New materials for Single Photon Emission from Colloidal Quantum Dots

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Colloidal quantum dots (QDs) are considered as a cost-effective alternative for optoelectronic applications compared to epitaxial QDs because of its economic & versatile method of synthesis and room temperature operation. CdSe based quantum dots are extensively studied for single photon emission and here we show the similar observation for our 'flash' synthesis of QDs. The newly synthesized InP based QDs are also observed to be photostable and seems to be a good single photon emitter with narrow emission linewidth. Such QDs show great promise to be integrated onto a chip as single photon sources for quantum information based devices.

Introduction

Nanoparticles from inorganic materials have shown considerable importance in various applications from electronics to biology because of their properties belonging in between atoms and bulk structures. Nanocrystals with the periodic arrangements of atoms can be made in an economic way in a solution phase using wet chemical synthesis. Such colloidal semiconductor nanocrystals exhibit unique optical and electronic properties when their charge carrier (electron/hole or exciton) is confined in a medium. Such a quantum confinement is achieved when the dimension of a material is smaller than the Bohr radius of the charge carrier and thus the presence of discrete energy levels compared to the continuous energy level in bulk structures. These materials are collectively called as quantum dots. Upon electro/photo-excitation, electron is excited from the ground states leaving a hole and thus an exciton (electron-hole pair) is created. When the electron and hole recombine, a photon is emitted with the energy equivalent to the band gap energy. The emission wavelength of the colloidal quantum dots can be tuned by simply changing the size of the material. The presence of dangling bonds on the surface of the quantum dot reduces the photoluminescence efficiency and the core material is prone to photo-degradation over the time. This is considerably reduced by growing a shell of larger band gap than the core. Type I structure with the confinement of both the charge carriers in the core are interesting for applications in single photon sources. Single photon sources have applications in quantum information processing, quantum cryptography and quantum metrology. Colloidal quantum dots (QDs) have advantage of tunable emission range, room temperature operation, economical synthesis method and industry supported nanolithographic integration onto devices. Such QDs as single photon sources should have narrow emission linewidth at room temperature operation with suppressed blinking. We have synthesized CdSe/CdS (10 nm diameter with the core of 3 nm) II-VI core/shell quantum dots [1] by the new efficient 'flash' method which show good antibunching. These quantum dots can be made in a shorter time (3 minutes) but still with a higher quantum yield over 70 %. The interest in using III-V QDs have also increased in the recent times with the InP based QDs considering that they are toxic Cd-free material. But the synthesis of InP QDs were relatively difficult with the limited choices for precursors. We also observed antibunching for InP/ZnS and InP/ZnSe QDs (8 and 10 nm diameter

respectively with the core of 3 nm) which are newly synthesized based on the method shown in [2] with the quantum yield around 60%.

Measurements & Discussion

The samples are prepared by spin-coating diluted quantum dots (less than a nanomolar concentration) on a clean quartz glass substrate with a single quantum dot on an area of 10 μm^2. Figure 1(a) shows the ensemble spectra of CdSe/CdS, InP/ZnSe, InP/ZnS with the spectral linewidth of 37 nm, 47 nm, 56 nm respectively. The lattice mismatch is around 3% for ZnSe shell with the InP core whereas the lattice mismatch is more for the ZnS shell with 7%. Figure 1(b) shows the single quantum dot spectra of CdSe/CdS, InP/ZnSe, InP/ZnS with the spectral linewidth of 21 nm, 20.8 nm, 25 nm respectively. It is observed that the CdSe QDs have narrower ensemble spectra than the InP QDs. But the single dot spectra are all comparable to each other with the narrower emission linewidth around 22±3 nm. It proves that the broader ensemble spectra of InP are not due to the broader single dot spectra. The observed result show that this is due to the inhomogeneous broadening just like the CdSe QDs. This observation further establishes that the III-V QDs could have the similar emission properties to the II-VI QDs.

