

Preparation of colloidal silver nanoparticles and structural characterization

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ABSTRACT

In this paper, we prepare silver nanoparticles colloids by using polyvinyl pyrrolidone (PVP) of four different molecular weights ($M_w = 10000, 29000, 40000, 55000$) as a protective agent, dextrose as reduction agent and by adding urea which produce intermediates $AgOCN$ and Ag_2CO_3 . Results indicated that PVP effects against agglomeration would depend to a great extent on the hydroxide and urea concentrations used in the reaction medium. When NaOH was dominant, the reaction rate was very fast and hence only PVP with large molecular weight produced small silver colloids of sizes around 20 nm. On the other hand, when urea was dominant, the reaction path was significantly changed and slowed down as well; under this circumstance, PVP with M_w of 10000 offered the best protection against agglomeration, it produced silver colloids of only 26 nm. A part of our silver nanoparticles was extracted as powder, to be characterized by XRD, and another part was deposited on glass substrates, by spin-coating, in order to be characterized by AFM. X-ray diffraction spectra confirmed the formation of metallic silver nanoparticles with preferred orientation along (111) plane. The AFM images showed that the silver nanoparticles are spherical and relatively uniform. After a proper washing process, much of PVP could be removed, and TGA characterization showed that the residual quantity of PVP on silver is about 5 wt% for most samples.

Keywords: Silver nanoparticles, atomic force microscopy, x-ray diffraction, thermo-gravimetric analysis, polyvinyl pyrrolidone, urea, dextrose.

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INTRODUCTION

Noble metal nanoparticles materials have been the focus of intense research in recent decade, and it is motivated by the exceptional properties that a material gains when its size is reduced to nanoscale lengths. The remarkable physical, chemical and optical properties of silver nanomaterial (Sen et al., 2003) allows for their utilization in various scientific applications such as sensors (Shao et al., 2009), nanophotonics devices (Prikulis et al., 2004), biology (Elechiguerra et al., 2005), drug delivery (Arruebo et al., 2007), cancer treatment (Jain, et al., 2007), photo-thermal therapy (Huang and El-Sayed, 2010), diabetic healing (Mishra et al., 2008), solar cells (Tong et al., 2008), catalysis (Sanchez, 2007), cooling system (Das et al., 2007), surface-enhanced Raman spectroscopy (Cui et al., 2006), inkjet-printer (Rianasari et al., 2008), imaging sensing, biology and medicine (Jain et al., 2008), optoelectronics and magnetic devices (Maarof and

Smith, 2005). These properties significantly depend on the size, shape and surface chemistry of the nanomaterial. Synthesis of silver particles is an important task. Several methods have been used in the past to prepare nanostructured silver particles, including chemical reduction (Marzan and Lado-Tourino, 1996; Glavee et al., 1993), electrochemical reduction (Khaydarov et al., 2009; Mallick et al., 2005; Keki et al., 2000), heat evaporation (Bae et al., 2002; Smetana et al., 2005), thermal decomposition in organic solvents (Lee et al., 2007) polyol process (Silvert et al., 1996) chemical and photo-reduction in reverse micelles (Ohde et al., 2001; Sun et al., 2001) and radiation chemical reduction (Henglein, 2001; Henglein, 1998). All these methods of preparation involve the reduction of relevant metal salts in the presence or absence of surfactants, which is necessary in controlling the growth of metal colloids

