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Reversible conversion of nanoparticles of metallic silver and silver oxide in ultrathin TiO_2 films: a chemical transformation in nano-space

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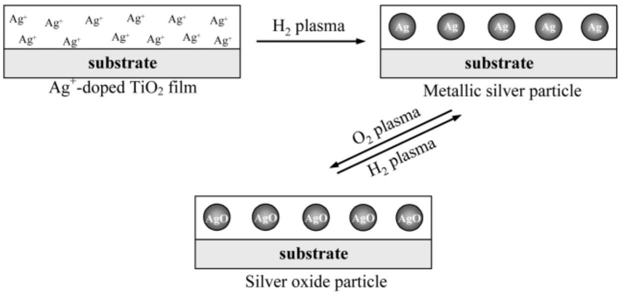
Received (in Cambridge, UK) 1st May 2002, Accepted 12th July 2002
First published as an Advance Article on the web 26th July 2002

The *in-situ* interconversion of silver and silver oxide nanoparticles was achieved in ultrathin TiO_2 films using hydrogen and oxygen plasmas as dry redox reagents. Absorption spectroscopy and transmission electron microscopy showed that the chemical transformation gave rise to narrowing of size distributions of both silver and silver oxide nanoparticles upon repeated interconversion.

Thin films that contain nanoparticles of semiconductors and metals play important roles in optical, electronic, magnetic and catalytic materials.[1–4] Several fabrication techniques have been reported, including ion implantation,[5] sputtering,[6] sol–gel process/spin-coating[7] and alternate layer-by-layer assembly.[8,9] Composition, size, shape and distribution of nanoparticles are key factors which influence physical and chemical properties of these thin films. Recently, Stietz *et al.* showed that the size distribution of Ag nanoparticles was narrowed by 40% by choosing the laser pulse frequency such that only the smallest and the largest particles selectively absorbed light.[10] El-Sayed *et al.* reported shape changes of colloidal gold nanorods by femtosecond and nanosecond laser pulses.[11] More recently, Mirkin *et al*. showed that silver nanospheres were converted to nanoprisms by conventional fluorescent light.[12] These conversions were carried out either on a quartz surface or in solution. Laser-induced fragmentation, melting, and partial melting[11] or a light-induced ripening process[12] was involved in these size and shape transformations. No chemical (*e.g.*, composition) changes were found.

We have recently shown successful preparation of metal nanoparticles from ion-exchanged ultrathin films of metal oxides. A variety of metal ions could be converted to metallic nanoparticles under several reductive conditions. We have also succeeded in preparation of bimetallic nanoparticles with a Pd-on-Ag morphology. An *in-situ* chemical and physical transformation of these nanoparticles would expand their uses to a considerable extent. As a first step towards this goal, we examined in this study plasma-induced conversion between nanoparticles of metallic silver and silver oxide. O_2 plasma is often used for surface modification. This process is dry and clean, and possesses many advantages over other chemical methods. Therefore, H_2 and O_2 plasmas are employed as dry redox reagents.

An ultrathin titania film that contains silver ions was prepared on a quartz substrate by doping Ag^+ ions into a nanoporous titania film by ion exchange.[13] It was then exposed to H_2 plasma for 150 s and to O_2 plasma for 150 s alternately (Scheme 1).[14] After each plasma treatment, UV-visible absorption spectra were recorded on a Shimadzu UV-3100PC UV-VIS-NIR scanning spectrophotometer with a quartz plate as the reference. As shown in Fig. 1, an as-prepared, Ag^+-doped TiO_2 film does not show any absorption band between 350 and 800 nm. After it was exposed to H_2 plasma, however, a broad band (Curve 1) appeared at 457 nm, which is attributed to the surface plasmon resonance of metallic Ag nanoparticles. The plasma-treated sample was brown-colored due to this surface plasmon absorption. When the sample was further exposed to O_2 plasma, the surface plasmon peak disappeared (Curve 1′) and the sample returned colorless. Six cycles each of H_2 (Curve *N*) and O_2 (Curve *N*′) plasma treatments were carried out (*N* = 1, 2, 3, 4, 5, and 6). Although the peak position at 447 nm remained almost unchanged for Curves 2–6 during these treatments, the peak shape became narrower with repetition of the H_2 plasma treatment. The spectral narrowing appears to result from more uniform size distribution of silver nanoparticles. It is possible that the silver moieties migrate among particles during the plasma treatment.



