Patterning Metal Nanowire-Based Transparent Electrodes by Seed Particle Printing

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ABSTRACT: This article describes a unique combination of inkjet printing of functional materials with an intricate self-assembly process. Gold–silver nanowire (NW) mesh films were produced by a sequential deposition process, in which small metal seed nanoparticle film was deposited at desired areas by inkjet printing, followed by coating with a thin film of NW growth solution. Two different types of NW growth solutions were used: the first, based on benzylhexadecyldimethylammonium chloride, exhibited a bulk solution growth mode and was thus suitable for coverage of large uniform areas. The second type was based on hexadecyltrimethylammonium bromide, which induced NW growth confined to the substrate–solution interface and thus enabled patterning of small transparent electrode features, which have the same dimensions as the deposited seed droplets. A selective silver plating bath was used to thicken the ultrathin NWs, stabilize them, and reduce the sheet resistance, resulting in films with sheet resistance in the range of 20–300 Ω/sq. 86–95% light transmission, and a relatively low haze. This simple patterning method of the NW film works at ambient conditions on many different types of substrates and has the potential to replace the conventional photolithography used for indium tin oxide patterning for applications such as touch sensors and flexible/stretchable electronics.

INTRODUCTION

The quest for controlling the synthesis of metal nanowires (NWs) and nanorods, produced by seeded growth techniques, has attracted vast attention in recent years.1−5 Such nanostructures may be useful for printed electronic devices as well as plasmonic/optical applications. One of the important applications of controlled deposition of metal NWs is the production of transparent electrodes (TEs).6−9

There is major interest among various companies developing next-generation displays to find a replacement for indium tin oxide (ITO) as the transparent electrode material, which is an essential part of displays, touch screens, and organic light-emitting diode (OLED) illumination devices.10 This interest is driven by the desire to avoid the need for indium, which is a rare element, to avoid expensive vacuum-based sputter coating technology, which is required for the ITO film production, and to produce highly flexible panels devoid of the brittle ITO.

Several interesting candidates for TE have been suggested during recent years. These include conducting polymers,11 carbon nanotubes,12 graphene films,13,14 nanoscale metallic gratings,15−18 and random networks of metal NWs15,20 made of copper,21 and silver.6,22

Different deposition techniques are used for the TE film materials listed above: The conducting polymers are spin-coated on the desired substrates and then possibly annealed and etched by oxygen plasma to enhance conductivity.11 The carbon nanotube network electrodes are deposited directly onto the surface of interest via spin-coating or drop-casting, and by introducing conjugated polymers to the nanotube suspensions, their dispersion in solvents and quality of deposition are improved.12 High-quality graphene films can be produced by chemical vapor deposition, which is prohibitively expensive.14 Nanoscale metal gratings can be fabricated using various techniques, such as simple deposition of metal nanorods/NWs.23 With the coffee ring effect, a micrometer-size droplet of liquid containing solid particles is pinned to a substrate, and upon drying of the droplet, the solid particles assemble into a ring. This enables obtaining 2D arrays composed of interconnected conductive rings using an inkjet printing technique.16 Another fabrication technique of nanoscale metal gratings is the deposition of silver nanoparticle dispersion on top of a stainless steel mesh that is placed on the substrate, and after the removal of the mesh, a grid pattern is left on the substrate.15

The random networks of metal NWs can be produced using copper, where further alloying copper with nickel makes it gray (instead of orange/red) and resistant to oxidation, and it is coated with poly(vinylpyrrolidone) (PVP) to prevent the aggregation of the NWs.21 Significant progress with copper nanowire synthesis enabled the formation of very thin NWs, ~15–35 nm in diameter, and consequent thin films with improved performance in terms of low sheet resistances with good optical transmission and low haze values.24−27

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AgNWs are synthesized by the reduction of Ag nitrate in the presence of PVP in ethylene glycol. Removal of the PVP residues between the silver NWs improves the junction conductance between silver NWs. An ink prepared using these NWs can coat glass slides with a wire-wound metering rod.22 Inkjet printing of silver NWs has been used to pattern conductive features, followed by thermal annealing or additional metal deposition to decrease the interwire resistivity of the overlapping NWs and increase the conductivity of the network.22,23 Alternatively, the silver NWs could be inkjet printed without any post-treatment on top of a conducting polymer film.28

Random networks of gold−silver NWs were produced directly on the substrates through surfactant-based soft-template systems,3,19 where the growth process occurred in a drying thin film containing the growth solution directly on the desired substrate. However, so far, all of the components of the NW growth process were mixed together prior to deposition on the substrate, thus limiting the shelf life of the solution to ~1 min and maintaining a complicated interdependence of different process parameters.

