Preparation of Periodic Arrays of Metallic Nanocrystals by Using Nanohoneycomb as Reaction Vessel

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There has been a great interest in fabricating nanocrystals because of their novel size- and shape-dependent properties.[1–6] Noble metal nanocrystals, like gold and silver, are particularly promising for potential applications in bioprobes,[2] optical devices,[3–5] and biosensors.[7,8] Gold nanoparticles are also a good catalyst for growing periodic arrays of aligned nanorods.[9,10]

Physical vapor deposition (PVD) methods, like inert-gas evaporation,[11] cosputtering,[12] and pulsed laser ablation,[3] are commonly used to grow nanoparticles, but the size distribution is relatively large. With the aid of nanoimprint lithography[9,13] and nanosphere lithography,[14] arrays of nanoparticles with a controllable size can be fabricated by using PVD. Filling the voids of the nanosphere template was suggested as a way to prepare periodic nanopatterns.[15] Xia's group developed a solution-based approach to prepare core–shell and hollow nanoparticles using nanospheres as a chemical template.[16] Chemical methods are also applied to grow uniform nanocrystals by carefully controlling the kinetics of nucleation and growth.[17–19] Small reaction vessels, such as polydimethylsiloxane (PDMS) microwell[20] and photoresist nanowell,[21] are suggested to provide better size control of nanocrystals. Barton and Odom used silica nanospheres as a mold to fabricate nanowells on silicon substrate by laser-assisted embossing.[22] NaCl and CdS nanocrystals were then grown by evaporating their precursor solutions into the silicon nanowells. The size of the nanocrystals depended on the well volume and concentration of the precursor solution.

Inhomogeneity in volume of the small reaction vessels, concentration of precursor solution, and reaction temperature may result in size dispersion of nanocrystals.[22] It is of great interest to uniformly deliver material into the small reaction vessels. In this study, we propose a new method using PVD to deliver gold or silver film into the small reaction vessels because of its ease in deposition control. The film is then annealed at an elevated temperature to grow nanocrystals. There are two requirements for the reaction vessel in this process, chemical inertness and thermal stability. Recently, we have developed a method called solution-based nanosphere lithography (s-NSL) to grow nickel oxide nanohoneycomb.[23] Nickel oxide is a thermally stable material with a high melting point (1955 °C). The nanohoneycomb has a concaved surface profile within the hexagons, which serves as a good small reaction vessel to grow arrays of gold or silver nanocrystals. Similar to other reaction vessels mentioned above, the nanohoneycomb can confine the crystallization of gold and silver films during annealing. The amount of gold and silver delivered into each hexagon is determined by the size of nanosphere and film thickness. Because gold and silver can form a complete solid solution, an experiment was also carried out to prepare alloy nanocrystals using the nanovessel.

The method to prepare nickel oxide honeycomb on Si substrate has been described previously.[23] Briefly, a template was prepared by spin-coating the PS nanospheres onto the substrate. A Ni organic solution was dropped onto the self-assembled nanosphere template that was then baked in air at 350 °C to remove the nanospheres and allow the formation of nickel oxide honeycomb. Gold film was deposited on the honeycomb by an ion sputter (E-1010, Hitachi) at a pressure of 50 mtorr Ar with a deposition rate of 10 nm/min. The silver film was prepared by using an electron gun deposition

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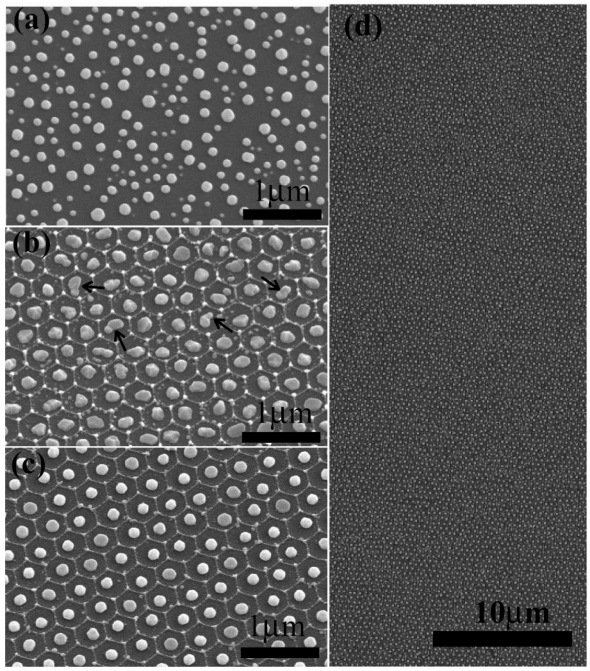

Figure 1. SEM images (30° tilted) of gold nanocrystals prepared by annealing films (a) without and (b–d) with NiO nanohoneycomb at various temperatures for 1 h. d is a low-magnification SEM image of c. The annealing temperatures for samples a–c were 1000, 600, and 1000 °C, respectively. The sputtering time was 60 s for all samples.

system (Temescal) with a growth rate of 6 nm/min. After the film was annealed at elevated temperatures under a flow of 200 sccm N_2 for 1 h, nanocrystals were formed inside the hexagons of nanohoneycomb. AFM (Nanoscope IIIa, Digital Instruments) and SEM (FE4300, Hitachi) were used to obtain the surface topography and morphology of the nano honeycomb, respectively. An energy-dispersion X-ray (EDX) analyzer (Emax Energy EX-350, Horiba Ltd.) was used to identify the component elements of the thin film.

