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Preparation and Characterization of Silver Nanoparticles

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Abstract: Using wet chemistry method, we have synthesized silver nanoparticles, with sizes going from 16 nm to 47 nm. Silver nanoparticles are formed in aqueous solution of silver nitrate, with dextrose as reducing agent; and polyvinylpyrrolidone (PVP)as a stabilizer. In this study we use urea as an additive to produce intermediates that slow the transformation of silver ions into silver by the reducing agent. We obtain silver colloids of small 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.

Key Words: silver nanoparticles, Atomic Force Microscopy (AFM), X-Ray Diffraction (XRD), Infra-Red spectra (FTIR), polyvinylpyrrolidone (PVP), Urea, Dextrose.

1. Introduction

Building small structures for advanced materials design, high performance nano devices and miniaturized electronics is one of the central goals of nano science[1]. Inorganic nanoparticles are particularly attractive building blocks for such purposes, owing to their unique optical, electronic, magnetic, and catalytic properties[2-7], many of which can be tailored simply by tuning size, shape, and surface functionality of nanoparticles without changing their material composition. Thus far, significant progress has been made using wet chemistry strategies to synthesize high-quality nanoparticles from a variety of inorganic materials, including gold, silver, iron oxide, and semiconductors[2-7].

Manipulating the synthesis conditions allows for rational control of nano particle morphology and provides a means to tailor material properties in the process. Noble metal nanoparticles, and specially silver nanoparticles, have potential uses in many applications[8-10], such photonic circuits[11,12], wave-guides[13-15], molecular rulers[16] and chemical/biological sensors[17-20].

Several methods have been used in the past to prepare nano structured silver particles, including chemical reduction of silver ions in aqueous solutions with or without surfactants[21], electrochemical reduction[22,23], heat evaporation[24,25], thermal decomposition in organic solvents[26], polyol process[26], chemical and photo-reduction in reverse micelles[27-33], and radiation chemical reduction[34-36]. 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.

From a practical point of view, the method of chemical reduction from aqueous silver nitrate solution is most preferable for obtaining silver nanoparticles. 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 on 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[37,38] . 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 reducing agent, such as formaldehyde, is used one can obtain silver particles with a mean size of27.8 nm and standard deviation of 9.9 nm from an initial silver concentration of 0.1 M[39,40]. Panigrahi et al.[41] tried a weak reducing agent, i.e. glucose, to obtain Ag particles of about 20 nm in size, but the products were not uniform enough. Nersisyan et al.[38] also used glucose, however their precursor was Ag_2O and the Ag particles were in the range of 10–50 nm. Hu et al.[42] used trisodium citrate to prepare silver nano rods and nano wires based on the principles of slow reduction rate and non-isotropic adsorption of surfactant. Silvert et al.[43] obtained fine-sized Ag particles whose size distribution was between 15 and36 nm by polyol reduction. Despite these efforts, it remains difficult to prepare silver particles of less than 20 nm and with a narrow distribution from an aqueous solution.

In our work we prepare silver nanoparticles from aqueous solution of silver nitrate. Our reducing agent is dextrose; and we employ polyvinylpyrrolidone (PVP) as a stabilizer (protective agent or capping agent). In this study we use urea as an additive to produce intermediates that slow the transformation of silver ions into silver by the reducing agent. We can obtain silver colloids of small 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 that this work is the first one at our country, in spite of the lake in characterization devices, and it could be completed with SEM and TEM characterization but we don’t have these techniques yet.

2. Experimental work

We prepare three separate solutions A, B and C:

- Solution A contains 0.156 M$AgNO_3$ with variable quantities of urea (the molar ratio of [Urea]/ [Ag^+] was between 0 and 12).
- Solution B contains PVP with its quantity fixed at 1 g of PVP/1g of AgNO3, and variable quantities of NaOH, whose concentration was from 0.2 to 1M.PVPhaving molecular weights of 10,000, 29,000, 40,000 and 55,000 are tested in this work for their capability to stabilize the silver colloidal suspensions.
- Solution C contains 0.334 M dextrose ($C_6H_{12}O_6$). The Particular experimental conditions are listed in Table 1.

