

Nanoparticles of Ag, Au, Pd, and Cu produced by alcohol reduction of the salts

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Nanoparticles of Ag, Au, Pd, and Cu have been prepared by the reduction of their salts by ethyl alcohol under refluxing conditions in the presence of polyvinylpyrrolidone (PVP). In the case of Au and Cu, it was necessary to use magnesium metal as a catalyst during the reduction. The nanoparticles are in the 5–35 nm range in the case of Ag, Au, and Pd, but there is considerable agglomeration in the case of Cu even in the presence of PVP.

I. INTRODUCTION

Fine metal particles of uniform size and shape and of high purity are of technological importance in the electronics industry and are used in conducting inks, paints, and adhesives.^{1,2} Monodispersed metal particles of near micron dimensions have been successfully prepared by the polyol process.² In the polyol process, a metal salt is reduced by a liquid polyol such as ethylene glycol under refluxing conditions. By this method, monodispersed microparticles of silver, gold, copper, and cobalt have been prepared.^{2,3} There has been some effort recently to prepare nanometric metal particles. For example, Puvvada *et al.*⁴ have used the bicontinuous cubic phase of glycerol mono-oleate for synthesizing Pd nanoparticles of ~4 nm diameter. Gold nanoparticles have been prepared by the reduction of H₂AuCl₄ by tetrakis (hydroxymethyl) phosphonium chloride by Duff *et al.*⁵ Nanoparticles of Ag–Pd and Cu–Pd alloys with diameters in the 5–40 nm range have been prepared over the entire range of compositions by employing the heterogeneous reaction between dry methanol or ethanol with intimate mixtures of AgNO₃ + PdO_x and CuO_x + PdO_x, respectively.⁶ We considered it fruitful to explore whether a simple alcohol such as ethanol can be used effectively as a reducing agent to prepare nanometric particles of various metals. In this paper,

we report the successful preparation of silver, gold, palladium, and copper nanoparticles using ethanol as the reducing agent. In preparing these nanoparticles, we have employed polyvinylpyrrolidone (PVP) as the protective agent to control the formation of the metal colloids and to stabilize them. PVP has been used as a protective agent by other workers in the preparation of colloidal metal particles of controlled size.^{6–8}

II. EXPERIMENTAL

In preparing the nanoparticles of Ag, Au, Pd, and Cu, the general procedure followed was as follows. A known quantity of the metal salt was taken to 100 ml of dry ethanol containing a predetermined quantity of polyvinylpyrrolidone (PVP), the salts being generally soluble in the alcohol. The weight ratio of the metal salt to PVP was generally 1:5 or 1:10. The ethanolic solution containing the metal salt and PVP was refluxed (~360 K) under stirring for a period of 12 h. This procedure was successful in yielding metal nanoparticles in the case of Ag and Pd, but it was necessary to add one equivalent of magnesium metal powder (relative to the metal salt) in the case of Au and Cu in order to facilitate the reduction. Here, the Mg metal acts as the reducing agent.⁹ Ethanol itself gets oxidized into acetaldehyde and other products in the reaction. At the end of the reaction period, a drop of the solution was placed on a holey carbon grid. After the evaporation of the alcohol,

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transmission electron microscope (TEM) images were recorded using a JEOL (200 kV) microscope. X-ray diffraction patterns of the particles were recorded with a JEOL diffractometer in the case of Pd, Au, and Cu where we could gather a sufficient quantity of the particles of relatively large size. These particles settle down after the reaction.

In order to prepare the Ag nanoparticles, we started with 0.1 g of AgNO_3 in 100 ml of ethanol and employed AgNO_3 :PVP weight ratios of 1:5 and 1:10. The starting materials in the case of Au, Pd, and Cu were chlorauric acid, palladium nitrate, and copper acetate, respectively. Refluxing was carried out in air for all the preparations except for Cu where we used high purity nitrogen gas to avoid formation of the oxides. The amount of the starting material was 0.1 g in the preparation of Au, Pd, and Cu particles as well. In the case of Pd, we employed palladium nitrate:PVP weight ratios of 1:1 and 1:2 besides 1:10.

