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# Coherent modulation of two-photon up-conversion from colloidal quantum dots by femtosecond laser

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**Using pulse shaping technique, we demonstrate the modulation of two-photon luminescence (TPL) of quantum dots through phase and polarization of the excitation femtosecond (fs) laser. The dependance of TPL intensity on the π phase step position, square phase modulation time, and polarization angle of the fs laser is revealed.**

Colloidal semiconductor nanocrystals (quantum dots, QDs) have been actively pursued as a new generation of luminescent materials because of their tunable, narrow-band, and efficient luminescence[1]. Their size/shape-dependent properties coupled with excellent solution processability are being actively explored for applications in biomedical labeling[2], solar cell[3], and light emitting diodes[4]. Recently, QDs have become a very interesting new type of nonlinear material for the study of multi-photon processes[5] and related applications, such as frequency up-conversion lasing and amplification[6], optical power limiting[7], frequency up-conversion imaging[8] and labeling[9], and optical switching[10]. In comparison with organic multi-photon active materials[11], inorganic semiconductor QDs possess significant advantages including high photo-chemical and photo-physical stabilities.

The ability to effectively control the up-conversion of QDs is very important for their future applications. Coherent quantum control by pulse shaping technique has been successfully used to control various optical processes in different fields, from physics to chemistry and biology[12]. Particularly, coherent control is attracting considerable interest as a new method to enhance or suppress specific multi-photon processes in atomic, molecular, and condensed-state systems through quantum interference[13-15]. Experimentally, the effective method to realize coherent control of the up-conversion luminescence is by varying the laser parameters, such as the laser spectral phase and polarization. Recently, Zhang et al.[16-18]experimentally and theoretically demonstrated that the femtosecond pulse shaping technique can serve as an effective method to control the up/down-conversion luminescence, and the up/down-conversion luminescence via single- and two-photon absorption in $Er^{3+}$ and $Dy^{3+}$ ions and molecular system can be enhanced, suppressed or tuned by a π or square phase modulation, as well as polarization. In order to achieve the quantum control of QDs, Steel et al.[19-21] have utilized pulse shaping technique to achieve the excitonic wave function manipulation, exciton qubits control and exciton dynamics control. QDs exhibit strong two-photon luminescence (TPL) and the two-photon pumped optical gain and lasing has been demonstrated recently[22]. The modulation of TPL for QDs by the fs phase-shaping technique would be of great interest.

In this paper, we demonstrate coherent control of the two-photon up-conversion PL of colloidal CdSe/CdS core/shell QDs by using phase-shaped and polarized fs pulse. We found that the TPL of QDs can be effectively modulated by phase shaped and polarized fs pulse, and the results can be nicely reproduced by theory. The results revealed here may have important implications for understanding photo-physical process in QDs.

Zinc-blende CdSe core and CdSe/CdS core/shell QDs were synthesized according to Peng's method [23, 24]. For the core/shell QDs, in a typical procedure a mixture of CdSe core solution (containing about $2\times10^{-7}$ mol of nanocrystals), dodecane (3.8 mL), octylamine (1.05 mL), and oleylamine (0.45 mL) was heated to 80°C in a three-neck flask under argon flow. CdS shell was then covered onto the CdSe core NCs layer after layer by stepwise injection of different amount of Cd(DDTC)2-amine solution. In the first step, 0.08 mL $Cd(DDTC)_2$-amine solution was injected and the solution was heated to 160 °C and kept there for 5 min before cooling to 80 °C. The second, third and fourth layer of CdS was synthesized under the same condition by using 0.12, 0.16, 0.21 mL of $Cd(DDTC)_2$-amine solution, respectively.

The as-synthesized QDs were examined by transmission electron microscopy (TEM) using a FEG-TEM (Tecnai G2 F30 S-Twin, Philips-FEI, Netherlands). Powder X-ray diffraction (XRD) analysis was

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carried out using a D/MAX-2550pc diffractometer with Cu Kα (λ=0.15418 nm) radiation at room temperature. Photoluminescence (PL) spectra and luminescence decay curves were recorded by using a FLS920 luminescence spectrophotometer (Edinburgh Instrument Ltd, UK).

