Glancing angle deposition meets colloidal lithography: a new evolution in the design of nanostructures

Abstract: The combination of colloidal lithography and glancing angle deposition facilitates a new powerful fabrication technique – shadow sphere lithography (SSL), which can greatly expand the variety and complexity of nanostructures fabricated using simple evaporation and colloidal monolayer templates. Their applications have been widely investigated in plasmonics and associated fields. Here, we present an overview of the principle of SSL, followed by different strategies of utilizing SSL to design various nanostructures by changing the nanosphere monolayer masks, deposition configurations, different ways to combine deposition and etching, etc. Typical nanostructures fabricated by SSL, including nanorods on nanospheres, patchy nanospheres, nanotriangles, nanoring, nanocrescents, etc., are introduced. Recent optical applications of these plasmonic nanostructures are also summarized. It is expected that this review will inspire more ingenious designs of plasmonic nanostructures by SSL for advanced and smart applications.

Keywords: shadow sphere lithography; plasmonic; glancing angle deposition; colloidal lithography; nanostructure.

1 Introduction

The periodical array of a close-packed microsphere monolayer was first used as a shadow mask in 1981 for the deposition of platinum disks by Fischer and Zingsheim [1]. Ever since then, this simple technique, termed as natural lithography [2], nanosphere lithography [3, 4], or colloidal lithography (CL) [5], to make microscale and nanoscale patterns has been widely investigated and has evolved to one of the simple and powerful nanostructure patterning processes. Such a CL method is based on the use of colloidal crystals [three-dimensional (3D) CCs] or monolayers [two-dimensional (2D) CCs] (to be general, later, we refer to both as CCs) as masks. In most cases, CCs used for CL mostly are close-packed; however, sometimes, dispersed colloidal layers have been applied. A CL method normally consists of four main procedures: (1) preparation of CCs; (2) modification of CCs; (3) colloidal mask assisted deposition; and (4) colloidal mask assisted etching. Monodisperse microspheres/nanospheres with sizes ranging from tens of micrometers down to tens of nanometers can easily be synthesized by conventional emulsion polymerization and sol-gel techniques or cheaply purchased from commercial companies [5]. Owing to their good monodispersity in size and shape, they can be self-assembled into 2D and 3D periodic CCs [6, 7]. Both the ordered arrays of microspheres/nanospheres and those of the interstices between the spheres of CCs can be used as templates or masks for surface patterning. The CCs can be either etched or deformed to increase the structural complexity of the template or mask. Such a CL process has paved a simple and low-cost route for nanopatterning with a flexibility of feature size <100 nm. Figure 1 shows some examples of typical CL processes to fabricate various nanostructures. Using 2D CCs as masks during evaporation, triangular nanoparticles [8], nanodots [9], and thin film with nanohole arrays [10] have been realized on the exposed substrates (Figure 1A). While using the 2D CCs as masks for etching, nanodisks [11], nanotips [12], or nanopillars [13] have been fabricated on polymer, silica, silicon, and other substrates (Figure 1B). By metal deposition, infiltration, or imprint using etched nanospheres as molds, ordered arrays of spherical voids [15, 21] and nanoshells [14, 22] have been produced (Figure 1C). Through dewetting around nanospheres, nanorings of polymers [16], carbon nanotubes (CNTs) [17], or nanoparticles [18] can be obtained (Figure 1D). In addition to nanostructure arrays...
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with simple geometric shapes, by combining other nanofabrication techniques to modify or sculpture individual nanospheres, more complicated or 3D nanostructures can be produced. For example, by site-selective deposition or etching, nanospheres with asymmetric shape or functional decoration have been realized \[19, 20\] (Figure 1E), which is difficult or impossible to be obtained by other synthetic routes.

Among the four common procedures for CL, material deposition is a key means to design and diversify the resulting nanostructures. Many physical vapor deposition (PVD) methods working in high vacuum or ultra-high vacuum, such as thermal evaporation, electron beam evaporation, and molecular beam epitaxy, as well as other low-vacuum deposition techniques, such as sputtering growth, pulsed laser deposition, and chemical vapor deposition, have been applied in CL. During the deposition, not only the structure of the CC template but also the deposition configuration can be tuned to design different nanostructures. In particular, most PVD deposition techniques can be readily converted into a glancing angle deposition (GLAD) configuration, if the deposition vapors can be intentionally engineered to be highly directional and the substrate temperature is low enough so that limited surface smoothening effects, i.e. low surface diffusion of adatoms, could occur. GLAD alone is another powerful micro-/nano-fabrication technique based on a PVD process where highly collimated incident vapor flux arrives on the substrate at a large angle with respect to the substrate surface normal, causing nanorod-like growth due to a self-shadowing effect \[23\]. Using GLAD, numerous nanostructures have been built by flexibly controlling the deposition parameters, such as incident angle \(\theta\), azimuthal angle \(\phi\), substrate rotation, deposition rate, substrate temperature, and deposition materials \[24–27\].

A typical GLAD configuration is shown in Figure 2A \[28\]. Basically, GLAD is an extension of the commonly used oblique angle deposition (OAD) \[29\] in the thin film deposition community, coupled with the azimuthal rotation of the substrate. In OAD, the incident vapor flux arrives at the substrate at a large angle \(\theta\) with respect to substrate surface normal, which can be tuned by changing the orientation of the substrate through a stepper motor.

**Figure 1**: CL methods to fabricate nanostructures.
(A) Colloidal mask-assisted deposition to fabricate triangular nanoparticles \[8\] (left), nanodots \[9\] (middle), and nanohole arrays \[10\] (right). (B) Colloidal mask-assisted etching to fabricate nanodisks (top left) \[11\], nanotips (top right), and nanopillars \[13\] (bottom). (C) Deposition or imprinting with nanospheres as molds to fabricate spherical nanoshells \[14\] (left) and nanovoids \[15\] (right). (D) Dewetting around nanospheres to fabricate nanorings of PS polymers (left) \[16\], carbon nanotubes (CNTs) \[17\] (middle), and CdSe nanoparticles \[18\] (right). (E) Site-selective deposition or etching to fabricate patchy spheres \[19\] (upper panel) and silica particle labeled with Au NPs \[20\] (bottom panel).
The geometric shadowing effect and surface diffusion of the adatoms account for the main mechanisms for the formation of the nanostructures (Figure 2B), revealing two characteristic features of OAD: self-shadow effect and self-alignment [30]. At the beginning of the deposition, islands with different sizes are randomly formed on the substrates. As the deposition proceeds, short islands will be shadowed by the nearby tall ones and cannot receive more vapor, while the tall islands continuously receive the vapor and grow longer and larger. In the meantime, the adatoms move along the surface due to the surface diffusion and intend to smoothen the islands. As long as the surface diffusion cannot dominate the self-shadowing effect, a layer of nanocolumns tilted toward the incident vapor direction is formed (Figure 3A and A’ [31]). When an additional motor is added to control the azimuthal rotation of the substrate holder, a so-called GLAD configuration is formed. By a single OAD deposition, tilted nanorods are fabricated by fixing the incident angle \( \theta \) at a relatively large value (>75°). When continuously rotating the substrate azimuthally with an appropriate constant speed, vertically aligned nanocolumns are formed (Figure 3B and B’ [31]). If the substrate rotation speed is intentionally slowed down compared to the deposition rate, a continuous formation of nanocolumns along different directions results, since at each rotation interval there will be enough amount of vapor deposited onto the substrate to form nanocolumns with a preferred orientation, this results in a continuous formation of nanocolumns along different directions. Thus, helical nanorod will be formed (Figure 3C and C’) [31]. By controlling the time interval between each revolution and the incident angle, one can control the length and diameter of the rod, the diameter of the helical pitch, and the number of turns of the helical nanorod structure or to even form zigzag nanorods (Figure 3D and D’) [23], C-shape nanorods (Figure 3E and E’) [32], and bead-like nanorods [31] (Figure 3F and F’). In addition to the diverse shapes of nanostructures that can be formed using GLAD, a wide variety of materials, including metals such as Ag, Mg, Ni, V, and Ta, semiconductors such as Si and Ge, and dielectrics such as MgF\(_{2}\), WO\(_3\), and TiO\(_2\), can be used in GLAD [38]. The only limit for the materials is their ability to be deposited via a PVD technique. By combining the morphological design and the depositions of different materials, composite and heterogeneous nanostructures have been realized (Figure 3G–K and G’–K’ [33–37]). The heterogeneous nanostructures can be obtained through a series of depositions of different materials by altering the deposition angle as well as the substrate rotation, while composite nanostructures can be fabricated through co-deposition, in which two or more materials are evaporated and deposited on the substrates simultaneously.

