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Near-IR Photoresponse in New Up-Converting CdSe/NaYF$_4$:Yb,Er Nanoheterostructures

Chenglin Yan,[†,‡] Afshin Dadvand,[†,‡] Federico Rosei,*[,‡] and Dmitrii F. Perepichka*[,†]

Department of Chemistry and Center for Self-Assembled Chemical Structures, McGill University, 801 Sherbrooke Street West, Montréal, QC, Canada H3A 2K6, and INRS−EMT and Center for Self-Assembled Chemical Structures, Université du Québec, 1650 Boul. Lionel Boulet, Varennes, QC, Canada J3X 1S2

Received May 2, 2010; E-mail: rosei@emt.inrs.ca; dmitrii.perepichka@mcgill.ca

Multicomponent heterostructures containing two or more nanoscale components arranged in a controlled manner are of fundamental and practical significance for many rapidly developing areas.[1] An interaction between the components of such systems may significantly improve the existing and induce new chemical[1c] and electronic properties.[1a] Here we report the synthesis of new nanoheterostructures consisting of lanthanide (Ln)-doped NaYF$_4$ nanocrystals dendritically decorated with CdSe quantum dots (QDs). These materials combine up-converting and semiconducting properties, resulting in the appearance of *sub-band-gap* photoconductivity.

Ln-doped nanocrystals have spurred significant recent interest because of their ability to convert low-energy near-infrared (NIR) photons to visible light.[2−6] The up-conversion in rare-earth compounds occurs by *sequential* absorption of two NIR photons (via a long-lived single excited state)[7] and is principally different from classical two-photon processes, which work via *simultaneous* absorption of two photons and require a very high photon flux. One of the most efficient up-converting nanocrystals is NaYF$_4$:Yb,Er, in which Yb dopant ions absorb NIR photons and the Er ions emit the up-converted visible light. While up-conversion is also present (and is even more efficient) in bulk materials, the solubility of nanocrystals is important for a number of applications, including sensors,[9] bioimaging,[10] and device fabrication. Many of these require efficient energy transfer (ET) from the up-converter to a suitable energy acceptor. However, studies of ET from up-converting lanthanide materials are still rare.[8,9]

We aimed to explore ET from lanthanide materials to CdSe because of its semiconducting properties.[10] Efficient up-conversion of photons with sub-band-gap energies to create a hole−electron pair in a semiconductor would allow a fundamental limitation of single-junction photovoltaic devices to be overcome. ET from NaYF$_4$:Yb,Er to CdSe QDs has recently been shown for a core−shell structure.[10a] However, using a silica shell to attach QDs to the lanthanide nanocrystals precludes electronic interactions and renders irrelevant the semiconducting properties of CdSe.

We used a seeded-growth method to synthesize heterostructures consisting of CdSe QDs attached to NaYF$_4$:Yb,Er nanocrystals (CSNY). Briefly, oleic acid-capped NaYF$_4$:Yb,Er nanocrystals prepared by Capobianco's method[4b] (Figure 1a) were used to direct the growth of CdSe from cadmium stearate and Bu$_3$PSe precursors in the presence of oleylamine [see the Supporting Information (SI)]. Use of two dissimilar ligands (oleylamine for CdSe and oleic acid for NaYF$_4$) is essential for linking the two materials. This might be due to electrostatic attraction between oppositely charged (acid and amine-capped) nanoparticles. Transmission electron microscopy (TEM) images show that the resulting material consisted of a NaYF$_4$:Yb,Er core decorated with CdSe QDs (Figure 1b). The average sizes of the NaYF$_4$:Yb,Er and CdSe nanocrystals were estimated to be 21.6 ± 1.2 and 7.1 ± 0.9 nm, respectively. There is a strong attachment between the two parts of CSNY heterostructures; these can be broken apart only by prolonged ultrasonication (see the SI). High-resolution TEM revealed an interlayer spacing of 0.32 ± 0.01 nm in the core region, in good agreement with the *d* spacing of the (111) lattice plane of NaYF$_4$ (Figure 1c). In the outer region, the interlayer spacing of 0.35 nm accords with the lattice spacing of the (001) plane of CdSe. Selected-area electron diffraction (SAED) obtained in the TEM setup (Figure 1d) and X-ray diffraction (XRD) of the bulk sample showed diffraction patterns assignable to both CdSe and NaYF$_4$:Yb,Er. The elemental composition of CSNY was confirmed by X-ray photoelectron spectroscopy (XPS) and energy-dispersive X-ray (EDX) analysis (see the SI).