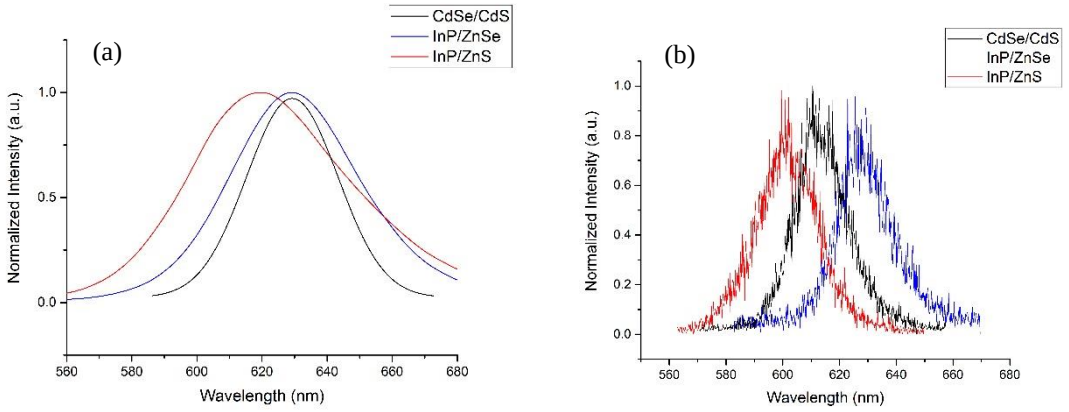

Figure 1 (a) Ensemble spectra of CdSe/CdS (black), InP/ZnSe (blue), InP/ZnS (red) (b) Single quantum dot spectra of CdSe/CdS (black), InP/ZnSe (blue), InP/ZnS (red)

Non-classical single photon emission from the QDs are proved by measuring the second order autocorrelation function. Figure 2(a) shows the antibunching measured for CdSe/CdS QD under continuous wave pumping from 10~500 W/cm^2 (P1 to P4). The second order auto-correlation function is fitted with the equation $A * [1 - C * \exp(-t/\tau)]$. The decay rate $(1/\tau)$ can be expressed as $(W + \Gamma)$ where the W is the effective pumping rate into the radiative state and the Γ is electron-hole recombination rate. As expected, τ decreases when going from P1 to P4 because the pumping rate increases. At the same time, the antibunching is less pronounced at high pump power: while $g^2(0)$ = 0.11 at power P2, it rises to 0.51 at power P4. This degradation of the antibunching is attributed to multi-excitonic emission (mostly bi-exciton) at higher excitation intensity and prevents CdSe/CdS quantum dots from being used in the so-called "photon-on-demand" regime. At low pump power (P2~50 W/cm^2) the probability to induce bi-excitons is low, such that the quantum dot shows good antibunching. This working intensity range is called as single-exciton regime. Figure 2(b) shows an intensity-time trace of the single CdSe/CdS quantum dot in the single-exciton regime. Even though the percentage of "on" counts is more than 90%, the blinking is not exactly 0-1 binary

states with the distinct bright and dark states. The presence of intermediate grey level is evident from the blinking trace in figure 2(b) with the dotted lines I, II and III representing the bright, grey and dark states respectively.