The experimental setup[17] for femtosecond (fs) pulse shaping and two-photon PL measurement is shown in Fig. 1 (a). A mode-locked Ti-sapphire femtosecond laser systems with pulse duration of 70 fs and peak wavelength of 800 nm is employed as the excitation. The repetition rate of the pulse can be either 1 kHz, or 80MHz before amplification. A programmable 4-f configuration zero-dispersion pulse shaper is used to vary the laser phase in the frequency domain, which is composed of a pair of diffraction gratings with 1200 lines/mm, a pair of concave mirrors with focal length of 200 mm and an one-dimension liquid-crystal spatial light modulator (SLM-S320d, JENOPTIK). The SLM is placed at the Fourier plane and used to control the spectral phase and/or amplitude. A λ/4 wave plate is used to vary the laser polarization from linear, elliptical to circular and vice-versa. The polarized and phase-shaped laser pulse is focused into the QDs solution with a lens of 500-mm focal length, and the laser intensity at the focus is estimated to be ~ $4\times10^{12}$ W/cm$^2$. All two-photon luminescence signal radiated from the sample is perpendicularly collected and measured by a telescope system and a spectrometer equipped with a charge-coupled device (CCD).

The colloidal solution of CdSe/CdS core/shell QDs were used directly for one-photon and two-photon PL measurement. As shown in Fig. 2 (a), the CdSe/CdS core/shell QDs exhibit narrow size distribution with an average diameter around 7 nm. XRD pattern

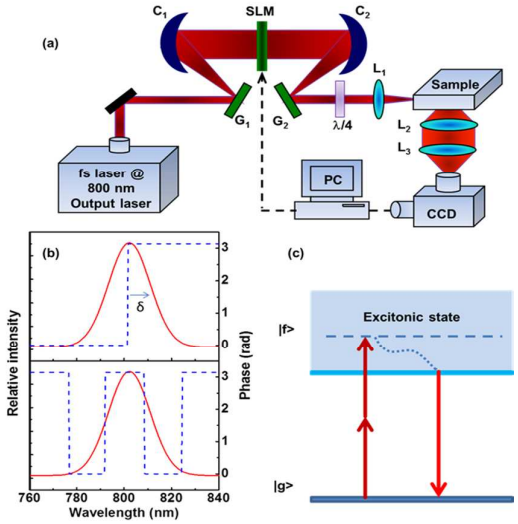


Fig. 1 (a) Schematic diagram of the experimental arrangement for the laser polarization and phase control of two-photon fluorescence in QDs. Here, a spatial light modulator (SLM) is used to modulate laser spectral phase and a λ/4 wave plate is employed to vary the laser polarization. (b) The laser spectrum is modulated by a π (upper panel) or square (lower panel) phase modulation. (c) Energy level diagram of the two-photon absorption and fluorescence detected schemes in QDs.

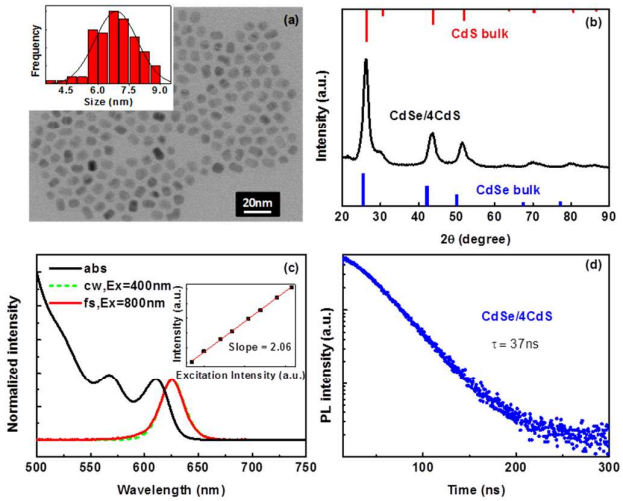


Fig. 2 (a) TEM images of CdSe/CdS core/shell QDs. The inset is the size distribution histograms of the QDs. (b) X-ray powder diffraction pattern of CdSe/CdS core/shell QDs (PDF of CdSe: 65-2891, CdS: 65-2887). (c) UV-vis ( black solid line) and PL spectra of CdSe/CdS core/shell QDs excited by 800nm fs laser (red solid line) and 400nm continuous wave laser (green dashed line). The inset is the fluorescence intensity as the function of the excitation intensity of 800 nm fs laser. (d) PL decay kinetics of CdSe/CdS core/shell QDs.