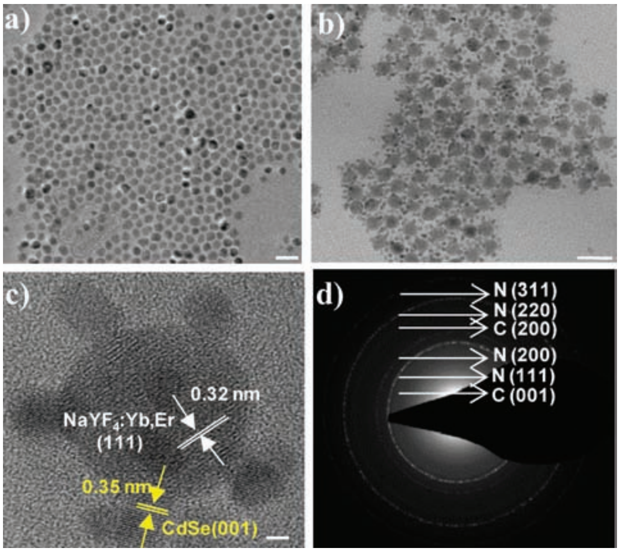

Figure 1. (a−c) TEM images of (a) the original NaYF$_4$:Yb,Er nanocrystals and (b, c) CSNY nanoheterostructures. (d) SAED pattern of a CSNY nanoheterostructure. Scale bars represent 50 nm in (a) and (b) and 3 nm in (c). N represents NaYF$_4$:Yb,Er and C represents CdSe.

The absorption and emission properties of CSNY upon UV excitation fully resemble those of CdSe QDs. The band-gap absorption peak at 623 nm and corresponding emission peak at 634 nm are shown in Figure 2a. The interaction between the CdSe and Ln parts was revealed under excitation at 980 nm. The up-converted fluorescence of the pristine NaYF$_4$:Yb,Er nanocrystals showed three characteristic Er^{3+} emission bands[4] at 524, 542, and 660 nm [due to the $^{2}H_{11/2} \rightarrow {}^{4}I_{15/2}$, $^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$, and $^{4}F_{9/2} \rightarrow {}^{4}I_{15/2}$ transitions, respectively (Figure 2b,c)]. Coupling of NaYF$_4$:Yb,Er to CdSe QDs resulted in efficient ET within the heterostructure. The two short-wavelength emission bands of Er^{3+} at 524 and 542

[†] McGill University.
[‡] Université du Québec.

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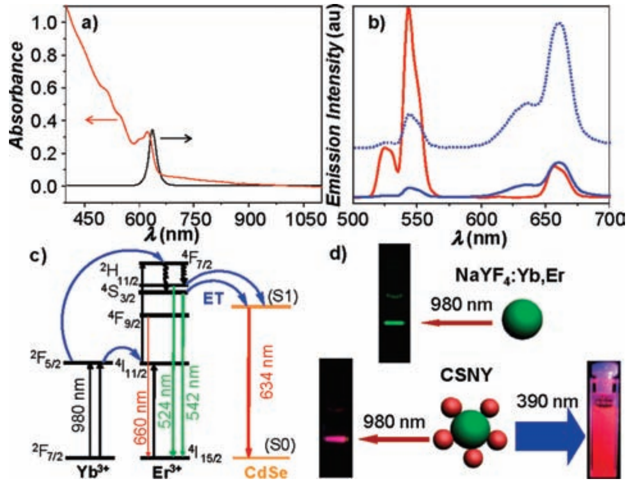

Figure 2. (a) Absorption (red) and emission (black) spectra of CSNY excited at 390 nm. (b) Emission spectra of the seed $NaYF_4$:Yb,Er nanocrystals (red) and the resulting CSNY (blue; the dotted line shows an expansion of the same) in toluene excited at 980 nm. (c) Schematic of the excitation and ET in CSNY. (d) Photographs of the emission from $NaYF_4$:Yb,Er nanocrystals (top) and CSNY heterostructures (bottom).

