yield nanoparticles soluble in organic agents or water. The amine in the oleylamine provides the reducing equivalents both for tetrachloroauric acid and silver acetate. The carbon double bond does not play a significant role in the process, since other aliphatic amines work equally in the reaction. Oleylamine was chosen because it is commercially available and is inexpensive, said the researchers. The reaction typically proceeds over the course of ~2–24 h. The size of the metal nanoparticles can be controlled by varying the concentrations of the metal precursor and the amine and by adequately choosing the growth temperature.

The researchers also show that the resulting particles have oleylamine weakly adsorbed on the surface and that this surfactant can be easily exchanged with aliphatic and functional thiols, thus allowing the solution of gold and silver nanoparticles in both aqueous and non-aqueous media.

ROSALÍA SERNA

## General Approach for Fabricating Inorganically Coupled Colloidal Quantum Dots and Rods Developed

A.P. Alivisatos of the University of California, Berkeley, and colleagues there and at Lawrence Berkeley National Laboratory (LBNL) have fabricated coupled quantum dots and segmented nanorods into tunable, linear, and multiple-branching forms. The linear and branched topology can be created at any point during the growth of heterostructures, not just at nucleation. To calculate the electronic interactions of the branches in three dimensions, the researchers developed a method that draws on the technique of local density approximation (LDA), extended to the entire system.

As reported in the July 8 issue of *Nature* (p. 190), the Alivisatos group used suspensions of cadmium, selenium, tellurium, sulfur, and other constituents. When these are assembled from liquid solution, crystals of different cadmium compounds are formed. A given structure begins with a quantum dot. The dot is then made to sprout four arms made of the same or a different compound. The arms of such a tetrapod can be lengthened into nanorods containing segments of different compounds. Nanorods, whether or not they are the arms of tetrapods, can be induced to branch into separate rods of the same or a different compound (see Figure 1a).

"Linear heterojunctions were formed when precursors for a second material were added to a growth solution containing preformed nanorods or tetrapods," said the researchers. The research group synthesized linearly extended rods with CdS rods and CdSe extensions. They synthesized branched rods with CdS rods and CdTe branches.

"Nanoprobe x-ray energy dispersive spectrometry…confirm[ed] the presence of Te at either end of branched-rod heterostructures, Se in the central rod, and Cd throughout," the researchers said. These results were further corroborated by powder x-ray diffraction, transmission electron microscopy (TEM), and high-resolution TEM (HRTEM). HRTEM revealed a continuation of anisotropic wurtzite growth in the second semiconductor, the researchers said.

They concluded that "a branched junction forms when the new material initially grows in the zinc-blende structure, followed by a reversion to anisotropic wurtzite growth, forming the branches. Zinc-blende formation is favored by a high supersaturation of the precursors immediately following injection, with wurtzite growth resuming as concentrations drop."

To calculate the electronic states of the nanostructures, L.-W. Wang of the Computational Research Division at LBNL said that LDA, which is sufficient for calculating electronic structures of small systems, would be impractical for a nanosystem. The memory needed for calculation increases as the square of the number of atoms in the system, while the needed processing power increases as the cube.

So, Wang and his colleagues developed a hybrid method. They drew on LDA to determine the charge density in one small region of a crystal, then by "charge patching," they extended the charge density to the entire system, in this case, a quantum dot or nanorod.

