PCCP

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/pccp

Fast fabrication of copper nanowire transparent electrodes by a high intensity pulsed light sintering technique in air

Su Ding, [a, b] Jinting Jiu, [*b] Yanhong Tian, [*a] Tohru Sugahara, [b] Shijo Nagao, [b] Katsuaki Suganuma [b]

[a] *State Key Laboratory of Advanced Welding and Joining, Harbin Institute of Technology, Harbin, 150001, China. E-mail: tianyh@hit.edu.cn*

[b] *The Institute of Scientific and Industrial Research (ISIR), Osaka University, Osaka, Japan. E-mail: jiu@eco.sanken.osaka-u.ac.jp*

Abstract:

Copper Nanowire transparent electrodes have received increasing interests due to the low price and nearly equal electrical conductivity comparing with other TEs based on silver nanowires and indium tin oxide (ITO). However, a post treatment at high temperature with insert atmosphere or vacuum environment was necessary to improve the conductivity of CuNW TEs due to the easy oxidation of copper in air atmosphere, which greatly cancelled out the low price advantage of CuNWs. Here, a high intensity pulsed light technique was introduced to sinter and simultaneously deoxygenate these CuNWs into highly conductive network at room temperature in air. The strong light adsorption capacity of CuNWs led to the welding of the nanowires at contact spots, as well as removing the thin layer of residual organics, oxides and hydroxide of copper even in air. CuNW TE with sheet resistance of 22.9 Ohm/sq and transparency of 81.8% at 550 nm has been successfully fabricated within only 6 milliseconds exposure treatment, which is superior to other films treated with high temperature in hydrogen atmosphere. The HIPL process was simple, convenient and fast to fabricate easily

oxidized CuNW TEs in large-scale in air atmosphere, which will largely extend the application of cheap CuNW TEs.

1. Introduction

Transparent electrodes (TEs) are essential components in touch screens, liquid crystal displays, organic solar cells, and light-emitting diodes (LEDs). Traditionally, the most widely used material for TE is indium tin oxide (ITO), however, ITO is becoming more and more expensive not only for the limited supply of indium but also for the rigorous vacuum-based processing methods including sputtering and chemical vapor deposition (CVD). Thus, researchers devote great efforts to develop new alternatives produced with cheap materials and low cost process. Recently, carbon nanotubes [1-4], graphene [5-9] and metal nanowires [10-13] transparent films have been demonstrated to be promising substitutions. Among them, films made from one dimensional (1D) metal nanowires (in particular, copper and silver nanowires) give superiority due to high electrical conductivity, amenability towards solution synthesis and cost effective manufacturing process. Silver nanowire (AgNW) TEs have been proved to have equal optoelectrical property to commercial ITO [14-17]. However, as precious metal silver is even more expensive than ITO and easily corroded due to vulcanization in air, both of which hinder the widely application in practical life. In contrast, copper is only 6% less conductive than silver, but 1000 times more abundant and 100 times less expensive. Thus, replacing AgNWs with CuNWs should offer comparable performance at much lower cost. Moreover, comparing with AgNWs, the aspect ratio of CuNWs is much larger which would improve the performance for high

transmittance networks [18]. So CuNWs based transparent film has been considered to be next generation of transparent conductor not only for economic consideration but also for excellent properties. However, CuNWs have a fatal oxidization drawback, which reduces even fails the conductivity of CuNWs. It is a key issue for CuNW TEs to effectively deoxidize CuNWs during the fabrication process.

Normally, CuNW transparent films are fabricated through Meyer rod- [19], spray-coating [20-21] or vacuum filtration [13, 22-23] using CuNWs inks on various substrates. After that, in order to improve the conductivity, these CuNWs films are always treated with high temperature (above 175 °C) in reducing atmosphere such as hydrogen [13, 19, 21-23], or mechanical pressure (up to 0.4 GPa) [20]. The annealing treatment in reducing atmosphere transformed the surface oxides into copper phase, however, the insert gas greatly increased the cost and complicated the operation. Although the mechanical press process avoided severe oxidation issue due to room temperature operation, the high pressure inevitably deformed devices. Recently, a washing method by organic acid, glycerol or $NaBH_4$ was developed to get rid of the residual organics and surface oxides on CuNWs before the films were formed. The washing process allowed the direct contact between pure CuNWs which effectively improved the electrical properties of CuNW TEs [21, 23-25]. However, the corrosion cleaning step made these CuNWs be more easily oxidized because of the newly generated fresh surface and defects during the etching process [26]. Obviously, there is still a need to develop a suitable post treatment technology for fabrication of CuNW TEs, which is simple, convenient and intelligent to deal with the oxidation issue.

