

Gold Nanostructures in Diacetylene Monolayer Templates

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Construction of controlled, organized nanostructure assemblies has been among the most challenging aspects of nanotechnology research and development. Diverse approaches for the design and fabrication of nanostructures on solid surfaces have been reported.^{1,2} Most strategies employ “top-down” lithography techniques,³ which are highly robust but exhibit shortcomings when attempted at smaller surface-length scales and for nonconventional configurations. “Bottom-up” self-assembly methods have attracted interest as alternatives to surface lithography.^{4–9} Promising self-assembly strategies have employed monolayers of amphiphilic substances for surface organization of metal nanoparticles (NPs) on water,^{10–12} but the reported approaches generally lack nanostructure organization. Here we demonstrate that diacetylene monomers¹³ that are isothermally compressed at the air/water interface can serve as templates for novel surface architectures of gold nanostructures. Specifically, we show that distinct patterns of alkylthiol-capped Au NPs can be formed within the diacetylene films. The surface patterns can be transferred from the water surface onto solid substrates and further annealed to remove the organic template, yielding organized Au patterns and pointing to the potential utilization of this approach for fabrication of surface nanostructures.

Figure 1 depicts the thermodynamic behavior and monolayer organization of diacetylene **1** at the air/water interface with and without embedded dodecanethiol-capped Au NPs (diameters of ~3 nm, produced through a modified Brust method¹⁴). The surface-pressure/area isotherm of **1** on water (solid curve in Figure 1A) exhibits the typical liquid-expanded/liquid-condensed transition (at ~4 mN/m) and liquid-condensed/trilayer-solid transition (at ~7 mN/m), which lead to formation of a diacetylene multilayer.¹⁵ The isotherm of the pure dodecanethiol-capped Au NPs (dotted curve in Figure 1A) spans a significantly greater surface area because of the particle size and features a collapse at ~10 mN/m.¹⁴

The isotherm of the mixed **1**/dodecanethiol–Au monolayer (0.17 mole % Au NPs; dashed curve in Figure 1A) is similar in shape to the isotherm of pure **1**, suggesting that the dodecanethiol-capped Au NPs do not significantly interfere with the organization and molecular interactions of the diacetylene monolayer. The shift of the isotherm of the mixed monolayer to higher molecular areas than for pure **1** reflects the small percentage of dodecanethiol-capped Au NPs within the diacetylene monolayer.

The Brewster-angle microscopy (BAM) images in Figure 1B provide dramatic visualization of the “templating” effect of **1** upon codeposited Au NPs. Specifically, the *mixed* Au NP/**1** film in Figure 1B(ii) yields a contrast image almost exactly complementary to the BAM image of *pure 1* [Figure 1B(i)], which features a branched monolayer organization as previously reported.¹⁵ The Au NPs (which appear brighter than the monolayer domains of **1** because of the high reflectance of the condensed Au core¹⁶) clearly seem to coalesce on water areas not occupied by the diacetylene domains, thus giving rise to more reflective regions in the BAM images (Figure 1B).

