Enhanced photocatalytic activity of TiO_2 thin film coating on microstructured silicon substrate

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Photocatalytic TiO_2 thin film is prepared by sol–gel technique on microstructured silicon substrate produced by femtosecond laser cumulative irradiation. The photocatalytic activity is evaluated by the degradation of methylene blue (MB) solution under ultraviolet (UV) irradiation. For 6-ml MB solution with initial concentration of 3.0×10^{-5} mol/L, the degradation rate caused by TiO_2 thin film of 2-cm^2 area is higher than 70% after 10-h UV irradiation. Microstructured silicon substrate is found to enhance photocatalytic activity of the TiO_2 thin film remarkably. The femtosecond laser microstructured silicon substrate is suitable to support TiO_2 thin film photocatalysts.

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The decomposition of gaseous and aqueous pollutants using TiO_2 photocatalysts is one of the most promising methods for dealing with certain environmental problems[1−5]. Unfortunately, using pure TiO_2 powders might be difficult for practical applications. For example, the small particle size of the catalyst powder in the solution results in high separation costs to remove once the reaction is completed. Therefore, efforts have been devoted to the development of supported photocatalysts with suitable recovery properties. Thin film consisting of immobilized TiO_2 particles onto various substrates is an efficient solution to the above problem. Many authors have reported the photocatalytic activities of TiO_2 thin films coated onto various substrates, such as glass, zeolite, and pumice[6−11]. For TiO_2 thin films coated onto substrates, surface morphology, including the particle shape and arrangement, is greatly affected by the substrate materials; different surface morphologies lead to different photocatalytic activities of TiO_2[12,13]. Femtosecond laser microstructured silicon has shown great potential for photodetectors and solar cells because of its novel light-absorption properties[14−16]. In addition, its special surface morphology with arrays of micrometer-sized conical spikes makes it promising for thin film and sensor applications[17−19].

In this letter, the photocatalytic activity of TiO_2 thin films coated onto femtosecond laser microstructured silicon is reported. The degradation rate of methylene blue (MB) solution under ultraviolet (UV) irradiation is evaluated. The result shows that the degradation activity of TiO_2 thin film on the microstructured silicon is remarkably enhanced compared with that using its unstructured counterpart.

All substrates were fabricated by cumulative pulsed (800 nm, 120 fs) irradiation of femtosecond laser on the surface of silicon (111) wafers (undoped, single-crystalline, 350-μm thick) in ambient gas of 70 kPa SF_6 at laser fluence of 1.0 J/cm^2. The focused laser beam had normal incidence upon the sample surface. The laser beam was scanned along the surface of silicon wafer at a certain speed to fabricate samples of large area (over 10×10 mm^2). The irradiation resulted in arrays of conical spikes formed on the surface. In our experiment, the average height of the spike was approximately 7–8 μm.

The TiO_2 films were fabricated by sol–gel technique. TiO_2 sol was prepared as described in Ref. [20]. Tetrabutyl orthotitanate (TPOT) and acetylacetone (AcAc) were dissolved in ethanol (Eth), the mixture of acetic acid (HAc), water and Eth was added into the solution with vigorous stirring. The obtained alkoxide solution was stirred at room temperature for 30 min. The mole ratio of TPOT, AcAc, HAc, H_2O, and Eth was 1:0.2:1.5:3:40. The sol solution was spread over the substrate surface by dip-coating method under atmosphere to form the TiO_2 film. The film was then dried at 70 °C for 5 min. The dip-coating procedure was repeated until the desired thickness of the film was obtained. (In our experiments, for the dip-coating, six repetitions were optimal. One should note that the photocatalytic activity will decrease if the dip-coating increases). Finally, the sample was kept under atmosphere at 500 °C for 60-min heat-treatment. The thickness of the TiO_2 film, estimated by scanning electron microscope (SEM), was approximately 500 nm; after dip-coating, the average height of the spike was approximately 4–5 μm.

The photocatalytic activity of the prepared samples was evaluated by the concentration of MB solution degraded under UV light irradiation. Samples with 2 cm^2 effective areas were immersed into the centrifuge tube containing 6 ml of 3.0×10^{-5}-mol/LMB solution, and then irradiated by UV rays. A 20-W UV light lamp was used as the UV source. The wavelength range of the UV source was from 320 to 400 nm with a peak wavelength of 365 nm. The MB concentration, as a function of the irradiation time, was determined by the light absorbance at 665 nm measured by the SpectraMax M5 (Molecular Devices, USA). The photocatalytic performance of TiO_2 thin films on unstructured silicon substrates was also measured for comparison. The dye adsorption properties of TiO_2 films were characterized by concentration variation of MB solution with 3.0×10^{-5}-mol/L concentration in the dark.

The structure of the sample was characterized by X-ray diffraction (XRD, Cu Kα line at 0.154 nm). The XRD spectra of microstructured silicon and the TiO_2 film coated onto microstructured silicon, together with those of TiO_2 powders, are shown in Fig. 1. In Fig. 1(a), one single peak of micro-structured Si(111) wafer appears at approximately 28.32°, indicating a highly ordered crystal structure on the surface, which is beneficial to the crystallization of TiO_2 thin films[21]. The XRD peak positions of the TiO_2 powder and their relative intensities, as shown in Fig. 1(c), with the position at 25.28° angle of A(101), is in good agreement with the known standard TiO_2 anatase pattern. For the TiO_2 film coated onto the substrate, the diffraction pattern (Fig. 1(b)) is nearly the same as that of the TiO_2 powders, except for the much weaker characteristic peak of Si(111) wafer. The XRD result suggests that the microstructured silicon used as a substrate of TiO_2 thin films does not introduce any significant change in the anatase structure.

