

In particular, film deposition by spin-coating onto an unpolished substrate^[11] is tricky, since the spin-coating solution does not wet the substrate and flies off the rotating surface. Since the OTS pattern after the lift-off technique is the inverse of the originally stamped ODT pattern, the sample in Figure 1d features macroscopically an oxide surface with printed OTS stripes on a micrometer lateral scale. Beyond the specific advantages of our technique, structured SAMs from OTS enjoy several advantages over their ODT analogs. The surface energy difference between OTS and silicon oxide is much larger than between ODT and Au,^[12] making patterned OTS substrates more suitable for structured wetting and demixing experiments. Potential applications for chemical and biological sensors^[13] also benefit from this increase in polarity. Furthermore, the silane bond is stronger than the chemisorbed thiols allowing experiments at higher temperatures.

In conclusion, we have combined the well-established μ CP technique of alkane-thiols on Au with a lift-off technique to transfer the stamped pattern onto a silicon-oxide surface. The main benefit of this approach compared to a direct printing technique is the improved control over environmental parameters during the deposition of the alkane-silanes, making the lift-off technique more reliable and reproducible. In addition, the lift-off technique does not depend on specific substrate materials. Therefore, extension to a wide range of surfaces and functionalized alkane chains is possible.

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Fabrication of Ordered Two-Dimensional Arrays of Micro- and Nanoparticles Using Patterned Self-Assembled Monolayers as Templates**

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This paper describes a method that uses patterned self-assembled monolayers (SAMs) of alkanethiols on gold as templates to fabricate ordered two-dimensional (2D) arrays of solid particles, with lateral dimensions ranging from ~50 nm to ~20 μ m. A large number of methods have been developed for producing particles of various materials with sizes from nm to μ m.^[1] Most of these methods produce particles as dispersions in solvents or polymeric matrixes, and most yield a mixture of sizes. Although these dispersions are useful in many applications (for example, in paints or coatings, in imaging systems, drug formulations, or as abrasives),^[2] they have not been useful electrically or optically in functional devices.^[3]

In fabricating devices, the location of functional materials is as important as their properties. Integration of solid particles into devices usually requires placing them in specific positions. We wish to develop new, parallel methods for the fabrication of ordered arrays of small particles. The simplest model systems with which to investigate such arrays are those in which the particles form on a regular grid. Several in situ deposition techniques—for example, molecular beam epitaxy (MBE),^[4] chemical vapor deposition (CVD),^[5] reactions in Langmuir–Blodgett (LB) films,^[6] and pulsed electrochemical deposition^[7]—have been investigated for making arrays of this type. These methods are flexible and capable of generating supported planar arrays of a variety of semiconductor nanocrystallites (some of which have been used to fabricate functional devices such as arrays of quantum dot lasers^[8]), but their accuracy in controlling size distribution and spatial arrangement still needs to be improved for demanding applications. Here we report a method that uses a combination of microcontact printing of SAMs, surface-templated self-assembly, and

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confined crystallization or precipitation to fabricate ordered 2D arrays of micro- and nanoparticles on gold substrates. We demonstrate this procedure using CuSO_4 and KNO_3 as examples. This approach can also be extended to other inorganic or organic materials.

Figure 1 outlines the procedure. We used microcontact printing (μCP)^[9] to pattern the gold surface into grids of hydrophobic (CH_3 -terminated) and hydrophilic (COOH -terminated) SAMs of alkanethiolates. When this patterned substrate is immersed in an aqueous solution of an organic or inorganic salt and then withdrawn, the solution wets and is retained exclusively on the hydrophilic regions of the surface.^[10] The size and shape of the pattern and the contact angle of the liquid fix the volume of liquid in each drop retained on the surface.^[11] The pattern of hydrophilic SAMs thus provides a way of distributing the solution in a regular array of drops that have volumes controllable between ~ 100 attoliters (from $4.0 \mu\text{m}^2$ square patterns) and ~ 1 nanoliter (from $1600 \mu\text{m}^2$ square patterns).^[12] Although we do not know the drop-to-drop reproducibility of the method, it is determined by physical parameters—interfacial free energy, viscosities, velocities, densities—and it should be reproducible in a carefully controlled system. When the water evaporates, a patterned array of particles of the dissolved materials forms. The distribution of parti-

