Directed Assembly

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Decoration of Microspheres with Gold Nanodots—Giving Colloidal Spheres Valences**

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To obtain a large variety of structures from colloids, one has to lend colloidal spheres a multiplicity of directed interactions that are analogous to those of atoms. This directionality is achieved in the work presented herein by combining the building of colloidal crystals with Au evaporation and plasma etching. The resulting colloidal spheres exhibit two, three, four, or five nanosized Au dots that are analogous to sp-hybridized atomic orbitals.

Colloidal spheres have been extensively investigated due to their broad spectrum of industrial and fundamental applications, especially their use in photonic crystals.[1–4] Various colloidal spheres, organic and inorganic, can be produced that are exceedingly monodisperse in terms of size and shape. Nevertheless, their surfaces still remain chemically homogeneous or heterogeneous in an undefined way despite there being well-established methods to modify surfaces. This surface chemistry renders the coupling of spheres spatially isotropic, so it is difficult to spatially direct the organization of the spheres. They self-assemble only into simple and energy-favorable structures such as face-centered-cubic (fcc) or hexagonal-close-packing (hcp) arrays. In this respect, colloidal spheres have changed little in at least a century.

The ability to spatially direct the integration of spheres or selectively link other nano-objects on spheres necessitates the spatially selective attachment of functional sites on colloidal spheres, thus creating analogues of valency of atoms and breaking the spatially isotropic coupling into anisotropic coupling. Up to date, however, little effort has been shown to address this challenge. Nelson theoretically testified the possibility of creating valences on microspheres by coating them with anisotropic objects such as nanorods.[5] Fitzmaurice and co-workers immobilized linear aggregates of Au nanoparticles on silica microspheres by fixing nanoporous membranes on microspheres to template the self-assembly of nanoparticles.[6] The controlled deposition of Au vapor allows capping of microspheres with half an Au shell.[7–9] Using the upper single layers of colloidal crystals as masks during Au vapor deposition, we recently demonstrated a simple and versatile way of fabricating various Au patterns on the upper halves of the lower spheres, whose dimension and feature are predominantly manipulated by the orientation of the template crystals.[10] Our methodology is demonstrably independent of the size and surface chemistry of the spheres. As the size of the Au patterns is comparable to that of the spheres, they may not be ideal as valences to direct the coupling of the spheres. Herein we have used the upper bilayers of polystyrene (PS) colloidal crystals that have been etched by O_2 plasma as masks for Au deposition on the spheres of the lower layers. This process allows decoration of microspheres with two, three, four, and five Au nanodots, whose arrangements are linear, trigonal, tetrahedral, or right-pyramidal in space, respectively. In terms of configuration, these Au nanodots might be considered as nanoscale analogues of the sp-hybridized chemical valences in, for example, carbon and silicon atoms.

Our previous study reported the formation of one Au nanodot on the upper half of a shell of microspheres by using the upper bilayers of their colloidal crystals.[10] However, the smaller interstices in the upper bilayers cause a non-uniform diffusion of Au vapor, so the dimension and features of the Au dots obtained in our previous study were not uniform or clear-cut as compared with those of patterns derived from a single-layer template.[10] To circumvent this non-uniform diffusion of Au vapor, in the present work we etched slightly PS colloidal crystals with O_2 plasma prior to Au vapor deposition. Yang and co-workers suggested that the shadow of the upper layers in the colloidal crystals renders the plasma etching anisotropic, which not only increases the interstice sizes between spheres but also allows the creation of new interstitial shapes.[11]

Figure 1 schematically represents our procedure for the fabrication of Au nanodots on microspheres by using the upper bilayers of O_2-plasma-etched colloidal crystals as masks for Au vapor deposition. In this work, we organized 270 or 920 nm PS spheres through a dip-coating process. After optimizing the withdrawing speed and the concentration of

