Surface Fabrication of Interconnected Hollow Spheres of nm-Thick Titania Shell

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(Received August 12, 2002; CL-020689)

Latex particles were adsorbed on solid substrate and then covered with ultrathin titania films by the surface sol-gel process. Hollow titania spheres formed after removal of the latex template by oxygen plasma treatment were connected with each other via nanotubes, reflecting the original disposition of the latex particles.

Design and preparation of hollow structures in the nanometer regime are the most interesting topics in nanotechnology, because of its potential for applications such as drug delivery. The template synthesis is a general technique for preparing hollow structures that are dispersed in solution. In this technique, thin films of organic polymers and metal oxides are prepared on the surface of templates, and hollow structures are obtained by removal of the template.[1–7] As a related example, Xia et al. have reported the preparation of inverse opals by using colloidal particles deposited on solid substrate as a template.[8] A metal alkoxide precursor was polymerized in the interparticle void, and the template particles were removed to form a pore array. In this approach, particles are not isolated and the interparticle voids are essential. Thus, the shape of the resulting frame is a negative copy of the original particle assembly. In contrast, we wanted to prepare a positive copy of latex templates by using a thin film technology. The positive copy approach can directly reflect the morphology and assembly of nanoparticles, leading to varied hollow structures upon removal of templates. Recently, Okuyama reported the formation of metallic domes by colloidal templating and over-sputtering.[9] Although this approach produced a positive copy of the particles, sputtered metal cannot cover the whole surface.

In this report, we employed the surface sol-gel process. This is based on chemsorption of metal alkoxides, and can fully cover the template surface with ultrathin films of metal oxide. Our approach consists of 3 steps. In the first step, nanoparticles are adsorbed onto a solid substrate. Ultrathin layers of metal oxide are then formed on the particle surface (Step 2), and template nanoparticles are finally removed to form hollow structures (Step 3). Oxygen plasma was used to remove organic templates. In the low-temperature oxygen plasma process, organic components are oxidatively decomposed into lower molecular weight components, such as CO_2 and water.[10]

More specifically, mica (Okabe Mica: natural mica grade), silicon wafer (TOKYO OHKA KOGYO) and silicon oxide-covered TEM grid (Ted Pella: Silicon Monoxide Type-A) were used as solid substrates. Prior to adsorption of latex particles, the substrate surfaces were covered with alternate layers of poly(diallyldimethylammonium chloride) (PDDA: Polymer Source: MW = 240000, 1 mg/ml) and poly(sodium styrene-4-sulfonate) (PSS) to generate a cationic surface. Latex particles which possess carboxylated surfaces and diameter of 500 nm (C-500 latex) (Polyscience: Polybeads carboxylate) were adsorbed from their aqueous dispersion (0.26 wt%)[11] onto the solid substrate. Titania thin films were then formed on the latex surface through the surface sol-gel process. This process was conducted by dipping a solid substrate in titanium(IV) tetra(isopropoxide) (Ti-(O-iPr)$_4$: Azmax, 100 mM) in ethanol for 1 min, rinsing by ethanol and ion-exchanged water for 1 min each, and drying by flushing nitrogen gas. This procedure was repeated 5 times. The solid substrate was subsequently exposed to oxygen plasma (South Bay Technology: PE-2000 Plasma Etcher, 20 W, radio frequency: 13.56 MHz, oxygen pressure: 180 mTorr) at room temperature, and subjected to scanning electron microscopy (SEM: Hitachi S-5200 scanning electron microscope, acceleration voltage at 1.0 kV without sample coating) observation.

The latex particles were randomly adsorbed onto the whole substrate surface, and most of the adsorbed particles were in contact with each other, forming domain structures. The formation of the titania layer on the substrate surface was confirmed by quartz crystal microbalance (QCM: USI system, Au-coated QCM resonator, 9 MHz) measurement. Regular frequency decreases were observed for each adsorption cycle, and the total frequency shift after 5 cycles was 33 Hz, corresponding to a calculated thickness of about 1 nm based on the bulk density (1.7 g/cm^3) of TiO_2-based gel.[12] As shown in Figure 1a, very smooth surfaces of the individual particles are preserved even after the sol-gel process and their diameter is essentially identical with that of the original particle (500 nm).

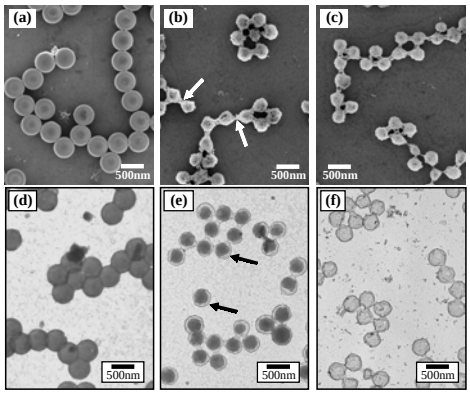

Figure 1. Morphological changes of titania/C-500 latex composites during oxygen plasma treatment. (a)–(c) are SEM images and (d)–(f) are TEM images. Exposure to O_2 plasma: (a) 0 min, (b) 30 min, (c) 60 min, (d) 10 min, (e) 30 min, (f) 70 min.