of the CdSe/CdS core/shell QDs shown in Fig. 2 (b) confirms the hexagonal zinc-blende crystal structure, and this structure is preserved after epitaxial growth of four monolayer of CdS[23, 24]. In Fig. 2 (c), the sharp absorption features in UV-vis spectra and narrow peak width of the corresponding PL spectrum indicate that the ensembles of QDs used for recording the spectra were nearly monodispersed. In addition, two sharp excitonic absorption peaks located at round 567 and 610 nm is the characteristic feature for CdSe/CdS core/shell QDs[23]. The PL peaks excited by 800 nm fs laser and 400 nm continuous wave laser are almost identical, suggesting that the two-photon luminescence and the one-photon luminescence both originate from the electronic transition from first excitonic state to ground state of the QDs. The inset of Fig. 2 (c) shows the power dependence of luminescence intensity excited by 800 nm fs laser. The experimental result is best fitted by a straight line with the slope of 2.06, which is the direct evidence of two-photon luminescence. The PL decay kinetics is shown in Fig. 2 (d), giving an ensemble lifetime of 37 ns for the colloidal QDs.

To enable coherent control of the two-photon PL for QDs, we firstly use the π phase modulated fs pulse (repetition rate 1 kHz) as the excitation source. Fig. 3 (a) shows the two-photon PL spectra recorded at different π phase step positions. It is shown that the PL intensity is changed with varying the π phase step position, while the spectra profile keeps almost unaffected. For both the 1 kHz and 80MHz pulse, the luminescence intensity show a w-shaped dependence on the π phase step position which is scanned between 780 nm and 820 nm. When excited by the fs laser with the repetition rate of 1 kHz, the luminescence intensity can be effectively suppressed by about 35%, which is different from that of

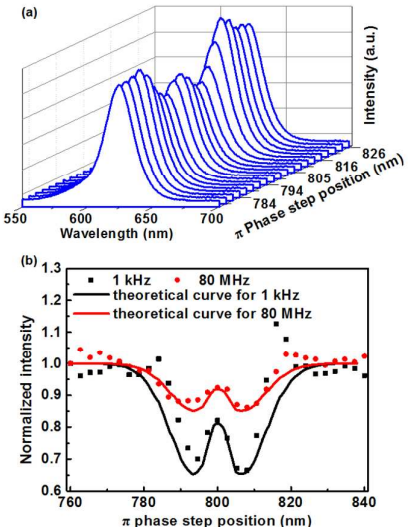


Fig. 3 (a) The two-photon fluorescence spectra modulated by the π phase step position excited by 800nm femtosecond laser with the repetition rate of 1 kHz. (b) The experimental (scatter) and theoretical (line) two-photon fluorescence intensity as a function of the π phase step position excited by femtosecond laser with the repetition rate of 1 kHz (black) and 80 MHz (red).

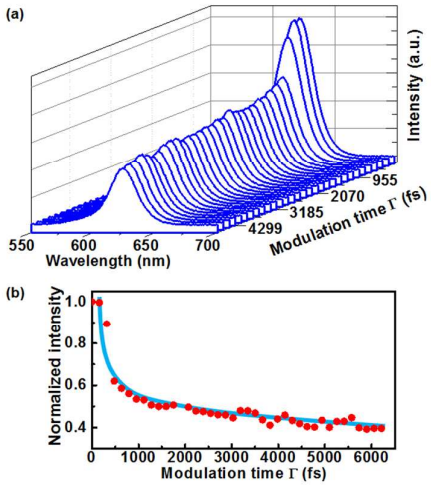


Fig. 4 (a) The two-photon fluorescence spectra controlled by the modulation time Γ excited by femtosecond laser with the repetition rate of 1 kHz. (b) The two-photon fluorescence intensity as a function of the modulation time Γ with the repetition rate of 1 kHz. The blue curve is provided as guidance for eye.