However, it is shown that most nanostructures formed by GLAD on a flat substrate are different variations of nanocolumns. If different 2D or 3D ordered templates/masks can be used in the GLAD deposition system, the variety and complexity of nanostructures fabricated via GLAD can be greatly expanded [39–41]. Such a strategy really depends on how templates/masks are made through conventional or nonconventional nanolithography methods. Among various nanolithography
methods, CL is a good candidate due to its low-cost and efficient fabrication process, as demonstrated in Figure 1. Thus, the combination of GLAD and CL could lead to a new powerful nanofabrication technique, and we call it the shadow sphere lithography (SSL). By replacing the flat substrates by 2D CCs or modified 2D CCs, the shadow effect due to GLAD becomes significantly more controllable. This can lead to sufficient degrees of freedom to design and fabricate a wide variety of nanostructures that incorporate complex geometry with small feature sizes and multiple materials and to generate a large variation of nanostructures for high-throughput screening that may yield unexpected properties. In the following sections, we present an overview of different strategies of utilizing SSL to design various nanostructures, including nanorods on nanospheres, patchy particles, nanotriangles, nano- ring, and nanocrescents, or other complex metasurfaces using either CCs or modified CCs as mask or CL-derived masks. The material of nanostructures can be uniform or heterogeneous, including semiconductors, metal oxides, plasmonic noble metals, magnetic materials, and others as long as they can be evaporated via a PVD technique. The material, mask, substrate, and parameters of the typical nanostructures are summarized in Table 1. A brief update of plasmonic applications of the nanostructures with plasmonic noble metals (Au and Ag) is provided.
Table 1: Parameters of the typical nanostructures fabricated by SSL.

<table>
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<tr>
<th>Strategy</th>
<th>Structure</th>
<th>Example</th>
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<td>PS sphere</td>
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<td>30</td>
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<td>Nanoantennas</td>
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<td>Au/Au/Ag/Pt/Cu/Ti/Cr/Ca/Ge/Ni</td>
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<td>Silver tetramer</td>
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Finally, the challenges and outlook of SSL are summarized to inspire more exciting developments in SSL and other applications.

2 Nanostructures using CCs as a template

2.1 Nanostructures on CCs

2.1.1 Nanorods on CCs

The straightforward combination of GLAD and CL is to use CC (referring to close-packed monolayer except where noted) as a template to grow regular arrays of nanorods, as summarized in Figure 4. For example, tilted nanorods can be fabricated on nanospheres by OAD (Figure 4A) [42, 43]. By changing the speed and phase of the azimuthal rotation, the polar rotation, and the deposition rate, nanorods grown on nanospheres can be sculptured into a single layer or multilayer vertical, zigzag, or helical shaped nanocolumn arrays (Figure 4B) [67]. With a dual-source deposition (co-deposition), the Y-shaped nanorods and the two-layer Janus hetero-nanorods have been easily fabricated (Figure 4C) [44, 45]. During the fabrication, different source materials, such as Cu [45], Cr [68], Ta [69], Si [67], SiO₂ [70], TiO₂ [71], GeSbSe [72], Ti₅Sn₁₅O₁₇ [73], Sn₅Ti₂O₇ [74], Pt [43], Ag [75], Ni [76], CoPt [42], and Fe₃O₄ [77], have been used. Although the basic principle and deposition procedure are the same for fabricating nanorods on flat substrates, there are also unique features for the nanorods grown on CC templates. The size and arrangement of the nanorods are significantly more uniform as compared with those fabricated on flat substrates. Especially, the size and arrangement of the nanorods can be controlled by the CC template [67]. This is explained by the shadowing effect of GLAD and the close-packed 2D CCs with a diameter of D as shown in Figure 5A. If the incident flux angle is fixed at θ and the shape of the nanosphere does not change during the deposition, due to the shadowing effect, the effective diameter d of the grown nanorod is given by [67]

\[ d = D \sin(\theta - \text{arc} \sin(1 - 2 \cos\theta)). \]  

As shown in Figure 5A, the ratio d/D decreases monotonically with the increase of the incident angle θ. Clearly, the diameter of the nanorod is determined by the diameter D of the colloidal particle and the flux incident angle θ. Based on this geometrical model, Dolatshahi-Pirouz et al. have controlled the shape of the individual nanorod by varying θ and the amount of deposited materials [43]. In addition, substrate temperature Tₛ is another important factor to greatly impact the nanorods grown on nanospheres. As shown by Gall et al., when Ta nanorods have been grown on 2D SiO₂ nanosphere CCs at θ = 84° at different Tₛ (from 200 to 900°C) [69, 78], the nanorod morphologies have been significantly different. At low Tₛ (≤300°C), individual nanorods have grown on each sphere, branches of sub-rods are formed near the nanorod tips, and regular hexagonal arrays of nanorods are produced. At high Tₛ (≥500°C), branching starts to emerge during the nucleation stage, and the fraction of branched nanorods decreases with increasing Tₛ [79]. These results are attributed to the increased adatom mobility at elevated Tₛ, leading to stronger inter-rod competition and a larger average separation of growth mounds and, in turn, lower nucleation probabilities for sub-rods.

In addition to experimental studies, the formation mechanisms of Ag nanorods on bare and 2D CC substrates by GLAD have also been investigated via a 3D kinetic Monte Carlo simulation [75]. Jiang et al. have demonstrated three growth stages of the nanorods on a
close-packed spherical seed layer. In the first stage, the Ag film is forced to grow on periodically aligned nanospheres instead of random distribution islands. A periodic seed layer can enforce the formation of uniform nanorod arrays within a certain film thickness. In the second stage, as nanorod height increases, taller nanorods broaden and short nanorods are extinct. In the final stage, the lateral modulation effect of seed layers on the growth vanishes and random Ag nanorods form on the top, which is similar to the nanorod growth on the bare substrate.

