CHAPTER 8

Optical Properties of Semiconductor Coated Au Nanoshells

8.1 Introduction

The optical properties of individual noble metal and semiconductor nanostructures have been studied extensively in the literature, (Kelly et al., 2003; Sosa et al., 2003; Baskoutas & Terzis, 2006; Ferreira et al., 2010) but their combined effect about optical properties has not been much explored. The present experimental expertise in the combined synthesis of metal-semiconductor nanohybrids (Pradhan et al., 2008; Li et al., 2011) has contributed to new optical properties which are different from individual materials. These new optical properties include the enhancement of the photocatalytic activities, optical absorption, photoluminescence, and nonlinear optical response of a given semiconductor material. The excitation of surface plasmons in noble metal enhances the local EF near the surface of the nanoparticle and when it is placed onto a semiconductor nanostructure, this leads to the enhancement in optical absorption and photoluminescence of the semiconductor nanoparticle (Pradhan et al., 2008). Many reports have proposed for increasing the optical properties of semiconductors due to this phenomenon. Schaadt et al. (2005) have reported the enhancement in optical absorption of Si photodiodes across the large spectral region by depositing Au NPs on its surface. Pradhan et al. (2008) prepared the CdSe semiconductor film with gold-coated nanoparticle surface of different sizes and showed an enhancement in Raman intensity and photoluminescence of CdSe film. In addition, Au nanoshells in the NIR region have been used for biological applications like drug delivery, optical imaging, photo-thermal therapy, etc. (Kalele et al., 2006; Huang et al., 2007; Jain et al., 2008). The Au shell
thickness can be controlled through the amount of gold deposited on the surface of the core. Many reports are available on optical properties of gold nanoshells in the NIR regime, for instance, Caruso et al. (2001) prepared the gold-coated silica nanoparticles with LSPR peaks in the NIR region of the EM spectrum. Hu et al. (2008) and Wu et al. (2008) studied the optical properties of gold-silica-gold and silica-gold(silver)-silver (gold) multilayer nanoshells for biomedical applications. Simultaneously from the available II-VI direct bandgap semiconductor materials, CdTe is considered to be the most widely used material for solar cell applications because its bandgap nearly matches to the solar spectrum. Moreover, CdTe is taken as the second most used material in solar cells after silicon (Afzaal & O’Brien, 2006), and also the nanocrystals of CdTe and CdSe have been successfully employed in applications like biosensing and bioimaging (Wang, 2008). Although, the cadmium materials have good utility but their toxic nature limits their practical usefulness. Therefore, to increase their potential and biocompatibility, these semiconductors are considered to be coated with Au so that their toxicity can be reduced because of the better biocompatibility of Au. Further, their efficiency can also be increased in the NIR region for better biomedical applications. Thus, there is a large tunability in optical properties from the visible to the infrared region as compared to CdTe/CdSe and almost in the same region as for Au nanorods (Ni et al., 2008) and nanoshells (Oldenburg et al., 1999). Therefore, the optical properties of semiconductor nanostructures can be enhanced by coated Au layer, and simultaneously, the plasmon resonance associated with Au nanoshells can be varied from the visible to the NIR regime which makes them potential materials for solar cells, optical imaging, photo-thermal, sensing, and biomedical applications. Hence, the aim of the present chapter is to tailor the LSPR-based optical properties of underlying semiconductor material by associating Au with it as nanoshells.
The most widely used materials are direct bandgap semiconductor materials because of relatively less loss of absorbed light from them. Further, as light is incident on the CdTe- and CdSe-coated Au nanoshells, the incoming photons interact with the conduction electrons of Au, which leads to the excitation of surface plasmons on the surface of coated nanoparticle. The energy associated with these surface plasmons can be efficiently collected by the Au nanoparticles due to strong EF enhancement in the vicinity of Au NPs and transferred to the underlying semiconductor nanoparticle, hence, enhances the optical properties of semiconductor nanoparticles (Pradhan et al., 2008). Therefore, it is possible to design semiconductor-Au nanoshells for solar cells, optical imaging, and photo-thermal applications, where high scattering efficiencies are suitable for optical imaging applications and high absorption efficiencies for photo-thermal applications in the NIR region and for solar cell applications in the visible region. By choosing the appropriate dimensions of the core and shell, the position of the absorption and scattering peak can be controlled across a wide range of wavelengths from the visible to the NIR region of the EM spectrum. In the present chapter, the optical properties of bare semiconductor spherical NPs are calculated by “MiePlot4.3” based on Mie theory and optical properties of semiconductor-metal core-shell nanoparticles are calculated using BHMIE code based on extended Mie theory as discussed in Chapter 3 to analyze the effects of dimensions and surrounding medium on the absorption and scattering efficiencies of the hybrid nanosphere.