Scheme 1 Schematic illustration of conversion of the silver moiety in TiO_2 matrix.

The spectral interpretation was confirmed by X-ray photoelectron spectroscopy (XPS). The thin film sample (Curve 6′ in Fig. 1) was cleaved into pieces of proper size, and XPS measurements were carried out.[13] Fig. 2 shows its full spectrum and the Auger peak. While the peak at 103.4 eV (Si 2p) originates from the quartz substrate, the peaks at 459.1 eV (Ti $2p_{3/2}$) and 463.6 eV (Ti $2p_{1/2}$) are attributed to the TiO_2 matrix. The peaks at 368.9 eV and 373.7 eV are assigned to Ag $3d_{5/2}$ and Ag $3d_{3/2}$, and that at 1132.2 eV is the AgO Auger peak. The Auger peak of metallic silver, which would have appeared at 1128.6 eV was not found under the current conditions of measurement. These results indicate that nanoparticles of silver oxide were formed in the ultrathin TiO_2 film after O_2 plasma treatment. The Ag/Ti ratio was estimated to be 1.45 : 1 from

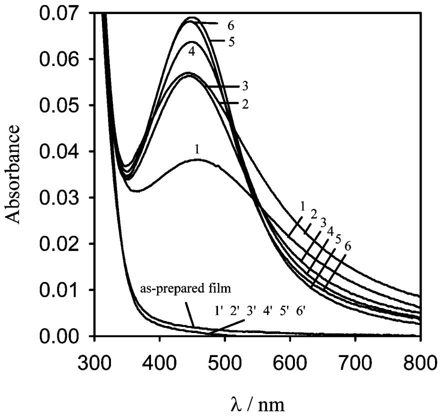


Fig. 1 UV-visible absorption spectra of silver ion-doped TiO_2 film during alternate H_2/O_2 plasma treatments. Curves 1–6: after H_2 plasma treatment, Curves 1′–6′: after O_2 plasma treatment.

DOI: 10.1039/b204227b

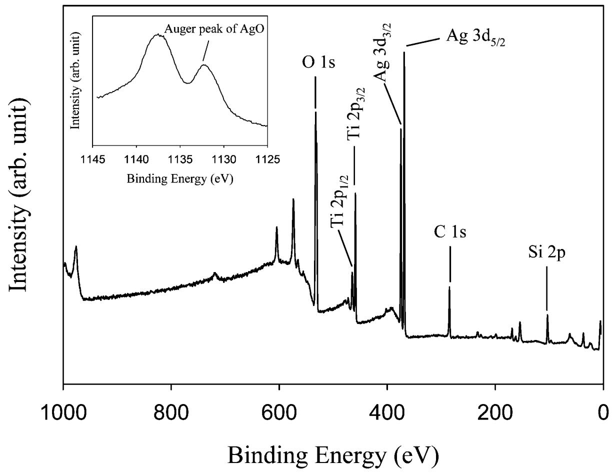


Fig. 2 XPS spectrum and Auger peak of the TiO_2 film (Curve 6′) with silver oxide nanoparticles. Monochromatic X-ray was used to increase the spectral resolution and an electron flood gun was used to avoid charge-up during the measurement. Due to the electron flood, all the peaks were shifted to lower binding energies. They were normalized to the C 1s peak (285 eV).

XPS data, showing that a large amount of silver existed in the thin film.

