Photocatalytic activity TiO_2 granular films prepared by layer-by-layer self-assembly method

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Many factors have influences on the photocatalytic activity of titanium dioxide, which mainly include recombination rate of charge carrier, diffuse time to surface, and trap of charge carrier. These favorable factors for diffusing toward surface and surface trapping of charge carrier, and decreasing recombination of photoexited electron–hole can promote the photocatalytic activity of TiO_2. Nanoporous granular films show high photocatalytic activity, because surface effects and quantum size effects are in favor of the separation and surface trap of charge carrier [1, 2].

The layer-by-layer self-assembly method has been studied by several groups for the formation of uniform molecular monolayer, and multilayer thin films incorporating organic components, inorganic colloids, biopolymer and virus particle and other molecules. The driving force of this process is ionic attraction between opposite charges. The use of polyelectrolytes that provide alternating electrostatic attractions between layers for fabrication of multilayer films reduces the defect formation. This method has an advantage in contrast to chemical self-assembly method that requires a reaction of 100% in order to maintain surface functional density in each layer. The Langmuir–Blodgett (L-B) self-assembly method can fabricate nanostructured uniform thin films too, but the L-B technique typically cannot form films thicker than several monolayers because defects occur and are replicated through the films structure as additional layers are added. In addition, layer-by-layer self-assembly method allows detailed molecular-level control over the films composition and thickness, and this technique is independent of the substrate size and topology [3, 4].

This letter reported fabrication and photocatalytic activity of nanoporous TiO_2 granular films. Nanoporous TiO_2 granular films were obtained by sintering TiO_2/PSS self-assembly multilayer films. The photocatalytic activity of nanoporous TiO_2 granular films was tested on the degradation of Rhodamine B (Rh.B) dye solution.

Poly(diallyldimethylammonium choride) (PDDA) and poly(sodium-4-styrenesulfonate) (PSS) were obtained from Aldrich Chemical Company. Titanium tetrabutoxide was purchased from Beijing Chemical Factory. All of these materials were used without further purification.

A modified substrate was immersed in the anionic solution (PSS solution) and the cationic solution (TiO_2 sol solution) separately in cyclic fashion, and rinsed extensively with water between the adjacent immerging. Then the ordered structure multilayer TiO_2/PSS films were obtained. The films deposited on the quartz substrate were heat-treated at different temperatures for 2 hrs in ambient atmosphere. Then, nanoporous TiO_2 granular films were gained. The chemical composition of the films was determined using VG ESCALAB MK II X-ray photoelectron spectroscopy (XPS) with Al Kα source. The photocatalytic activity of the heat-treated thin films was studied on the degradation of Rhodamine B (Rh.B) dye solution. Experimental details were as follows: the thin films with 4.5 cm^2 were immersed into 5 ml aqueous Rh.B solution with a concentration of 0.5 mg/l in a beaker. An UV lamp (8 W) was used as the irradiation source with the center wavelength 254 nm. The films were irradiated in the perpendicular direction and the distance between the UV source and the thin films was 15 cm. The concentration of Rh.B, which was decolorized, was monitored on an UV-Vis-NIR spectrophotometer.

Fig. 1(a) and (b) shows the XPS spectra of Ti and S in the surface of multilayer films before heat-treatment, and after treatment, respectively. The Ti2p peak shows that the Ti element mainly existed as Ti4+, and a little existed as Ti3+ according to the fitted peak position before heat-treatment. After treatment, Ti element existed as Ti4+, and Ti2p peak has a shift toward high energy direction, which is almost the same as bulk TiO_2 materials. The S signal of PSS appears in the peak of S2p before treatment, but it disappears after heat treatment. The changes of Ti2p, S2p peak are attributed to the decreasing of the oxygen vacancy, and disappearance of PSS.

