

Optical and Electron Microscopy of Au core/CdS shell nanoparticles

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Abstract

The combining of metal and semiconductor nanostructures as core/shell have attracted great interest due to their complementary optical properties; the localized Plasmon in the core and the exciton in semiconductor. The first, results in the enhancement of local fields and the second, are the nonradiative damping due to electron transfer from semiconductor to metal. Composite nanostructures of metal-core/semiconductor-shell configuration were prepared using organometallic method. UV-Vis spectra for the colloids show two distinct bands, one for the gold (Au) metal core surface plasmon at lower energy and the second for the excitons of semiconductor Cadmium Sulfide (CdS) shell at higher energy. Second derivative methods were used to determine the precise absorption peaks in UV-Vis spectra. The shell size was estimated using two methods, effective mass approximation (EMA), and polynomial fitting function (PFF), both give shell thickness dimension in the range of few nanometers. These dimensions were confirmed by imaging the nanostructure using high resolution transmission electron microscope (HRTEM).

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. The ability to tailor the optical properties or tune the sensing properties of the semiconductor nanoshell is a major goal of designing these nanocomposite systems [4]. Core/shell Au/CdS nanostructure are of special interest in light energy conversion systems. The surface plasmon of a metal nanostructure is dependent on both the nanostructure size and chemical surroundings [5]. In this work we have used nanostructure gold core of the same dimension and of CdS shell of varying thickness.

UV-Vis spectra for the nanocomposites show the CdS exciton peak where as the peak corresponding to the Au core plasmon is relatively quenched. The surface plasmon field of the core enhancement the local field in the nanostructure. Organometallic synthesis method was used to control Au-core size and CdS shell thickness. The dimensions of nanostructure were determined using the effective mass approximation (EMA) and also polynomial fitting function (PFF). The dimension were also measured directly using high resolution transmission electron microscope (HRTEM), and the calculated dimension are in good agreement with the experimentally measured once.

Experiential

Preparation of Au core nanoparticles:

Gold acetyl acetate (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 °C, and adding 0.5 ml of acetyl acetone (Alpha Chemical) till we obtain red color. The

temperature was raised until the liquid evaporates to get (Au ac ac) powder. 2 ml di-phenyl ether (Riedel-Dehaen), 2 gm of Hexadecylamine (HDA, Aldrich) and 2 gm Trioctylphosphine oxide (TOPO, Fluka), are added to the prepared Au ac ac at temperature 90 °C and by raising the temperature to 100°C, the Au nanoparticles is formed. The absorption spectra were measured using UV-Vis spectrophotometer (Jasco 670).

Preparation of Au /CdS core shell nanoparticle:

The prepared Au core was put in tri-neck flask and heated to 140 °C. A 0.3g of cadmium oxide (CdO, Aldrich), was dissolved in 2g (stearic acid) at 170 °C then a mixture of 2g of TOPO and 2g of HDA was added and held at 180 °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. Then 1 ml of the Cd source and 1 ml of S source were added drop wise into the Au core colloids and we waiting for 1min to collect the first sample. Repeating the previous steps after adding more Cd and S and waiting 1 min 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 spectra were measured using UV-Vis spectrophotometer. 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)).

Results and Discussions:

In Fig (1) we show UV-Vis spectra for the gold core spectra superposed on the spectra of Au/CdS core/Shell nanoparticles. The peak corresponding to the plasmon excitation in the gold nanoparticles occur around 524 nm. The surface plasmon is caused by the oscillation of the core

