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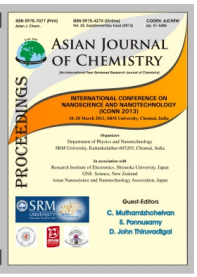

Mechanism of Poly(vinyl pyrrolidone) in the Stabilization of Silver Particles†

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Silver particles were prepared by chemical reduction method using sodium borohydride ($NaBH_4$) as a reducing agent. The synthesized particles were introduced into the poly(vinyl pyrrolidone) (PVP) polymer, which acted as a stabilizer for silver particles. The resulting collidal solution was characterized using UV-Visible (UV-Vis) spectroscopy which confirmed the presence of silver particles through the characteristic plasmon peak around 400 nm. X-Ray diffraction (XRD) analysis also corroborated the formation of metallic silver particles. The stability of silver particles with and without poly(vinyl pyrrolidone) polymer was compared using UV-visible spectroscopy and scanning electron microscopy (SEM) studies. Silver particles protected by polymer showed better stability than the unprotected metal colloid. Additionally, several other roles of poly(vinyl pyrrolidone) on silver particles were discussed.

Key Words: Silver, Poly(vinyl pyrrolidone), Stabilization, Silver particles.

INTRODUCTION

Metal nano/micro particles have attracted a great deal of attention of the researchers due to their fascinating properties with applications in wide research areas such as optical, electronic and catalytic properties[1-4]. Their quantum size and surface effects makes them attractive[5,6] and especially silver particles were widely recognized for their usefulness in the field of biology, medicine and sensor development[7,8]. Though there are many methods to produce metal micro/nano particles such as photochemical method[9], microwave irradiation[10], electrochemical method[11] *etc*., chemical reduction method is preferred because of the good control of it over the particle size and shape, metal purity, good distribution and simplicity than other methods[7,12]. The two most commonly used reducing agents for the reduction of silver salts are sodium borohydride and sodium citrate[13,14]. The latter yields uneven shapes and relatively larger sizes[12] while sodium borohydride permits formation of fine spherical particles of uniform size.

It is of utmost importance to protect the nano metal colloid from aggregation due to the high surface energy possesed by nanodimensioned particles and hence a stabilizer was used to serve such purposes. A wide variety of polymeric protective agents have been used in the stabilization of silver micro/nano particles, but amongst them, vinyl polymers such as poly(vinyl alcohol) (PVA), poly(vinyl pyrrolidone) (PVP), polymethyl-vinyl ether (PMVE) were preferred[15] since their side chains have high density polar groups that prevent the particles from aggregation[16]. Further narrowing it down, PVP was regarded as an excellent stabilizer over other vinyl group polymers[17-19] owing to its structural effects. The nitrogen (N) and oxygen (O) atoms in the PVP polymer form chemical bonds and hence bind silver ions and particles, and the hydrophilic pendant groups of the vinyl polymer coordinate with the solvent thereby providing the steric effect[20]. Hence the particle growth was retarded and agglomeration was prevented.

Almost, all the recently reported works reduces silver salt in the presence of stabilizer but the current work specializes in a two step process in which silver particles are synthesized separately and then added into the polymer. In this study, we present a detailed report on the synthesis of silver particles using chemical reduction method and its stabilization using PVP polymer. The effect of the stabilizer on the metal colloid is discussed and the results are compared with the unprotected metal colloid.

EXPERIMENTAL

All chemicals utilized in the current study were analytical grade and used without any further purification. Silver nitrate ($AgNO_3$), sodium borohydride ($NaBH_4$) and poly(vinyl pyrrolidone) (PVP k 40) were purchased from Sigma Aldrich.

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Deionized water was used throughout the experiment. Aqua regia was used to clean the glass wares and oven dried prior to use.

The optical studies of the synthesized particles were carried out using UV-visible spectroscopy with a Jasco V-630 spectrophotometer in the range between 300-800 nm in a quartz cuvette with a path length of 1 cm. The X-ray diffraction analyis of metallic particles was carried out using PANalytical X'pert-PRO diffractometer using CuK_{α} as a radation source at 40 kV and 30 mA. The morphology of the prepared particles was observed using a scanning electron microscope (Tescan Vega-3 LMU) with a suitable accelerating voltage of 30 kV.

