Hydrothermal Synthesis of Silver Nanowires and Application as Transparent Conductive Materials

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ABSTRACT

A scalable hydrothermal synthesis for silver nanowires has been developed. The new synthetic route is expected to be compatible with industrially available reactor systems and offer environmental and safety advantages due to use of aqueous solutions. Resulting silver nanowire product contains high aspect ratio particles (length:diameter ≥1000:1) with mean nanowire diameters of ~35 nm. The silver nanowires are processed into highly conductive, transparent thin films with sheet resistance of 50 Ω/□ at 1% haze and >97% transparency. The conductive silver nanowire films are envisioned for various applications such as touch panel displays, photovoltaics, OLEDs, conductive composites, and flexible electronics in the future.

Keywords: silver nanowires, hydrothermal synthesis, transparent conductor, thin film, nanotechnology

1 INTRODUCTION

Optically transparent films with high electrical conductivity are applied as electrodes and/or coatings in a wide range of applications including flat panel displays, touch screens, and photovoltaic cells. Most commercial products containing transparent electrodes currently use indium tin oxide (ITO) thin films. While ITO provides high electrical conductivity (sheet resistance <100 Ω/□) and high transparency (>90%), the metal oxide thin films are disadvantaged by their mechanical properties and high deposition temperature (≥ 200 °C) [1]. These properties are especially critical for light weight and/or flexible electronics where polymeric substrates impose ITO deposition temperature limitations, and as a result, the conductivity suffers at equivalent transparencies [2]. Several alternative technologies are under investigation as ITO substitutes, but of these approaches metallic nanowires, particularly silver nanowires, provide the best comparative electrical and optical properties to ITO [3]. Films composed of random silver nanowire networks combine the benefit of the bulk electrical conductivity of silver with small feature sizes and optical transparency inherent in a dilute network of nanoparticles. The work presented herein details efforts in the synthesis of silver nanowires for use in transparent conductive electrodes.

The most widely cited method in the literature for making silver nanowires is the polyol synthesis in which a silver salt such as silver nitrate is reduced in the presence of poly(vinylpyrrolidone) (PVP) in a glycol solvent system [4]. PVP provides steric stabilization of the silver nanoparticle in solution, and the polymer has been shown to more strongly bind to <100> crystal facets of silver as compared to <111> facets. This difference in binding strengths leads to preferential adsorption of PVP on the nanoparticles and allows pentagonally twinned Ag seeds to grow anisotropically into nanowires. The reducing agent during the polyol synthesis is glycol aldehyde formed by high temperature (~160 °C) oxidation of the glycol solvent. While the polyol synthesis has been extensively studied, a novel hydrothermal synthesis of silver nanowires has been developed within The Dow Chemical Company (Dow). The silver nanowire synthesis uses water as solvent, and Dow has filed patent applications for the preparation method [5].

2 EXPERIMENTAL

The hydrothermal synthesis utilizes silver nitrate and PVP, as in the case of the polyol synthesis. However, the method developed within Dow uses D-glucose as the reducing agent. Trace amounts of copper (II) chloride and sodium chloride are also added to the aqueous synthesis. The proposed reaction scheme shown in Figure 1 describes the hydrothermal synthesis reactants and products.

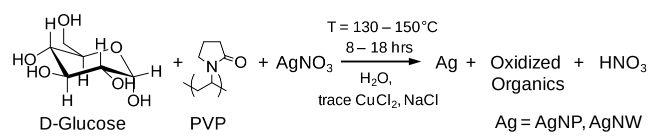

Figure 1. Reaction scheme for the hydrothermal synthesis of silver nanowires.

2.1 Reagents

ACS reagent grade (≥99.0%) silver nitrate, D-(+)-glucose, copper chloride dihydrate, and sodium chloride were purchased from Sigma Aldrich and used as received. Sokalan K30 grade PVP (average Mw 45,000-55,000 Da) was obtained from BASF. The sourcing and molecular weight of PVP were found to be important for dimensions and distributions of nanowires obtained in the synthesis. ACS reagent grade nitric acid (70%) was used in pH adjustment of solutions prior to loading into the reactor and was purchased from Sigma Aldrich. ACS plus reagent grade nitric acid (70%) used in the reactor cleanouts was obtained from Fisher Scientific. Ultra-purified water with a resistance ≥18.0 MΩ-cm, supplied by a Millipore Super-Q Plus water purification system, was used for aqueous solution preparation and reactor cleaning.

2.2 Synthesis & Purification

The hydrothermal silver nanowire synthesis was conducted in a 8 L 316 stainless steel reactor manufactured by Pressure Products Industries (PPI), with a pressure rating of 2000 psi, and a temperature control module with an external mantle for heating and internal cooling coil for cooling. The reactor was equipped with three propeller type blades. The system also included a diaphragm pump for D-glucose/sodium chloride/copper chloride solution addition, and a 500D Isco syringe pump for $AgNO_3$ and PVP solution addition with flowrate control.

