Chapter 6

Selective Quantum Confinement Effect

Addition of a shell layer on semiconducting quantum dots is an approach to control the optical bandgap of core/shell systems. In this direction, we have grown several core/shell nanostructures having a type-I heterostructure configuration. The nature of the energy-offsets has been varied by a suitable shell-material with an aim to control the conduction and the valence band-offsets separately. Confined holes or electrons could hence be relaxed selectively leading to an increase in the valence band-edge or a decrease in the conduction band-edge. In this work, after forming such core/shell systems with a control over the shell thickness, we characterized the nanostructures with scanning tunneling spectroscopy in order to determine the density of states and finally the conduction and the valence band-edges of the core/shell systems. We find that while a large band-offset strictly localizes the carriers in the core, a small perturbation indeed delocalizes the carriers up to the shell-layer shifting the relevant band-edge towards the Fermi energy and thereby decreasing the transport gap. The decrease in the transport gap was in agreement with the optical absorption spectra. The results provide a novel route to delocalize a selective type of carriers up to the shell layer of core/shell nanostructure systems.
6.1. Introduction

Quantum structures caught the fancy of researchers primarily due to the ability to tune the bandgap with their diameter. Apart from the bandgap, locating the conduction and the valence band-edges of these low-dimensional systems has became equally important in designing a device-architecture.\(^1\) Tuning of the bandgap and band-edges has been achieved through a range of routes, such as the size and shape of quantum structures, composition of ternary and multinary systems, an introduction of core/shell approach, and so on.\(^2,3\) In each of the cases, the rationale behind the energy of band-edges and hence the bandgap of the final system has been immensely interesting involving rich chemical physics.

In core/shell nanostructures, the core and shell materials have unequal bandgaps. This leads to formation of one of the three types of heterojunctions, namely, straddling gap (type-I), staggered gap (type-II), or broken gap (type-III).\(^4\) In the former two heterojunctions, the conduction band-edges may at times relax the confined electrons of core quantum crystals by delocalizing them up to the shell layer.\(^4,5\) Similarly, a suitable valence band-offset may partially delocalize the holes. With an apparent diameter-extension for one of the charge carriers, only one of the band-edges will be affected thereby decreasing the bandgap of the quantum dots. With a change in the composition, a transition between the heterojunctions is also possible.\(^6\)

It has been proposed that the possibility of lifting of quantum confinement in type-I core/shell systems would depend on the magnitude of the band-offset. When the conduction (or valence) bands of the core and shell differ by a large extent, the electrons (or holes) would remain confined in the core. On the contrary, if the band-offset is small, the carriers would be extended till the shell layer.\(^4,5\) In this direction, a theoretical model dealt with charge localization/delocalization that depended on the band-offset in heterostructured nanomaterials.\(^7\) Experimental efforts in this context spanned from the mapping of wave functions of semiconducting nanoparticles\(^8,9\) or Fermi-level pinning of doped nanocrystals,\(^10,11\) to the understanding of atom-like discrete energy states of core/shell nanoparticles\(^12\) or band-offset in “dot in a nanorod” heterostructures.\(^1,9\)
Chapter 6

It is hence very important to determine the bandgap and more importantly the band-offsets in core/shell systems, so that a suitable heterostructure could be engineered for an application. While the optical spectrum provides energies corresponding to the allowed transition between the bands, the scanning tunneling spectroscopy (STS) is a powerful experimental technique to provide valuable information on conduction and the valence band-edges separately.\textsuperscript{13,14} To study the role of band-offsets at the heterojunction on the band-edges of the nanostructures, we have grown a set of type-I core/shell nanoparticles. With the same core, we have varied the material on the shell layer (and the shell's thickness) in order to design three type-I core/shell systems. The shell materials have been chosen in such a manner that the magnitude of the band-offset or the difference between conduction (or valence) band-edges ranged from a low to a high value. In this work, we report growth and STS of such core/shell nanoparticles as an experimental evidence of type-selective quantum confinement effect.

