Rare-earth-doped nanoparticles prove illuminating

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Nanoparticles doped with lanthanides such as holmium and thulium possess useful optical properties for a range of applications including computer displays, lasers, and bioimaging.

We currently live in the age of the nano, with nanoscale science and technology providing challenges for fundamental research and creating opportunities for development of new technologies. One nanometer is one billionth of a meter—around the size of individual atoms and molecules—and on this scale particles behave very differently from bulk-size materials.

Trivalent ions of the lanthanide series (rare-earth metals from cerium to lutetium) trapped in host materials have attracted a great deal of attention for over half a century. Recently, interest has been growing in nanoscale materials trapped (doped) with such ions, because they possess unique particle-size-dependent optical and electrical properties. These materials have potential applications in display monitors, optical communications, lasers, bioimaging, and biolabeling.

One of their most interesting properties, energy upconversion, occurs when low-energy light in the form of infrared or visible radiation is converted to higher-energy ultraviolet or violet radiation by means of multiple absorptions or energy transfers. Upconversion has been observed in transition, lanthanide, and actinide ions, but the highest efficiencies are found in trivalent rare-earth ions trapped in a host lattice. Energy upconversion in bulk materials (like crystals, glasses, or gels) doped with trivalent lanthanide ions has therefore been investigated for some time.

However, rare-earth-doped nanoparticles offer a lot of advantages over bulk materials. For a start, they can be dispersed in glass or plastic for display purposes. They can also be surface modified for distribution into aqueous or non-aqueous media for bioimaging. Furthermore, the spontaneous-emission probability of optical transitions from rare-earth-doped ions in nanoparticles can be significantly different from that of their bulk counterparts.

Many kinds of nanoparticles made from a range of host materials and doped with different lanthanides and of various shapes and size distributions have been synthesized using different methods. Our group uses yttrium oxide ($\text{Y}_2\text{O}_3$) as a lattice for the synthesis of nanoparticles because of its low phonon energy compared to aluminum oxide and silicon dioxide.

Several techniques have been developed to synthesize nanocrystals, including the sol-gel method, coprecipitation, and chemical-vapor and flame synthesis. Our group synthesizes...
Y$_2$O$_3$ nanopowders doped with holmium (Ho) and thulium (Tm) using coprecipitation. Production of nanoparticles of less than 50nm has been a major challenge because smaller nanoparticles have enhanced optical-fluorescence properties. We have now successfully synthesized nanoparticles of this size in our laboratory.

Using an atomic-force microscope (AFM) we surface characterized our rare-earth-doped nanopowders. Figures 1 and 2 show topographical images of holmium- and thulium-ion-doped Y$_2$O$_3$ (Ho$^{3+}$:Y$_2$O$_3$ and Tm$^{3+}$:Y$_2$O$_3$) nanopowders respectively, while the corresponding software-generated size distributions are shown in Figures 3 and 4. AFM analysis indicates that the average size of the Ho$^{3+}$:Y$_2$O$_3$ and Tm$^{3+}$:Y$_2$O$_3$ nanoparticles is 46.35 and 42.91nm, respectively.

Upconversion luminescence depends on particle size and crystal structure. Patra and coworkers have shown that the emission spectra for Y$_2$O$_3$ nanoparticles containing ion pairs of thulium and ytterbium, and erbium and ytterbium cover the visible spectrum from blue to red. These small nanoparticles can be dispersed in a homogeneous medium like glass, plastic, or some aqueous medium for bioimaging applications and will still have efficient upconversion luminescence.

We investigated our nanopowders at room temperature by recording their absorption and emission spectra. A Ho-doped sample was pumped with a 532nm laser to resonantly excite the $^5S_2$ energy level in Ho$^{3+}$:Y$_2$O$_3$. We observed emission at 314nm for the energy transition $^3P_1 \rightarrow ^5I_6$, 345nm (for $^5K_7 \rightarrow ^5I_6$), 412nm (for $^5G_5 \rightarrow ^5I_6$), 771nm (for $^5G_4 \rightarrow ^5I_5$), and 890nm (for $^5F_3 \rightarrow ^5I_6$). Figure 5 shows the upconversion signal at 412 nm. Our studies indicate that a sequential two-photon excitation process is responsible for all energy-upconversion signals from these Ho$^{3+}$:Y$_2$O$_3$ nanopowders.

**Figure 2.** ATM image of thulium-ion-doped Y$_2$O$_3$ (Tm$^{3+}$:Y$_2$O$_3$) nanopowders.

**Figure 3.** Size distribution of Ho$^{3+}$:Y$_2$O$_3$ nanopowder (in Å).

**Figure 4.** Size distribution of Tm$^{3+}$:Y$_2$O$_3$ nanopowder (in Å).

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We are now trying to synthesize rare-earth-doped nanoparticles on the basis of other host matrices to discover candidates with very high upconversion efficiencies. Eventually, we intend to use these nanoparticles in fluorescence labeling and bioimaging.

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References

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