Complex Colloidal Assembly

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ate separation anxiety in young animals (*6*)? Perhaps affective urges for maternal caregiving are triggered as mothers' brains experience psychological pain engendered by their infants' cries. It may be that empathic coordination of social motivations is mediated by emotional resonances among nearby animals, allowing receivers to experience the emotions of transmitters. At such deep affective levels, emotional states may reverberate among animals, with no need for learned re-representations arising from mirror neurons. Mammals may have intrinsic abilities to resonate with the pains and joys of nearby others through primal emotional contagion.

Much deep-brain research remains to be done to understand the degree to which mammalian empathy is achieved more through higher social-cognitive processes or primal affective processes in the brain. Simplified models of empathy, as in mice and rats, offer new inroads for understanding our own social-emotional nature and nurture. Such knowledge may eventually help us promote nurturant behaviors in humans.

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MATERIALS SCIENCE

Complex Colloidal Assembly

A colloidal chemistry approach is used to fabricate complex three-dimensional objects on the nanometer scale.

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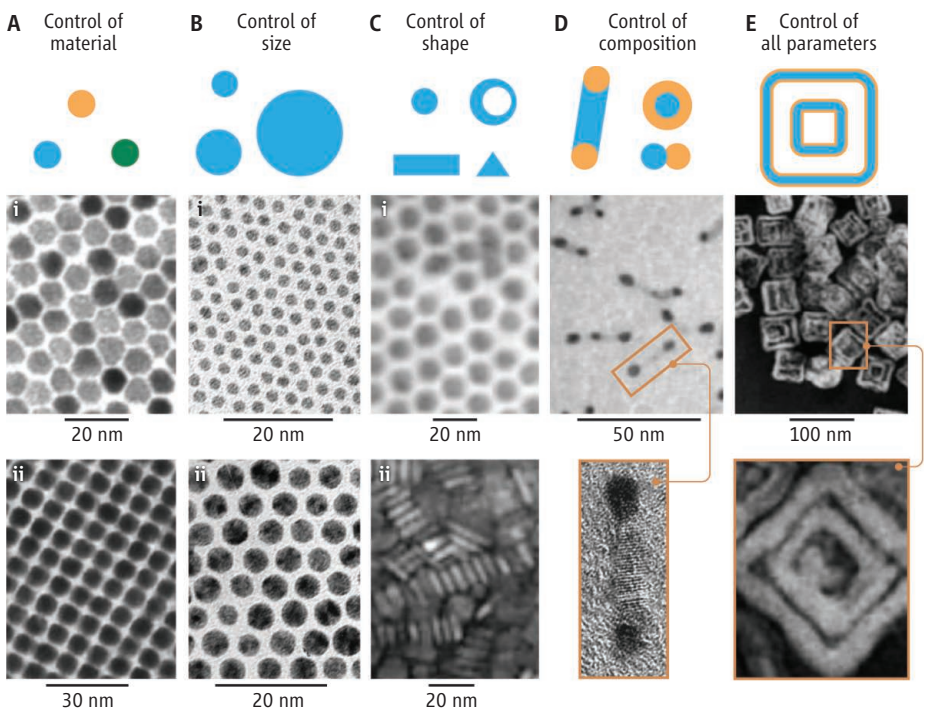
Since the popularization of nanotechnology almost two decades ago, the public has been fascinated by the prospect of a "nano-assembler" for the construction of complex three-dimensional (3D) objects. Such a device would assemble objects atom-by-atom or molecule-by-molecule. Indeed, small objects have been assembled on a 2D surface by picking up individual atoms and molecules with the tip of a scanning tunneling microscope or an atomic force microscope, respectively (*1*, *2*). However, it is not only the action of gripping an object that presents a challenge, but also its release at the designated position. The Nobel laureate Richard Smalley described this as a problem of "sticky fingers" (*3*). There is, however, an alternative approach for bottom-up assembly on the nanometer scale that originates from colloidal chemistry. On page 1377 of this issue, González *et al*. (*4*) report on the synthesis of complex 3D colloidal nanoparticles, a route that may circumvent the problem of the sticky nano-finger.

In colloidal chemistry, 3D objects are formed by self-assembly of atomic or molecular precursors (crystallization). Although this is a parallel approach that allows for producing many objects, the complexity of such objects so far has been limited; the degrees of freedom to design the structure and composition of the object were relatively low. In contrast, González *et al*. demonstrate the complexity with which colloidal nano-objects can be synthesized, how colloidal nanoparticles (NPs) are formed, and how their geometry and composition can be designed.

Colloidal NPs are self-assembled in solution by nucleation and further growth of atomic or molecular precursors. Different precursors will obviously lead to NPs made of different materials (see the figure, panel A). Size uniformity, achieved through the interplay of van der Waals forces and surface tension, can be externally controlled



Putting it together. (**A**) Nanoparticles (NPs) can be synthesized out of different materials, such as (i) CdSe (*10*) and (ii) FePt (*8*). (**B**) The size of the NPs can be controlled, such as for Au NPs with diameters of (i) 4.5 nm and (ii) 9.6 nm (*7*). (**C**) NPs can be made with different shapes, such as (i) disk-shaped and (ii) spherical Co NPs (*11*). (**D**) NPs can also be synthesized with defined domains of different materials, such as CdSe nanorods with spherical Au on their tips (*14*). (**E**) Control of all parameters leads to complex objects, such as the Ag/Au NP composites demonstrated by González *et al*.

