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STRUCTURAL DEPENDENCE OF SILVER NANOWIRES ON DIFFERENT MEDIATED SALT

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Abstract

Silver nanowires (AgNWs) has been synthesized by polyol process through different mediated salts such as Copper II Chloride ($CuCl_2$), Sodium Chloride (NaCl), Potassium Chloride (KCl). The presence of cations and anions (Cu (II)+, Na+, K+ and Cl-) makes strong impact on the shape of silver nano structures. The surface morphologies and crystallinity of silver structure are analyzed by Scanning Electron Microscopy (SEM) and X- Ray Diffraction (XRD). SEM results revealed that the diameter and length of silver nanowires. XRD pattern displayed the final product was highly crystallized and pure. The synthesis of silver nanowires is important to achieve high performance transparent conductive films.

Keywords: Polyol synthesis method, mediated salt, silver nanoparicles, silver nanowires

Introduction

One-dimensional (1-D) metal nanostructures such as nanowires have attracted extensive attention due to their unique magnetic, optical, and electronic properties compared to zero-dimensional (0-D) nanostructures (Xiao, Y.A, 2007). Current noteworthy materials for ITO substitution are carbon nanotubes (CNTs), graphene, transparent conductive polymers, metal grids, and random meshes of metal nanowires. Ag NWs with well-defined shapes such as lengths and diameters are particularly interesting, as they have superior optical and electrical properties, thus making them excellent candidates for transparent electrodes (Lee, H-H, 2005). Transparent conductive polymers have interesting properties like high flexibility, low cost and light weight. Several companies have been trying to use them in various devices such as touch panels and organic electronics. However, in order to implement the optical and electrical features required for transparent electrodes, there is still a need to develop more effective processes for synthesizing Ag NWs with controllable shapes and sizes. In these regards, the synthesis of nanowires has attracted attention from a broad range of researchers (Dang, C. M., 2012). Over the last decade, various methods had been used to synthesize AgNWs such as polyol process, wet chemical synthesis, hydrothermal method and ultraviolet irradiation photo reduction techniques (Młoniak, A, 2011). Among these methods, the polyol process is considered due to simple, effective, low cost, and high yield. By controlling the parameters such as reaction time, molar ratio between capping agent and metallic precursor, temperature, and addition of control agent, a reasonable control growth of AgNWs may be achieved. In this work, silver nanowire preparing by this methods strongly depends on the parameters of the synthesis procedure such as the reaction temperature, the molar ratio between PVP and $AgNO_3$, PVPs with different chain lengths, the seeding condition and shielding gas, the additive of the control agents and the stirring speed (Maringan,C.S, 2016). AgNWs were synthesized through reducing silver nitrate ($AgNO_3$) and ethylene glycol (EG) in the presence of polyvinylpyrrolidone (PVP) as the surfactant which can direct the growth of AgNWs and protect them from aggregation. The mediated agents such

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as $CuCl_2$, NaCl and KCl are added to facilitate the growth of AgNWs. We believe Cu (II), Na+, and Cl− ions are necessary for AgNWs production.

Experimental

2.1 Materials

All chemicals such as Silver Nitrate ($AgNO_3$, 99.9%), Ethylene Glycol (EG, 95.5 %), PVP (MW: 1300000), and Potassium Chloride (KCl), Sodium Chloride (NaCl) and Copper (II) Chloride ($CuCl_2$ anhydrous, 99.0%), anhydrous Ethanol (Ethos) and acetone were used as received without any purification.

2.2 Synthesis of Silver Nanowires

The polyol method is a cheap and simple method of synthesizing high quality silver nanowires in solution. In this method, a solution of ethylene glycol (EG), polyvinyl pyrrolidone (PVP) and different mediated salts (KCl, NaCl and $CuCL_2$) is heated to 170 °C and a mixture of $AgNO_3$ and EG is gradually added. Adding $AgNO_3$ to the solution leads to the creation of Ag^+ ions which results in the formation of nanoparticles. Silver nanowire were synthesized by reducing $AgNO_3$ as metal precursor salt in Ethylene Glycol (EG) which was used as not only reducing agent but also solvent and PVP as a capping agent. The first sample (Sample 1) is synthesized without any mediated salt. $AgNO_3$ solution (94 mM, in EG) and PVP solution (1300K) (147 mM, in EG) were completely dissolved by using magnetic stirring at room temperature. First, 30 mL of EG in a flask was heated at 170°C in a heating mantle with stirring rate 150 rpm for 30 minutes. After 30 minutes, mixed PVP/ethylene glycol was added to prepared solution, followed by $AgNO_3$ /ethylene glycol drop wise to the solution over dropping at a rate of 1ml min^{-1}. After adding all reagents, the mixture turned yellow indicating the appearance of silver nanoparticles. The reaction continue for 2 hours until the reaction finished completely with formed slightly gray-white suspensions. The sample marked as Sample 1 (S1).