As reported previously,[23] a nickel oxide nanohoneycomb was formed after removal of the nanospheres. From the AFM observation, the surface within each hexagon in the nanohoneycomb was concaved. For the honeycomb prepared by using 400 nm PS nanospheres, the height difference between the border and center of the hexagon was approximately 20 nm. Therefore, the nanohoneycomb was a natural reaction vessel to confine the formation of nanocrystals.

After being annealed for 1 h, the gold film became nanocrystals, as shown in Figure 1. Without using the nanovessel as a control specimen, gold nanocrystals are randomly formed and have a large size variation, as shown in Figure 1a. With the aid of nanovessels, formation of gold nanocrystals is confined, as shown in images b and c in Figure 1. As marked by arrows in Figure 1b, the presence of necks in gold nanocrystals indicates that the sintering process is not completed after 1 h of annealing at 600 °C. On the contrary, the gold nanocrystals prepared by annealing at 1000 °C are nearly spherical and identical, Figure 1c. This can be explained by faster mass transport of atoms at high annealing temperatures. Figure 1d shows a low-magnification SEM image, indicating that a large area (at least 50 μm × 50 μm) of nanohoneycomb and periodic gold nanocrystal arrays can be obtained by this method. The minimum

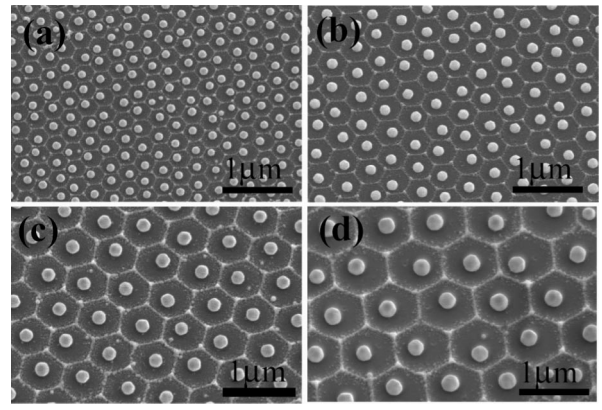

Figure 2. SEM images (30° tilted) of gold nanocrystals prepared by using (a) 300, (b) 400, (c) 600, and (d) 800nm PS nanospheres. The sputtering time was 60 s and all samples were annealed at 1050 °C for 1 h.

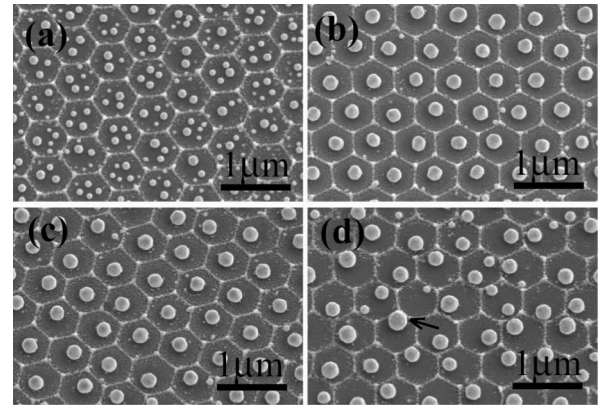

Figure 3. SEM images (30° tilted) of gold nanocrystals prepared by using different lengths of sputtering time. (a) 40, (b) 70, (c) 80, and (d) 90 s. The diameter of PS nanosphere was 600 nm, and all samples were annealed at 1050 °C for 1 h.

annealing temperature needed to convert the gold film into one single nanocrystal within each 400 nm vessel is approximately 700 °C, i.e., 0.73 T_m of Au.

The influence of nanosphere size on the diameter of gold nanocrystals was then studied. As shown in Figure 2, after the films were annealed at 1050 °C for 1 h, spherical and identical gold nanocrystals were obtained with the vessels of various sizes. The diameter of gold nanocrystals increases with the nanosphere size. The effect of sputtering time or film thickness on the diameter of gold nanocrystals was also examined. Figure 3a shows that the gold film prepared from a shorter sputtering time of 40 s, i.e., 6.7 nm thick, became several nanocrystals within every vessel after annealing at 1050 °C for 1 h. If a suitable sputtering time was used, e.g., 70 and 80 s, only one single nanocrystal was formed within each vessel, as shown in images b and c in Figure 3, respectively. When a longer sputtering time, 90 s, was applied, neighboring nanocrystals might further merge together on the boundary of hexagons, as indicated by the arrow in Figure 3d.

