Influence of surfactant on the patterning behavior of nanosilver within polyacrylamide nanogels

Sadiya Anjum, Shamayita Patra, Bhuvanesh Gupta*

Bioengineering Laboratory, Department of Textile Technology, Indian Institute of Technology, New Delhi 110016, India

*Corresponding author: Tel: (+91) 11-26591416; E-mail: sadiya2203@gmail.com, bgupta@textile.iitd.ernet.in

DOI: 10.5185/amlett.2019.2120 www.vbripress.com/aml

Abstract

Functional patterning and alignment of metallic nanoparticles are gaining enormous interest in electronics, photonics and sensing areas. In the present work, we have investigated the water-in-oil emulsion polymerization for the growth of functional silver nanoparticles within polyacrylamide chains. These functional nanoparticles undergo different alignment and patterning with the variation of surfactant concentration. As the surfactant in the emulsion increases, the resultant nanoparticles are linearly aligned into nanofiber with some branching. However, at 10% concentration of surfactant, these fibers are fused and quasi-circular pattern was observed. The average size of the nanoparticles was observed to be in the range of 5 to 25 nm. Whereas, the size of line pattern was observed in some microns with branching or interconnectivity of nanometer range. Copyright © 2019 VBRI Press.

Keywords: Polyacrylamide, radiation, nanosilver, emulsion, patterning, alignment.

Introduction

Silver nanoparticles have gained excessive interest in biomedical applications due to its remarkable antimicrobial property against a wide spectrum of microorganisms [1, 2]. Apart from this property, nanosilver persists unique optical, electronic, magnetic and catalytic properties [1, 3-5]. These nanoparticles could be used as individual particles or may be assembled with any template for the fabrication of the devices, films or substrates for various applications. However, the major disadvantage with nanosilver particles is the lack of functionality and they tend to agglomerate with each other. Agglomerated particles diminish their activity due to the large size. This interest has driven the development of functional nanosilver particles by using stabilizers especially hydrogels. We have recently reported the formation of functional nanosilver particles using hydrogels, polymethacrylic acid, polyacrylamide and polyvinyl alcohol [2, 6-8].

While designing such kind of functional nanoparticles, it is important to keep in mind that the hydrogel concentration is relatively low to avoid the formation of film templates and composite structures. In the previous report related to this work, the influence of various reaction conditions on the growth of nanoparticles within hydrogel chains was observed [7-9]. Gamma (γ)-radiation source was used for the reduction of silver ions and simultaneous polymerization of monomers. Whereas, in another

Copyright © 2019 VBRI Press

study, fructose was used for the growth of nanosilver particles in polyvinyl alcohol chains [2]. In this study, the very low concentration of hydrogel was used and resultant core-shell of spherical nanosilver particles was observed. In this study, the nanosilver particles within polyacrylamide chains were synthesized in Nano emulsion using radiation source. The

TEM images was demonstrated the variation in shape and alignment of the nanoparticles.

Experimental

Silver nitrate and sodium bis(2-ethylhexyl) sulfosuccinate (AOT) were received from Sigma Aldrich. Acrylamide (AAm), ethyl methyl ketone (EMK), heptane, and sodium chloride (NaCI) were purchased from Merck India. The chemicals were used as received. ⁶⁰Co gamma radiation source of 800 curies (dose rate of 0.16 kGy/h), supplied by Bhabha Atomic Research Centre, India, was used for the irradiation of the samples.

The oil phase of water-in-oil emulsion was prepared by dissolving varying concentration of surfactant in heptane. The water phase of the emulsion was prepared by the mixing of acrylamide and silver nitrate in water. The emulsion was transferred into polymerization tube, deaerated by purging nitrogen gas for 15 min and the tube was sealed properly and was placed in γ -radiation source for 2 h. After polymerization, the emulsion was destabilized by adding the aqueous solution of sodium chloride. The particles were, repeatedly washed with ethyl methyl ketone (EMK) to remove AOT and dried under vacuum. Transmission electron microscopy measurements were carried out in a TECNAI TEM (Fei, Electron Optics) TEM, operated at 200 kV, equipped with Olympus Soft Imaging Solutions GmbH (software: iTEM; TEM Camera: Morada 4008×2672 pixel max) recording system. Samples were prepared by placing one drop of the aqueous nanogel on top of a carbon coated copper grid.

Results and discussions

The water-in-oil emulsions were prepared by mixing heptane, AOT, acrylamide and silver nitrate. The γ -radiation source has been used for the polymerization of the monomer, crosslinking of chains as well as reduction of silver ions [**7**, **9**].



Fig. 1. TEM images of nanosilver particles within PAAm chains at different AOT concentration (a and a') 6%, (b and b') 8% and (c and c') 10%.