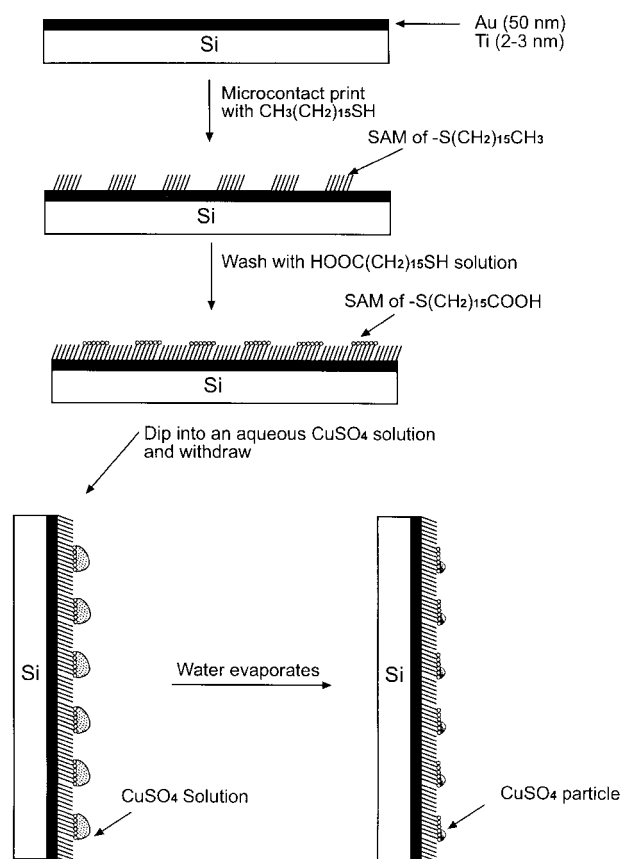


Fig. 1. Schematic procedure for the formation of regular arrays of μm - and nm-sized particles of solid CuSO_4 . The concentrations of the CuSO_4 solutions range from 25 mM to 0.5 M (pH = 5).

cles in hydrophilic regions can be manipulated by withdrawing the substrate from the aqueous solution with different orientations of the pattern relative to the direction of shear on the liquid film. Evaporation of liquid from the drops occurs as and after the substrate is withdrawn, and the solid particles of salt form in the parts of the patterns that are “down” in the gravitational field. The size of these particles can be controlled by the concentrations and compositions of the solution, the shape and area of the hydrophilic region, and the variety of parameters that influence the volume of liquid deposited on each hydrophilic region. Using this procedure, uniformly patterned arrays of solid particles can be formed over areas of square centimeters. Figure 2

