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Chloride Ion Addition for Controlling Shapes and Properties of Silver Nanorods Capped by Polyvinyl Alcohol Synthesized by Polyol Method

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Abstract: We report our investigation on the effect of chloride ions oncontrolling the shapes and properties of silver nanorods(AgNRs) synthesized using a polyol method. In this study, we used polyvinyl alcohol (PVA) as a capping agent and sodium chloride (NaCl) as asalt precursor and performed at the oilbath temperature of 140 °C. The chloride ions originating from the NaCl serve to control the growth of the silver nanorods. Furthermore, the synthesized silver nanorodswere characterized using UV-VIS, XRD, SEM and TEM. The results showed that besides being able to control the growth of AgCl atoms, the chloride ions were also able to control the growth of multi-twinned-particles into the single crystalline silver nanorods by micrometer-length. At an appropriate concentration of NaCl, the diameter of silver nanorodsdecreased significantly compared to that of without chloride ion addition. This technique may be useful since a particular diameter of silver nanorods affects a particular application in the future.

INTRODUCTION

Synthesis of metal nanowires or nanorodsusing polyol method has attracted many researchers due to high feasibilities for many applications such as catalysts, optoelectronic devices, organic solar cells and photonics nanodevices [1-2]. Synthesis ofsilver nanowires (AgNWs) is often performed using ethylene glycol as a solvent and a reducing agent, polyvinyl pyrrolidone (PVP) as capping agent and stabilizer, and platinum chloride (PtCl2) as diameter controller of AgNWs. Moreover, it is usually carried out at a temperature of 160 °C [3-6].

A lot of efforts have been made to control the diameter and length, high aspect ratio, and uniform orientation of AgNWs [7]. When using PVP capping agent, the AgNWsformation has been successfully controlled using salt precursors addition in the form of chloride ions and bromide ions from sodium chloride, copper chloride, potassium bromide, or iron chloride. In this case, the addition of Cl or Br can control the process of growing AgCl or AgBrnanocubes as multi-twin-seed particles (MTPs) that subsequently growing into AgNWs. Such conditions lead to the AgNWsformation become more stable and uniform. However, there are several problems related to the addition of salt precursors, such as the volume and concentration of precursor salt should not be optimized [8-10]. As polymer matrix, PVP acts as a reducing and capping agent for some metal nanoparticles or nanorods [11]. On the other hand, polyvinyl Alcohol (PVA) has properties as a hydrophilic, biodegradable and biocompatible synthetic polymer [12]. Since their properties are similar, the PVA has a role as polymer matrix for nanoparticles or nanorods formation.

This paper describes AgNRs formation using PVA and chloride ion addition synthesizedusing polyols method. In this study, PVA acts as a capping agent and stabilizer as well as a controller chloride ion AgNRs growth. The chlorine ions resulted from sodium chloride (NaCl) was varied from 0 mM to 20 mM.

MATERIALS AND METHODS

Materials and Synthesis of AgNRs: Silver nitrate ($AgNO_3$, 99%, Merck), polyvinyl alcohol (PVA, Sigma-Aldrich, Mw. 31.000-50.000 g/mol), sodium chloride (NaCl, 80%, Sigma-Aldrich),ethylene glycol (EG, 99%, Merck), and ethanol (EtOH, 98%, Merck).The same polyol method for synthesizing AgNRsused in this study was carried out as in our previous studiesthat schematically as shown in Fig.1 [13]. The amount of10 mLof EG was heated in an Erlenmeyer flask at 140 °C and stirred at 350 rpm for 20 minutes. Furthermore, asolution of $AgNO_3$and PVA (0.5 M and 2 M in 10 mL EG, respectively) were injected into EG solution drop by drop at 0.5 cc/min flow

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rate. After stirred for 1 hour, theamount of 0.5 mL NaCl/EG was added to the solution. The stirring process in the solution was kept for 2 hours at a constant temperature of 140 °C. The solution containing produced AgNRs of this process was then cooled naturally to room temperature. It was followed by being separated and washed in ethanol through several times of centrifugation at a speed of 6000 rpm. Finally, the AgNRs were stored in an ethanol solution for further characterization process.

