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Superficies y vacío, núm. 15, diciembre, 2002, pp. 16-18,
Sociedad Mexicana de Ciencia y Tecnología de Superficies y Materiales A.C.
México

Superficies y vacío,
ISSN (Printed Version): 1665-3521
alex@fis.cinvestav.mx
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Preparation and optical absorption of colloidal dispersion of Au/Cu nanoparticles

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Colloidal dispersions of Au/Cu nanoparticles are synthesized by the simultaneous reduction technique from their corresponding metallic ions in presence of poly(N-vinil-2-pirrolidone). The UV-VIS optical absorption spectra of alloy nanoparticles prepared with different Au/Cu molar ratio revealed that the colloidal dispersions prepared are not a simple mixture of Cu and Au monometallic nanoparticles, but the particles are composed of both the Au and Cu metals in the same structural boundary. A liner law was found in the position of the surface plasmon resonance (SPR) band with the composition of the bimetallic particles.

Keywords: Nanoparticles; Alloy; Colloids; Optical properties

1. Introduction

Linear and nonlinear optical properties of nanoscale metal particles have attracted much interest recently[1]. As the linear and nonlinear optical properties are dependent on the frequency at which the surface plasmon resonance (SPR) occurs [2], the ability to modify the SPR frequency is of great significance. The SPR frequency of a metal particle can be altered by the incorporation another metal element in it [2]. Several techniques have been employed to synthesize nanoscale bimetallic particles. Miner et al.[3] synthesized gold/Platinum alloy by simultaneously reducing chloroplatinic and chloroauric acid in aqueous solution with citrate, and they found that the absorption spectra of the alloy particles are not additive of those of the pure components. Mazzoldi et al. [4,5] have synthesized glasses containing Cu/Ni alloy nanoparticles by ion implantation. Other workers have reported the preparation of alloy nanoparticles (Au/Pd, Au/Ag, Pt/Rh, Pd/Pt, and Pt/Ru) prepared by reducing two kinds of metal ions with alcohols in the presence of poly(N-vinyl-2-pirrolidone) (PVP)[6-14]. However, to our knowledge, there is no study on the colloidal dispersions of Au/Cu alloy nanoparticles and seems the material is attractive for catalytic applications.

We have synthesized Au/Cu alloy nanoparticles, protected by polymer, by refluxing the metal ions in the methanol solution of the two kinds of metal ions in the presence of poly(N-vinyl-2-pirrolidone). In this new nanoparticles, the SPR frequency can be modulated in the range from SPR frequency of Au monometallic colloidal to that of the Cu monometallic colloidal, by changing the concentration of Au/Cu molar ratio, and hence, is controllable, which is of great theoretical and practical importance.

2. Experimental preparation of colloidal dispersions

Colloidal dispersions of Au/Cu alloy nanoparticles were prepared under inert atmosphere by an improved simultaneous reduction method [15]. Solutions of tetrachloroauric acid (99.9 % Aldrich, 0.033 mmol in 25 ml of methanol) were prepared by dissolving the corresponding crystalline material in methanol. Methanol solutions of copper (II) chloride (99.9 % Aldrich, 0.033 mmol in 25 ml of methanol) were prepared in the similar way. Both the solutions were mixed at room temperature at various ratios to produced the mixture methanol (100 ml) solutions containing poly(N-vinil-2-pirrolidone) (99.9% Aldrich, PVP, K-30, 300 mg. MW 10,000) as a protecting polymer. The extra 50 ml of methanol was added in mixture solution to make a total volume 100 ml to keep the total ion concentration in the mixture fixed. The mixture solutions were refluxed at about 50 °C for 1 h in nitrogen atmosphere. Then, an aqueous solution of $NaBH_4$ (3 ml of 0.022 M soln.) was added to the resulting solution at 25°C. A homogeneous colloidal dispersion in methanol was formed immediate after the addition of $NaBH_4$ solution in the mixture. For preparing the colloidal dispersions of the Au monometallic nanoparticles, a 25 ml of PVP solution (150 grams in 25 ml) was added to the methanol solution of $AuCl_2$ (0.033 mmol in 25 ml of methanol) and refluxed at about 50 °C for 1 h. Then, the aqueous solution of $NaBH_4$ (1.5 ml) was added to the resulting solution at 25°C. The same procedure was used to prepare the Cu monometallic nanoparticle dispersions.

