

Synthesis of nanosized silver colloids by microwave dielectric heating

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Abstract. Silver nanosized crystallites have been synthesized in aqueous and polyols viz., ethylene glycol and glycerol, using a microwave technique. Dispersions of colloidal silver have been prepared by the reduction of silver nitrate both in the presence and absence of stabilizer poly(vinylpyrrolidone) (PVP). It was observed that PVP is capable of complexing and stabilizing Ag nanoparticles formed through the reduction of Ag⁺ ions in water and ethylene glycol. In the case of ethylene glycol, it has been shown that the use of PVP leads to particles with a high degree of stability. The colloids are stable in glycerol for months even in the absence of stabilizer.

Keywords. Silver nanoparticles; microwave; optical absorption.

1. Introduction

Nanoparticles have a variety of unique spectroscopic, electronic and chemical properties that arise from their small sizes and high surface/volume ratio. Thus, the preparation of nanometre- and monodisperse-sized particles is one of the most important challenges and is an endless endeavour.^{1–4} Nanoparticles have found uses in many applications such as catalysis, sensors, drug delivery, optoelectronics and magnetic devices.^{5–11} Therefore, new methods for the preparation of nanoparticles are frequently reported in the literature. El-Sayed *et al*¹² have shown that the shape of metal particles can be controlled by changing the capping ratio of stabilizer to metal ions.¹² This in fact can be utilized for catalytic reactions as they depend not only on the size but also on the shape of the particles.

Nanoparticles also exhibit new optical properties, which are observed neither in molecules nor in bulk metals.^{13–15} One particular example is the presence of a strong absorption band in the visible region. This arises due to the surface-plasmon-oscillation modes of conduction electrons that are coupled through the surface to external electromagnetic fields.^{16–19} Because of this plasmon band, the optical properties of copper, silver and gold nanoparticles have received consid-

erable attention. It has been shown that colour of noble metal nanoparticles depends on both size and shape of the particles, as well as the refractive index of the surrounding medium.^{13,16,20} So far, many methods have been used to prepare nanostructured materials from the liquid phase and thus the solvent plays an important role in the process of reaction. Very recently, an alcohol reduction method has been developed to prepare metal nanoparticles. In this process, solution of the metal ions is refluxed at a particular temperature under an inert atmosphere. Various alcohols as well as polyols and organic solvents have been attempted for preparation of metal nanoparticles^{21–27} using the reflux technique and/or oil bath heating.

Microwaves are electromagnetic waves. Microwave heating is well known in the food industry and of late has found a number of applications in chemistry especially in organic chemistry.²⁸ In a microwave device, heating is created by the interaction of the permanent dipole moment of the molecule with high frequency (2–45 GHz) electromagnetic radiation. In comparison with conventional heating, this novel method can shorten reaction time by a factor of approximately 20. Using microwaves, heating is not only quick but also uniform. This is particularly being exploited for making both metal and semiconductor nanoparticles,^{29–39} as uniform heating may result in narrowly distributed particles. Recently,

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polychrome silver nanoparticles have been prepared using the microwave technique.⁴⁰ Formation of silver nanoparticles in ethylene glycol in the presence of NaOH is also reported.⁴¹ It has been suggested that ethylene glycol due to its high dipole moment can serve as a good solvent for microwave heating. However, no detailed study exists in literature for the reaction in the absence of NaOH. As there are apprehensions in the literature that stabilizers used in the preparation of metal particles can inhibit their catalytic activity, therefore, it is pertinent to explore the possibility of avoiding use of stabilizers. Due to high viscosity of polyols, they can also act as stabilizers in addition to being the medium in which the reaction is carried out. In the present article, we report on the preparation of metallic silver particles in the three solvents, nanopure water, ethylene glycol and glycerol. Effect of poly(vinylpyrrolidone) on the stabilization of metallic particles is also discussed and the results are compared with that reported by using the reflux technique.

2. Experimental

All reagents were of the highest purity. AgNO₃ (BDH), ethylene glycol (UV spectroscopy grade, Spectrochem, India), glycerol (UV spectroscopy grade, Spectrochem, India), and polyvinyl pyrrolidone (PVP) (Sigma) were used as received. Reactions were carried out in a domestic microwave oven (Kenstar, MO-9706 A) operating in a cycling mode (on 15 s, off 5 s) to prevent intense boiling of solvents as well as aggregation of metals. Samples for transmission electron microscopy (TEM) were prepared by putting a drop of the colloidal solution on a copper grid coated with a thin amorphous carbon film. Samples were dried and kept under vacuum in a desiccator before loading them onto a specimen holder. TEM characterization was carried out using a JEOL JEM-2000FX electron microscope. Particle sizes were measured from TEM micrographs. Particle size is defined as the average of the largest and shortest diameter of the particle. Absorption measurements were carried out on a UV 160 A Shimadzu spectrophotometer. The spectra were recorded at room temperature using a one-centimetre quartz cuvette.

