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## Solvothermal approaches on synthesis of silver nanowires

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### ABSTRACT

Development of reliable and stable process for synthesis of nanowires is an important step in the field of application on nanotechnology. One of the options to achieve this objective is to use chemical process such as solvothermal method. Silver nanowires have been successfully synthesized by reducing silver nitrate ( $\text{AgNO}_3$ ) with ethylene glycol (EG) in the presence of Trioctyl phosphine oxide (TOPO) as the capping agent at  $120^\circ\text{C}$  for 2 hrs. Electron microscopy, X-ray diffraction, and absorption spectra have been used to investigate the products, and the mechanism is proposed to interpret the controlled synthesis of silver nanowires. The results indicate that this approach provides a versatile route to prepare silver nanowires with controllable diameters. The formation of nano products by this method is rapid, simple and stable.

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### KEYWORDS

Silver nanowire;  
Solvothermal method;  
Ethylene glycol;  
TOPO.

### INTRODUCTION

Nanoparticles are being viewed as fundamental building blocks of nanotechnology. The most important and distinct properties is that they exhibit larger surface area to volume ratio. Advances over the past two decades have been revealing that silver nanoparticles (NPs) possess unique optical, electrical and catalytic properties<sup>[1,2]</sup>. They have many actual and potential applications in surface-enhanced Raman spectroscopy, metal-enhanced fluorescence, electrochemistry, micro-electronics and can serve as building blocks of nanodevices<sup>[3-6]</sup>. During the past few years the field of silver NPs preparation has witnessed tremendous growth in synthetic sophistication and depth of characterization. Many techniques of silver NPs synthesis have

been reported, such as the chemical reduction of silver ions in reverse micelles<sup>[7]</sup>, in two-phase water-oil systems (Brust-Schiffirin technique)<sup>[8,9]</sup>, in water solutions<sup>[10]</sup> and in the presence of shape-controlling capping agents<sup>[11]</sup>. Different approaches have been used to synthesize silver nanowires. The template-directed approaches were the most effective and widely used. Macroporous membranes<sup>[12]</sup>, mesoporous materials<sup>[13]</sup>, carbon nanotubes<sup>[14]</sup>, DNA channels<sup>[15]</sup>, organic nanotubes arrays<sup>[16]</sup> and silica gels<sup>[17]</sup> have been used as physical templates to guide the growth of nanowires. Though above-mentioned methods can ensure a good control over morphology of final products and allow obtaining metal nanowires with high aspect ratios, the additional removal of these physical templates may complicate the synthetic procedures and limit the scale at

which materials can be synthesized.

The purpose of this paper is to describe a facile way for synthesis of silver nanowires through the solvothermal method by reducing silver nitrate ( $\text{AgNO}_3$ ) with ethylene glycol (EG) and using TOPO as an adsorption agent and characterized herein.

## MATERIALS AND METHODS

### Preparation

All chemicals were of analar grade commercially available and used without further purification. In a typical synthesis procedure, 20 mL EG was added with 0.5 M TOPO and then stirred vigorously. This mixed solution was injected drop by drop using a syringe into 20 mL of a magnetically stirred EG solution of  $\text{AgNO}_3$  (0.1 M). The solution became wine. Afterward, the solution was put into a 25 mL Teflon-lined autoclave tube. This tube was sealed and maintained at  $120^\circ\text{C}$  for 2 hrs, followed by natural cooling to room temperature. The products were washed with acetone and then with water to remove most of the EG and TOPO. During the washing process, the suspension was centrifuged at 6000 rpm for 20 min to make sure that most of the products taken from the reaction were recovered. Then they were dispersed in deionized water for further characterization.

### Characterization

The UV-vis absorbance spectra were recorded using a Shimadzu UV-1800 spectrophotometer (Japan), and 1mm path length quartz cuvettes were used for the measurement of visible spectra. The electronic images were made on Hitachi S-4500 SEM analyzer. Fourier transform infrared (FTIR) spectroscopy was performed using a Nicolet IR-200 instrument (Thermo Scientific, USA). Infrared spectra of synthesized silver NPs in the range of  $400\text{--}4000\text{cm}^{-1}$  were recorded at 100 scans per spectrum and a  $4\text{cm}^{-1}$  resolution. Samples were dispersed in spectroscopically grade potassium bromide and compressed into pellets. X-ray diffraction was carried out on a Philips diffractometer of 'X'pert company with nano chromatized using Cu K $\alpha$  radiation at a step of  $0.02^\circ$  ( $2\theta$ ) at room temperature. The background was subtracted with the linear interpolation method.