Gall et al. have built a simultaneous opposite glancing-angle deposition (SO-GLAD) system (Figure 5B) to fabricate nanorod arrays on CCs with laterally stacked components (or Janus nanorods) [44]. During SO-GLAD, two different materials are deposited simultaneously.
from opposite directions both at oblique angles onto a 2D CC template. The shadowing effect caused by the nanospheres allows the selective deposition of only one material on one side of each nanosphere, leading to the formation of nanorods with two laterally separated components. In addition, other nanorod arrays, such as Cu Y-shaped nanorods (Figure 4C') [45], Cr-Si two-component multi-stack nanorods [68], Si-Ta two-component rods (Figure 4C'') [37], zigzag two-component nanosprings [37], vertical multilayer nanorods [37], and a checkerboard arranged nanorod array [37], have also been fabricated based on this SO-GLAD technique.

2.1.2 Patchy particles

Patchy particles, defined as particles with precisely controlled dual or multiple patches of varying surface and interaction properties, are a special type of particle used to assemble photonic crystals, fabricate targeted drug delivery system, and produce components for nanoelectronics [81, 82]. In SSL, upon deposition, the nanospheres in 2D or 3D CCs will receive evaporated vapors, and patches of different shapes can be formed on the nanospheres. In general, during SSL, the vapor incident angle \( \theta \) determines the coverage of the patch on a nanosphere; i.e. the patch coverage decreases with increasing \( \theta \), and the azimuthal angle \( \phi \) determines the shape of the patch. As shown in Figure 6A, through a single OAD, partial shells covering half spheres can be fabricated [83–85]. With increasing \( \theta \), the surface coverage (patchiness) of the shells can be reduced from 50% to 3.7% (Figure 6B–D) [46]. The shape of the patches is very sensitive to the azimuthal angle \( \phi \) and is repeated within a period of \( \Delta \phi = 60^\circ \) for the hexagonally arranged CCs. The change in incident and azimuthal angle leads to a large variety of patchy particles (Figure 6B–D) [86–90]. Thus, the SSL is a powerful technique to prepare patchy particles and can control the shape and surface coverage. When the azimuthal angle is sequentially or continuously changed during patchy particle preparation, patchy particles with complicated shapes can be produced. Zhao et al. have used a swinging GLAD strategy to produce patchy particles with uniform size, shape, and plasmonic response (Figure 7A) [47]. Swinging the colloid substrate azimuthally causes the domain orientation to rotate away from the initial orientation \( (\phi_0) \) through a prescribed angle range \( (\Delta \phi) \) during the deposition. Thus, during a deposition, the symmetry inherent in the close-packed colloidal monolayer can be utilized to produce patchy particles with the desired uniformity without the complications of a prefabricated template or other special colloid layer preparation steps.

Through two subsequent OAD depositions with different \( \phi \), the shape of the patches on the patchy particles has been further widened [91–93]. For example, Lei et al. used stepwise OAD of two metal layers on a
centimeter-scale self-assembled dielectric microsphere array to produce large-area stacked-patch plasmonic chiral metamaterials (SPPCMs) [94]. Kretzschmar et al. used two sequential vapor depositions with $\Delta \varphi = 60^\circ$ to fabricate overlapping patches on the same hemisphere of the particle, as shown in Figure 7B [48]. In such a way, L-shaped Ag nanostructures composed of two rectangular shaped stripes with different thicknesses are prepared by controlling substrate azimuth angle and deposition time [95]. These ordered patchy particles show strong optical chirality in visible and near-infrared (IR) regions. If three subsequent OADs are performed at three different $\varphi$, three patches will be deposited on the nanospheres to form fan-shaped structures. For example, through three OADs with $\theta = 86^\circ$ and $\Delta \varphi = 120^\circ$, three identical patches are overlapped onto hexagonal close-packed CCs, forming fan structures (Figure 7C) [49, 96–99]. The Ag fan structures on 500-nm-diameter polystyrene (PS) spheres demonstrated a strong, visible, light circular dichroism response. In addition, during multiple OAD processes of patch formation, if the deposition materials can be alternated, the chemical ordering of the resulting patch can be modulated, and even more complicated patchy particles can be designed. By seven OADs and controlling the azimuthal rotations of the 2D CC substrate, Ag and SiO$_2$ layers can be helically stacked in left-handed and right-handed fashions to form a continuous helically stacked structure (Figure 7D) [50]. The wavelength range of the circular dichroism response of these helical structures can be tuned by the diameter of the nanospheres. Furthermore, more complicated 3D patchy structures, such as conical Swiss roll structures on nanospheres, can also be fabricated by combining swing GLAD and multiple alternating depositions of Ag and SiO$_2$ (Figure 7E) [51]. The resulting chiral plasmonic structures show a broadband circular dichroism response.

If the nanosphere template is manipulated or altered during the multiple depositions, additional types of patchy particles can be fabricated. One method is to use polydimethylsiloxane (PDMS) stamping to inverse the CC monolayers for two subsequent depositions onto the upper and lower half surfaces of the nanospheres (Figure 8A) [100]. Hollow spheres with windows of controlled size and number have been fabricated, which can be used as nano-carrier, for drug transport, and as nano-research containers. In addition, by changing the lattice structure of the CCs, the patches on the nanospheres can be altered. For example, linear chains of nanospheres can be self-assembled by the V-shaped or square-shaped grooves in a Si wafer [101, 103]. The patch shape and size on those nanospheres can be controlled by the vapor incident angle $\theta$, nanosphere...
diameter $D$, the dimensions of the grooves, the vapor flux azimuthal direction with respect to the groove direction ($\alpha$), and the number of deposition and evaporated materials (Figure 8B). The dimensions of the grooves add another degree of freedom to design a large variety of asymmetric patchy particles. The nanosphere monolayer can also be replaced by two-layered or multilayered CCs to form different patches on lower layered nanospheres. Zhang et al. used this strategy to produce diverse Au nanosized dots on the lower layer spheres by using the upper layer nanospheres as masks for deposition (Figure 8C) [102]. Such a strategy uses the top nanosphere monolayer(s) as a mask and the lower nanosphere monolayer(s) as a template.

