Communication

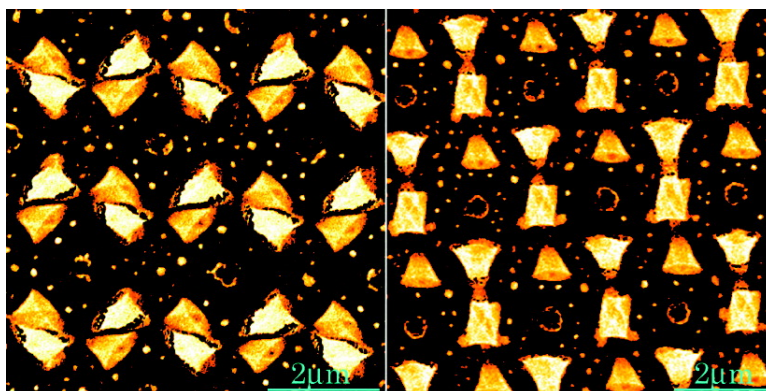# Fabrication of Heterogeneous Binary Arrays of Nanoparticles via Colloidal Lithography

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Fabrication of Heterogeneous Binary Arrays of Nanoparticles via Colloidal Lithography

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Surface patterning is the center of the entire microelectronics industry.[1,2] The past decades have witnessed a rapid progress of surface patterning mainly based on lithography driven by the increasing demand of high performance and miniaturization of electronic and optoelectronic devices. In terms of forming devices, increasing the heterogeneity of surface patterns is of paramount importance,[3] but it remains a formidable challenge especially when the pattern features are scaled down to nanometers.

Up to date, laterally heterogeneous binary arrays of nanoparticles (NPs) have been demonstrated via co-self-assembly of different NPs with different sizes and/or chemical compositions.[4–7] However, the applicability of a bottom-up strategy in surface patterning is usually limited by their materials-specific character and the deliberate control of solvent evaporation during self-assembly of NPs. Nevertheless, there are few simple lithographic techniques capable of constructing such laterally heterogeneous binary arrays. Herein we present a facile and rather versatile approach to circumvent this challenge based on stepwise angle-resolved colloidal lithography.

Thanks to the process simplicity, the low cost, and the accessibility of scaling down the feature size into nanometers, colloidal lithography has drawn a great deal of attention once being developed.[8–18] Using highly ordered interstitial arrays within colloidal crystals as masks for deposition allows fabrication of ordered arrays of NPs with circular and triangular shapes, for instance. The geometry, dimension, and arrangement symmetry of NPs derived from colloidal lithography are dependent on the crystal structure of the colloidal templates, the template particle sizes, and the experimental conditions mainly including the plasma etching time, the incidence angle of the vapor beam, and the registry of the colloidal templates with respect to the vapor beam. In the present work, we demonstrate the feasibility of consecutively depositing two different metal vapors, gold and silver, at two different incidence angles, to construct ordered binary arrays of gold and silver NPs.

Prior to metal vapor deposition, the crystal orientation of the colloidal masks, hexagonally close-packed monolayers of 830 nm polystyrene (PS) microspheres, was identified by scanning electron microscopy (SEM). According to their crystal orientation, the masks were first registered so that the vector between nearest-neighboring PS spheres was in line with the projection of the incident vapor beam on the mask, as shown in Figure
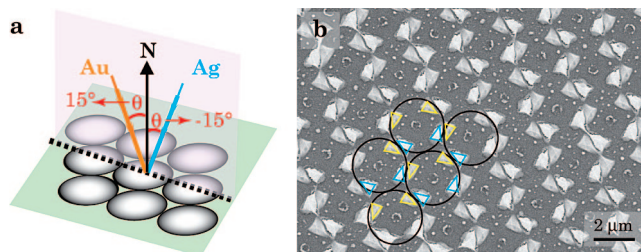
Figure 1. (a) Schematic illustration of depositing gold and silver onto a hexagonally close-packed sphere monolayer at the incidence angles (θ) of 15 and $-15°$, respectively. The colloidal mask is registered so that the vector between nearest-neighbor spheres is in line with the projection of the incidence beam on the mask, highlighted by a black dotted line. The incidence beam of gold, the incidence beam of silver, and the normal direction of the colloidal template are highlighted by yellow, blue, and black arrows, respectively. The incidence angles (θ) of the vapor beam with respect to the normal direction of the colloidal masks are marked as red. Gold and silver NPs deposited on the substrate are highlighted by yellow and blue. (b) SEM image of the resulting heterogeneous binary array. The mask is a monolayer of hexagonally close-packed 830 nm PS spheres. The original location of PS spheres, gold NPs, and silver NPs are highlighted by black circles, yellow triangles, and blue triangles, respectively.

1a. Afterward, gold was deposited at the incidence angle (θ) of 15° (with respect to the normal direction of the colloidal masks) for 40 min at a deposition rate of 0.02 nm/S, corresponding to a 50 nm thick film. Silver was consecutively deposited at θ of $-15°$ for 85 min, corresponding to a 100 nm thick film. After peeling off the colloidal masks using Scotch tape, the resulting nanostructures were visualized by SEM.

