Optical absorption of colloidal dispersion of bimetallic nanoparticles Au/Pd

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Colloidal bimetallic Au/Pd nanoparticles are synthesized by the simultaneous reduction technique from their corresponding metallic salts in presence of poly(N-vinyl-2-pirrolidone). Depending upon the Au/Pd concentration ratio, bimetallic nanoparticles of different average size are formed. The UV-VIS optical absorption spectra of bimetallic nanoparticles prepared with different Au/Pd molar ratios revealed that the colloidal dispersions prepared by simultaneous reduction are not a simple mixture of monometallic Au and Pd nanoparticles, but the particles are composed of both the Au and Pd metals in the same structural boundary. The same trend is found in their XRD spectra. The average size of the bimetallic particles strongly depended on the molar concentration of Pd in the reaction mixture. The effect of Pd concentration on the size of bimetallic nanoparticles is studied.

Keywords: Colloidal dispersion; Bimetallic nanoparticles; Optical absorption

1. Introduction

Investigations on bimetallic nanoparticles in colloidal solution are of great interest due to their applications in catalysis[1-3], electronics[4] optical[4], and the change in the surface plasma band energy[5,6] relative to the component monometallic particles. Several methods have been reported on their preparation. Miner *et al*.[7] have synthesized bimetallic particles of gold/platinum by simultaneously reducing chloroplatinic and chloroauric acid in aqueous solution with citrate, and found that the absorption spectra of the alloy particles were not the sum of those of the pure components. Yonezawa and Toshima[8] have refluxed ethanol/water solutions of the two materials in the presence of poly (N-vinyl-2-pirrolidone) and obtained particles that they interpreted as being of the Au_{core}-Pt_{shell} type. Rémita *et al*.[9] used ionizing radiation to simultaneously reduce $HAuCl_4$ and K_2PtCl_4 in an aqueous solution-containing poly (acrylic acid) as stabilizer. In the present work, we report the preliminary results on the preparation of the colloidal dispersions of bimetallic Au/Pd nanoparticles. Their optical properties, size and structure were characterized by UV-VIS spectroscopy and X-ray diffraction (XRD). The effect of Pd concentration on the size of bimetallic nanoparticles is studied.

2. Experimental Section

Preparation of Colloidal Dispersions

The colloidal dispersions were prepared by an improved simultaneous reduction method[10]. Solutions of tetrachloroauric acid (99.9% Aldrich, 0.033 mmol in 25 ml of water) were prepared by dissolving the corresponding crystalline material in deionized distilled water. Ethanol solutions of palladium (II) chloride (99.9% Aldrich, 0.033 mmol in 25 ml of ethanol) were prepared by stirring the dispersions of $PdCl_2$ powder in ethanol (99.9% J. T. Baker). Both solutions were mixed at room temperature at various ratios to produce bimetallic ethanol/water (1/1 v/v) (50 ml) solutions containing poly (N-vinyl-2-pyrrolidone) (99.9% Aldrich, PVP, K-30, 151 mg. MW 10 000) as a protecting polymer. The total amount of both the metals was always kept $3.3X10^{-5}$ mol in 50 ml of the mixture solution. The mixture solutions were refluxed at about 100 °C for 2 h. For the preparation of the physical mixture of Au and Pd colloidal nanoparticles, the colloidal solutions prepared separately were mixed by stirring at room temperature.

Characterization

A Shimadzu UV-3101PC double beam spectrophotometer with slit wavelength of 2 nm and light path length of 1cm was used to record the absorption spectra of the colloids. Samples (20 ml of concentrated colloidal solution) for x-ray diffraction (XRD) study were prepared by evaporating the colloid solutions on quartz glass substrates (1cm^2) in vacuum at room temperature. A Simens D5000 x-ray diffractometer with monochromatic CuK_{α} radiation source was used for recording the XRD spectra of the samples with a step width of 0.01°. The average particle size was estimated from the XRD spectra of the corresponding sample, using Scherrer´s equation.

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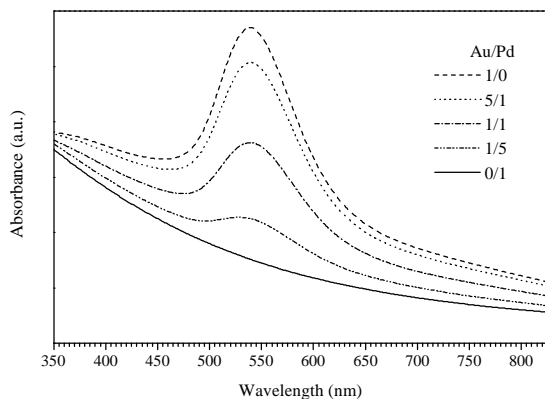[2]*Corresponding author, e-mail: upal@sirio.ifuap.buap.mx Tel: +52 22 45 76 45*

Figure 1.   UV-vis absorption spectra of the physical mixtures of individual Au and Pd nanoparticles at Au/Pd = 1/0, 5/1, 1/1, 1/5 and 0/1.
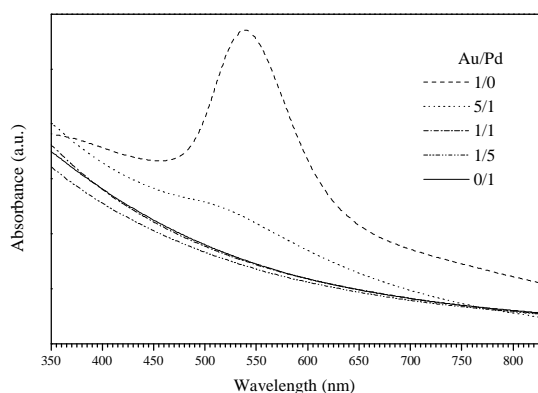