In this article, we present a significant advancement in the above-mentioned NW deposition scheme, splitting the NW film preparation into three stages of controllable transparency, sheet resistance, and spatial NW distribution. Ultrathin gold−silver NWs (from now on will be called UTNWs) are formed on top of the substrate of interest (glass or various polymers), at selected areas, defined by inkjet printing (or possibly other printing techniques). The process is illustrated in Figure 1: First, very small metal seed particles ("Nanogold", 1.4 nm) are printed where the growth of the NW film is desired. Second, a thin film of the NW growth solution is deposited. The growth solution is a surfactant-based soft-template system, where the surfactants used are either benzylhexadecyldimethylammonium chloride (BDAC) or hexadecyltrimethylammonium bromide (CTAB), which is the more common surfactant for the preparation of metal nanorods and NWs and has different properties from BDAC.29 Whereas CTAB leads to the formation of UTNWs strictly at the solution−substrate interface,3 the BDAC-based process produces UTNWs in the bulk solution.29 The gold−silver UTNWs formed at this stage would typically be ~2−4 nm in diameter and occur in bundles consisting of anywhere between single wires to hundreds of wires. Due to their small diameter, these UTNWs would not be stable over time and spontaneously fragment (Rayleigh instability).30 Therefore, a third metal deposition step would be required to make them thicker, hence stable, and lower their resistance. The last step has to be selective to thicken the preformed UTNWs without depositing metal elsewhere on the substrate. We have developed a selective catalytic electroless silver-plating process to thicken and stabilize the UTNWs. The parameters of the electroless metal deposition step would determine the final thickness of the silver-coated NWs (to be called AgNWs for the rest of the article), hence controlling the final film’s sheet resistance and transparency.

**RESULTS AND DISCUSSION**

**Preparation of Uniform Films. Seeding.** The density of seed particles deposited (by droplet jetting) on the substrate could be controlled by the concentration of the seed solution,
droplet size (via the diameter of the capillary used for jetting), and the droplet spacing. Typical dispensing capillary size was 80 μm (producing droplets of ~200 pL) and seed concentration was in the range 4.2 × 10⁻⁸–1.8 × 10⁻⁷ M. The droplets were typically printed with their rims nearly touching or slightly overlapping to obtain an average surface density of ~1–500 seeds/μm².

**NW Growth.** The NW growth process can be done either with CTAB- or BDAC-based solutions. In a previous work, Azulai et al. have studied the seed concentration dependence of CTAB-based NW growth. They found that UTNWs bundles were formed at high enough concentration, and when this concentration was reduced below some threshold, the morphology changed to less uniform, thicker NWs. It has also been confirmed in several studies that this type of NWs grew only at the solution–substrate interface (surface growth).

In the present work, we studied the seed concentration dependence of the BDAC-based NW growth (bulk growth): After drying the seed solution droplets on the substrate, a typical volume of ~50 μL of the BDAC-based growth solution per 1 cm² of seed-coated surface was deposited. This resulted in bundles of UTNWs with average diameter of 3.4 ± 0.8 nm, and about 75:25% Au/Ag atomic ratio, as shown in Figure 2a,b. These UTNWs bundles look identical to those grown in CTAB. The bundles typically consist of single up to hundreds of UTNWs, with typical total lateral dimensions ~3–200 nm, and single UTNW height. We have previously observed that in the CTAB-based nanowires, the silver was evenly distributed along the NWs.

The formation of UTNWs using BDAC (or CTAB) as the templating surfactant is initiated in the solution with the reduction of Au(III) ions to Au(I) state by the ascorbic acid molecules (or ascorbate ions). The Au and Ag ions form complexes with the BDAC or CTAB molecules, which allows for the reduction to the final metallic state only in the presence of the catalytic metal seeds particles printed on the surface of the substrate. The mechanism of formation of UTNWs is a self-assembly process occurring in the thin layer of growth solution deposited on the substrate. It should be emphasized that the BDAC-based growth solution leads to bulk growth of UTNWs in the thin solution film volume, as reported by Qian et al. Hence, we believe that the UTNW network, which grows within the whole volume of the BDAC-based solution, weakly attaches to the substrate at random locations, and, finally, after washing, flattens down on the surface, held by strong van der Waals attraction to the substrate. This will be further illustrated in the discussion of patterned deposition later on.

