

Preparation and Growth Mechanism Study of Polymer Protected Au/Pd Bimetallic Nanoparticles by Simultaneous Reduction of HAuCl_4 and PdCl_2

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Abstract: We report on the preparation of polymer-protected gold-palladium bimetallic particles in colloidal form by the reduction of corresponding metal ions simultaneously. Formation of nanoparticles and their constitution were studied by x-ray diffraction (XRD), transmission electron microscopy (TEM) and optical absorption spectroscopy techniques. The average size of the particles depended strongly on the molar ratio of two metal ions in the reaction mixture. XRD study revealed that the Au/Pd colloids prepared with different molar ratios form some partially alloyed structure of those metals. A high concentration of Pd ions in the reaction mixture produces non-dispersed small bimetallic colloids. Mechanism of formation of bimetallic Au/Pd particles has been studied.

Key words : Clusters, Nanoparticles, Bimetallic colloids, Optical properties, Growth mechanism.

1. INTRODUCTION

The metal clusters composed of two different metallic elements are of great interest from the viewpoint of variation of electronic structure and the ensemble effect in catalysis. Since the last 20 years, several reports have been published on the preparation of polymer protected bimetallic colloidal dispersions of two noble metals¹⁻³. Mulvaney et al.⁴ have prepared the Au/Ag bimetallic particles via electron transfer onto the silver particles by radiolytically generated free radicals and subsequent reduction of dissolved $\text{Au}(\text{CN})_2^-$ by stored electrons. Bimetallic clusters such as Pt/Re⁵, In/Pt⁶, and Pt/Sn⁷ dispersed in metal oxide such as Al_2O_3 , SiO_2 , TiO_2 and MgO , have been prepared and studied by several groups for their application in petroleum industry for hydrocarbon restoring. However, bimetallic clusters composed of a noble metal and a light transition metal should be

more prospective than those composed of only noble metals as the former can provide higher potential than latter for tailoring the structures and the catalytic properties. Bradley et al.⁸ and Esumi et al.⁹ have reported the preparation of Cu/Pd bimetallic colloids by thermal decomposition of the mixture of the corresponding metal acetates in presence or absence of polymer protective agents. Recently Mizukoshi et al.¹⁰ have prepared Au/Pd bimetallic nanoparticles by sonochemical method. Harada et al.¹¹ have prepared Au/Pd bimetallic clusters by simultaneous reduction of their corresponding salts.

The colloidal dispersions of noble metals, protected by polymer, can be prepared by reducing the noble metal ions in the refluxing solution of alcohol/water containing water soluble polymers such as poly(vinyl alcohol) and poly(N-vinyl-2-pyrrolidone)¹². The colloidal dispersions thus prepared are stable and 1-3 nm in average diameter with narrow size distributions. Such nanoparticles are very useful in catalysts with high activity and selec-

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tivity for the hydrogenation of olefins,¹³ selective partial hydrogenation of diene to monoene,^{14,15} light induced hydrogen generation from water,^{16,17} etc.

In the present paper, we report on the preparation and growth mechanism study of the colloidal dispersions of the polymer protected gold/palladium bimetallic clusters by simultaneous reduction process and their characterization. Both the monometallic and bimetallic clusters were grown with poly(N-vinyl-2-pyrrolidone) protector. Bimetallic clusters with different molar ratios of Au-Pd were prepared and characterized by x-ray diffraction (XRD), transmission electron microscopy (TEM) and optical absorption spectroscopy. Mechanism of formation of Au/Pd bimetallic particles is studied by optical absorption spectroscopy during growth.

2. EXPERIMENTAL

Colloidal dispersions of the Au/Pd bimetallic clusters were prepared by simultaneous reduction of the two metal ions in presence of poly(N-vinyl-2-pyrrolidone) (PVP) by using ethanol as a reducing agent. Ethanol solutions of palladium (II) chloride (0.033 mmol in 25 ml of ethanol) were prepared in advance by stirring dispersions of PdCl₂ powder in ethanol for 48 hrs. Solutions of tetrachloroauric acid (0.033 mmol in 25 of water) were prepared by dissolving the HAuCl₄ crystals in water.

