

Chemical Resistant Silver Nanowire/Cellulose Nanofibril Flexible Transparent Conductive Film

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Keywords: silver nanowire, cellulose nanofibrils, Flexible TCF, electrochromic, one-step coating, anti-corrosion.

ABSTRACT

In this research, a simple coating method was developed to produce a chemical-resistant transparent conductive thin film. Ultrasonicated CNF, as a binder, is mixed with Silver nanowires to provide a stable coating fluid. The mixture was coated on a flexible plastic substrate by a one-step blade coating procedure. As a result, the coating not only shows low sheet resistance of 11.7 Ω/square , great transparency of 91.48% transmittance. Additionally, The film can be further improved in chemical & mechanical stability by cross-linking reaction to exhibit great chemical resistance.

1 Introduction

Transparent conductive films (TCF) have been widely used in various electronic applications, such as touch panels, solar industry, and LED. Recently, demands of flexible TCFs surge with the increasing needs in portable touch screen devices. The most commonly used TCF nowadays is made of indium tin oxide (ITO) [1], which has outstanding visible light transmittance and an excellent conductivity up to 5714 S/cm. However, owing to its ceramic nature, ITO TCF is brittle and has low bending durability for further flexible electronic applications. Moreover, ITO is susceptible to acids and therefore limits its application in certain working environments. Hence, recent studies start to seek for ITO replacement materials for flexible TCF fabrication. Several alternative materials, such as carbon nanomaterials [1], conductive polymers [2], and nanometals [3], have been proposed. Among these options, silver nanowire (AgNW) shows the most promising performance in many aspects. First, silver has the best conductivity among all conductive materials. Therefore, TCF made of AgNW can achieve required conductivity with little material consumption. Secondly, AgNW can be synthesized with a large quantity and well suspended in common solvents, such as water or isopropyl alcohol, as a coating solution for TCF manufacturing. Thus, various coating methods, including roll-to-roll coating, can be applied to produce TCF at large scale. Finally, AgNW coating can form a percolating conductive mesh network under low areal density to provide not only great flexibility but also high transmittance for visible lights.

Despite the merits mentioned above, poor adhesion

and low oxide resistance while exposed to air highly restrain the application of AgNW for TCF coatings. The most common solution to this issue is coating an embedder layer over AgNW coatings to protect AgNW from air exposure and also serve as an adhesive layer to keep AgNW on the substrate as well. For example, Chen et al. [3] sputtered ZnO on AgNW TCF as a transparent surface protector to prevent AgNW from detachment under bending conditions. Similarly, Zhang et al. [4] cover AgNW coatings with a graphene layer to provide oxidation protection while maintaining surface conductivity. Other protection layers, such as including epoxy [5] and other polymers, have also been proposed in the literature. But these polymeric embedders, although showing great adhesion and oxidation protection, tend to result in a lower electrical conductivity. Despite materials for protection layers, production of AgNW TCF needs two or three coating steps to enhance adhesion and chemical stability of AgNW. To shorten the process time, a better coating formula is needed to provide adhesion and oxidation protection for AgNW at the same time.

Among various coating materials, cellulose nanofibers (CNFs), an environmental-friendly material from natural biomass, recently catch wide attention due to its good mechanical strength and high transparency. Besides high mechanical strength, CNF thin films possess compact nanofiber stacking to prevent gas penetration, and have been widely used for oxygen penetration barrier. The CNF coatings also provide good adhesion to various flexible polymer substrates, and can be used as a binder in ink formulation. Furthermore, recent research shows that CNFs can be mechanically separated into smaller units through ultrasonication to help the suspension stability of AgNWs in water. Therefore, CNFs can serve as a dispersant and binder for AgNW coatings to enhance coating uniformity, adhesion and oxidation protection. However, owing to the hydrophilic groups on CNF, dried CNF thin films are hygroscopic and absorb humidity easily. Water molecules can penetrate through CNF films easily, leading to swelling or curling, and deteriorate the film structural stability. To reduce water absorbance, CNF thin films can be processed via esterification process with crosslinking agents, such as citric acid, to remove

the hydroxy groups on CNFs. The crosslinking reaction not only reduce the polarity of CNFs, but can also build chemical bonds between CNFs to form stronger structures against chemical erosion.

