

## Study of interaction of ethylene glycol/PVP phase on noble metal powders prepared by polyol process

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**Abstract.** Noble metal powders (Au, Ag, Pt, Pd and Ru) have been synthesized by the polyol process in both the nanometer and submicron scales (*sans* Pd, Pt and Ru). They have been characterized by both microscopic (TEM and SEM) as well as spectroscopic techniques (FT-IR and XPS). Infrared spectroscopy was employed to study the colloid particles in the presence of ethylene glycol and PVP and the results show that the interaction between the organic phase and the metal particles vary according to the particle size. The role of the solvent, ethylene glycol, during the reduction process was also investigated and we observe formation of  $>C=O$  vibration band after the reduction process implying that the solvent reduces the metal ions thereby getting oxidized. XPS measurements carried out on the colloidal sols have shown the presence of the organic phase adsorbed onto the metal particles.

**Keywords.** Metal nanoparticles; infrared spectroscopy.

### 1. Introduction

Noble metal powders are extremely important materials for their possible applications in diverse fields such as catalysis, electronic or optical industry. Their physical and chemical properties of these powders depend strongly on the manufacturing process (Rousset 1996). The control of the size, the monodispersity of the particles and the shape of the metal particles are important parameters for the required application. As an example, in the case of submicron Pd and Pt powders which are employed in the manufacture of certain electronic components (production of internal electrodes for multi-layer ceramic capacitor), the packing characteristics of the powder depend on the spherical shape as well as monodispersity of the particle as these are critical parameters to obtain smoother electrodes possible (Warnecke 1992).

Several methods for the synthesis of metal particles of varying sizes have been devised (Rao 1994). For example, specific reducing agents such as  $NaBH_4$  (Brust *et al* 1994), and tetrakis (hydroxymethyl) phosphonium chloride (Duff *et al* 1993) have been employed to produce metal colloids of nanometer or micron dimensions. Citric acid has been used as a reducing agent to synthesize micron-sized Au particles (Turkevich *et al* 1951). Alcohols are also found to be good reducing agents to prepare nanometer metal nanoparticles (Ayyapan *et al* 1997). The

conditions of reduction such as the salt concentration and the time of reaction are generally varied to obtain a range of sizes. In some instances, protecting agents such as poly(vinylpyrrolidone) (PVP) are used to control or stop the growth of metal colloids.

One of the well-known methods for the preparation of metal colloids is by employing ethylene glycol (Fievet *et al* 1989a, b) as the reducing agent. This method seems very attractive as it allows the synthesis of numerous metal powders with a good control in size and shape with the same general protocol. However, synthesis occurs in organic media, e.g. ethylene glycol and surfactant (generally PVP for noble metal synthesis) and this phase may play a non-negligible role on the characteristic of the metal powder (such as reactivity toward a specific process). In order to understand the interaction between the organic phase and the metal particles, we have synthesized metal particles of Ag, Au, Pt, Pd, Ru (Ducamp-Sanguesa *et al* 1990; Silvert and Tekaiia-Elhsissen 1995) in the nano and submicron scale (with exception of Pd, Pt and Ru powders which were obtained only in the nanosize domain) and characterized the powders by X-ray photoelectron spectroscopy (XPS). The metal sols were also investigated by diffuse reflectance infrared fourier transform (DRIFT).

### 2. Experimental

All chemicals used were reagent grade materials. Silver nitrate (Aldrich) and tetrachloroauric acid monohydrate

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(ABCR) were used as received for the synthesis of both nano- and submicron sized particles. Ruthenium chloride hydrate, hexachloroplatinic acid hexahydrate and palladium nitrate (ABCR) were used as metallic compounds to synthesize the corresponding metal nano-particles. The polymer PVP employed had average molecular weight of the polymer 14,000.

