Evaluation of Optical Properties of Ag, Cu, and Co Nanoparticles Synthesized in Organic Medium

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The surface plasmon resonance evaluation of colloidal metal nanoparticles, synthesized in organic medium, is reported in this work. Metal salts were dissolved in dioxane/AOT solution and reduced by hydrazine hydrate under vigorous stirring. Optical properties of obtained colloidal nanoparticles were investigated by UV–VIS spectroscopy. Theoretical predictions of optical properties of metal nanoparticles were made by means of the Mie theory and the Drude free-electron model. Geometrical parameters and distribution of metal nanoparticles in colloidal solutions were characterized by atomic force microscopy. The results show that Ag, Cu, and Co nanoparticles, synthesized in organic medium distinguish plasmonic properties. Surface plasmon resonance bands were obtained in all cases: Ag — at 430 nm, Cu — at 570 nm, Co — at 350 nm (SPR1) and 430 nm (SPR2). Comparing theoretical evaluation of nanoparticles size with atomic force microscopy analysis, we can assume that our calculations are accurate. It was found that dominating nanoparticles diameter in Ag colloidal solution is $\approx$ 150 nm, in Cu colloidal solution is $\approx$ 70–80 nm and in Co colloidal solution is $\approx$ 150 nm. It can be concluded that nanoparticles with enhanced plasmonic properties synthesized in organic medium can be widely used in order to increase efficiency of various optical elements.

1. Introduction

Plasmonics is a rapidly emerging subfield of nanotechnologies, which gives a possibility to control and guide light interaction with matter more effectively. During the last decade many methods for plasmonic nanoparticles synthesis, including microemulsion techniques, organic--water two-phase synthesis and aqueous solution reduction were developed and well investigated [1–3]. Generally, nanoparticles synthesis methods are divided into two groups: physical and chemical synthesis techniques. In the first one, nanoparticles are assembled from atoms in the process of metal vaporization and condensation on various supports or obtained from bigger particles in colloidal dispersions by means of colloidal mills. Physical methods are relatively complex processes and require sophisticated equipment and technologies, that is why chemical nanoparticles preparations methods are mostly used for stable colloidal nanoparticles preparation. Chemical techniques group may be subdivided into two categories: aqueous solutions with stabilizers and reverse micelles systems with aggregation processes, where growing nanoparticles are surrounded by surfactant molecules. Main disadvantages of synthesis in aqueous solution are low stability of nanoparticles and their broad size distribution. The stability of nanoparticles in colloidal solution is amplified for the synthesis in reverse micelles using chemical reducing agents (hydrazine, borohydride, quercetin etc.) [3].

Generally, for plasmonic nanoparticles synthesis noble metals (Au, Ag, Pt, etc.) are widely used because of their ability to support plasmon resonances at visible wavelengths [4]. But during last years, the interest in transition metals, like cobalt and nickel has arisen because of possibility to combine both magnetic and optical properties. Many authors report in their works preparation, optical and magnetic properties of Co nanometals [5–8].

Unlike gold and silver, metallic cobalt nanoparticles are very sensitive to air, moisture and reaction conditions, though the synthesis methods applied for noble metals are also possible [9].

In this paper we present synthesis of plasmonic Ag, Cu, and Co nanoparticles in organic solvent (1,4-dioxane) by reverse micelles method. In order to evaluate optical properties of colloidal metal nanoparticles UV–VIS analysis was performed. The optical absorbance spectra of Ag and Cu colloidal solutions were analyzed by means of the Mie theory, and size-dependent surface plasmon resonance (SPR) bands were easily evaluated. For Co colloidal nanoparticles size-dependent SPR bands determination, the Mie approximation model was insufficient because of high damping and interband transitions in Co nanoparticles. For this purpose extended Drude free-electron model was used. Additionally, atomic force microscopy (AFM) analysis was performed in order to estimate the real geometrical parameters of colloidal nanoparticles.