The pH of the solution was adjusted using phosphate buffers (KH₂PO₄ and Na₂HPO₄) or by NaOH. Solutions were prepared a fresh each time to avoid any photochemical reactions. All experiments were carried out in air.

3. Results and discussion

3.1 Formation of silver nanoparticles in water

In the first set of experiments, a constant PVP concentration was used in aqueous solution at pH 9. Concentration of AgNO₃ was varied from 0.1 mM to 1.0 mM. The effect of Ag⁺ concentration on the reaction rate was studied by monitoring the UV-visible absorption spectrum. Plotted in figure 1 are the spectra measured for higher silver concentrations at different times of irradiation. Initially the surface plasmon absorption band was observed at around 450 nm. The colour of the sol obtained was orange. It can be seen that the plasmon band is red-shifted as compared to that reported for the yellow sol of silver having small particles.¹⁶ The surface plasmon absorption band obtained in figure 1 is also broad. There is some blue-shift of the plasmon band during the initial stages of the reaction. This could be due to the adsorption of Ag⁺ ions which are excess in solution. However, as the reduction proceeds the reduction of silver ions take place without any shift in the plasmon band. The colour of silver sol was roughly similar at all concentrations of Ag⁺ ions. The size of the particles obtained at different concentration of Ag⁺ ions after 45 min of irradiation is tabulated in table 1.

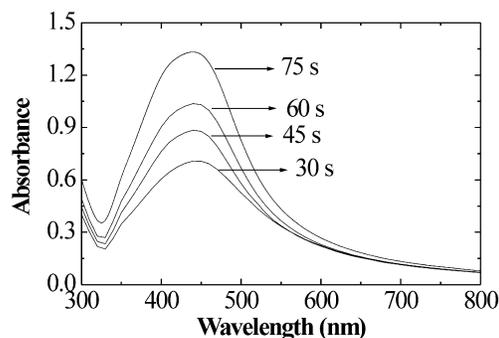


Figure 1. Evolution of UV spectra during the formation of silver colloids in aqueous solution containing 1 mM Ag⁺ and PVP (1 wt%) at pH 9. The time of irradiation is shown on the traces.

Table 1. Colloidal silver dispersions obtained in aqueous solution at pH 9.

AgNO ₃ (mmol/l)	PVP (wt %)	Mean size (nm)	SD (%)
0.1	1	35	16
0.5	1	25	20
1.0	1	15 ^{a,b}	20

^aThese appear to be agglomerates of smaller particles of about 10 nm dia.; ^bagglomerates of 20 nm dia are also found with a few isolated particles

3.2 Formation of silver nanoparticles in ethylene glycol

The process of particle formation by UV-vis spectrometry was also monitored in glycol. It was observed that in the absence of protective agent PVP the surface plasmon absorption band of Ag particles was quite broad (figure 2). The colour of the sol was yellow only when Ag^+ concentration was 0.5 mM. At all the concentrations of Ag^+ that mentioned, the sol had some opalescence showing that particles have aggregated. The mean size obtained was 30 nm.

Figure 3a shows the time evolution of the absorption spectra for a sample with AgNO_3 concentration = 0.1 mM in ethylene glycol in the presence of PVP. It can be seen that no sign of colloidal silver was observed up to 60 s of irradiation. Further irradiation leads to the development of colloidal silver that show an absorption band centred at around 420 nm. The size of the particles obtained after 70 s of irradiation is shown in table 2. On increasing the Ag^+ concentration to 0.5 mM change in the colour of the sol was observed from 30 s of irradiation. The maximum absorption was reached after 60 s of irradiation. Further irradiation does not increase the absorbance significantly (figure 3b). The size of the particles obtained after 45 s of irradiation is shown in table 2.

