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Plasmonic Absorption Enhancement in Au/CdS Nanocomposite

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***Abstract*—**Composite nanostructures of metal core/semiconductor shell (Au/CdS) configuration were prepared using organometalic method. UV-Vis spectra for the Au/CdS colloids show initially two well separated bands, corresponding to surface plasmon of the Au core, and the exciton of CdS shell. The absorption of CdS shell is enhanced, while the Au plasmon band is suppressed as the shell thickness increases. The shell sizes were estimated from the optical spectra using the effective mass approximation model (EMA), and compared to the sizes of the Au core and CdS shell measured by high resolution transmission electron microscope (HRTEM). The changes in the absorption features are discussed in terms of gradual increase in the coupling strength of the Au core surface plasmon and the exciton in the CdS. leading to charge transfer and modification of electron oscillation in Au core.

***Keywords*—**Nanocomposites, Plasmonics.

I. Introduction

RECENTLY, the growing ability to fabricate Metal/Semiconductor (M/S) composites on a nanoscale has opened up new opportunities for designing multifunctional materials with properties that cannot be obtained in the bulk phase. Over the past decade, a wide variety of nanocomposite morphologies, including metal-core/semiconductor-shell heterostructures were synthesized [1-3]. The fundamental interaction between semiconductor-shell excitons and surface plasmon (SP) of metal- core nanoparticles is of particular interest, due to their unique coupling interaction. Such an interaction may fall in two regimes; a week or a strong coupling regime [4]. In the weak coupling regime, excitons wave functions and plasmons electromagnetic modes are considered unperturbed. In the strong coupling regime, excitons-plasmon interaction modifies exciton wave function and SP modes which leads to changes of their energies. The surface plasmon of a metal nanostructure is dependent on both the nanostructure size and chemical surroundings [5] which helps to tailor their optical properties to tune with the sensing properties of the semiconductor nanoshell. This composite nanostructure has a great potential for utilization in the areas of photovoltaic [6] and solar cell production [7], lasers [8], sensors and memory devices.

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Organometalic synthesis method was used to have a good control of Au-core size and CdS shell thickness in this study, we are concerned with the coupling of the exciton dipole and the surface plasmon electromagnetic field in Au/CdS core/shell and their effect on the absorption of the CdS shell and the Au core. The shell dimensions were calculated using the UV-Vis spectra and the effective mass approximation model (EMA)[10], and were compared with the direct dimension measurement using high resolution transmission electron microscope (HRTEM). The SP absorption peak was observed to be suppressed as the thickness of the CdS shell increases while there is an enhancement in the CdS absorption. These observations are discussed in terms of the varying strength of the coupling of the SP and the exciton fields.

II. Experiment

A. Preparation of Au Core Nanoparticles

Gold acetyl acetenate (Au ac ac) was prepared by mixing 3ml ethyl alcohol and 0.1 gm of Gold (III) chloride (HAuCl4, Aldrich), at room temperature, then raising the temperature slowly to 90 ^{o}C, and adding 0.5 ml of acetyl acetone (Alpha Chemika) till we obtain the red color. By increasing the temperature until the liquid evaporates we get Au ac ac powder. Adding 2 ml di-phenyl ether (Riedel-Dehaen), 2 gm of Hexadecylamine (HDA, Aldrich) and 2 gm Trioctylphosphine oxide (TOPO, Fluka), to the prepared Au ac ac at temperature 90 ^{o}C, by raising the temperature to 100^{o}C, the Au nanoparticles is formed. The absorption spectra were measured using UV-Vis spectrophotometer (Jasco 670). The particle size and shape was determined using high-resolution transmission electron microscopy (HRTEM, JEOL JEM-2100 operated at 200KV with high resolution Gatan CCD bottom camera, Orius SC200).

B. Preparation of Cadmium Sulfide (CdS) Nanoparticle

A 0.3g of Cadmium oxide (CdO, Aldrich), was dissolved in 2g (stearic acid) at 170 ^{o}C, then a mixture of 2g of TOPO and 2g of HDA was added and held at 180 ^{o}C for 5 min to get a clear solution. The resultant solution was kept warm and stored in a syringe to use as a Cadmium (Cd) source. A 0.3 g of Sulfur (S) was dissolved in 6 ml of Trioctylphosphine (TOP, Fluka), then stored in another syringe to use as a S source, this solution was quickly injected into the prepared Cd source, and the reaction mixture was raised to 130 ^{o}C for the growth of CdS. Six samples were collected at increasing time intervals and labeled from 1 to 6. The absorption spectra were measured Using UV-Vis spectrophotometer.