Although the mechanism by which gold nanorods or UTNWs evolve from gold seed particles using CTAB as surfactant has been studied in the past, it is still partly unknown. Because the reduction of gold (and also silver) ions by ascorbic acid (or ascorbate ions) can only occur catalytically at the surface of the seed particles, it is clear that the seed particles are incorporated within the grown nanorods or UTNWs. In the case of the UTNWs, it seems that their formation, at least in the CTAB-based process, involves the joining of short segments of the UTNWs into continuous ones. This topic will be further studied in the future.

We assume that the seed particles have to be detached from the surface to be incorporated in the surfactant template and evolve into nanowires. The difference between the two surfactants is that BDAC is more soluble than CTAB. Hence, CTAB accumulates faster at the surface, as the growth solution is brought in contact with the seed-coated substrate and immobilizes the seed particles at the interface region, whereas in the case of BDAC, they can diffuse farther into the solution.

**Silver Plating.** We have used a selective electroless silver-plating process (also called “silver enhancement”) to thicken and stabilize the UTNWs and to enhance the film conductivity. Silver deposition was preferred over the previously used gold deposition because, unlike gold, silver does not have interband transitions in the visible range and is therefore more transparent across this wavelength range.

A TEM image of the AgNWs grown with the BDAC-based growth solution, after the silver enhancement process, can be seen in Figure 2c. The UTNWs bundles coated with silver now became unified stripes of silver nanowires, about 20–200 nm wide. Before the silver enhancement, the sample sheet resistance was of the order 1 kΩ/sq (which degraded over time), the visible transmission was about 98–99%, and the haze was same as that of bare substrate within the ~0.3% haze measurement accuracy, both on poly(ethylene terephthalate) (PET) and glass. Figure 2d–f (see also the Supporting Information, Figure S3) provides the topographic AFM data for a AgNW film prepared on a PET substrate. The height of the AgNWs varies between 10 and 40

![Figure 2](image-url)
nm, with the most frequent height at ~25–30 nm, which is the result of thickening of bundles consisting of single UTNWs layer.

Figure 3 presents the results of a study of the influence of the areal density of printed seeds on the AgNWs final density (using BDAC-based process) and hence on the final sheet resistance. Due to charging of the insulating substrate, it is not possible to reliably image the UTNWs grown on glass or PET substrates by high-resolution scanning electron microscopy (SEM); hence, all of the SEM imaging was done on the AgNWs. When the density of seeds is very large (~>500 seeds/μm²) or very small (<5 seeds/μm²), the sheet resistance rises to very high values (>1 kΩ/sq), with good correlation to low AgNWs density (shown in the inset SEM images). Between ~8 and ~100 seeds/μm², we obtained relatively low sheet resistance values (≤100 Ω/sq) with high AgNWs density but with a nonmonotonous dependence of sheet resistance on seed density.

As the seed areal density is increased from ~4 to ~8 seeds/μm², a significant improvement in conductance and NWs density occurs, reaching less than 50 Ω/sq for ~8 seeds/μm². Further increase in the seed density seems to initially deteriorate the NW density and increase the sheet resistance, but then toward ~60 seeds/μm², the NW density increases to a higher value and sheet resistance drops. With further increase in seed density, it becomes clear that too high concentration of seed particles reduces the aspect ratio of the grown NWs (200–300 seeds/μm²), and, finally, completely inhibits NW formation (>500 seeds/μm²), probably due to distribution of the deposited gold and silver atoms over too many seed particles. The two local minima of the curve in Figure 3 correspond to different NW densities, but apparently the lower one (8 seeds/μm²) is compensated by higher aspect ratios and better connectivity of the NW network.