Figure 3c shows the evolution of surface plasmon absorption band of Ag obtained on irradiation of 1 mM AgNO_3 in ethylene glycol in the presence of PVP. It can be seen from the figure that the surface plasmon absorption band of Ag particles was observed just after 15 s of irradiation and increased with further irradiation. The absorbance observed at 75 s of irradiation is roughly similar to that obtained in 0.5 mM

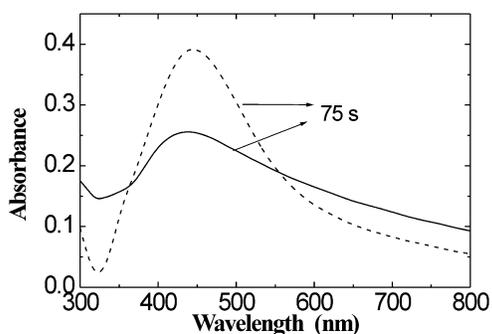


Figure 2. UV spectra of dispersions during colloidal silver formation in ethylene glycol: solid line 1 mM Ag^+ , dashed line 0.5 mM Ag^+ . The time period of irradiation was 75 s.

Ag^+ under identical irradiation time. The size of the particles obtained after 45 s of irradiation is shown in table 2. The general mechanism of metal reduction in ethylene glycol can be represented by the following reactions.

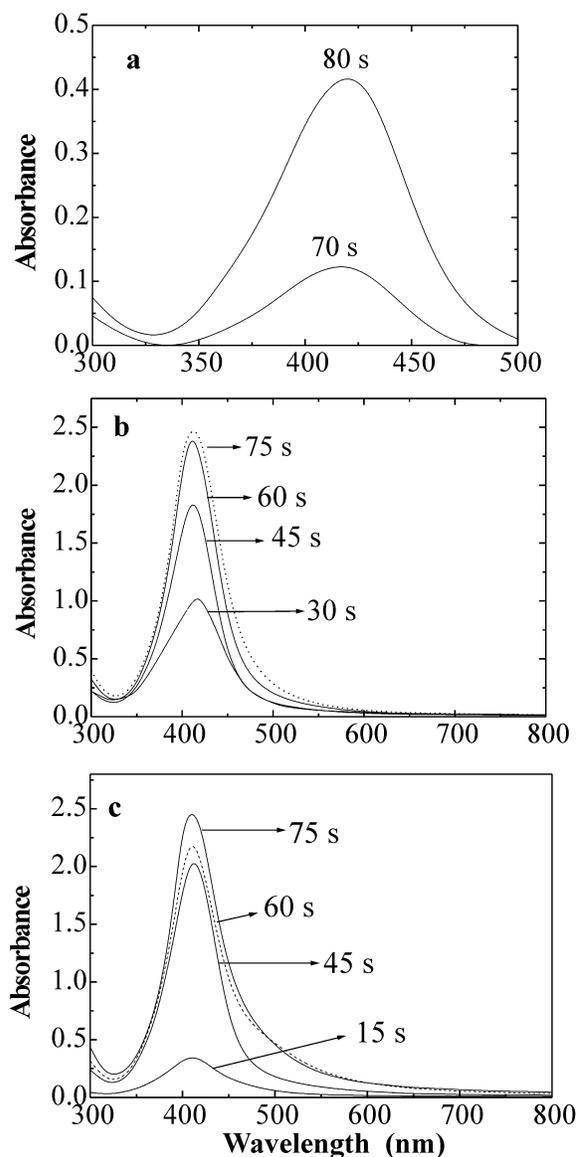
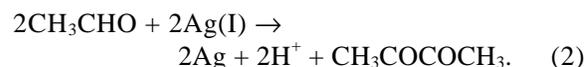


Figure 3. UV spectra of dispersions during colloidal silver formation in ethylene glycol in the presence of PVP (1 wt%). (a) 0.1 mM, (b) 0.5 mM, and (c) 1 mM Ag^+ . Time duration of irradiation is shown on the traces.

