

# Effects of protective agents (PVA & PVP) on the formation of silver nanoparticles

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## **Abstract:**

*In this study silver/poly vinyl alcohol (PVA) and silver/poly vinyl pyrrolidone (PVP) Nanocomposites were prepared via reduction of silver salt by employing DMF (N, N'- dimethyl formamide) as a reducing agent. Effects of protective agents such as PVA and PVP were also described here. We show that the acidic pH of PVP solution also affects the interaction between protective agents and silver nanoparticles. The nanoparticles were characterized by ultra violet-visible spectroscopy (UV-vis), FTIR spectroscopy, X-ray diffraction (XRD) and transmission electron microscopy (TEM). From the figures, it can be concluded that PVP is somewhat better than PVA for preventing silver nanoparticles from their agglomeration.*

**Keywords:** Silver nanoparticles; Chemical synthesis; Transmission Electron Microscopy (TEM)

## 1. INTRODUCTION

In the past few years, metal nanostructures in various compositions, structures, sizes, and shapes have been of great interest because of their unique and enhanced electronic, catalytic, and optical properties [1-6]. Controlled synthesis of monodisperse inorganic nanoparticles (NPs) in terms of size and shape has been strongly motivated by the requirements to uncover and map their size- and shape-dependent properties and to achieve their practical applications ranging from biosensing to catalysis, optics, and data storage [7-9].

The unique properties of nanometer-scale particles can be utilized in a broad range of fields from catalyst to optical filters or nanolithography. Small particles differ from the bulk materials due to surface shape and quantum size effects. The method of layer by layer was usually used to prepare this type of materials. The basis of this method is the electrostatic attraction between the charged species deposited [10]. The surface modification of these colloidal nanoparticles is very important to facilitate their application to biotechnology, catalysis, and nanocomposites. Silvert and et al. observed the promoting effect of nucleation of

PVP in the formation of silver particles using ethylene glycol as the reducing agent [11]. There are few reports about the reducing properties of the polymer to the fabrication of metal nanoparticles [12]. Organic solvents and reducing agents such as ethanol [13], *N,N'*-dimethyl formamide (DMF) [14], sodium borohydride [15], glucose [16], and sodium formaldehyde sulfoxylate [17] have been successfully used to reduce silver salts to zero valent silver. Silver nanoparticles protected by polymers, namely poly (ethylene glycol), poly(vinylpyrrolidone) (PVP) [11,18-20], poly (vinyl alcohol) (PVA) [18,21], poly(ethylene glycol) [22], or poly styrene [23], and by organics (e.g., trioctylphosphine oxide and amines capped) [24] have also been extensively reported. Ethylene glycol and diols can be used as reducing agents to prepare metal particles [25, 26].

Recently, the fabrication of silver nanowire in the presence of stabilizer of poly vinyl pyrrolidone (PVP) and seeding solid of platinum nanoparticles was reported by using EG at 160 °C [27]. Fine silver powder with small particle diameter can also be prepared *via* the displacement method using copper [28]. Thus silver powder of modified surfaces with controlled morphology can be prepared by several methods [29-33].

Although dilute solution of metal salt, surfactant and reducing reagent leads to the formation of clear golden-yellow colloidal solution by a 'bottom-up' approach, it is the scale-up that needs careful control of experimental conditions in order to avoid disparity from batch to batch as well as agglomeration leading to hard crystalline particles. An increase in molar concentration of the reagents generally results in an increase in particle size and agglomeration among the particles.

Subsequent experiments suggested that the morphology of the product depends on the reaction conditions.

Herein, we report the dramatic effect of stabilizer to the formation of silver-nanoparticles. In this work, we employed poly vinyl alcohol (PVA) and poly vinyl pyrrolidone (PVP) as protecting agents to synthesize silver (Ag) nanoparticles with an average diameter of 15 nm by reduction of silver nitrate. In this paper, we focus on the effect of the PVP and PVA protective agents on the silver particle size and

its distribution.