In a typical synthesis, 2.3 L of aqueous solution containing 13.5 g D-glucose, 5 mg sodium chloride, and 5 mg copper chloride is charged into the reactor via the diaphragm pump. A total of 52.2 g of PVP in water is subsequently added to the reactor. The reactor is heated to 150 °C under agitation. A portion ($1/5^{th}$) of an aqueous solution containing silver nitrate (12.7 g $AgNO_3$) is added via the Isco syringe pump and held at temperature for several minutes. The reactor contents are cooled to 130 °C, and the remaining $AgNO_3$ solution is metered into the reaction mixture. A total of 0.85 L water is added with the PVP and $AgNO_3$ solutions. After all the reactants are pumped into the reactor, the reaction is allowed to run for between 8 and 18 hours. The reaction products are cooled to room temperature and drained out of the reactor.

Crude reaction mixture produced from the synthesis procedure described above contains a range of silver particles and unreacted reagents. To purify and extract the silver nanowires from the crude reaction mixture, decanting and filtration are used.

2.3 Characterization

UV-Visible spectroscopy of the silver nanowire dispersions was conducted on a Shimadzu UV-2401 spectrometer to characterize the nanostructures present. Prior to performing UV-Vis spectroscopy analysis, crude reaction mixture was centrifuged, solids redispersed in water, and diluted with water in a UV/Vis cuvette. One drop of the suspension prepared for UV-Vis measurement was placed onto a piece of clean silicon wafer and dried overnight under vacuum at room temperature for use in scanning electron microscopy (SEM) imaging. Backscatter electron images were acquired using an FEI Nova NanoSEM field emission gun scanning electron microscope using FEI's Automated Image Acquisition (AIA) software. Semi-automated image analysis for nanowire width measurments was done using ImageJ software.

Nanowire thin films were prepared by making a formulation from 1% Methocel K100 solution in Milli-Q deionized water, 1% Silwet L7604 solution in Dowanol PM, Milli-Q deionized water, and the purified silver nanowires. Coatings were prepared on 2"x3" microscope glass slides or 2"x2" PET films using a spin coater (Laurell, model WS-400BZ-GNPP). The coatings were tested for haze and transmittance using a BYK Haze Guard Plus instrument. Film conductivity (also referred to as Sheet Resistance) was measured using 4-point probe tested at 10.00µÅ and reported in ohms per square (Ω/ □).

3 RESULTS & DISCUSSION

The hydrothermal silver nanowire synthesis produces a mix of nanowires, nanoparticles, and other low aspect ratio particles. Normalized UV-Vis spectroscopy enables analysis of nanowire-to-particle relative populations, and also provides a qualitative assessment of the relative nanowire diameters. Figure 2 shows the normalized spectra for the crude reaction mixture and filtered product from the hydrothermal synthesis. The adsorbance between 400 – 550 nm is attributed to nanoparticles, while the adsorbance peaks between 350 – 390 nm are attributed to silver nanowires [4]. The crude reaction mixture exhibits plasmon peaks at 353 nm and 374 nm, but there are also broad peaks between 400 – 550 nm indicating the presence of nanoparticles. After filtration, the nanowire dispersion shows a significant decrease in nanoparticle absorbance. Furthermore, the transverse plasmon mode shifts to 371 nm, suggesting a decrease in nanowire diameter.

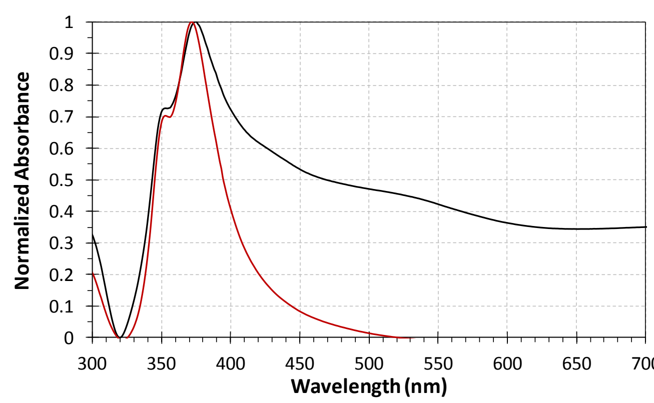

Figure 2. UV-Vis spectra of crude reaction (black) and filtered (red) siver nanowire mixtures.

