Solvatochromic behavior of gold nanoparticles in different solvents

Al-Sayed Abdel-Majied Al-Sherbini

Department of environmental, Photochemical and Agriculture Applications,
National Institute of Laser Enhanced Science (NILES) Cairo University, Cairo-12631 (EGYPT)
E-mail : elsayed_s2000@yahoo.com
Received: 3rd March, 2008 ; Accepted: 10th March, 2008

ABSTRACT

Gold nanoparticles were prepared in different solvents of different polarities by laser-induced breakdown of the gold metal plate. The results showed that the position of the surface plasmon bands depends on the optical dielectric constant (ε_m) and dielectric permittivity (ε_o) with respect to the polarity of the medium. In polar solvents a blue shift was observed when we go from water ($\varepsilon_m = 1.77$, $Z = 94.6$, $\varepsilon_o = 78.3$) to butanol ($\varepsilon_m = 1.97$, $Z = 77.7$, $\varepsilon_o = 17.5$) while in nonpolar solvents the blue shifts are observed when we go from THF ($\varepsilon_m = 1.98$, $Z = 58.8$, $\varepsilon_o = 7.5$) to cyclohexane ($\varepsilon_m = 2.03$, $Z = 60.1$, $\varepsilon_o = 2.02$). The Particle sizes were determined by using transmission electron microscope(TEM).   © 2008 Trade Science Inc. - INDIA

INTRODUCTION

Ultrafine noble metal particles have been prepared by various methods and studies of their physicochemical properties have been a very active field of research due to their potential applications not only in the field of catalysts but also in the development of efficient sensors, drug deliverers, optoelectronics, and magnetic devices[1-5]. They exhibit new optical properties[6] which are neither observed in molecules nor in bulk metals. In particular, optical properties of metallic nanoparticles have been extensively studied since they strongly absorb light in the visible region, caused by the surface plasmon oscillation modes of conduction electrons that are coupled through the surface to external electromagnetic field. In fact, the color of the noble metal nanoparticles is known to depend on both the sizes and shapes of the particles as well as on the refractive index of the surrounding medium[1,7-9]. The wavelength and absorbance of the spectrum are also reported to depend on the nature and the concentration of the species[10,11]. Most of the early studies in the area of metal clusters have focused on the preparation of gold colloids in aqueous media. Colloidal gold prepared in aqueous medium, by chemical reduction, are usually capped with anions (e.g., citrate), and the negative surface charges provide the repulsive force between the particles, which prevents them from agglomeration[12].

The study of nanoparticles in various solvents were carried out to extend their application capabilities upon derivatives with organic molecules[1,13,14]. For instance alkanethiolization of metal nanoparticles occurs by forming a covalent bond between the sulfur atom of alkanethiol and the surface of particles or with chemisorbing to the metal particle by donating electron cloud to the thiolate functional group[13].

In the present study, we report the experimental observations of gold nanoparticles by laser ablation of

Full Paper

a gold metal plate in different solvents of different physical properties.

EXPERIMENTAL

Gold nanoparticles were prepared by laser ablation of a metal gold plate in aqueous micellar solution of cetyltrimethyl ammonium bromide (CTAB), (Fluka) and in different solvents, (Fluka). The solvents used were of spectroscopic quality. Double distilled water was used. The solvents parameters were taken from the literature[20,21]. As shown in figure (1), the gold plate (>99.9%) was placed on the wall of a glass tube filled with 3mL of a solvent. Laser pulses (τ = 8 ns at 10 HZ) from a Nd-YAG laser (continuum SLI-10) at λ = 1064 nm were focused onto the surface of a gold plate using a fused silica cylindrical lense (p = 100nm). The focused region on the gold plate has a rectangular shape of 6 nm leng and 0.5 nm wide. The position of the laser beam on the surface of the pre polished metal plate could be varied, to obtain a fresh surface and help to provide ~ homogeneous nanoparticles. The energy of Nd-YAG laser was 100 mJ/pulse measured by power energy meter (molectron-EPM 2000:Tar5). The colored solution was measured by *Perkin Elmer Lmbda-40* spectrophotometer after irradiation with the laser beam. Transmission electron microscopy (TEM) of the produced samples was formed by drying a drop of the solution on a carbon-coated copper grid. Particles sizes were determined from the micrographs of the Joel-100S transmission electron microscope, of resolution of 0.3 nm.

