

Linear Optical Properties of Gold Colloid

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Gold colloid was prepared by reducing $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ with $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$. The morphology, size of gold nanoparticles and the optical property of colloid were characterized by transmission electron microscope and UV-Vis spectrophotometer, respectively. It shows that the gold nanoparticles are in the shape of spheres with diameters less than 8 nm, and the surface plasmon resonance absorption peak is located at about 438 nm. As the volume fraction of gold particles increases, the intensity of absorption peak strengthens. The optical property of gold colloid was analyzed by Maxwell-Garnett (MG) effective medium theory in the company of Drude dispersion model. The results show that the matrix dielectric constant is a main factor, which influences the optical property of gold colloid.

Keywords: gold nanoparticle, aqueous-phase reduction, Drude dispersion model, Maxwell-Garnett effective medium theory.

1. INTRODUCTION

When a ray of light is incident on metallic surface with a certain angle, the surface plasmon resonance (SPR) phenomenon takes place. In the biomedical application, there is a tremendous development on the sensitivity of SPR to the medium refraction index of metallic surface. This can not only be applied to the ligand-receptor real-time dynamics interaction, the screening study of the lead compound in pharmacy industry, but also can be applied to the testing of the DNA hybridization, the enzyme-radical interaction, the polyclonal-antibody specialty, the epitope mapping, the construction of protein and the nontracer immunoassay [1]. In recent years, some papers have reported research achievements of gold nanoparticles applied in DNA detection, nucleic acid alignment detection, chromatic sensation, catalysing, photoelectron device and so on [2–6]. Recently, a convenient method for preparing supported Au nanoparticles has been suggested without any need for external reducing agent [7].

Due to the resonance absorption and scattering, colloid like gold and silver metallic nanoparticles dissolved in water will perform different optical properties. In this article, we have chosen the $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ aqueous-phase reduction method with $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$ to produce gold colloid [8–9]. In our work, gold nanoparticles are in the shape of spheres with diameters less than 8 nm. Moreover, in order to explore the optical properties in detail, some studies on its optical properties have been done by using spectrophotometer and Maxwell-Garnett effective medium theory [10].

2. EXPERIMENT

In our experiment, some reagents were used: chloroauric acid ($\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$, AR, Shang Hai Fine Chemical Engineering Material Research Institute),

trisodium citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$, AR, Beijing Institute of chemical reagents), deionized water (made by laboratory); 1-dodecanethiol ($\text{C}_{12}\text{H}_{25}\text{SH}$, CP, Sinopharm Chemical Reagent limited corporation). FEI Tecnal G² F20 S-Twin transmission electron microscope (TEM) and Rigaku X-ray diffractometer (XRD) were used to characterize the morphology and size of gold nanoparticles. HITACHI U-2810 type ultraviolet visible (UV-Vis) spectrophotometer was used to measure the optical properties of gold colloid. 85-2 digital thermostat magnetic stirrer (Shanghai Jun Zhu Instrument Manufacturing Co.Ltd.) was used to prepare the gold colloid.

The gold colloid was prepared in the following processes: 6 ml $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ aqueous solution with concentration of 0.034 mol/L and 10 mL deionized water were added to the conical flask. The solution was stirred at the rate of 650 rpm when it is boiling. Meanwhile, a 0.024 mol/L HAuCl_4 solution was added rapidly. When the reactive time ran up to 6 min, the heating and stirring was stopped and the solution was cooled to room temperature. Finally, some 1-dodecanethiol was added as the stabilizer, and we obtained the gold colloid. It was kept in a cold (4 °C) and dark environment.