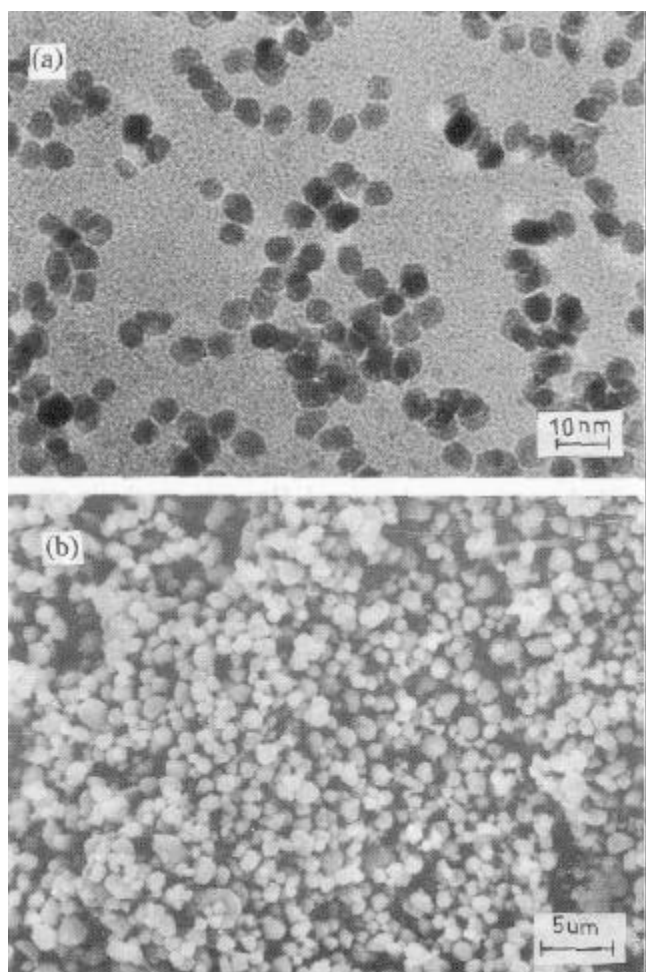
Characterization was carried out employing both microscopic as well as spectroscopic techniques. Transmission electron microscopy (TEM) images were recorded with a JEOL-3010 microscope operating at 300 keV. A small drop of the sample was placed on a holey carbon grid (dia. 3 mm) and evaporated before imaging was performed. Scanning electron microscopy (SEM) was performed using a LEICA-S440i instrument. For this purpose, the metal colloid was centrifuged, the particles separated, dried and then placed on the sample holder. X-ray photoelectron spectroscopic (XPS) measurements were performed using a ESCALAB MKIV (VG Scientific) instrument. A few drops of the metal sol were evapo-

rated on an amorphized graphite substrate before recording the spectrum.  $\text{AlK}_\alpha$  (1486.6 eV) radiation was used as the X-ray source. Fourier transform infrared spectroscopy (FT-IR) was performed in diffuse reflectance mode with a BRUKER IFS66v/S. FT-IR measurements were carried out in the range 4000–400  $\text{cm}^{-1}$ . A few drops of the metal particles in glycol solution containing the metal sol were thoroughly mixed with KBr before the diffuse reflectance spectrum of the pellet was recorded.

### 3. Results and discussion

The morphology of the metal particles was observed by employing TEM and SEM techniques. In figures 1a and 1b, we exhibit the typical micrographs of nano- and submicron particles of platinum and silver metal, respectively. The shape of all the synthesized metal particles irrespective of the size were spherical in nature. In table 1, the mean dia. of the different particles synthesized are summarized.

In order to characterize the surfaces of particles, we employed core-level X-ray photoelectron spectroscopic (XPS) technique. The spectra in the case of Au colloids are shown typically in figure 2. The binding energies of the different core-levels were fixed with respect to the binding energy of the bulk metal core-level. The oxygen, nitrogen and carbon signals confirm the presence of PVP and possibly ethylene glycol on the surface of the colloids. In table 2, we list the binding energies of the C(1s), N(1s) and O(1s) core-levels due to the surface coatings on the metal colloids. The shift observed in the binding energies has a component that is also due to charging effect of the sample.



**Figure 1.** Micrographs of metal powders obtained by polyol process. (a) TEM images of Pt nano-particles; and (b) SEM images of silver sub-micron powder.

