

## Langmuir–Blodgett of Nanocrystals and Nanowires

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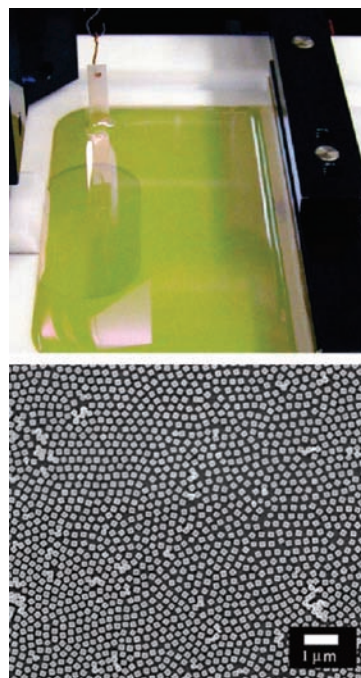
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### CONSPECTUS

**A**lthough nanocrystals and nanowires have proliferated new scientific avenues in the study of their physics and chemistries, the bottom-up assembly of these small-scale building blocks remains a formidable challenge for device fabrication and processing. An attractive nanoscale assembly strategy should be cheap, fast, defect tolerant, compatible with a variety of materials, and parallel in nature, ideally utilizing the self-assembly to generate the core of a device, such as a memory chip or optical display. Langmuir–Blodgett (LB) assembly is a good candidate for arranging vast numbers of nanostructures on solid surfaces. In the LB technique, uniaxial compression of a nanocrystal or nanowire monolayer floating on an aqueous subphase causes the nanostructures to assemble and pack over a large area. The ordered monolayer can then be transferred to a solid surface en masse and with fidelity.

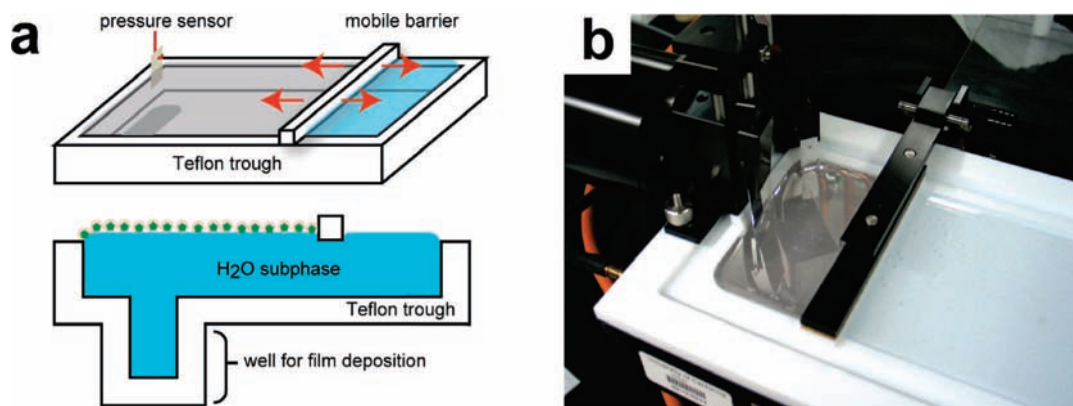
In this Account, we present the Langmuir–Blodgett technique as a low-cost method for the massively parallel, controlled organization of nanostructures. The isothermal compression of fluid-supported nanoparticles or nanowires is unique in its ability to achieve control over nanoscale assembly by tuning a macroscopic property such as surface pressure. Under optimized conditions (e.g., surface pressure, substrate hydrophobicity, and pulling speed), it allows continuous variation of particle density, spacing, and even arrangement. For practical application and device fabrication, LB compression is ideal for forming highly dense assemblies of nanowires and nanocrystals over unprecedented surface areas. In addition, the dewetting properties of LB monolayers can be used to further achieve patterning within the range of micrometers to tens of nanometers without a predefined template. The LB method should allow for easy integration of nanomaterials into current manufacturing schemes, in addition to fast device prototyping and multiplexing capability.



### Introduction

Assembly presents one of the most fundamental issues in nanoscience. Rational assembly strategies are needed not only to build complex structures with novel collective properties but also to pattern nanoscale building blocks for device fabrication at a practical scale. Although top-down approaches toward these architectures such as

nanoimprint lithography, near-field lithography, and scanning probe techniques have demonstrated high spatial resolution, bottom-up methods are still highly desirable for their simplicity and compatibility with large-scale, heterogeneous integration processes. In the past several decades, significant advancement has been made in the chemical synthesis of nanomaterials: building



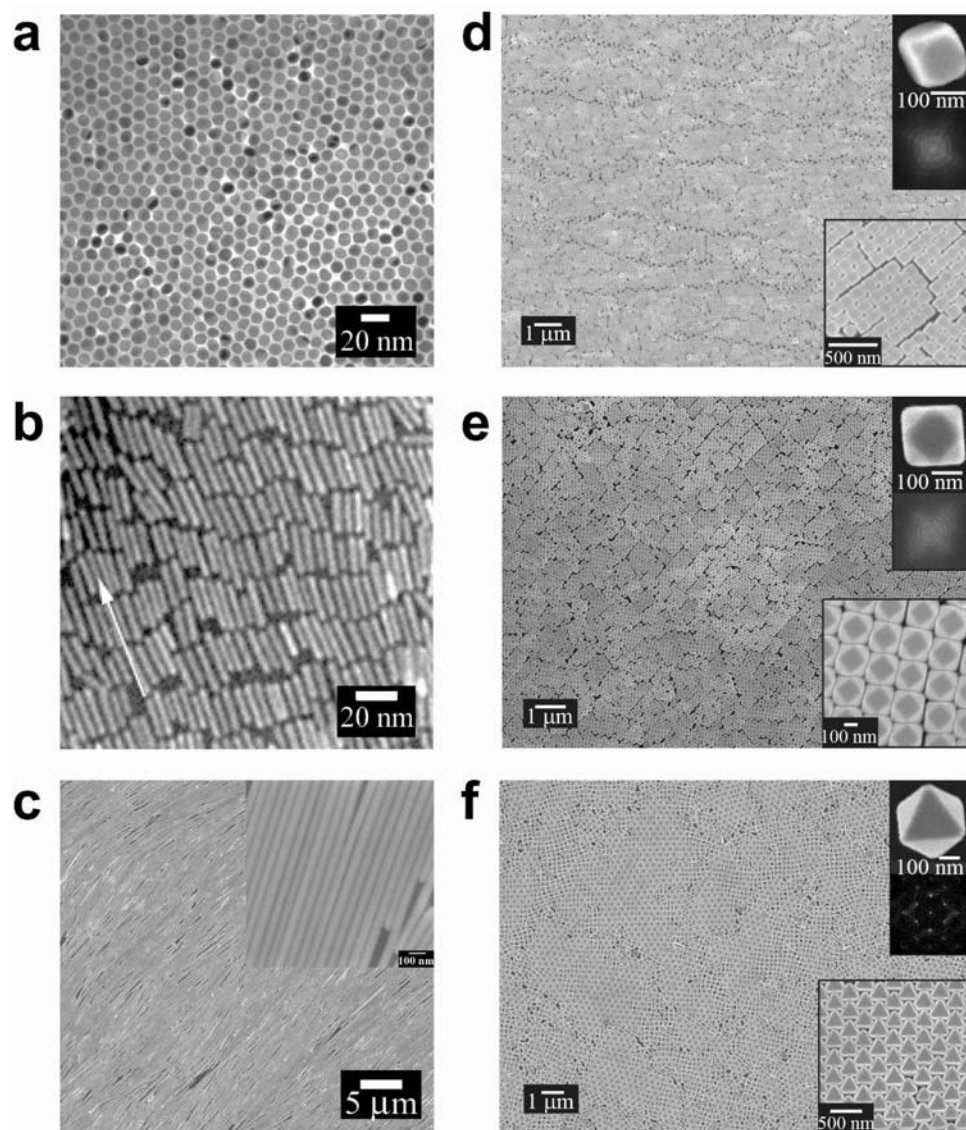
**FIGURE 1.** Langmuir–Blodgett trough: (A) schematic of a water-filled Langmuir–Blodgett trough from the top and side views; (B) image of a substrate being pulled vertically through a Langmuir monolayer of silver nanowires. The speed of both the dip-coater and the mobile barrier are mechanically controlled.

