PLASMONIC ENHANCEMENT IN PbS QUANTUM DOT SOLAR CELLS

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ABSTRACT

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Third generation quantum dot solar cells are one of the promising sources of clean energy. However, poor efficiency is a major issue; they are in a positive direction of optimization. To optimize their performance, we should select the materials which can absorb more light radiation in visible and infrared regions. To this regard, the gold plasmonic enhancement shows a promise to improve the efficiency of photovoltaics. Here, we report a solution process of depleted heterojunction PbS solar cells in the presence of gold nanoparticles. In our experiment, the solar cells show a better absorption and efficiency in the presence of the Au nanoparticles. The fabricated solar cell in the addition of Au nanoparticles has the average efficiency of 4.15%, where as the solar cell without plasmons has the average efficiency of 4.00%.
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CHAPTER 1

INTRODUCTION

The current problem of global warming and limited fossil fuels emphasizes the importance of alternative environmentally friendly energy sources. Since solar energy is a natural, clean and renewable energy source, it has become an important issue in the scientific world [14]. In addition, solar radiation is the most abundant form of energy on the Earth. The energy absorbed by the Earth’s atmosphere in one hour is greater than the world’s annual energy consumption [20]. The power of sun radiation striking on the surface of the Earth is 120, 00 TW. If we could make 10.00% efficient solar cells covering 0.16% of the Earth’s land, it could produce 20TW of power, which is double the amount of annual global energy consumption [28]. The development of new technology for converting sunlight into chemical energy has become important, but it is a challenging problem for researchers. Since solar energy is free, clean and abundant in nature, photovoltaic cells have a significant contribution among the other renewable discoveries.

Photovoltaic (PV) is the method of generating electric power by using sunlight. The photovoltaic devices, which convert solar radiation into electricity, are called solar cells. They are specific in their characteristics to convert light into useful energy without any environmental pollution. The photovoltaic technique was discovered in 1950, and its development was so rapid that it contributed significantly to the world’s power production in a short
time. Since 1980, when research in silicon solar cells began, scientists have tried to increase solar efficiencies in many ways. Their efficiency reached 20.00% in 1985, which was a record at that time [3]. In the next ten years, their efficiency increased in a steady manner from 15.00% to 20.00% [8] and became 38.00% in 1997 [5]. The theoretical maximum efficiency seems to be 40.80% as done by Shockley and Queisser in the presence of concentrated artificial sunlight. Then, many solar cell industries were built so that everyone received a chance to utilize its facilities.

Solar cell technology was developed in such a way that three generations of solar cells had already been implemented by the 1950s. The first generation of photovoltaics are made of silicon wafers. They are large in size and are made from a single crystal fabricated at a high temperature. Their manufacturing price is high because of a lot of work needed in the purification of bulk silicon into crystalline form, but they have high efficiency because of homojunction structure with control defects and interface problems. The silicon cells have two layers: one is a positive layer (p-type), which is formed from the doping of trivalent impurity like Boron, and the other is a negative layer (n-type), which is formed from the pentavalent impurity like Phosphorus. The illustration of the general design of the first generation silicon solar cell is shown in fig(1.1). The glass on the top of the cell is used to protect the cell, the anti-reflecting coating is used to maximize the number of incident photons on the cells and metal backing is used to transfer energy. The valance and conduction edges of silicon are not aligned in K-space; therefore, it has an indirect band gap of energy 1.12 eV. Regarding the efficiency, the cost of electricity produced by the first generation solar cells is ten times greater than the electricity generated by fossils fuels [30]. The technology for bulk Si solar cells is so advanced that it is impossible to lower its price. Currently, these heavy Si solar cells cover 86.00% of the current solar cells market production [20,25,27].

Due to the high price of the first generation solar cell, second generation solar cells emerged. The second generation PVs are commonly called thin-film solar cells. They are basically categorized into three types: amorphous silicon, copper indium gallium diselenide
Figure 1.1: First Generation Silicon Solar Cell [23].

(CIGS) and cadmium telluride (CdTe); among them, amorphous silicon is more popular in the market. Although the design of the second generation solar cells is p-n junction, like the first generation, they are notably different from the first generation because of the direct band gap of the material used in this cell. Their manufacturing price is lower than the first generation solar cells, but they have lower efficiencies than the first generation photovoltaics. Now, they have maximum efficiency of 20.00%. The general design of a CdTe thin film solar cell is shown in fig(1.2). The top layer (winder layer) of thin film solar cells is made with a material of a larger band gap, like CdS(2.4eV), to absorb light of higher frequency, and a lower layer (absorber layer) is made with a material of a lower band gap to absorb light of lower frequency. In this structure, CdTe has the band gap of 1.45eV, which is thus considered as an absorber layer. Soda lime coated with indium tin oxide(ITO) helps to increase the conductivity, and metal back contact is used to transfer the energy. Even though the cells are cheaper, they cannot absorb light as much as the first generation and
photodegrade with time. More importantly, most of the materials used are highly toxic and rarely available \cite{20, 27}. These defects in second generation solar cells have inspired scientists to explore a new generation of solar cells.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{second_generation_silicon_solar_cell.png}
\caption{Second Generation Silicon Solar Cell \cite{23}.}
\end{figure}