In this study, CNFs are first ultrasonicated into smaller units to serve as a dispersion agent. AgNWs are then mixed and stabilized in the aqueous CNF solution to prepare a stable coating solution. A blade coating process is used to create uniform TCF thin film over transparent polymeric substrates. After drying, the hygroscopic AgNW/CNF coatings are then crosslinked with citric acid to prepare chemical-resistant TCFs. The conductivity, adhesion, and chemical resistance of the esterified CNFs will be carefully examined.

2 Experiment

CNF solution (9 g) was placed in a 20 ml glass bottle and was sonicated with a homogenizer (Ruptor 4000, Omni) for 15 minutes. The sonicated CNF solution was then mixed with AgNW solution (1 g) and mixed with a planetary centrifugal mixer for 2 minutes followed by a 30-second defoaming process at 2000 rpm. PET film was cut into pieces with a dimension of 9 × 9 cm. The cut PET films were rinsed with ethanol and cleaned with a sonication bath cleaner (DC300, Delta). After drying the PET, these PET films were then treated with a low-pressure plasma for 2 minutes before coating. A blade coating machine was used to coat AgNW/CNF solution over the PET films. The coated AgNW/CNF on PET was then dried for 12 hours in a vacuum oven at 80 °C. The dried AgNW/CNF was further immersed in 20 wt% citric acid solution to crosslink for 1 hour followed by another 12-hour drying process. The cross-linked AgNW/CNF on PET was then collected for further analysis.

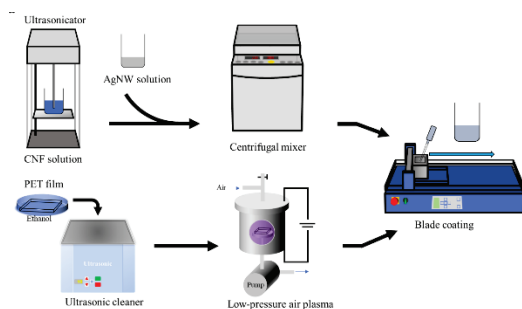


Fig. 1 Schematic diagram of AgNW/CNF TCF fabrication.

3 Results

The CNF network in water unwind after ultrasonication. To analyze the changes in the configuration after the ultrasonication, the rheological properties of sonicated CNF solutions are examined (Fig. 2(a)). The dependence of the viscosity with shear rate decreases, which can be observed from the increasing n value in the power law

model (inset figure in Fig. 2a).

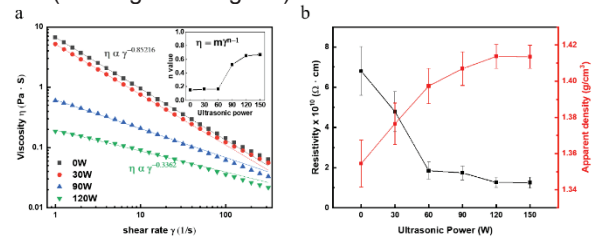


Fig. 2 (a) Viscosity of 1 wt% CNF aqueous solution after ultrasonication for 15 min at different power input conditions. (b) Resistivity and apparent density of CNF dry films made by sonicated CNF solutions.

To observe the ultrasonication effect the film surface and AgNWs alignment. AFM and SEM analyses for AgNW/CNF and AgNW/uCNF dry films on PET is shown in Fig. 3.

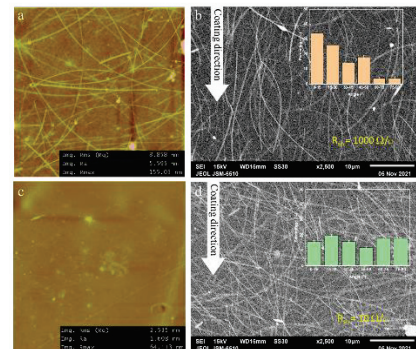


Fig. 3 AFM and SEM analyses for AgNW/CNF and AgNW/uCNF dry films on PET. The inset figures in (b) and (d) show the angles between AgNWs and coating direction.

Various durability tests are operated to analyze the enhancement of chemical and mechanical properties. As shown in Fig. 4 and Fig. 5.

