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# Spatially Confined Assembly of Nanoparticles

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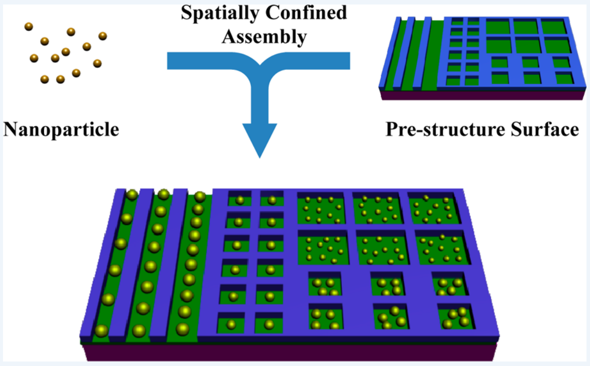

**CONSPECTUS:** The ability to assemble NPs into ordered structures that are expected to yield collective physical or chemical properties has afforded new and exciting opportunities in the field of nanotechnology. Among the various configurations of nanoparticle assemblies, two-dimensional (2D) NP patterns and one-dimensional (1D) NP arrays on surfaces are regarded as the ideal assembly configurations for many technological devices, for example, solar cells, magnetic memory, switching devices, and sensing devices, due to their unique transport phenomena and the cooperative properties of NPs in assemblies. To realize the potential applications of NP assemblies, especially in nanodevice-related applications, certain key issues must still be resolved, for example, ordering and alignment, manipulating and positioning in nanodevices, and multicomponent or hierarchical structures of NP assemblies for device integration. Additionally, the assembly of NPs with high precision and high levels of integration and uniformity for devices with scaled-down dimensions has become a key and challenging issue.

Two-dimensional NP patterns and 1D NP arrays are obtained using traditional lithography techniques (top-down strategies) or interfacial assembly techniques (bottom-up strategies). However, a formidable challenge that persists is the controllable assembly of NPs in desired locations over large areas with high precision and high levels of integration. The difficulty of this assembly is due to the low efficiency of small features over large areas in lithography techniques or the inevitable structural defects that occur during the assembly process. The combination of self-assembly strategies with existing nanofabrication techniques could potentially provide effective and distinctive solutions for fabricating NPs with precise position control and high resolution. Furthermore, the synergistic combination of spatially mediated interactions between nanoparticles and prestructures on surfaces may play an increasingly important role in the controllable assembly of NPs.

In this Account, we summarize our approaches and progress in fabricating spatially confined assemblies of NPs that allow for the positioning of NPs with high resolution and considerable throughput. The spatially selective assembly of NPs at the desired location can be achieved by various mechanisms, such as, a controlled dewetting process, electrostatically mediated assembly of particles, and confined deposition and growth of NPs. Three nanofabrication techniques used to produce prepatterns on a substrate are summarized: the Langmuir–Blodgett (LB) patterning technique, e-beam lithography (EBL), and nanoimprint lithography (NPL). The particle density, particle size, or interparticle distance in NP assemblies strongly depends on the geometric parameters of the template structure due to spatial confinement. In addition, with smart design template structures, multiplexed NPs can be assembled into a defined structure, thus demonstrating the structural and functional complexity required for highly integrated and multifunction applications.

## ■ INTRODUCTION

Currently, nanotechnology research has reached the stage in which the subjects of advanced studies are assemblies of nanoentities, particularly groups of nanoparticles (NPs) rather than individual NPs because the former possess much greater structural and functional complexity.[1−3] The assembled systems are expected to result in qualitative and quantitative improvements in their properties due to the collective physical or chemical properties that depend on particle components, size, spacing, and higher-order structure, which may play important roles for emerging advanced device applications in the areas of photonics, plasmonics, electronics, information storage, catalysis, cancer diagnostics, and biological sensors.[4−6] Among the various configurations of NP assemblies, two-dimensional (2D) NP patterns and one-dimensional (1D) NP arrays on surfaces may serve as platforms for realizing functionalities enabled by the physical (i.e., optical, electrical, and magnetic) properties of both individual particles and their arrangements.[7,8] For example, 1D NP arrays provide model systems for the study of transport phenomena and cooperative properties between NPs, that is, strong surface plasmon resonance coupling,