To overcome the defects of first and second generation of solar cells, a third generation of solar cells came into existence. Most of the third generation solar cells are still being researched, and their designs are completely different than traditional p-n junction. Their popularity is due to the lower manufacturing cost, and they have the potential to break the conversion rate limit of single band gap solar cells. Dye-sensitized solar cells (DSSC), organic solar cells, inorganic solar cells, quantum dot solar cells, tandem cells, intermediate band solar cells, hot-carrier cells, thermophotovoltaic and thermophotonic devices are some popular models in this category. Among them, DSSC was very popular in its early stage. Its highest efficiency is reported as 11.00%. Although these cells are inexpensive, reversible and regenerative, they photodegrade very quickly and have the problem of dye leakage. Because of these drawbacks, scientists discovered a new design of solar cells called organic solar cells.
They are cheap and have the efficiency of about 8.00%, but this efficiency is very low to commercialize. In addition, they are not thermally and chemically stable. In the search for low cost and stable photovoltaics, researchers explored a colloidal quantum dot solar cell based on solution processed semiconductor nanoparticles, which offer to harvest a full spectrum of solar radiation [25]. Because of the fascinating size dependence characteristic of quantum dots, these solar cells are becoming a subject of increasing interest in the scientific world. The quantum dots are "artificial atoms" having the smaller size than exciton Bohr’s radius, and energy carried by electrons inside the quantum dots are similar to the energy of the atom. Therefore, by changing the size of quantum dots, band-gaps can be altered, and hence they can tune in a wide range of the solar spectrum [4]. The distribution of solar radiation is illustrated in fig(1.3).

Several models of colloidal quantum dot solar cells have been developed. Among them, Schottky Solar Cell is the simplest one in which a thin layer of quantum dots is sandwiched between an ITO conducting glass substrate and metal. In addition to the conducting ITO
glass substrate, a layer of a wide band gap titanium dioxide ($\text{TiO}_2$) is deposited on the depleted heterojunction colloidal quantum dot solar cells. Then, the several layers of quantum dots are formed on the glass substrate, and finally a gold contact is made at the top of it for the extraction of the majority charge carriers [32]. The basic structure of the depleted heterojunction quantum dot solar cell is shown in fig(1.4). A high band gap titanium dioxide is used on one part of the glass substrate to produce high photocurrents in inorganic nano-structured solar cells, and charge selective heterojunctions are required on the other part to minimize losses in the photo voltage because of the potential drops and recombination at interfaces. The efficiency of depleted heterojunction colloidal QD photovoltaic cells is controlled by the separation of exciton between the QD layer and the transparent glass substrate in a type-II heterojunction and by exciton diffusion in a QD layer [26].

A method of surface passivation is used to replace high exciton diffusion lengths adding a sufficient number of ligands. Moreover, the average distance between QDs should be small enough to preserve specific electronic states of quantum dots [10]. Even a removal of a small fraction of ligands affects the performance of film significantly due to the formation
of trap states. To enhance the thermal and chemical stability of the film, the quantum dots (PbS) are encapsulated into a matrix of wide band gap semiconductors (CdS) totally in an inorganic medium, which also maintains some degree of quantum confinement of the quantum dots without changing their optoelectronic properties [12]. Although these solar cells are inexpensive and thermally and chemically stable, their characteristics are not ideal. Further modification and optimization of the method could increase the efficiency and make these solar cells commercially attractive.

The power conversion efficiency ($\eta$) for solar cells is given by

$$\eta = \frac{P_{\text{max}}}{P_{\text{in}}} = \frac{V_{oc}J_{sc}FF}{P_{\text{solar}}}$$

Where, $V_{oc}$ = Open-circuit voltage
$J_{sc}$ = Current density
FF = Fill factor
and $P_{\text{solar}}$ = Solar intensity

The above relation shows that when the solar cell absorbs more light, more excitons will be produced; these excitons will cause the higher current, and this higher current will finally give us a better efficiency of the cell. The fill factor and open-circuit voltage depend mostly on the architecture of the cell, quality of the contacts, electrodes, and so on. The J-V characteristic of the cell is illustrated in fig(1.5).