2.1. Characterization

A Shimadzu UV-3101PC double beam spectrophotometer with slit wavelength of 2 nm and light

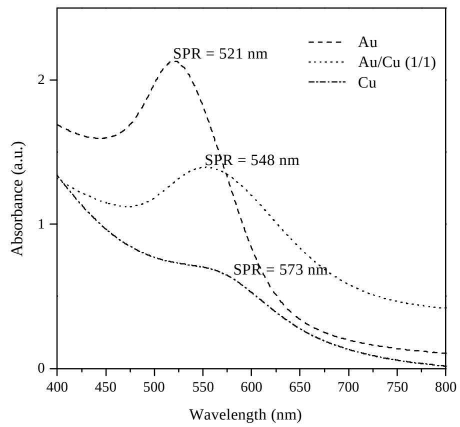

Figure 1. Absorption spectra for the colloidal dispersions of Au monometallic nanoparticles, Au/Cu (1/1) alloy nanoparticles and Cu monometallic nanoparticles.

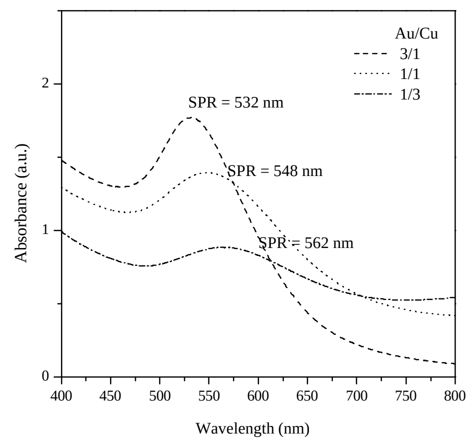

Figure 2. Absorption spectra for Au/Cu alloy colloids of three different ratios: 3/1, 1/1 and 1/3.

path length of 1 cm was used to record the absorption spectra in the wavelength range 250-800 nm of the colloids.

3. Results and discussion UV-VIS absorption spectra

Figure 1 shows the absorption spectra for three kinds of samples; colloidal dispersions of Au monometallic nanoparticles, bimetallic Au/Cu alloy, and Cu monometallic nanoparticles. The colloidal dispersion of Au monometallic nanoparticles exhibits a well defined absorption peak at 521 nm, which is consistent with the SPR of gold metal particles with size in the nanometer range [16] and the absorption band near 572 nm indicates the production of copper colloids, with size in the nanometer interval [17]. For the dispersions of Au/Cu (1/1) bimetallic nanoparticles only a single SPR absorption band is revealed, and the peak position is different from the peak position either of Au and Cu monometallic nanoparticles. The absorption curve of the alloy dispersion could not be obtained by simple overlapping of the the absorption curves of Au and Cu monometallic colloidal dispersions. It is to mention that, the wavelength 548 nm (obtained for bimetallic alloy dispersions) is the arithmetic mean value of 521 nm and 573 nm. Therefore, it is reasonable to conclude that the Au/Cu bimetallic nanoparticles are homogeneous alloy ones, and the novel absorption band, 548 nm, for Au/Cu (1/1) is attributed to SPR band of Au/Cu alloy nanoparticles and the composition of the alloy colloids is equal to the initial concentration of metal ions dissolved in methanol.

