

## Poly(vinyl pyrrolidone) coated silver nano powder via displacement reaction

P. K. KHANNA\*, R. GOKHALE, V. V. V. S. SUBBARAO

Nanomaterials Laboratory, Centre for Materials for Electronics Technology (C-MET), Off Dr. Bhabha Road, Panchawati, Pune 411 008, India

E-mail: pkk@cmetindia.org; pawankhanna2002@yahoo.co.in

Nanoscale metal particles such as silver and gold provide a very exciting research field due to their interesting optical, electronic, magnetic, and catalytic properties. Silver exhibits the highest electrical and thermal conductivities among all the metals [1] and has applications in a variety of areas such as in catalysis [2], conductive inks and pastes & adhesives for electronic components [3], photonics and photography [4, 5].

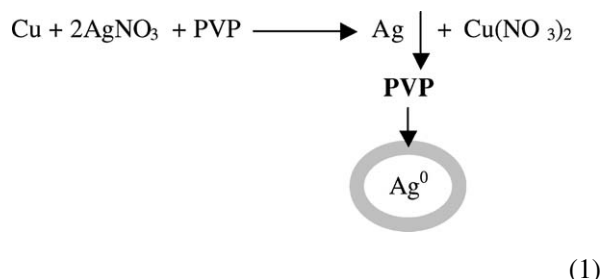
Several chemical methods using different reducing agents are reported for the preparation of silver nanoparticles/powder. Organic solvents such as ethanol [6], *N,N'*-dimethyl formamide [7], ethylene glycol [8, 9] have been successfully used to reduce silver salts to zero valent silver besides other reducing agents such as sodium borohydride [10], glucose [11], and sodium formaldehyde sulfoxylate [12]. Silver nanoparticles protected by polymers, namely poly(vinyl alcohol) (PVA) [13, 14], poly(vinyl pyrrolidone) (PVP) [14–17], or poly styrene [18], and by organics (e.g., trioctylphosphine oxide and amines capped) [19] have also been extensively reported. However, the synthesis of coated silver nanoparticles of desired shape and size and by simpler and easier synthetic routes continues to be a challenging area of research for materials scientists.

In this communication, the production of silver particles coated with poly(vinyl pyrrolidone) is described via reduction of silver nitrate by copper turnings in aqueous medium. All the chemicals and reagents used were of analytical grade. The powders were characterized by various techniques. UV–visible measurements were done on a Hitachi Spectrophotometer model No. 3210, infrared (IR) analysis was obtained on Spectrum 2000 Perkin Elmer instrument, powder X-ray diffraction (XRD) was done using  $\text{Cu K}\alpha$  on a Mini Flex Philips Rigaku Model, and EDAX and scanning electron microscopy (SEM) was done on Philips XL30 series instrument.

It is well known that copper displaces silver from its salt in solution state [20]. However, to date organically or polymeric coated silver powder has not been reported by this method. PVP has a basic functionality to interact with metal ions thus forming chemical bonds with silver and therefore is very useful as a matrix for embedded metal particles as well as acting as nucleating agent. We herein report the use of a simple displacement

method for synthesizing silver powder coated with PVP.

In a typical procedure, an aqueous solution containing the appropriate amount of polymer (PVP) was prepared followed by the addition of silver nitrate into it. The weight ratio of PVP:AgNO<sub>3</sub> was kept at 0:1, 1:1, and 2:1, respectively. Copper turnings were introduced in the reaction vessel in required quantities. The reaction was carried out at room temperature for about 1 hr by which time gray colored silver powder precipitated, which was filtered off, washed with distilled water and ethanol. The product was then dried in an electrically heated oven for 3 hr. The reaction proceeded as shown in Equation 1.



It is well known that PVP can have use as a reducing agent as well as a surface-capping agent to the particles to avoid agglomeration. In the present work, it is used as a surface-coating or surface-capping agent. It has been observed in the present study that the particles have different morphology when no PVP is used. In the absence of PVP, the particles are agglomerated and are bigger in size than in the presence of PVP. Scanning electron microscopy (SEM) of these powders showed that spherical silver particles are much better separated from each other in the presence of PVP. Electronic absorption measurements (UV–visible) and infrared spectroscopy (IR) data along with SEM indicate that the probable chemical bonding between PVP and silver powder has played a significant role in preparing PVP-coated silver powder.

The IR spectrum (Fig. 1b) of isolated powder showed that there is a chemical bonding between PVP and silver. PVP has C–N and C=O bonds due to functional groups in its individual unit and it is reported that these groups have affinity for silver ions and metallic silver coordination due to the N and O atoms in the molecule

\* Author to whom all correspondence should be addressed.