**Table 1.** Average diameters of the metal colloids.

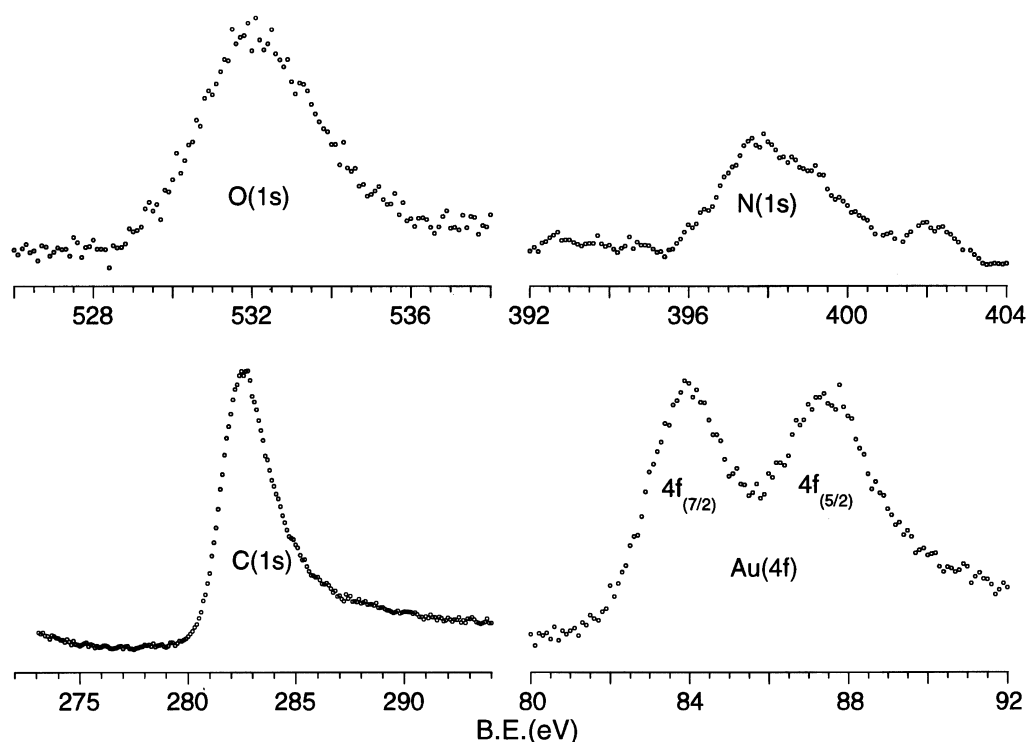
Metal	Nanoparticles* (nm)	Submicron particles† (μm)
Au	15.0	0.38
Ag	20.1	0.8
Pt	6.5	–
Pd	–	0.4
Ru	16.9	–

\*As determined by TEM images analysis.

†As determined by SEM images analysis.

**Table 2.** Core-level binding energies of the surface coating on the metal colloids.

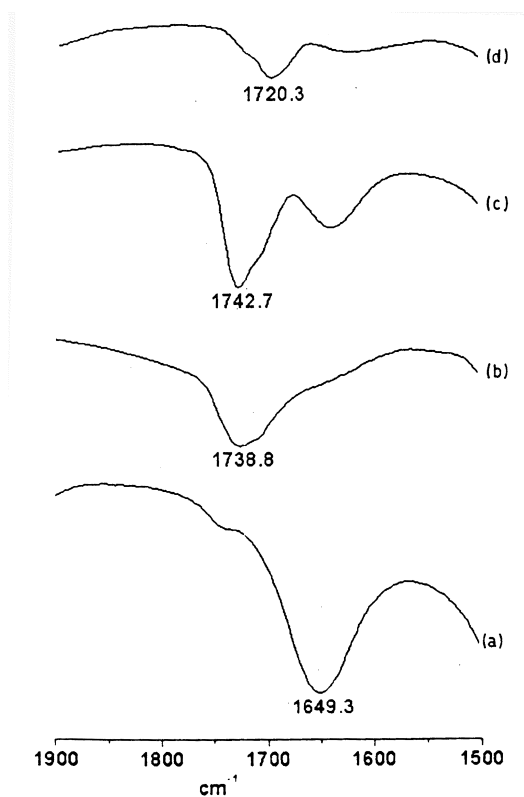
Metal	Particle diameter	O(1s) (eV)	N(1s) (eV)	C(1s) (eV)
Au	0.38 μm	532.0	398.0	282.4
Pt	6.5 nm	531.9	397.9	282.7
Pd	0.4 μm	532.0	397.9	282.8



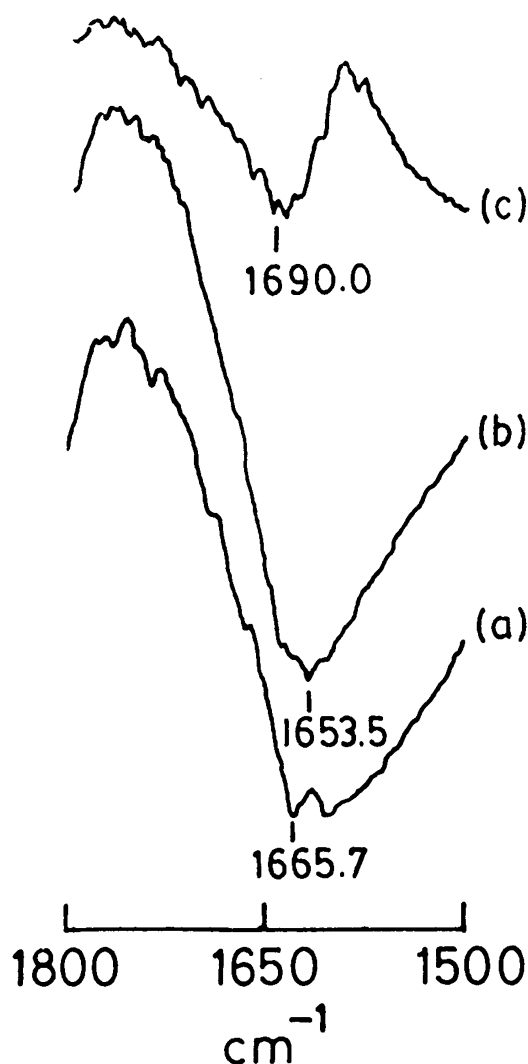
**Figure 2.** X-ray photoelectron spectra of Au colloid with mean dia. 0.38  $\mu\text{m}$ . The figure shows core-level spectra in O(1s), N(1s), C(1s) and Au(4f) regions.

