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Study on Photocatalysis Properties of Nanocrystalline Titanium Dioxide

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Abstract Nano-TiO_2 powders with pure anatase structure were prepared by the method of precipitation-solution-gelation, using H_2TiO_3, hydrogen peroxide and ammonia as reactants. Active red X-3B dye solution was selected as a model pollutant for the photocatalysis degradation experiments. The effects of grain sizes, dosage and microstructure of nano-TiO_2 on its photocatalysis properties were studied. The results show that photo-activity of the nano-TiO_2 is enhanced with the grain sizes reducing or dosages increasing of nano-TiO_2. However, excess increase in nano-TiO_2 concentration is not advantageous to the enhancement of the photo-activity. Anatase TiO_2 demonstrated a higher photo-activity than rutile TiO_2. The dye solution hardly degraded without nano-TiO_2 powders being added into it or under sunlight irradiation.

Key words nanocrystalline, TiO_2, photocatalysis property.

1 Introduction

In traditional wastewater treatment techniques, including activated carbon adsorption, chemical oxidation, biological digestion, *etc*, there are somc limitations and disadvantages. For instance, activated carbon adsorption only involves phase transfer of pollutants without decomposition. Chemical oxidation is unable to mineralize all organic substances and is only economically suitable for the removal of pollutants in high concentrations. Biological digestion requires disposal of active sludges and control of proper pH and temperature. Furthermore its reaction rate is slow. For the photocatalysis process of TiO_2 used as a semiconductor catalyst under UV-light in wastewater treatment, it shares the following advantages: complete oxidation of organic pollutants in a few hours, without production of polycyclic products, degradation of pollutants in ppb range, *etc*[1]. Thus, studies on photocatalysis properties of TiO_2 have been in focus in recent years. Photocatalysis properties of TiO_2 have been suggested to depend on quite a number of parameters including particle size, surface area, the ratio between the anatase and rutile phase, light intensity and materials to be degraded. For most photocatalysis reaction systems, it is generally accepted that anatase demonstrates a higher activity than rutile[2].

In this paper, nanocrystalline TiO_2 powders with pure anatase structure were prepared. Active red X-3B dye solution was selected as a model pollutant for the photocatalysis degradation experiments. The effects of grain sizes, dosage and microstructure of nano-TiO_2 on its photocatalysis properties were studied.

2 Experiments

2.1 Preparation of nanocrystalline TiO_2

Nanocrystalline TiO_2 powders were prepared by the method of precipitation-solution-gelation, An amount of H_2TiO_3, hydrogen peroxide and ammonia were mixed with the molar ratio of 1:6:2 under continuously stirring in an ice-water bath. After a yellow clear solution was formed, a little surfactant was added into it with stirring for additional 2 hours. A gelation was obtained after the solution was placed at room temperature for several hours. Then the gelation was washed with distilled water, filtered and dried at 80～120℃. After mechanically grinding, the dry-gel powders were calcinated at 550～650℃ for 3 hours to obtain nanocrystalline TiO_2 powders with different grain sizes.

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2.2 Characterization of nanocrystalline TiO_2

The structure and grain sizes of nanocrystalline TiO_2 powders, and the ratio of anatase and rutile were determined by X-ray diffraction (XRD), using Rigaku D/max-C XRD diffractrometer at 40 kV /100 mA with Cu K_α radiation. The percentage of rutile in the powders can be estimated using the equation $x = (1 + 0.8\ I_A / I_R)^{-1}$, where I_A and I_R are the integrated intensities of anatase and rutile diffraction peaks, respectively, and x is the weight fraction of rutile in the powders. Grain sizes can be determined from the broadening of corresponding X-ray spectral peaks by Scherrer's formula $L = 0.90\lambda/(\beta\cos\theta)$, where L is the grain size, λ is the wavelength of the X-ray radiation, and β is the line width at half maximum height. The line width can be corrected for instrumental broadening by employing the patterns obtained for standard-sample silicon under the same experimental conditions.

As-prepared TiO_2 powders are pure antase based on XRD analysis. The average grain size is in the range of 12—30 nm, due to different calcinating temperatures.