blocks of a wide range of materials can now be made with good control over their size, shape, and crystallinity. However, major advances in the field of assembly must be made in order to fully utilize the functionality offered by nanoscale materials and to realize their practical application toward optical, electronic, and magnetic devices.

Parallel organization, rather than serial manipulation, is a necessity. In addition to patterning and placement with high fidelity, the ideal assembly technique must be easily integrated into current fabrication schemes, such as roll-to-roll processing. Such techniques typically involve strategic design of solvent flow, liquid interfaces, and wetting properties. For microscale devices, self-assembly of three-dimensional electrical networks and large device arrays have been demonstrated using capillary forces driven by hydrophobic interactions or liquid menisci.<sup>1,2</sup> For the assembly of nanoscale building blocks, large efforts have been focused on spontaneous organization of colloidal solutions. Early examples include the fabrication of photonic bandgap “opals” composed of silica spheres packed by sedimentation or slow evaporation.<sup>3</sup> In addition, superlattices of colloidal semiconductor quantum dots,<sup>4</sup> magnetic nanoparticles,<sup>5</sup> and metal nanocrystals<sup>6–8</sup> have been demonstrated using solvent evaporation. Spontaneous crystallization of these structures results from tuning interparticle forces by optimization of solvent composition, evaporation rate, particle concentration, and particle surface chemistry. Microfluidic channels, as well as convective flow cells, have been used to direct solvent flow during the assembly process.<sup>9,10</sup> However, large-scale patterning of nanostructures with these methods is difficult to achieve. In addition, superlattice crystallization can be extremely sensitive

to sample quality and often requires nanostructures exhibiting high monodispersity and near-spherical shapes.

To address these difficulties, a common strategy is to employ a predefined template to control deposition during solvent evaporation. Templating methods apply the fact that colloidal assembly is driven by capillary forces at the drying front. For planar fabrication, the surface of a substrate can be modified chemically or geometrically to assist nanostructure assembly. For example, substrates patterned with alternating regions of hydrophobic and hydrophilic molecular layers result in selective deposition of small particles into hydrophilic sections.<sup>11</sup> Physical templates such as wells and trenches can be used to confine an evaporating suspension, forming organized clusters of particles.<sup>12,13</sup> These techniques are also compatible with anisotropic nanostructures.<sup>14</sup> However, because template fabrication typically involves lithographic processing, this assembly method is often limited to what can be currently achieved using top-down approaches. In this Account, we summarize our efforts in the assembly and patterning of nanomaterials by the Langmuir–Blodgett (LB) technique, which has proved to be a very versatile tool to fabricate both closely packed nanoparticle superstructures and well-defined patterns with low particle density. First, we discuss the basic method of LB compression and dip-coating in the framework of nanoscale assembly. We cover the fabrication of two-dimensional arrays of nanorods, nanowires, and nanocrystals that adopt unique close-packed architectures. We then discuss how LB monolayer transfer can be used as a patterning technique by utilizing general dewetting principles. It should be noted that this Account does not review methods where nanoparticles are synthesized *in situ* within or at the surface of a molecular LB film.



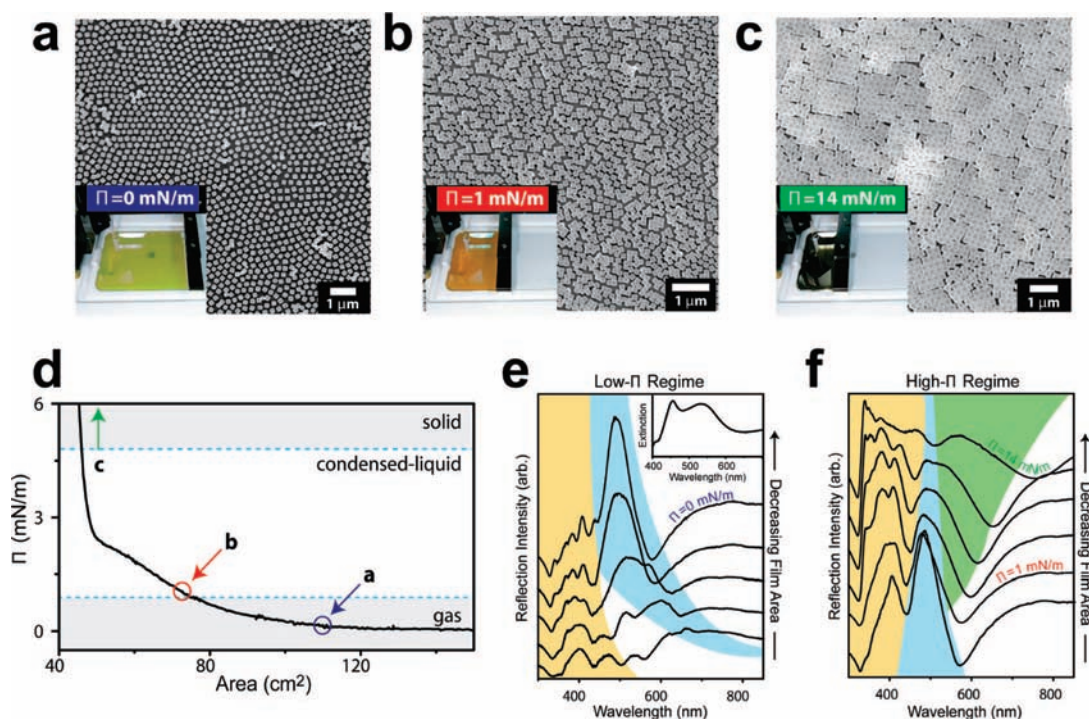
**FIGURE 2.** Selected examples of close-packed Langmuir–Blodgett monolayers of nanocrystals and nanowires: (a) Pt nanocrystal arrays used as 2D model catalysts;<sup>29</sup> (b) BaCrO<sub>4</sub> nanorods arranged into liquid crystalline patterns;<sup>30</sup> (c) densely packed Ag nanowire arrays for molecular sensing using surface-enhanced Raman spectroscopy—the inset shows an area of close-packed nanowires;<sup>31</sup> (d–f) superlattice architectures assembled from Ag nanocrystal building blocks of different polyhedral shapes, (d) truncated cubes, (e) cuboctahedra, and (f) octahedra. The insets in panels d–f show individual nanocrystal geometry (top), fast Fourier transform images indicating long-range order within each monolayer (middle), and close-up views of the nanocrystal unit cell (bottom). Panels a and b are TEM images, while the microscopy graphs in (c–f) are SEM images. Reprinted with permission from ref 27. Copyright 2007 Nature Publishing Group.