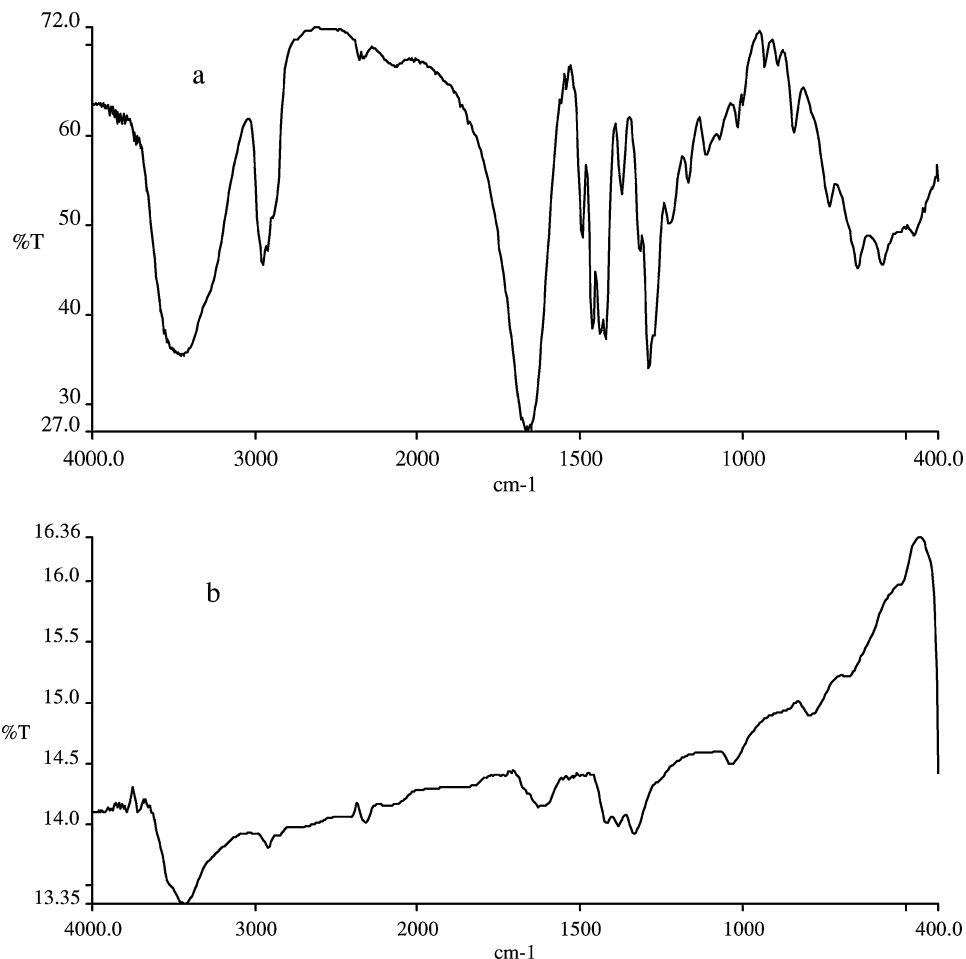


Figure 1 IR spectra of (a) PVP alone and (b) Ag/PVP composite.

[15]. The C–N absorption peak at  $\nu 1019\text{ cm}^{-1}$  in pure PVP alone (Fig. 1b) is shifted to  $\nu 1035\text{ cm}^{-1}$  with a slight broadening in the Ag/PVP composite. Similarly, the peak at  $\nu 1663\text{ cm}^{-1}$  corresponding to the C=O bond in PVP is also shifted to  $\nu 1634\text{ cm}^{-1}$  in the composite. These two shifts are consistent with those reported by Zhang *et al.* [16]. The shift in the  $\nu\text{C–N}$  wavelength implies a weak coordinative chemical bonding of C–N to Ag at the interface between PVP and the powder. The decrease in wave numbers for C=O absorption may result from bond weakening due to back bonding via partial donation of lone pair electrons from oxygen in PVP to the vacant orbital of silver [16].

The UV–visible spectra of the silver particles in the presence of PVP showed two initial absorption bands  $\lambda_{(\text{max})}$  340 and 456 nm when the concentration of silver nitrate is small, i.e., close to 25% with respect to the 2:1 ratio between silver nitrate and copper (Fig. 2a). The band at about 340 nm is due to the formation of  $\text{Ag}^+$  ions bonded to PVP and a broad band at 456 nm was observed earlier also for  $\text{Ag}^{(0)}$  in PVP [15, 16] due to surface plasmon resonance. These bands are however much sharper when the silver nanoparticles are prepared by other methods by using low concentration of silver ions in organic or polymer matrices for capping, and normally centered at

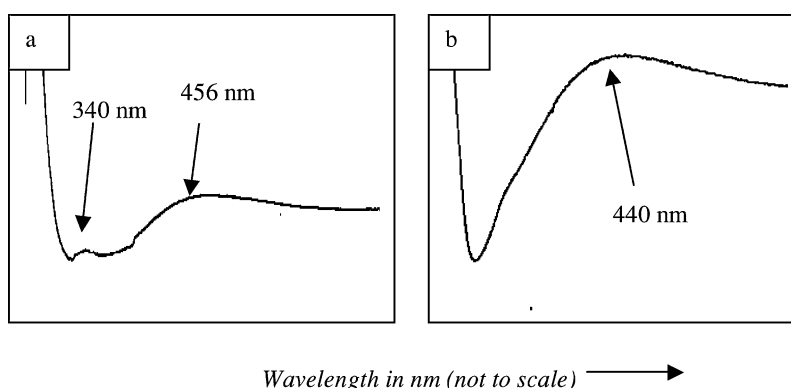


Figure 2 UV–visible spectra of (a) 25% silver nitrate in PVP and (b) Ag/PVP suspension.

