

IR-to-UV Upconversion Occurs through Simultaneous Three-Photon Absorption in $\text{Ce}^{3+}:\text{Lu}_2\text{Si}_2\text{O}_7$ 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 $\text{Ce}^{3+}:\text{Lu}_2\text{Si}_2\text{O}_7$.

As reported in the July 15 issue of *Optics Letters* (p. 2175), Ren, Xu, and co-researchers used an established technique to grow $\text{Ce}^{3+}:\text{Lu}_2\text{Si}_2\text{O}_7$ 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 $\text{Lu}_2\text{Si}_2\text{O}_7$ 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 $2.44 \times 10^{-77} \text{ cm}^6 \text{ s}^2$.

The researchers said that their result “extends the application of $\text{Ce}^{3+}:\text{Lu}_2\text{Si}_2\text{O}_7$ 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

of the microcapsules from $\sim 4.5 \mu\text{m}$ to $\sim 3 \mu\text{m}$ and significantly increases the structural integrity of the capsules, which is attributed to the increase in wall thickness that accompanies the shrinking. They verified the structural integrity of the thermally-treated microcapsules by noting the percentage of capsules that were not deformed upon ingestion by cells; the capsules with thicker walls are reinforced and thus are more suited to the delivery of encapsulated materials.

Using optical transmission microscopy, the researchers demonstrated the activation of a microcapsule inside a cancer cell using a laser with a wavelength of 830 nm and an incident intensity of 50 mW. The capsules had silver nanoparticles (diameter $> 20 \text{ nm}$) embedded in the walls, but had no encapsulated material. Silver nanoparticles were chosen in part because they absorb the 830 nm light and in part because they provide dark contrast in the optical transmission microscope. The researchers also performed release experiments on AF-488 dextran encapsulated microcapsules that had gold or gold sulfide nanoparticles embedded in the walls. These studies showed that ingested living cells adhere to the substrate both before and after the release of the encapsulated polymer, demonstrating that this method is feasible for the delivery of materials into specific cells. The studies also showed that microcapsules that were merely adhered to the outer membrane were lifted up and away from the cells during illumination and were not disrupted, demonstrating that only the ingested microcapsules release their encapsulated material upon irradiation.

THAD AWEKA

Pitting Sites on Al Controlled by Microcontact Printing Using Poly(chloroprene) Rubber Mask Film

The arrangement of uniform tunnel pits at regular intervals is essential to maximize the surface area of Al electrodes for electrolytic capacitors. However, tunnel pits obtained by conventional anodic etching are not regularly distributed on an Al foil. Recently, K. Nishio and colleagues at Tokyo Metropolitan University developed a method to precisely control the initiation sites of tunnel pits on Al.

As described in their article in the September issue of *Electrochemical and Solid-State Letters* (p. B39; DOI: 10.1149/1.2214364), the researchers used poly(chloroprene) rubber (CR) as a masking material for the elastomeric stamp to control the pitting sites on Al. The researchers first cast a prepolymer of poly(dimethyl-

siloxane) (PDMS) on a metal mold with an ideally ordered array of convex protrusions on its surface and cured it for 12 h at room temperature. After they mechanically detached the PDMS hole array (stamp) from the metal mold, the researchers dipped the stamp in a 1 wt% toluene solution of CR and pulled it at a constant rate. When the toluene evaporated, a thin CR film was formed on the stamp. They then transferred the CR film on the stamp to an Al foil through physical contact and detachment since the adhesion of CR to Al is much stronger than to PDMS. They then etched the Al foil covered with the patterned CR film in HCl solution under a constant dc current condition. The CR film printed on the Al foil masks against the anodic etching of the Al so that no pits are initiated on the CR film. Using this method, the researchers fabricated uniform pits arranged in an ideal array over the Al film with the same $\langle 100 \rangle$ orientation, a width of $\sim 3 \mu\text{m}$, a depth of $\sim 1.5 \mu\text{m}$, and an interval of $5.0 \mu\text{m}$. While the width and interval of the pits can be precisely controlled, the researchers could not control the depth of the pits, because prolonged etching induces a substantial dissolution of the sidewalls of the pits. Further study is needed to make the pits sufficiently deep.

The researchers said that using this process, they can optimize the surface area of an Al electrode for electrolytic capacitors by forming ordered arrays of fine and deep tunnel pits. They also said that their technique can be applied in other electrochemical and photoelectrochemical etching of semiconductors such as Si, InP, GaAs, and GaN for simple site control of pitting.

TAO XU

Sol-Gel Hybrid Film with Benzotriazole-Doped SiO_2 Nanoreservoirs Provides Corrosion Protection to Al Alloy by Controlled Release of Inhibitor

Thin sol-gel films containing inhibitors have emerged as a potential adhesive for polymer-based coating systems with self-healing capabilities, but the integrity of the film is affected unless the inhibitor is isolated from the matrix. The concept developed to overcome this problem is based on placing the inhibitor in a reservoir or container that would slowly release it as corrosion is initiated. The addition of nanometer-sized reservoirs ensures a homogeneous distribution of corrosion protection along the film.

Using a layer-by-layer technique to fabricate reservoirs, D.G. Shchukin of the Max Planck Institute of Colloids and Interfaces in Germany; M. Zheludkevich of the

University of Aveiro, Portugal; and their colleagues created a hybrid $\text{ZrO}_2/\text{SiO}_2$ sol-gel film in which SiO_2 nanoparticles coated with polyelectrolyte layers act as nanoreservoirs of the inhibitor benzotriazole, protecting an aluminum AA2024 alloy from corrosion. The layer-by-layer technique consists of depositing layers of solutions with opposite charge, leading to a multilayer assembly in which permeability can vary depending on the nature of the solutions involved. The researchers said that if polyelectrolytes are used as a shield for the inhibitor, the fact that its permeability changes with pH and humidity would allow controlled release of the inhibitor, depending on the very variables that determine corrosion initiation.

As explained in the July issue of *Advanced Materials* (p. 1672; DOI:10.1002/adma.200502053), the research team, led by H. Möhwald of MPI, deposited positively charged polyethyleneimine (PEI) on the negatively charged SiO_2 nanoparticles, with subsequent layers of polystyrene sulfonate (PSS) and benzotriazole, resulting in a multilayer structure of the form PEI/PSS/inhibitor/PSS/inhibitor. In order to evaluate the corrosion-protection abilities of the nanoreservoir-doped film, the researchers compared its performance in a NaCl aqueous solution with an undoped $\text{ZrO}_2/\text{SiO}_2$ film and a film containing freely added benzotriazole (0.13 wt% and 0.63 wt%). Impedance measurements along a range of frequencies revealed some corrosion activity occurring in both films with free inhibitor, showing a decrease of one order of magnitude in the resistance of the film containing 0.13 wt% benzotriazole, and two orders of magnitude for the one containing 0.65 wt% benzotriazole, when compared with the undoped film. Other signs of structural degradation were found when evaluating capacitance: after 20 h in the corrosive environment, the undoped film capacitance increased by one order of magnitude while the 0.13 wt% free-inhibitor film increased by four orders of magnitude, highlighting the damaging effect of the free inhibitor in the film.

At this point, the undoped and nanoreservoir-doped films had demonstrated similar corrosion resistance in a 48 h period. The added benefit of the nanoreservoirs was then confirmed after the investigators introduced an identical defect on each film. Local measurements of corrosion activity using the scanning vibrating electrode technique revealed in both cases an initial severe drop in resistance, with the undoped film showing a continuous decrease in a slower ramp. For the doped film, the severe initial drop was