Nickel concentration-dependent opto-electrical performances and stability of Cu@CuNi nanowire transparent conductors

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Supporting Information

Materials Characterization

The micro morphology of NWs were obtained by a scanning electron microscope (SEM) (FEI Quant 250FEG) instrument. For Transmission Electron Microscope (TEM), High Resolution Transmission Electron Microscopy (HRTEM) and Selected Area Electron Diffraction (SAED), a copper grid was used to hold the NWs which were detected by a TECNAI G2 20 LaB6 instrument operated at an acceleration voltage of 200 kV. X-ray diffractometer (XRD) patterns were acquired using a Bruker-AXS D8 Advance XRD operating with Cu Kα radiation (λ=1.5406 Å). Ultraviolet–visible spectroscopy (UV/Vis) transmission spectra were obtained using a Shimadzu 3600 UV/Vis spectrophotometer (in the 250-800 nm spectral range). Sheet resistance of the NWs films were obtained via four-point probe measurements and the van der Pauw method at room temperature and the final values were averaged over a minimum of five measurements for each sample.

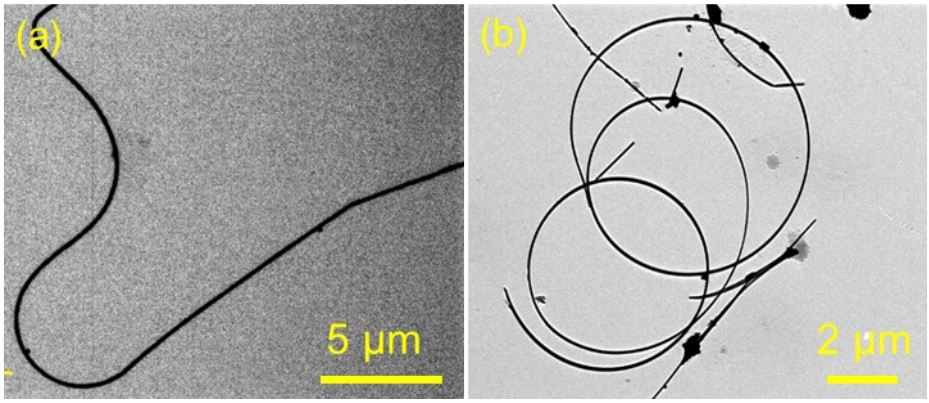

Figure S1. TEM image of prepared Cu@Cu–Ni net work via a simple one- pot method

Table S1. The molar ratio of Cu to Ni was detected by ICP-AES

Sample	1	2	3	4	5
Reaction time（h）at 210 ºC	0	1	2	3	4
Ni (at.%)	0.1	3.4	5.1	9.6	17.2