The main advantage of fabricating patchy particles by SSL technique is that it can accurately position patches onto the surfaces of nanospheres controlled by
simple geometric rules and the patch materials can be widely altered as long as the material can be evaporated. However, there are still many challenges for using SSL to fabricate high-quality patchy particles. The biggest challenge is the domain orientation and alignment of the nanosphere monolayer. The nanosphere monolayer used in most studies has a hexagonal lattice, which possesses a sixfold symmetry. The patch shape depends on the domain orientation, leading to diverse nanostructures. Figure 9 shows a true-color optical image captured for a stacked-patch nanosphere monolayer under unpolarized white light illumination [94]. The micro-sized regions of different reflection colors represent microscale domains with different lattice orientations and geometric morphologies, which means that the nanostructures on the nanospheres are different. According to Figure 6, as long as one performs a single OAD, since different domains have different \( \phi \) with respect to the azimuthal vapor incident direction, the shape of the patches on nanospheres in different domains will be different. Especially if the \( \theta \) is closer to 90°, the significance of the difference in patch shape will become greater. One way to resolve this issue is to make large-area, single-domain monolayers and pre-align the domain orientation with respect to the azimuthal direction of the incident vapor flux. However, large-area, single-domain monolayers are not easy to achieve experimentally and the alignment needs extra work. There are also alternative ways that have been developed to reduce the influence of domain orientation. A template can be used to assist the self-assembly of nanosphere monolayers so that small patches of monolayers with the same orientation can be formed, thus leading to the same shadow effect [101, 103]. In addition, if the substrate with 2D CCs is swung (rotated azimuthally back and forth) azimuthally during the deposition, symmetry inherent in the close-packed nanosphere monolayer can be utilized to produce patchy particles with uniform size, shape, and plasmonic response (Figure 7D) [47]. Finally, if subsequent multiple depositions can cover a 360° azimuthal rotation, since different shaped patches can be produced at different depositions at various monolayer domains, the resulting patchy particles inherently have the same morphology and thus demonstrate the same property. For example, the conical Swiss roll structures (Figure 7E) have properties independent of the orientations of monolayer domains, which leads to a very uniform array [51]. Recently, with multiple depositions of Ag and SiO₂ at different relative \( \phi \), a uniform large area broadband optical absorber has been designed based on the plasmonic response of different shapes of Ag patches on nanospheres [104]. While the presence of multiple domains complicates the fabrication of large-area homogeneous patchy particles, it is useful in high-throughput screening of patchy particles when a diverse set of patch features on a single sample is required. For instance, the multiple domains created on a single SSL-fabricated surface with multiple domains can be characterized locally to establish a patch shape-property relationship via a one-step deposition so that a desired patch shape can be easily identified for specific property optimization.

2.2 Nanopatterns on substrates using CCs as mask

2.2.1 Nanotriangles

Using CCs as a shadow mask, different nanopatterns can be designed and produced on substrates through direct deposition. Like the formation of different patchy particles, multiple depositions or multilayer deposition can also be used to design complex nanopatterns on the substrates. One typical structure that forms through such a strategy is a nanotriangle array, which can be fabricated by direct vertical deposition through close-packed nanosphere monolayers [3]. The shape and size of the nanotriangles strongly depend on vapor incident angle \( \theta \) and azimuthal angle \( \phi \) (with respect to the orientation of
monolayer domains) due to a simple geometric shadowing effect [52]. By a single OAD deposition, elongated triangles are formed (Figure 10A). Such a deposition not only can change the size of the resulting nanotriangles but also introduce anisotropy in produced nanostructures, leading to anisotropic physical and chemical properties [52]. By two subsequent depositions with different relative $\theta$ and $\varphi$, nanotriangles with overlap, nanocontacts, and nanogaps were fabricated [105]. When the $\theta$ was the same, but with two opposite deposition directions (+$\theta$/$-\theta$), bow-tie-like triangles with small gaps have been fabricated [106]. By three subsequent depositions with different relative $\theta$, chains of nanotriangles are formed [105]. By four subsequent depositions and carefully adjusting of $\varphi$ and the deposition thickness, complicated structures such as chiral plasmonic oligomers composed of four achiral triangles have been successfully produced and demonstrated [107]. Examples of the triangular dimers, trimers, and quadrumers can be seen in Figure 10B [53]. In addition, the triangular shape can be modulated when the substrate is continuously rotated azimuthally at different vapor incident angle $\theta$ during deposition. A transition from triangles to polygonal shapes then to triangle network-like structures has been observed when $\theta$ changes from 0° to 20° during the deposition of Ag by continuously rotating the substrates (Figure 10C) [54, 108, 109]. For the triangle network-like structures with $\theta = 20°$, if a second deposition was implemented, nanoparticle-in-ring arrays would be fabricated [110].

2.2.2 Nanorings and nanocrescents

Another typical structure fabricated on substrates by SSL is nanocrescent. Nanocrescent is a symmetry-broken structure and has shown a range of interesting phenomena due to the reduction of symmetry. Figure 11A shows a typical process to fabricate nanocrescents based on SSL [55, 112, 114–116]. First, randomly dispersed or ordered nanospheres are formed on substrates to act as template [or for close-packed 2D CCs, the nanospheres are usually etched via a reactive ion etching (RIE) process to introduce the separations between nanospheres]. Then, metal is deposited on the nanosphere-covered substrate.

![Figure 10](image_url)  
**Figure 10:** SEM images of the nanotriangles fabricated by SSL.  
(A) SEM images of triangular NPs and images with simulated geometry superimposed, respectively. (A1, A2) $\theta = 10°$, $\varphi = 28°$, (B1, B2) $\theta = 20°$, $\varphi = 2°$, (C1, C2) $\theta = 26°$, $\varphi = 16°$, and (D1, D2) $\theta = 40°$, $\varphi = 2°$ [52]. All samples are Cr deposited onto Si (111) substrates. (B) SEM images of the touching triangular dimers, trimers, and quadrumers fabricated by two, three, and four OADs, respectively. The evaporation and rotation angles $\theta$ and $\varphi$ are depicted below each image [53]. (C) SEM images of the triangular NPs fabricated by GLAD with continuous rotation at $\theta = 0°$, 10°, 15°, and 20°, respectively [54].
with an adjusted incident angle $\theta$. After deposition, ion beam milling is performed vertically to remove the metal layer that is not masked by the nanospheres. Here, the nanospheres are acting as masks that prevent anything inside the projected areas being etched. Finally, the nanospheres are removed and the metal layers left under the projected areas of the nanospheres form nanocrescents on substrates (Figure 11B). In the process, the size and shape of nanocrescents can be controlled by the size of nanospheres, deposited thickness of metal, incident angle $\theta$, as well as the azimuthal rotation. In fact, the desired nanocrescent shapes can be modeled by a 3D profile simulation [56], which can provide the guidance in fabrication of nanocrescents.

The typical process has been extended to fabricate various nanocrescent-derived nanostructures. When the substrate is rotated with respect to the surface normal by an azimuthal angle $\phi$ ($\phi < 180^\circ$) with subsequent multidepositions, stacked nanocrescents from an open crescent to a fully connected ring are obtained (Figure 11C) [111]. When $\phi = 180^\circ$, opposing nanocrescent dimers with sub-10-nm gap between the tips of the final crescent can be fabricated [117]. If a dielectric layer is deposited prior to the second deposition, one can obtain stacked double-crescent arrays [118]. In such a way, 3D densely packed arrays of nanocrescents have been fabricated by applying the above process twice with a SiO$_2$ space layer at two different $\phi$ [119]. In addition to changing $\theta$ and $\phi$, the etching process can also be varied; e.g. perpendicular metal etching can be expanded to tilted etching to provide more opportunities to produce nanocrescents in various shapes [120]. The final profiles after perpendicular or tilted etching can also be calculated as references for the fabrications [57].