At ambient temperature, and with stirring at 600 rpm, solution A is rapidly poured into solution B. Light yellow precipitates are formed immediately. After 10 min of reaction, solution C is poured into the mixed solution of A and B. When the color of the solution changes from yellow to black, we transfer the mixture to a water bath at 70^0C to accelerate the reduction reaction.

After30 min of reaction, we separate the silver colloids from the solution by robust centrifugation at 10000 rpm for 60 min, to get rid of any excess protecting agent, and were-disperse the obtained silver in D.I. water. We repeat the previous operation at the speed of 10000 rpm, for another period of 30 min, to remove as much of the PVP as possible, then we re-disperse the separated silver colloids in D.I. water again.

Finally, we deposited the Ag colloidal suspension on glass slides by spin-coating. For further analysis, the precipitate was also separated by centrifugation at 10000 rpm for another 30 min and dewatered by heating at 100^oC for several hours.

We characterize the deposited films by Atomic Force Microscopy (AFM, NanosurfeasyScan2, Switzerland), and the powder is characterized by X-ray diffraction (XRD, Philips, PW3710, Netherlands),TGA (SETARAMLABSYSOP-1A, France) was used to examine the residual quantity of PVP of these silver colloids, and Infrared (IR) spectrum was measured on a EQUINAX55Fourier transform infrared (FTIR) spectrometer, where the particles were grind with $MgBr_2$ particles together, and pressed to a circle flake.

Table 1: Experimental conditions for the synthesis of silver nanoparticles at 70 ^{0}C.
In all these samples: $[AgNo_3]$=0.156 M, [dextrose]=0.334 M and PVP/AgNO3 is 1g/1g.

Sample number	Molecular weight of PVP	Urea/$AgNO_3$ (molar ratio)	NaOH (M)
1	10000	0	0.0125
2	29000	0	0.0125
3	40000	0	0.0125
4	55000	0	0.0125
5	10000	4	0.025
6	29000	4	0.025
7	40000	4	0.025
8	55000	4	0.025
9	10000	12	0.05
10	29000	12	0.05
11	40000	12	0.05
12	55000	12	0.05

3. Results and discussion

3.1. XRD study

XRD data were collected using a Cu (K• 1) radiation, with 2• in the interval [10^0-100^0], a step of 0.02^0, and a scan time per step of 1 s. X-ray diffraction patterns of the various components, *i.e.* pure silver, and Ag nanoparticles, are presented in Figure 1.

Comparing these patterns with that of pure silver, we deduce that our samples are effectively contains Ag, and only Ag. We see, in preference, diffraction peaks at crystalline plans (111), (200), (220), (311) and (222).

We analyzed all these patterns by the Rietveld method, using the refinement system GSAS and EXPGUI[44,45]: For every pattern, we determined FWHM values of XRD peaks, taking in account the instrumentation contribution in the broadening of those peaks. In order to separate this instrumentation contribution$\beta_{\text{ins.}}$, we measured an XRD pattern of a bulk sample of Si furnished with our PW3710 XRD-PHILLIPS system, then we refined its profile to determine the Caglioti-Paoletti-Ricci coefficients(U,V,W)[46]: $\beta_{\text{ins.}} = \sqrt{U\tan^2\theta + V\tan\theta + W}$. We obtained U=0.02591, V=-0.02159 and W=0.01398 (units: rad^2).

Then crystallite sizes of our silver nanoparticles were determined using Scherrer equation: $D = K\lambda/(\beta\cos\theta)$, where $\beta = \sqrt{\beta_{\text{m}}^2 - \beta_{\text{ins.}}^2}$, $\beta_{\text{m}}$is the FWHM of an analyzed peak at the positionθ, and K is a constant depending on the shape of the crystallites (here we supposed a spherical shape, so$K = \left(\frac{4}{3}\right)\sqrt[3]{\pi/6} \cong 1.0747$[47]. We deduced a crystallite sizes between 16 nm to 47 nm, as resumed in **Error! Reference source not found.**.