For the preparation of the monometallic clusters of palladium, 75.5 mg of the PVP was added to the ethanol solution of PdCl₂ (0.033 mmol in 25 ml of ethanol) and refluxed for 2 hrs at 100°C. Monometallic Au particles prepared with ethanol as the reducing agent, were unstable. So, methanol was used as the reducing agent for the preparation of monometallic Au particles. Methanol solution of HAuCl₄ (0.033 mmol in 25 ml of methanol) was mixed with the methanol solution of PVP (75.5 mg in 25 ml of methanol) and the mixture solution was refluxed for 1hr at 100°C. As the alcohols (reducing agents) contain α -hydrogen and are oxidized to the corresponding carbonyl compound (e.g. methanol to formaldehyde, ethanol to acetaldehyde), it requires the addition of a hydroxide ion in order to be effective¹⁸. Therefore, a solution of sodium hydroxide (0.17 mol of NaOH in 5 ml of water) was added drop by drop to the pre-refluxed solution and refluxed again at 100°C for 10 minutes. Addition of the hydroxide solution to the mixture produced a homogeneous dispersion of Au particles (of red color) in the solution.

For preparing bimetallic clusters, solutions containing two metal ions were mixed in 50 ml of pure ethanol/water (1/1 v/v) mixture containing 151 mg of PVP (K-30, average molecular weight 10,000) with a total metal ion content of 6.6×10^{-5} mol. The mixture solution was stirred and refluxed at about 100°C for 2 hrs.

For the preparation of bimetallic clusters with different metal content ratios, metal ion solutions of corresponding ratios were mixed in ethanol/water mixture containing PVP, maintaining the total metal ion content in the final mixture fixed (6.6×10^{-5} mol) and then refluxed at 100°C for 2 hrs.

For the study of growth mechanism of bimetallic clusters, separately an ethanol solution of Au and a mixture solution of Au and Pd (4/1) ions were refluxed. During the refluxing process a few ml solutions were collected from the refluxing container at different temperatures (during the increase of temperature) and studied by optical absorption spectroscopy at room temperature.

A Shimadzu UV-VIS 3101PC double beam spectrophotometer was used to record the absorption spectra of the colloids. For transmission electron microscopic (TEM) observations, a drop of colloidal solution was spread on a carbon coated copper microgrid and dried subsequently in vacuum. A JEOL-JEM200 microscope was used for TEM observations. Samples for x-ray diffraction (XRD) were prepared by evaporating the concentrated colloid solution on quartz glass substrates in vacuum at room temperature. A Siemens D5000 x-ray diffractometer with CuK α radiation was used for recording the XRD spectra of the samples. For the high resolution electron microscopy (HREM) study, a Jeol-4000EX electron microscope with 1.7 Å point-to-point resolution was used.

3. RESULTS AND DISCUSSION

Figure 1 shows the TEM images and corresponding size distributions of the monometallic and bimetallic nanoparticles prepared with different metal ion concentrations. Formation of nanoparticles is clear from the TEM micrographs. The size distributions followed a Gaussian fit with narrow size distribution for the bimetallic particles. We can observe that the monometallic Au particles (figure 1a) are very big with a broad size distribution in comparison with the monometallic Pd particles (figure 1d). The average size of the particles is lowest for monometallic Pd and it increased with the increase of Au/Pd ratio. TEM images of the monometallic Pd and bimetallic Au/Pd did not reveal the formation of aggregates in contrast with the monometallic Au particles. The increase of particle size on increasing the Au content in the bimetallic nanoparticles can be explained by considering the reduction kinetics of the individual metal ions. As the ionization potential of Pd (8.33 eV) is smaller than the ionization potential of Au (9.22 eV), the velocity of reduction of Au ions is faster than the velocity of reduction of Pd ions. So, an increase in the Pd ion content in the mixture solution inhibits the growth rate of the bimetallic nanoparticles and as the consequence, the bimetallic particles grow homogeneously. However a more clear understanding of the size control mechanism is revealed from the growth mechanism study of the particles, discussed latter in this section.