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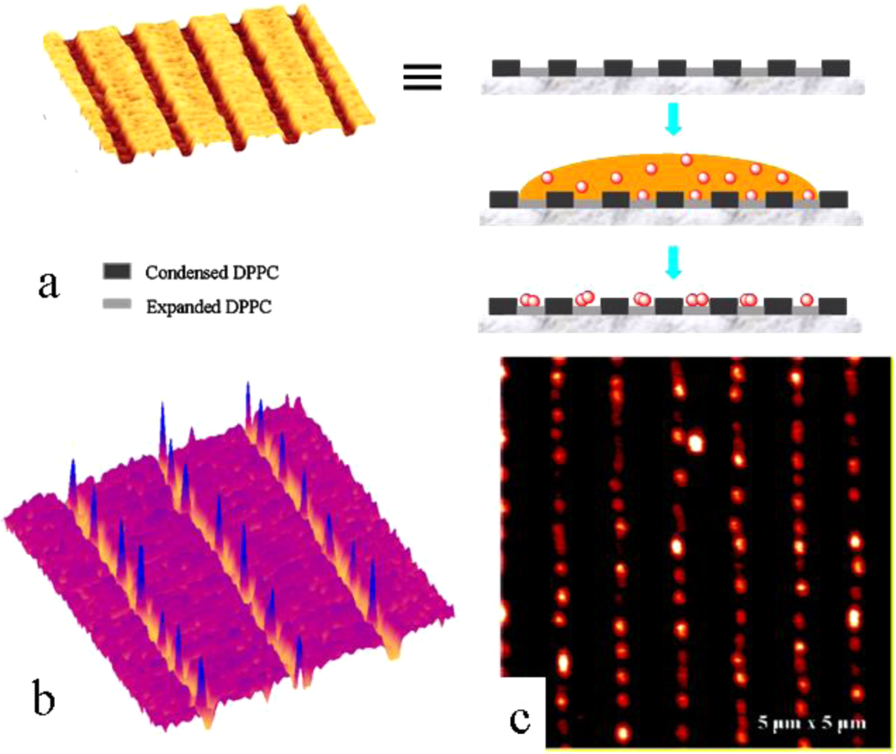

Figure 1. (a) Generalized schematic outline of the procedure used to pattern nanoparticles on a DPPC stripe pattern. Selective deposition of (b) $Au_{55}$ clusters and (c) CdSe nanocrystals aligned along the channels on a mica surface. Reproduced with permission from ref 19. Copyright 2007 American Chemical Society.

directional single electron transport, and waveguiding.[9−11] Moreover, the assembly of NPs into 2D patterns and 1D arrays on surfaces is of interest for the development of many technological devices, for example, solar cells, magnetic memory, switching, and sensing devices. With the steady trend of functional devices on increasingly smaller scales, assemblies of NPs formed with high precision and high levels of integration as well as uniformity have begun to take on more prominent roles.[12,13]

Compared with top-down lithography-based nanofabrication, the bottom-up assembly approach can produce ordered 2D and 1D nanostructures with desirable functionalities and smaller feature dimensions.[14−17] However, due to the inevitable structural defects that form during the assembly process, a formidable challenge that persists is the controllable assembly and positioning of NPs at desired locations over large areas with high precision and high levels of integration.[18] The combination of self-assembly strategies with existing nanofabrication techniques, that is, Langmuir−Blodgett (LB) patterning and lithography, may potentially provide tools for the construction of reliable nanomaterial-based devices that may potentially meet industrial requirements. In particular, with LB patterning, a simple method that is less instrumentation demanding, surface patterns with feature size down to 100 nm over wafer size area can be created based on the phase separation of organic molecules in an ordered manner.[19] In this Account, we focus on our recent progress in fabricating spatially confined assemblies of NPs on a prestructured surface fabricated via LB and lithography techniques (e-beam and nanoimprint lithography) for positioning particles with high resolution and considerable throughput. We recognize that spatially mediated interactions between nanoparticles and prestructures on surfaces play a critical role in the controllable assembly of NPs. Finally, the main conclusions, current challenges, and future prospects in this field are presented in the final section.

## ■ SPATIAL CONFINED ASSEMBLY OF NANOPARTICLES BASED ON THE LANGMUIR−BLODGETT TECHNIQUE

The LB technique is a sophisticated and advanced method for interfacial assembly, which is widely used for organizing organic molecules into ordered structures.[20] It has been further extended to organize nanoentities such as nanoparticles, for example, to obtain regular nanoparticle arrays on solid substrates.[19] Using self-patterned molecular aggregates as templates for interfacial assembly provides a general method for assembling NPs into ordered structures.[21,22] For example, poly(vinylpyrrolidone) (PVP) can adsorb $Au_{55}(PPh_3)_{12}Cl_6$ [$Au_{55}$] clusters via its phenyl groups. When PVP molecules were incorporated into an aqueous subphase as a linear template, a quasi-1D arrangement of the gold clusters formed and gave rise to 2D networks at the air/water interface. Consequently, these NP assemblies could be transferred onto a $Si/SiO_2$ substrate. When the material transfer was carried out on a structured $Si/SiO_2$ surface with metal patterns (which serves as a model for a nanoelectrode), single-chain structures could be located between the metal patterns.[23] Moffitt and coworkers applied self-assembled amphiphilic block copolymers (polystyrene-*block*-poly(ethylene oxide)) with incorporated polystyrene-coated CdS NPs to form strand-like structures on a surface featuring hydrophilic/hydrophobic stripe prepatterns.[24] The assemblies were selectively positioned within the hydrophilic stripes when the hydrophilic/hydrophobic stripes were oriented perpendicular to the water surface during LB transfer. This process has been explained by considering the selective dewetting along the three-phase contact line. In such a system, the NPs and template molecules must first be mixed and subsequently transferred together to the substrate, which makes the controlled alignment of NPs difficult.