After 30 min of the oxygen plasma treatment, the particle diameter decreased to 200–300 nm, almost one half of the original diameter. At the same time, there appeared tubular structures with 10–100 nm widths that bridge adjacent particles (Figure 1b, arrow). This morphology remained unaltered after prolonged treatment of 60 min (Figure 1c).

The inner structure of the particles during oxygen plasma treatment was made clear by transmission electron microscopy

(TEM, JEOL JEM-2000EX instrument, acceleration voltage of 100 kV, without staining) (Figure 1d–1f). After 10 min oxygen plasma treatment, dark spherical structures with a diameter of about 500 nm are seen (Figure 1d). In 30 min, the particles are converted to spherical shells with diameter of about 300 nm and thickness of several nanometers (Figure 1e, arrow), and the shell contains particles with diameter of about 250 nm. This inner particle appears to be a partially decomposed latex particle by plasma oxidation. After 70 min, this inner particle is not observed anymore, but the morphology of the interconnected spherical shell remains unchanged (Figure 1f). Clearly, the organic particle component was totally decomposed at this stage, leaving only the titania shell behind. Though the wall thickness cannot be precisely determined from Figure 1f, it is estimated to be less than 10 nm. Although the QCM data suggest the formation of a much thinner shell (~1 nm), the TEM observation is more reliable. It is remarkable that such ultrathin shells maintain their morphologies after oxygen plasma treatment. The shell has mechanical strength sufficient to maintain hollow spherical and tubular morphologies. This robustness implies that we can construct self-supporting 3D architectures with components of several nanometer thick. To our best knowledge, such nano-hollow structures have not reported to date. Metal oxides appear to be unique in this respect, since other materials such as metals and polymers would not produce stable films with this ultimate thickness.

We additionally employed an amine-modified latex particle with diameter of 100 nm (A-100 latex: Polyscience, Polybeads amine), instead of C-500 latex template. In this case, the mica substrate was first modified by layer-by-layer adsorption of PDDA and PSS to generate a negatively charged surface, and then subjected to adsorption of A-100 latex particles (2.73 wt%, 10 min immersion). Though most of A-100 latex particles were randomly adsorbed, domains of hexagonally packed particles existed (data not shown). After additional adsorption of poly(acrylic acid) (PAA, Polymer Source: MW = 1240, 1 mg/ml), titania layers were adsorbed for 5 cycles, and the sample was exposed to oxygen plasma for 60 min. In the area of randomly adsorbed particles, the shape of the titania hollow structure was essentially identical to that of the plasma treated C-500 latex particle. On the other hand, the domain of hexagonally packed particles gave regularly interconnected titania spheres after oxygen plasma treatment (Figure 2). According to Figure 2, the interconnection is made of broken spheres and the diameter of the individual titania sphere is 50–80 nm. All the joints are connected by titania tubes of 10–30 nm. Thus, hexagonally interconnected titania hollow structures were produced from hexagonally packed particles.

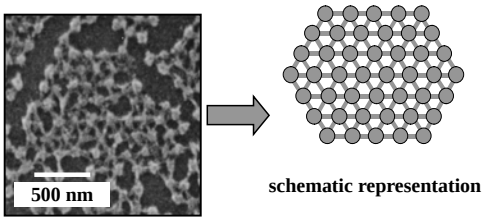

Figure 2. SEM observation of hexagonally interconnected titania nanospheres prepared from A-100 latex template.

The interconnected hollow structure may be generated by the following mechanism (Figure 3). A titania thin film is formed on the surface of latex particles on a solid substrate to give a core/shell structure (Figure 3a). Upon exposing this solid substrate to oxygen plasma, the latex particle core is gradually removed by oxidative decomposition (Figure 3b). The removal of the latex core causes shrinking of spherical titania shells to 50–80% of the original size. This spherical titania shell is firmly attached to the substrate surface, and cannot move away from the original adsorption site of the latex. The titania tubes are produced as a result of elongation of the interconnecting titania layer. Further elongation may cause structural changes from tube to wire, though not confirmed. Interconnected titania hollow structures are thus formed (Figure 3c).

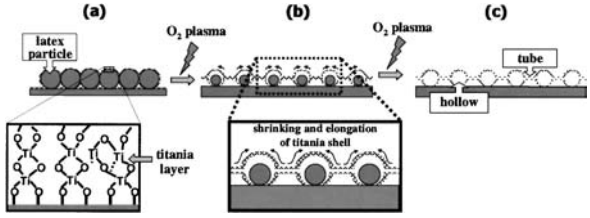

Figure 3. Generation scheme of interconnected titania hollow structures.

In conclusion, it is clear that the current approach offers a great potential for fabrication of nano-architectures. The surface sol-gel process we employed here gives positive copies of template morphology, whereas void filling as in inverse opal formation produces negative copies. The plasticity and robustness of ultrathin metal oxide layers have not been put to proper use in the past. The present finding is important in showing that flexible, robust nano-layers become available for nano-architectures. We used in this research a simple template morphology in order to test the feasibility of our approach. More elaborate nano-architectures may be created on the basis of sophisticated patterns.

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