8.2 Results and discussion

The absorption spectrum of semiconductor nanoparticles is greatly affected by the size of NPs as shown in Figure 8.1. Here, the investigation has been taken for NPs with the radius below 100 nm and found a slight increase in the absorption efficiency of each
cadmium nanoparticle along with redshift in the peak position as the size of the nanoparticle increases, a similar trend as reported by Duan & Xuan (2011).

Figure 8.1: Simulated absorption spectra of different radii nanoparticles of a) CdSe, b) CdS, and c) CdTe, respectively.

It can be seen that the absorption efficiency for each cadmium semiconductor NPs such as CdSe, CdS, and CdTe drops suddenly at wavelengths (energies) around 712 nm (1.74 eV), 512 nm (2.42 eV), and 861 nm (1.44 eV), respectively, which is associated with the band gap of the respective semiconductor material. As light at wavelengths below the band gap is incident on the semiconductor material, the electrons in the valence band absorb energy from the light and make transitions to the conduction band.
by leaving holes in the valence band. These electrons in the conduction band and holes in the valence band result in induction of current in the semiconductor material that can be used for various applications. The number of electron-hole pairs increases if absorption of light at wavelengths below the band gap is enhanced and hence, increases current in the material. Therefore, the higher the absorption of light below the band gap, the larger is the current induced in the semiconductor material and hence, enhances optical properties. Further, a much broadened spectra has been observed at large particle sizes because at such sizes, the radiation damping retardation effect originates which leads to dampen the spectra and hence, to broaden it. It may be noted that due to this broadening of spectra, the absorption of light enhances below the band gap edge wavelength for each semiconductor, and can be tuned over the visible region of the spectrum with change in size of the nanoparticle. Among all, CdTe shows better absorption efficiency and has low cost in comparison to the present silicon based solar cells which could be preferred as an ideal absorbing material for cadmium based solar cell applications.

In order to enhance the absorption and scattering efficiencies of these semiconductor materials in the visible to infrared region of the spectrum, Au may be considered as a shell over the semiconductor core in further studies. Therefore, in the next part of the study, shell layer thickness and core size have been optimized to achieve high absorption and scattering efficiencies. The core-shell nanoparticle consists of a spherical homogeneous core of CdTe or CdSe semiconductor nanoparticle having radius $r_1$ enveloped by a spherically symmetric homogeneous shell of the Au metal nanoparticle having radius $r_2$. This coated nanoparticle is supposed to be located in surrounding media of air or glass having refractive index 1.0 or 1.5, respectively. The input parameters for the extended Mie theory were the values of the core and shell radii, $r_1$
and \( r_2 \); their experimentally determined complex dielectric functions taken from Palik (1991); and the surrounding medium refractive index.

The calculations on the optical efficiencies of CdTe- and CdSe-coated Au nanoshells were studied at a fixed core radius of 20 nm with varying Au shell thicknesses i.e., \( t = r_2 - r_1 \) from 2 nm to 10 nm and further, at a fixed shell thickness, where the absorption and scattering are maximum with varying core radii i.e. \( r_1 \) from 20 nm to 40 nm in the surrounding refractive indices of 1.0 or 1.5.

The effect of Au shell thickness on the absorption efficiency of CdTe-coated Au nanoparticles has been examined in surrounding media having refractive indices of 1.0 or 1.5 as shown in Figure 8.2.