III. RESULTS AND DISCUSSION

Reduction of AgNO_3 by ethanol in the presence of PVP gave nice colloidal solutions of very small particles in the nanometric range. In Fig. 1, we show the TEM images of silver nanoparticles obtained by employing AgNO_3 :PVP ratios of 1:5 and 1:10. Next to the

micrographs we have provided the histograms showing the particle size distributions. With a AgNO_3 :PVP ratio of 1:10, we see that the particles are small with a narrow size distribution, the mean diameter being ~ 5 nm. With a AgNO_3 :PVP ratio of 1:5, we obtain Au particles with a mean diameter of 13–15 nm. The particle size distribution is clearly sensitive to the concentration of PVP. It may be noted that refluxing AgNO_3 in ethanol alone in the absence of PVP does not yield Ag nanoparticles. We could not record the XRD patterns of Ag particles because the nanoparticles were finely dispersed in colloid form in the solution. Electron diffraction patterns, however, show the fcc structure of Ag. The absorption band of the colloidal solutions was found to be around 415 nm. This band is characteristic of the plasmon band of Ag colloids.^{6,7}

On refluxing HAuCl_4 in ethanol in the presence of PVP, we could not obtain Au nanoparticles. However, on refluxing HAuCl_4 with ethanol/PVP in the presence of magnesium (one equivalent with respect to HAuCl_4), we could obtain fine Au nanoparticles. We show a TEM image of the Au nanoparticles (obtained with a HAuCl_4 :PVP weight ratio of 1:10) in Fig. 2 along with the histogram giving the particle size distribution. The mean particle size is 5 nm. The TEM image of the particles obtained with a HAuCl_4 :PVP weight ratio of 1:5 gave a mean particle size of 12 nm. The particle size

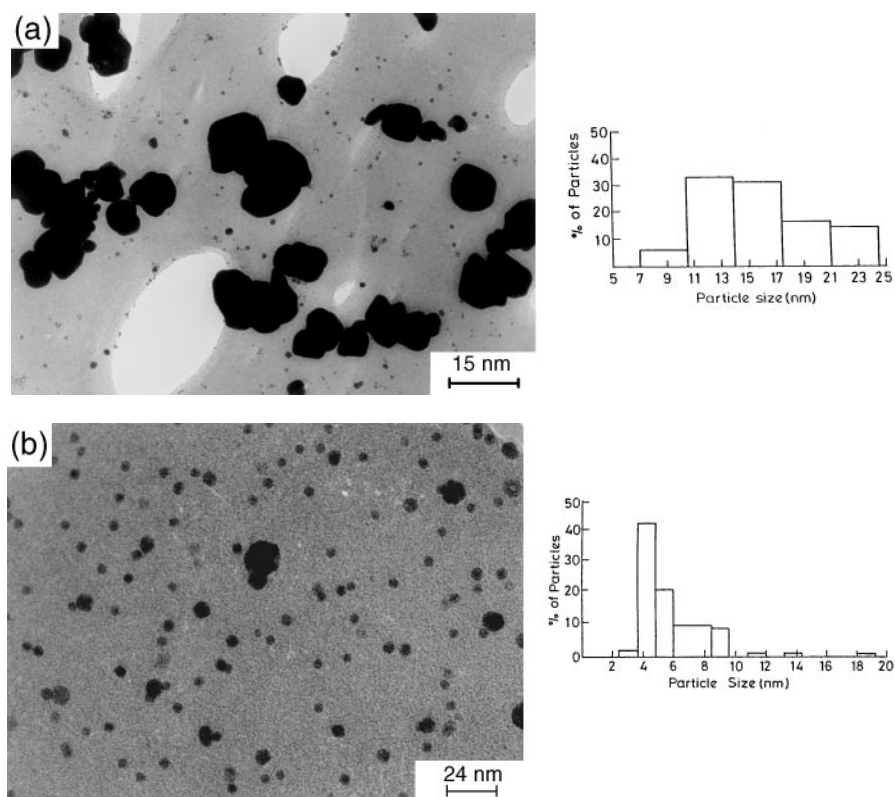


FIG. 1. TEM images of silver nanoparticles along with the histograms showing particle size distributions: (a) 1:4 sample, and (b) 1:10 sample.

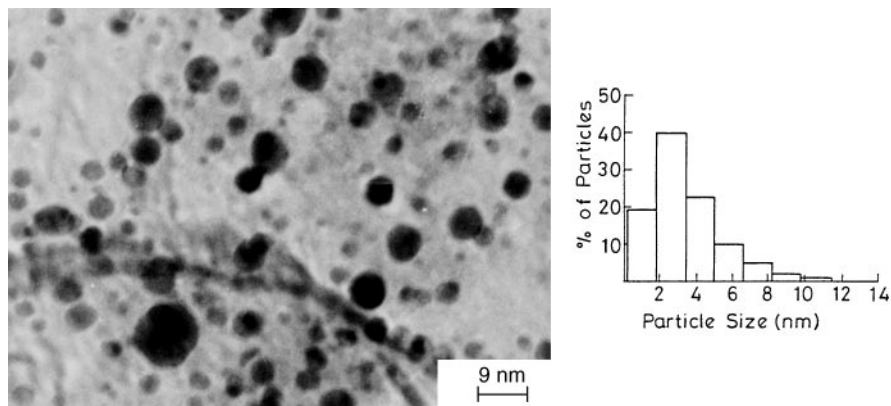


FIG. 2. TEM image of gold nanoparticles along with the histogram showing the particle size distribution (1 : 10 sample).

distribution of the Au nanoparticles is sensitive to the PVP concentration, just as in the case of Ag particles. We could record the x-ray diffraction (XRD) patterns of the Au nanoparticles [Fig. 3(a)]. The XRD pattern clearly indicates crystallinity of the particles. The particle size found from the x-ray line broadening is 18 nm.