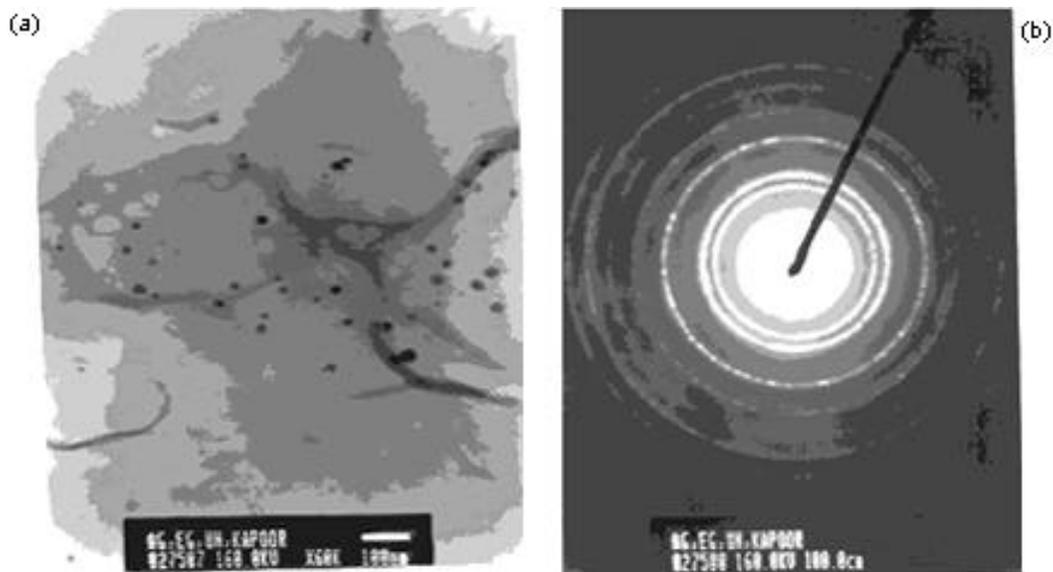


Figure 4. Transmission electron micrograph (a) and corresponding diffraction pattern (b) for silver particles prepared in ethylene glycol after 45 s of irradiation. Other conditions are the same as that of figure 3b.

Table 2. Colloidal silver dispersions obtained in ethylene glycol.

AgNO ₃ (mmol/l)	PVP (wt %)	Mean size (nm)	SD (%)
0.1	1	25	16
0.5	1	15	10
1.0	1	12 ^a	10

^aThese appear to be agglomerates of smaller particles of about 10 nm dia

Comparison of spectra obtained in figure 3 with those in figures 1 and 2 clearly show that in the presence of PVP in ethylene glycol there is better control on the reaction when compared to reaction in aqueous solution as well as in its absence in ethylene glycol. It can be seen that the absorbance due to silver sol increases sharply in presence of PVP and the size of the particles decreases. It is known that PVP is a homo polymer in which the individual units contain imide groups. It has been shown that the N and O atoms of this polar group bind to the silver ions and metallic silver.⁴² Also, PVP is known to reduce silver ions. The combined effect of PVP thus helps in controlling the size of the particles because it is known that if reduction takes place fast, the size of the particles can be controlled better.^{43–46}

With respect to the shift in the plasmon band during the reduction, we did not observe any blue-shift dur-

ing the reaction. The position of the band remains almost constant, probably because the plasmon band shifts before the first absorption spectrum was taken. It can be seen from figure 3 that the bands are sharper and more symmetrical, which reflects more uniform size distributions. In addition, with stabilizer PVP higher absorbance values are achieved and the plasmon bands are centred at lower wavelengths, which also points towards a smaller particle size. A representative TEM micrograph for silver particles in ethylene glycol in the presence of PVP is shown in figure 4. Rings obtained in diffraction pattern confirm the presence of silver particles having FCC structure.

3.3 Formation of silver nanoparticles in glycerol

Figure 5 shows the evolution of the surface plasmon absorption band at various concentrations of Ag⁺ ions in glycerol in the absence of stabilizer PVP. The change in the absorption band of silver particles is clearly seen at 0.5 mmol Ag⁺ concentration. It can be seen from figure 5 that with irradiation the surface plasmon band at 410 nm becomes sharper and a new shoulder appears at 500 nm. This is probably due to the plasmon resonance of the aggregates. It can be seen that as the concentration of Ag⁺ ions increases from 0.5 mM to 1 mM the shape of the spec-

trum becomes sharper. The size of the particles obtained after 45 s of irradiation is shown in table 3. A representative micrograph is shown in figure 6. Rings obtained in diffraction pattern confirm the presence of silver particles having *FCC* structure. At 1 mM concentration of Ag^+ ions, after 60 s of irradiation, the colour of the solution turned slightly violet with the appearance of opalescence indicating aggregation of the particles. A large number of products can be formed from glycerol oxidation. The general mechanism of metal reduction in glycerol can be represented by the following reactions:

