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Silver nanowire purification and separation by size and shape using multi-pass filtration.

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Abstract

Silver Nanowire (AgNW) meshes produced by soft solution polyol synthesis offer a low-cost low-temperature solution deposited alternative to indium tin oxide transparent conductors for use in solar cells. However, polyol synthesis typically produces both nanoparticles and nanowires during synthesis. Nanoparticles reduce optical transmission of nanowire meshes without any beneficial reduction to sheet resistance. This work describes a combined purification and separation multi-pass filtration process to efficiently remove nanoparticles from nanowire solutions prior to deposition. The filtered samples typically contains 86% nanowires (14% nanoparticles) compared to 67% nanowires in the standard centrifuge process and 55% nanowires in the original sample. The filtration method offers further benefits of reduced nanowire breakage and a generally lower sheet resistance after nanowire deposition.

Keywords: AgNW, separation, nanowires, filtration

1. Introduction

Transparent Conductive Electrodes (TCEs) have many uses, primarily in photovoltaic cells, organic light emitting diodes and flat panel displays. The most common TCE is the Transparent Conductive Oxide (TCO) Indium Tin Oxide (ITO) with merits of good optical transmission (> 90%) in the visible region of the spectrum and a low sheet resistance, (R_{Sh} =10 Ω/□) [1]. However, with its multiple uses and low number of sources indium has a high risk associated with its supply leading to a high cost [2]. Further to these issues it also suffers from brittleness and the need for high temperature processing to achieve optimal properties [1, 35]. These factors make ITO unsuitable for use with new low cost solar cells such as organic solar cells in which deposition is slow and often damages the substrate [6].

An alternative material showing merits as a TCE is silver nanowire (AgNW) meshes which have been previously fabricated with transparency of 80%, observed over the entire visible spectrum, and sheet resistance 10 Ω/□ [1]. AgNW meshes also have the merits of being flexible over multiple bending cycles which allows for their use with flexible solar cells [7]. Furthermore, deposition and treatment of AgNW meshes can be achieved without the need for high temperatures which allows for good suitability with organic cells [8].

AgNW meshes also display plasmonic behaviour observed in noble metal nanomaterials, such as Localised surface plasmon resonances (LSPR) produced by incident light. This produces increased absorption in thin solar cells by scattering [9]. It has also been observed that a larger proportion of light can transmitted compared to the clear aperture presented by AgNW meshes [10]. The light frequency at which the LSPR occurs is highly dependent on the size and shape of the metal nanoparticle as well as the dielectric environment [11].

AgNWs can be produced via many template methods as well as soft solution processes [12-23]. A popular soft synthesis method is the Polyol process which is able to produce high aspect ratio nanowires by reducing silver chloride with Ethylene Glycol (EG), utilising a poly vinyl pyrollidone (PVP) surfactant and copper chloride growth facilitator [24]. The polyol process produces nanowires as its major product, but also produces significant quantities of spherical nanoparticles, nanoplates and nanobars. The quantity of these products is controlled by thermodynamic and kinetic factors during the synthesis with a maximum - 70% nanowire product having been reported [25].

Low or unity aspect ratio nanoparticles don't improve electrical percolation within the mesh while reducing overall light transmission and so need to be removed [26]. Post synthesis purification, to remove the EG and PVP from the nanowires surface, and separation is usually completed by a centrifuge process [25, 27-29]. However, centrifugation can encourage the formation of entangled agglomerates which are subsequently difficult to re-disperse in to isolated nanowires prior to deposition [30]. Centrifugation can also be an expensive process to scale up with long duration runs required.

Other nanowire nanoparticle separation techniques previously reported to separate nanowires include; cross-flow filtration, where a cross-flow filter utilises the nanowire alignment with flow direction to separate nanowires and nanoparticles and centrifugation of samples in multiphase immiscible liquids, which exploits the difference in hydrodynamic behaviour of different geometries [30, 31].

This work introduces a new separation and purification process. This process, unlike previous methods, uses cheap and available PolyPropylene (PP) filters in a simple filtration process which separates nanoparticles and low aspect ratio nanowires. The method improves upon centrifugation by reducing time to extract and cost whilst reducing nanowire breakage and improving separation of nanowires and nanoparticles.

2. Methods

2.1. Polyol Synthesis

The AgNW synthesis method used by Korte et al. was followed [24]. 5 ml of EG was placed in a 20 ml glass vial and a stirring bar inserted. The vial was placed in an oil bath and heated at 150 ^{o}C for 60 minutes with stirring. 40 µl of 4 mM $CuCl_2 \circ H_2O$ in EG was added next. After a further 15 minutes of heating 1.5 ml of 147 mM PVP in EG followed by 1.5 ml of 94 mM

$AgNO_3$ in EG were added. The solution was heated with stirring for another 60 minutes before the reaction was quenched in room temperature water [24].