3. RESULTS AND DISCUSSION

Gold colloid was dropped onto a copper grid by micropipette. The TEM image Fig. 1 a of gold nanoparticles was taken by TEM at the accelerating voltage of 200 kV. Fig. 1 b reveals the TEM image of a single gold nanoparticle with the diameter of about 6 nm. The spacing of inter lattice plane is around 0.23 nm, corresponding to the (111) planes of the gold face-centered-cubic structure. Fig. 1 c shows the size distribution of monolayer gold nanoparticles in Fig. 1 a. The gold nanoparticles are in the range of 2.0 nm–7.0 nm in diameter and the average is 6.0 nm. A XRD test was carried out on the dried gold colloid transferred to a glass substrate. The diffraction spectrum of gold particles was

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obtained as Fig. 1 d shows. The diffraction peak is located at about 38° corresponding to the (111) planes of the gold face-centered-cubic structure, which is identical to the TEM result.

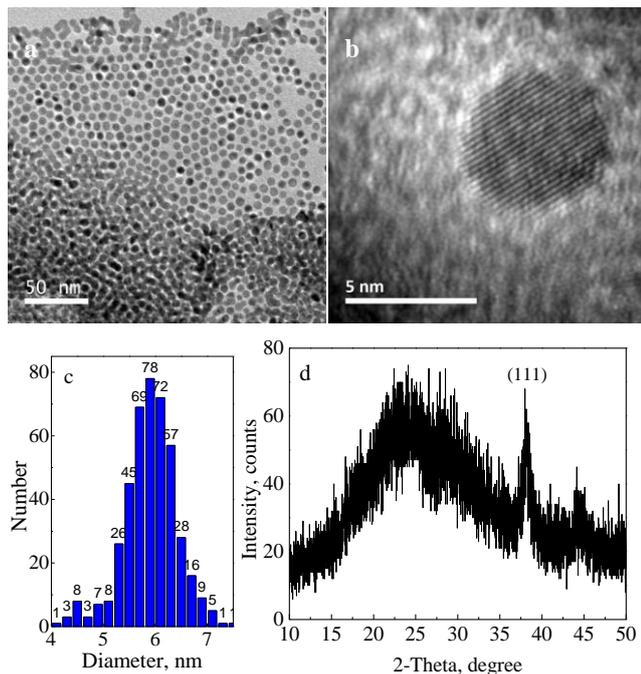


Fig. 1. TEM image of a–gold particles of gold colloid; b–a single gold particle; c–size distribution of monolayer gold particles in a; d–XRD spectrum of gold particles

The gold colloid (diameter of around 6 nm) of different volumes, which were 0.5, 0.75, 1.0, 1.25 and 1.5 mL, were added to five cuvettes (#a–#e) (Fig. 2 c), respectively. Then we continued to add the solvent until the volumes of these five cuvettes attain 4.0 mL.

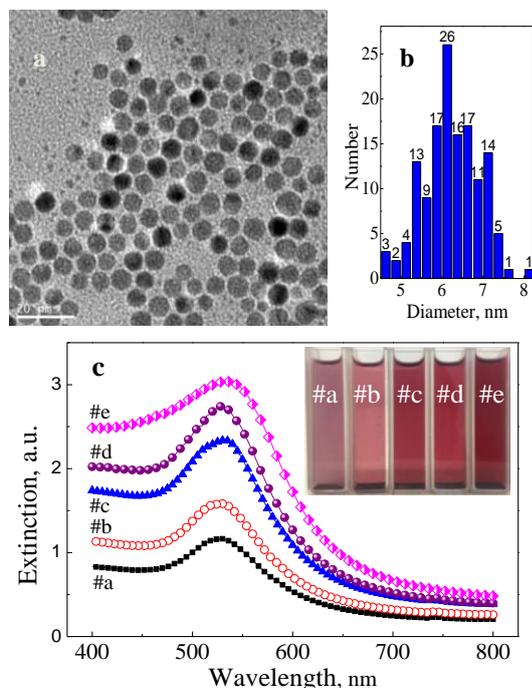


Fig. 2. a–TEM image of gold colloid; b–size distribution of monolayer gold particles in (a); c–absorption spectra of gold colloid with concentration varied as the inserted photo shows

The TEM image (Fig. 2 a) was obtained and the size distribution of monolayer gold colloid (Fig. 2 b) was measured. By using HITACHI U-2810 liquid sample spectrophotometer, we got the absorption spectra as Fig. 2 c shows. The results indicate that the concentration of gold colloid does not change the location of absorption peak. However, as the concentration increases, the intensity of absorption peak strengthens. This effect is simply due to the Beer's law.

