IR-to-UV Upconversion Occurs through Simultaneous Three-Photon Absorption in Ce^{3+}:$Lu_2Si_2O_7$ Single Crystals

New materials for IR-to-UV frequency-upconversion luminescence are currently sought. Most research has focused on organic compounds, semiconductors, nanocrystals, and optical fibers performed with nanosecond- or picosecond-pulsed lasers. Recently, however, Q. Ren of Shanghai Jiao Tong University, China, and J. Xu and co-researchers at the Chinese Academy of Sciences used a femtosecond-pulsed laser to demonstrate three-photon-excited violet upconversion luminescence in single crystals of Ce^{3+}:$Lu_2Si_2O_7$.

As reported in the July 15 issue of *Optics Letters* (p. 2175), Ren, Xu, and co-researchers used an established technique to grow Ce^{3+}:$Lu_2Si_2O_7$ single crystals and then sliced 2-mm-thick disks for laser radiation and spectral measurements at room temperature. Focusing their 800-nm Ti:sapphire laser on the sample, the researchers easily observed with the naked eye strong violet emission, which suggested to them that violet upconversion fluorescence could be excited with an IR source without UV optics. The researchers said that the Ce^{3+} substitutes for Lu^{3+} in the $Lu_2Si_2O_7$ host lattice and acts as the luminescence center. The emission spectra for optical excitation at 800 nm and at 267 (i.e., 800/3) nm were nearly identical. Furthermore, for both UV and IR excitation, the fluorescence yield ratios and corresponding spectral distributions were essentially the same, indicating to the researchers that emission occurs from the same state independent of the excitation wavelength. The researchers showed that the emission intensity depends on the cube of the laser power, thereby demonstrating a three-photon excitation process.

Noting that there is no linear absorption at 800 nm, the researchers discounted a mechanism consisting of one-photon absorption followed by two-photon absorption. The researchers also precluded two-photon absorption followed by one-photon absorption because this requires an intermediate state corresponding to a 400-nm absorption, which was not observed. However, the researchers expect simultaneous three-photon absorption, because the three-photon energy of the 800-nm radiation falls into a strong UV absorption band. In addition, the researchers excluded the possibility of other upconversion mechanisms for rare-earth-doped materials, including energy transfer upconversion, excited state absorption, cooperative upconversion, and photon avalanche. The three-photon cross section was determined to be 2.44×10^{-77} cm^6 s^2.

The researchers said that their result "extends the application of Ce^{3+}:$Lu_2Si_2O_7$ single crystals and suggests opportunities for a three-photon process in frequency-upconversion lasers, optical communication, high-density three-dimensional optical data storage, display, IR quantum counters, and three-dimensional fluorescence imaging."

STEVEN TROHALAKI

pH Sensor Fabricated from Single-Walled Carbon Nanotubes

Monitoring the pH of biological and chemical processes is important in order to effectively control their outcome. In the September issue of *Electrochemical and Solid State Letters* (p. H85; DOI: 10.1149/1.2217131), J.-H. Kwon and co-workers at Korea University in Seoul describe how they use single-walled carbon nanotubes (SWCNTs) to fabricate an aqueous-phase pH sensor. The researchers indicated that the sensor functionality arises from the fact that the electronic properties of carbon nanotubes (CNTs) are modified by the hydroxyl ion (OH^-) concentration in the solution.

The sensing device is prepared on a SiO_2-coated silicon substrate, and consists of two chromium electrodes separated by a 4-μm gap. It is fabricated by a standard photolithography process: a photoresist is spun onto the substrate and patterned, chromium is deposited on top, and the sacrificial photoresist layer is etched off. The gap between the electrodes is sprayed with a 0.4 mg/ml solution of SWCNTs in ethanol and therefore bridged by randomly overlapped bundles of SWCNTs. The vinelike morphology of the SWCNTs between the metal electrodes allows foreign molecules to readily access the nanotube network.

Measurement of the current–voltage characteristics of the device reveals that the conductivity of SWCNTs is higher when a buffer solution (0.5 μl) with a higher pH value is poured on top of the sensing area. This happens because the energy gap of the OH^--absorbed SWCNTs is much smaller than that of the bare SWCNTs. The unpaired electron in an OH^- group readily participates in hybridization near the carbon atom when the OH^- group is attached to the nanotube, forming an acceptor level and enhancing the conductivity of the CNTs. Also, real-time current measurements at one of the electrodes shows that changes in current can be observed even when the OH^- concentration in the poured buffer solution is increased by an amount as small as 0.01 pM, confirming the sensitivity of SWCNT conductivity to pH value. Hence, changes in the conductivity of the device can be measured by monitoring the pH value of the concerned solution. The researchers said that conductance change of the device is small at a low pH range (1–5) and large at a high pH range (7–11). Besides pH sensing, the OH^- doping mechanism can also be exploited for modifying the electronic properties of SWCNTs for their use in chemical and biological sensing, the researchers said.

TUSHAR PRASAD

Potential of Laser Delivery of Therapy at the Cellular Level Demonstrated

Medicine and pharmacology are advancing toward providing patients with targeted therapies, and a growing area in this arena is releasing materials directly to affected cells. Recently, A.G. Skirtach of Max-Planck-Institut für Kolloid und Grenzflächenforschung, W.J. Parak of Ludwig-Maximilians-Universität München, G.B. Sukhorukov of Queen Mary University of London, and their colleagues have used laser-generated, near infrared (NIR) radiation to remotely activate polyelectrolyte microcapsules and release encapsulated material inside living cells. The capsules are doped with metal nanoparticles (e.g., Ag), which serve as absorption centers for the radiation. The researchers published their findings in the July 10 issue of *Angewandte Chemie International Edition* (p. 4612; DOI: 10.1002/anie.200504599). This study is different from previous work reported by other researchers in that it was performed at the single-microcapsule level, which the researchers said "is the method ideally suited to applications where precise control is necessary."

When using lasers to illuminate cells and tissues, it is important to minimize the absorption of laser light in order to prevent damage. This can be accomplished by choosing a laser wavelength in the "biologically friendly" window, the NIR part of the spectrum, because of the minimal effect it has on the temperature of water, which makes up 80–85% of eukaryotic cells, i. e., complex cells in which genetic material is contained in a nucleus or nuclei bound by a membrane. Microcapsules containing Ag nanoparticles in the capsule walls, however, absorb the NIR radiation, which causes local heating and deformation of the capsules, thus releasing the encapsulated material into the cell.

The researchers used a thermal treatment method to encapsulate Alexa Fluor 488 dextran conjugate inside microcapsules. They found that their thermal treatment method produces a reduction in size