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Nanoscale Laser Processing of Hollow Silica Microbeads Assisted by Surface Plasmon Resonance of Gold Particles

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Irradiation with a nanosecond pulse laser ($\lambda = 532$ nm) was performed on spherical hollow silica particles modified with gold nanoparticles to photoexcite the localized surface plasmon resonance, resulting in the formation of pores on the shell wall accompanied with the fragmentation of the original Au particles to much smaller ones. The size of pores was tunable from 17 to 56 nm by varying the size of original Au particles on SiO_2 shell from 6 to 39 nm.

Recently hollow particles with a micrometer- or nanometer-size range have attracted much attention for their potential applications,[1–3] such as supports for catalysts and drug delivery systems. Catalytic reaction systems using these particles, in which nanoparticles of catalysts[4,5] or photocatalysts[6] are incorporated inside the hollow shells to prevent the coalescence between catalyst particles, require efficient exchange of target substances between the void space inside hollow particles and the bulk solutions outside particles. One possible way to solve this problem is to prepare pores of a desired size in the shell of hollow particles. Several strategies such as preparation of a shell with mesoporous silica[7,8] and removal of template molecules incorporated in the shell wall[9,10] have been reported. The pore size could be controlled by selecting the kind of surfactants[7,8] and block polymers[9] in the range from ca. 2 to 9 nm. Though a pore size much larger than ca. 10 nm is also attractive for the permeation of polymers or biomolecules, there have been few reports of the preparation strategies of hollow particles having such large pores.

Laser processing techniques have been developed as tools for top-down fabrication of various materials. Besides micrometer-scale fabrication, the morphology in nanometer scale could be modified by a laser technique with assistance of photoexcitation of localized surface plasmon resonance (LSPR) of gold (Au) particles.[11–16] For example, as demonstrated by Obara and co-workers,[11] holes of tens of nanometers in diameter were produced on the surface of silicon substrates by irradiation with a single femtosecond laser pulse to Au particles immobilized on the substrates. Hashimoto et al.[15] reported that a nanosecond pulsed laser irradiation to Au particle-immobilized glass substrates resulted in pulverization of the Au particles into smaller ones along with formation of nanoholes on the glass substrates. We have also prepared nanoholes on thin organic polymer films with photoexcitation of LSPR of Au particles by irradiation with nanosecond pulsed laser at the wavelength of 532 nm, the size of the holes formed in the polymer films being increased by increasing the size of Au particles used.[14] The Au particle-assisted laser processing is a powerful and versatile method for precise top-down fabrication on flat substrate surfaces. This technique is also applicable to prepare pores of a desired size on the shell wall of hollow silica (SiO_2) microspheres, but such attempt has not been done.

We report here a new method for preparing hollow particles having pores of the size from 17 to 56 nm in the shell. Hollow SiO_2 particles, the inner surface of which is modified with Au particles, are irradiated with nanosecond pulsed laser at 532 nm to photoexcite the LSPR, resulting in the formation of pores in the SiO_2 shell.

The strategy for preparing hollow particles with pores, which is schematically shown in Figure 1, consists of four steps. In the first step, Au nanoparticles are deposited on amino group-functionalized polystyrene (PS) (diameter: 1.0 µm) particles as a template by the reduction of $H[AuCl_4]$, using a previously reported method with a slight modification.[17] The resulting Au-deposited PS (Au/PS) particles are covered with a thin SiO_2 layer produced by the hydrolysis of tetraethyl orthosilicate (TEOS). Calcination of SiO_2-coated Au/PS particles at 723 K in air for 2 h produces hollow SiO_2 particles having the inner shell surface modified with Au particles. Finally, irradiation with a nanosecond pulsed laser at the wavelength of 532 nm (pulse width: ca. 7 ns, repetition: 10 Hz, fluence: 700 mJ cm^{-2} pulse^{-1}) is carried out on the thus-obtained Au–SiO_2 composite particles