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C. Preparation of Au /CdS Core Shell Nanoparticle

The prepared Au core was put in tri-neck flask and heated to 140 ^{o}C then 1 ml of the Cd source and 1 ml of S source was added drop wise into the Au core colloids. The first sample is collected after 1 minute, by repeating the previous step after adding more Cd and S and waiting for extra minutes for each injection to collect the samples. At constant temperature, 4 samples were collected at increasing time intervals and labeled from 1 to 4. All samples were immediately cooled and diluted with toluene to stop CdS shell growth. The absorption spectrum for each sample was recorded using UV-Vis spectrophotometer. The particle size and shape were also determined using (HRTEM). Care was taken in the preparation of the colloid sample such that the absorption measurement would not depend on the concentration.

III. Results and Discussions

In Fig. 1, we show UV-Vis spectra for Au-core nanoparticles. The spectrum shows a peak corresponding to the plasmon excitation in the Au nanoparticles around 524 nm. The SP is caused by the oscillation of the free electrons resonating with the incident light. The Au nanoparticles were of the same batch as the seeds used later for the Au-core/CdS-shell nanocomposite. Fig. 2 gives the HRTEM image for these Au nano seeds, showing symmetric spherical particle shape with an average size of ~16 nm.

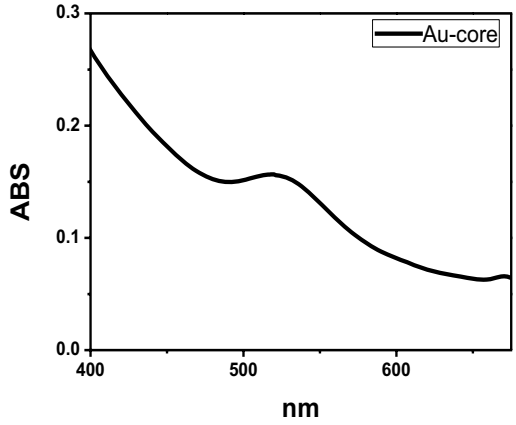


Fig. 1 UV-Vis absorption of Au-core nanoparticles

The absorption spectra for CdS Q.D that were prepared separately, at increasing time intervals as mentied above, are shown in Fig. 3. The resulting Q.D. of varying sizes show peaks due to the first excitonic transition that red shifts as the particle size increases. To determine the peak position with more precision, we use the second derivative analysis.

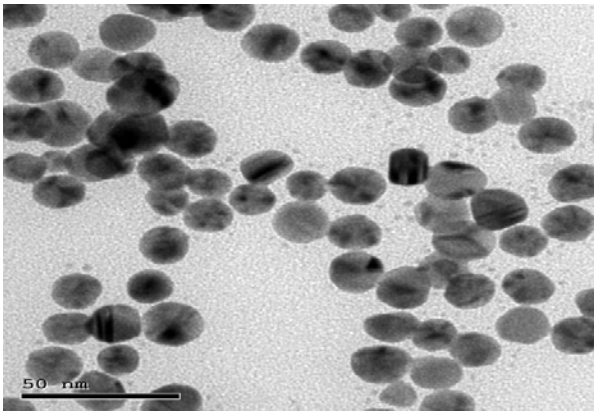


Fig. 2 HRTEM image for Au-Core nanoparticles

From the second derivative spectra, we find that the first absorption peak shifts from 390 nm for the smallest size (least time of growth) to 468 nm for the largest size (the longest time of growth).