6.2. Experimental

6.2.1. Materials

Cadmium oxide (CdO) and zinc stearate (ZnSt\textsubscript{2}) were purchased from Loba Chemie, trioctylphosphine oxide (TOPO, 90% pure), trioctylphosphine (TOP, 95% pure), selenium (99.5%), sulfur powder, oleic acid (OA), 1-octadecene (ODE), and octadecylamine (ODA, 97%), were purchased from Aldrich Chemical Co. All the chemicals were directly used without further purification.

6.2.2. Growth of CdSe nanocrystals

To grow CdSe quantum dots, we followed reported colloidal synthesis routes\textsuperscript{2,3,15-17}. In a typical synthesis, 20 mmol (5.649 g) of OA and 9 mL of ODE were mixed with 0.256 g (2.0 mmol) of CdO in a three-neck flask. The mixture was heated to 220 °C with a continuous flow of nitrogen. The solution turned clear that was cooled to room temperature; 3 g each of TOPO and ODA were added at this stage. The mixture was heated to 285 °C when 3 mL of
trioctylphosphine selenide (TOPSe) solution, formed by dissolving 1.8 g of Se in 8.5 mL TOP in a dry container under a nitrogen environment, was swiftly injected to the flask. The reaction that led to formation of CdSe nanocrystals was stopped after 2 min by a rapid cooling down to 30-50 °C. The nanocrystals were extracted from unreacted precursors through repeated precipitation by adding ethanol in presence of acetone followed by centrifugation at 8000 rpm. The growth process generated almost monodispersed (diameter = 3.5 nm, as obtained from transmission electron microscope, TEM image) CdSe nanocrystals with the optical absorption band at around 540 nm. The resulted CdSe nanoparticles were re-dissolved in hexane to use as a stock solution for the synthesis of core/shell nanoparticles. The concentration of the stock solution could be measured using Beer–Lambert law, since the extinction coefficient of the material was known.  

6.2.3. Cadmium, zinc, sulfur, and selenium precursor solutions

A cadmium precursor solution (40 mM) was formed by dissolving 154 mg of CdO in 2.7 g OA and 30 ml ODE at 220 °C under prolonged nitrogen purging through the solvent. Similarly, a sulfur solution (40 mM) was prepared by dissolving 12.8 mg of sulfur in 10 mL ODE at 120 °C under the same condition. The solutions after cooling down to room temperature were used for the growth of CdS shell-layer on CdSe quantum dots. As a zinc precursor solution, 0.4 mmol of ZnSt$_2$ was dissolved in 10 mL ODE at 180 °C. Injection solution (40 mM) of Se was made by dissolving 15.8 mg of Se in 5 mL TOP in a dry container under a nitrogen atmosphere.

6.2.4. Growth of a shell layer on CdSe quantum dots

We have grown metal-chalcogen (MeCh) shell layers on CdSe quantum dots following successive ion layer adsorption and reaction (SILAR) method. For this synthesis, 2 mL of hexane solution containing almost $1 \times 10^{-4}$ mmol of as synthesized CdSe nanoparticles were mixed with 2 g of ODA and 5 g of ODE in a three-neck reaction flask. The flask was then heated to 100 °C for 30 min under nitrogen atmosphere to remove hexane from the reactants. The
reaction mixture was then further heated to a desired temperature (250 °C for CdS, 230 °C for ZnSe and 210 °C for ZnS ) to grow shell layers. The MeCh shell layers were grown monolayer-after-monolayer (SILAR method) by alternate injection of a metal and a chalcogenic precursor in sequence. Growth time was 4 min after injection of each precursor solution. The exact amount of metal (Cd, Zn) or chalcogen (S, Se) precursors required for each monolayer (ML) was determined by calculating the total surface area of nanoparticles present in the solution. Average thickness of one monolayer of CdS would increase the diameter of the nanoparticles by about 0.7 nm as measured from TEM. While 0.49 mL of Cd-precursor was injected for the growth of the first layer, the volume of subsequent injection solutions were determined by calculating the total surface area of the nanoparticles. To monitor the growth of a shell-layer, we measured the UV-Vis absorption and photoluminescence spectra 3 min after injection of each pair of precursor solutions. In this process, we have alternately injected the metal and chalcogenic precursors up to seven times. Such shell layers have been denoted as ML1 to ML7. When we achieved the desired number of shell layers, the growth solution was cooled to room temperature. The nanocrystals were repeatedly precipitated by adding ethanol in hexane solution in presence of acetone followed by centrifugation at 8000 rpm and finally dissolving in toluene. The reaction at the end generated core-shell nanoparticles with a shell layer of seven monolayers having a total diameter of 8.0-8.5 nm. A small amount of the reaction solution was taken out of the flask after second and fourth round of precursor-injection so that the core/shell systems with 2 ML and 4 ML thick shell-layers could be characterized. All the nanoparticles had oleic acid as the stabilizing agent.

