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ORIGINAL ARTICLE

Synthesis and thermal study of octahedral silver nano-plates in polyvinyl alcohol (PVA)

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Abstract Octahedral silver nano-plates were synthesized from aqueous solution of silver nitrate and polyvinyl alcohol. The colloid formed is dried on glass plates by simple dip-coating method to inhibit the growth of the particles, and to analyze the samples. Samples were characterized by X-ray diffractometer, transmission electron microscope (TEM), thermo-gravimetric analysis (TGA), and differential scanning calorimetry (DSC) techniques. The UV–Vis absorption spectra of these silver nano-plates revealed a high intense plasmon absorption peak near 425 nm. In addition three emission peaks were observed when the excitation was fixed at 222 nm.

1. Introduction

Thermal analysis of polyvinyl alcohol-stabilized silver nano-plates is very significant as optical biosensors. Optical biosensing (Haes and Duyne, 2003; Liu et al., 2007; Chen et al., 2007) is well established analytical tool for the diagnosis and monitoring of diseases, drug discovery, proteomics and detection of environmental pollutants or biological agents.

The polymer polyvinyl alcohol (PVA) is used as a size controlling agent and stabilizing agent in this experiment to inhibit the growth of silver nanoparticles. Polyvinyl alcohol (PVA) is an important water-soluble polymer, and is extensively used in industries due to its excellent chemical and physical properties, non-toxicity, good chemical resistance, good film formation capacity, biodegradability and high crystal modulus. PVA is used here in hydrolyzed form with degree of 85% hydrolysis (Wang et al., 1999). The polymer acts as surface capping agent when the nanoparticles are embedded or enclosed in polymer. In addition, film preparation becomes easier using PVA, and the particle size can be controlled well within the desired regime when a thin film is formed. It worth mentioning that, the control of particle size, particle shape and their uniform distribution within the polymer are the hurdles before the researchers and nano-engineers for opto-electronic and electronics applications.

There are a number of reports on synthesis of silver nanoparticles using polymers as capping agents with the possibility of variation in optical properties depending on the optical activity of polymers and the shape and size of the silver

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nanoparticles (Deng et al., 2008; Navaldian et al., 2007; Jinag et al., 2007; Jun et al., 2007; Zou et al., 2007; Slistan-Grijalva et al., 2007; Jin et al., 2007; Yan et al., 2007; Wang et al., 2007; Dubas et al., 2006), but there are only a few literatures available describing PVA as a size controlling agent and stabilizer (Gautam et al., 2007). Besides, this is the first report of thermal behavior of octahedral silver nano-plates embedded polyvinyl alcohol (PVA) where the PVA is used as a size controlling agent and a stabilizer and is reported to have melting point depression because the total surface energy of the nanoparticles increases due to the reduction in the particle' size. PVA has been widely used for polymer nanocomposite due to its high transmittance and its solubility in water and the nanoparticles of silver can be easily prepared in aqueous medium, thus making the preparation non-toxic and environmentally friendly because of the zero solid byproduct.

Khanna et al. (2005) prepared silver Ag-PVA nanocomposites by reducing silver nitrate using two different reducing agents such as sodium formaldehyde sulfoxylate (SFS) and hydrazine hydrate (HH) in aqueous PVA solution and reported both of their optical absorption and thermal behavior. Thermal degradation of gamma radiolytically synthesized Ag-PVA nanocomposites were studied by Krkljes et al. (2007), and Mbhele et al. (2003) studied the thermal behavior of PVA in the presence of silver nanofillers reduced by $NaBH_4$. The thermal decomposition of silver oxalate to single crystalline Ag nanoparticles in PVA was studied by Navaldian et al. (2007). These investigations suggest that the introduction of nano-sized silver into PVA altered its properties. For example, the glass transition temperature of the Ag-PVA nanocomposites prepared by Mbhele et al. (2003) shifted toward higher temperatures by 20 °C and the thermal stability improved about 40 °C. The aim of the present work is to study the thermal and optical absorption properties of octahedral silver nano-plates in polyvinyl alcohol (PVA) using differential scanning calorimetry (DSC), thermo-gravimetric analysis (TGA) and UV–Vis absorption spectroscopy. In addition, the pyrolysis of the PVA-stabilized AgNP is investigated using TGA.

In this paper an easy route for the synthesis of octahedral silver nanoparticles embedded in polyvinyl alcohol is described. Here, we have followed the preparation method of silver nanoparticles proposed by Gautam et al. (2007) but with a slight modification. Then a thin film of these nanoparticles is formed on a glass plate and air-dried to inhibit the further growth of the nanoparticles. Silver nitrate is used as a precursor because its decomposition temperature is very low and the product of the reaction is silver metal (Jinag et al., 2007). Silver nitrate has been reduced to silver in aqueous PVA solution. The polymer nanocomposite was characterized by various techniques. The preparation and characterization of these nanocomposite films are discussed.