2. Experimental

2.1. Theoretical prediction of size of nanoparticles

Optical properties of noble metals are widely studied by the Mie theory. According to the Mie theory the SPR band is simply calculated from the frequency dependence

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of the bulk dielectric constant of the metal [10]. On the basis of the Mie theory nanoparticles size can be derived from obtained optical absorption band. In the case, when nanoparticles are assumed as uniformly dispersed spherical objects, according to the Mie theory their cross--section can be calculated from [1]:

$$\sigma(\lambda) = \left(\frac{18\pi V N l \varepsilon_m^{3/2}}{2.303\lambda}\right)\frac{\varepsilon_2}{(\varepsilon_1 + 2\varepsilon_m)^2 + \varepsilon_2^2}, \qquad (1)$$

where V is the volume of one particle, ε_m — dielectric constant of the medium (in our case 1,4-dioxane), ε_1 and ε_2 — real and imaginary parts of dielectric constant of metal ($\varepsilon_1 = n^2 - k^2$; $\varepsilon_2 = 2nk$) and λ — wavelength in vacuum. For noble metals Lorentzian shape of absorbance curve is expected with a resonance when the condition $\varepsilon_1 = -2\varepsilon_m$ is satisfied.

For transition metals the Mie theory stands only when neglecting damping constants and interband transitions, which are quite high due to weak interaction of electrons from s and d shells. For accurate SPR determination in transition metals Drude free-electron model is used for metals dielectric constants ε_{D1} (real) and ε_{D2} (imaginary) evaluation, considering relaxation and plasmon frequencies [11], which are given by expressions

$$\varepsilon_{D1} = 1 - \omega_p^2/(\omega^2 + \gamma^2), \qquad (2)$$

$$\varepsilon_{D2} = \omega_p^2\gamma/[\omega(\omega^2 + \gamma^2)], \qquad (3)$$

where ω_p and γ are plasmon and relaxation frequencies, respectively.

For metals where there is a substantial bound electron component, like cobalt, the dielectric function can be decomposed into two terms: free-electron term and interband term [12]. Consequently, dielectric function becomes additive from two components: free-electron term and bound-electron term [12]:

$$\varepsilon_{D1size}(r) = 1 - \frac{\omega_p^2}{\omega^2 + \gamma^2(r)} + \varepsilon_{1bound\text{-}electrons}, \qquad (4)$$

$$\varepsilon_{D2size}(r) = 1 - \frac{\omega_p^2\gamma(r)}{\omega(\omega^2 + \gamma^2(r))} + \varepsilon_{2bound\text{-}electrons}. \qquad (5)$$

Additional collisions of particles γ can be calculated from [12]:

$$\gamma(r) = \gamma_{bulk} + C\frac{v_F}{r}. \qquad (6)$$

Interband dielectric constants are calculated from [12]:

$$\varepsilon_{bulk}(\omega) = \varepsilon_{bound\text{-}electrons}(\omega) + 1 - \frac{\omega_p^2}{\omega^2 + i\omega\gamma_{bulk}}. \qquad (7)$$

Additionally, theoretical predictions of SPR bands for Ag and Cu nanoparticles were made with MiePlot v4.2 software [13].
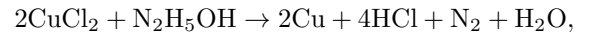
2.2. Reagents

All chemical reagents were of analytical grade and were supplied by Sigma-Aldrich. For synthesis we have used silver nitrate ($AgNO_3$), cobalt(II) nitrate hexahydrate ($Co(NO_3)_2$), copper(II) chloride ($CuCl_2$), dioctyl sulfosuccinate sodium salt (AOT) (96%), hydrazine hydrate (50–60%), 1,4-dioxane and deionized water (made

in Millipore-Q system). Acetone was used for preparation of samples for AFM.

2.3. Preparation of samples

Colloidal solutions of metal nanoparticles were prepared by modifying synthesis method presented in [1]. 330 mg of AOT were dissolved in 50 ml of 1,4-dioxane. Then, 10 μl of aqueous metal salts solutions were added to 1,4-dioxane/AOT solutions and obtained reaction mixtures were reduced by 0.2 ml of hydrazine hydrate under vigorous stirring. Quantities of metal salts were taken according to chemical reaction formula with hydrazine hydrate. General chemical reactions formulae describing synthesis of metal nanoparticles in reverse micelles with hydrazine as reducing agent are presented below

$$4AgNO_3 + N_2H_5OH \rightarrow 4Ag + 4HNO_3 + N_2 + H_2O,$$

$$2CuCl_2 + N_2H_5OH \rightarrow 2Cu + 4HCl + N_2 + H_2O,$$

$$2Co(NO_3)_2 + N_2H_5OH \rightarrow 2Co + 4HNO_3 + N_2 + H_2O.$$

Obtained colloidal solutions were left for stabilization for 24 h. Change in color of all three colloidal solutions from light yellow to caramel indicates the formation of nanoparticles with characteristic plasmon resonance band in visible range.