RESULTS AND DISCUSSION

The spherical gold nanoparticles were prepared following a method introduced by Turkevich[15]. It is well known that, the optical absorption spectra of gold nanoparticles is due to of the surface plasmon (SP) resonance band(s) and the nanoparticles of 5-50 nm showed a sharp band in the 520-530 nm region[16]. As the particles grow bigger or agglomerated, the absorption band broadens and covers the whole visible range[17]. Figure (2a) showes that, the spherical gold nanoparticles prepared by the chemical method[15] have only one plasmon absorption band $\lambda_{max.}$ = 524 nm without a detectable broad band at longer wavelength of the visible region.
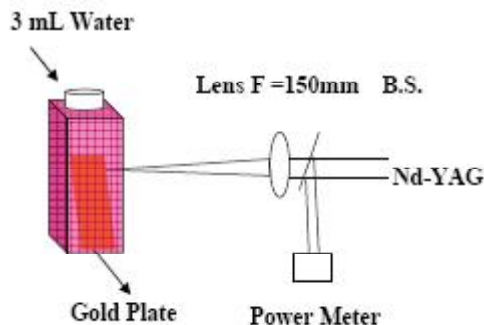

Figure 1 : Schematic diagram of the experimental set up

TABLE 1: The different solvent parameters

	Solvents	λ_{max}(nm)	z	ε_o	ε_m
1.	Water	522	94.6	78.3	1.77
2.	Methanol	524	83.6	32.7	1.76
3.	Isopropanol	537	76.3	21.6	1.89
4.	Butanol	538	77.7	17.5	1.97
5.	Dmso	539	70.2	46.6	2.18
6.	Acetone	534	65.7	20.75	1.84
7.	Chloroform	555	63.2	4.81	2.08
8.	Cyclohexane	550	60.1	2.03	2.03
9.	Thf	591	58.8	7.58	1.98

Z = Solvent polarity, ε_o = dielectric permittivity, ε_m = optical dielectric constant

1. Effect of optical dielectric constant ($\varepsilon\infty, \varepsilon_m$)

The absorption spectra of gold nanoparticles prepared by laser ablation in different solvents are characterized by different position of the maximum absorption bands depending on the collection bands of the gold nanoparticles and the optical dielectric constant of the surrounding medium($\varepsilon\infty, \varepsilon_m$) as shown in TABLE 1, figure (2b). The figure showes only one absorption band for water similar to that prepared by Turkevich[15]. It is documented that, the plasmon absorption of the gold nanoparticles is sensitive to both dielectric constants and refractive indexes of the surrounding solvents[17]. In addition the surface plasmon position may depend on the polarity as well as the ability of the solvent to donate or accept electrons. The greater the value of the solvent polarity, the smaller the is interaction between the particles. This might be due to the fact that the interaction between the particles and the polar solvent is more favorable than particle-particle interaction. The shape and size of the nanoparticles are affected and accordingly the absorption band broadens[18]. The position of the plasmon absorption band can be discussed within the framework of Drude model[19]. According to Drude model, the surface plasmon peak position for a

Full Paper

spherical particle depends on the refractive index of the surrounding medium[17,19].