Gold colloid liquids of different average grain diameters, which were around 2 nm, 6 nm and 20 nm (Fig. 3 a–c), were added to three different cuvettes (#A–#C) (Fig. 3 d), respectively. The absorption spectra were measured as Fig. 3 d shows. The results show that the absorption peak of gold colloid is affected by the size of gold grain. It occurs to be a redshift of absorption peak as the size increases. The absorption peak broadens in the extinction spectra reflects the size homogeneity of gold nanoparticles. Thus in Fig. 3 d, the size homogeneity of gold grain in #A is better than that in #B. This behavior has been well studied and reported to be one of the characteristics of metal nanoparticles with tunable size and surface plasmon resonance frequency [11–12].

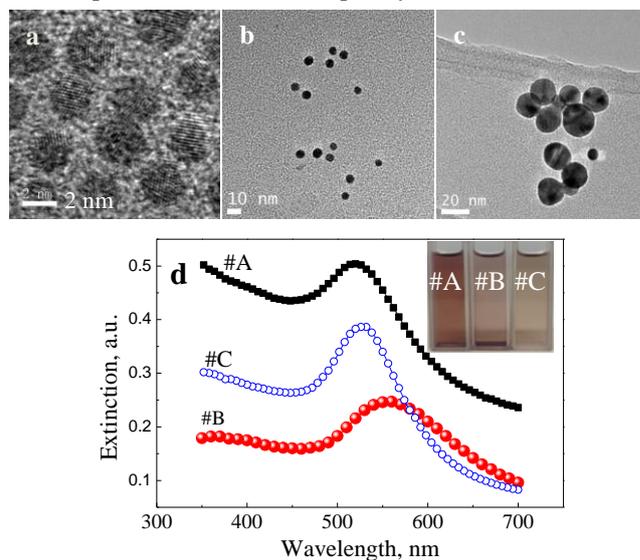


Fig. 3. a–c: TEM image of gold grain in cuvette #A–#C; d–the absorption spectra of gold colloid with grain diameters varied as the insert photo shows

Fig. 4 indicates that the absorption peak position of absorbance curve in Fig. 3 has a simple linear relation with the diameter of gold grain.

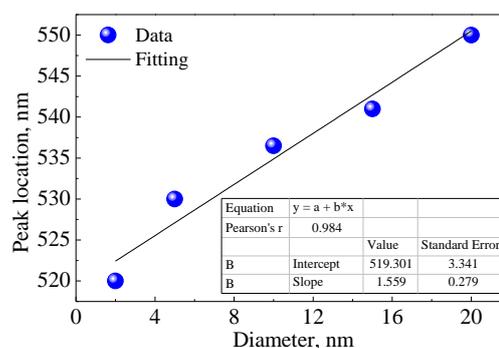


Fig. 4. The relationship between the peak location and grain diameter

TEM is a common method of measuring the size distribution of gold colloid nanoparticles. However, it requires complicated operating and delicate operation at fairly high cost. Therefore, if we establish the empirical formula between the spectrum and the diameter of gold colloid particles, by using a large amount of statistical analysis, then we can simplify the measuring procedure enormously.

Since there are a large number of free electrons in metal, we generally adopt the Drude dispersion theory to describe the dielectric properties of metallic particles in external electric field. Employing damped oscillators approximately, we get the dynamic equation of electron in gold particles.

$$m \frac{d^2 x}{dt^2} = e^* E_0 e^{-i\omega t} - m\gamma \frac{dx}{dt}, \quad (1)$$

where $e^* E_0 e^{-i\omega t}$ represents driving force of light wave in electric-magnetic field, $-m\gamma dx/dt$ represents the damping force, e^* represents the effective charge of harmonic oscillator, ω represents the angular frequency of incident light, m represents the quality of harmonic oscillator, and γ represents the damping coefficient.