Recently, photonic sintering technique has been proved to be an effective method to sinter metal nanoparticles to make conductive patterns with an extremely fast speed in air [27-30]. Silver nanowire TEs have been fabricated with a high intensity pulsed light (HIPL) technique in our previous reports which not only improved the junctions between nanowires but also enhanced adhesion between Ag nanowires and flexible substrates due to the transient heat effect [31-32]. Due to the strong light adsorption of metal nanomaterials, the transient temperature is even over 1000 °C, which is pretty enough for welding metal nanowires to improve junctions. However, the application of this method to CuNW TEs has not been realized. It will be a great achievement to fabricate CuNW TEs by the HIPL technique due to its fast speed, room temperature operation and obedience of roll-to-roll assembly line, which will greatly accelerate the application of cheap CuNW TEs. Besides the enhancing of junctions between nanowires, even more exciting, the biggest weakness of CuNWs -- oxidation issue is very likely to be avoided or removed which have been proved in Cu nanoparticles [29]. These results encourage us to make CuNW TEs with the rapid HIPL technique.

In this paper, CuNWs were firstly prepared using a simple hydrothermal method and then dispersed in isopropanol to make CuNWs ink. After the CuNWs ink was coated on glass substrates using spray method with different thickness, the CuNW films were sintered with HIPL to achieve highly conductive TEs in a short duration in air. The relationship between transmittance and conductivity, the dependence of conductivity on the number of exposure have been demonstrated. The microstructure of CuNWs has been observed to discuss the sintering mechanism of CuNWs in air.

2. Experimental

2.1 Preparation of CuNWs

Anhydrous copper dichloride ($CuCl_2$, 95%), glucose (98%), octadecylamine (ODA), hexane and isopropanol were obtained from Wako Chemicals. All of the chemicals were used as received without further purification. CuNWs were synthesized by a simple hydrothermal method according to previous reports [33-35]. First, 0.4mmol $CuCl_2$, 0.4 mmol glucose and 2.4 mmol ODA were mixed in 30 mL water at room temperature for 2 hours under magnetic stirring until the solution gradually became into blue emulsion. Then the emulsion was transferred into a 50 mL capacity Teflon-lined autoclave and kept at 120 °C for 24 hours. After the autoclave cooled down to room temperature, the reddish product was collected and washed for 3 times by water, hexane and isopropanol, respectively. Finally, the CuNWs were dispersed in isopropanol to make an ink with concentration of about 0.5 g/L for further use.

2.2 Fabrication of CuNW TEs

Before the CuNWs ink was coated on the substrates, the ink was normally treated with ultrasonic vibration for 10~15 minutes to ensure the homogeneous distribution. The CuNWs ink was coated on glass slices placed on a hot plate with temperature of 60 °C by home-made spray method (Fig. S1). It effectively avoided the aggregation of CuNWs due to the rapid evaporation of solvent on the hot plate. The distance between spray nozzle and substrates is around 10 cm. The loading amount of CuNWs on substrates was varied by the spray cycles to obtain films with various transparencies. After that, these CuNW films were treated with HIPL equipment (PulseForge 3300,

Novacentrix, Austin, TX, USA) by adjusting the energy and duration of light. During this process, a mirror was set under the substrates in order to reflect the light back again to the surface of the CuNW meshes. The mirror effectively reduced the dissipation of light and heat.

2.3 Characterization

The morphology of CuNW films was characterized by field-emission scanning electron microscopy (SEM, Hitachi SU8020, Hitachi High Technologies America, Inc.) and transmission electron microscopy analysis (TEM, JEOL-2100, JEOL Ltd.). Transmittance spectra were measured using UV-visible-near infrared spectrophotometer (V670, JASCO Corp.) employing glasses as reference. The sheet resistance was measured by the four probe method with a surface resistivity meter (LorestaGP T610, Mitsubishi Chemical Analytech Co. Ltd.). The oxidation state was also investigated by X-ray diffractometer (XRD, Rigaku Smart Lab, Rigaku Americas Holding Company, Inc.) and X-ray photoelectron spectroscopy (XPS, PHI Quantera Ⅱ, ULVAC-PHI, Inc.).

3. Results and discussion

Fig. 1a gives the SEM images of as-synthesized CuNWs, which have an average diameter of 40 nm and length over 50 μm. Fig. 1b shows the SEM image of CuNW films on glass substrate with transmittance around 80%. These CuNWs have been randomly distributed on the glass substrate to form a uniform network structure. Fig 1c and d show the tilted images of CuNW films before and after the HIPL treatment, respectively. Before the HIPL treatment, the sheet resistance of the CuNWs network

was around 10^5 Ohm/sq, which was much higher than AgNW films by simple coating method. The possible reasons were analyzed in the following. The resistance of CuNW films was mainly determined by the contact resistance of junctions between CuNWs. Close contact was expected to facilitate the electrical connection between wires which will achieve low resistance. Without any treatment, the junctions were mainly driven by gravity, Van der Waals between the CuNWs, air pressure from the airbrush, and capillary forces due to solvent evaporation during the preparation process. These interactions were very weak and the junctions were not firm enough as shown in Fig. 1c, which clearly gave a soft and loose stacked structure between nanowires leading to a low conductivity. After treatment, although no apparent differences have been observed in the plan view of the CuNWs network with transmittance around 80% (Fig. S2), the distance between nanowires has been largely changed from loose overlap to clearly tight contact as shown in 1d. Most top wires were partly embedded into the bottom ones at the contact spots, which greatly enlarged the contact area between CuNWs. It is known that the CuNWs have a strong optical adsorption at 580 nm as indicated in the Uv-vis spectroscopy of Fig. S3. The HIPL xenon lamp has a wide spectrum in the range from 100 to 1000 nm. When the CuNWs films were exposed to the xenon lamp of HIPL, the light energy was absorbed by the CuNWs. The energy induced the diffusion and assembly of Cu atoms on the surface of nanowires, which caused the re-crystallization of Cu atoms. Combining the surface plasmon resonance (SPR) [36-38], the diffusion and assembly of Cu atoms on the surface contributed to tight connection. The energy also can be

