

Full Length Research Paper

A study of the surface plasmon absorption band for nanoparticles

A. R. Bijanzadeh^{1*}, M. R. Vakili² and R. Khordad³

¹Department of Physics, Islamic Azad University, Firoozabad Branch, Iran.

²Department of Chemistry, Islamic Azad University, Firoozabad Branch, Iran.

³Department of Physics, Yasouj University, Yasouj, 75914-353 Iran.

Accepted 24 February, 2012

In this work, we have performed the theoretical calculations of the absorbance of spherical silver nanoparticles dispersed in deionized water and in n-propanol, computed from a summation of the Mie series for different particle radius in the range from 1 to 17 nm. In both solvents, the maximum absorbance increases and the bandwidth at half-maximum absorption and number of particles decrease. Maximum absorbance of silver nanoparticles is higher in n-propanol than in deionized water. These results are due to high refractive index of n-propanol.

Key words: Silver nanoparticles, absorbance, particle radius.

INTRODUCTION

In recent years, with advances in nanofabrication technology, a great deal of experimental interest has been devoted to study metal nanoparticles. Gold, silver, iron and cobalt nanoparticles have a significant role in science and technology (Ling and KeFu, 2007; Fan et al., 2009; Ashkarran, et al 2009; Siwach and Sen, 2008). Nanoparticles show great potential in material science, physics and chemistry fields (Zhang and Mou, 2001). Since, the carbon nanotubes (Ijima, 1991) and nanoballs (Kroto et al., 1985) were discovered for the first time, researchers have been increasingly studying new nanoparticles and nanostructures (Aliabad et al., 2012).

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 (Hwang et al., 2000; Narayanan and El-Sayed, 2003; Bjerneld et al., 2003). Among nanoparticles, metal nanoparticles have become an important target for modern chemistry, physics, technology and bio-engineering. Fabrication and characterization of silver nanoparticles has attracted considerable attention as a result of their significant applications in the fundamental sciences and

nano-technology.

The optical properties of silver nanoparticles have been extensively investigated by ultraviolet-visible (UV/VIS) spectroscopy technique (Grijalva et al., 2005; Liu et al., 2003; Wilcoxon et al., 2001; Cai et al., 2001), because of their potential application in opto-electronics (Hughes and Jain, 1979; Kreibig and Vollmer, 1995).

It can be noted that the silver nanoparticles exhibit an intense absorption band in UV/VIS 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 silver nanoparticles depend on their size, shape, surrounding medium, coupling of the colloids and adsorbed solutes.

So far, some researchers obtained experimental information concerning the interpretation of the absorption spectra for ionic silver clusters (Linnert et al., 1990; Gutierrez and Henglein, 1993; Janata et al., 1994; Ershov et al., 1993). For example, Mulvaney (1996) 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. Mie (1908) developed the theory of absorption and scattering of light

*Corresponding author. E-mail: bijanzadehalireza@yahoo.com.

by spherical nanoparticles. Calculations of absorption spectra of metallic nanoparticles are presented as the extinction cross-section or extinction efficiency of a single nanoparticle (Kreibig and Vollmer, 1995; Mulvaney, 1996; Creighton and Eadon, 1991), 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 the fundamental characteristics of the surface plasmon absorption band. The knowledge of the effect that the particle size and surrounding medium have none of 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 silver nanoparticles was computed using a full summation of the Mie series for the extinction cross section of spherical silver particles in the range of radius from 1 to 17 nm.

THEORY AND MODEL

As we know, nanoscale materials are offering new opportunities to photonics, because of their enhanced linear and nonlinear optical properties and because of the ability to convert light into other forms of energy, as surface plasmons excitations. For these reasons, silver nanoparticles are key materials in nanophotonics (Amendola, 2008).

Collective oscillation of conduction electrons in metals are known as plasmons. According to the Fermi liquid model, plasmons can be satisfactorily described as a negatively charged electron cloud displaced from its equilibrium position around a lattice made of positively charged ions, in analogy to real plasma.