6.2.5. Characterization of the quantum dots

The nanocrystals were characterized by UV-Vis absorption and photoluminescence spectroscopy. Diameter of the nanoparticles was estimated from transmission electron microscope (TEM) images. Crystalline nature of the nanoparticles could be observed from high-resolution TEM (HR-TEM) images and selected area electron diffraction (SAED) patterns.
Elemental mapping from scanning transmission electron microscopy (STEM) images were used to determine the composition of the nanoparticles.

6.2.6. Scanning tunneling spectroscopy (STS)

For scanning tunneling microscopy (STM), the nanoparticles were deposited on a freshly cleaved highly ordered pyrolytic graphite (HOPG) by drop cast method. In order to address single particles or a sub-monolayer of particles, we used an ultra dilute solution of the nanoparticles in hexane or toluene. The HOPG substrates were annealed at 60 °C in a glove box for 2 h before STM characterization. Measurement of tunneling current was carried out with a Nanosurf easyScan2 STM under an ambient condition. For each core/shell system, current-voltage (I-V) characteristics were recorded at many different points.

6.3. Results and discussion

6.3.1. Characterization of the nanocrystals

Crystalline nature of the nanoparticles was studied by HR-TEM and SAED. To determine the size distribution of the nanoparticles, we have recorded the TEM images of the core and also the core/shell nanoparticles at various scale of interest. Figure 6.1.(a) and 6.1.(b) represent the size distribution of CdSe nanoparticles and CdSe/CdS core/shell nanoparticles having 7 layers of CdS, respectively. HR-TEM image of a core/shell nanoparticle has been presented in the inset of figure 6.1.(b). Lattice fringes of the nanoparticles with a spacing of 0.36 nm, clearly visible in the HR-TEM image, matched well with the lattice spacing of the <100> plane of CdS crystals. To know the level of monodispersity of CdSe core and CdSe/CdS core-shell nanoparticles, histograms computed from 60 nanoparticles each have been clubbed in figure 6.1.(c). The results show that while the CdSe core had an average diameter of 3.5 nm, the diameter of the core/shell nanoparticles was 8.5 nm. The dark-field STEM images for CdSe/CdS core/shell nanoparticles are shown in figure 6.1.(d). From the elemental mapping, it can be observed that all the elements, that is, cadmium, selenium, and sulfur were homogeneously distributed over the field of view. A closer look of the images for selenium and
sulfur shows that the core-shell nanoparticles were slightly rich in sulfur as compared to selenium presumably due to larger volume of the material on the shell (CdS) as compared to that of the core (CdSe).

**Figure 6.1.** TEM images of (a) CdSe and (b) CdSe/CdS core/shell nanostructures. The latter systems had 7 monolayers of the shell material. Inset of (b) shows a HR-TEM image of CdSe/CdS (7ML). (c) Histograms for size distributions of CdSe and CdSe/CdS nanoparticles as extracted from TEM images. (d) Dark-field STEM image of core-shell nanoparticles, as presented in part (i) and elemental mappings for (ii) Cd, (iii) S and (iv) Se. The scale bar for the selected region of the elemental mapping was 500 nm × 400 nm.