To solve this problem, NPs were selectively deposited onto prepatterned surfaces, which provided a fast and easy route to obtaining ordered structures with controlled alignment, size, and shape. Complementary surface interactions between nanoparticles and surface patterns such as hydrogen bonds, biomacromolecular hybridization, electrostatic forces, and hydrophobic interactions afford substantial selectivity for directing the assembly of NPs.[25−28] Ohtani and co-workers developed a simple method for fabricating well-aligned necklace-like assemblies of Au NPs on substrates using well-stretched strands of DNA as templates.[29] The wetting properties of patterned templates have most frequently been exploited to assemble NPs via selective positioning based on the interaction between the dispersion medium phase (e.g., dispersing solution) and the patterned template structures. We used another strategy based on the patterning of a phosphor lipid L-*R*-dipalmitoylphosphatidylcholine (DPPC) as the template. The DPPC could form a pattern composed of stripes measuring approximately 800 nm in width separated by channels of approximately 200 nm in width on a substrate surface using the LB technique (see Figure 1a).[30,31] The stripe region consisted of DPPC in the liquid condensed (LC) phase, and the channel region consisted of DPPC in the liquid expanded (LE) phase. This type of pattern could serve as a template for the selective deposition of NPs. The stripe pattern exhibited the anisotropic wetting properties of 1-phenyloctane due to the different interfacial energies for the channels and stripes, allowing for the selective deposition of NPs, as shown in Figure 1a.[19] As a result, the NPs accumulated in the channels, and the density of NP coverage was determined by the NP concentration and the deposition time; in addition, quasi-1D aggregate arrays of $Au_{55}$ clusters were generated (see Figure 1b).[31] Using the same method, semiconductor nanocrystals (CdSe and core/shell CdSe/ZnS) could be selectively deposited in the channels as well, with their strong luminescence preserved (Figure 1c).[32] Furthermore, by studying the wetting behavior of the delivered solvent on the stripe pattern and determining the adhesion energy between semiconductor nanocrystals and the substrate, two consecutive steps were proposed for the selective adsorption of nanocrystals onto the stripe pattern.[33] The first step consists of molecular exchange between 1-phenyloctane and lipid molecules to form the adsorption sites for nanocrystals, and the second step involves the adsorption of nanocrystals onto the adsorption sites due to the strong interaction between the nanocrystals and the substrate.[33] Moreover, the physisorbed DPPC molecules in the channels and the stripes on the substrate could also be selectively substituted with two different silane molecules ($NH_2$-terminated and $CH_3$-terminated silanes), which covalently bond to the surface to form a robust chemical pattern.[34] Next, negatively charged $Au_{55}$ clusters could selectively assemble onto the $NH_2$-terminated silane stripes with positive charges via electrostatic interaction. These examples principally demonstrate that pattern contrast affords substantial flexibility in controlling the assembly of NPs at desired locations. However, these methods still present a formidable challenge in terms of controlling the assembly of NPs with high precision and high resolution.

In addition, the LB technique has proven to be a versatile tool for achieving both closely packed nanoparticle superstructures and well-defined patterns with low particle density without the use of a predefined template.[35,36] Schmid and co-workers first used the LB technique to generate quasi-1D parallel rows of $Au_{55}(PPh_3)_{12}Cl_6$ clusters at the air−water interface.[37] Furthermore, Yang and co-workers applied the LB technique for the 1D controllable assembly of nanoparticles using a simple dip-coating process.[38,39] Well-spaced, parallel, single-particle lines with different shapes, sizes, and compositions can be readily deposited on a substrate by the controlled stick−slip motion of the contact line of the water and substrate.[39] This low-cost, scalable method also enables the creation of spatially confined arrays of NPs and the selective deposition of nanoparticles onto the desired location.