Samples for AFM analysis were made by dissolving of 5 μl of each metal colloidal solution in 100 μl of acetone. Then, 2 μl of obtained solution were dripped onto silicon plates and dried out in desiccator for 48 h.

2.4. Instruments

Optical absorption spectra were recorded on "Avantes AvaSpec-2048" UV/VIS/NIR spectrometer at room temperature in wavelength range 300–800 nm. Spectrometer is based on AvaBench-75 symmetrical Czerny-Turner construction with 2048 pixel CCD detector. Colloidal solutions were analyzed in quartz cuvettes (optical path length — 10 mm), resolution 1.4 nm.

AFM analysis was done with atomic force microscope NT-206 in contact mode (Si V form probe, NSC11/15, force constant - 3 N/m, resonance frequency 28 kHz), lateral resolution — 2 nm, vertical resolution — 0.1–0.2 nm.

3. Results and discussions
3.1. UV–VIS study

Optical absorbance spectra of metal colloidal solutions were measured at 21 °C temperature. Figure 1 shows theoretical Mie curve (dotted line) versus experimental optical absorbance curve (solid line) of silver colloidal solution. Ag SPR band has a maximum at 430 nm, which coincides with the theoretical Mie SPR band maximum for silver nanoparticles with $r = 75$ nm dispersed in water.

According to the Mie theory the intensity and the width of the absorbance peak of noble metals depend on diameter of the particle [14]. Considering obtained results we can assume that predictable diameter of Ag nanoparticles in colloidal solution corresponds to theoretical one.

In Fig. 2 optical absorbance curve of Cu colloidal solution versus theoretical Mie curve for Cu nanoparticles with $r = 35$ nm are shown. The position of SPR band
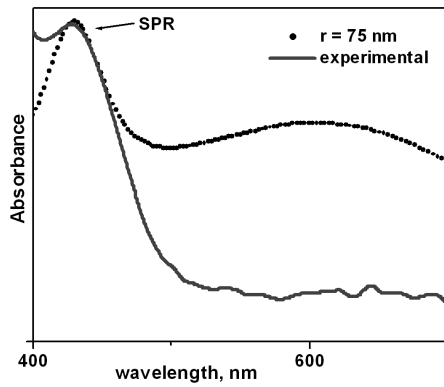
Fig. 1. Comparison of UV–VIS spectra of Ag colloidal solution with theoretical Mie cross-section extinction curve.

of Cu colloidal solution is at 570 nm. The intensity and width of the band denote the presence of spherical copper nanoparticles [4], which also coincides with the Mie theory. Comparing experimental and theoretical SPR bands width we can assume that theoretical evaluation of possible nanoparticle diameter in Cu colloidal solution is quite accurate, but peaks intensity differs, which can be explained by temperature-dependent dielectric constant of medium (1,4-dioxane).
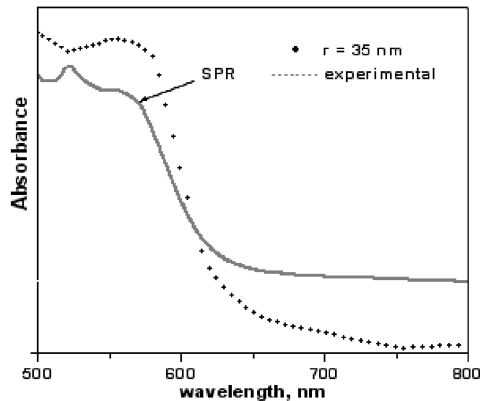

Fig. 2. Comparison of experimental UV–VIS spectra of Cu colloidal solution with theoretical absorption cross-section curve calculated by the Mie approximation model.

Obtained multiband spectra of Co colloidal solution is shown in Fig. 3 (solid line). To explain the origin of Co SPR bands, we have calculated cross-section extinction spectrum of Co nanoparticles in 1,4-dioxane (Fig. 3) by dipole approximation of the Mie theory [15]. For calculations optical constants of bulk cobalt were taken from [16].