The second sample (S2) is synthesized with KCl as the mediated agent. First 30 mL of EG in a flask was heated at 170°C in a heating mantle with stirring rate 150 rpm for 30 minutes. After 30 minutes, KCl solution was dropped into heated EG and then the reaction temperature was reduced to 110°C. At 110°C, mixed PVP/ethylene glycol was added to prepared solution, followed by AgNO3 /ethylene glycol drop wise to the solution over dropping at a rate of 1ml min-1. After adding all reagents, the mixture turned yellow indicating the appearance of silver nanoparticle. The reaction mixture was maintained at 110°C for 10 minutes until all $AgNO_3$ had been completely reduced. And then, the temperature was increased to 170ºC within 10 min for nanowire growth and the solution became gray gradually. The reaction continue to down at 150ºC for 40 minutes until the reaction finished completely with formed slightly gray-white suspensions. The sample marked as Sample 2 (S2). For Sample 3 (S3) and Sample 4 (S4) was synthesized by using NaCl and $CuCl_2$ as a mediated salt. The synthesis procedure was exactly the same as Sample 2 (S2). The product was diluted with acetone (1:5 by volume) and centrifuged at 3000 rpm for 20 min. The supernatant containing silver particles could be removed using a pipette. This centrifugation procedure could be repeated three times with ethanol. Purified silver nanowires solution was mixed with 2-propanol (1:1v/v) and sonicated for 15 minutes to get homogeneous ink solution. This solution was coated on glass substrates by rod coating method. This method is inexpensive and easy to use; just one wire-wound rod is enough for fabrication so there is no need for any complex equipment. The thickness of the deposited solution is determined by the diameter of the wire that is wound around the main rod. The density of the nanowires in the electrode was controlled both by the concentration of the nanowire solution and the number of layers deposited. After nanowire deposition, the film was dried in air. Nanowire films on glass substrates were annealed at 200°C for 30 minutes to get maximum conductivity by sintering the nanowire junctions.

Results and Discussions

This research provide the easiest way to synthesize thin and long silver nanowires with high yield within one hour after adding all reagents. In this synthesis procedure, 90% of the major product was wires and the less was different size of rod and particles. This experimental result shows that, without adding other metal salts as the source of seeds and appropriately reducing the molar concentration of silver nitrate, it is possible to produce silver nanoparticles. Other metal salt such as Potassium Chloride (KCl), Sodium Chloride (NaCl) and Copper (II) Chloride ($CuCl_2$) are necessary to produce silver nanowires.

3.1. XRD and SEM Analysis of Silver Nanostructures

XRD analysis are performed to determine the nature of silver nanostructures. After the preparation of nanowires, the suspension of nanowires in ethanol was used for SEM analysis by fabricating a drop of suspension onto a clean glass substrate and allowing ethanol to completely evaporate. The surface morphology of silver nanowires were observed by using Scanning Electron Microscope (JEOL- JSM 5610 LV) with the accelerating voltage of 15 kV, the beam current of 50 mA and 10000 time of photo multiplication. SEM showed that the silver products varied with the type of mediated salts used in the $AgNO_3$, PVP, mediated salts, Ethylene glycol and water.

Simple silver nanoparticles were obtained from no salts. Figure 1 shows the absorption spectra of silver nanostructures by using the precursor of PVP to $AgNO_3$ without mediated salt. SEM images show that spherical shaped silver nanoparticles have relatively uniform average diameter equal to 120 nm.