Sutherland et al. have also developed an alternative method to fabricate nanocrescents by continuously rotating the substrate, eliminating the metal milling step [113]. The concept is to use the nanospheres to deposit a structured sacrificial layer (e.g. SiO$_2$) around the nanoparticle to define an adhesive region (e.g. Ti) on the surface. Then, OAD is used to deposit a metal nanostructure onto the adhesive domain. The shape is determined by the gap between the nanospheres and the sacrificial layer. Nanostructures of nanorings or nanocrescents are formed after the removal of the nanospheres and the sacrificial material (Figure 11D). The process step of changing the deposition angle of the sacrificial layer gives the opportunity to systematically control the shape of the final pattern. In addition, other processes have also been developed to fabricate nanocrescents based on SSL. For example, SSL and parallel imprint have been combined to fabricate long-range ordered crescent structure arrays [121]. First, silicon crescent nanohole arrays have been fabricated based on SSL, whose complementary structure can be replicated by PDMS. After metal deposition on the PDMS model, nanocrescent particle arrays can be duplicated onto various substrates by parallel imprinting. The parallel printing method greatly improves the reproducibility of the fabrication process and also reduces the cost. In addition, by incorporating a sacrificial copper layer in.
SSL, aluminum plasmonic nanocrescent antennas have been fabricated over large substrate areas [122]. The addition of the copper mask eliminates the argon ion milling step, which is challenging to implement for aluminum nanostructures because of the robust native oxide layer.

In addition to SSL, other templates can also be used to create nanoring and nanocrescent structures. Jiang et al. have reported a scalable bottom-up approach for fabricating periodic arrays of metal nanorings and nanocrescents [123]. First, nanoring-shaped trenches between templated polymer posts and sacrificial nanoholes have been created. Then directional deposition of metals in the trenches, followed by liftoff of the polymer posts and the sacrificial nanoholes, results in ordered metal nanorings. By simply controlling the vapor deposition angle $\theta$ of the metal beams, continuous geometric transition from concentric nanorings to eccentric nanorings and even to nanocrescents has been achieved. Giersig et al. have fabricated nanorings and nanocrescents based on the deposition through the circular aperture formed using the close-packed CCs [124, 125]. In addition to the nanocrescent particles, crescent nanohole arrays have also been realized by varying the SSL fabrication processes [115, 121].

### 2.2.3 Other nanostructures fabricated on substrates

Besides the two representative structures, the nanotriangles and nanocrescents, other complex nanopatterns can also be generated by controlling the parameters in the SSL process [126, 127]. Kostinski et al. considered a set of possible 2D patterns accessible via periodic SSL [128]. A topological characterization based on overlap of shadows has been proposed and a variety of patterns is reduced to $4 + 1$ topologically distinct groups. The authors have developed phase diagrams linking the five topological groups from any lattice geometry to experimental rotation and tilt angles. The phase diagrams are readily constructed for a variety of configurations by plotting contours of zero-valued Cayley-Menger determinants containing the desired sphere radii and lattice vectors and can guide CL experiments.

Experimentally, by using $O_2$-plasma etched bilayers of hexagonally packed spheres as templates, Wang et al. have fabricated highly ordered binary arrays of gold nanoparticles with varied shapes, such as a shuttlecock-like shape composed of a small crescent-shaped nanoparticle and a big fan-shaped one [129], and two different triangular nanoparticles interspaced by a tiny gap [130]. The size and shape of both small and big nanoparticles obtained are manipulated by the plasma etching time and the incidence angle $\theta$ of Au vapor. The subsequent thermal annealing leads to binary arrays of round Au nanoparticles with a rather narrow distribution in terms of size and shape. Based on a similar strategy, they have successfully demonstrated a stepwise SSL process to grow highly ordered multiplex quasi-3D grids of metallic one-dimensional nanostructures, e.g. nanowires and nanorods [131]. In addition, elliptical holes can be created by simply tilting the substrate during the metal deposition [10, 132]. The ellipticity of the holes depends on the size of the nanospheres and the vapor incident angle $\theta$; smaller nanospheres with a larger $\theta$ produce ellipses with higher aspect ratios.

Recently, Whitesides’s group presented a detailed and systematic work on producing an extensive variety of complex 2D metasurfaces based on SSL (Figure 12) [58]. They showed that rationalizing the vast and almost entirely unexplored parameter space of shadow-derived shapes enables a substantial expansion of the spectrum of structures that can be generated by projection through 2D CCs. Their approach uses custom-designed software to predict the shadows that guide multiangled deposition of one or multiple materials through a plasma-etched 2D CC. Through a comprehensive exploration of the space of available shadow-derived shapes, they have found that the patterns that result from different combinations of $\theta$ and $\phi$ generally belong to a set of five classes: (1) interconnected lines, (2) asymmetric bars, (3) symmetric bars, (4) triangular islands, or (5) an interconnected, honeycomb-like lattice. Each feature can be duplicated at $\phi = 60^\circ$ intervals due to the sixfold (C6) rotation symmetry of the hexagonal lattice. Varying the azimuthal angle $\phi$ produces continuous transitions between the different classes of shadows and offers many intermediate positions and shapes; varying the polar (incident) angle $\theta$ or the gap between the spheres controls the position, length, and width of each feature.

Although numerous structures have been fabricated on substrates based on SSL, challenges still exist. The major obstacle encountered when using SSL to fabricate patterns on substrates is the inability to control mask registry $\phi$, i.e. the orientation of the 2D CC domains. Because 2D CC growth results in multiple hexagonally close-packed domains with random orientations (Figure 9), the shape, size, and spacing of the resulting structures could vary in different domains since the detailed shadowing effect is different for different deposition configurations. While the presence of multiple domains introduces the inhomogeneity in the fabrication of large-area homogeneous structures, it could be useful in high-throughput
screening a diverse set of nanostructures. For instance, if a local property characterization technique can be used and the location of a substrate can be registered, then a quick structure-property relationship can be established using the structures fabricated via a multi-domain 2D CC. If the resulting CC is a single domain, the alignment of the domain orientation with respect to vapor deposition direction $\phi$ becomes important. However, for small-diameter nanospheres such as diameter $<500$ nm, it is a big technical challenge to achieve such an alignment. Moreover, for multiple depositions, in most simulation programs, only the shadowing effect due to bare nanospheres is considered, and the additional shadowing effect due to the deposited layers on top of the nanospheres or side walls of previous deposition is usually not considered. The additional shadowing effect could produce structures with distorted shape/pattern compared to those predicted by the simulations. To minimize the effect, sometimes, multiple depositions with smaller thickness at different $\theta$ and $\phi$ conditions can be used [49].