Several models are used to describe the surface plasmon absorption (SPA). One of the models is the Mie theory. In the last 99 years, Mie theory has been successfully applied to the calculation of noble metal nanoparticles extinction cross section. Gustav Mie solved the problem of light diffraction by a single sphere using classic electrodynamics. In Mie theory, there are three cross sections as (Mie, 1908):

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

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

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

where σ_{ext} is the extinction cross section, σ_{sca} is the scattering

cross section and σ_{abs} is the absorption cross section. 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:

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

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

$m = \frac{n}{n_m}$ where n_m and $x = kR$. Note that R is the sphere radius. In these equations, n is the complex refractive index of the sphere, n_m is the real refractive 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 dipolar sphere excitation, $m=2$ corresponds to quadrupolar oscillation, etc.

The complete mathematical basis has already been published in Bohren and Huffman (1998). 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 metal spheres, excitations due to photons electric field are plasmons-polaritons, while those due to photons magnetic field are electric currents. The UV/Vis absorption spectrum of N identical metal nanoparticles for unit volume can be determined by the extinction cross section. In the case of spherical silver nanoparticles separated by a long distance, with clean surfaces and considering that they have silver's bulk density, their absorbance can be obtained with the following relation:

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

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

Contrary to extrinsic size effects on the extinction cross section, that are bare electromagnetic phenomena, intrinsic size effects are only due to the dependence of metal dielectric constant on the size. When the particle size is smaller than the mean free path of the conduction electrons, the magnitude of the real $\epsilon'(\omega)$ and

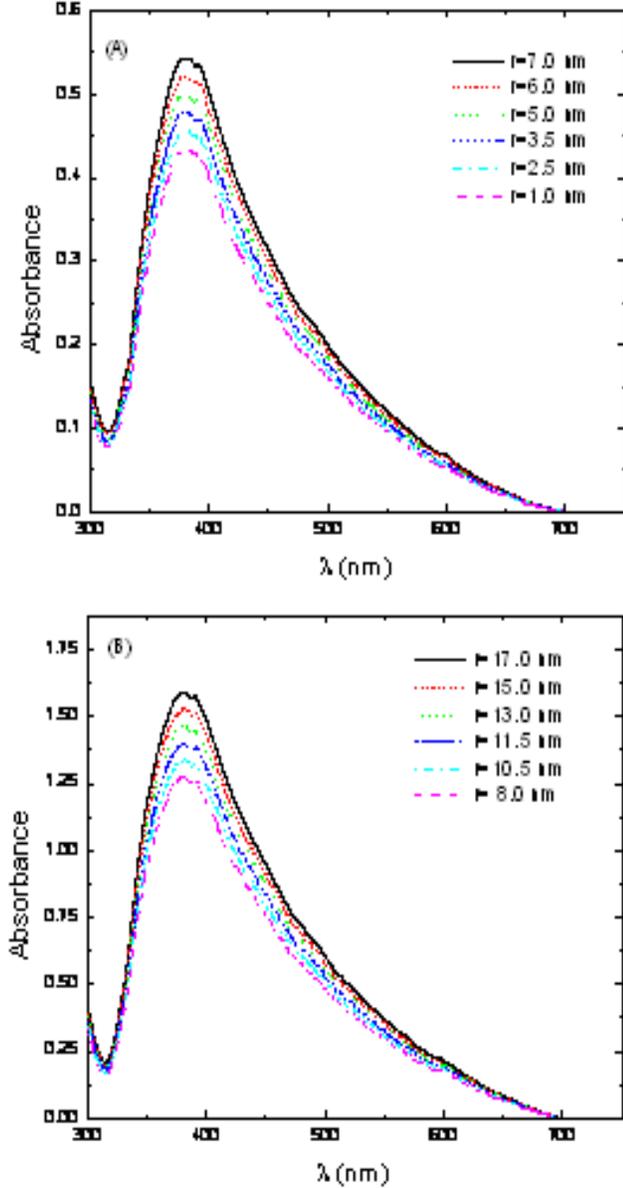


Figure 1. The surface plasmon absorption band of silver nanoparticles as a function of wavelength λ in deionized water for several particle sizes.

imaginary parts $\varepsilon''(\omega)$ of the dielectric function of the particle is affected, and become size-dependent. Using the size effect and based on the Drude model, the size-dependent dielectric functions may be calculated with (Kreibig and Vollmer, 1995):

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

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

frequency and the bulk metal damping constant, respectively.

Suppose 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:

$$\omega_r = \omega_d + B \frac{v_f}{r} \quad (9)$$

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, we can apply a value of 1 for B (Kreibig and Vollmer, 1995). One can obtain the surface plasmon absorption of silver nanoparticles by using Equations 1 to 7. In the following, we briefly present numerical procedure to obtain our results.