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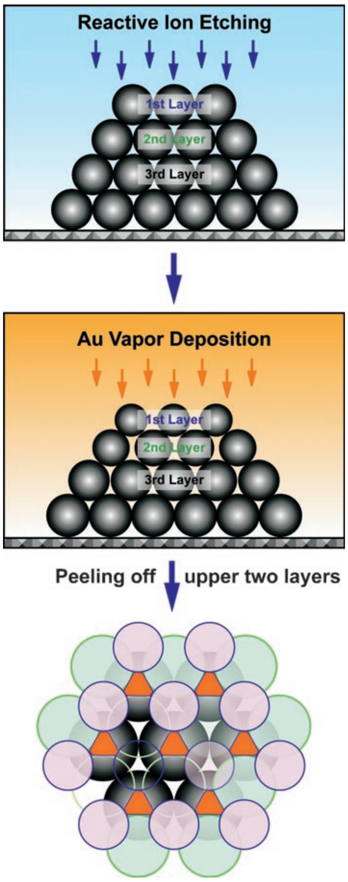

Figure 1. Construction of Au nanodots on microspheres by combining Au vapor deposition and the use of the upper bilayers of O_2-plasma-etched colloidal crystals with (111) facets parallel to the substrates as masks. The orange areas represent Au domains that remained on spheres after removal of the upper two layers.

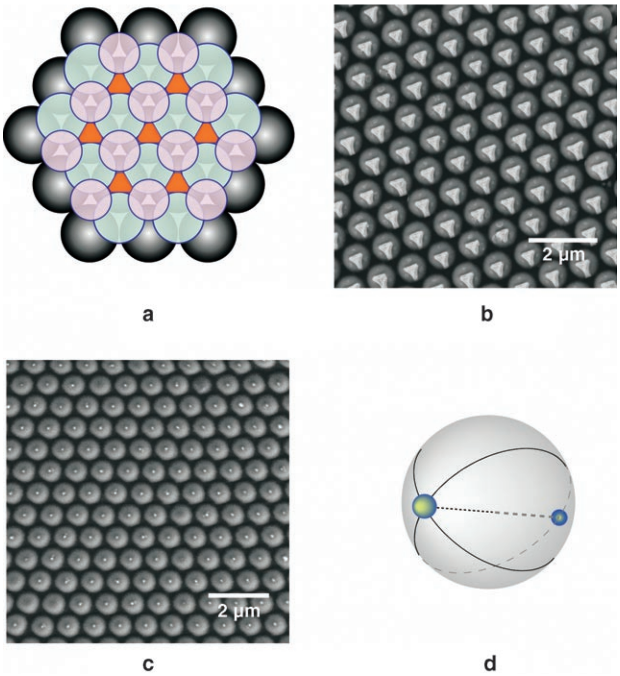

Figure 2. a) Au patterns obtained atop spheres in the third layer in O_2-plasma-etched colloidal crystals with an fcc structure by using the upper bilayers as a mask during Au vapor deposition. The stacking symmetry of the crystals is ABCABC and their (111) facets are parallel to the substrates. The spheres in the first, second, and third layers are highlighted by pink, light green, and black, respectively; the Au patterns on the third layer spheres are orange. The incidence angle between Au vapor flow and the normal direction of the crystals films is set as 0°. b) SEM image of the resulting Au patterns deposited on the upper halves of 925 nm PS spheres in the third layer obtained by templating their fcc colloidal crystals that had been etched by O_2 plasma for 10 min and coated with a 100 nm thick Au layer. The size of the resulting Au dots is in the range of 350–400 nm. c) SEM image of the Au patterns obtained on the lower halves of these spheres; the size of the resulting dots is around 80 nm. d) Schematic illustration of the spatial configuration of two Au nanodots constructed on microspheres.

PS suspensions, we constructed colloidal crystals with four or five layers of PS spheres on silicon wafers, in which single-crystal domains of a pure fcc structure extended over 50 µm and the preferential orientation parallel to the substrate was (111). In this packing structure, the spheres in the third layer are located just underneath the interstices in the upper bilayers, thus allowing Au vapor to reach them. After O_2-plasma etching, the PS spheres in the top layers are reduced in size due to direct exposure to O_2-plasma flow (see Figure 2a and Supporting Information), thus increasing the interstitial sizes between PS spheres. In this work, however, we found that prolonged plasma etching usually caused fusion of the spheres in colloidal crystals, which made it difficult to remove the upper layers. Hence the plasma-etching period was fixed at 3 min for 270 nm PS spheres and 10 min for 920 nm PS spheres. After Au vapor deposition and removal of the upper two layers with adhesive tape, a triangular Au dot was found exclusively atop the spheres. This can be seen by scanning electron microscopy (SEM, Figure 2b). The structural profiles of the resulting triangular dots were analyzed by atomic force microscopy (AFM; see Supporting Information), which indicated that the thicknesses of the triangular dots increase with an increase in the period of Au deposition.