$$\lambda^2 = \lambda_p^2 (\varepsilon\infty + 2\varepsilon_m) \qquad (1)$$

since

$$E_T = hc/\lambda = 2.859 \times 10^{-3}\, \nu \qquad (2)$$

where E_T is the observed transition energy in kilocalories, ν is the wave number in cm^{-1}[20]. So, the equation could be calculated depending on the transition energy as follow:

$$E_s^2 = E_p^2 (\varepsilon\infty + 2\varepsilon_m)^{-1} \qquad (3)$$

Where E_s is the energy of the surface plasmon band, E_p is the energy of the bulk plasma band, $\varepsilon\infty$ is the high-frequency dielectric constant due to inter-band and core transitions, and ε_m is the optical dielectric constant (medium dielectric constant, $n = (\varepsilon_m)^{1/2}$). The reciprocal of both dielectric constants illustrate the sensitivity of the maximum absorption position toward the observed energy of the surface plasmon resonance of the nanoparticles. Figure 3 shown the Plot of the square of the observed energy of the maximum position of the surface plasmon bands of the gold nanoparticles in different solvents as a function of reciprocal of the double optical dielectric constants. A remarkable red shift is observed showing that the optical dielectric constant of the medium influences the energy of the surface plasmon of the nanoparticles according to eq.(3). The results observed in the figure illustrated that the solvents could be divided to two categories depending on the refractive index and accordingly on the high frequency dielectric constants and the solvent polarity with respect to the hydrogen bond donor(protic) and acceptor(aprotic) solvents. In case of protic solvents, the nanoparticles showed red shifts ~33 nm with increasing the optical dielectric constant and decreasing the solvent polarity. The red shifts observed when we go from water, $\lambda_{max.} = 522$ nm ($\varepsilon_m = 1.77$, $Z = 94.6$) to butanol ($\varepsilon_m = 1.97$, $Z = 77.7$) and CHCl$_3$($\varepsilon_m = 2.085$, $Z = 63.2$). It is of interest to illustrate that the solvents which contain OH group is more favorable to interact with the nanoparticles than nonoparticles-nanoparticles interaction preventing them from the aggregation, figure (2b). In contrary to chloroform, which has low polarity and remains inert, with no noticeable chemical interactions with the gold surface, such aggregation was observed. In case of aprotic solvents the figure shows red shifts of ~ 52 nm with decreasing both the optical dielectric constant and the solvent polarity. This shifts was
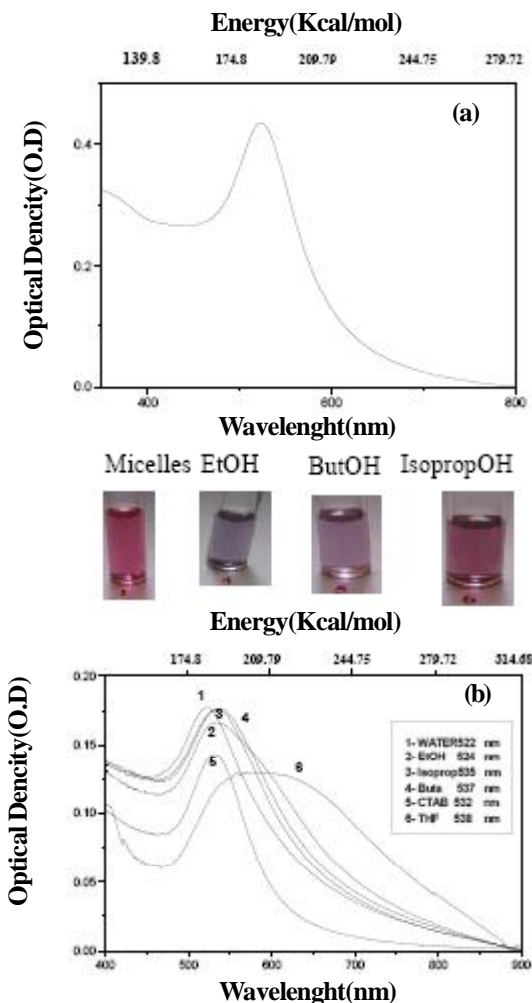

