Coupling of CdSe/ZnS quantum dots: among themselves and with matrices

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ABSTRACT

We investigate the photoluminescence (PL) properties of CdSe/ZnS quantum dots (QDs) deposited on Si, fused silica, Au film, and silica nanospheres. The red shifts of the PL peak were observed with increasing density of QDs on various matrices: Si, fused silica, and Au film. This red shift is attributed to coupling between QDs forming bonding and anti-bonding states with PL emerging from the lower bonding states. The second peak is attributed to molecular complexes on the surface of QD interacting with its surrounding matrices. The second peak is too weak on native oxide due to very low surface roughness compared to others. Our results also demonstrated the enhanced bonding of QDs to the surface of the silica spheres with the thiolation process.

Keywords: CdSe quantum dots, photoluminescence, shift

1. INTRODUCTION

Colloidal II-VI semiconductor quantum dots (QDs) have been extensively used in optical and optoelectronic devices [1], chemical sensing [2], and biomedical labeling [3], *etc.* For these applications, QDs are incorporated into a dielectric matrix, and show interesting optical non-linear properties from quantum confined excitons. Interaction of light with nano-sized CdS and CdSe particles suspended in a He gas medium and ethylene-glycol was studied more than ten years ago. Even though sulfur has electro-negativity just below oxygen, nanoscaled CdS still require capping for protection in a matrix such as ZnS [4], a material for the TV screens. QDs are usually passivated by a shell of ZnS, CdSe/ZnS or CdS/ZnS QDs, for photo-stability and quantum yield improvement.

The electronic and photonic properties of a semiconductor nanoparticle usually depend not only on the properties of the particle itself but also on the nature of its surrounding matrices. The effects of coupling interactions between QDs and between QDs /dielectric interface are certainly as important. M. Xiao *et al.* studied the spontaneous-emission lifetime of CdSe/CdS core-shell QDs interacting with a SiO_2/Si interface, and observed a damped oscillatory behavior for the lifetime [5]. O. Kulakovich *et al.* presented the photoluminescence (PL) enhancement of CdSe/ZnS QDs on gold colloids, and the locally enhanced electromagnetic field due to the plasmon resonance of colloidal gold nanoparticle results in a more effective QD excitation [6].

Colloidal monodispersed silica spheres is an attractive material and widely used as a model system in fields such as ceramics, catalysis, and pigments, *etc.* They are usually prepared by Stöber-Fink-Bohn method [7], and the surface properties of these spheres can easily be tuned by using siloxane chemistry. It is well know that silica nanospheres can be used to form three-dimensional (3D) photonic crystals using a self-assembly approach [8]. Quantum dots combining with photonic crystals represent a powerful new device application mainly for lasers and parametric devices. Y. A. Vlasov *et al.* observed an enhanced optical gain of CdS QDs embedded inside the interstitials of 3D photonic crystals of silica spheres [9]. Modified PL properties from CdSe QDs on these silica nanospheres have been reported [10][11]. Also, M. Y. Gao *et al.* and N. Murase *et al.* demonstrated luminescence characteristics of $CdTe/SiO_2$ composite nanoparticles, and observed a slightly blue-shifted PL peak compared to that of CdTe nanocrystals [12][13]. W. T. Ford *et al.* also found a blue-shifted fluorescence spectrum for polystyrene latexes of 80nm diameter with CdSe/CdS nanoparticles [14]. An explanation of the blue shift has not been given by these authors.

In this work, we investigate the PL properties of CdSe/ZnS QDs deposited on Si, fused silica, Au film, and silica nanospheres, respectively. The red shifts of the PL peak with increasing density of QDs were observed on Si, fused silica, and Au film. However, we found blue shift whenever a second peak at a lower energy is detected. The red shift is simply due to the coupling among QDs themselves, and the blue shift results from the molecular complexes on the surface of the QD interacting with the surrounding matrices.

