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Preparation and characterization of high photoactive TiO_2 catalyst using the UV irradiation-induced sol-gel method

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Abstract: High photoactive TiO_2 catalyst was prepared using the sol-gel method through UV irradiation during the formation stage of nuclei. The surface morphology and microstructure of the prepared catalyst were characterized using scanning electron microscopy (SEM), X-ray diffraction patterns (XRD), and Fourier transform infrared spectroscopy (FT-IR). The photoactivity was evaluated by the degradation of methylene blue. The results show that the photocatalysis of the prepared catalyst is higher than that of conventional heat-treated particles. The higher photoactivity is a combined result of favorable microstructure, appropriate hydroxyl groups, and active sites of Ti^{3+} ions on the surface of TiO_2. It is concluded that the ultraviolet irradiation-induced sol-gel method is an effective method to enhance the photocatalysis of TiO_2.

Key words: titanium oxide; photocatalysis; sol-gel; ultraviolet irradiation

1. Introduction

TiO_2 is the most promising photocatalyst due to its facile and cheap application in removing inorganic and organic pollutants from waste waters [1]. Among many methods that are used to prepare TiO_2 catalyst, the sol-gel method is the most widely applied [2-4]. In the traditional sol-gel method, the xerogel requires to be calcined at several hundred degrees to decompose the remnant organic solvent and organic groups, and transform the amorphous TiO_2 particles to anatase crystal phase with high photocatalysis. However, the dispersed nanosized particles tend to conglomerate during calcination, resulting in the loss of quantum effect [5]. Although many researches have been carried out for enhancing the TiO_2 photocatalytic activity, most of them have focused on the enhancement of photoactivity of TiO_2 by doping or by the use of a composite [6-7]. Yu reported that high photoactive nanocrystalline TiO_2 was prepared by a solvent evaporation-induced crystallization method [8]. In this work, a novel and simple preparation method for high photoactive TiO_2 using the UV irradiation-induced sol-gel method was studied. Using the sufficient energy provided by UV irradiation, notable nuclei were formed rapidly during the preliminary process of the sol-gel method, more active points were formed by rearranged gelatin network that is formed during the formation stage of framework, and the amorphous particles crystallized at room temperature. The photocatalytic activity of the prepared particles was evaluated by degradation of methylene blue (MB). The activity of the as-prepared TiO_2 catalyst exceeds that of the samples prepared using conventional furnace treatment.

2. Experimental

Nanosized anatase TiO_2 catalyst was prepared using a sol-gel method. Titanium tetrapropoxide [$Ti(PrO)_4$] was used as the precursor. In a typical preparation, 5 mL of titanium tetrapropoxide was mixed with 20 mL of ethanol under stirring. The solution containing 1 mL of H_2O, 3 mL of ethanol, and a drop of hydrochloric acid was then added into the titanium-ethanol solution. Six series of samples were prepared, and the preparation conditions are shown in Table 1.

The formation process of the sol-gel was analyzed by measuring the conductivity. The thermal behavior of the conventionally prepared catalyst was analyzed using simultaneous differential scanning calorimetric analysis and thermogravimetric analysis (DSC-TG, Germany Netzsch, STA449 C). The crystal phases of TiO_2 particles were characterized by X-ray diffraction patterns (XRD, Japan Rigakn, D/max 2200PC), and the crystal size was determined using the Scherrer equation based on the (101) peak. The surface morphology of the prepared catalyst was observed using scanning electron microscope (SEM, Holland Philips JSM-5800) at 15 keV. Fourier transform infrared spectroscopy (FT-IR, U.S. Nicolet, Avatar 360) was measured in the

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range of 450-4000 cm^{-1}.

Table 1. Preparation conditions of different samples

No.	Preparation of nano TiO_2 sol	Aging time / day	Desiccation	Calcination
1	Irradiated by ultraviolet lamp for 1 h under stirring	7	100°C for 4 h	—
2	Irradiated by infrared lamp for 1 h under stirring	7	100°C for 4 h	—
3	Irradiated by ultraviolet lamp for 1 h under stirring	7	100°C for 4 h	500°C for 2 h
4	Irradiated by infrared lamp for 1 h under stirring	7	100°C for 4 h	500°C for 2 h
5	Stirring	7	100°C for 4 h	500°C for 2 h
6	Stirring	7	100°C for 24 h[6]	—

Photocatalytic activities of the samples were evaluated by measuring the degradation rates of methylene blue (MB) solution. Proper amount of the catalyst was placed in a beaker filled with 10 mg/L MB solution, and the solution was kept for 6 h to equilibrate the adsorption-desorption processes of MB on the catalyst. The system was reacted under a near-ultraviolet source with a peak wavelength at 380 nm. A drop of the MB solution was taken out and separated by a centrifugal instrument at 10-min intervals. The absorption intensities of the filtrate were measured using UV-Vis spectroscopy at 664 nm, where MB showed a major absorption peak. To compare with the photocatalytic reactions, the catalytic reaction without UV irradiation and the UV photolysis of MB in the absence of TiO_2 were tested.