## Langmuir–Blodgett Monolayers: From Molecules to Nanoparticles

Research on water-supported thin films dates back to the nineteenth century.<sup>15</sup> When amphiphilic molecules, usually dissolved in an immiscible volatile solvent, are spread onto a water surface, a Langmuir thin film consisting of a water-supported monolayer of the molecules can be obtained.<sup>16,17</sup> The molecular density in the monolayer can be readily altered by compressing or expanding the film using a barrier. Such a thin film can be transferred onto a substrate (e.g., by dip-coating) and a solid-state thin film is obtained upon evaporation of the

underlying water layer. This has led to numerous applications based on ultrathin films.<sup>18–20</sup> Traditionally, LB assembly and deposition has been used for generating films of organic species, including long-chain aliphatic compounds, aromatic compounds, porphyrins, dyes, and large biological molecules.<sup>21</sup> Fatty acids, however, are the quintessential monolayer material having been studied by Irving Langmuir in the early 1900s. Langmuir was able to relate pressure-induced force to the phase transitions of long-chain surfactant monolayers, expanding upon the idea of surface tension and free energy using a molecular picture that involved steric hindrance,





**FIGURE 3.** The optical response of a silver nanoparticle film can be tuned using Langmuir–Blodgett assembly: (a–c) SEM images of transferred LB films and their corresponding visual appearances (inset) at surface pressures of 0, 1, and 14 mN/m; (d) the surface pressure isotherm curve taken during compression of a nanoparticle film; (e, f) the optical reflectance of Langmuir–Blodgett nanoparticle films while supported on the fluid subphase. In the low surface pressure regime (panel e), the optical response of the film is dominated by Bragg scattering. In the high surface pressure regime (panel f), near-field plasmon coupling leads to a continuum of resonances rather than distinct resonant wavelengths. Reprinted with permission from ref 27. Copyright 2007 Nature Publishing Group.

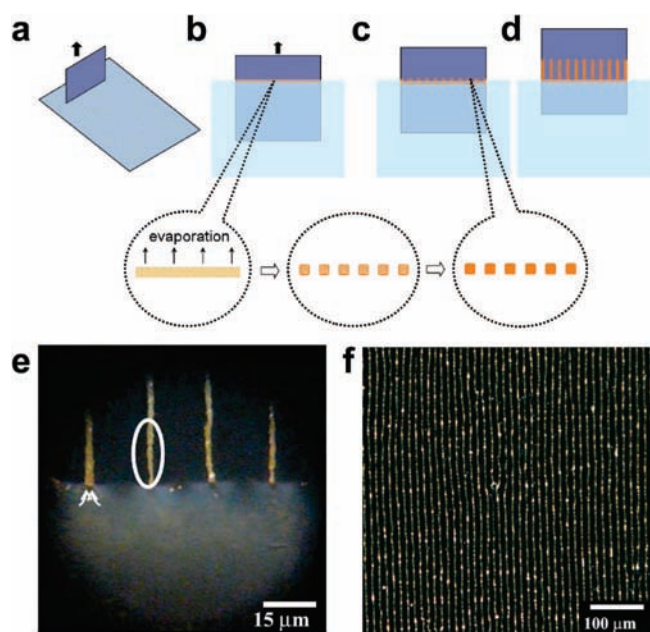
molecular orientation, and rearrangement.<sup>16</sup> Having been extensively applied by Katharine Blodgett, the LB technique refers to the passing of a solid barrier vertically through the air/water interface to achieve monolayer or multilayer deposition.<sup>22</sup>

Nanoparticles can also be processed in the same fashion as traditional LB molecules. This is a general, but versatile, method for arranging nanoscale building blocks of different compositions, morphologies, and sizes. A wide variety of nanoscale materials have been organized into two-dimensional monolayers using the LB technique, including CdSe,<sup>23</sup> Fe<sub>3</sub>O<sub>4</sub>,<sup>24</sup> Ag,<sup>25–27</sup> Au,<sup>28</sup> and Pt<sup>29</sup> nanoparticles; Au, BaCrO<sub>4</sub>, and BaWO<sub>4</sub> nanorods;<sup>30</sup> Ag,<sup>31</sup> Si,<sup>32</sup> Mo<sub>3</sub>Se<sub>3</sub><sup>–</sup>,<sup>33</sup> ZnSe,<sup>34</sup> WO<sub>x</sub>,<sup>35</sup> and Ge<sup>36</sup> nanowires; and carbon nanotubes.<sup>37</sup> The isothermal compression of fluid-supported nanoparticles or nanowires is unique in its ability to achieve control over nanoscale assembly by tuning a macroscopic property such as surface pressure. Under optimized conditions, it allows continuous variation of particle density, spacing, and even arrangement. LB compression is ideal for forming highly dense assemblies of nanowires and nanocrystals over unprecedented surface areas. In addition, the dewetting properties of

LB monolayers can be used to achieve patterning from micrometer to tens of nanometers range without a predefined template.