nm were drastically attenuated (by >90%), and a new broad peak appeared at 634 nm, corresponding to emission from CdSe. The total emission intensity (measured at the same concentration) decreased by an order of magnitude as a result of the low photoluminescence quantum yield of CdSe QDs lacking a protective shell.[10] The red emission of Er^{3+} at 660 nm did not change, as the energy of this excited state is *lower* than that of the CdSe acceptor. Although weak two-photon absorption is known for CdSe,[11] a control experiment with pure CdSe QDs at the same laser power did not give any detectable fluorescence. The whole process of excitation, up-conversion, ET, and emission is depicted in Figure 2c. The color change of up-converted fluorescence upon conjugation with CdSe QDs is shown in Figure 2d.

To demonstrate the use of up-conversion in electronic devices, we studied CSNY photoconductivity upon NIR excitation. Two-contact devices were prepared by spin-coating a solution of nanoparticles in toluene onto Si/SiO_2 substrates prepatterned with Au electrodes. As the oleylamine shell of CdSe creates a large barrier for electron tunneling, the films were pretreated with hydrazine (which cross-links the QDs[12]). Even then, scanning the voltage from −25 to +25 V in the dark showed a very low current of up to 14 pA (the "off" state in Figure 3a). When the device was illuminated with a 980 nm laser, a much higher current of up to 5 nA was measured (the "on" state), giving a significant on/off ratio of up to 360. The switching between the two states was reversible over a number of cycles (Figure 3b). The nonlinear power−photocurrent relationship is due to "saturation" of the up-conversion processes of Ln-based materials (Figure 3a inset).[13]

The excellent NIR photoresponse of CSNY nanoheterostructures is a combined effect of up-conversion and ET. The energy of 980 nm photons up-converted by the $NaYF_4$:Yb,Er core can be (partially) transferred to the attached CdSe QDs (Figure 2c). The dissociation of the resulting QD exciton in the external bias field creates charge carriers ($h\nu \rightarrow e^- + h^+$) that are responsible for the observed photocurrent. Photoconductivity could also be induced using a green laser (532 nm; see the SI), which directly excites the CdSe. Control experiments with analogous devices prepared with pure CdSe QDs showed only marginal NIR photoconductivity, with a maximum on−off ratio of <10. Direct two-photon excitation of CdSe QDs[14] is likely responsible for the weak photoconductivity of such devices. The much higher on−off ratio of CSNY implies that the up-converting $NaYF_4$:Yb,Er core is responsible for its remarkable NIR photoswitching behavior. Another control experiment with a mixture of individual CdSe and $NaYF_4$:Yb,Er nanocrystals showed ∼1 order of magnitude weaker response, highlighting the importance of an intimate contact between the two parts of CSNY.

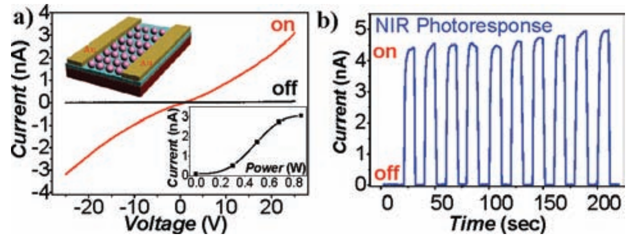

Figure 3. (a) $I-V$ characteristics of the CSNY-based device (the channel width was 6 μm and the length 1880 μm) in the dark (black line) and under 980 nm radiation (red line). The bottom inset shows the dependence of the photocurrent on the laser power. (b) On−off switching characteristics.

In conclusion, we have prepared a new nanoheterostructure, CdSe/$NaYF_4$:Yb,Er, that up-converts NIR photons and uses the created excitons to generate charge carriers in CdSe-based films, leading to a reversible and stable NIR photoconductivity switch. To our knowledge, this is the first example of the use of up-converting nanocrystals in electronic devices. The concept is potentially applicable in photovoltaics to harvest photons with sub-band-gap energies.[14]

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Supporting Information Available: Experimental details; results of XRD, EDX, TEM, and XPS analyses; and control device experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

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