through agglomeration (Sahoo et al., 2009). In a typical process, one can choose the reducing agent and corresponding protective agent to obtain a uniform dispersion of products. In an aqueous reaction medium, when a strong reducing agent such as sodium borohydride (NaBH_4) or hydrazine (N_2H_4) is used, the fast reaction produces very small primary particles, and when the precursor (i.e. AgNO_3) concentration is relatively high, it becomes difficult for the protective agent, e.g. PVP molecules, to fully adsorb onto the silver colloidal surface in time due to the diffusion limit. As a result, the conversion might prove high, but the size distribution of the final product is often very broad (Nersisyan et al., 2003; Pradhan et al., 2002). In order to avoid too much agglomeration, the silver ion concentration must be kept low, which in turn compromises the productivity of the process. However, when a moderate reductant such as formaldehyde is used, one can obtain silver particles with a mean size of 27.8 nm and standard deviation of 9.9 nm from an initial silver concentration of 0.1 M (Chou and Lai, 2004; Chou et al., 2005). Panigrahi et al. (2004) tried a weak reductant, that is, glucose, to obtain Ag particles of about 20 nm in size, but the products were not uniform enough. Nersisyan et al. (2003) also used glucose, however their precursor was Ag_2O and the Ag particles were in the range of 10 to 50 nm. Hu et al. (2004) used trisodium citrate to prepare silver nanorods and nanowires based on the principles of slow reduction rate and non-isotropic adsorption of surfactant (Lu and Chou, 2008).

Lu and Chou (2008) used dextrose as a reducing agent, polyvinyl pyrrolidone with single molecular weight as a protective agent, and urea to slow down the reduction reaction through the formation of intermediate compounds. Finally, they got silver colloids of average 22 nm. Chou and Lai (2004) used formaldehyde (37%, Tedia) as a reducing agent and polyvinyl pyrrolidone of three different molecular weights ($M_w = 8000, 29,000, 55,000$) as a stabilizing agent. Finally, they got silver colloids which size ranges between 5 and 20 nm depending on the power of used promoter (Chou and Lai, 2004).

In our work, we study the effect of the PVP molecular weight on the formation of silver nanoparticles. We employed dextrose as reducing agent, and as a stabilizer (protective agent or capping agent) we used polyvinyl pyrrolidone with different molecular weights (PVP10000, PVP29000, PVP40000, and PVP55000). We used urea as an additive to produce intermediates that slow the transformation of silver ions into silver by the reducing agent. We got silver colloids of small particle sizes and a narrow distribution using only a small amount of protective agent while maintaining high conversion rates at reasonable silver concentrations at the same time.

We should mention here that our work is the first one in Syria, and its results are obtained for the first time in our country, in spite of the leak of characterization devices available in our university and institute.

MATERIALS AND METHODS

Chemicals

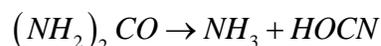
All of the chemicals used in the experiment were analytic reagent (AR). The silver nitrate was used as the precursor to prepare silver colloids and provided by Hubei Xinying Noble Metal Co. Ltd. Dextrose, was used as the reducing agent and polyvinyl pyrrolidone (PVP) of four different molecular weights ($M_w = 10000, 29000, 40000, 55000$) as the stabilizing agent for these Ag colloids were obtained from Sigma-Aldrich.

Preparation of nano-Ag

We prepared three separate solutions, that is, A, B and C. Solution A contained 0.156 M AgNO_3 with variable quantities of urea (the molar ratio of $[\text{Urea}] / [\text{Ag}^+]$ was between 0 and 12). Solution B contained polyvinyl pyrrolidone (PVP) with its quantity fixed at 1 g PVP/1 g AgNO_3 and variable quantities of NaOH, whose concentration was from 0.2 to 1 M PVP having molecular weights (MW) of 10,000, 29,000, 40,000 and 55,000 were tested in this work for their capability to stabilize the silver colloidal suspensions. Solution C contained 0.334 M dextrose ($\text{C}_6\text{H}_{12}\text{O}_6$). The particular experimental conditions are listed in Table 1 (sample nos: 1 to 12). At the ambient temperature, and with stirring at 600 rpm, solution A was rapidly poured into solution B. Light yellow precipitates formed immediately. After reacting for 10 min, solution C was poured into the mixed solution of A and B. After 5 min of interaction we transferred the mixture to water bath at 70°C to accelerate the reduction reaction. It was noted that the color changed from yellow to black. After half an hour, the silver colloids were separated from the solution by vigorous centrifugation at 10,000 rpm for 60 min to remove any excess protecting agent and then re-dispersed in D.I. water. Then repeat the previous operation at the speed 10,000 for a period of half an hour, to remove as much of the PVP as possible, then re-dispersion in D.I. water again. For further analysis, the precipitate was also separated by centrifugation at 10,000 rpm for 30 min and dewatered by heating at 100°C for several hours.

