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Absorbance of Iron Nanoparticles Dispersed in the Ethylene Glycol and n-Propanol

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Abstract. In the present work, the theoretical calculations of the absorbance of spherical Fe nanoparticles dispersed in the ethylene glycol and n-propanol, computed from a summation of the Mie series for different particle radius in the range from 1 to 17 nm, is presented. In both solvents, the maximum absorbance increases and the bandwidth at half-maximum absorption and number of particles decrease. Maximum absorbance of Fe nanoparticles is higher in ethylene glycol than in n-propanol. In addition, the scanning electron microscopy (SEM) and the size histograms of two samples are presented.

Keywords: plasmon absorption, Fe nanoparticles, particle radius

1. Introduction

Over the last two decades, the interest in metal nanoparticles such as Ag, Au, and Fe has grown significantly [1-4]. Metal nanoparticles show great potential in material science, physics, and chemistry fields [5]. The more general term nanoparticle includes small clusters or giant molecules and larger particles consisting of tens to hundreds of thousands of atoms and having a diameter in the range of tens to hundreds of nanometers. The word of nanoparticle is for all particles falling in the size regime of 10^{-9} m.

Nanoparticles have been studied intensively in the last decade because of their unique physical properties like magnetic, electric, optical and mechanical properties that are different from bulk materials [6-8]. Among nanoparticles, metal nanoparticles have become an important target for modern chemistry, physics, technology and bioengineering. Preparation methods of metallic nanoparticles range from chemical methods to metal vapor synthesis [9-11]. Fabrication and characterization of Fe nanoparticles has attracted considerable attention because of their significant applications in the fundamental sciences and nanotechnology.

As we know, a reduction in particle size leads to different electronic and optical properties. When a metal nanoparticle is made up, a noticeable separation in energy levels within the conduction band is observed. In fact, this energy separation increases rapidly with decreasing size [12]. Due to this energy separation, the electronic and optical properties of metal nanoparticles are different from their bulk. In the past few years, the optical properties of Fe nanoparticles have been investigated by ultraviolet-visible (UV/VIS) spectroscopy technique [13-15], because of their potential application in optoelectronics [16, 17].

It is to be noted that the Fe nanoparticles exhibit an intense absorption band in ultraviolet-visible region. Their UV/VIS spectrum, known as the surface plasmon absorption band, is produced by the movement of the conduction electrons in the particles as a consequence of the incident electric field light, which results in a displacement of the negative and positive charges in the metal. The surface plasmon absorption band properties of Fe nanoparticles depend on their size, shape, surrounding medium, coupling of the colloids and adsorbed solutes.

So far, some researchers obtained experimental information concerning to the interpretation of the absorption spectra for metal nanoparticles [18-21]. For example, Mulvaney [22] has indicated that many of the optical properties of silver nanoparticles are reasonably well understood, but there are discrepancies between the properties of these colloids prepared in water and other matrices.

In 1908, the theory of absorption and scattering of light by spherical nanoparticles has been developed by Mie [23]. Calculations of absorption spectra of metallic nanoparticles are presented as the extinction cross-section or extinction efficiency of a single nanoparticle [17, 22, 24], but for interpretation of experimental UV/VIS results, it is more useful to know the absorption spectra themselves. We know that the peak position, maximum absorbance and bandwidth at half-maximum absorption are fundamental characteristics of the surface plasmon absorption band. Knowledge of the effect that the particle size and surrounding medium have on these characteristics is needed for understanding the optical properties of metallic colloidal systems.

Transmission electron microscopy is used to know both the shape and size of nanoparticles, and when this information is combined with the theoretical-experimental surface plasmon absorption band, it is possible to characterize some interfacial phenomena and to delineate particle growth processes. In the present work, the surface plasmon absorption band of Fe nanoparticles was computed using a full summation of the Mie series for the extinction cross section of spherical Fe particles in the range of radius from 1 to 17 nm.