After these third-layer PS spheres with a triangular Au nanodot on their upper halves were peeled off from the crystals, we observed a round Au nanodot on the apex of their lower halves (Figure 2c). According to the AFM analysis (see Supporting Information), the size and thickness of the resulting round Au nanodots increases with an increase in the Au vapor-deposition time. Thus, from a combination of the results shown in Figures 2b and c, we conclude that the PS spheres in the third layer are decorated with two Au nandots. These two dots are arranged opposite each other in the great circle of the sphere, as illustrated schematically in Figure 2d. In this scenario, the configuration of these two Au nanodots on a microsphere resembles that of the sp-hybridized atomic orbital of carbon atoms.

When the colloidal crystals with four layers of spheres were used, we found that round Au nanodots were visible on the lower halves not only of the third-layer spheres but also of the second-layer spheres and of the first-layer spheres, but not of the fourth-layer spheres that are attached directly to the substrate. The formation of these round Au dots is not entirely explained so far. We speculate that when the Au vapor diffuses from the top layers into the lower layers in colloidal crystals through the interstitial voids between the spheres, it might be scattered or reflected back by the surface of the spheres or the substrate. The scattered or reflected vapor should condense on the lower halves of the spheres, opposite to the flow of the Au vapor, which should lead to the formation of the round Au dots. An investigation into the origin of this round Au nanodot is underway.

The features of Au patterns constructed on the spheres in the third layers in colloidal crystals are expected to be strongly dependent on the stacking structure of the colloidal crystals, ABCABC (fcc) or ABAB (hcp). However, so far we have had difficulty in controlling the stacking structures of colloidal crystals due to the exceedingly narrow energy difference between these two stacking structures.[12] The crystals, constructed by the existing methods, usually are a mixture of ABCABC (fcc) or ABAB (hcp) stacking structures. In the dip-coating process, we found that the rapid withdrawing speed led to the formation of more ABAB stacking structures. In an hcp array, the spheres in the third layer are positioned just under the spheres of the first layer, thus leaving air channels behind that allow Au vapor to penetrate freely through the whole crystal with little deposition on the lower-layer spheres. After plasma etching, the spheres in the first layer were smaller than those in the third layer, which may allow Au deposition on the edges of the latter (Figure 3a). After Au vapor deposition and removal of the upper two layers, three small triangular Au nanodots were observed on the edge of the upper halves of the spheres, which were arranged in a trigonal array (Figure 3c). In the current work, we learned that the number of Au dots atop the spheres is dependent on the incidence angle of the Au evaporation, the angle between the vapor flow and the normal direction of the sample surfaces.[13,14] If the incidence angle is increased from 0° to 10° (Figure 3b), the number of Au dots is reduced from three to two. Figure 3d reveals that the edges of the upper halves of the spheres are decorated with one large and one small triangular nanodots. In this case, one round Au nanodot was also found on the lower halves of the spheres in third layer in a way similar to that shown in Figure 2c. As shown in Figures 3e and f, the arrangement of Au nanodots on spheres can be expected to be tetrahedral (four dots) and trigonal (three dots), thus resembling nanoscale analogues of sp^3- and sp^2-hybridized molecular orbitals.

Thanks to enormous efforts in the past decade, it is possible to grow colloidal crystals with defined crystal orientation parallel to substrates. By use of substrates with V-shaped grooves, one can construct fcc colloidal crystals with a preferential plane of (100) parallel to the substrates.[15,16] In this square close-packing structure (ABAB stacking), the spheres in the third layers are located exclusively underneath those of the top layers. Therefore, no Au vapor may reach the third layer.[10] After plasma etching, four air gaps were opened up in the upper bilayers to allow the penetration of Au vapor (Figure 4a and Supporting Information). After Au vapor deposition and removal of the upper two layers, we constructed four rectangular Au nanodots on the edges of the upper halves of the PS spheres on the third layer (Figure 4b). One round Au dot also formed on the center of the lower half of the spheres (see Supporting Information). As depicted in Figure 4c, five Au nanodots with a right-pyramidal configuration are therefore linked on one PS sphere. When the incidence angle of the Au vapor flow was set as 10°, only three rectangular Au nanodots—one big and two small—were obtained (Figure 4d). The spatial configuration of these three dots is expected to be similar to that shown in Figure 3e.