Protocol

Theoretically, urea in solution can decompose to ammonium and cyanate ions:



In an alkaline solution, cyanate ions react with hydroxide ions to form carbonate ions and ammonium according to:

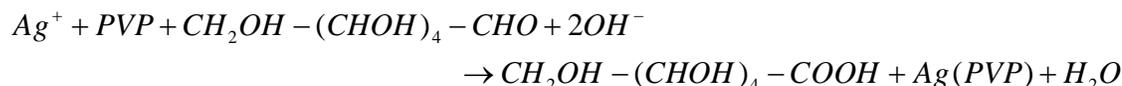


Table 1. Experimental conditions for the synthesis of SNP at 70°.

No.	AgNO ₃ (M)	PVP/AgNO ₃ (g/g)	MW PVP	Urea/AgNO ₃ (molar ratio)	Dextrose (M)	NaOH (M)
G1	0.156	1/1	10000	0	0.334	0.0125
G2	0.156	1/1	29000	0	0.334	0.0125
G3	0.156	1/1	40000	0	0.334	0.0125
G4	0.156	1/1	55000	0	0.334	0.0125
G5	0.156	1/1	10000	4	0.334	0.025
G6	0.156	1/1	29000	4	0.334	0.025
G7	0.156	1/1	40000	4	0.334	0.025
G8	0.156	1/1	55000	4	0.334	0.025
G9	0.156	1/1	10000	12	0.334	0.05
G10	0.156	1/1	29000	12	0.334	0.05
G11	0.156	1/1	40000	12	0.334	0.05
G12	0.156	1/1	55000	12	0.334	0.05

The decomposition rate of urea increases as pH or temperature increases (Larson, 1932; Warner, 1942); therefore, when solution A was injected into solution B whose pH was increase gradually, the alkaline solution accelerated the urea decomposition greatly and immediately produced many cyanate ions and carbonate ions. In addition, the K_{sp} values of AgOCN and Ag₂CO₃

were both smaller than that of Ag₂O. As a result, the intermediates of AgOCN and Ag₂CO₃ were observed, instead of Ag₂O. In the presence of a reducing agent (that is, after adding solution C), this intermediate proved unstable, and it gradually converted into silver leading to a change of color from yellow to brown to black.



Characterizations

The structural properties of NSPs were investigated by X-ray diffraction (XRD, Philips, PW1710, Netherlands) that was operated at a voltage of 40 kV and a current of 30 mA with an excitation source of CuK_α radiation ($\lambda = 1.54060 \text{ \AA}$), in the range of scanning angle 30 to 85° at a scan rate of 1°/min with the step width 0.02°. The surface morphology was determined by the Atomic Force Microscopy measurements (AFM, Nanosurf easyScan2, Switzerland). The AFM measurements were performed in contact mode.

Deposition of silver nanoparticles

Deposition of silver nanoparticles was performed by spin-coating. We coated the Ag colloidal onto glass substrates of the dimension of 25.4 mm × 76.2 mm × 1 mm were degreased in ethanol for 10 min and then ultrasonically cleaned with distilled water for another 15 min before deposition of films. The spin-coating process was used for the deposition of the silver sols on to the substrates. Typically, a few drops of solution are placed on to the surface of the substrate; the initial amount of silver sol

has little effect on the final film properties. The substrate is then rotated at several thousand rpm in order to obtain a homogeneous film.

RESULTS AND DISCUSSION

X-ray diffraction analysis

The X-ray diffraction pattern measurements of spin-coating silver nanoparticles film on glass substrate. The XRD measurements were performed in order to investigate the structural properties of the SNP_s. X-ray diffraction patterns of the various components, that is, pure silver, and Ag nanoparticles, are presented in Figure 1; the value of the Ag lattice constant has been estimated to be $a = 4.078 \text{ \AA}$, a value which is consistent with $a = 4.0862 \text{ \AA}$ reported by the (JCPDS cards 4-0783). XRD patterns of silver particles will yield five peaks from 30 to 85°, 2θ 38, 44, 64, 77, and 81° reveal that it is a face centered cubic (FCC) structure.