atomic system, where the two-photon absorption can be completely suppressed and also effectively enhanced. The reason is that the broadband absorption in QDs greatly suppresses the constructive or destructive interference of two-photon excitation pathways[17]. In comparison, with 80 MHz pulse excitation, the PL intensity is reduced by only 15% at maxima. This difference arising from the repetition rate of the fs pulse is associated with the lifetime of the excitonic state of the QDs. For fs laser of 1 kHz, the excited state lifetime (in the order of ns) is much shorter than the laser pulse separation, while the excited state lifetime is longer than the laser pulse separation for 80 MHz (12.5 ns). That is to say, the two-photon absorption process takes place within only one laser pulse duration at 1 kHz. However, when excited by 80 MHz pulse, the excitation pathways are induced by two or more laser pulses, and there may be constructive interference between these electrons excited from two-photon absorption process, that will compensate the destructive interference of π phase modulation. Therefore, the mechanisms involved in the two-photon PL of QDs are different when excited by laser pulses of different repetition rate and energy, and this difference is account for the different modulation efficiency by pulse-shaping as we observed in Fig. 3 (b).

The w-shaped dependence of two-photon PL for the colloidal QDs can be reproduced by the second-order time-dependent perturbation theory. Concerning the nonlinear interaction between a linearly polarized femtosecond laser field E(t) and a quantum system with broad absorption line, the multi-photon absorption is proportional to a sum of each individual transition[16-18]. For QDs, the energy levels can be considered as an approximate two-level system (shown in Fig. 1 (c)), and the two-photon absorption $S^{(1+1)}$ can be expressed as

$$S^{(1+1)} \propto \int_{-\infty}^{+\infty} A(\omega_f)\left|\int_{-\infty}^{+\infty} E^2(t) exp(i\omega_f t)\, dt\right|^2 d\omega_f \propto \int_{-\infty}^{+\infty} A(\omega_f)\left|\int_{-\infty}^{+\infty} E(\omega)\, E(\omega_f-\omega)\, d\omega\right|^2 d\omega_f \quad (1)$$

where $A(\omega_f)$ is the absorption line-shape function in the final state $|f\rangle$, and $\omega_f$ is the resonant frequencies of the $|f\rangle$ states. $E(\omega)$ is the Fourier transform of E(t) with $E(\omega) = E_0(\omega)exp[i\Phi(\omega)]$, and $E_0(\omega)$ and $\Phi(\omega)$ are the spectral amplitude and phase, respectively. The π phase or square phase modulation has been successfully applied in quantum coherent control of atomic and molecular system[14, 25] and the simple spectral phase modulation is shown in Fig. 2 (b). Here, the π phase modulation is defined by a function of $\Phi(\omega) = \pi\sigma(\omega-\delta)/2$, where σ(ω-δ) denotes the signum function which takes the value -1 for ω<δ and 1 for ω>δ, and thus $\Phi(\omega)$ is characterized by a phase jump from 0 to π at the phase step position δ. From Fig. 3 (b), a nice agreement is found between the observed date and theory. The π phase step modulation has been proved to be a well-established tool in quantum coherent control because it can induce a constructive or destructive interference between different excitation pathways[14].

We then examined the two-photon PL under excitation of square phase modulated pulses. As shown in Fig. 4 (a), the PL spectra profile keeps constant while the PL intensity decreases monotonously as the modulation time Γ increase. In the first 500 fs, the PL intensity drops rapidly by around 30%; it is then further actuated, reaching a total reduction by around 60% up to 5000 fs. This result can be also explained in terms of the destructive interference of phase modulation in time-dependent perturbation theory. The square phase modulation is defined by the function of $\Phi(\omega) = \frac{\pi}{2} + 2\sum_{m=0}^{\infty}\frac{sin[\Gamma(2m+1)(\omega-\omega_0)]}{2m+1}$, where Γ is the modulation time and $\omega_0$ is the laser central frequency, and thus the modulation period of square phase modulation can be continuously changed by varying the modulation time Γ. Although fitting the I-Γ relation is not provided in Fig. 4, from the equations the suppression of PL with increased Γ can be understood without difficulty.