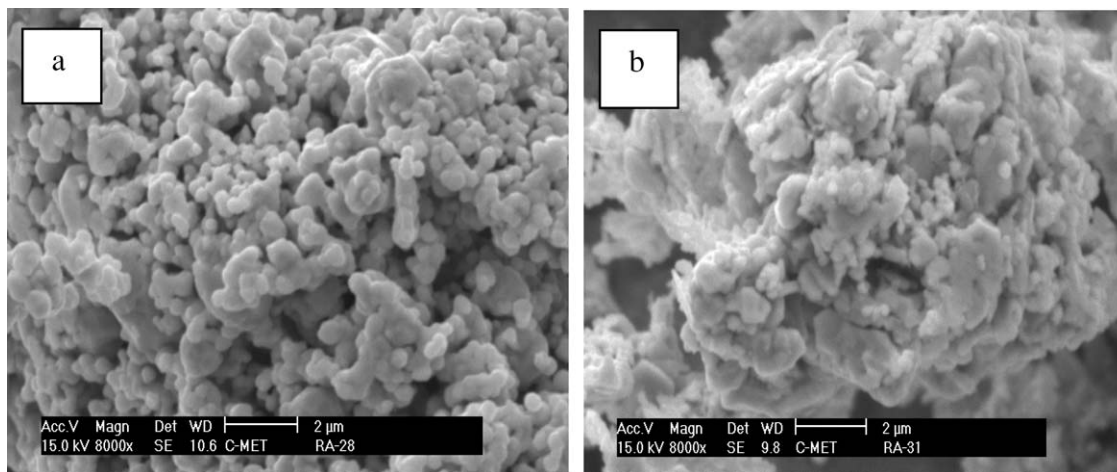


Figure 3 SEM of silver powder in the absence of polymer (a) and in the presence of polymer (b), respectively, at 2- $\mu$ m bar.

around 400–425 nm (depending on the particle size) [19, 21].

As the concentration of silver nitrate is increased and brought to the 2:1 ratio with respect to copper, the precipitation is instant due to the formation of bigger silver particles, thus producing a suspension of silver particles in PVP that showed a single broad band at about 440 nm (Fig. 2b). To check the authenticity of the absorption band a neat experiment with only copper suspended in PVP was performed to find that no absorption bands were present in the spectrum. This suggested that PVP had not formed any intermediate complex with copper within the reaction time.

SEM showed agglomeration of silver in the absence of polymer. The particles of spherical nature seem to be of submicron size diameter typically in the range of 100–300 nm with reasonable uniformity (Fig. 3a). However, in the presence of polymer, the SEM showed slightly elongated particles with much less agglomeration. The polymer has perhaps caused formation of layers that has resulted in formation of big blocks due to drying of the powder as can be seen in Fig. 3b. EDAX was recorded to check elemental analysis of the powder. This proved valuable in understanding the reduction of silver salt to metallic silver by copper. It was found that the end product in EDAX analysis shows that silver is formed without any contamination of copper. Thus a complete conversion of silver salt to silver is ensured via reduction of silver ions to zero valent silver. The absence of copper suggested quantitative formation of silver powder.

The XRD pattern of silver powder is shown in Fig. 4. All the diffraction peaks were for silver in the cubic phase [22]. A very small peak broadening was observed in the pattern. This suggested that the particles are of smaller dimensions than the bulk silver. Scherrer's formula was applied to calculate the particle diameter and it was found that the size is less than 50 nm. This, however, was not in agreement with SEM results where the size appeared to be larger than that was calculated by XRD peak broadening. In fact, based on XRD pattern, the spherical particles were coated with PVP with variable size distribution.

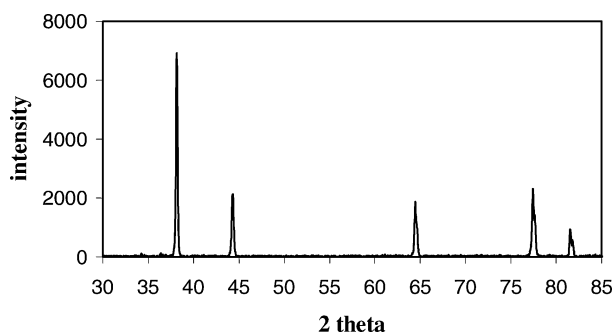


Figure 4 XRD of PVP/Ag with the weight ratio of 2:1.

To conclude, the synthesis of PVP protected/coated silver nano-powder by a simple and easy route is described and the presence of PVP around the silver particles has been established.

### Acknowledgments

We thank Dr. B. K. Das, Executive Director, C-MET for permission and technical staff of C-MET for SEM/EDAX analysis of the samples.

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*Received 3 October 2003  
and accepted 15 November 2004*