Near-IR Photoresponse in New Up-Conveting CdSe/NaYF₄:Yb,Er Nanoheterostructures

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Multicomponent heterostructures containing two or more nanoscale components arranged in a controlled manner are of fundamental and practical significance for many rapidly developing areas. An interaction between the components of such systems may significantly improve the existing and induce new chemical and electronic properties. Here we report the synthesis of new nanoheterostructures consisting of lanthanide (Ln)-doped NaYF₄ 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. The up-conversion in rare-earth compounds occurs by sequential absorption of two NIR photons (via a long-lived single excited state) 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 NaYF₄: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, bioimaging, 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.

We aimed to explore ET from lanthanide materials to CdSe because of its semiconducting properties. 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 the absorption of two photons and require a very high photon flux. One of the most efficient up-converting nanocrystals is NaYF₄: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, bioimaging, 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.

We used a seeded-growth method to synthesize heterostructures consisting of CdSe QDs attached to NaYF₄:Yb,Er nanocrystals (CSNY). Briefly, oleic acid-capped NaYF₄:Yb,Er nanocrystals prepared by Capobianco’s method were directed to the growth of CdSe from cadmium stearate and Bu₄PSe precursors in the presence of oleylamine [see the Supporting Information (SI)]. Use of two dissimilar ligands (oleylamine for CdSe and oleic acid for NaYF₄) 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

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Figure 1. (a–c) TEM images of (a) the original NaYF₄: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 NaYF₄:Yb,Er and C represents CdSe.

NaYF₄:Yb,Er core decorated with CdSe QDs (Figure 1b). The average sizes of the NaYF₄: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 spacing of the (111) lattice plane of NaYF₄ (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 NaYF₄: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).

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 NaYF₄:Yb,Er nanocrystals showed three characteristic Er fluorescence transitions, respectively (Figure 2b,c). Coupling of NaYF₄:Yb,Er to CdSe QDs resulted in efficient ET within the heterostructure. The two short-wavelength emission bands of Er²⁺ at 524 and 542

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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.\textsuperscript{10} The red emission of Er\textsuperscript{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,\textsuperscript{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 nanocrystals with CdSe QDs is shown in Figure 2d.

In conclusion, we have prepared a new nanoheterostructure, CdSe/NaYF\textsubscript{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 photococonductivity 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.\textsuperscript{1,4}

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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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