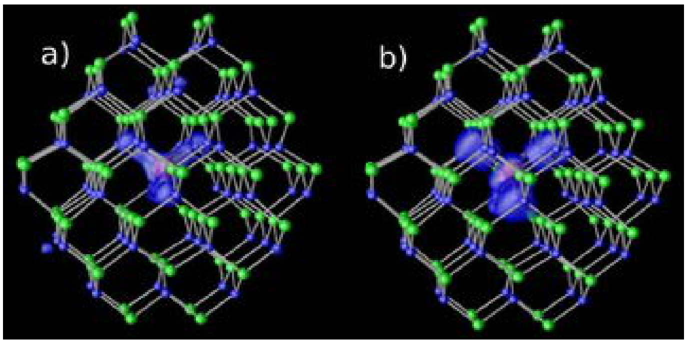
Nanocrystals' 'self-purification' mechanisms explained by energetics



In an example of doped nanocrystals, this charge density plot shows magnesium impurities in cadmium-selenium nanocrystals at two different gap levels: (a) resonant and (b) hybrid. Image credit: Gustavo Dalpian and James Chelikowsky.

Doping semiconductor nanocrystals will likely provide a basis for a wide variety of nano applications. But since the tiny nanocrystals tend to repel impurities, scientists must first find a way to overcome nanocrystals' "self-purification" mechanisms and exploit them for doping.

On the macroscale, doping led to the transistor. On the nanoscale, scientists believe that doping could lead to an assortment of technologies, including solar cells, electroluminescent devices and electronic devices. Doping, which means adding impurities containing electrons, can enable electric conductance in a controlled way. But the miniscule size of semiconductor nanocrystals – also described as one-dimensional "quantum dots" – means that scientists must explore new methods for doping.

Because nanocrystals have very little interior volume and are virtually all surface, scientists in the past believed that inner impurities can easily migrate the short distance to the surface and be ejected.

"People used to believe that nanocrystals had fewer defects due to their limited size," explains Gustavo Dalpian, coauthor with James Chelikowsky of a recent publication in *Physical Review Letters* on the energetics of doping. "People believed that defects could be annealed away from the nanocrystal in an easy way due to its limited size. After a few jumps, the impurity will be out of the nanocrystal."

In 2005, scientists (Erwin et al.) proposed that the difficulties in doping nanocrystals could be explained by the crystals' surface topology and how easily impurities could bind to the surface. For these reasons, these scientists determined that the smaller the size of a nanocrystal, the less binding energy, and the more difficult doping becomes.

Dalpian and Chelikowsky, from the University of Texas, have shown that understanding doping in semiconductor nanocrystals requires an understanding of both kinetic and thermodynamic/energetic properties. By explaining nanocrystals' tendency toward self-purification in terms of the energy needed to form impurities in nanocrystals, the scientists hope to find new ways to increase the dopability of these materials.

"Annealing was basically a kinetic argument," Dalpian said to *PhysOrg.com*. "[Erwin et al.] show that, changing their solution to an anion-rich (negatively-charged) environment, they could put more impurities into the nanocrystals. Their argument was that there is a shape change in their nanocrystal that increases the binding energy of the impurity into the surface. We show that the difficulty of nanocrystal doping can also be explained through energetic arguments: when you change the solution to an anion-rich environment, the formation energy of the defects is decreased.

"In principle, an energetic argument should be better because it is simpler:" he continued. "To discuss kinetics, one needs energy barriers, diffusion coefficients, exact shape of the nanocrystal, etc. However, in our model, supposing the system is under thermodynamic equilibrium, we just need the formation energy of the defect."

When an impurity enters a nanocrystal, a level is created in the gap of the nanocrystal, which (along with structural properties) affects the formation energy of the impurity. Dalpian and Chelikowsky found that a defect's structural properties do not depend on nanocrystal size, but that the level in the gap is deeper (energy difference is larger) for smaller nanocrystals.

"Suppose you have two different systems that create levels in the gap, and one is deeper than the other," said Dalpian. "If you want to populate these levels (put electrons on them), it will cost more energy to populate the one that is deeper. That is why it costs more energy to put impurities in the small nanocrystals than the larger ones: the level created in the gap is filled and is deeper for smaller nanocrystals."

Because smaller nanocrystals contain deeper impurity levels, more energy is required for doping and the lower the population of defects. This explanation supports the idea that self-purification is an intrinsic property of nanocrystals, but also a property that can be overcome.

"In order to make doping easier, we also propose that the sample should be grown in an anion-rich solution," said Dalpian. "Since manganese impurities like to go to the cation (positively-charged) site in cadmium-selenium nanocrystals, a lot of cations create ´competition´ between the impurities and the cadmium (a cation precursor) to occupy the cation site. In an anion-rich environment (the other thermodynamic limit), you have a lot of selenium (an anion precursor) and a deficiency of cadmium, reducing the competition between impurities and cadmium, and making it more likely for the impurities to go to the cadmium site."

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