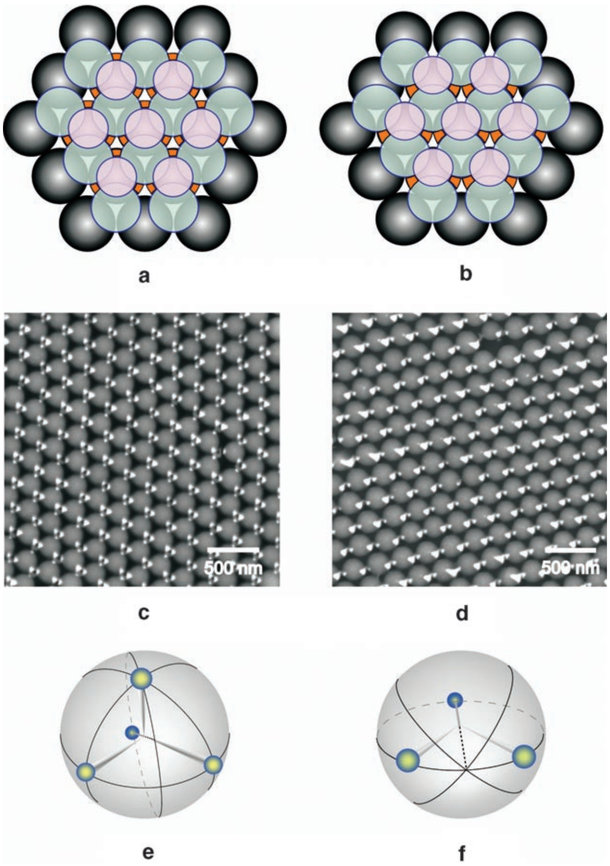

Figure 3. a, b) Au patterns atop the spheres in the third layer obtained by using the upper bilayers as a mask during Au vapor deposition in O_2-plasma-etched colloidal crystals with an ABAB stacking symmetry. The incidence angle between Au vapor flow and the normal direction of the crystal films is set as 0° (a) and 10° (b). c, d) SEM images of the Au patterns on the upper halves of 270 nm PS spheres in their hcp colloidal crystals, constructed at an incidence angle of 0° (c) and 10° (d). The crystals were etched by O_2 plasma for 3 min and coated by an Au layer 30 nm thick. c) Three Au dots of 20–45 nm in size on the edge of the PS spheres. d) One 90 nm and one 25 nm dot on the sphere edge. e, f) Spatial configurations of the resulting four (e) and three Au nanodots (f) on microspheres.

It is worth noting that the decoration of Au nanodots on microspheres is independent of the diameter of the spheres and is extendable to other polymer spheres. Nevertheless, the mechanical stability of the Au nanodots deposited on PS microspheres is currently poor. Redispersion of the PS spheres coated with Au dots into water resulted in the detachment of the Au dots, thus limiting their usage for directing self-assembly of spheres. To circumvent this drawback, we are currently extending our procedure to silica spheres with the aid of highly reactive ion etching. Further-