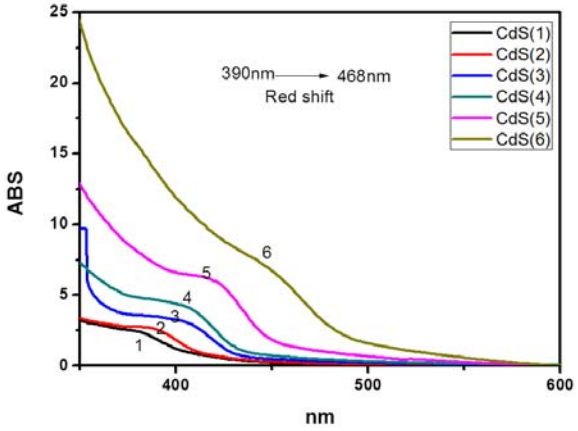


Fig. 3 Absorption bands for CdS QD nanoparticles

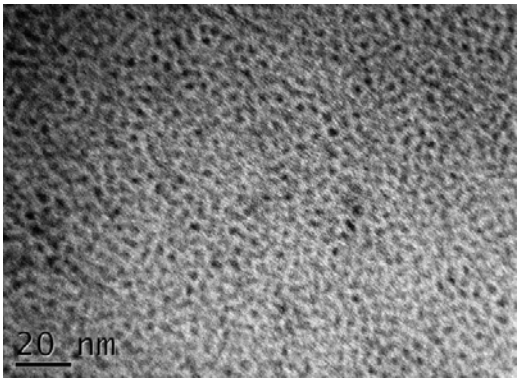


Fig. 4 HRTEM image for CdS Q.D nanoparticles

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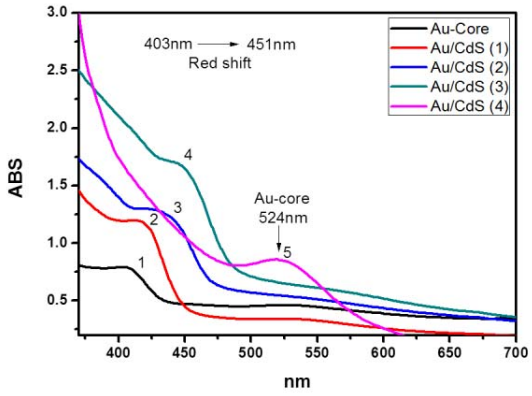


Fig. 5 UV-vis of Au/CdS core shell nanoparticles

The dimensions of the generated CdS Q.D nanoparticles were also measured using HRTEM, Fig. 4 shows the case for sample 2 of the spectra in Fig. 3, where the estimated particle size for CdS QD from the graph was 3.2 nm.

The absorption spectra for Au/CdS core/shell nanoparticles with the same Au core size but with increasing CdS shell thickness are shown in Fig. 5. The absorption peak for the bare Au core is superposed on the spectra for comparison. It is clear from the spectra, that the SP absorption corresponding to the Au core of Au/CdS show suppression in the intensity and red shift as the CdS shell increase in thickness. There is also an increase in the intensity of the CdS shell exciton peak with increasing thickness. The second derivative analysis of the compound spectra in this case was employed to the two regions separately; the exciton region is traced in Fig. 6, and the plasmon is traced in Fig. 7. The second derivative spectra show that there is a red shift in the peak of the excitonic band of CdS-shell from 403nm to 451nm as the shell thickness increase. At the same time the suppressed of the plasmon band of the Au core is accompanied by a red shift increasing (532 nm to 566 nm) as the CdS shell thickness increasing (1.9 nm to 2.7 nm).

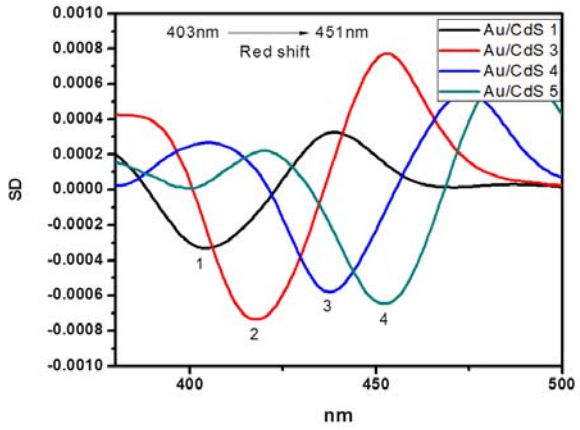


Fig. 6 Second derivative for CdS-shell region of Au/CdS nanoparticles absorption spectra

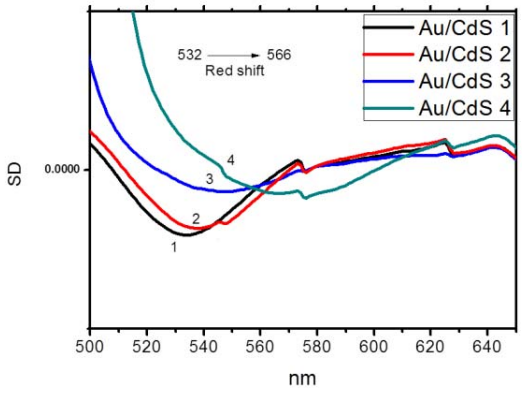


Fig. 7 Second derivative for Au–core region of Au/CdS nanoparticles

The sizes and structures of Au/CdS nanocomposites were imaged by HRTEM, Fig. 8 presents the case for sample 4 in the optical spectra. It is clear that metallic Au cores have higher contrast than the semiconductor CdS shell; for this sample, the core size is about 16 nm, and the CdS shell size is about 3.5 nm.