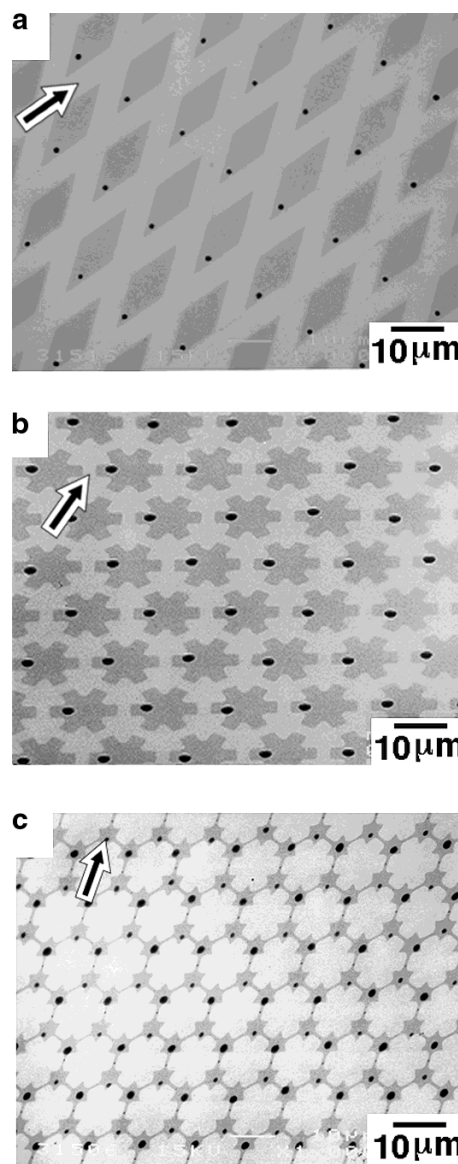


Fig. 2. SEM images of ordered arrays of CuSO_4 particles formed by withdrawing the patterned surfaces from a 0.5 M CuSO_4 solution along the direction as shown by the arrows (the arrow points “up” in the gravitational field). The substrate was held in that orientation while water evaporated. The black dots are CuSO_4 particles; the dark regions represent COOH -terminated SAMs; the bright regions are CH_3 -terminated SAMs.

shows scanning electron microscopy (SEM) images of regular arrays of CuSO_4 particles that formed on the hydrophilic regions. The patterned substrate was withdrawn slowly (less than 1 cm/s) from an aqueous solution along a particular direction (as indicated by the arrow); the orientation of the sample was maintained in that direction while the water was allowed to evaporate at room temperature (~ 30 s).

The SEM images in Figure 2 demonstrate the capability of this procedure to generate highly ordered 2D arrays of particles on the surfaces of solid substrates. Three different test patterns (Fig. 2a–c) with increasingly complex structures were tried, and ordered arrays of CuSO_4 particles were formed on all of these patterned surfaces. Note that Figure 2c has a continuous network (rather than isolated areas) of hydrophilic SAMs. Immediately after the substrate is withdrawn from the CuSO_4 solution, water covers all the hydrophilic areas. As water starts to evaporate, the continuous network of water breaks into arrays of isolated droplets (on the hydrophilic triangular areas) from the narrow lines that bridge the triangles. Because of gravity, those triangles that are oriented parallel to the arrow showing

the direction of withdrawal have more water than those oriented perpendicular to the arrow. As a result, the CuSO_4 particles in these two sets of triangular areas have different sizes; the spatial order of the CuSO_4 particles is, however, still maintained in the array. Even smaller particles are also formed on those “bridges” between triangles that lie along the vertical direction.

One way to control the lateral dimensions of particles or crystals is to change the size of patterned hydrophilic regions in the SAMs. Figure 3 shows SEM images of arrays of CuSO_4 particles and KNO_3 crystals that were formed on gold surfaces patterned with SAMs of various feature sizes. These SEM images show that the lateral dimensions of the CuSO_4 particles or KNO_3 crystals decrease from ~ 20 μm to ~ 150 nm as the area of COOH-terminated SAMs decreases from ~ 2500 to ~ 1.0 μm^2 .

The dimensions of the particles can also be controlled by the concentration of the aqueous solution. Figures 4a and 4b show atomic force microscopy (AFM) images of arrays of CuSO_4 particles that were formed on gold surfaces patterned with 5×5 μm^2 square grids of COOH-terminated