Transmission electron microscopy (TEM), The Powder X-ray diffraction (XRD), FTIR and UV-visible spectrum measurements were combined to elucidate the structure and the growth mechanism of silvernanoparticle.

## 2. EXPERIMENTAL

### 2.1. *Materials and apparatus*

All the chemicals and reagents used were of analytical grade. The experimental investigation was carried out under atmospheric pressure. In this communication, the production of silver particles coated with poly vinyl alcohol (PVA) ( $M_w=72000$ ) and poly vinyl pyrrolidone (PVP) ( $M_w=72000$ ) are described via reduction of silver nitrate by DMF in aqueous medium. The product was characterized by using XRD, TEM, UV-vis and IR spectrometer.

The Powder X-ray diffraction (XRD) patterns were recorded on a Seisert Argon 3003 PTC using nickel-filtered XD-3a  $CuK\alpha$  radiations ( $\lambda=1.5418 \text{ \AA}$ ).

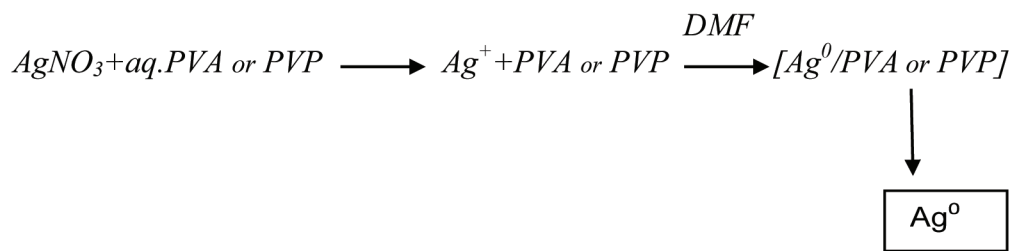
The UV-visible spectrum in absorbance mode was recorded on an UV-visible Hitachi spectrophotometer model U-2101 PC. Spectrum was recorded in the solution form by suspending small amount of powder in aqueous medium.

FTIR spectra were obtained using a Bomem MB 100 spectrophotometer with universal ATR sampling accessory.

Transmission electron microscopy (TEM) was performed on a Philips EM208 and microscope operated at 100 kV. The sample was prepared by dispersing the powder in ethanol. Imaging was enabled by depositing few drops of suspension on a carbon coated 400 mesh Cu grid. The solvent was allowed to evaporate before imaging.

### 2.2. *Preparation of silver nanoparticles using poly vinyl alcohol (PVA) and poly vinyl pyrrolidone (PVP)*

Firstly, 5 ml *N,N'*-Dimethyl formamide (DMF) was refluxed in three-necked round-bottom flask at 80 °C for 2h, then 5 ml DMF solution of 0.02 M silver nitrate and 5 ml DMF solution of 0.05 mM PVA(or PVP) were simultaneously injected drop wise. When the first drops of silver nitrate and



**Scheme 1:** Preparation of (Silver/PVA or PVP) nanocomposites via reduction of silver nitrate by DMF

PVA/DMF (or PVP/DMF) solutions were added, the mixture turned yellow immediately. With the continuing of injection, the solution became opaque gradually (Scheme.1).

By finishing the injection, the solution turned turbid with a golden-yellow color in about 15 min, indicating the appearance of Ag nanoparticles. When the reaction finished, the supernatant was removed; the gray precipitate remained and needed no further purification.

### 3. RESULTS AND DISCUSSION

In the present work, PVA and PVP are used as a surface-coating or surface –capping agents. It has been observed in the present study that the particles have different morphology when no PVA or PVP are used. In the absence of protecting agents, the particles are agglomerated and are bigger in size than in the presence of protecting agents.

Feng et al. [34] prepared nanoparticles which were scattered uniformly. From the previous reports, nano-particles in the composites have not been scattered uniformly [35], and agglomeration of particles being very prominent. Diameter of their particles often exceeds 100 nm.

