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Effect of Stirring Rate on The Synthesis Silver Nanowires using Polyvinyl Alcohol as A Capping Agent by Polyol Process

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***Abstract*— Effect of stirring rate on the formation of silver nanowires (AgNWs) have been successfully synthesized by using polyol process. In this study, the materials used are ethylene glycol (EG) as solvent and reductant, silver nitrate ($AgNO_3$) as the metal precursors, and polyvinyl alcohol (PVA) as a capping agent and stabilizer without adding chloride ions. The synthesis AgNWs was done by varying the stirring rate about 125, 350, 500, 700, and 1100 rpm. The scanning electron microscopy (SEM) showed that the AgNWs optimally formed at a stirring rate of 350 rpm with a diameter of (190 ± 40) nm and a length about (70 ± 20) µm, resfectively. The silver nanorods (AgNRs) formed with diameter and length about (500 ± 20) nm and (20 ± 10) µm for stirring rate of 500 rpm, and (700 ± 30) nm and (20 ± 5) µm for 700 rpm. For the stirring rate of 125 and 1100 rpm only produced silver nanoparticles (AgNPs) with a diameter of 2 to 3 µm. The X-ray diffraction (XRD) showed a high crystalline with face-center-cubic (fcc) structures. The UV-vis spectra of AgNWs shows that the absorbance peaks at a wavelength of 358 and 380 nm. PVA can be used as a capping agent and stabilizer for the synthesis AgNWs and AgNRs with high aspect ratio.**

***Keywords*— Silver nanowires; silver nanorods; polyvinyl alcohol; stirring rate; polyol process**

I. INTRODUCTION

The research on nanowires (NWs) is one of the nanomaterial research that attracted in recent years. NWs is one-dimensional (1D) nanostructures that have a diameter of less than 100 nm and length by ranging from a few hundred nanometers to micrometers [1]. The silver nanowires (AgNWs) is one material that developed due to it has an interesting study of the mechanical, magnetic, electrical, optical properties, and its application as a catalyst, scanning probes, nanoelectronics, and photonic devices [2]. In comparison with other metal, silver in bulk is the highest electrical and thermal conductivity among all metals. The silver have electrical and thermal conductivity about 6.3×10^7 Sm^{-1} and 429 $Wm^{-1}K^{-1}$, respectively [3]–[5]. The AgNWs is very good for the application of transparent conductive electrodes (TCEs) [6].

The polyol process was used to synthesize AgNWs because it is simple, easy process, can produce AgNWs with high aspect ratio and low cost [7]. However, the constraints of polyol process are the difficulty to produce AgNWs with homogeneous shapes and sizes. The results obtained are not pure AgNWs, but there are still nanoparticles (NPs) so that the necessary of centrifugation process to separate between NPs and NWS.

Some of the parameters that influence the formation AgNWs including the molar ratio of polyvinyl pyrrolidone: silver nitrate [PVP:$AgNO_3$], oil bath temperature, injection rate, and stirring rate [3]. Polyol process is a method used an oil bath as the medium for heat transfer in the synthesis AgNWs. Synthesis AgNWs carried out with the aid of solvents and reducing agents, as well as polymer capping agent such as PVP. The solvents that have been successfully used in the synthesis AgNWs are ethylene glycol [8],[10] water [11],[12], 1,2-propanediol [7], glycerol [13],[14], and propylene glycol [15]. Ethylene glycol (EG) is more commonly used as a solvent because it can decompose to glycolaldehyde and water which play a role in the reduction of Ag^+ ions into Ag^0 atoms. EG has a melting point of about 197 °C which is approaching the melting point of $AgNO_3$, namely 209 °C so as to produce AgNWs with a high aspect ratio. The polymer capping agent used in the synthesis AgNWs is polyvinyl alcohol (PVA) with a melting point of about 180 to 240 ^oC. PVA role is to control the formation of seeds (seeds) Ag nanostructures, such as polycrystals, single-crystal, single-twin particle (STP), and multiple-twin particles (MTPs) [16].

