SYNTHESIS OF SILVER NANOWIRES USING NACL ASSISTED ETHYLENE GLYCOL MEDIATED POLYOL METHOD

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Abstract

The synthesis of silver nanowires (AgNWs) from $AgNO_3$ through ethylene glycol mediated polyol process with the assisted of polyvinylpyrrolidone (PVP) and a NaCl. The surface morphologies and crystallinity of silver nanoparticles are analyzed by Scanning Electron Microscopy (SEM), XRD and UV-Vis. The UV-Vis spectra showed the typical surface plasmon absorption maxima around 465 nm, 436 nm, 414 nm, 399 nm and 350nm. SEM results revealed that the diameter of silver nanowires (AgNWs) were 100 nm and length up to 150μm accompanied with silver nanoparticles (AgNps). XRD studies reveal a high degree of crystallinity and monophase silver nanowires (AgNWs). The polyol synthesis of silver nanowires (AgNWs) produce ultralong and thin nanowires.

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

Introduction

Materials with high transparency, flexibility, and conductivity are important for progressing optoelectronic applications such as solar cells, infrared reflectors, flat panel displays, touch screens, and organic light emitting diodes. Ideally transparent electrodes would be highly transparent, easily fabricated, and serve as efficient electron acceptors with low resistivity. To date, the dominant material of the transparent conductive electrode (TCE) is indium tin oxide (ITO). However, limitation of ITO such as its scarcity, expensive price, brittleness and complicated process in the vacuum environment resulted in not only extremely intensive energy but also economically expensive of using ITO during thin film fabrication process. Moreover, flexing of ITO electrodes alters the homogenous coverage over the flexible substrate resulting in cracking and reduced performance over time. Therefore, there are some emerging alternatives, such as carbon nanotubes, graphene, conducting polymers, and metal nanowires with high conductivity

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and transmissivity to replace with ITO. One-dimensional (1-D) metallic nanostructure, namely silver nanowires (AgNWs), has exhibited for their unique materials in building macroscale flexible conductors because of their high conductivity, good flexibility, and mature preparation technology, and various flexible conductive materials and devices have been fabricated on the basis of silver nanowires. However, in order to implement the optical and electrical features required for flexible and transparent electrodes, there is still a need to develop more effective processes for synthesizing AgNWs with controllable shapes and sizes, which can be grown continuously up to get long and thin AgNWs. For wider industrial applications of AgNWs, a simple and scalable preparation process is required.

Various synthetic methods for AgNWs have been investigated over the past decade. Until now, the most widely used methods is polyol method. The polyol method is becoming the most promising synthesis for preparing AgNWs by virtue of their various advantages such as their homogeneous reaction. This method is simple, but the great attention must be needed to make stable and reproducible colloid. Solution temperature, concentrations of the metal salt and reducing agent, reaction time influences particle size. Controlling size and shape of metal nanoparticles remains a challenge.

Silver nanowires 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.

In this paper, one pot synthesis of modified polyol-mediated processes have been used for the synthesis of ultralong silver nanowires within reaction time one hour after completing the all reagents. Moreover, optical and electrical properties of air dried ultralong AgNWs thin films are reported. Further, the structural, chemical properties of these two different structures of ultralong AgNWs were examined.

Experimental

Silver Nitrate (AgNO3, 99.9 %), Ethylene Glycol (EG, 95.5 %), Polyvinyl pyrrolidone (PVP) (MW: 1300,000), and sodium chloride (NaCl anhydrous, 99.0%), anhydrous ethanol (EtOH), Acetone were used as received without any purification.

Silver nanowires 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) was synthesized without any mediated salt, NaCl. $AgNO_3$ 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, NaCl solution was dropped into heated EG and then the reaction temperature was reduced to 110°C. After 10 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}. The magnetic stirring was completely stopped when the $AgNO_3$ solution was added. After adding all reagents, the mixture turned yellow indicating the appearance of AgNps. 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 minutes 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 S1 (S1). For Sample 2 (S2), Sample 3 (S3) and Sample 4 (S4) was synthesized by using Sodium Chloride (NaCl 10 mM, 20 mM and 30 mM, in EG) as a mediated salt before adding starting precursor. The synthesis procedure was exactly the same as Sample 1 (S1). The product was diluted with acetone (1:5 by volume) and centrifuged at 3000 rpm for 20 minutes. The supernatant containing silver particles could be removed using a pipette. This centrifugation procedure could be repeated three times with ethanol until the supernatant became colorless. The collected precipitates redispersed in ethanol for further used and some were dried oven at 60ºC for further characterization.