3. Results and discussion

The formation of nanosized TiO_2 follows three stages: the formation stage of nuclei, the growth stage of nuclei, and the steady stage of particles. The conductivity of the system increases rapidly in the formation stage of nuclei due to the formation of large numbers of $Ti(OH)_4$ and BuOH. It then drops gradually in the growth stage of nuclei. Balanced conductivity depends on the steady stage of particles. Fig. 1 shows the conductivity change with time of sol-gel processing of sample 5. The conductivity of the titanium-ethanol solution is 26.4 $\mu s \cdot cm^{-1}$ at the beginning of the reaction. As the water-acid-ethanol solution is added to this solution, the conductivity increases rapidly, and reaches 630 $\mu s \cdot cm^{-1}$ at 5 min. Then the conductivity continuously increases with time, and reaches the maximum of 698 $\mu s \cdot cm^{-1}$ at 11 min. As the reaction proceeds, the solution becomes viscous gradually. Then the conductivity curve drops, and tends to flatten after 30 min. The conductivity is steady at 487 $\mu s \cdot cm^{-1}$ after 1 h and the gel becomes opalescent. The change of conductivity suggests that the formation and growth of nuclei occurs mainly in the initial 0.5 h. Therefore the duration of UV and IR irradiation is determined as 1 h. The gels of samples 1 and 3 are lilac, which is the characteristic color of Ti^{3+}, whereas those of the others are opalescent.

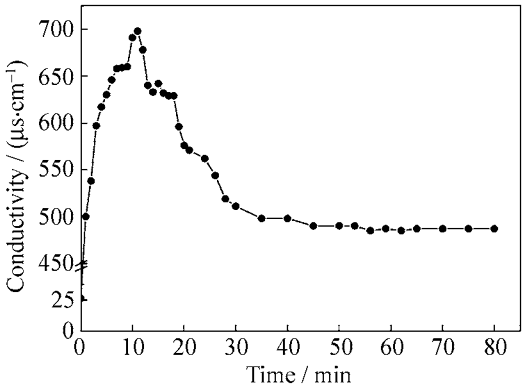

Fig. 1. Change of conductivity of TiO_2 sol-gel processing with time.

The typical DSC-TG curves in Fig. 2 show four stages based on the thermal and mass loss behavior of sample 5. A broad endothermic peak appears in the range of 100-160°C with a mass loss of 3.85wt%. It is attributed to the loss of absorbed water and to the volatilization of low-molecular weight compounds in the titanium peroxide gel [9]. The mass loss of 20.52wt% that is characterized by a weak exothermal peak can be seen in the range of 160-270°C with a maximum at 227°C. It may be due to the combustion and decomposition of organic solvents [10]. The sharp exothermic peak in the range of 270-450°C with a maximum at 353°C corresponding to the mass loss of 2.54wt% is a result of the transformation of amorphous TiO_2 to anatase phase. There is no further mass loss; however, some weak exothermic peaks appear in the range of 450-800°C. It indicates the slow transformation of anatase phase TiO_2 to rutile phase. It is suggested that TiO_2 photocatalyst prepared by conventional furnace treatment needs to be calcined above 450°C.

As shown in Fig. 3, the similar XRD spectra of samples 2 and 6 reveal some degree of anatase crystallinity. The crystalline sizes of samples 2 and 6 are 9 and 13 nm respectively, which are calculated by the Scherrer formula from (101) peak. The crystallization of sample 1 is better than that of the two above-mentioned samples, with an average crystal size of 5 nm. When conventional furnace treatment is used, crystallization is found to occur at approximately 350-400°C. If not, the particles remain completely amorphous for heat treatments at lower temperatures. It shows that the crystallization mechanism by IR irradiation is similar to the conventional heat treatment as seen from the result of Fig. 3. However, the better crystallization and finer crystal size of sample 1 than those of sample 2 under the same irradiation condition indicate probably a different mechanism. Further investigation are underway.

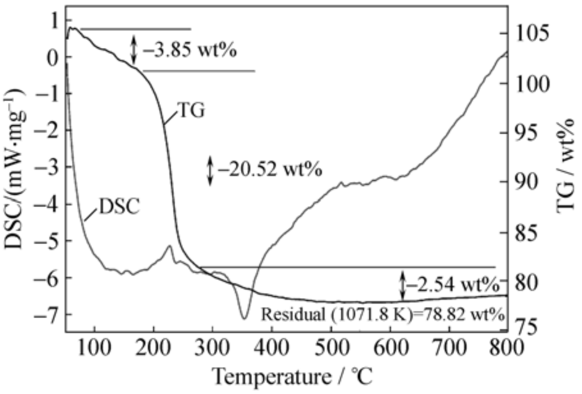

Fig. 2. DSC-TG curves of TiO_2 xerogel.