One of the reasons for low efficiency of the colloidal quantum dot solar cell is the incomplete absorption of sunlight. Thus, we need to look for nanoparticles which can assist to absorb more light. Recently, Localized Surface Plasmon Resonance (LSPR) of metallic nanoparticles has been reported as a promising technique for the optimization of photovoltaic performance. It is responsible for an electromagnetic field enhancement in near-field, which increases the photocurrent in the circuit and hence the efficiency of the solar cells [21].

Localized Surface Plasmons (LSPs) are fictitious electron cloud oscillations confined to
Figure 1.5: J-V Characteristics of Solar Cells
the metal nanoparticles, which is shown in fig(1.6). When external field (light) is applied on the surface of metal, the phenomenon of resonance occurs, which results in the enhancement of near field with intense scattering [6]. The frequency and intensity of light absorbed are highly sensitive to the shape, size and nature of surface plasmons, and the surrounding environment. These unique characteristics of plasmons are the fingerprints in detecting and sensing of the materials [9].

![Diagram of metal sphere with electron cloud and electric field](image.png)

**Figure 1.6: Schematics for Plasmons Oscillation**

In this project, we evaluate the plasmonic enhancement of PbS quantum dot solar cells using gold plasmons by measuring the efficiency of solar cells before and after doping gold plasmons on them. We mix PbS/CdS core/shell with Au/Cds plamons in different proportions and deposit them on a TiO$_2$ glass substrate. Here, we use smaller gold nanoparticles than the traditional size used in solar cells where researchers mostly focus on the intense scattering of light. More interestingly in this experiment, we have observed a significant enhancement in the solar cell power efficiency using smaller nanoparticles, which is a very different concept than the scattering. It is a very new concept of energy transfer to the near field instead of charge. Our small gold nanoparticles absorb light in the visible range allowing the energy transfer to the near field while the electrons are dexcited from higher
to lower energy states. This transfer energy to the near fields is responsible for plasmonic enhancement in the solar cells.
CHAPTER 2

EXPERIMENTAL SECTION

2.1 MATERIALS

Lead(II) oxide powder (PbO, 99.999% Aldrich), cadmium oxide (CdO, 99.99%, Aldrich), 1-octadecene (ODE, 90% Aldrich), Oleic acid (OA, 90% Aldrich), bis-(trimethylsilyl) sulfide (TMS2, Aldrich, synthetic grade), acetone (anhydrous Amresco, ACS grade), hexane (anhydrous, 95% Aldrich), ethanol (anhydrous, 95% Aldrich), Sulfur (S, 99.999% Acros), methanol (anhydrous, 99.8% Aldrich), isopropanol (anhydrous, 99.8% Acros), toluene (anhydrous, 99.8% Aldrich), 3-mercaptopropionic acid (3-MPA, 99%, Alfa Aesar), sodium sulfide nonahydrate (Na2S.9H2O, 98% Alfa Aesar), cadmium acetate dihydrate ((CH3COO)2Cd.2H2O, 98%, Acros), Silver nitrate (99%, sigma-Aldrich), titanium chloride (TiCl4, 99.99% Aldrich), gold(III) chloride (99%, Acros Organics), and Cadmium nitrate tetrahydrate (99.999%, Aldrich) were used as received without any further purification. All reactions were performed under Argon environment using the standard Schlenk technique. Fluorine doped tin oxide (FTO) glass substrates were received from Pilkington Glass.
2.2 METHODS

2.2.1 SYNTHESIS OF NANOCRYSTALS.

Synthesis of PbS Nanocrystals.

PbS NCs were synthesized according to the procedure reported by Kinder et al. [12] explained here. A mixture of 0.49g of PbO, 18mL of ODE (1-octadecene) and 1.5mL of OA (oleic acid) were degassed in a 3-neck flask at 120°C for 2 hours. Then, the flask was switched to argon flow and kept at 135°C until injection. At the same time, 10 mL of ODE was degassed at 120°C for 2 hours in 3-neck flask, then switched to argon flow, and kept at room temperature. Later, 0.21mL of TMS$_2$ was added at lab temperature under argon. After that, the mixture of ODE and TMS$_2$ was added to the first flask and cooked for 2 min and cooled down at lab temperature using an ice water bath. The synthesized PbS NCs then were equally divided into four centrifuge tubes and filled with acetone to 15 mL. The solution in the tubes was shaken well and centrifuged. The precipitate obtained in centrifuge was dissolved in hexane and cleaned two or three more times with acetone using the same procedure and NCs were finally re-dispersed into hexane. The prepared NCs had 1S peak at 1020 nm.

