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Size-independent peak shift between normal and upconversion photoluminescence in MPA-capped CdTe nanoparticles

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Abstract. In this article, we report size-dependent measurement of the shift in peak of upconversion photoluminescence spectra compared to that of normal photoluminescence using a 800 nm femtosecond laser and its second harmonic. It has been shown that the upconversion photoluminescence is always red-shifted compared to that of normal PL in all the samples. By measuring the power-dependent upconversion photoluminescence (UCPL), it has been shown that the origin of UCPL from MPA-capped CdTe nanoparticles is mainly of two-photon absorption

Keywords. Upconversion photoluminescence; CdTe nanoparticles; femtosecond laser.

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1. Introduction

Unlike bulk semiconductors, the light absorbing and emitting properties of semiconductor nanoparticles can be tuned in a wide spectral range by varying their sizes [1]. Such tunability in the optical properties make semiconductor nanoparticles a potential candidate for applications as emitters (light emitting diodes and lasers), light harvesters (photodiodes and solar cells) and as biological labels [2–5]. In addition to their linear optical properties, semiconductor nanoparticles have large nonlinearities making them efficient nonlinear absorbers of light. Similar to the case of linear absorption, the light absorbed by the semiconductor nanoparticles through the nonlinear process is also emitted as photoluminescence [5,6]. Thus, in the case of upconversion photoluminescence (UCPL) the emitted photon has larger energy than the input photon. For the past few years, studies

are being carried out on the UCPL in semiconductor nanoparticles like CdTe, CdSe and CdS [5–7]. The UCPL peak wavelength has been found to be red-shifted compared to that of normal PL [5,6]. The origin of such difference between the peak wavelength of UCPL and normal PL is still under study. In this article, we report a comparative study of the UCPL emission (when excited at 800 nm) with that of the normal PL emission (when excited at 400 nm) for different sizes of MPA-capped CdTe nanoparticles. We show that the UCPL in MPA-capped CdTe nanoparticles is induced by two-photon absorption. The origin of shift between the UCPL and PL is also discussed.

The MPA-capped CdTe nanoparticles were prepared by the following procedure. Cadmium chloride ($CdCl_2$) (1 mM) was dissolved in 150 ml water and 3-mercaptopropionic acid ($C_3H_6O_2S$) (5 mM) was added with it in drops, under vigorous stirring condition. The white turbid coloured solution immediately turned into a clear solution when the pH of the solution was adjusted to 11.2 by 1 M sodium hydroxide (NaOH). Following this, a measured amount of sodium citrate tribasic dihydrate ($C_6H_5Na_3O_7{\cdot}2H_2O$) was added to the solution. The entire solution was kept under nitrogen atmosphere in a three-necked flask system. Then, potassium tellurite (K_2TeO_3) (0.5 mM) solution reduced by excessive sodium borohydride ($NaBH_4$) was injected into it and the entire solution was heated to 100°C. The immediate appearance of yellow colour indicated the formation of CdTe cores in the solution. The colour of the solution was changed after strong refluxing. Aliquots of the samples were taken at different time intervals to study the properties of the prepared CdTe nanoparticles.

Figure 1 shows the linear absorption spectra of the MPA-capped CdTe nanoparticles prepared at different reflux times (3 h, 5 h, 12 h and 18 h). The average sizes of the nanoparticles can be estimated from the measured linear absorption coefficients by considering the size-dependent quantum confinement effects. We estimate the average size of nanoparticles to be 2.4 nm, 3.0 nm, 3.3 nm and 3.7 nm for the samples CdTe-530,

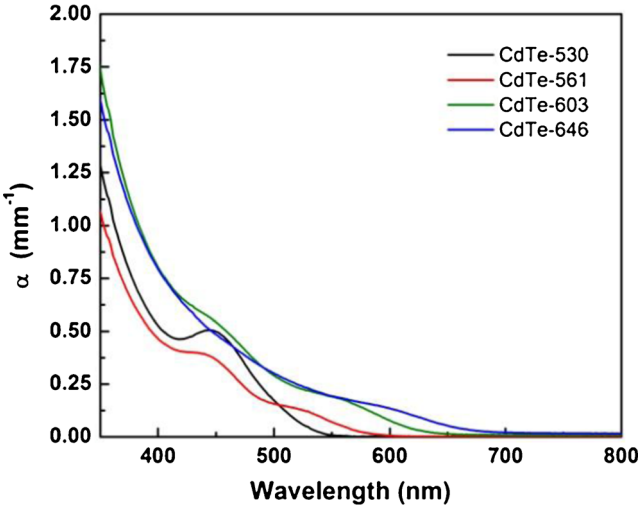

Figure 1. The wavelength dependence of the linear absorption coefficient of MPA-capped CdTe nanoparticles prepared at different reflux times.