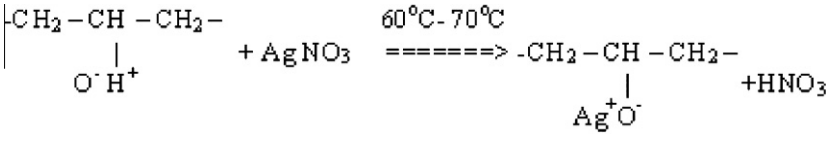
2. Experimental section

2.1. Preparation of Ag-PVA nanocomposite

The precursor Silver nitrate ($AgNO_3$, 99.99% purity) and the size controlling agent polyvinyl alcohol (PVA, 9000–10000 molecular weight, 88% hydrolysis) were purchased from Sigma–Aldrich Chemicals. Samples with 0.1 and 0.2 weight percentages of silver were prepared by silver nitrate in 5 ml of de-ionized water and 0.03 g/ml of PVA in 50 ml of de-ionized water and the temperature of PVA solution was maintained between 60 °C and 70 °C during the preparation. When the PVA becomes completely dissolved, the solution transforms into a transparent liquid, and then silver nitrate solution was added drop by drop (one drop/second) by using a burette while the temperature was maintained between 60 °C and 70 °C and with continuous stirring. Magnetic stirring continued until the solution became a faint brownish viscous liquid. The byproduct nitric acid is evaporated and small particles of metal Ag is capped in PVA polymer molecules. External heating is very important to obtain pure Ag metals of dispersed particles (Gautam et al., 2007). At this hot condition, the hydrogen de-bonds from the OH of the dispersed PVA and this hydrogen de-bonded PVA serves as a template to form Ag^+ reaction, surface stabilizer and a protective agent for silver nanoparticles. This interaction can be schematically represented as in the Scheme 1. Silicate glass slides were then dipped into this viscous solution to form a fine thin film for characterizing the silver nanoparticles. Final color of the solution depends upon the concentration of silver (Huang et al., 1996), and the film became dark yellow when it was dried out on the glass slides. The formation of the silver nanoparticles is evident from the variation in the color of the slides dipped as the experiment progresses to the final stage as shown in Fig. 1. The clear brownish yellow color is seen in the bottom picture of Fig. 1.

2.2. Characterization

The samples have been named as S1 and S2 for the 0.05 and 0.1weight percentages of silver, respectively. The content of the silver in PVA-stabilized silver nanocomposite was determined from the UV–Vis-NIR absorption spectra using 'JASCO UV–Vis Spectro-Photometer V-570' and Bruker AXS D8 advance X-ray diffractometer. Photoluminescence studies were carried out using Varian Cary Eclipse Fluorescence Spectrophotometer. The transmission electron microscope (TEM) image was obtained by JEOL 3010 instrument by dispersing the prepared particles in de-ionized water. TGA was used here to provide an understanding of the thermal behavior and the decomposition of the sample. Thermo-gravimetric analysis (TGA) is an analytical technique used to determine a mate-



Scheme 1 Schematic representation of the formation of Ag nanoparticles with the help of polyvinyl alcohol.