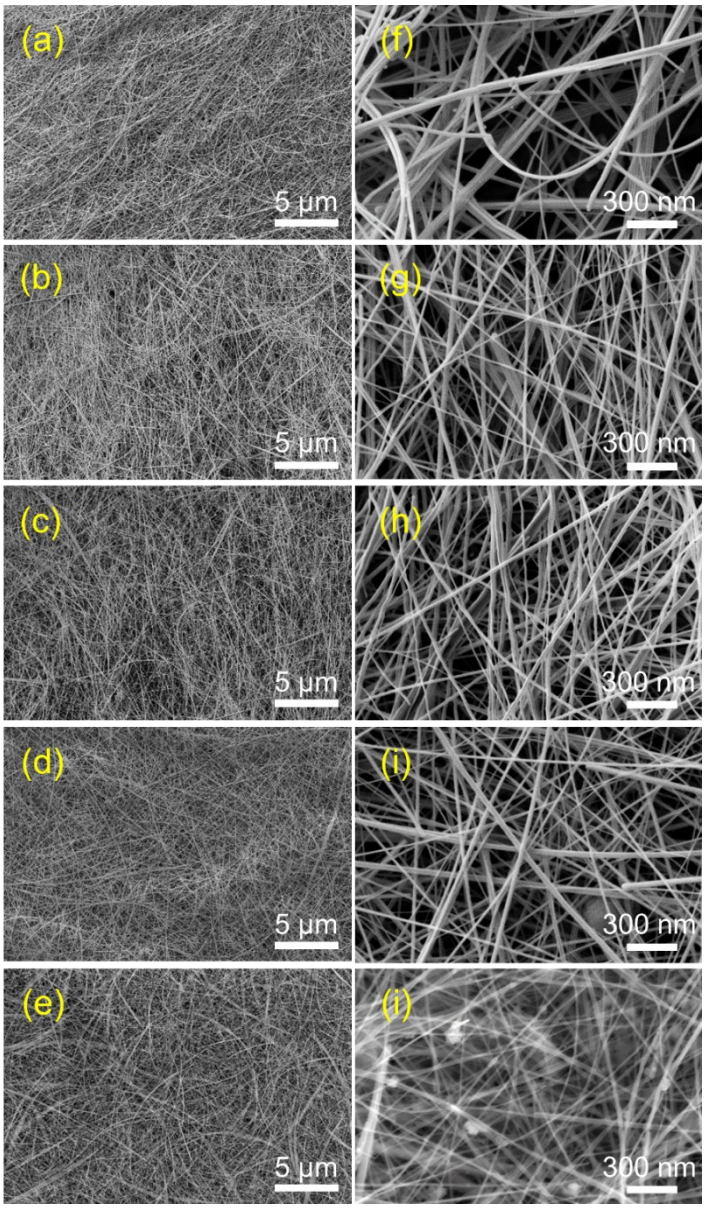

Figure S2 (a)-(e) SEM images and (f)-(j) High-resolution SEM images of Cu NWs alloyed with different nickel content.

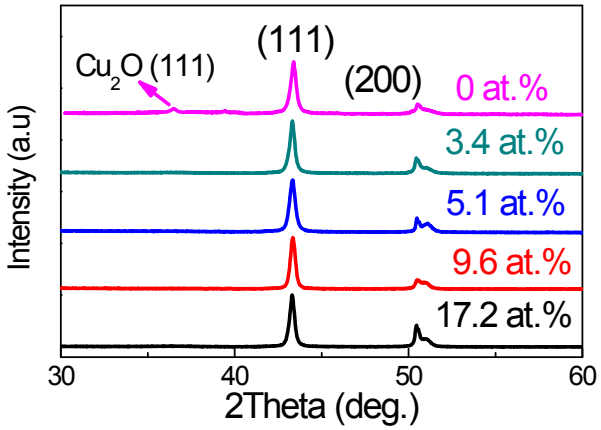

Figure S3 XRD patterns of Cu and core-shell NW films on glasses.

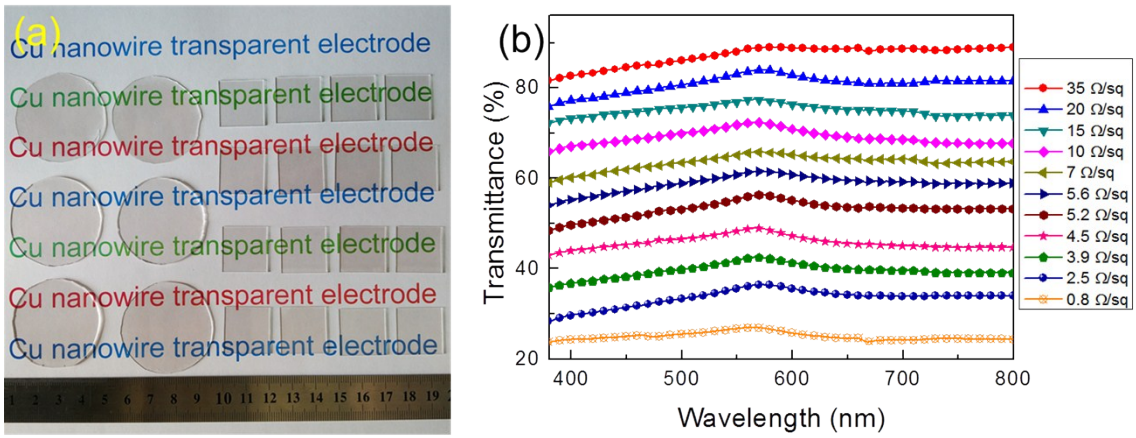

Figure S4. (a) Cu@Cu-Ni NW films on glasses and PDMS with controlled transparency adjusted by thickness. (b) UV-Vis-NIR transmission spectra of Cu NW films on glasses with controlled transparency adjusted by thickness. The resistances decrease from 35 to 0.8 ohm/sq with the decrease of transparency and with the increase of thickness.

