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Enhancing photocatalytic activity by using TiO_2–MgO core-shell-structured nanoparticles

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Hygroscopic $Mg(OH)_2$ gel was topotactically decomposed on TiO_2 particle surfaces, resulting in highly nanoporous MgO-coated TiO_2 particles. The highly hygroscopic and nanoporous MgO shell absorbed more water molecules and hydroxyl groups from the environment to yield an improved photocatalytic property of the core-shell particles as compared to the uncoated TiO_2 counterpart. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2159562]

The discovery of the Honda-Fujishima effect[1] has stimulated intensive research on the titanium dioxide as a semiconducting photocatalyst to purify the environmental pollutants for the last a few decades. The strong oxidation capability of the photogenerated holes from TiO_2 as well as the chemical inertness and nontoxicity of TiO_2 itself makes it (1) a superior photocatalyst for removing water/air pollutants and (2) a superior antibacteriant.[2,3]

The photogenerated holes in illuminated TiO_2 surfaces and hydroxyl ions in the environment combine to produce hydroxyl radicals (e.g., $h^+ + OH^- \rightarrow \cdot OH$). The highly oxidizing capability of $\cdot OH$ radicals, resulting from such indirect photochemical reaction, attacks to decompose neighboring pollutants. Thus, the degree of hydroxylation on the surface of TiO_2 critically influences its photoactivity, especially in the case of the photodecomposition of air pollutants. Stemming from this importance of hydroxylation, extensive studies have been performed to enhance the hydroxylation of TiO_2 film surfaces, which includes acid treatment of TiO_2 thin film, SiO_2 addition, and fabrication of mesoporous structures.[4,5]

In this regard, the use of an ultrathin MgO nanolayer on TiO_2 is very promising since MgO has a huge hygroscopic nature.[6] Moreover, the specific surface area of MgO can be greatly enlarged by controlling its preparation route. Preparation of MgO from a topotactic thermal decomposition of hygroscopic $Mg(OH)_2$ gel, yields nanoporous MgO particles due to the difference in density between the $Mg(OH)_2$ gel and MgO.[6–8] In the present study, therefore, the topotactic reaction route was adopted to produce a nanoporous MgO coating on TiO_2 core particles. The improvement of the degree of hydroxylation and subsequently the photoactivity was experimentally demonstrated.

For the preparation of MgO-coated TiO_2 nanoparticles (P25, DEGUSSA), magnesium methoxide (ALDRICH, 7.6 wt. % in methanol) was used as a coating solution. Mixtures containing 3 g of TiO_2 powder, varying amounts of magnesium methoxide as prescribed (0 and 0.6 wt. %), and 10 ml of methanol were ball-milled. The mixture was then hydrolyzed with 20 ml of deionized water at 80 °C. The hydrolysate was centrifuged and redispersed in the mixture of 40 ml ethanol and a 0.4 ml of acetyl acetone, followed by a further ball-milling process, yielding a homogeneous particulate sol. The resultant sol was spread on the quartz substrate by employing the spin-coating method at 3000 rpm for 2 min. The coated films were heated to 400 °C for 1 h. The thickness of the annealed films was in the range of 400–500 nm.

The morphology of MgO itself, prepared by the hydrolysis/condensation of magnesium methoxide and thermal decomposition of the resultant $Mg(OH)_2$, has been investigated first to test the feasibility of the intended topotactic reaction for a high specific surface area resulting from nanopores. As seen in the transmission electron microscopy shown in Fig. 1(a), MgO nanocrystals (dark spots) and nanopores (bright areas) are shown in a hexagonal-shaped platelet. This nanoporous feature indicates that the intended topotactic thermal decomposition from $Mg(OH)_2$ to MgO has been achieved: the selected area diffraction patterns in the insets of Fig. 1(a) show the transformation from $Mg(OH)_2$ into MgO. Figure 1(b) shows the transmission electron microscopy (TEM) image of the core-shell structure for the case when 2.0 wt. % MgO coated TiO_2 surfaces. This figure confirms that TiO_2 particles are homogeneously covered by a MgO layer having thickness of approximately 2–4 nm (TEM observation was performed using a separately prepared 2.0 wt. % MgO instead of 0.6 wt. % in order to clearly demonstrate the MgO coating on TiO_2 surfaces).

The nanoporous TiO_2–MgO core-shell structured particles exhibited a high surface area 55.4 m^2/g, which was larger than that of the uncoated TiO_2 particles (47.5 m^2/g). As the most of the weight of the core-shell particles is taken by the TiO_2 core, the increase in specific surface area indicates that the coated MgO layer itself, obtained by the topotactic reaction, has a very high nanoporous structure.