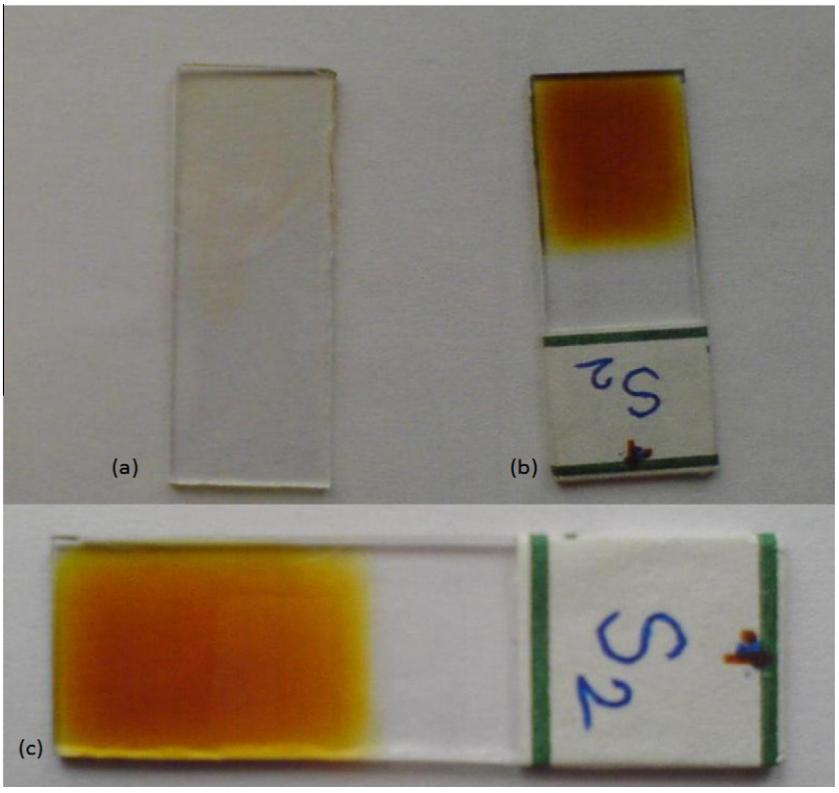


Figure 1 (a) Film formed after seven hr of stirring the solution, (b) after 9 h and (c) a closer view of film b.

rial's thermal stability and its fraction of volatile components by monitoring the weight change that occurs as the sample is heated. Thermal studies were carried out using SDT Q600 V8.3 Build 101 of TA Instruments which provides a true simultaneous measurement of weight change (TGA) and true differential heat flow (DSC) on the same sample and fully controlled by computer software. The films were peeled from the silicate glass plate for thermal analysis and each sample of 2.7370 mg (S1) and 2.1120 mg (S2) was placed into an experimental sample pan with a sensitive microbalance and the furnace was able to provide an accurate heating from ambient to 1500 °C while the measurement was taking place.

3. Results and discussion

3.1. Optical and structural characterization

UV–Vis absorption is performed to verify the presence of silver nanoparticles in the prepared samples of PVA-stabilized silver nanocomposites. Silver nanoparticles has a surface plasmon absorption between 400 nm and 450 nm as reported in the previous literatures (Navaldian et al., 2007; Zou et al., 2007; Slistan-Grijalva et al., 2007; Jin et al., 2007; Dubas et al., 2006; Siwach and Sen, 2008; Xu et al., 2006; Temgire and Joshi, 2004). Surface plasmon resonance (SPR) is the coherent excitation of all the "free" electrons within the conduction band, leading to an in-phase oscillation. When the size of a metal nanocrystal is smaller than the wavelength of incident radiation, surface plasmon resonance is generated. The electric field of an incoming light induces a polarization of the free electrons relative to the cationic lattice. A net charge difference occurs at the nanoparticles boundaries (the surface), which in turn acts as a restoring force, in this manner a dipolar oscillation of electrons is created with a certain frequency. Surface plasmon resonance peak depends upon particle size, shape of the particle, refractive index of surrounding medium and dielectric properties (Huang et al., 1996; Elechiguerra et al., 2005).

Sample S1 (0.05 wt% of silver) shows plasmon absorption at 425.72 nm and of S2 (0.1 wt% of silver) is at 423.05 nm and the absorption spectra is shown in Fig. 2. The presence

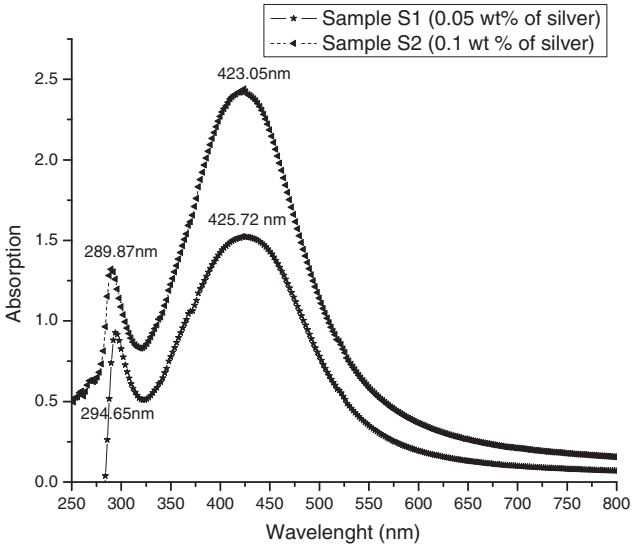


Figure 2 UV–Vis absorption spectra.

of SPR confirms the formation of silver nanoparticles in these samples; whereas the small peaks observed at 294.65 nm (S1) and 289.87 nm (S2) are attributed to the formation of Ag clusters in the samples (Temgire and Joshi, 2004).

The nanocomposite of octahedral silver nanoplate shows three emission peaks at 300 nm, 324 nm and 337 nm when the excitation wavelength is fixed at 222 nm as shown in Fig. 3. The luminescent study of this nanocomposite yields new insight into the energy band structure of the nanoplates. Jiang et al. (2005) reported fluorescence peak at 465 nm for excitation at 290 nm for silver nanoparticles dispersed in water and this has been assigned to the interface electron energy bands of fluorescence. Fluorescence emission is observed at 300 nm for excitations at 215 nm and 270 nm in the water dispersed silver nanoparticles which was reported by Siwach and Sen (2008)). He further reported that the emission in this range is due to the transition in Ag nanoparticles to higher energy levels. According to the literature (Siwach and Sen, 2008) the intensity maximum at 222 nm observed in Fig. 4 indicates a maximum transition probability and this absorption yields fluorescence at three regions such as 300 nm, 324 nm, and 337 nm.

