Supporting Information for:

Synthesis of ultra-thin copper nanowires using tris(trimethylsilyl)silane for high-performance and low-haze transparent conductors

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Materials and Methods

Regents:

Tris(trimethylsilyl)silane (TTMSS, 97%), copper (II) chloride dihydrate ($CuCl_2 \cdot 2H_2O$, 99.999%), oleylamine (70%), oleic acid (90%), and nitrocellulose filter membranes (25 mm diameter, 220 nm pore size), were purchased from Sigma-Aldrich and used as received. Unless otherwise stated, all of other chemicals were purchased from Sigma-Aldrich and used as received.

Experimental details:

Synthesis of copper nanowires:

In a typical reaction, 85 mg of $CuCl_2 \cdot 2H_2O$ (0.5 mmol) and 5 g of oleylamine were mixed in a reaction vessel and then sonicated at room temperature to fully dissolve copper precursor. 0.5 g of tris(trimethylsily)silane (2 mmol) was added in to the solution as reducing regent. The resulting clear blue mixture was heated up to 120 °C until the solution turned into light yellow. Afterwards, the reaction temperature was slowly turned up to and kept at 165 ℃ for 10 h while stirring. The color of the solution turned reddish brown, indicating formation of copper nanowires. The product was harvested by centrifugation at 6000 rmp for 5 mins. Then, the nanowires were washed repeatedly with toluene using centrifugation-redispersion cycles to remove excess oleylamine. Finally, the product was dispersed in toluene for further characterization and film fabrication.

Synthesis of silver nanowires[1]

Silver nanowires were synthesized following reported method in literature1. 0.34 g of PVP (poly vinylpyrrolidone) was dissolved in 20 ml ethylene glycol in a reaction tube. The solution was heated up and kept at 170 °C. Then, 0.025 g of AgCl was added to the mixture upon vigorous stirring. After three minutes, 0.1 g of $AgNO_3$ dissolved in ethylene glycol was added drop wise to the mixture. The reaction was allowed to carry out for another 30min when it was cooled down. Ag nanowires was centrifuged down

and washed with methanol 3 times. Finally, the nanowires were redispersed in methanol for further characterization and film fabrication.

Fabrication of copper nanowire transparent conductor

To make a conductive thin film, copper nanowires were diluted using toluene and sonicated for 15 min to form a homogenous suspension. The thin film was constructed by filtering down the nanowires from the dispersion onto a nitrocellose porous membrane (pore size 220 nm) via vacuum filtration. The nanowire network was transferred to a transparent substrate (glass or PET) by applying pressure to the back side of the membrane and forcing an intimate contact with the substrate. The copper nanowire thin film was then annealed under forming gas (10% H_2 and 90% Ar) at 200 ℃ for 30 min to improve junction contact.

Fabrication of silver nanowire transparent conductor

Ag nanowires were diluted using methanol and sonicated for 15min to form a homogenous suspension. The thin film was constructed by filtering down the nanowires from the dispersion onto a polytetrafluorethylene (PTFE) membrane filter (purchased from Sartorius, pore size 450nm). The nanowire network was transferred on to a transparent substrate (glass) by applying pressure to the back side of the membrane.

Characterizations:

The morphologies of the as-grown copper nanowires were examined using a transmission electron microscope (TEM, Hitachi H7650) and scanning electron microscope (SEM, JOEL JSM - 6340F). The structure of copper nanowires was analyzed using high resolution transmission electron microscopy (HRTEM, FEI Tecnai G20), selected area electron diffraction (SAED) and X-ray diffraction pattern analysis (Bruker D8 Advance). Exit-wave reconstruction was performed using MacTempas software. Sheet resistance of nanowire thin film was measured using a four-point probe method (CDE-RESMAP-270). The transmittance and haze measurement was carried out on an ultraviolet-visible near-infrared spectrophotometer with an integrating sphere (Shimadzu UV-2550). AFM images of the copper nanowires and their junction were taken using an Asylum MFP 3D

in tapping mode. The as-made Cu nanowire film on glass without heat treatment and the one with 30 minutes forming gas annealing were used for the measurements.

Haze measurement

The haze measurement is carried out by D1003-13 standard[2]. Shimadzu UV-2550 ultraviolet-visible near-infrared spectrophotometer with an integrating sphere was used for haze measurement. Four transmittance scans of a sample with different configurations were acquired for its haze calculations: T_1, incident light; T_2, total light transmitted by the specimen; T_3, light scattered by the instrument and T_4, light scattered by the instrument and specimen. The haze factor of one specimen can be calculated by the equation: Haze, % = $[(T_4/T_2) - (T_3/T_1)]$.

Unless specified, all haze factors in discussion is the value measured at 550 nm of wavelength. The contribution of glass substrate is already excluded.

References:

1. Hu, L., Kim, H. S., Lee, J., Peumans, P.; Cui, Y. *ACS Nano* **2010**, *4*, 2955–2963.
2. ASTM D1003-13, **2013**. Standard Test Method for Haze and Luminous Transmittance of Transparent Plastics, The American Society for Testing and Materials, West Conshohocken, PA.