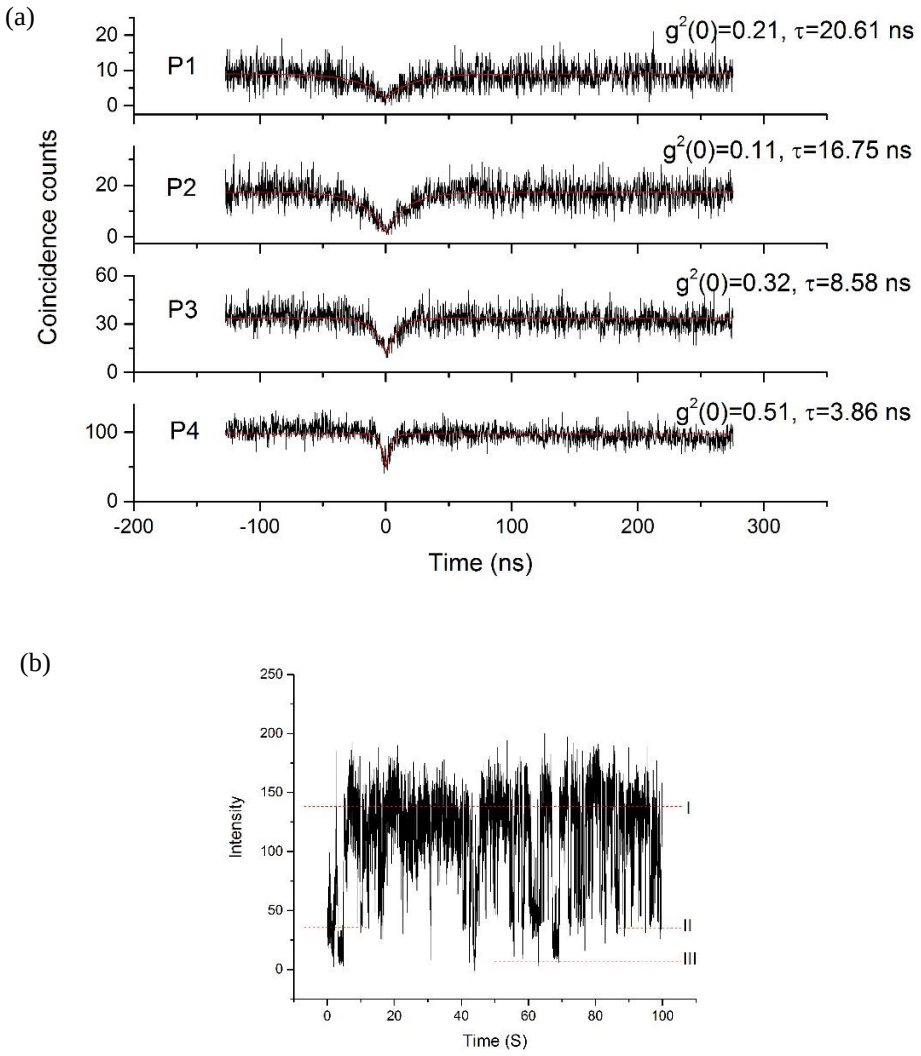

Figure 2 (a) Antibunching under continuous wave pumping from 10 to 500 W/cm^2 which is shown from P1 to P4. The $g^2(0)$ values and the factor τ is also shown for the fit. (b) Intensity-time trace recorded for CdSe/CdS QD with the time-bin of 10 ms. The dotted lines I, II and III represent the bright, grey and dark states.

CdSe/ZnS QD was shown to have good antibunching with strong Auger process [3], but they also had a poor blinking behavior. By replacing Zn by Cd in the shell, CdSe/CdS QDs were shown to have better blinking performance while maintaining antibunching at low pump power. The reduction of the Auger effect speculated to be is responsible of bi-exciton emission (which prevents antibunching at high pump power) and trion formation (responsible of grey emission states) [4]. Our above observation on CdSe/CdS QD also show the presence of grey states as shown in figure 2(b).

InP QD may offer a good alternative to the CdSe QDs but they have been little studied for single photon emission. Figure 3(a) and 3(b) show the antibunching observed for

InP/ZnS and InP/ZnSe QDs respectively. The input excitation intensity was set at very low power at 30 W/cm^2. The antibunching fit gives the value of $g^2(0) = 0.49$ for InP/ZnS QD while a much better value of $g^2(0) = 0.12$ for InP/ZnSe QD. The ZnSe shell on InP QD were also comparatively highly stable. The observation of a slightly narrower spectra in the figure 1(a) for InP/ZnSe QD also shows the highly passivated surface compared to the ZnS shell. Thus the newly synthesized InP/ZnS and InP/ZnSe core/shell QD emits single photon and thus opens the possibility of further investigation into their optical properties.

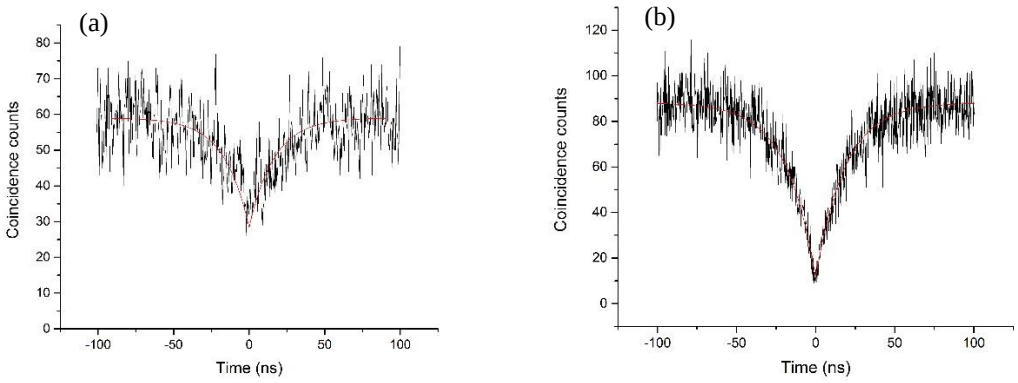

Figure 3 Antibunching under continuous wave pumping at low power (~30 W/cm^2) shown for (a) InP/ZnS with $g^2(0) = 0.49$ and (b) InP/ZnSe with $g^2(0) = 0.12$

Conclusion

We showed the single quantum dot spectroscopy of CdSe based QDs synthesized using the 'flash' method and the newly synthesized InP based QDs. The characterization study show promising results for the new InP QDs which is comparable to the high quality CdSe QDs. The single photon emission was observed for InP/ZnS and InP/ZnSe QDs. This opens perspectives for using these new materials as single photon sources and integrating them onto a chip for applications in optoelectronics.

Acknowledgements

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References

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