X-ray diffractogram shown in Fig. 5 corroborates the presence of hexagonal silver nanoparticles in the samples. It is found that the crystals are oriented along (1 0 0), (1 0 1), (1 1 2) and (1 0 3) planes and the interplanar spacing of these planes have been calculated as 0.249 nm, 0.242 nm, 0.226 nm and 0.197 nm, respectively by using Bragg equation ($2d\sin\theta = n\lambda$).

The TEM image of Sample S1 (Fig. 6) shows the growth of truncated octahedral structure. The largest side has 33.33 nm length and shortest 27.77 nm length. A truncated octahedral nanoplate (Wiley et al., 2004) is seen in the TEM image (Fig. 7) of the S2 sample, with a clear bright boundary. This bright boundary may be due to the strong surface plasmon absorption of silver nanoplate (Chen and Carroll, 2002) when the electron beam interact with the metal surface which was also seen in the UV–Vis optical absorption spectra (Fig. 2). It is the first report of truncated octahedral nano silver prepared in PVA alone and this truncated octahedral disk does not have perfect corners but round corners. The longest sides have a length of around 64.52 nm and the shortest have 32.25 nm just half of the longest sides. The interplanar spacing has been measured as 0.29 nm and 0.25 nm from the HRTEM image (Fig. 8) and these crystals may be oriented along (1 0 0) and (1 0 1) as seen from JCPDS Card No. 41.1402 for hexagonal silver. This truncated octahedral structure may be originated from this hexagonal structure of silver crystals.

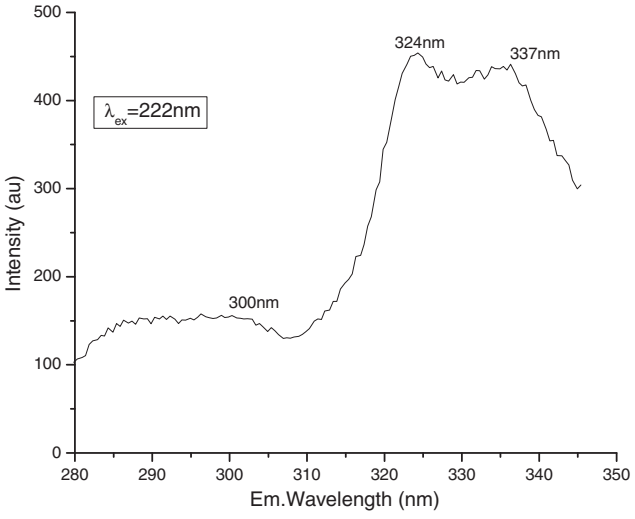


Figure 3 Emission spectra of octahedral silver nano-plate (Sample S2) when the excitation fixed at 222 nm.

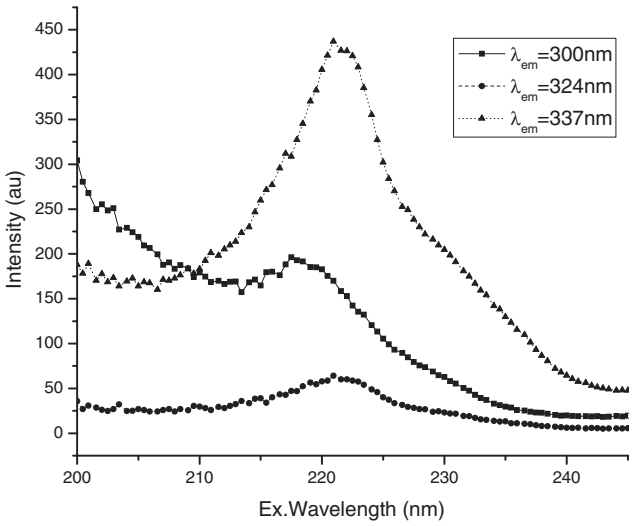


Figure 4 Excitation spectra of octahedral silver nano-plate (Sample S2).

4. Thermal characterization

4.1. Thermo-gravy metric analysis (TGA)

TGA is an established technique which measures the weight changes as a function of temperature or time. It provides information of the thermal behavior such as pyrolysis and thermal decomposition of the samples. Decomposition profiles were obtained while heating at a rate of 20 °C/min in air between 20 °C and 1000 °C. The relation between temperature and weight loss of the samples in the TGA curve is shown in Fig. 9. In air atmosphere, the thermogram resulting from the TGA of the samples shows that there are four obvious regions in the temperature range 51 °C to 500 °C indicating that these two samples had almost identical decomposition temperatures (Chang et al., 2007).