From Fig. 2, it can be seen that heat-treated TiO_2 granular films show a higher photocatalytic activity than TiO_2/PSS films. After 135 min irradiation under UV light, the Rh.B solution is degraded to 78%, and 52% by TiO_2 granular films and TiO_2/PSS films, respectively. The higher photocatalytic activity is ascribed to phase change of TiO_2 films from amorphous to anatase at heat-treatment process. In our viewpoint, anatase phase has lesser defect compared with amorphous phase, which can decrease trap and

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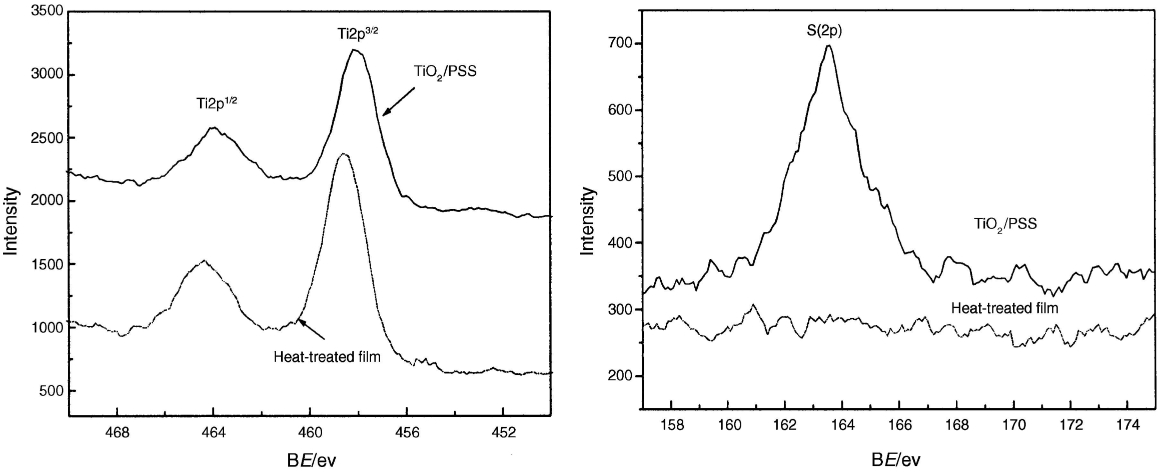

(a) (b)

Figure 1 High resolution XPS spectra of (a) Ti2p and (b) S2p peaks of the films.

recombination probability of charge carrier inside semiconductor [5]. Therefore, the TiO_2 granular films show higher photocatalytic activity.

At certain heat-treatment temperature, holding time can influence the structure of films. Fig. 3 shows the reduction of Rh.B dye concentration with reaction time for samples heat-treated at 400 °C in 10, 30, 60, 90, and 120 min, respectively. A very sharp increase of photocatalytic activity is observed for TiO_2 granular films with heat-treatment time from 10 min to 60 min. The photocatalytic activity of TiO_2 thin film has no further changes after 60 min. This change was attributed to crystallization and growth of TiO_2 particle has completed in certain time; further increasing holding time has no effects on the structure of TiO_2 films. So, the photocatalytic activity of TiO_2 granular films has little change after 60 min heat-treatment. In order to get the sufficient crystallization films, the holding time generally adopts 90 min.

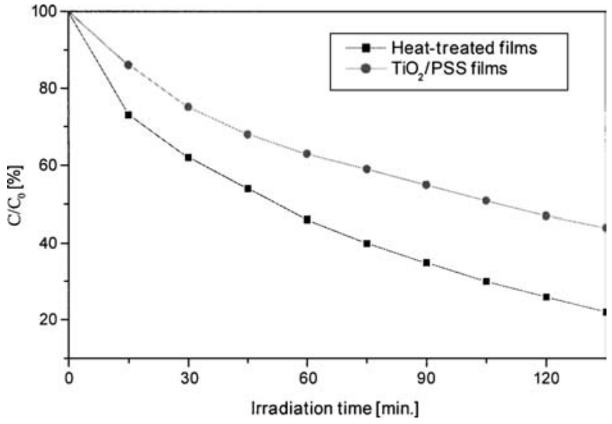

Figure 2 Comparison of photocatalytic activity of films before and after heat-treatment.