Solving the Eq. 1, then the displacement of harmonic oscillator is $x = -e^* E_0 e^{-i\omega t} / (m(\omega^2 + i\gamma\omega))$. Supposing that the number of harmonic oscillator in a unit volume is N . According to the intensity of polarization formula, we can get the dielectric function as follows: $\epsilon_r = 1 - w_p^2 / (\omega^2 + \gamma^2)$, $\epsilon_i = \gamma w_p^2 / (\omega(\omega^2 + \gamma^2))$, where $w_p^2 = Ne^{*2} / (m\epsilon_0)$ represents the plasma frequency. Damping coefficient γ indicates the interaction such as collision and scattering between free electrons, which means when the size of particles is smaller than the mean free path of electrons, γ can be a function of the size expressed as $\gamma(r) = \gamma_0 + Av_f/r = v_f/l_\infty + Av_f/r$, where r represents the radius of particles, γ_0 represents the frequency of the interaction, A is a constant determined by the interaction of electronic surface, the morphology of particles and the properties associated with scattering, v_f represents the Fermi rate of electrons, l_∞ represents the mean free path [13–15] of electrons in bulk materials.

As for the aqueous solution of gold colloid, the diameter of gold particles is much less than the wavelength of incident light, matching the “dispersion microstructure” microscope-particle model of MG effective medium theory. The field feature can be expressed as a single dipole term, so the total electric displacement vector is $\vec{D} = \epsilon_e \vec{E} = \epsilon_2 \vec{E} + \vec{P}$, where ϵ_e represents the effective dielectric function of the medium materials, ϵ_2 represents the dielectric function of matrix medium materials, \vec{E} represents the mean macroscopic electron field generated in medium, \vec{P} represents the intensity of polarization. $\vec{P} = n_0 \alpha \vec{E}_e = v_0 (\epsilon_1 - \epsilon_2) \vec{E}$, where n_0 represents the number of particles in a unit volume, v_0 represents the volume of a particle, ϵ_1 represents the dielectric function of gold nanoparticles, α represents the polarizability.

Judged from the TEM image in Fig. 1, the morphology of gold particles manifested as a sphere. When the incident light is parallel to a plane, the Lorentz depolarization factor q equals to 1/3 and the shield parameter κ related to the

morphology equals to 2 [16], then we can get the MG relation expression [17]:

$$\epsilon_e = \epsilon_2 + \frac{3f_m \epsilon_2 (\epsilon_1 - \epsilon_2)}{(\epsilon_1 + 2\epsilon_2) - f_m (\epsilon_1 - \epsilon_2)}, \quad (2)$$

where f_m represents the volume fraction of metal particles, $f_m = n_0 v_0$.

Due to the Maxwell theory, the complex index of refraction \tilde{n} (equals to $n + ik$) is related to the complex dielectric function ($\epsilon_e = \epsilon_r + i\epsilon_i$), $\tilde{n} = (\epsilon_e)^{1/2}$, where ϵ_r and ϵ_i are the real part and the imaginary part of ϵ_e , respectively. Then we can get the dispersion relation of refractive index and extinction coefficient as:

$$n = \sqrt{\frac{1}{2} (\sqrt{\epsilon_r^2 + \epsilon_i^2} + \epsilon_r)}, k = \sqrt{\frac{1}{2} (\sqrt{\epsilon_r^2 + \epsilon_i^2} - \epsilon_r)}. \quad (3)$$

In consideration of the aqueous solution of gold colloid, we assume some relevant parameters [18] of gold nanoparticles like N as $5.9 \times 10^{28} \text{ m}^{-3}$, A as 0.43, v_f as $1.39 \times 10^6 \text{ m/s}$, γ_0 as $4 \times 10^{14} \text{ Hz}$. If the radius r of gold nanoparticles remains unchanged as 3 nm while the volume fraction of matrix medium changes, the refractive index spectra and the extinction coefficient spectra are calculated as Fig. 5 shows.