## RESULTS AND DISCUSSION

A drop wise addition of ethylene glycol-TOPO to silver nitrate solution resulted in the immediate change in color from light brown to dark. The latter corresponded to the silver colloid.

To further confirm the structure of the obtained nanowires, typical XRD patterns of the products taken with a bigger quantity of the dried sample and shown in Figure 1. The patterns indicate the presence of three diffraction peaks, which agreed well with the (111), (200) and (220) diffractions of face centered cubic silver (JCPDS File No. 04-0783 from ASTM). The diameter of the nanowires is calculated by using Debye-Scherrer's formula and it was found as 9.99nm. The final product is all composed of metallic silver, indicating that the high purity of fcc silver could be prepared by solution-phase method.

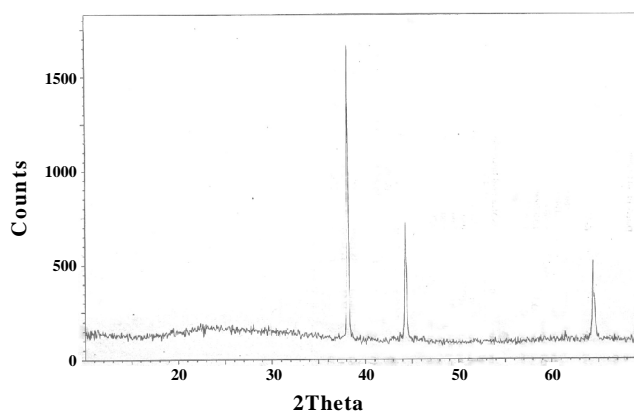


Figure 1: XRD pattern for silver nanowires in ethylene glycol  
Optical characterization of silver nanowires

The SEM image of synthesized silver nanowires was shown in Figure 2 and clearly indicates that the formation of uniform sized silver nanowires. The band gap energy is measured with the help of absorption spectra and a graph of  $\alpha^2$  versus  $h\nu$  were plotted (Figure 3). The extrapolation of the straight line to  $\alpha^2=0$  gives the value of the band gap energy of prepared materials and obtained as 0.095eV. This shows that the formation of nano silver wires sample in the ethylene glycol medium is significant and reveals that the size of the silver wire is in nano. From the absorption spectra, it is also observed that the silver surface plasmon resonance band occurs at 214 nm and steadily increases in intensity as a function of time of reaction without any shift in the peak

## Full Paper

wavelength. Similar results have been observed by Mukherjee *et.al*<sup>[18]</sup> and Gonzalo *et.al*<sup>[19]</sup>.

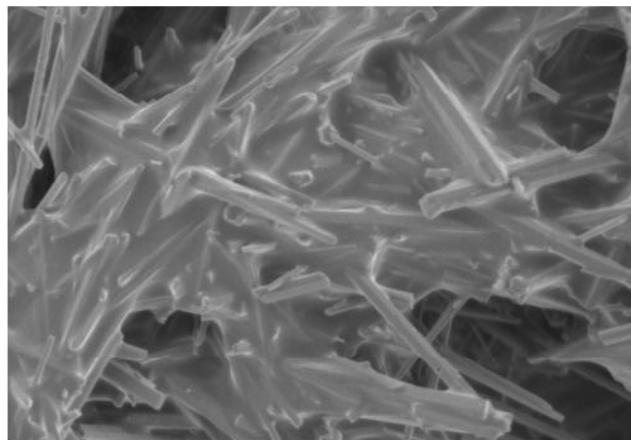


Figure 2 : SEM images of silver nanowire

FT-IR absorption spectra (Figure 4) show the nature of the particle through different absorption peaks of various samples. The stretching frequency of N-O is observed at above  $1385\text{ cm}^{-1}$ . The characteristic absorption peak of silver is observed at  $413.21\text{ cm}^{-1}$  in ethylene glycol medium. This is confirmed by the changes