## SPATIALLY CONFINED ASSEMBLY OF NPS IN COMBINATION WITH LITHOGRAPHY PATTERNING

Advances in lithography have enabled the precise and reproducible patterning of features ranging in size from tens of nanometers to the macroscopic scale, and the topographic structure defined by lithography can be used to trap nanoparticles into defined positions.[40,41] A synergistic combination of colloidal nanostructures with lithographic patterning allows for the precise control necessary to produce highly integrated nanostructure assemblies with high resolution on all length scales via the intrinsic magnetic or electric dipoles of NPs, dewetting, solvent evaporation, etc.[42−44] The spatial confinement parameters, that is, height, width, and length, of templates play key roles in determining the arrangement of NPs.[45] Normally, the packing of colloidal NPs on patterned structures depends on the deposition method used as well as the commensurability between the particle diameter and the geometric size of the template.[12] Kumacheva et al. observed that colloidal NPs formed an ordered assembly if the template size was commensurate with the particle size and became disordered when the template size was incommensurate due to capillary force, that is, the gas−liquid interfacial tension in the meniscus region.[46] Although template-assisted self-assembly of colloidal NPs has been shown to produce ordered arrays of colloidal NPs, the need to extend this technique to particles much smaller than 30 nm, a size regime in which the thermoshift of particles may affect the positioning, and to develop robust fabrication techniques that lead to defect-free large-area arrays still exists. To obtain a 1D single-particle array, the width of channel templates must be approximately the same as the diameter of the NPs. Therefore, the arrangement of sub-30 nm NPs remains technically difficult due to the resolution limit of lithography techniques under conventional research laboratory conditions.

Recently, the fabrication of ordered particle arrays across a large-scale surface was achieved via the electrostatic assembly of charge-stabilized colloidal nanoparticles on a modified substrate.[47,48] In a conventional diluted colloidal system, the thickness of the electric double layer ($1/\kappa$) can be well described by the Helmholtz and Gouy−Chapman model, as shown in Figure 2a. The parameter $\kappa$ can be calculated from the following rearrangement of the original Helmholtz and Gouy−Chapman model:

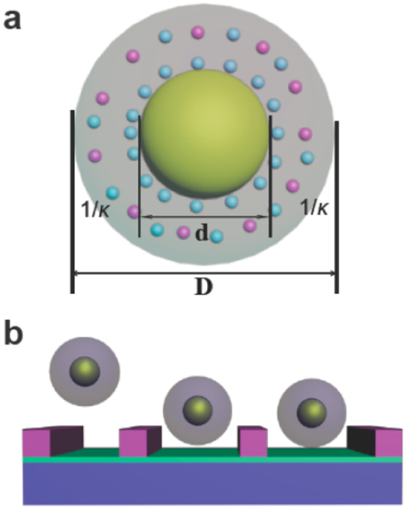

**Figure 2.** (a) Effective diameter of a Au particle composed of a rigid core and an electric double layer. (b) Deposition of Au nanoparticles into the channels can occur only if the channel width is larger than the effective diameter of the Au particles.

$$\kappa^2 = \frac{4\pi e^2}{\varepsilon kT} \sum_i n_{i0} Z_i^{\,2} \tag{1}$$

The reciprocal $1/\kappa$ is the so-called thickness of the double layer. Therefore, the effective diameter of the particle is a combination of the diameter of the rigid core and the double charge layers ($D = d + 2/\kappa$) and is a key factor in controlling the deposition of a Au nanoparticle onto the template structure in solution. Taking a 30 nm Au particle as an example, when the ionic strength of the Au solution is approximately $5.24 \times 10^{-5}$ mol $L^{-1}$, the calculated value of the double-layer thickness is approximately 40 nm according to eq 1, which results in an effective diameter that is larger than the core diameter of the Au particle. Consequently, Au nanoparticles can be deposited into the channel structures only if the width of the channels is larger than the particles' effective diameter (see Figure 2b). Based on this principle, we demonstrated a facile approach to the fabrication of 1D single-particle arrays of 32 nm Au particles in large channels (up to 220 nm in width) as well as 13 nm Au particle arrays.[49] The main advantage of this approach is the application of templates with feature sizes larger than the particle size, thus requiring lower technological costs for lithography.

With this concept, 32 nm Au NPs could be site-selectively deposited into broad channels (160 nm) but would not enter the narrow channels located nearby (100 nm) because the channel width was smaller than the effective particle size, as shown in Figure 3a. In this work, the surface of the silicon substrate used was first functionalized with a monolayer of aminopropyltriethoxysilane (APTES), which provided positively charged amine groups (+35 ± 3 mV; $\zeta$-potential). These groups subsequently attracted the negatively charged, citrate-stabilized Au nanoparticles when immersed in the colloidal Au NP solution. It should be noted that the particles cannot be deposited in the channels without surface treatment with APTES. Furthermore, this concept can also be applied to 2D single-particle arrangements as well, as shown in Figure 3b; only one 32 nm Au particle could be deposited in the hole by adjusting the size of the opening (210 nm), which was much larger than the diameter of the Au particles.

