Characterization of core/shell (Ag/CdSe) nanostructure using photoacoustic spectroscopy

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Abstract. Photoacoustic (PA) technique has been used to study the optical and thermal properties of core/shell (Ag/CdSe) nanostructure. Core shell Ag/CdSe nanostructure particles were prepared using organometallic method, having a core of (12 -14 nm) and CdSe shell thickness ranging from (2.59 nm to 5 nm) as determined by TEM. The PA spectra were compared with regular UV-Vis absorption which gave comparable results, though the UV-Vis is for colloidal form and the PA spectra is for powder form. The obtained spectra are combination of the surface plasmon (SP) absorption bands of the Ag core and the band gap of CdSe shell. Second derivative fitting method and Gaussian peak fitting were used to determine precise absorption peaks and band of the PA spectra. The SP bands of the Ag core show a decrease in amplitude, broadening of the width and red shift as the CdSe shell thickness increases. The CdSe absorption band edge also shows an increasing red shift from (517 nm to 604) nm with the increases in the thickness. The thermal diffusivity of the Ag/CdSe core shell samples increase by an order of magnitude larger than the CdSe bulk value which is caused by Ag core.

1. Introduction
Recent interest in synthesis and characterization of core/shell nanoparticles raised from the varied attributes of functional activities involving optical, electronic, magnetic, catalytic and chemical/biological phenomenon. Core/shell Ag/CdSe of metal semiconductor nanostructures of are of special interest in light energy conversion systems. The surface plasmon absorption band of a metal nanostructure is dependent on both the nanostructur size and chemical surroundings [1-2]. Core/shell nanostructures have gained considerable importance, hence careful choice of core-to–shell ratio makes it possible to design nanostructures of varied absorption to suit application or scatter light efficiently. Strong absorber at wide range can be used in efficient photovoltaic [2]. Organometalic synthesis method was used in this work to give a good control of core size and shell thickness. Using the nondestructive characterization PA technique to determine the optical and thermal properties allows us to study the material in the powder form without any special sample preparation and gives results that are in full agreement with direct measurements like TEM.
2. Experimental

Core/shell Ag/CdSe nanoparticles were synthesized in two steps. First the Ag core is prepared by the method of Elizabeth Williams [3], then, the CdSe shell is synthesized by the method of Talapin et al. [4], using the Ag nanoparticles from the first step as seeds. Hexadecylamine (HDA) was used as a capping agent, together with trioctylphosphine oxide (TOPO). The injection temperature of CdSe materials into a tri-neck flask is very critical in starting CdSe shell over the Ag core. Samples with different shell thicknesses from (a) to (e) were obtained from the same synthesis pot by collecting samples at longer time intervals during growth of the CdSe shell. The size of the core and the thickness of the shell, were measured by TEM, to compare the calculated dimensions using PA Technique with the direct measurement of TEM. Fig. (1) shows TEM images of the pure Ag core of diameter (12-14 nm) and Fig (2) shows TEM images for the core shell Ag/CdSe nanoparticles (5 nm) shell thickness. Fig. (3) Shows measurement of the optical absorption of the obtained samples in colloidal solution for the pure Ag core and the absorption for the core shell Ag/CdSe nanoparticles are shown in Fig (4). The obtained optical spectra are combination of the surface plasmon (SP) absorption bands of the Ag core and the band gap of CdSe shell.

Figure 1. TEM of pure 14-16 nm Ag.

Figure 2. TEM of core/shell Ag/CdSe of 14 nm core and 5 nm shell thickness.

Figure 3. Optical absorption for the Ag core (12-14nm).

Figure 4. Optical absorption for Ag/CdSe core/ shell samples of shell thickness as indicated.

