SYNTHESIS OF MONODISPERSE Au, Pt, Pd, Ru AND Ir NANOPARTICLES IN ETHYLENE GLYCOL

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Abstract—Au, Pt, Pd, Ru and Ir nanoparticles with a narrow size distribution have been synthesized by chemical reduction of their corresponding metal species in ethylene glycol. In all cases, the average particle size was found to be smaller than 10 nm. Particle size was mainly controlled by varying the initial total metal concentration, the reaction temperature, and the concentration of PVP. With the exception of Ir, metal particle agglomeration and sintering was prevented by the addition of PVP, a well known protective agent that also aids particle dispersion. *©2000 Acta Metallurgica Inc.*

Introduction

Many physical and chemical properties of modern materials for electronics, optics, catalysis, and other high-tech applications depend closely on the manufacturing process (1). To meet the stringent properties and characteristics of these materials, seldom achieved by classical high temperature synthesis of solids, precise control of the synthesis method is always crucial. One characteristic that gives special properties to solid materials, whether in the form of powders or thin films, is its size. When at least one dimension is in the nanometer range, the material exhibits remarkable and unusual properties, absent in the bulk phase. The preparation of these small size materials at relatively low temperature is possible using soft-chemistry methods, which offer the possibility of producing tailor-made materials. In the case of nanosize metal powders, their synthesis by chemical reduction of metal species in both aqueous and nonaqueous solutions has been amply reported (2–5). Electrochemical reduction has been also used to produce Pd and Ni nanoparticles (6).

Synthesis and processing of nanoparticles pose a number of difficulties, especially in terms of reactivity and agglomeration (7). The remarkable reactivity of nanoparticles, which makes them potential candidates as catalysts, is associated to their high fraction of surface atoms as compared to conventional particles. In certain applications, a uniform dispersion of nanoparticles is required. Unsupported nanosize particles of Pt-group metals, for example, are excellent catalysts for many chemical reactions, but their catalytic properties depend on their average size. An effective control of particle size continues to be the most difficult challenge for researchers involved in the synthesis of colloidal metal dispersions (8). In addition, since individual nanoparticles have a tendency to form agglomerates during the preparation process, control of particle-particle interaction is critical for obtaining a stable dispersion. To ensure the preparation of individual nanoparticles, it is particularly

important to inhibit the formation of hard agglomerates through a physical bond, or neck (7). In the present investigation we have prepared metallic dispersions of finely divided Pt, Pd, Au, Ru and Ir in ethylene glycol. This polyol serves both as solvent and reducing agent of metal species. Synthesis of these nanosize metals was achieved by varying the reaction temperature, the initial concentration of metal compounds, and the mode and order of addition of reactants.

Experimental Materials and Methods

Materials

All chemicals used in this research work were reagent grade materials. Ethylene glycol (Prolabo) served as solvent and reducing agent. PVP (K15, M.W. 10 000, Aldrich) was used as protective agent. Metal particles were formed from the following compounds: palladium nitrate, palladium tetraammine nitrate, ruthenium chloride, hexachloroplatinic acid, tetrachloroauric acid and hexachloroiridic acid (ABCR).

Methods

Palladium, Ruthenium and Iridium Nanoparticles

These metal colloids were synthesized in a four-neck round flask as follows. A chosen amount of PVP was dissolved in 75 mL ethylene glycol at room temperature and under magnetic stirring, then the metal compound was added. After dissolution of the solid, the solution was heated up to the selected temperature at a rate of 1 °C/min. The reaction was allowed to proceed at constant temperature for a fixed time. A heating mantle connected to a Eurotherm regulator was used to carry out the metal synthesis under controlled heating rate and at constant temperature.

Platinum Nanoparticles

45 ml of ethylene glycol were heated up to 150 °C at a rate of 5 °C/min, then a 5ml solution of EG-H_2PtCl_6 (500 mg) are injected into the hot ethyelene glycol and 25 ml EG-PVP solution (100 mg or 500 mg) are added drop by drop with the aid of a peristaltic pump. The addition of PVP takes about 13 min, and then the reaction is stopped after one hour.