The seed density/concentration used here for the BDAC-based process is similar to that used by Azulai et al. in CTAB-based UTNWs formation. Their seeds concentration was in the range of 0.67–2.1 × 10⁻⁸ M. Taking such a concentration in a growth solution comparable to the present work (50 μL/1 cm²), one obtains the equivalent of ~50–100 seeds/μm². This concentration is similar to the second sheet resistance minimum (~60 seeds/μm²). In light of the knowledge accumulated for the CTAB-based surface growth process, we believe that similarly, this second minimum in the BDAC-based process may combine surface/interface growth mode, which requires nearly an order of magnitude larger concentration of seed particles compared with the BDAC-based bulk solution growth mode. The latter is probably responsible for the first sheet resistance minimum at ~8 seeds/μm².

After silver plating, the sheet resistance of the samples (prepared with suitable seed density) was in the range of 20–300 Ω/sq, with visible transmission in the range of ~86–95% on PET and glass substrate areas between 4 and 100 cm². Optical transmission values are given for a wavelength of 550 nm (for full spectrum, see the Supporting Information, Figure S7). The SEM images of AgNW films, prepared using BDAC- and CTAB-based processes, on 2.5 × 2.5 cm² PET substrates can be seen in Figure 4 (see also the Supporting Information, Figures S4–S6). The sheet resistance of these samples was 40 and 30 Ω/sq, respectively. It can be clearly seen that the silver deposition process was selective, and only the UTNWs were thickened without metal deposition directly on the substrate (see also the Supporting Information, Figures S1 and S2), and with almost no low aspect ratio particles of significant size contaminating the sample after the silver-enhancement step. It is highly probable that some metal particles adsorbed to the substrate before the silver coating were washed away from the substrate during the silver deposition or washing steps.

Using TEM-energy-dispersive X-ray spectroscopy (EDS) and SEM-EDS, we found that the Au/Ag composition in the UTNWs before the silver plating was ~75/25% and changed to 60–95% Ag after the silver deposition, depending on the amount of Ag plated on the UTNWs (see EDS data in the Supporting
Information, Figures S1 and S2), which together with the TEM and AFM images of the AgNWs proves that a substantial silver layer (∼10−30 nm) was formed on top of the UTNWs.

Figure 5a,c displays the optical transmission versus sheet resistance for different AgNW films deposited on glass and PET for both the CTAB- and BDAC-based processes. Tunability of the two parameters is achieved through the timings of nanowire growth and silver deposited on top of the wires. It can be seen that even at relatively low sheet resistance (∼70 Ω/sq) the transparency is ∼90% for BDAC-grown NWs and >90% for CTAB-based process.

Moreover, the haze versus sheet resistance graphs in Figure 5b,d show that a relatively low haze (fraction of the scattered light out of the total transmitted) is achieved for our films (∼0.6−0.8%) at ∼100 Ω/sq, and ∼1% haze was reached at lower sheet resistance values (∼50 Ω/sq). The haze level higher than 1% is considered disruptive for display application, as it reduces the sharpness and clarity of the image, but it is acceptable for organic photovoltaic and light-emitting diode devices in which lower sheet resistance is required.

The slopes of the haze and transmission graphs change with sheet resistance, especially in the case of the CTAB-based AgNWs (Figure 5c,d). Because haze (and partly the extinction) originates in light scattering, we can check whether the nonlinearity in the curves may be related to light scattering: Assuming a roughly cylindrical cross section of radius r for the AgNWs, the resistance of the AgNWs is given by \( R = \rho \times \frac{L}{A} \), where \( \rho \) is the resistivity, \( L \) is the NW length, and \( A \) is the cross-sectional area, which scales as \( A \propto r^2 \). Hence, the sheet resistance drops (and conductance increases) with the increase in AgNW thickness as the diameter is squared. The magnitude of Rayleigh scattering (I) increases as the square of the polarizability \( \alpha \), \( I \propto \alpha^2 \), which scales as the square of the volume \( \alpha \propto V \), and \( V \propto r^2 \) for a cylinder of constant length.35 This results in a higher power (∼4) dependence of light scattering on the AgNW diameter. We would therefore expect that as the radii of the nanowires increase (by more silver deposition), the light scattering (haze) would increase as the square of the conductance, as roughly demonstrated in the inset of Figure 5d. The same should roughly hold for the extinction if it is dominated by scattering (inset of Figure 5c).