### Close-Packed Nanoparticle Superlattices by Compression

The LB technique has been shown to be a high-throughput, low-cost, easily integrated method for the controlled assembly and patterning of nanoparticles and nanowires. A schematic of the process is shown in Figure 1. The assembly process is carried out in a water-filled trough equipped with a mobile barrier and a pressure sensor (Wilhemmy plate). Nanoparticles are dispersed in a volatile solvent that is immiscible in water, typically chloroform or hexane. The solution is then spread dropwise onto the water surface where it spreads to an equilibrium surface pressure and evaporates, leaving behind a water-supported film of particles. The high surface tension of water allows the interfacial region to easily support nanostructures with dense material compositions that are otherwise not buoyant. The mobile barrier is then used to laterally compress the monolayer at a controlled speed, typically at a rate of 1–40 cm<sup>2</sup>/min. Ordered arrays are achieved at high surface pressures, where the colloidal nanostructures are con-



**FIGURE 4.** Ordered nanoparticle stripe patterns via dewetting a dilute particle monolayer: (a–d) a schematic drawing illustrating the formation of an aligned gold nanoparticle stripe pattern by dip coating. Only the nanoparticles at the water–substrate contact line (gold dots in b–d) are shown for clarity. The substrate is raised slowly (a, b) so that water is evaporated when a new surface is exposed. The “wet” contact line containing uniformly dispersed nanoparticles breaks up into aggregates of nanoparticles (b, c) owing to the fingering instability during the initial dewetting stage. These fingertips then guide further deposition of nanoparticles, finally forming the extended stripe pattern (d). (e) Direct optical microscopy observation of the water front reveals a rapid motion of nanoparticles toward the wet tips (circled area) of the stripes as indicated by the arrows. This leads to the unidirectional growth of the stripes across the entire substrate as shown in the optical microscopy image in panel f. Reprinted with permission from ref 43. Copyright 2005 Nature Publishing Group.

densed into a solid, cohesive film. At low surface pressures, convective flow can be induced by a temperature gradient or by intentionally agitating the interface. This is particularly beneficial for metal nanoparticles that experience size-dependent dispersion forces, leading to the self-segregation of monodisperse nanoparticle lattices.<sup>38</sup> The resulting 2-D superlattices can then be transferred onto solid substrates by vertical dip-coating.

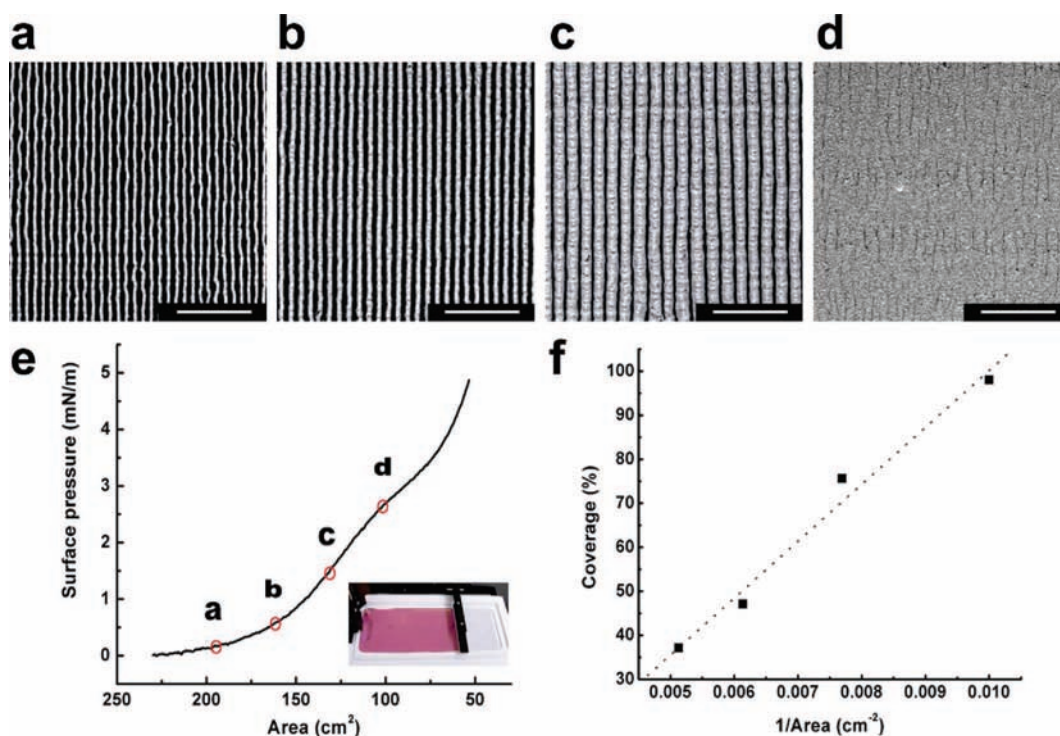
In addition to surface pressure, the resulting nanoparticle arrays are greatly affected by particle size, shape, and passivating ligand. While spherical nanoparticles form close-packed superstructures, faceted particles can generate 2D lattices with alternative symmetries determined by the shape of the particles.<sup>27</sup> Of particular note are the interlocked architectures formed by LB films of Ag octahedral nanocrystals. For highly anisotropic structures, such as the rods and wires in Figure

2b,c, oriented films with textures resembling liquid crystals can be achieved. Nanorods with short aspect ratios adopt smectic ordering;<sup>33</sup> as aspect ratio increases, order is lost in one dimension such that the film adopts nematic-like order.<sup>31</sup> Deposition of the nanowire films onto arbitrary substrates allows for a versatile processing method for creating ultrahigh-density aligned nanowire arrays that can accommodate flexible substrates.<sup>31,39</sup>

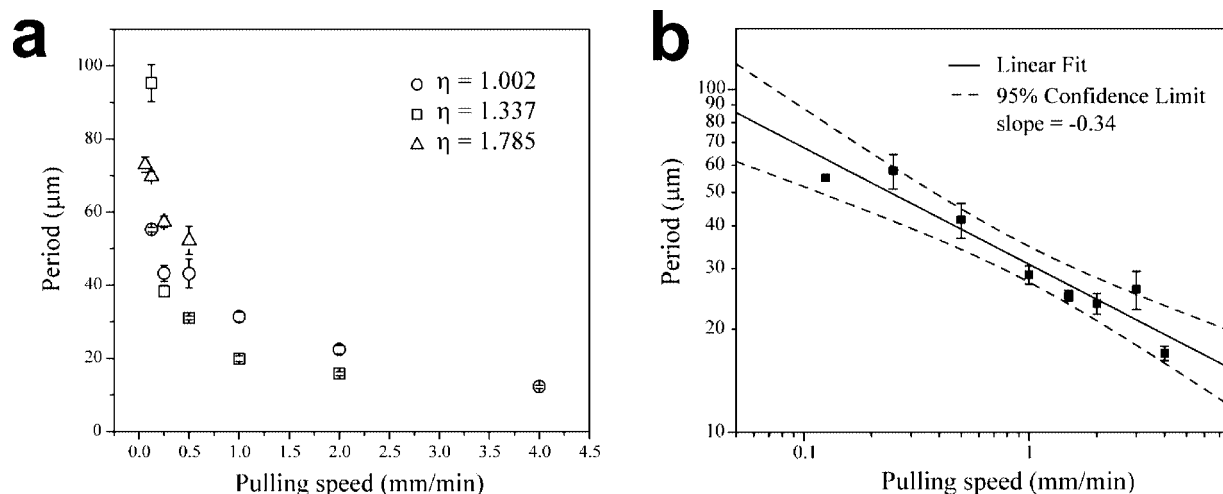
The area of the monolayer can be tuned continuously by moving the barrier, effectively changing the interparticle spacing within the nanoparticle film. This makes it possible to observe the transition between uncoupled and coupled nanoparticle arrays as the interparticle spacing is reduced. For example, Collier et al. demonstrated that as the spacing between small Ag quantum dots ( $d \approx 2.7$  nm) was decreased, increased electronic coupling between the nanoparticles lead to a metal-to-insulator transition at separation distances below 5 Å.<sup>25</sup> With larger faceted Ag nanocrystals ( $d \approx 100$ –250 nm) that exhibit intense light scattering due to localized plasmon resonances, we demonstrated that interparticle separation could be used to completely tune the optical response of the LB film.<sup>27</sup> For particle separations greater than the diameter, Bragg scattering is observed; for particles spaced as far as 40 nm apart, near-field plasmon coupling results; at shorter distances of  $\sim 2$  nm, surface plasmons can be delocalized over the entire nanocrystal monolayer (Figure 3). The observation of these cooperative effects demonstrates the LB technique as a powerful tool for constructing a large-scale, bottom-up material whose collective properties can be tuned by controlling organization at the nanoscopic level. In addition, these close-packed arrays of metal nanoparticles can find immediate application as sensing substrates for surface-enhanced Raman spectroscopy (SERS). Such metallic layers are expected to exhibit large local electromagnetic field enhancement, particularly for anisotropic building blocks with sharp tips and non-circular cross-sections. LB deposition has been demonstrated as a successful tool for the fabrication of high-response SERS substrates by assembling a high density of electromagnetic hot spots that are readily accessible for analyte adsorption.<sup>31,40–42</sup>