3.2. AFM characterization

We present in Figure 4, the AFM images of silver nanoparticles films deposited on glass slides by spin coating. These images have been measured on scanning probe microscope in tapping mode under ambient conditions.

In these AFM images, we see pseudo-spherical particles with different sizes in the studied samples. The height and width of the silver nanoparticles were measured using the software attached with the AFM microscope. In order to estimate an average width and an average height of the imaged nanoparticles, we have arbitrarily chosen, and analyzed, about 15 particles on each image. We got the results presented in

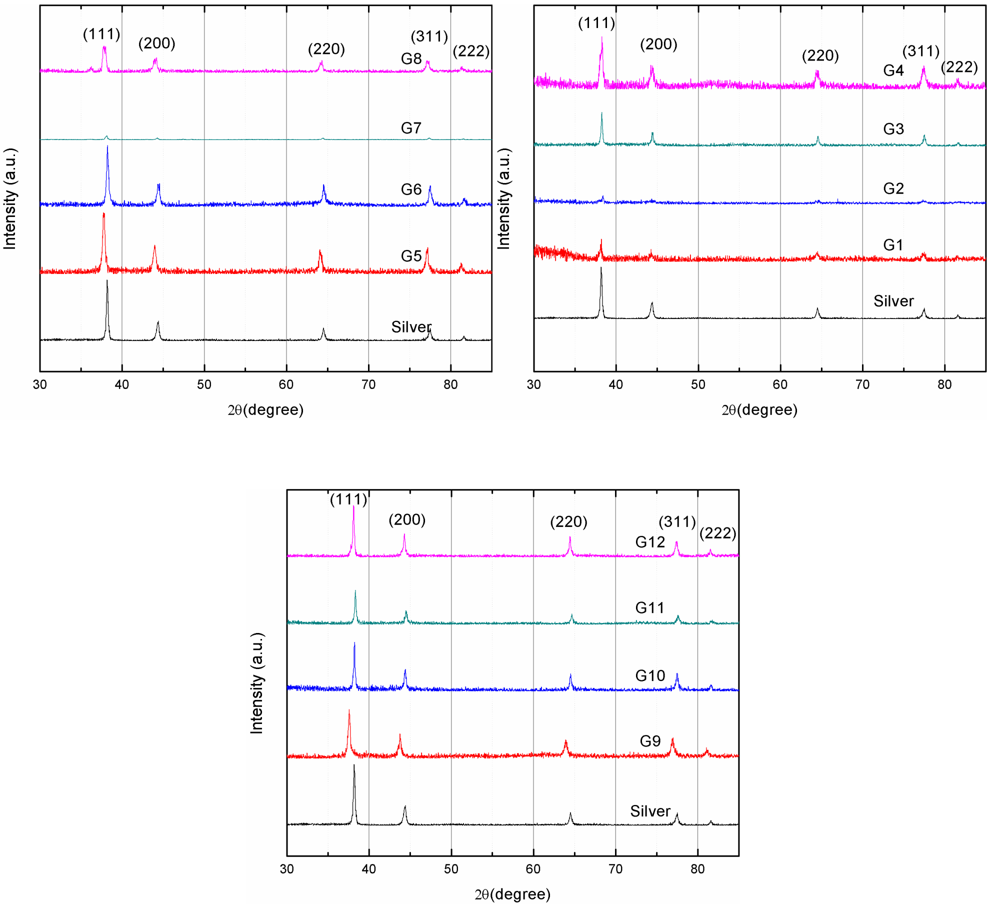


Figure 1: XRD patterns of all synthesised silvernanoparticles and a pure silver.