**Patterning of the NW Films.** To optimize the UTNW deposition process for narrow stripe patterns, we compared the two UTNW growth modes, "surface growth" using CTAB-based solution versus "bulk growth" using BDAC-based solution.29 In these experiments, single seed droplet wide lines were printed on the PET substrates followed by the deposition of the UTNW growth solution over the whole substrate, followed by the silver plating bath.

Figure 6a displays the deposited and dried seed droplet lines after silver enhancement of the seed particles to make them visible in the high-resolution SEM. The 80:20% water/ethanol droplets, deposited from a 40 μm orifice (droplet volume ∼70 pL), were spread on the PET substrate in ∼70 μm diameter spots. The AgNW film stripes grown from continuous seed lines, formed by overlapping seed solution droplets, were confined to the same dimension (Figure 6b−d). To further learn about the confined UTNW surface growth mode, a single seed droplet spot

![Figure 5. Optical transmission for BDAC-based (a) and CTAB-based (c) processes, and (b, d) haze vs sheet resistance for continuous AgNW films prepared with different levels of NW density and/or silver plating timing. The transmission and haze were measured at a wavelength of 550 nm. The insets in the graphs corresponding to the CTAB-based process show the same data points plotted as (inset c) extinction (=100% − transmittance) and (inset d) haze as a function of conductance (1/Rs, where Rs is the sheet resistance), which are fitted to a parabola.](https://example.com/f5.png)
was deposited on a PET substrate and the grown NWs were imaged. As seen in Figure 7, the AgNWs were tightly confined to the ∼100 μm seed spot with a fairly sharp edge, where the AgNWs abruptly terminate, except for occasional small protrusions of the order of ∼10 μm.

Figure 8 displays the results of growing the NWs over a single seed droplet wide line using a BDAC growth solution. The BDAC-based UTNWs growth clearly occurred in the bulk solution by seed particles that detached from the substrate and became mobile in the solution through convection and diffusion. BDAC is substantially more soluble in water compared with CTAB and thus accumulates more slowly on the surface when the growth solution touches the substrate. Hence, with BDAC-based growth solution, most of the seed particle may diffuse deeper into bulk solution film and lead to the UTNW formation away from their original position. In the CTAB-based growth solution, most of the seeds are confined to the proximity of the surface due to very fast accumulation of CTAB on the surface and, thus, grow at the substrate—solution interface.

Accordingly, in the CTAB-based process, the surface-confined UTNW growth is found to be highly suitable for patterning the NW films on the substrates. As seen in Figures 6 and 7, the formed AgNWs are constricted to the original spots where the seed particles were deposited.

The difference between the obtained line patterns in the two UTNW growth modes is also demonstrated through conductance measurements. The AgNW stripes grown with the CTAB-based solution showed sheet resistance of ∼50 Ω/sq along the lines, and no conductivity was measured in the perpendicular direction (across the printed lines). On the other hand, the lines grown with BDAC showed a higher sheet resistance along the lines (>100 Ω/sq), and finite conductance was also measured perpendicular to the printed lines.

Various combinations of the two surfactants within the growth solution may be used to control the UTNW density and their spread on the substrate. The thickness of the growth solution

Figure 6. SEM images of CTAB-based AgNW stripes, patterned on a PET substrate in lines of ∼70 μm wide seed droplets and separated by ∼1 mm. (a) Printed lines of seed droplets imaged after silver enhancement. The droplets were printed partially overlapping along the lines to produce continuous seed lines. (b–d) Increasing magnification of grown AgNW stripes, confined to the same width as the seed droplets. The droplets were printed with a slight overlap. The blurred bright areas seen in (c) and (d) are due to charging of the insulating areas out of the NW stripes.

Figure 7. (a) SEM image of CTAB-based AgNW film grown on a single seed droplet printed by a 80 μm orifice on a PET substrate. (b) A higher-magnification image of the droplet border.

Figure 8. SEM images of BDAC-based AgNW films deposited on a PET substrate, with seeds patterned in ∼100 μm wide lines (single seed droplet width) and separated by ∼1 mm. (a, b) Low-magnification SEM images showing a higher metal density along the patterned seed lines due to some seed particles remaining attached to the surface and silver enhanced. (c, d) Higher-magnification SEM images showing that the resulting AgNW film extends far beyond the deposited seed droplet lines, demonstrating bulk solution UTNW growth. The border of the printed seed stripe is marked with the blue lines (seeds were deposited on the right side of the blue lines).
needed for optimal UTNW growth, especially in the bulk growth mode using BDAC, is also an important parameter that was not optimized in the current work.

