

TiO₂ coating photocatalysts with nanostructure and preferred orientation showing excellent activity for decomposition of aqueous acetic acid

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TiO₂ coatings are attractive materials for use as photocatalysts, photoelectrodes and solar cells. Structural modification, quantum size effects, and large surface-to-volume make the coatings interesting. We have described the effects of crystal structure [1], crystallinity [2] and morphology [3] of TiO₂ coatings on photocatalytic properties, and shown that a TiO₂ coating prepared from a chemically-modified alkoxide solution had characteristic structures [4]. Here we report the photocatalytic properties of TiO₂ coatings prepared by the chemically modified alkoxide method, which have nanostructure and show preferred orientation along the *c* axis. We also report the effect of oxygen vacancies in the TiO₂ coatings on the photocatalytic properties.

Decomposition of acetic acid is a very important reaction because during decomposition acetic acid usually generates organic compounds containing more than two carbons. Decomposition of aqueous acetic acid by use of oxygen and photocatalysts is known to proceed differently from the photo-Kolbe reaction [5] with a product of ethane. During the photocatalytic decomposition of aqueous acetic acid with oxygen, formaldehyde is generated as an intermediate compound and this oxidizes readily to carbon dioxide. Chemical oxygen demand (COD) decreases to zero characteristically in the process. Therefore, the photocatalytic decomposition of aqueous acetic acid with oxygen is a key reaction for purification and treatment of water.

TiO₂ coatings were prepared by the chemically modified alkoxide method. The method has been described in detail elsewhere [4]. The precursor solution for the coatings was prepared from titanium tetraisopropoxide, anhydrous ethanol, diethanol amine, water and polyethylene glycol (molecular weight; $M_w = 2000$). The concentration of titanium tetraisopropoxide in ethanol was 0.5 mol dm^{-3} . The molar ratios of water and diethanolamine to titanium tetraisopropoxide were 1 and 2, respectively. The concentration of polyethylene glycol to titanium tetraisopropoxide was 20 wt%. Gel coating, which was prepared on a quartz glass plate by a dip-coating method, crystallized to anatase during elevation on

temperature to 650 °C and heating at that temperature for 1 h in air or oxygen flow. The thickness of the coating was increased by repeating the cycle of dip-coating and heating.

Transmission electron microscopy (TEM) measurements were performed with an accelerating voltage of 200 kV to observe the microstructural development in the TiO₂ coating. Fig. 1 shows a TEM photograph of the TiO₂ coating. It was found that the TiO₂ coating consisted of nanocrystallites and nano spaces between the crystallites. The diameter of the nanocrystallites was less than 30 nm. The nano spaces were formed by the elimination of carbon dioxide, generated by the decomposition of polyethylene glycol coordinating to titanium tetraisopropoxide [4]. Therefore, the coating was considered to contain a significant number of oxygen vacancies. X-ray powder diffraction (XRD) measurements were performed under an applied voltage of 35 kV and a current of 20 mA. Fig. 2 shows the XRD profile of a TiO₂ coating with a thickness of 1 μm, together with

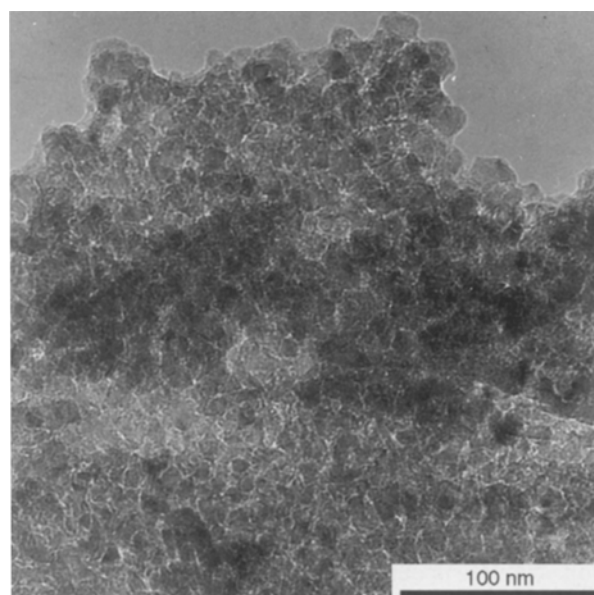


Figure 1 TEM photograph of a TiO₂ coating prepared from the chemically modified alkoxide solution.