From Fig. 3 it is seen that SPR1 band from experimental spectrum has maximum at 350 nm, which is close to calculated SPR value at 320 nm (for cobalt sphere with $r = 75$ nm). SPR2 band (430 nm) might be induced by
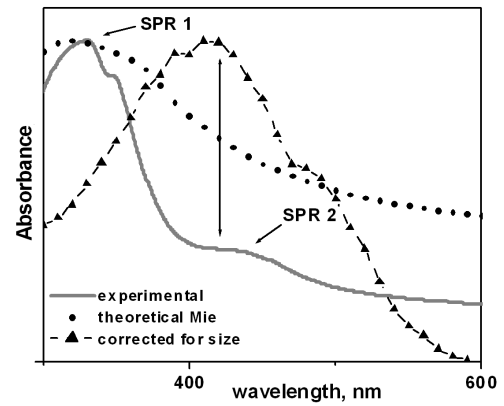

Fig. 3. Comparison of experimental UV–VIS spectra of Co colloidal solution with theoretical absorption cross-section curves calculated by the Mie approximation and the Drude free-electron models.

cobalt oxide nanoparticles or cobalt nanoclusters [17].

Calculations by the Mie approximation for Co nanoparticles show that SPR mostly depends on dielectric constant of surrounding medium, but not on the dielectric constants of cobalt. That is why the condition $\varepsilon_1 = -2\varepsilon_m$ cannot be satisfied for cobalt nanoparticles. This is explained by high damping and contribution of interband transitions in cobalt. Therefore, it means that the Mie approximation model is not accurate in this case. For accurate SPR evaluation of Co nanoparticles, damping constant (relaxation frequency) must be taken into account. This could be easily done by using extended Drude free-electron model where dielectric function $\varepsilon = \varepsilon_{D1} + i\varepsilon_{D2}$ is determined by plasmon and relaxation frequencies ω_p and γ, respectively ((2) and (3)), which is explained in detail in [11].

If we want to evaluate size-dependent optical absorbance curve of Co nanoparticles, we have to assume that dielectric function is additive and also dependent on bound-electrons dielectric constant ($\varepsilon_{bound\text{-}electrons}$). Then, the relations (2) and (3) take the form (4) and (5). Additional collisions of particles were calculated from (6). The Fermi velocity v_F for bulk cobalt was taken from [18], and r is the radius of the particle ($r = 75$ nm). Interband dielectric constants were calculated from (7). Damping constant γ_{bulk} for bulk cobalt was taken from [19]. Size-dependent real and imaginary parts of complex dielectric function was calculated from (4) and (5) and corrected for size optical absorbance curve was constructed.

From Fig. 3 (corrected for size curve) it is visible that maximum optical absorbance band is located at ≈ 420 nm, which is similar to SPR2 band (430 nm), but the intensity of bands differs significantly, which could be also explained by dielectric properties of medium.

Generally, our calculations have shown that Drude-free-electron theory is more accurate for Co SPR determination, but it is necessary to mention that calculations were done for bulk cobalt, and difference in inten-

sity of bands is better explained by dielectric properties of medium and surrounding conditions during synthesis.

3.2. AFM analysis

In Fig. 4 AFM images of silver, copper and cobalt nanolayers formed from colloidal solutions are presented. From that figure it is visible that single spherical nanoparticles and μm size clusters are formed in all cases. The results show that the size of nanoparticles is similar in Ag and Co cases and the average diameter is $\approx$ 150–160 nm, while Cu nanoparticles are hardly visible. The average diameter of Cu nanoparticles is $\approx$ 70–80 nm, which partially corresponds to theoretical size evaluation by the Mie approximation model. μm size clusters are assumed to be AOT particles.
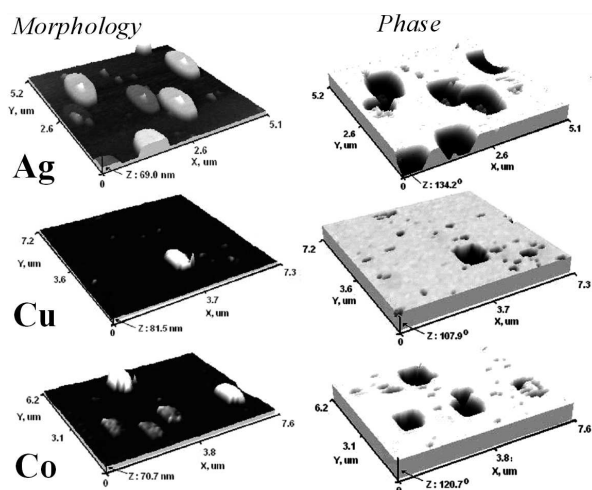

Fig. 4. AFM images of composites formed from metal colloidal solutions.