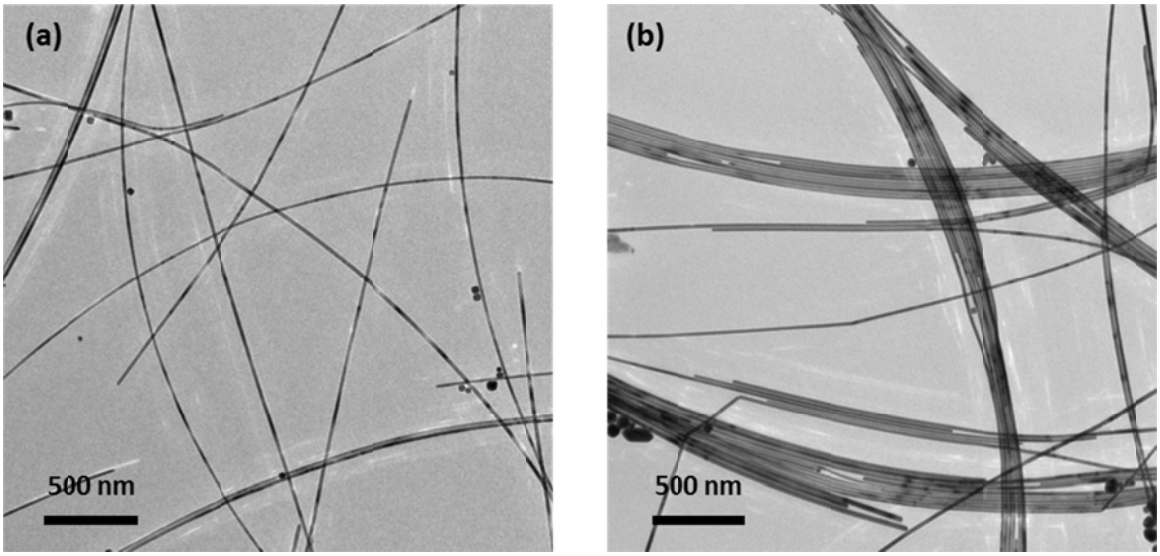

Figure S1. The effect of oleic acid as a secondary ligand. TEM images of copper nanowires synthesize (a) with oleic acid (0.1 g), and (b), without oleic acid. Small amount of oleic acid in the reaction system can greatly improve copper nanowires' dispersion. Copper nanowire synthesized with oleylamine as the sole ligands (as shown in b) show severe aggregation which is not suitable for the formation of loose nanowire network.

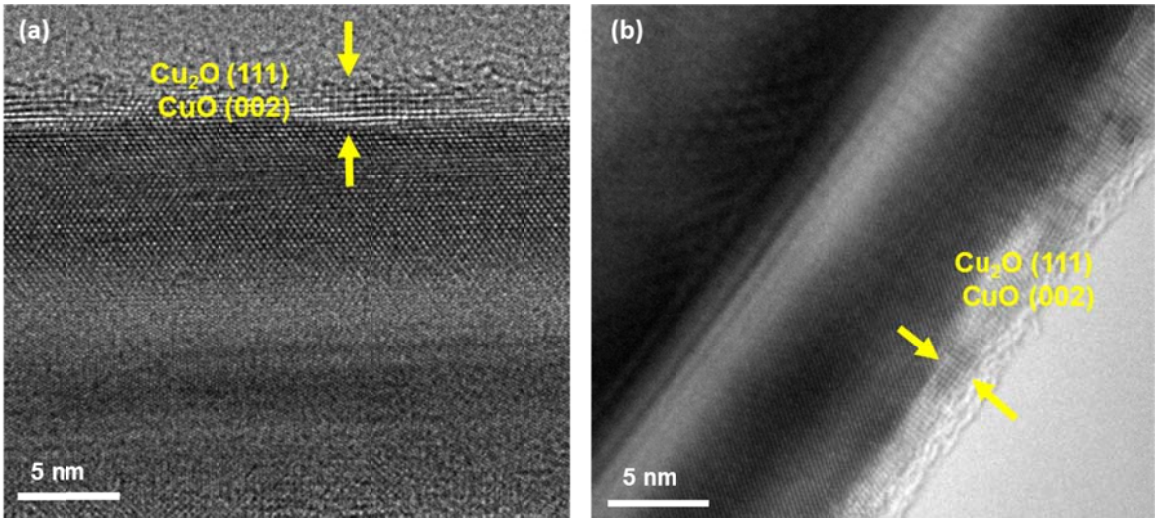

Figure S2. Nanowire surface oxides. HRTEM images of the surface of the Cu nanowire after exposed in air for (a), 2 hours and (b), 5 days. A thin layer of native oxides is

observed on the as grown copper nanowires after washing procedure. The oxide layer thickness is around 2 to 3 nanometer and is consist of a mixture of Cu_2O and CuO. No further growth of oxide layer was seen after 5 days exposure in ambient air. This implies the initial native oxide layer would stop further oxidation of the copper nanowire.