The two-photon PL of colloidal QDs can be also modulated by the polarization of fs pulse. This is quite unusual as particle ensemble,

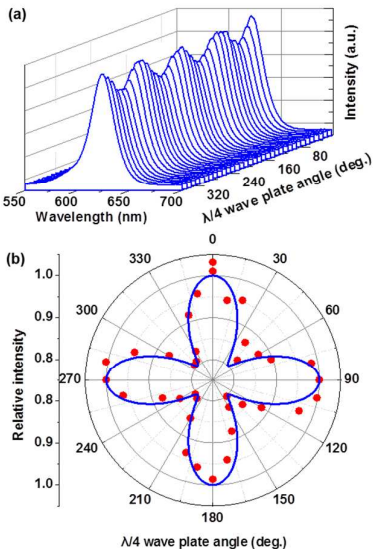


Fig. 5 (a) The two-photon fluorescence spectra controlled by the λ/4 wave plate angle excited by femtosecond laser with the repetition rate of 1 kHz. (b) The experimental (red circles) and theoretical (blue line) two-photon fluorescence intensity by varying the λ/4 wave plate angle.

here as colloidal dispersion, where colloids are usually randomly distributed in solution, and hence does not show polarization dependence which is typical for only single crystals and chiral structures. In our measurement, we used a λ/4 wave plate to change the polarization of fs pulse, and we found that the PL intensity of the QDs showed a periodical dependence with a period of π/2 on the rotation angle of the λ/4 wave plate (shown in Fig. 5 (a)). The maxima and minima PL intensities are observed at the rotation angles of mπ/2 and (2m+1)π/4, and the difference is around 20% (shown in Fig. 5 (b)). In other words, the two-photon luminescence intensity is suppressed as the laser polarization is changed from linear through elliptical to circular.

The polarization behaviour can be again theoretically explained as follows. As the quantum system is three-dimensional, the laser polarization should have a significant effect on nonlinear optical process. When propagating through a λ/4 wave plate, the linearly polarized laser field $\vec{E}(t) = E_0(t)\,cos(\omega t)\,\vec{e_x}$ can be decomposed to two orthogonal polarization directions $\vec{\mathbf{e}}_\mathbf{x}$ and $\vec{\mathbf{e}}_\mathbf{y}$ which is expressed by

$$\vec{E}_{\lambda/4}(t) = \boldsymbol{E_0(t)\,cos(\theta)\,cos(\omega t)}\vec{e}_x + \boldsymbol{E_0(t)\,sin(\theta)\,cos(\omega t)}\vec{e}_y \qquad (2)$$

where θ is the rotation angle of the input laser polarization direction and the λ/4 wave plate optical axis. This equation tell us that the output laser is linearly polarized for θ=nπ/2 (n=0, 1, 2…), or circular polarization for θ=(2n+1)π/4, and elliptical polarization for other rotation angle θ. And the $S^{(1+1)}$ can be further written as

$$\boldsymbol{S^{(1+1)} \propto [cos(\theta)^4 + sin(\theta)^4]} \times \int_{-\infty}^{+\infty} \boldsymbol{A(\omega_f)}\left|\int_{-\infty}^{+\infty}[\boldsymbol{E_0(t)\cos(\omega t)}]^2 \boldsymbol{exp(i\omega_f t)dt}\right|^2 \boldsymbol{d\omega_f} \qquad (3)$$

From this equation, $S^{(1+1)}$ reaches maximal value for θ=nπ/2 (the linear polarization) and minimal value for θ=(2n+1)π/4 (the circular polarization), giving a period of π/2 for the I-θ relation, as shown in Fig. 5 (b). Therefore, laser polarization can be applied to control the two-photon luminescence from ensemble of QDs, which is mechanistically different from the polarization UC emission from rare earth doped single nanocrystals[26].