transferred into heat energy which similarly induced the atoms diffusion and further enhanced the connection between CuNWs. Furthermore, the organic ODA layer, ODA used in the synthesizing process was tightly adsorbed on the surface of tiny CuNWs (Fig. S4) and attributed to the high resistance due to the obstruction of contacts between nanowires [26, 39-40], might be removed by the function of light to give a better contact between nanowires. It has been confirmed the PVP could be photodegraded into alcohol and acid under the function of high intensity pulsed light [30]. As organic, ODA might be decomposed under the irradiation of HIPL to enhance the junctions as well as improve the conductivity of CuNW films [41]. Due to these reasons, the HIPL technique rapidly transformed the soft and loose stacking CuNWs networks into a tightly connected network which was supposed to improve the conductivity.

Fig. 2 shows the transmittance (T) at 550 nm versus sheet resistance (R_{sh}) curve of CuNW TEs using different numbers of exposure. Before HIPL treatment, the R_{sh} of newly prepared CuNW films was around 10^5 Ohm/sq as mentioned above. The light was set with energy of 2.393 J/cm^2 and pulse duration of 300 μs in present work unless otherwise noted. It is clear that the resistance was drastically decreased to several hundred when a single exposure was applied as shown in Fig. 2. When the number of exposure was further increased to no more than 20, the R_{sh} was always declined. For example, when the CuNW films were treated with 1 pulse, the resistance was over 200 Ohm/sq at transmittance of 77%. Increase the pulse number to 5, the resistance has been decreased to about 36 Ohm/sq. Further increase the pulse

number to 10 and 20 times, the resistance has been reduced to 25 and 20 Ohm/sq. The improvement in conductivity depended on the enhanced junctions between nanowires formed by the photonic sintering. More pulses meant prolonging sintering time, would more effectively enhance the re-crystallization of Cu atoms in junctions to decrease the contact resistance.

The heat generation was confirmed by the simulation of temperature evolution on the CuNW films at transparency of 80% using some parameters of thermal conductivity, density and thickness of both Cu and glass as given in Tab. S1. The used parameters of light were also given in Tab. S2. The thickness of CuNWs networks and glass was set as 0.2 μm and 900 μm, respectively. According to the simulation result, the temperature on the surface of films was about 600°C as shown in Fig. S5. However, the estimated temperature is based on a dense bulk Cu film. In fact, CuNW TE with transparency of 80% was a mesh network. The actual temperature was far lower than the simulated temperature. Otherwise, the generation of heat was confirmed and estimated below 600°C. When the single exposure was finished, the heat was released to around air to cool the sample. In the continuous pulse procedure, the heat could not be totally released before the next pulse and led to a slightly higher temperature on the CuNW films. The CuNWs were instantaneously sintered to form conductive networks due to the welding between nanowires through atoms diffusion and assembly, thus, the conductivity was improved by increasing exposure times. The adsorptive capacity of light for highly transparent films with less CuNWs loading was weak, multiply exposure was necessary to achieve low resistance. Pulses number over

10 was needed to achieve highly transparent and conductive TEs with *T* over 80% under power of 2.393 J/cm^2 as shown in Fig. 2. A higher power with short pulse or low power with long pulse may be suitable with the simple HIPL technique. Through adjusting the parameters of light, highly conductive CuNW TEs could be obtained.

Besides the loose contact and obstruction of ODA which could be improved using HIPL technique, there is still a reason for the high resistance of CuNW films. CuNWs are highly sensitive to oxidation even at room temperature during the post washing and short-term storage process, which would reduce the conductivity [42]. The nonconductive oxidation at the surface of CuNWs blocked the transfer of electrons. The CuNW films, therefore, always were much less conductive than normal AgNW films due to the inevitable oxidation. Molares et.al have reported that the resistance of CuNWs exposed to the aerial oxygen for only several hours was much larger than the original value due to the gradual oxidization of copper [43]. Same phenomenon has been encountered in our case. When the CuNWs films were kept in atmospheric environment for only 2-3 hours before HIPL treatment, the sheet resistance has exceeded the measurement range ($9.9*10^6$ Ohm/sq) from original 10^5 Ohm/sq. To observe the surface state of CuNWs, fresh made CuNWs were immediately dropped onto TEM grid to analyze the surface oxide. It can be seen there were two clear layers at the surface as shown in Fig. S6. The outer layer was amorphous organics with thickness of 3.9 nm which was assigned to residual ODA, and an extreme thin layer of 1.4 nm was also presented. The high resolution TEM image shows two different space distances of 0.21 nm and 0.24 nm along the same direction as marked by dashes,

which corresponded to the (111) facets of Cu and Cu_2O (cuprite), respectively. A same oxide layer covered on the surface of CuNWs has been observed when the CuNWs were kept in vacuum desiccator for only 1 week [40]. It implied that these CuNWs were easily oxidized in air to show high resistance, thus, simple washing method was able to achieve highly conductive CuNW films by resolving surface oxides and purifying CuNWs [23, 26].