The discernible peaks can be indexed to (111), (200), (220), (311) and (222) planes of a cubic unit cell, which corresponds to cubic structure of silver (JCPDS card. No. 89-3722). Crystallite size calculations were done at (111) plane for all samples using Scherrer equation and results

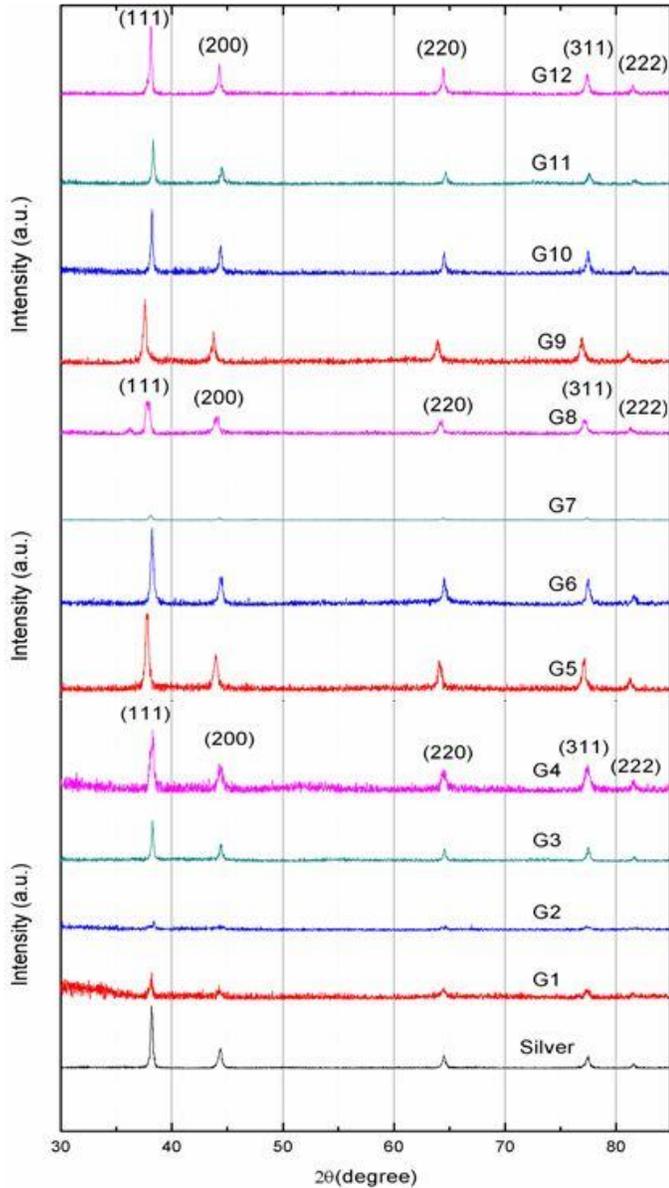


Figure 1. XRD patterns of a pure silver with all synthesized silver nanoparticles.

are given in Table 2.

$$D = \frac{K \lambda}{\beta \cos \theta}, \quad \beta = \sqrt{\beta_m^2 - \beta_a^2}$$

Where K is a constant ($k = 0.9$), β_m is full width at half maximum (FWHM) in degree (get it from fitting peaks according to Gaussian), β_a is a constant ($\beta_a = 2.74 \times 10^{-3} \text{ rad}$) determine from the instrument broadening, $\lambda = 1.54060 \text{ \AA}$ is the CuK α wavelength of x-ray used, θ is the Bragg angle. The

Table 2. Crystallite sizes, diffraction angle and FWHM of synthesized silver nanoparticle.

