Digest Journal of Nanomaterials and Biostructures Vol. 6, No 2, April - June, 2011, p. 709 - 716

SIZE MEASUREMENT OF METAL AND SEMICONDUCTOR NANOPARTICLES VIA UV-Vis ABSORPTION SPECTRA

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In this paper we present a technique for size measurement of metal and semiconductor nanoparticles. The technique includes comparison between UV-Vis spectra fitting of the colloidal nanoparticles and theoretical calculation of absorption spectra. For metal colloidal nanoparticles, Mie theory is used to obtain the Lorentzian profile of absorption. It is shown that the width of this profile is related to the size of nanoparticles. The intensity of absorption spectra is related to the liquid dielectric constant and real part of interband transition of metal nanoparticles. This allows us to measure the size of colloidal Ag nanoparticles in distilled water. Our results given this method are in excellent agreement with size measurement which is taken from Transmission Electron Microscopy (TEM). For colloidal semiconductor nanoparticles, effective mass model is used to measure the nanoparticles size. This method can be calculated shift of energy band gap between the bulk and nano-size semiconductor material. We have applied this method to measure the size and energy band gap of CdS nanoparticles. Our results from the effective mass model are in good agreement with the nanoparticle size measurement using TEM image.

(Received December 1, 2010; Accepted April 1, 2011)

Keywords: Colloidal, Absorption Spectra, Lorentzian, Band Gap, Effective Mass

1. Introduction

The preparation and study of nano-size material is interest in research and technology because of increasing their applications in electronic industry [1] and medical science [2-4] and partly because of increasing their unique character differing from the bulk state of those [5]. In the published reports have been proven the size and shape have an important role to brings unique properties for the nanoparticles [1, 6, 7]. Metals colloidal are one important nano-size-material, and laser ablation in solutions is a new promising technique to obtain metal colloids [7-9]. One advantage of this method compared to other is producing pure colloids, which will be useful for further applications. With using UV-Vis absorption spectra we can characterize the nanoparticles prepared by laser ablation and survey their stability. By using Mie theory we are obtained a Lorentzian profile from UV-Vis spectra of Ag nanoparticles and estimated the size of these nanoparticles between 4nm-8nm and also these results are compared with the size measurement obtained from TEM image. In this work we have applied the effective mass model for size measurement of CdS nanoparticles as a semiconductor. The quantum size effect in CdS nanoparticles was evidenced from the blue shifts of optical absorption edge and the average size of CdS nanoparticles was estimated by the magnitude of blue shift according to the effective mass model [21-24]

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2. Theoretical approaches

2.1. Metal nanoparticles

Mie theory based on the solid state which applies classical electrodynamics to cluster of simple shapes likes spheres. So we have assumed the resultant nanoparticles from ablation in distilled water to be spherical and widely spatially separated. The resulting Mie resonance cause selective optical extinction bands in the visible spectral range for the alkali and noble metals which usually depend strongly on the cluster diameter. For large size particles they are interpreted as spherical Plasmon polaritons, where as in small clusters they are referred to as collective electron excitations [10-12]. In following we summarized the predictions of the Mie theory for metal clusters that show cluster size effects in the optical spectra. This leads to theoretical models for the size dependencies of the dielectric functions and the definition of a relevant parameter which can be compared to experiment [10-14]. If particles are assumed to be spherical objects, widely dispersed (the average distance much larger than their radius) their cross section express as:

$$\sigma_{abs} = 9\frac{\omega}{c}\varepsilon_m^{3/2} v_0 \frac{\varepsilon_2(\omega)}{[\varepsilon_1(\omega)+2\varepsilon_m]^2+\varepsilon_2^2(\omega)} \tag{1}$$

Where υ_0 is the spherical particles volume, ε_m and $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$ denoted the dielectric function of the surrounding medium and particle material. The dipole resonance frequency is determined by the condition $\varepsilon_1(\omega) = -2\varepsilon_m$ provided. $\varepsilon_2(\omega)$ is not too large and dose not vary much near the resonance frequency. This crass section has a resonance peak whose position ω_1 is dependence on the dielectric functions. Within the Drude-Lorentz-Sommerfield free electron model [15] $\varepsilon(\omega)$ is given by

$$\varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\omega\gamma} \tag{2}$$

Where the plasma frequency (ω_p) depends on the electron density (n) on the proper electron effective mass (m_{eff}). Using Eq. (2) and with new condition $\omega \approx \omega_1$ we can rewrite Eq. (1) in terms of a simple Loretzian, where the (FWHM) being given by the phenomenological damping constant γ .

