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Effect of different polymers on morphology and particle size of silver nanoparticles synthesized by modified polyol method

Zeinab Fereshteh [a, *], Ramin Rojaee [b], Ali Sharifnabi [b]

[a] Department of Ceramic, Institute of Science and High Technology and Environmental Sciences, Graduate University of Advanced Technology, 76315117, Kerman, Iran

[b] Biomaterials Research Group, Department of Materials Engineering, Isfahan University of Technology, Isfahan, 8415683111, Iran

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ABSTRACT

In this work, simple, economic, eco-friendly modified method with high efficiency was applied for synthesis of silver nanoparticles (Ag NPs) by using polyethylene glycol (PEG) as a capping agent, reductant, and media agent. In order to preparation uniform and small Ag NPs, the reaction parameters such as type of polymer, $AgNO_3$/Polymer weight concentration ratio, and $AgNO_3/NaBH_4$ molar concentration ratio were modified. The best condition was optimized in concentration ratio of $AgNO_3$: PEG: $NaBH_4$ where are 1:10:0.01, respectively with 82% efficiency and 98.95% purity. Therefore, this modified polyol method can also be scaled up for synthesis of Ag NPs appropriately. Due to polymeric coating on the Ag NPs, they can be employed as a promising candidate for drug delivery systems.

1. Introduction

In the recent years, silver nanoparticles (Ag NPs) is one of the most important nanoparticles due to its widespread applications in many different areas such as catalysts, photocatalysis, lubricating materials, and anti-bacterial materials [1–4]. The most widely used and known applications of Ag NPs are in the medical applications including medical device, implants, antibacterial gels/creams and other similar items [5,6]. Therefore, synthesis of size-controlled Ag NPs with high purity and high yield via a simple and cost effective method is interested by many researchers [5–7]. There are various methods to prepare Ag NPs including microwave irradiation, sonoelectrochemical methods, atom beam sputtering, chemical reduction, biological methods etc [5,8–12]. Among of these methods, wet chemical procedures are the most prevalent methods for synthesis Ag NPs regarding to be simple and rapid. However, toxic chemicals and surfactants are used in many of which. On account of using Ag NPs in biotechnology contacted directly with human life, there is an essential require to produce silver nanoparticles via environmentally friendly methods. It should be noticed that green ingredients especially solvent and surfactant must be applied for synthesis of nanoparticles [13–15]. Polyol method is an easy, simple, and environmentally friendly method to synthesis of nanoparticles which applies polymers as green surfactants. By using different type or weight molecules of polymer, synthesis of nanoparticles with different shapes and sizes can be accomplished in the versatile single step polyol method [2,11–15].

* Corresponding author.
E-mail address: z.fereshteh@kgut.ac.ir (Z. Fereshteh).

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Zhao's group synthesized Ag NPs with different shapes and sizes by controlling the mass ratios of polyvinyl pyrrolidone (PVP; MW: 40,000) in $AgNO_3$ solutions. Owing to increasing the viscosity of the reaction system, when the mass ratio of PVP to $AgNO_3$ was above 10:1, the particle size was not dramatically decreased and it was independent of the PVP concentration. By employing ammonia as a complexing agent, the reduction of $[Ag(NH_3)_2]^+$ to silver metal is harder Ag^+ which in turn leads to prepare smaller particle size of Ag NPs [2]. In addition, by ethylene glycol (EG) and PVP, silver nanowires were synthesized in two steps [16]. Lin et al. indicated that several factors; including silver nitrate concentration, temperature, reaction rate, and PVP/$AgNO_3$ molar concentration ratio; had an influence on size and shape of the silver nanowires. A high aspect ratios of PVP employed as a capping agent which guided the growth orientation of the silver nanowires in 1D [16]. Moreover, by thermal decomposition of $Ag_2C_2O_4$ - polyvinyl alcohol (PVA), Navaladian's group synthesized silver nanoparticles in different sizes. PVA, similar to PVP in the former study, played as a capping agent thereby the particle size decreased. They also illustrated increasing PVA concentration causes to decline the particle size; it was approximately decreased twice when the concentration was doubled [17]. Despite attractive properties of polyethylene glycol (PEG) in Ag NPs production process, it is occasionally employed as a capping agent. Chen et al. synthesized Ag NPs by PEG, plying role as a reducing as well as a capping agent, and Dimethylacetamide, as a solvent. By increasing molecule weight of PEG, there is a slight descending tendency of the mean diameter, being sufficiently high for the protection of Ag NPs in Mw~1000 [18].