In this paper, we studied effect of stirring rate on the formation of AgNWs. The stirring rate plays an important parameter on the formation of silver nanostructures. The stirring rate is too low or high causing AgNWs difficult formed with high aspect ratios [17]. The AgNWs are widely characterized using UV-vis spectrocopy, Fourier transform infrared (FTIR) spectrocopy, X-ray diffraction (XRD), and scanning electron microscope (SEM).

II. Materials and Methods

A. Materials

The materials were used for synthesizing of silver nanowires through polyol method included silver nitrate ($AgNO_3$, 99%, Merck), polyvinyl alcohol (PVA, Mw. 31000-50000 g/mol, Sigma-Aldrich), ethylene glycol (EG, 99%, Merck), and ethanol (EtOH, 98%, Merck).

B. Method

The synthesis AgNWs with polyol process is carried out in three steps (Fig. 1), which are a dissolving process of the sample, synthesis AgNWs, and centrifugation [18].

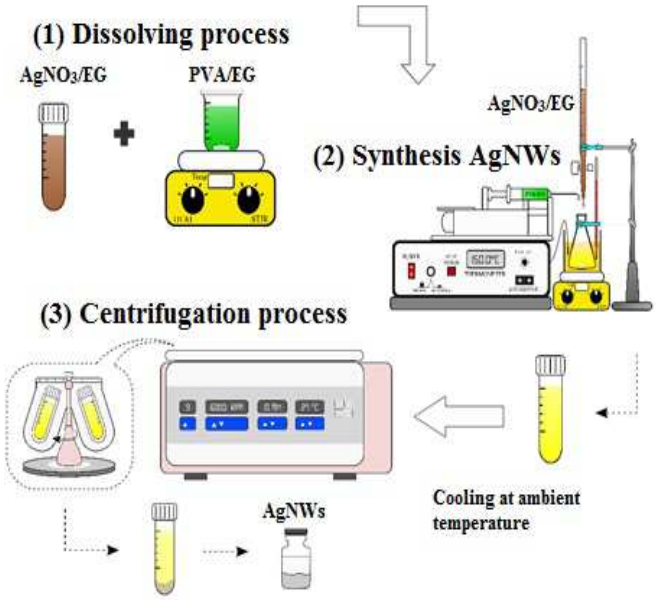

Fig. 1 Synthesis AgNWs by polyol process.

Firstly, PVA of 1.62 g was dissolved in 20 mL of ethylene glycol into an Erlenmeyer flask immersed in controllable magnetic stirrer oil bath for 1 hour. After that, ten mL of a 0.5 M $AgNO_3$/EG was added dropwise using a syringe pump for about 20 minutes (0.5 cc/min), followed by stirring the mixture of these solutions at 350 rpm for 90 min. The color changed to yellow and became brownish-gray after $AgNO_3$/EG added. The solution containing produced of silver nanowires then cooled naturally to room temperature. It followed by being separate with ethanol through several times of centrifugation at a speed of 6000 rpm.

C. Characterization

UV-vis spectroscopy (Shimadzu, UV-1700) was used to measure the absorption spectrum of silver nanowires solution in the wavelength range of 300 to 700 nm. The FTIR spectrum was performed using an ABB-MB3000 with a wavenumber of 500 to 4000 cm^{-1}. The crystal structure of silver nanowires was analyzed using XRD (Shimadzu R6000) by CuKα (λ = 1.54184 Å) with a scanning 2θ in the range of 20^o to 90^o. Furthermore, the morphology and size of silver nanowires were observed using SEM (JEOL, JSM-6510) by accelerating voltage of 10 kV.