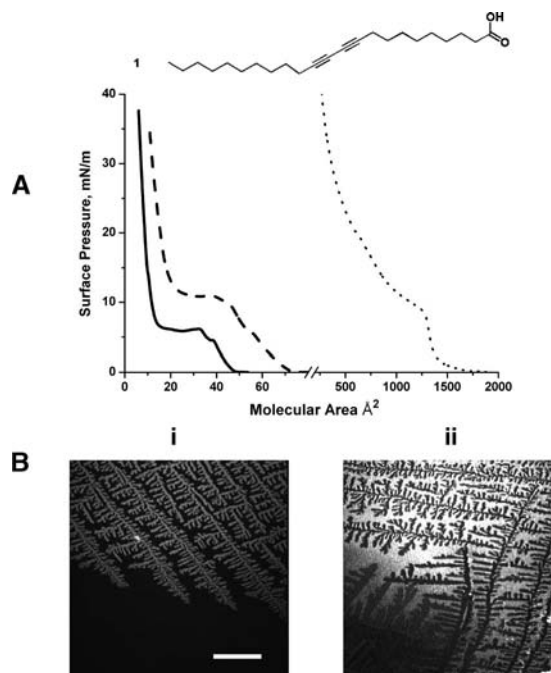


Figure 1. Monolayers of **1** and dodecanethiol–Au NPs at the air/water interface. (A) Surface-pressure/area isotherms recorded at 18 °C for pure **1** (solid curve), pure dodecanethiol–Au NPs (dotted curve), and mixed **1**/dodecanethiol–Au NPs (0.17 mole % Au NPs; dashed curve). (B) BAM images of (i) pure **1** and (ii) **1**/dodecanethiol–Au NPs. The images were taken at a surface pressure of 4 mN/m. The bar corresponds to 100 μm .

While the BAM analysis in Figure 1B illuminates the *micrometer*-scale organization of the alkylthiol-capped Au NPs and the diacetylene template at the air/water interface, we further investigated the mixed films at the *nanometer* scale. Figure 2 depicts transmission electron microscopy (TEM) and atomic force microscopy (AFM) images of the **1**/dodecanethiol–Au NP films transferred by the Langmuir method onto a copper–carbon grid and mica slides, respectively. The TEM data in Figure 2A demonstrate that the Au NPs self-assemble at the boundaries of the condensed (slightly darker) diacetylene domains. The lengths of the Au NP strips are essentially determined by the sizes of the diacetylene domains and can reach several microns. The widths of the bands appear to be highly uniform and can vary from tens of nanometers down to few nanometers, comprising a single file of Au NPs (Figure 2A, rightmost TEM image).

The AFM images depicted in Figure 2B show the structural features of the Au NP assemblies following removal of both the diacetylene template and the alkylthiol capping through plasma etching.¹⁷ The AFM data demonstrate that transfer of the **1**/Au NP film from water onto solid substrates and subsequent removal of all organic and polymer residues (via plasma etching) do not adversely affect the surface organization of the Au NP assemblies, yielding uniform Au nanowires.

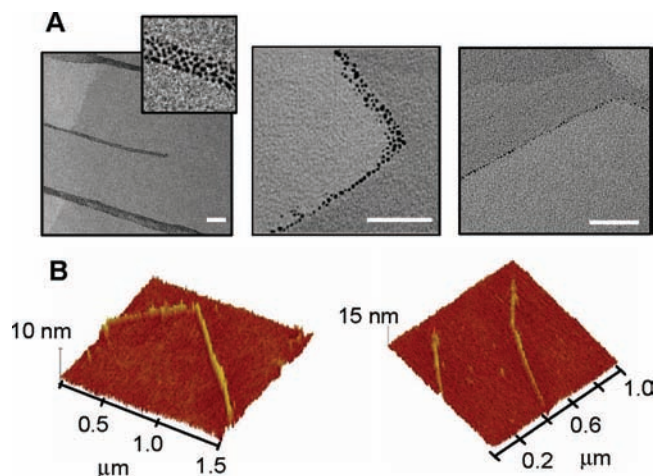


Figure 2. Patterns of Au NPs embedded in templates of diacetylene **1**. The **1**/Au NP films (0.11 mole % Au NPs) were transferred from the water subphase at surface pressures of ~ 15 mN/m. (A) TEM images. The black strips constitute the Au NP assemblies (the inset depicts an enlargement of a strip region showing the distinct Au NPs). Scale bars correspond to 50 nm. (B) AFM images (recorded after plasma etching) that depict Au nanowires.