General procedure: In a typical synthesis, solution A was prepared by dissolving 4 mg of silver nitrate in deionized water. The silver salt was reduced into metallic particles by introducing the salt solution into ice-cooled sodium borohydride. Simultaneously solution B was prepared by dissolving 500 mg of PVP in 25 mL of deionized water and was mixed under magnetic stirring for 1 h. As soon as the metallic silver particles were formed, it was added into the PVP polymer solution to avoid aggregation and sonicated for 0.5 h. The colourless PVP solution gradually turned to pale yellow, attaining dirty yellow as time proceeds and finally to wine-red colour, thereby indicating the completion of the reaction, as shown in Fig. 1b. The wine-red transparent solution was stable for 3 months without precipitation but the unprotected metal colloid aggregated into black precipitate within 0.5 h of synthesis as shown in Fig. 1a.

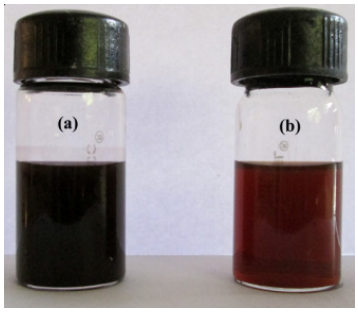

Fig. 1. Photographs of (a) unstabilized and (b) polymer stabilized silver particles colloid

RESULTS AND DISCUSSION

X-ray diffraction analysis: The formation of metallic silver from precursor salt solution was confirmed by X-ray diffraction analysis. The characteristic diffraction peak was observed around 38.08º, 44.24º, 64.38º, 77.36º corresponding to (111) (200) (220) (311) crystallographic planes of face centered cubic silver. This result is consistent with the JCPDS file number 04-0783[21-24]. And also, the sample possesses good crystalline nature, which can be ascertained from the intense, sharp diffraction peaks[23] as shown in Fig. 2.

UV-Visible spectroscopy studies: UV-visible spectroscopy had been extensively used to confirm the presence of the metal nanoparticles and its stability because of its quick, time saving and user-friendly conveniences. Fig. 3. shows the UV-Vis spectrum of pure PVP (a), polymer protected silver particle colloid (b) and the unprotected metal colloid (c). The pure PVP did not show any peak at all, whereas the metallic

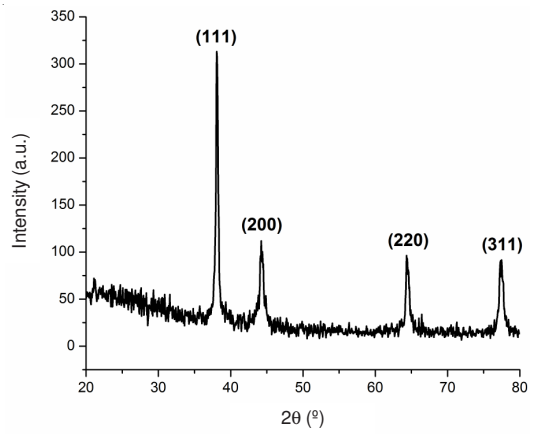

Fig. 2. X-Ray diffraction pattern of silver particles+

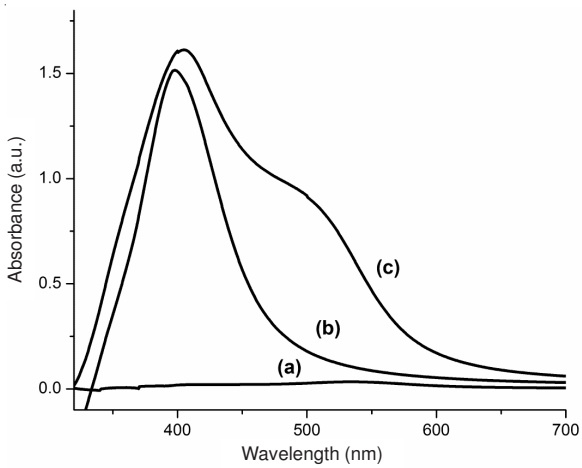

Fig. 3. UV-Vis absorption spectrum of (a) pure PVP (b) polymer protected colloidal silver particles and (c) unprotected colloidal silver particles

colloids show broad band around 400 nm which arised from the surface plasmon resonance (SPR) of silver colloids[25]. The polymer protected metal colloid showed single strong absorption peak whereas for the unprotected metal colloid, an additional weak shoulder was observed around 510 nm. Sun *et al.*[26] had observed that the number of SPR band increases when the nanoparticles had lost its symmetry. Therefore, there is a possibility that the unprotected metal colloid has been aggregated which was also confirmed by the observed colour of the precipitated colloid shown in photographs in Fig. 1a.

