Fig. 4 Comparison of the apparent rate constants (k/min⁻¹) of P25, TiO₂ wet gel and xerogel powder prepared by solvent evaporation-induced crystallization method at 100 °C for 24 h.

In summary, the bi-phase (anatase and brookite phase) nano-sized TiO₂ particle photocatalyst with high specific surface area and small grain size was synthesized at relatively low temperature by using solvent evaporation-induced crystallization method. Experimental results indicated that the formation of anatase and brookite phases could be promoted by solvent evaporation during drying at 100 °C. The photocatalytic activity of TiO₂ powder prepared by this method showed high photocatalytic activity and approached that of Degussa P25. This work may provide a new approach to the synthesis of other oxide nanocrystalline catalysts with small particle size and high specific surface area.

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