III. Result and Discussion

A. UV-vis spectroscopy analysis

Stirring rate in the synthesis AgNWs conducted at 125, 350, 500, 700, and 1100 rpm. Stirrer speed is closely related to the kinetic energy on the surface of nanostructured Ag. For silver nanoparticles (AgNPs) has one absorption peak at a wavelength of ~420 nm. The AgNWs has two absorption peaks at a wavelength of around 350 to 380 nm [19]-[21]. UV-vis spectra at higher energy associated with symptoms of absorption and scattering of light in the short axis (transverse) of NWs. Meanwhile, for the UV-vis spectra at a lower energy-related symptoms absorption and scattering along the long axis (longitudinal) of the NWs. The difference of the absorption peak can be used to identify the shapes and properties of Ag nanostructures. UV-vis spectra of samples AgNWs for various stirrer speeds shown in Fig. 2.

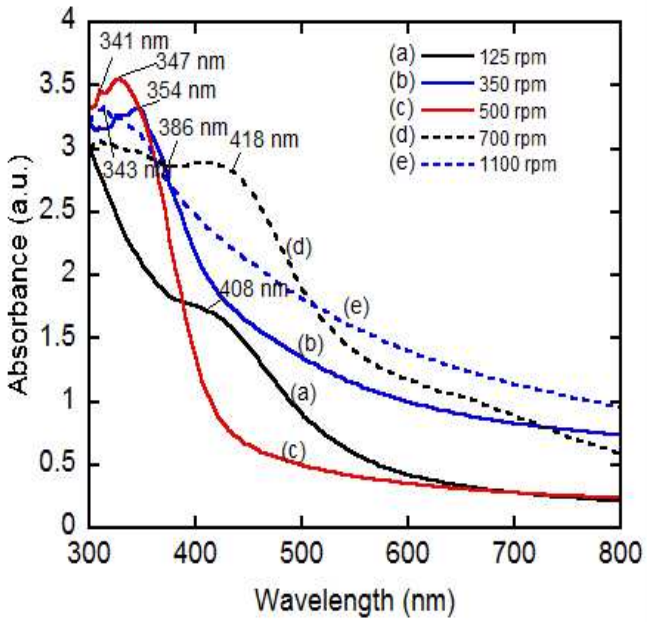

Fig. 1 UV-vis spectra of AgNWs with variation of stirring rate.

For AgNWs at stirring rate of 125 rpm showed one absorption peak at a wavelength of 408 nm which is the absorption peak of AgNPs. The absorption peaks at a wavelength around 354 nm and 386 nm formed at AgNWs synthesized with a stirring rate of 350 rpm. When synthesized with a stirring rate of 500 rpm, the absorption peaks are formed at a wavelength 341 nm and 347 nm.

For AgNWs at a stirring rate of 700 rpm contained absorption peak at a wavelength of 343 nm and 418 nm which indicates the formation of the AgNWs and AgNPs.

Meanwhile, for AgNWs at the stirring rate of 1100 rpm is still dominated by PVA as indicated by the absorbance peaks similar to PVA. The absorbance peaks of PVA showed absorbance peaks are not very significant in the visible region, but the significant region around at a wavelength of 197 nm [22].

B. FTIR spectroscopy analysis

Results of FTIR characterization of PVA and AgNWs at a stirring rate of 350 rpm can show in Fig. 3. The type of molecular vibration that occurs in the sample can show in Table 1.