The photocatalytic activities of the bare TiO_2 and nanoporous MgO-coated TiO_2 films were measured by the de-

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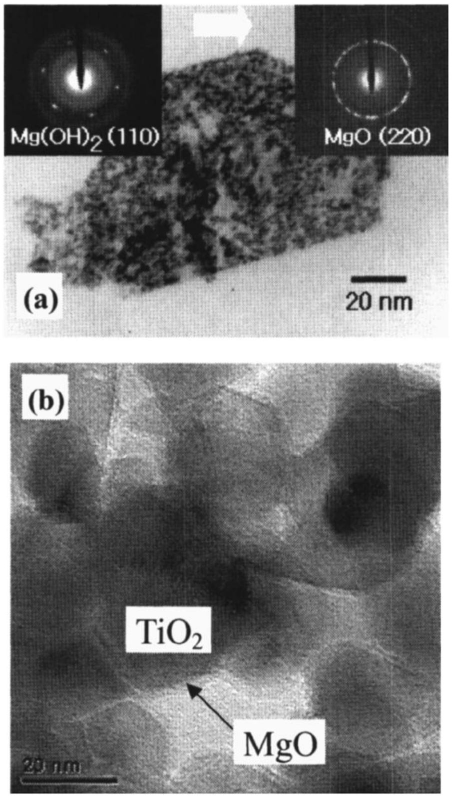

FIG. 1. TEM images of (a) topotactically decomposed MgO and (b) topotactic MgO-coated TiO_2 nanoparticles.

composition rate of a 100 μL (0.07 M in ethanol) of stearic acid $[CH_3(CH_2)_{16}COOH]$, which was casted on each film, following the method reported by Paz *et al.*[9] The decomposition behavior of the stearic acid was observed by measuring the rate of decrease in the integrated IR absorbance of the ensemble of the C–H stretching vibrations between 2800 and 3000 cm^{-1}.[10] A 10 W lamp (306 nm, SANKYO) was used as the UV light source. Figure 2(a) shows representative Fourier transform infrared (FT-IR) spectra from photodegraded stearic acid on bare TiO_2 film at varying reaction times. The changes in the integrated IR absorbance with time are compared for the cases of bare TiO_2 and MgO-coated TiO_2 in Fig. 2(b). The employment of porous MgO layer enhances photocatalytic activity. Eighty-nine percent of stearic acids on MgO-coated TiO_2 film decomposed in 18 min compared to only 54% of the acids on bare TiO_2 film.

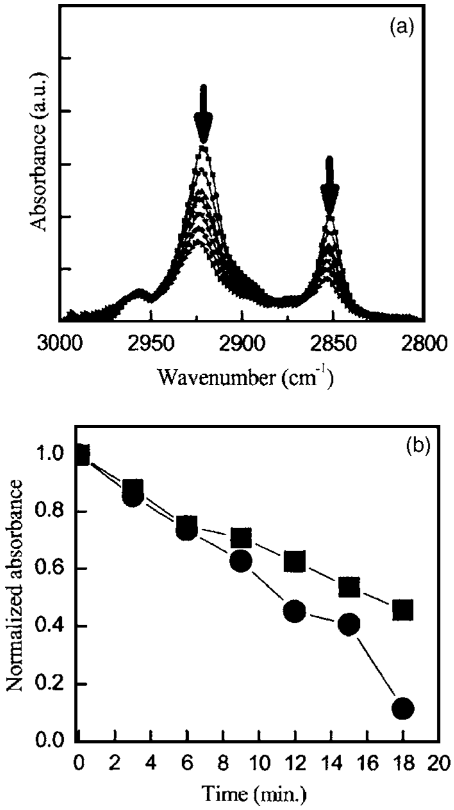

FIG. 2. FT-IR spectral changes (in the C–H stretching region) for the photodegradation of stearic acid on bare TiO_2 film. (b) Normalized absorbance for stearic acid on bare TiO_2 (■) and 0.6 wt. % MgO-coated TiO_2 (●) films as a function of UV irradiation time.