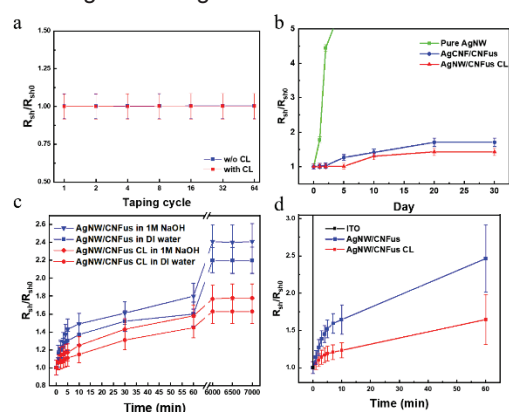


Fig. 4 R_{sh} ratio change of AgNW/uCNF, AgNW/uCNF CL (a) as a function of taping cycle (b) As a function of time after 3 hours of UV irradiation compared with pure AgNW film(c) As a function of time under aqueous and 1M NaOH solution. (d) As a function of time under 1M HCl solution compared with pure AgNW film.

with ITO PET film.

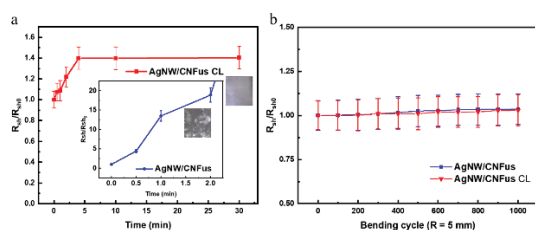


Fig. 5 R_{sh} ratio change of AgNW/UCNF, AgNW/UCNF CL film. (a) As a function of time under ultrasonic cleaner. (b) as a function of the bending cycle.

4 Discussion

4.1 Ultrasonication treatment for CNF

The original CNF solution is a shear-thinning fluid, whose viscosity follows a power law and decreases with shear rate with an exponent of -0.85. This shear thinning characteristic is commonly observed in polymer solutions, and the exponent observed here is quite close to those for cellulose solutions. After sonicated at low power (30-60 W), the rheological behavior of the CNF solution remains nearly the same, indicating that the CNF network remain intact in the solution. When the sonication power reaches 90W, a drastic viscosity drop occurs, possibly due to the sufficient energy density to break CNF rods apart into thinner units. Moreover, the dependence of the viscosity with shear rate decreases, which can be observed from the increasing n value in the power law model (inset figure in Fig. 2a). These rheological changes indicate less entanglement between CNFs and the sonication above certain power density level (90 W in this case) can unwind CNFs into smaller units with less contact-dragging forces. When most of the CNF rods are physically separated, the viscosity drop tendency slows down and therefore one can find the n value plateaus for sonication power levels higher than 120 W.

The CNF untangling behavior after ultrasonication also results in more compact CNF packing after drying. Because CNF unwind into thinner units after ultrasonication, a more compact dried film structure is expected for the sonicated samples. As shown in Fig. 2(b), the apparent density of CNF dried films is 1.35 g/cm³ before sonication, and increases 1.41 g/cm³ after sonication. Moreover, the density also plateaus at sonication power of 120 W, sharing the same characteristic as Fig. 2(a). The electrical resistivity of dried films is also strongly affected by CNF packing and drops to 1/4 for samples from sonicated CNF. With the dense structure and lower resistivity, the dried film from ultrasonicated CNF solution can work as a better embedder for AgNW TCF.

4.2 CNF/AgNW Coating

From AFM analysis (Fig. 3), obvious AgNWs texture are

observed on the thin film made by coating (AgNW/pristine CNF) solution with a surface roughness of ~ 9 nm, which is about half of the AgNW radius (~20 nm). Thus, one can hypothesize that the pristine CNF cannot wrap over the AgNW to provide total embedment in the drying process. On the other hand, using the untangled CNF after sonication as an embedded, a uniform smooth surface with a roughness of 2.5 nm is obtained. Moreover, the AFM image shows nearly no AgNW textures. This can be explained by the fact that untangled CNFs can wrap over AgNWs in the drying process and stack up around AgNWs to form a uniform and smooth layer.

