Impurities Enhance Semiconductor Nanocrystal Performance
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chemokines, and provide costimulatory and antigen processing and presentation signals to instruct the adaptive immune response cells to secrete IL-17. These IL-17–producing cells are predominantly T_H17 cells, but there are other cells from both the innate and adaptive immune system [(T cells (γδ), natural killer cells, neutrophils, T cells (CD8 subtype), and eosinophils] that also produce IL-17. Moreover, T_H17 cells secrete several chemokines (CXCL1, CXCL5, and IL-8) that in turn act on cells of the innate immune system, stimulating their migration to the site of infection. IL-17 stimulates mucosal epithelial cells to secrete proinflammatory cytokines, chemokines, and antimicrobial peptides.

Puel *et al*. describe two case reports with two different genetic etiologies for these chronic *Candida* infections. In one case, a child diagnosed with chronic mucocutaneous candidiasis had an autosomal recessive mutation in the gene encoding IL-17RA. This receptor binds both IL-17A and IL-17F, and is expressed in multiple tissues, such as vascular endothelial cells, peripheral T cells, B cells, fibroblasts, lung, myelomonocytic cells, and bone marrow stromal cells. The authors sequenced genes encoding the key cytokines produced by T_H17 cells from this patient (IL-22, IL-17A, and IL-17F) and their corresponding receptors, and found a homozygotic nonsense mutation in the *IL17RA* gene that abrogated IL-17RA receptor expression in fibroblasts and peripheral blood mononuclear cells. This mutation caused fibroblasts and leukocytes isolated from this patient to be unresponsive to IL-17A and IL-17F (homo- or heterodimers). In the second case report, the authors found a missense mutation in *IL17F* gene in a multiplex family with autosomal dominant inheritance of chronic mucocutaneous candidiasis. This mutation was located in the cavity of the cytokine, a region implicated in receptor binding. Cytokines that were genetically engineered to express the mutated form of the cytokine (in the context of either an IL-17F homodimer or IL-17A–IL-17F heterodimer) did not bind to IL-17RA on fibroblasts. These mutant cytokines also altered the stimulation of cytokine secretion by peripheral blood mononuclear cells, suggesting that the mutation caused a partial loss of *IL17F* gene function.

The discovery of genetic defects in chronic mucocutaneous candidiasis that are related to T_H17 cells supports previous data from mouse models and humans suggesting the importance of this cell type for protection against *Candida* infections. It further indicates that other genetic etiologies related to this lineage could underly chronic mucocutaneous candidiasis in other subjects, opening an important field for developing therapeutic strategies that target T_H17 cells in these patients. Puel *et al*. also demonstrate that the percentage of total T cells (defined by CD3 expression) that secretes IL-17A was not altered in the patients from both case reports compared to healthy individuals. However, it is unknown whether afferent defects in immune responses to *Candida* mediated by defects in IL-17A and IL-17F production by T cells, or loss of the efferent effects of IL-17 on mucosal and epithelial surfaces, underlie the chronic mucocutaneous fungal infection.

Although thrush and vaginitis occur in only a subset of the population, the findings of Puel *et al*. suggest that allelic variations in key components of the IL-17 signaling pathways may predispose to common candidiasis infection. Nevertheless, these data clearly link evolution of the IL-17 pathway with host responses to *Candida*.

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MATERIALS SCIENCE

Impurities Enhance Semiconductor Nanocrystal Performance

The electronic properties of free-standing semiconductor nanocrystals can be tuned by diffusing metallic impurities into them.

Y. Charles Cao

The semiconductor industry annually spends billions of dollars deliberately adding atomic impurities, called dopants, into very pure semiconductors. Dopants can make devices run faster by increasing the number of negatively (n) or positively (p) charged mobile carriers. They can also determine the predominant type of charge carrier: electrons in n-type semiconductors, "holes" in p-type semiconductors (the dopant atom accepts an electron, resulting in the formation of a "hole"). Without doping, the fabrication of key transistor components such as p-n junctions would not be possible (*1*). Doping has had less impact on lower-cost devices in which semiconductor nanocrystals may be used, such as solar cells, printable low-power devices, and light-emitting diodes (*2*). Our knowledge of the doping effects on the electronic properties of semiconductor nanocrystals has been incomplete because of a lack of robust synthetic methods for doping free-standing nanocrystals (as opposed to thin films of nanocrystals). On page 77 of this issue, Mocatta *et al*. (*3*) report a solution-phase synthesis of metallically doped, free-standing indium arsenide (InAs) nanocrystals. They present strong evidence that both n- and p-type nanocrystals were formed, as well as insights into the electronic and optical effects of doping small nanocrystals (less than 10 nm in diameter).

The light emission and electronic structures of a semiconductor nanocrystal can differ from those of bulk samples or thin films because of quantum confinement effects created by its small size (*4*). These properties have already led to applications; for example, colloidal semiconductor nanocrystals can be used as fluorescent labels for the long-term monitoring of biological pathways in living cells (*5*). It has been predicted that intentional