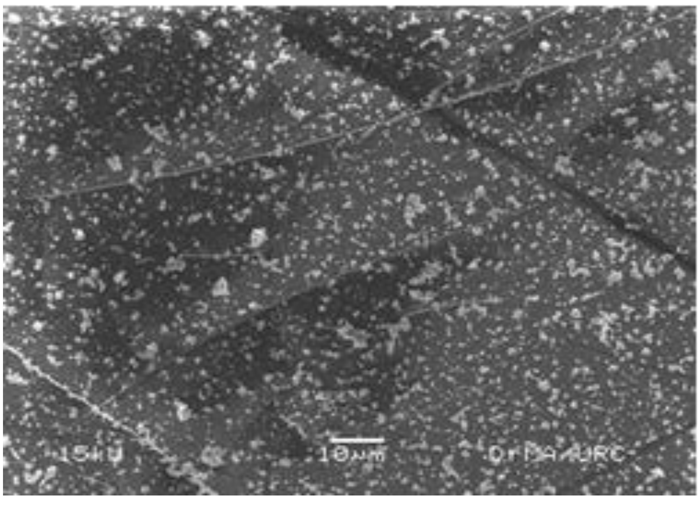

Figure 1 SEM image of silver nanoparticles (without any salt)

Figure 2 shows the final product synthesized under this particular condition that is using mediated salt KCl was a mixture of AgNps and AgNWs. This implies that the final product synthesized under this particular condition that is using mediated salt was a mixture of AgNps and AgNWs. Figure 2(a) XRD pattern reveals that the ratio of intensity between (111) and (200) peaks reveals a relatively high value of 4.5. It is obvious that using of KCl as mediated agent affected ratio of intensity between panels and it shows the crystallinity in this method increased. Figure 2(b) shows SEM images of silver nanostructures synthesized with KCl as mediated agent. SEM image show that the high yield of spherical shaped silver nanoparticles accompanied with some nanowires. AgNWs with very low yield and relatively uniform average diameter equal to 100 nm length around 10 μm.

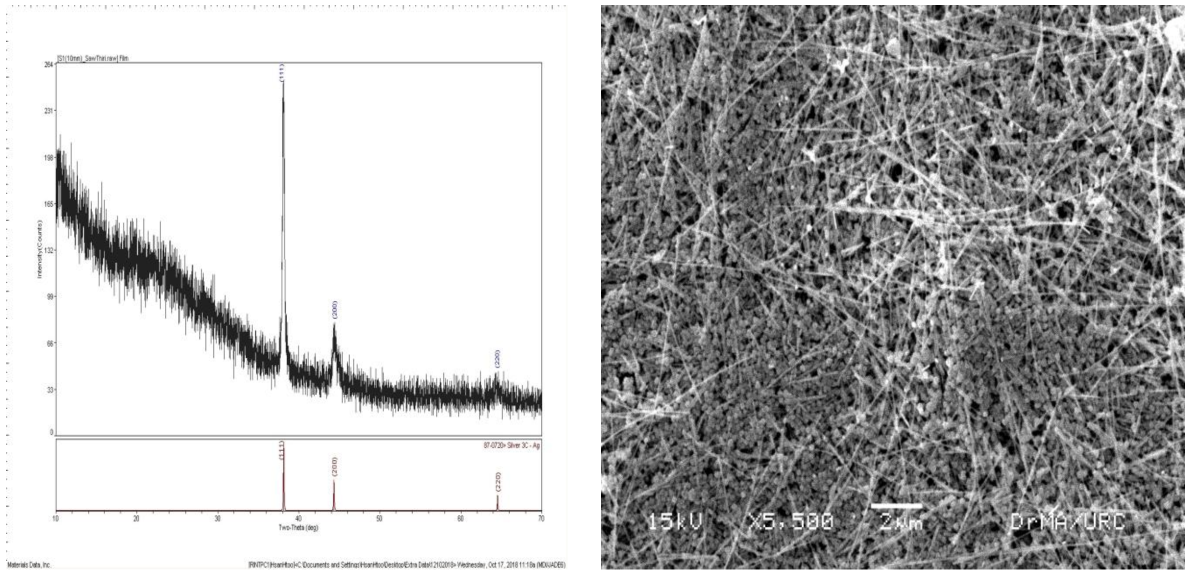

Figure 2 (a) XRD pattern of purified silver nanostructure
(b) SEM image of silver nanostructures with mediated salt KCl

Figure 3 shows the silver nanowires synthesized from the procedure in which $CuCl_2$ as the mediated salt. The final product synthesized under this particular condition that is using $CuCl_2$ of mediated salt gives mixture of nanowires and nanoparticles. Figure 3(a) XRD pattern reveals that the ratio of intensity between (111) and (200) peaks reveals a relatively high value of 6.5. Figure 3(b) shows the SEM image of silver nanostructures synthesized with $CuCl_2$ mediated salt. By using $CuCl_2$ mediated salt, the main products are the spherical silver nanoparticles (25%) besides there is a long wire shaped form with very low yield and relatively uniform average diameter equal to 88 nm and length more than 120 μm.