The embedded AgNWs underneath the surface can be observed through SEM analysis. To quantitatively describe the AgNW arrangement, the angle between the coating direction and each AgNW is measured individually. For AgNW coated with pristine CNF, the highly viscous fluid generates strong dragging force in the coating process, and thus the slender AgNWs are pulled along the coating direction. As a result, most AgNWs are parallel to coating direction after drying. Such parallel AgNW arrangement weakens the conductive network and therefore the dry film made of pristine CNF shows a high sheet resistance ~1000 Ω /square. On the other hand, because of the lower viscosity, the nanowire directions using the untangled CNFs are highly uniform in all directions. The interlacing network of the AgNW provides effective percolating paths for electron transfer and thus the AgNW/UCNF film shows a great sheet resistance of ~ 10 Ω /square.

4.3 Durability of Crosslinked AgNW/uCNF films

After crosslinking, the AgNW/UCNF films exhibit great durability against mechanical disturbance and chemical erosions. First, the uCNF embedder enhances the adhesion and creates a protection layer over the AgNWs. Standard taping and bending tests (Fig. 4(a) and Fig. 5(d)) show that the uCNF layer can generate great adhesion on PET. The resistance of the AgNW/UCNF coatings remains unchanged after 64 tape removing cycles or 1000 bending cycles. However, after crosslinking, the AgNW/UCNF coatings have a tougher structure and can resist strong sonication under water. As shown in Figure 5(a), the AgNW/UCNF film breaks apart after in less than 2 minutes in sonication bath. On the other hand, the crosslinked AgNW/UCNF remains intact and only shows a slight resistance increase after sonication for 30 minutes. This stronger mechanical stability shows more compact CNFs together and less hydrophilic groups, which prevent the solution from penetrating the film, and the continuous chained structure keeps the fibrils from breaking apart by cavitation bubbles.

The AgNW/UCNF films resist oxygen exposure for long term usage (Fig. 4(b)). The conductivity of

AgNW/CNF thin film fades significantly after 2-3 days due to the fast oxidation in air. With uCNF embedder layer, the AgNW/uCNF has a thin and sealed protection layer over AgNWs and can prevent exposure to air. Thus, the sheet resistance remains nearly the same in 5 days, and slowly increases. Besides oxygen protection, the film is expected to function under a wide range of solutions. Therefore, it is immersed under DI water, 1M NaOH, 1M HCl for stability test. As shown in Fig. 4(c)(d), AgNW/UCNF film shows great improvement in all aspects after the cross-linking treatment. In comparison to ITO film, the AgNW/UCNF CL film can tolerate a more acidic condition.

4.4 Figure of merit (FOM)

To compare the TCF performance with others in the literature, a common figure of merit equation is used as below

$$FOM = \frac{Z_0}{2R_{sh}(T^{-1/2} - 1)}$$

where Z_0 is the impedance of free space with a value of 377Ω , R_{sh} is the sheet resistance, and T is the transmittance of the TCF film at the wavelength of 550 nm. A great transmittance performance in comparison with ITO glass The AgNW/uCNF CL film shows great transmittance of 91.48% with a sheet resistance of 15.1 Ohm/square. Our research shows a rather high performance among the TCFs. The specific data is illustrated in the following Table. 1

Table 1.Comparison of TCF [6] [7] [8] [9] [10] [11] [12] [13]

Material size	Coating method	Additional method	Sheet resistance(Ω/square)	Transmittance at 550nm (%)	substrate	FOM
D = 70nm, L = 8μm	Drop coating	Rinsing and pressing	8.6	80.0	PET	185.70
D = 60nm, L = 6μm		Film transfer	100/30/12	91/86/82	polyacrylate	80.22
D = 90nm, L = 20-40μm		Polymer(SR540) composite	10.0	≈80	glass	159.70
D = 115nm, L = 30μm	Spray coating	Spray coating with PEDOT:PSS	10.76	84.3	PET	196.52
D = 60nm, L = 20μm		Spin coating with PEDOT:PSS	30.8	≈80.0	PET	51.85
D = 223nm, L = 143μm		Plasma treatment	13	91	PET	300.30
D = 50-100μm	Mayer rod coating	Nano soldering	25	85	PET	89.07
D = 40nm, L = 35μm		Ultrasonic spray coating	1.03	88.22	glass	193.92
D = 30-65nm, L = 10-90μm	Blade coating	Covered with polymer matrix	50/10	90/78	PET	142.50
D = 40-50nm, L = 10-20μm		Pre-mixing polymer composite/cross-linking	15.1*	91.48*	PET	318.46