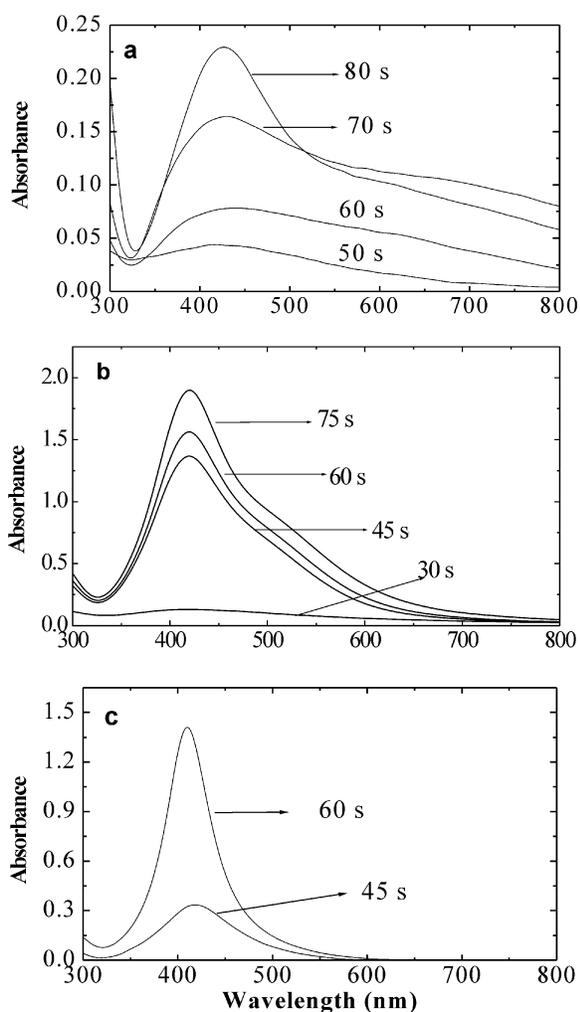
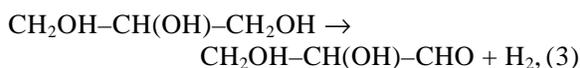
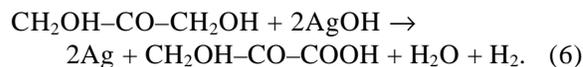
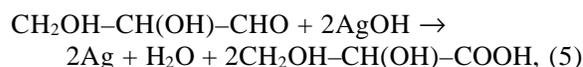
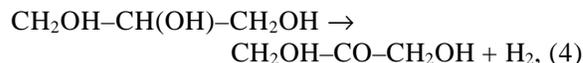


Figure 5. UV spectra of dispersions during colloidal silver formation in glycerol: (a) 0.1 mM, (b) 0.5 mM, and (c) 1 mM Ag^+ . Time duration of irradiation is shown on the traces.



It is known that precious metals sinter at relatively low temperature when synthesized in organic media.⁴⁷ With respect to colloid stability, we observed that the dispersions prepared in glycerol are more stable than those prepared in water and ethylene glycol under similar experimental conditions, that is, without stabilizer. We did not see any precipitate in our metal sol even on keeping for 45 days. Also, the TEM does not reveal any sintered particle. When the reaction was carried out in glycerol (b.p. 285°C) as the solvent and reducing agent, the absorption spectrum as well as TEM results and diffraction pattern showed that nanoparticles of perfect *FCC* phase were obtained.

The most intriguing fact is the dependence of absorption spectra on the nature of the solvent. In the case of silver colloids, prepared by photochemical reduction, a red-shift of 14 nm was observed when the particle size changed from 15.2 to 22.4 nm.⁴⁸ This is consistent with the general trend that the peak shifts towards longer wavelengths as the particles become bigger.⁴⁹ Theoretical studies have shown that dipolar absorption is dominant for particles smaller than 20 nm.⁵⁰ Above 30 nm, dipolar scattering and quadrupolar absorption play important roles. This leads to a significant broadening in the absorption peak. In fact, the position and the number of peaks in the absorption spectra also indicate the shape of the particles. For example, spherical particles show only one band centred at about 400 nm, whereas for ellipsoid particles two peaks appear in the absorption band.⁵¹ The aggregation of particles take place when particles

Table 3. Colloidal silver dispersions obtained in glycerol.