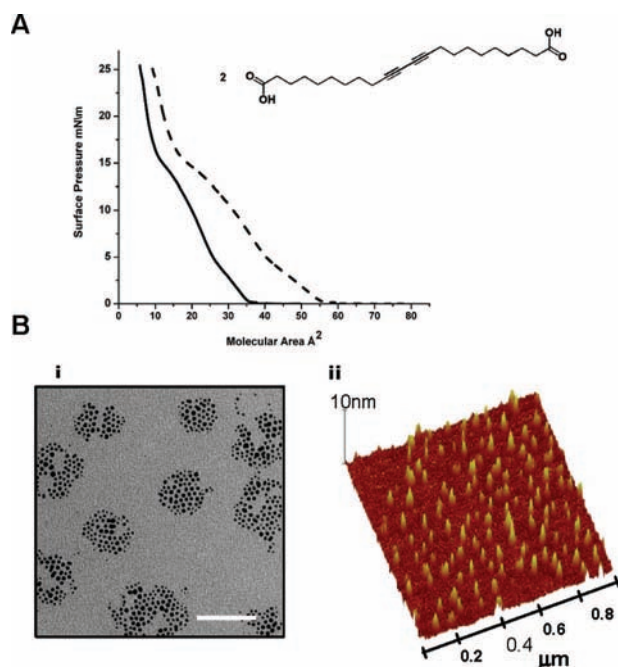


Figure 3. Mixed **2**/dodecanethiol–Au NP films. (A) Surface-area/pressure isotherms of pure **2** (solid curve) and **2**/dodecanethiol–Au NPs (0.14 mole % Au NPs; dashed curve) recorded at 18 °C. (B) Patterns of Au NPs embedded in templates of diacetylene **2** (0.14 mole % Au NPs): (i) TEM image, scale bar 50 nm; (ii) AFM image recorded after plasma etching.

To explore the dependence of the surface Au NP configurations on the molecular properties of the diacetylene template, we further analyzed mixed films comprising dodecanethiol-capped Au NPs and diacetylene **2**, which displays *two* carboxylic residues (one at each end of the molecule). The surface-pressure/area isotherms in Figure 3A indicate that **2** immediately forms a condensed phase after deposition on the water subphase. The isotherm of the mixed film of **2** and dodecanethiol-capped Au NPs (0.14 mole % Au NPs; Figure 3A, dashed curve) retains the overall shape observed for pure **2** and exhibits a shift to higher surface areas, qualitatively similar to the result obtained for the mixed **1**/dodecanethiol-capped Au NP monolayer discussed above (Figure 1).

The TEM and AFM images in Figure 3B show that organized assemblies of the Au NPs are formed in the mixed films of **2** and the dodecanethiol-capped Au NPs. However, the self-assembled Au NPs exhibit dramatically different organization within the template of diacetylene **2** than within **1**. Specifically, Figure 3B indicates that the dodecanethiol-capped Au NPs form “nanoislets” with diameters of ~ 50 nm, with some of the islets enclosing smaller internal voids. The AFM image in Figure 3B(ii) demonstrates that the nanoislet organization is retained after plasma etching, resulting in the formation of relatively uniform dispersed gold protrusions ~ 5 nm in height above the mica surface.

Segregation of self-assembled Au NPs through condensation of amphiphilic molecules has been reported.¹² However, the organization and structural features of the Au NPs embedded within the diacetylene template (Figures 2 and 3) are unique. These structures are directly related to the formation of condensed diacetylene domains at the air/water interface and the existence of significant interactions between the alkyl-capped Au NPs and the diacetylene template. In particular, the Au NPs appear to aggregate at the interfaces, or edges, of the rigid diacetylene domains, thus resulting in the remarkable “templating” effects. The restriction of the alkylthiol-capped Au NPs within the diacetylene template is most likely facilitated through gradual transformations of the mixed monolayers from a liquid-expanded phase to rigid assemblies.

This work describes a new approach for creating organized Au NP patterns using diacetylene Langmuir monolayers as templates. Utilizing varied microscopy techniques (BAM, TEM, and AFM), we identified organized nanostructures of the Au NPs formed within the diacetylene templates, including strips, nanowires, and nanoislets. Importantly, these structures were retained after transfer onto solid substrates and further surface annealing through plasma etching. The molecular diversity and readily available routes for synthetic modifications of diacetylene monomers point to the potential of this new patterning approach for creating varied, ordered nanostructures on surfaces.

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Supporting Information Available: Experimental protocols. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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