3 Nanostructures using CL-derived masks

3.1 Using a CL-derived hole as mask

In SSL, not only the configuration of the deposition and the locations of materials deposited on CCs are important, but also the masks or templates used are critical. As discussed above, the nanosphere monolayers or multilayers (3D CCs) can serve as templates or masks to design various nanostructures. They can also be used as templates or masks to design other templates or masks to fabricate more complicated nanostructures using the shadowing effect. For example, the nanohole arrays fabricated by CL constitute one of the most used masks, and nanofabrication using holes as mask can be called as hole-mask CL (HCL) [62, 133, 134]. The basic fabrication steps in HCL are shown in Figure 13 [134]: (1) A sacrificial thin film [e.g. polymer such as poly (methyl methacrylate) (PMMA) or dielectric

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Figure 12: SEM images of nanoantennas designed and fabricated by SSL. Patterns composed of two to three (A), four (B), and five to six (C) different angles of deposition. (D) Subset of possible unit cells categorized according to optical function as designed (left) and fabricated (right), adapted from Ref. [58].
such as SiO$_2$] is spin-coated or deposited onto a flat surface (Figure 13A). (2) Nanoholes are fabricated by a typical CL process [10] on the sacrificial layer (Figure 13B and C). It should be noted that the nanoholes are usually dispersed. (3) Reactive plasma etching is applied to selectively and isotropically remove the sacrificial polymer or dielectric layer exposed underneath the nanoholes (Figure 13D). The etching selectivity of the double-layer film (the mask material and the sacrificial film) leads to a partial undercut of the sacrificial film. (4) GLADs with varied configuration parameters are carried out (Figure 13E). (5) The sacrificial layer and the mask are removed to leave the nanostructures on the substrates (Figure 13F). The essential feature of HCL is the presence of a sacrificial layer combined with a thin film mask with nanoholes. The hole mask is used in shadowing evaporation and/or etching to define a nano-pattern. The sacrificial layer is used not only to define the projected pattern and boundary but also to remove the hole mask in the last processing step. By using the process with only one simple OAD, nanodisks (Figure 14A) [133] and tilted pillars [138] have been fabricated. If two OADs have been performed at opposite azimuthal directions, nanodisk dimers with overlaps or gaps can be designed (Figure 14B) [60, 61, 139]. Heterotrimers (Figure 14C) and heterotetramers (Figure 14D) composed of closely spaced silver and/or gold nanodisks of different heights have also been prepared through HCL by three and four OAD depositions, respectively [136]. The parameters of the disk can be well controlled by the hole size and the OAD configuration parameters $\theta$ and $\phi$. If the hole mask can be rotated in both the polar and azimuthal directions, ring or split-ring structures can be produced (Figure 14E) [134, 140, 141]. Clearly with the HCL, the materials are not limited to evaporation but they can also be deposited via electroplating or other methods [63]. In addition, heterostructures such as Ag/Au [139], Au/Co [141], and Pt/Ru [60] hetero-nanodisk dimers can be produced with multilayer depositions.

The shape and related geometric parameters of the nanostructures fabricated by HCL can be calculated based on the simple geometric shadow model. The control of the azimuthal angle $\phi$ and the incident angle $\theta$ in combination with the sacrificial layer thickness $h_0$ determines the outer radius of the ring ($r$) and the gap size $s$ (opening of the ring), with the parameters defined in Figure 13. The radius $r$ is given by

$$r = h_0 \tan \theta,$$

and the gap size $s$ is determined by

$$s = 2\pi r \frac{360^\circ - \phi}{360^\circ} = 2\pi h_0 \tan \theta \frac{360^\circ - \phi}{360^\circ}.$$

The width $w$ is determined by the mask-hole diameter. The structure height $h$ can be calculated by the equation

$$h = h_1 \frac{45^\circ w}{\nu h_0 \tan \theta}.$$

Here, $h_1$ is the evaporated material thickness. By applying two rotated depositions based on this geometric model, asymmetric double split-rings have been fabricated (Figure 14F) [137]. By varying the polar rotating speed of the samples during gold evaporation, Giessen et al. have fabricated spiral-type ramp split-ring structures [142].
Also, a series of split-ring nanoantenna placed directly on top of a magneto-plasmonic ring element have also been produced using a similar strategy [143]. Other complex plasmonic nanostructures (e.g. split-ring with different orientations) can be fabricated using multiple repetitions of HCL [59].

The typical fabrication process shown in Figure 13 can be modified by dynamically changing the hole size or sacrificial layer thickness during the deposition. For example, the diameter of the hole can be shrunk by evaporating Ti at a high $\theta$ angle ($\geq 70^\circ$) with continuous azimuthal rotation [135]. Due to the shadowing effect around the hole, Ti will only be deposited around the side wall of the holes, and such a lateral growth continuously makes the hole diameter smaller. Such a strategy could ensure a continuum modification of the mask during the deposition. In addition, Sutherland et al. have reported an extension of HCL to fabricate gradients of nanostructures with systematically varied nanostructure features to screen the properties of plasmonic arrays by modulating the polymer sacrificial layer thickness across the sample prior to creation of the hole mask [144]. A gradient in polymer film thickness can be translated into a gradient of the nanostructure feature size by using OAD [see Equations (2) and (3)]. Käll et al. introduced another SSL methodology – evaporation on a partially exposed rotating substrate with hole mask – to generate continuous and precise gradients in nanoscale structure parameters, including vertical thickness, lateral positioning, and orientation, based on controlling the relative movement between a supporting substrate and a partial shutter during material evaporation [64]. Nanodisks with continuously varying thicknesses, sandwich structures with a gradient in the spacer thickness, nanoparticle dimers with continuously increasing gap distances, and split-ring nanoparticles with continuously changing orientations have been fabricated based on this strategy. In addition, SSL using hole as mask can also be used to fabricate an array of plasmonic opposite metal spindles in nanowells (Figure 15A) [65], nanopores containing nano-crescent particles (Figure 15B) [66], and 3D nanodishes that serve as small plasmonic containers to host guest nanoparticles (Figure 15C) [145].

### 3.2 Using other CL-derived masks

In addition to using holes as templates or masks in SSL, other different kinds of templates and masks derived from nanosphere monolayers have also been investigated. By using inverted hemispheres as a template for...
SSL, Jin et al. have fabricated a periodic array of 3D crescent-like holes [146]. First, a PS film perforated with a hexagonally non-close-packed dimple array is generated by heating a silica nanosphere monolayer on top of the PS film. Then, an OAD is employed to deposit a layer of silver on the patterned PS film to form a 3D crescent-like hole array. The silver covered area within each individual dimple is controlled by the vapor incident angle $\theta$. If a second OAD has been employed from the opposite azimuthal direction, an array of non-planar nano-arc-gaps will be formed [147, 148]. The gap width of the nano-arc-gaps can be tuned via the angle $\theta$. If $\theta$ becomes bigger, the width of the gap can be larger.

