Research Paper

Optical, Structural and Catalytic Studies of Silver Nanoparticle Embedded PVA Films

E. V. Chandan, Kirthesh Kumar, B. Madhura and K. Sanath Shetty
Materials Science Dept., Mangalore University, Mangalagangothri - 574 199, Karnataka

Abstract

Stable silver nanocomposite lms were synthesized by mixing aqueous solutions of $AgNO_3$ and PVA which acts as both reducing and stabilizing agent, without using any toxic chemicals. Composite lms of appropriate weight percentage with dierent contents of inorganic phase were obtained by heating, followed by solvent evaporation. The eect of temperature and the duration of heat treatment were explored.

The synthesized composite lms, characterized by UV-visible spectroscopy, revealed the increase in number of Ag nanoparticles with heating time and the intensity plots showed a red shift. Scanning electron microscopy (SEM) revealed the increase in average diameter of particles with increase in the duration of heating. Energy dispersive X-ray spectroscopy (EDS) authenticates the presence of Ag whose concentration increased with increase in the duration of heat treatment as well as increasing weight percentage of $AgNO_3$. Catalytic activity of the nanocomposite lms for the reduction of the organic dye Rhodamine B and Methylene Blue was investigated in the presence of excess $NaBH_4$ and good catalytic activ-ity towards the reduction of Rhodamine B was observed. The simple and fast preparation methodology makes the Ag-PVA lms cost-eective catalysts in the decolouriza-tion of organic dyes.

Keywords: In-situ and ex-situ methods, Rhodamine, UV-Vis spectroscopy.

1 Introduction

Nanoscale study of noble metals such as silver and gold are of great signicance due to their attractive optical, electrical and catalytic properties. Nanoparticles (NPs) nd wide applications in catalysis, drug delivery, data storage, non-linear optics, microelectronics and bio-imaging. Synthesis of silver nanoparticles is of research interest not only due to its size dependent properties but also due to its antimicrobial and antifungal activity. For the preparations of AgNPs, polymers like PVA, PVP are being used as the matrix due to its easy processability, high optical clarity, biocompatibility, and reducing ability of secondary alcohol groups[1, 2]. Ag-PVA nanocompos-ite nds applications as catalytic agents, biosensors, Sur-face Enhanced Raman Spectroscopy (SERC) detectors etc. There are various physical and chemical methods to produce AgNPs like chemical reduction, laser abla-tion, UV irradiation, gamma irradiation, microwave and photochemical methods [3]. Basically, a metal-polymer nanocomposite can be made by both in-situ and ex-situ methods. In in-situ techniques, metal particles are generated inside a matrix by dissolving the precursor in the polymer. In ex-situ, the metal particles are produced separately rst and then dispersed into the polymeric matrix. The aim of this work is to synthesize silver nanoparticles in PVA matrix by simple heat treatments and to investigate the catalysis property of silver in the reduction of rhodamine in the presence of $NaBH_4$. Synthetic dyes are used in many industries such as textile, paper and chemical industries etc. Rhodamine is one of these toxic and carcinogenic chemicals found in waste water from these industries. It is necessary to separate this dye from water before they get into our environment[4, 5].

Several samples were prepared by varying the weight ra-tios of precursor to matrix and the time of reaction. The nanocomposites were characterized by various tech-niques such as UV-Vis spectroscopy, Scanning Electron Microscopy and EDS.

2 Experimental

2.1 Preparation of Ag-PVA nanocompos-ite

PVA solution was initially prepared by dissolving 1.2g of PVA (M.W 125000) in 25ml of distilled water with continuous stirring until the polymer is completely dissolved. $AgNO_3$ solution is prepared by dissolving 0.144g of $AgNO_3$ in 10ml of distilled water. 5ml of aqueous $AgNO_3$ solution was then pipetted out into a beaker con-taining PVA solution (0.384mM) to obtain weight ratio of 0.06%. The $AgNO_3$ solution was added dropwise and the solution was constantly stirred for two hours. Care was taken to protect the solutions from sunlight until heat treatment. Similarly, weight ratio of 0.1% is obtained by taking 0.240g of $AgNO_3$ and 1.2g PVA [6, 7].
The colloidal solution was then poured on to glass substrates and dishes and then heated in an oven. Ag-PVA composite lms were maintained at 100 C and samples (lms) were removed at the intervals of 1hr, 2hrs and 3hrs.

2.2 Reduction of rhodamine

0.01mM of rhodamine solution was prepared by dissolving 0.005g of rhodamine in 1000ml of distilled water. 10mg of nanocomposite were placed into 12.5ml of rhodamine solution. As a reducing agent, 1ml of aqueous $NaBH_4$

(0.05M) was added to the same solution drop wise, under constant stirring [8]. The reduction of rhodamine with silver nanocomposite as the catalyst was monitored using UV-Vis spectrophotometer.

