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How to dope a semiconductor nanocrystal?

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Doping of bulk semiconductors, the process of intentional introduction of impurity atoms into a crystal discovered back in the 1940s, is a key enabling route for tuning their properties. Its introduction allowed the wide-spread application of semiconductors in electronic and electro-optic components. Controlling the size and dimensionality of semiconductor structures is an additional powerful way to tune their properties via quantum confinement effects. In this respect, colloidal semiconductor nanocrystals have emerged as a family of materials with size dependent optical and electronic properties that have attracted significant attention due to their unique attributes and potential applications. Impurity doping in such colloidal nanocrystals still remains an open challenge. From the synthesis side, the introduction of a few impurity atoms into a nanocrystal which contains only a few hundred atoms may lead to their expulsion to the surface or compromise the crystal structure. From a physical viewpoint, impurities inherently create a heavily doped nanocrystal under strong quantum confinement, and the electronic and optical properties in such circumstances are still unresolved.

We developed a solution based method to dope semiconductor nanocrystals with metal impurities providing control of the band gap and Fermi energy (Figure 1).[1] A combination of optical measurements, scanning tunnelling spectroscopy and theory revealed the emergence of a confined impurity band and band-tailing effects. Structural studies using Xray Absorption Spectroscopy techniques provide a model for the location of the induced impurities.

An additional approach we used for doping semiconductor nanocrystals employs the fact that lattice vacancies may also introduce charge carriers that provide a route for doping semiconductor nanocrystals. This has been demonstrated by us for Cu_2S that is a semiconductor that exhibits a tendency towards formation of copper vacancies. We are able to tune the electrical conductance of Cu_2S nanocrystal films by controllably inducing vacancies. This is achieved by thermally annealing the Cu_2S nanocrystal arraysin a process that does not require high temperatures. This process has yielded a significant irreversible increase in the film conductance of up to 6 orders of magnitude. The combination of controlled annealing and temperature dependent transport measurements allowed us to extract the Cu vacancy enthalpy of formation and its activation energy for diffusion.

Conductive atomic force microscope measurements confirmed significant conductance increase at the single nanocrystal level while scanning tunneling spectroscopy measurements verified electrical band gap offsets toward positive values and the appearance of in-gap states.

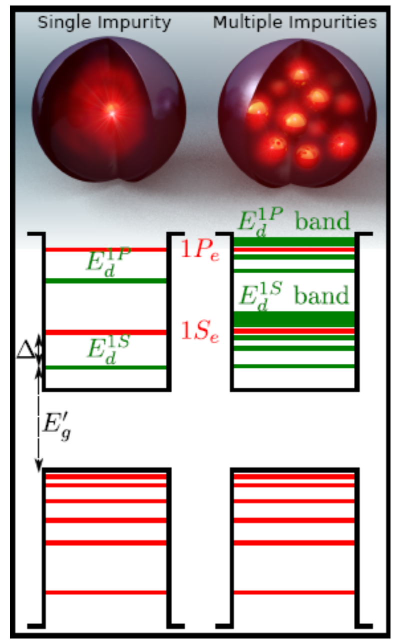

Figure 1: Effects of doping in semiconductor nanocrystals. Shown is a sketch for n-doped nanocrystal quantum dot with confined energy levels, red and green lines correspond to the QD and impurity levels, respectively. Left: The level diagram for a single impurity effective mass model, Right: Impurity levels develop into impurity bands as the number of impurities increases.

These measurements support induced vacancies as *p*-type doping mechanism in the single nanocrystal level. Vacancies induced tuning of electrical properties may benefit various solution-based devices such as transistors, solar cells and displays in which electrical properties of deposited nanocrystal films are typically much less controllable than traditionally fabricated devices.

Successful control of doping and its understanding provide *n*- and *p*-doped semiconductor nanocrystals which greatly enhance the potential application of such materials in solar cells, thin-film transistors, and optoelectronic devices prepared by facile bottom-up methods.

References

1. D. Mocatta, G. Cohen, J. Schattner, O. Millo, E. Rabani and U. Banin, “Heavily Doped Semiconductor Nanocrystal Quantum Dots”, *Science* **332**, 77-81 (2011).