The amount of the end product after the pyrolysis of the sample was 3.717% (0.1017 mg) for Sample S1 and 3.990% (0.09226 mg) for Sample S2. The initial weight loss from 51 °C to 130 °C is attributed to the vaporization of the absorbed surface and interlayer water (weight loss is 6%). Even the pure polyvinyl alcohol shows about 4% of weight loss of water for this region (Carrado et al., 1996).

Thermogram (Fig. 9) unambiguously shows that the PVA-stabilized silver nanocomposite is thermally stable until 288 °C, the onset temperature of degradation. Then, the material continues its degradation as the temperature is increased. The weight loss observed at higher temperatures can be attributed to the pyrolysis process. Pyrolysis takes place between 288 °C and 498 °C and it is superimposed later. Decomposi-

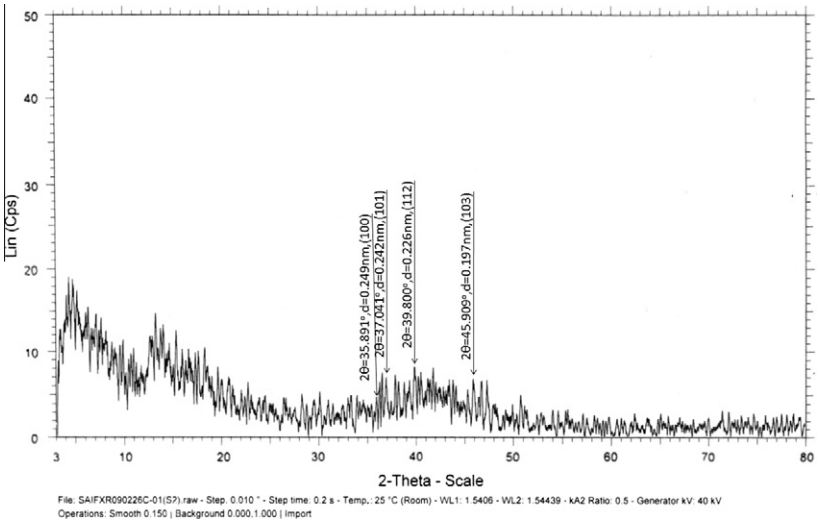


Figure 5 X-ray diffractogram of Sample S2 (wt% of silver is 0.1).

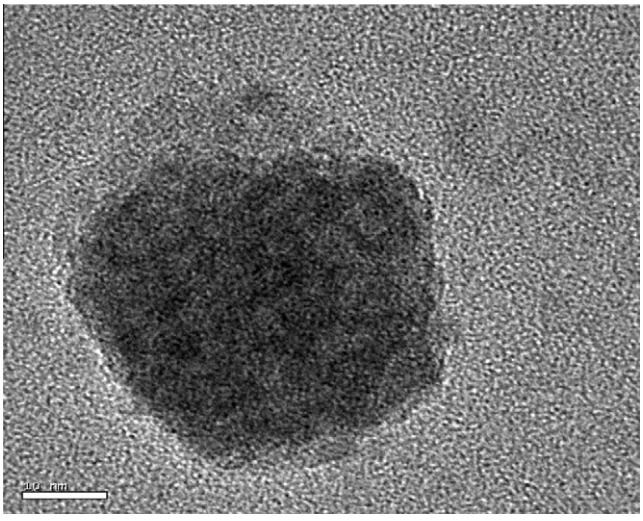


Figure 6 TEM image of Sample S1 (wt% of silver is 0.05).

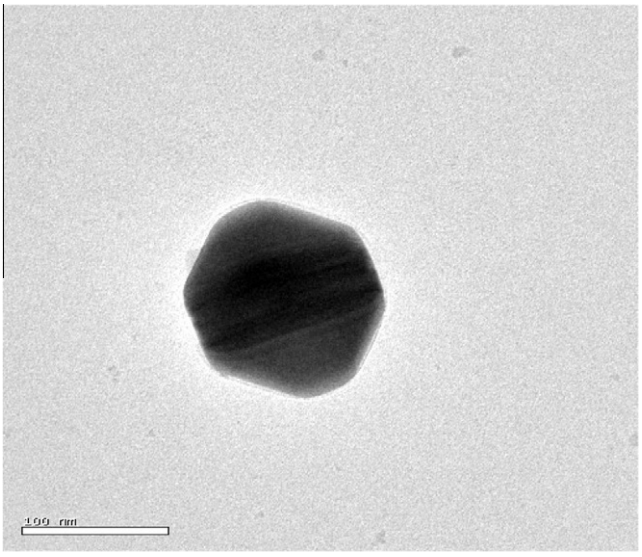


Figure 7 TEM image of Sample S2 (wt% of silver is 0.1).

tion of the materials is similar for all the two samples and shows multistep decomposition events at temperatures near 288 °C, 360 °C, 450 °C, and 498 °C. These events may be involved due to the loss of isobutyl groups, backbone fragments and finally charred. The incorporation of silver nanoplates improved the thermal stability of the polymer little when we consider the decomposition of PVA alone at about 250 °C as Mbhele et al. (2003) reported in his paper. The improvement of thermal stability of the PVA-stabilized silver nanocomposite is also reported by Khanna et al. (2005).