In this study, size-controlled silver nanoparticles were synthesized by an elegant and simple modified polyol process applying PVP, PVA, and PEG as a surfactant and effect of different varieties of polymer on shape and size of Ag NPs were investigated. In order to achieving of a rapid, single step, and economical method with the highest yield, $NaBH_4$ employed as a reductant. In addition, the effective parameters of synthesizing Ag NPs and its formation mechanism have been studied in details.

2. Experimental procedure

Silver nitrate ($AgNO_3$, 99.9%) (Merck), polyvinyl pyrrolidone (PVP), polyvinyl alcohol (PVA), polyethylene glycol (PEG), with molecular weight (Mw), 30,000, 70,000, and 1000, respectively, ethylene glycol (EG), acetone and ethanol were purchased from Merck and used without further purification.

$AgNO_3$ (0.1 M) was dissolved in distilled water and heated up to 160 °C in an oil bath with a stirring speed of 250 rpm; afterwards, an appropriate amount of polymer solved in EG was added dropwise into the solution, and the reaction continued for 4 h. Emerging a brown colloidal dispersion indicated the formation of the silver nanoparticles (Ag-NPs). The solution was cooled down to room temperature; then, it was admixed with acetone to precipitate Ag-NPs. The nanoparticles were centrifuged by acetone in 8000 rpm for 30 min until the supernatant solution was clear; they were followed by drying at 60 °C for 24 h in a vacuum oven.

In the obtained samples by using $NaBH_4$, $NaBH_4$ dissolved in ethanol and add into solution after mixing polymer solution. Finally, the obtained sediment decomposed at 450 °C for 30 min, in order to eliminate leftover polymer and achieve Ag-NPs with high purity. The schematic diagram of the silver nanoparticles synthesis process is presented in Fig. 1. Table 1 shows the modified reaction parameters and their effect on the particle size and process yield in the synthesis process of the silver nanoparticles by the modified polyol method.

The functional groups of the samples were identified by Fourier transform infrared spectroscopy (FT-IR: Bruker-Tensor 27, Jasco-680 spectrophotometer, Japan) in the range of 400–4000 cm^{-1}. The phase composition of the samples was analyzed by X-ray diffraction patterns (XRD, Philips XPert) with the voltage of 40 kV, and Cu Kα radiation (λ = 0.15,406 nm). The XRD patterns were recorded in 2θ range of 5–100° (step size of 0.02° and time per step of 1s). The morphology and size of NPs were examined using transmission electron microscopy (TEM: EM 109, ZEISS, Germany, with the accelerating voltage of 100 kV), scanning electron microscope (SEM: LEO 435VP), and field emission scanning electron microscopy (FE-SEM: Hitachi, S-4160).

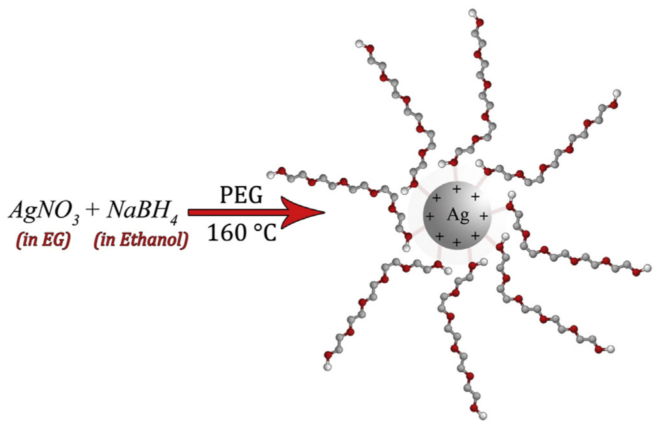

Fig. 1. The schematic diagram of the synthesis process of the Ag NPs by the modified polyol method.