2.3 Degradation experiments

Degradation experiments of active red X-3B dye solution were carried out in the same cylindrical annular batch photoreactor, employing GGZ-125W high pressure mercury lamp as UV light source. A quantity of as-prepared nano-TiO_2 powders was added into the dye solution, whose initial concentration in the mixture was fixed at 30 mg/L. The mixture was dispersed uniformly by sonicating and stirring, and then taken into the reactor. Air was continuously bubbled into the stirred suspensions at a flow rate of 25 L/h. Samples were taken out every 5 min and centrifuged twice at 16000 r/min, 15 min each time. The supernatants were collected for absorbency measurements with 752 UV-vis detector. Photocatalysis properties of nanocrystalline TiO_2 powders were characterized by A or $(A_0 - A)/A_0$, where A_0 was the initial absorbency of the dye solution and A was its absorbency at different irradiation times.

3 Results and Discussions

3.1 Effect of nano-TiO_2 dosage

A certain amount of pure anatase nano-TiO_2 powders with the average grain size of 22 nm was added into the dye solution. The concentrations of TiO_2 in the solution were 0, 0.4, 1, 2, 4, 6 g/L, respectively. Fig.1 shows the effects of irradiation time on the photoactivity of TiO_2 with different concentrations. It can be seen that absorbance of the dye solution changes at an extremely slow rate with increasing irradiation time(curve a), when no nano-TiO_2 powders is added into the dye solution, *e.g.*, TiO_2 concentration is 0 g/L. The decoloration percent$((A_0 - A)/A_0)$ of the dye solution remains nearly zero after being irradiated for 10 min and then reaches 4.3% after 25 min. When nano-TiO_2 powders is added into it, the decoloration percent of the dye solution obviously enlarges and gradually increases with irradiation time. But with prolonging irradiation time, the decoloration rate slows down, which suggests that the effect of nano-TiO_2 dosage on the degradation of the dye solution weakens.

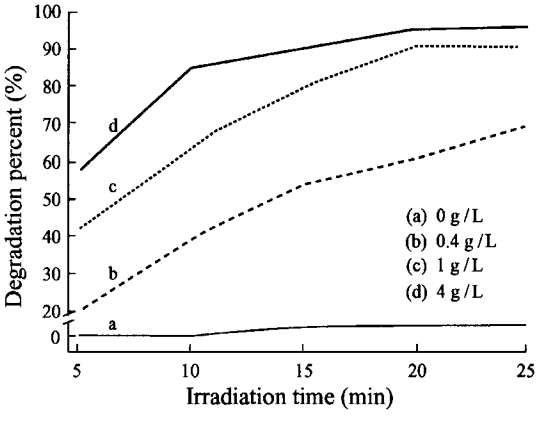

Fig.1 Effect of irradiation time on photoactivity of TiO_2 with different concentrations

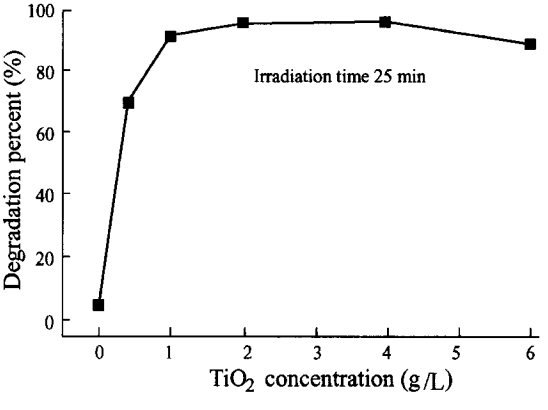

Fig.2 Effect of TiO_2 concentration on photoactivity at a constant irradiation time

In addition, at a certain irradiation time (for instance, 25 min), the decoloration percent of the dye solution increases with TiO_2 dosage rising until a plateau, whereas further increase in TiO_2 dosage results in reduction of the decoloration percent, as shown in Fig. 2. This indicates that excess nano-TiO_2 is of little advantage to the enhancement of the photoactivity, due to less homogeneous light distribution. This effectively restricts the photons to a very small region near the UV-lamp and under such conditions the small ratio of irradiated volume to total reactor volume is unfavorable for an efficient photochemical process[3]. Too low concentration of TiO_2 also leads to the decoloration percent reducing, due to less photogenerated electron-hole pairs. Therefore, there is an optimal range of TiO_2 dosage.