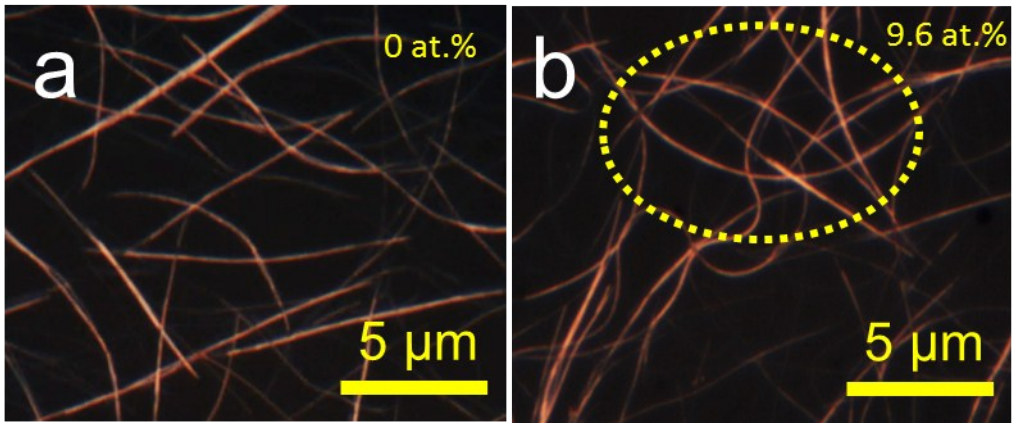

Figure S5 (a), (b) Dark-field optical microscope image of Cu, cupronickel NWs on

glass, respectively.

Analysis of the composition of Cu -Ni alloy:

Here, the density and the molar mass of Cu and Ni are considered to be the same. The alloy of Cu-Ni was defined as Cu_xNi.

The mass of Ni: $m_{Ni} = \rho v = \rho\pi r^2 * h = [1/(1+ x)]\rho\ \pi[(45/2)^2-(35/2)^2] * h$

The total mass of the NWs: $m_{total} = \rho v = \rho\pi\ r^2 * h = \rho\pi(45/2)^2 * h$

The molar ratio of Ni: m_{Ni} / m_{total} = 9.6% (ICP data); x ~ 4

The Cu-Ni alloy is Cu_4Ni , matching with the matching with the matching with the matching with the matching with the XRD pdf card No 09 -0205.

Concentration of CuNWs:

To measure the concentration of the well-dispersed CuNWs, a set volume of the solution was dissolved in concentrated nitric acid (1 ml) and the solution will be layered. The dissolved copper was then diluted to a set volume and then take the following solution. An atomic absorption spectrometer (AAS, Perkin Elmer 3100) was then used to measure the concentration.

Measuring the Density of Wires in the Film:

This section describes how we determined the relationship between the transmittance as well as sheet resistance of Cu NW films and thereby the amount of nanowires in the films. The transmittance of the films was measured with a UV-Vis-NIR spectrometer (Cary 6000i). The number of wires in a given volume of solution, N, is given by Equation S1:

$$N = \frac{C_{Cu} V_T}{\rho_{Cu} L r^2 \pi} \qquad \text{(Equation S1)}$$

where C_{Cu} is the concentration of copper in the solution (as measured by AAS), V_T is the total volume of the solution, ρ_{Cu} is the bulk density of copper, L is the average length of the Cu NWs, and r is the average radius of the Cu NWs. The number density, N_D, of Cu NWs in a film can then be calculated with Equation S2:

$$N_D = \frac{N}{A} \qquad \text{(Equation S2)}$$

where A is the area of the CuNW film.

Calculation of the ratio σ_{op}/σ_{dc} of copper nanowire films with different nickel contents.

For fast and convenient calculation, we convert the formula

$$T = (1 + \frac{188.5}{R_s} \frac{\sigma_{op}}{\sigma_{dc}})^{-2}$$

into a formula

$$\frac{1}{\sqrt{T}} = 1 + 188.5 \frac{\sigma_{op}}{\sigma_{dc}} \frac{1}{R_s}$$

We plotted $\frac{1}{\sqrt{T}}$ versus $\frac{1}{R_s}$ in Figure S3-S7. We determined the ratio σ_{op}/σ_{dc} for the quality factor of nanowire films from the slopes of the lines in Figure S5-S9.