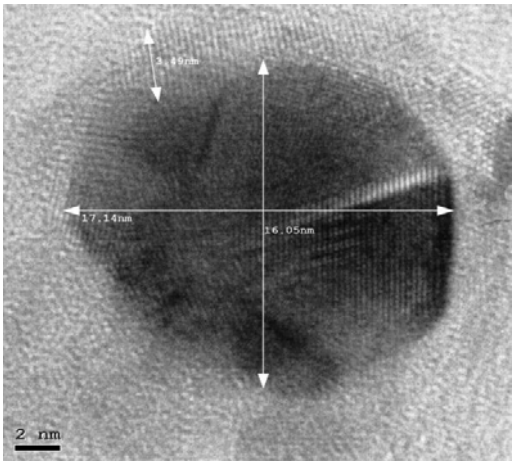


Fig. 8 HRTEM of sample (4) of Au/CdS

The nanoparticles sizes on the other hand, were estimated from the absorption spectra using the effective mass approximation (EMA) model [10].

$$E(NC) = E_g(bulk) + \frac{\hbar^2 \pi^2}{2R^2}\left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right) - \frac{1.8e^2}{\varepsilon\ R} \qquad (1)$$

where, E (NC) is the lowest energy for electronic transition for nanocrystals, E_g is the band gap of bulk CdS (2.42 ev), R is the average radius of nanoparticles, m^*_e is the effective mass of electron (0.19 me), m^*_h is the effective mass of hole (0.8 me) and ε is the dielectric constant for CdS nanocrystals. The calculated CdS shell thicknesses of Au/CdS core/shell nanoparticles are shown in Table I together with values that were obtained using HRTEM. The directly measured values of

samples 2 and 4 are in reasonable agreement with the calculated dimensions obtained by EMA model.

TABLE I
THE CALCULATED CDS SHELL THICKNESS OF AU/CDS CORE/SHELL NANOPARTICLES USING THE OPTICAL SPECTRA AND THE EMA MODEL, AND THE SHELL THICKNESS AS MEASURED BY HRTEM

Samples	*EMA (nm)*	*HRTEM (nm)*
	UV-Vis	
Au/CdS 1	1.9	-
Au/CdS 2	2.1	2.6
Au/CdS 3	2.4	-
Au/CdS 4	2.7	3.5

It can be observed from the absorption spectra for the bare Au core Fig. 1, the CdS QD Fig. 3, that the absorption of the nanocomposites Au/CdS Fig. 5 is not a simple superposition of the first two. This is attributed to a gradual increase in the coupling strength of the interaction of excitons in the CdS shell and the SP in the Au core. This varying coupling strength mechanism of the Au-core surface plasmon and the excitons in CdS-shell results from the close proximity of the Au core and the CdS shell in the colloidal nanocomposites and the increase in the overlap of the exciton absorption band and surface plasmon band. The HRTEM images (Fig. 8) also indicates that at Au/CdS interface there is regular lattice fringes of the two crystals phases showing that there is no lattice alloying. This leads to quick transfer of the photoinduced electrons in CdS to the Au core [11] causing the suppression the SP absorption. The Au cores act as an electron sink enhancing the charge seperation in CdS shell. This process also leads to large increase in the absorption of the CdS shell in the visible region. However, similar suppression of the plasmon peak and enhancement of the CdS absorption in Au/CdS has also been observed [12]. The suppression of the SP feature was explained in terms of the modification of electron oscillation in Au and the increase in CdS absorption as due to the photoinduced absorption of carriers in the CdS.

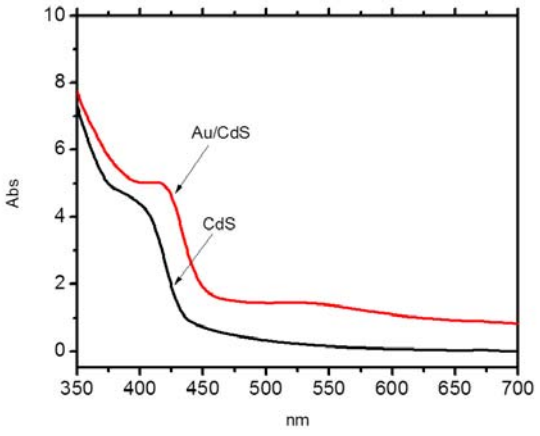


Fig. 9 Relative absorption of Au/CdS core/shell samples shell thickness comparing to CdS Q.D of the same particle size (4.2 nm)

To further examine this explanation of experimental results, the absorption spectra were measured for particular CdS QD samples of size (4.2 nm) and Au/CdS with equal CdS shell thicknesses, and the results are shown in Fig. 9. The second derivative analysis show the CdS excitons band is at the same energy for CdS QD and CdS shell with no shift. However, there is a clear enhancement of the CdS absorption and suppression of the Au plasmon absorption. The observed results are clear evidence of the strong coupling mechanism of the Au plasmon and CdS exciton and confirmation of the above explanation.

IV. CONCLUSION

We present a new approach for direct synthesis of Au/CdS core/shell nanoparticles that have the same size core but with different shell thicknesses. The CdS-shell thicknesses were calculated using EMA model and are in full agreement with the directly measured values using HRTEM. The increasing coupling strength of plasmon-exciton has resulted in enhancement of the absorption of CdS shell and suppression of the plasmon absorption. This enhancement would benefit in the construction of the active layer of photovoltaic solar cell to increase their efficiency.

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