In order to testify the universality of coherent modulation of two-photon up-conversion from different types of QDs by femtosecond laser, the same measurement was carried out for CdSe core-only QDs, CdSe/ZnS core/shell QDs and CdS QDs doped glass. The results are shown in Figs. S1, S2 and S3 in Supplementary Information. As can be seen from these spectra, similar features appear in the π phase, square phase, as well as the polarization modulated spectra, implying that the coherent spectral modulation is independent of material characteristics.

## Conclusions

In summary, we have demonstrated coherent control of two-photon PL for colloidal solution of QDs. The up-conversion luminescence via two-photon absorption of QDs can be controlled by varying the phase and polarization of the femtosecond laser pulse. For π phase modulated pulse, we found 1 kHz fs pulse with much higher energy produces higher actuation of PL as compared to fs pulse of high repetition rate (80 MHz). In square phase modulation, the luminescence can be suppressed by more than 60% by varying the modulation time Γ. Furthermore, by rotating the λ/4 wave plate angle, the luminescence is suppressed as the laser polarization is changed from linear through elliptical to circular. Our present work opens a new gate to control the luminescence of QDs and other materials, which is helpful for further understanding and controlling more complex multi-photon absorption process in different materials. This novel and simple method has significant applications on fluorescence imaging and fluorescence correlation spectroscopy.

## Acknowledgement

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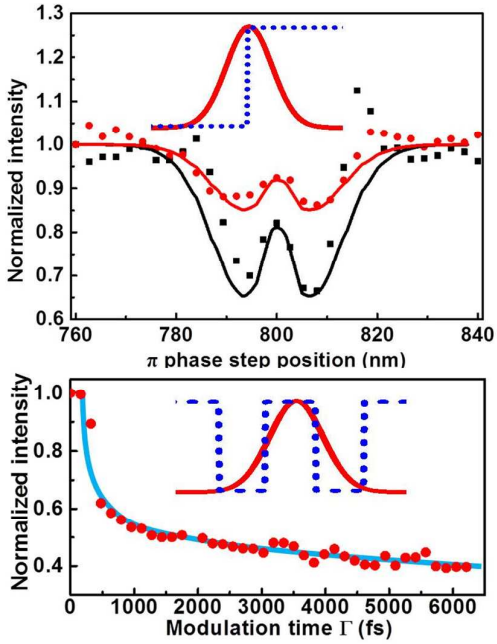
**Graphical Abstract**

The ability to effectively control the up-conversion of quantum dots, which have become a very interesting new type of nonlinear material for the study of multi-photon processe, is very important for their future applications. The coherent modulation of up-conversion fluorescence from colloidal quantum dots by femtosecond laser has been experimentally and theoretically achieved , which proves that the femtosecond pulse shaping technique can provide an effective method to control two-photon fluorescence.



# Supplementary Information

## Coherent modulation of two-photon up-conversion from colloidal quantum dots by femtosecond laser

Cheng Xu,[a] Yunhua Yao,[b] Chaodan Pu,[c] Shian Zhang,[b] Xiaofeng Liu,*[a,] and Jianrong Qiu*[a,d]

1. Sample preparation

CdSe core QDs were synthesized according to the method introduced in ref. 1 and ref. 2. CdSe/ZnS core/shell QDs were purchased from Najing Technology Corporation Limited. CdS QDs doped glass was synthesized by a modified melt-quenching method[3]. A potassium borosilicate glass with the composition of $SiO_2$ (72%), $B_2O_3$ (9%), and $K_2O$ (19%) (in mol% of each oxide) was chosen as the matrix and CdS (1 wt%) was added to raw material mixture. The glass sample was melted in alumina crucible at 1400 °C for 1 h and then cast into a brass mold followed by annealing at 650 °C for 8 h.