The end product after the pyrolysis is carbon coated silver nanoparticles (Gautam et al., 2007) and the weight percentage of residue is higher in the Sample S2 because the weight percentage of silver is higher than in Sample S1. It is very clear from the Fig. 9 that the carbon coated silver nanoparticles do not evaporate at the temperature range between 498 °C and 700 °C.

4.2. Differential scanning calorimetric (DSC) studies

Differential scanning calorimetry or DSC is a thermo analytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference are measured as a function of temperature. The basic principle of this technique is that, when the sample undergoes a physical transformation such as phase transitions, more (or less) heat will need to flow to it than the reference to maintain both at the same temperature. This is due to the absorption of heat by the sample as it undergoes the endothermic phase transition from solid to liquid and this curve can be used to calculate enthalpies of transitions.

Fig. 10 shows the glass transition temperatures of the Samples S1 and S2 as 155.70 °C and 156.76 °C. Glass transitions occur by increasing the temperature where a change in the heat

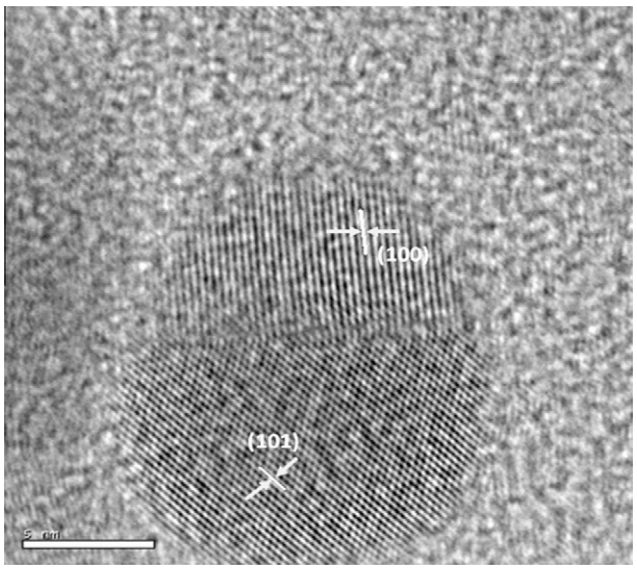


Figure 8 HRTEM image of Sample S2 (wt% of silver is 0.1).

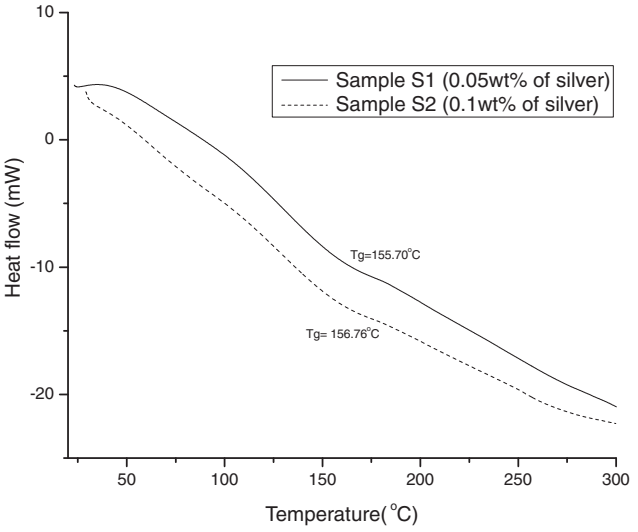


Figure 10 DSC curve of Samples S1 and S2 in the range of 20 °C to 300 °C.

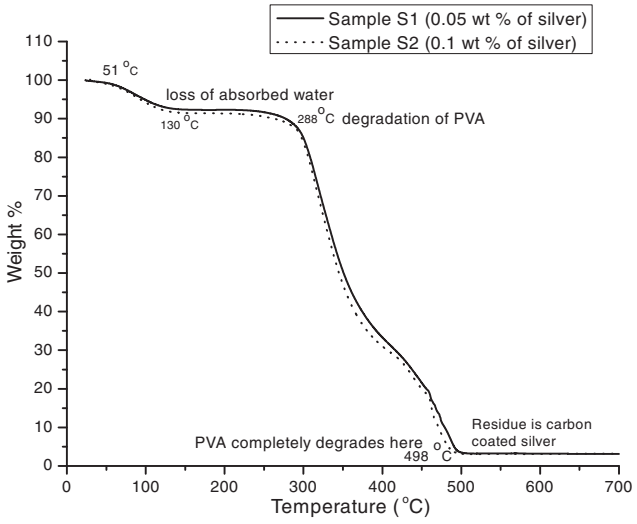


Figure 9 Thermogram of Samples S1 and S2.