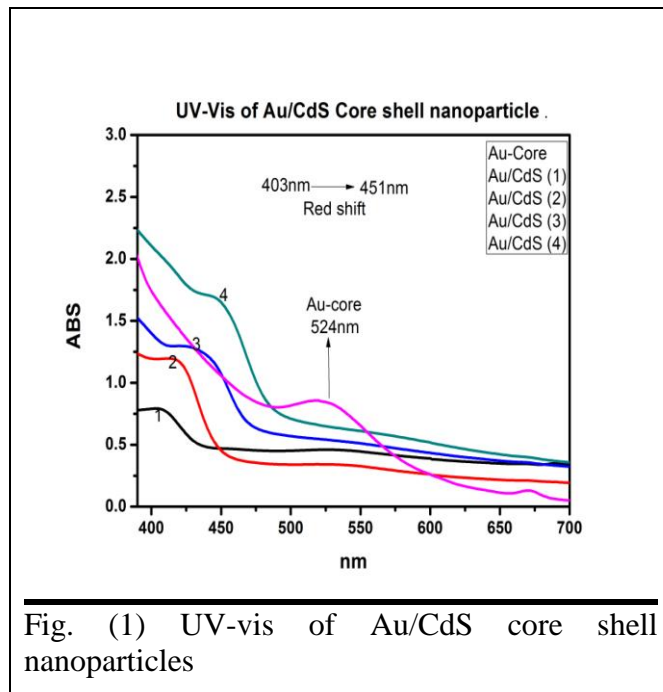


Fig. (1) UV-vis of Au/CdS core shell nanoparticles

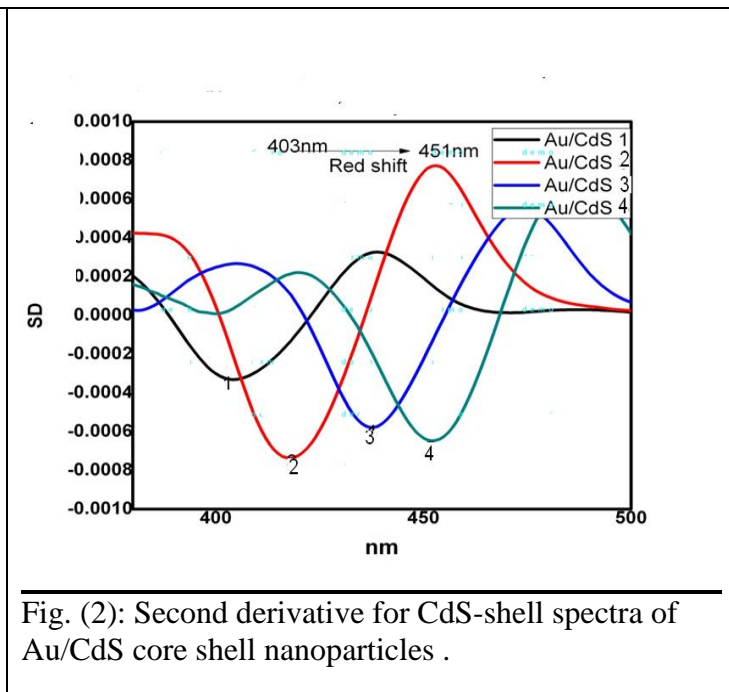
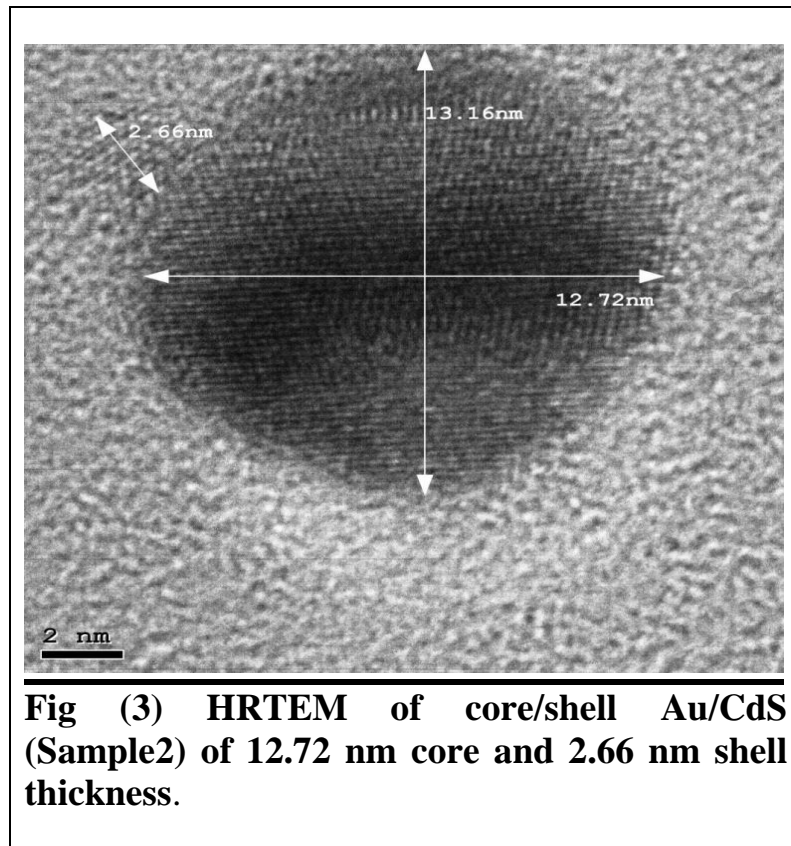


Fig. (2): Second derivative for CdS-shell spectra of Au/CdS core shell nanoparticles .

free electrons resonating with the incident light. The Au nanoparticles of the same batch were used as the seeds for the CdS shell nanocomposites .