Figure 2.   UV-vis absorption spectra of the Au/Pd bimetallic nanoparticles at Au/Pd = 1/0, 5/1, 1/1, 1/5 and 0/1.
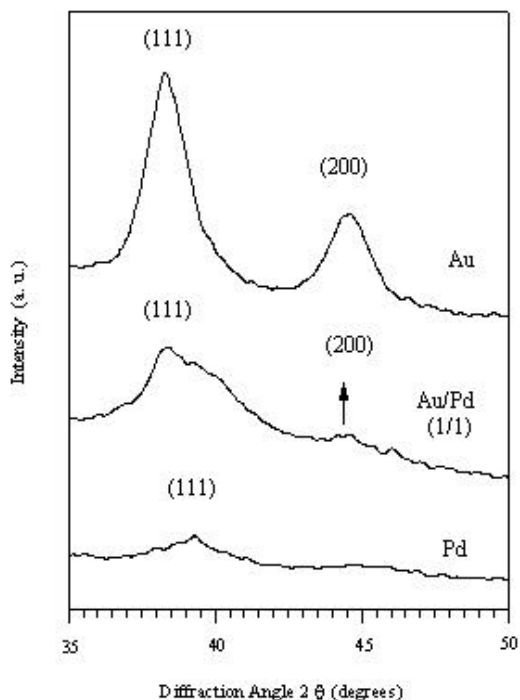

Figure 3. XRD pattern spectra of the Au/Pd bimetallic nanoparticles, Au and Pd monometallic nanoparticles

3. Results and discussion

UV-VIS Absorption Spectra

Figure 1 shows a series of the UV-VIS absorption spectra for the physical mixtures of Au and Pd monometallic nanoparticles. The spectra for monometallic Au and monometallic Pd are also presented as reference. The absorption peak revealed at around 540 nm is the surface plasma absorption of Au particles[11]. The intensity of the absorption band increased with the increase of Au/Pd ratio, and is prominent even at small Au/Pd ratio. The absorption spectra for the bimetallic systems, as illustrated in Figure 2, revealed no significant surface plasmon absorption band except for the Au/Pd (5/1) system where a very small absorption peak appeared. This phenomenon was consistent with the previous observations that the presence of a group 10 metal (d^8s^2) in bimetallic nanoparticles suppress the surface plasma energies of group 11 metal ($d^{10}s^1$) [12-14] and implied the formation of Au/Pd bimetallic nanoparticles in our samples. Furthermore, the sudden disappearance of the surface plasma absorption band of Au in our other samples (apart from Au/Pd = 5/1) implied that the surface of the Au/Pd bimetallic nanoparticles obtained in this work have more Pd atoms than the inner core.

XRD Spectra

  Figure 3 shows the XRD patterns of the monometallic Au and Pd , and bimetallic Au/Pd (1/1) nanoparticles. The spectrum of monometallic Au reveled two sharp scattering peaks at 38.2°and 44.6°, which can be assigned to (111) and (200) planes, respectively. This revealed that the resultant Au particles were in the face-centered cubic (fcc) structure. On the other hand, the scattering peaks were sharp unlike the results for the other two samples. According to Scherrer's equation, it implies that the crystallite size is large for monometallic Au particles. It is well know that gold particles drastically grow by coalescence during condensation of the colloid[15]. The monometallic Pd colloid revealed one broad peak centering at about 39.2°, which is identified as the (111) plane palladium. The bimetallic Au/Pd (1/1) colloid revealed scattering peaks at 38.5° and 44.5° which are very close to the peak positions of (111) and (200) planes of gold. Although the two peaks are very broad, the position of the first peak clearly indicates an intermediate scattering angle between those of the monometallic colloids. Consequently, it was found that alloying of the two metal atoms was taking place throughout. The same trend is found in their UV-VIS absorption spectra. Using the Scherrer's equation different authors[16] have calculated the size particle, we estimated he size for both monometallic and bimetallic particles. The broad line width of the XRD peaks may be due to fluctuations in the composition as well as due to the small particle size. The estimated particle size for the monometallic Au, Pd and bimetallic Au/Pd (1/1) were of

8.44 ± 0.03 nm, 3.02 ± 0.01 nm and 3.2 ± 0.07 nm respectively. The decrease of the size of the bimetallic Au/Pd (1/1) colloid, with respect to the monometallic Au, can be explained considering the velocity of growth of the individual metal particles. The ionization potential of Pd (8.33 eV) is known to be lower than the ionization potential of Au (9.22 eV)[17]. So, the incorporation of more Pd in the reaction mixture inhibits the growth of bimetallic particles.

4. Conclusion

Colloidal dispersions of bimetallic Au/Pd nanoparticles have been successfully prepared by the simultaneous reduction of the corresponding ions in presence of the poly(N-vinyl-2-pirrolidone). The comparison of the UV-VIS absorption spectra for the bimetallic system and the physical mixture of monometallic nanoparticles revealed that the nature of the structural compositions of the complex particles formed by those two processes are different. In the latter case, the complex particles were formed by physical adherence of two monometallic particles, whereas, in the earlier case, the particles were formed with a Au core surrounded by a Pd cap layer. The XRD analysis also suggested the formation of bimetallic nanoparticles through the simultaneous reduction process and revealed that the average particle size of the bimetallic nanoparticles is inversely proportional to the content of Pd in them.

Acknowledgments

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