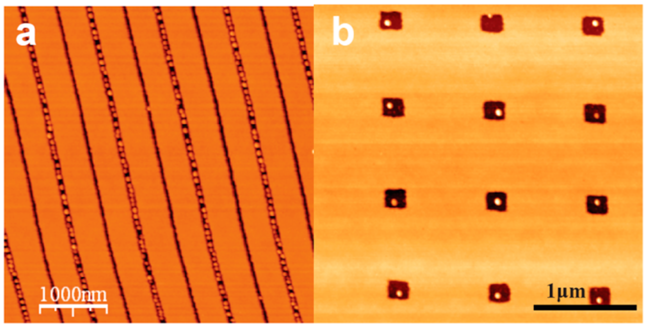

**Figure 3.** a) Atomic force microscopy (AFM) images of 1D arrays of 32 nm Au nanoparticles site-selectively self-assembled in broad grooves (160 nm) but not in narrow grooves (100 nm). (b) Spaced (1-$\mu$m) 2D array of 32 nm Au particles. Reproduced with permission from ref 49. Copyright 2009 Wiley-VCH.

The thickness of the electrical double layer surrounding colloidal NPs in solution can be adjusted by varying the ionic strength of the solution.[50] Therefore, the interparticle distance of Au NPs deposited onto the template structure can be adjusted by varying the ionic strength of the Au NP solution, as demonstrated on unstructured surfaces (Figure 4).[51] We observed that with an increase in the ionic strength of the Au NP solution, the effective diameter of the Au NPs decreased, thus allowing deposition of the Au NPs into channels of narrower width. Therefore, we can adjust the average interparticle distance of a 1D single-particle array of Au particles by simultaneously adjusting the width of the channel and the electrical layer thickness of the NPs. It should be noted that the smallest width (70 nm) of the channel used to deposit 13 nm Au NPs was still larger than the diameter of the Au NPs and that this method is applicable on the wafer scale for use with other types of lithography techniques, that is, nanoimprinting. This strategy provides a versatile means for producing nanoparticle arrays on a substrate with a defined particle distance and position control. However, it remains a challenge to fabricate NP arrays with tunable interparticle distances or NP arrays with different particle sizes on the same substrate.

We further developed a strategy for assembling NPs into multiplexed 1D arrays on a surface based on spatially confined electrostatic potential.[52] It is important to note that the profile of the generated 1D channel was negatively charged by e-beam irradiation (Figure 5a). Taking 32 nm Au particles with an effective diameter of 60 nm as an example, to obtain 1D single-particle arrays, the channel width ($W$) must be in the range of 60 nm < $W$ < 120 nm. Therefore, 1D channel patterns with different groove widths ranging from 65 to 110 nm were designed. It was observed that the 32 nm Au NPs could form multiplexed 1D single-particle arrays with tunable interparticle distances on the same substrate via simple modulation of the channel widths (Figure 5b).

The electrostatic potential distribution in a single channel determined from a numerical solution of the two-dimensional Poisson−Boltzmann equation, as shown in Figure 6a (channel with depth $d$ = 110 nm and height $h$ = 40 nm), was used to interpret the above-mentioned results.[53] It is clearly shown that the channel width largely affects the electrostatic potential distribution in the 1D channel, and the APTES-functionalized surface on the bottom of channel is at an energy minimum, which facilitates the trapping of the NPs. For the same density

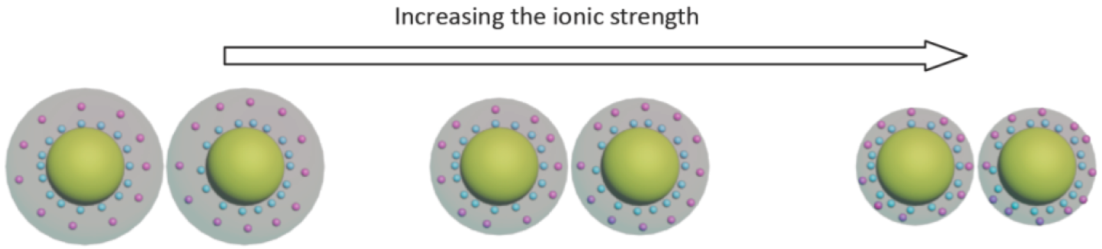

**Figure 4.** Schematic illustration of the variation in the interparticle distance between negatively charged colloidal Au nanoparticles with increasing ionic strength of the solution.