- 1) We consider different particle radius, between 1 and 17 nm.
- 2) Using the bulk metal damping constant ($\omega_d = 2.67 \times 10^{13} \text{ s}^{-1}$) and the electron velocity at Fermi level ($v_f = 1.39 \times 10^8 \text{ cm/s}$), we

can obtain the metal particle damping constant (ω_r) in Equation 9.

- 3) For a given light frequency (or light wavelength), we can calculate the size-dependent dielectric functions using Equations 7 and 8. In the equations, the value of the plasmon frequency for silver is $\omega_p = 1.37 \times 10^{16} \text{ s}^{-1}$

- 4) Finally, we apply Equations 1 and 4 to 6 to obtain the surface plasmon absorption of silver nanoparticles. The value of silver concentration is 10^5 g/cm^3 .

RESULTS AND DISCUSSION

The surface plasmon absorption spectra of silver nanoparticles in deionized water and n-propanol are as shown in Figures 1 and 2. The results have been obtained for different particle sizes, between 1 and 17 nm, and a silver concentration of 10^{-6} g/cm^3 . As seen from the figures, that the silver nanoparticles give a strong surface plasmon band in the visible region, centered at wavelengths between 395 and 425 nm, and that the maximum absorption is higher in n-propanol than in deionized water. It can noted that our results are in agreement with previous theoretical calculations (Grijalva et al., 2005). Grijalva et al. (2005) calculated the surface plasmon absorption band for silver nanoparticles suspended in water and ethylene glycol with a silver concentration of 10^{-5} g/cm^3 . They obtained a strong surface plasmon absorption in the visible region, centered at wavelengths between 395 and 445 nm, for different particle sizes between 3 and 80 nm. In other previous works (Cai et al., 2001; Liu et al., 2003; Wilcoxon et al., 2001), we found the experimental data for the optical absorption spectra of silver nanoparticles. The experimental results showed that the absorption spectra were centered at wavelengths from 395 to 510

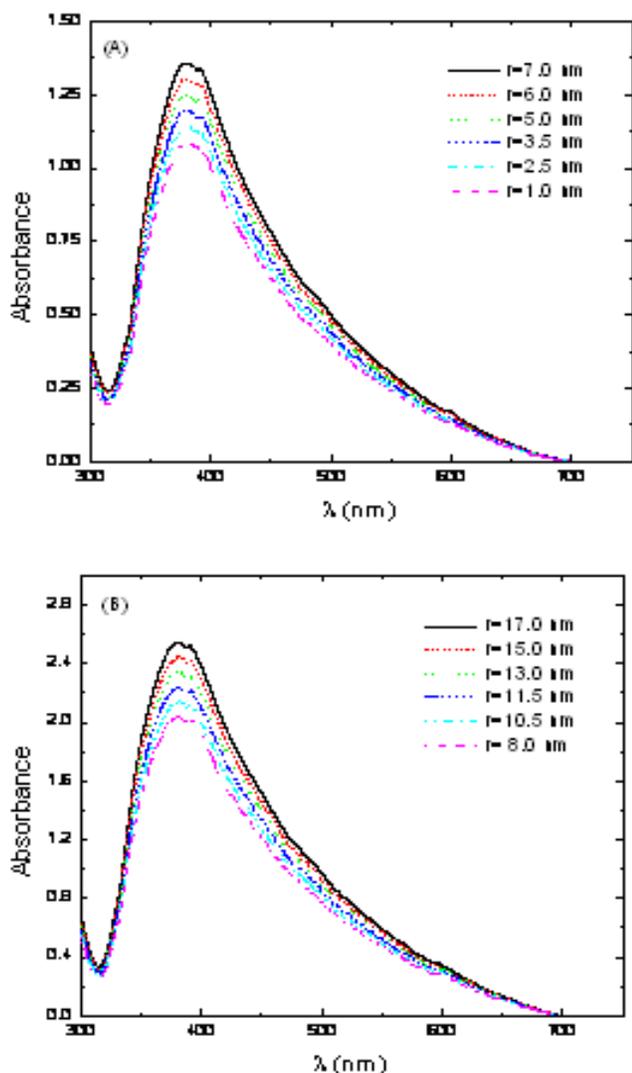


Figure 2. surface plasmon absorption band of silver nanoparticles as a function of wavelength λ in n-propanol for several particle sizes,

nm. The absorption spectra around 510 nm has been observed for the silver sol with different transition metal cations like Cd^{2+} , Cr^{3+} , Cu^{2+} and Zn^{2+} .

