Nano Focus

Energy migration in core–shell nanoparticles allows expansion of the range of upconversion emissions

Photon upconversion is used to convert long-wavelength sources into short-wavelength emission, and has potential applications in compact solid-state lasers, optical data storage, biological imaging, and solar energy conversion. As reported in the December 2011 issue of *Nature Materials* (DOI: 10.1038/NMAT3149; p. 968), a team of researchers led by X. Liu from the National University of Singapore, Y. Han from the King Abdullah University of Science and Technology (Saudi Arabia), and X. Chen from the Chinese Academy of Science have developed a system which displays efficient upconversion emission. This was based on photon upconversion in core–shell nanoparticles doped with a series of lanthanide ions. In particular, tunable emission was achieved by controlling gadolinium sublattice-mediated energy migration in $NaGdF_4$ nanoparticles with well-defined core–shell structures.

The researchers used a sensitizer (Yb^{3+}) that harvests pump photons and subsequently promotes a neighboring accumulator ion (Tm^{3+}) to excited states. This energy is then transferred to a migrator (Gd^{3+}) from high-lying energy states of the accumulator, and finally, by random energy hopping through the migratory ion sublattice and trapping of the migrating energy by an activation ion (Tb^{3+}, Eu^{3+}, Dy^{3+}, and Sm^{3+}). Importantly, the researchers achieved efficient upconversion emission at room temperature and moderate excitation densities. To regulate the energy exchange interaction between the accumulator and the activator, the researchers confined the sensitizer and the accumulator in the core level of the nanoparticles, while the activator was confined in the shell. The presence of Gd^{3+} in both core and shell levels created an array of migratory ions that bridged the energy transfer from the accumulator to the activator.

Additional experiments were also performed which revealed that confinement of the sensitizer, accumulator, and activator in the same layer quenched the upconversion emissions, therefore demonstrating the necessity of the core–shell structures. It was also found that Gd^{3+} was crucial for this energy transfer and that the luminescence could be varied according to the Gd^{3+}-Gd^{3+} interionic distance. The researchers additionally observed that the excitation energy could travel long distances through the Gd^{3+} sublattice, which allowed design interparticle energy migration transfer to lanthanide-doped inorganic nanoparticle acceptors.

This work was used to demonstrate different phenomena including upconversion emissions that cover almost the entire visible spectral range, simultaneous excitation of two different dyes by conventional Förster resonance energy transfer, and tunable upconversion emissions. The ability to tune upconversion properties by combining energy migration and core–shell structural engineering could expand the range of applications for lanthanide-doped nanoparticles, and may stimulate the development of lanthanide-based luminescent materials.

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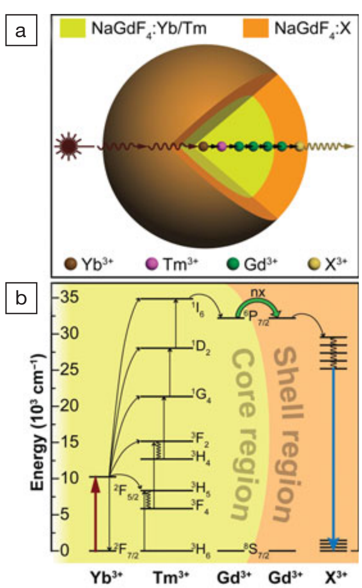

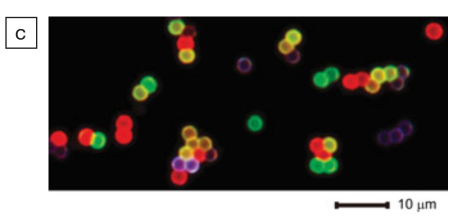

Tuning upconversion through energy migration in core–shell nanoparticles. (a) Schematic design of a lanthanide-doped $NaGdF_4$@$NaGdF_4$ core–shell nanoparticle for energy migration-mediated upconversion (X: activator ion). (b) Proposed energy transfer mechanisms in the core–shell nanoparticles. (c) Luminescence in core–shell $NaGdF_4$:Yb/Tm@$NaGdF_4$ (blue), $NaGdF_4$:Yb/Tm@$NaGdF_4$:Tb (green), $NaGdF_4$:Yb/Tm@$NaGdF_4$:Eu (red), and $NaGdF_4$:Yb/Tm@$NaGdF_4$:Tb+NaGdF4:Yb/Tm@$NaGdF_4$:Eu (yellow) nanoparticles attached to polystyrene bead. Reproduced with permission from *Nature Mater.* **10** (12) (2011), DOI: 10.1038/NMAT3149; p. 968. © 2011 Macmillan Publishers Ltd.

Nano Focus

Step-by-step synthesis approach leads to complex hybrid nanoparticles

Colloidal, hybrid nanoparticles are single particles comprising several active domains, for example, of metallic, semiconducting, or magnetic materials, and have potential applications in a wide variety of fields including solar energy conversion, catalysis, medical therapies, and electronics. The domain boundaries allow for direct electronic and magnetic communication between the component materials, and this intimate contact and selective arrangement of domains provides a unique pathway to tuning the particle properties. Predictive and controlled arrangement of these domains is clearly a nontrivial challenge. However, M.R. Buck, J.F. Bondi, and R.E. Schaak from the Pennsylvania State University have recently reported a stepwise and robust synthetic approach for generating complex hybrid nanoparticle structures, as published in the November 13,

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