$$\sigma_{abs} = \sigma_0 \frac{1}{[\omega-\omega_1]^2+(\frac{\gamma}{2})^2} \tag{3}$$

With ω_1 being the Mie resonance frequency $(\omega_1 = \frac{\omega_p}{\sqrt{1+2\varepsilon m}})$. So the Drude γ of Eq. (2) equals the band width of the dipole Plasmon polariton in Eq. (3) for the case of free electron (only for the free electron metals) [16-18]. In the classical theory of free-electron metal, the damping is due to the scattering of the electrons with phonons, electrons, lattice defects, or impurities. The relation $\gamma = \frac{\upsilon_f}{L_\infty}$ holds where υ_f is the Fermi velocity and L_∞ is the mean free path of the electron in bulk material [17-18]. If the cluster size becomes comparable with L_∞, the interaction of the conduction electrons with the particle surface becomes important as an additional collision process and increased γ which depends on the cluster size (expanded versions of Mie theory [10-14]).

$$\gamma(R) = \gamma_0 + (A\nu_F)/R \tag{4}$$

Where A attributed to scattering process (is $\frac{3}{4}$ for silver [19-20]) and γ_0 is the velocity of bulk scattering (for silver $5 \times 10^{12} s^{-1}$) and v_f is the Fermi velocity (for silver $1.39 \times 10^6 m/s$) [17, 21, 23]. Size depending of γ, leads to size depending of polarizability $\alpha(\omega, r)$ or equivalently the dielectric function $\varepsilon(\omega, r)$ of the cluster material. When the size of particles is smaller than the average free path of the electrons (52 nm for silver metal [17, 22]), the complex part of the silver dielectric function $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$ modifies to

$$(\varepsilon_2 = \varepsilon_{2,bulk} + \frac{3\omega_p^2 v_f}{4\omega^3 r}) \tag{5}$$

Here we have the angular frequency ω and the plasma frequency ω_p (for silver $\omega_p = 1.38 \times 10^{16} s^{-1}$ [15]).The mean free path limitation leads to an increased Plasmon bandwidth with decreasing size of particle.

2.2. Semiconductor particles

A number of theoretical models have been proposed in the literature, aiming to give a quantitative agreement of the predicted dependence of energy band gap on the crystal size (R) with the experimental data for a wide variety of semiconductor (with bulk band gap values within a wide rang). The most used theoretical model analysis of the experimental data for the energy band gap $\mathrm{E}_g(R)$ dependencies is the Brus model (i.e. the effective mass approximation) [21, 24, 25]. According to the effective mass approximation model, the band gap of semiconductor nanoparticles (considered as a sphere with radius R) is given by:

$$\mathrm{E}_g(R) = \mathrm{E}_{g,bulk} + \frac{h^2}{8m_0R^2}\left(\frac{1}{m_e^*}+\frac{1}{m_h^*}\right) - \frac{1.8e^2}{\varepsilon_0\varepsilon_r R} - 0.248\frac{4\pi^2 e^4 m_0}{2\left(4\pi\varepsilon_0\varepsilon_R\right)^2 h^2\left(\frac{1}{m_e^*}+\frac{1}{m_h^*}\right)} \tag{6}$$

Where $\mathrm{E}_{g,bulk}$ is the bulk band gap value, h the plank's constant, m_0 the electron mass, while m_e^* and m_h^* are the electron and hole relative effective mass respectively, e the electron charge, ε_0 the permittivity of vacuum and ε_r the relative dielectric constant of the semiconductor on the basis of Eq.(6) the band gap shift with respect to the bulk value

$$\Delta E_g = \frac{h^2}{8m_0R^2}\left(\frac{1}{m_e^*}+\frac{1}{m_h^*}\right) - \frac{1.8e^2}{\varepsilon_0\varepsilon_r R} - 0.248\frac{4\pi^2 e^4 m_0}{2\left(4\pi\varepsilon_0\varepsilon_R\right)^2 h^2\left(\frac{1}{m_e^*}+\frac{1}{m_h^*}\right)} \tag{7}$$

The first term in Eq. (7) referred to as the quantum localization term (i.e. the kinetic energy term), which shifts the $E_g(R)$ to higher energies proportionally to R^{-2} .The second term in Eq. (7) arises due to the screened coulomb interaction between the electron and hole, it shifts the $E_g(R)$ to lower energy as R^{-1}. The third, size-independent term in Eq. (7) is the salvation energy loss and is usually small and ignored [24].

