

Nano Focus

Lifetime variation in giant nonblinking QDs due to switching between neutral and negatively charged states

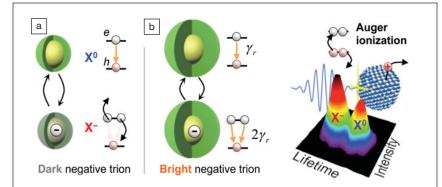
Quantum dots (QDs) are attractive as nanoscale light sources, but the fluctuations in emission intensity from individual dots, which is known as "blinking," can limit their application. It has recently been shown that CdS/ CdSe core-shell nanoparticles with thick shells do not exhibit blinking. However, as reported by a Los Alamos team, Christophe Galland (now at the University of Delaware), Yagnaseni Ghosh, Andrea Steinbrück, Jennifer A. Hollingsworth, Han Htoon, and Victor I. Klimov in the June 19 issue of Nature Communications (DOI: 10.1038/ncomms1916), giant nonblinking QDs (g-QDs) exhibit a pronounced variation in their emission lifetimes due to a switching between negatively charged and neutral states.

In their study, the researchers investigated the optical behavior of individual CdSe/CdS g-QDs with a \geq 15 monolayer thick shell. Individual g-QDs produced stable photoluminescence intensities with variations fitting a single-peak Poisson distribution. Such behavior suggests emission occurred from a single state. However, lifetime measurements revealed the presence of two equally weighted lifetimes (19 ns and 39 ns), thereby demonstrating that two distinct states contribute to the emission.

This behavior was linked to the process of nonradiative Auger recombination and its different effect on negatively charged excitons (negative trions) versus positively charged excitons (positive trions). Neutral QDs correspond to the bright optical state. In thin-shell QDs, charged excitons are essentially nonemissive because Auger decay is fast. However, in g-QDs, Auger processes are largely suppressed for negative trions. By adding a single electron to the QD, the number of radiative recombination pathways is doubled, as is the radiative decay rate. Charging is thus accompanied by a decrease in the photoluminescence lifetime without affecting the intensity ("lifetime blinking").

The investigators confirmed this scenario by studying the effect of controlled electrochemical charge injection on the QD photoluminescence and relaxation rates. At 0 V, the equal distribution between the two lifetimes was again observed. When either -0.5 V or -0.8 V was applied, electron injection was more favorable, and the shorter lifetime (19 ns) predominated without any change in photoluminescence intensity. The research team concluded that observed lifetime fluctuations are connected to random charging of the g-QDs with excess electrons. Moreover, they found that charging occurs by Auger ionization through ejection of a hole. This Auger decay pathway is favored in g-QDs because of a greater degree of confinement for holes than for electrons. These results show that nonblinking behavior is not incompatible with random charge fluctuations in the QD.

Anthony S. Stender



In thin-shell QDs (a) charging is one of the mechanisms causing luminescence intensity fluctuations known as blinking. This is because light emission from the negatively charged exciton (X-) is quenched by very fast Auger decay (negative trion pathway, curved arrows). In contrast, in g-QDs (b), nonblinking emission intensity is observed because Auger recombination of the negative trion is suppressed. The only signature of charging is a doubling of the radiative decay rate compared to the neutral exciton $(\gamma_r \rightarrow 2\gamma_r ;$ double orange arrow). This is indicated by the plot of time-resolved photon-counting data on the lifetime-intensity distribution map (lower right). Charge fluctuations are caused by Auger ionization of the g-QD, that is, by the decay of a biexciton through the fast positive trion pathway with ejection of the hole. This pathway is favored in g-QDs because of a pronounced asymmetry in spatial distributions of electron and hole wave functions in these nanostructures.