To accurately model a nanostructure, Wang began by "passivating" its surface with fractionally charged pseudohydro-
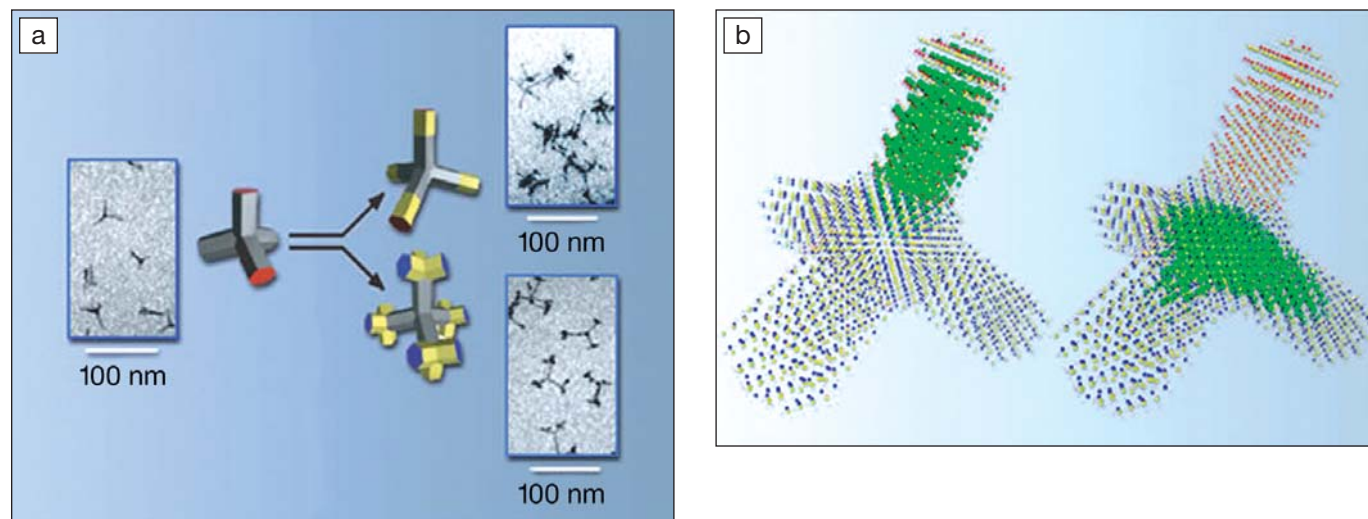


Figure 1. (a) Tetrapods of CdSe (left) extended with segments of CdTe (upper right), which can be made to branch in turn (lower right). (b) Calculations using local density approximation, the charge-patching method, and the folded spectrum method yield atom-by-atom electronic maps of a tetrapod with one leg of CdSe and three of CdTe. On the left, green marks the conduction band's lowest energy state, which is physically separated in the structure from the valence band's highest energy state, shown in green on the right. For the calculated tetrapod, each branch has a diameter of 2.2 nm and a length of 4.2 nm.

gen atoms—mathematical entities that assign the surface atoms the same reactivity as that of a real nanoparticle in suspension. The positions of the interior atoms were calculated with the valence force field method, which models the strength, elasticity, and direction of bonds among atoms.

Then LDA was used to determine the charge "motifs" around a number of representative atoms, including the surface pseudohydrogens. Through charge patching, the calculation is extended to include the entire nanostructure. In a final step, a "folded spectrum" method that Wang developed 10 years ago is used to determine the material's electronic states near the bandgap, including the highest energy state of the valence band and the lowest energy state of the conduction band (see Figure 1b).

Mapping the ways different compounds are assembled into different structures reveals the structures' optical and electronic properties.

Wang said, "The charge-patching method allows us to model thousand-atom structures with *ab initio* accuracy in about one hour."

## High Purity and Controllable Growth of $Mg_2B_2O_5$ Nanowires Accomplished by CVD

Magnesium borate ($Mg_2B_2O_5$) is a remarkable ceramic material that has been shown to be a thermoluminescent phosphor, a friction-reducing additive, and a ferroelastic material that may find application in nanocomposites, nanomechanics, and nanoelectronics. Synthesis of $MgB_4O_7$ (another form of magnesium borate) nanowires has been previously attempted by heating mixed powers of MgO, $B_2O_3$, and B with catalysts, but the result was a mixture of precursors or fiberlike agglomerates, necessitating a further purification process. Furthermore, with this kind of process, it is difficult to control size and location of the nanowires. Recently, researchers Y. Li and R.P.H. Chang of Northwestern University, and Z. Fan and J.G. Lu of the University of California, Irvine, have attained controllable growth and pure fibers by using chemical vapor deposition (CVD) to grow $Mg_2B_2O_5$ nanowires on MgO substrates.

As reported in the June 29 issue of *Chemistry of Materials* (p. 2512), they first coated a polished MgO substrate with a 2–3 nm layer of Pt/Pd nanoparticles as catalysts. The substrate was then heated in a tube furnace to 750–1100°C under Ar flow. $BI_3/H_3BO_3$ vapor was carried by Ar to the substrate. Straight nanowires with uniform diameters were grown on the substrate after several hours of reaction for substrate temperatures between 850–1050°C. The diameter of the nanowires is in the rang0e of 30–150 nm and the length is 1–10 μm. The researchers said that the dimensions of the nanowires can be manipulated by growth time, substrate temperature, and $BI_3/H_3BO_3$ vapor concentration. Each nanowire usually has a Pt/Pd nanoparticle attached to its end, suggesting a vapor–liquid–solid growth mechanism. Electrical transport measurement on a single nanowire indicates that the $Mg_2B_2O_5$ is a semiconductor at room temperature, and its bandgap is 5.44 eV, according to theoretical calculation.

