Advanced Materials Research Vol. 1123 (2015) pp 256-259
© (2015) Trans Tech Publications, Switzerland
doi:10.4028/www.scientific.net/AMR.1123.256

Submitted: 2015-02-15
Revised: 2015-03-15
Accepted: 2015-03-27

Effect of Temperature on Silver Nanorods Synthesized by Polyol Method

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Keywords: polyol method, silver nanorods, capping agent, mediated agent, morphological evolution

Abstract: Effect of temperature on the formation of silver nanorods (AgNRs) synthesized using polyol method has been investigated. In this experiment, materials were used silver nitrate ($AgNO_3$) as main raw material, ethylene glycol (EG) as a solvent, small amount of sodium chloride (NaCl) as a mediated agent, while polyvinyl alcohol (PVA) as a capping agent to assist the growth of AgNRs. To apply a constant temperature at each synthesis process, an Erlenmeyer flask containing the sample was immersed in a controllable magnetic stirrer oil bath. It is found that the presence of heat as represented by the temperature of oil bath has been shown to have a strong impact on the AgNRs formation. The scanning electron microscope (SEM) confirmed uniform and high density of AgNRs when the oil bath temperature during polyol process was 140°C. In the same condition, the UV-vis spectra also confirmed formation process of AgNRs with appearance of the transverse plasmon peak about 350 nm. Finally, the X-ray diffraction (XRD) pattern represented that the final product of AgNRs was highly crystallized.

Introduction

The change in size of material from macro-scale to nano-scale causes affects significantly material properties [1]. Products of material science and engineering in nano-scale may be in the form as nanoparticles (NPs), nanowires (NWs), nanorods (NRs) and nanotubes (NTs). Such nano-scale materials like carbon nanotubes (CNTs) and graphene, silver nanorods (AgNRs) and others can be produced by chemical synthesis [2], electrochemical techniques [3], hydrothermal or solvothermal [4], ultraviolet radiation [5], DNA template [6], and polyol method [7,8]. The polyol is a method to produce metal colloids by heating technique using salt and a solvent like ethylene glycol (EG). In this case, the EG has roles as a solvent and reducing agent, while the salt has role as precursors or mediated agent. Most reports show that polyvinyl pyrrolidone (PVP) is often used as capping agents and stabilizer of metal nanorods formation [9].

In this work, AgNRs were synthesized by dissolving $AgNO_3$ and salt in EG. The presence of PVA in EG has a role as the capping agent for assisting the growth of AgNRs and protecting from aggregation. Compared to the most often used capping agent and stabilizer of PVP, the PVA has many advantages for this method such as non-toxicity, mechanical strength, electrochemical stability, and good film-forming ability, biocompatibility, low membrane permeability, and highly crystallized [10].

Experimental

Materials and Preparation of AgNRs: Materials used in this study consisted of silver nitrate ($AgNO_3$, Mw. 169.87, PT. Aneka Tambang, Indonesia), ethylene glycol (EG, 99%, Merck), poly-vinyl alcohol (PVA, Mw. 36000, PT. Brataco, Indonesia), sodium chloride (NaCl, 80%, Sigma Aldrich), and ethanol (EtOH, 98%, Merck). AgNRs were synthesized using polyol method as shown in Fig. 1, which is comprised of six steps (see Fig. 1). (1): PVA of 0.880 g was dissolved in 20 mL of EG in an Erlenmeyer immersed in controllable magnetic stirrer oil bath for 15 min. (2):

Addition with 0.5 mL of NaCl/EG solution (1 mM in EG). (3): Addition with 5 mL of $AgNO_3$/EG (0.5 M in EG) dropwise using a syringe for about 10 min., followed by stirring the mixture of these solutions at speed of 700 rpm for 1 h. (4): The AgNRs were chilled at air ambient (27 ± 2)°C for 30 min. (5): The AgNRs were filtered and washed with ethanol using centrifuge treatment at speed of 6000 rpm for 10 min. The washing step was repeated four times to remove non AgNRs. (6): The pure AgNRs was then stored in an ethanol solution for next process.