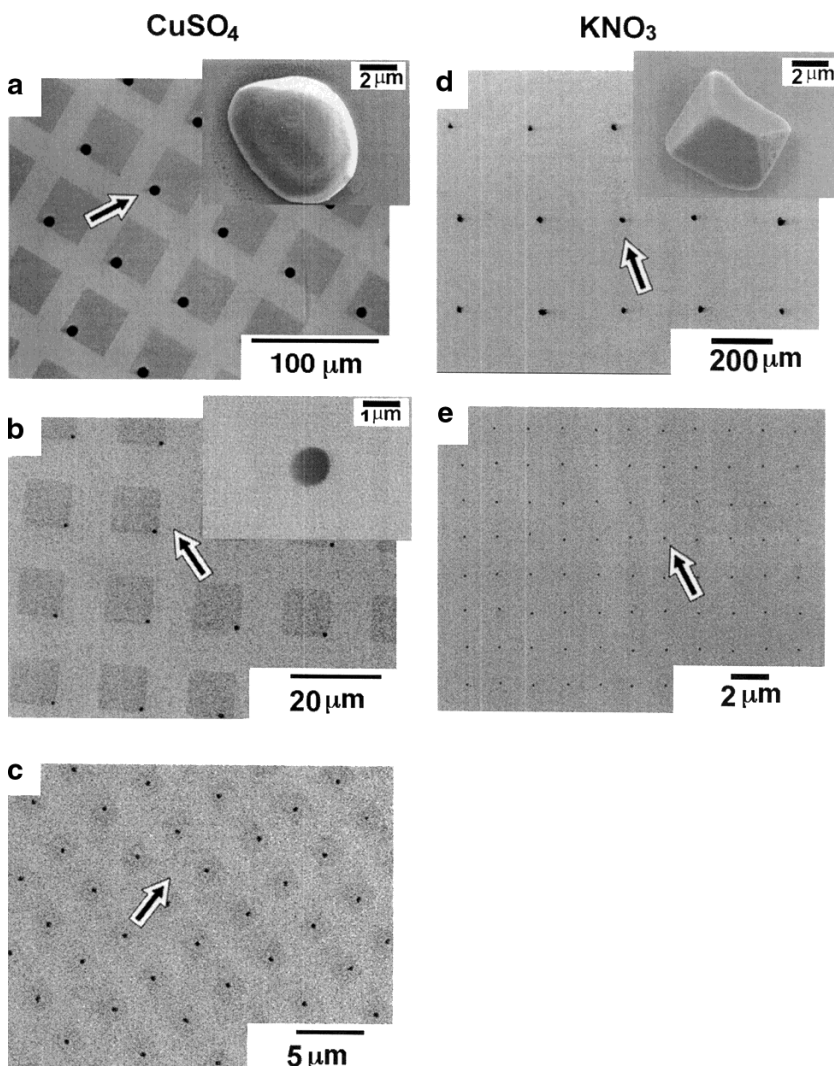


Fig. 3. SEM images of CuSO_4 particles and KNO_3 crystals formed on surfaces patterned with SAMs having different feature sizes. a), b), c): CuSO_4 particles on COOH-terminated SAM. d), e): KNO_3 crystals on COOH-terminated SAM. The crystal facets and planes of the KNO_3 crystal are well defined, although its perimeter is irregular.