AgNO_3 (mmol/l)	Mean size (nm)	SD (%)
0.1	35	20
0.5	20	10
1.0	18 ^a	10

^aThese appear to be agglomerates of smaller particles of about 6 nm dia

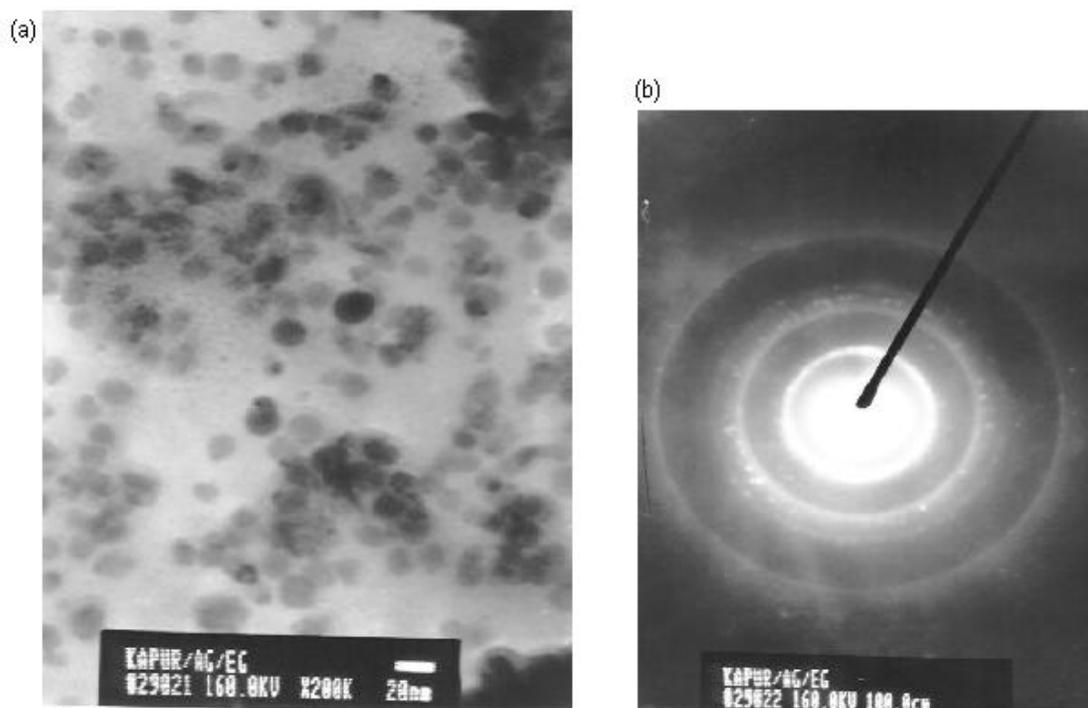


Figure 6. Transmission electron micrograph (a) and corresponding diffraction pattern (b) for silver particles prepared in glycerol after 45 s of irradiation. Other conditions are the same as that of figure 5b.

of different sizes bump into one another. Satoh *et al*⁵² have shown that there is a tendency for ions to dissolve from the surface of smaller particles and precipitate on the surface of larger ones. Therefore, to reduce the possibility of bumps between particles and to prevent the aggregation of particles, polymeric stabilizer and/or organic solvent should be used. In the present work, metallic silver particles prepared in glycerol were much smaller than those in water and glycol under identical irradiation conditions, that is, in the absence of PVP. As viscosity of ethylene glycol and glycerol is approximately 26 and 1000 times more than that of water⁵³ some stabilization was seen in ethylene glycol without PVP. However, it appears that glycerol molecules inhibit the diffusion of silver particles which enhances the stability and hence prevents Ag particles from aggregating effectively. It is pertinent to mention here that recently Pillai and Kamat⁵⁴ have shown that citrate ions undergo strong surface interaction with Ag nanocrystallites. It has been suggested that this plays an important role in dictating the size and shape of the Ag nanocrystallites. In the present case also, the adsorption of glycerol over nanocrystallites of Ag makes it possible to stabilize them even in the absence of

stabilizer. In microwave irradiation, the interaction between dielectric materials, solids or liquids, and microwaves leads to dielectric heating in which electric dipoles of materials respond to an electric field. In liquids, the constant reorientation leads to friction between the molecules. Due to this, heat is generated subsequently. This in turn may affect the morphology and size of the particles. Thus the observed differences could be due to (i) the difference in the boiling points of the solvents (glycerol boils at a temperature 87°C higher than ethylene glycol which boils at a temperature 98°C higher than water) and (ii) the difference in the complexing power of solvents. However, the exact nature of this is yet to be elucidated.

The general conclusions from the present report are the following.