### 6.3.2. Optical absorption and photoluminescence spectroscopy

Optical absorption and photoluminescence (PL) spectra of CdSe and different core/shell nanoparticles are shown in figures 6.2.(a)-(c). Thickness of the CdS, ZnSe, and ZnS shell layer has been varied from 1 to 7 layers. With the introduction of a shell layer, the optical
band of CdSe at 540 nm shifted to the lower energies. The magnitude of the red-shift depends strongly on the material that formed the shell-layers. The shift is meager in CdSe/ZnS core/shell systems (only 7 nm); for the CdSe/CdS system, the shift is as large as 78 nm. The red-shift in the optical absorption in the CdSe/ZnSe core/shell system is intermediate to the two extremes (51 nm). The shift moreover increases monotonically with the thickness of the shell-layer followed by saturation. Optical absorption spectra and the shift in the band positions can be explained by considering energy band diagrams (figure 6.3.).

**Figure 6.2.** Optical absorption (solid lines) and photoluminescence spectra (broken lines) of bare CdSe and different core/shell systems with 2, 4, and 7 monolayers of shell. While CdSe has been represented by black lines, the core/shell systems have been represented by red, green, and blue lines, respectively. A Y-offset has been added to the spectra for clarity of presentation.

With the core/shell systems being CdSe in the core and a higher bandgap material in the shell, the ground-state electrons or holes or both may remain confined in the core or become delocalized up to the shell layer depending on the band-offsets between the core and the material on the shell. In CdSe/CdS core/shell systems, due to a small conduction band-offset, ground state electrons of CdSe would be able to overcome the tunneling barrier between the core and the shell systems. The holes, on the other hand, facing a large barrier (due to a large valence band-offset) would be unable to become delocalized up to the shell. In other
In CdSe/ZnSe system, on the other hand, the valence band-offset is small prompting holes to be delocalized up to the shell layer; the electrons remained confined in the core due to a large conduction band-offset. Such a selective delocalization (of holes) led to an increase in the valence band-edge energy without a change in the conduction band-edge. That is, the decrease in the bandgap of CdSe/ZnSe system would occur due to a change in the valence band-offset. In CdSe/ZnS core/shell systems, both the band-offsets are large enough (~0.9 eV) reducing the probability of tunneling of both types of carriers. The electrons and the holes remained confined strictly to the core without relaxing the quantum confinement effect. With the addition of the ZnS shell layer, the valence and conduction band-edges hence did not change leaving the bandgap of the core/shell system unaltered.

Figure 6.3. Schematic representation of energy band-diagram along with the radial wave function of ground state electrons and holes in CdSe/CdS, CdSe/ZnSe, and CdSe/ZnS type-I core/shell nanoparticles. The shift in the conduction or valence band-edges upon selective delocalization of electron or holes are shown as dotted lines.
6.3.3. Scanning tunneling spectroscopy (STS)

It can be intriguing if the band-edges of the core/shell systems could be located with the aid of scanning tunneling spectroscopy. We hence recorded the tunneling current through the nanoparticles; the measurements have been carried out for the three core/shell systems. The dependence of the tunneling current with the shell thickness has also been studied. Tip approaching current has been kept low so that the tip does not influence the band-edges of the nanoparticles. Current-voltage characteristics of the three core/shell systems are shown in figure 6.4. Here, we presented results from the core/shells having seven layers of shell material. To bring out the effect of the shell layer, we included the characteristics of the nanoparticles without the shell layer. The figures also include STM topography of a monolayer and a freshly cleaved HOPG surface. The topographies display presence of the nanoparticles on the HOPG substrate. The size of the nanoparticles that can be estimated from the topography also matches the diameter obtained from the HR-TEM image.