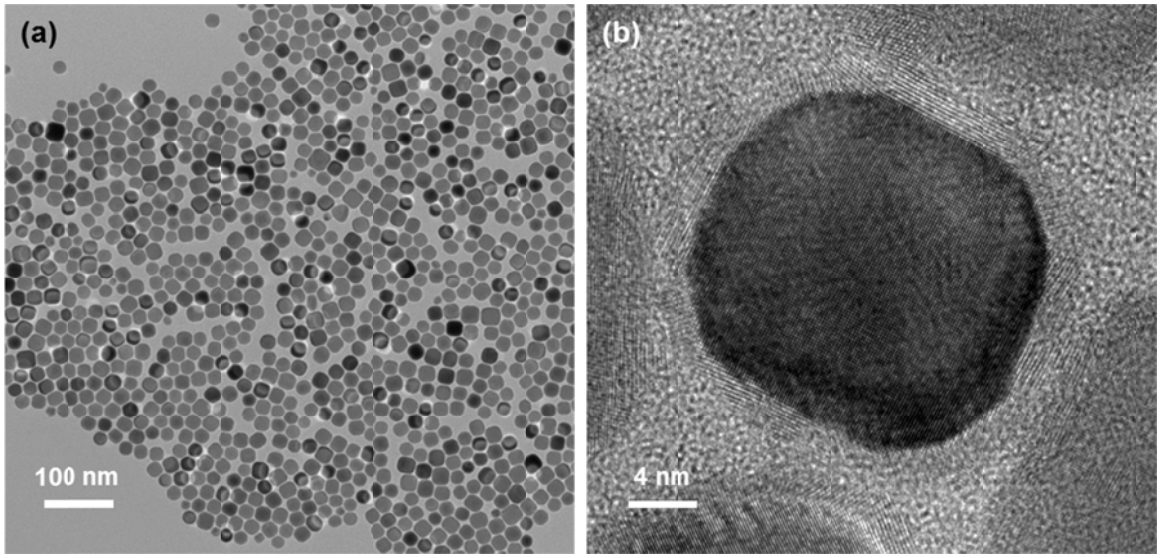

Figure S3. Single crystalline cubic copper particle. (a) TEM image of the majority of copper product before the appearance of five twinned particles. (b) HRTEM image of the cubic copper nanoparticle

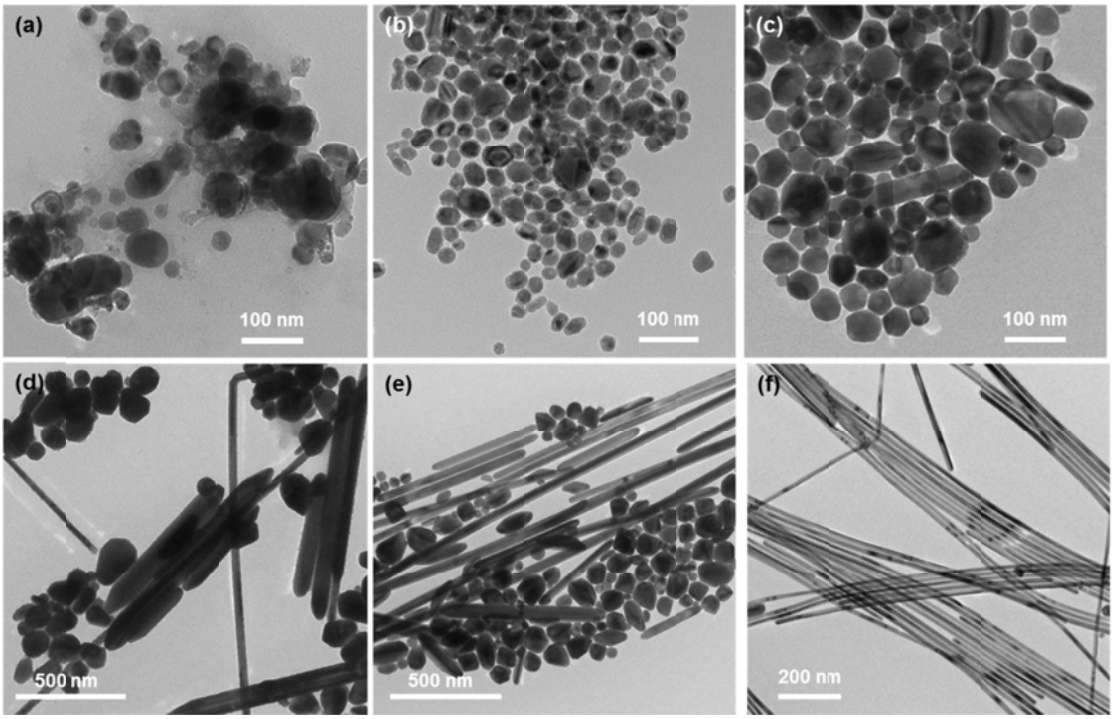

Figure S4. The role of oleylamine in copper nanowire shape control. TEM images of copper products with different amount of oleylamine within the reaction system. From (a) to (f), 0 g, 0.5 g, 1 g, 2 g, 3 g, and 5 g of oleylamine were in presence of the reactants. With presence of non-coordinate solvent only, the reduction of copper ion to copper metal particles is also possible which proves that tristrimethylsiylsilane acts as the effective reducing regent in this system. With the increasing amount of oleylamine concentration, the shape of copper products becomes better defined. An increasing tendency of anisotropic growth can also be seen correlated with the increasing amount of oleylamine.

In the absence of "catalyzed growth", one dimensional nanomaterial growth mechanisms are mainly attributed to two possible routes: oriented attachment and selective monomer deposition on preferentially protected facets. According to our experimental data, the later explanation is more plausible for the following reasons. Firstly, different stages of the reaction products were extracted from the reaction and their morphologies were characterized by TEM. We did not observe any chain-like intermediates which are the characteristic intermediate of an oriented attachment directed synthesis. Secondly, we did detailed high-resolution TEM study on the as grown nanowire and it shows that the

nanowire adopts a five-fold twinned structure. The tips of the nanowires are bounded by five (111) facets and it looks like a five-fold pyramid. If the growing mechanism were to follow the oriented attachment mechanism, two segments would need to attach pyramidal tips with one another to form a continuous wire which is not energetically favorable. Thirdly, there are compelling evidences suggesting that the five-fold twin nanoparticles we observed during the early stage of the reaction should serve as the seeds of the nanowire growth. Besides the fact that they have strong correlation in tense of size distribution, their five-fold nature and exposed facets (the nanoparticles are also bounded by (111) facets at the tip) are all strongly correlated.