Measurements of the PA spectra were carried out at room temperature in the wavelength range 400–700 nm at modulation frequency 16Hz using a mechanical chopper. The PA spectra were normalized (light intensity normalization) using carbon black. The data were averaged to improve the signal to noise ratios and the conditions for each of the PA measurements were kept the same (see Fig. (5)). Typical example of the PA spectra for sample (b) of Ag core (14 - 16 nm) and shell thickness (2.37 nm) and sample (d) same Ag core and shell thickness (3.52 nm), are shown in Fig. (5). The obtained PA spectra are combination of the surface plasmon (SP) absorption bands of the Ag core and the band gap of CdSe shell. The 2nd derivative of the experimental data, coupled with Gaussian fitting to give
precise $\lambda$ at peak absorption. The polynomial fitting functions given by Peng[5] were used to give values for the thickness of CdSe nanoshell. These values were then compared to direct measurements by TEM. In order to measure the thermal diffusivity, powder of each size of Ag/CdSe core/shell were compressed into a disk of 0.5 mm thickness. PA signal amplitude is recorded at various chopping frequencies for each sample using the same incident laser wavelength.

3. Results and discussion

Though the UV-Vis spectra are for colloidal form, and the PA spectra are for powder form, the two spectra gave peaks that are very close. The SP bands of the Ag core (at 420 nm) show a decrease in amplitude and broadening of the width as well as slight red shift as the shell thickness increases. The plasmon band of metal involves oscillations of the free electrons in the conduction band that occupy energy states immediately above the Fermi level. Hence, loading these oscillations with CdSe shell leads to an increase in the shift and a decrease in the amplitude. The CdSe absorption band edge shows an increasing red shift from 517 nm to 604 nm with the increase in the thickness. The determination of the second exciton of CdSe was made difficult by the presence of the Ag core SP absorption band. The 2nd derivative of the PA spectra Fig.(6) coupled with Gaussian peak fitting, and using the resulting $\lambda$ in the polynomial fitting functions [6], the particles size are calculated from:

$$\text{CdSe : } D = \left( 1.6122 \times 10^{-8} \right) \lambda^4 - \left( 2.6575 \times 10^{-6} \right) \lambda^3 + \left( 1.6242 \times 10^{-3} \right) \lambda^2 - \left( 0.4277 \right) \lambda + \left( 41.57 \right)$$  \hspace{1cm} (1)

where D is the particle size in nm. The calculated shell thicknesses were (2.57 nm, 2.8 nm, 3.21 nm, 4.25 nm and 4.77 nm) for samples (a), (b), (c), (d), and (e) respectively. The value of sample (e) matches well with that measured by TEM (5 nm) as shown in Fig. (2).

![Fig.(5) PA spectra of sample(b) and sample(d) of the Ag/CdSe Core/Shell.](image)

![Fig.(6) 2nd derivative The PA spectra of the Ag/CdSe Core/Shell.](image)

The thermal diffusivity (D), is calculated using the relation [6].

$$D = f_c L^2 \text{ cm}^2/\text{s}$$  \hspace{1cm} (2)

where L is the thickness of the sample and $f_c$ is the characteristic frequency [6]. The calculated values of thermal diffusivity for the core/shell Ag/CdSe samples are between (0.098 cm$^2$/s and 0.14 cm$^2$/s) for all the samples. These values are an order of magnitude larger than the bulk CdSe value (0.014 cm$^2$/s) [7]. This is caused by the presence of the Ag core. This higher diffusivity for Ag/CdSe core/shell materials are more suitable for solar conversion devices.
4. Conclusion
The PA spectra for the core/shell Ag/CdSe nanostructure in the powder form have shown a combined absorption of Ag core SP band and the CdSe nanoshell. Increasing the CdSe shell in the Ag/CdSe nanoparticles gives the opportunity to tune the band gap of the nanoparticles to harvest a wide range of visible solar spectra. Using the 2nd derivative of the experimental data coupled with Gaussian peak fitting and the polynomial functional fitting, give the thickness of the CdSe nanoshell in agreement with the measured value by TEM. The thermal diffusivity of the Ag/CdSe core shell shows an increase by an order of magnitude than the CdSe bulk due to the presence of the Ag core.

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