This approach involves the chemical-free route for the development of functional nanosilver in which nanosilver particles are stabilized and protected by polyacrylamide chains. In this work, we investigated the influence of AOT as a surfactant for the growth of nanoparticles. In the emulsion process, surfactant play a dominating role in the stabilization of the emulsion. Due to its amphiphilic nature, it protects the water phase by creating polar-organic phase boundary and forms the micelles structure. AOT as surfactant, controls the shape, size and the alignment of the nanoparticles. The TEM images of the nanoparticles clearly describe the influence of AOT, at low AOT concentration of 6%, the quasi-spherical shape of nanoparticles are randomly aligned in a zig-zag manner with short lines (Fig. 1a and a'). Although the particle size was observed in the range of 10-25 nm with the line alignment of within 100 nm. But upon increasing AOT concentration, 8%, the nanoparticles are clear ordering of the particles in highly parallel linear nanostructures with some branching. These alignments are as long as several microns, consisting the particle size of 5 to 12 nm. In Fig. 1b and b', the magnified image of the linear alignment clearly depicted the single

particle and the branching of the lines. At higher concentration of AOT (10%), the most striking feature of the nanoparticles was observed. The ring or cyclic like alignment and pattern of the nanoparticles was observed, in which the hydrophilic interaction of the functional nanoparticles play a synergistic role with AOT for the formation of this type of image (Fig. 1c and c'). In this pattern the particle size was slightly bigger than the previous concentration of AOT, the average particle size was found to be in the range of 15-30 nm. Similar results were observed in the previous study in which polyvinylpyrrolidone produces stable and branched chains of gold nanoparticles at room temperature [10]. In another study, the impact of surfactant concentration was observed with respect to the alignment and branching of the nanoparticles [11].

Conclusions

In this work, the method for the synthesis of silver nanoparticles with the different arrangement in welldefined linear patterns of ring or cyclic was observed. The patterning and alignment of the nanoparticles depend on the AOT concentration as well as the presence of polyacrylamide chains. Among all concentration, 8% AOT concentration showed a line pattern of nanoparticles with some degree of branching and interconnectivity. These different structures smart nanoparticles would be used as promising material in various applications such as electrical, magnetic, optical and where some anisotropy in chemical composition is required.

References

- 1. Sotiriou, G.A.; Pratsinis, S.E.; *Curr Opin Chem Eng*, **2011**, *1*, 3. **DOI:** 10.1016/j.coche.2011.07.001
- Anjum, S.; Sharma, A.; Tummalapalli, M.; Joy, J.; Bhan, S.; Gupta, B.; Int. J. Polym. Mater. Polym. Biomater., 2015, 64, 894.
- DOI: 10.1080/00914037.2015.1030660
- Dong, X.Y.; Gao, Z.W.; Yang, K.F.; Zhang, W.Q.; Xu, L.W.; *Catal. Sci. Technol.*, **2015**, *5*, 2554.
 DOI: 10.1039/C5CY00285K.
- Zhang, X.F.; Liu, Z.G.; Shen, W.; Gurunathan, S.; Int. J. Mol. Sci., 2016, 17, 1534.
 DOI:10.3390/ijms17091534.
- Wen, G.; Luo, Y.; Liang, A.; Jiang, Z.; *Sci. Rep.*, **2014**, *4*, 3990.
 DOI: 10.1038/srep03990.
- Anjum, S.; Gupta, A.; Sharma, D.; Gautam, D.; Bhan, S.; Sharma, A.; Kapil, A.; Gupta, B.; *Mater. Sci. Eng. C*, 2016, 64, 166.
- DOI: 10.1016/j.msec.2016.03.069.
 7. Gupta, B.; Gautam, D.; Anjum, S.; Saxena, S.; Kapil, A.; *Rad. Phys. Chem.*, 2013, 92, 60.
- DOI: 10.1016/ j.radphyschem.2013.07.020.
 8. Anjum, S.; Gupta, A.; Sharma, D.; Dalal, P.; Gupta, B.; *Mater. Sci. Eng. C*, 2016, *69*, 1050.
 DOI: 10.1016/j.msec.2016.08.009.
- Anjum, S.; Patra, S.; Gupta, B.; *Adv. Mat. Lett.*, **2017**, *8*, 13.
 DOI: 10.5185/amlett.2017.6562.
- Zhang, D.F.; Niu, L.Y.; Jiang, L.; Yin, P.G.; Sun, L.D.; Zhang, H.; Zhang, R.; Guo, L.; Yan, C.H.; *J. Phys. Chem. C*, **2008**, *112*, 16011.
 DOI: 10.1021/jp803102h.
- Ericka, R.L.; Ramón, Í.P.; Efraín, U.B.; Ronaldo, H.U.; Judith, T.; Amir, M.; *Nanoscale Res. Lett.*, **2015**, *10*, 101. **DOI:** 10.1186/s11671-015-0804-8