In order to prepare Pd nanoparticles, palladium nitrate was refluxed with ethanol in the presence of various

amounts of PVP. In Fig. 4 we show the TEM images of Pd nanoparticles obtained with metal salt : PVP weight ratios of 1 : 1 and 1 : 10. The TEM images suggest clustering of nanoparticles. In spite of the clustering, however, the particle sizes are still in the nanometric regime with an average diameter of ~ 25 nm in the

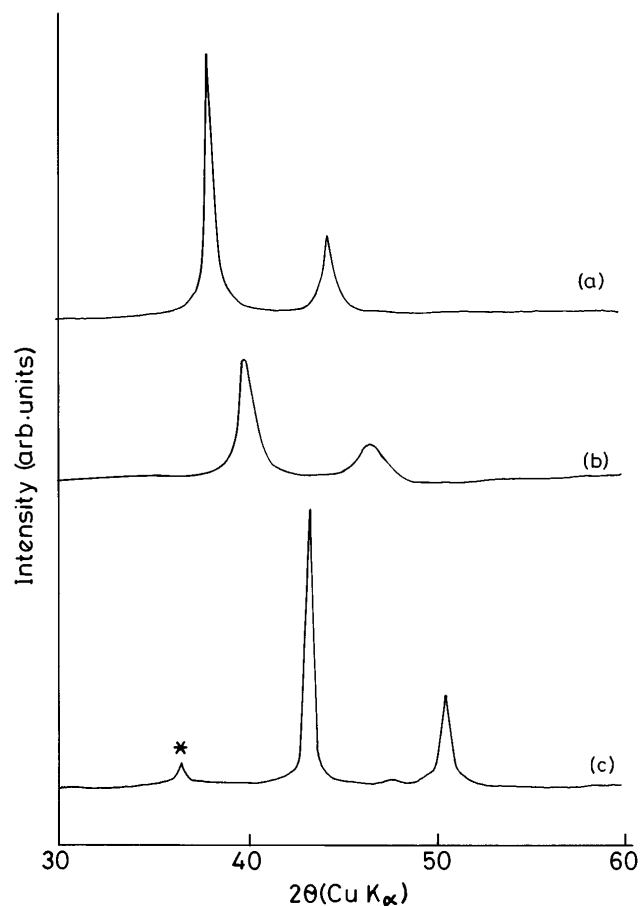


FIG. 3. XRD patterns of the nanoparticles of (a) gold (1 : 5), (b) palladium (1 : 1), and (c) copper (1 : 10).

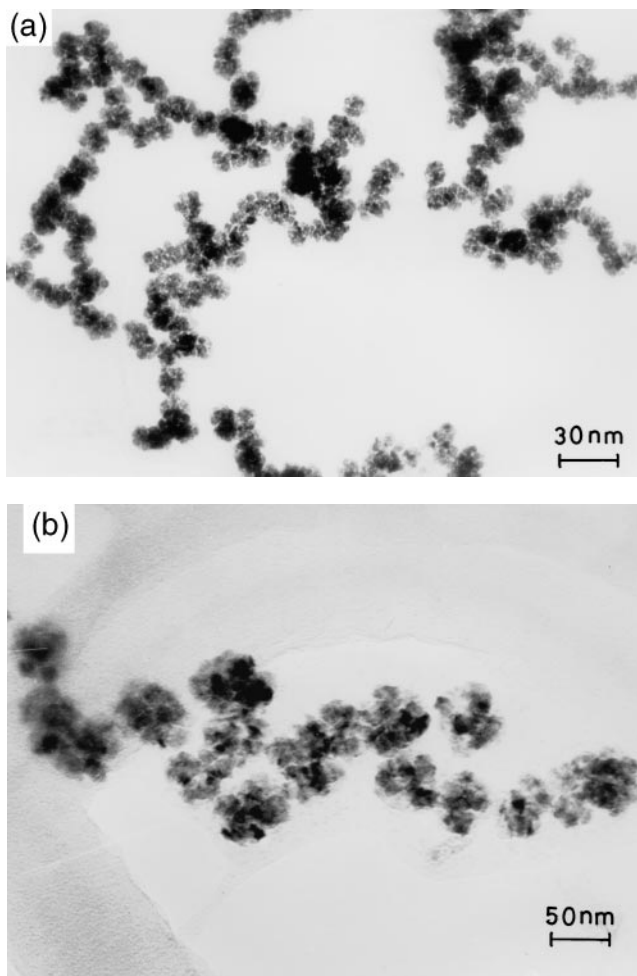


FIG. 4. TEM images of palladium nanoparticles: (a) 1 : 1 sample, and (b) 1 : 10 sample.

case of the 1:10 sample and ~ 35 nm in the case of the 1:1 sample. The individual particles in the cluster are considerably smaller (~ 10 nm). The XRD pattern of the Pd particles obtained with a palladium nitrate:PVP weight ratio of 1:1 is shown in Fig. 3(b). From the x-ray line broadening, we estimate the particle to be 9 nm.