Based on the high purity and controllable growth of $Mg_2B_2O_5$ nanowires this experiment demonstrates, the researchers said, "Metal borate nanowires can be synthesized by introducing boron and boron oxide sources to a metal oxide substrate coated with a thin film of some catalyst."

SHIMING WU

## Models of Failure in Brittle Solids Supported by *In Situ* Observation of Crack Behavior in Plasma-Sprayed YSZ Tube

Plasma-sprayed yttria-stabilized zirconia (YSZ) is commonly used as a thermal barrier coating. It produces coatings with a microstructure containing high porosity and microcracks that will have an effect on the mechanical behavior of the material. As reported in the May issue of the *Journal of the American Ceramic Society* (p. 960), J.P. Levin, G.R. Dickinson, and R.W. Trice at Purdue University observed *in situ* the microstructure evolution of a plasma-sprayed YSZ stand-alone tube under incremental compressive load while simultaneously viewing it in a scanning electron microscope (SEM). They found that cracks oriented parallel to the loading direction have opened, while cracks oriented perpendicular to the applied stress have partially closed. They also observed that new cracks nucleated and then propagated parallel to the direction of the applied load.

Previous observations indicated that plasma spraying forms a microstructure dominated by lamellae with significant porosity and cracks both in and between the lamellae. The sample was prepared by plasma-spraying aluminum powder onto an alumina rod, followed by plasma-spraying a 280 μm YSZ layer. After dissolving the aluminum, the scientists obtained YSZ stand-alone tubes consisting of an yttrium-rich, nonequilibrium tetragonal zirconia phase with a bulk density of ~5.2 g/cm³ and a porosity of 15%. To measure the axial strain, two strain gauges were attached to the outer surface of the YSZ tubes, which were then placed in a load frame located inside the SEM. The samples were compressed incrementally using stress increments of ~13 MPa and 8 MPa, until fracture; SEM images were taken after each stress increment.

The stress–strain curve showed variable slope, but the researchers reported the data as having two slopes, corresponding to the two main regions. The first slope, up to stresses of 46 ± 1 MPa, had a modulus of 30 GPa; at higher stresses, a modulus of 60 GPa was measured. The region of the outer tube that was investigated by SEM had cracks of various widths and orientations: parallel, perpendicular, and off-axis with respect to the applied load.

The scientists' observation supports the hypothesis that the increase in modulus of the material under compression was caused by cracks oriented perpendicular to the applied load that close partially or completely, thus increasing the planar density of the sample. Cracks parallel to the applied load widen as the crack faces slide relative to one another under the shear stress. The formation of microcracks was observed at approximately half the failure stress of the tube. The researchers' observations agree with previous research done on the failure of brittle solids.

MARIA CORTALEZZI

## Charge Transfer across Nanocrystalline Metal Oxide/DNA Interfaces Enables DNA Recognition

Molecular recognition of biological molecules has become an active area of research, partly due to the increasing importance of the fields of molecular patterning, genome sequencing, and drug affinity studies and their applications in bioelectronics. A necessary step in molecular recognition is control of the spatial positioning of the biomolecules. T. Rajh and co-workers at Argonne National Laboratory and N.F. Scherer of the University of Chicago have reported the use of $TiO_2$ nanoparticles (5 nm diameter) in conjunction with DNA strands in the development of biosensing technology. As reported in the June 9 issue of *Nano Letters* (p. 1017), the researchers linked the metal oxide nanoparticles to DNA oligonucleotides by using bridging enediol ligands such as dopamine (DA). The researchers said that the oxygen-rich DA ligands bond readily to $TiO_2$ nanoparticles smaller than 20 nm because their coordination sphere is incomplete and exhibits high affinity for the oxygen-containing ligands. Dopamine repairs undercoordination of the Ti atoms at the surface, thus forming strongly coupled conjugated structures.