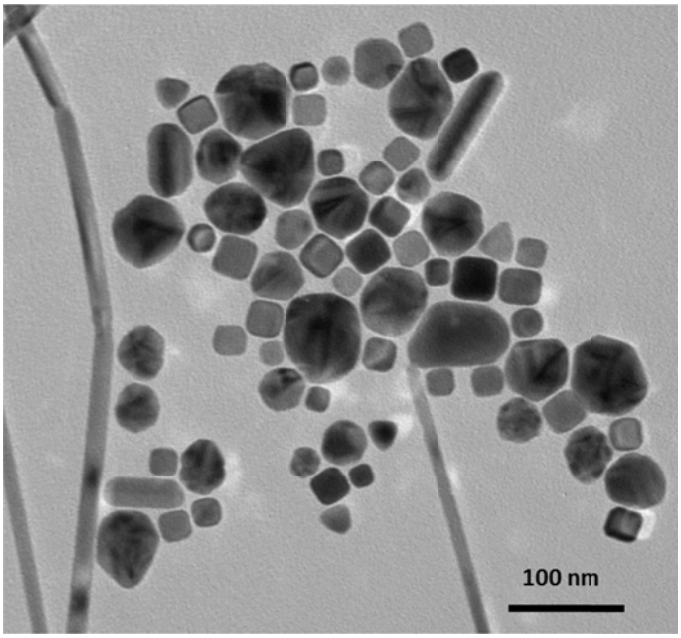

Figure S5. TEM image of nanoparticle byproducts. The majority of byproducts are nanoparticles with the dimension ranging from 30-100 nm in diameter. The yield of copper nanomaterials (all morphology included) of a typical synthesis is around 50% by weight. Nanowires take up around 90% (by count) among all morphologies of all copper products.

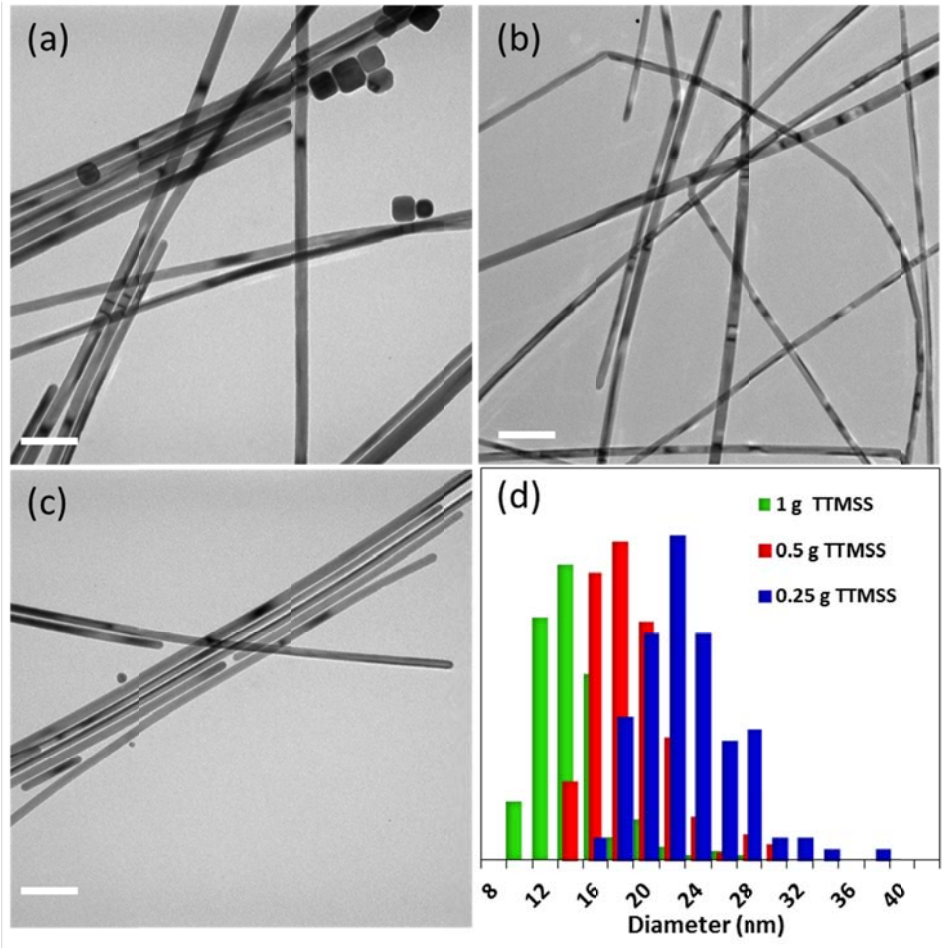

Figure S6. Tuning of nanowire diameter by changing reducing agent quantity. TEM images (Scale bar 100nm) of copper nanowire when the TTMSS adding amount is (a), 1g; (b), 0.5 g; and (c), 0.25 g. (d), diameter distribution statistics of copper nanowire in the above three reaction conditions. During the nucleation, the more reducing regent, the more nuclei it will generate, the smaller the seeds.

Table S1. The effect of TTMSS quantity, copper precursor concentration and reaction temperature on copper nanowire synthesis. The red highlighted condition is the optimized reaction condition used for copper film fabrication.

$CuCl_2$ (mmol)	TTMSS (mmol)	Temperature (℃)	Results
0.5	**0**	**165**	**No Copper product**
0.5	**0.05**	**165**	**Copper cubes only**
0.5	**1**	**165**	**Nanowires with D ~ 22.5 ± 3.9 nm**
0.5	**2**	**165**	**Nanowires with D ~ 17.5 ± 3.0 nm**
0.5	**4**	**165**	**Nanowires with D ~ 15.5 ± 2.7 nm**
0.25	**1**	**165**	**Nanowires with D ~ 32.3 ± 11.0 nm**
1	**4**	**165**	**Nanowires with D ~ 18.5 ± 4.7 nm**
0.5	**2**	**135**	**No copper product**

When no TTMSS in the reaction system, copper chloride cannot be reduced to copper metal. When small amount of TTMSS (10 % of $CuCl_2$) is added, copper cubic nanoparticles are observed in the product. However, the yield of Cu (0) is very low. These imply that TTMSS does act as the effective reducing reagent of copper precursor, and insufficient loading of silane cannot fully reduce $CuCl_2$. The nanowire diameter can be tuned by controlling the molar ratio of TTMSS/$CuCl_2$. With set amount of $CuCl_2$, the nanowire diameter decreases as TTMSS increases. The size of the nanowire is also sensitive about reactant concentration. Smaller concentration results in thicker nanowires. The red highlighted condition is chosen as the optimized condition for typical nanowire growth in this work for the reason that it gives less particle byproducts.