Our attempt to prepare Cu nanoparticles by refluxing copper acetate with ethanol in the presence of PVP was not successful. The reaction always gave copper oxides. However, on adding one equivalent of magnesium metal to the reaction mixture (as in the case of preparation of Au nanoparticles), we could obtain metallic Cu particles. These preparations were carried out in a pure nitrogen atmosphere to minimize oxide formation. The TEM image of Cu particles obtained with a copper acetate:PVP ratio of 1:10 is shown in Fig. 5. We do not see well-separated Cu nanoparticles extensively. There are some isolated nanoparticles of 5–10 nm diameter, but most of the metal particles are loosely clustered, giving rise to particles in the 20–100 nm range. The XRD pattern of these particles is shown in Fig. 3(c). The reflection due to copper (I) oxide impurity is marked with an asterisk. The particle diameter estimated from x-ray line broadening is 21 nm.

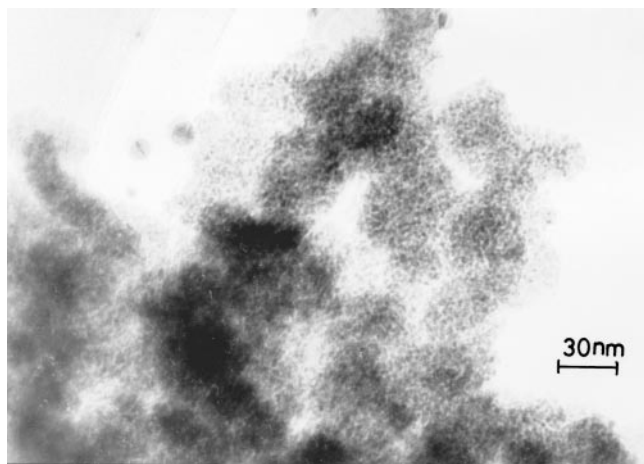


FIG. 5. TEM image of copper nanoparticles (1:10 sample).

IV. CONCLUSIONS

We have been able to successfully prepare nanoparticles of Ag, Au, and Pd by using ethyl alcohol as the reducing agent in a medium containing PVP (Table I). In the case of Cu, the nanoparticles were not as good although the particles obtained are in the right size range. Where ethyl alcohol alone fails, addition of magnesium catalyzes the reduction of the metal salt. It is necessary to use an appropriate proportion of PVP in order to obtain a narrow size distribution of the metal particles.

TABLE I. Sizes of the metal nanoparticles.

Metal	Metal salt:PVP (weight ratio)	Mean particle diameter (nm) from TEM	Particle diameter (nm) from XRD
Ag	1:5	13	...
	1:10	5	...
Au	1:5	12	18
	1:10	5	...
Pd	1:1	35 ^a	9
	1:10	25 ^a	...
Cu	1:10	5–100 ^b	21

^aThese appear to be agglomerates of smaller particles of ~ 10 nm diam.

^bAgglomerates of 20–100 nm diam. are found with a few isolated particles of 5–10 nm diam.

REFERENCES

1. C. Ducamp-Sanguesa, R. Herrera-Urbina, and M. Figlarz, *J. Solid State Chem.* **100**, 272 (1992).
2. F. Fieret, J.P. Lagier, and M. Figlarz, *MRS Bull.* **29** (1989).
3. R. Seshadri and C.N.R. Rao, *Mater. Res. Bull.* **29**, 795 (1994).
4. S. Puvvada, S. Baral, G.M. Chow, S.B. Qudri, and B.R. Ratna, *J. Am. Chem. Soc.* **116**, 2135 (1994).
5. D.G. Duff, A. Baiker, I. Gamson, and P.P. Edwards, *Langmuir* **9**, 2310 (1993).
6. H.N. Vasan and C.N.R. Rao, *J. Mater. Chem.* **5**, 1755 (1995).
7. H. Torigoe and K. Esumi, *Langmuir* **9**, 1664 (1993).
8. K. Meduro, Y. Nakamura, Y. Hayashi, M. Torizuka, and K. Esumi, *Bull. Chem. Soc. Jpn.* **61**, 347 (1988).
9. P.P. Alphonse, M. Brieu, M. Gillet, and P. Mauret, *J. Chim. Phys.* **85**, 6 (1988).