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Enhanced oxidation-resistance Cu-Ni core-shell nanowires: Controllable one-pot synthesis and solution processing to transparent flexible heaters

Jianyu Chen[§, a], Jun Chen[§, a], Yi Li[§, a], Weixin Zhou[a], Xiaomiao Feng[a], Qingli Huang[b], Jian-Guo Zheng[*, c], Ruiqing Liu[a], Yanwen Ma[*, a], Wei Huang[a]

[a] Key Laboratory for Organic Electronics and Information Displays & Institute of Advanced Materials (IAM), Jiangsu National Synergistic Innovation Center for Advanced Materials (SICAM), Nanjing University of Posts and Telecommunications, 9 Wenyuan Road, Nanjing 210023, China. **email: iamywma@njupt.edu.cn.*

[b] Testing center, Yangzhou University, Yangzhou city, Jiangsu 225009, China

[c] Irvine Materials Research Institute (IMRI), University of California, Irvine, CA 92697, USA *email:jzheng@uci.edu,

Table S1 Detailed experimental conditions for one-pot synthesis of Cu-Ni NWs

xpt.	NaOH solution		Ni^{2+} solution		Cu^{2+} solution		Volume of EDA	Volume of N_2H_4	Temperature	Time
	V(mL)	c(mol/L)	V (mL)	c (mol/L)	V (mL)	c (mol/L)	V (mL)	V (uL)	(°C)	(min)
A1	1000	12	10	0.3	10	0.1	3	25	80	60
A2	1000	10	10	0.3	10	0.1	6	25	80	60
A3	1000	7	10	0.3	10	0.1	12	25	80	60
B1	1000	12	10	0.2	10	0.1	3	25	75	60
B2	1000	10	10	0.2	10	0.1	6	25	75	60
B3	1000	7	10	0.2	10	0.1	12	25	75	60
C1	1000	12	10	0.15	10	0.1	3	25	75	60
C2	1000	10	10	0.15	10	0.1	6	25	75	60
C3	1000	7	10	0.15	10	0.1	12	25	75	60
D1	1000	12	10	0.1	10	0.1	3	25	70	90
D2	1000	10	10	0.1	10	0.1	6	25	70	90
D3	1000	7	10	0.1	10	0.1	12	25	70	90
E1	1000	12	10	0.1	10	0.15	3	25	65	90
E2	1000	10	10	0.1	10	0.15	6	25	65	90
E3	1000	7	10	0.1	10	0.15	12	25	65	90
F1	1000	12	10	0.1	10	0.2	3	25	60	120
F1	1000	10	10	0.1	10	0.2	6	25	60	120
F3	1000	7	10	0.1	10	0.2	12	25	60	120
G1	1000	12	10	0.1	10	0.3	3	25	60	120
G2	1000	10	10	0.1	10	0.3	6	25	60	120
G3	1000	7	10	0.1	10	0.3	12	25	60	120

Table S2 Cu and Ni contents of Cu-Ni NWs measured by EDS

Feeding molar ratio of Cu^{2+}/Ni^{2+}	Element content		Measurment molar ratio of Cu/Ni
	Cu (at. %)	Ni (at. %)	
3:1	77.84	22.16	3.5:1
2:1	67.28	32.72	2.1:1
1.5:1	61.13	38.87	1.6:1
1:1	51.33	48.67	1:1
1:1.5	41.18	58.82	1:1.4
1:2	33.82	66.18	1:2.0
1:3	23.09	76.91	1:3.3

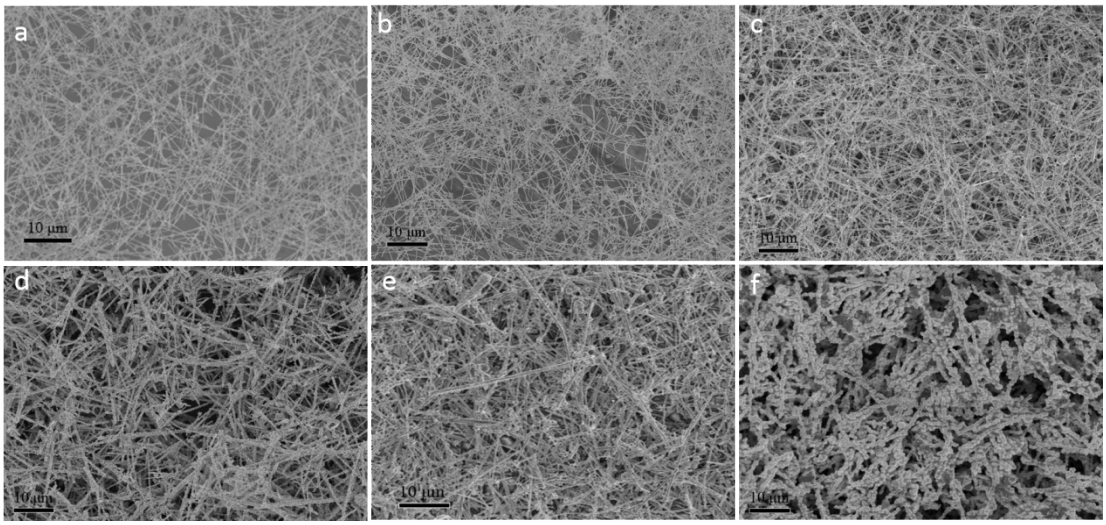

Fig. S1 SEM images of Cu-Ni NWs with Cu/Ni molar ratio of (a) 3.5:1, (b) 2.1:1, (c)1.6:1, (d) 1:1.4, (e) 1:2 and (f) 1:3.3.