OF PbS/CdS CORE/SHELL NCS THROUGH CATION EXCHANGE. The nanocrystals were synthesized using the procedure adapted by Moroz et al. [18] explained here. A mixture of 0.2g of CdO (cadmium oxide), 1.5mL of OA and 6ml of ODE was heated at 235°C under Argon until the solution became clear. Then, it was kept at 55°C under argon before injection. 4-5 mL of PbS NCs were injected to the Cd precursor. After that, the solution was immediately quenched using an ice water bath. The PbS/CdS NCs were then separated from the reaction mixture by centrifuging with ethanol. The precipitate obtained during centrifuge was dissolved in a minimal amount of hexane. The NCs were cleaned two or three times using the same procedure and finally re-dispersed into a minimal amount of hexane. The blue shift was observed in the prepared NCs with the value of $\Delta \lambda = 60 nm$. 
SYNTHESIS OF OLEYLAMINE-CAPPED Au NANOCRYSTALS (NCs).

The NCs were synthesized according to the procedure adopted from Lambright et al. [13] explained here. First, a mixture of 0.011g of AuCl₃ and 3 mL of Oleylamine in 1-neck flask was sonicated for 10-15 min. During sonication, the color of the reaction mixture was turned to the orange, which indicates the manufacture of Au-Oleate complexes. The flask was then placed on a heating mantle and heated for 30 min at 100°C. The reaction mixture was then turned to deep purple from orange. The flask was removed from the mantle to cool down the reaction mixture at lab temperature. The reaction mixture was equally divided into two centrifuge tubes. The nanocrystals from the reaction mixture then were isolated by centrifuging the tubes with an excess of ethanol. The precipitate obtained after centrifuging was dissolved in toluene. These NCs were cleaned two more times using the same procedure and finally re-dispersed into a minimal amount of toluene.

SYNTHESIS OF OLEYLAMINE-CAPPED Au/Ag CORE/SHELL NCs.

The NCs were synthesized using the procedure adopted by Shore et al. [29]. In a typical reaction, a mixture of Au NCs and 5 mL Oleylamine was heated at 120°C while stirring until all the toluene was evaporated. Meanwhile, a solution of 1.05 × 10⁻² M AgNO₃ was prepared in de-ionized water by sonication. A 0.1 mL or 0.2 mL of the AgNO₃ solution was injected very slowly, drop by drop, into Au precursor. After injection, the temperature was dropped by 10-15°C due to the cold water and its evaporation at a high temperature. Again, the temperature was increased to 120°C, and the mixture was cooked for 10 minutes. The concentration of silver ions was carefully watched in order to prevent it from the formation of isolated silver nanoparticles.

The thickness of the Ag shell could be observed by studying the absorption peak of Localised Surface Plasmon Resonance (LSPR). The blue shift of 15-20 nm was observed in addition of 0.5 mL of AgNO₃ solution. A 40 nm blue shift was observed with the injection
of 0.9 mL of AgNO₃ solution.

After observing the desired LSPR peak, the mixture was cooled down at atmospheric temperature with the help of a cold water bath. The mixture was equally divided into two centrifuge tubes. The NCs then were isolated by centrifuging the reaction mixture with an excess of ethanol. The precipitate obtained in the process of centrifuge was then dissolved into toluene. The Au NCs were cleaned two more times using the same procedure with ethanol and finally re-dispersed into a minimal amount of toluene.

**SYNTHESIS OF Au/Ag₂S NCs FROM Au/Ag.**

The Au/Ag₂S NCs were synthesized using the procedure adapted by Zhang et al. [33] explained here. First, a sulfur solution was prepared by sonicking a mixture of 1.22 × 10⁻⁶ M sulfur and Oleyamine under argon. The Au/Ag core/shell prepared in previous step was transferred to the flask under argon. The sulfur solution was injected slowly, drop by drop, (maximum 0.2mL) into the vigorously stirring Au/Ag core/shell, and the mixture was left for 10 minutes for the proper reaction. Injection of sulfur was stopped when LSPR absorption peak observed to be shifted to 630 nm. To isolate the NCs from the reaction mixture, the reaction mixture was centrifuged, precipitated and re-dispersed into the minimal amount of toluene.

**SYNTHESIS OF Au/CdS NCS FROM Au/Ag₂S.**

This procedure was adapted from Zhang et al. [33]. A mixture of 3.8 mL Au/Ag₂S (95units) and 1 mL of oleylamine was heated up to 50°C in 25 mL flask. Then, 0.12 g of CdNO₃.4H₂O in 1 ml of MeOH was added. After 10 minutes, 0.3 mL of TBP was injected to the mixture, and the reaction mixture was heated at 50°C for 120 minutes. After that, the reaction mixture was cooled down to a lab temperature. The NCs were isolated from the reaction mixture by centrifuging with an excess of methanol, precipitating, and re-dispersing in the minimal toluene. A few drops of Oleylamine were added for stability.
2.2.2 DEPOSITION OF TiO$_2$ on FTO GLASS SUBSTRATES.