3. Experimental

Silver target (99.9% , 2 mm thickness) first cleaned in detergent and then immersed in quartz cell with 20 ml distilled water. The synthesis of silver nanoparticles were obtained by radiation of the ND:YAG laser. Laser radiation (532 nm wavelength, 1Hz pulse repetition and 3 mj pulse energy) was focused on the silver target by a local lens (F=50 mm) through a liquid layer. The duration of the laser ablation experiment was 40 min. To make homogeneous distribution of the nanoparticles, the ablated solution was constantly stirred. After laser ablation experiment, the colloidal Ag nanoparticles were analyzed by UV-Vis spectrophotometer (Varian-Cary 100) in the range of 300 nm to 800 nm. Transmission electron microscopy (TEM: LEO-Model 912 AB) measurements were performed by at 115 kV on Ag nanoparticles which were drop-costed onto a carbon-coated Au grid. For surveying the size changes of nanoparticles with the time, we measure UV-Vis absorption spectra in 10 days.

4. Results and discussion

Fig.1a shows the optical absorption spectra of colloidal solutions prepared at first day. The UV-Vis spectra reveal a characteristic absorption peak of the Ag colloidal located at 410 nm due to surface Plasmon resonance. On the basis of Mie theory and its expanded versions [10-14] information concerning Ag particle size can be derived from analysis of this spectrum. According to the Eq. (1), a Lorentzian fit (Fig.1b) of the absorption cross-section is expected with a resonance when the relationship $\varepsilon_1(\omega) = -2\varepsilon_m$ is satisfied. The band width is strongly dependent on $\varepsilon_2(\omega, R)$ and thus, on the particle size by Eq. (4) [10]. So with information presented in section 2.1 about metallic nanoparticles, we have been calculated the size of Ag nanoparticles 4.1 nm (at first day).

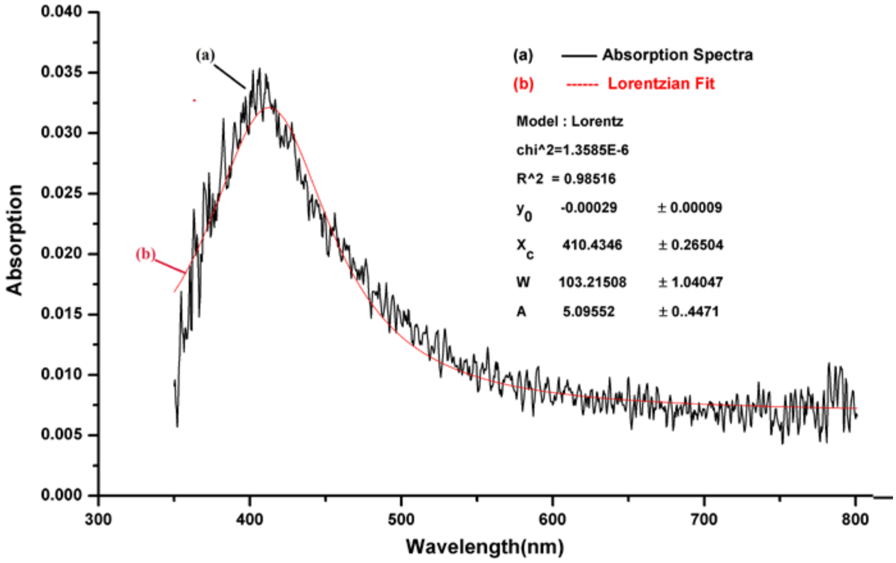


Fig. 1. (a) Optical absorption spectra of colloidal Ag nanoparticles prepared by laser ablation at first day. (b) Best fit of the optical surface Plasmon absorption spectra using Mie equation.

As seen in Fig. 2 aging of colloidal solution was done for 10 days. After 10 days the maximum peak of absorption spectra is shifted up to 414 nm probably due to cluster density increasement. But width and intensity of the absorption spectra is broaden and smaller than located at 410 nm. A red shift of metallic particles (located at 414 nm) has been attributed to enlarge Ag particles.