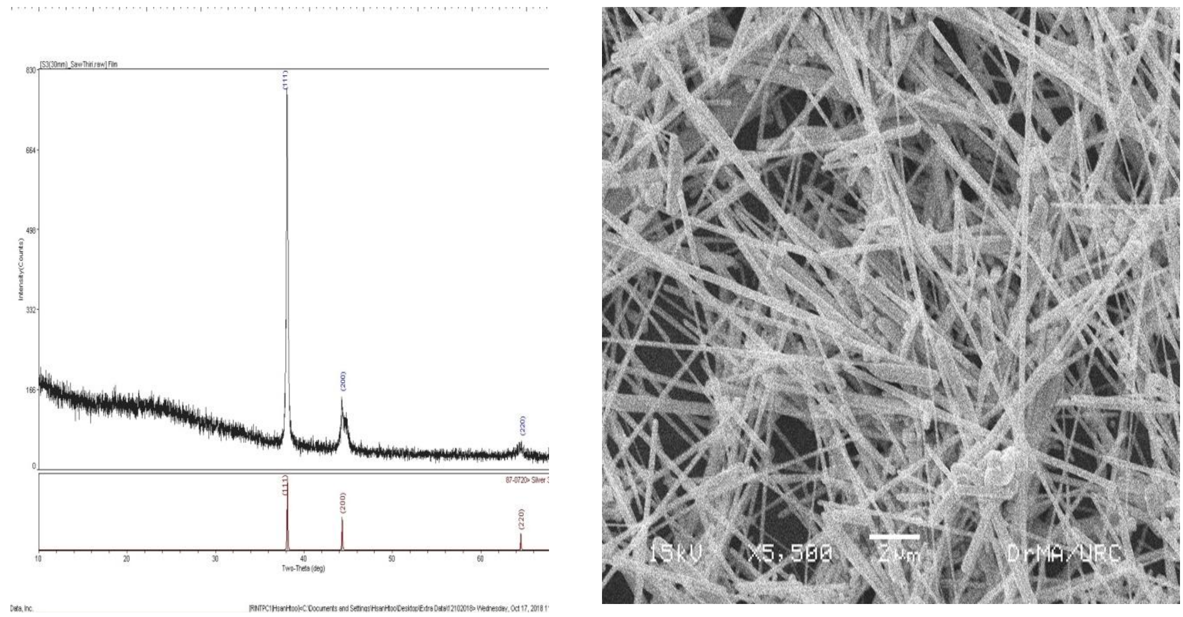

Figure 3 (a) XRD pattern of purified silver nanostructure
(b) SEM image of silver nanowires with $CuCl_2$ as the mediated agent

Figure 4 shows the SEM image of silver nanowires with NaCl as the mediated agent. Figure 4(a) the ratio of intensity between (111) and (200) peaks reveal a relatively high value of 6.8. It is obvious that using of NaCl as mediated agent affected ratio of intensity between panels and it shows the crystallinity in this method increased. Figure 4(b) shows SEM images of silver nanowires synthesized with NaCl as mediated agent. The image reveals that the product is entirely composed of uniform nanowires with very high yield and relatively uniform average diameter equal to 88 nm and length up to 150 μm.