Table 2: Crystallite sizes of silver nanoparticles samples, obtained by analyzing XRD patterns of Figure 1.

Sample	Size (nm)	Sample	Size (nm)
G1	27	G7	**35**
G2	16	G8	**21**
G3	39	G9	**33**
G4	20	G10	**47**
G5	28	G11	**42**
G6	32	G12	**34**

Table 3: Average width and height of the silver nanoparticles obtained from AFM images.

Sample	Height (nm)	Width (nm)	Sample	Height (nm)	Width (nm)
G1	9	86	G7	14	**102**
G2	10	79	G8	10	**90**
G3	26	114	G9	13	**95**
G4	10	81	G10	14	**103**
G5	13	93	G11	12	**116**
G6	12	95	G12	11	**98**

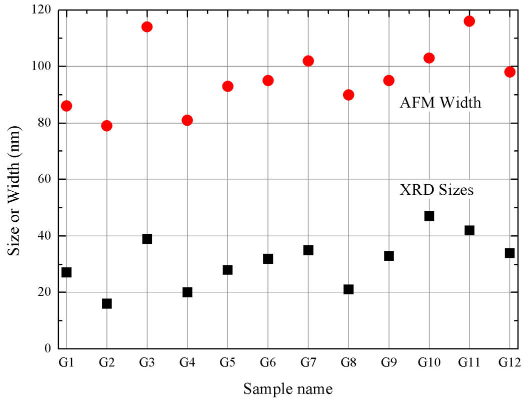
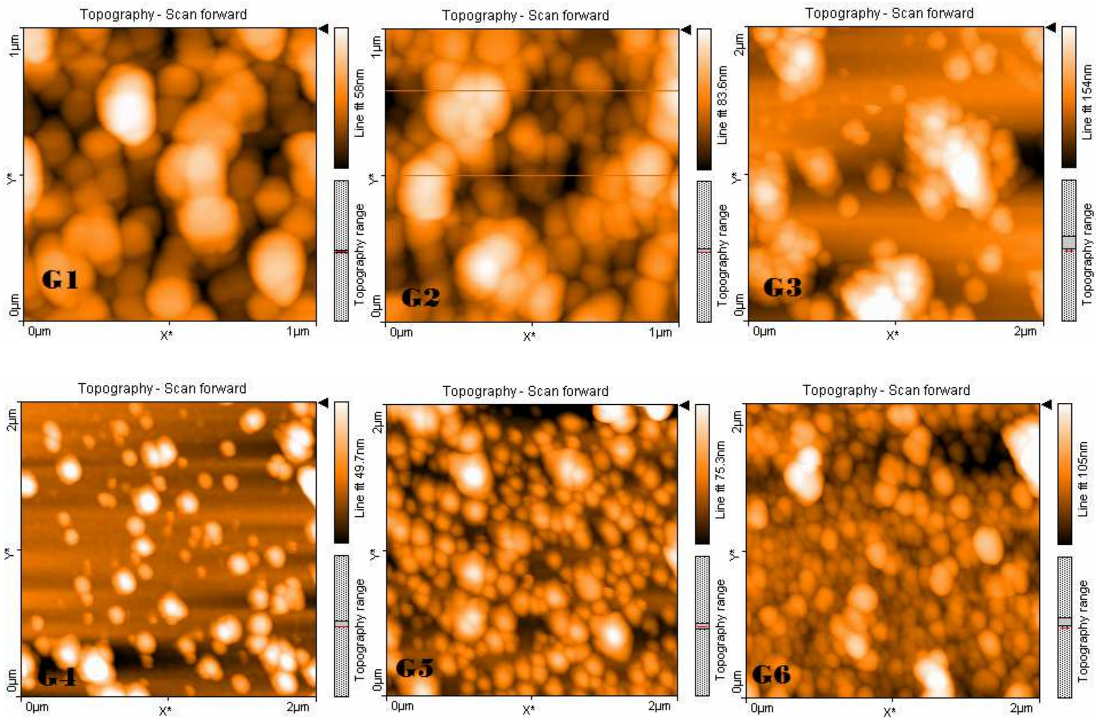


Figure 2: Comparison between silver nanoparticles "sizes" as obtained from AFM images and XRD analysis.