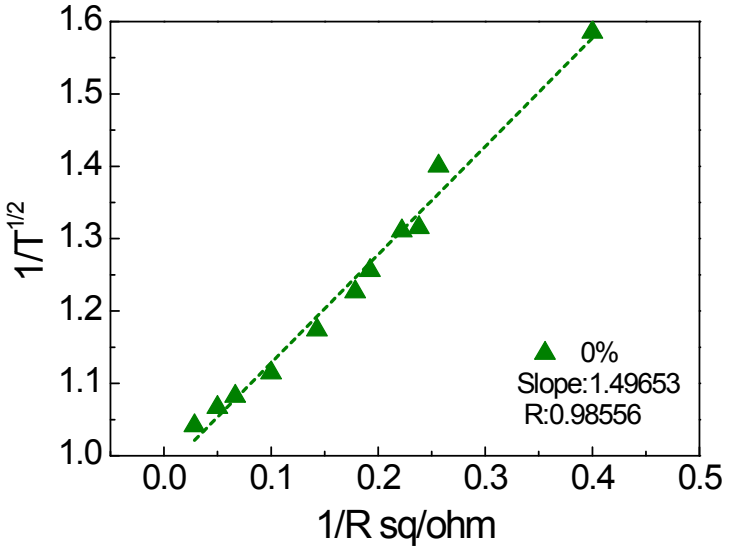

Figure S6: Plot of $\frac{1}{\sqrt{T}}$ versus $\frac{1}{R_s}$ for Cu NW films

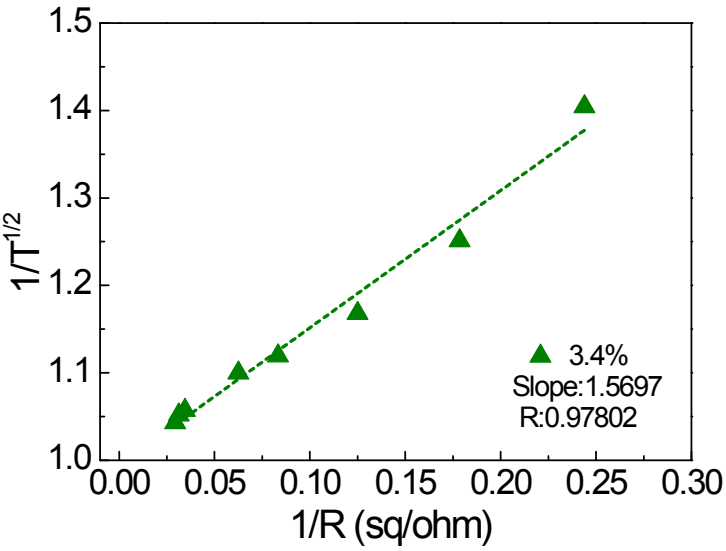

Figure S7: Plot of $\frac{1}{\sqrt{T}}$ versus $\frac{1}{R_s}$ for Cu NW films coated with 3.4mol % nickel

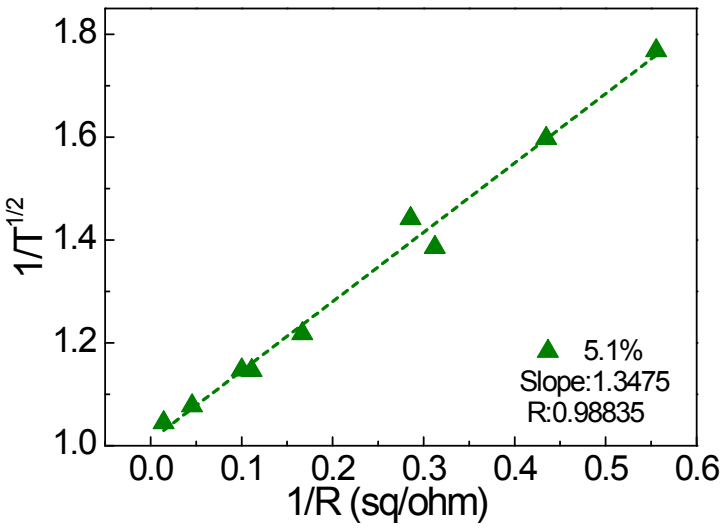

Figure S8: Plot of $\frac{1}{\sqrt{T}}$ versus $\frac{1}{R_s}$ for Cu NW films coated with 5.1mol % nickel