The separated seed deposition and UTNW growth steps allow a tightly controllable printing mode on a variety of substrates. In particular, use of small-diameter orifices for inkjet printing of the seed solution combined with control of solvent wetting of the substrate should enable patterning of the NW films with <70 μm features (probably down to 20–30 μm). The density of the NWs on the surface can be controlled by the amount of the deposited seed particles and the time of growth. The parameters of the silver-plating step would determine the final thickness of the AgNWs, and, hence, the final film sheet resistance, transparency, and haze level.

This method has several advantages over other metal NW deposition techniques: first, in some of the other techniques, the nanorods/NWs are coated by an insulating polymer (typically PVP), and it is necessary to form electrical contacts between them through heating, other postdeposition treatments, or additional conducting polymer films, whereas in the technique described here, interwire contacts are spontaneously formed under ambient conditions during UTNW formation. Also, preformed, typically micronscale long NWs can clog inkjet nozzles (of the order of 10 μm or less) are used for high-resolution pattern deposition, whereas with the current technique, the largest printed objects are the 1.4 nm seed particles.

The standard methods of patterning the preformed Ag or Cu nanowire films are laser patterning or chemical etching through a polymer mask formed by photolithography. Laser patterning is a serial technique (as inkjet printing). The photolithographic process is a parallel one, which is more efficient but involves several steps: spinning the photosist, baking it, exposing to UV light through a mask, development of resist, applying the etching solution, and removal of the resist pattern. Thus, it seems that for certain applications, the direct inkjet NW patterning using a suitable fast printer would have several advantages over the postdeposition patterning done in the case of the standard Ag/Cu NW technology. One of the advantages would be the ambient conditions used for our process, in contrast to higher temperatures used for different stages of the other patterning processes.

## CONCLUSIONS

A scalable printing process for the preparation of metal NW films has been developed. It is a highly versatile process, where in one version it allows uniformly coating large area surfaces of different kinds (glass, polymer) through growth of the NWs in the bulk of a thin solution film based on BDAC template. In a second version, a CTAB-based growth solution enables surface UTNW growth mode, which tightly confines the grown UTNWs to inkjet-printed seed particle patterns on the surface. Although we used ~70 μm seed spots, it may be possible to reduce the jetting device to orifices of the order of 10 μm in diameter and thus reduce the NW stripe dimension to such widths, which should suffice for standard touch screen patterns (as used with ITO). Alternatively, other high-resolution printing techniques could be used to pattern the seed particles, such as microcontact printing. In addition, the final silver-plating process can be replaced by catalytic deposition of other metals, such as nickel, to change the properties of the NWs.

## MATERIALS AND METHODS

### Materials

The reagents used for the metal NW film preparation, i.e., BDAC, CTAB, HAuCl₄, AgNO₃, ascorbic acid, sodium ascorbate, bovine serum albumin (BSA), citric acid, trisodium citrate, and hydroquinone, were purchased from Sigma-Aldrich and used without further purification. The Au seed particles (NanoGold) were purchased from Nanoprobe Inc. The water used was ultrapure (18 MΩ cm), obtained from a USF ELGA UHQ system.

**Deposition of the Gold—Silver NW Films.**

**Step 1: Metal Seed Particle Solution Was Printed on the Desired Area on the Substrate.** Au seed nanoparticles of size ~1.4 nm (NanoGold, ~55 gold atoms) were used. A 10⁻⁷ M solution of seeds in a mixture of 50:50% water/ethanol by volume (or 80:20% water/ethanol for patterning) was used for printing a pattern, where the growth of the NW film is desired, on different substrates such as glass, polyimide, and different types of PET and conducting polymers. Inkjet printing of seed solution was done using a MicroFab Jetlab-4 system, with 80 and 40 μm internal diameter piezoactuated jetting devices.

**Step 2: Growth Solution Deposited on the Substrate Was Used To Form the UTNWs.** This step involves deposition of a UTNW growth solution either in the same places where the seed solution was deposited or uniformly over the whole substrate. In both cases, the UTNW film would grow only in areas where the seed particles were deposited.