(1) As a result of microwave irradiation on AgNO₃ dissolved in three different solvents (water, glycol and glycerol), particles of metallic silver of different sizes were obtained. It appears that it is necessary to have a stabilizer in the case of water and glycol to restrain the growth of Ag particles. Size of the metallic silver particles is better controlled in organic solvents.

(2) On comparing the results obtained in the present study using the microwave technique with that reported for ethylene glycol/PVP system by the reflux technique, it can be said that almost the same or slightly lower standard deviation was observed in the present work. The other major advantage noticed is the time of reaction; the reaction proceeds at a much faster rate when irradiation is done using microwaves. The study corroborates the results obtained in the case of Pt, Ag and Au nanoparticles in aqueous and N,N-dimethylformamide solutions.^{41,55,56}

4. Conclusions

Silver sols have been prepared in water, ethylene glycol and glycerol using the microwave technique. Each colloidal solution was characterized by UV-Vis spectroscopy. The presence of silver particles in solution is related to a broad absorbance peak whose maximum occurs at 410 nm. The height of the peak gives direct information about the metallic silver concentration in the medium. The average particle size of different preparations is found to be between 15 and 30 nm. The silver sols have a regular and polyhedral particle shape. This indicates that there is isotropic growth of silver particles. The polymer and the amount of precursor added, as well as the solvent used for the preparation of silver sol, determine the average particle size and the amount of silver reduced in a constant time period of irradiation.

Nanometre-size dispersion in a non-aqueous system is of current interest because of its importance both scientific and technological fields. Many semiconductor nanoparticles studies are reported in the literature in organic liquids. Hence, the dispersion/aggregation phenomenon in non-aqueous media is a very contemporary subject. Silver particles prepared in ethylene glycol and glycerol are very stable. It is important to mention here that the particles prepared in glycerol without stabilizer show enormous stability towards coagulation/aggregation as compared to that in water.

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References

- Schmid G 1992 *Chem. Rev.* **92** 1709
- Lewis L N 1993 *Chem. Rev.* **93** 2693
- Gates B C 1995 *Chem. Rev.* **95** 511
- Fendler J H 1996 *Chem. Mater.* **8** 1616
- Schmid G, West H, Mehles H and Lehnert A 1999 *Inorg. Chem.* **36** 891
- Crooks R M and Ricco A 1998 *Acc. Chem. Res.* **31** 219
- Thomas J M 1998 *Pure Appl. Chem.* **60** 1517
- Toshima N, Yonezawa T and Kushihashi K 1998 *J. Chem. Soc., Faraday Trans.* **89** 2537
- Chan W C and Nie S 1998 *Science* **281** 2016
- Nashner M S, Frenkel A I, Adler D L, Shapley J R and Nuzzo R G 1997 *J. Am. Chem. Soc.* **119** 7760
- Kuno M, Lee J K, Dabbousi B O, Mikulec F V and Bawendi M G 1997 *J. Chem. Phys.* **106** 9869
- Ahmadi T S, Wang Z L, Green T C, Henglein A and El-Sayed M A 1996 *Science* **272** 1924
- Underwood S and Mulvaney P 1994 *Langmuir* **10** 3427
- Hostetler M J, Zhong C J, Yen B K H, Andereg J, Gross S M, Evans N D, Porter M and Murray R W 1998 *J. Am. Chem. Soc.* **120** 9396
- Belloni J, Amblard J, Marignier J L and Mostafavi M 1994 in *Clusters of atoms and molecules* (ed.) H Haberland (New York: Springer-Verlag) vol. 2, p. 290
- (a) Henglein A 1989 *Chem. Rev.* **89** 1861; (b) Henglein A and Meisel D 1998 *J. Phys. Chem.* **B102** 8364
- Mulvaney P 1996 *Langmuir* **12** 788
- Taleb A, Petit C and Pileni M P 1998 *J. Phys. Chem.* **B102** 2214
- Keibig U and Vollmer M 1995 *Optical properties of metal clusters* (Springer: Berlin) ch. 2
- Dimitrijevic N M, Bartels D M, Jonah C D, Takahashi K and Rajh T 2001 *J. Phys. Chem.* **B105** 954
- Ayyappan S, Gopalan R S, Subanna G N and Rao C N R 1997 *J. Mater. Res.* **12** 398
- Kurihara L K, Chow G M and Schoen P E 1995 *Nanostruct. Mater.* **5** 607
- Chow G M, Kurihara L K, Kemner K M, Schoen P E, Elam W T, Ervin A, Keller S, Zhang Y D, Budnik J and Ambrose T 1995 *J. Mater. Res.* **10** 1546
- Silvert P-Y, Herrera-Urbina R, Duvauchelle N, Vijayakrishnan V and Tekaia-Elhissien K 1996 *J. Mater. Chem.* **6** 573
- Silvert P-Y, Herrera-Urbina R and Tekaia-Elhissien K 1997 *J. Mater. Chem.* **7** 293
- Lu P, Teranishi T, Asakura K, Miyake M and Toshima N 1999 *J. Phys. Chem.* **B103** 9673
- Kimura K and Bandow S 1983 *Bull. Chem. Soc. Jpn.* **56** 3578
- (a) Mingos D M P and Baghurst D 1991 *Chem. Soc. Rev.* **20** 1; (b) Mingos D M P and Whittaker A G 1996 In *Microwave dielectric heating effects in chemical synthesis, chemistry under extreme or non-classical conditions* (eds) R Van Eldik and C D Hubbard (New York: Wiley) p. 11
- Ma J, Huang X, Cheng H, Zhao Z and Qi L 1996 *J. Mater. Sci. Lett.* **15** 1247
- Zhu J, Palchik O, Chen S and Gedanken A 2000 *J. Phys. Chem.* **B104** 7344