Centrifuge machine (Kokusan H-200 series) was used to separate the nanowires from the solutions. The surface morphology of AgNWs 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. The crystalline properties for drop coated glass thin film of silver nanostructures were analyzed by using Cu K-α 1 radiation (40 kV, 40 mA) in 2θ range from 10°C to 70° C on a Rigaku powder X-ray diffractometer (RINT 2000) equipped with a diffracted-beam graphite monochromator.

Results and Discussions

The merit of this research provide the easiest way to synthesize thin and long AgNWs with high yield within one hour after adding all reagents. Different aspect ratios of AgNWs were obtained by using different amount of NaCl with exactly the same experimental procedure.

After the preparation of samples, 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 crystallite domain diameters D were obtained from XRD peaks according to the Scherrer equation: $D = \frac{0.9\lambda}{W cos\theta}$ where λ is the wavelength of the incident X-ray beam (1.54056 Å for Cu K-α 1), θ is the Bragg's reflection angle , ΔW is the full width at half maximum. Crystallinity is evaluated through comparison of crystallite size as ascertained by SEM particle size determination. Crystallinity index Equation is presented as following $I_{crystal} = \frac{D_{p(SEM,TEM)}}{D_{XRD}}$ where $I_{crystal}$ is the crystallinity index; D_p is the particle size (obtained from either TEM or SEM morphological analysis); D_{XRD} is the crystallite size (calculated from the Scherrer equation).

Sample 1

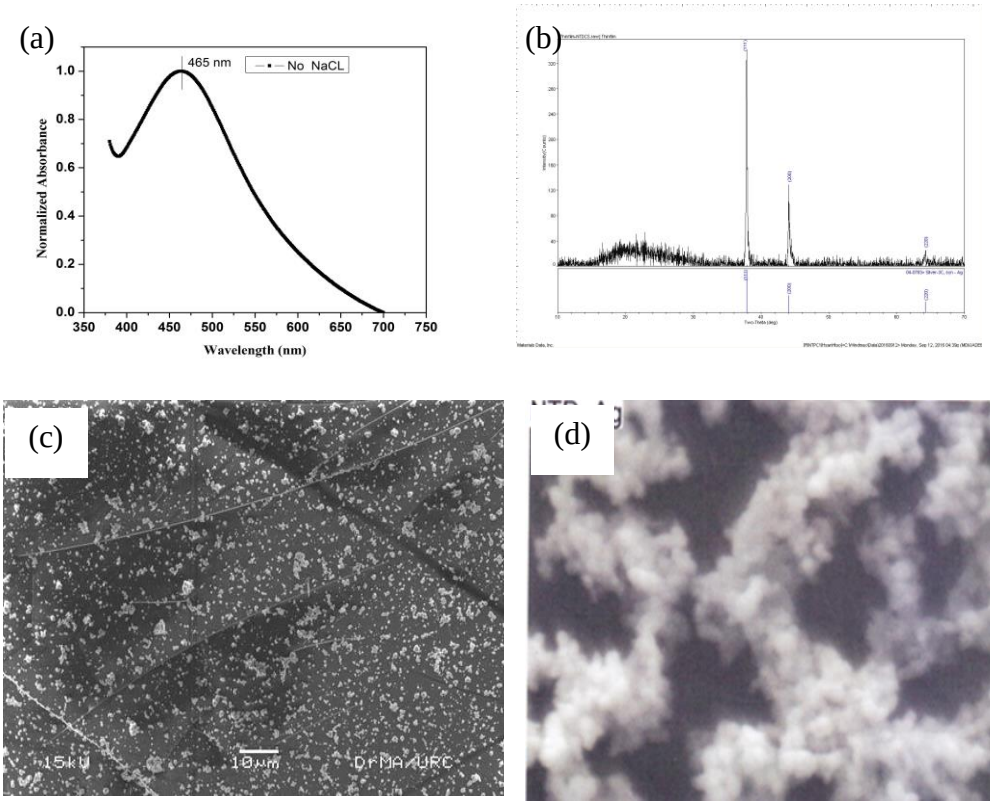


Figure1: (a) The UV-Vis absorption spectrum of AgNps without any mediated salt (b) XRD pattern of purified AgNps (c) low (d) high magnification SEM micrograph of AgNps solution without any mediated salt