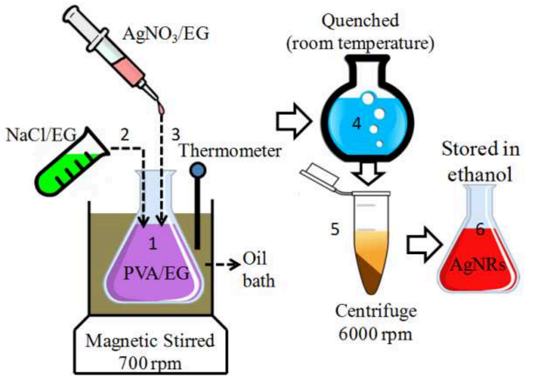

Fig. 1. Schematic of experiment procedure of polyol method.

Characterization: The morphology and evolution of AgNRs were characterized using scanning electron microscope (SEM) and UV-Vis spectrophotometer. Finally, the crystal structure of AgNRs was analyzed using XRD with a scanning 2θ in the range of 30-90°.

Results and Discussion

The polyol method used for synthesizing AgNRs in this study was adopted from the previous report with different capping agent from polyvinyl-pyrrolidone (PVP) to polyvinyl-alcohol (PVA) [2]. The formation of nanorods is generally affected by temperature. In this study, the temperature of $AgNO_3$/EG solution as represented by the oil bath temperature was varied to be 100, 120, 140, and 160°C. Unfortunately, there was no AgNR formed at the oil bath temperatures of 100 and 120°C. The microstructure of Ag nanowires had been characterized by scanning electron microscope (SEM, JSM-6510, JEOL) at an acceleration voltage of 10 kV. Figure 2 shows the morphologies and sizes of AgNRs. Therefore, there is no available SEM image of AgNRs at these temperatures. Oppositely, the AgNRs were formed high density when the oil bath temperature of 140°C (Fig. 2.(a)). The diameter of AgNRs is ranging from 200 to 500 nm with a length of 5 to 10 µm. Meanwhile, a mixture of low density AgNRs and agglomerates formed at oil bath temperature of 160°C (Fig. 2.(b)).

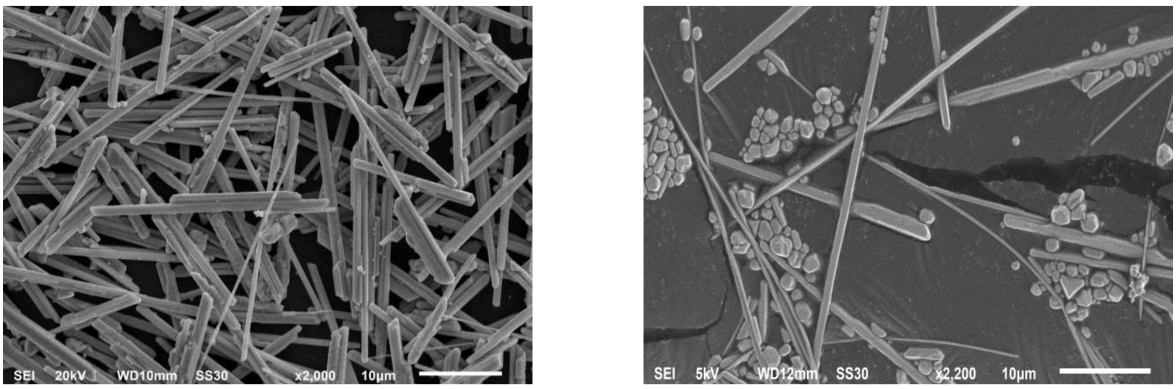

Fig. 2. SEM images of AgNRs syntesized at temperature of (a) 140°C and (b) 160°C.

The morphological evolution of AgNRs was investigated using UV-Vis spectrophotometer (UV-1700, Shimadzu) as shown Fig. 3.(a). This phenomenon is related to the appearance of a surface plasmon resonance (SPR), where the peak of the absorption spectrum indicates its transverse plasmon resonance. Based on literatures, the absorption peak for silver nanoparticles is approximately 420 nm, while that of silver nanorods is approximately 350 nm [11,12]. In this study, there is no absorption peak in Fig. 3.(a) when the oil bath temperatures were 100 and 120°C. It indicates that at these conditions there is no formation of either Ag nanoparticle or AgNRs. Meanwhile, the appearance of absorption peaks at around 350 nm when the oil bath temperatures were 140 and 160°C indicates that using these temperatures can create AgNRs. From the description, both SEM images and UV-Vis spectra are correlated for confirming AgNRs formation.