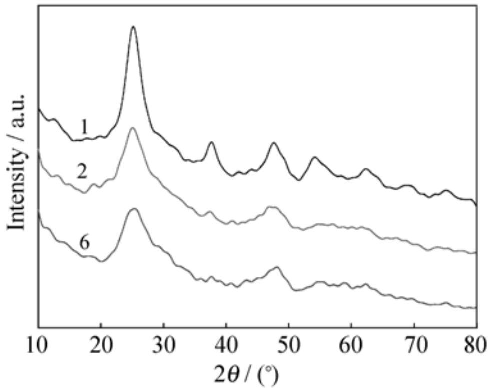

Fig. 3. XRD patterns of the TiO_2 samples.

SEM images of the TiO_2 samples (1 and 5) are shown in Fig. 4. It is notable that sample 1 is more uniform, finer, and less conglomerate than sample 5, which is in agreement with the patterns of XRD. It is concluded that UV irradiation plays an essential role in the growth of nanoparticles: it induces the formation of abundant nuclei in the initiation stage of sol-gel by supplying necessary energy. Therefore, the formation rate of nuclei is higher than the growth of nuclei. Because of the nearly coinstantaneous formation of plentiful nuclei, the crystals with finer and narrower size distribution are obtained.

As seen in Fig. 5, the incorporation of water molecules is characterized by two strong peaks centered at 3411 and 1624 cm^{-1}, which are the characteristic peaks of stretching vibrations of O–H and bending vibrations of H–O–H, respectively. It indicates that a large number of hydrogen bonds are formed in hydroxyl groups on the surfaces of the samples. It suggests that the samples contain a number of surface hydroxyl groups, although sample 3 has been calcined at 500°C. Appropriate surface hydroxyl groups may be the active sites of catalyst [11], but superfluous surface hydroxyl groups are adverse to catalysis [12]. The three peaks around 2950 cm^{-1} are attributed to the stretching vibration of the C–H bond of the organic compounds. On the basis of the intensity of peaks, it is deduced that the organic solvent and organic group in samples 1-3 and 6 are removed mainly. The 1630 cm^{-1} band is considered to be the C=O monomer stretching vibrations. The presence of the two bands at 1650 and 1300 cm^{-1} are attributed to the v(COO) vibrations of residual precursors. The absorption bands, which appear in the spectra between 1000 and 1100 cm^{-1}, are attributed to the O–R groups linked to Ti [13]. These bonds can be seen in both types of samples. The characteristic absorption peak of titanium ethoxide is at 930 cm^{-1}, which appears only in the spectrum of sample xerogel. The main absorption peak of pure TiO_2 assigned to the Ti–O–Ti bond appears at 600 cm^{-1}, which is rather large in samples 1-3 and 6. Samples 1-3 and 6 have similar IR spectra except the xerogel of sample 5, which has more peaks (the peaks do not correspond that of the Ti–O–Ti bond). Thus it is concluded that UV irradiation for 1 h is sufficient to decompose the organic matters added to the system.

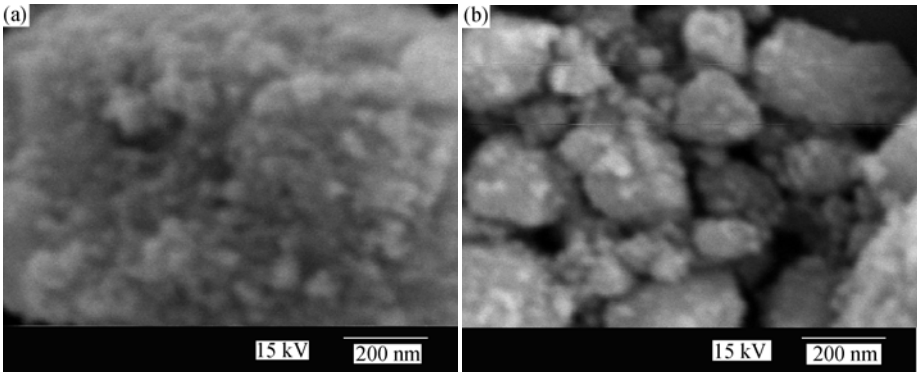

Fig. 4. SEM images of the TiO_2 samples: (a) sample 1; (b) sample 5.