![Figure 8.2: Simulated absorption spectra of CdTe-coated Au NPs having a core radius of 20 nm with varying shell thickness for a) \( n = 1.0 \) and b) \( n = 1.5 \).](image)

It has been found that the absorption efficiency improves along with the shifting of peak position towards smaller region of the wavelength as the Au shell thickness increases from 2 nm to 10 nm on the CdTe core of fixed radius 20 nm. This improvement in absorption efficiency is due to the large EF enhancement near the
surface of Au metal nanoparticle (Maier, 2007). The absorption efficiency is found to be maximized for the higher Au shell thickness of 10 nm in both the surrounding media and also maximizes in the surrounding medium having a higher refractive index. The greater the Au shell thickness (10 nm) over the fixed core radius, larger is the absorption efficiency. This is because of increased density of free electrons as the size of Au nanoparticle increases. This increased density of free electrons influences the surface plasmon absorption of Au nanoparticle that provides the enhancement of the absorption process to the semiconductor core NPs (Pradhan et al., 2008). The absorption spectra in the air as embedding medium (Figure 8.2a) is quite different from that of higher refractive index medium (Figure 8.2b). It can be clearly seen that as the surrounding medium refractive index increases, the corresponding absorption spectra are red-shifted with a significant enhancement in absorption efficiency (i.e., almost three times) as compared to air medium. This behavior can be explained because of the resonance condition $\varepsilon_i = -2\varepsilon_s$, where $\varepsilon_i$ and $\varepsilon_s$ represents the real part of the metal and surrounding medium dielectric function, respectively.

Figure 8.3 represents the absorption spectra by changing the core material to CdSe having the same dimensions and in the same surrounding media. It has been found that the absorption efficiency is maximized with the Au shell thickness of 4 nm and 6 nm in the surrounding medium refractive index of 1.0 or 1.5, respectively. However, the efficiency is larger in the embedding medium having a larger value of refractive index for all Au shell thicknesses. Much enhancement in absorption efficiency has been found with the Au shell thickness of 8 nm as the surrounding medium refractive index increases from 1.0 to 1.5.
Therefore, the absorption efficiency of CdTe (Figure 8.2) and CdSe (Figure 8.3) can be enhanced in near the visible region of the spectrum by varying Au shell thickness from 6 nm to 10 nm and improved further by controlling the surrounding medium refractive index. The optimized Au shell thickness, where the absorption efficiency is found to be maximized in air as surrounding medium is 10 nm and 4 nm over the CdTe and CdSe core radius of 20 nm, respectively.

Further, the absorption properties have been elaborated by varying the CdTe and CdSe core radius \( r_1 \) from 20 nm to 40 nm while keeping fixed Au shell thickness of 10 nm in the case of CdTe (Figure 8.4) and 4 nm in the case of CdSe (Figure 8.5). It has been found that the absorption efficiency is improved in near infrared (NIR) region of the spectrum along with red shift of the peak position as core radius varies from 20 nm to 40 nm.
**Figure 8.4:** Simulated absorption spectra of CdTe-coated Au NPs having a shell thickness of 10 nm with varying core radius for n = 1.0.

**Figure 8.5:** Simulated absorption spectra of CdSe-coated Au NPs having a shell thickness of 4 nm with varying core radius for n = 1.0.

Hence, the absorption efficiencies associated with the CdTe- and CdSe-coated Au nanoparticles can be tuned from the visible to the infrared region of the electromagnetic spectrum. In the visible region, these nanoshells can be useful for the solar cell technology because in this region, the solar spectrum is highly intense, ([http://upload.wikimedia.org/wikipedia/commons/4/4c/Solar_Spectrum.png](http://upload.wikimedia.org/wikipedia/commons/4/4c/Solar_Spectrum.png)) and in the
NIR region, these nanoshells could be used for photo-thermal applications. Moreover, from Figures 8.2 to 8.5, it is clear that the Au coating on the surface of CdTe and CdSe NPs leads to the increase in the optical absorption in both the cases but larger enhancement has been seen in the case of CdSe nanoparticles of the same dimensions in the same surrounding environment. Therefore, for solar cell applications, the CdSe-based Au nanoshells can be used with larger absorption efficiency as compared to the CdTe-based Au nanoshells.