Diffuse reflectance FT-IR spectra of the metal colloids were compared with the spectra of EG and PVP employed in the synthesis. The spectra showed that the  $-\text{OH}$  stretching band shifts to higher frequencies after the formation of the powders, suggesting a decrease in hydrogen bonding in the glycol medium after formation of the metal. More interestingly, the carbonyl region of spectra showed distinct changes. In figure 3, we see typical diffuse reflectance IR spectra to illustrate the nature of changes in the carbonyl-stretching band. Submicron sized colloids generally show a positive amide group frequency shift, while the nanometric colloids show negative shifts. It is known from the infrared spectra of metal complexes of amides, ureas and related compounds (Nakamoto 1978) that a positive shift of the amides stretching band implies coordination of the nitrogen atom to the metal while a negative shift implies coordination of the carbonyl group of the amide to the metal. It seems therefore possible that the coordination of the PVP to the metal colloids depends on the size of the colloid particle. In the case of submicron sized particles, the nitrogen-containing heterocyclic ring of the PVP may coordinate more strongly than the carbonyl group whereas the opposite may occur in the case of nanometre size particles.

Since ethylene glycol acts as a reducing agent, it was interesting to find out how it transforms in the reduction process. In order to understand this transformation, we recorded the IR spectra of the reaction mixture (ions



**Figure 3.** FT-IR diffuse reflectance spectra in the region of 1500–1800  $\text{cm}^{-1}$  of (a) ethylene glycol, (b) Pt colloid, (c) Pd and (d) Ru colloid.



**Figure 4.** FT-IR diffuse reflectance spectra in the region of 1500–1900  $\text{cm}^{-1}$  for (a) ethylene glycol; ethylene glycol oxidation after formation of (b) Pt, (c) palladium and (d) ruthenium.

of Pt, Pd and Ru compounds in EG) by carrying out the reduction of the metal compound in the absence of the polymer. The spectra in the carbonyl region so obtained are shown in figure 4. The reduction of the metal salt is accompanied by the appearance of a carbonyl-stretching band between 1730  $\text{cm}^{-1}$  and 1750  $\text{cm}^{-1}$  characteristic of aldehydes and ketones. This observation suggests that ethylene glycol gets oxidized during the reduction process, as expected. Clearly, as ethylene glycol reduces the

metal compound, it undergoes oxidation to a carbonyl compound.

#### 4. Conclusions

XPS investigations have shown the presence of ethylene glycol/PVP on the metal particle surface, an observation confirmed by the absence of metal oxide. Infrared spectroscopy studies utilized to study the interaction between the organic phase and noble metal particles seem to exhibit dependency on the particles size, particularly with respect to bands relating to PVP. Finally, the role of ethylene glycol was also investigated by IR wherein the ethylene glycol plays the role of the reducing agent thereby getting oxidized into carbonyl species.

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#### References

- Ayyapan S, Gopalan R S, Subbanna G N and Rao C N R 1997 *J. Mater. Res.* **2** 398
- Brust M, Walker M, Bethel D, Schiffrin D J and Whyman R 1994 *J. Chem. Soc. Chem. Commun.* 801
- Duff D G, Baiker A and Edwards P P 1993 *J. Chem. Soc. Chem. Commun.* 96
- Ducamp-Sanguesa C, Herrera-Urbina R and Figlarz M 1990 *J. Solid State Chem.* **100** 272
- Fievet F, Blin L B, Beaudoin B and Figlarz M 1989 *Solid State Ionics* **32/33** 198
- Fievet F, Lagler J P and Figlarz M 1989 *MRS Bull.* 29
- Nakamoto K 1978 *Infrared and Raman spectra of inorganic and co-ordination complexes* (New York: John Wiley)
- Rao C N R 1994 *Chemical approaches to the synthesis of inorganic materials* (New York: John Wiley)
- Rousset A 1996 *Solid State Ionics* **84** 293
- Silvert P-Y and Tekaia-Elhsissen 1995 *Solid State Ionics* **82** 53
- Turkevich J, Stevenson P C and Miller J 1951 *Discuss. Faraday Soc.* **11** 55
- Warnecke H 1992 *Precious Metal for Electronics* 283