The glass plates were cut into the size of 2.5 cm × 2.5 cm and washed with the detergent and clean water. Then, these FTO glass substrates were cleaned one more time with de-ionized water. These substrates were dried for a few minutes. Next, they were sonicated for 5 minutes in methanol, then in acetone and 2-propanol respectively. These cleaned glass plates were placed into the solution of 75 mM TiCl$_4$ in the de-ionized water and heated at 70°C for 30 minutes. After that, the glass substrates were washed with the de-ionized water. They were then dried under argon, heated at 400°C for one hour, and cooled down to lab temperature.

A solution was prepared by dissolving Dye Sol paste into terpinol in a ratio of 1:3 by weight. The 3-4 drops of the Dye Sol solution were put on each TiO$_2$ treated glass substrate and spun at 700 RPM for 30 seconds. Then, it was spun at 2000 RPM for 1 minute inside the glove box. Finally, the glass substrates were heated outside the glove box to anneal all the organic materials.

2.2.3 FABRICATION OF THE MISTURE OF PbS/CdS AND Au/CdS FROM THE SOLUTION.

The fabrication of NCs was done totally in an inorganic medium according to the procedure of layer by layer deposition adapted by Kinder et al. [12]. First, the colloidal solution of PbS/CdS and Au/CdS was made mixing in the ratio of 2:1 (by units). 3-5 drops of NCs were put on the glass substrate spinning in the speed of 3000 RPM until the substrate was fully covered with the NCs. Then, 5-10 drops of MPA solution (i.e. MPA:Methanol = 3:1) were put on the surface of the substrates for a couple of seconds so that the film soaked the solution well, and spun for 10 seconds at the speed of 3000 RPM. This was done to replace the organic OA ligands by thermally-degradable MPA ligands. These MPA ligands were washed away by adding 8-10 drops of Methanol followed by 8-10 drops of octane, and
spinning at 3000 RPM for 30 seconds respectively. After each three layers of NCs deposition, the films were heated at 150°C for 15 minutes to anneal all organic materials. The 9 layers of NCs were deposited in total.

### 2.2.4 PORE FILLING WITH CdS.

The successive ionic layer absorption and reaction (SILAR) technique was used for the pore filling, reported by Sankapal et al. [24]. In this technique, the cadmium and sulfur precursors were prepared by sonicating 0.113 g of Cadmium acetate in 20 mL of methanol, and 0.096 g of Na₂S·9H₂O in 20 mL of methanol respectively. First, the inorganic NC film was immersed in cadmium precursor for 1 minute, then it was rinsed with methanol; immersed into the sulfur precursor for 1 minute and finally washed with methanol again. This cycle was repeated for 2-10 times, and the films were heated to anneal the organic materials at 150°C for 15 minutes.

### 2.2.5 DEPOSITION OF Au/Pd COUNTER ELECTRODES ON THE FILMS.

The counter electrodes of 60-90 nm of Au/Pd (Au-Pu, 60/100) were deposited on the films by using the Polaron E500 sputter. The equipment had the shadow mask with a diameter of about 2mm, which had sixteen pixels in each film. The calculated area of one pixel was 0.03 cm².

### 2.3 CHARACTERIZATION.

The absorption spectra were measured using CARY 50 scan and simadzu UV-vis-NIR spectrometers. High-resolution transmission electron microscopy (HR-TEM) images were taken using JEOL 3011UHR and 2010 transmission electron microscopes, set at 300 and 200 KV.
respectively. A small fragment of NCs from FTO glass substrate were scratched out and dissolved in hexane or toluene. The prepared sample of NCs were put into a carbon coated copper grid, which were then dried. The currents and voltages were measured by using the 2400 SourceMeter KEITHLEY under AM 1.5 G (100 mW/cm²) solar simulator, which had IV data acquisition system from PV measurement, Inc.
CHAPTER 3

RESULTS AND DISCUSSION

The procedure of the synthesis of PbS/CdS NCs was explained in detail in Chapter 2. The NCs were synthesized using a method of hot injection reported by Kinder et al. [12]. The shells on the PbS NCs were grown by the method of cations exchange through the reaction Pb$^{2+}$ $\rightarrow$ Cd$^{2+}$ [19][22]. In this method, the shells of CdS were grown on the surface of PbS NCs by displacing the Pb ions on the surface without affecting the size of NCs during the ions exchange. During the growth of monolayers of CdS shell on the NCs, the dispersion in the diameters of PbS NCs was found to be very small (i.e. s.d. = 6% to 7%) [12]. The thickness of CdS shells grown on the PbS NCs was controlled by changing the reaction temperature of the solution and time during the cations exchange. The observation of HR-TEM images revealed that the shell of CdS was grown uniformly on the surface of the core of PbS NCs. The lattice mismatch observed in the interface of PbS/CdS was negligible (i.e. strain 1.7%). The 14-16 monolayers of CdS were grown around the PbS NCs without any noticeable lattice defects; this is strong evidence of the lattice matching of PbS between CdS with low strain [12].