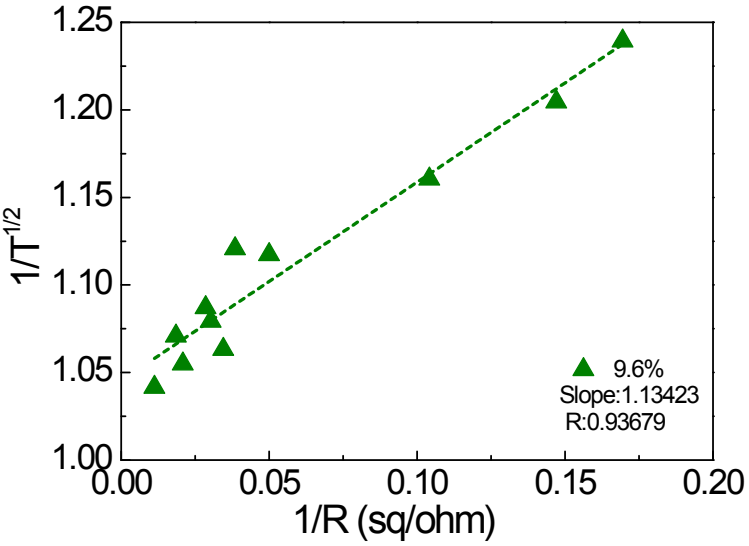

Figure S9: Plot of $\frac{1}{\sqrt{T}}$ versus $\frac{1}{R_s}$ for Cu NW films coated with 9.6mol % nickel

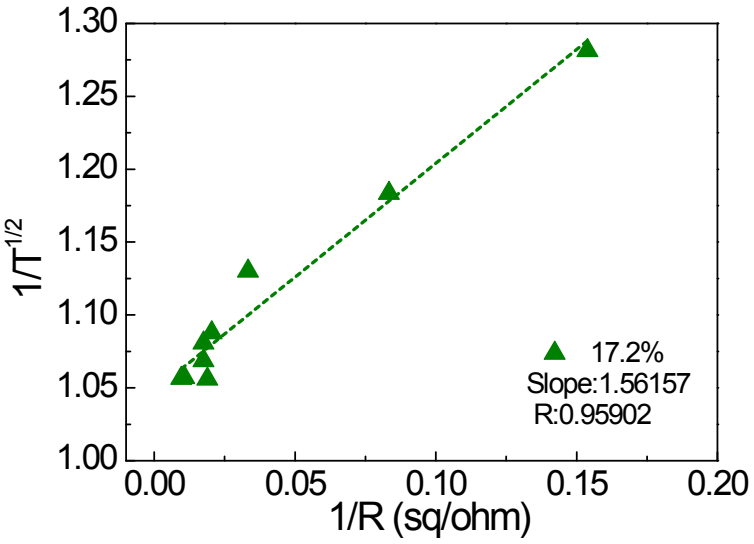

Figure S10: Plot of $\frac{1}{\sqrt{T}}$ versus $\frac{1}{R_s}$ for Cu NW films coated with 17.2mol % nickel