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by the concentration of the precursors and by temperature. Size control is important for exploiting quantum effects of NPs, such as the size-dependent fluorescence of semiconductor NPs. Current size control methods enable the production of NPs with size distributions sufficient to crystallize and form 2D and 3D lattices (*5*–*8*) (see the figure, panel B). Protocols for the synthesis of NPs of most inorganic materials already exist. In order to keep NP colloids stable, their surfaces are typically covered with charged molecules or with molecules that provide steric repulsion (ligands). These ligand molecules can be highly ordered, so that x-ray diffraction structures of crystallized ligand-coated NPs can be recorded. Even when proteins adsorb onto the NP surface under physiological conditions, the so-called protein corona possesses remarkable order (*9*).

By performing NP synthesis in templates or by making use of the fact that different crystalline facets of NPs can grow with different speeds, control of the NP shape is also possible (see the figure, panel C). Besides spherical NPs, NPs in the shape of rods (*10*), disks (*11*), cubes, and prisms (*12*) have been demonstrated, as have hollow (*13*) and branched NPs. Moreover, the material composition of NPs can be locally tuned. This began with core-shell structures, whereby the NP core and shell are composed of different materials and culminate in rod- or tetrapod-shaped NPs with attached spherical NPs (*14*) or branched structures of different materials (see the figure, panel D). The diversity of examples illustrates the control of material, size, shape, and composition of NPs that is now possible.

González *et al*. use a combination of all degrees of control, in addition to using clever concepts. One such concept is based on galvanic deposition. If a material (such as a metal) in reduced state A is present in a solution of atoms or molecules of B^+ in its oxidized state, which have a higher electrochemical potential, then the surface of the material A will be oxidized ($A \rightarrow A^+$) and driven to solution, whereas atoms or molecules from solution are reduced and deposited at the surface ($B^+ \rightarrow B$). For example, this process occurs for the case of an iron nail placed in a solution of copper ions. Some iron on the surface will go to solution, whereas the surface of the nail will be covered with elemental copper. On the other hand, the Kirkendall effect, which is based on different diffusion rates of a diffusion couple, has been used to create NPs with defined cavities (*13*). González *et al*. report a protocol in which they first synthesize Ag NPs and then create, by subsequent application of the Kirkendall effect and galvanic deposition, controlled cavities and coating of the Ag surface with Au (see the figure, panel E). By addition of Pd, even a third material could be integrated in the NPs.

Taking into account all the different parameters for the designed growth of colloidal NPs, we can conclude that modern synthesis techniques allow for excellent control of geometry and composition with maze-like interiors that are not available to physical growth techniques such as molecular beam epitaxy. Colloidal NPs may never be amenable to atom-by-atom control as demonstrated for small 2D assemblies, but larger 3D objects can be obtained in parallel. This paves the way for designing NPs to perfectly match their desired application.

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CLIMATE CHANGE

Using the Past to Predict the Future?

Reconstructions of climatic conditions on Earth during the Last Glacial Maximum may help to constrain the likely magnitude of global warming.

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Predictions of future climate change are subject to considerable uncertainty, for two main reasons: Future factors that may influence climate—such as emissions of greenhouse gases, volcanic eruptions, and changing solar activity—are uncertain; and knowledge of how strongly the climate system responds to external influences, particularly increases in greenhouse gases, is incomplete. One way to summarize this latter type of uncertainty is by estimating the equilibrium climate sensitivity (ECS), which is defined as the equilibrium response of global surface temperature to a doubling of the atmospheric CO_2 concentration. On page 1385 of this issue, Schmittner *et al*. (*1*) report that the use of spatially more complete paleoclimate data for the Last Glacial Maximum (LGM) shows promise for narrowing the ECS uncertainty ranges relative to previous estimates.

The lower limit for ECS values is quite well constrained. A range of observational data shows a substantial change in global temperature in response to changes in Earth's energy balance (*2*, *3*). However, the upper limit has proven more difficult to estimate. This is reflected in the conclusions of the Intergovernmental Panel on Climate Change (IPCC) that the ECS "is likely to be in the range 2 to 4.5°C with a best estimate of about 3°C, and is very unlikely to be less than 1.5°C. Values substantially higher than 4.5°C cannot be excluded, but agreement of models with observations is not as good for those values" (*2*). This situation makes it difficult to rule out large temperature increases in response to greenhouse gas increases, or to estimate the atmospheric CO_2 concentrations that would allow certain warming thresholds to be avoided (*4*, *5*).

Estimates of ECS can be obtained from climate models, observations of modern climate change, and reconstructions of past climatic (paleoclimatic) conditions. The usefulness of paleoclimatic constraints has been questioned because the uncertainties associated with proxy-based climate information are much greater than those within the observational record. Furthermore, there may be no paleoclimatic analogs for the forcing or boundary conditions of the current cli-

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