The maximum absorbance of these bands increases as the particle radius increases. The absorption bands presented in Figures 1 and 2 can be explained if one considers Equation 1, which can also be written as:

$$A(C_{ext}, r) = a \frac{C_{ext}}{r^3} \tag{10}$$

where a is a constant. According to this relation, the absorbance increases as C_{ext} increases, while an

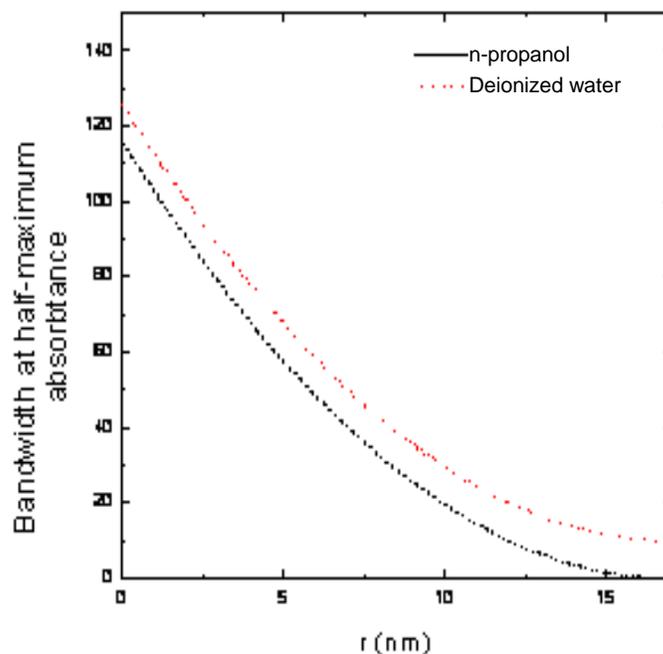


Figure 3. The bandwidth of the surface plasmon absorption band at half-maximum absorbance as a function of particle radius in deionized water and n-propanol.

increase in the particle radius decreases the absorbance.

C_{ext} determines the position of the plasmon peak and the shape of the absorption band.

Figure 3 shows the bandwidth of the surface plasmon band of silver 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 can also be seen that the bandwidth also depends on the solvent (water or n-propanol). Similar calculations have been performed for silver nanoparticles with different sizes between 3 and 80 nm suspended in water and ethylene glycol (Grijalva et al., 2005). It can be seen from the figure that our results are in agreement with previous work (Grijalva et al., 2005).

Figure 4 displays the number of particles per m^3 as a function of particle radius for deionized water and n-propanol. It was observed that the number of particles decrease as the particle radius increases from 1 to 20 nm. The decrease of particle numbers for water is from 2.5×10^{20} to 4.0×10^{17} . This decrease for n-propanol is from 2.6×10^{20} to 6.0×10^{17} . We note that for the used particle concentrations, the separation between particles is approximately 50 and 60 times the particle diameter. This value is about 4 and 7 times higher than the value reported by Creighton and Eadon (1991). They reported their results for metallic nanoparticles, in general, without specifying the type of metal. Our results are fairly in agreement with the obtained results for the silver

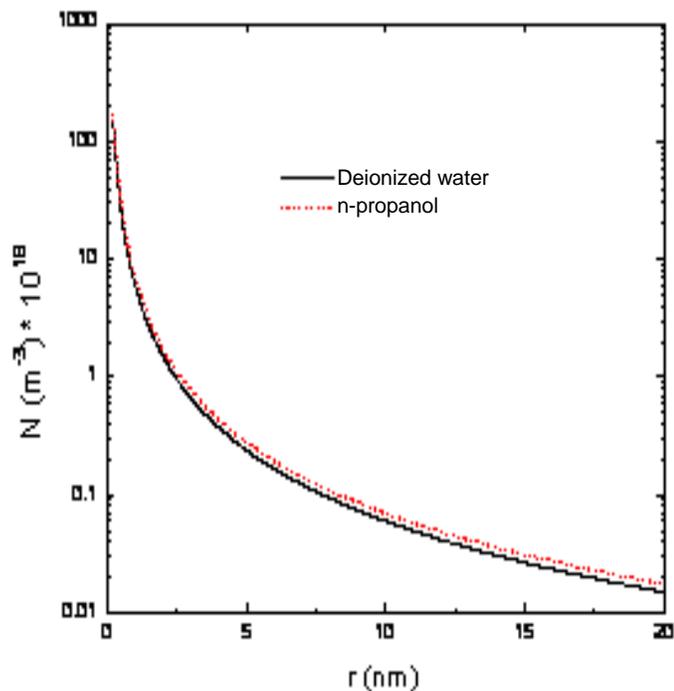


Figure 4. Number of silver nanoparticles as a function of particle radius in deionized water and n-propanol.