In this paper, HIPL method was used to deoxidize and purify CuNWs in air atmosphere. In order to confirm the oxide layer could be removed after the HIPL process, CuNWs ink was stored in isopropanol solution and put into fridge for two months for sufficient growth of oxides on the surface of CuNWs. Then these CuNWs were employed to fabricate films and treated with HIPL technique. The X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) patterns were collected after long term storage as shown in Fig. 3. Besides Cu, the copper oxide (CuO), cuprous oxide (Cu_2O) and hydroxides of Cu ($Cu(OH)_2$) were detected as marked in the insert of Fig. 3a, although the amount was still so small. The presence of the oxides and hydroxides of Cu was further confirmed by the XPS curve (Fig. 3b). Before HIPL treatment, the Cu 2p photoelectron peaks of Cu/Cu_2O (932.1 eV), CuO (933.0 and 943.0 eV) and $Cu(OH)_2$ (935.0 eV) were observed. After the HIP treatment, only one peak at 932.1 eV, which was corresponding to Cu/Cu_2O, was observed, other peaks attributing to CuO and $Cu(OH)_2$ have been disappeared. Moreover, Cu_2O peak was also detected according the Cu LMM peak analysis (Fig. S7), which was probably ascribed to continuous oxidation once exposed in air atmosphere. The results

suggested that the oxide containment has been reduced with the HIPL treatment.

To further verify the capacity of deoxidization of HIPL technique, the electrical property of TEs fabricated using the oxidized CuNWs was also examined. Films fabricated with the severely oxidized CuNWs were nonconductive due to the inhibiting conduction across pure Cu-Cu. After HIPL treatment these films show high conductivity with the R_{sh} of about dozens Ohm/sq depending on the transmittance (Fig. S8). The R_{sh} was higher than that of TEs fabricated using newly prepared CuNWs in Fig. 2. It was probably due to the thicker oxides and hydroxide layer could not be totally removed before welding, moreover, the additional ultrasonic procedure decreased the length of CuNWs that would lead to an inferior conductivity. On the other hand, although conductive CuNW films have been obtained by annealing at 200°C in vacuum environment using fresh CuNWs [44], same vacuum treatment achieved non-conductive CuNW films in our work even at 220°C and loading much more CuNWs on the substrates, which implied the residual of oxides on surface. To obtain highly conductive CuNW films, it was imperative not only welding the copper nanowires but also removing surface oxides and hydroxide. These results strongly indicated that the HIPL process effectively removed the oxides and hydroxide on the surface of CuNWs and improved the conductivity. It has been reported that oxides on the surface of Cu nanoparticles could be reduced into Cu with light irradiation in the existence of reactive organics, such as poly (N-vinylpyrrolidone) (PVP) which played a role of reduce agent [29]. In present process, the residual ODA shown in Fig. S4 might play similar role in the HIPL process. These organics was supposed to be

photochemically decomposed to produce active H, N radical, which reacted with those oxides and cleaned the surface to improve the junctions between CuNWs.

From the above, HIPL technique is an effective method to improve the conductivity of CuNW TEs due to the welding between nanowires and removal of ODA and oxides. Transparency is another important parameter for TEs. Fortunately, the transparency of CuNW films was increased slightly after the HIPL treatment (Fig. 4). Two samples with transmittance of 82% and 72% at 550 nm were tested. The transmittance was improved to 84% and 75% after HIPL treatment after 20 pulses, respectively. In the present work, 20 pulses have been used to sinter the CuNWs films, which produced a lot of heat on the surface of CuNWs film. The heat not only effectively sintered the CuNWs, but also led to thermal stress in the CuNW films. The stress would result in broken of the CuNWs network and separation between CuNWs and glass due to the bad adhesion. Moreover, the uneven distribution of CuNWs on the glass might lead to a non-uniform heat distribution. CuNWs at overheat area would be "blow" away from the glass substrates to achieve a high transmittance film. Hence, correctly controlling the light intensity of the HIPL process is important to achieve ideal TEs.