### Micrometer-Scale Nanoparticle Fingering Patterns by Dip Coating

While most research efforts in nanoparticle LB films have been directed to produce high-density nanoparticle arrays, little has been done to study low-density nanoparticle monolayers and their transfer onto substrates. Compared with a close-packed nanoparticle monolayer, the dewetting process of a dilute



**FIGURE 5.** Tuning stripe dimension by changing the surface pressure of the water-supported nanoparticle film. (a–d) The SEM images (scale bars = 100  $\mu\text{m}$ ) show that the thickness of the stripes increases with higher particle density on water. (e) The isotherm of the nanoparticle film. The inset shows the typical color of the gold nanoparticle film on water. (f) The coverage of the stripes on the substrate is linearly dependent on the particle density of the particle monolayer. Reprinted with permission from ref 43. Copyright 2005 Nature Publishing Group.



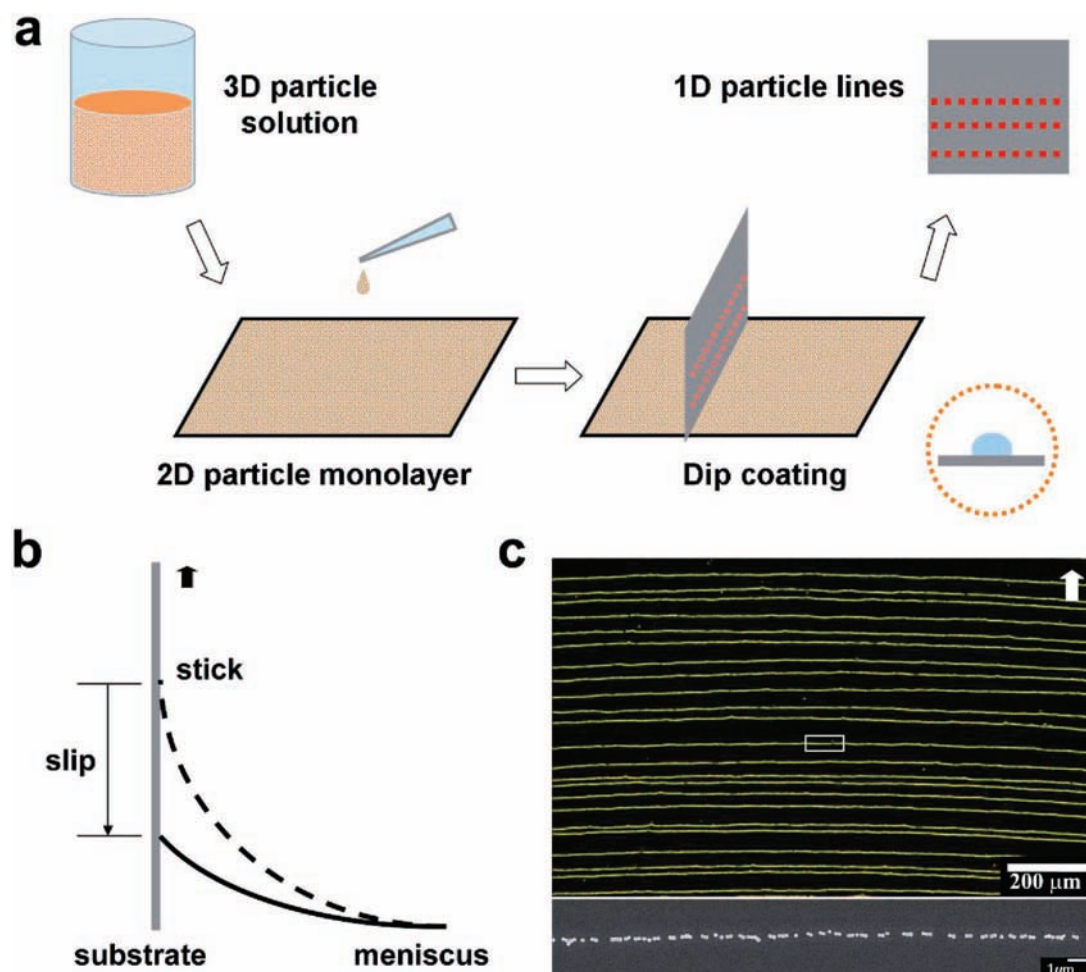
**FIGURE 6.** The periodicity of the fingering instability is highly dependent on the velocity of the moving contact line and can be readily tuned by changing parameters of  $C_a$ : (a) the periodicity of generated stripe patterns is plotted against substrate pulling speed for various viscosities of the aqueous subphase; (b) the period of the stripe pattern is plotted with respect to pulling speed on a log scale.

monolayer is especially interesting because the free space between particles allows a higher degree of convection-induced motion during evaporation. In this manner, LB films can also be utilized to fabricate regular patterns of nanostructures by controlling the deposition process.