2. Theory and model

The problem of light absorption and scattering by small particles is described by the Mie theory. In 1908, Mie solved Maxwell's equation for an electromagnetic light wave interacting with small spheres having the same macroscopic frequency-dependent material dielectric constant as the bulk metal. The solution of this electrodynamic calculation with appropriate boundary conditions for a spherical object leads to a series of multipole oscillations for the extinction cross-section of the nanoparticles [17, 25-27]. By series expansion of the involved fields into partial waves, one obtains the following expressions for the extinction cross-section σ_{ext}, scattering cross section σ_{sca}, and the absorption cross section σ_{abs} [17]:

$$\sigma_{ext} = 2\frac{\pi}{k^2}\sum_{s=1}^{\infty}(2s+1)\,\mathrm{Re}(a_s + b_s) \tag{1}$$

$$\sigma_{sca} = 2\frac{\pi}{k^2}\sum_{s=1}^{\infty}(2s+1)(|a_s|^2 + |b_s|^2) \tag{2}$$

$$\sigma_{abs} = \sigma_{ext} - \sigma_{sca} \tag{3}$$

Re is the real part of the scattering coefficients a_s and b_s, which depend on the particle radius. Also, $k = 2\pi N / \lambda$ is the incident photon wave-*vector*. The coefficients a_s and b_s are given as

$$a_s = \frac{m\psi_s(mx)\psi_s'(x) - \psi_s'(mx)\psi_s(x)}{m\psi_s(mx)\eta_s'(x) - \psi_s'(mx)\eta_s(x)} \tag{4}$$

$$b_s = \frac{\psi_s(mx)\psi_s'(x) - m\psi_s'(mx)\psi_s(x)}{\psi_s(mx)\eta_s'(x) - m\psi_s'(mx)\eta_s(x)} \tag{5}$$

where $m = \frac{n}{n_m}$ and $x = kR$. Note that R is the sphere radius.

In above equations, n is the complex refraction index of the particle, n_m is the real refraction index of the non-absorbing surrounding medium, ψ_s and η_s are the spherical Riccati-Bessel functions. The electric and magnetic field resultant inside the sphere are expressed as a multipolar series of spherical harmonics with different symmetry. We note that $m=1$ corresponds to dipole oscillation, $m=2$ corresponds to quadrupole oscillation and so on. The complete mathematical basis has already been published in [27].

When a beam of light irradiates a metallic nanoparticle, the oscillating electric field causes a collective excitation of the conduction electrons. The displacement of the electrons against the immobile positive charges leads to the polarization of the nanoparticle. Absorption and scattering of light by the particle depend on its chemical composition, size, shape, surrounding dielectric medium, coupling of colloids and adsorbed solutes.

In the case of spherical Fe nanoparticles separated by a long distance, with clean surfaces and considering that they have iron's bulk density; their absorbance can be obtained with the following relation:

$$A = l\sigma_{ext}\frac{C_{Fe}}{101.273r^3}, \tag{6}$$

where r is the particle radius, l is the optical path length in nm, C_{Fe} is the concentration of Fe^0 in gcm^{-3}, and σ_{ext} is the extinction cross section of a single particle in nm^2.

When the particle size is smaller than the mean free path of the conduction electrons, electron-surface scattering is believed to be important as well. Therefore, the magnitude of the real $\varepsilon'(\omega)$ and imaginary $\varepsilon''(\omega)$ parts of the dielectric function of the particle are affected, and become size-dependent. Using the size effect and based on the Drude model, the size-dependent dielectric functions may be calculated with [17]

$$\varepsilon'(\omega,r) = \varepsilon'_{bulk} + \frac{\omega_p^2}{(\omega^2+\omega_d^2)} - \frac{\omega_p^2}{(\omega^2+\omega_r^2)}, \tag{7}$$

$$\varepsilon''(\omega,r) = \varepsilon''_{bulk} + \frac{i\omega_p^2\omega_r}{\omega(\omega^2+\omega_r^2)} - \frac{i\omega_p^2\omega_d}{\omega(\omega^2+\omega_d^2)}, \tag{8}$$

where ω, ω_p, and ω_d are the light frequency, the Plasmon frequency, and the bulk damping constant, respectively. In above equations, ω_r is introduced as a phenomenological damping constant. It is equal to the Plasmon absorption bandwidth for the case of a perfectly free-electron gas [17]. The damping constant ω_r is related to the lifetimes of all electron scattering processes, which are mainly electron-electron, electron-phonon and electron-defect scattering in the bulk material [17].

