Preparation of a New Nanostructured TiO_2 Surface Using a Two-Dimensional Array-Based Template

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Nanoporous, nanostructured semiconducting films of photocatalytic titanium dioxide (TiO_2) were fabricated by molding from two-dimensionally ordered arrays. We were able to control the structures of the periodic surfaces by varying the annealing temperature of the films.

Nanoporous semiconducting materials have recently attracted much attention because of their various applications in electronic, electrochemical and photocatalytic systems, including photoelectrochemical solar cells, electrocatalysts, sensors and high performance photocatalytic films.[1,2] Many efforts have been made to prepare nanoporous semiconducting materials with textured surfaces of controlled periodicity in order to optimize the mass transport properties.[3,4,5] For example, if we would like to prepare porous films for liquid junction solar cell applications or for faster gas diffusion in sensors, the widths of the hollow channels needs to be on the order of tens of nanometers.[6] Therefore, Masuda et al. reported the preparation of porous films with hollows of this type by a replication process using nanostructured anodic porous alumina.[3]

Two-dimensionally ordered arrays are also new types of nanoscale architecture.[7] In such arrays, fine particles or molecules are packed over a wide surface area. Herein we report a new process for fabricating porous semiconducting (TiO_2) films with periodic surface structure, also by a type of replication, using the intrinsic nanostructures of two-dimensionally ordered arrays. The size of the hollows can be controlled by varying the diameters of the fine particles from several hundreds nanometers to micrometers.

We selected silica (SiO_2) particles to be used in the form of an ordered array as a replica template, because they are stable at TiO_2 annealing temperature (400-500℃). Fine silica particles were obtained from Nihon Syokubai, Japan (Seahostar® KE-P). The silica particles were suspended (4.8 wt%) in 2-propanol. The detailed process is shown schematically in Figure 1. After a silica particle array was prepared on cover glass (Takahashi Giken Glass, Japan) from the suspension,[8] 0.05 M titanyl acetylacetonate (Tokyo Kasei) in ethanol solution was deposited by a spray-pyrolysis technique at controlled annealing temperatures.[9] After the annealing, the titanyl acetylacetonate mist was converted to TiO_2. The thicknesses of the TiO_2 film overlayers as deposited on the SiO_2 two-dimensional arrays were 1-2 μm. Finally, the TiO_2-SiO_2 hybrid film on a Ni substrate (Nilaco, Co., Japan) was removed from the glass substrate using 55% HF solution (Koso Chemical Co., Ltd., Tokyo, Japan). The surface topology of the film was observed by scanning electron microscopy (JSM-5400, JEOL Ltd., Tokyo, Japan).

The HF solution dissolves the SiO_2 but not the TiO_2 or the

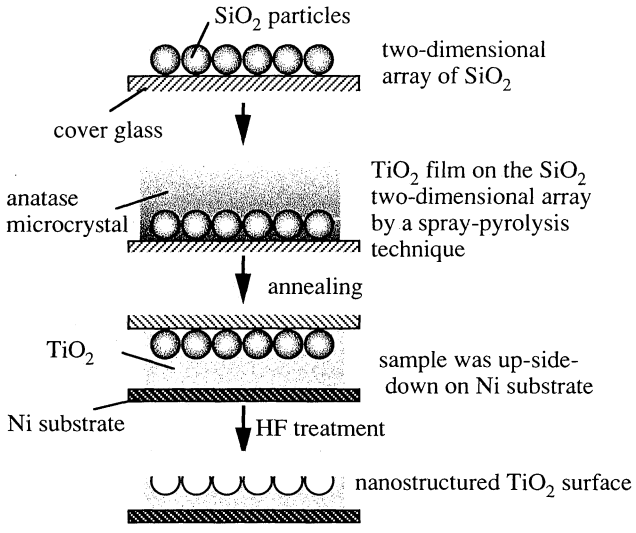

Figure 1. Schematic process for fabrication of new nanostructured TiO_2 films.

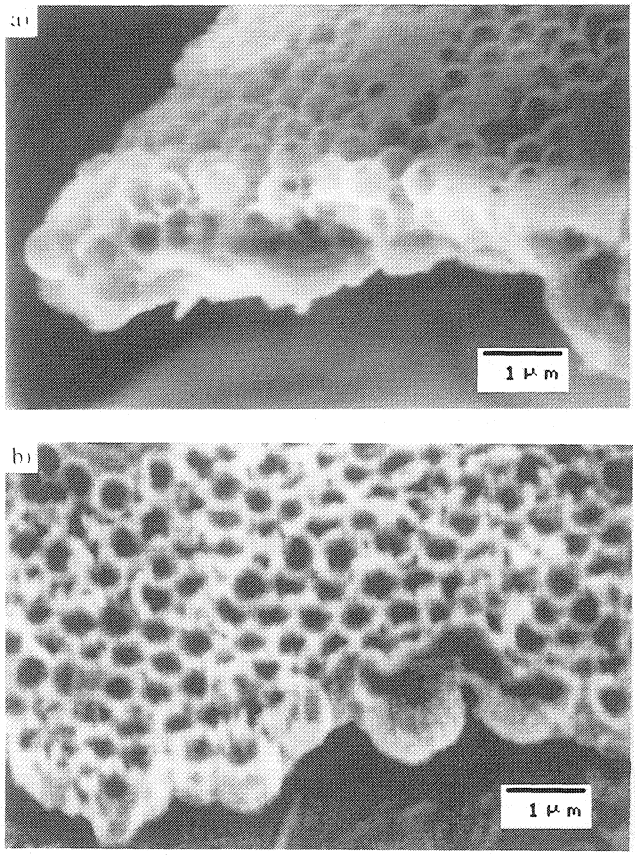

Figure 2. SEM images of replicated TiO_2 films annealed at (a) 450℃, (b) 430℃.

Ni substrate. Therefore, by HF treatment, we were able to obtain TiO_2 films which were replicas of the SiO_2 two-dimensional arrays. Figure 2a shows an SEM image of the surface taken from the silica particle (530 ± 50 nm dia.) side after annealing at 450℃. High-density hollow spheres can be seen to exist in a regular array. The hollow spheres which were formed had almost the same shapes as the SiO_2 spheres in the template array, as shown in Figure 2a. When the annealing temperature was decreased to 430℃, another type of structure was observed (Figure 2b). We observed some cells with barnacle-like morphology, also with an average diameter of 530 nm. The side-walls of these cells are thicker than those in the image in Figure 2a. We can also observe some needles on the surface. We considered that the titanyl acetylacetonate solution soaked into the particles in the second or third layers during the spray process, giving rise to needle-like structures after removal of the silica particles.

As previously mentioned, one type of application involves photocatalysis. We were concerned that there is a possibility of substitution of -OH groups with -F on the TiO_2 surface, which could degrade the photocatalytic activity.[10] We examined the photocatalytic activity of the porous periodic semiconducting (TiO_2) films after the 55% HF treatment. The films were placed in 50 μM $AgNO_3$ aqueous solution under UV (365 nm) irradiation for 30 min. After UV irradiation, we observed the surface with optical microscopy and SEM. Ag deposition was observed using optical microscopy. Using SEM in the secondary electron probe mode, we confirmed that the surface topology was unchanged after UV irradiation. Using SEM in the reflected electron probe mode, we observed strong circular-shaped reflections due to Ag on the sample. On the basis of these observations, we conclude that Ag was deposited mainly in the pores on the surface. Therefore, there was no significant inhibition of the photocatalytic activity even after HF treatment.

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