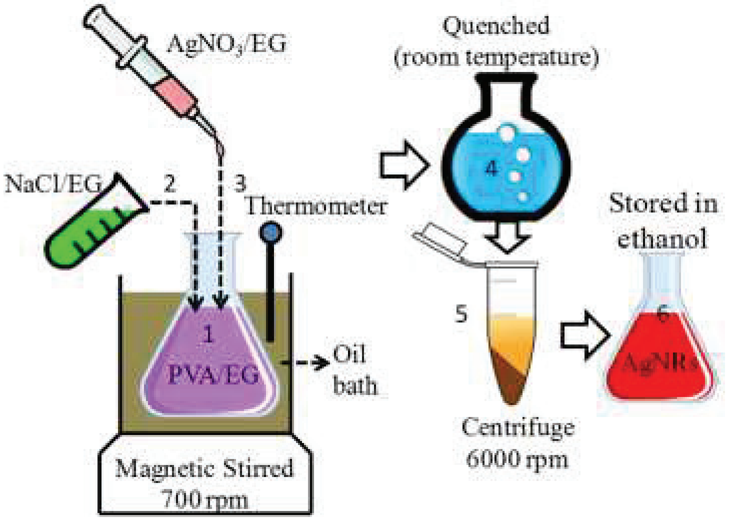

Fig. 1. Schematic of experiment procedure of polyol method [13]

Characterization of AgNRs: UV-vis spectrometer (Shimadzu, UV-1700) was used to measure the absorption spectrum of AgNRs solution in the wavelength range of 300 to 800 nm. Furthermore, the crystal structure of AgNRs was analyzed using XRD (Shimadzu R6000) by CuKα ($\lambda = 1.54184$ Å) with a scanning 2θ in the range of 20° to 90°. The morphology and size of AgNRs were observed using scanning electron microscopy (JEOL, JSM-6510) by accelerating voltage of 10 kV.

RESULT AND DISCUSSION

Many studies have investigated the effect of chloride ions on the synthesis of silver nanowires using polyol method.The research has been done by Wiley et al. showed the chloride ions isessentialfor the formation and growth ofAgNRs.When NaCl is added to the solution of ethylene glycol, then NaCl will unravel into ions of Na^+ and Cl^-. The sodium ions serve forremove oxygen from the solvent (EG) and prevent twinned seed decomposed and damaged by anoxidative etching process. When $AgNO_3$ was added drop by drop, Chloride ions will bind to Ag^+ ions and form silver chloride (AgCl) particles [14].

The chloride ion used forstabilizeon the growth process of the silver nanoparticles from aggregation and it can growth into AgNRs through Oswalt ripening [10]. The addition amount of chloride ions can also inhibit the formation of nitrate acid (HNO_3) during the synthesis process. With the addition of chloride ions, AgCl will be formed in a stable and in orderto form the multi-twin-particles. The formation process of AgCl nanoparticles can be controlled by controlling the reaction rate. Controlling the reaction rate may include temperature control, stirrer, and injection rate of $AgNO_3$ solution during the synthesis of AgNRs [15].

The use of PVA as a capping agent also should be extra attention. The presence of H^+ ions originating from the ring hydroxyl group from PVA may interfere with the formation process of MTPs into silver nanowires. Hydrogen ions can bind with NO_3 ions, thus multiplying the amount of nitric acid which can erode togenerateof MTPs. The best solution at this time to do is to give ethylene glycol in more amount. The addition of ethylene glycol volume will assist in the formation of Ag-O structure becomes more stable and orderly. Moreover, the addition of salt precursors in the form of sodium chloride, potassium bromide, copper (II) chloride, or iron (III) chloride to minimize the formation of nitric acid [16-18].