Supposing that the metal particle damping constant ω_r, which is the inverse of the collision time for conduction electrons, is increased because of additional collisions with the boundary of the particle, ω_r can be obtained by

$$\omega_r = \omega_d + B\frac{v_f}{r} \tag{9}$$

where v_f is the electron velocity at Fermi level, and B is the theory-dependent quantity of order 1. Using the Maxwell theory and the isotropic scattering [17], we can use a value of 1 for B.

One can obtain the surface plasmon absorption of Fe nanoparticles by using Eqs. (1) to (9). In the following, we briefly present numerical procedure to obtain our results.

i) We consider different particle radius, between 1 and 17 nm.

ii) Using the bulk metal damping constant ($\omega_d = 2.54\times10^{13}\,s^{-1}$) and the electron velocity at Fermi level ($v_f = 1.98\times10^{8}\,cm/s$), we can obtain the metal particle damping constant (ω_r) in Eq. (9).

iii) For a given light frequency (or the light wavelength), we can calculate the size-dependent dielectric functions using Eqs. (7) and (8). In equations, the value of the Plasmon frequency for Fe is $\omega_p = 1.49\times10^{16}\,s^{-1}$.

iv) We apply Esq. (1)-(6) to obtain the surface plasmon absorption of Fe nanoparticles. The value of Fe concentration is 10^{-6} g cm^{-3}.

3. Results and discussion

The surface plasmon absorption spectra of Fe nanoparticles in ethylene glycol and n-propanol are shown in Figs. 1 and 2. The results have been obtained for different particle radius, between 1 and 17 nm, and an iron concentration of 10^{-6} gcm^{-3}. It is seen from the figures that the Fe nanoparticles give a strong surface plasmon band in the visible region and that the maximum absorption is higher in ethylene glycol than in n-propanol.

The maximum absorbance of these bands increases as the particle radius increases. The absorption bands presented in Figs. 1 and 2 can be explained if one considers Eq. (6), which can also be written as

$$A(C_{ext}, r) = a\frac{C_{ext}}{r^3} \tag{6}$$

where a is a constant. According to this relation, the absorbance increases as C_{ext} increase, while an increase in the particle radius decreases the absorbance. C_{ext} determines the position of the plasmon peak and the shape of the absorption band.

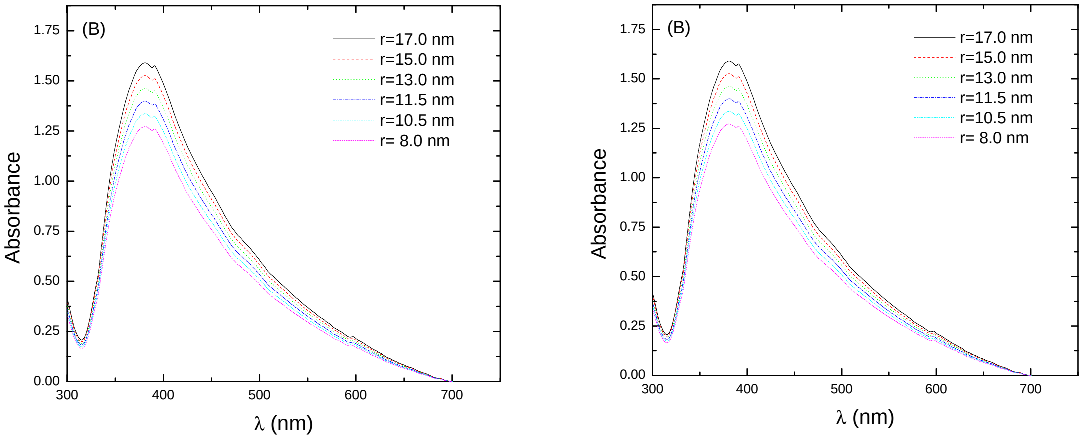

Fig. 1. The surface plasmon absorption band of iron nanoparticles as a function of wavelength λ in ethylene glycol for several particle radius: (a) r=1 nm to r=7 nm, and (b) r=8 nm to r=17 nm.