2. EXPERIMENTS

The CdSe/ZnS core-shell QDs with ~2.4nm size used were commercially available from *Evident Technologies Inc*. Au film with ~30nm was deposited onto Si substrates using Varian 3125 e-beam evaporator. In order to study evaluation of thiolation effect on the PL properties of QDs, several substrate surfaces, e.g. Si substrate, Au film on Si, and fused silica, with sulfur and without sulfur were introduced, and the root-mean-square (RMS) surface roughness of these samples was measured with the use of Veeco Dimension 3100 atomic force microscope (AFM). Substrates were first immersed in a solution of 5mM (3-mercaptopropyl)-trimethoxysilane in ethanol for 24h. The thiolation process for introducing sulfur onto a substrate surface followed. To study the coupling among the QDs themselves, low, middle, and

high concentrations of QDs in toluene solution were used to deposit the QDs thin film onto the above substrates via evaporation of the toluene solvent.

The details of thiolation process of silica spheres were followed by a procedure reported by K.S. Kang [10], and this process is used for QDs close attachment. The packed sphere crystals were prepared using a convective method [8]. Silica powder with QDs was re-dispersed in ethanol solution, having a concentration of 1.0wt%. The substrates were then immersed into the colloid sphere solution vertically. 3D photonic crystals of silica spheres were self-assembled onto the substrate via evaporation of the ethanol. For the case of QDs on silica nanospheres, the samples of two different depositions were prepared by the incorporation of QDs into unpacked silica spheres and packed silica spheres, respectively. PL was taken with the excitation of a 266nm quasi-CW source of UV laser.
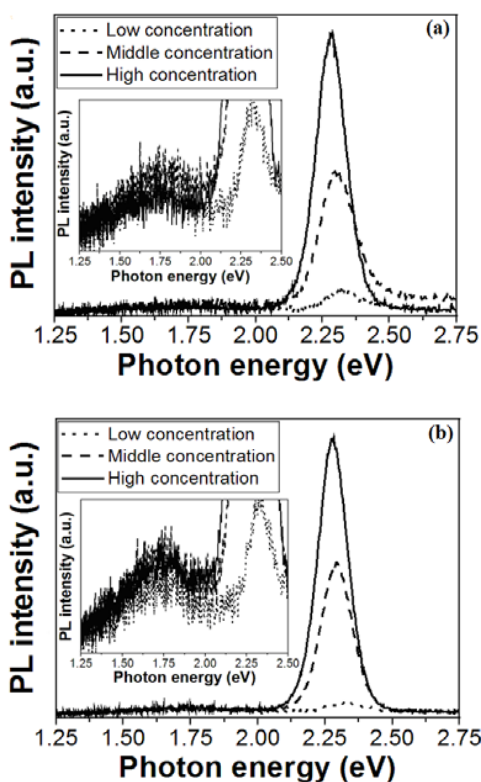
3.RESULTS AND DISCUSSION

Fig. 1 Comparison of PL spectra of CdSe/ZnS QDs deposited on a) a cleaned fused silica, b) a thiolated fused silica, and three different concentrations were used. The insets depict an enlarged figure of the lower peak near the higher PL peak.

Figure 1 shows the comparison of PL spectra of CdSe/ZnS QDs deposited on a cleaned and a thiolated fused silica, respectively, and three different QDs concentrations were used. Putting the QDs on fused silica results in the appearance of an additional lower peak, and the insets depict an enlarged figure of the lower peak near the higher PL peak. The red shift of the higher emission peaks are ~2.1% and ~2.6% for the cleaned surface and the thiolated surface, respectively. However, a single

symmetrical PL peak on Si substrate was observed, and the red shift of ~1.3% was obtained compared to the peak energy of QDs with low concentrations. This comparison between fused silica and Si confirmed that the fused silica itself is forming interaction with the QDs. Fig. 2 (a) shows the schematic illustration of transitions as the coupling between QDs (ground state: $|G\rangle$, excited state: $|E\rangle$), and the red shift with increasing density of QDs for both cases is attributed to coupling between QDs forming bonding and anti-bonding states with PL emerging from the lower bonding states.
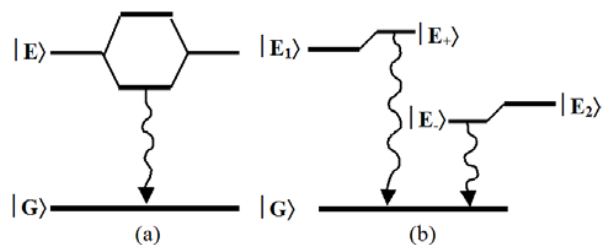