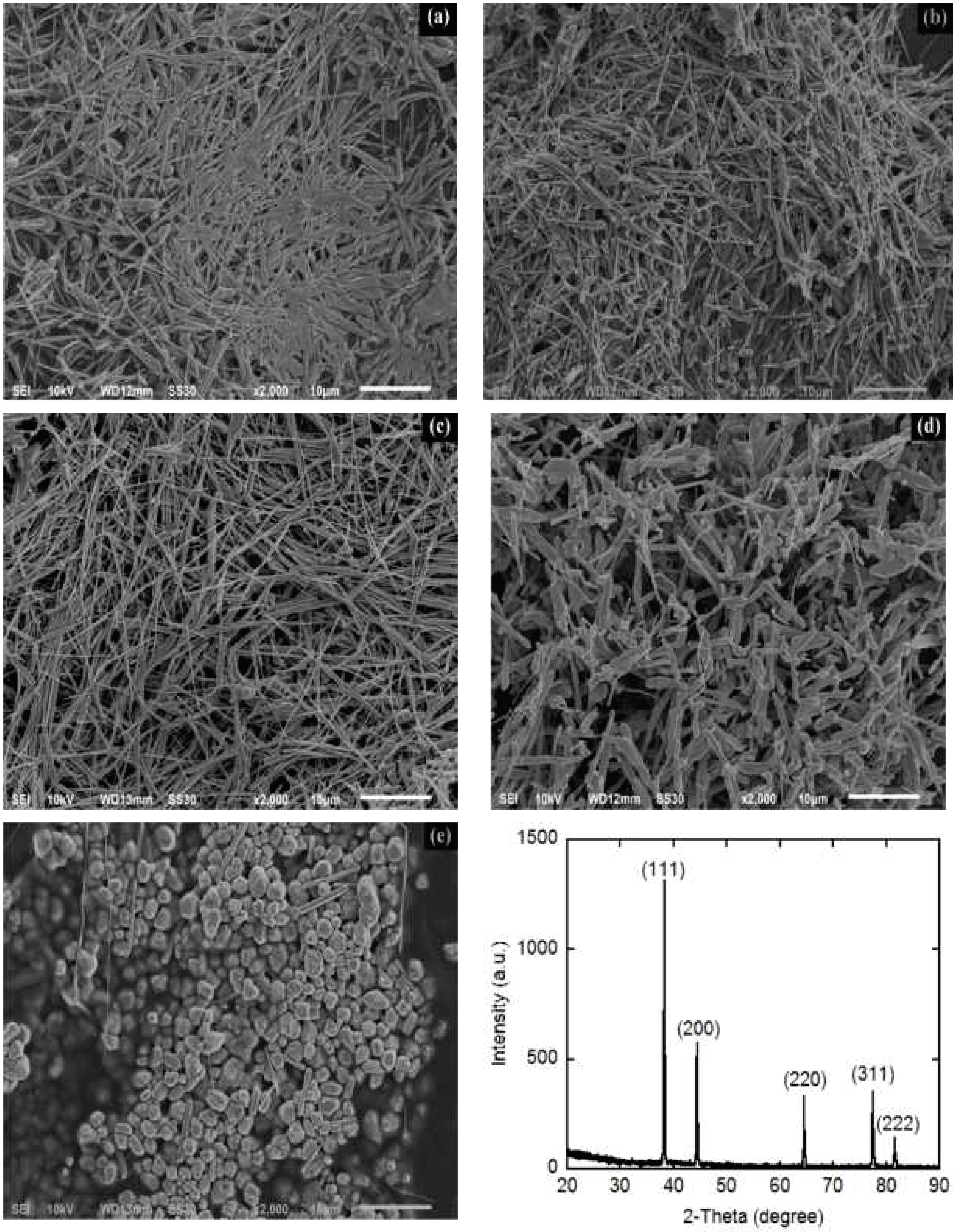

FIGURE 2. SEM images of silver nanorods (a) without ion chloride, (b) with ion chloride 5 mM, (c) with ion chloride 10 mM, (d) with ion chloride 15 mM, (e) with ion chloride 20 mM, and (f) XRD pattern of silver nanorods

