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Tunable Giant Multi-Photon Absorption using Seeded CdSe/CdS Nanorod Heterostructures

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Abstract: A clear strategy to enhance the MPA cross-sections whilst independently tuning the emissive wavelengths of semiconductor QDs using seeded CdSe/CdS nanorod heterostructures is presented. MPA cross-sections as large as 2-3 orders and two-photon pumped ASE with threshold fluence 1-2 orders smaller compared to CdSe/CdS QDs were achieved using these heterostructures.

OCIS codes: (160.4236) Nanomaterials; (190.4180) Multiphoton processes; (300.6530) Spectroscopy, ultrafast

Over the last two decades, multi-photon absorption (MPA) in colloidal semiconductor quantum dots (QDs) has been intensively investigated for potential applications in bio-imaging, upconversion lasing, three dimensional data storage and optical limiting [1-2]. These applications leverage on the unique characteristics of QDs: size-dependent optoelectronic properties, large MPA cross-sections, relatively high quantum yields, good photostability and flexible surface chemistry. Recently, the MPA cross-sections of QDs have been found to increase with size, and this general trend has been attributed to a corresponding increase in the density of states [2]. Increasing the MPA cross-sections of QDs without significantly degrading its quantum yield or altering its emission wavelength can be highly desirable for example, in multi-photon fluorescence imaging where greater signal may be achieved using less average incident power, thus minimizing sample damage. While the pronounced size-dependence of the emission of fluorescent QDs in the strong confinement regime presents a convenient way to achieve desired emission wavelengths by simply changing the dot size, however, it also simultaneously imposes severe restrictions on the ability to vary the absorption cross-section while maintaining the emission at a required wavelength. Thus from the stand point of wavelength-specific applications, increasing the MPA cross-section of a QD without significantly modifying its size-dependent emission is an important and yet non-trivial challenge to overcome.

Fig 1: TEM images of the CdSe/CdS nanodot/nanorod heterostructures with (a) 8.5 nm, (b) 34 nm, (c) 39 nm and (d) 180 nm average lengths. (e) Images of R6G and 39 nm CdSe/CdS heterostructures of the same concentration under the same intensity 800 nm laser pulse excitation. These photographs were taken with the same camera exposure time and settings.

Herein we present a method that permits the independent tuning of the MPA cross-section and its corresponding luminescence properties using semiconductor core/enlarged-shell QDs. We demonstrate this with a representative CdSe/CdS nanodot/nanorod system. The elongated CdS shell is used as a photon-capturing “antenna”, which can greatly enhance the overall MPA cross-section of the QD. Photoexcitation of the CdS shell leads to ultrafast carrier transfer to the CdSe core where radiative recombination subsequently occurs [3]. We show that further elongating the CdS shell in rods of a certain length result in substantial gains in the MPA cross-section without significantly red-shifting their emission. The emission peak, on the other hand, can be tuned by appropriately changing the core

size. Importantly, these results suggest a strategy for enhancing the MPA whilst independently tuning the emissive wavelengths of semiconductor QDs in a way which is highly relevant to their applications in multi-photon bio-imaging and upconversion lasing.

Fig. 2 (a) – (c) shows the 800 nm, 150 fs laser pulses excited upconversion PL spectra (red). These results indicate that the PL is always determined by the size of the CdSe core, regardless of single- or multi-photon excitation. The emission spectrum is tailorable through engineering the size of the CdSe core. Under relatively low light excitation ($< 1 \text{ GW/cm}^2$), the 2PA process manifests itself in the quadratic power dependence (Fig. 2(d)). To quantitatively determine the 2PA capability of these elongated shell nanostructures, we have also performed open aperture Z-scan experiments on these samples. The results clearly show that the 2PA cross-sections are greatly enhanced to 1.3, 1.9 and $2.3 (\times 10^{-45} \text{ cm}^4 \text{ s photon}^{-1})$ for 24 nm, 34 nm and 39 nm heterostructures, respectively. In the case of the 39 nm CdSe/CdS heterostructures, the 2PA cross-section is one- to two-orders of magnitude larger than that of spherical CdSe QDs of similar core size and is three-orders of magnitude larger than that of Rhodamine 6G (R6G) dye.

Fig 2: (a), (b), (c) and (d) show the normalized UV-visible absorption spectra (black) and its magnified (x10) region (green), as well as PL spectra corresponding to 400 nm (blue) and 800 nm (red) excitation of the 8.5 nm, 34 nm, 39 nm and 180 nm long CdSe/CdS rods respectively. (e) The corresponding log-log plots of the PL signals (normalized by particle number concentration) as a function of excitation power at 800 nm. The solid lines in (e) are the linear fittings. (f) Graph of emission intensity versus incident pump fluence with two photon (800 nm) excitation.

Two-photon pumped amplified spontaneous emission (ASE) was also demonstrated using these samples. Fig 2(e) shows a graph of the emission intensity against the incident pump fluence. The threshold fluence to achieve ASE in the 15 nm, 34 nm and 39 nm rods are 0.67, 0.35 and 0.3 mJ/cm^2 respectively, consistent with the increasing TPA cross-sections. Our results show that the threshold fluence needed to achieve two-photon pumped ASE in these samples is 1 – 2 orders smaller than that for CdSe/CdS quantum dots. Ultrafast optical spectroscopy such as time-resolved photoluminescence and transient absorption techniques were also employed to probe the charge carrier dynamics in these samples in a bid to gain a clear understanding of the competing radiative and non-radiative recombination pathways (e.g. Auger recombination) in these samples. Our latest results on the charge transfer mechanisms as well as the 3PA work will be presented at the conference. In addition, a unifying picture that provides a clear basis of comparison between the 3PA cross-sections of various II-VI semiconductor nano-materials is proposed so as to facilitate a more judicious choice of their use in 3PA applications.

In summary, we have presented a clear strategy to enhance the MPA cross-sections whilst independently tuning the emissive wavelengths of semiconductor QDs using seeded CdSe/CdS nanorod heterostructures; which is highly relevant to their applications in multi-photon bio-imaging and upconversion lasing. TPA cross-sections as large as 2-3 orders and two-photon pump ASE with threshold fluence 1-2 orders smaller compared to CdSe/CdS QDs were achieved using these seeded CdSe/CdS nanorod heterostructures.

[1] D. R. Larson, W. R. Zipfel, R. M. Williams, S. W. Clark, M. P. Bruchez, F. W. Wise, W. W. Webb, *Science* 300, 1434 (2003).

[2] G. S. He, K. T. Yong, Q. D. Zheng, Y. Sahoo, A. Baev, A. I. Ryasnyanskiy, and P. N. Prasad, *Opt. Express* 15, 12818 (2007).

[3] D. V. Talapin, R. Koeppel, S. Gotzinger, A. Kornowski, J. M. Lupton, A. L. Rogach, O. Benson, J. Feldmann, and H. Weller, *Nano Lett.* 3, 1677 (2003).