Well-aligned stripe patterns with tunable orientation, thickness, and periodicity at the micrometer scale can be obtained

by a facile dip-coating process (Figure 4).<sup>43</sup> Stripe formation results from convective flows at the moving contact line of a colloidal LB monolayer, where film dewetting onto a hydrophilic substrate produces fingering instabilities. The resulting pattern is explicitly determined by factors that affect the meniscus formed between the monolayer and the vertically moving substrate. Nanoparticles are loosely arranged within





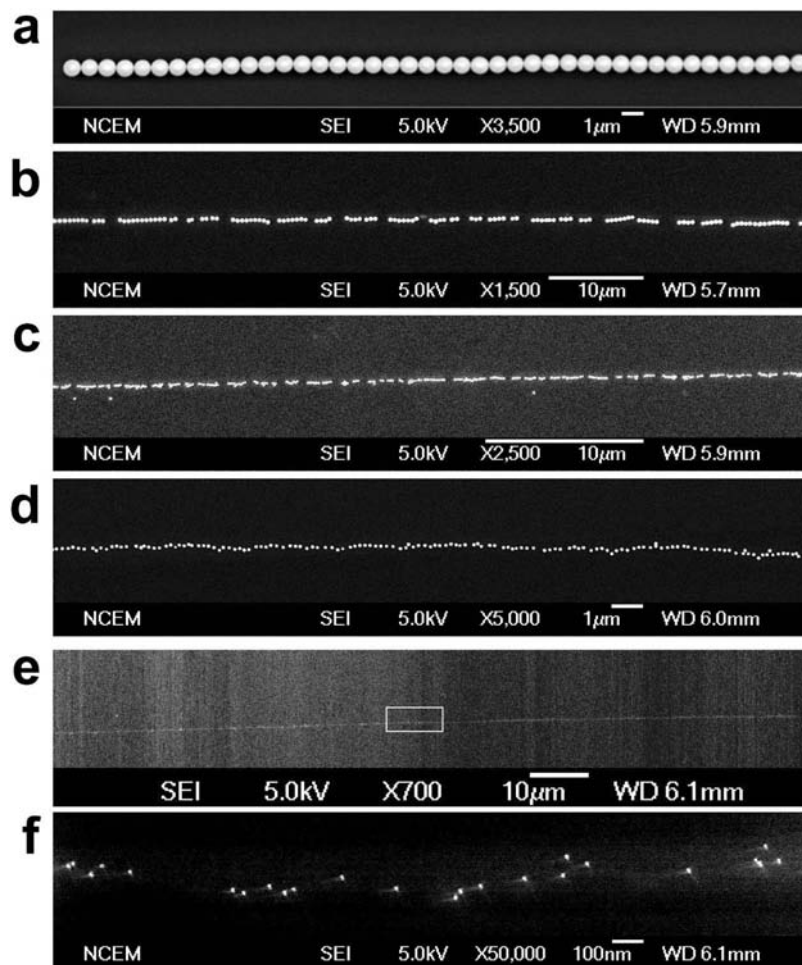
**FIGURE 7.** A general method for assembling 1D arrays of colloidal particles from their dilute monolayer: (a) Schematic illustration showing colloidal particle dispersions with sequentially reduced dimensionality. First, a 3D colloidal solution is spread on to a water surface, forming a 2D particle monolayer. An immersed substrate intersects the monolayer and creates a contact line. With partially wettable substrates, parallel 1D arrays of particles can be deposited on the substrate upon lifting through (b) a stick–slip motion of the contact line. (c) A typical optical microscopy image of thus prepared Au single nanoparticle (diameter 50 nm) lines on a Si substrate. The curvature of the lines replicates that of the water meniscus. The typical line width is approximately one nanoparticle as revealed by the SEM image in panel c. Reprinted with permission from ref 51. Copyright 2006 American Chemical Society.

the stripe pattern. Because dewetting is a general process that involves no special template, this patterning technique is ideal for macroscopic patterning of nanoparticle arrays within small-scale analytical devices such as “lab-on-a-chip.” Specifically, ordered nanoparticle stripes could easily be overlaid with microfluidic channels to create multiplexed, addressable areas for quantitative chemical analysis.

A schematic of the dip-coating process is shown in Figure 4. The retreating meniscus is unidirectional, with evaporation rate controlled by the speed of the moving substrate. Nanoparticles at the contact line are carried off the surface film and dried onto the substrate. During this step, nanoparticles at the water–substrate contact line segregate into periodically distributed domains of nanoparticles due to the fingering instability of the drying front.<sup>44–47</sup> The uniform size of these

domains is likely due to the local depletion of available nanoparticles at the drying edge. As the substrate continues to be raised, more nanoparticles precipitate out of the LB film to form aligned stripes parallel to the pulling direction.

These nanoparticle monolayers present complex points of study in two-fluid systems, where parameters such as viscoelasticity, fluid height, and surface tension are intimately coupled to the chemical and physical nature of the monolayer itself. Hydrodynamic instabilities have been observed for monolayers of brush polymers, which change conformation at the spreading edge,<sup>48</sup> and Langmuir films of lipid molecules give rise to unique patterns dependent on monolayer density.<sup>49</sup> For nanoparticles and nanowires, a wide variety of experimental parameters can be changed during LB film transfer to tailor the resulting stripe pattern. Stripe width is dependent on



**FIGURE 8.** The stick–slip method can readily produce 1D arrays of colloidal particles with a wide range of sizes and materials. A couple of examples are shown in the SEM images: (a) 0.9  $\mu\text{m}$ , (b) 450 nm, and (c) 160 nm  $\text{SiO}_2$  spheres, (d) 50 nm Ag nanocubes, and (e, f) 7 nm Pt nanoparticles. Panel f is a higher magnification image showing the details of the Pt line in panel e. Reprinted with permission from ref 51. Copyright 2006 American Chemical Society.

the particle density on the water surface, which is readily controlled by increasing or decreasing the surface pressure at the air/water interface. When the film is compressed, the stripes become thicker (Figure 5).