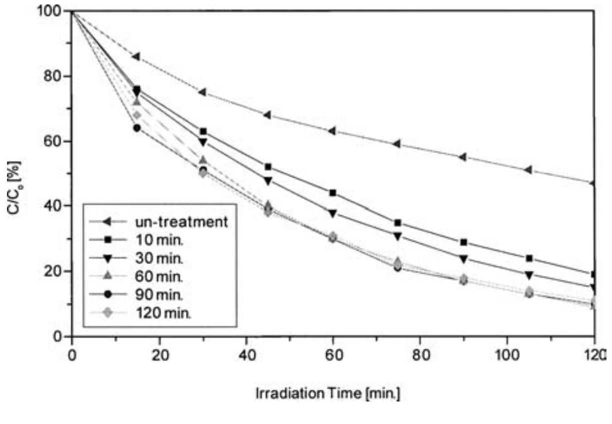

Figure 3 The effects of heat-treatment time on the photocatalytic activity of granular films.

Fig. 4 shows the effects of heat-treatment temperature on the photocatalytic activity of granular films. From Fig. 4, we can see that the TiO_2 films heat-treated at 600 °C and 400 °C show much higher photocatalytic activity than those heat-treated at 500 °C and 800 °C. We think that it can be ascribed to the different phase structure. The photocatalytic activity of films treated at 800 °C is lowest, because the phase of films is rutile under this heat-treatment temperature. The phase of films treated at 400 °C is anatase, and appears rutile in the films treated at 500 °C and 600 °C. On the basis of research results of R. I. Bickley for TiO_2 powder [6], growing a thin layer rutile phase on the surface of anatase particle can effectively promote separation of photoexited electron–hole in the anatase structure. Therefore, the powder with mixed crystal structure shows higher photocatalytic activity. The band gap of anatase is 3.2 eV, which is 0.1 eV wider than rutile. When two kinds of phase structure coexist, the edge of band gap will bend because of difference of Fermi level. It will have benefit to diffusing of photoexited hole to the surface, and reducing the recombination of charge carrier. In addition, the mixed crystal films have higher absorption in UV waveband, and defects reduce with increasing heat-treatment temperature. These facts result in the films treated at 600 °C, which show highest photocatalytic activity. But the films treated at 500 °C have lower photocatalytic activity. It may attribute to the rutile phase which is further less than anatase at 600 °C. In this condition, the impurity energy level appears, which is harmful to separation of photoexited electron–hole. The influences of heat-treatment temperature on the photocatalytic activity are complicated because it could bring influences on the particle size, crystallization, and phase structure.

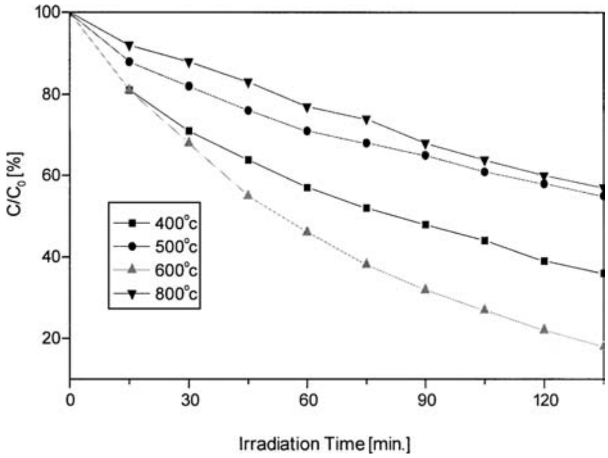

Figure 4 The effects of heat-treatment temperature on the photocatalytic activity of granular films.

In summary, nanoporous TiO_2 granular films were prepared by layer-by-layer self-assembly method. The heat-treatment process can influence the particle size, phase structure, and surface properties. The heat-treated TiO_2 films show higher photocatalytic activity than TiO_2/PSS films. A very sharp increase of photocatalytic activity is observed for TiO_2 granular films with heat-treatment time from 10 min to 60 min. In order to get the sufficient crystallization films, the holding time generally adopts 120 min. TiO_2 films heat-treated at 600 °C and 400 °C show much higher photocatalytic activity than those heat-treated at 500 °C and 800 °C. The influences of heat-treatment temperature on the photocatalytic activity are complicated because it can bring effects on the particle size, crystallization and phase structure.

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