## Abstract

The *present Thesis* discusses various Titanium dioxide (TiO2) - Cadmium Sulfide (CdS) assemblies for efficient harvesting of the solar photon. Inorganic semiconductor nanocrystals such as CdS have attracted considerable attention in the realm of solar photon harvesting mainly due to beneficial properties such as easy tunability of their optical, electrical, magnetic properties, functional stability i.e. non-degradability under atmospheric conditions, materials synthesis and device fabrication by benchtop methods. However, a major detrimental issue that prevails in semiconductor nanocrystals is charge recombination. Tailored semiconductor assemblies with favourable energetics can significantly alleviate the effect of charge recombination. Improved charge separation in an optimum semiconductor assembly may aid in decrease in charge recombination and hence, result in enhanced photoelectrochemical function. Owing to the band structure, CdS can harvest solar photon and when attached with wide band gap semiconductor TiO2. The photogenerated electron in the CdS conduction band can be injected at ultrafast timescales to the conduction band of the TiO2. The thesis discusses easy and cost-effective synthesis of various TiO2 and CdS assemblies and explores application of them in photovoltaics, photocatalysis and (photo conducting) image sensor. Various interactions and physical properties are also studied including the ultrafast photoinduced electron dynamics from CdS to TiO2.

Sun is a great source of alternative energy especially, electrical energy. In this context, nanostructured semiconductor assemblies have demonstrated great potential towards efficient harvest of the solar photon. In Chapter 1, general properties and scope of nanostructured assemblies in the context of few applications namely liquid junction semiconductor sensitized solar cell (for solar photon conversion to electricity), visible light photocatalysis (to degrade pollutants using solar photon) and large area image sensor (sensitive to white light) are discussed. The Chapter also discusses the various characterization and quantification methods which not only provide detailed analysis of properties of the novel semiconductor assemblies but also throw light on the prospects for industrial applications.

Chapters 2 to 5 comprises of discussions on the electronic and photovoltaic properties of various shaped semiconductor nanocrystals (average size ⍰ 30 nm). In Chapter 2, cadmium sulfide (CdS) semiconductor nanocrystals of various shapes (tetrapod, tetrahedron, sphere and rod) obtained using an optimized solvothermal process exhibited a mixed cubic (zinc blende) and hexagonal (wurtzite) crystal structure. The various nanocrystal shapes obtained here are a consequence of the simultaneous presence of wurtzite and zinc blende phases in varying amounts. The simultaneous presence of the two crystal phases in varying amounts is observed to play a pivotal role in not only determining the final nanocrystal shape but also both the electronic and photovoltaic properties of the CdS nanocrystals. Light to electrical energy conversion efficiencies measured in two-electrode configuration laboratory solar cells remarkably decreased by one order in magnitude from tetrapod ⍰

tetrahedron □ sphere □ rod. The tetrapod-CdS nanocrystals, which displayed the highest light to electrical energy conversion efficiency, showed a favourable shift in position of the conduction band edge leading to highest rate of electron injection (from CdS to TiO2) and lowest rate of electron-hole recombination (higher free electron lifetimes).

Chapter 2 successfully demonstrated that the photovoltaic (PV) efficiency of a device can be influenced by tuning the shape of the light harvester nanocrystal. While the light to electricity conversion efficiencies varied by one order in magnitude between the various nanocrystal shapes (average size □ 30 nm), the magnitude of the efficiencies was itself not very high. In Chapter 3, the same nanocrystal shapes are used to sensitize multi-layered Titania films and liquid junction solar cells are then fabricated using them. This optimization of the cell configuration showed tremendous enhancement in the light to electricity conversion efficiency by nearly one order in magnitude compared to the ones discussed in Chapter 2. The semiconductor-electrolyte interface is also studied in detail by performing ac-impedance spectroscopy on the full cell to estimate the electron lifetime of the device. The estimated recombination resistance and the electron lifetime are observed to follow the same trend as of the PV-performances of the cells composed of various shaped nanocrystals in the new configuration.