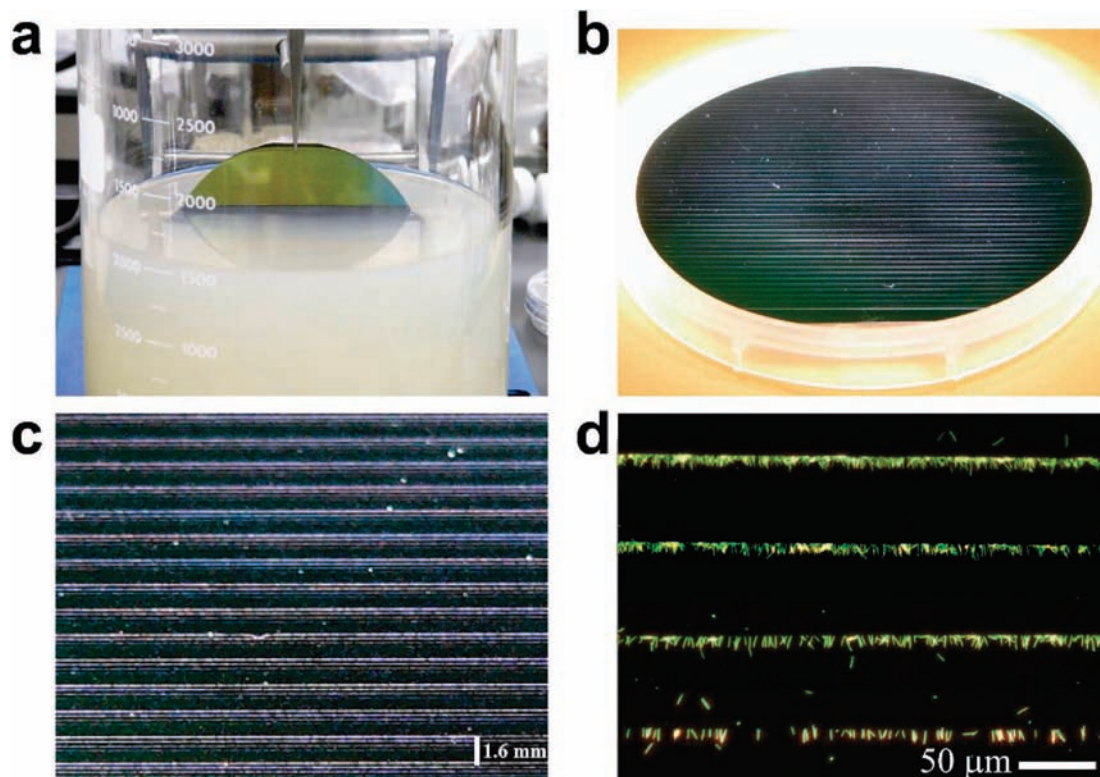
Pulling speed of the substrate is another important factor and can be used to tune the periodicity of the stripe patterns: periodicity increases for decreased pulling speed (Figure 6). The highly periodic pattern of stripes indicates that the contact line instability responsible for fingering adopts a characteristic wavelength. Interparticle interaction plays no observable role in this pattern formation, with the only requirement being an isotropic particle distribution within the LB monolayer. A similar trend has also been observed in other fluidic systems where fingering instabilities occur at the solvent spreading front, evidenced by stripe patterns that undergo bifurcation, coalescence, and widening.<sup>50</sup> For a Newtonian fluid, this wavelength is inversely proportional to the capillary number,  $C_a = V\eta/\gamma$ , where  $V$  is the contact line velocity,

$\eta$  is viscosity, and  $\gamma$  is surface tension. For the stripe pattern generated by our LB nanoparticle monolayers, the experimentally obtained dispersion relation between substrate pulling speed and periodicity gives a dependence of  $\lambda \approx V^{-1/3}$  (Figure 6b), in agreement with the findings by Cazabat et al.<sup>50</sup> Extending this dependence on  $C_a$ , stripe patterns can also be modulated by changing the viscosity of the underlying liquid subphase (Figure 6a).

### Single-Nanoparticle Lines by Stick-Slip Deposition

Furthering this application of monolayer dewetting, extended control over nanoparticle and nanowire placement can be achieved by performing LB film transfer onto a substrate where wetting at the contact line is unfavorable. As previously discussed, when a completely wettable substrate (water contact angle  $< 10^\circ$ ) is pulled vertically through a LB monolayer, ordered micrometer-scale stripes are deposited perpendicular to the contact line.





**FIGURE 9.** One-step patterning of aligned nanowire arrays by programmed dip coating: (a) an oxygen plasma cleaned silicon wafer was immersed in a Ag nanowire dispersion in methylene chloride and pulled out by a programmable mechanical dipper to control the stick–slip motion of the solvent–substrate contact line; (b) nanowire arrays with tunable density and arbitrary spacing over the entire 4-in. wafer were obtained; (c) a magnified view of panel b showing that each repeating set of nanowires is composed of four equally spaced arrays with decreased nanowire density as shown in the optical microscopy images in panel d corresponding to sticking times of 20, 15, 10, and 5 s, respectively. Reprinted with permission from ref 59. Copyright 2007 Wiley-VCH.

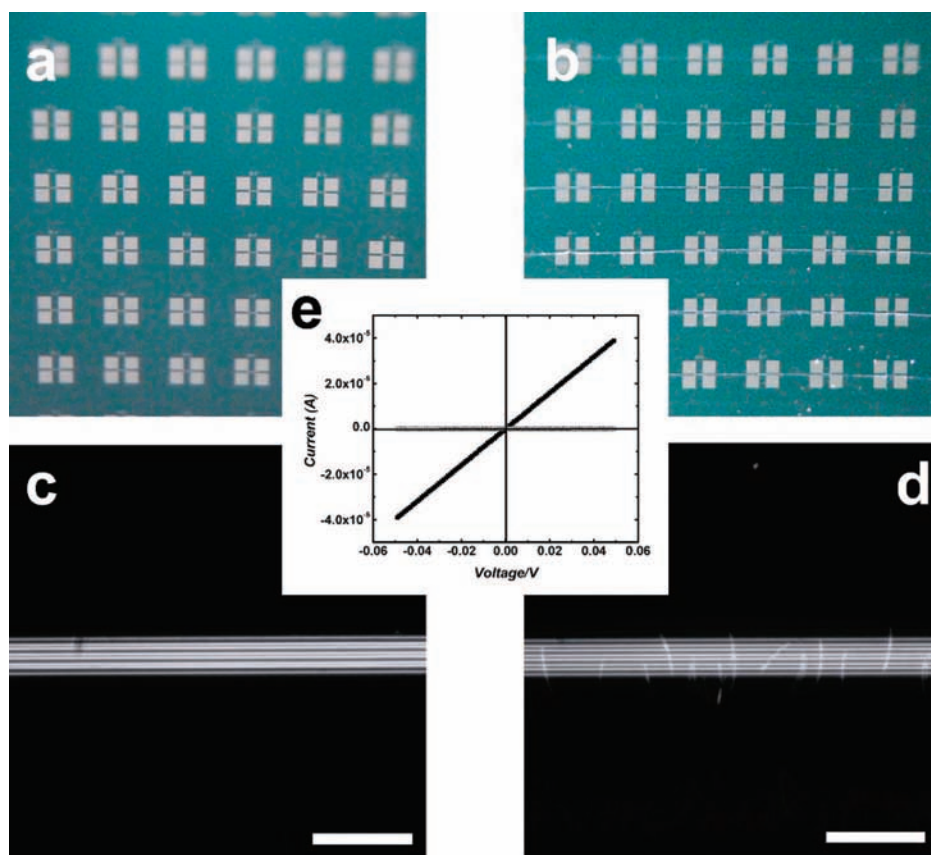
lar to the meniscus.<sup>43</sup> Dip-coating onto a more hydrophobic substrate (water contact angle  $>20^\circ$ ) instead produces patterns of single-particle lines (Figure 7) oriented parallel to the meniscus. Here, contact line pinning occurs at the meniscus formed between the dilute particle monolayer and the partially wettable substrate. During the dip-coating process, the pinned meniscus is dragged by the raising substrate and becomes stretched. Eventually, it breaks and recedes to a new pinning site on the substrate. This stick–slip motion leads to deposition of one-dimensional arrays of nanoparticles that are spatially resolved, where the nanoparticle lines are deposited during a “stick” event and the spacing is due to the “slip” of the meniscus (Figure 7). In this manner, one-dimensional arrays of nanoparticles of varying shape, size, and composition can be controlled in the absence of any lithographic processing (Figure 8).<sup>51</sup> This patterning process has been demonstrated to produce these lines over large areas, with particle diameters ranging from micrometers down to a few nanometers.