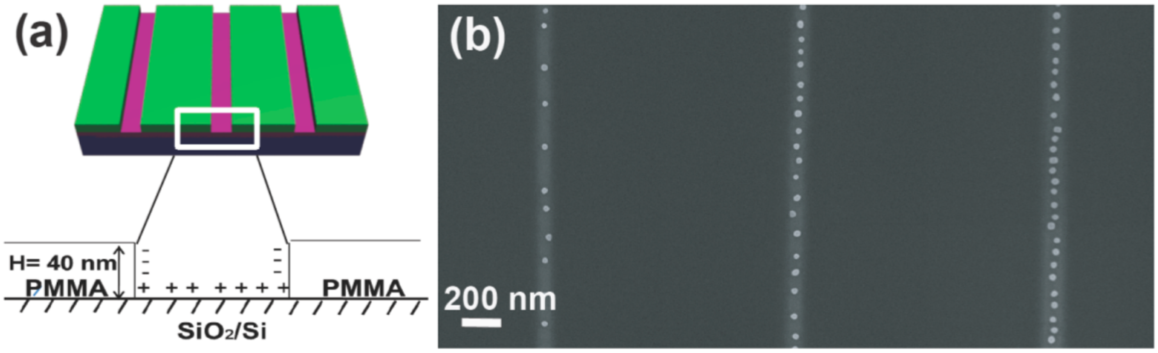

**Figure 5.** (a) Schematic illustration of a 1D channel with a positively charged silicon substrate surface and negatively charged PMMA layer. (b) SEM image of single-particle chains with tunable interparticle distances depending on the channel width on the same chip. Reproduced with permission from ref 52. Copyright 2011 American Chemical Society.

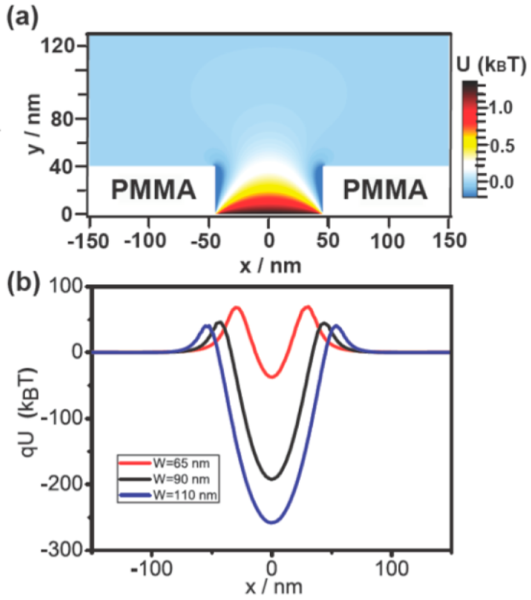

**Figure 6.** (a) Two-dimensional electrostatic potential distribution obtained by solving the Poisson−Boltzmann equation. (b) Electrostatic energy of a point charge of $q$ ($-38e$) as a function of $x$ along a contour of $y = -50$ nm and the effect of the channel width on the electrostatic potential distribution. Reproduced with permission from ref 52. Copyright 2011 American Chemical Society.

of the positively charged surface, the wider the channel is, the larger the electrostatic interaction between the nanoparticles and the substrate will be (Figure 6b) such that we can adjust the average interparticle distance of the 1D single-particle array by simply modulating the channel width on the same chip.

Based on the concept of a spatially modulated electrostatic potential, we can also control multiplexed 1D nanoparticle arrays with different particle sizes on the same substrate. Channels of three different widths, that is, 170 nm (broad, B), 130 nm (medium, M), and 100 nm (narrow, N), were designed to form multiplexed 1D nanoparticle arrays with different particle sizes (Figure 7). First, we immersed a patterned substrate into a solution containing 32 nm Au nanoparticles (effective diameter of approximately 102 nm). Due to spatial confinement, the Au nanoparticles could only be deposited in the broad channels and in the channels of medium width with larger interparticle distances. Next, the same chip was immersed into a solution containing 13 nm Au nanoparticles (effective diameter of approximately 83 nm). The Au nanoparticles were selectively deposited into the medium-sized and narrow channels, which resulted in multiplexed 1D arrays with different particle sizes that induced a multiplex SERS response on the patterned substrate. Vaia and co-workers demonstrated that the local orientation of anisotropic gold nanorods and the interparticle spacing can be tuned by controlling the Debye length of Au nanorods in solution and the dimensions of a confined strip of poly(2-vinylpyridine) with a polystyrene contrast pattern.[54] The method of combining top-down lithography and the bottom-up electrostatic assembly of colloidal NPs offers an effective approach to producing high-quality encoded nanostructures with multiplex 1D periodic nanoparticle arrays at desired locations on a single chip, which can be rearranged to suit many desired multifunctional applications in nanoscale electronics, photonics, or biology.