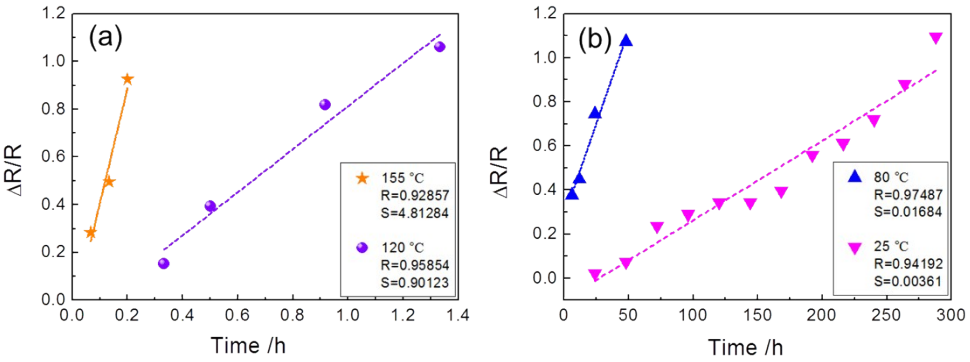

Figure S11. Plot of $\Delta R/R_0$ vs. time for Cu NW films

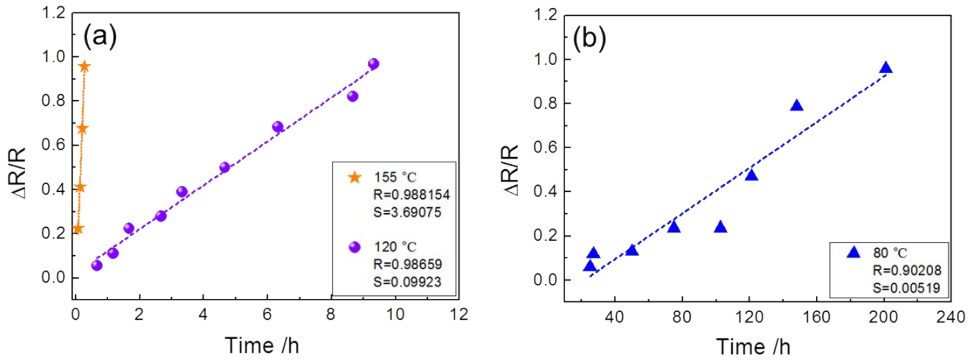

Figure S12. Plot of $\Delta R/R_0$ vs. time for Cu NW films coated with 3.4mol % nickel

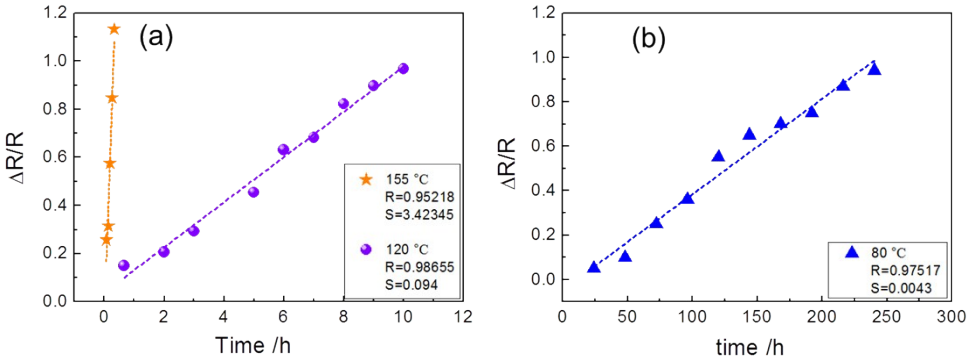

Figure S13. Plot of $\Delta R/R_0$ vs. time for Cu NW films coated with 5. 1mol % nickel.

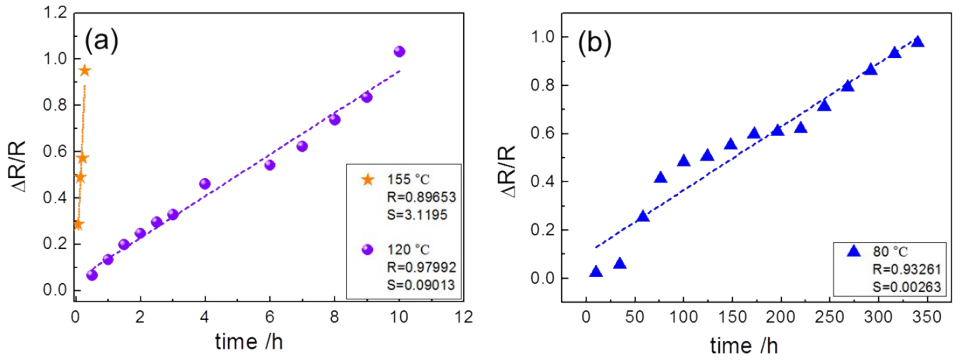

Figure S14. Plot of $\Delta R/R_0$ vs. time for Cu NW films coated with 9.6mol % nickel

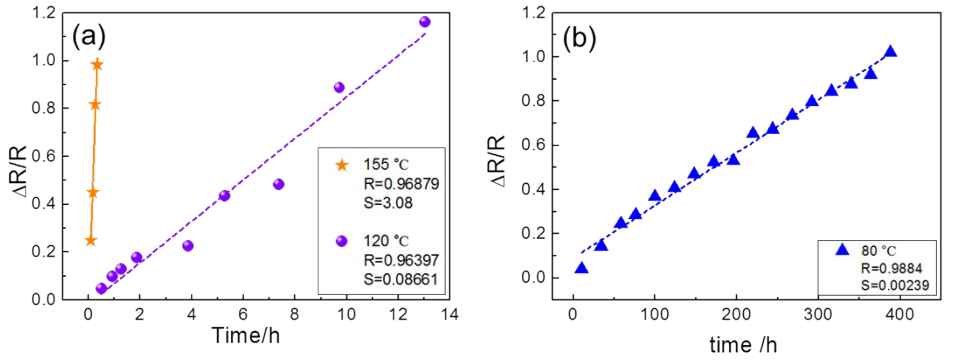

Figure S15. Plot of $\Delta R/R_0$vs. time for Cu NW films coated with 17.2mol % nickel