Fig. 2 Schematic illustration of transitions as (a) the coupling between QDs, and (b) the interaction between QDs and matrices.
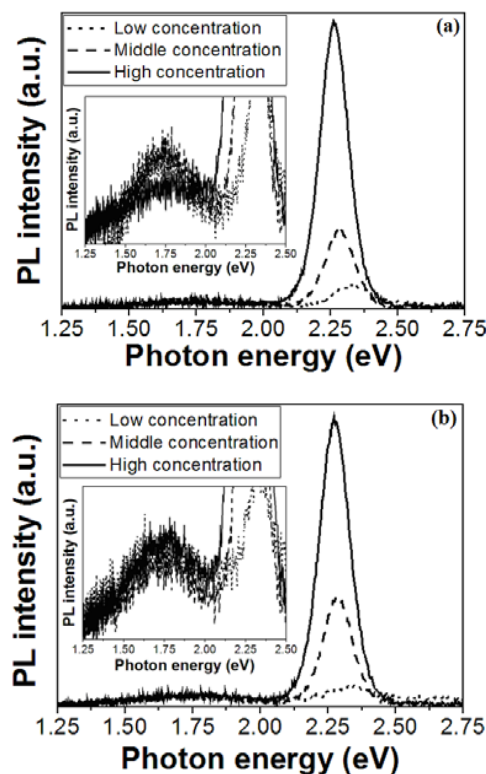

Fig. 3 Comparison of PL spectra of CdSe/ZnS QDs deposited on a) a cleaned Au film surface, b) a thiolated Au film surface, and three different concentrations were used as well. The insets depict an enlarged figure of the lower peak near the higher PL peak.

Figure 3 shows the comparison of PL spectra of QDs deposited on a cleaned and a thiolated Au film surface, respectively, for three different QDs concentrations. The insets depict an enlarged figure of the lower peak near the

higher PL peak. The peak shift results are also similar to those shown in Fig. 1, and the red shift of the higher peaks are ~2.7% and ~2.9% for the cleaned Au film and the thiolated Au film surface, respectively, indicating that the thiolation does not play a significant role.

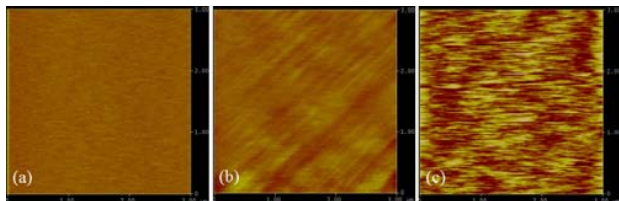Fig. 4 AFM surface images of (a) Si with native oxide (b) fused silica (c) Au plated Si with a scanning area of 3.0μm ×3.0μm.

In this case, we assume that the lower second peak results from molecular complexes on the surface of the QD interacting with the matrices, clearly the higher peak is shifted up and the lower peak is shifted down, dictated by the solution from quadratic equation. Why then we have not observed the second peak on Si with ~3nm of native oxide? Fig. 4 shows the AFM surface images of Si, fused silica, and Au plated Si with native oxide, and the RMS roughness have the following values: <0.4nm, 8nm, and 16nm, respectively. The roughness of the fused silica is ~20 times greater than that of the Si substrate, which serves to enhance the emission. Therefore, surface roughness enhancement explains why we have an extra peak on the fused silica but not on the native oxides of Si. Furthermore, with Au on Si substrate, the measured roughness is ~40 times larger, resulting in even larger enhancement. Thus, the second peak originates from the interface of the QDs and the substrate, interacting with the QDs.
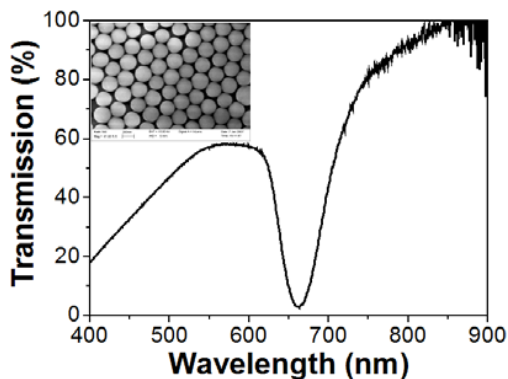

Fig. 6 Transmission spectra at normal incidence of photonic crystal of silica spheres with a diameter of ~300nm. The inset shows a close packed stacking of crystal in one dimension.