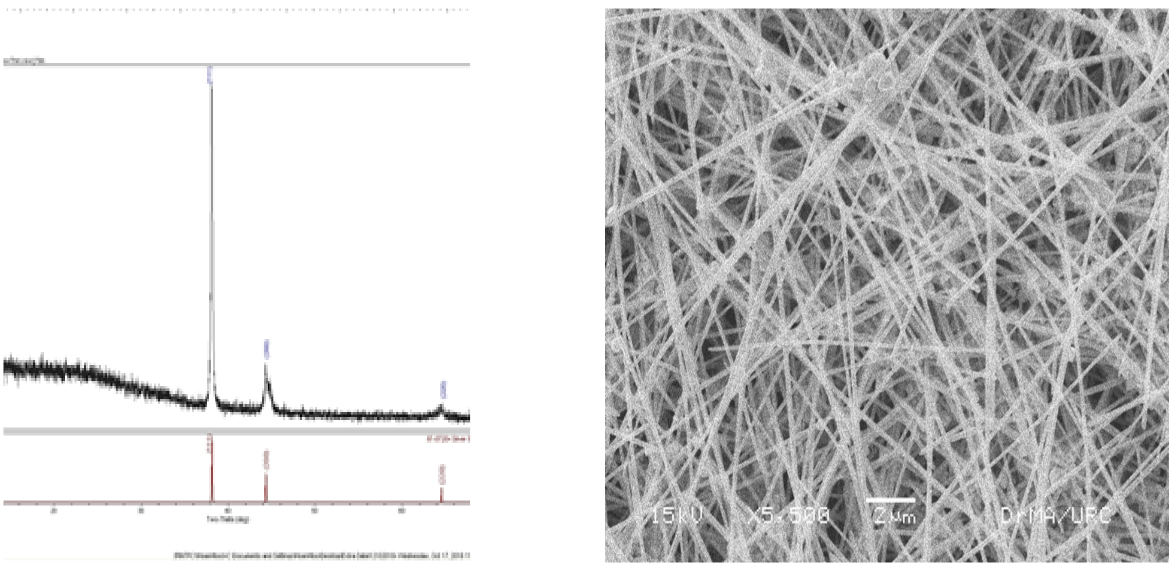

Figure 4 (a) XRD pattern of purified silver nanowires
(b) SEM image of silver nanowires with NaCl as the mediated agent

SEM showed that the structure and yield silver products varied with different of mediated salts used in the $AgNO_3$/PVP/mediated salts/Ethylene glycol system. The SEM images show that there are no mediated salt in synthesis procedure, the AgNWs are not achieved, and the majority of the structures are AgNps. By using KCl mediated salt, the main products are the spherical AgNps (50%) besides there are different length of silver nanostructure. As the $CuCl_2$ salt amount increases from the main products are the spherical silver nanoparticles (25%) besides there are different shaped of metal nanostructure. The average diameter of the nanowire is equal to 100 nm and length up to 100 μm. Figure 4 show the SEM image of AgNWs with NaCl as the mediated agent. The image reveals that the product is entirely composed of AgNWs. The diameter of the nanowire is around 88 nm and length up to 150 μm.

The phase composition and the crystallite size of the prepared samples were evaluated by X-ray diffraction analysis. The peaks of samples were identified by comparison with PDF-71-1166 according 2θ which confirmed that an anatase structure at angles of 2θ = 37.924°, 44.126° and 64.207° correspond to the (111), (200), and (220) crystal planes of the face center cubic (FCC) Ag, respectively. The lattice constant calculated from the diffraction pattern was 24.48 nm. The XRD pattern reveals that the synthesis silver nanowires through polyol process comprise pure phase. It exhibits well-defined peaks without any impurity element peaks detected. This indicated the success in the formation of the crystalline silver nanowires.

Table Silver nanostructures By Using Different Mediated Salts

Sample	**Different Mediated Salts**	**Structure**	**Diameter**	**Length**
S 1	No salt	Nano Particles	120nm	_
S 2	KCl	Particles and short wires	100nm	10μm
S 3	$CuCl_2$	Particles and long wires	88nm	120μm
S 4	NaCl	High yield	88nm	150μm

Conclusion

AgNWs were successfully synthesized by using polyol technique with different salt-mediated process. Without the mediated agents, the final product synthesized was AgNps. It was found that the addition of KCl or NaCl and $CuCl_2$ to the polyol reduction of $AgNO_3$ in the presence of PVP greatly facilitated the formation of AgNWs. Both the cation and the anions are crucial for the successful production of silver nanowires. A certain amount KCl or $CuCl_2$ mediated salts produce high yield of ultralong AgNWs, otherwise, a mixture of AgNps and AgNWs were obtained. The right amount of NaCl mediated salt is crucial for the successful production of AgNWs.

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