Gold Nanoparticles

Colloidal gold has been synthesized following the procedure described elsewhere (9).

Characterization of Colloidal Dispersions

An aliquot of the nanoparticles dispersion (about 2 ml) was taken and introduced into a small test-tube, which was rapidly cooled in tap water. Then, a volume of acetone (5:1, acetone:dispersion) was added and the system agitated before centrifugation. The supernatant was discarded, replaced by distilled water, and then the particles were redispersed under ultrasound. This cycle was repeated several times until a clear supernatant was obtained.

A drop of the washed colloidal metal dispersion was deposited onto a carbon-coated copper grid and observed using a Philips CM12 transmission electron microscope. Particle shape, average size and size distribution were determined from electron micrographs. By using the "Biocom" program, image

analyses of these micrographs allowed the construction of histograms, from which both the average particle size and standard deviation were calculated.

Nanoparticles were also characterized by X-ray powder diffraction using a Philips PW 17/29 diffractometer and CuKα radiation (1.5418 Å).

Results and Discussion

Palladium Nanoparticles

Upon dissolution of palladium nitrate in ethylene glycol at room temperature, finely divided metallic palladium is formed indicating that free Pd(II) ions are instantaneously reduced by this solvent to elemental metal. The formation of palladium nanoparticles at room temperature, however, is a slow process. After several hours of reaction, the solids were separated from the supernatant, which was then tested for Pd(II) ions in solution. Upon the addition of a few drops of hydrazine, a black precipitate was observed to form indicating the presence of unreduced metal ions in solution. To speed up the reduction of Pd(II) by ethylene glycol, the reaction temperature was increased up to 100 °C. The material prepared at this temperature, however, exhibits a high degree of particle sintering. It was therefore necessary to add PVP, a well known particle-protecting polymer agent that effectively adsorbs onto colloidal particles thus inhibiting particle sintering. Surprisingly, as the amount of PVP increased the average particle size also increased. When $Pd(NH_3)_4(NO_3)_2$ is used to synthesize palladium metal, however, its
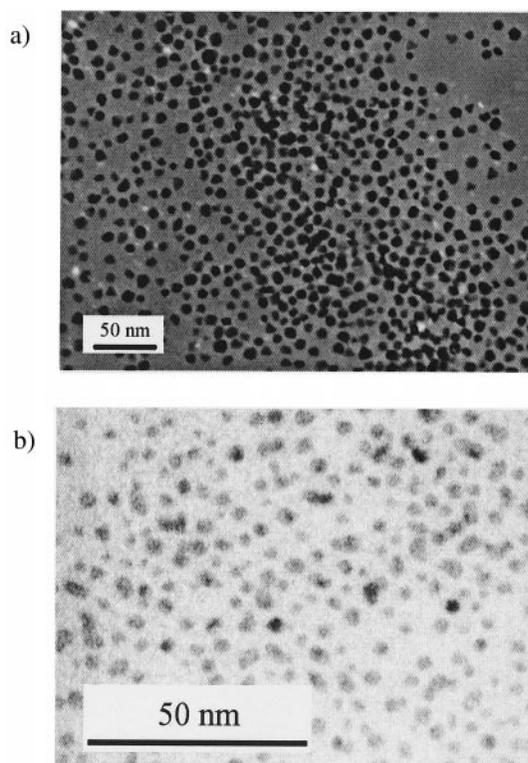