No.	2 θ by degree	β_m (FWHM)	Crystallite size (nm)
G1	38.134	0.322	30
G2	38.386	0.235	48
G3	38.254	0.245	45
G4	38.224	0.446	20
G5	37.775	0.372	25
G6	38.229	0.341	28
G7	38.3122	0.332	30
G8	37.837	0.476	19
G9	37.581	0.356	26
G10	38.205	0.236	48
G11	38.31	0.253	42
G12	38.109	0.239	47

particle sizes of all the samples in our study have been estimated by using the above Scherrer's equation and was found to be ~ 19 nm for the molar ratio $[Urea]/[Ag^+] = 4$ and molecular weight of PVP = 55000.

AFM characterization

A $2 \mu\text{m} \times 2 \mu\text{m}$, AFM image is reported on Figure 2. A statistical treatment of AFM images was performed using specially designed image processing software. To further exploit these measures should be extracted from these images the main geometrical characteristics of these nanostructures. These are summarized in Table 3. The silver nanoparticles have an average diameter ranged from 79 to 116 nm and an average height varied from 9 to 26 nm.

From the AFM pictures we can see that the size of nanoparticles is bigger. Silver nanoparticles tend to form aggregates on the surface during deposition. The sizes of nanoparticles obtained from the AFM images appear bigger than the values that we get from XRD measurements. We interpret those results to several reasons; first explanation relates the silver nanoparticles appear to be clustered together. Second explanation due to the wafers was not completely cleaned for PVP. Third reason related to the shape of the tip AFM may cause misleading cross sectional views of the sample. So, the width of the nanoparticle depends on probe shape; however, the nanoparticle height is independent of the probe shape. The finally explanation relates residual amount of PVP on the both wafer and nanoparticles which could distort the results obtained from the AFM images. We recognize a very good agreement between the two results: a larger XRD-size corresponds effectively to a large AFM-diameter.