The scattering efficiency for both semiconductor coated Au nanoshells has also been calculated because of their intense use in optical imaging applications in the NIR region. In this regime, the absorption of all the biomolecules is minimum that gives relatively a clear window for optical imaging (Frangioni, 2003). The scattering efficiency spectrum of CdTe-coated Au NPs as a function of Au shell thickness from 1 nm to 10 nm in the surrounding medium of refractive index 1.0 or 1.5 is shown in Figure 8.6.

![Simulated scattering spectra of CdTe-coated Au NPs](image)

**Figure 8.6**: Simulated scattering spectra of CdTe-coated Au NPs having a core radius of 20 nm with varying shell thickness for **a)** $n = 1.0$ and **b)** $n = 1.5$.

The similar behavior as that of absorption efficiency (Figure 8.2) has been observed as the Au shell thickness varies from 1 nm to 10 nm on CdTe core nanoparticle of fixed
radius 20 nm. The maximum scattering efficiency has been found for the higher Au shell thickness of 10 nm in both the surrounding media and also maximizes with higher surrounding medium refractive index. Moreover, with increasing surrounding medium refractive index from 1.0 to 1.5, the corresponding scattering peaks are red-shifted with significant enhancement in the scattering efficiency.

Figure 8.7 shows the scattering spectrum of CdSe-coated Au NPs having same dimensions in the same surrounding environment. The scattering efficiency is found to be maximum with Au shell thickness of 6 nm and 8 nm on CdSe core nanoparticle having a radius of 20 nm in the surrounding medium refractive index of 1.0 or 1.5, respectively. Moreover, the scattering efficiency is significantly enhanced and corresponding scattering peaks are red-shifted with an increase in the surrounding refractive index from 1.0 to 1.5.

![Simulated scattering spectra of CdSe-coated Au NPs having a core radius of 20 nm with varying shell thicknesses for a) n = 1.0 and b) n = 1.5.](image)

**Figure 8.7**: Simulated scattering spectra of CdSe-coated Au NPs having a core radius of 20 nm with varying shell thicknesses for a) n = 1.0 and b) n = 1.5.

Therefore, the scattering efficiency of semiconductor-based Au nanoshells can be enhanced in the NIR region by varying Au shell thickness from 4 nm to 8 nm and can
be effectively enhanced further by changing surrounding medium. The Au shell thickness of 10 nm and 6 nm over the CdTe and CdSe core has been optimized, respectively, where, the scattering efficiency is found to be maximum in air as surrounding medium. From Figures 8.2, 8.3, 8.6, and 8.7, it is observed that the scattering enhancement is very small as compared to the absorption enhancement with an increase in Au shell thickness in both the semiconductor nanoparticles.

Further, the scattering properties have also been elaborated by varying the CdTe and CdSe core radius \( (r_{c}) \) from 20 nm to 40 nm while keeping fixed Au shell thickness of 10 nm in the case of CdTe (Figure 8.8) and 6 nm in case of CdSe (Figure 8.9). As the core radius varies from 20 nm to 40 nm, the scattering efficiency is improved in the NIR region of the spectrum and also shows the red-shift in the peak position for both the cases.

![Simulated scattering spectra of CdTe-coated Au NPs having a shell thickness of 10 nm with varying core radius for n = 1.0.](image)

**Figure 8.8:** Simulated scattering spectra of CdTe-coated Au NPs having a shell thickness of 10 nm with varying core radius for \( n = 1.0 \).
Figure 8.9: Simulated scattering spectra of CdSe-coated Au NPs having a shell thickness of 6 nm with varying core radius for n = 1.0.

Thus, CdTe- and CdSe-coated Au nanoshells with the shell thickness of about 4 to 8 nm are more useful in optical imaging, because, in this size range, the scattering associated with surface plasmons of nanoshells lies in the NIR regime of the EM spectrum and shows significant scattering efficiency which is basically needed for optical imaging applications (Frangioni et al., 2003). Moreover, from Figures 8.6, to 8.9, it is clear that the Au coating on the surface of CdTe and CdSe nanoparticles leads to increase in the scattering for both the cases but larger enhancement has been seen in the case of CdSe-coated Au NPs with same dimensions and embedded in the same surrounding environment. Therefore, for optical imaging applications, the CdSe-based Au nanoshells can be used more favorably as compared to the CdTe-based Au nanoshells.
The effects of Au shell thickness on the absorption peak position and full width at half maxima of the absorption spectrum have been presented in Figures 8.10 and 8.11, respectively. It has been found that the absorption and scattering peak positions shifts regularly from the infrared to the visible regime of the spectrum with increasing Au shell thickness from 2 nm to 10 nm with the same trends therefore not shown here. The absorption and scattering peak positions of CdTe-coated Au nanoshells lie at longer wavelength region as compared to the peak positions of CdSe-coated Au nanoshells in the same surrounding environment for the entire range of Au shell thickness. Moreover, the peak position of Au nanoshells shifts to the higher value of wavelength with increase in the surrounding medium refractive index from 1.0 to 1.5 in both the cases.