2.2. Separation Techniques

2.2.1. Centrifuge Separation

Two centrifuge methods were employed. A 6000RPM method, used by Hu et al. and referred to as 6000RPM, was employed to separate all nanowires and nanoparticles from solution [27]. In this method the synthesis product was centrifuged twice at 6000RPM for 30 minutes, pipetting off the supernatant in-between runs. The Precipitate was then re-dispersed in ethanol.

A second lower speed method, adapted from that used by Sun et al. and referred to as 2000RPM, used 10 times volume acetone added to the synthesis products and centrifuged at 2000RPM for twenty minutes [25]. The supernatant was pipetted off and the process repeated once more with acetone and a further time with de-ionised water. The final precipitate was again re-dispersed in ethanol.

2.2.2. Filtration Separation

In the standard process 2 ml of synthesis product was drawn into a 2.5 ml luer-lok syringe. The filter housing with appropriate filter was then attached and the solution filtered through it. After this 1 ml of acetone was drawn into the syringe through the filter. The acetone was used to purify the nanowires as well as dislodge nanowires and nanoparticles from the filter membrane. The purification was completed with a further 2 ml of acetone followed by 15 ml of de-ionised water. After purification and separation the filter membrane was removed from its housing and placed in a 20 ml vial with 1 ml of ethanol and placed in an ultrasonic bath for 10 mins to remove nanowires from the surface of the membrane. The membrane was then removed from the solution. The standard process was completed with 200 nm and 450 nm PP filters and the methods are referred to as the 200PPST and 450PPST respectively.

A second process was used with the 450 nm PP filters. The same initial filtration process as the standard process was completed in which acetone and then de-ionised water are drawn through the filter. After the completion of purification the nanowires were re-dispersed into ethanol by drawing 1ml of ethanol into the syringe through the filter, compared to the filter membrane being placed in the ethanol and the nanomaterial removed in an ultrasonic bath in the 450PPST method. This method is referred to as the pull-back method (450PPPB).

2.3 Sample Deposition and Annealing

Before deposition the mass of nanowires per unit volume was ascertained and all samples were deposited at the same concentration. Samples were drop cast at 80 ^{o}C onto glass substrates. Samples were deposited at different masses determined by the number of drops cast on the sample, with continued heating at 80 ^{o}C between drops to evaporate solvent.

Samples were annealed at 180 ^{o}C for 20 minutes under an air atmosphere. This step was utilised to evaporate off any remaining solvent and surfactant alongside sintering the nanowire junctions to reduce the AgNW mesh R_{Sh}.

3. Results and Discussion

Figure 1 shows SEM high magnification images of the extracted samples. The 6000RPM centrifuge separation which intended to separate the entire reaction product shows the multiple silver nanoparticle geometries that can be produced in the polyol synthesis, including a large variation in size between the nanoparticles. It is clear just from the observation of the lower magnification images in figure 2 that the 2000RPM centrifuge method has not resulted in a good nanoparticle and nanowire separation. This is similarly observed for the 450PPB method and the 200PPST methods. The 450PPST shows fairly good separation of the nanowires and nanoparticles with only few large nanoparticles observed.

3.1. Nanoparticle and Nanowire Statistics

The percentage of nanoparticles and nanowires in the extracted samples, measured using Scanning Electron Microscope (SEM) imaging, are shown in figure 3. The 6000RPM method was used as a control in which all nanoparticles and nanowires produced in the polyol process were collected. This shows that 55 ± 18% of the samples produced in the polyol process were high aspect ratio nanowires. Note that a small number of nanoparticles remained in the supernatant even after 6000RPM centrifugation, observed by slight colouration of the supernatant. When comparing the other methods it is observed that using the larger 450 nm filter achieved better separation than the 200 nm filter during the standard filtration process as expected due to the large number of nanoparticles with diameters greater than 200 nm. When comparing the 450PPST, 450PPPB and 2000RPM results it is observed that the 450PPST method has the highest separation efficiency with 86 ± 8% nanowires in the extracted sample. The 450PPPB and 2000RPM methods are seen to have similar but lower extraction efficiency with 68 ± 10% and 67±5% nanowires in the extracted samples respectively. It potentially could be possible to increase the percentage content of nanowires of the 2000RPM process with an increased number of runs. However, this would lengthen an already time consuming process with diminishing returns for each extra centrifuge run.

Nanowire breakage is an important factor to consider in the separation process. Shorter nanowires have previously been simulated to result in diminished electrical percolation and hence higher sheet resistance [33]. To quantify breakage nanowire length distributions were produced for the 6000RPM, 450PPST and 2000RPM samples using SEM imaging, these are shown in figure 4. The process aimed to quantify the nanowire size distributions in the initial synthesis, from the 6000RPM sample, and the distributions obtained from separating the nanowires and nanoparticles by centrifuge and filtration, 450PPST, 200PPST, 450PPPB and 2000RPM samples.

