Concluding Remarks and Future Perspectives

“Happy is the person who knows what to remember of the past, what to enjoy in the present, and what to plan for in the future.”

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The thesis as presented in Chapters 1-6 has probably achieved its limited objective. The main objective of the thesis as presented in Chapter 3-6 was to employ “state of the art” theoretical methods to study the electronic structure of CdTe nanoparticles viz. quantum dots, nanowires and nanotubes. In this context, we have employed the self-consistent-charge density-functional tight-binding (SCC-DFTB) method. The study reveals some new and interesting features for CdTe nanoparticles which we believe will be very useful for further exploration of these nanomaterials.

In Chapter 3, we have described the complete SCC-DFTB parametrization for cadmium and its interaction with hydrogen, carbon, oxygen, sulfur, selenium, tellurium etc. The calculated structural, energetic and electronic properties of the relevant bulk phases, surfaces and nanowires of CdX (X = S, Se and Te), using our derived SCC-DFTB parameters have been discussed and compared with reference DFT calculations as well as available experimental data. We also discussed the results of structural and energetic properties of some simple diatomic molecules and small molecular systems using our derived SCC-DFTB parameters and tested with DFT calculations and available reference data. The calculated values using our SCC-DFTB parameters are in good agreement with the reference DFT calculations and also with experimental results. We show that our parameters are able to reproduce atomic geometries, binding energies and energy dispersion quite well in comparison to first-principle calculations, demonstrating a good transferability among different chemical environments [325]. Using these SCC-DFTB parameters, one can now be able to calculate the structural, energetic and electronic properties of larger size various cadmium chalcogenides (CdX) nanoparticles such as quantum dots (QDs), nanowires (NWs), nanotubes (NTs), nanoribbons (NRs), surfaces and also bulk systems. One can also investigate the lattice defects as well as electronic structure of core/shell nanoparticles like CdTe/CdSe, CdTe/CdS, CdSe/CdS etc. and also alloy nanoparticles such as CdTe\textsubscript{1−x}Se\textsubscript{x}, CdTe\textsubscript{1−x}S\textsubscript{x}, CdSe\textsubscript{1−x}S\textsubscript{x} etc. By employing these SCC-DFTB parameters, we have calculated the stability, structural relaxations and electronic structures of relatively larger size CdTe nanoparticles (QDs, NWs and NTs), and also investigated the electronic properties of CdTe based inorganic-organic hybrid nanostructures viz. CdTe QDs-CNT,
NWs-dye and NTs-fullerene, which are discussed in Chapters 4-6.

Chapter 4 offered the electronic structure of thiol-capped CdTe QDs and CdTe QD-CNT hybrid nanostructures. We have discussed the stability, structural relaxation, density of states (DOS), energy gap between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) and Mulliken population as a function of both size and crystal structure. We show that an overall trend of an increasing binding energy when the cluster size increases. This can be taken as a direct consequence of the reduction in the ratio of surface atoms to bulk atoms. We also observed that depending on the size of the QDs there is a possibility of switching the structure from zinc-blende to wurtzite and vice-versa. We have also shown the structural relaxations of both the unpassivated and passivated CdTe QDs. The surface passivation essentially reduces the size of the QDs and our study suggests a surface region of about 3 Å, almost independent of the size of the QD where the structural relaxations are mostly found. From the density of states analysis we show that the surface passivation plays an important role in controlling the luminescence properties of QDs. The values of the HOMO-LUMO gap of both zinc-blende and wurtzite CdTe QDs of different sizes suggested that the absorption of thiol-capped CdTe QDs has the superior tunability over a broad spectral range. This will make CdTe QDs very useful material for solar cells, and in FRET based devices. An understanding of the surface charge of the nanoparticle is very crucial to study the transport processes within the living cells. In view of this, we have studied the Mulliken charge distributions for individual atoms as a function of their radial distance for stoichiometric zinc-blende and wurtzite Cd\(_n\)Te\(_n\)(SH)\(_m\)H\(_m\) QDs of different sizes and found that the relatively more charge transfer occurred from Cd to Te in the inner region as compared to surface region. We also discussed the electronic structure of CdTe QD-CNT hybrid nanostructures and found that the band gap of the CdTe QD-CNT nanocomposites could be controlled by the CNT [351]. Thus we conclude that the onset of photocurrent generation in these particular nanocomposites occurs at the wavelength corresponding to band gap of the CNT. We observed one interesting feature that the difference between the LUMO of the QD and conduction band maximum of the CNT (the
energy difference between the donor and the acceptor is the driving force) decreases with increasing the size of the QDs and we could expect faster electron transfer rate for smaller CdTe QD as compared to larger QDs when they are coupled with the CNT. Finally we could expect that these hybrid nanomaterials may be suitable candidates for designing the next generation of photovoltaic devices.