Figure 2 shows SEM images during the reaction process without the addition of chloride ions. In this condition, only a small portion of HNO_3 degradable.The remainder of HNO_3 will continue to exist and can disrupt the process for establishingof multi-twinned-crystal seeds.The amount of HNO_3 is too much lead-crystal multi-twinned seeds can't grow into a silver nanowires.The nitric acid is poison that can damage the MTPs. If the nitric acid is not immediately eliminated, then the ability of the etching solution mixture will increase rapidly. When without the addition of chloride ions, diameter and length of AgNRsare about 365 nm and 10 to 15 µm, respectively (Fig 2(a)).

The concentrations of $HNO_3$are very high will destroy MTPs before growing into a silver nanowires and leaving a single crystal.In order to HNO_3 not formed in significant amounts, it must be the addition of alkalisuch as Na, K, Fe, or Pt. These metals will bind nitrate ions so as not to form nitric acid [19,20].Another method is to add oxygen or nitrogen gas during the reaction process. The addition of gases such as oxygen or nitrogen is able to prevent the formation of nitric acid. When oxygen or nitrogen gas is passed into the solution, then the NO_3^- ion will be oxidized and disappeared. This causes the decomposition process between the metallic silver with nitric acid occurs rapidly, so that MTPs can be maintained to grow into silver nanowires [21,22].

From the SEM images, the absence of chloride ions in solution during the reaction process led to the growth of Ag^+ ions into atoms Ag^0 be very fast and uncontrolled. This led, multi-twin-seeds can't grow optimally and the amount generated AgNRsbe a little amount because of the aggregation process. Therefore, we try to conduct experiments on the synthesis of AgNRs without and with the addition of the chloride ion concentration variations. In Fig 2(b), AgNRs addition, Ag nanoparticles in the micrometer size are still formed. This condition can be caused due to the concentration of chloride ions is lower, so that the rate of decomposition reaction Ag^+ ions into atoms Ag^0 to the formation of AgCl still faster. In this study, we obtain the optimum conditions for concentration of Cl^- ion is about 10 mM (Fig 2.c). For this condition, the AgNRs formed homogenously by diameter and length about 200 nm and 10 to 20 µm, respectively.

When the NaCl concentration was raised above 10 mM, the experimental results show that Ag nanoparticles with micrometer-order again dominate. In this condition, the size of AgNRs about 5 to 10 µm in length and ~670 nm in diameter (Fig 2(d)). As shown in Fig. 2(e), only slightly AgNRs formedfortheconcentrationof chloride ion of 20 mM. The final product is dominated by MTPs with micrometer sizes (1 to 3 µm).This can be attributed because of too many AgClparticlesformed and didn't grow into AgNRs so that these particles undergo precipitation. In addition, when the NaCl concentration is too high can lead to particle formation process AgClexperiencing saturation. Therefore, if the reaction rate becomes very slow, and MTPs can't grow into AgNRs.

Figure 2(f) shows the XRD pattern of AgNRs. There are five diffraction peaks representing peaks of Ag, which each angle of diffraction 2θ were at38.25° (111), 44.43° (200), 64.55° (220), 77.51° (311), and 81.65° (222). Compared with JCPDF-card number 04-0783 of ASTM, all the peaks identify the crystal structure of a face-centered cubic (fcc).The calculated lattice constant according to the spacing distance (d_{hkl}) of the {311} and {222} planes were 4.085 Å. This calculated lattice constant is very close to the literature value of 4.086 Å [13,24].

CONCLUSION

The addition of chloride ions for thesynthesisof the AgNRs can control the growth of silver chloride. When a number of chloride ions are added, the process of forming a multi-twined seeds more stable and prevent aggregation. Moreover, the presence of chloride ions, the amount of Ag nanoparticles be less because almost all Ag atoms are growing into AgNRs. In this study, the AgNRs have a length of 10 to 20 µm with diameter AgNRs decreased from 365 nm to 200 nm and uniformly.

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