3.2 Effect of grain size

Nanocrystalline anatase powders with different grain sizes were added into the dye solution. The effect of grain size of TiO_2 on its photoactivity is illustrated in Fig. 3. TiO_2 concentrations were fixed at 1 g/L and the average grain sizes were 15, 22 and 30 nm, respectively. In Fig. 3, the decoloration percent of the dye solution increases with reducing of TiO_2 grain sizes. According to Brus equation[4]:

$$\Delta E = \frac{h^2\pi^2}{2R^2}\left(\frac{1}{m_e}+\frac{1}{m_h}\right) - \frac{1.786e^2}{R\varepsilon} - 0.248E_{R_y}$$

where ΔE, R and ε are band-gap energy, grain size and dielectric constant of TiO_2, respectively. It is demonstrated that TiO_2 with smaller grain size has larger band-gap energy, and thus high photoactivity. In addition, reducing grain size leads to more surface atoms and active positions, larger surface area, and faster charge-transferring rate, which also are beneficial to strengthening photoactivity. Therefore, TiO_2 with smaller grain size shows higher photoactivity and degradation capability than those with larger grain sizes.

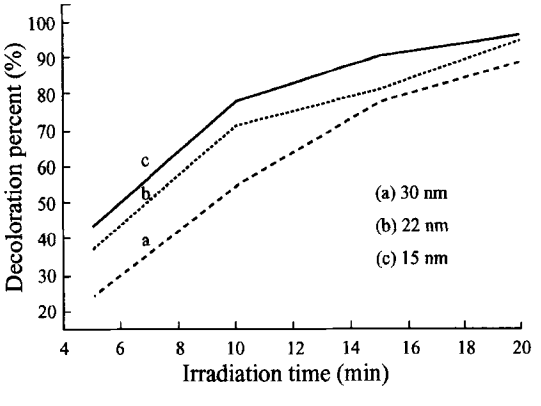

Fig. 3 Effect of TiO_2 grain size on its photoactivity

Photoactivity of the nano-TiO_2 powders (with the average grain size of 22 nm) was compared with that of conventional TiO_2 powders (anatase, chemical purity). The concentrations of TiO_2 were 2 g/L. The result shows that conventional TiO_2 powders also have relatively high photoactivity, and the decoloration percent of the dye solution gradually increases with irradiation time and amounts to 69.7% after 20 min of irradiation time. While the decoloration percent of the dye solution degraded by nano-TiO_2 powders reaches 91% under the same conditions, which is 1.3 times as that by conventional TiO_2 powders. Obviously, photoactivity of the nano-TiO_2 is higher than that of conventional TiO_2.

3.3 Effect of microstructure

As-prepared nano-TiO_2 powders were annealed at 600, 800, 900 and 1 000℃ for 2 hours, respectively. As shown in Fig. 4, XRD results indicate that nano-TiO_2 powders annealed at 600℃ still remains anatase phase. At 800℃, the transformation from anatase to rutile takes place and a small amount of anatase changes into rutile. With annealing temperature rising, more anatase phase transforms to rutile phase. At 1000℃, all the anatase phase transforms to rutile phase. It is estimated that after nano-TiO_2 powders were annealed at the temperatures of 600, 800, 900 and 1 000℃, there are 0%, 14%, 90% and 100% rutile in it, respectively. The effect of the structure of nano-TiO_2 on its photoactivity was examined by adding the heat-treated nano-TiO_2 into the dye solution. The concentrations of TiO_2 were 1 g/L and irradiation time was fixed at 20 min.