3 Characterization

Figure 1(a) shows UV-Vis spectra of a sample with C for 1hr, $AgNO_3$:PVA (0.06 weight ratio) heated at 100 2hr and 3hr. The peak of samples heated for 1hr appears at 418nm which reveals the formation of silver nanoparticles. Lesser absorbance value indicates the formation of smaller amount of nanoparticles. Futher heat treatment results in the formation of more amount of nanoparticles of increased diameter,which is conrmed by SEM images. Figure 1(b) shows the absorption spectra of the sample 0.1 wt% heated for dierent time intervals.

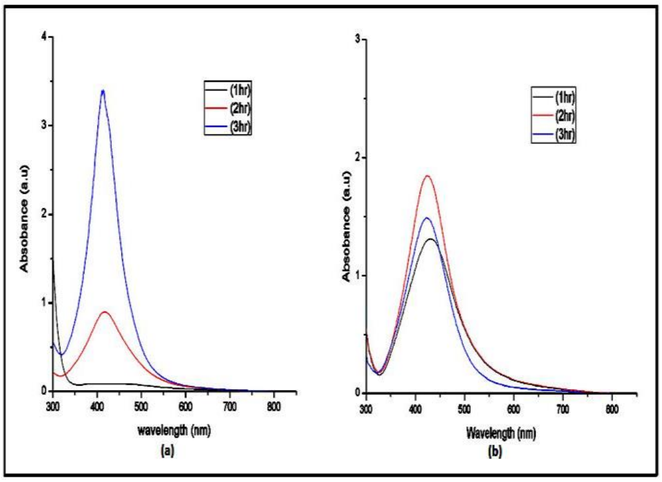

Figure 1: UV-Vis spectra of samples with (a) 0.06wt% ($AgNO_3$:PVA) and (b) 0.1wt%.

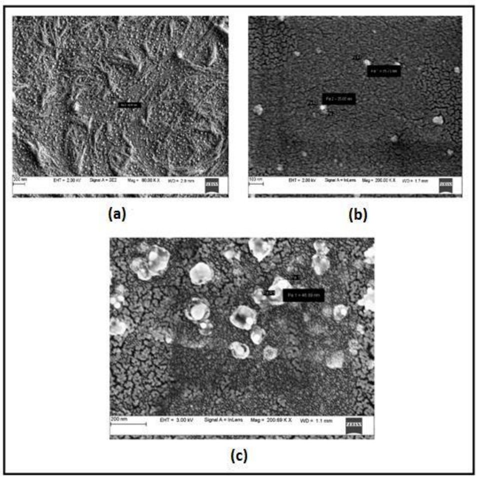

Figure 2: SEM photographs of (a) 0.06wt% with 1 hr heating. (b) 0.06wt% with 3hr heating. (c) 0.1wt% with 1hr heating.

SEM photographs of above mentioned weight percentages are shown in Figure 2(a), (b) and (c). It can be seen that the particle size increases with increase in heating time and also with increase in weight percentage. Particles with average diameter of 8nm and 25nm are observed in samples of 0.06wt% heated for 1hr and 3hr respectively. Nanoparticles with average diameter of 46nm are seen in nanocomposites of 0.1wt%.

Table 1: Correlation of max and Particle size

Weight percentage	Heating time (hrs)	max (nm)	Avg Particle size (nm)
0.06	1	415.7	8
0.06	3	424.0	30
0.1	1	430.9	46

The presence of Ag in the samples was veried with Energy Dispersive Spectroscopy (EDS). Figure 3 shows EDS image of sample 0.1wt% with 1hr heating.

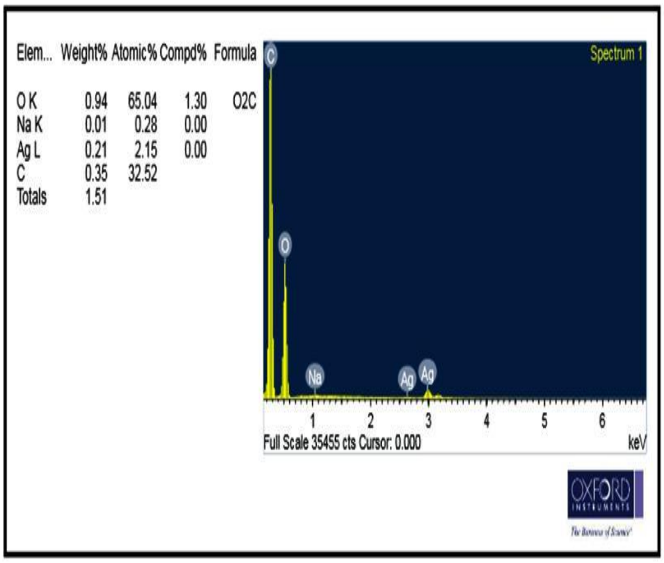

Figure 3: EDS Photograph of 0.1wt% sample with 1hr heating.