The properties of CuNW TEs using HIPL technique were compared with some representative results of other groups as shown in Fig. 5. The R_{sh} increased quickly with increasing transmittance for all the curves. HIPL treated films were same or superior to those films fabricated by annealing or acid washing method when the transparency was lower than 84%. For example, the CuNW TEs fabricated by

mechanical press methods only achieved a R_{sh} of 57 Ohm/sq even with T of 50%, which was marked by block in Fig. 5. With the same transmittance, the resistance of CuNW TEs drastically decreased into only 8.7 Ohm/sq using the HIPL method. Moreover, the CuNW TEs treated with HIPL exhibited excellent optoelectronic performance with R_{sh} of 22.9 Ohm/sq at T of 81.8%, which is superior to other reported works. For example, the transmittance was only 80% with same R_{sh} of 22.9 Ohm/sq under annealing method at 175 °C, and R_{sh} was 25 Ohm/sq at T of 81.2%with annealing process at even 300 °C. However, when the transmittance was around 90%, the R_{sh} was quickly raised up to 10^3 Ohm/sq using HIPL method.

Although, the annealing method was widely used in fabrication of CuNW TEs since first introduced by Wiley's group [13], hydrogen flow must be introduced to avoid oxidization of copper at a fairly high temperature, which was dangerous and complicated, also limited the use of heat-sensitive substrates. HIPL technique was intelligent to control the reaction happened in an ultra-short time (300 microseconds every pulse in our experiment) and avoid the long-time heat which could apply on heat-sensitive substrates. It also has been demonstrated the oxidation issue could be totally avoided in air atmosphere, even more, the HIPL technique enable deoxidize and purify CuNWs to achieve high conductivity. Therefore, the HIPL technique is a simple and powerful route for the fabrication of high performance CuNWs TE in air. However, the improvement of conductivity mainly depended on the connection between nanowires, which was determined by the light absorbability of CuNWs in the HIPL process. When the transmittance is higher than 84%, the amount of CuNWs on

substrates have been largely reduced leading to weak light absorption which resulted in bad junctions corresponding to high R_{sh} value seen in Fig. 4. However, the quickly increase of R_{sh} of CuNW TEs was inevitable for all the methods, the HIPL technique was intelligent to achieve CuNW TEs with superior or equal property compared with other works in ambient environment with suitable transmittance.

4. Conclusions

In summary, HIPL technique was demonstrated to be a fast and powerful method to fabricate highly conductive CuNWs TEs on glass substrate at room temperature in ambient conditions without any protective atmosphere. A high performance TE with high transmittance of 81.8% and resistance of 22.9 Ohm/sq was achieved. In addition to the welding between CuNWs, more excitingly, the oxide and hydroxide layer on the surface of CuNWs were removed by the intense light even when these nanowires have been stored for long time. Finally, comparing with other vacuum sintering and acid washing, the HIPL process provides convenient method to fabricate CuNW TEs with superior or equal properties. The HIPL process is expected to be the most charming technique to apply CuNWs in many devices, such as LED, solar cell, e-paper and so on.

Acknowledgement

Su Ding thanks the financial support from China Scholarship Council for her PhD research in Osaka University. We are very much thankful to Ms. Emi Yokoi for the observation of TEM. This work was partly supported by the COI Stream Project, Showa Denko K. K. and Grant-in-Aid for Scientific Research (Kaken S, 24226017).

The authors are also grateful for financial support from the National Science Foundation of China (Grant No. 51522503) and support from Program for New Century Excellent Talents in University (NCET-13-0175).

References

1. Z. Wu, Z. Chen, X. Du, J. M. Logan, J. Sippel, M. Nikolou, K. Kamaras, J. R. Reynolds, D. B. Tanner, A. F. Hebard and A. G. Rinzler, *nature*, 2004, **305**, 1273-1276.
2. M. W. Rowell, M. A. Topinka and M. D. McGehee, *Appl. Phys. Lett.*, 2006, **88**, 233506.
3. D. Zhang, K. Ryu, X. Liu, E. Polikarpov, J. Ly, M. E. Tompson and C. Zhou, *Nano Lett.*, 2006, **6**, 1880-1886.
4. D. J. Lipomi, M.l Vosgueritchia1, B. C. Tee, S. L. Hellstrom, J. A. Lee, C. H. Fox and Z. Bao, *Nat. Nanotechnol.*, 2011, **6**, 788-792.
5. G. Eda, G. Fanchini and M. Chhowalla, *Nat. Nanotechnol.*, 2008, **3**, 270-274.
6. K. S. Kim, Y. Zhao, H. Jang, S. Y. Lee, J. M. Kim, K. S. Kim, J. H. Ahn, P. Kim, J. Y. Choi and B. H. Hong, *Nature*, 2009, **457**, 706-710.
7. S. Bae, H. Kim, Y. Lee, X. Xu, J. S. Park, Y. Zheng, J. Balakrishnan, T. Lei, H. Kim, Y. Song, Y. J. Kim, K. S. Kim, B. Ozyilmaz, J. H. Ahn, B. H. Hong and S. Iijima, *Nat. Nanotechnol.*, 2010, **5**, 574-578.
8. X. Li, Y. Zhu, W. Cai, M. Borysiak, B. Han, D. Chen, R. D. Piner, L. Colombo and R. S. Ruoff, *Nano Lett.*, 2009, **9**, 4359-4363.
9. X. Li, G. Zhang, X. Bai X. Sun, X. Wang, E. Wang and H. Dai, *Nat. Nanotechnol.*,

2008, **3**, 538-542.