As shown in Fig. 5, the decoloration percent of the dye solution gradually decreases with annealing temperature increasing. When annealing temperature is above 800℃, the decoloration percent dramatically decreases, from 97.8% at 600℃ to 8.1% at 1000℃. The decreasing of photoactivity is caused partialy by grain size increasing, but primarily by the anatase-rutile transformation. Grains of anatase phase grow from 13.4 nm at 600℃ to 33.5 nm at 900℃ and the decoloration percent decreases to 13.6%, which is far

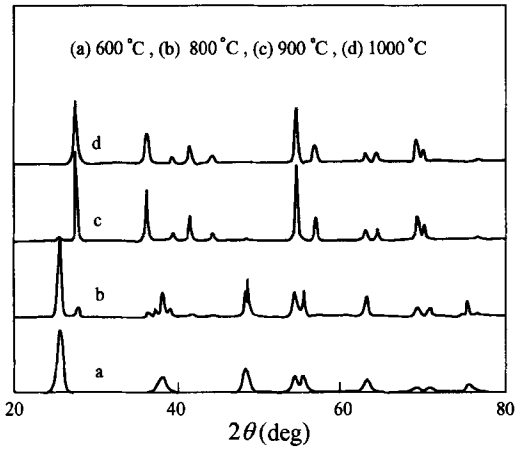

Fig.4 XRD diffraction patterns of nano- TiO_2 annealed at different temperature for 2 hours

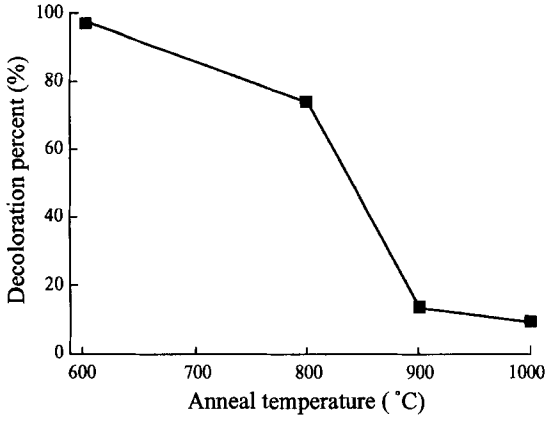

Fig.5 Effect of nano-TiO_2 microstructure on photoactivity, TiO_2 concentration 1 g/L, irradiation time 20 min

smaller than that by pure anatase nano-TiO_2 with the similar grain size of 30 nm under the same conditions (as shown in Fig.3(a), the decoloration percent was 89.7% by pure anatase TiO_2). This demonstrates that the smaller decoloration percent is due to the transformation of most anatase to rutile at 900℃. Rutile has a smaller band-gap than anatase and thus it has a lower oxide-reduction capability[5]. Therefore, anatase exhibites higher photoactivity than rutile, as a result of the two phases having different electronic band structures.

3.4 Effect of irradiation

Photocatalysis degradation experiments of the dye solution were performed, using sunlight and 125W high-pressure mercury lamp as UV irradiation source. The concentrations of the nano-TiO_2 were 2 g/L. It was found that absorbance of the dye solution hardly changed with increasing irradiation time, when it was irradiated by sunlight. However, the absorbance remarkably reduced when it was irradiated by the high-pressure mercury lamp and the degradation percent reached 99% after irradiating for 40 min.

4 Conclusions

Nano-TiO_2 powders with pure anatase structure were prepared by the method of precipitation-solution-gelation, using H_2TiO_3, hydrogen peroxide and ammonia as reactants. Active red X-3B dye solution was selected as a model pollutant for the photocatalysis degradation experiments. The effects of grain sizes, dosage and structure of nano-TiO_2 on its photocatalysis properties were studied. The results show that the photoactivity of nano-TiO_2 is enhanced with the grain sizes reducing and dosages increasing of nano-TiO_2. However, excess increase in nano-TiO_2 dosage is unfavorable for the enhancement of the photoactivity. Anatase nano-TiO_2 exhibited a higher photoactivity than rutile TiO_2. The dye solution hardly degraded without nano-TiO_2 powders being added into it or under sunlight irradiation.

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