Fig. S2a-f shows EDS elemental maps of Cu-Ni NWs synthesized with Cu^{2+}/Ni^{2+} molar ratio of 3:1, 2:1, 1.5:1, 1:1.5, 1:2 and 1:3, respectively. The sample synthesized from the Cu^{2+}/Ni^{2+} molar ratio of 1:3 presents a necklace-like morphology, but other samples show a typical NW structure, in accordance with the results revealed by SEM images (Fig. S1). The Ni maps indicate that continuous Ni shell layer could be formed when the Ni content in precursor is increased to 1:2 or greater. Obviously, the thickness of Ni layer is increased with Ni content. In addition, oxide species always accompanied Ni as reflected by O element maps. Here oxide species is NiO, which forms dense oxide layer to prevent the diffusion of exterior oxygen.

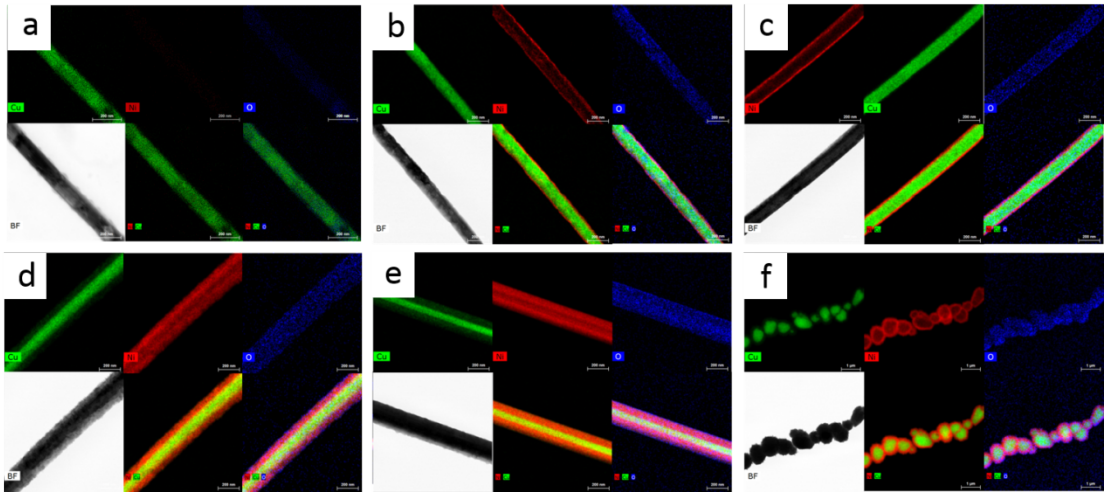

Fig. S2 EDS element maps of Cu-Ni NWs with Cu/Ni molar ratio of (a) 3.5:1, (b) 2.1:1, (c) 1.6:1, (d) 1:1.4, (e) 1:2 and (f) 1:3.3.

"The core-shell nanowire growth is affected by both thermodynamics and kinetics. To understand the effect of thermodynamics, a serial of temperature gradient experiments (80 °C, 75 °C, 70 °C, 65 °C and 60 °C) listed in Table S1 were carried out. The experimental result indicates that at high 80 °C, Cu^{2+} is easily reduced while the reduction of Ni^{2+} is sluggish. The reduction of Ni^{2+} is preferred to take place at 60 °C. Therefore, the reaction temperature is varied according to the change of Cu/Ni ratio, e.g., 80 °C for neat 3/1, 70 °C for 1/1 and 60 °C for 1/3. As for kinetics effect, varying Cu/Ni molar ratio can synthesize different structural Cu-Ni nanowires. When Cu/Ni molar ratio is 1/2 or greater, Ni will grow on the preformed Cu nanowires. At higher Ni^{2+} content, its reduction rate is increased. The excessive Ni^{0} would be reduced to cover Cu^{0} surface before formation of Cu axis, and thus neck-like nanowires were formed.