From phase AFM images it is visible that the surface of nanolayers is heterogeneous which is consistent to μm size clusters and nanoparticles on AFM morphology images. In phase diagram of composite formed from silver colloidal solution we see that not only small nanoparticles and μm size clusters are formed on the surface, but additional nanoparticles formed inside of clusters, which let us assume that the composite is formed from several compounds.

Generally, from AFM results it can be said that size of nanoparticles in all cases approximately satisfies the theoretical size evaluation values.

4. Conclusions

In conclusion, Ag, Cu, and Co nanoparticles, synthesized in organic medium by reverse micelles method, distinguish unique optical properties. UV–VIS spectra of studied colloidal solutions have revealed characteristic SPR bands in all cases. The observed behavior was quantitatively explained by theoretical Mie approximation and Drude free-electrons models. Using the Mie approximation, possible nanoparticles diameter was easily calculated for Ag and Cu nanoparticles: $\approx$ 150 and $\approx$ 70 nm, respectively. But in case of Co we had to

use extended Drude free-electron model to evaluate size--dependent SPR band, and we have found disagreement with the Mie theory. For the same diameter SPR band occurs at different wavelengths, which explains its dependence from dielectric properties of medium and interband transitions in cobalt.

For real geometrical parameters evaluation we have performed AFM analysis of nanolayers formed from metal colloidal solutions. The average diameter of nanoparticles was found to be close to theoretical calculations.

Summarizing results of our experiment we can emphasize that synthesis of Ag, Co, and Cu nanoparticles in reverse micelles is valuable method for plasmonic nanoparticles synthesis. The results of our experiment may be used for further investigations of plasmonic nanoparticles and their applications for commercial optical elements.

References

[1] E.M. Egorova, A.A. Revina, *Colloids Surf. A* **168**, 87 (2000).

[2] T. Dadosh, *Mater. Lett.* **63**, 2236 (2009).

[3] M.P. Pileni, *Langmuir* **13**, 3266 (1997).

[4] V.S. Tiwari, O. Tovmachenko, G.K. Darbha, W. Hardy, J.P. Singh, P.C. Ray, *Chem. Phys. Lett.* **446**, 77 (2007).

[5] G. Balaji, R. Desilva, V. Palshin, N. Desilva, G. Palmer, S.S.R.K. Challa, *Mater. Sci. Eng. B* **167**, 107 (2010).

[6] J. Zhang, C.Q. Lan, *Mater. Lett.* **62**, 1521 (2008).

[7] E. Cattaruzza, G. Battaglin, P. Canton, C.M. De Julian Fernandez Ferroni, T. Finotto, C. Maurizio, C. Sada, *J. Non-Cryst. Solids* **336**, 148 (2004).

[8] S.R. Ahmed, P. Kofinas, *J. Magn. Magn. Mater.* **288**, 219 (2005).

[9] J.M. Nusrat, S. Mazumdar, S. Mazumdar, *Langmuir* **24**, 3439 (2008).

[10] E. Cottancin, G. Celep, J. Lerme, M. Pellarin, J.R. Huntzinger, J.L. Vialle, M. Broyer, *Theor. Chem. Acc.* **116**, 514 (2006).

[11] P.B. Jonson, R.W. Christy, *Phys. Rev. B* **6**, 4370 (1972).

[12] L.B. Scaffardi, N. Pellegri, O. de Sanctis, J.O. Tocho, *Nanotechnology* **16**, 158 (2005).

[13] *MiePlot*, www.philiplaven.com/mieplot.htm.

[14] L. Balan, J.P. Malval, R. Schneider, D. Burget, *Mater. Chem. Phys.* **104**, 417 (2007).

[15] C. Petit, P. Lizon, M.P. Pileni, *J. Phys. Chem.* **97**, 12974 (1993).

[16] P.B. Jonson, R.W. Christy, *Phys. Rev. B* **9**, 5056 (1974).

[17] O. Yeshchenko, I. Dmitruk, A. Alexeenko, A. Dmytruk, V. Tinkov, *Physica E* **41**, 60 (2008).

[18] Y. Petrovykh, K.N. Altmann, H. Hochst, M. Laubscher, S. Maat, G.J. Mankey, *Appl. Phys. Lett.* **73**, 3459 (1998).

[19] V.G. Kravets, A.K. Petford-Long, X. Portier, L.V. Poperenko, M. Kolesnik, *J. Magn. Magn. Mater.* **217**, 129 (2000).