Macromolecular chains of PVA and PVP coated on the Ag nanoparticles surface, and particles can't be agglomerate [34, 35]. Then through gelling and drying, the films are made. Reagent concentration, reaction temperature and time, all of them affect the preparation of Ag nano-particles. It is observed that the reduction process is quite rapid irrespective of reducing agents without any aggregation among the particles. The golden-yellow solutions are stable over a long period of time thereby indicating that the nanoparticles have no tendency to agglomerate because of effective capping by PVA and PVP.

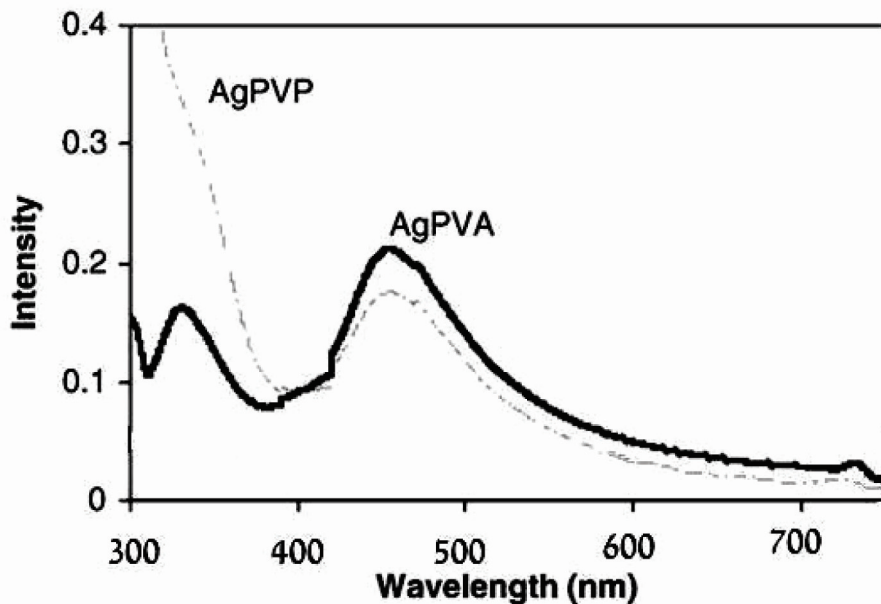
Protecting agents PVA and PVP restricts the mobility of silver ions during the reaction; it avoids agglomeration (Scheme 1).

Mechanism of PVP protection was divided into three stages. First, PVP donates lone pair electrons of oxygen and nitrogen atoms to sp orbitals of silver ions, and thus the coordinative complex of Ag ions and PVP forms in aqueous solution. Second, PVP promotes the nucleation of the metallic silver because the Ag ions-PVP complex is more easily reduced by DMF than the pure Ag ions owing to Ag ions receiving more electronic clouds from PVP than from H<sub>2</sub>O ( $\epsilon^\circ = -0.8277$  v). Third, PVP prohibits silver particle aggregation and grain growth as a result of its strict effect [19].

Poly vinyl alcohol is known to be a good stabilizer of small metal particles [36] and has been frequently used as particle stabilizers in chemical synthesis of metal nanoparticles as also it is advantageous from the point of view of film casting. The role of PVA remains as one of the holding matrix and OH functional group of PVA may temporarily bind with the metal ion through van der Waals forces. The Ag (I) cations are reduced to zero valent silver by DMF thus changing the color. In other words, colour of silver salt changes from its original clear yellow to golden yellow due to chemical reduction process.

The UV-visible spectra of the samples are illustrated in (Fig.1), where the peak at about 454 nm is the silver particle. The band at about 340 nm is due to the formation of Ag<sup>+</sup> ions bonded to (PVP, PVA) and a broad band at 454 nm (depending on the particle size) [37], was observed earlier also for Ag<sup>(0)</sup> in (PVP, PVA) [38,39] due to surface plasmon resonance.