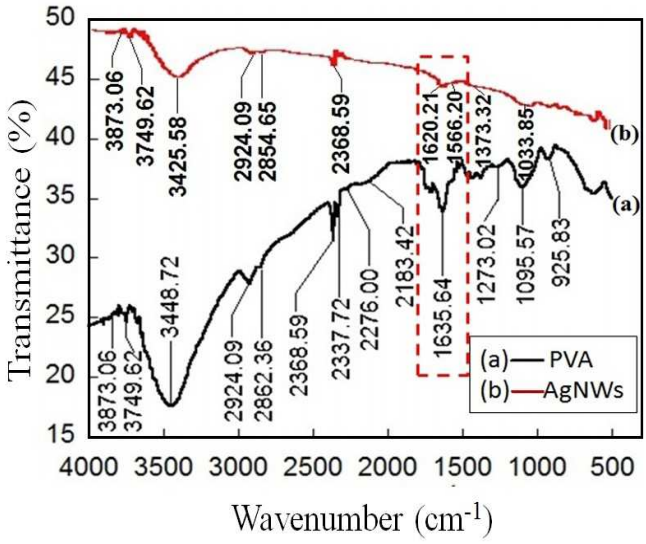

Fig. 3 FTIR spectra of PVA and AgNWs.

TABLE I
BOND OF PVA AND AGNWS FROM FTIR SPECTRA

Functional groups	PVA	AgNWs	Kind of bond
O – H	3448,72	3321,18	*stretching*
C – H	2931,80	2916,16	*stretching*
C = O	1720,50	1735,81	*stretching*
C – H	1442,75	1411,79	*bending*
C – C	1265,30	1207,35	*stretching*
C – O	1095,57	1083,92	*stretching*
C – H	848,68	817,76	*rocking*
C – H	609,51	590,17	*bending*

FTIR spectra of PVA in Fig. 3(a) indicate that PVA has broad absorption peaks at wave number around 3448.72 and 3748.62 cm^{-1}. The wave number is the culmination of a hydroxyl group (O-H) stretching. Weak peaks at wave number around 2924 and 2924.09 cm^{-1} are the culmination of CH_3 and $-H_2-$ stretching. Vibration peak from the group C=O stretching occurs in wave numbers around 1635.64 $cm^{-1,}$ and C-H bending occurs in wave numbers around 1442.75 cm^{-1}. There is a lower energy vibration peak at wave number 1273.02 cm^{-1} from the group C-C stretching and the wave number 1095.97 cm^{-1} from the group C-O stretching. Vibration peak for the group C-H rocking and bending occurs in wave numbers 848.68 and 609.51 cm^{-1} [23]–[25].

Fig. 3(b) is a FTIR spectra of AgNWs. The transmittance peaks of AgNWs are not much different from the PVA. The FTIR spectra of AgNWs experienced a shift toward smaller wave number of the FTIR spectra of PVA. These indicate that the vibrational energy molecular bond between PVA and AgNWs is getting smaller. The similarity of vibration peak between AgNWs and PVA indicate that PVA only coated AgNWs without the formation of new compounds. This phenomenon also indicates that the PVA and AgNWs experience interaction marked by a huge shift of the vibration of the hydroxyl group (O-H). Fig. 3(b) shows the red-shifted owned PVA of 1635.64 cm^{-1} to 1620.21 cm^{-1} due to the interaction of the oxygen atom of the hydroxyl groups with Ag atoms form Ag-O bonds [26],[27].

C. XRD analysis

XRD analysis performed to determine the crystal structure of AgNWs. The AgNWs powder dried through evaporation process analyzed by using XRD (Rigaku diffractometer) in CuKα radiation with a wavelength of 1.54060 Å. Measurements conducted at an angle of diffraction patterns 2θ of 20 to 90°. XRD diffraction patterns for AgNWs at stirring rate of 350 rpm as shown in Fig. 4.