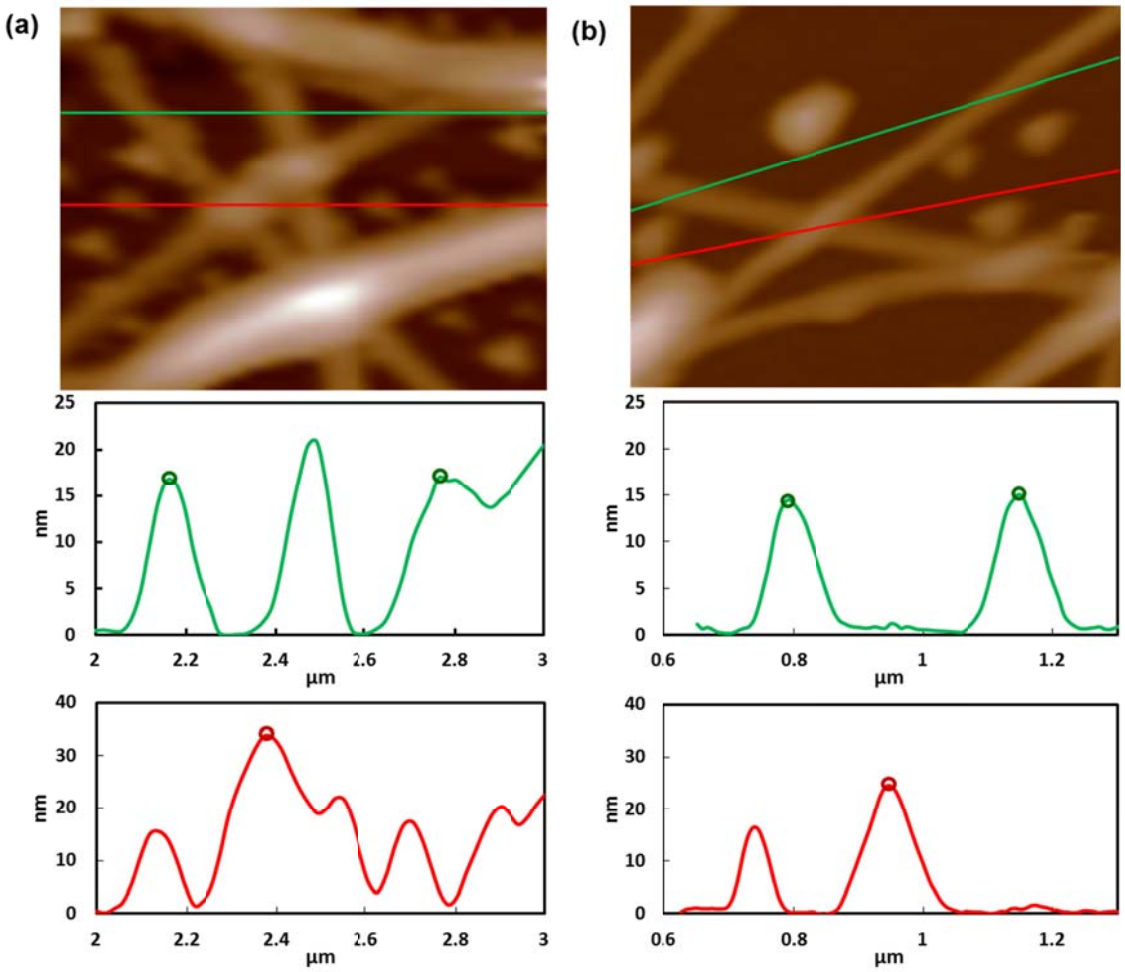

Figure S7. AFM images of copper nanowire film (a), before annealing and (b), after annealing. Before annealing, the two measure nanowires have diameter of 16.66 nm and 16.98 nm. The measured junction height is 33.74 nm which is almost the same with the summation of two individual nanowire diameters (33.64 nm). In the case annealed nanowire film, the measured diameters of the two individual wires are 14.50 nm and 15.00 nm which add up to 29.50nm. The annealed junction has the height of 24.46nm which is 5 nm short of the summation. This shows that the thermal annealing can partially wield nanowire together which can enhance the junction contact.

