Super-hydrophilic SiO\textsubscript{2}-doped TiO\textsubscript{2} photocatalysts for self-cleaning applications

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Abstract

The self-cleaning of glasses can be realized by coating the photoinduced super-hydrophilic nanoporous thin films based on TiO\textsubscript{2} photocatalysts via sol–gel route. In this study, a new method to enhance the photocatalytic activity of TiO\textsubscript{2} thin films direct coated on the glass was developed by doping SiO\textsubscript{2} in the films. The effects of post-annealing and the SiO\textsubscript{2} content of TiO\textsubscript{2} film on the photocatalytic activity were investigated. The microstructure and hydrophilic properties of the film were studied using differential X-ray diffraction, scanning electron microscope and contact angle measurement. After illuminated by ultraviolet light, the SiO\textsubscript{2} doped TiO\textsubscript{2} film are superhydrophilic with water contact angle less than 1°, which favors greatly the self-cleaning function of the films.

Keywords: Sol–gel; Spin-coating; SiO\textsubscript{2} doped TiO\textsubscript{2}; Self-cleaning glass
Super-hydrophobic or hydrophobic coatings have been used in the recent years for several applications, such as easy-to-clean surfaces. These products are based on the photocatalytic property of a thin layer of TiO$_2$ deposited at the surface of the glass. When exposed under UV light irradiation, TiO$_2$ reacts with the oxygen and water molecules present in the atmosphere to produce free radicals leading to oxidative species. These species are able to degrade organic material causing stains adsorbed on the surface into volatile molecules. Both technologies cover products designated by the general term of “self-cleaning”. In previous works, it has been observed that SiO$_2$ addition in TiO$_2$ films enables to increase in-time persistence of the photo-induced super-hydrophilicity. In this study, Silica–titania composite films containing from 1 to 10 mol% of SiO$_2$ were deposited from mixtures of TiO$_2$ and SiO$_2$ precursor sols and subsequently heat-treated for 1 h at 600 °C.

In Fig. 1 are shown the glancing incidence X-ray diffraction (XRD) patterns of the pure TiO$_2$ films prepared at a temperature varying from 300 to 800 °C. These XRD patterns are given in the figure along with the peaks reported in the literature for anatase and rutile structural. It was found that the pure TiO$_2$ films with anatase phase increase when annealing temperature increased. The pure TiO$_2$ films formed of anatase phase show a very high efficiency photocatalytic activity due to their large internal surface. Both the optical properties and the photocatalytic activity of TiO$_2$ coatings depend strongly on the crystalline phase, the crystallite size and the porosity of the coatings. On the other hand, the TiO$_2$ films formed of rutile phase when the sample annealed at a temperature more than 700 °C.

Surface hydrophilicity of the films was quantified from measurements of the water contact angle. This measurement was first performed on pure TiO$_2$ films in order study wetting behaviors under different annealing temperature. Fig. 2 shows a hydrophilic character immediately after annealed at 600 °C and UV-light illuminates for 20 min, which is illustrated by contact angle close to 5 degree. Then, contact angle increase after annealed more than 700 °C, which is explained by rutile phase formation of the film. Fig. 3 illustrates the wettability behaviors of SiO$_2$-TiO$_2$ composite films from the silica–titania mixed sols studied in this work. The behavior of a pure TiO$_2$ film is also presented as a reference. Wettability studies show that a suitable control of the TiO$_2$–SiO$_2$ mixed sol formulations noticeably enhances persistence of the natural super-hydrophilicity in composite films. The process of hydrophobic to hydrophilic conversion is fast, the water contact angle quickly decreases with time of UV irradiation. The composite films with SiO$_2$/TiO$_2$=5 mol% shows a natural super-hydrophilic character with a contact angle of 0.8 degree.

The film morphology was characterized by field emission scanning electron microscopy (SEM). Fig. 4a–d show SEM images of a pure TiO$_2$ film, as well as 1 mol%, 5 mol% and 10 mol% SiO$_2$ doped TiO$_2$ composite films, respectively. The image of a pure TiO$_2$ film indicates a fairly homogeneous granular surface with fine grain boundaries (Fig. 6a). In contrast, SEM images (Fig. 6b–d) show that composite films exhibit a sponge-like morphology with rather large cavities, which indicates an important surface porosity of these films. It shows that enhancement of the surface porosity from 1 to 10 mol% SiO$_2$ doped TiO$_2$ composite films with increase of the roughness. The performance of self-clean glass (SiO$_2$/TiO$_2$= 5 mol%) and conventional glass are shown in Fig. 5. The self-clean glass (light) has super-hydrophilic properties make windows easier to clean.

Subject of our research is detailed investigation of the dependence of the photocatalytic activity of SiO$_2$ doped TiO$_2$ composite films. This paper provides a new low cost method to product a super-hydrophilic film for self-clean glass.
Fig. 1. X-ray diffraction patterns of pure TiO$_2$ films after annealed at different temperature.

Fig. 2. Evolution of the water contact of pure TiO$_2$ films after annealed at different temperature.

Fig. 3. Evolution of the water contact with UV light illuminates for pure TiO$_2$ and SiO$_2$ doped TiO$_2$ composite films.

Fig. 4. SEM images of the SiO$_2$-doped TiO$_2$ films with different SiO$_2$ doping ratio as shown in figure and the films annealed at 600 °C for 1 h.

Fig. 5. The photo illustrates the sheeting effect of self-clean glass (right) compared to conventional glass (left).