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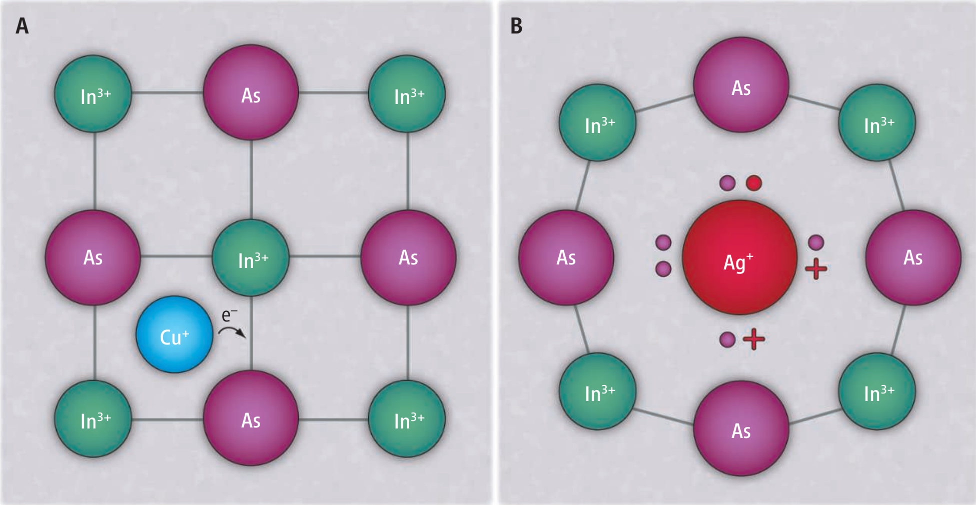
addition of impurities in nanocrystals might lead to effects not observed in the bulk. For example, magnetic impurities such as manganese (Mn) can be positioned inside a colloidal nanocrystal with angstrom-scale precision (*6*) to tune optical and magnetic properties. Nanocrystals doped with magnetic impurities are of interest for their potential use in spin-based electronic devices (*7*).

Little progress has been made in the n- or p-type impurity doping of free-standing semiconductor nanocrystals. Instead of using an impurity, Shim and Guyot-Sionnest (*8*) made undoped semiconductor nanocrystals n-type by injecting extra electrons into them. These extra electrons occupy the discrete conduction-band state of the nanocrystals (in bulk semiconductors, energy states of mobile electrons form a conduction band that lies above the states of the bound electrons in the valence band; the energy separation between them is the band gap). In studies of thin films of nanocrystals, Talapin and Murray (*9*) reported a general method to control the carrier type in lead selenide nanocrystals with hydrazine treatments, and Bawendi and co-workers (*10*) switched InAs nanocrystals from n-type to p-type conduction via doping with cadmium ions. However, the carrier type determined in these transport experiments is a collective property of many nanocrystals, and may not necessarily be the same as the carrier type of the individual nanocrystals in the film.



Moving in. Lewis chemical structure diagrams illustrate a simplified two-dimensional view of the bonding in an InAs lattice containing metallic impurities. Mocatta *et al*. introduced metallic dopants, which modify the electronic properties of InAs nanocrystals, through diffusion. Bonding electrons are represented either by black lines or by paired dots, whose color aims to indicate the atom to which it belongs. Plus signs indicate the lack of an electron in a bonding orbital. (**A**) A Cu impurity in an interstitial site in the InAs lattice donates valence electrons to the crystal and causes n-type doping. (**B**) A substitutional Ag impurity occupying an indium site in the InAs lattice. The Ag causes InAs lattice disorder and introduces two electron acceptor sites into the lattice. The resulting deficiency of valence electrons causes p-type doping.

Mocatta *et al*. doped free-standing colloidal InAs nanocrystals with metallic impurities—copper (Cu) or silver (Ag)—by solid-state diffusion (see the figure). Although Cu and Ag impurities show similar diffusion properties inside the InAs crystal lattice, they produce opposite electronic doping effects in bulk InAs. Copper is an n-type interstitial impurity (it squeezes into empty sites between atoms in the crystal) and donates electrons that become the main charge carrier. Silver is a p-type substitutional impurity (it replaces an In ion), and the lower charge of its ion relative to In causes holes to be the main carrier (*11*).

Optical measurements by Mocatta *et al.* suggest that, unlike the n-type nanocrystals made by carrier injection (*8*), new impurity states are formed that increase the density of energy states near the semiconductor band gap. They also used scanning tunneling spectroscopy (STS) to characterize the doped InAs nanocrystals. This method can directly measure the electronic energy levels with respect to the Fermi level, which is the energy of the highest state occupied with electrons (*12*). In general, shifts of the Fermi level up toward the conduction band characterize a semiconductor as n-type, and shifts down toward the valence band characterize it as p-type. The STS measurements show that the Cu-doped InAs nanocrystals are indeed n-type, and that the Ag-doped ones are p-type.

Modeling by Mocatta *et al*. suggests that the electronic doping effects in small semiconductor nanocrystals strongly depend on the low density of states in their conduction band (an effect of quantum confinement) as well as being "heavily doped"—a 4-nm nanocrystal containing just one impurity atom is comparable to the most heavily doped regime for a bulk semiconductor. Their theoretical analysis reveals that the heavy doping modifies the nanocrystal electronic states through the interplay of two fundamental effects. One is the creation of the quantum-confined impurity band, which is partially filled by charge carriers from the impurity. The other is called band-tailing, which is related to disordering of the crystal lattice by the introduction of dopants.

It will be interesting to correlate the electronic nature of these individual n- or p-type semiconductor nanocrystals with the carrier type in the thin films made of these nanocrystals. One open question is whether Stark effects (shifts in energy levels created by internal electrical fields) might also be responsible for the electronic properties of heavily doped semiconductor nanocrystals. A second issue concerns the location of the impurities within the doped InAs nanocrystals, as both copper and silver ions have large room-temperature solid-state diffusion coefficients. Although some impurity atoms may stay on the surface, the work of Mocatta *et al.* strongly argues that only the impurities inside nanocrystals play a major role in determining the electronic properties of these nanocrystals. Despite these issues, the ability to control the position of the Fermi level in semiconductor nanocrystals via impurity doping should enhance their performance in electronic devices that can be prepared by scalable bottom-up manufacturing.

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