Catalytic activity of Ag nanocomposite lms with Rhodamine was monitored by UV-Vis Spectrophotometry. Figure 4 shows catalytic activity of lms with 0.1wt% of $AgNO_3$:PVA with heating time 1hr. The absorption peak at 554 nm, corresponding to rhodamine dye de-creases to a very small value within 5 minutes, after which the decrease is not very signicant. The inset shows the decrease in the rhodamine peak at 554 nm monitored after 5 minutes. It is seen that a very low intense peak corre-sponding to Ag nanoparticles also appears after 15 min-utes . This may indicate slow dissolution of the nanopar-ticles from the lm. We also observed faster dissolution of Ag particles from the sample with a smaller weight ratio of $AgNO_3$:PVA. Eorts are being made to impede this behaviour by varying the rate of heating or by crosslinking the polymer.

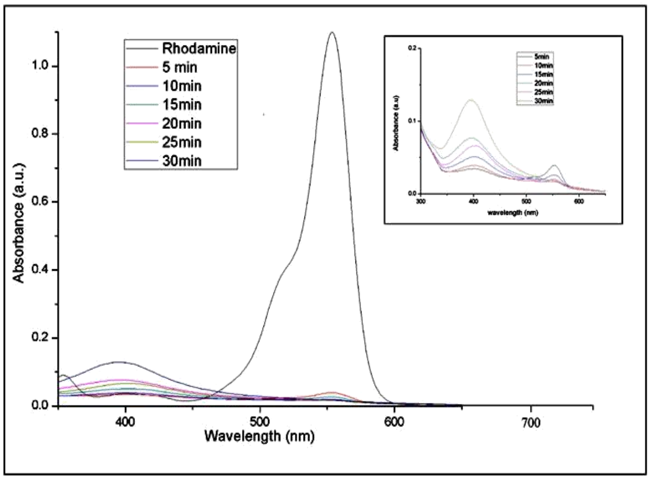

Figure 4: Catalytic activity of Ag nanocomposite with Rhodamine.

4 Conclusion

This work shows a simple and cost eective method for the synthesis of silver nanoparticles embedded on a PVA matrix by heat treatment. The study also demonstrates the catalytic activity of nano silver in the reduction of rhodamine using $NaBH_4$. $AgNO_3$ was used as the precur-sor. PVA acted not only as the polymer supporting tem-plate but also as stabilizing and reducing agent. Results from UV-Vis spectrophotometer, EDS and SEM analysis proved the presence of silver in the composite.

References

[1] Z. I. Ali, H. H. Saleh and T. A. Afy, "Optical, structural and catalytic evaluation of gamma-irradiation synthesized Ag/PVA nanocomposite lms", Chem.Mater. Vol. 4, pp. 1527-1538, 2014.

[2] M. Ghanipour and D. Dorranian, "Eect of Ag-nanoparticles doped in polyvinyl alcohol on the structural and optical properties of PVA lms", J. Nano-Mater. pp. 1-10, 2013.

[3] Guozhong Cao, "Nanostructures and nanomaterials; synthesis, properties & application", Published by Imperial College Press, London, 2004.

[4] J. Y. Cheon, Y. O. Kang and W. H. Park, "Formation of Ag nanoparticles in PVA solution and catalytic activity of their electrospun PVA nanobers", Chem.Poly. Vol. 4, pp. 840-849, 2015.

[5] Y. Meng, "A sustainable approach to fabricating Ag nanoparticles/PVA hybrid nanober and its catalytic activity", NanoMater, Vol. 5, pp. 1124-1135, 2015.

[6] S. Porel, S. Singh, S. S. Harsha, D. N. Rao and T. P. Radhakrishnan, "Nanoparticle-embedded polymer: In-situ synthesis, free-standing lms with highly monodisperse silver nanoparticles and optical limiting", Chem. Mater. Vol. 17, pp. 9-12, 2005.

[7] M. Pattabi, R. M. Pattabi and G. Sanjeev, "Studies on the growth and stability of silver nanoparticles synthesized by electron beam irradiation", J. Mater. Sci: Mater. Electron. Vol. 20, pp. 1233-1238, 2009.

[8] L. Ai, C. Zeng and Q. Wang, "One step solvothermal synthsis of Ag-Fe_3O_4 composite as a magnetically recyclable catalyst for reduction of rhodamine", B. Cat.Com. Vol. 14, pp. 68-73, 2011.

[9] Z. H. Mbhele, M. G. Salemane, C. G. C. E. van Sittert, J. M. Nedeljkovic, V. Djokovic and A. S Luyt, "Fabrication and characterization of silver-polyvinyl alcohol nanocomposites", Chem. Mater. Vol. 15, pp. 5019-5024, 2003.

[10] M. Venkatesham, D. Ayodhya, A. Madhusudhan, N. V. Babu and G. Veerabhadram, "A novel green one-step synthesis of silver nanoparticles using chitosan: catalytic activity and antimicrobial studies", Appl Nanosci. Vol. 4, pp. 113-119, 2014.