The following simple explanation can help us to understand the physics mechanism of AgNRs formation using polyol method. When the $AgNO_3$/EG solution is injected into PVA/EG solution, the amount of Ag particles is reduced quickly by NaCl and results in AgCl. At a particular temperature (e.g. 140°C), the EG solution starts to break AgCl into Ag^+ and Cl^- ions, and then nucleate to form Ag particles. The Ag particles are then capped by PVA to form Ag nanorods (AgNRs). Due to some difficulties in controlling ambient perfectly in this study, however, some Ag particles or agglomerates remain in mixing with AgNRs. The centrifuge treatment is then very important process for separating the AgNRs from Ag particles, agglomerates, EG solvent and supernatant of PVA. For higher temperature of oil bath (160°C), the AgNRs may be broken and results in both agglomerates and nanorods. The importance of temperature can be attributed to the deficiency of thermal energy for the formation of specific faces [13, 14].

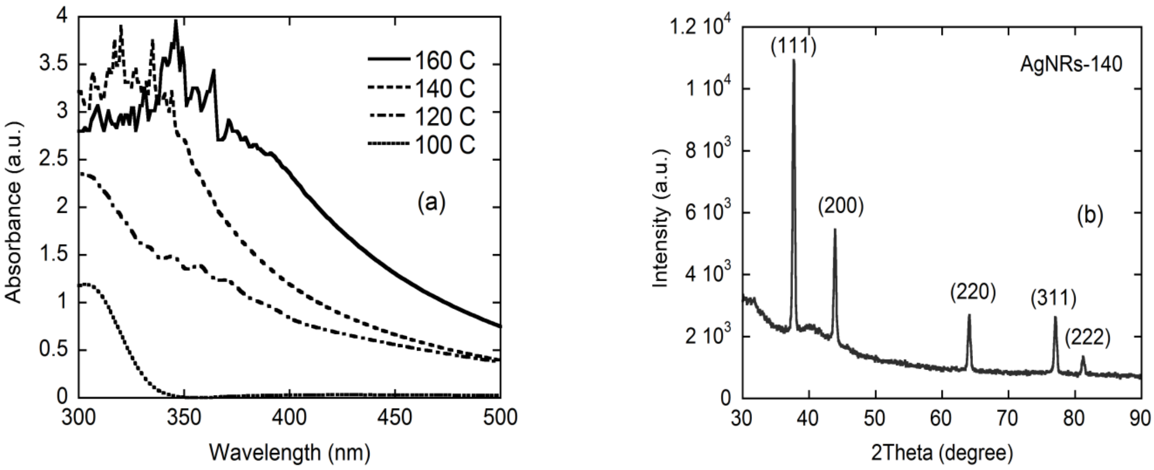

Fig. 3. (a) Absorbance spectra of AgNRs in ethanol solution at different oil bath temperatures, and (b) XRD pattern of AgNRs synthesized at 140 °C.

Figure 3.(b) shows the X-ray powder diffraction (XRD) patterns were recorded using a Rigaku diffractometer with the CuKa radiation (λ = 1.54060 Å). The XRD pattern of AgNRs synthesized at 140°C. The ratio of peak intensity at 37.67° and 43.88° is about 2.4, while the theoretical ratio is 2.5 [15]. The peak at angles of 2θ = 37.67°, 43.88°, 64.04°, 77.01°, and 81.06°, based on JCPDS card 04-0783, correspond to the (111), (200), (220), (311), and (222) crystal planes of the face center cubic (fcc) Ag, respectively. The calculated lattice constants according to the spacing distance d_{hkl} of the {111} planes and the equation: $d_{hkl}^2 = a^2/(h^2+k++l^2)$ is 4.132 Å [16]. This calculated lattice constant is very close to the literature value of 4.086 Å. The silver nanorods location of (111) was preferred because, in the fcc lattice structure, the atom density of {111} crystal surface was 91.04% [17].

Conclusion

The AgNRs were successfully synthesized using polyol method with different temperatures. It is found that the temperature of oil bath during the synthesis process influences significantly to the formation AgNRs. In the oil bath temperature of 140°C, it can form high density AgNRs with the diameter and length about 200 to 500 nm and 5 to 10 μm, respectively. For higher temperature of 160°C, the AgNRs may be broken and results in both agglomerates and AgNRs.

Acknowledgement

This work was supported by research grant of "International Research Collaboration and Scientific Publication, Contract No.: LPPM-UGM/998/LIT/2014" by the Directorate General of Higher Education (DIKTI), Ministry of Education and Culture, the Republic of Indonesia.

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