nanoparticles suspended in ethylene glycol (Grijalva et al., 2005).

To check the applicability of Equation 1 for explaining the experimental UV/VIS spectra of silver dispersion, we recently produced the silver nanoparticles by spark method in deionized water and n-propanol and obtained the nanoparticles with an average diameter of 4 nm. The results for the silver nanoparticles in deionized water have been reported in the work of Khordad et al. (2012). Figure 5 shows the absorbance of silver nanoparticles as a function of wavelength. It can be seen that the experimental and theoretical results have differences. This difference is due to the used equations and errors in the theoretical calculations. For example, Equation 1 is valid only when the nanoparticles dispersion is sufficiently dilute.

Conclusion

In the present paper, we tried to study the surface plasmon absorption band for silver nanoparticles suspended in deionized water and n-propanol. For this purpose, we first used a theoretical procedure based on a summation of the Mie series. Then, we calculated this series for different nanoparticle sizes between 1 and 17 nm. We applied two different solvents, deionized water and n-propanol, in our theoretical calculations. According to the results, it was deduced that: (1) the maximum absorbance increases when the particle sizes increase

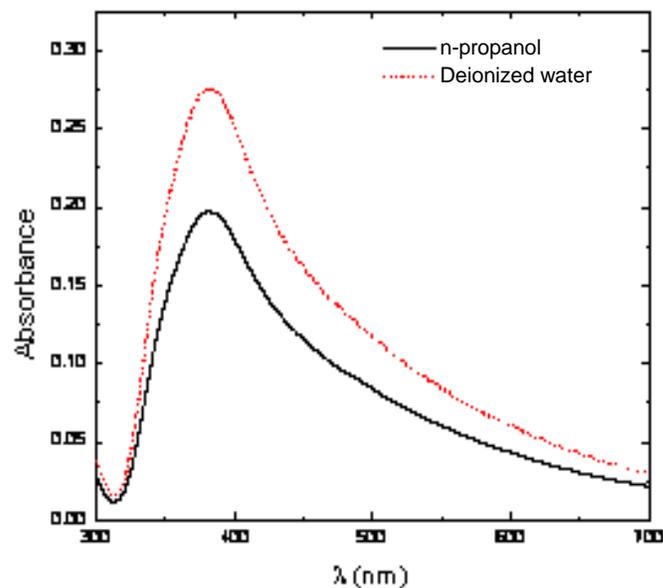


Figure 5. Experimental UV/VIS spectra of silver nanoparticles with an average size of 4 nm, dissolved in deionized water and n-propanol.

for both solvents, (2) by increasing the particle size, the bandwidth at half-maximum absorbance and number of particles decrease for both solvents, (3) the results obtained for n-propanol (maximum absorbance, the bandwidth at half-maximum absorbance and number of particles) are higher than the deionized water. These differences are due to high refractive index of n-propanol.

ACKNOWLEDGEMENT

This work was financially supported by the Islamic Azad University, Firoozabad Branch, under Grant No. 51293880310001.

REFERENCES

- Aliabad HAR, Arabshahi H, Aliabadi AH (2012). The effect of Hubbard potential on effective mass of carriers in doped Indium oxide. *Int. J. Phys. Sci.*, 7: 696-708.
- Amendola DV (2008). Synthesis of gold and silver nanoparticles for photonic Applications. PhD thesis.,
- Ashkarran AA, Irajizad A, Mahdavi SM, Ahadian MM (2009). ZnO nanoparticles prepared by electrical arc discharge method in water. *Mater. Chem. Phys.*, 118: 6-8.
- Bjorneld EJ, Svedberg F, Kall M (2003). Laser-induced growth and deposition of noble-metal nanoparticles for surface-enhanced Raman scattering. *Nano Lett.*, 3: 593-596.
- Bohren CF, Huffman DR (1998). 'Absorption and Scattering of Light by Small Particles.' New York: Wiley, p. 275.
- Cai W, Hofmeister H, Rainer T (2001). Surface effect on the size evolution of surface plasmon resonances of Ag and Au nanoparticles dispersed within mesoporous silica. *Phys. E.*, 11: 339-344.
- Creighton JA, Eadon DG (1991). Ultraviolet-visible absorption spectra of the colloidal metallic elements. *J. Chem. Soc. Faraday Trans.*, 87: 3881-3891.