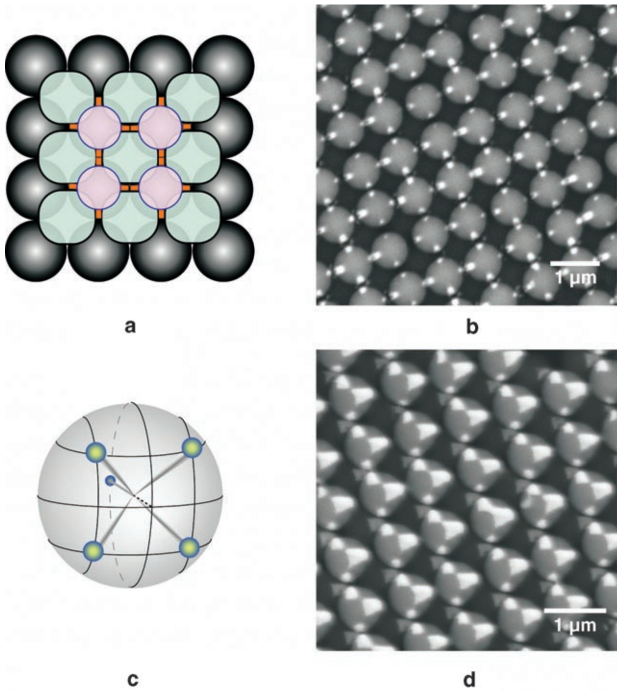

Figure 4. a) Au patterns atop the spheres in the third layers obtained by using the upper bilayers as a mask during Au vapor deposition in O_2-plasma-etched fcc colloidal crystals with (100) facets parallel to the substrates. The incidence angle is 0°. b) SEM image of the resulting Au patterns on the upper halves of 925 nm PS spheres in the third layer obtained by templating their colloidal crystals that had been etched by O_2 plasma for 10 min and coated with an Au layer 100 nm thick. The size of the resulting dots is in the range of 50–150 nm. c) Spatial configuration of the five Au nanodots constructed on the spheres. d) SEM image of the Au patterns atop the spheres in the third layer obtained at an incidence angle of 10°, which reveals a large Au dots (200 nm × 400 nm) and two small dots (about 150 nm).

more, the selective fabrication of colloidal crystals with either fcc or hcp structures is also a promising extension of this work.

In summary, we have demonstrated the feasibility of the decoration of PS microspheres with two, three, four, or five Au nanodots by using their colloidal crystals, etched by O_2 plasma, as masks for Au vapor deposition. The number of dots per sphere can be manipulated by use of different crystal structures and by altering the conditions of Au vapor deposition. The Au nanodots deposited on the spheres are arranged in a linear, trigonal, tetrahedral, or right-pyramidal fashion, which provides the nanoscale analogues of sp-hybridized atomic orbitals of carbon. The Au nanodots obtained on microspheres can be used as the bonding site to dictate the integration of the spheres, thus paving a new way to colloidal self-assembly—colloidal valent chemistry of spheres[5]—to create hierarchical and complex "supraparticles".[17]

Experimental Section

Aqueous suspensions (10 wt %) of polystyrene of 270 and 925 nm in diameter were purchased from Microparticles GmbH, Germany. The crystallization of these spheres on silicon wafers was conducted by a dip-coating process. The withdrawing speeds were optimized in the range of 0.5–5 $\mu m\,s^{-1}$ and the concentration of these spheres in the range of 1.0–2.0 wt % for 270 nm spheres and 3.0–5.0 wt % for 925 nm spheres to produce crystals with four or five layers of spheres. By using a plasma cleaner (PDC-32G, Germany), O_2-plasma etching was performed at a pressure of 0.2 mbar and a power density of 100 W. The optimal etching period was adjusted to 3 min for 270 nm PS colloidal crystals and 10 min for those of 925 nm. Au vapor deposition was conducted in a high-vacuum coater (Edwards Auto 306, UK) at a pressure of 10^{-7} mbar and a deposition speed of 0.02 $nm\,s^{-1}$. By varying the deposition time, Au layers of 30, 50, 100, and 200 nm thick were deposited within the plasma-etched colloidal crystals. Note that prior to Au deposition, the crystals were coated with chromium layers 5 nm thick. The incidence angles between the Au vapor flow and the normal direction of the samples were adjusted by tilting the samples on the sample holding blocks within the thermal deposition chamber.

After Au deposition, we placed double-sided adhesive tapes on the Au-coated surfaces of colloidal crystals and subsequently covered glass slides atop the adhesive tapes.[10] The glass slides were pressed at a pressure of 0.2 $kg\,cm^{-2}$ for 5 min, then the upper two layers were stripped off to leave an Au pattern on the spheres in the third layers. A similar process allowed the spheres in the third layers to be removed from the crystals. Both sides of the third-layer spheres were visualized by SEM. SEM images were recorded with a Gemini LEO 1550 instrument operated at 3 kV. To directly reveal the Au patterns on colloidal spheres, the samples were not sputtered by thin Au films before SEM measurements. AFM imaging was performed by using the Nanoscope Dimension 3100 system operating in tapping mode.

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