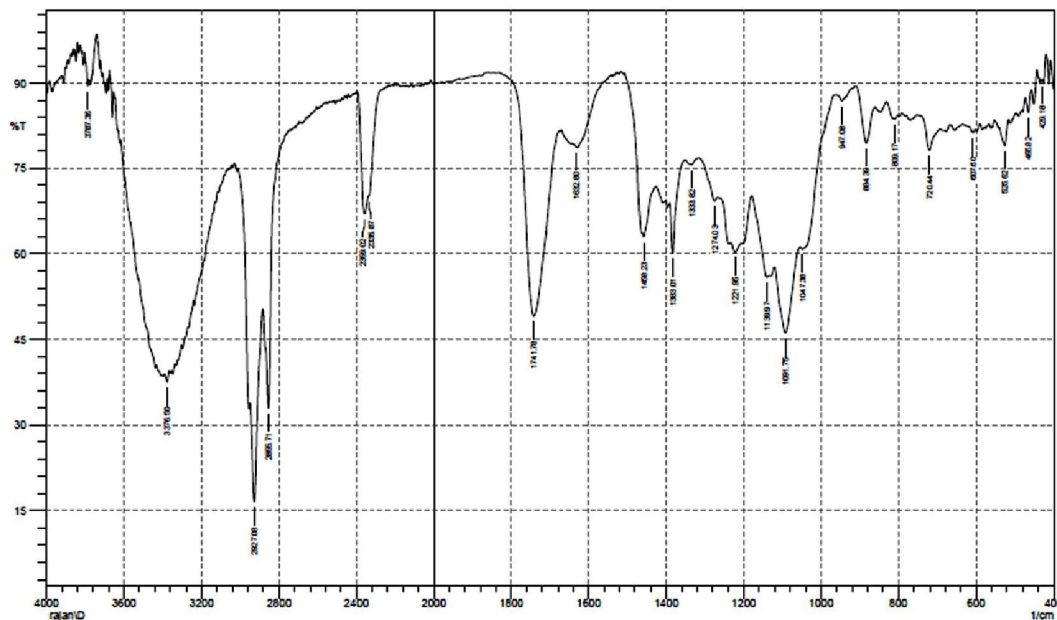


Figure 4 : FT-IR spectra of silver nanowires in ethylene glycol

## CONCLUSION

In summary, the present work shows that the silver nanowires were synthesized using the TOPO-mediated solvothermal process. The capping agents have the capability of effective covering and stabilize the newly

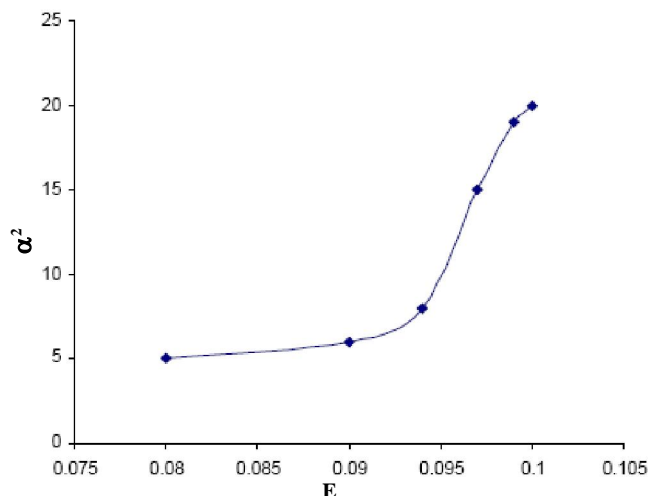


Figure 3 : Absorption spectra for silver nanowires in ethylene glycol

in the peak shift of the silver nitrate and silver nanowires appeared in the ethylene glycol medium. In this regard, the mechanism of solvothermal process seems to be similar to that of the polyol process demonstrated for the synthesis of highly crystalline nanowires from III to V semi-conductors and silicon<sup>[20,21]</sup>.

formed nanowires. The face centered cubic structure and use of TOPO with a proper concentration; both play an important role in confining the growth of silver nanowires to the 1D mode. Silver nanowires with a uniform diameter of 9.99 nm were obtained. The end-to-end assemblies of silver nanorods were formed during the reaction process, and the obvious spacing be-

tween two straight silver nanorods would gradually disappear and probably be filled with silver atoms. This method can be used to select the appropriate solvent for the preparation of silver nanowires with desired aspect ratio, indicating preferential potential for applications in fabricating future nanoelectronic devices.

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