Morphology changes as suspected from the spectral narrowing were directly observed using transmission electron microscopy. Nanoparticle-containing TiO_2 film was scratched off from its quartz substrate in 2-ethoxyethanol and transferred to TEM grids (carbon-coated copper grid) by dispenser. The fragmented films were then observed on a JEOL JEM-2000EX transmission electron microscope at 100 kV. Fig. 3a shows a TEM image and a histogram[15] of metallic Ag nanoparticles in TiO_2 film after the first H_2 plasma treatment (Curve 1 in Fig. 1). The shape of Ag nanoparticles is not quite spherical. The mean diameter, d, is 8.6 nm and the standard deviation, σ, is estimated to be 3.0 nm, indicating that the size distribution is broad. In contrast, uniform spherical nanoparticles of silver oxide were formed after 6 cycles of H_2/O_2 plasma treatments (Fig. 3b). The mean diameter was estimated to be 3.9 nm and the standard deviation to be 0.7 nm. In order to compare the morphologies of particles of the same composition, the sample of Fig. 3b was further exposed to H_2 plasma and observed by TEM. As shown in Fig. 3c, uniform spherical Ag particles were found with a mean diameter of 3.6 nm and a standard deviation of 0.8 nm. It is clear that the number of larger nanoparticles decreased during the alternate H_2/O_2 plasma treatments. The decrease led to narrowing of their size distribution. These TEM results agree well with the UV-visible spectroscopic observation.

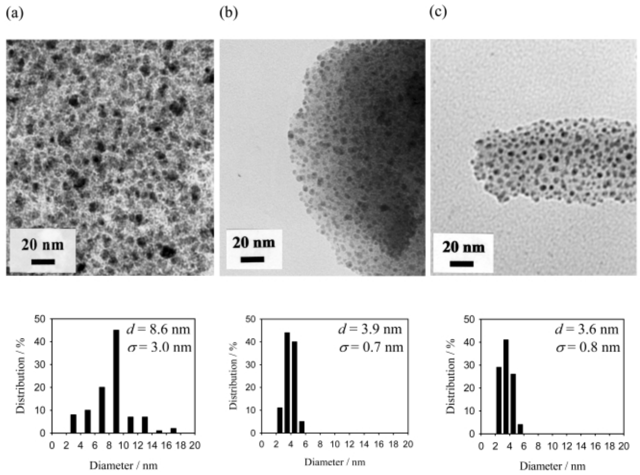


Fig. 3 TEM images and histograms of silver nanoparticles after the 1st (Fig. 3a, Curve 1 in Fig. 1) and 7th (Fig. 3c) H_2 plasma treatment, and silver oxide nanoparticles after the 6th O_2 plasma treatment (Fig. 3b, Curve 6′ in Fig. 1) in TiO_2 film.

In electron beam diffraction experiments, the metallic silver nanoparticle gave crystalline diffractions, but the silver oxide nanoparticle gave diffuse hollows, indicating formation of amorphous oxide particles.

In summary, *in-situ* conversion of nanoparticles between the metallic and metal oxide forms was achieved for the first time by alternate H_2/O_2 plasma treatments. The implication of the present results is at least twofold. One is that the TiO_2 gel film serves as effective nano-flasks for *in-situ* chemical transformation of nano-sized materials. Such materials can be confined in the film without fusion, coagulation and growth. The migration of atoms, ions and small atomic clusters within the gel film cannot be denied, as demonstrated by altered size distributions of silver and silver oxide nanoparticles. However, direct fusion of nanoparticles does not proceed in this matrix, since nanoparticles themselves are apparently not capable of penetration through the TiO_2 network. A second implication is that the *in-situ* transformation is a useful tool for the preparation of nano-sized materials that are not readily accessible by other means. For example, metallic silver nanoparticles are converted to the corresponding oxide form and other chemical species by the current approach. The importance of such nano-sized materials in catalytic and electronic applications is obvious.

We thank Dr M. Shimizu (Exciton Laboratory, FRS, RIKEN) for helpful discussions on physical aspects. J. He is grateful to the Japan Science and Technology Corporation (JST) for a STA fellowship.

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14 H_2 and O_2 plasma treatment were carried out on a PE-2000 Plasma Etcher (South Bay Technology, USA). The operating pressure was regulated at *ca.* 180 mTorr. The forward power was set at 10 W, while the reflected power was optimized. N_2 gas at 2.5 l min^{-1} was introduced into the pump for the purpose of safety when H_2 was used as the carrier gas.
15 Histogram, mean diameter and standard deviation were obtained by sampling 100 nanoparticles in TEM images of 3×10^5 magnification, followed by analyses using a commercial statistics software.