10. S. Ye, A. R. Rathmell , Z. Chen , I. E. Stewart and B. J. Wiley, *Adv. Mater.*, 2014, **26**, 6670-6687.
11. L. Hu, H. S. Kim, J. Y. Lee, P. Peumans and Y Cui, *ACS nano*, 2010, **4**, 2955-2963.
12. T. Tokuno, M. Nogi, M. Karakawa, J. Jiu, T. T. Nge, Y. Aso and K. Suganuma, *J. Mater. Chem.*, 2012, **22**, 23561-23567.
13. A. R. Rathmell, S. M. Bergin , Y. Hua , Z. Li and B. J. Wiley, *Adv. Mater.*, 2010, **22**, 3558-3563.
14. S. De, T. M. Higgins, P. E. Lyons, E. M. Doherty, P. N. Nirmalraj, W. J. Blau, J. J. Boland and J. N. Coleman, *ACS nano*, 2009, **3**, 1767-1774.
15. L. Hu, H. S. Kim, J. Y. Lee, P. Peumans and Y. Cui, *ACS nano*, 2010, **4**, 2955-2963.
16. T. Tokuno, M. Nogi, M. Karakawa, J. Jiu, T. T. Nge, Y. Aso and K. Suganuma, *Nano Res.*, 2011, **4**, 1215-1222.
17. C. Liu and X. Yu, *Nanoscale Res. Lett.*, 2011, **6**, 75.
18. S. M. Bergin, Y. H. Chen, A. R. Rathmell, P. Charbonneau, Z. Y. Li and B. J. Wiley, *Nanoscale*, 2012, **4**, 1996-2004.
19. A. R. Rathmell and B. J. Wiley, *Adv. Mater.*, 2011, **23**, 4798-4803.
20. C. Sachse, N. Weiß, N. Gaponik, L. M. Meskamp, A. Eychmüller and K. Leo, *Adv. Energy Mater.*, 2014, **4**, 1300737.
21. M. Kevin, G. Y. R. Lim and G. W. Ho, *Green Chem.*, 2015, **17**, 1120-1126.

22. D. Zhang, R. Wang, M. Wen, D. Weng, X. Cui, J. Sun, H. Li and Y. Lu, *J. Am. Chem. Soc.*, 2012, **134**, 14283-14286.

23. Y. Won, A. Kim, D. Lee, W. Yang, K. Woo, S. Jeong and J. Moon, *NPG Asia Mater.*, 2014, **6**, e105.

24. Y. Won, A. Kim, W. Yang, S. Jeong and J. Moon, *NPG Asia Mater.*, 2014, **6**, e132.

25. Z. Yin, S. K. Song, D. J. You, Y. Ko, S. Cho, J. Yoo, S. Y. Park, Y. Piao, S. T. Chang and Y. S. Kim, *Small*, 2015, DOI: 10.1002/smll.201500855.

26. C. Mayousse, C. Celle, A. Carella and J. P. Simonato, *Nano Res.*, 2014, **7**, 315-324.

27. H. S. Kim, S. R. Dhage, D. E. Shim and H. T. Hahn, *Appl. Phys. A*, 2009, **97**, 791-798.

28. B. Y. Wang, T. H. Yoo, Y. W. Song, D. S. Lim and Y. J. Oh, *ACS Appl. Mater. Inter.*, 2013, **5**, 4113-4119.

29. J. Ryu, H. S. Kim and H. T. Hahn, *J. Electron. Mater.*, 2011, **40**, 42-50.

30. J. S. Kang, J. Ryu, H.S. Kim and H.T. Hahn, *J. Electron. Mater.*, 2011, **40**, 2268-2277.

31. J. Jiu, M. Nogi, T. Sugahara, T. Tokuno, Teppei Araki, N. Komoda, K. Suganuma, H. Uchida and K. Shinozaki, *J. Mater. Chem.*, 2012, **22**, 23561-23567.

32. J. Jiu, T. Sugahara, M. Nogi, T. Araki, K. Suganuma, H. Uchida and K. Shinozaki, *Nanoscale*, 2013, **5**, 11820-11828.

33. M. Mohl, P. Pusztai, A. Kukovecz and Z. Konya, *Langmuir*, 2010, **26**, 16496-16502.

34. D.V.R. Kumar, I. Kim, Z. Zhong, K. Kim, D. Lee, and J. Moon, *Phys. Chem. Chem. Phys.*, 2014, **16**, 22107-22115.

35. Z. Jiang, Y. Tian, S. Ding, Mater. Lett., 2014, **136**, 310-313.

36. W. S. Han, J. M. Hong, H. S. Kim and Y. W. Song, *Nanotechnology*, 2010, **22**, 395705.

37. E. C. Garnett, W. Cai, J. J. Cha, F. Mahmood, S. T. Connor, M. G. Christoforo, Y. Cui, M. D. McGehee and M. L. Brongersma, *Nat. Mater.*, 2012, **11**, 241-249.