Figure 5 (a) and (b) show the PL spectra of CdSe/ZnS QDs deposited for the unpacked and packed silica spheres on Si and fused silica substrates, respectively. To eliminate the effect of photonic band gap on the PL of the QDs at 540nm wavelength, the stop-band of the packed sphere crystals was measured at ~660nm

using a Cary 300 Bio UV-Visible spectrophotometer, as shown in Fig. 6. The inset shows a close packed stacking of crystal in one dimension, and only face-centered cubic stacking prefers to exist because of its more stable. The higher PL peaks shifts to higher photon energy with respect to the peak energy of QDs itself on Si substrate, and a maximum blue shift of ~176meV was obtained as shown in Fig. 5 (a). The up-shifts are higher with higher packing. A maximum blue shift of ~194meV was observed with QDs on the silica spheres, as shown in Fig. 5 (b).
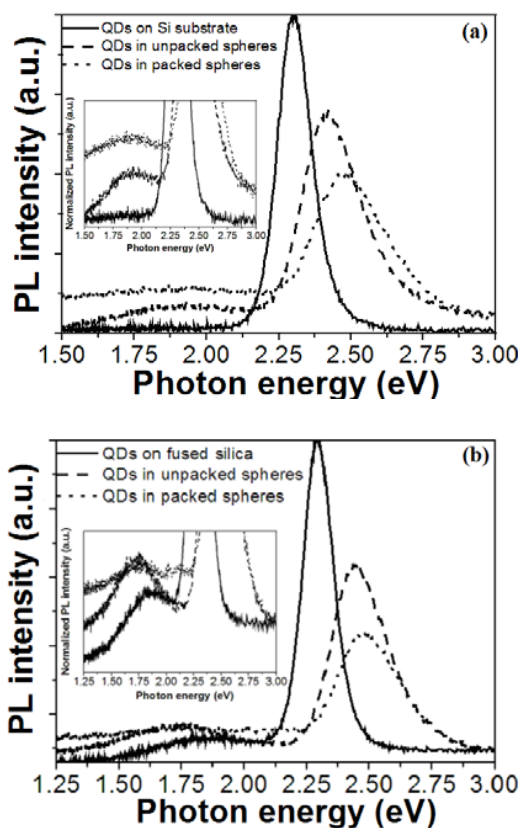

Fig. 5 (a) PL spectra of CdSe/ZnS QDs deposited on 1) the surface of a Si substrate, 2) the unpacked silica spheres, and 3) the packed crystals of silica spheres. (b) PL spectra of CdSe/ZnS QDs deposited on 1) the surface of a fused silica substrate, 2) the unpacked silica spheres, and 3) the packed crystals of silica spheres. The inset depicts an enlarged figure of the second lower peak near the higher PL peak, respectively. These silica spheres used were thiolated for both substrates.

In order to understand the two peaks, we recognize that there are two ways to shift the emission peak, one way shift caused by pressure, temperature, etc., and two way shift, one up-shift of the higher peak and another down-shift of the lower peak. The electron wavefunctions for QDs and its surrounding matrix are given by $H_o|1\rangle = E_1|1\rangle$ and $H_o|2\rangle = E_2|2\rangle$, where E_1 is the energy state of CdSe, and E_2 is the energy state of the complex. In $H\Psi = E\Psi$, with $H = H_o + H_1$, where H_1 represents interaction with matrix elements $C = \langle 1|H_1|2\rangle$ and $C^+ = \langle 2|H_1|1\rangle$. The

wavefunction Ψ can be expressed as $\Psi = a|1\rangle + b|2\rangle$, where a and b being constant parameters. The secular determinant gives