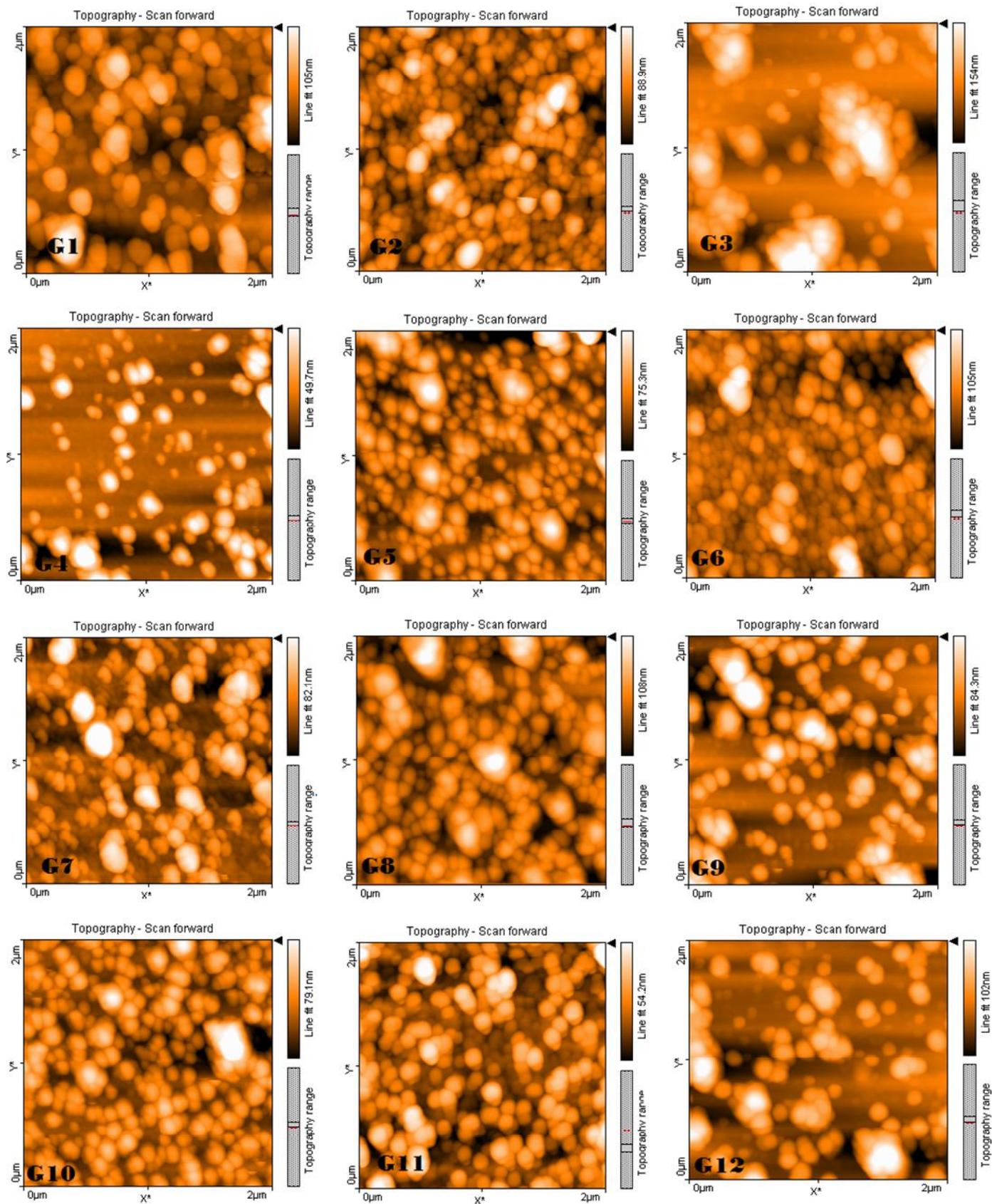


Figure 2. Two-dimensional AFM surface images of SNPs colloids deposited on a glass slide.

Table 3. Average diameter and height of the silver nanoparticles calculated by AFM.

No.	Mean AFM diameter (nm)	Mean AFM height (nm)
G1	86	9
G2	79	10
G3	114	26
G4	81	10
G5	93	13
G6	95	12
G7	102	14
G8	90	10
G9	95	13
G10	103	14
G11	116	12
G12	98	11

When NaOH was used alone without presence urea, the reduction reaction is quick because NaOH promote the reduction reaction. So when the reaction rate was fast, PVP which having molecular weight of 10000 or 29000 would not have plenty of time to coat newly formed silver colloids, thus unable to prevent the agglomeration. Here, we got on the particle size of about 30 and 48 nm, respectively. Whereas PVP which having molecular weight of 55000 probably caused some physical disability and thus slowed agglomeration process, so enabling the coating and stabilization process to those silver colloids. Therefore, we got on the particle size of about 20 nm. When the urea concentration is low (Urea/AgNO₃ = 4) and concentration of sodium hydroxide is high (0.025 M), the impact of sodium hydroxide remains the dominant in reaction medium and therefore we got the same result above. While when the urea concentration is high, urea dominates, and the reaction clearly slows. So PVP which having molecular weight of 10000 would having sufficient time to coat and protect silver colloids, where we got on a particle size of about 26 nm. Whereas PVP which having molecular weight of 55000 gave us a larger particle size around 47 nm. We attribute this result to the fact that small polymer molecules gives better coverage on the surfaces of silver colloids than large polymer molecules.

Thermo-gravimetric analysis (TGA)

TGA measurements were carried out on the Ag/PVP nanoparticles and pure PVP. A known weight of the samples was heated at a rate of 10°C min⁻¹ in flowing N₂, from room temperature up to 700°C, which is in between the boiling point of the solvent and the degradation temperature of the polymer. Figure 3 shows three distinct stages of weight loss were observed for PVP. An initial weight loss was calculated to be around 7.3% in the range of room temperature up to 250°C. The weight loss