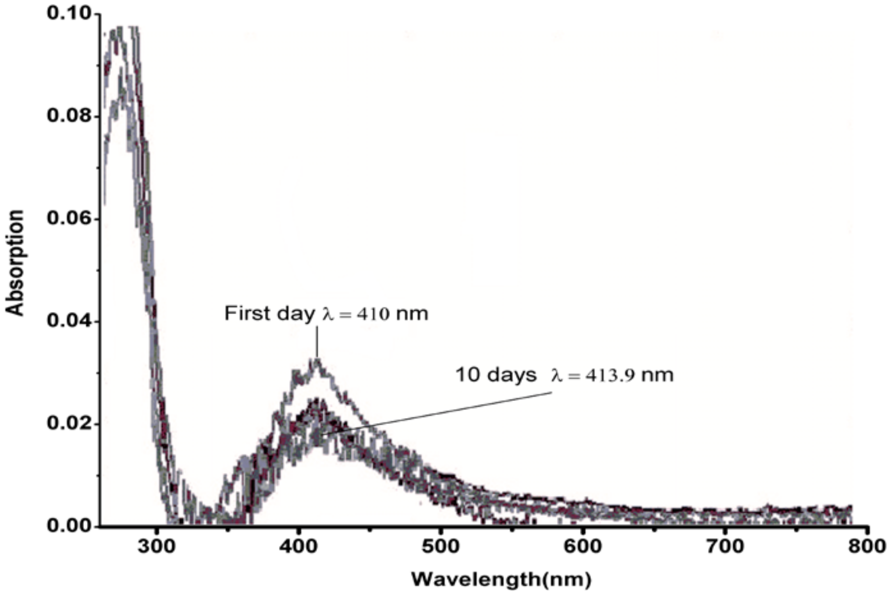


Fig. 2. Evaluation of colloidal Ag absorption spectra during 10 days.

Results of size measurements for Ag nanoparticles using Mie theory during 10 days listed in Table 1.

Table 1. Results of size measurements using Mie theory during 10 days.

Date	Position of peak	Width(nm)	Width(s^{-1})	Estimated size
First day	410 nm	108.21 nm	2.8×10^{14}	4.1 nm
Second day	411.91 nm	92.7 nm	2.6×10^{14}	4.4 nm
Third day	412.28 nm	75.1 nm	2.0×10^{14}	6.0 nm
Fourth day	413.8 nm	65 nm	1.6×10^{14}	7.9 nm
Tenth day	413.9 nm	60 nm	1.56×10^{14}	8.1 nm

As seen in Table 1. The width of the peak is decreased too from 108.21 nm to 60 nm after 10 days. It was shown previously, the surface Plasmon resonance is centered in the vicinity of 415 nm-425 nm which chemically technique was used to synthesis of Ag nanoparticles [26], whereas the absorption spectra of such structure prepared by laser ablation shown difference, in case the surface plasmon resonance is shifted toward a short wavelength range between 400 nm-415 nm due to influence of small-sized nanoparticles [27]. Our results confirmed this shift. The TEM image of Ag naoparticles provided at first day in Fig. 3 has a good agreement with our estimation derived by Mie theory.