38. S. Han, S. Hong, J. Ham, J. Yeo, J. Lee, B. Kang, P. Lee, J. Kwon, S. S. Lee, M. Yang and S. H. Ko, *Adv. Mater.*, 2014, **26**, 5808-5814.

39. J. Wang, J. Jiu, T. Araki, M. Nogi, T. Sugahara, S. Nagao, H. Koga, P. He and K. Suganuma, *Nano-Micro Lett.*, 2015, **7**, 51-58.

40. E. Ye, S. Y. Zhang, S. Liu and M. Y. Han, *Chem. Eur. J.*, 2011, **17**, 3074-3077.

41. Y. Chen, C. Hu, X. Hu and J. Qu, *Environ. Sci. Technol.*, 2009, **43**, 2760-2765.

42. P. Lignier, R. Bellabarba and R. P. Tooze, *Chem. Soc. Rev.*, 2012, **41**, 1708-1720.

43. M.E.T. Molares, E. M. Höhberger, C. Schaeflein, R. H. Blick, R. Neumann and C. Trautmann, *Appl. Phys. Lett.*, 2003, **82**, 2139-2141.

44. H. Guo, N. Lin, Y. Chen, Z. Wang, Q. Xie, T. Zheng, N. Gao, S. Li, J. Kang, D. Cai and D. Peng, *Sci. Rep.*, 2013, **3**, 2323.

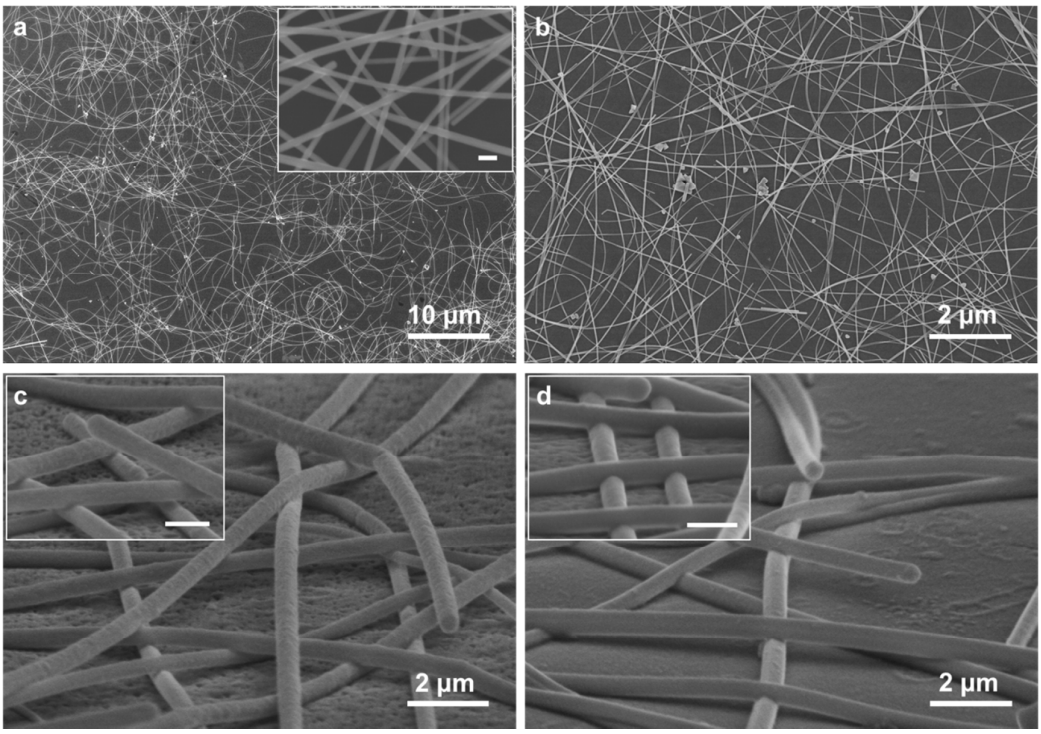

Fig. 1 SEM images of as prepared Cu NWs (a); CuNWs network on glass substrate after spray coating (b). Tilted SEM images of CuNW film before (c) and after (d) the HIPL treatment. The scale bars in insert images is 100 nm.

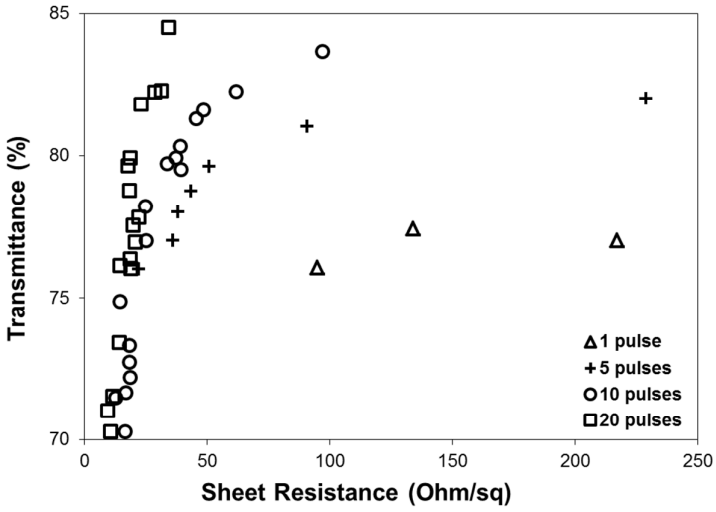

Fig. 2 Sheet resistance depending on transmittance for CuNW TEs treated with different times of pulse.