Scanning electron microscopy studies: To further validate the stabilizing role of poly(vinyl pyrrolidone) (PVP) on metallic silver, scanning electron microscopy study was carried out. Fig. 4 shows the metallic silver particles protected/unprotected by polymer. It was clear from the figure that the unprotected metallic silver colloids have anisotropic structures with uneven shapes and distribution and shows agglomeration at some places whereas the metallic particles protected by polymer shows well defined smooth spherical structures with identical sizes (around 500 nm) and good dispersity. The SEM results agree well with the UV-Visible spectrum obtained for protected and unprotected metal colloids by polymer. The stabilizing effect of PVP was due to the N and O atoms which have combined with silver particles, resulting in the formation of protective layer on the surface of silver particles inhibiting its growth and aggregation[23 27-29]. Apart from that, it may

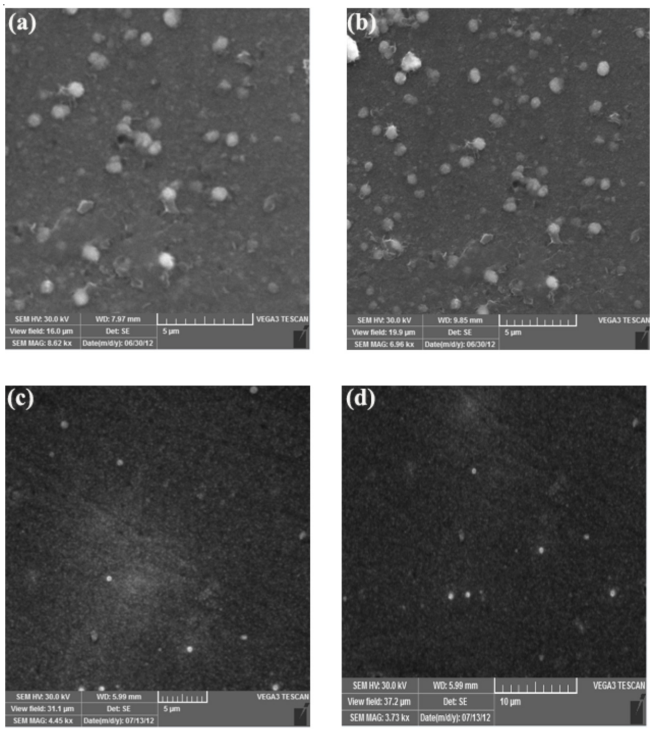

Fig. 4. Scanning electron microscopy images of silver particles: (a, b) unprotected colloidal silver particles and (c, d) polymer protected colloidal silver particles

also be due to the steric effect[20] and viscosity of the polymer solution[30] which made it intricate for the silver particles to accumulate into clusters and hence homogenity in particle size and shape were observed. The vital role played by polymer here was to protect the metal colloid from aggregation. Besides the polymer had also hindered the growth of the particle and showed good dispersion[17,23,31,32].

Conclusion

In summary, silver particles were prepared and a comparision between polymer protected and unprotected metal colloid was made. X-Ray diffraction analysis substantiated the formation of metallic silver. The surface plasmon resonance band observed in UV-VIS spectroscopy study assured the formation of silver particles and an additional shoulder observed in the case of the unprotected metal colloid maybe due to the aggregation of silver particles which was validated through the colour of the colloid and morphological study. The SEM studies showed uniform, well dispersed, smooth spherical particles for polymer protected metal colloid while on the contrary, for the unprotected colloid, the particle lacks uniformity and shows some degree of aggregation. The N and O atoms in the polar group of PVP may have binded metallic silver particles preventing further growth and aggregation, in addition to steric and viscosity effect, thereby stabilizing the metal colloid for months without decomposition.

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