A first look at this table shows a small height values compared with the corresponding width values. The measured height is expected to be as large as the width, assuming a spherical nanoparticle shape, but here it is smaller than the width. This difference is practically due to the fact that particles are diving in a continuous background on the substrate, and to the shape and dimensions of the tip of the cantilever used in AFM imaging[48]. Because of that the height value obtained here is not a typical characteristic of the nanoparticle size.

In contrast, we see on Figure 2 that the nanoparticle width values, obtained from AFM images, are almost larger than the corresponding values obtained by XRD. In fact a primary purpose of the introducing PVP was to protect the silver nanoparticles from growing and agglomerating, but with the introduction of PVP, silver ions or particles would coordinate with N or O in PVP, and a covered layer would generate on the surface of nanoparticles, and this in turns is reflected in a greater dimension when measured by AFM. In spite of that, we recognize at Figure 2 a very good agreement between the two results: a larger XRD-size corresponds effectively to a large AFM-width.

Figure 3:



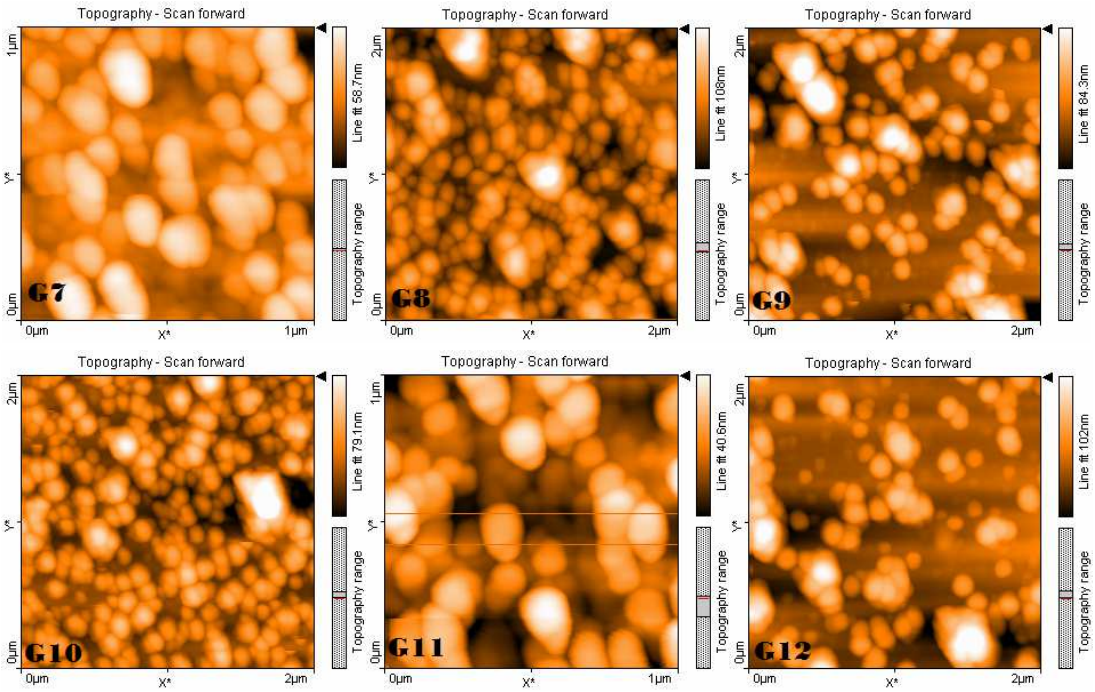


Figure 4: AFM images of silver nanoparticles films deposited on glass slides by spin coating Scan scale: 2 µm×2 µm or 1 µm×1 µm; height scale: 5.0 nm.