As shown in Figure 1b, two different triangular NPs, white and gray NPs interspaced by a tiny gap, were obtained. Each of them was arranged in an array with *P6mm* symmetry. The resulting structures are similar to those derived from metal vapor deposition at zero incidence angle (Figure S1), despite deformation of the NP shape from equilateral to isosceles triangle. The pairs comprising neighboring white and gray NPs were arranged in a rectangular array. Since the SEM imaging mainly arises from the height difference, the gray NPs are thinner than the white NPs. This was further confirmed by atomic force microscopy (AFM) (Figure S2). The energy-disperse X-ray (EDX) spectra of the resulting samples demonstrate coexistence of gold and silver (Figure S3). According to the current experimental conditions, we can therefore conclude that the gray NPs are gold and the white ones silver, demonstrating a lateral heterogeneity of the resulting binary arrays. After post-annealing at 700 °C for 2 h under nitrogen, the white NPs retracted into smaller NPs, while the gray NPs were little changed (Figure
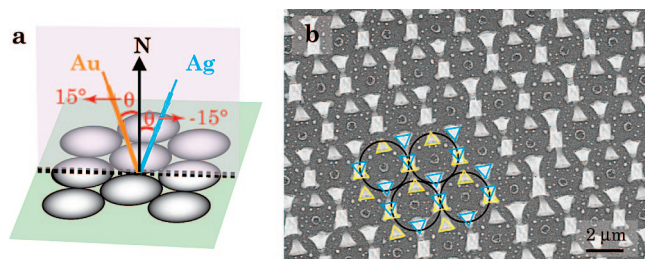
Figure 2. (a) Schematic illustration of depositing gold and silver at the incidence angles (θ) of 15 and $-15°$, respectively, onto a hexagonally close-packed sphere monolayer with the vector between next-nearest-neighbor spheres in line with the projection of the incidence beam on the sphere monolayer. (b) SEM image of the resulting heterogeneous binary array. The mask was a monolayer of hexagonally close-packed 830 nm PS spheres.

S4). This further demonstrates that the white NPs were of silver and the gray ones of gold due to the difference of their melting points.

Since the use of Scotch tape was not able to completely remove the PS spheres, the residuals of the PS spheres were visible in Figure 1b. This provides an easy identification of the original location of PS sphere masks, leading to a better comprehension of formation of the heterogeneous binary arrays. Over the course of metal vapor deposition on a close-packed sphere monolayer, only the voids between three neighboring spheres allow the vapor to reach a substrate, so the geometry of the projections of the voids on the substrate determines the feature of the pattern obtained so. The deviation of the incidence angle of the metal vapor from zero degree is envisaged to cause not only deformation but also the shift from the center of the triangular interstitial projection on the substrates to one vertex. As such, the two-step angle resolved metal deposition led to two different isosceles triangular metallic NPs located with two different vertices of one triangular interstice, leading to heterogeneous binary arrays. Since the vector between nearest-neighboring triangular interstices is not collinear with that between nearest-neighboring spheres, either isosceles triangular gold NPs or silver ones alternately changed their orientation, as shown in Figure 1b.

In the current work, we also registered the colloidal mask so that the projection of the incident beam on the substrates was coincident with the vector between the next-nearest-neighboring spheres prior to metal vapor deposition. Following a similar procedure as mentioned above, afterward, gold and silver films were subsequently deposited on the colloidal mask at θ of 15 and $-15°$, respectively (Figure 2a). The removal of the colloidal mask by Scotch tape led to a new type of heterogeneous binary arrays of metal NPs (Figure 2b), which were composed of gray triangular NPs, white triangular NPs, and white rectangular NPs; each of them was arranged in a hexagonal array. From the topographic analysis by AFM (Figure S5), we learned that triangular gray NPs were of gold and triangular white ones of silver, and rectangular gray NPs were formed owing to superposition composed of one triangular gold NP and one triangular silver NP. This was also clearly demonstrated by the annealing treatment of the resulting binary arrays (Figure S6).

Distinct from those shown in Figure 1, either gold or silver NPs in the new binary arrays obtained kept an equilateral triangular shape with a similar orientation because the incident beam was coincident with the vector of nearest-neighboring triangular interstices. The gold and silver NPs had opposite orientation due to the opposite incidence direction.

In summary, we succeeded in fabricating heterogeneous binary arrays of metallic NPs via stepwise angle-resolved colloidal lithography. The present approach is independent of the sphere sizes of colloidal masks and the chemical nature of materials deposited, while it shows a profound dependence on the registry of colloidal masks with respect to the incident vapor beam and the incidence angle. Such heterogeneous binary arrays are hard to construct otherwise by lithographic techniques. Due to the distinguished lateral heterogeneity, the resulting heterogeneous binary arrays should find promising applications in microelectronics. Thanks to distinct chemical coupling affinity of each constituent NP, they also should provide appealing patterned substrates for chemical or biological sensing. Our ongoing work is to extend the present strategy to other materials to fabricate homogeneous and especially heterogeneous binary arrays of NPs with varied chemical composition and dimension in order to diversify the binary pattern complexity.

Supporting Information Available: Details of experimental method, SEM images of gold/silver nanostructure derived from metal deposition at the incidence angle of zero and gold/silver binary arrays obtained after post-annealing, and EDX spectra and AFM images of gold/silver binary arrays. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA710771J