Figure 2: (a) Optical absorption spectra of the spherical nanoparticles prepared by sodium citrate, (b) : Optical absorption spectra of the nanoparticles prepared by laser ablation in different solvents
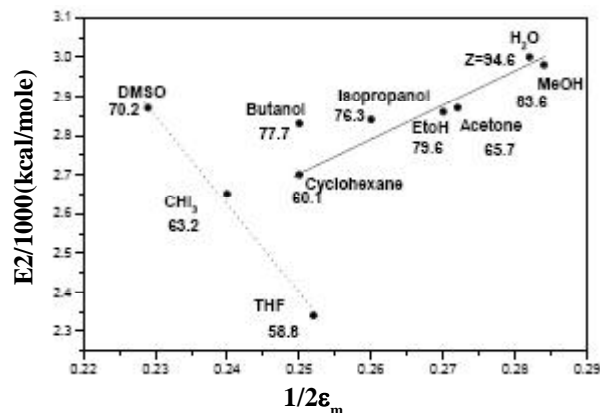

Figure 3 : Normalized surface energy of the surface Plasmon absorption bands of the gold nanoparticles in different solvents as a function of reciprocal of the double of the optical dielectric constant.
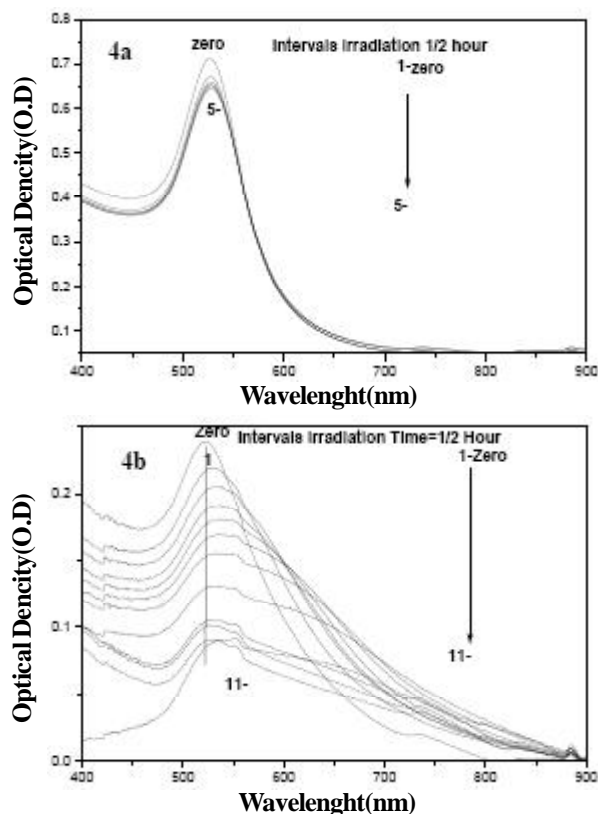
Nano Science and Nano Technology
An Indian Journal

Full Paper

Figure 4 : Absorption bands of the gold nanoparticles in (a) miceller solution and in (b) water at different irradiation time(1/2 hour)
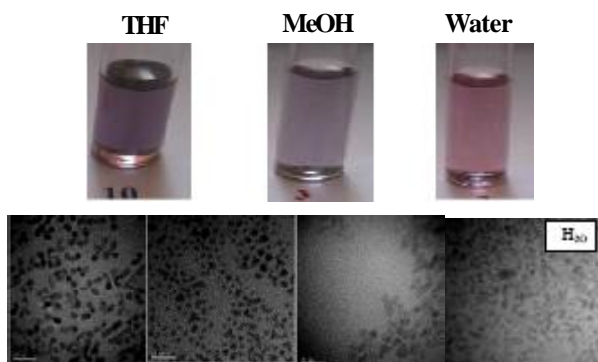

Figuer 5 : TEM of the gold nanoparticles in different solvents

observed when we go from DMSO ($\varepsilon_m = 2.18$, Z = 70.2),cyclohexane ($\varepsilon_m = 2.03$, Z = 60.1) to THF ($\varepsilon_m = 1.98$, Z = 58.8). As shown in the figure (2b) the absorption spectra of nanoparticles in tetrahydrofuran, cyclohexane and DMSO showed broad absorption spectra extended to 900 nm region. The absorption maximum was at 591nm, 550 and 539 nm respectively and the half-height width of the band was ~100 nm.