3.3. FTIR Analysis

Figure 5 shows FTIR spectra of the PVPs of different molecular weights used in our preparation of silver nanoparticles. These spectra have absorption peaks at identical wave numbers, as expected[49-51] .

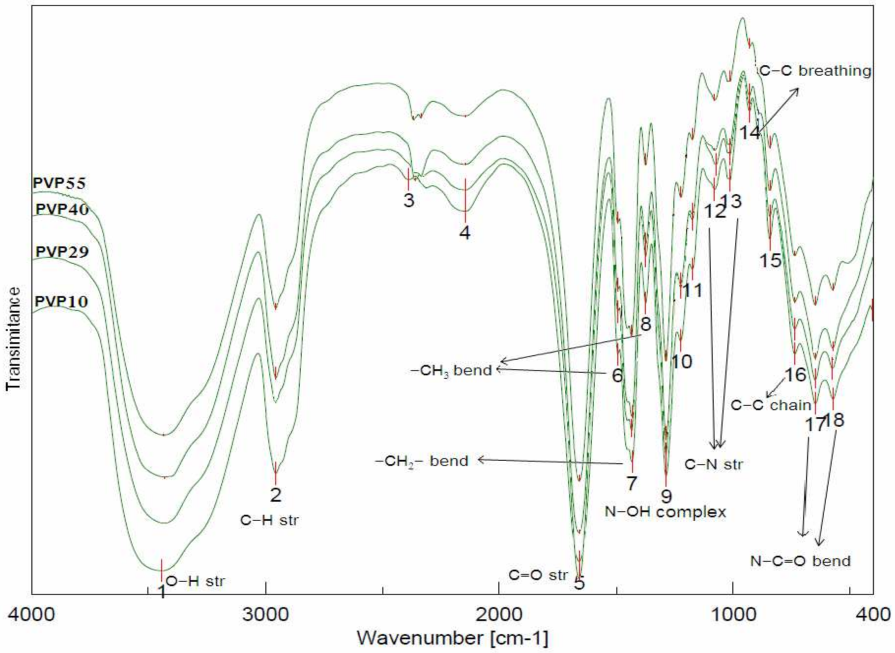
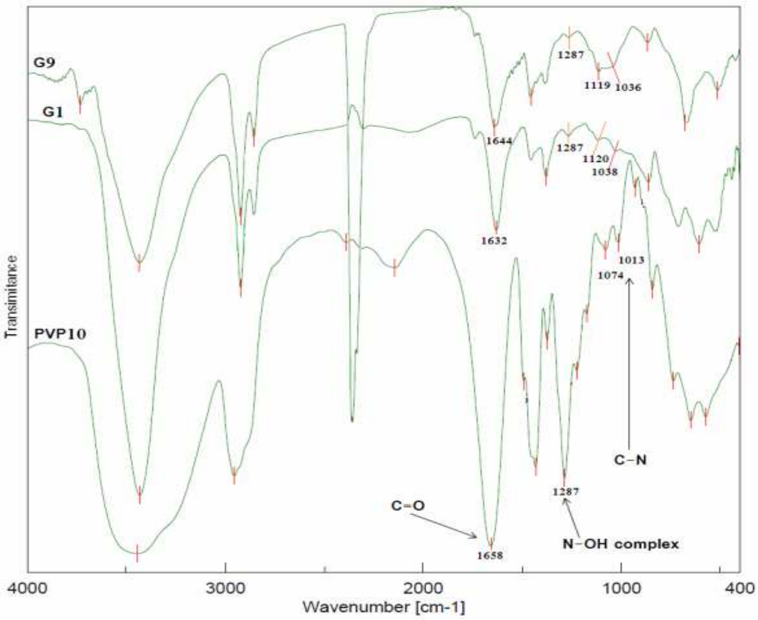