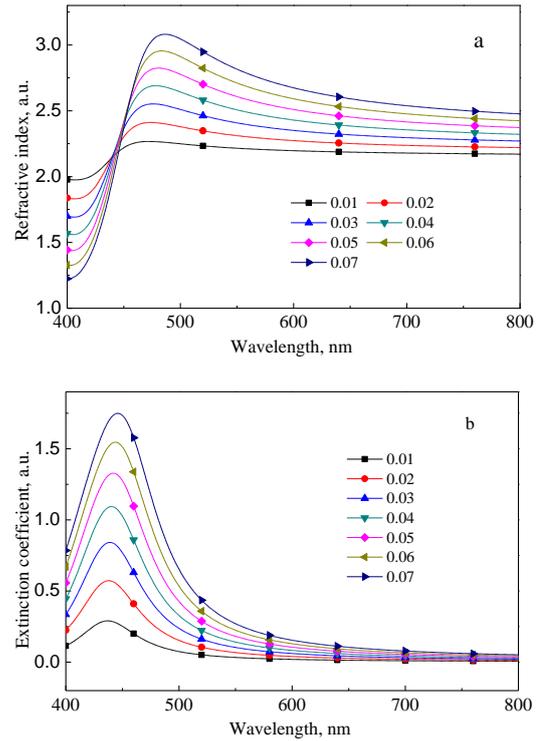


Fig. 5. Simulated: a–refractive index spectra; b–extinction spectra of gold colloid with volume fraction of gold particles

With the volume fraction increases, the former spectra have a redshift, the intensity of the latter spectrum strengthens, the half-peak-width increases and there is a faint redshift in the peak position. All the results are identical to the result of Fig. 2. If the volume fraction f_m remains unchanged at 0.01 while the size of gold nanoparticles changes, the refractive index spectra and the extinction coefficient spectra are shown in Fig. 6.

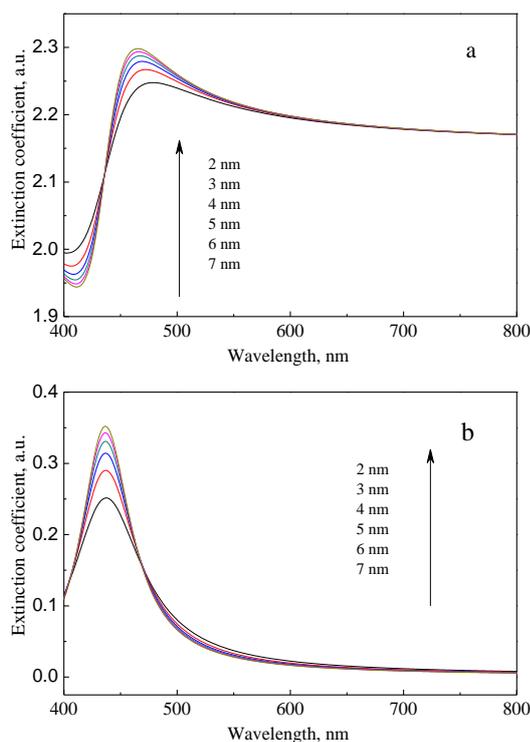


Fig. 6. Simulated: a—refractive index spectra; b—extinction spectra of gold colloid with radius of gold particles varied