The absorption pattern is sharp when the reduction of silver nitrate is done by PVP, indicating that the particle size distribution is quite narrow while it



**Figure 1:** UV-vis absorption spectra of Ag/PVA and Ag/PVP nanocomposites, prepared by using DMF.

is slightly broader when PVA is used as reducing agent, indicating uneven particle size distribution. Under identical experimental and measurement conditions, the  $\lambda_{(abs)}$  is found to be same for PVA and PVP reaction. The formation of better quality particles is believed to be due to fast reduction rate process in comparison to the dispersion carried out using PVA.

The peak width at half of maxima (PWHM) is considered to be quite useful in understanding the particle size and their distribution within the medium matrix. By adopting the concept of Brown et al. [40], in the present work, the PWHM for PVA reactions turn out to be about 25 nm which is much higher than the nanocomposite solution that is prepared by using PVP where the PWHM are of the magnitude of 15 nm only. This showed that the narrow size distribution of the particles in DMF can be accomplished by use of PVP.

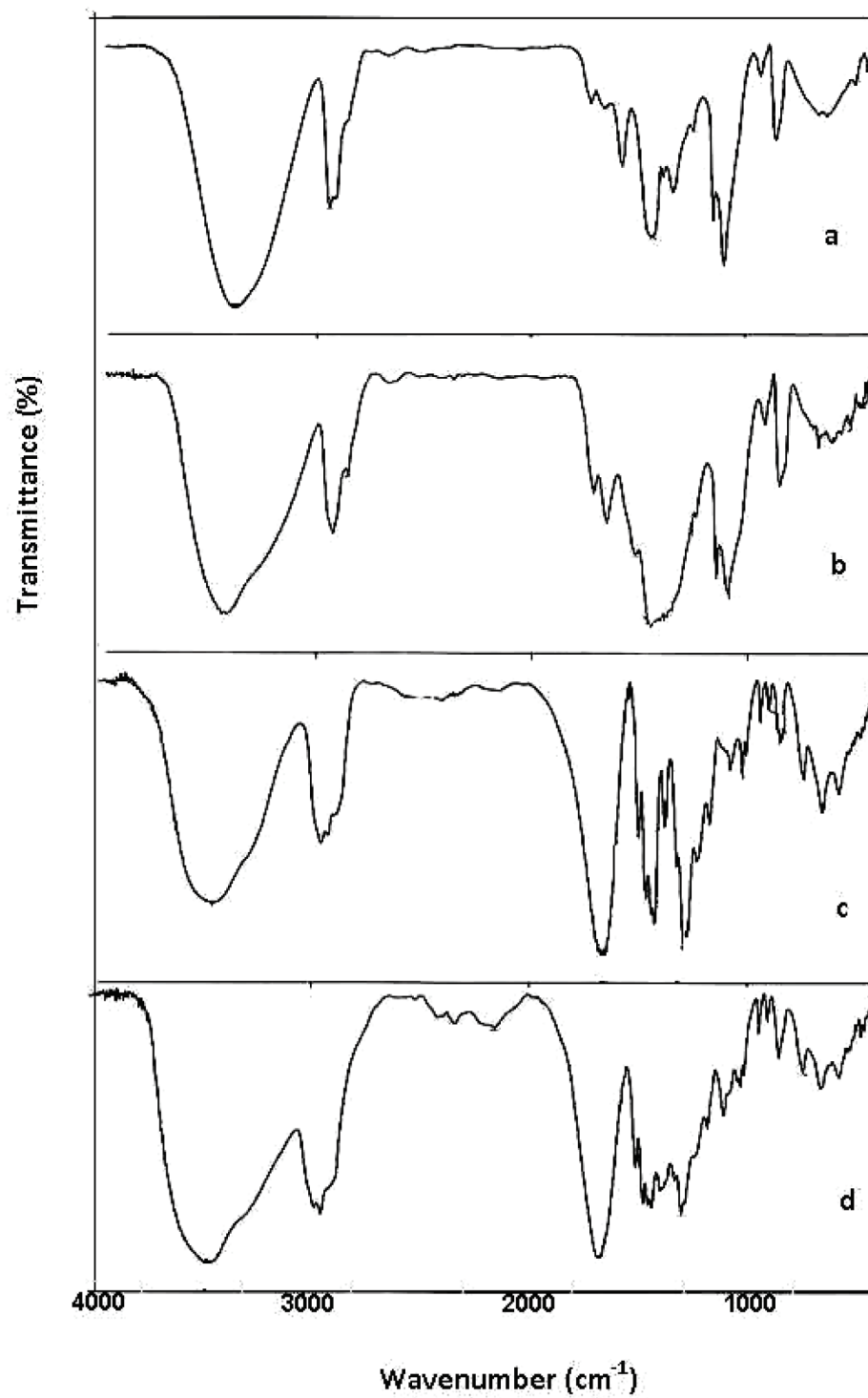
The FTIR spectrum of films of Ag/PVA and Ag/PVP Fig.2 showed that the peaks have become broad and these are shifted in their wave numbers with respect to their original value in PVA and PVP.