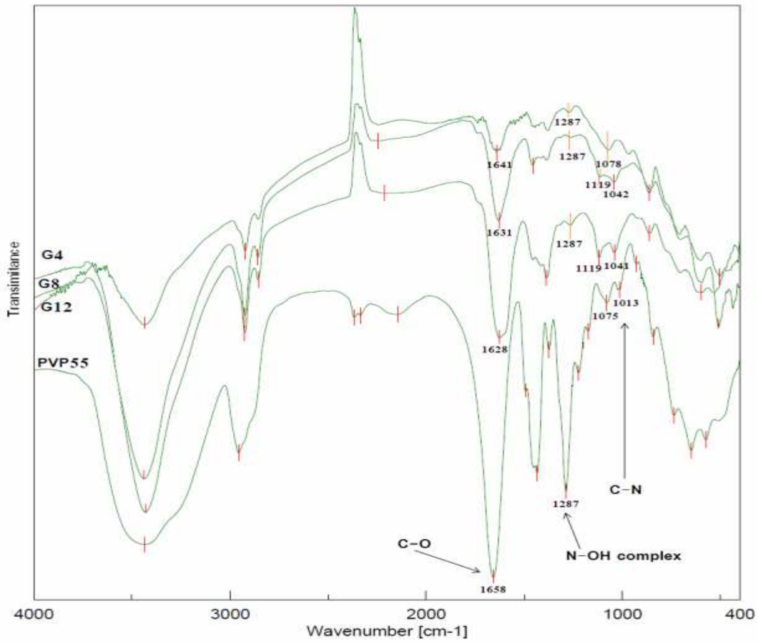
Figure 5: FTIR spectra of the used PVPs of different molecular weights.

In order to understand the mechanism of adsorption of PVP on the surface of nanoparticles, FTIR analysis of Ag nanoparticles within PVP matrix were carried out and the obtained data were compared to the FTIR spectrum of the pure PVP.

Figure 7 shows the FTIR spectra of PVP only and PVP-embedded Ag nanoparticles prepared using Wet Chemical Route. Comparing the FTIR spectra of the PVP and PVP- embedded Ag nanoparticles in this figure, it is observed that absorption peak at 1658 cm^{-1} (Curves pvp10,pvp29 ,pvp40,pvp55) represents the functional unit C=O present in PVP, shift to 1628-1645 cm^{-1} (The remaining curves in Figure 7)[51,52]. Such a decrease in wave number of C=O bond may occur due to the bond weakening as a result of the partial bond formation with the surface Ag atoms which eventually passivate the surface of Ag nanoparticles. Moreover, the peaks at 1013 and 1074 cm^{-1} (Curves pvp10, pvp29, pvp40, pvp55) due to C–N bond red shift to 1024-1043 cm^{-1} and 1074-1120 cm^{-1} for PVP- embedded Ag (The remaining curves in Figure 4) [51,52]. The peak shifting corresponding to C–N bonds towards higher wave number may be attributed due to chemical coordination of Ag nanoparticles with C–N bond. We also note that the peak of N-OH complex (at 1288)was weakened greatly[51,52]. Changing in optical behavior of PVP confirms the coordination of Ag nanoparticles with N and O atoms of C=O and C–N bonds of this polymer.

Figure 6:





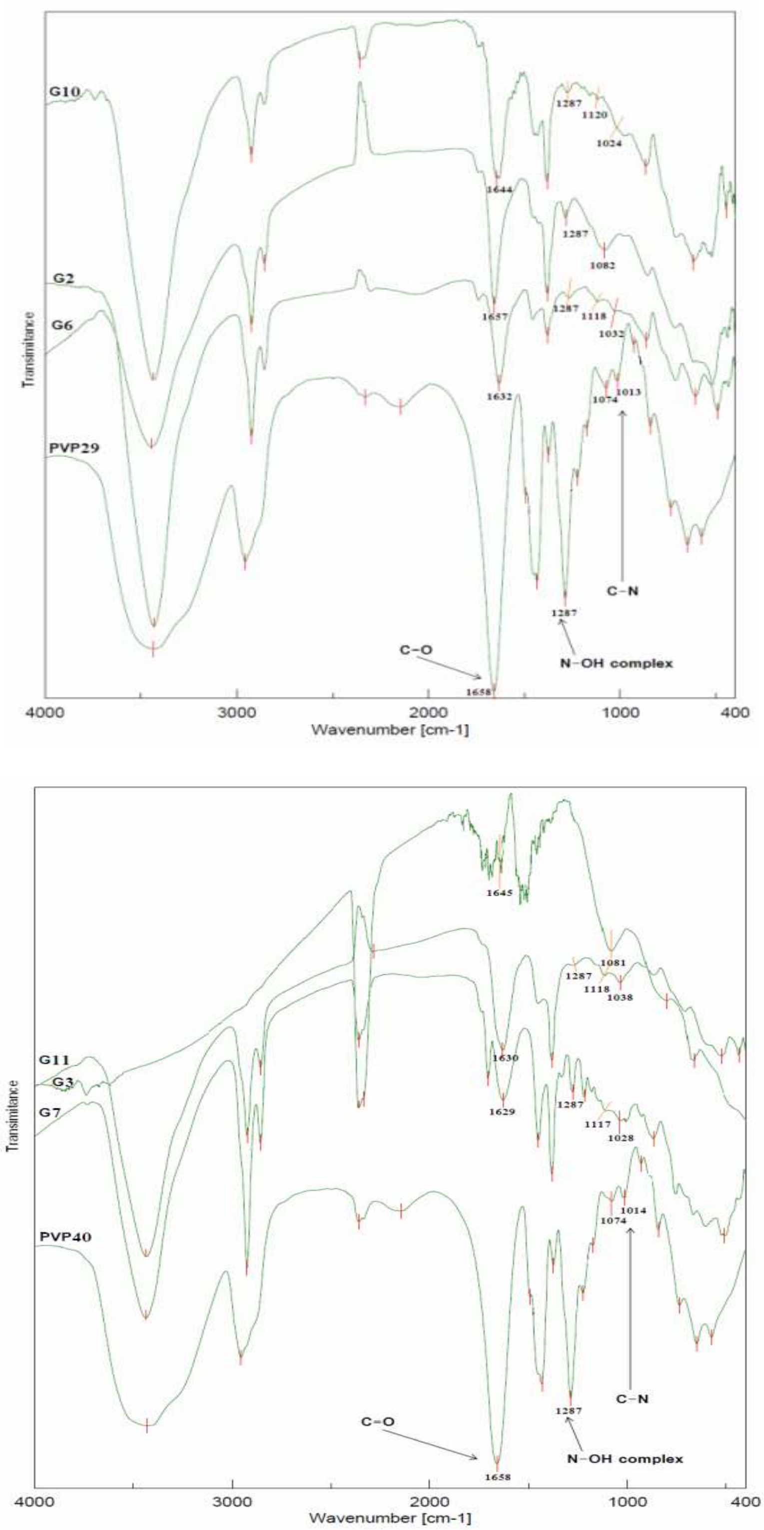


Figure 7: FTIR spectrum for pure PVP and silver nanoparticles synthesized in the presence of PVP using dextrose as reducing agent at 70^0C

4. Conclusion

We presented here, how to prepare silver nanoparticles using wet chemical method, under optimized conditions. Our method uses aqueous solution of silver nitrate, dextrose, PVP and sodium hydroxide. We characterized the obtained nanoparticles by XRD, and we used spin coating method to make thin films of silver nanoparticles which are imaged by AFM. We deduced that we obtained crystallized silver nanoparticles of sizes between 16 nm and 47 nm. FTIR spectra where analyzed to study the mechanism of adsorption of PVP on the nanoparticles.

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