Figure 1(a) shows the absorption spectra of silver nanostructures by using the precursor of PVP to $AgNO_3$ without mediated salt. The appearance of surface plasmon resonance (SPR) which can be attributed to the collective oscillation of conduction electrons that is induced by an electromagnetic field at 465 nm indicated the formation of AgNps. The symmetric shape of the SPR band indicates the formation of spherically shaped Nps, and the long tail in the red region indicates the formation of polydisperse size of Nps. The X-ray diffraction pattern of the silver nanoparticles synthesized by polyol method is shown in Figure 1 (b). A number of strong Bragg reflections can be seen

which correspond to the (111), (200), and (311) reflections of FCC silver. No spurious diffractions due to crystallographic impurities are found, only monophase silver agrees with the XRD data (ICDD-PDF#04-0783). The high intense peak for FCC materials is generally (111) reflection, which is observed in the sample. The lattice constant calculated from the diffraction pattern was 0.4086 nm, which is in agreement with the reported value of silver (JCPDS 04-0783). From XRD data, the ratio of intensity between (111) and (200) peaks reveals a relatively same value of 2.25 compared to the theoretical ratio value of 2.5. The crystallite size of the silver nanoparticles estimated from the Debye–Scherrer formula is 24 nm. SEM images show that the spherical shaped silver nanoparticles have relatively uniform average diameter equal to 100 nm.

Sample 2

Figure 2(a) shows the UV-Vis absorption spectra of AgNWs with NaCl 10 mM as mediated agent. As NaCl salt 10 mM was added to synthesis procedure, the SPR peak around 465 nm (sample 1) is blue-shifted to 414 nm. This implies that the final product synthesized under this particular condition that is using mediated salt was a mixture of AgNps and AgNWs. The UV spectrum had a main absorption at 414 nm with a shoulder at 350 nm. These two absorption bands were ascribed to the surface plasmon resonance bands of the transverse and longitudinal modes of the silver nanowires and nanoparticles. Figure 2(b) 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 NaCl 10 mM as mediated agent affected ratio of intensity between panels and it shows the crystallinity in this method increased. Figures 2(c) and 2(d) show high and low magnification SEM images of silver nanostructures synthesized with NaCl 10 mM as mediated agent. SEM images 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.