$$(E - E_1)(E - E_2) - C^2 = 0 . \qquad (1)$$

The roots give the two shifted energy states, $E_{\pm}$. Lacking a pronounced peak for the silica spheres higher than that of the CdSe QDs, $E_2 > E_1$ cannot be applied. For blue shift, we must have $E_1 > E_2$ such that E_1 is shifted to a higher level, e.g. E_+, and E_2 is shifted to a lower level, e.g. E_-, as shown in Fig. 2(b). This indicates that the PL modification was induced by the interfacial coupling between QDs/silica spheres with the molecular complexes.
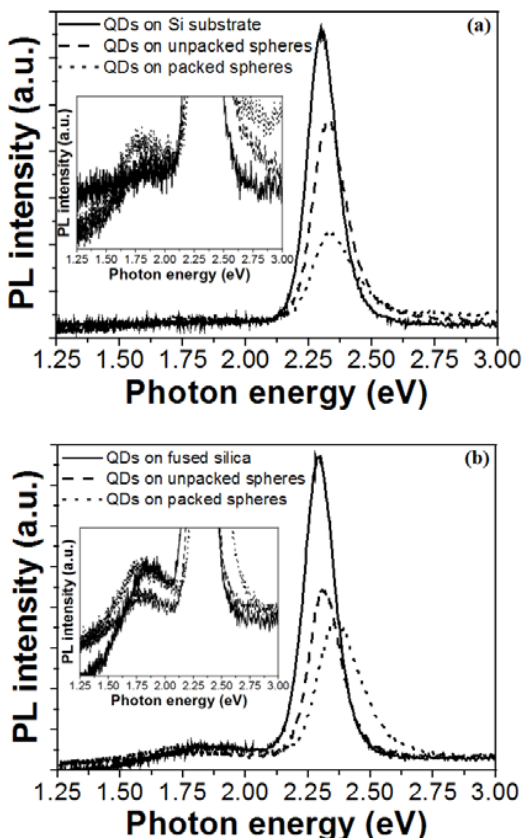

Fig. 6 (a) PL spectra of CdSe/ZnS QDs deposited on 1) the surface of a Si substrate, 2) the unpacked silica spheres, and 3) the packed crystals of silica spheres. (b) PL spectra of CdSe/ZnS QDs deposited on 1) the surface of a fused silica substrate, 2) the unpacked silica spheres, and 3) the packed crystals of silica spheres. The inset depicts an enlarged figure of the second lower peak near the higher PL peak, respectively. These silica spheres used were not thiolated for both substrates before the deposition.

Figure 6 (a) and (b) show the PL spectra of CdSe/ZnS QDs deposited for the unpacked and packed silica spheres on Si and fused silica substrates, respectively, and the thiolation process was not performed for these silica spheres before deposition. The peak shift results were also similar to those shown in Fig. 5. However, the energy shifts were smaller. We thus estimate that the thiolation process on silica spheres make those QDs strongly bond on the surface of spheres. This will

produce molecular complexes on the QDs surface properly via oxygen atoms, and the molecular complexes interacting with the sphere matrix results in the blue shift of PL peaks. For QDs on the silica spheres our pre-thiolated process ensures that QDs are separated so that the QD/QD coupling is not significant, leaving the large interaction between the QDs and the surface complexes to dominate.

4. CONCLUSION

In conclusion, the coupling interaction of quantum dots among themselves and with matrices are important to the development of lasers and parametric devices incorporating quantum dots, and our results give the fundamental understanding of luminescence shifts due to these interaction. The red shift with increasing density of QDs is attributed to the coupling between QDs forming bonding and anti-bonding states with PL emerging from the lower bonding states. The second lower peaks observed on fused silica and Au film result from the molecular complexes on the surface of the QD interacting with the state of the QD. Increasing the surface roughness results in substantially enhanced surface coupling due to both increase of surface areas and increase of effective surface electric field. PL properties of QDs are enhanced in the QDs/sphere system. Our results also demonstrated the enhanced bonding of QDs to the surface of the spheres with the thiolation process.

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