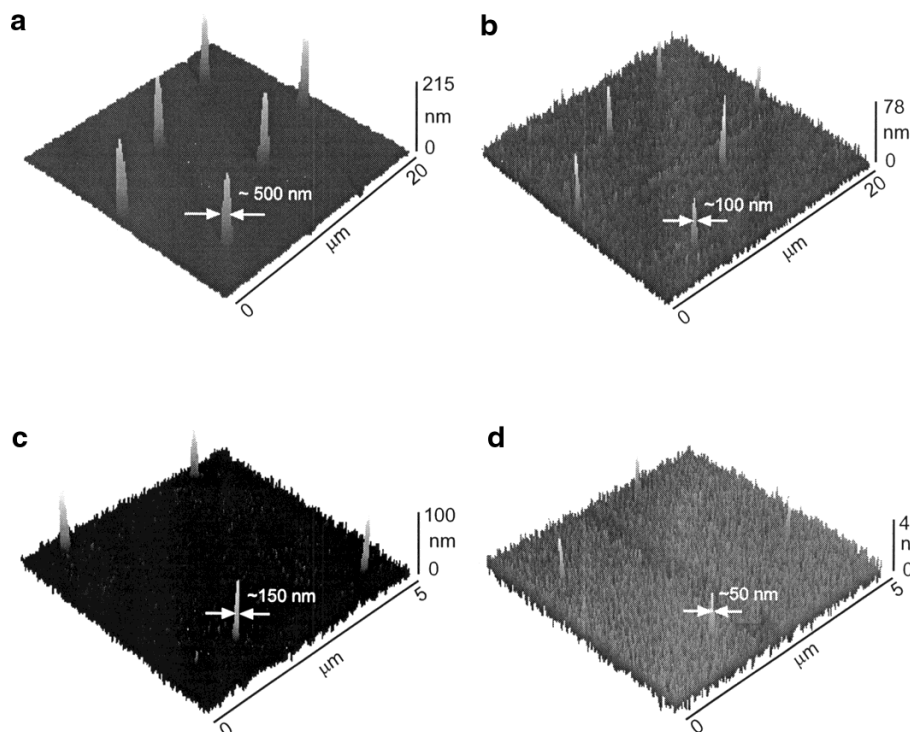


Fig. 4. a,b) AFM images of regular arrays of CuSO_4 particles formed on surfaces patterned with $5 \times 5 \mu\text{m}$ square grids of COOH-terminated SAMs from a 0.5 M and a 0.05 M CuSO_4 solution, respectively. c,d) AFM images of CuSO_4 particles formed on surfaces patterned with $2 \times 2 \mu\text{m}$ square grids of COOH-terminated SAMs from a 0.5 M and a 0.05 M CuSO_4 solution, respectively.

SAMs from a 0.5 M and a 0.05 M CuSO_4 solution, respectively. Figures 4c and 4d show AFM images of arrays of CuSO_4 particles that were formed on surfaces patterned with $2 \times 2 \mu\text{m}^2$ square grids of COOH-terminated SAMs from a 0.5 M and a 0.05 M CuSO_4 solution, respectively. When the concentration of CuSO_4 decreased by a factor of 10, the lateral dimensions of the CuSO_4 particles decreased by a factor of ~ 3 – 5 and the vertical dimension decreased by a factor of two. We note that the ~ 50 nm CuSO_4 particle (the smallest we have prepared in terms of lateral dimension) contains only $\sim 10^{17}$ mole of the material ($\sim 6 \times 10^6$ Cu^{II} ions). It should be possible to prepare ordered 2D arrays of CuSO_4 particles with lateral dimensions smaller than 50 nm using patterns with smaller feature sizes and/or salt solutions with lower concentrations. The surface roughness of the polycrystalline gold films makes it difficult to resolve the particles by electron microscopy. By working with different substrates, it should be possible to circumvent this problem.

We have demonstrated the concept of formation of patterned solid particles from confined droplets primarily using CuSO_4 and KNO_3 as examples, but we have also extended this procedure to other systems where regular arrays of particles of functional materials can be fabricated. For example, we patterned arrays of an organic dye (Fig. 5a) and particles of gold colloid (Fig. 5b) on the gold surface. By patterning CdCl_2 crystals on the gold surface, then reacting these particles with gaseous H_2S , we generated arrays of CdS particles (Fig. 5c); these particles are potentially useful as patterned light-emitters or absorbers.^[14]

In summary, gold surfaces patterned with regions of hydrophobic and hydrophilic SAMs have been used to generate regular arrays of droplets of aqueous solutions^[14] (as small as 100 attoliters in volume) on the surfaces of gold substrates. Subsequent crystallization (or precipitation) from these droplets yielded spatially ordered 2D arrays of micro- and nanoparticles. Both the spatial distribution and the dimension of the solid particles can be controlled in this procedure. These patterning methods also provide routes to arrays of particles of other simple inorganic salts, which may be useful in nanoscience/technology. For example, these arrays might be used as a diffraction grating; or as masks in reactive ion etching or metastable atom lithography to transfer nanopatterns into the underlying substrates.^[15,16] These arrays can also, in principle, be converted into arrays of functional materials (for example, ZnO, a good luminescent material) through solid-state reactions such as thermal decomposition.