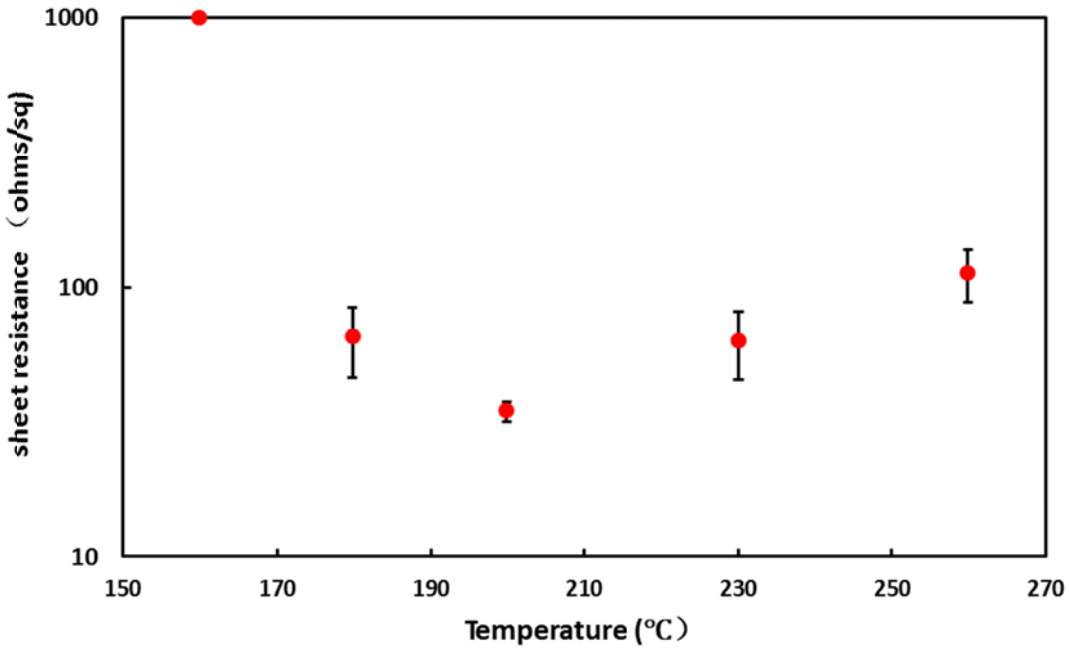

Figure S8. Dependency between film sheet resistance and annealing temperature. 200℃ is the optimized annealing temperature. If the temperature is lower, it cannot effectively melt the nanowire to form intimate contact at the wire-wire junction. An increase in sheet resistance is observed. When the annealing temperature is lower than 150 ℃, the nanowire film is almost insolated due to the presence of oxides on the surface of the nanowire. The temperature cannot be too high either. Overheating will severely melt nanowire and damage the nanowire percolation, which will result in degrading in film conductivity

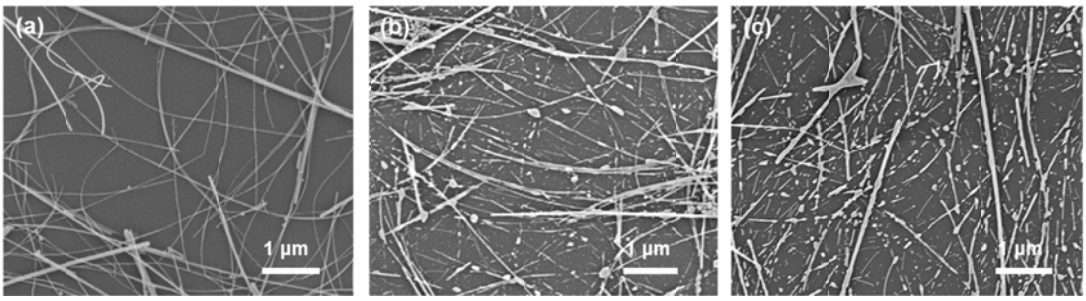

Figure S9. SEM images of nanowire conducting film when annealed at (a) 200 ℃ when most nanowires are intact; (b) 230 ℃, when some of the nanowires are visibly melted; and (c) 260 ℃, when most of the nanowires are deformed.

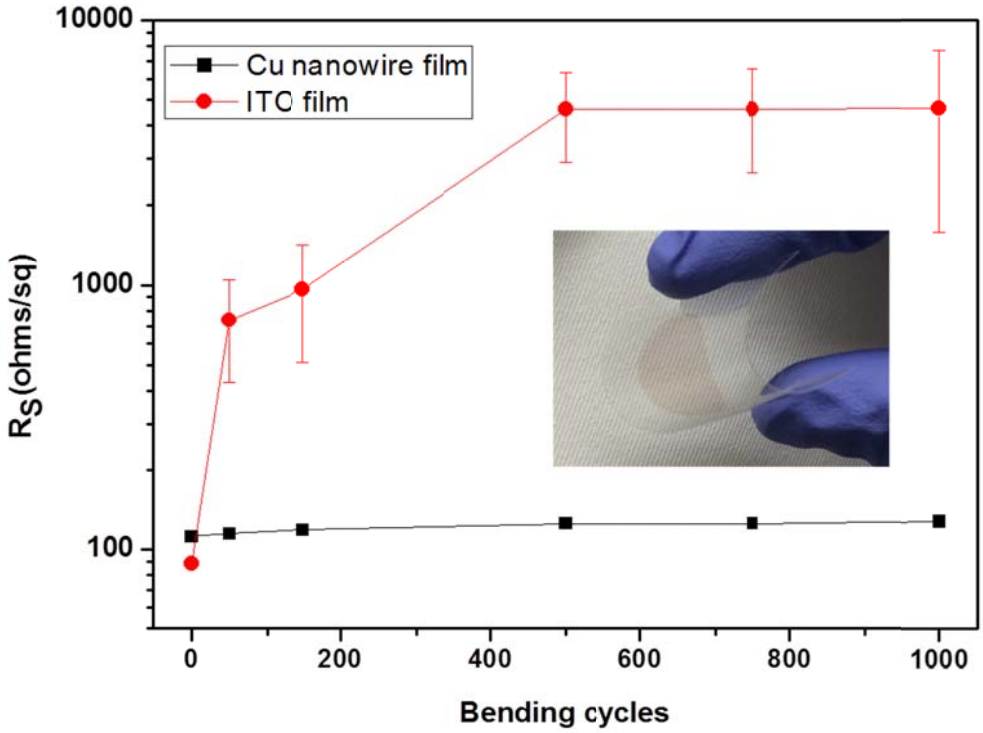

Figure S10. Conductivity performance of ITO and Cu nanowire conductor upon mechanical bending. Inset, flexible copper nanowire conducting film fabricated on polyethylene terephthalate (PET). Transparent PET (175 micron) substrates (MELINEX® ST506) were purchased from TEKRA. ITO (sheet resistance at the range of 80~90 ohms/sq) on PET (175 micron) was purchased from Sigma-Aldrich. Bending angle is around 90 degree. ITO on PET shows severe degradation in conductivity when it is applied with mechanical bending. The sheet resistance increased almost 100 times when the sheet was bended 500 cycles. In comparison, copper nanowire film exhibit extraordinary flexibility. The sheet resistance shows almost no change even after 1000 cycles of bending.