The change in size and density of gold nanocrystals can be explained by the deposition and sintering processes of the film. The annealing results in formation of crystals to reduce the total surface energy. The concaved surface profile confines the sintering within each vessel to form only a single nanocrystal if an optimum sputtering time is used, as shown

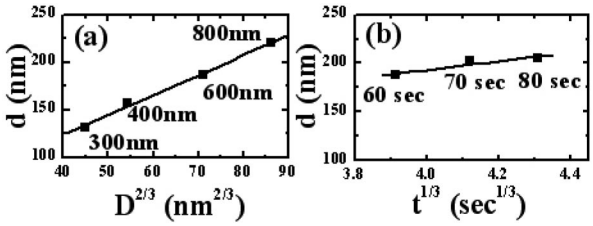

Figure 4. Dependence of gold nanocrystal diameter *d* on (a) nanosphere size *D* and (b) sputtering time *t*. The sputtering time for sample a was 60 s, and the nanosphere size for sample b was 600 nm.

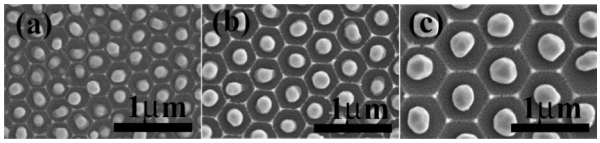

Figure 5. SEM images of silver nanocrystals prepared using (a) 300, (b) 400, and (c) 600 nm PS nanospheres. The thicknesses of silver film were 15, 20, and 30 nm for a–c, respectively. All samples were annealed at 700 °C for 1 h.

in Figure 3. Assuming that the gold nanocrystals are perfectly spherical, the diameter of nanocrystals formed in the vessel is determined by the volume of deposited film, which is given by

$$V = (\pi/4)D^2st \quad (1)$$

where V is the volume, D the size of nanosphere, s the deposition rate, and t the sputtering time. If only one spherical nanocrystal is formed in each vessel, the diameter can be derived as follows

$$d = (3s/2)^{1/3}D^{2/3}t^{1/3} \quad (2)$$

where d is the diameter of nanocrystal. The dependences of the average diameter of gold nanocrystals on nanosphere size and sputtering time are plotted in panels a and b in Figure 4, respectively, which are in good agreement with the prediction of eq 2.

It was also demonstrated that periodic arrays of silver nanocrystals could be prepared using the same NiO nanohoneycomb as reaction vessels. Compared with the process for gold nanocrystals, the thickness window to form a single silver nanocrystal in each vessel was relatively smaller. However, we were able to obtain single nanocrystals in the 300, 400, and 600 nm nanohoneycomb vessels with 15, 20, and 30 nm silver films, respectively, as shown in Figure 5.

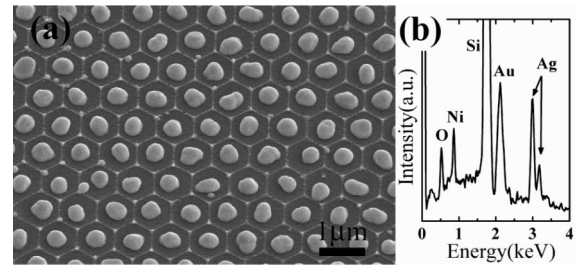

Figure 6. (a) SEM image (30° tilted) and (b) EDX spectrum for gold–silver alloy nanocrystals prepared by using 800 nm PS nanospheres. The thickness of Ag and Au films are 30 and 6.7 nm, respectively. The sample was annealed at 700 °C for 1 h.

The reason for the small thickness window could be explained by a shorter distance between the silver nanocrystals, as indicated by the larger *d*/*D* ratio. In an attempt to fabricate Au–Ag alloy nanocrystals within each vessel, we deposited an additional gold film on top of the silver film. The thicknesses of Ag and Au films were 30 and 6.7 nm, respectively. Figure 6a shows that, indeed, gold–silver alloy nanocrystals could be prepared by using 800 nm PS nanospheres. The EDX spectrum in Figure 6b shows that the nanocrystals are composed of gold and silver. In additon, both selected-area diffraction by TEM and X-ray diffraction analyses indicate that the nanocrystals are polycrystalline and have alloy structure. To prepare alloy nanocrystals with different gold/silver ratios in different sized vessels would require more study.

In summary, we have developed a method to fabricate periodic arrays of gold, silver, and gold–silver alloy nanocrystals by using NiO nanohoneycomb as small reaction vessels. The nickel oxide nano honeycomb is very stable and does not react with gold and silver at high temperatures. The diameter of nanocrystals formed in the nanovessel could be controlled by the film thickness and nanosphere size. High-temperature annealing provides fast mass transport of atoms and results in the formation of nearly spherical and identical nanocrystals. It is also expected that the nanohoneycomb can be used to prepare other elemental or alloy nanocrystals with desired patterns, size, and composition.

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