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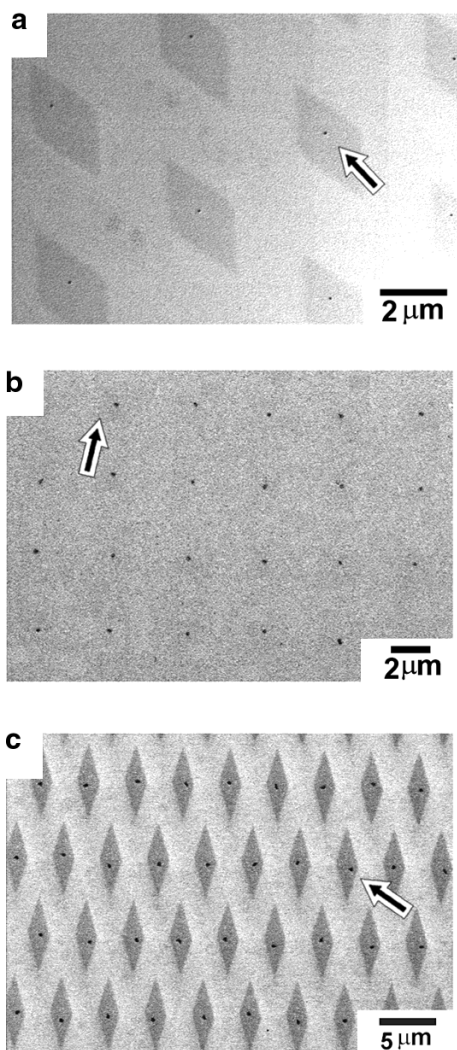


Fig. 5. a) SEM images of Nile Red particles formed on Au surfaces with COOH-terminated SAMs from 0.01 M ethanol solution. b) SEM images of clusters of gold colloids formed on Au surfaces with COOH-terminated SAMs from the solution of gold colloid (10 nm). Each cluster contains ~300 colloid particles. c) SEM images of CdS particles formed on Au surfaces, after reacting CdCl₂ particles (from 0.1 M CdCl₂ solution) with gaseous H₂S.

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Electrodeposited Quantum Dots: Metastable Rocksalt CdSe Nanocrystals on {111} Gold Alloys**

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Many materials exist in more than one crystal form. Often, one or more of these forms is unstable under normal ambient conditions. In some cases, these thermodynamically unstable forms may be kinetically stable in ambient conditions, a state known as metastability.^[1]

Bulk CdS and CdSe are known to undergo a phase transition from the tetrahedral Wurtzite (WZ) structure to an octahedral rocksalt (RS) form under high pressure. The lattice parameters of the RS form depend on the pressure, but are typically 5% smaller than those of the WZ or Zincblende (ZB) (also tetrahedral) structures.^[2] Upon release of the pressure, the structure reverts to a mixture of WZ and ZB with some hysteresis (the pressure at which RS transforms to WZ/ZB is lower than the reverse transition). Nanocrystals exhibit special properties with regard to phase transformations. CdSe nanocrystals were shown to undergo the WZ to RS transition at higher pressures than bulk CdSe and the hysteresis range was much larger.^[3,4] Tolbert and Alivisatos^[4] and Brus et al.^[1] discussed the differences between solid–solid phase changes in bulk and nanocrystalline materials in terms of two main factors. 1) The absence of defects in nanocrystals (phase change in bulk material is usually initiated at defects), which introduces a

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