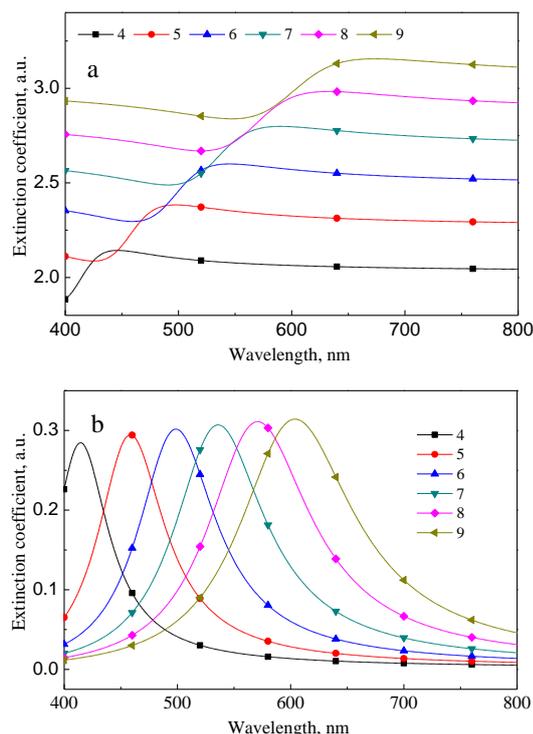


Fig. 7. Simulated: a—refractive index spectra; b—extinction spectra of gold colloid with matrix dielectric constant varied

With the size increase, the former spectra have a blue shift and the intensity of the latter spectra peak strengthens while the peak-width and the peak position are basically unchanged. If the radius and the volume fraction remains unchanged ($r=3$ nm, $f_m=0.01$) but the dielectric constant ϵ_2 of the matrix medium changes, we get the refractive index spectra and the extinction coefficient spectra as

Fig. 7 shows. With the dielectric constant increasing, the former spectra have a remarkable redshift. The peak intensity and peak-width are basically unchanged while the peak position has a redshift.

4. CONCLUSIONS

We synthesized a kind of aqueous solution of gold colloid, where the diameter of particles is below 8 nm and the resonance absorption peak locates at 438 nm. Utilizing Drude dispersion theory and MG effective medium theory, we analyzed the optical properties of gold colloid. Results show that: the surface plasmon resonance is affected by the volume fraction, the size of gold nanoparticles and the dielectric constant of matrix medium. With the volume fraction of gold particles magnifying, the refractive index spectra have a redshift while the peak intensity of the extinction coefficient spectra strengthens. With the radius of gold particles expanding, the refractive index spectra have a blue shift while there is only a small change in the extinction coefficient spectra. With the dielectric constant of matrix medium increasing, it occurs that there is a remarkable redshift in both refractive index spectra and the extinction coefficient spectra. Meanwhile, we conclude that the matrix dielectric constant is the main factor that influences the optical properties of gold colloid solution.

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REFERENCES

1. Patrick, E., Anne Van, H., Michel, V. Surface Plasmon Resonance: Principles, Methods And Applications In Biomedical Sciences *Spectroscopy* 17 2003: pp. 255–273. <http://dx.doi.org/10.1155/2003/372913>
2. Zhang, J., Song, S.P., Wang, L.H., Pan, D., Fan, C.H. A Gold Nanoparticle-Based Chronocoulometric DNA Sensor For Amplified Detection of DNA *Nature* 2 (11) 2007: pp. 2888–2895.
3. James, J.S., Adam, D.L., Viswanadham, G., Bao, Y.P., Müller, U.R. Homogeneous Detection of Unamplified Genomic DNA Sequences Based On Colorimetric Scatter of Gold Nanoparticle Probes *Nature Biotechnology* 22 (7) 2004: pp. 883–887. <http://dx.doi.org/10.1038/nbt977>
4. Liu, J.W., Lu, Y. Preparation of Aptamer-Linked Gold Nanoparticle Purple Aggregates for Colorimetric Sensing of Analytes *Nature Protocols* 1 (1) 2006: pp. 246–252. <http://dx.doi.org/10.1038/nprot.2006.38>
5. Mark, T., Vladimir, B.G., Owain, P.H.V., Pavel, A., Angel, B.M., Mintcho, S.T., Brian, F.G.J., Richard, M.L. Selective Oxidation with Dioxygen by Gold Nanoparticle Catalysts Derived from 5-Atom Clusters *Nature* 07194 2008: pp. 981–984.
6. Hu, M.S., Chen, H.L., Shen, C.H., Hong, L.S., Huang, B.R., Chen, K.H., Chen, L.C. Photosensitive Gold-Nanoparticle-Embedded Dielectric Nanowires *Nature Materials* 5 2006: pp. 102–106. <http://dx.doi.org/10.1038/nmat1564>