## ■ SPATIALLY CONFINED DEPOSITION OF NPS BY COMBINATION WITH NANOIMPRINTING

As previously mentioned, spatial confinement has pronounced effects on the controllable assembly of NPs on prepatterned surfaces with high resolution and considerable throughput. In the above-described approaches, the NPs were synthesized

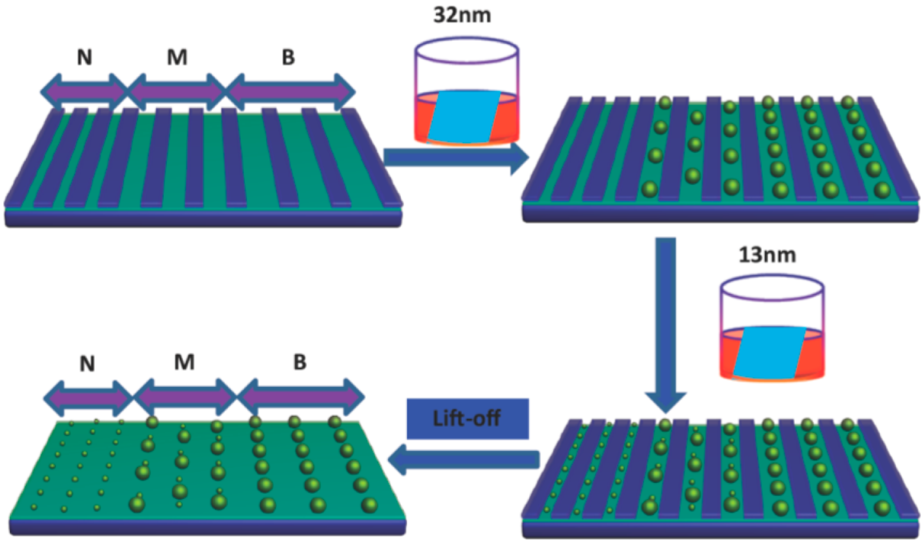

**Figure 7.** Schematic illustration of fabrication of multiplexed 1D nanoparticle arrays with different particle sizes in channels of different widths on the same substrate.

prior to spatial patterning. The direct in situ growth and deposition of NPs in the template structure provide an alternative approach to producing NP arrays on a large scale.[55] It was revealed that the effects of spatial confinement also play a key role in NP selective growth on prestructured surfaces. Recently, template-assisted electrochemical deposition (ECD) was applied to generate metallic nanostructures due to the facile nature of the process.[56,57] We fabricated arrays of silver NPs using ECD on predefined positions generated by nanoimprinting lithography (NIL), as shown in Figure 8.[58] The fabrication of multiple patterns on an ITO slide and the growth of silver NPs were achieved in a one-step ECD process using a designed template (see Figure 9a). The particle density, particle size, and interparticle distance in the silver NPs arrays could be controlled and tuned by adjusting the template size and spacing.[58] With the same spacing of the templates, the particle density on the templates increased exponentially with the decrease in the feature size of the templates (see Figure 9b).[59] Moreover, with templates exhibiting the same feature size, the density of silver NPs was higher on patterns with a large spacing than on those with a smaller spacing, as summarized in Figure 9b (comparison of the black line and red line). It was observed that the metal-enhanced fluorescence intensity could be tuned by adjusting the feature size of the NPs arrays. Furthermore, space-mediated deposition of NPs also provided a simple and efficient method for fabricating gold nanoparticle (Au NP) arrays.[60] The size of the Au NPs could be adjusted from 130 to 420 nm by varying the potential and duration of ECD. A stamp for NIL was fabricated using cost-efficient nanosphere lithography (NSL), which allowed for the production of NPs arrays in the desired positions with high throughput, low cost, and easy control. This method presents a simple but efficient technique for the fabrication of nanostructures with tunable properties that can be developed for useful applications in sensor and integrated devices.