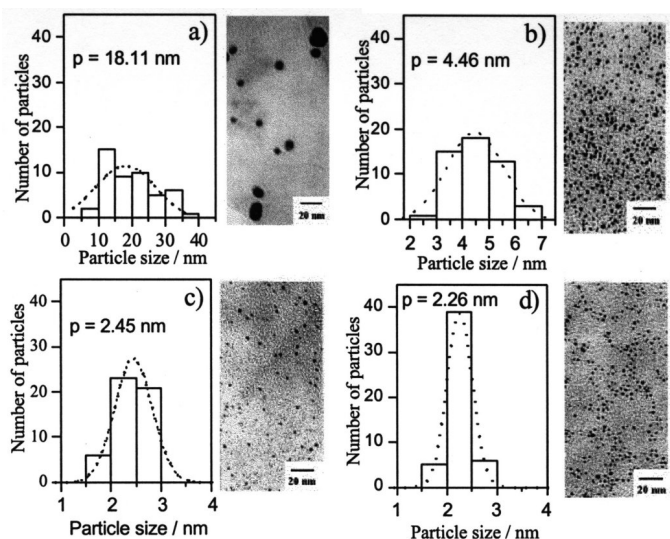


Figure 1: Electron micrographs and normalized size distribution of particles of the metal colloids: a) monometallic gold, b) bimetallic Au/Pd (mole ratio = 4/1), c) bimetallic Au/Pd (mole ratio 1/4), and d) monometallic palladium.

Figure 2 shows the XRD profiles of the bimetallic Au/Pd (1/1) nanoparticles and of monometallic Au and Pd particles. The XRD pattern for monometallic Au revealed two sharp peaks at about 38.2° and 44.6° which were assigned to the (111) and (200) planes of gold respectively. Whereas, the monometallic Pd revealed only one peak at about 39.5° correspond to the (111) plane of Pd metal. In the bimetallic dispersions of Au/Pd, all those three peaks were revealed. However, the peak positions were not exactly the same as that of monometallic samples (i.e. 38.5° and 44.5° for Au/Pd=1/1), which demonstrates the formation of an alloy of two metals in bimetallic colloids. Using the Scherrer formula:

$$P = 0.9\lambda / (B \cos \theta_B)$$

(where P is the average particles size, B is the angular width of the diffraction peak and θ_B is the Bragg angle at the peak position), and using $\lambda = 1.5408 \text{ \AA}$ for the $\text{CuK}\alpha$ radiation, we calculated the size for both monometallic and bimetallic particles. The calculated particle size for the monometallic Au, Pd and bimetallic Au/Pd (1/1) were 12.5 nm, 2.95 nm and 3.85 nm respectively; whereas, the average particle size calculated from the TEM micrographs were 18.1 nm, 2.26 nm and 4.46 nm respectively.

In figure 3, the absorption spectra of the colloidal dispersions of bimetallic Au/Pd are presented. The spectra for monometallic Au and monometallic Pd are also presented as reference. All

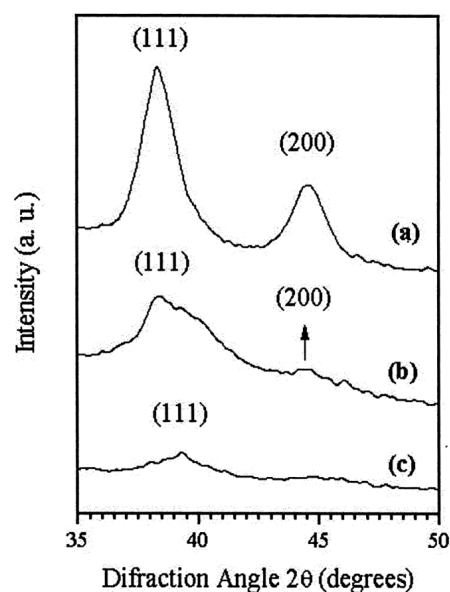


Figure 2: XRD profiles of a) monometallic Au, b) bimetallic Au/Pd (mole ratio = 1/1) and c) monometallic Pd Colloids.

the spectra were recorded at room temperature. The absorption spectrum for monometallic Pd is monotonous revealing no absorption peak. An absorption peak at about 547 nm was revealed for the colloidal dispersions of Au clusters, which is generally assigned to the surface plasmon resonance (SPR) absorption of small Au clusters. On increasing the Pd ion content in the mixture solutions, along with the decrease in intensity, the position of the peak shifted towards lower wavelengths. Such a shift of the SPR band position is generally assigned to the reduction of the size of the Au particles. The peak did not reveal for the colloidal solutions containing less than 50% of Au. Our TEM observations have also revealed such a trend of size variation in bimetallic colloids. So, the content of Pd ions in the reaction mixture could control the size of the bimetallic particles. Sudden disappearance of plasmon absorption band in bimetallic colloids prepared with Au/Pd mole ratio $< 4/1$ indicates that the surface of the Au/Pd bimetallic particles prepared by this technique have more Pd atoms than the inner part, which in turn predicts the formation of a core-shell structure of the these particles, where Au remains as the core and Pd forms the shell structure around it. A similar core-shell structure in Au/Pd bimetallic particles has also been observed by other workers¹⁹. However, our HREM study did not reveal such a core-shell structure for most of the bimetallic particles. For example, in figure 4a, the HREM image for the Au/Pd (4/1) particle revealed a crystalline core of Au (111) (fcc) and an incomplete shell of crystalline Pd (111) (decahedral). Figure 4b shows the formation of Au/Pd alloy structure for the particles prepared with Au/Pd = 1/1 molar ratio. The formation of those structures is more clear from