Figure 3 shows the bandwidth of the surface plasmon band of Fe at half-maximum absorption as a function of particle radius (r). It is obvious from the figure that the bandwidth decreases when the particle radius increases. It is also seen that the bandwidth also depends on the solvent (ethylene glycol or n-propanol).

Figure 4 displays the number of particles per m^3 as a function of particle radius for ethylene glycol and n-propanol. It is observed that the number of particles decreases as the particle radius increases.

It is worth mentioning that we recently produced the Fe nanoparticles in ethylene glycol and n-propanol. Fig. 5 shows the absorbance of Fe nanoparticles as a function of wavelength. It can be seen that the experimental and theoretical results (compare Fig. 5 with previous figures) have differences. These differences are due to the used equations and errors in the theoretical calculations. In particularly, Eq. (1) is valid only when the nanoparticles dispersion is sufficiently dilute.

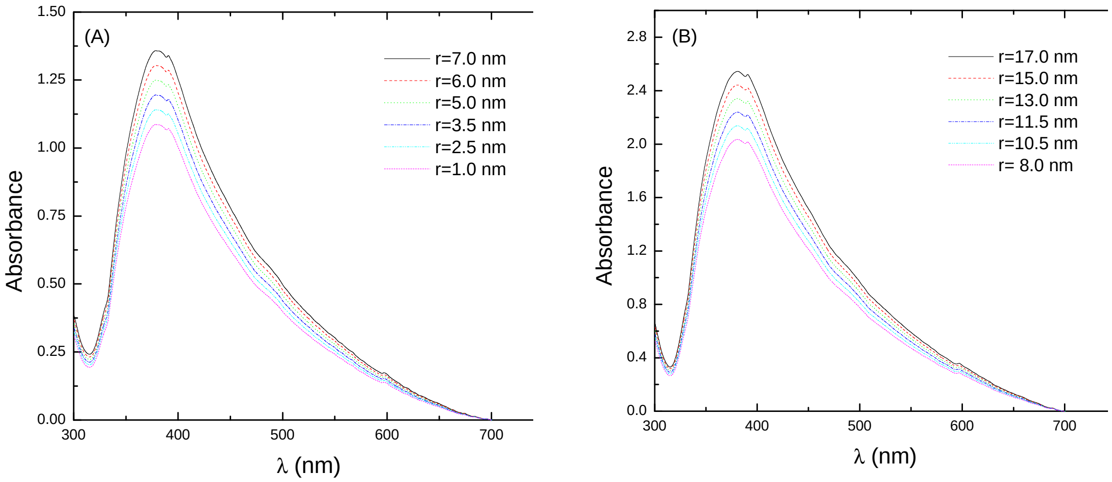

Fig. 2. The same as Fig. 1, but in n-propanol. The particle radius are (a) r=1 nm to r=7 nm, and (b) r=8 nm to r=17 nm.

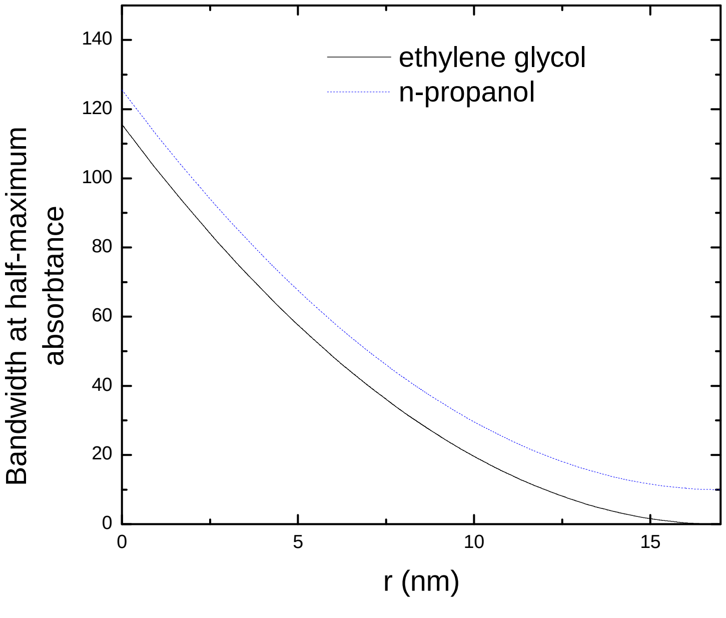

Fig. 3. The bandwidth of the surface plasmon absorption band at half-maximum absorbance as a function of particle radius in ethylene glycol and n-propanol.