In the FTIR spectrum of pure PVA Fig.2a the band  $\nu$  1333  $\text{cm}^{-1}$  is due to the coupling of O-H vibrations at  $\nu$  1428  $\text{cm}^{-1}$  with the C-H wagging vibrations. The FTIR spectrum of Ag/PVA Fig.2b nanocomposite

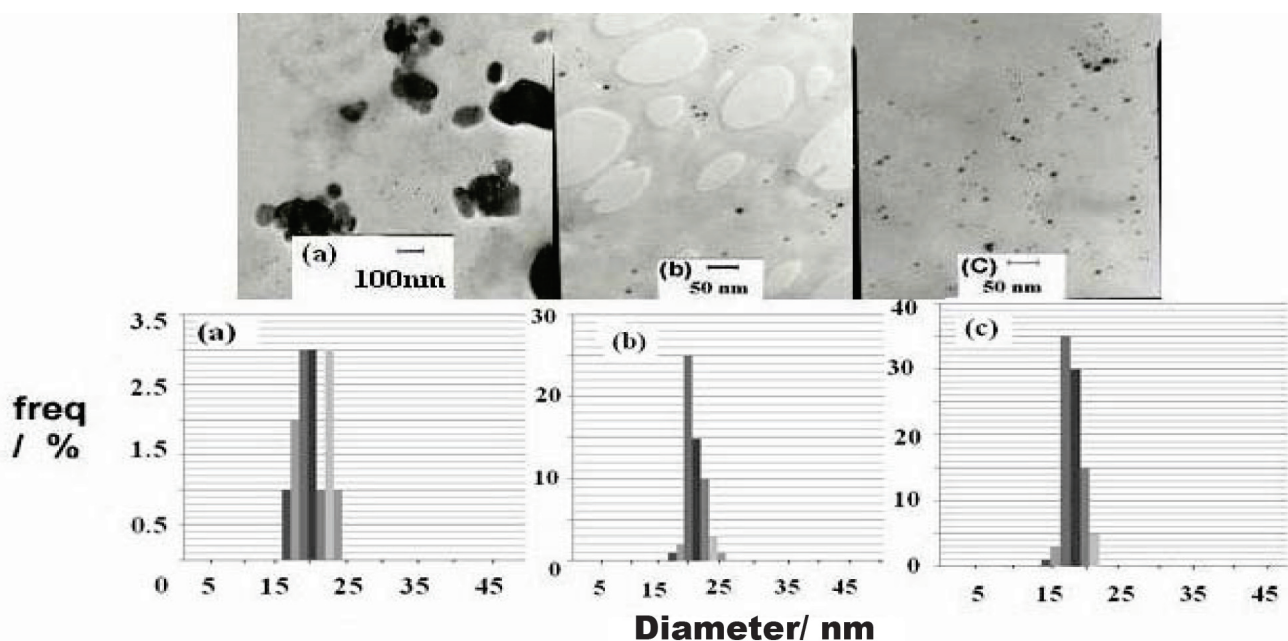
showed an increase in the transmittance of the band at  $\nu$  1333  $\text{cm}^{-1}$ , in comparison with band at  $\nu$  1428  $\text{cm}^{-1}$ , which indicates the decoupling between O-H and C-H vibrations due to bonding interaction between O-H and silver nanoparticles. This finding is consistent with the observation reported by Mbhele et al. [41]. The bands at  $\nu$  610  $\text{cm}^{-1}$  and  $\nu$  850  $\text{cm}^{-1}$  indicate the out of plane vibrations of O-H and C-H in PVA.