**Figure 8.10:** Effect of shell thickness on the absorption peak position for both the coated NPs in \( n = 1.0 \) and \( n = 1.5 \).
Figure 8.11: Effect of shell thickness on the resonant linewidth for both the coated NPs in $n = 1.0$ and $n = 1.5$.

Figure 8.11 represents the variation of absorption linewidth (FWHM) at resonance with Au shell thickness. It has been found that the linewidth is much higher for CdTe-coated Au nanoshell as compared to the CdSe-coated Au nanoshell. Moreover, in case of CdTe-coated Au nanoshell, the linewidth decreases regularly with increasing Au shell thickness in both the surrounding media. Initially, it is clear that the linewidth is slightly higher in air as surrounding medium but when the Au shell thickness is 6 nm or higher, the linewidth increases as the surrounding medium varies from $n = 1.0$ to $n = 1.5$. In case of CdSe-coated Au nanoshell, the linewidth varies randomly w.r.t. the Au shell thickness and has a small value in comparison to the linewidth of CdTe coated Au nanoshells but their absorption efficiency is almost two times the absorption efficiency of CdTe-coated Au nanoshells in the visible region and scattering efficiency is more than two times in the NIR region of the EM spectrum. Therefore, CdSe-coated Au nanoshells can be used favorably to increase the efficiency of solar cells as well as in the optical imaging applications.
The optical properties of semiconductor-coated Au nanoshells having a small thickness from 2 nm to 10 nm have been studied by using the bulk dielectric functions of semiconductor and Au metal but the applicability of a bulk dielectric function to a small Au shell thickness is debatable, (Wu et al., 2008) and in the present calculations, the effect of surface scattering on the dielectric function of Au have not been included. However, the effect of surface scattering is to increase the linewidth of both the absorption and scattering spectra but at the cost of small reduction in both the efficiencies. Moreover, it does not affect the peak position so far (Noguez, 2007). The increase in linewidth is beneficial for solar cell applications because larger spectral region is covered by the absorption spectra (Catchpole & Polman, 2008) but at the cost of some reduced efficiency, which can further be improved by controlling the surrounding medium. In the present chapter, the size of semiconductor-coated Au nanoshells and its surrounding medium have been optimized for the maximum absorption and scattering efficiency in the visible to the NIR region of the EM spectrum based upon their considered applications.

8.3 Conclusions

Cadmium based semiconductors are important materials for various applications based on light absorption and scattering characteristics such as solar cells, light emitting diodes, photoluminescence, photocatalytic water splitting and biological field, etc. Therefore, it is important to improve the absorption and scattering properties at wavelengths below or equal to the band gap edge wavelength to use them for these applications. These properties can be enhanced by coating the semiconductor material with Au NPs due to the near field enhancement of surface plasmon resonance on the Au surface. In this chapter, the optical absorption and scattering properties of CdTe- and CdSe-coated Au nanoshells have been discussed using extended Mie theory for solar
cells and biological applications. The optical properties are significantly enhanced due to the excitation of surface plasmons in the Au shell. The increased absorption in the visible region can be useful for solar cell applications, whereas in NIR it can be useful for photo-thermal application, whereas the increased scattering in the NIR region could be useful in optical imaging applications. In conclusion, by varying Au shell thickness, semiconductor core radius, and surrounding medium, it has been observed that CdSe-coated Au nanoshells in comparison to CdTe-coated Au nanoshells shows better enhancement in optical properties over the entire visible to NIR region of the spectrum, therefore, preferred as better material for absorption and scattering based applications.