the Fourier-transform TED pattern of the corresponding microscopic images. Surprisingly, the core-shell structure is favored for higher concentration of Au in the bimetallic particles. In the figure 4b, we can also observe the multiple twinned Au/Pd alloy particle with intermediate inter-planer spacing. However, the detailed analysis of the structure of the bimetallic particles is under study and will be reported later.

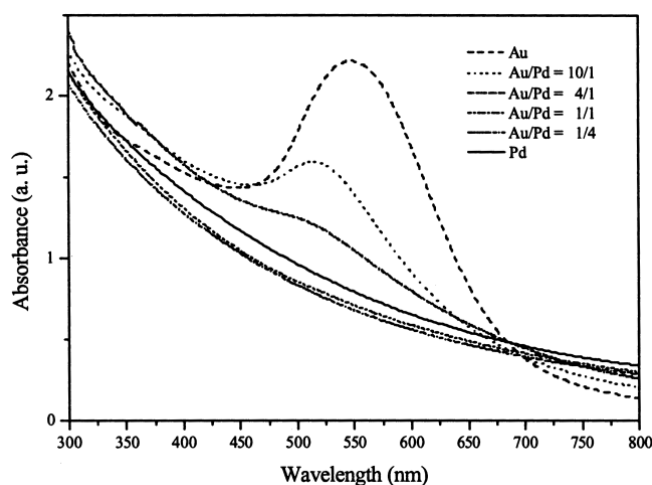


Figure 3: Optical absorption spectra of bimetallic colloids prepared with different Au/Pd mole ratios.

Figure 5 shows the absorption spectra at different stages of reduction of Au ions and Pd ions. At the initial stage of reduction, the absorption spectra of ethanol solution of Au revealed a band at about 320 nm corresponds to the presence of Au ions in the solution. On increasing the temperature of the solution during reflux, the intensity of the band decreased, indicating the reduction of Au ions to form neutral Au atoms. On increasing the temperature up to 100°C, though the reduction of Au ions continued, the formation of Au clusters did not occur (the color of the solution did not change and the SPR band in the absorption spectra did not reveal). If we compare the evolution of this band in figure 5a and 5b, we can observe that the rate of reduction of intensity of this band is faster when the Pd solution was added to the Au solution and the SPR band of Au clusters revealed. This, in turn, indicates that the rate of reduction of Au ions is favored by the addition of Pd solution in it. This phenomenon explains the size control process in the bimetallic Au/Pd colloids. Previously we have demonstrated that the increase of Pd content in the mixture solution reduces the size of the Au/Pd clusters, even when the total ion content in the mixture solution remained fixed. Addition of Pd in the Au solution accelerates the reduction process of Au, i.e. the nucleation rate of Au clusters increases, which is the main reason for the formation of smaller and less dispersive bimetallic particles for higher Pd contents²⁰.

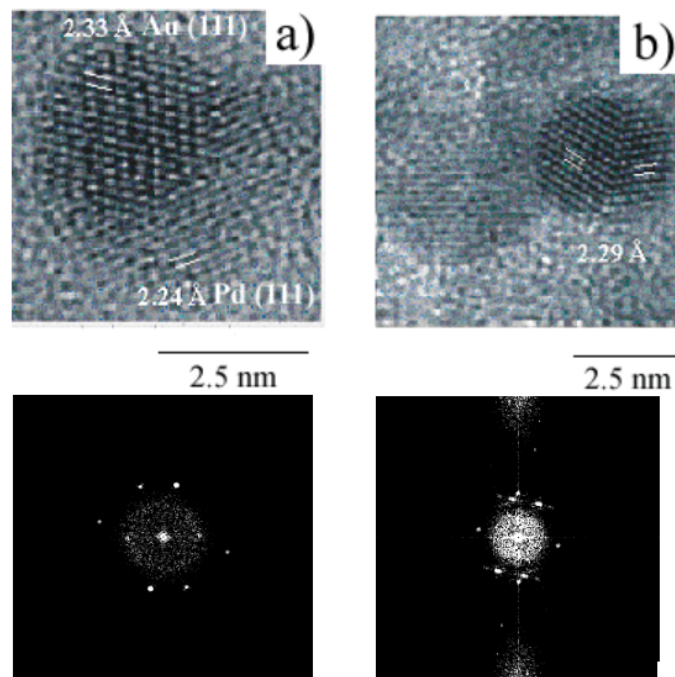


Figure 4: High-resolution electron micrographs of bimetallic colloidal particles: (a) Au/Pd = 4/1 and (b) Au/Pd = 1/1 and their corresponding Fourier-transform TED patterns (at the bottom).