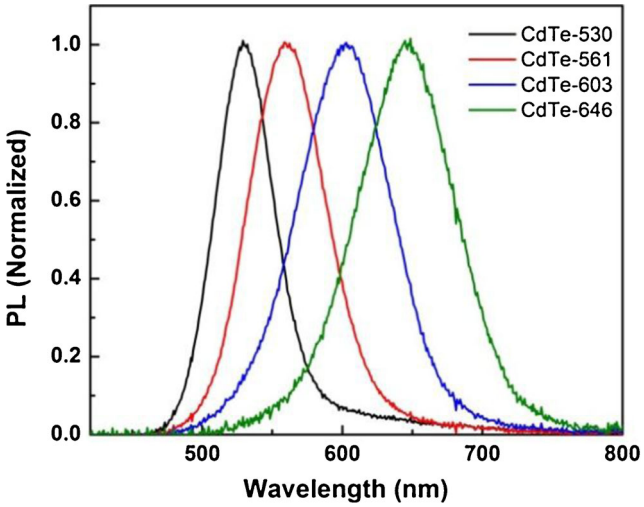

Figure 2. The photoluminescence spectra of CdTe nanoparticles of different sizes. The wavelength of the pump laser is 400 nm.

CdTe-561, CdTe-603 and CdTe-646 respectively [8,9]. Note that in all the cases the sample has very low absorption at 800 nm and very large absorption at 400 nm.

Figure 2 shows the measured photoluminescence spectra of the CdTe nanoparticles when excited at ∼400 nm. The 400 nm pump was generated from 100 fs, 800 nm wavelength, Ti-sapphire laser operating at 82 MHz by second harmonic generation. Note that as the size of the particles increase, the peak wavelength of the PL red-shifts, which is consistent with earlier reports [1]. In figure 3, we show the UCPL of the samples when

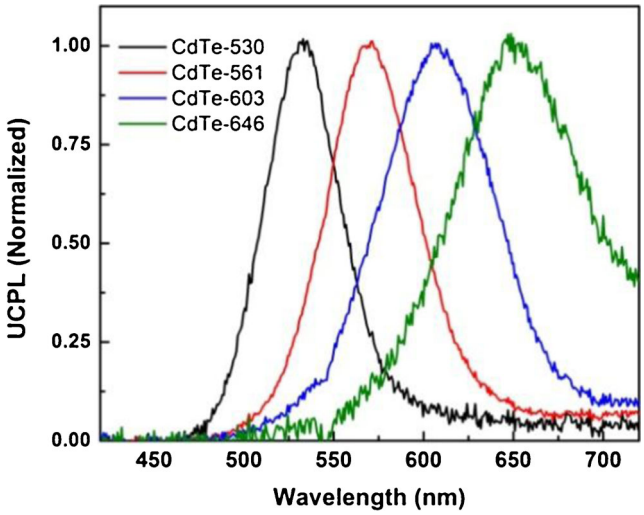

Figure 3. The UPCL spectra of CdTe nanoparticles of different sizes excited at 800 nm.

excited directly by the femtosecond laser at 800 nm wavelength. Similar to the above-mentioned normal PL, the peak wavelength of UCPL red-shifts with the increase in size of the particles. Before discussing the origin of shift in the PL peaks, we look at the input power dependence of PL emission in both of these cases.

In the case of CdTe nanoparticles, the output power of upconversion photoluminescence has been reported to depend linearly on the input power while in some other cases quadratic dependence has also been observed [5,10,11]. In order to understand the origin of the UCPL in our case, we have measured the pump energy dependence of UCPL emission. Figure 4 shows the input power dependence of UCPL when pumped at 800 nm for the sample CdTe-530 at its peak emission, 533 nm. Clearly, the increase in UCPL is not linear with the input intensity. By fitting a simple power-dependent function, I^p, to the variation of output UCPL with the input power (I), we find the value of p to be 1.8. For comparison, we have also measured the power dependence of PL emission when pumped at 400 nm and is shown in figure 5. The linear dependence of the peak PL emission on pump power shows that it is originating from linear absorption. Thus, we attribute the origin of UCPL in the present case to two-photon absorption.