The photocatalytic activity of TiO_2 was evaluated by measuring the degradation rate of MB. All tests were conducted under analogous conditions to compare the performance of different prepared samples. The intensity of the absorption spectrum at λ=664 nm corresponded to the concentration of MB solution. The curves of MB degradation under UV irradiation are shown in Fig. 6. The MB solution shows little fading without UV irradiation although equiponderant TiO_2 catalyst is added (not shown in the figure). The MB degradation under UV irradiation without catalyst, *i.e.* photolysis, is found to be only 50% after 100 min. The degradation rate of the samples containing catalysts reaches almost 100% after 100 min. Sample 2 shows relatively poor activity for MB degradation, whereas sample 3 presents the best activity. Sample 1 shows relative high activity, reaches 77% of MB degradation when the reaction occurs for 10 min. From the comparison of MB degradation, it is seen that samples 1 and 3 act much faster than other samples as the system reacts for 20 min; however, samples 3-5 show more thorough degradation rate. It suggests that the calcination above 400°C is needed for high photocatalytic activity. Overall, sample 3 is the best catalyst. Almost 100% of MB degradation in simple 3 is observed after 20 min, while samples 4 and 5 need 50 min, and others need at least 100 min. Samples 1 and 3 were repeatedly tested under the same condition, and showed the same photoactivity as that in the first run, which indicated good reproducibility.

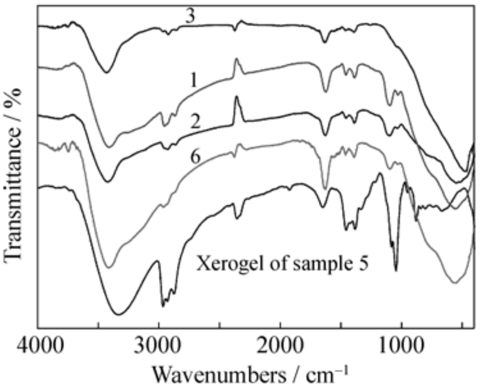

Fig. 5. FT-IR spectra of the TiO_2 samples.

From the above results, sample 3 presents the best active photocatalysis, followed by sample 1. It is concluded that the preparation method of TiO_2 plays an essential role in determining photocatalytic activity, and UV irradiation plays an important role in the preparation of TiO_2 catalyst. There are many factors affecting the photocatalytic activity of TiO_2, for example, electronic traps for electrons or holes, surface state, and the concentration of Ti^{3+} on the surface. In the formation stage of the framework, ultraviolet irradiation may induce the gel network to rearrange, and create surface oxygen vacancies at bridging sites. The presence of oxygen vacancies result in the transformation of relevant Ti^{4+} sites to Ti^{3+} sites, which is favorable for the adsorption of dissociating water molecules [14]. The presence of Ti^{3+} may be proved by the special lilac that appeared in samples 1 and 3, whereas the other samples show opalescence under the same condition. Hence, the high photoactivity of samples 1 and 3 is attributed to the presence of Ti^{3+} ions.

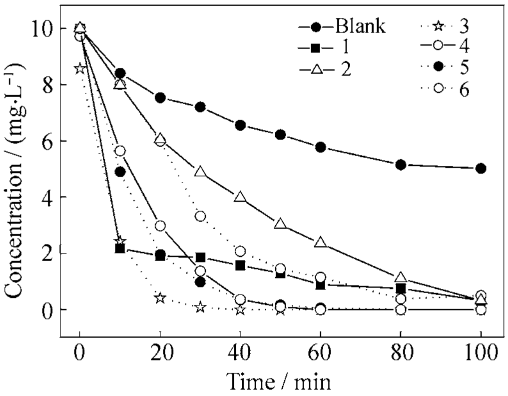

Fig. 6. MB degradation curves with TiO_2 samples.

4. Conclusions

TiO_2 particles prepared using the UV irradiation-induced sol-gel method show anatase crystal phase, and the crystalline size is 5 nm. TiO_2 catalyst calcined at 500°C after irradiation by ultraviolet light for 1 h shows the best photoactivity. After the reaction occurs for 20 min, almost 100% of MB degradation is observed, whereas that using the other methods needs at least 50-100 min. The results show that ultraviolet irradiation plays an important role in the preparation of high photoactive TiO_2 catalyst. Under ultraviolet irradiation, the remnant hydroxyl and organic groups are removed completely, and the titanium oxide particles are transformed from amorphous to anatase phase at relatively low temperatures, which can effectively avoid the conglomeration. In the formation stage of the framework, ultraviolet irradiation may induce the gel network to rearrange, and create surface oxygen vacancies at bridging sites. Oxygen vacancies result in the transformation of relevant Ti^{4+} sites to Ti^{3+} sites, which is favorable for the adsorption of dissociating water molecules.

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