We produced the Au/Cu alloy colloids of arbitrary composition and found a liner law in the SPR band position in their absorption spectra with the composition of the constituents. Figure 2 shows the absorption spectra for three kinds of samples containing gold and copper of 3/1, 1/1 and 1/3 molar ratios. All three absorption curves are of Au/Cu alloys with different compositions. The maximum of the SPR absorption peak position is equal to the weighted mean of the wavelength of 521nm for Au colloids and 573 nm for Cu monometallic colloids. For example, the calculated wavelength for Au/Cu (3/1) alloy colloids is 534 nm and the measured value is 532 nm. similarly, they are 547 nm and 548 nm for Au/Cu (1/1) alloy colloids and 560 nm and 562 nm for Au/Cu (1/3) alloy colloids. In the figure 3, the calculated and experimental peak position of the SPR bands are shown. These data infer that the composition of the alloy colloids correspond to the initial concentrations of gold and copper ions in the mixture reaction solution. So, from the peak position of SPR band, we can determine the concentration Au and Cu in the Au/Cu alloy of any arbitrary composition.

To obtain information on the mechanism of formation of the Au/Cu alloy colloids we studied the step-by-step reduction of the metals ions by drop wise addition of $NaBH_4$ solution in the mixture reaction solution.

Figure 4 shows the kinetics of absorption for the bimetallic alloy colloids prepared with gold and copper ion solutions in 3/1 molar ratio. The absorbance increases linearly witch the increasing concentration of the added redactor ($NaBH_4$). During the addition of $NaBH_4$ solution form 4 ml to 32 ml, the SPR peak position (at about 548 nm) varied only about 3 nm in the early stage. The intensity of the SPR peak increased linearly with the increase of added $NaBH_4$. The other two samples with different concentration ratios showed similar features. There appeared two more bands at about 320 nm and 269 nm in the absorption spectra which are correspond to the presence of Au and Cu ions in the reaction mixtures. On increasing the amount of redactor in the mixture, the content of the free Au ions decreased rapidly and then the Cu ions, which is due to the higher reduction potential of Cu than Au.

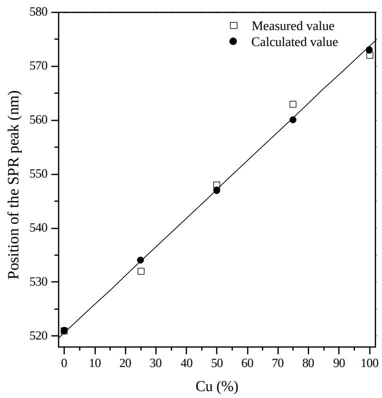

Figure 3. Variation of SPR peak position in the Au/Cu bimetallic nanoparticles on the variation of Au/Cu molar ratio.

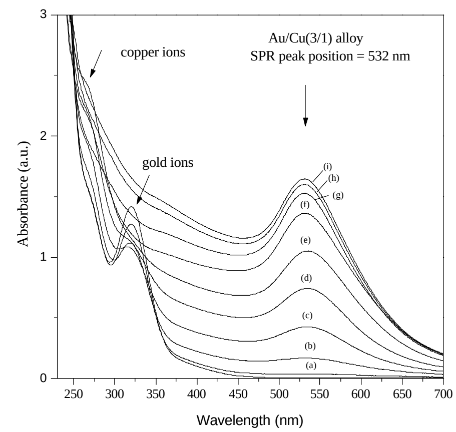

Figure 4. The change in absorption spectra for Au/Cu (3/1) alloy at various stages of reduction with $NaBH_4$ (0.022 M): (a) 0 ml, (b) 4 ml, (c) 8 ml, (d) 12 ml, (e) 16 ml, (f) 20 ml, (g) 24 ml, (h) 28 ml and (i) 32 ml.

4. Conclusion

Colloidal dispersions of bimetallic Au/Cu nanoparticles have been prepared. UV-VIS absorption spectra suggested the formation of bimetallic nanoparticles through the simultaneous reduction process. The SPR frequency of Au/Cu alloy particles can easily be tailored to any value in between the SRP frequency value of monometallic Au and monometallic Cu by changing the initial concentration of Au/Cu ions in the mixture solution.

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