Figure 6.4. Tunneling current versus tip voltage characteristics of a monolayer of CdSe quantum dots and (a) CdSe/CdS, (b) CdSe/ZnSe, and (c) CdSe/ZnS core/shell systems. Results from 10 measurements have been included for each case with the average shown as solid lines. STM topographies of a couple of CdSe/CdS core/shell nanoparticles on the HOPG (32.5 nm × 32.5 nm) and a freshly cleaved HOPG substrate (7.93 nm × 7.93 nm) are shown in inset of (a) and (b), respectively.
To record the tunneling spectra of the nanoparticles, the Pt/Ir tip was first approached through a feedback loop; the feedback control was disabled before recording of the spectra. In the spectra, a region of suppressed tunneling could be observed around the zero bias followed by current onsets at both positive and negative tip-voltages. The negative voltage corresponding to the current-onset, which is due to an injection of electrons from the STM tip to the conduction band of nanoparticles, locates the conduction band-edge of the nanoparticles. The positive voltage of current-onset, on the other hand, appearing due to withdrawal of electrons from the valence band-edge of nanoparticles to the STM tip, is a measure of the energy of valence band-edge of the nanoparticles. A comparison of the tunneling spectroscopy of bare CdSe and core/shell systems, as presented in figure 6.4., includes results from 10 measurements each that show a high-level of reproducibility. With an addition of a shell layer, the change in the magnitude of tunneling current depends on the material on the shell and the direction of tip-bias. For example, with an addition CdS in the shell, the (amplitude of) current in the negative voltage increased. The current in the positive bias increased with an addition of a ZnSe shell layer. On the other hand, there was little or no change in the tunneling current in the both bias directions upon addition of a ZnS shell layer. The change in tunneling current with an addition of a shell layer, occurring primarily due to the level of alignment of the band-edges and the Fermi energy of the tip metal, in fact depends on the nature of core/shell heterostructures. The results presented in figure 6.4. would hence indicate the change or shift in the conduction and the valence band-edges of the nanoparticles upon formation of type-I band-offsets. The change was however always progressively more with the increase in the thickness of the shell-layer.

6.3.4. Role of energy-offsets on band-edges

To analyze the tunneling current of nanoparticles, we have plotted the conductance ($\frac{dI}{dV}$), as obtained by numerical differentiation of the tunneling current, versus tip bias for different core/shell systems. Figure 6.5. represents the average conductance spectra for 10 different measurements of bare CdSe and different core/shell systems with three different
Selective Quantum Confinement Effect

shell thicknesses in each system. In a conductance spectrum, the first onset in the negative tip voltage represents the conduction band-edge. The first onset in the positive bias, on the other hand, identifies the valance band-edge of the nanoparticles in a monolayer. The gap between the two onsets is a measure of the transport gap of the nanoparticles. The measured gap of CdSe nanocrystals from STS has been 2.46 eV (figure 6.5.) which is in close agreement with the band gap (2.29 eV) obtained from optical absorption spectrum. Here, the optical bandgap and the transport gap did not differ much due to low exciton binding energy in these materials. As such, the optical bandgap exceeds the transport gap by energy equal to the binding energy.

Figure 6.5. Tunneling conductance spectra (dI/dV vs V), as derived from the numerical derivative of I-V characteristics, of a bare CdSe and increasingly more thickness of (a) CdS, (b) ZnSe, and (c) ZnS shell-layer. A Y-offset has been added to the spectra for clarity of presentation.

The results of CdSe/CdS and CdSe/ZnSe core/shell systems, where band-edges responded to the formation of shell layers, have been summarized in figure 6.6. The change in optical bandgap and the band-edge responsible for the change in transport gap with reference
to the parameters of bare CdSe nanoparticles have been plotted as a function of the number of shell layers. Error bars have been added to the points denoting the change in band-edges, as obtained from STM measurements. The deviation in locating band-edges primarily occurs due to a variation in the diameter of the nanoparticles.