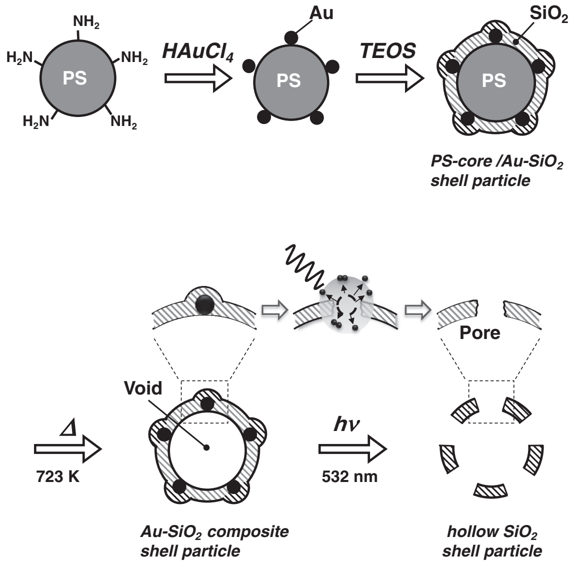

Figure 1. Schematic illustration of the strategy for preparation of a hollow Au–SiO_2 composite particle and a porous SiO_2 shell particle.

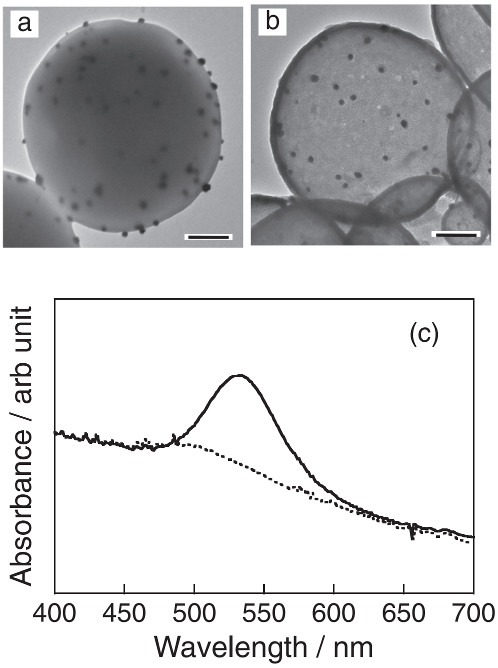

Figure 2. (a, b) Typical TEM images of Au-particle-deposited PS particles (a) and hollow Au–SiO_2 composite particles (b). Scale bar in each image represents a length of 200 nm. (c) Extinction spectra of Au–SiO_2 composite hollow particles before (solid line) and after irradiation with 700 mJ cm^{-2} $pulse^{-1}$ for 3 min (dashed line).

suspended in water for 3 min under gentle agitation with N_2 bubbling. Experimental details are written in the Supporting Information.[21]

The original amino group-functionalized PS spheres had a smooth surface without any protrusions. By reacting these particles with $H[AuCl_4]$ (30 μmol dm^{-3}), spherical Au nanoparticles, observed as small black islands on the surface of the PS spheres in Figure 2a, were uniformly deposited on the PS surfaces. The average diameter (d_{av}) of Au particles was ca. 28 nm with a standard deviation (σ) of 8.6 nm. The d_{av} of Au particles could be controlled from ca. 6 to 40 nm by changing the concentration of $H[AuCl_4]$ added from 1.0 to 50 μmol dm^{-3}. After coating Au/PS with SiO_2 shell of 30 nm in thickness, the PS core was removed through combustion at 723 K in air. As shown in Figure 2b, hollow particles of Au–SiO_2 composite were observed, the void size of which was the same as the diameter of PS spheres (ca. 1.0 μm) used as a core. The d_{av} of Au particles in the shells (28 nm) was almost the same as that before removal of the PS core, indicating that the removal of the PS core did not cause the coalescence between Au particles. It should be noted that some white spots were also observed on the hollow sphere in Figure 2b. SEM measurements revealed that the spheres in Figure 2b had no large pores penetrating the shell wall (not shown). These white spots would be assigned to the cavities on the interior surface of hollow sphere, which were probably formed by the partial desorption of Au particles from SiO_2 shell wall, being similar to the results reported by Xia et al.[18] Furthermore, it is well known that the SiO_2 shell prepared by the sol–gel method has micropores with size less than ca. 3 nm.[7] In the present study, there must be several micropores in the thus-obtained SiO_2 shell (Figure 2b), through which small molecules could diffuse into the void space in the hollow sphere from the bulk solution. However, in our TEM measurements, such micropores could not be observed in the shell wall due to the low resolution of our instrument.