Figure 1. Micrographs of palladium nanoparticles synthesized from two different metal compounds in ehtylene glycol-PVP solutions. a) palladium tetraammine nitrate and b) palladium nitrate.
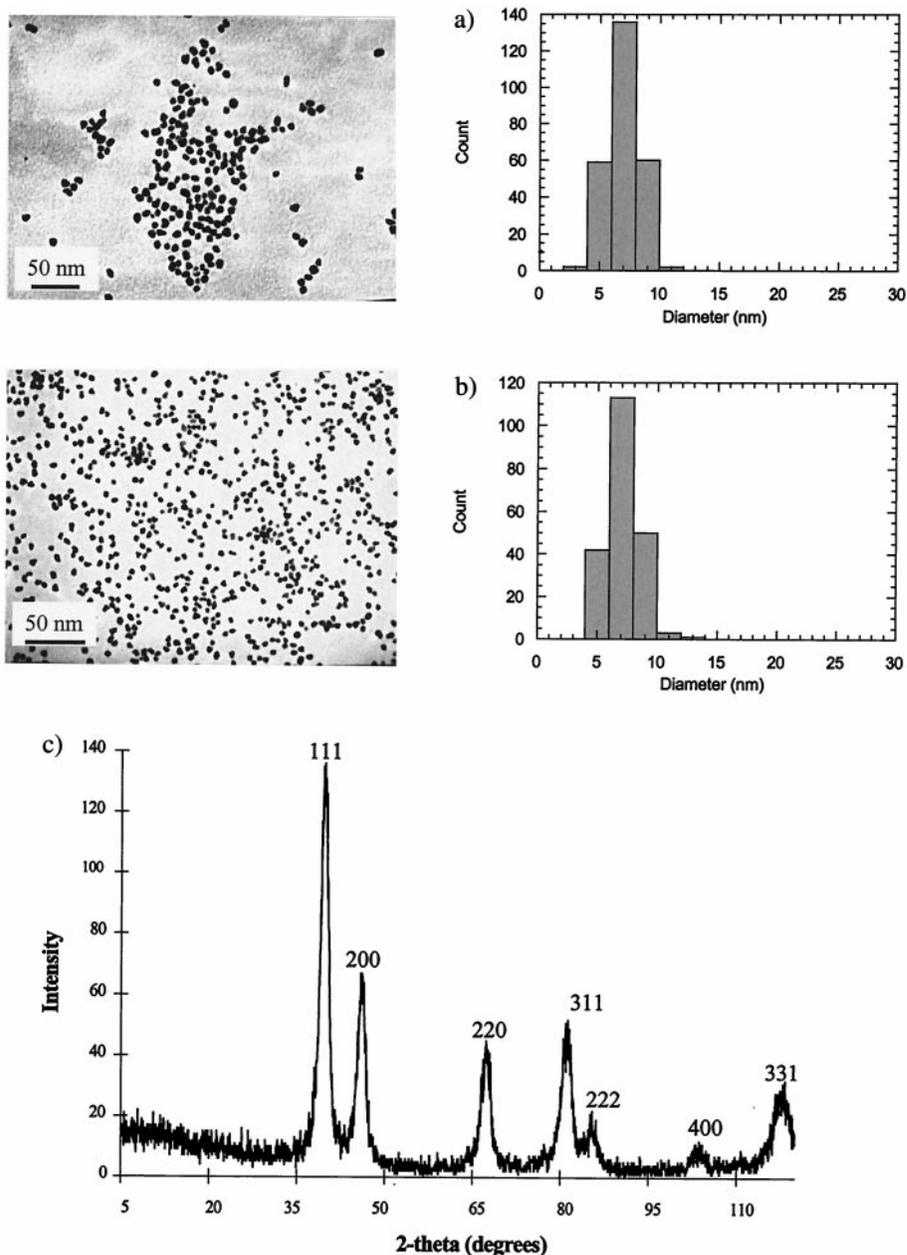
Figure 2. Micrographs and the corresponding histograms of platinum nanoparticles synthesized from hexachloro platinic acid in ethylene glycol in the presence of two different quantities of PVP. a) 100 mg and b) 500 mg. c) the corresponding X-ray diffraction pattern of platinum nanoparticles.