- Ershov BG, Janata E, Henglein A, Fojtik A (1993). Silver atoms and clusters in aqueous solution: Absorption spectra and the particle growth in the absence of stabilizing Ag⁺ ions. *J. Phys. Chem.*, 97: 4589-4594.
- Fan HM, You GJ, Li Y, Zheng Z, Tan HR, Shen ZX, Tang SH, Feng YP (2009). Shape-controlled synthesis of single-crystalline Fe₂O₃ hollow nanocrystals and their tunable optical properties. *J. Phys. Chem. C.*, 113: 9928-9935.
- Grijalva AS, Urbina RH, Silva JFR, Borja MA, Barraza FFC, Amarillas AP (2005). Classical theoretical characterization of the surface plasmon absorption band for silver spherical nanoparticles suspended in water and ethylene glycol. *Phys. E*, 27: 104-112.
- Gutierrez M, Henglein A (1993). Formation of colloidal silver by "push-pull" reduction of silver (1+). *J. Phys. Chem.*, 97: 11368-11370.
- Hughes AE, Jain SC (1979). Metal colloids in ionic crystals. *Adv. Phys.*, 28: 717-828.
- Hwang CB, Fu YS, Lu YL, Jang SW, Chou PT, Wang CRC, Yu SJ (2000). Synthesis, characterization, and highly efficient catalytic reactivity of suspended palladium nanoparticles. *J. Catal.*, 195: 336-341.
- Iijima S (1991). Helical microtubules of graphitic carbon. *Nature*, 354: 56-58.
- Janata E, Henglein A, Ershov BG (1994). First clusters of Ag⁺ ions reduction in aqueous solution. *J. Phys. Chem.*, 98: 10888-10890.
- Khordad R, Vakili MR, Bijanzadeh AR (2012). Investigation of size distribution of silver nanoparticles. *Superlatt. Microstruc.*, 51: 223-231
- Kreibig U, Vollmer M (1995). 'Optical Properties of Metal Clusters.' New York: Springer, p. 335.
- Kroto HW, O'Brein SR, Curl RF, Smalley RE (1985). C₆₀: Buckminsterfullerene. *Nature*, 318: 162-163.
- Ling FX, KeFu Y (2007). Structural and magnetic properties of Fe₃O₄ nanoparticles prepared by arc-discharge in water. *Chin. Sci. Bull.*, 52: 2866-2870.
- Linnert T, Mulvaney P, Henglein A, Weller H (1990). Long-lived nonmetallic silver clusters in aqueous solution: Preparation and photolysis. *J. Am. Chem. Soc.*, 112: 4657-4664.
- Liu GY, Liu C, Chen L, Zhang Z (2003). Adsorption of cations onto the surfaces of silver nanoparticles. *J. Colloid Interf. Sci.*, 257: 188-194.
- Mie G (1908). Contribution to the optics of turbid media, particularly of colloidal metal solutions. *Ann. Phys.*, 25:377-445.
- Mulvaney P (1996). Surface plasmon spectroscopy of nanosized metal particles. *Langmuir*, 12: 788-800.
- Narayanan R, El-Sayed MA (2003). Effect of catalysis on the stability of metallic nanoparticles: Suzuki reaction catalyzed by PVP-palladium nanoparticles. *J. Am. Chem. Soc.*, 125: 8340-8347.
- Siwach OP, Sen P (2008). Fluorescence properties of Fe nanoparticles prepared by electro-explosion of wires. *Mater. Sci. Eng. B.*, 149: 99-104.
- Wilcoxon JP, Martin JE, Provencio P (2001). Optical properties of gold and silver nanoclusters investigated by liquid chromatography. *J. Chem. Phys.*, 115: 998-1008.
- Zhang LD, Mou JM (2001). *Nano-Material and Nanostructure*. Beijing: Sci. Press, p. 115. In Chinese.'