The nanowire length distributions of the 2000RPM and 6000RPM samples are similar with mean lengths of 1.8 ± 0.2 µm and 2.1 ± 0.2 µm respectively. The larger distribution of the 450PPST sample, with an increased mean of 4.3 ± 0.4 µm, is an interesting result as the 6000RPM sample is assumed to include the entire reaction product and so should have a similar distribution and mean. It is possible that nanowires could be damaged in the centrifuge process from the agglomeration and entanglement which are then broken when placed in the ultrasonic bath to separate. This could explain the absence of longer nanowires observed in the 450PPST sample. A further explanation, and possible merit of the filtration method, is that low aspect ratios nanowires with mean length 0.91 ± 0.05 µm, were observed in the filtrate of the 450PPST method having passed through the filter. The 2000RPM centrifuge supernatant was also observed to have nanowires present, with a mean length of 1.1±0.1 µm. This suggests that a combination of damage produced in the centrifuge process as well as the removal of lower aspect ratio nanowires occurring in the filtration process produces the larger mean nanowire lengths in the filtered samples.

3.2. UV-Vis Spectrometry

Ultra Violet Visible spectrometry was completed on each sample as well as the filtrate or supernatant. Figure 5 shows the transmission profile for the 450PPST sample. The extracted samples show an absorbance peak at 380 nm with a shoulder at 355 nm, showing similarities to other results and simulations for dipole and quadrupole resonances [30, 34]. The broad absorption peak can be attributed to the wide distribution in nanowire size and nanoparticle interactions [35]. Both the filtrate samples show peak absorption at a larger wavelengths of 425 nm and 435 nm. This is indicative of a larger proportion of nanoparticles which have a peak absorption at a longer wavelength [36]. The relative absorbance of the products is unimportant due to the variant concentrations.

3.3. Sheet Resistance

The sheet resistance of deposited samples was measured with a 4-point probe instrument which has the ability to measure the R_{Sh} without encountering a contact resistance. R_{Sh} values plotted against deposited mass of the samples are shown in figure 6. With the exception of the 450PPPB sample the expected reduction in R_{Sh} with increased mass deposited is generally observed. The errors measured in both R_{Sh} are noted to be large. The sheet resistance error values are indicative of the uniformity of deposition issues with drop-casting nanomaterials. The comparative values of R_{Sh} between methods doesn’t follow the order that might be expected when taking the nanowire size and the nanoparticle and nanowire percentages of the samples into account. However an overall trend of reduced R_{Sh} is observed for filtered samples compared to centrifuged samples. R_{Sh} values not following the expected trend could again be linked to the poor uniformity of deposition observed. One of the factors that could cause varying deposition characteristics is remnant surfactant on the samples, with both centrifuge and the 450PPPB samples still appearing to have a possible organic content when viewed during SEM imaging, previously shown in figure 1. Further to affecting the deposition uniformity surfactant would also hinder connections between nanowires again affecting R_{Sh} values [32]. To achieve more reliable R_{Sh} measurements and so be able to separate between remaining surfactant issues from the nanowire characteristics of the samples necessitates an improved deposition process to be utilised.

3.4. Conclusions

In conclusion, a multi-pass filtration method was developed which used multiple solvent washes to allow for a good separation efficiency and prevent filter clogging. Multi-pass filtration was shown to produce final samples comprising of 86% nanowires, compared to 67% nanowires in centrifuge separated samples. It is likely that increasing the number of washing cycles could reduce the number of particles in the centrifuge samples. This would, however, increase the already lengthy centrifuge procedure with diminishing returns. The multi-pass filtration technique also showed little wire breakage when compared to the centrifuge method, important for producing a high transparency low sheet resistance TCE. Further merits of the multi-pass filtration method are its separation of low aspect nanowires from the final sample, which would again be advantageous for the use of nanowires in a TCE. This fast and efficient multi-pass filtration method shows good promise as a straight forward method to separate and purify the reaction product of the silver nanowire salt mediated polyol process before the fabrication of silver nanowire meshes. Nanowire annealing reduced sheet resistance by improving contact between nanowire junctions.

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Figure Captions

Figure 1: SEM images of separated nanowires by filtration: a) 200PPST, b) 450PPST, c) 450PPPB and by centrifugation: d) 2000RPM, e) 6000RPM.

Figure 2: Large area SEM images of separated nanowire samples: a) 2000RPM, b) 6000RPM, c) 200PPST, d) 450PPST.

Figure 3: The nanoparticle and nanowire areas of deposition measured using SEM imaging for the 450PPST, 200PPST, 450PPPB, 2000RPM and 6000RPM methods.

Figure 4: Nanowire length probability distribution for 6000RPM, 450PPST and 2000RPM methods, amd associated filtrate and supernatant.

Figure 5: Transmission spectrum for 450PPST separated nanowires and acetone and water filtrate.

Figure 6: Sheet resistance values for the 450PPST, 200PPST, 450PPPB, 2000RPM and 6000RPM deposited samples.