dissolution in ethylene glycol is not followed by the reduction of Pd(II) species. In this system, complexation of Pd(II) by ammonia stabilizes the metal species against reduction by ethylene glycol. Heating the palladium solution up to 100 °C yields colloidal palladium, but this dispersion contains a large proportion of sintered particles. The formation of palladium metal may involve first the thermal
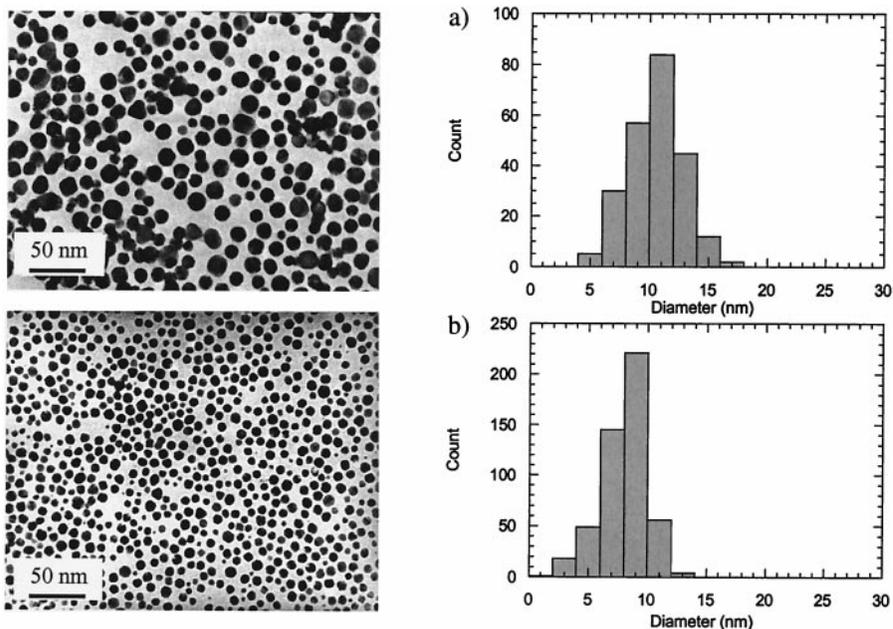
Figure 3. Micrographs and the corresponding histograms of gold nanoparticles synthesized from tetrachloro auric acid in ethylene glycol in the presence of two different quantities of PVP. a) 5 g and b) 7 g.

decomposition of the palladium-ammine complex and the subsequent reduction of the free palladium by ethylene glycol. Again, addition of PVP inhibits particle sintering and allows the preparation of colloidal dispersions containing discret particles. Depending on the mass of palladium tetraammine nitrate used, the average particle size obtained was 19 nm and 10 nm for 0.48 g and 0.06 g, respectively. Examples of these products are presented in Figures 1a and 1b.
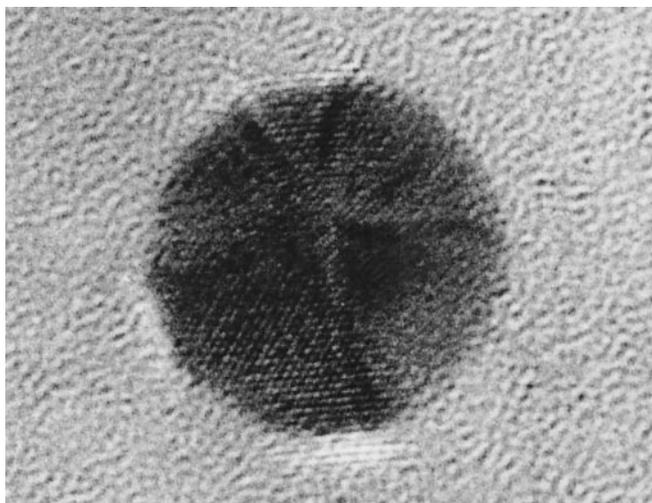