The concept of charge confinement in the NCs was explained on the basis of absorption and emission spectra. The absorption spectra are illustrated in fig(3.1). From the observation of these spectras, we noticed the clear blue shift, which indicates the decrease in the
length of carrier confinement during the growth of a shell by cations exchange. The value of blue shifts in the spectra is directly proportional to the decrease in the diameter of PbS NCs; this was used to determine the thickness of CdS shell around the PbS NCs. Moreover, the intensity of emission spectra was increased by five times its original value, which clearly indicates the significant decrease in the possibility of the localized surface charge trapping \[12\]. This phenomenon is very important to develop SMENA solids, it maintains the quantum confinement of the charges to some extent inside the matrix encapsulated NCs, and allows the localized charge to flow through nearby dot-to-dot during the excitation.

Figure 3.1: Absorption Spectra of PbS and PbS/CdS NCs

The detailed explanation of the preparation Au/CdS core/shell was described in the experimental section of Chapter 2, according to the procedure reported by Lambright et al. \[13\]. This method basically involved four different steps: (a) preparation of 6-16 nm of Au NCs, (b) growth of Ag shell on the surface of Au, (c) conversion of Au/Ag into Au/Ag\(_2\)S, and (d) conversion of Au/Ag\(_2\)S into Au/CdS. The schematic representation of steps involved
in the synthesis of Au/CdS is shown in fig(3.2).

![Diagram of synthesis process](image)

Figure 3.2: (a) Schematic Representation of the Synthesis of Au/CdS NCs [13], and (b) HR-TEM Images of Au/CdS SMENA.

First, Au NCs were prepared by the thermal reduction of Au salt in oleylamine. The plasmon resonance of Au NCs was about at 525 nm. The uniform shell of Ag was grown on the surface of Au NCs by adding Ag precursor drop by drop, which also helped to prevent the formation of an isolated silver. The growth of Ag shell was confirmed by the gradual shift of absorption peak from 525 nm to the plasmon resonance wavelength of Ag (i.e. 415 nm). The presence of some isolated silver NCs were discarded by size-selective precipitation. Further, the conversion of Au/Ag into Au/Ag$_2$S was completed at the room temperature by allowing Au/Ag in oleylamine to react with sulfur. This transformation of NCs were confirmed by the
gradual red shift as explained by Mie theory \[17\]. Finally, the conversion of Au/Ag\(_2\)S into Au/CdS was carried out by the method of cations exchange i.e. \(2\text{Ag}^+ \rightarrow \text{Cd}^{2+}\), which was accompanied by the blue shift from 630 nm to 590 nm.

The colloidal NCs were fabricated from the solution on a conducting FTO glass substrate into an all-inorganic medium using the layer by layer method \[16\]. The colloidal NCs of PbS/CdS and Au/CdS were mixed in the ratio of 2:1 by units. The five drops of colloidal NCs with OA ligands were put on the substrate and spun at 2500 RPM. Then, OA ligands were replaced by the thermally-degradable molecules, like MPA (\(T=111^\circ\text{C}\)) during the layer by layer deposition of nanocrystals. After each three layers of NCs deposition, the films were heated at 150\(^\circ\text{C}\) for 15 minutes. The general strategy of NCs fabrication is shown in fig(3.3).