The broadening of the spectral line may be due to the particle-particle interaction since in aprotic solvent the ability of the aggregation of the nanoparticles is more favorable than the interaction between the solvent molecules and the nanoparticles. Some results (17) illustrated that there is interaction between nanoparticles and nopaolar solvent molecules preventing the nanoparticles from aggregations. This may be due to the differences between the two methods of the prepared nanoparticles. In case of the chemical method, the capping materials prevent the nanoparticles from aggregation such results illustrated that the nanoparticles changed from metallic state to ionic state in some solvents or with raising the temperatures[24]. While incase of laser ablation the metallic nanoparticles are stable under the observed conditions. In addition, features study on the effect of UV-light on the gold nanoparticles showed that no changes in the optical density in case of the chemical method while an aggregation is observed in case of laser ablation method as clear from figure 4(a,b).

Figure 5 showed a significant aggregation in case of metallic nanoparticles after irradiating with UV-light in aqueous solution,

The same results were observed in case of cyclohexane which has a poor hydrogen bond donor acceptor with low polarity (Z=60.1). Particles aggregation were seen in the TEM, figure 5 where the nanoparticles appear as rods or clusters compared with water and MeOH which appear as sphericals with a slight aggregation in case of MeOH, the aggregation appeared as a shoulder at around 650 nm in the absorption spectra. Indeed the aggregation of the nanoparticles in nonpolar solvents (THF, $CHCl_3$, Cycloheane) was observed due to sedimentation within several days after the preparation.

2. Effect of dielectric permittivity (ε_o)

It is of interest to consider the effect of dielectric permittivity (ε_o) of the medium on the spectral position of the gold nanoparticles. This is because the surface plasmon resonance depends on the polarity of the solvent. Since, the most common measure of solvent polarity is the low frequency dielectric constant ε_0 (dielectric permittivity). The greater the value of the solvent polarity, the greater the interaction between the particles and the polar solvent. The Plot of the square of
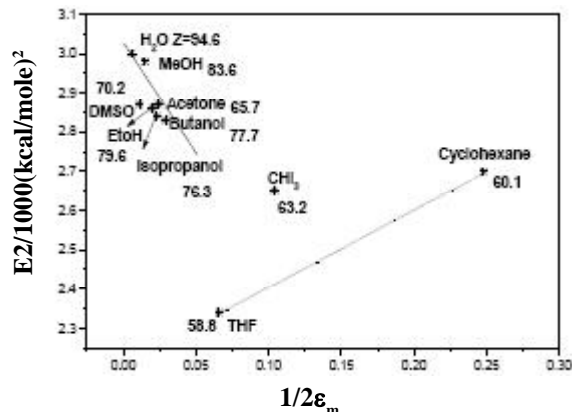
$\rightarrow$ *Full Paper*

Figure 6 : Normalized surface energy of the surface Plasmon absorption bands of the gold nanoparticles in different solvents as a function of reciprocal of the double medium dielectric permittivity (ε_o)

the observed energy of the maximum position of the surface plasmon bands of the gold nanoparticles in different solvents as a function of reciprocal of the double of the dielectric permittivity (ε_o)is shown in figure 6. The results showed that the position of the surface plasmon band depends on the surrounding medium and the polarity. In polar solvents red shifts were observed accompanying the decrease of the dielectric permittivity (ε_o) where the spectral bands show a slight aggregation. The red shift of about 16 nm when we go from water ($\lambda_{max.} = 522$ nm and $\varepsilon_o = 78.3$) to butanol ($\lambda_{max.} = 538$nm and $\varepsilon_o = 17.5$) can be ascribed to the interaction between the gold nanoparticles and the polar solvents. DMSO showed some aggregation which may be due to that DMSO ia an aprotic solvent. In nonpolar solvent such as THF, $CHCl_3$ and cyclohexane the normalized curve shows a red shift with increasing the dielectric permittivity (ε_o) on the contrary of polar solvents. The changes indicate that the surface plasmon position band of the gold nanoparticles depends on both the static and the dynamic dielectric constants[22]. Al-sherbini studied the effect dielectric constants of binary solvents at different ratio volume/volume (v/v) on the gold nanorods and the results showed that the longitudinal plasmon band depends on the both $\varepsilon\infty$ and ε_o dielectric constants[23].