6.3.5. Selective quantum confinement

In type-I core/shell systems, both conduction and the valence band-edges of the core lie within the band gap of the shell materials. The first onsets of conductance spectra at both biases hence are associated with the core material. Nevertheless, the spectra of the CdSe core and different core/shell systems were clearly different. In the CdSe/Cds core/shell systems (Fig. 5a), holes remained confined to the core and the electrons were delocalized up to the shell layer. Upon growth of the CdS shell, while the valence band energy remained invariant, the conduction band-edge shifted to a lower energy. These two events resulted in a red-shift in the optical absorption spectra of the CdSe/Cds core/shell nanoparticles upon addition of the shell layers. In CdSe/ZnSe core/shell systems (figure 6.5.b), where electrons remained confined and holes were delocalized, the valence band-edge shifted towards a higher energy and the conduction band remained invariant leading to a red-shift in optical absorption spectra. That is, even though the optical bandgap of CdSe/Cds and CdSe/ZnSe decreased, the rationale behind the shift has been different in the two cases. In CdSe/ZnS core/shell systems (figure 6.5.c), both types of carriers are strictly confined to the core prompting the band-edges of the core to become almost unaffected by the growth of the shell layer as also observed in absorption spectra.

With an increase in the thickness of the shell layer, the shifts in the optical bandgap and the relevant band-edge increase. Apart from the excellent correlation between the scanning tunneling spectroscopy and optical spectroscopy results, the shift observed in the STS results has been consistently more than that from the optical spectroscopy. This could be due to an electron-charging effect and an absence of excitonic coulomb-interaction in the tunneling spectra. When we compare the shifts in CdSe/Cds and Cdse/ZnSe core/shell systems, we
observe that both the shifts are higher for the CdSe/CdS system at every shell thickness. The decrease in the conduction band-edge energy for a 7-layered thick shell in the CdSe/CdS system has been around 0.39 (±0.02) eV; for the CdSe/ZnSe system, the shift in the valence band-edge energy reached up to 0.29 (±0.02) eV. The change in the band-edge energy of CdSe/CdS system has been larger presumably due to one or more of the following reasons: (1) electrons in the core of the CdSe/CdS system face a smaller barrier to tunnel in comparison to the barrier for holes in the CdSe/ZnSe system, (2) lattice mismatch in the CdSe/ZnSe system is somewhat larger (~7%) as compared to the CdSe/CdS system (~5%), and (3) the mobility of electrons is higher than that of holes due to a favorable effective mass of the former types of carriers. Overall, the changes observed in optical and STS spectroscopies for a range of core/shell systems and shell-thickness have a high-degree of correlation.

**Figure 6.6.** Dependence of the shift of first absorbance peaks on their shell thicknesses of (a) CdSe/CdS and (b) CdSe/ZnSe. Error bars in the tunneling measurements represents the maximum range of shift measured on 10 nanoparticles of each sample. This error is mainly due to size distribution of the nanoparticles and the level of accuracy of our experimental set up.
6.4. Conclusions

In conclusion, we have grown core/shell nanostructures in order to selectively create a conduction or a valence band-offset. With CdSe quantum dots in the core and a range of materials with varying and controllable thickness as the shell layer, the core/shell systems formed type-I heterostructures. From the tunneling spectroscopy and density of states of the isolated nanostructures recorded with a scanning tunneling microscope tip, we have observed that the change in the band-edge energy of the core/shell systems was selective. The (band-edge) energies of core/shell systems change only when a band-offset was small enough allowing delocalization of that type of carriers up to the shell layer. A large band-offset in the valence and/or conduction bands of the core and the shell keep the respective carriers localized in the core. In other words, we showed that quantum confinement effect could be relaxed for a selective (type of) carriers in these core/shell systems. The core/shell systems provided interesting examples of type-selective delocalization of carriers.
Selective Quantum Confinement Effect

References