Construction of solar cell (=4.15%): First, the FTO conducting glass substrates were cleaned, which was described above. On the conducting FTO substrate, the two layers of TiO\(_2\) were deposited by TiCl\(_4\) treatment. For the first layer of TiO\(_2\), the solution of TiCl\(_4\) was put on the FTO glass substrate and heated on air at 70\(^\circ\text{C}\) to oxidize. Then, the paste of TiO\(_2\) DyeSol was deposited by spin coating methods and finally heated at 450\(^\circ\text{C}\) to remove all organic materials. The core/shell of PbS/CdS nanocrystals (i.e. diameter of PbS = 5 nm, 1S absorption peak of PbS = 1020, thickness of CdS shell = 0.12 nm, 1S absorption peak of PbS/CdS = 960 nm) were synthesized. On the other hand, Au/CdS NCs (i.e. diameter of Au = 10 nm, 1S absorption peak of Au = 525 nm, thickness of CdS = 5nm and 1S peak absorption of Au/CdS = 590 nm) were also synthesized. Then, these two nanocrystals were mixed in the proportion of 2:1. To deposit the NCs on the substrate, the layer by layer method was used. In this method, 4-5 drops of NCs were placed on the substrate during spinning at 2000-3000 RPM. Then, the whole film was covered by adding 8-10 drops of MPA solution (i.e. MPA : methanol = 3:1), and the substrate was spun at the speed of 2500 RPM for 15 seconds. Next, the substrate was rinsed with 8-10 drops of methanol, and spun at 2500 RPM for 15 seconds. Finally, the film was washed with 8-10 drops of octane spinning at 2500 RPM for 15 seconds. The three layers of NCs were made. After each three layers
Figure 3.3: General Strategy of NCs Fabrication to develop the Semiconductor Matrix-Encapsulated Nanocrystal Arrays (SMENA). Steps involved: Step-1: Collodidal synthesis of PbS and Au Nanocrystals; Step-2: The shells of CdS were grown around each of these NCs, Step-3: Mixing and spin-coating of colloidal NCs into films using layer by layer method; and Step-4: Pores of NCs solids were filled with an additional CdS using SILAR technique.
of NCs, the film was heated at 150°C for 15 minutes for the crystallographic fusion. When repeating the same procedure 2 more times, nine layers of NCs were made. The pores on the film were filled by the SILAR technique. The 60-90 nm of Au-Pd sputters were deposited as the electrodes at the backside of the glass substrate. For J-V characteristics measurement, a corner of film was scraped with wetted acetone cotton to make good contact with the FTO conducting surface.

The morphology of ligands desorption into a film was examined by using TEM images. To make a sample for TEM images, a small amount of SMENA films was scraped out and dissolved in toluene by sonicating, then it was put on a carbon grid. On the TEM images shown in fig(3.4(a)), the matrix encapsulation of PbS NCs is seen due to the crystallographic fusion of CdS shells heating at 150°C for 15 minutes. The figure(3.4(b)), which has darker continuous fringes than the first TEM image, is the TEM image of Au NCs. The TEM images of SMENA films of PbS/CdS solar cells after adding a small amount of Au nanoparticles, are shown in fig(3.4(c) and (d)). These images show the continuous fringes pattern of PbS NCS in the presence of some Au NCs matrix encapsulated with the crystallographic fusion of CdS. These TEM images also reveal that the PbS/CdS and Au/CdS NCs were uniformly mixed in a colloidal solution during the fabrication of NCs in the glass substrates.

The conductance of the film can be improved by decreasing the scattering and trapping of electronic charges. This structure of NCs is achieved when there are smooth interfaces at PbS-CdS [22], CdS-CdS [15] and Au-CdS, during the crystallographic fusion of the NCs core/shells. However, eventhough the surfaces of different NCs are interfused, there might be some surfaces unpassivated, which causes surface trapping of charges. The exposed unpassivated surfaces are because of less order in the packing of round NCs. These unpassivated surfaces were filled by the method of SILAR technique. In this technique, the cadmium and sulfur ions go inside the nanoparticles films and passivated the trapping states. This pore filling technique does not affect the inter-NC distance and the electrical coupling of quantum dots, but it decreases the trapping of charges [1].
Figure 3.4: (a) TEM Images of PbS/CdS SMENA, (b) TEM Images of AuCdS (c) and (d) TEM Images of Au/CdS SMENA.
One of the most important factors to be improved for the applications of light emitting and photovoltaic devices, is the thermal stability of the materials at high temperature. If the NCs are organically interlinked in the arrays, the temperature of degradation is reported about $150^\circ C - 170^\circ C$ [7]. For the SMENA films, the thermal degradation of the film occurs at a higher temperature than the organically inter-linked NCs films due to the state conversion of the lattice. The stability of the films against temperature was tested by comparing the thermal stability of PbS NCs interlinked with MPA ligands film with that of PbS NCs films matrix encapsulated with high band gap materials CdS. The difference in temperature $T_c(\text{PbS/CdS}) - T_c(\text{PbS/MPA})$ was found to be $80^\circ C$. In addition, the thermal degradation temperature was increased by $18^\circ C$ after filling SMENA pores with CdS by SILAR technique [7].