2. Experimental results

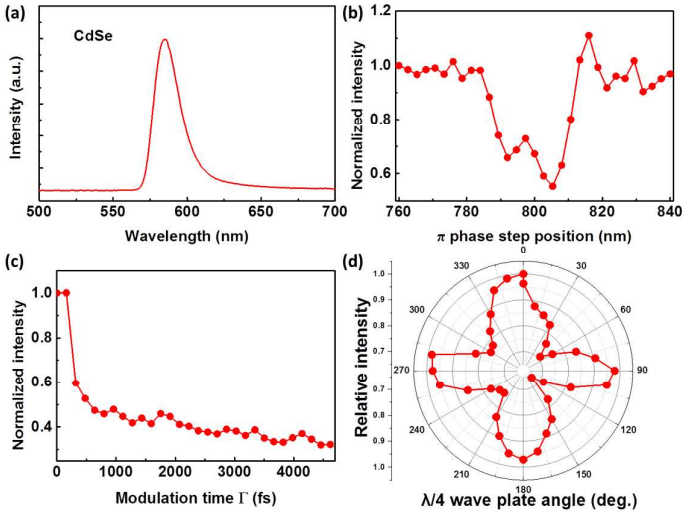



Fig. S1 (a) The two-photon fluorescence spectrum of CdSe core QDs, and two-photon fluorescence intensity as a function of (b) the π phase step position, (c) the modulation time Γ and (d) the λ/4 wave plate angle excited by 800nm femtosecond laser with the repetition rate of 1 kHz.

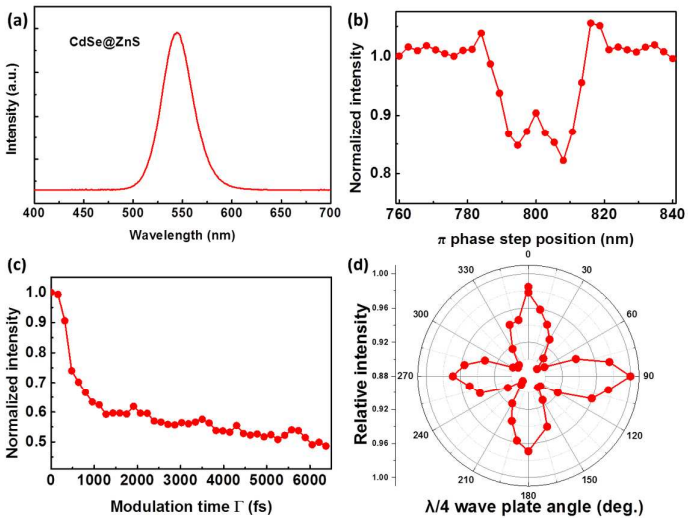



Fig. S2 (a) The two-photon fluorescence spectrum of CdSe/ZnS core/shell QDs, and two-photon fluorescence intensity as a function of (b) the π phase step position, (c) the modulation time Γ and (d) the λ/4 wave plate angle excited by 800nm femtosecond laser with the repetition rate of 1 kHz.

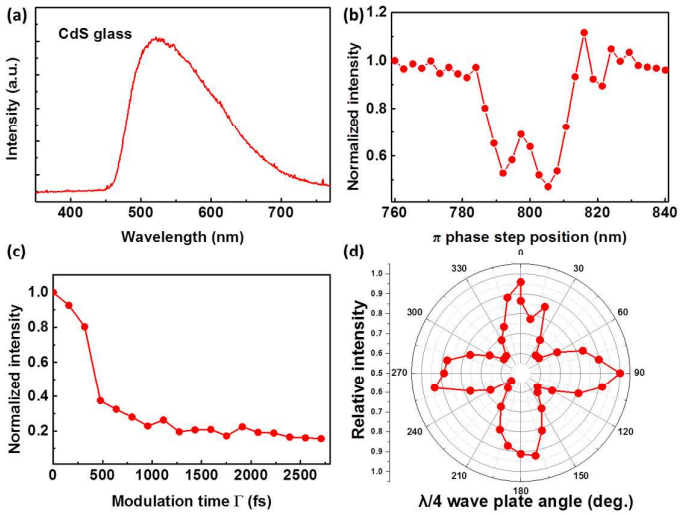



Fig. S3 (a) The two-photon fluorescence spectrum of CdS glass, and two-photon fluorescence intensity as a function of (b) the π phase step position, (c) the modulation time Γ and (d) the λ/4 wave plate angle excited by 800nm femtosecond laser with the repetition rate of 1 kHz.

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