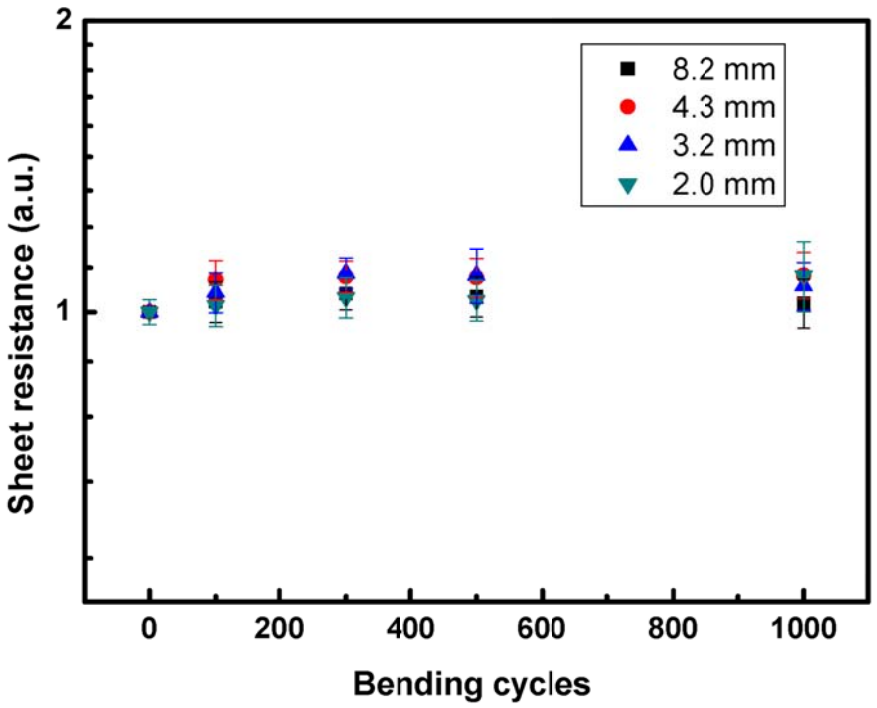

Figure S11. Sheet resistance (normalized for clear comparison) performance of flexible transparent films after applied with multiple bending cycles with various bending radius. Transparent PET (175 micron) substrates (MELINEX® ST506) were used as the supporting substrate. Four bending radii were tested: 8.2mm, 4.3mm, 3.2mm and 2.0mm. The bending angle is 180 degree for tests with bending radius smaller than 5 mm. The bending angle is 90 degree of the test with bending radius of 8.2 mm due to the small size of our as made film. The films show great resistance towards mechanical bending and the conductivity remains its original value during the whole experiment. All the films tested were made from the same batch of copper nanowires and underwent the same fabrication process. The four films tests have the sheet resistance of 33 $\pm$ 3 ohms/sq.

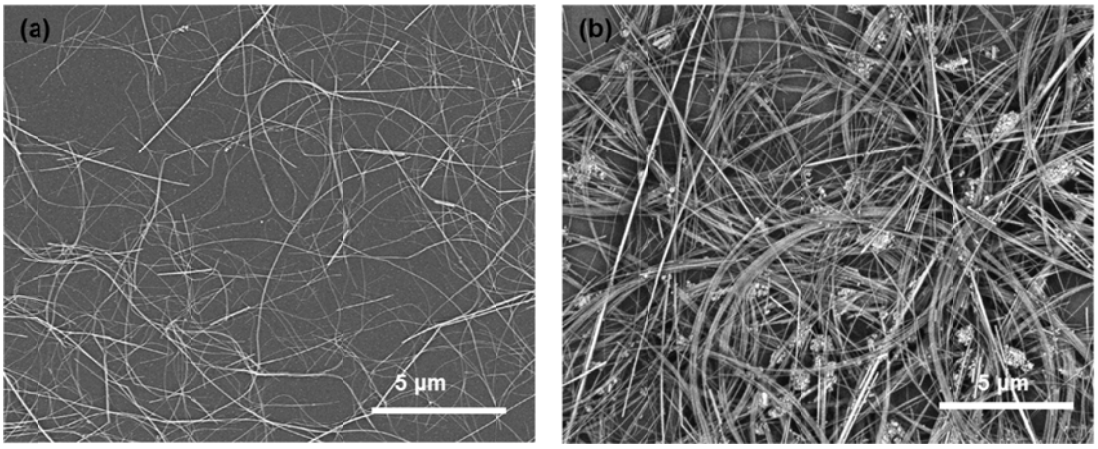

Figure S12. SEM images of (a) copper nanowires which were filtered by 220 nm pore-sized nitrocellulose membranes and (b) copper nanowires drop casted on silicon wafer. Vacuum filtration can effectively remove most of the nanoparticle byproducts.