In conclusion the surface plasmon bands of the gold nanoparticles depends on both dielectric properties ($\varepsilon\infty$ and ε_m) as well as on ε_o dielectric constants and the polarity.

REFERENCES

[1] Chil Seong Ah, Hyouk Soo Han, Kwan Kim, Du-Jeon; Pure.Appl.Chem., **72**, 91 **(2000)**.

[2] G.Schmid, H.West, H.Mehles, A.Lehnert; Inorg. Chem., **36**, 891 **(1997)**.

[3] M.S.Nashner, I.Frenkel, D.L.Adler, J.R.Shapley, M.M. Alvarez, J.T.Khoury, T.G.Schaaff, M.N.Shafigullin, I.Vezmar, R.L.Whetten; J.Chem.Chem.B., **101**, 3706 **(1997)**.

[4] A.K.Boal, V.M.Rotello; J.Am.Chem.Soc., **121**, 4914 **(1999)**.

[5] R.M.Crooks, A.J.Ricco; Acc.Chem.Res., **31**, 219 **(1998)**.

[6] J.M.Thomas; Pure Appl.Chem., **60**, 1517 **(1988)**.

[7] S.Underwood, P.Mulvaney; Langmuir, **10**, 3427 **(1994)**.

[8] J.H.Hodak, I.Martini, G.V.Hartland; J.Phys.Chem. B., **102**, 6958 **(1998)**.

[9] R.G.Nuzzo; J.Am.Chem.Soc., **119**, 7760 **(1997)**.

[10] T.Linnert, P.Mulvaney, A.Henglein; J.Phys.Chem., **97**, 679 **(1993)**.

[11] F.Strelow, A.Henglein; J.Phys.Chem., **99**, 11834 **(1995)**.

[12] N.Shipway, E.Katz, I.Willner; Chem.Phys.Chem., **1**, 18 **(2000)**.

[13] S.L.Logunov, T.S.Ahmadi, M.A.El-Sayed, J.T. Khoury, R.L.Whetten; J.Phys.Chem.B., **101**, 3713 **(1997)**.

[14] S.Y.Kang, K.Kim; Langmuir, **14**, 226 **(1998)**.

[15] J.Turkevich, P.C.Stevenson, J.Hillier; Dscuss. Faraday Soc., **11**, 55 **(1951)**.

[16] A.Henglein, D.Meisel; Langmuir, **14**, 7392 **(1998)**.

[17] P.V.Kamat; J.Phys.Chem.B., **106**, 7729 **(2002)**.

[18] K.George Tomas, Binil Ltty Lpe, P.K.sudeep; Pure Appl.Chem., **74(9)**, 1731 **(2002)**.

[19] P.Mulvancy; Longmuir, **1**2, 788 **(1996)**.

[20] M.Roses, J.Rafols, J.Ortega, E.Bosch; J.Chem.Soc. Perkin Trans, **2**, 1607 **(1995)**.

[21] Y.Marcus; Chem.Soc.Rev., 409 **(1993)**.

[22] E.Prodan, P.Nordlander; J.Chem.Phys., **120**, 5444-5454 **(2004)**.

[23] S.A.M.Al-Sherbini; Colloids and Surfaces A: Physicochemical Engineering Aspect, **246**, 61 **(2004)**.

[24] M.B.Mohamed, K.Z.Ismail, S.Link, M.A.El-Sayed; J.Phys.Chem.B., **102**, 9370 **(1998)**.