

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 Abdulah 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 NaGdF₄ nanoparticles with well-defined core-shell structures.

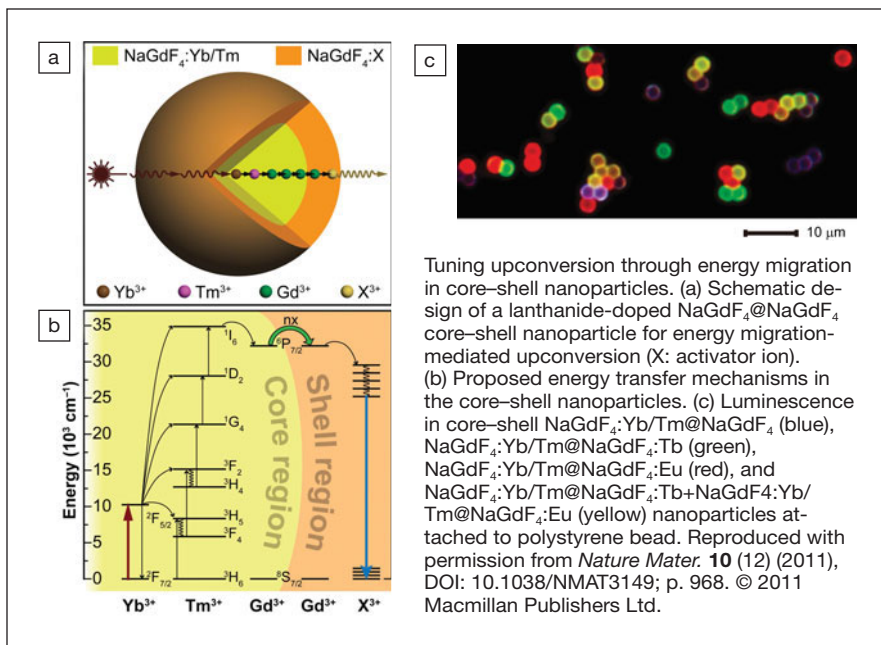
The researchers used a sensitizer (Yb³⁺) that harvests pump photons and subsequently promotes a neighboring accumulator ion (Tm³⁺) to excited states. This energy is then transferred to a migrator (Gd³⁺) from high-lying energy states of the accumulator, and finally, by random energy hopping through the migratory ion sublattice and trapping of the migrating energy by an activation ion (Tb³⁺, Eu³⁺, Dy³⁺, and Sm³⁺). Importantly, the researchers achieved efficient upconversion emission at room temperature and moderate excitation densities. To regulate the energy exchange inter-

action 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 Gd³⁺ 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 Gd³⁺ was crucial for this energy transfer and that the luminescence could be varied according to the Gd³⁺-Gd³⁺ interionic distance. The researchers additionally observed that the excitation energy could travel long distances through the Gd³⁺ 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.

Joan J. Carvajal


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,



2011 online edition of *Nature Chemistry* (DOI: 10.1038/NCHEM.1195).

The researchers first generate a class of metal-Pt-Fe₃O₄ heterotrimers. Step-wise thermal decomposition of Fe(CO)₅ in the presence of Pt seed particles generates Pt-Fe₃O₄ dimers, and subsequent reduction of a chosen metal precursor (for Au, Ag, Ni, or Pd) in the presence of these dimers then results in a high yield of heterotrimer structures. Surprisingly, each reduction reaction resulted in heterogeneous nucleation of the Au, Ag, Ni, or Pd exclusively on the Pt domain of the Pt-Fe₃O₄ dimers. This occurs as direct contact between the Pt and Fe₃O₄

domains facilitates electron transfer to the Pt domain, leading to the observed chemoselective deposition of the metal at the Pt surface.

Heterotetrameric particles were also synthesized by depositing Cu_xS or PbS domains on Au-Pt-Fe₃O₄ heterotrimer seeds. Again, while many products would appear to be possible, in both cases the new domain was located exclusively on the Au domain. It was suggested that while sulfur adsorbs to all domains of the heterotrimer, it was selectively localized on the Au due to differences in the rate of sulfur adsorption and reaction with Cu⁺ ions at the Au versus Pt surfaces.

The Au-Pt-Fe₃O₄ heterotrimers were also used to generate higher order oligomers of 2–5 trimers by heating them in the presence of sulfur.

Through this study, the researchers demonstrated that a sequential reaction approach can provide a powerful route to the synthesis of complex hybrid nanoparticles. In combination with existing mechanistic understanding of the reactions involved, this strategy can lead to the rational synthesis of larger multidomain hybrid nanoparticles with increasing architectural complexities.

Alia P. Schoen

Electrochemically formed gas bubbles serve as propulsion fuel

The design of artificial swimmers and other motion-controlled objects often involves asymmetrical or charged objects. G. Loget and A. Kuhn, from the University of Bordeaux, used

the polarization of conducting materials in an external electric field to operate their swimmers. Bipolar electrochemical reactions at the surfaces of the objects results in the asymmetric production of gas bubbles, which propels the objects.

As reported in the November 15, 2011 online edition of *Nature Communications* (DOI: 10.1038/ncomms1550),

the researchers achieved linear and rotational motions of millimeter-sized conducting objects, due to gas bubble formation. Placing the swimmer between an anode and a cathode induces a potential difference between two opposite sides of the swimmer and electrochemical reactions such as water splitting result in differential gas bubble formation on the object surface. Other electrochemical reactions could also be used to enhance the asymmetry of the propulsion and therefore produce higher speeds. The bubble propulsion was also shown to be more efficient for larger objects where larger potential differences across the surfaces and smaller viscosity effects combine and increase the propulsion.

Macroscopic rotors were also developed based on a similar principle, where exposure of only one small conducting part on each blade causes asymmetrical bubble production. Vertical rotors can also take advantage of the buoyancy of bubbles, pushing the rotor blades up and reaching speeds of 0.70 rpm. Tuning the adherence of the bubbles to the sails then allows optimization of the rotation speed.

Elsa Couderc