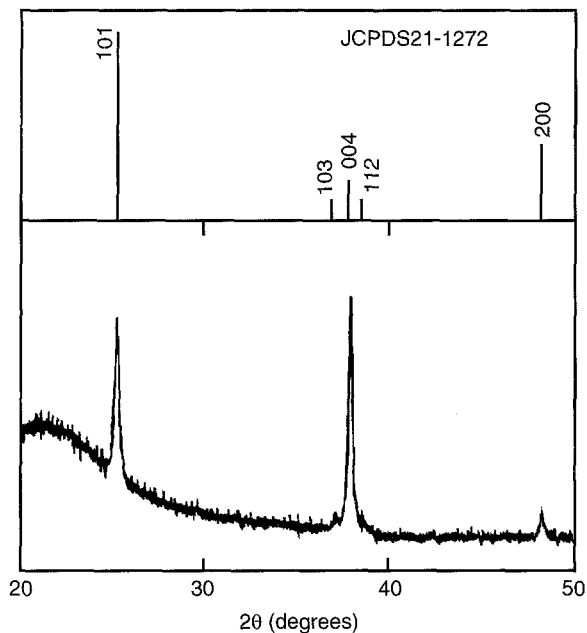


Figure 2 XRD profile of a TiO₂ coating prepared from the chemically modified alkoxide solution and the JCPDS diffraction anatase data.

the JCPDS anatase diffraction data. The coating was single-phase anatase. Comparing the intensities of diffraction lines of the coating with the data from JCPDS, it was observed that the intensity of the 101 diffraction line was relatively weak and the intensity of the 004 diffraction line was relatively strong. This means that the crystallographic orientation of the coating is different from that of anatase powders and coatings prepared by the conventional sol-gel method [1]. The transmittance of the coatings in the visible wavelength range was higher than 80%.

The photocatalytic decomposition of aqueous acetic acid by the TiO₂ coatings was examined using a method described in detail elsewhere [1-3]. A TiO₂ coating with a thickness of 500 nm and aqueous acetic acid (6 wt%) were put in a quartz glass container, and irradiation performed using a high-pressure mercury lamp while bubbling aqueous acetic acid with oxygen. Fig. 3 shows the change in the acetic acid content with irradiation time. The concentration of acetic acid did not change under dark conditions. Immediately after the lamp was switched on, the concentration of acetic acid decreased. On the surface of the TiO₂ coating prepared by heating in air, acetic acid decomposed very rapidly. The time for decomposition was shorter than on surfaces of anatase coatings with dense structure and submicron pores as reported in [1] and [3]. High photocatalytic activity was due to the nanostructure of the TiO₂ coating. In the coatings composed of nano crystallites and nano spaces, charge separation may occur because of differing rates of hole and electron transfer to the species in the solution, rather than build-up of conventional space-charge layer [6, 7]. This is because recombination cannot occur during migration in the nano crystallites and the species in the solution can diffuse effectively through the nano spaces.

On the surface of the TiO₂ coating prepared by

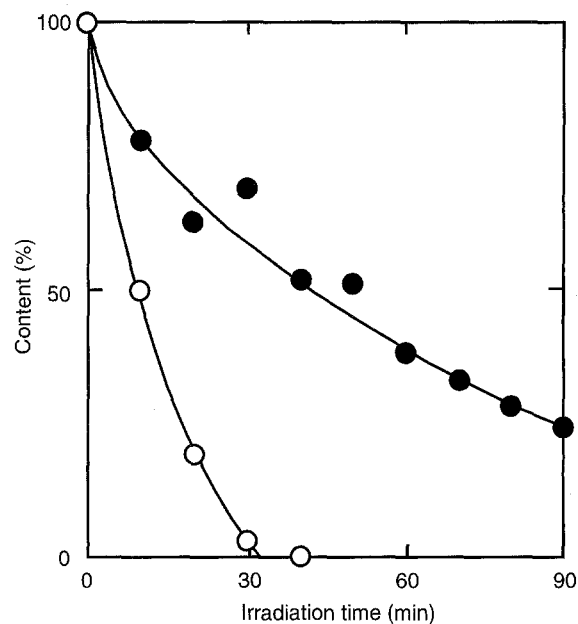


Figure 3 Changes in the content of acetic acid with irradiation time. Photocatalytic activity of TiO₂ coating prepared by heating (○) in air, (●) in oxygen flow.

heating in oxygen flow, acetic acid decomposed relatively slowly. This result suggests that oxygen vacancies relate to photocatalytic property. Surface Ti³⁺, which has been reported to act as a photoelectrochemically active site for photocleavage of water, appeared to exist in TiO₂ coatings prepared by heating in air. Decrease in the number of the surface active sites by heating in oxygen flow resulted in a diminution of the number of OH radicals and a lowering of the rate of decomposition of aqueous acetic acid.

Recently, Lu *et al.* have reported the chemical detection of Ti³⁺ defect sites on TiO₂(110) [8]. Production of Ti³⁺ sites is expected to depend on the crystal face. Investigation of the dependence of photoelectrochemical properties on crystallographic orientation of TiO₂ coatings is in progress.

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