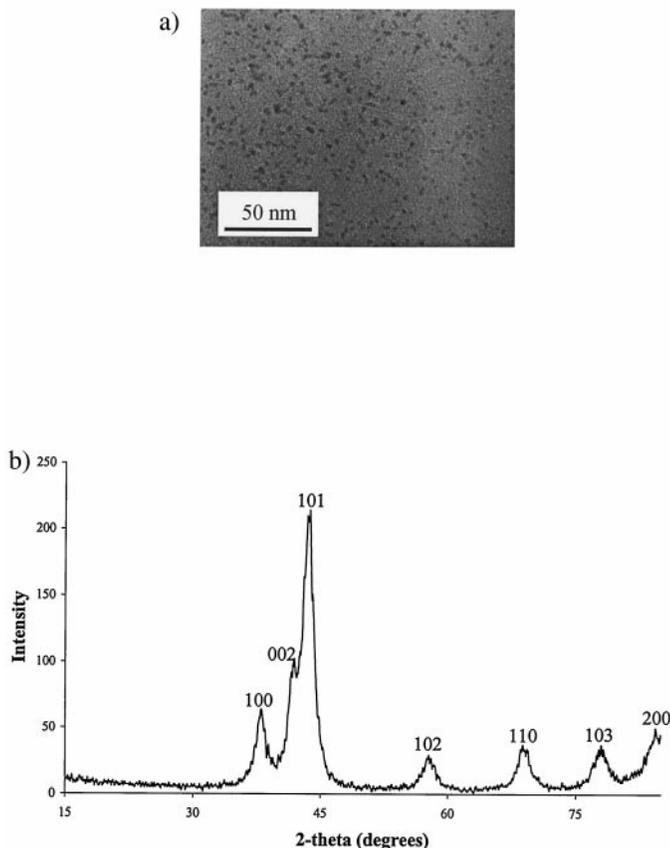Figure 4. High resolution electron micrograph of a gold nanoparticle (11.6 Å).

Figure 5. a) Micrograph of ruthenium nanoparticles synthesized from ruthenium chloride in ethylene glycol in the presence of 2.0 g PVP, and b) the corresponding X-ray diffraction pattern of ruthenium nanoparticles.

Platinum Nanoparticles

The hexachloroplatinic complex is stable towards reduction by ethylene glycol at room temperature, but it is reduced at 110 °C into elemental platinum. After 30 min of reaction at this temperature, the solution becomes progressively brown and then it turns into a black dispersion. The product obtained after four hours of reaction was found to be composed of colloidal particles with a size smaller than 10 nm and with a considerable degree of sintering. To achieve colloidal platinum dispersions with a narrow size distribution and free of sintering, small amounts of PVP were required. An excess PVP (between 1 g and 3 g) inhibitted completely the reduction of $PtCl_6^{2-}$ perhaps due to the formation of a stable complex. Under these conditions the color of the solution does not change, even after several hours, and metallic platinum is not detected. Regardless of the experimental conditions used, the size of platinum colloids obtained was always about 7 nm. Figures 2a and 2b show micrographs of colloidal platinum synthesized from 500 mg $H_2PtCl_6.6H_2O$ at 150 °C in the presence of 100 mg and 500 mg PVP. The corresponding histogram is also presented in this figure. Even though the particle size distribution of colloidal platinum is very narrow, it exhibits no regular particle shape. X-ray powder diffraction of these nanoparticles revealed a well crystallized material; its diffractogram (presented as Figure 2c) shows broad peaks, characteristic of small crystallites, and it correspond to metallic fcc platinum according to

the JCPDS (4–802). A mathematical analysis of the Bragg peaks was undertaken to calculate the crystallite size using the Scherrer formula. The obtained result was 5.4 Å, in good agreement with the mean particle size of 7.5 Å calculated from the image analysis of TEM micrographs. Since the Scherrer calculation always underestimates the real crystallite size, these results seem to corroborate the monocrystaline nature of platinum nanoparticles.

Gold Nanoparticles

Micrographs of colloidal gold prepared at 120 °C from 50 mg $HAuCl_4.3H_2O$ in the presence of 5 g and 7 g PVP are presented in Figures 3a and 3b, respectively. The corresponding histograms of these particle assemblies, which are also presented in these figures, show a narrow size distribution. From these micrographs, it is also clear that as the amount of PVP increases the average particle size decreases: from 11 nm for 5 g PVP to 8 nm for 7 g PVP. When the amount of added PVP is smaller than 5 g, colloidal gold prepared under these conditions shows a wide particle size distribution and a significant degree of sintering. These findings confirm the role of PVP as an effective colloidal protecting agent that also limits particle growth. In addition, since PVP has also been found to act as reducing agent of aqueous $AuCl_4^{2-}$ (10), it could also reduce this gold complex in ethylene glycol. Two experiments performed with 10 g added PVP indicate that indeed this polymer induces the reduction of gold tetrachloro complex in ethylene glycol and speeds up the kinetics of particle formation. At 120 °C, the solution becomes dark red upon the addition of the gold precursor while at 4 °C it becomes red overnight. In both cases colloidal gold (particle sizes between 5 nm and 13 nm) was detected by transmission electron microscopy.