31. Liang J, Deng Z, Jiang X, Li F and Li Y 2002 *Inorg. Chem.* **41** 3602
32. Komarneni S, Bruno M and Mariani E 2000 *Mater. Res. Bull.* **35** 1843
33. Liao Xue-Hong, Zhu Jian-Min, Zhu Jun-Jie, Xu Jing-Zhong and Chen Hong-Yuan 2001 *Chem. Commun.* 937
34. Palchik O, Kerner R, Gedanken A, Wiess A M, Slifkin M A and Palchik V 2001 *J. Mater. Chem.* **11** 873
35. Grisaru H, Palchik O, Gedanken A, Palchik V, Slifkin M A, Wiess A M and Hacoheh Y R 2001 *Inorg. Chem.* **40** 484
36. Zhu Jun-Jie, Wang H, Zhu Jian-Ming and Wang J 2002 *Mater. Sci. Eng.* **B136**
37. Tsuji M, Hashimoto M and Tsuji T 2002 *Chem. Lett.* 1232
38. Zhy Ying-Jie and Hu Xian-luo 2004 *Mater. Lett.* **58** 1234
39. Yin H, Yamamoto T, Wada Y and Yanagida S 2004 *Mater. Chem. Phys.* **83** 66
40. He R, Qian X, Yin J and Zhu Z 2002 *J. Mater. Chem.* **12** 3783
41. Komarneni S, Li D, Newalkar B, Katsuki H and Bhalla A S 2002 *Langmuir* **18** 5959
42. Rao K J and Ramesh P D 1995 *Bull. Mater. Sci.* **18** 447
43. La Mer V K and Dinegar R H 1967 *J. Chem. Soc. Jpn.* **40** 85
44. Zhang Z, Zhao B and Hu L 1996 *J. Solid State Chem.* **121** 105
45. Kapoor S 1998 *Langmuir* **14** 1021
46. Kapoor S and Mukherjee T 2003 *Chem. Phys. Lett.* **370** 83
47. Ducamp-Sanguesa C, Herrera-Urbina R and Figlarz M 1992 *J. Solid State Chem.* **100** 272
48. Huang H H, Ni X P, Loy G, Chew C H, Tan K L, Loh F C, Deng J F and Xu G 1996 *Langmuir* **12** 909
49. Heard S M, Grieser F, Barraclough C G and Sanders J V 1983 *J. Colloid Interface Sci.* **93** 545
50. Kreibig U, Quinten M and Schoenauer D 1986 *Physica* **A157** 244
51. Creighton J A and Eadon D G 1981 *J. Chem. Soc., Faraday Trans. 2* **87** 3881
52. Satoh N, Hasegawa H, Tsuji K and Kimura K 1994 *J. Phys. Chem.* **B98** 2143
53. Weast R C (ed.) 1970 *Handbook of chemistry and physics* (Cleveland, OH: The Chemical Rubber Co.)
54. Pillai Z S and Kamat P V 2004 *J. Phys. Chem.* **B108** 945
55. Yu W, Tu W and Liu H 1999 *Langmuir* **15** 6
56. Pastoriza-Santos I and Liz-Marzan L M 2002 *Langmuir* **18** 2888