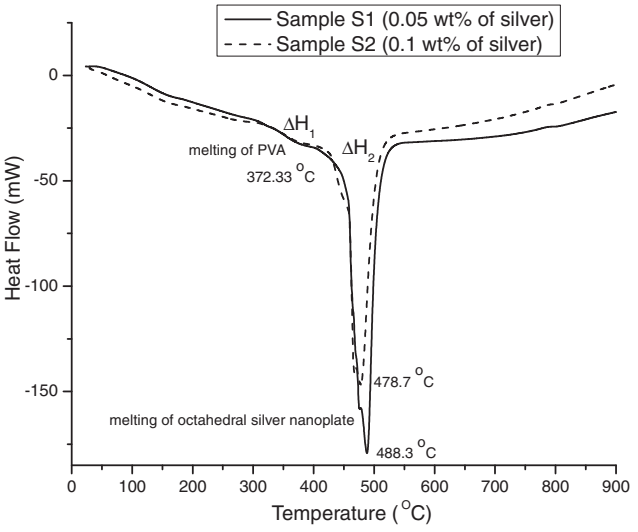


Figure 11 DSC curve of the Samples S1 and S2.

capacity (not a formal phase) occurs. As the temperature increases, this amorphous PVA becomes less viscous. The glass transition temperature, T_g, is the temperature at which an amorphous solid such as a polymer becomes fragile on cooling, or soft on heating. The glass transition of this octahedral silver nanocomposite samples are shifted from 85 °C for pure PVA to 155.70 °C and 156.76 °C for the S1 and S2 samples. Shifting in T_g to a higher temperature is previously reported in the case of copper doped PVA by Linga Raju et al. (2007). Linga Raju et al. (2007) explained the reason for shifting in T_g towards higher temperature region as it is because of the increased lateral forces in the bulk state due to the restricted steric effect of –OH groups by the branching of Ag^+ ions with the chain of PVA molecules.

From Fig. 11 it is seen that a broad peak is observed near 372.33 °C which may be attributed to the melting of the polymer PVA. It is interesting that melting point of PVA in the PVA-stabilized AgNP displays a broad melting endotherm and is shifted to a higher temperature in comparison to 230 °C of pure PVA.

The temperature increases further from the melting of PVA and it reaches to the melting point of the metal silver particles which are in octahedral shape. When the temperature reaches to the melting of the octahedral silver nanoplates, more heat energy flows to the material and the temperature rising of the material stops for a while because melting requires energy. All the energy added at this point goes into melting, and none of it is given to raise the temperature. When the metal particles are completely melted then the temperature of the samples begins to increase again which is evident from the Fig. 11.

It is observed that the melting points of the octahedral silver nanoplates are 488.3 °C and 478.7 °C for Samples S1 and S2, respectively. The melting point is depressed to this lower value from 961 °C due to the size reduction and the peculiar shape of the formed silver nanoplates (Nanda et al., 2002).

Table 1 Thermal data observed from TGA and DSC studies.

Sample name	Wt% of Ag mg	Glass transition (°C)	Melting point of PVA (°C)	Melting enthalpy (ΔH_1 J/g) of PVA	Melting point of octahedral silver nanoplate (°C)	Melting enthalpy (ΔH_2 J/g)
S1	0.05	156.13	371.38	91.96	478.70	6174
S2	0.1	159.44	371.38	91.96	488.23	6065

Melting point depression is evident in nanowires, nanotubes and nanoparticles, which all melt at lower temperatures than bulk amounts of the same material. Changes in melting point occur because of the larger surface to volume ratio of the nanomaterials which alter their thermodynamic and thermal properties. The observed enthalpies of the melting and other thermal information are tabulated in Table 1.

5. Conclusion

Octahedral silver nanoplates have been prepared by aqueous chemical reduction method using poly vinyl alcohol alone at hot condition and coated on a glass plate to inhibit the further growth of the particles. The UV–Vis absorption spectrum of this material is studied and the appeared surface plasmon absorption confirmed the presence of silver nanoparticles. TEM observations showed that the particles have acquired a peculiar octahedral shape. Thermogravimetric studies have been performed to analyze the pyrolysis of the PVA-stabilized silver nanocomposite and it is observed that the decomposition of the PVA is correlated with previous literatures. The DSC studies further confirmed the reduced size of the silver metals and found that the melting point is depressed to lower temperatures.