up to this range of temperature is attributed to low molecular weight oligomers, loss of moisture and residual solvent in this range of temperature. Second stage was 11.5% in the range of 250 to 396°C, and third stage was 61% in the range of 396 to 695°C for PVP. Figure 3 also shows one distinct stages of weight loss were observed for Ag/PVP nanoparticles. The only weight loss was about 4.1% in the range of room temperature up to 510°C. The second weight loss for PVP indicates that the pure PVP began to degrade above 300°C and is completely decomposed at above 695°C. The second major weight loss was attributed to structural decomposition of polymer. However, the thermo gravimetric analysis of the Ag/PVP nanoparticles showed decomposition profile starting at about 350°C and continuing until about 510°C. This shows that the thermal stability of the polymer is improved due to presence of Ag as nano-filler. This observation is consistent with the results obtained by Mbhele et al. (2003), where it has been shown that the PVA alone starts decomposing at about 280°C and its composite with about <1% Ag starts decomposing at higher temperature than the PVA alone, typically about 40°C more. In our experiments, though the content of Ag is expected to be more but it appears that the degradation temperature of our composite is sparingly higher to that it is reported. Finally, from TGA data in Figure 3, it is shown that the residual PVP on silver is about 5 wt% for most samples, which is estimated to be the weight loss between 350 and 700°C. In general, the residual quantity of PVP greatly depends upon the washing procedure.

Conclusion

In conclusion, the Ag nanoparticles have been prepared by the wet chemical technique under optimized conditions of preparation. Deposition of silver sols was

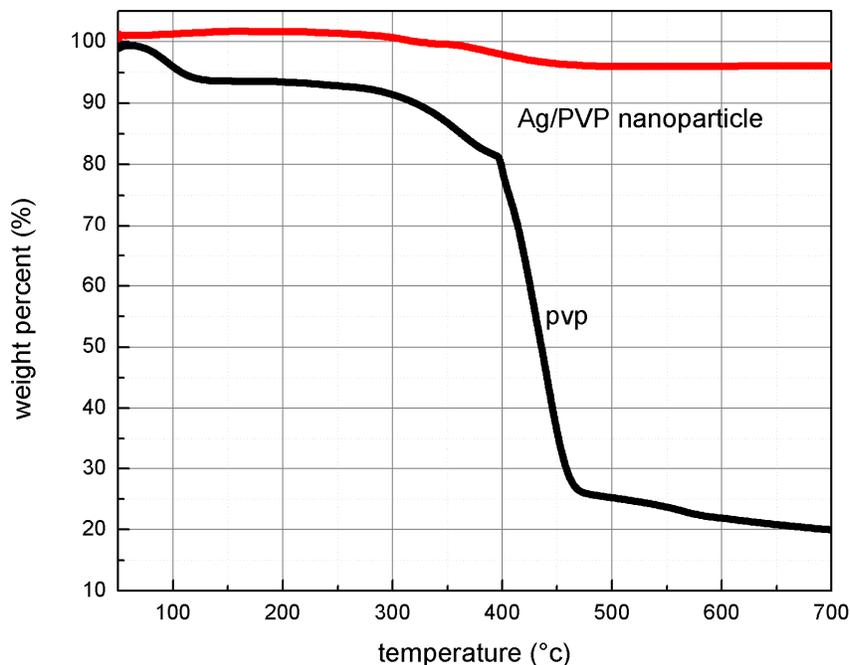


Figure 3. TGA analysis of an Ag/PVP nanoparticle sample.

carried out from aqueous solutions using silver nitrate, dextrose, PVP of four molecular weight ($M_w = 10000, 29000, 40000, 55000$) and sodium hydroxide. XRD as well as Atomic AFM image studies confirmed the nanometer size Ag particles. XRD analysis showed the nanoparticles were crystalline and metallic with minimum size ~ 19 nm. AFM analysis showed that most of the particles were spherical in shape with and their size appears larger than the calculated value from XRD. However, the nano-size particles calculated by XRD correspond reasonably well with the real values of the size SNPs.

When the reaction rate was fast because the effect of sodium hydroxide is the one who dominates in the reaction medium, PVP with molecular weight of 55000 can offer protection against agglomeration to produce silver colloids of size around 20 nm. While PVP having molecular weight 10000 was found unable to protect against agglomeration. Whereas the reaction was slow because the effect of urea is the one who dominates in the reaction medium. PVP of 10000 molecular weight showed the best protection against agglomeration to produce silver colloids of size around 26 nm.

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