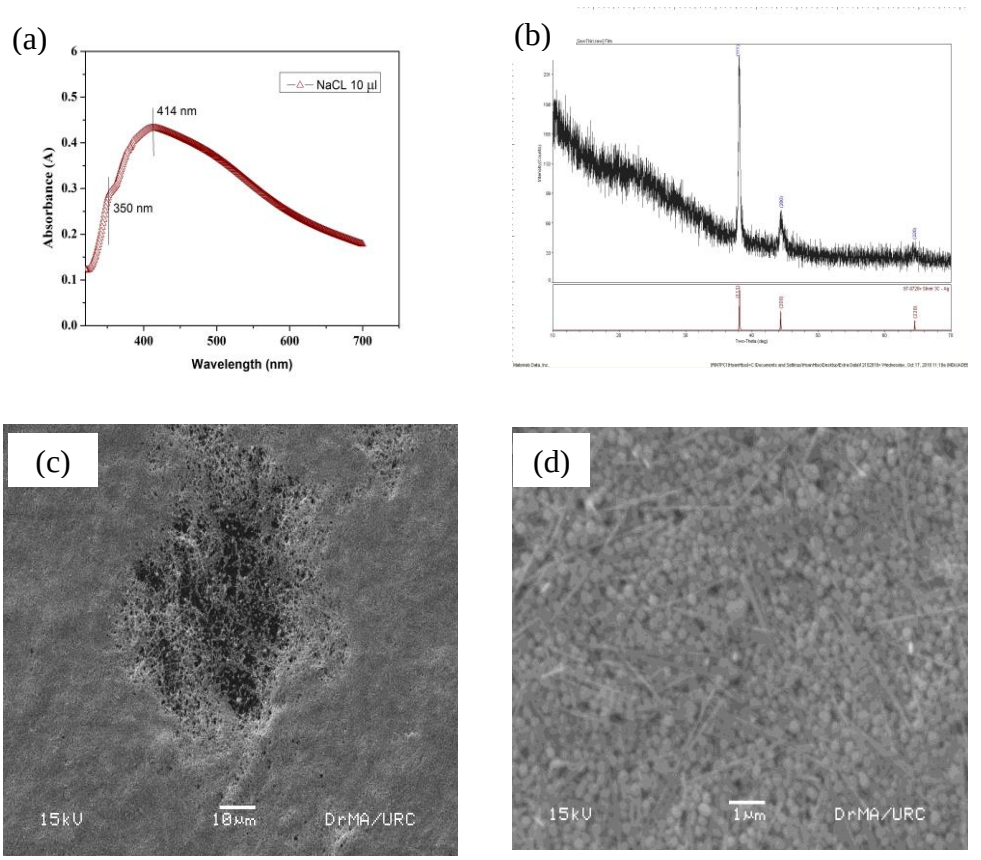


Figure 2: (a) The UV-Vis absorption spectrum of AgNWs : at 414 nm and 350 nm were attributed to the plasmon resonance peaks of silver with various origins: surface plasmon of nanoparticles, long nanowires similar to the bulk silver (b) XRD pattern of purified silver nanostructure (c) low and (d) high magnification SEM micrograph of Ag nanostructure solution with 10 mM of NaCl mediated salt

Sample 3

Figure 3(a) shows the UV-Vis absorption spectra of AgNWs with NaCl 20 mM as mediated agent. As NaCl salt 20 mM was added to synthesis procedure, the SPR peak around 414 nm (sample 2) is blue-shifted to 399 nm.

The peak positioned at 399 nm could be considered as the optical signature of relatively long AgNWs. This implies that the final product synthesized under this particular condition that is using 20 mM mediated gives a high of yield of AgNWs. Figure 3(b), XRD pattern reveals that the ratio of intensity between (111) and (200) peaks reveals a relatively high value of 6.5. It is obvious that using of NaCl 20 mM as mediated agent affected ratio of intensity between panels and it shows the crystallinity in this method increased. Figures 3(c) and 3(d) show high and low magnification SEM images of silver nanostructures synthesized with NaCl 20 mM as mediated agent. SEM images show AgNWs with very high yield and relatively uniform average diameter equal to 100 nm and length up to 150 µm.