Silver nanostructures present in hydrothermal synthesis products were also evaluated via scanning electron microscopy. As depicted in Figure 3a, SEM image of the crude reaction mixture shows high aspect ratio nanowires as well as other faceted nanoparticles. The observation of a mixture of nanowires and nanoparticles is in agreement with that of the UV-Vis spectrum for the crude reaction mixture. Furthermore, ImageJ analysis of multiple micrographs of the crude reaction mixture yields a mean nanowire diameter of 37 nm. In contrast, SEM images from the filtered nanowire dispersion (Figure 3b) show very few nanoparticles, in agreement with the low absorbance between 400 – 550 nm (Figure 2, red curve). ImageJ analysis of SEM images from the filtered nanowire dispersion resulted in a mean nanowire diameter of 31 nm. A decrease in the mean nanowire diameter after filtration, as observed in the SEM micrographs, is consistent with the blue-shift observed for the transverse plasmon mode peak from 374 nm to 371 nm in the UV-Vis spectra. It is hypothesized that the decrease in mean nanowire diameter after filtration is due to removal of thicker, short nanorods.

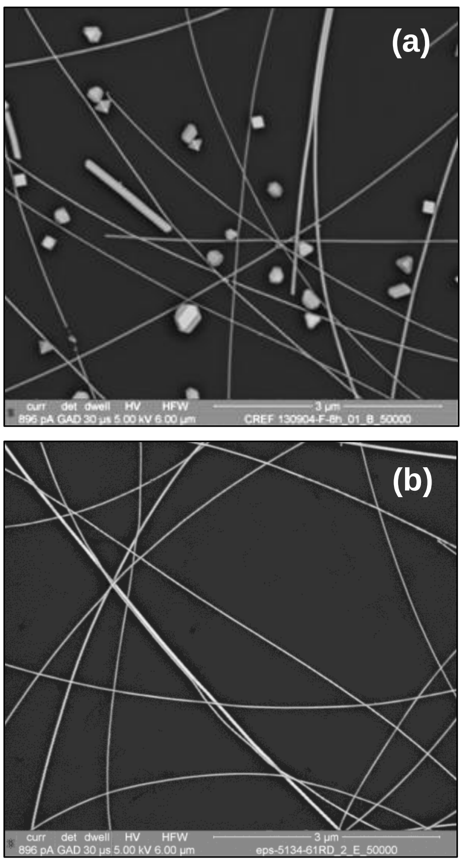

Figure 3. Scanning electron micrographs of (a) crude reaction and (b) filtered silver nanowire mixtures.

High aspect ratios observed for silver nanowires is expected to improve performance as transparent conductive films. Thinner and longer nanowires have been shown to improve optical properties of the films at a given sheet resistance [6]. In particular, as the nanowire diameter approaches the same magnitude as visible light wavelength, light scattering is expected to increase producing a higher haze for the film [6]. Therefore, optical (transmittance and haze) and electrical properties of nanowire films generated using the hydrothermally derived, filtered nanowires were evaluated.

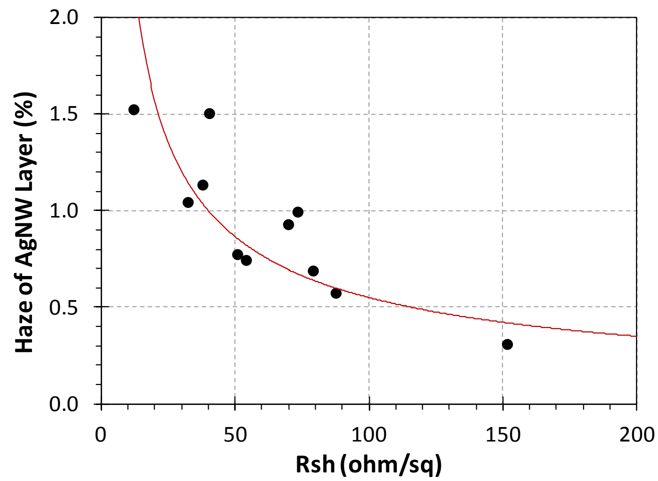

Figure 4. Silver nanowire layer performance as a transparent conductive thin film.

Silver nanowire films deposited via spin coating at varying metal loadings were produced to evaluate performance as transparent conductors. All films tested possess transmittance between 97.5 – 99.5%. Figure 4 shows the haze as a function of sheet resistance for the nanowire films. Several films exhibit sheet resistance values < 100 Ω/□ at haze ≤ 1%. Electrical and optical properties such as these meet the requirements for several transparent conductive electrode applications such as touch panels, lighting, photovoltaics, displays, and electromagnetic shielding [7]. In fact, sheet resistance down to 50 Ω/□ have been demonstrated while still maintaining high performance optical properties (0.8% haze and 99.2% transmittance).

4 CONCLUSIONS

A novel hydrothermal synthetic route to silver nanowires has been developed at The Dow Chemical Company, and performance of these nanowires in transparent conductive films was evaluated. Filtration of the reaction product produced highly purified nanowire dispersions with mean nanowire diameters of ~30 nm. Thin films deposited from these purified nanowire dispersions have low sheet resistance of 50 – 100 Ω/□ at haze ≤ 1% and transmittance > 97%. This combination of high electrical conductivity and optical transparency make thes materials promising candidate materials in transparent conductive electrode applications.

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