On increasing the temperature of the mixture solution during the refluxing process beyond 52°C, clusters of Au formed revealing a SPR band of Au at about 545 nm. Higher the temperature of the solution, more and bigger is the size of the Au clusters (figure 5b). Until a temperature of 60°C of the mixture solution, the clusters were monometallic Au, i.e. Pd ions were not reduced up to that temperature. Increase of the intensity of the band located at about 545 nm, and its slow displacement towards higher wavelengths indicates the growth of more and bigger Au clusters. The reduction of Pd ions starts at about 63°C of the reaction mixture. In figure 5b, we can observe a sudden shift of the SPR band of Au towards lower wavelengths (for the solution temperature of 64°C). Such a shift of the SPR band of Au is due the formation of bimetallic clusters. The contact between two metals, differing not only their electron configuration but also in their electronegativities, causes the electron transfer process from the electropositive Pd to the electronegative Au. The increase of electron density in Au causes a blue shift of the surface plasmon resonance band. The last spectrum in the figure 5b revealed a band at about 510 nm due to the formation of stable Au/Pd bimetallic clusters.

4. CONCLUSION

Polymer protected colloidal dispersions of bimetallic Au/Pd nanoparticles have been prepared by simultaneous reduction of

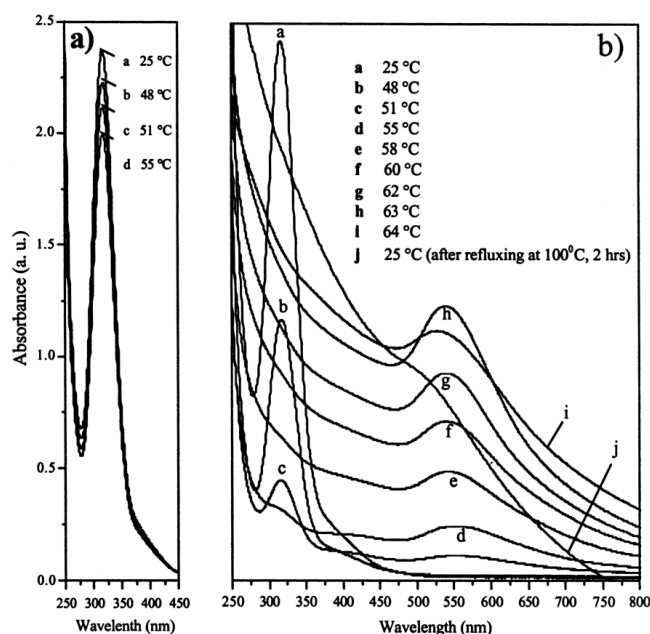


Figure 5: Uv-Vis spectra at various reduction temperatures of (a) HAuCl_4 and (b) $\text{PdCl}_2/\text{HAuCl}_4$ (4/1) in ethanol/water (1/1) in the presence of PVP.

HAuCl_4 and PdCl_2 in presence of poly(N-vinyl-2-pyrrolidone). XRD and optical absorption spectra of the samples revealed that the bimetallic nanoparticles are not the simple mixture of Au and Pd particles. Due to the faster velocity of reduction of Au, it forms the inner core and Pd forms the outer shell of the compound particles. However, for lower mole concentration of Au the bimetallic clusters do not form a core-shell like structure. Incorporation of Pd onto the Au clusters starts at about 64⁰C of the refluxing mixture. The size of the bimetallic particles depends strongly on the Au/Pd mole ratio in the mixture solutions. Increase of Pd content in the mixture solution accelerates the nucleation rate of Au clusters, causing the formation of monodisperse bimetallic particles. The position of the SPR band of Au clusters shifts towards lower wavelengths due to the electron transfer for Pd to Au in the bimetallic clusters.

5. ACKNOWLEDGMENTS

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