Colloidal gold particles were also characterized by high resolution electron microscopy. Figure 4 presents a micrograph of a single gold particle (size = 116 Å), multiply twinned, with a decahedral shape. Observation of other particles also revealed a polyhedral shape. These results seem to indicate that colloidal gold is monocrystalline.

Ruthenium Nanoparticles

Nanosize ruthenium particles with a very narrow size distribution are obtained by ethylene glycol reduction of ruthenium chloride at 150 °C in the presence of PVP. Figure 5a is a micrograph of these particles, which are clearly free of sintering. The average size of monodisperse ruthenium particles was
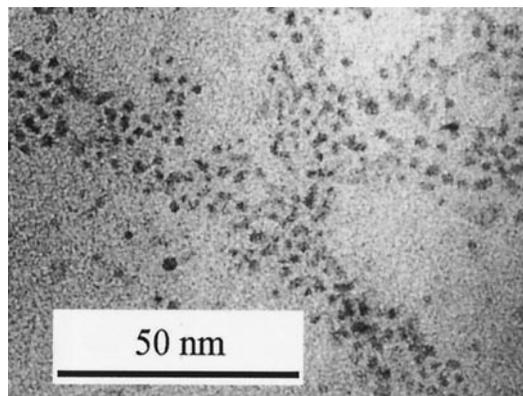

Figure 6. Micrograph of iridum nanoparticles synthesized from hexachloro iridic acid in ethylene glycol.

determined to be 2 nm. The X-ray diffractogram presented in Figure 5b shows peaks characteristic of finely divided metallic ruthenium according to the JCPDS (6–663): they are very broad at the base.

Iridium Nanoparticles

As opposed to the synthesis of all metallic nanoparticles reported in this work, iridium particles synthesized at 100 °C in the absence of PVP are free of sintering. The average size of these particles, which are shown in the micrograph presented as Figure 6, was found to be about 3 nm.

Conclusions

Nanosize dispersions of Pt-group metals with a narrow particle size distribution can be synthesized by chemical reduction of selected metal compounds with ethylene glyclol in the presence of PVP. With the exception of Ir nanoparticles, the addition of PVP is necessary to prevent interparticle sintering. In the case of Pt, however, the amount of PVP added was found to be critical because an excess inhibits completely the reduction of the metal complex, thus preventing the formation of metallic platinum. Control of the average particle size and degree of sintering of these dispersions was possible by using different quantities of metal starting materials and PVP, and by modifying the experimental mode of particle preparation. Colloidal dispersions of Pt, Pd, Au, Ru and Ir remain stable after several months. The X-ray diffractograms of these metallic particles indicate that they are crystalline, and show broad peaks characteristic of materials with a small crystallite size.

Acknowledgments

References

1. A. Rousset, Solid State Ionics. 84, 293 (1996).
2. P. R. Van Rheenen, M. J. McKelvy, and W. S. Glaunsinger, J. Solid State Chem. 67, 151 (1987).
3. K. Esumi, O. Sadakane, K. Torigoe, and K. Meguro, Colloids Surf. 62, 255 (1992).
4. J. H. Clint, I. R. Collins, J. A. Williams, B. H. Robinson, Th. F. Towey, Ph. Cajean, and A. Khan-Lodhi, Faraday Discuss. 95, 219 (1993).
5. S. Ayyappan, R. S. Gopalan, G. N. Subbanna, and C. N. R. Rao, J. Mater. Res. 12, 398 (1997).
6. M. T. Reetz and W. Helbig, J. Am. Chem. Soc. 116, 7401 (1994).
7. M. N. Rittner and Th. Abraham, Int. J. Powder Metall. 34, 33 (1998).
8. J. S. Bradley, in Clusters and Colloids, ed. G. Schmid, Chap. 6, VCH, Weinheim (1994).
9. P. Y. Silvert and K. Tekaia-Elhsissen, Solid State Ionics. 82, 53 (1995).
10. P. Y. Silvert, Ph.D. Thesis, Université de Picardie Jules Verne, 157 pp. (1996).