5 Conclusions

In this research, a simple fabrication method is developed to prepare chemical-resistant AgNW transparent conductive films on a flexible substrate. By using ultrasonicated CNF as a dispersion agent and an embedder, forming a well-dispersed solution. This can provide a one-step coating procedure to insert the CF into AgNW meshes, which generates enough adhesion force and also a thin layer that both protects the AgNW and allows good electrical conductivity. Moreover, the structural stability of the film can be further enhanced by cross-linking reaction. AgNW/UCNF CL film shows performance enhancement in all aspects of our investigation.

References

- [1] E. J. López-Naranjo, L. J. González-Ortiz, L. M. Apátiga, E. M. Rivera-Muñoz, and A. Manzano-Ramírez, "Transparent electrodes: a review of

the use of carbon-based nanomaterials," *J Nanomater*, vol. 2016, 2016.

- [2] K. Sun *et al.*, "Review on application of PEDOTs and PEDOT: PSS in energy conversion and storage devices," *Journal of Materials Science: Materials in Electronics*, vol. 26, no. 7, pp. 4438-4462, 2015.
- [3] Y. Chen *et al.*, "Highly flexible, transparent, conductive and antibacterial films made of spin-coated silver nanowires and a protective ZnO layer," *Physica E: Low-dimensional Systems and Nanostructures*, vol. 76, pp. 88-94, 2016.
- [4] X. Zhang, X. Yan, J. Chen, and J. Zhao, "Large-size graphene microsheets as a protective layer for transparent conductive silver nanowire film heaters," *Carbon*, vol. 69, pp. 437-443, 2014.
- [5] L. Miao, G. Liu, K. McEleney, and J. Wang, "Epoxy-embedded silver nanowire meshes for transparent flexible electrodes," *J Mater Sci*, vol. 54, no. 14, pp. 10355-10370, 2019.
- [6] S. Huang *et al.*, "A facile way for scalable fabrication of silver nanowire network electrodes for high-performance and foldable smart windows," *J Mater Chem A*, vol. 8, no. 17, pp. 8620-8628, 2020.
- [7] T. Tokuno *et al.*, "Fabrication of silver nanowire transparent electrodes at room temperature," *Nano Res*, vol. 4, no. 12, pp. 1215-1222, 2011.
- [8] Z. Yu *et al.*, "Highly flexible silver nanowire electrodes for shape-memory polymer light-emitting diodes," *Adv Mater*, vol. 23, no. 5, pp. 664-668, 2011.
- [9] Z. Yu, L. Li, Q. Zhang, W. Hu, and Q. Pei, "Silver nanowire-polymer composite electrodes for efficient polymer solar cells," *Adv Mater*, vol. 23, no. 38, pp. 4453-4457, 2011.
- [10] S. Zhu *et al.*, "Transferable self-welding silver nanowire network as high performance transparent flexible electrode," *Nanotechnology*, vol. 24, no. 33, p. 335202, 2013.
- [11] J. Lee *et al.*, "Room-temperature nanosoldering of a very long metal nanowire network by conducting-polymer-assisted joining for a flexible touch-panel application," *Adv Funct Mater*, vol. 23, no. 34, pp. 4171-4176, 2013.
- [12] D. Y. Choi, H. W. Kang, H. J. Sung, and S. S. Kim, "Annealing-free, flexible silver nanowire-polymer composite electrodes via a continuous two-step spray-coating method," *Nanoscale*, vol. 5, no. 3, pp. 977-983, 2013.
- [13] L. Yang, T. Zhang, H. Zhou, S. C. Price, B. J. Wiley, and W. You, "Solution-processed flexible polymer solar cells with silver nanowire electrodes," *ACS applied materials & interfaces*, vol. 3, no. 10, pp. 4075-4084, 2011.