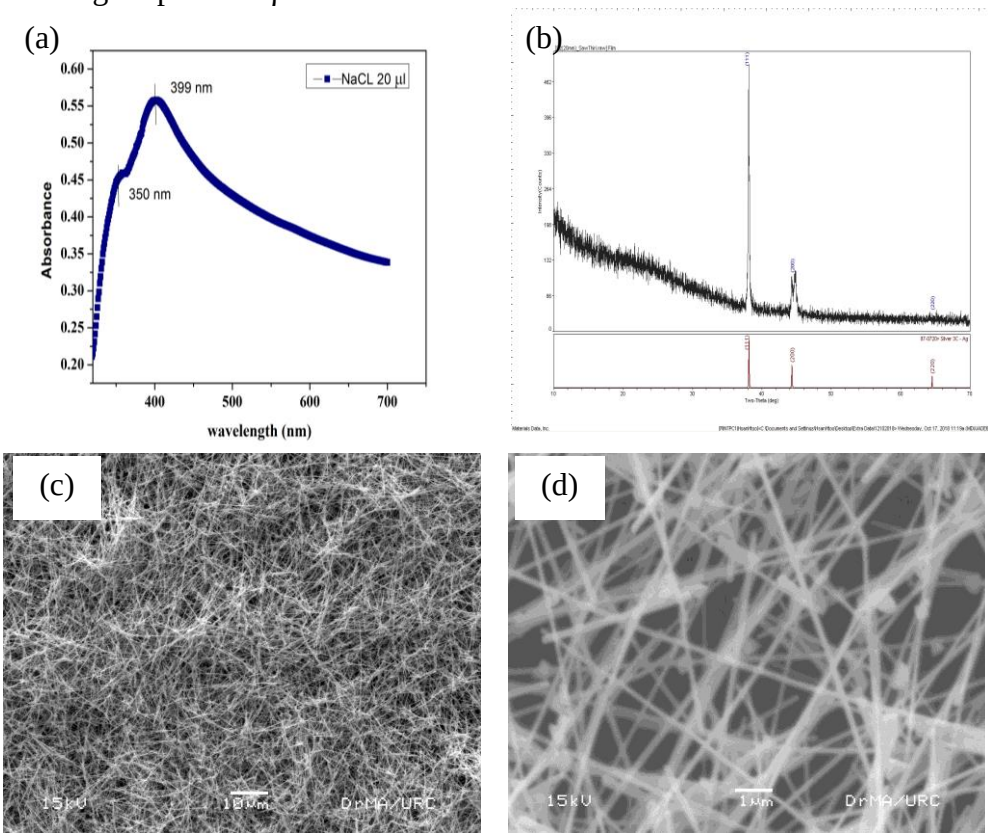
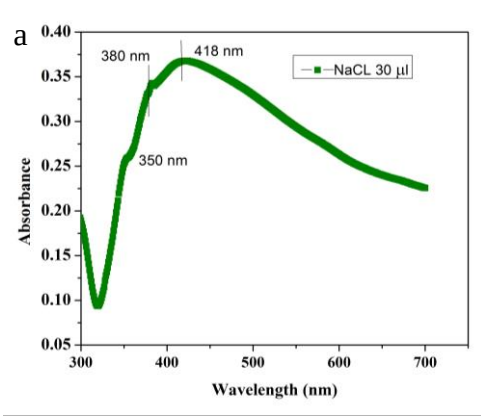
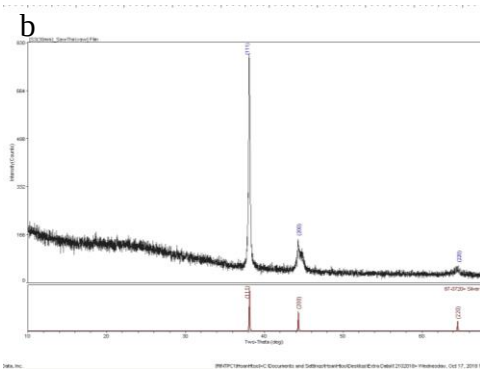


Figure 3: (a)The UV-Vis absorption spectrum of AgNWs: at 399, and 350 nm were attributed to the plasmon resonance peaks of silver with various origins: transverse mode of nanowire, long nanowires similar to the bulk silver (b) XRD pattern of purified silver nanostructure (c) low and (d) high magnification SEM micrograph of AgNWs solution with 20 mM NaCl mediated salt

Sample 4

Figure 4(a) shows the UV-Vis absorption spectra of AgNWs with NaCl 30 mM as mediated agent. As the NaCl salt amount increases from 20 mM to 30 mM, the SPR peak around 399 nm is red-shifted to 411 nm. The UV spectrum had a main absorption at 418 nm with a shoulder at 380 nm and 350 nm. The main absorption 418 nm indicated the formation of AgNps and shoulder peak at 380 nm and 350 nm ascribe to the surface plasmon resonance bands of the transverse and longitudinal modes of the AgNWs. The final product synthesized under this particular condition that is using 30 mM of mediated salt gives mixture of nanowires and nanoparticles. Figure 4(b) the ratio of intensity between (111) and (200) peaks reveals a relatively high value of 6.8. It is obvious that using of NaCl 30 mM as mediated agent affected ratio of intensity between panels and it shows the crystallinity in this method increased. Figures 4(c) and 4(d) show high and low magnification SEM images of silver nanostructures synthesized with NaCl 30 mM as mediated agent. SEM images show AgNWs with very low yield and relatively uniform average diameter equal to 88 nm.