Figure 2(a) shows the SEM image (view on 45°) of TiO_2 film coated onto the surface microstructured silicon. The image shows micron-sized structures, such as micron-sized spikes and interconnected micron-cavities. Figure 2(b) shows the cross-section of the sample, where many cracks are evident, not only on the surface, but also at the bottom of the spikes. These microstructures are beneficial to the MB molecules diffusing and then being adsorbed effectively by the photocatalyst.

The photocatalytic activity of the TiO_2 thin films was evaluated by MB solution degradation. We assume C_0 and C to be the initial and reacted concentration of MB solution, respectively. Much higher photodegradation efficiency of TiO_2 films on microstructured silicon substrates was observed than of the films on unstructured substrates. As shown in Fig. 3(a), the

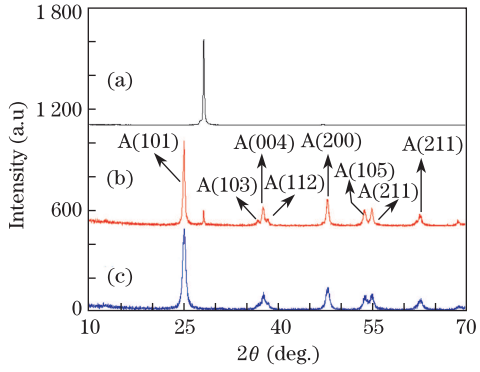

Fig. 1. XRD spectra of the samples. (a) Microstructured silicon; (b) TiO_2 film coated onto microstructured silicon, the position at angel of 25.28° of A(101) is TiO_2 anatase pattern; (c) TiO_2 powders.

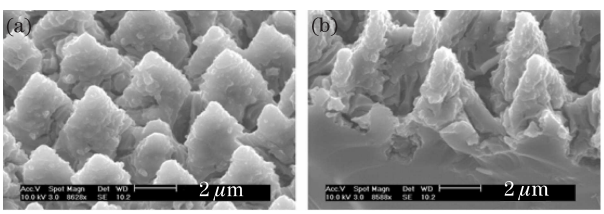

Fig. 2. SEM images of TiO_2 thin films coated onto microstructured silicon. (a) Viewed at 45°; (b) cross-section.

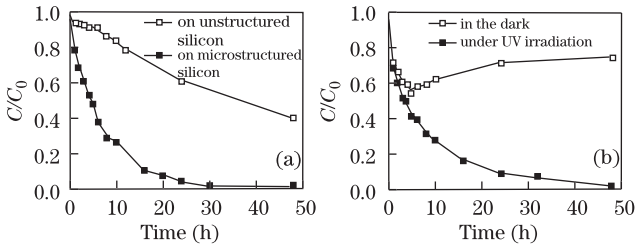

Fig. 3. MB concentration versus irradiation time. (a) TiO_2 films coated onto unstructured and microstructured silicon; (b) TiO_2 thin films coated onto microstructured silicon in the dark and under UV irradiation.

degradation rate caused by TiO_2 thin films on microstructured silicon substrates with 10-h UV irradiation was higher than 70%, while it was merely 15% in the films coated onto unstructured substrates. After 30-h UV irradiation. nearly all of the MB was degraded by TiO_2 films coated onto microstructured silicon, whereas approximately 60% MB still remained in the solution for the substrates unstructured. The improvement of the photodegradation efficiency of TiO_2 thin films coated onto microstructured silicon can be explained. (Note: The variation of black curves in Figs. 3(a) and (b) is from the difference of samples used in different experiments.) In fact, the SEM image (Fig. 2) shows a large amount of micron-spikes and micron-cavities formed on the film surface, indicating that the TiO_2 thin films have highly porous and interconnected structures. Such structure type remarkably increases the effective surface areas, and is beneficial to the rapid diffusion and adsorption of MB molecules on the photocatalyst. In addition, the spikes arrays also improve the efficiency of light utilization[14]. All these result in the enhanced photocatalytic reaction rate.

The adsorptive capacity of TiO_2 thin films coated onto microstructured silicon was also evaluated by decolorization of the MB solution in the dark. The result is shown in Fig. 3(b). Without UV irradiation, the concentration of MB solution decreased slowly during the first few hours due to the adsorption of MB molecules on the surface of the film. After the concentration of MB solution reached its lowest point, the concentration increased slightly, indicating that the redissolution of a few adsorbed MB molecules occurred. Within the reaction time duration of 50 h, the concentration was not changed markedly, showing equilibrium adsorption was reached. Under UV irradiation, however, the MB concentration decreased abruptly during the first 5 h. This decrease was much more rapid than that in the dark because, under UV irradiation, the adsorption and photocatalytic reaction play the role simultaneously in the initial degradation process.

In conclusion, TiO_2 thin films are prepared on the microstructured silicon substrates via sol–gel method. The photocatalytic activity of samples is evaluated with the MB concentration under UV radiation. Compared with the unstructured silicon substrates, the microstructured silicon substrates greatly enhanced the photodegradation efficiency of TiO_2 thin film photocatalysts. The improvement of the photodegradation efficiency might be attributed to the special structure of the substrates surface. Highly porous and interconnected structures

are beneficial to rapid diffusion and adsorption of MB molecules, and also to enlarge the effective surface areas. As a result, the rate of photocatalytic reaction is enhanced. Thus, femtosecond laser microstructured silicon substrate is a new substrate suitable for coating TiO_2 thin film photocatalysts.

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