The IR spectrum (Fig.2d) 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 [42]. It seems 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 nanometer size particles [38]. The C-N absorption peak at  $\nu$ 1017  $\text{cm}^{-1}$  in pure PVP alone (Fig. 2c) is shifted to  $\nu$ 1096  $\text{cm}^{-1}$  with a slight broadening in the Ag/PVP composite. Similarly, the peak at  $\nu$ 1660  $\text{cm}^{-1}$  corresponding to the C=O bond in PVP is also



**Figure 2:** FTIR spectra of a) PVA, b) Ag/PVA nanocomposite, c) PVP and d) Ag/PVP nanocomposite.



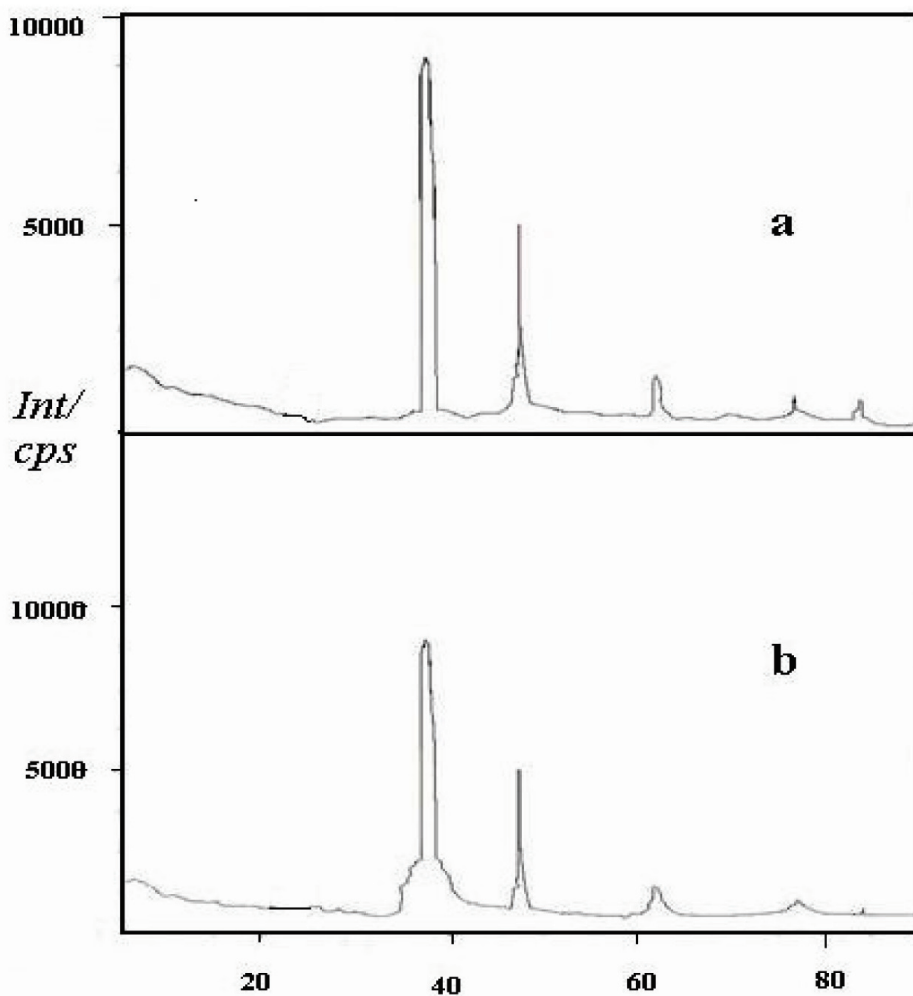
**Figure 3:** TEM picture and size distributions of the silver nanoparticles, a) without polymer, b) by PVA polymer, c) by PVP polymer, prepared by DMF.