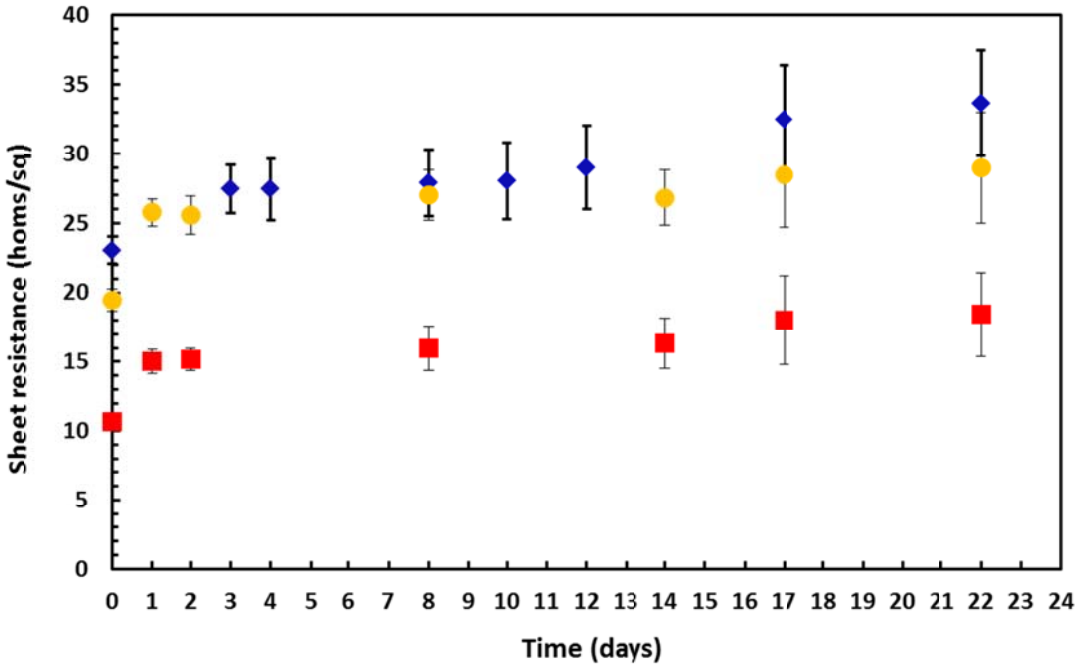

Figure S13. Stability test of copper nanowire transparent conductors. Each color represents a different loading amount. It is also worth to note that the Cu NW film cannot keep the high conductivity permanently. After several months' exposure in ambient air, the conductivity of the copper film degrades significantly.

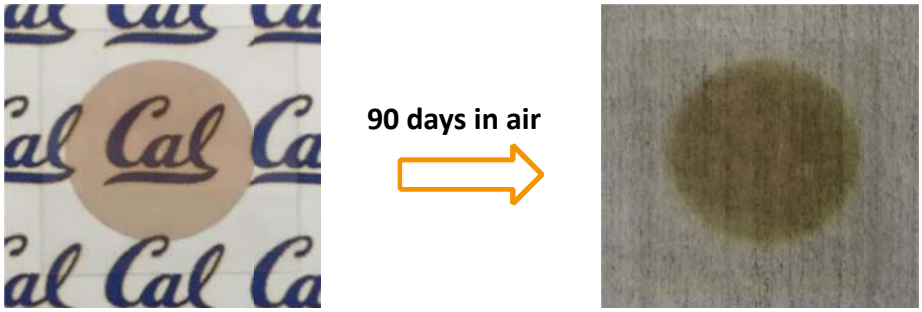

Figure S14. Copper film is fully oxidized after 3 months storage in air

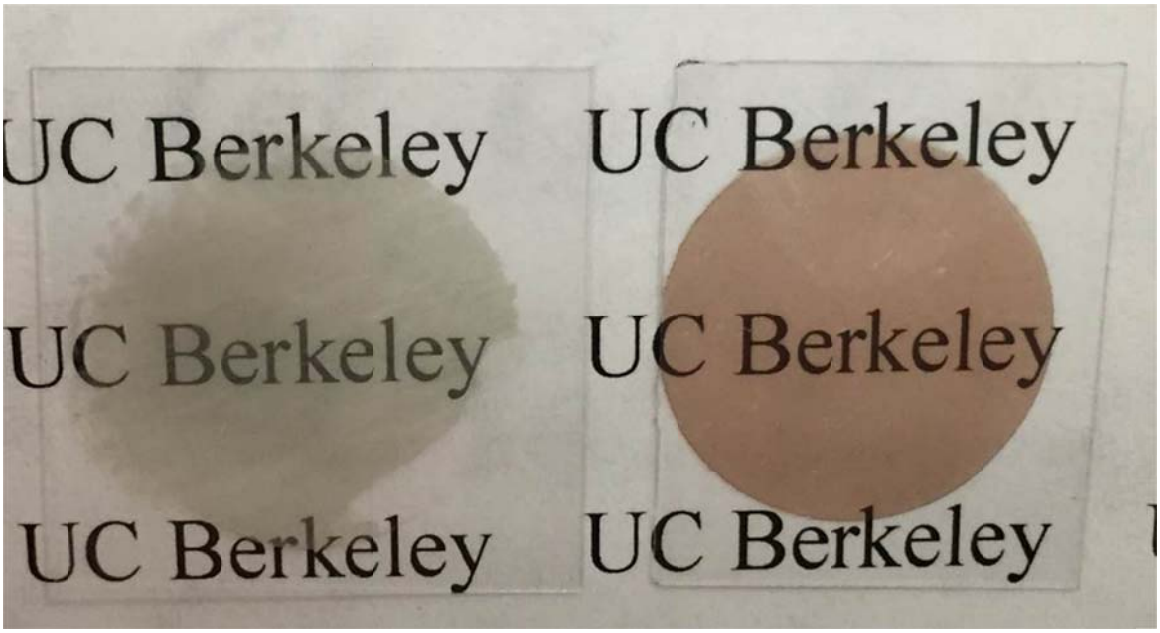

Figure S15. Visual comparison between a silver nanowire (with mean diameter of 50nm) transparent conductor and an ultra-thin copper nanowire conducting film with the same total transmittance.