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References

Carrado, K.A., Thiyagarajan, P., Elder, D.L., 1996. Clays and Clay Minerals 44 (4), 506–514.
Chang, Y.W., Wang1y, E., Shin, G., Han, J.E., Mather, P.T., 2007. Polym. Adv. Technol. 18, 535–543.
Chen, S., Carroll, D.L., 2002. Nano Lett. 2 (9), 1003–1007.
Chen, H., Kim, Y.S., Keum, S.R., Kim, S.H., Choi, H.J., Le, J., An, W.G., Koh, K., 2007. Sensors 7, 1216–1223.
Deng, Y., Sun, Y., Wang, P., Zhang, D., Ming, H., Zhang, Q., 2008. Phys. E 40, 911–914.
Dubas, S.T., Kumlangdudsana, P., Potiyaraj, P., 2006. Colloids and surfaces A: physicochem. Eng. Aspects 287, 105–109.
Elechiguerra, J.L., Burt, J.L., Morones, J.R., Bargado, A.C., Gao, X., Lara, H.H., Yacaman, M.J., 2005. J. Nanobiotechnol. 3, 6.
Gautam, A., Singh, G.P., Ram, S., 2007. Synthetic Metals 157, 5–10.
Haes, A.J., Duyne, R.P.V., 2003. Proceedings of SPIE 5221, 47–58.
Huang, H.H., X, P.N., Loy, G.L., Chew, C.H., Tan, K.L., Loh, F.L., Deng, J.F., Xu, G.Q., 1996. Langmuir 128, 909–912.
Jiang, Z., Yuan, W., Pan, H., 2005. Spectrochim. Acta A 61, 2488.
Jin, W., Jeon, H.J., Kim, J.H., Youk, J.H., 2007. Synthetic Metals 157, 454–459.
Jinag, L., Wang, W., Wu, D., Zhang, J., Wang, Q., Wu, Z., Jin, R., 2007. Mater. Chem. Phys. 104, 230–234.
Jun, J., Yuan-Yuan, D., Shao-hai, W., Shao-feng, Z., Zhong-yi, W., 2007. J. US-China Med. Sci. 4 (2), 52–54.
Khanna, P.K., Singh, N., Charan, S., Subbarao, V.V.V.S., Gokhale, R., Mulik, U.P., 2005. Mater. Chem. Phys. 93, 117–121.
Krkljes, A.N., Marinovic-cincovic, M.T., Kacarevic-popovic, Z.M., Nedeljkovic, J.M., 2007. Thermochim. Acta 460, 28–34.
Linga Raju, C.H., Rao, J.L., Reddy, B.C.V., Veera Brahmam, K., 2007. Bull. Mater. Sci. 30 (3), 215–218.
Liu, C., Yang, X., Yuan, H., Zhou, Z., Xiao, D., 2007. Sensors 7, 708–718.
Mbhele, Z.H., Salemane, M.G., van Sittert, C.G.C.E., Nedeljkovic, J.M., Djokovic, V., Luyt, A.S., 2003. Chem. Matter 15, 5019–5024.
Nanda, K.K., Sahu, S.N., Behera, S.N., 2002. Phys. Rev. A. 66, 013208.
Navaldian, S., Viswanathan, B., Viswanath, R.P., Varadarajan, T.K., 2007. Nanoscale Res. Lett. 2, 44–48.
Siwach, O.P., Sen, P., 2008. Spectrochim. Acta Part A 69, 659–663.
Slistan-Grijalva, A., Herrera-Urbina, R., Rivas-Silva, J.F., Avalos-Borja, M., Castillon-Barraza, F.F., Posada-Amarillas, A., 2007. Mater. Res. Bull., doi.10.1016/j.materresbull.2007.02.013.
Temgire, Joshi, S.S., 2004. Radiat. Phys. Chem. 71, 1039–1044.
Wang, H.H., Shyr, T.W., Hu, M.S., 1999. J. Appl. Polym. Sci. 74, 3046–3052.
Wang, X., Zhang, S., Zhang, Z., 2007. Mater. Chem. Phys., doi.10.1016/j.matechemphys.2007.07.015.
Wiley, B., Herricks, T., Sun, Y., Xia, Y., 2004. Nano Lett. 4 (9), 1733–1739.
Xu, J., Han, X., Liu, H., Hu, Y., 2006. Colloids Surfaces A: Physicochem. Eng. Aspects 273, 179–183.
Yan, W., Feng, X., Chen, X., Li, X., Zhu, J., 2007. Bioelechem. doi.10.1016/j.bioelechem2007.07.003
Zou, J., Xu, Y., Hou, B., Wu, D., Sun, Y., 2007. China Particuology 5, 206–212.