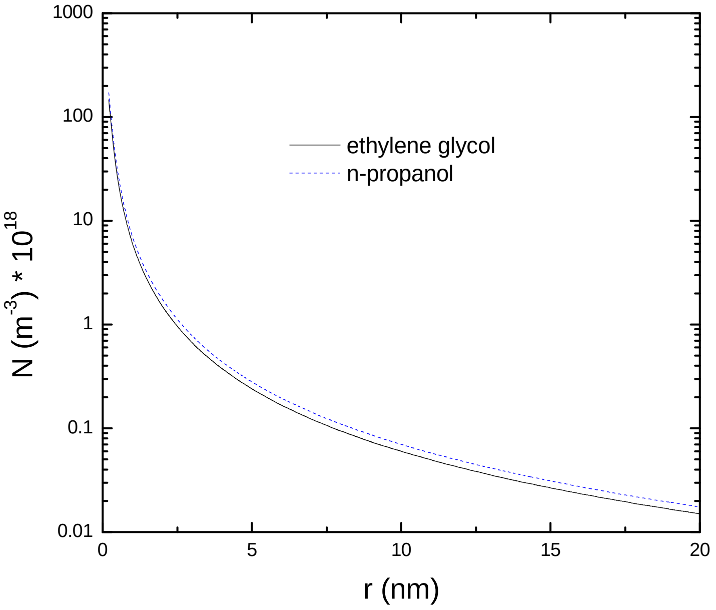

Fig. 4. Number of iron nanoparticles as a function of particle radius in ethylene glycol and n-propanol.

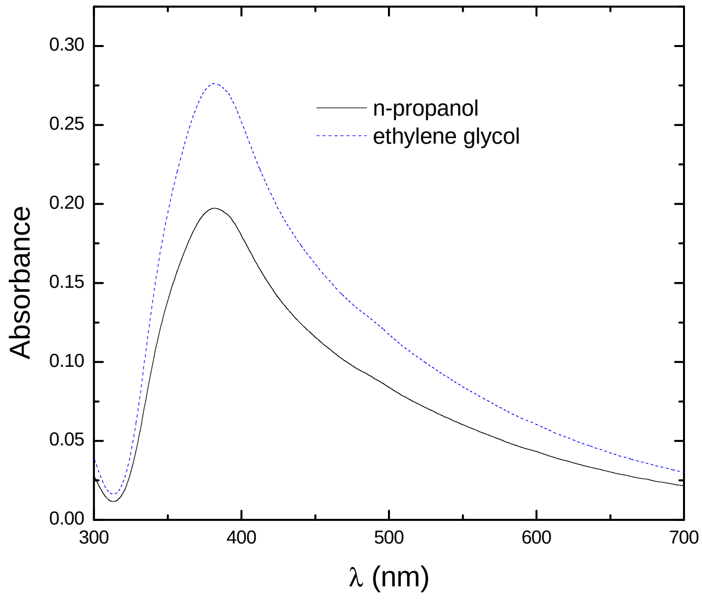

Fig. 5. Experimental UV/VIS spectra of iron nanoparticles with an average size of 4 nm, dissolved in ethylene glycol and n-propanol.

4. Conclusions

Thus, in this work, we have performed the theoretical calculations of the absorbance of spherical iron nanoparticles dispersed in ethylene glycol and in n-propanol, computed from a summation of the Mie series for different particle radius in the range from 1to 17 nm. In both solvents, the maximum absorbance increases. In addition, the bandwidth at half-maximum absorption and number of particles decreases. Maximum absorbance of Fe nanoparticles is higher in ethylene glycol than in n-propanol. These results are due to the difference in the refractive indexes of two materials.

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