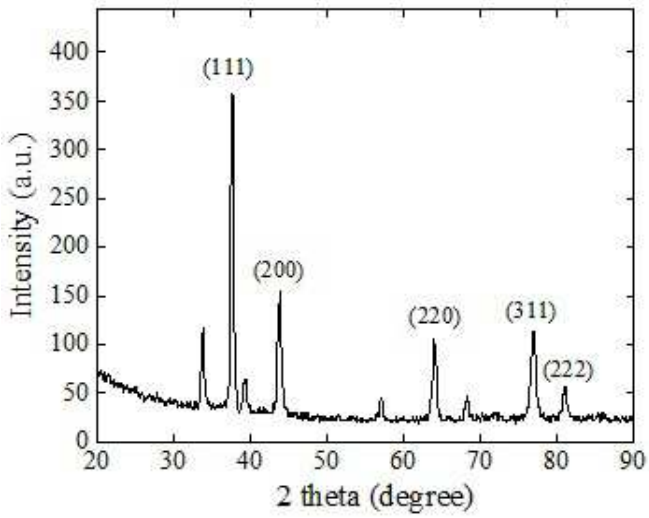

Fig. 4 XRD pattern of AgNWs at stirring rate of 350 rpm.

XRD pattern (Fig. 5) shows the diffraction peaks at 2θ angles, i.e., 37.58°, 43.77°, 63.98°, 76.96°, and 81.11°. The magnitude of the values of the diffraction angles corresponding to the crystal structure with Miller index of (111), (200), (220), (311) and (222) (JCPDS File 04-0783), with its crystalline structure is face-center-cubic (fcc). The high diffraction peaks of AgNWs indicated that formed has a high crystallinity.

In addition to the diffraction peak of AgNWs, on the outcome of the XRD pattern, there are also other peaks at 2θ angles, i.e., 33.75°, 39.28°, 57.07°, and 68.26°. From the analysis using software Match 2 shows that the peaks are characteristic of Scandium (Sc), which indicate the presence of impurities samples. From these results are also obtained lattice constant (a) is about (4.14 ± 0.01) Å. This value is close enough to the lattice constant from reference (a = 4.0862 Å, File JCPDS 04-0783) [28],[29].

D. SEM analysis

SEM analysis was used to observe morphology and size of AgNWs. Fig. 5 is SEM images of AgNWs for optimization of stirring rate. Fig. 5(a) shows that for stirring rate of 125 rpm still dominated by AgNPs with a diameter of (1950 ± 275) nm. AgNPs with large size formed due to the agglomeration. When synthesis AgNWs conducted with stirring rate is too low, the rate of reduction of Ag^+ ions into atoms Ag^0 rapidly. This condition causes the Ag seeds are a clot and not disperse in solution. The reduction of Ag^+ ions that quickly cause AgNPs more reactive and form larger Ag particles.