There is an increase in intensity of the CdS shell exciton peak with increasing thickness. However, the peaks corresponding to the Au core show large decreases. The second derivative

analysis was employed to the two regions, the plasmon and the exciton. The second derivative spectra, are given in figs.(2) for the exciton of CdS shell region. There is a peak red shift of the excitonic band of CdS-shell from 403nm to 451nm as the shell thickness increase. There is also a red shift of the plasmon band of the gold core (about 30nm) as CdS shell increase. The red shift of the exciton can be explained in terms of the increasing of the shell width. On the other hand the red shift of the plasmonic absorption peak could be understood in terms of the loading of Au core with the increasing the shell thickness.



The size and structure of Au/CdS were imaged by HRTEM, Fig (3) presents the case for sample 2 in the optical spectra. It is clear that metallic gold nanoparticles have higher contrast than the semiconductor CdS shell. For this case, the core size is about 12.72 nm, and the CdS shell size is about 2.66nm.

The nanoparticles size was estimated from the UV-Vis absorption spectra peaks using two methods:

(1) The Polynomial Fitting Functions (PFF) [6].

$$D = (-6.6524 \times 10^{-8})\lambda^3 + (1.9557 \times 10^{-4})\lambda^2 - (9.2352 \times 10^{-2})\lambda + (13.29) \rightarrow (1)$$

D (nm) is a size of a given nanocrystals sample, $\lambda_{(nm)}$ is the wave length of the first excitonic absorption peak.

(2)The Effective Mass Approximation (EMA) [7].

$$E_{gn} = E_{gb} + \frac{\hbar^2 \pi^2}{2R^2} \left(\frac{1}{m_e^*} + \frac{1}{m_h^*} \right) - \frac{1.8e^2}{\epsilon R} \rightarrow (2)$$

where E_{gn} (NC) is the lowest energy for electronic transition for nanocrystals, E_{gb} is the band gap of bulk CdS(2.42 eV), and R is the average radius of nanoparticles. m_e^* is the effective mass of electron (0.19 m_e), m_h^* is the effective mass of hole (0.8 m_e) ϵ is the dielectric constant for CdS nanocrystals. In table (1) we show the dimension of CdS shell thickness as determined from the PPF and EMA methods. Also the table indicates the dimension as determined by HRTEM.

Samples	PPF(nm)	EMA(nm)	HRTEM(nm)
	UV-Vis	UV-Vis	
Au/CdS 1	1.8	1.92	-
Au/CdS 2	1.96	2.1	2.66
Au/CdS 3	2.36	2.4	-
Au/CdS 4	2.68	2.75	3.49

Table (1) The calculated CdS shell thickness in Au/CdS core/shell nanoparticles by two methods (PPF) and (EMA) from the optical spectra of UV-Vis and then the shell thickness as measured by (HRTEM).

Conclusion:

We present a new approach for synthesis of Au/CdS by directly assembling CdS of different shell thickness on same size Au core nanoparticles. The calculation methods using EMA and PPF give dimensions of CdS shell in good agreement with the directly measured dimension using HRTEM. It is concluded that increasing the CdS shell in the Au/CdS core/shell nanoparticles gives us the ability to tune the band gap of the nanoparticles to harvest a wide range of visible solar spectra.

Reference:

[1] Zhang, J.Tang, Y, lee, K,Ouyang, M.science 2010,327,1634-1638

[2]Shi, W.L,Zeng,H,,Sahoo,Y,Ohulchannnnsky,T.Y,Ding, Y,Wang,Z,L,Swihart,M,Prasad,P.N. Naaaaaaano lett. 2006,6,875.

[3]Kim,H,Achermann,M,Balet,L.P,Hollingsworth,J.A,KlimovV.I.J.am.Chem,Soc 2005,127,544-546.

[4] Yanfei Wang, Minjie Li, Spectrochimica Acta Part A 64 (2006) 101-105 .

[5] C.Zhong, M.M.Maye, Adv. Mater. 13 (2001) 1507

[6] *A.M.Okasha, Mona B.Mohamed, T.Abdallah, Anis B Basily, S.Negm, H.Talaat Journal of Physics: Conference Series 214, 012131(2010)*

[7] *Brus, L. E.; "Electronic Wave-Functions in Semiconductor Clusters Experiment and Theory". J. Phys Chem., 90, 2555 (1986).*