The photovoltaic characteristics of the NCs films were studied using a depleted heterojunction structure illustrated in fig(3.5). This structure of solar cells provides high open circuit voltage ($V_{oc}$) because the semiconductor-metal interface does not affect the fermi level of the metal electrode [31]. In this design, the deposited TiO$_2$ layer increases the fill factor (FF) of the device by obstructing induced holes from recombination. The layer of TiO$_2$, which was 60 to 180 nm thick, was measured by SEM. The SEM images of the PbS/CdS film, and PbS/CdS film after adding the Au plasmons, are shown in fig(3.6(a) and (b)) respectively. To absorb light radiations, 8-10 layers of a mixture of PbS and Au NCs were deposited by the method of spin coating. After each three layers, the films were heated at $150^\circ C$ for 15 minutes for crystallographic fusion. Next, the pores of the films were filled by CdS using SILAR techniques. Finally, a shadow mask was used to deposit Au/Pd electrodes on the top of the film.

In order to study the effects of Au plasmons on the absorption of solar cells of PbS/CdS, the solar cells of PbS/CdS were fabricated mixing with the Au nanoparticles in the different proportions. These fabricated solar cells were then put on the absorption machine to observe
Figure 3.5: Illustration of a Depleted Heterojunction Solar Cell consisting of a FTO/glass Electrode, a layer of TiO$_2$(60-180nm), PbS/CdS and Au/CdS SMENA and Au/Pd Counter Electrodes.
the absorption spectra. The intensity of the absorption spectra was gradually increased with the gradual increase in the proportion of Au nanoparticles in the solar cells, which is shown in fig(3.7). This is the evidence with which we could say the plasmons are one of the promising materials which assist to absorb more light in the enhancement of the efficiency of solar cells. The experiment was started with the addition of a very small amount of Au nanoparticles on the PbS/CdS solar cells. The experiment was continued with the addition of more and more Au nanoparticles. We could not add a lot of Au nanoparticles for the enhancement purpose because there is a limit so that the added Au nanoparticles could not obstruct the hopping of electrons from dot to dot. The optimization of the efficiency of solar cells was becoming the maximum when the ratio of PbS/CdS and Au/CdS reached 2:1 by units.

The J-V characteristics of two different models of solar cells is shown in fig(3.8). The red curve is a J-V characteristic of a pure PbS/CdS solar cell and the blue curve for the PbS/CdS with doping of Au nanoparticles. The study of J-V characteristics clearly showed that there is a significant contribution of plasmons doping in the enhancement of solar cells efficiency.
Figure 3.7: Illustration of Intensity Variation of Absorption Spectra of PbS/CdS Solar Cells with the Gradual Increase in Plasmons Proportion during the Fabrication of Solar Cells.
This enhancement in the solar cell’s efficiency agrees with our initial hypothesis. It was assumed that when the solar cells are shone by the light, the PbS nanoparticles absorb light in a infrared region, and Au nanoparticles absorb light radiations in a visible region. The Au nanoparticles are excited in the presence of an external field, like light; then the Localized Surface Plasmons Resonance (LSPR) occurs. In LSPR, the plasmons transfer energy to the near field which helps to enhance the nearby electromagnetic field, and it generates more excitons. This results in the enhancement of the efficiency of the solar cells.

To test the hypothesis of plasmons enhancement of the solar cells, two thin films of solar cells were fabricated from the same core/shell of PbS/CdS using the same procedure we explained in the experimental section of Chapter 2. The first solar cell was fabricated with a pure PbS/CdS core/shell (i.e. diameter of PbS = 5 nm), whereas the other one was fabricated from the mixture of same PbS/CdS and Au nanoparticles in the ratio of 2:1. After depositing NCs, the pores were filled by the SILAR technique, and finally Au electrodes (Au-Pd, 60/100) were deposited to observe J-V characteristics of the films. The J-V characteristics of these films were performed by using a 2400 SourceMeter, KEITHLEY. From the J-V characteristics measurement, the average efficiency of a pure PbS/CdS was found to be 4.00%, whereas the efficiency of Au nanoparticles dopped PbS/CdS solar cell was found to be 4.15%.
Figure 3.8: J-V Characteristics of a Pure PbS/CdS Solar Cell and Plasmons Doped PbS/CdS Solar Cell.
CHAPTER 4

CONCLUSION

To sum up, the plasmons showed the promise to enhance the efficiency of solar cells. The solar cells are considered to be better solar cells only when they have a good combination of lower price and higher efficiency than the solar cells of the same classes. Here, the Au nanoparticles were reported as a promising candidate to meet these criteria to some extent. On the addition of more and more Au nanoparticles on the PbS/CdS a matrix encapsulated solar cells, the intensity of absorption of solar cells was increased gradually. Regarding the efficiency of the solar cells, the plasmons were significantly contributed. The average efficiency of the PbS/CdS solar cell was increased by 0.15% with the addition of Au nanoparticles.
BIBLIOGRAPHY


