NANOMATERIALS

The art of empty space

Nanoparticle assemblies can be transformed into regular and stable nanoporous materials

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Porous metals, semiconductors, and ceramics are widely used in optoelectronics, biological sensing, catalysis, and energy conversion and storage. Materials with pore diameters ranging from less than a nanometer to a few nanometers include zeolites (1), metal-organic frameworks (2), supramolecular coordination frameworks (3), and DNA lattices (4). Alternatively, colloidal crystals can be used to create micrometer-scale pores. However, voids that are several nanometers to several tens of nanometers in size make atomic lattices unstable and often collapse; such materials are therefore difficult to synthesize. On page 514 of this issue, Udayabhaskararao et al. (5) report a method for engineering primarily two-dimensional and, in some instances, three-dimensional materials that have regular nanometer-scale spaces between 5 and 25 nm and do not collapse.

The authors use inorganic nanoparticles, which have previously been shown to assemble into frameworks with nanoscale pores; however, nonuniform particle sizes led to variable pore sizes (6). Udayabhaskararao et al.'s method involves mixtures of inorganic nanoparticles, one type of which is dissolved ("sacrificed") to create pores. Such a sacrificial strategy has been used in the past to make singular nanoshells (7, 8), but not for binary nanoparticle constructs that make possible a wide variety of atom-like superlattices.
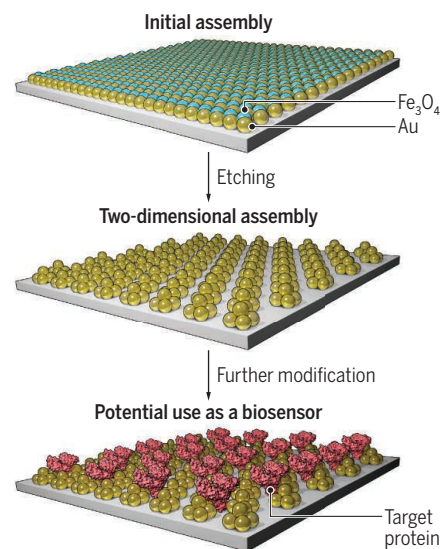
The authors start from monolayers and multilayers of two chemically dissimilar nanoparticles—gold (Au) and magnetite (Fe_3O_4)—formed at the interface of diethylene glycol and air. They used the Langmuir-Blodgett lift-off technique (9, 10) to create binary nanoparticle superlattices that could cover any solid surface (see the figure). Dissolution of one nanoparticle type would produce non–close-packed nanoparticle arrays of the other type, with nanoscale vacancies. However, the nanoparticles are coated with surfactant molecules, providing partial protection from etching agents. The authors deprotected them by gently heating the nanoparticle films to 70°C; at this temperature, the surfactant layers migrate from the nanoparticles to the underlying carbon films. After this step, exposure of the closely packed superlattices to hydrogen chloride or hydrogen cyanide successfully etched away Fe_3O_4 or Au, respectively.

With this method, as much as half of the particles in two-dimensional lattices can be removed without collapse into a disorga-

Nano-vacancies by self-assembly

Etching away iron oxide particles leaves regular gold nanoparticle assemblies. The gaps are of ideal size for biomolecular sensing and other applications.

Initial assembly

Fe_3O_4
Au

Etching

Two-dimensional assembly

Further modification

Potential use as a biosensor

Target protein

nized or closely packed solid. However, the nanoparticles reorganize during this process. For example, Au nanoparticles cluster together to form tetrahedral quintets when the supporting Fe_3O_4 nanoparticles are dissolved. After heat treatment, the nanoparticles coalesce further into supraparticles that are held together primarily by van der Waals forces (see the figure). This secondary reassembly opens up more space in the nanoparticle lattice while maintaining long-range organization. Superlattices with high Au content show variable coalescence patterns; one of them leads to the long-range assembly of a conductive membrane with nearly perfect hexagonal elements.

The computational design of nanoparticle assemblies with vacancies requires consideration of the collective motions of a nanoparticle in three dimensions. Full description of the close-range interactions of nanoparticles with surfactant layers in solution (where most self-assembly processes take place) is challenging because nanoscale interactions are not additive in the traditional sense of colloidal science (11), they cannot, therefore, be computed by separation into familiar electrostatic, van der Waals, and hydrophobic components. The authors were nevertheless able to successfully model the nanoparticle reorganization because vacuum conditions and etching simplify the computations by removing the surfactant and solvent molecules from the calculations.

The ability to create stable, non–close-packed particle arrays with nanoscale pores opens multiple pathways for future scientific inquiries and emerging technologies. The authors demonstrated, for instance, the drastic—more than one order of magnitude—improvement in Raman scattering intensity for superlattices with vacancies of specific shape and size. Nanoscale pores are also needed for biomedical applications such as continuous biomonitoring of cancer markers, biomimetic catalysis, and drug delivery because nanoscale dimensions are typical for biomacromolecules. The formation of host-guest complexes (see the figure) in these arrays may be identified with Raman scattering, electrical conductance surface capacitance, magnetic measurements, and reflectivity (12).

A key challenge for some of these non–close-packed arrays will be to ensure solvent stability. Bridges between the nanoparticles will increase the robustness of the superstructure, although at the expense of pore size uniformity. The possibility of field-driven subwavelength phenomena in electrically conductive networks is intellectually stimulating and has far-reaching practical implications for electro-optics and energy storage (13). ∎

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