Doping Semiconductor Nanocrystals: Theory and Experiment

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Doping—the intentional introduction of impurities into a material—is fundamental to controlling the properties of bulk semiconductors. The prospect of new technologies has motivated similar efforts to dope semiconductor nanocrystals since their discovery two decades ago. Despite some successes [1–5], many of these efforts have failed, for reasons that remain mysterious. For example, individual Mn atoms can be incorporated into nanocrystals of CdS and ZnSe [3–5], but not into CdSe [6]—despite comparable solubility limits near 50 percent in the bulk crystals. These difficulties have hindered the development of important new materials, including p- and n-type [7], and even magnetic [8], nanocrystals. Such failures have often been attributed to "self-purification," an allegedly intrinsic mechanism in nanocrystals whereby impurities are expelled to the nearby surface. Here we propose a very different view: that doping is controlled instead by the initial adsorption of impurities on the nanocrystal surface during growth. We show that impurity adsorption—and therefore doping efficiency—is determined by two main factors: the crystal structure and equilibrium shape of the nanocrystal. Calculated Mn adsorption energies and equilibrium shapes for several cubic and hexagonal nanocrystals lead to specific doping predictions. These are confirmed by measuring how the Mn concentration in ZnSe varies with nanocrystal size and shape. Finally, we use our predictions to incorporate individual Mn impurities into previously undopable CdSe nanocrystals. This success establishes that earlier difficulties with doping are not intrinsic, and suggests that a variety of doped nanocrystals—for applications from solar cells to spintronics—can be anticipated.