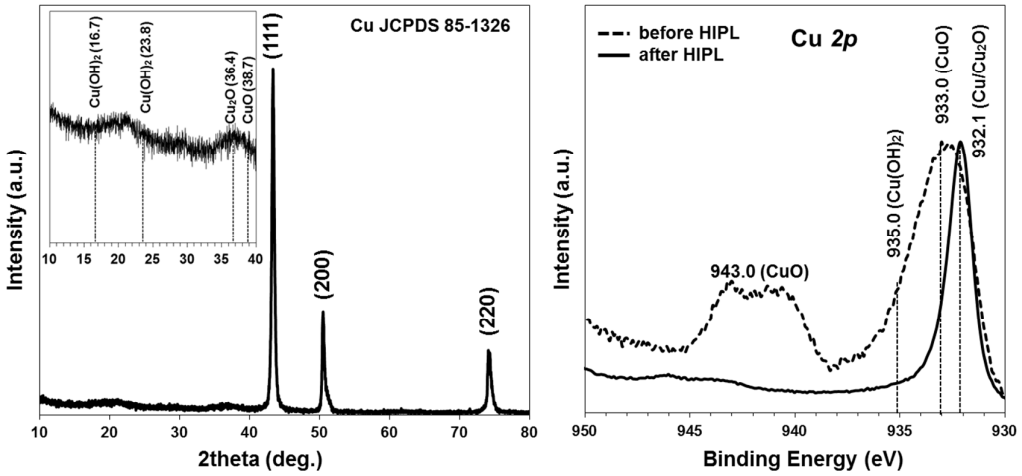

Fig. 3 XRD pattern of CuNWs kept in isopropanol for two months (a) and Cu 2p XPS spectra of oxidized CuNW films before and after HIPL treatment.

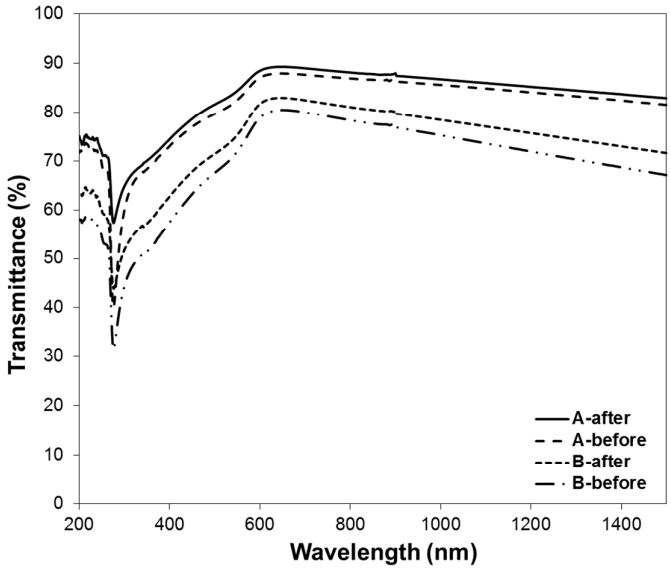

Fig. 4 Transmission spectra before and after HIPL irradiation.

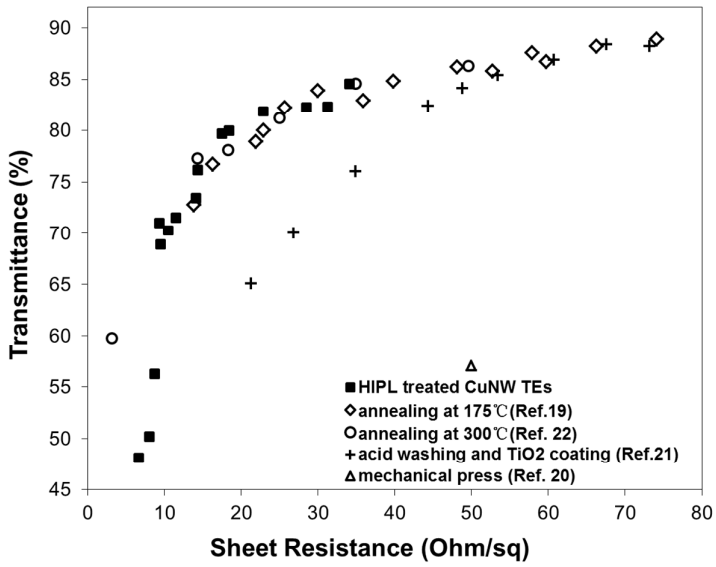

Fig. 5 Plot of transmittance verse sheet resistance for CuNW TEs in the work and references.