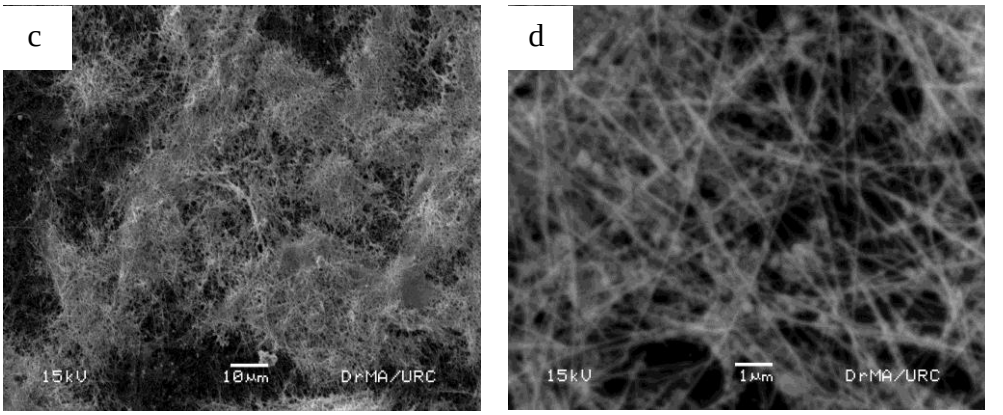


Figure 4 (a) The UV-Vis absorption spectrum of AgNWs: at 399, and 350 nm were attributed to the plasmon resonance peaks of silver with various origins: transverse mode of nanowire, long nanowires similar to the bulk silver (b) XRD pattern of purified silver nanostructure and the intensity of two distinct peaks show high aspect ratio (c) low and (d) high magnification SEM micrograph of AgNWs solution with 30 mM NaCl mediated salt

Different amounts (0 mM, 10 mM , 20 mM and 30 mM) of NaCl mediated salts in the synthesis procedure give the maximum SPR peak around 465 nm, 414 nm, 399 nm and 418m. The maximum of the plasmon peaks ~ 418 nm, ~ 399 nm, and 414 nm which were always described as the transverse mode of AgNWs or nanorods. The shoulder peaks at 350 nm could be considered as the optical signature of ultralong AgNWs. This implies that the final product synthesized under this particular condition that is using mediated salt was a mixture of AgNps and AgNWs. Moreover, with fragmentation of rod-like branches, the trunks of silver dendrites can convert into long NWs, which would support a blue-shift optical style of the plasmon peak. These results are consistent with the XRD results: with increasing the aspect ratio, the transverse SPR band shifts slightly to the blue side. By using 20 mM salt in the synthesis procedure, the plasmon peak shifts to ~ 399 nm and the plasmon band becomes relatively narrow.

SEM showed that the structure and yield silver products varied with the molarity 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 10 mM NaCl mediated salt, the main products are the spherical AgNps (96%) besides there are different length of silver nanostructure. Figure 3(c) and (d) show the SEM image of AgNWs with NaCl (20 mM,in EG) as the mediated agent. The image reveals that the product is entirely composed of AgNWs. The diameter of the nanowire is around 100 nm and length up to 150 μm. As the NaCl salt amount increases from 20 mM to 30 mM, the main products are the spherical silver nanoparticles (50%) besides there are different shaped of metal nanostructure. The average diameter of the nanowire is equal to 88 nm and length up to 100 μm.

According to XRD results, all the reflections correspond to pure silver metal with face centered cubic symmetry. The high intense peak for FCC materials is generally (111) reflection, which is observed in the sample. The intensity of peaks reflected the high degree of crystallinity of the silver nanoparticles. The calculation results shows that the crystallinity index of the sample that scored higher than 4.0 by using mediated salt; NaCl. If $I_{crystal}$ value is close to 1, then it is assumed that the crystallite size represents monocrystalline whereas a polycrystalline have a much larger crystallinity index greater than 1. The silver nanostructures show poly crystalline nature. The intensity ratio of (111) to (200) of around 6.5 is much larger than the theoretical value of 2.2, indicating that the intensity of the (200) peak was much smaller than expected. The XRD data suggest that the silver nanowires grew preferentially along the [110] direction.

Conclusion

In conclusion, a simple, fast, and economical polyol method to synthesize silver nanoparticles is presented. There is no need to use high pressure, energy, temperature, toxic chemicals, downstream processing etc. Handling of the nanowires is also much easier than other methods. AgNWs were successfully synthesized by using polyol technique with mediated

agents. It was found that the addition of NaCl to the polyol reduction of $AgNO_3$ in the presence of PVP greatly facilitated the formation of AgNWs. Without the mediated agents, the final product synthesized was AgNps. A certain amount 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. The synthesized AgNWs are in diameter of around 100 nm and length up to 150 μm. Their characterizations have been successfully done using XRD, SEM and UV-Vis spectroscopic techniques. XRD studies reveal a high degree of crystallinity and monophase silver nanoparticles.

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