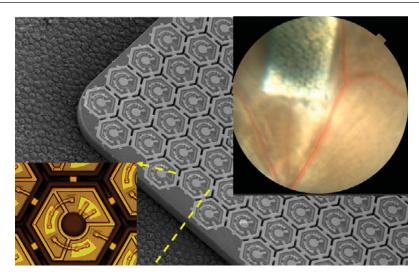
Bio Focus

Wireless PV retinal prosthesis shows promise for restoration of sight

etinal degenerative diseases lead to blindness due to the loss of photoreceptors even though the inner retinal neurons remain largely intact. Visual percepts, also called "phosphenes," can

be produced by electrical activation of the inner retinal neurons. This alternate route to visual information has the potential for restoring sight to the blind. Current retinal prosthesis designs, with electrode arrays implanted in the retina facing either the ganglion cells or the inner nuclear layer, rely on serial telemetry to deliver stimulation signals to the electrodes, requiring bulky receiving and

processing electronics and a trans-scleral cable. Surgery is complex and the design is difficult to scale up to attain higher visual acuity. In addition, patients cannot use natural eye movements to scan the visual scene because retinal stimulation patterns are transmitted from an external camera to the retinal implant, independent of eye orientation. These limitations can be overcome by devices that use



Subretinal photodiode array with triple-diode pixels arranged in a hexagonal pattern. Pixels of 70 µm and 140 µm in size were made. Left inset: Central electrodes are surrounded by three diodes connected in series, and by the common return electrode. Right inset: The subretinal implant.

photosensitive pixels but they depend on an external power source. Recently, however, researchers from the Palanker group at the Hansen Experimental Physics Laboratory and the Department of Ophthalmology at Stanford University designed a photovoltaic retinal prosthesis where video goggles were used to deliver both power and visual information through pulsed NIR illumination, preserving the natural link between image perception and eye movement without complex electronics and wiring.

In an article published in the June issue of *Nature Photonics* (DOI: 10.1038/nphoton.2012.104; p. 391), Keith Mathieson, James Loudin, and co-research-

ers from Stanford University and the University of California–Santa Cruz, describe their prosthesis design in which video images captured by a head-mounted camera are processed by a portable computer. The video goggles use a liquid-crystal display (LCD) illuminated by pulsed near-infrared light (880–915 nm) to project the images onto a subretinal photodiode array (consisting of 70 µm pixels, each with ~20 µm stimulating electrodes), which converts the light to local currents that stimulate the nearby neurons in the inner nuclear layer of the retina.

The researchers fabricated silicon photodiode arrays consisting of pixels with

single diodes as well as those consisting of pixels with three diodes connected in series. These triple-diode pixels can produce 1.5 V, which triples the charge injection on the sputtered iridium oxide film electrodes (from 0.5 mC cm⁻² for a single-diode pixel to 1.5 mC cm⁻²). The triple-diode pixels require light intensities three times higher than single-diode pixels because the photosensitive pixel area is divided into three subunits. However, the researchers found that their single-and triple-diode devices had very similar thresholds for eliciting retinal responses.

The researchers tested their design concept by stimulating healthy and degenerate rat retinas in vitro with NIR light intensities at least two orders of magnitude below the ocular safety limit. They showed that the elicited retinal responses can be modulated by both light intensity and pulse width, although their current optical design allows only for intensity modulation within each video frame. However, if the retinal response is modulated by varying the pulse width, the researchers said that digital light processing technology can also be used, adding, "Such a device would allow both the duration and timing of exposure to be precisely controlled on the scale of individual pixels. In addition to higher throughput compared to an LCD, this high-speed control would allow the sequential activation of nearby pixels to further reduce pixel crosstalk—interference of currents from nearby pixels."

Steven Trohalaki

Nano Focus

Optical confinement modifies graphene transistor characteristics

The interaction between light and matter can be greatly enhanced within an optical cavity in which the spacing of two mirrors defines a standing electromagnetic wave. Placing a sheet of graphene in such a cavity can therefore have profound effects on its optoelectronic properties, as shown by

M. Engel of the Karlsruhe Institute of Technology, M. Steiner of the IBM T.J. Watson Research Center in New York, A. Lombardo of the University of Cambridge, and their colleagues. Their article in the June 19 issue of *Nature Communications* (DOI: 10.1038/ncomms1911) describes how such optical confinement of a graphene transistor allows spectrally selective generation of photocurrent and even alters the electrical transport properties of the material.

The team embedded a sheet of gra-

phene between two optically transparent dielectric materials, $\mathrm{Si_3N_4}$ and $\mathrm{Al_2O_3}$, which are in turn enclosed by silver mirrors with a spacing equal to one-half of the resonant wavelength of the cavity. At the center of this optical cavity the anti-node in the optical field enhances the absorption or emission of photons by the graphene at the resonant wavelength, and inhibits it at other wavelengths. Applying a voltage across the graphene and illuminating the device with a laser generated 20 times more photocurrent at the