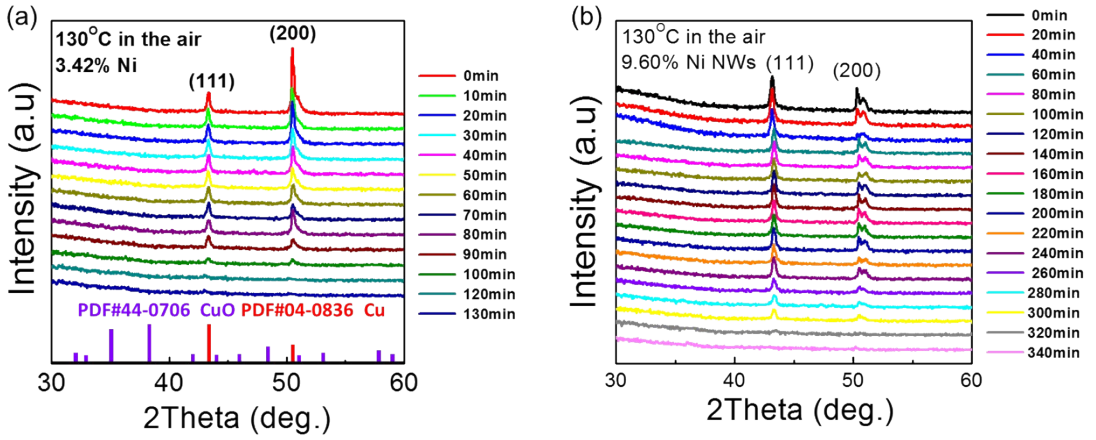

Figure S16. In situ XRD patterns of Cu (a) and Cu-Ni NW (b) films on the heating plate at 130°C in the air.

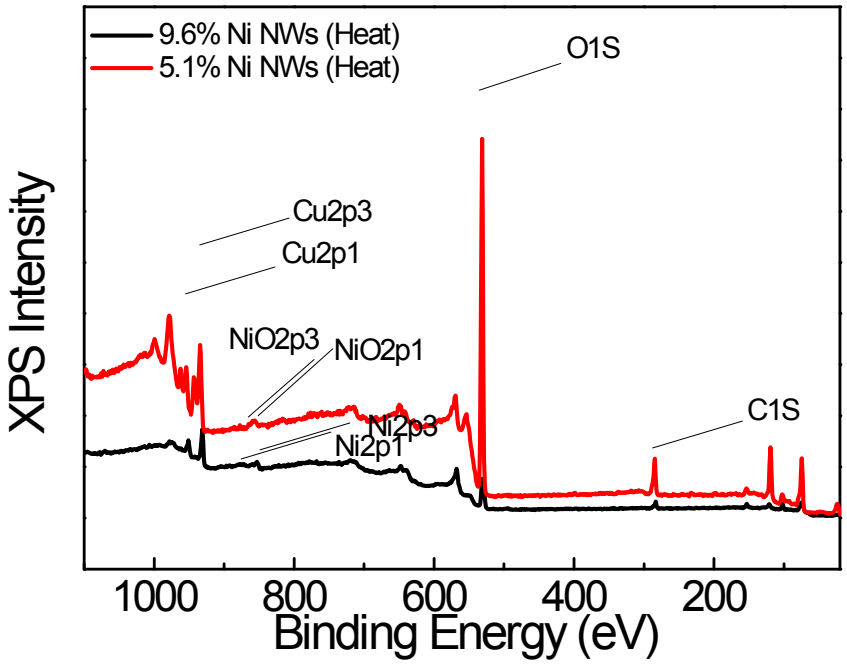

Figure S17. XPS survey full spectra of Cu NWs containing 5.1 at.% Ni and 9.6 at.% Ni that heated to 130 °C for 80 min