shifted to  $\nu 1655 \text{ cm}^{-1}$  in the composite. These two shifts are consistent with those reported by Zhang *et al.* [19]. The shift in the  $\nu$  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 [19]. The wavenumbers 2955 and 3454  $\text{cm}^{-1}$  corresponds to C-H and O-H bond vibrations, respectively. The values 1463 and 1422  $\text{cm}^{-1}$  are obtained for  $\text{C}_4\text{N}$ - of PVP bond absorption. The wavenumbers 1373 and 1289  $\text{cm}^{-1}$  are due to bond vibrations of the  $\text{NO}_3^{-1}$  group and N→H-O complex, respectively.

Fig.3 showed TEM micrographs of silver powders. It can be seen that the particle shape and degree of aggregation distinctly depend on different (PVA or PVP)/ $\text{AgNO}_3$  mole ratios. When (PVA or PVP)/ $\text{AgNO}_3=0$ , it reveals irregular shape and strong sinter-like particles several micrometers in size (Fig.3a). In contrast, the well-dispersed quasi-spherical-shaped silver particles and a narrow

particle size distribution (Figs.3b, 3c) were obtained by presence of PVA or PVP. The distribution of particles further narrows down between 15 and 25 nm showing that the particle nucleation can be controlled by the use of suitable polymers such as PVA and PVP [19]. The morphology of the particles is spherical with homogeneous distribution. The role of polymer for better surface protection of the nano-particle is therefore highlighted.

The X-ray diffractograms (Fig. 4) of the nanocomposites are well in agreement with the literature values for silver nanoparticles [39, 43]. All the prominent peaks at  $2\theta$  values of about 38, 47.2, 62.2, 77.1 and 84° representing the 111, 200, 220, 311 and 222 Bragg's reflections of fcc structure of silver. The peaks are comparatively broader when PVP is used for preparation of nanoparticles and Scherrer's equation resulted in an average particle size of about 15 nm where as they are sharper when PVA is used giving rise to an average particle diameter of about 22 nm. The broadening of peaks in X-ray diffraction pattern is generally related to smaller particle size.



**Figure 4:** XRD of a) Ag/PVA and b) Ag/PVP nanocomposites, generated by DMF.

On the other hand, when PVP was added to the starting  $\text{AgNO}_3$  solution, we noticed that the PH would decrease to some extent. An acid-base titration performed on PVP solution indicated that PVP is actually a weak acid. This result suggested that PVP molecules are capable of combining with hydroxyl ions. This interaction would then reduce the effective quantity of PVP toward protecting silver nanoparticles. Thus, the silver nanoparticles prepared by using PVP are uniformly dispersed with narrow size distribution as evidenced by XRD, UV-vis spectroscopy and TEM.

#### 4. CONCLUSION

To summarize, this paper describes the use of two different protecting agents such as PVA and PVP for the synthesis of silver nanoparticles reduced by DMF. Silver particles in the nanometer size range are formed in DMF solution and progressively attach to protecting agents, until sufficient material has been deposited, for reduction to occur directly on the surface.

It was found that the addition of protecting agents played a very important role in determining silver conversion, its particle size and stability. Infrared spectroscopy studies utilized to study the interaction between the organic phase and noble metal particles

seem to exhibit dependency on the particles size. Well-dispersed crystalline silver particle with 5-25 nm size and spherical shape has been prepared by reducing silver nitrate with DMF in the presence of PVA and PVP as protective agent. With regard to the optical properties of the dispersions, the silver plasmon absorption band is shifted toward longer wavelength in virtually all cases, due to particle growth and the formation of agglomerates. The increasingly better contact between particles is observed in an increase of absorbance at higher wavelengths. From the figures, we can conclude that both PVP and PVA can function satisfactorily as protective agents for silver nanoparticles. However, according to our experience, PVP is somewhat better (in terms of longer stability) than PVA for preventing silver nanoparticles from their agglomeration.

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