In Chapter 5, we have explored the electronic properties of $10\overline{1}0$ faceted CdTe nanowires (NWs) and also the molecular control over the band gap of CdTe NWs. The dependence of the formation energy, electronic band gap, and tendency for surface atoms to reorient are assessed as a function of the cross-sectional topology and diameter for a series of unpassivated, infinitely long, [0001] CdTe nanowires. We have shown that the formation energies of the nanowires decreases with increasing wire diameter, due to the decrease of surface atom ratio. As surface atom ratio increases, the strain in the system increases dramatically and surface restructuring alone is not enough to eliminate the large strain and therefore formation energy increases. So, nanowires of larger diameter are more stable that the smaller one. As the size of the nanowire decreases, $E_g$, the band gap increases, reflecting the impact of the quantum confinement effect. A close inspection of the band structures revealed that for both triangular and hexagonal CdTe nanowires, the conduction band minimum shifted downward as the diameter of the nanowire increases but the valence band top almost remain unshifted. Because of the downward shift of the conduction band minimum, the band gap value decreases as the size of the nanowire increases. We have also discussed about the spatial charge density distributions of unpassivated and H-passivated NWs and shown that although the passivation does not affect the band gap too much but it greatly influences the spatial distribution of charge densities. The knowledge of the spatial distribution of charge densities of the nanowire helps to identify the surface atoms to which the densities of these reactive orbitals are high and accordingly the adsorption of organic molecules will takes place through these atoms. The performance of the semiconductor containing electronic and opto-electronic devices depend very much on the surface properties of the corresponding semiconductor nanostructures.
The modification of the surface structure allows one to tune the properties of the semiconductor devices and enhance their performances. In view of this we performed a study on the adsorption of a series of dicarboxylic acid derivatives on the 10$\bar{1}$0 surface of CdTe nanowires. We have shown that chemisorption of these molecules on the surface of CdTe nanowires can systematically modify the electronic band gap and depending on the nature of the molecule in the NW-Molecule system, electronic structures are quite different [406]. The idea of the position of frontier orbitals of the hybrid systems have great impact on the characteristic properties of the final device such as the polarization offset of photodiodes or the open-circuit voltage in excitonic solar cells. We hope that our theoretical prediction will stimulate experimentalists to design CdTe nanowire based dye sensitized solar cells.

In Chapter 6, we have discussed the structural, energetic and electronic properties of CdTe NTs of various sizes and also the electronic structure of CdTe NT-Fullerene (coupled via thiol group) hybrid system. We have shown that the thin-walled nanotubes have large formation energy due to the high density dangling bonds (three coordinated atoms) and thus they are very difficult to synthesized experimentally. A close inspection of the band structures of these CdTe nanotubes reveals that the conduction band minimum shifted downward and the valence band top shifted upward as the wall thickness of the nanotube increased keeping the inner tube radius fixed, reflecting the impact of the quantum confinement. From our study we found that, one can adjust both the light absorption and the energetics at the interfaces of the nanotubes with the surrounding media by controlling the size and wall-thickness of the nanotubes. We also modified the electronic structures of CdTe NTs by designing the NT-C$_{60}$ hybrid nanostructures. We observed that one could increase the electron transfer rate by increasing the wall-thickness of the CdTe NTs when coupled with electron acceptor C$_{60}$. Furthermore, we could also maximize the light harvesting efficiency of these nanohybrids with increasing the concentration of C$_{60}$-thiol moieties. Finally we have designed the different types of CdTe NT-fullerene hybrid nanostructures using various types of fullerenes e.g. C$_{60}$, C$_{68}$, C$_{70}$, C$_{76}$, C$_{80}$ and C$_{84}$ and have shown that the depending on the nature of the fullerenes
in the hybrid systems, electronic structures are quite different [445] and may utilize in multifarious photovoltaic applications.

Before concluding we venture to add that the investigation reported in the thesis has tried to explore some of the interesting aspects of semiconductor nanoparticles of different size and shape and the study opened up quit a few possibilities for further exploration. These includes the integration of QDs into large nanostructures, exploring the dynamics of electron injection and electron-hole recombination in hybrid systems using time-dependent density-functional theory. It will be the author’s endeavor to pursue these possibilities to their logical conclusions.