In figure 6 we plot the photoluminescence peak wavelengths of the normal PL and UCPL (obtained from figures 2 and 3). The peak wavelength of UCPL is always red-shifted compared to that of the normal PL. This result shows that the direction of the peak shift is independent of the size of the CdTe nanoparticles. As mentioned before, the difference between the peak wavelength of normal PL and UCPL is attributed to several different processes involving electronic surface states, hole surface states, phonons, size and trap states dependence of two-photon absorption coefficients in CdTe nanoparticles. In the present case, since the origin of UCPL is two-photon absorption, we attribute the shift observed in the UCPL compared to PL to the size dependence of two-photon absorption coefficient of CdTe nanoparticles. It has been shown that the TPA coefficient of CdTe

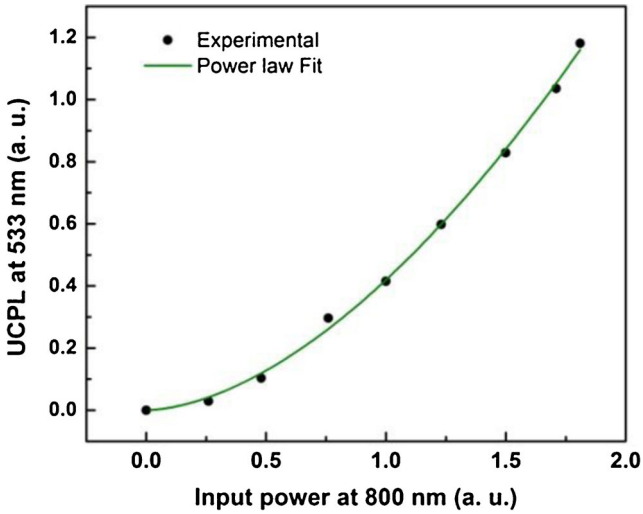

Figure 4. 800 nm pump power dependence of UCPL peak emission for the sample CdTe-530.

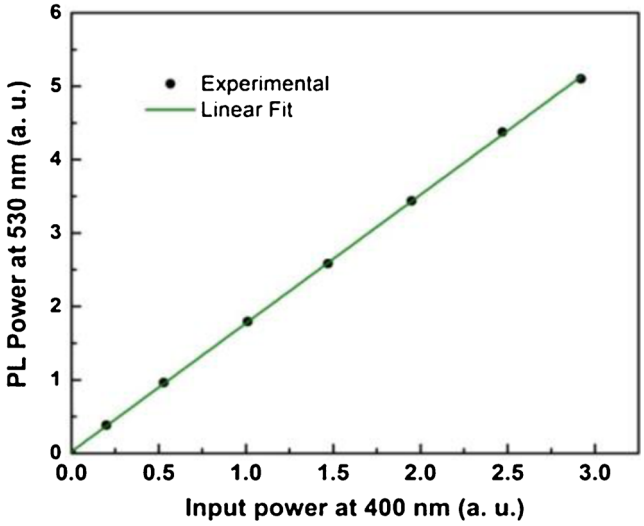

Figure 5. 400 nm pump power dependence of PL peak emission for the sample CdTe-530.

nanoparticles depends strongly on the size of the nanoparticles and increases with increase in particle size [12]. Thus, in a given distribution of size of the nanoparticles around an average value, the larger particles will have a higher two-photon absorption leading to a red-shifted UCPL emission. However, since the variation in the peak shift with the size of the particle is not uniform, we believe a contribution from trap states dependent TPA may also play a role in the observed peak shift.

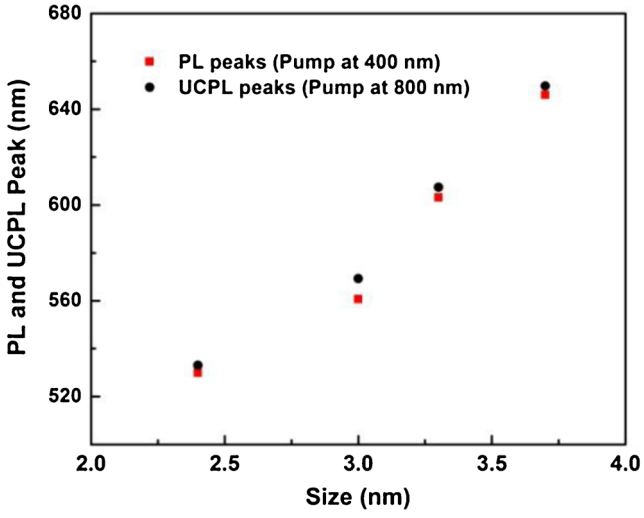

Figure 6. The variation of peak wavelengths of the normal PL and UCPL with size of the CdTe particles.

2. Conclusion

We have measured upconversion photoluminescence from MPA-capped CdTe nanoparticles of different sizes. It has been shown that the UCPL is always red-shifted compared to that of normal PL in all the samples. By measuring the power-dependent UCPL, it has been shown that the origin of UCPL from MPA-capped CdTe nanoparticles is mainly of two-photon absorption.

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