The photoinduced electron transfer processes in a nano-heterostructure semiconductor assembly are complex and depend on various parameters of the constituents of the assembly. Chapter 4 discusses the ultrafast electron transfer characteristics of an assembly comprising of a wide band gap semiconductor, titanium dioxide (TiO2) attached to light harvesting cadmium sulfide (CdS) nanocrystals of varying crystallographic phase content. The nanocrystals employed here are the same as that discussed in Chapters 2 and 3. Quantitative analysis of synchrotron high resolution X-ray diffraction data of CdS nanocrystals precisely reveal the presence of both wurtzite and zinc blende phases in varying amounts. The biphasic nature of CdS influences directly the shape of the nanocrystal at long reaction times (as also highlighted in Chapters 2 and 3) as well as the transfer of the photo-excited electrons from the CdS to TiO2 as obtained from transient absorption spectroscopy. Higher amount of zinc blende phase is observed to be beneficial for fast electron transfer across the CdS-TiO2 interface. The electron transfer rate constant differs by one order in magnitude between the CdS nanocrystals and varies linearly with the fraction of the phases.

Chapters 2-4 show that the electron recombination lifetime in a sensitized semiconductor assembly, which has a major impact on the performance in a solar cell, is greatly influenced by the crystal structure and geometric form of the light harvesting semiconductor nanocrystal. In Chapter 5, the final Thesis Chapter related to semiconductor assemblies for liquid junction based semiconductor sensitized solar cells, deals with the influence of downsizing of light harvester nanocrystals on the electron recombination lifetime and its eventual influence on the light to electricity conversion efficiency of the solar cell. The semiconductor (photoanode)-electrolyte interface in a liquid junction semiconductor sensitized solar cell which has a direct impact on the photovoltaic performance is probed here systematically. The light harvesting cadmium sulfide (CdS) nanocrystals (average size  6-12 nm) of distinctly different and controlled shapes are obtained using a novel and simple liquid-gas phase synthesis method performed at different temperatures involving very short reaction times. High resolution synchrotron X-ray diffraction and spectroscopic studies respectively exhibit different crystallographic phase content and optical properties. When assembled on a mesoscopic TiO2 film by a linker molecule, they exhibit remarkable variation in electron recombination lifetime by one order in magnitude, as determined by ac-impedance spectroscopy. This also drastically affects the photovoltaic efficiency of the differently shaped nanocrystals sensitized solar cells.

In Chapter 6, focus shifts from liquid junction semiconductor sensitized solar cells to visible light photocatalysis. The possibility of harvesting light via a semiconductor assembly of the same chemical compositions (as in Chapters 2-5) however, in a different spatial configuration is again explored. An unprecedented morphology of titanium dioxide (TiO2) and cadmium sulfide (CdS) self-assembly obtained using a 'truly' one-pot and highly cost-effective method with a multi-gram scale yield is discussed here. The TiO2– CdS assembly comprised of TiO2 and CdS nanoparticles residing next to each other homogeneously self-assemble into 'woollen knitting ball' like microspheres. The microspheres exhibited remarkable potential as a visible light photocatalysts with high recyclability.

Finally, in Chapter 7, a semiconductors assembly comprising of titanium dioxide (TiO2) rods sensitized by cadmium sulfide (CdS) nanocrystals for potential applications in large area electronics on three dimensional (3-D) substrates is discussed. Vertically aligned TiO2 rods are grown on a substrate using a 1500C process flow and then sensitized with CdS by SILAR method at room temperature. This structure forms an effective photoconductor as the photo-generated electrons are rapidly removed from the CdS ('carpet') via the TiO2 thereby permitting a hole rich CdS. Current-voltage characteristics are measured, and models illustrate space charge limited photo-current as the mechanism of charge transport at moderate voltage bias. With this stable assembly, high speed can be achieved. The frequency response with a loading of 10 pF and 9 M shows a half power frequency of 100 Hz.