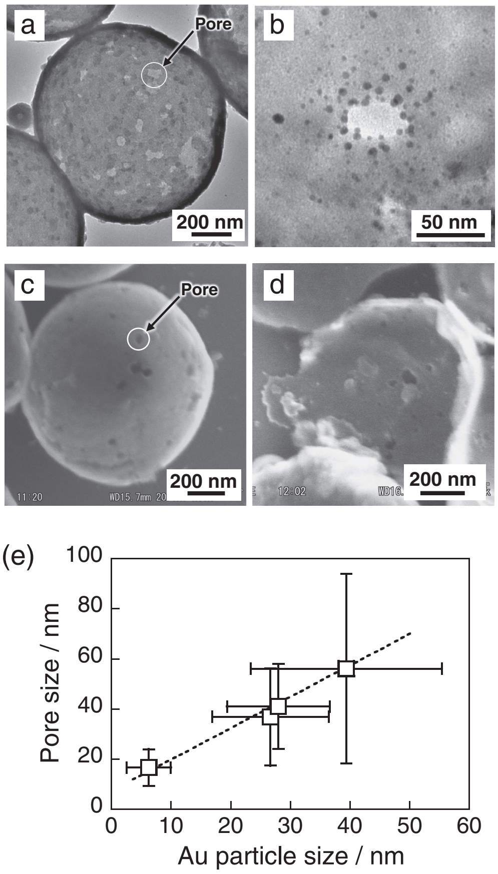

Figure 3. (a, b) Typical TEM images and (c, d) SEM images of hollow SiO_2 particles with pores, obtained by laser irradiation. The image in (b) is a high-magnification TEM image around a pore. The inner shell surface of accidentally broken particles is observed in the image in (d). (e) Relationship between pore size in the obtained SiO_2 shell and Au particle size in Au–SiO_2 composite particles. Error bars represent the standard deviations.

Figure 2c shows the change in the extinction spectra of Au–SiO_2 composite particles dispersed in water before and after laser irradiation at 532 nm. The extinction spectra of the original suspension exhibited an LSPR peak of Au particles at 530 nm. By laser irradiation, the intensity of the LSPR peak decreased remarkably, accompanied by a blue shift of the peak wavelength from 530 to 500 nm. It is well known that the LSPR peak of spherical Au particles becomes broad and that its intensity is lessened as the particle size decreases from that of ca. 8 nm.[19] So the observed optical changes originated from the decrease in the size of Au particles by laser irradiation.

Figures 3a–3d show typical TEM and SEM images of hollow particles obtained after pulsed-laser irradiation. The original Au particles ($d_{av} = 28$ nm) incorporated in SiO_2 shell wall disappeared with laser irradiation, resulting in the formation of pores (average size: 41 nm) in the SiO_2 shell, which were observed as small round areas having brighter contrast in the