Using nanodisks (e.g. Figure 14A) or the triangular shaped nanodots (e.g. Figure 10A) formed via SSL as templates, ordered arrays of Si nanorods and nanospirals have been produced [149–152]. Prepatterned honeycomb-like and hexagonal closed-packed arranged Au nanodots have been obtained by CL using self-assembled mono- and double layers of PS nanospheres, and Si nanostructures have been deposited onto these nanopatterns via GLAD. The morphology of the Si nanostructures deposited on the nanodots depends strongly on the deposition angle $\theta$ [151]. A continuous film with honeycomb-like arranged hillocks has been produced at $\theta = 0^\circ$. With the increased $\theta$ ($\leq 70^\circ$), the nanostructure changes to dense columnar films with a mesh of hexagonally arranged pores. Finally, when $\theta$ becomes larger than $85^\circ$, separated rod-like structures with a triangular cross-section are formed. The nanodots or nanodisks can also serve as an etching mask (or nanostructured seed layer) for GLAD via an RIE or a chemical etching process [153]. The nanodots or nanodisks formed after RIE can have a much higher aspect ratio (i.e. depth) compared to similar structures formed via direct SSL, so that when a Si GLAD is performed on these templates, a better self-alignment effect can be achieved and less growth of Si nanostructures in between the nanodots could occur. Similarly, inverted pyramid hole patterns have been created as templates for GLAD via anisotropic etching of Si (001) substrates, leading to the formation of a network of nanochannels surrounded by arrays of vertically aligned nanorods after a subsequent GLAD [150, 154]. Here, nano-triangular-shaped Cr masks have been fabricated onto the Si (100) substrates via a conventional CL, and inverted-pyramidal pit arrays are formed using an anisotropic chemical etching process. Many other nanostructures have been also designed using similar strategies. For example, nanocones and nanopillars formed via an RIE process by CL have been used as mask in SSL to fabricate half-cone shells [155, 156] and Janus nanopillars [157–159], respectively. All these results demonstrate that substrate patterning by CL is very useful in SSL to design more complicated nanostructures.

### 4 Plasmonic properties of the nanostructures fabricated by SSL

The nanostructures fabricated by SSL have been widely exploited in various fields, including nanomotors based on Janus nanorods on spheres [70, 71], self-assembly based on patchy spheres [81, 160], magneto-optical activity [143], anisotropic wettability [156, 157], cell growth behaviors on nanotopographies [144], electrocatalytic properties [60, 144], plasmonics, etc. Among these applications, plasmonics is one of the most widely investigated fields due to the fact that numerous noble metal nanostructures can be easily fabricated by SSL. In the following, we will mainly show some examples of the applications of the above structures (as classified in patchy particles, nanotriangles, nanocrescents, and structures fabricated by HCL) in plasmonics.

Patchy particles have been designed to show strong chiral optical properties by controlling the patch shape and material deposited on the spheres, which can be used for chiral optics and sensors. Fan-shaped Ag
nanostructures (Figure 7C) have been designed on nanoparticles by three subsequent OADs with a relative difference of 120° in azimuthal angle based on the shape of the patch [49]. The relative rotation direction during OADs breaks the racemic symmetry, leading to a different distribution of the amount of Ag on three patches of the fan shape, which results in the chirality of the optical response. However, structural handedness varies locally due to the sixfold symmetry of the lattice and different orientations of the monolayer domains (see discussions in Section 2.2.3). Thus it is very hard to realize the same handedness within a large substrate area [97]. To address this issue, other improved methods have been developed. By controlling the azimuthal rotation of substrates as well as the deposition materials, Ag and SiO₂ layers have been alternatively deposited by OADs on to nanoparticles and helically stacked in left-handed and right-handed fashions to form helices of Ag patches (Figure 7D), called helically stacked plasmonic layers [50]. The pitch and diameter of the stacked helices are determined by the diameter of nanoparticles, the vapor incident angle θ, and the layer thicknesses of Ag and SiO₂. These plasmonic helices exhibit strong chiroptical responses in the visible to near-IR region, which can be tuned by changing the diameter of nanoparticles. With such flexibility in the design, helically stacked plasmonic layers may act as tunable chiral metamaterials, as well as serve as different building blocks for chiral assemblies. Based on stepwise

**Figure 16:** Stacked-patch plasmonic chiral particles.
(A) Left: Schematic diagram of two-step GLAD on a self-assembled microsphere monolayer. The black dashed lines labeled with “Projection 1”, “Projection 2”, and “Projection 2’” are the in-plane projections of the material vapor beams 1, 2, and 2’ in the substrate plane, respectively; θ is the deposition angle of the vapor beam with respect to the normal of the substrate (red dashed line); ϕ is the azimuthal angle with respect to the reference direction of the microsphere array (black dashed line labeled by “Reference line” overlapped with “Projection 1’); and Δϕ = ϕ₁ - ϕ₂ is the relative change in azimuthal orientation of the substrate between the first (ϕ₁) and second (ϕ₂) material deposition processes. Right: left-hand (LH) (upper-right) and right-hand (RH) SPPCMs (lower-right) can be prepared, respectively, by two sequential coatings of Ag films following either a clockwise (Δϕ = +45°) or anticlockwise (Δϕ = −45°) direction. (B) Top-view SEM image of a 90 nm-thick LH-SPPCM prepared at θ = 60°, Δϕ = +45°. The scale bar in all panels is 1 μm. (C) Measured CD spectra for an LH- (black) and an RH- (red) SPPCM prepared at θ = 60° and ϕ₁ = 0° with Δϕ = ±45°, respectively. The deposition thickness of two Ag films is 90 nm and the diameter of PS spheres used here is 430 nm, adapted from Ref. [94].
GLADs of two metal layers, 3D SPPCMs with high structural degree of freedom have been fabricated, as shown in Figure 16 [94]. Sophisticated modifications based on symmetry considerations to the deposition parameters used in previous GLAD recipes eliminate the undesirable yet unavoidable nature of racemic mixture induced by the long-range disorder of the monolayer domains, resulting in plasmonic chiral metamaterials with definite handedness over macroscopic areas and consequently an order of magnitude enhancement of circular dichroism (CD) over nearly the whole visible spectrum. The CD response can be flexibly controlled by adjusting the deposition conditions and used in refractive index sensing [99].

2D plasmonic structures fabricated on substrates by SSL have been investigated extensively during the past decades. Fano resonance and chiral response have been obtained by the nanotriangles fabricated by SSL, either improving figure of merit (FOM) or showing great potentials for sensing chiral molecules. Giessen et al. utilized triangular building blocks fabricated by SSL to build large-area (10 x 10 mm²), high-quality dimers, trimers, and quadrumers (Figure 10B) with reproducibly small gaps and desired well-defined structural gapless shapes [53]. The triangle oligomers can excite “self-induced” coupling between fundamental dipolar modes and higher-order modes within the same structure that lead to Fano resonances. Fundamental modes, higher-order modes, as well as Fano resonances due to coupling between bright and dark modes within the same complex structure depend on the polarization of incident light and the geometry of the plasmonic structures. Fano resonances occur, in particular, for the case when the plasmonic triangles touch each other by controlling the θ and φ. For this situation, structural symmetry breaking allows for tuning the modes and the shapes of the Fano resonances. These plasmonic triangle oligomers have been used as a refractive index sensor with a theoretical FOM exceeding 15. The triangles can also be used as building blocks to form chiral plasmonic oligomers based on the stepwise SSL [107]. Their chirality is dependent on the anticlockwise or clockwise deposition sequence of the achiral particles. A large chiroptical resonance in the visible region was achieved, and this resonance can be easily adjusted by using CCs with different nanosphere diameters.