**BDAC Growth Solution.** The growth solution was prepared by mixing aqueous solutions of BDAC (0.1 M, 10 mL), HAuCl₄ (0.01 M, 421 μL), AgNO₃ (0.01 M, 512 μL), and ascorbic acid (0.1 M, 268 μL) sequentially at 30 °C in a 20 mL glass vial. The usable time of the solution was at least 1 h. About 50 μL of the growth solution per 1 cm² of substrate area was deposited and incubated for 20 min at ~30 °C. Then, the substrate was washed by dipping for 1 min in methanol and 1 min in water.

**CTAB Growth Solution.** For the CTAB-based growth procedure, we used a mixture of 10⁻⁷ M seeds with 2.8 M sodium ascorbate in an aqueous solution. The growth solution was prepared by mixing aqueous solutions of CTAB (0.25 M, 10 mL), HAuCl₄ (0.025 M, 500 μL), and AgNO₃ (0.1 M, 250 μL) sequentially at 35 °C in a 20 mL glass vial. About 50 μL of the growth solution per 1 cm² of substrate area was deposited on the substrate for 1–5 min at room temperature. Then, the substrate was washed by dipping for 1 min in 70% ethanol/water and 1 min in water.

**Step 3: Selective Silver Deposition To Enhance the Film’s Conductivity and Stabilize the UTNWs, and Obtain the AgNWs.** A catalytic electroless silver-plating process was used to thicken and stabilize the UTNWs. The silver-plating solution was prepared by mixing aqueous solutions of BSA (0.5% w/v, 200 mL), AgNO₃ (0.1 M, 1.11 mL), citric acid and sodium citrate buffer (1.2 and 1.6 M, respectively, 11.1 mL), and hydroquinone (0.3 M, 33 mL) sequentially at 26 °C.

The substrates with NW films were dipped for 1–6 min in the silver-plating solution. Then, the samples were washed for 1 min in methanol and 1 min in water.

**Microscopy.** Transmission Electron Microscopy (TEM). NW film samples were deposited on carbon-coated copper grids (SPI). For the silver-coated NWs, we used carbon-coated nickel grids. Images were recorded using a Philips FEI Tecnai F20 TEM. Energy-dispersive X-ray spectroscopy (EDS) was used to determine the nanowire composition.
Scanning Electron Microscopy (SEM). SEM imaging was carried out in a Quanta200 field emission gun environmental SEM using the FEI wet-STEM detector. To examine the AgNW films deposited on nonconducting substrates (glass, PET), we used water vapor environment (low vacuum). Also, in the SEM, EDS was used to determine AgNW composition, either averaging over relatively large areas of the coating or measuring over individual AgNWs, or background.

Atomic Force Microscopy (AFM). Topography imaging was done using a NT-MDT P47 AFM using standard silicon tips (HQ-NSC35, MikroMasch) in tapping mode.

Sheet Resistance, Transparency, and Haze Characterization. The optical transmission and haze of the films were measured against a reference blank substrate in a fiber-coupled array spectrophotometer (Ocean Optics, S2000) connected to an integrating sphere, at a wavelength range of 400–900 nm. The transmission values are reported in the paper for a wavelength of 550 nm. The haze (fraction of scattered light) was calculated from four optical transmission measurements made by mounting the specimen at the input of the integrating sphere: haze = [(T1/T0) − (T2/T0)] × 100%, where T1 is a measurement of the incident light with no specimen and closed sphere, T2 is a measurement of the total light transmitted through the specimen with a closed sphere, T0 is a measurement of the light scattered by the instrument with no specimen, with an open sphere (light passing through the sphere) and a light trap, and T4 is a measurement of the light scattered by the instrument and the specimen, with an open sphere and a light trap.

Sheet resistance measurements were carried out by two-terminal measurements using silver paint at the edges of the substrates for defining the contacts and employing a Fluke multimeter. The silver paint lines defined a square measurement cell (typically 2 × 2 cm²) over the whole coated area. Therefore, the measured resistance value was roughly also the sheet resistance value. We estimate an error of the order of 5% in the estimation of Rₛ using this method due to film edge effects. Occasional comparisons to four-terminal measurements agreed with the two-terminal measurements to an accuracy of ~20%.

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