To enhance the photocatalytic activities of TiO_2, several fundamental characteristics including (1) light absorption, (2) charge generation, (3) charge injection into surface, and (4) degree of hydroxylation could be involved. Since MgO has high band-gap energy (8–9 eV), the MgO layer does not change the light absorption characteristics, as has been confirmed by using diffuse reflectance UV-visible spectra of MgO-coated and uncoated TiO_2 particles in a separate analysis (Fig. 3). Subsequently, the charge generation in UV-exposed TiO_2 should not be changed by coating the MgO layer. The charge injection behaviors were also compared indirectly by measuring the photocurrent of MgO-coated TiO_2 and bare TiO_2 films. The photocurrents of MgO-coated and bare TiO_2 films were measured with a potentiostat (Model CHI 608A, CH Instruments) under an illumination of UV light (306 nm, SANKYO). The electrolyte solution containing tri-iodide (SOLARONIX) was used. The results showed that the MgO coating on the TiO_2 surface decreased the photocurrent from 4.9 to 2.86 μA/cm^2. The decrease in the photocurrent in MgO-coated TiO_2 is attributed to the insulating nature of MgO coating layer which prohibits the charge injection from inner TiO_2 to the interface between MgO coating layer and the environment. This effect is detrimental to the photocatalytic activity of MgO-coated TiO_2. However, the experimental result herein (Fig. 2) is quite the opposite. As the other three conceivable sources are not responsible for the increase in the photocatalytic activity, the highly hygroscopic and highly nanoporous MgO characteristics are mainly responsible for the enhancement in the photocatalytic activity: the MgO layer contains more H_2O and hydroxyl groups and offers a larger surface area.

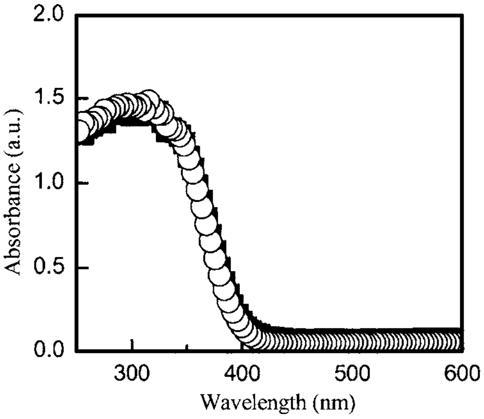

FIG. 3. UV-visible absorption spectra of TiO_2 films (■:bare TiO_2 and (○): 0.6 wt. % MgO-coated TiO_2).

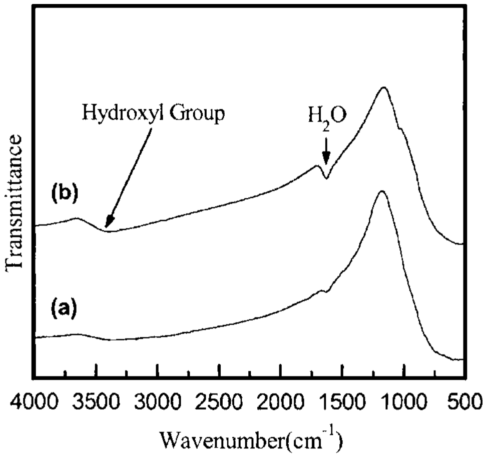

FIG. 4. FT-IR spectra for (a) bare TiO_2 and (b) 0.6 wt. % MgO-coated TiO_2 nanoparticles.

Having shown the higher photocatalytic activity of the MgO-coated TiO_2 in decomposing stearic acid (Fig. 2), the potential of the MgO coating in photodecomposition of air pollutants is further checked hereinafter. In the case of the photodecomposition of air pollutants, the presence of hydroxyl group and water molecule has been well documented to enhance the photocatalytic activity of TiO_2. Thus, their presence has been analyzed via FT-IR and the result is compared in Fig. 4. The MgO-coated TiO_2 possesses a larger amount of hydroxyl group ($3600 \sim 3000\ cm^{-1}$) as well as water molecule ($1624\ cm^{-1}$), confirming that the MgO coating has a potential in photodecomposition of air pollutants as well. The role of these two species (hydroxyl group and water molecule) has been reportedly known as follows. The abundance in hydroxyl groups allows for more radicals on the surface, facilitating the decomposition process of organic materials. For the case of MgO-coated TiO_2, the photogenerated holes from the TiO_2 core are simply assumed to reach the outer surface of ultrathin MgO shell via quantum tunneling to form a highly active hydroxyl radical.[11,12] An excess water may remove the strongly adsorbed by-products of the decompositions, which prevents the photocatalyst from deactivation by keeping the photocatalytic active sites clean.[13] Although the identification of the more dominant influence from the two species is not pursued herein, it is certain that the capability of MgO-coated TiO_2 in possessing the two species originates from highly nanoporous and hygroscopic nature of the MgO shell.

In conclusion, an ultrathin MgO layer, obtained by topotactic decomposition of $Mg(OH)_2$, was applied to TiO_2 particles to form a TiO_2 core-MgO shell structure. The MgO shell was highly nanoporous and possessed a larger amount of hydroxyl groups and water molecules as compared to bare TiO_2, which, in turn, improved the photocatalytic activity of the core-shell structured particles.

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