Nanocrescents fabricated by SSL can exhibit strong polarization-dependent resonances in the visible and IR regions of the electromagnetic spectrum. The spectra can be controlled by the structural parameters, which are good for optical filter and localized surface plasmon resonance (LSPR) sensors. Due to the sharp corners of these structures, the crescents are expected to produce a highly enhanced optical near-field and behave as optical antennas [114]. These resonances are strongly dependent on the electric-field polarization of the incident light and were of the same type as required for magnetic resonators. As shown in Figure 17, four extinction peak maxima have been measured for crescents. Most of the extinction peaks are highly sensitive to the orientation of the particle in the polarized light beam. When the long axis of the crescent is orthogonal to the electrical-field polarization, the particles exhibit a strong resonance at 830 nm. When the long axis of the crescent is parallel to the electric field of the polarized beam, the resonance at 830 nm disappears and resonances appear at 1300 nm and 1958 nm. All four resonances have been excited when the crescent orientation is rotated by 45° with respect to the electric-field polarization, as expected for dipolar resonances parallel and perpendicular to the symmetry plane of the crescents. The plasmonic properties can be controlled by the parameters of size, film thickness, opening, and metal deposition angles of the structures [115]. Significant shifts in resonance position are observed when the size or the opening angle of the structures was varied, allowing for a fine tuning of specific resonances in a desired wavelength range. Fundamentally, different responses can be seen for crescents that have clearly separated tips, tips separated by only a small gap, and overlapping tips. One additional peak in the visible range has been identified as the transverse resonance of a rod. The main resonances change upon variations in metal layer thickness and diameter of the masking colloid in a way that was in qualitative agreement with this interpretation. Unique plasmonic properties are also observed from the nanocrescent variations of...
of cm²-sized chiral plasmonic templates for chiroptical methods offers a simple, low-cost manufacturing method in the region (750–3000 nm), with CD values of up to 13%. This chiroptical resonances in the 100–400 THz frequency SSL using hole as mask [142]. The optical properties show that plasmonic modes. This novel substrate has been employed for antenna-assisted surface-enhanced IR absorption measurements using octadecanethiol (ODT) and deuterated ODT [134]. The method has the potential to make resonant plasmon enhanced IR spectroscopy a standard lab tool in biology, pharmacology, and medicine. Moreover, large-area 3D chiral plasmonic structures can be fabricated by SSL using hole as mask [142]. The optical properties show chiroptical resonances in the 100–400 THz frequency region (750–3000 nm), with CD values of up to 13%. This method offers a simple, low-cost manufacturing method of cm²-sized chiral plasmonic templates for chiroptical applications such as stereochiral enantiomer sensors.

5 Conclusions and outlook

This review summarizes the principle of SSL and gives some exciting design strategies to produce the various nanostructures as well as their promising plasmonic performances. The understanding of the fundamental principle and configuration of SSL is a foundation to flexibly create various nanostructures. As discussed, different and complex nanostructures can be constructed by adjusting parameters such as vapor incident angle θ, azimuthal rotation angle φ, how to rotate θ and φ, deposition materials, the number of deposition, and template or mask. Nanostructures with various shapes or topologies, such as nanorods on nanospheres, patchy nanospheres, nanotriangles, nanodisks, nanocrescents, etc., as well as their assemblies such as dimers, trimers, quadrupers, split-rings, metasurfaces, etc., have been realized. Simple geometrical models based on shadowing effect can be used to predict the formed nanostructures and assemblies and can serve as a designing guide for SSL fabrication. These nanostructures demonstrate different plasmonic properties and can be used in different applications such as LSPR index sensors, extraordinary optical transmission sensors, chiral sensors, SERS, metamaterials, plasmonic heating, optics, light trapping, and color display. It is expected that by varying the SSL parameters and combining SSL with other nanofabrication processes, new and advanced nanostructures can be designed and their novel plasmonic properties and applications will be exploited.

Based on above discussions, the advantages of SSL can be summarized as the following: (1) patterning large areas at low cost and in parallel fashion; (2) fabricating sub-100-nm nanostructures with high resolutions, which are hard to be implemented sometimes by conventional nanolithography techniques; (3) having the flexibility in designing ordered or non-ordered 2D and 3D nanostructures; and (4) depositing materials with almost no limit as long as the materials can be evaporated.

Although investigations have progressed rapidly, challenges in this field still exist. The major obstacle encountered when using SSL is the inability to control mask registry φ. As discussed in Section 2.2.3, in most 2D CC growth, there exists multiple hexagonally close-packed domains with random orientations, and the shape, size, and spacing of nanostructures produced by SSL in different domains could vary significantly at different locations of the substrates. More elaborate nanosphere mask preparation techniques should be developed to allow fabrication of large-area, single-domain nanosphere monolayers. However, multiple domains provide an advantage to simultaneously fabricate multiple nanostructures so that a high throughput screening of nanostructures is possible. Second, the crystallinity of the nanostructure fabricated by SSL may be poor. In order to form the nanostructure with defined geometries predicted by the shadowing effect, the substrate temperature during the deposition should be much lower than the bulk melting temperature of the evaporated material. The films grown at near room temperature are usually amorphous for most semiconductor and compound materials and polycrystalline for metals. For applications requiring high-quality crystalline nanostructures, post-deposition annealing is usually performed (if nanospheres are kept with the nanostructures, the nanospheres should also have high melting temperature such as silica nanospheres). However, the improvement in crystallinity
is typically insignificant. Third, high-quality interfaces are lacking for hetero-structures. The low-temperature grown nanostructures usually have fairly roughened surfaces. Many defects could exist at the interfaces that can impair the charge transport properties or other properties across the interfaces. The adatom diffusion has to be increased to improve the quality of the nanostructures.

It is worth noting that simulation models play an important role in SSL due to the fact that nanostructures could become complicated when multiple parameters are changed so that direct visualization of resulted nanostructures is not straightforward. Models based on the geometrical shadowing effect can disclose the basic relationship between the fabricated nanostructure profiles and the process parameters during the deposition and provide a design guide to the fabrication (or potentially could be used to predict the plasmonic properties). One has to be aware that most simulation models only count for the shadowing effect due to the initial CC lattice and do not take into account the growing shadow effect during the deposition. Therefore, it could introduce discrepancies between the model and real structures. In addition, compared to the experimentally resulting nanostructures, other effects such as the surface diffusion of adatom, nucleation, polycrystallinity and roughness of the films, etc., can play a significant role in determining the final structures. To better predict the resulting nanostructures, a kinematic Monte Carlo or molecular dynamic simulation model that accounts for different growth effects could be developed [54]. Clearly, a better simulation model to predict the real structures would be useful.

There is much room left to use SSL to design and fabricate complicated nanostructures and explore different applications. In order to unravel the full power of SSL, a close collaboration among the researchers from different disciplines is crucial. Further research on SSL is believed to mainly focus on four aspects: first, further improvement on the preparation of large-area, high-quality 2D/3D CCs; second, better control of adatom diffusion in the deposition process to better utilize the shadow effect and simultaneously achieve smooth interfaces; third, successful advancement in simulation models to reflect the real fabricated structure; and last, ingenious strategies on designing novel structures. Further exploration on the applications based on the novel nanostructures fabricated by SSL will be carried out. We envision that SSL will continue to evolve and that an increasing number of novel nanostructures with surprising effects/properties will be designed and fabricated. This simple, inexpensive, large-scale nanofabrication and design tool will greatly benefit the field of plasmonics and impact other nanotechnology-related fields such as medical diagnostics, environmental monitoring, food safety, security, etc.

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