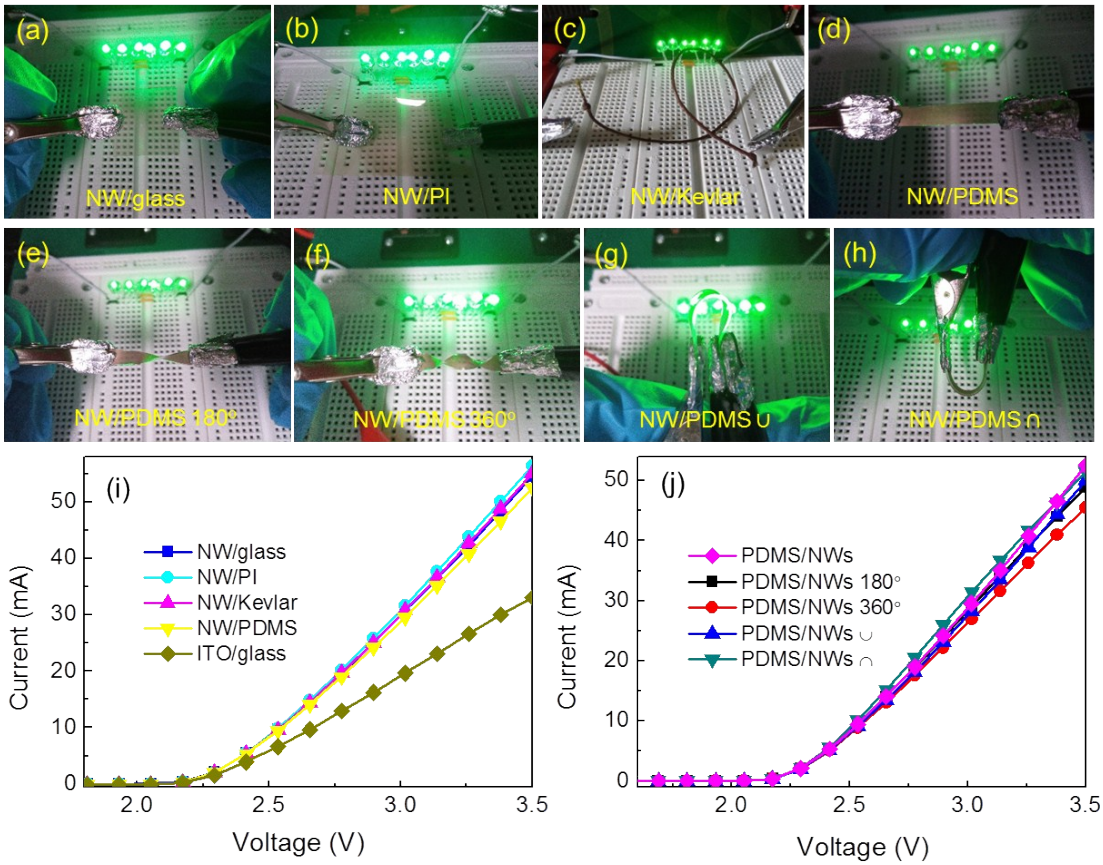

Figure S18 LED applications of cupronickel NWs containing 9.6 at.% Ni. Photographic images of working LEDs with cupronickel NW film conductors on (a) glass, (b) PI, (c) kevlar fiber, and (d-h) elastomeric PDMS as segments of external circuits. (i,j) Plot of current density versus voltage for LEDs using the NW conductors as described in (a-h).

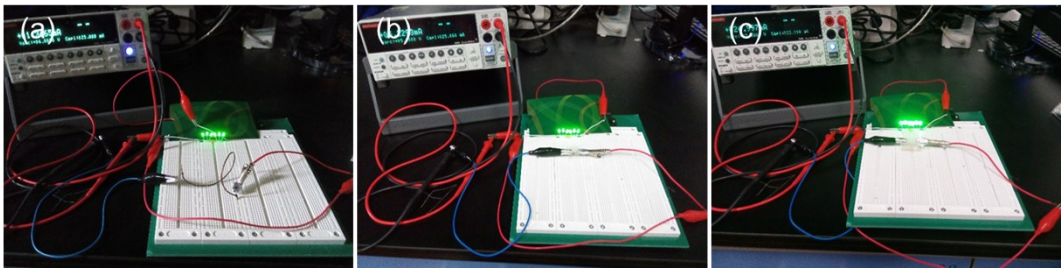

Figure S19. Photographic images of working LEDs with (a) conductive fiber coating with cupronickel nanowires, (b) cupronickel nanowire films on glass , (c) cupronickel nanowire films on PI.