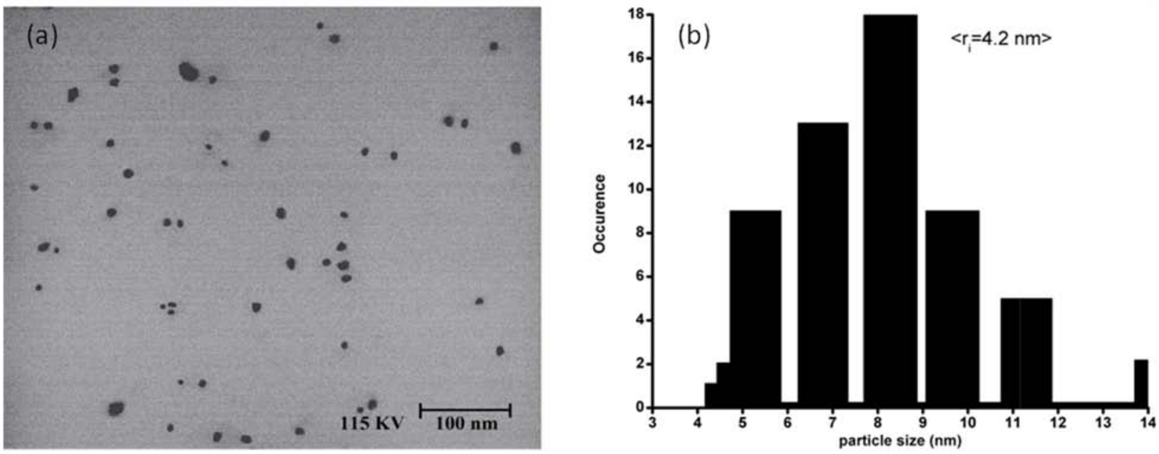


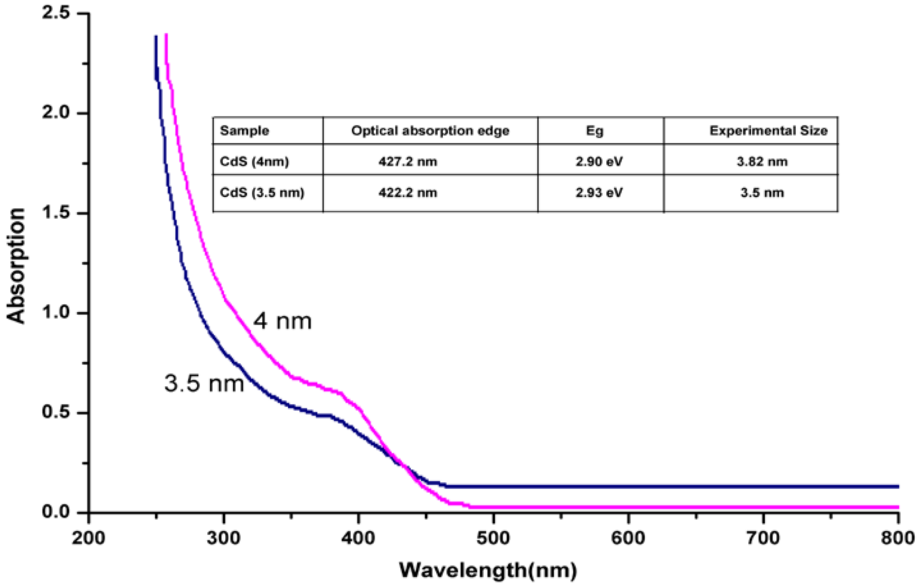
Fig. 3. (a) TEM image and (b) size distribution of colloidal Ag nanoparticles at first day (<r>=4.2nm).

Different liquids such as THF, Acetone, Ethanol and Deionized water have been used to make different concentration of colloidal solution (Table 2). Size measurement obtained from Mie theory by Loretzian fit and TEM image is compared in Table 2. From the presented results excellent agreement have found in theory and experimental whereas the diversion theory and experiment is about 0.1 nm.

Table 2. Comparison the result of theory and experimental for size measurement of Ag nanoparticles.

Liquid	Position of peak	Band width	Estimated size	TEM image
THF	411 nm	3.77×10^{14}	1.5 nm	1.6 nm
Acetone	400 nm	2.46×10^{14}	2.4 nm	2.5 nm
Ethanol	411 nm	0.8×10^{14}	10 nm	10.5 nm
Deionized water	405 nm	1.14×10^{14}	6 nm	6.5 nm

For semiconductor measurements we selected CdS nanoparticles and estimated their size from UV-Vis absorption spectra with effective mass model because these semiconductors have a large band gap and good blue shift between bulk and nano-size. We measured the optical absorption edge of two CdS samples with different size 3.5nm and 4nm, and calculated the magnitude of blue shift [28-32] with using the information of section 2.2 and Eq. 7. The results of this estimation and size measurement of these nanoparticles are in Fig. 4.



Sample	Optical absorption edge	Eg	Experimental Size
CdS (4nm)	427.2 nm	2.90 eV	3.82 nm
CdS (3.5 nm)	422.2 nm	2.93 eV	3.5 nm

Fig. 4. UV-Vis absorption spectra and absorption edge measurement for two samples of CdS. (In set Table: Result of size measurement using UV-Vis absorption and effective mass model)

5. Conclusions

In this paper we present a novel and simple method for measurement of the size of metal and semiconductor nanoparticles. For metallic nanoparticles we selected Ag nanoparticles and synthesized these particles by laser ablation method. For size measurement of metal nanoparticles, Mie theory was used and found excellent agreement with image taken from TEM observation by experimental method. For semiconductor nanoparticles we was chosen the CdS nanoparticles and same way prepared by experimental method. For size measurement, the effective mass model was used. Comparison between the result of theory and experiment has shown a good agreement for CdS nanoparticles. With this method we can be measure, also, the energy band gap of semiconductor in a simply way..

Acknowledgments

One of authors (Somaye) thanks all of her friends at Shahid Beheshti University (nanocenter), Tehran, Iran for encouragement and kindly help to perform this work.

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