Changing the nanoparticle density within the water-supported monolayer is again a convenient means of tailoring

particle density within the patterned lines. With a LB trough, the monolayer can be controllably expanded or compressed by moving a barrier, thus changing the particle concentration. Performing LB monolayer transfer at varying surface pressures results in small groups or chains of nanoparticle oligomers, whereas at higher pressures continuous one-dimensional arrays are obtained. Upon further compression, branched and buckled lines can also be collected. This control over nanoparticle placement allows for the design of hierarchical device structures that otherwise require top-down or serial approaches to patterning. For example, one-dimensional arrays of gold nanoparticles patterned by this stick–slip method have been successfully used to catalyze and template the growth of vertical silicon nanowires arrays.<sup>51</sup>

### One-Step Patterning of Aligned Nanowire Arrays

The concepts of contact line deposition<sup>52–54</sup> and the stick–slip behavior of menisci<sup>55–58</sup> can be extended to a more general method for the patterning of nanowires. While a Langmuir monolayer is necessary for obtaining single-par-



**FIGURE 10.** Selective positioning and addressing of nanowire arrays on prefabricated electrodes by programmed dip coating: (a) optical microscopy image showing a  $6 \times 6$  array of Cr/Pt electrodes on a  $\text{SiO}_2/\text{Si}$  wafer; (b) after selective nanowire deposition, the six parallel nanowire arrays can be seen lying across the electrodes; the center-to-center distance between the neighboring electrodes is 1 mm; (c, d) optical microscopy images showing a set of four probe electrodes before and after nanowire deposition, respectively; (e)  $I$ – $V$  measurement of a thus-made device showing the successful addressing of the deposited nanowire arrays. Reprinted with permission from ref 59. Copyright 2007 Wiley-VCH.

ticle lines, aligned single-nanowire arrays can be obtained by controlled stick–slip deposition from both the 2D monolayer and an isotropic colloidal dispersion if nanowire lengths are in the micrometer range. When a solvent meniscus is pinned on a substrate, capillary flow toward the meniscus is responsible for the highly selective deposition along the contact line, most commonly observed as a coffee ring stain.<sup>53</sup> Uniquely for an evaporating nanowire dispersion, this capillary flow can also orient the nanowires along the flow direction, thus generating aligned arrays deposited selectively at the meniscus. Utilizing this property, we achieved massive patterning of aligned nanowires over large areas such as on a 4-in. wafer as shown in Figure 9.<sup>59</sup> Both nanowire density and line spacing can be programmed using a mechanical dipper to regulate the sticking time and slipping distance, respectively. This low-cost, entirely scalable method also enables the selective positioning of nanowires onto prefabricated electrodes as shown in Figure 10. This assembly method is advantageous because it is produced directly from a nanowire dispersion, the most

common form of nanowire “stock,” with minimal material consumption. This programmed stick–slip deposition clearly demonstrates the potential of controlled dewetting for patterning nanostructures.

## Conclusions

In order to realize the integration of nanoscale materials into devices that have practical significance, nanoscale patterning techniques that are scalable, massively parallel, low-cost, and high throughput must be developed. The use of LB monolayers to produce ordered nanoparticle and nanowire arrays presents a readily implemented solution to these manufacturing obstacles. Transfer of a fluid-supported LB film to a substrate by dip-coating allows added control over nanoparticle and nanowire placement, producing patterns of stripes and lines with variable densities and high fidelity.

The techniques discussed in this review meet the challenges for new production tools that enable device flexibility and functionality, employing the dewetting properties of LB

monolayers rather than relying on templates or serial manipulation. It is most likely, however, that these techniques will not completely supersede top-down approaches but instead will provide a complementary tool for nanoscale patterning. The greatest advantage of the techniques presented here is that no specialized equipment is necessary. In principle, LB assembly and patterning will allow both manufacturers and researchers to rapidly prototype devices using simple bench-top fabrication, furthering the exploration of new device physics and design for nanoscale materials.

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#### BIOGRAPHICAL INFORMATION

**Andrea Tao** is currently a postdoctoral researcher at the University of California, Santa Barbara, where she holds a UC Office of the President's Postdoctoral Fellowship. She received her A.B in Chemistry and Physics from Harvard in 2002 and her Ph.D. in Chemistry from UC Berkeley in 2007, where she worked on the synthesis and assembly of nanocrystals for plasmonic applications. She is the recipient of a Young Chemists Prize from the International Union of Pure and Applied Chemistry and a National Science Foundation Graduate Research Fellowship. Her current research interests include adaptive biophotonics and self-assembling nanoscale systems.

**Jiaxing Huang** received a B.S. in Chemical Physics from University of Science and Technology of China in 2000 and a Ph.D. in chemistry from the University of California, Los Angeles, in 2004. He then became a Miller Fellow to carry out postdoctoral research in Professor Peidong Yang's group at the University of California, Berkeley. He joined the Materials Science and Engineering Department at Northwestern University as an Assistant Professor in 2007. He is the recipient of a Young Chemists Prize from the International Union of Pure and Applied Chemistry and the National Starch & Chemical Award in Polymer Science and Engineering from the American Chemical Society. His current research focuses on the chemical synthesis and assembly of nanostructured materials for tailoring properties and applications; examples include anisotropic plasmonic nanostructures, high-performance conducting polymers, and controlled assembly of soft nanomaterials.

**Peidong Yang** received a B.S. in chemistry from University of Science and Technology of China in 1993 and a Ph.D. in chemistry from Harvard University in 1997. He did postdoctoral research at University of California, Santa Barbara, before joining the faculty in the department of Chemistry at the University of California, Berkeley, in 1999. He is the recipient of Alfred P. Sloan research fellowship, the Arnold and Mabel Beckman Young Investigator

Award, National Science Foundation Young Investigator Award, MRS Young Investigator Award, Julius Springer Prize for Applied Physics, ACS Pure Chemistry Award, and NSF A. T. Waterman Award. His main research interest is in the area of low-dimensional semiconductor and metal nanostructures and their applications in nanophotonics, energy conversion and nanofluidics. More about the Yang group research can be found in <http://www.cchem.berkeley.edu/pdygrp/main.html>.

#### FOOTNOTES

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