SiO_2 layer in TEM images (Figures 3a and 3b) or those with darker contrast in SEM images (Figures 3c and 3d). As shown in Figure 3d, some of the spheres are not intact and exhibit the hollow interior. The inner shell surface of broken particles had pores similar to those observed on the outer surface in Figure 3c, suggesting that the thus-produced pores have penetrated the SiO_2 wall. Furthermore, it was observed in a high-magnification image of a pore (Figure 3b) that Au nanoparticles of less than ca. 4 nm in size were radially scattered on the shell wall around a pore. These small particles were probably formed by the fragmentation of original Au particles of 28 nm in size with the intense photoexcitation of their LSPR, being in good agreement with the decrease in LSPR intensity after irradiation (Figure 2c). It should be noted that the treatment of hollow Au–SiO_2 composite particles with aqua regia enabled selective chemical etching of Au particles on the SiO_2 layer but did not produce large pores penetrating the shell wall. Furthermore, in the absence of deposited Au particles, the surfaces of hollow particles exhibited no detectable change in morphology and no pores were formed on the shell, even when a pulsed laser irradiation with the same fluence ($700\,\mathrm{mJ\,cm^{-2}\,pulse^{-1}}$) was carried out. These results indicated that the laser fluence used here was below the damage threshold of the present thin SiO_2 shell in water and that pores were produced in the shell by laser-induced fragmentation of Au particles.

Recently, Hashimoto and co-workers reported that the nanosecond laser pulse irradiation with intensity of 470 $\mathrm{mJ\,cm^{-2}\,pulse^{-1}}$, which can raise the temperature of irradiated Au particles of 40 nm in size over the boiling point, was performed on Au particle-immobilized glass substrates, resulting in the pulverization of Au particles into smaller ones along with the formation of nanometer-sized holes on the glass substrates.[15] This coincides with the present case of irradiated hollow SiO_2 particles; as shown in TEM images (Figure 3b), Au nanoparticles that were much smaller than the original particles were formed around the pores. Furthermore it was estimated in our previous study[14] that irradiation with a pulsed laser at 532 nm (pulse width of 8 ns) with fluence of $700\,\mathrm{mJ\,cm^{-2}}$, similar to the experimental conditions used in this study, heated Au particles of 20 nm in diameter to 1.21×10^5 K, which is much higher than the boiling temperature of Au (2856 K for bulk[20]). Therefore, these suggested that the explosive fragmentation via superheating of Au particles was a possible mechanism for formation of pores in the SiO_2 shell with laser irradiation.

Irradiation of Au–SiO_2 composite particles with different Au particle sizes could produce various sizes of the pores in hollow SiO_2 particles, as shown in Figure 3e, in which the error bars represent the standard deviation of the size distribution. The pore size increased from 17 to 56 nm with an increase in d_{av} of original Au particles from 6 to 39 nm. In each case, the pore size was ca. 1.5-times larger than the size of Au particles used. This was probably due to partial destruction of the SiO_2 shell wall in the vicinity of Au particles via their explosive fragmentation and/or thermal diffusion in the lateral direction. Similar phenomena were observed in our previous case for irradiation of Au particle-incorporated polymer films, in which the etched nanoholes, produced by the laser irradiation to Au particles (d_{av} = ca. 40 nm), had diameters (50–90 nm) slightly larger than those of Au particles incorporated in the films.[14] Thus, we can conclude that a desired size of pores in the hollow SiO_2 particles is obtained just by selecting the size of Au particles deposited on PS spheres used for a template.

In conclusion, the laser processing technique assisted by Au nanoparticles enables fabrication of nanostructured spherical hollow SiO_2 particles. Nanometer-sized pores penetrating the SiO_2 layer were produced via explosive fragmentation of Au particles with photoexcitation of LSPR. The size of the pore could be controlled by adjusting the size of Au particles used. This was not achieved by conventional chemical preparation methods. The precise size control of Au particles used for a template can produce pores of a desired size in the shell that enable size-selective penetration of large molecules, such as quantum dots, biomolecules, and polymers. Thus, the obtained porous hollow particles will be useful as host materials for applications, such as chemical sensing, chromatography, and catalysis for biomolecules.

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21 Supporting Information is also available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.