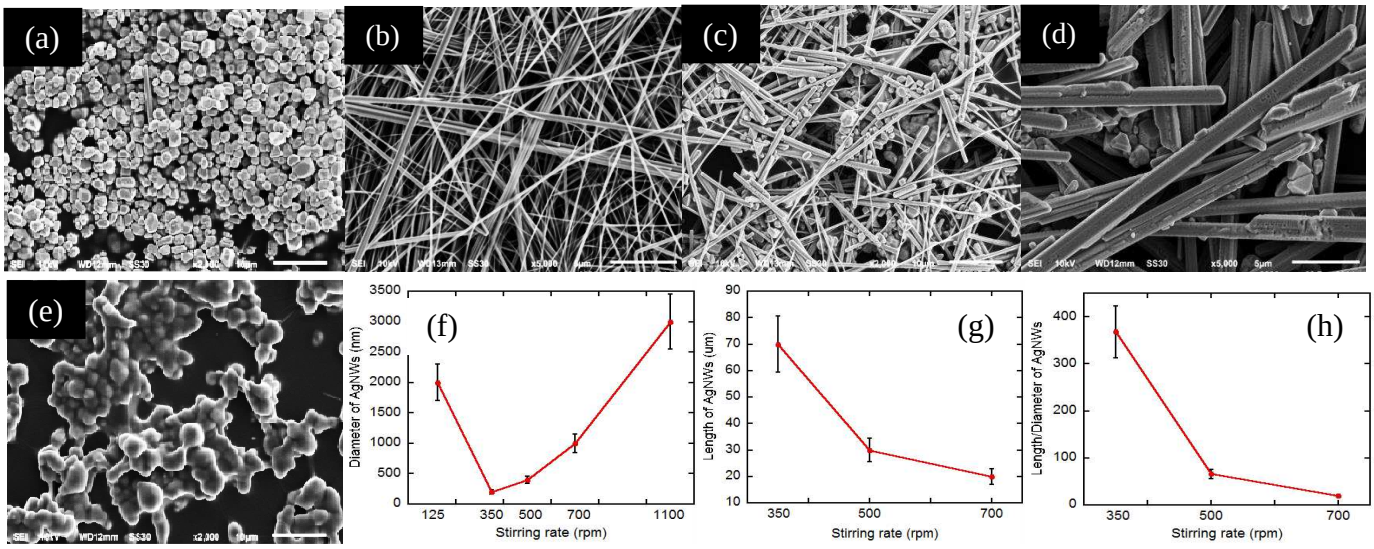

Fig. 5 SEM images of AgNWs at stirring rate of (a) 125, (b) 350, (c) 500, (d) 700, (e) 1100 rpm, effect of stirring rate on the (f) diameter, (g) length, and (h) ratio (*l*/*d*) of AgNWs.

The synthesis AgNWs with a stirring rate of 350 rpm can produce AgNWs with high ratios as shown in Fig. 5(b). The diameter and length of AgNWs obtained (190 ± 30) nm and (80 ± 10) µm with a ratio length/diameter (*l*/*d*) about 368, respectively (Fig. 5(f-h)). These results indicate that AgNWs formed longer than using PVP as a capping agent. This condition due to the mechanical strength of PVA higher than PVP. The high mechanical strength of PVP cause AgNWs not easily broken when synthesized at a high stirring rate [3],[15],[30].

The synthesis AgNWs for stirring rate of 500 rpm is a transition condition between stirring rate of 350 and 700 rpm as shown in Fig. 5(c). Diameter and length of AgNWs for stirring rate of 500 rpm about (300 ± 170) nm and (20 ± 10) µm with the ratio *l*/*d* about 67 (Fig. 5(f-h)). The diameter of AgNWs is greater than the stirring rate of 350 rpm. The diameter of AgNWs increases with increasing the stirring rate. Compared with AgNWs at the stirring rate 350 and 500 rpm, AgNWs for stirring rate of 700 rpm indicate a change significantly diameter and length. In these conditions, the AgNRs produced with diameter and a length of t (700 ± 200) nm and (20 ± 5) µm as shown in Fig. 5(d). The Ag seeds can be scattered randomly across the surface of Erlenmeyer flask with the high stirring rate. The synthesis AgNWs with the stirring rate is too high proved unable to produce AgNWs and AgNRs. Fig. 5(e) indicates that at a high stirring rate (1100 rpm) was formed Ag particles by large diameter, i.e., (2800 ± 500) nm.

The stirring rate too high can lead to a high surface energy on the (111) facets of MTPs Ag seeds. PVA is difficult to stabilize the surface in the (100) facets. This condition causes the growth of the (100) facets becomes massive and stop. MTPs Ag seeds are still reactive will bind AgNPs from the addition of Ag^+ ions continuously.

IV. Conclusions

The stirring rate plays an important parameter on the formation of silver nanostructures. The synthesis AgNWs with optimizations of stirring rate obtained the optimum condition at stirring rate of 350 rpm with a high aspect ratio. For a stirring rate of 500 and 700 rpm generated AgNRs. The stirring rate is too low or high produced AgNPs. XRD pattern of AgNWs shows the surface structure resembling a pentagonal-shaped with the crystal structure of face center cubic (fcc). UV-vis spectra of AgNWs shows absorbance peak at a wavelength of 354 and 386 nm. The anisotropic growth process of AgNWs caused by PVA is surrounding and covering the (100) facets so that the Ag atoms combine on the (111) facets. Therefore, there will be growth process that stretches on AgNWs and AgNRs.

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