7. **Silvia, F., Daniele, N., Barbara, B., Maria, C.C., Marco, G., Chiara, M., Angela, T., Giuliana, A., Sameh, I.A.** Straightforward Synthesis of Gold Nanoparticles Supported on Commercial Silica-Polyethyleneimine Beads *Journal of Physical Chemistry C* 116 2012: pp. 25434–25443.
<http://dx.doi.org/10.1021/jp309518a>
8. **Frens, G.** Controlled Nucleation for Regulation of Particle-Size in Monodisperse Gold Suspensions *Nature-Physical Science* 241 (105) 1973: pp. 20–22.
9. **Mao, B., Liu, B., Wang, Y.F., Li, G.N., Song, Y.Z., Ma, L.P., Liu, G.H.** Preparation of Au Colloid of Small Size in Aqueous Solution *Rare Metal Materials and Engineering* 38 (3) 2009: pp. 515–518.
10. **Ruppig, R.** Evaluation of Extended Maxwell-Garnett Theories *Optics Communications* 182 2000: pp. 273–279. [http://dx.doi.org/10.1016/S0030-4018\(00\)00825-7](http://dx.doi.org/10.1016/S0030-4018(00)00825-7)
11. **Liu, S., Chen, G.Y., Prasad, P.N., Swihart, M.T.** Synthesis of Monodisperse Au, Ag, and Au–Ag Alloy Nanoparticles with Tunable Size and Surface Plasmon Resonance Frequency *Chemistry of Materials* 23 2011: pp. 4098–4101.
12. **Zijlstra, P., Orrit, M.** Single Metal Nanoparticles: Optical Detection, Spectroscopy and Applications *Reports on Progress in Physics* 74 2011: pp. 106401–106455.
<http://dx.doi.org/10.1088/0034-4885/74/10/106401>
13. **Kreibig, U.** Interface-Induced Dephasing of Mie Plasmon Polaritons *Applied Physics B* 93 2008: pp. 79–89.
<http://dx.doi.org/10.1007/s00340-008-3213-1>
14. **Pinchuk, A., Kreibig, U., Hilger, A.** Optical Properties of Metallic Nanoparticles: Influence of Interface Effects and Interband Transitions *Surface Science* 557 2004: pp. 269–280.
<http://dx.doi.org/10.1016/j.susc.2004.03.056>
15. **Zaremba, E., Persson, B.N.J.** Dynamic Polarizability of Small Metal Particles *Physics Review B* 35 (2) 1987: pp. 596–606.
<http://dx.doi.org/10.1103/PhysRevB.35.596>
16. **Bohren, C.F., Huffman, D.R.** Absorption and Scattering of Light by Small Particles. New York: John Wiley & Sons Inc, 1983.
17. **Hornyak, G.L., Patrissi, C.J., Martin, C.R., Valmalette, J.C., Dutta, J., Hofmann, H.** Dynamical Maxwell-Garnett Optical Modeling of Nanogold-Porous Alumina Composites: Mie And Kappa Influence on Absorption Maxima *NanoStructured Materials* 9 1997: pp. 575–578.
[http://dx.doi.org/10.1016/S0965-9773\(97\)00128-1](http://dx.doi.org/10.1016/S0965-9773(97)00128-1)
18. **Hodak, J.H., Henglein, A., Hartland, G.V.** Electron-Phonon Coupling Dynamics in Very Small (Between 2 And 8 nm Diameter) Au Nanoparticles *Journal of Chemical Physics* 112 (13) 2000: pp. 5942–5947.
<http://dx.doi.org/10.1063/1.481167>