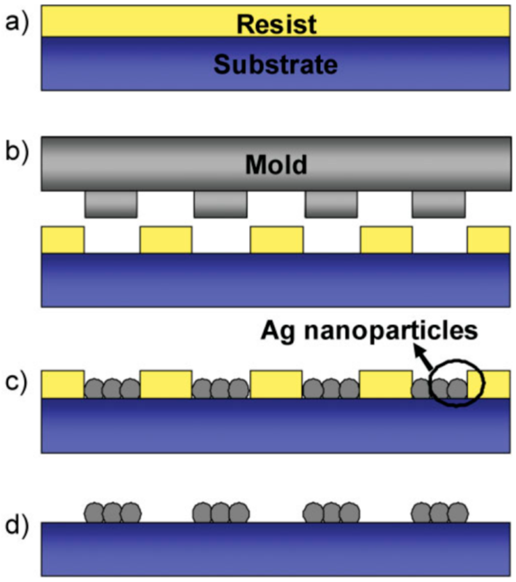

**Figure 8.** Schematic illustration of the procedure used to fabricate arrays of silver NPs (SPNs). (a) Spin-coating of the resist polymer onto ITO substrates. (b) Imprinting and etching process. (c) ECD of Ag NPs. (d) "Lift-off" of the resist layer. Reproduced with permission from ref 58. Copyright 2010 Wiley-VCH.

## ■ CONCLUSIONS AND OUTLOOK

A fundamental challenge in the development of nanotechnology is the assembly of nanoscale building blocks into functional nanostructured materials or devices with high precision and high levels of integration and uniformity. The spatially confined assembly of NPs on prestructured surfaces discussed in this Account provides an effective and distinguished solution for fabricating 1D or 2D highly ordered arrays of NPs with positioning control and high resolution. The synergistic combination of spatially mediated interactions between nanoparticles and a confined structure on a surface may play an increasingly significant role in the controllable assembly of NPs for the construction of reliable nanomaterial-based devices. The development of controllable assembly methods that are simple, reliable, versatile, and scalable for large-scale arrays of nanoparticles is thus highly important for advanced applications in electronics, photonics, and biology. In addition, a high demand exists for building more complex architectures, that is, multicomponent or more hierarchical

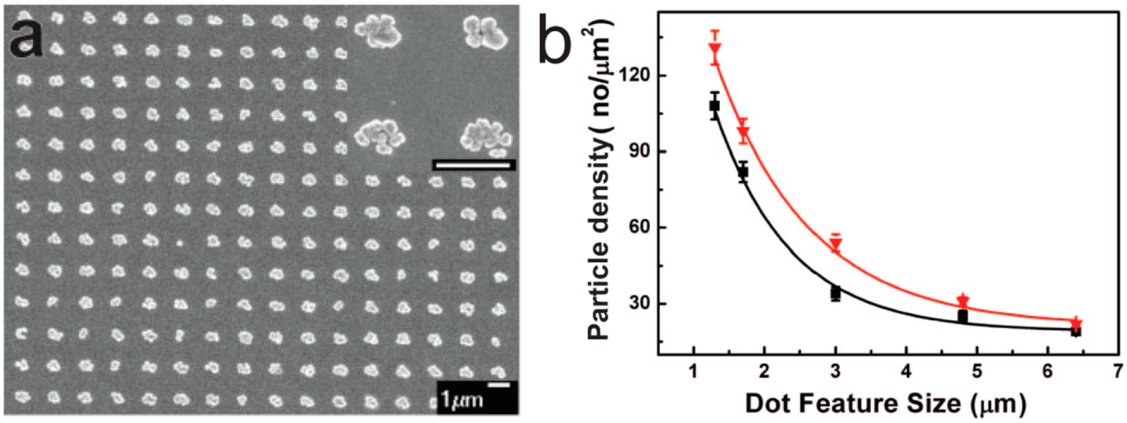

**Figure 9.** FE-SEM images of (a) 500 nm dots. Reproduced from ref 58. Copyright 2010 Wiley-VCH. (b) Correlation of the density of the confined SNPs and the feature size of the pattern. Black line, 1.9-*μ*m spacing; red line, 3.8-*μ*m spacing. Reproduced with permission from ref 59. Copyright 2009 American Chemical Society.

structures for integration, which are still in the embryonic stage of development. Through the smart design of template structures, both the structural and functional complexity of highly integrated, multifunctional applications are becoming possible.

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### Notes

The authors declare no competing financial interest.

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**Lifeng Chi** received her B.S. degree in physics and M.S. degree in physical chemistry from Jilin University, China. She earned her Ph.D. degree in 1989 in Göttingen, Germany, working on electron/energy transfer in thin organic films. After a postdoctoral tenure at the University of Mainz and BASF, she moved to the University of Münster and received a Lise Meitner scholarship in 1997. In 2000, she finished her habilitation in physics in the area of nanostructuring through self-organization. She became a professor in physics at the University of Münster in 2004 and was appointed as Chair Professor at Suzhou University, China, in 2012. Her research interests include surface (nano)patterning, molecular self-assembly on structured surfaces, low-dimensional molecular electronics, and on-surface chemistry. She has coauthored approximately 300 original scientific papers, coauthored 5 books, edited 1 book, and filed more than 10 patents.

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