According to the structural changes of Cu and Cu-Ni NWs with the increase of Ni^{2+} in precursor, their possible growth process is deduced and depicted in Fig. S3. Neat Cu NWs start growing from the pre-formed seeds of aggregated Cu nanoparticles (Route 1). The NWs first grow in longitudinal direction and then act as template for Cu deposition in axial direction. When Ni^{2+} cations are incorporated in Cu^{2+} solution, the reduction of Cu^{2+} cations undergo significantly faster than Ni^{2+} cations because $E^{\ominus}(Cu^{2+}/Cu)$ is much higher than $E^{\ominus}(Ni^{2+}/Ni)$. The NWs would grow through Route 2 if Ni was deposited on the pre-grown Cu NWs, forming Cu-Ni core-shell (cable) NWs. At high Ni^{2+} concentration, Cu seeds are surrounded by Ni^{2+} cations and sequentially coated by Ni layer. These core-shell nanoparticles are connected together under the direction of EDA capping agents and formed a one-dimensional necklace-like structure (Route 3).

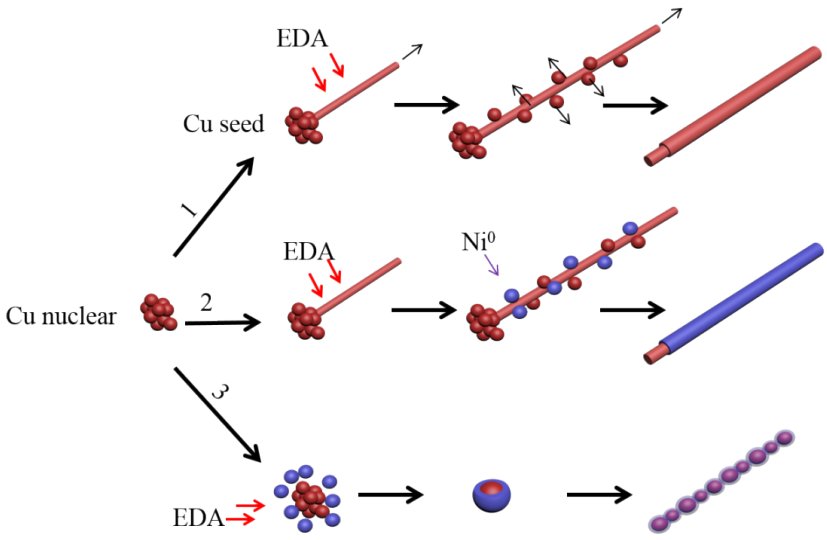

Fig. S3 Schematic of neat Cu and Cu-Ni NW growth process.

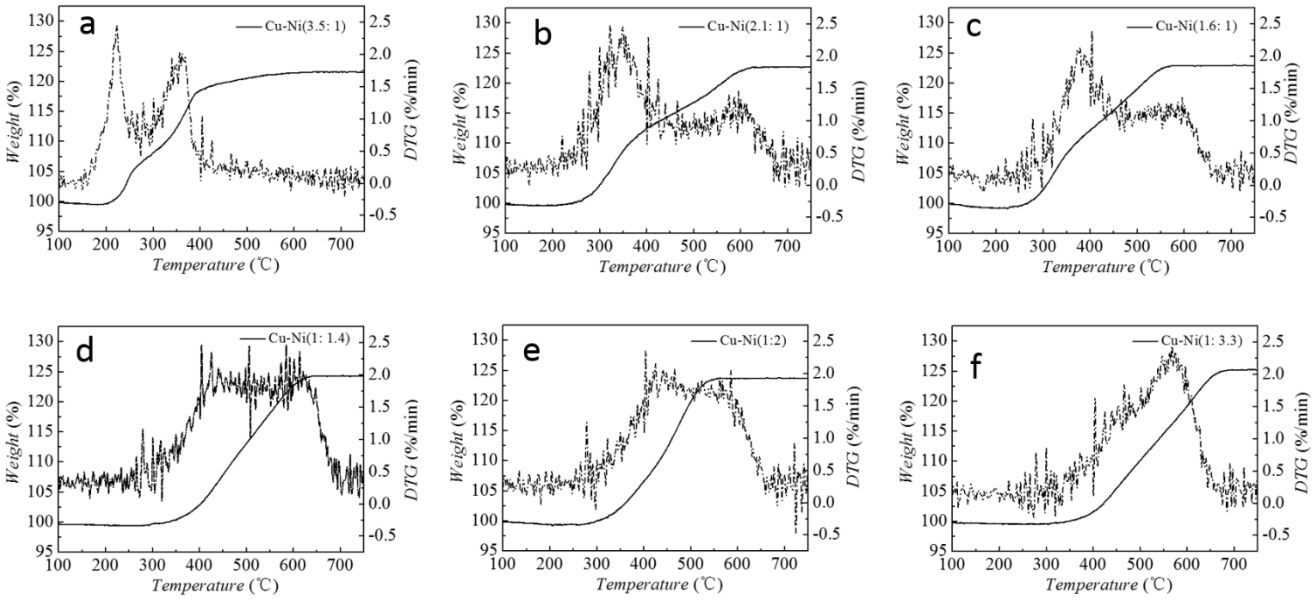

Fig. S4 TG and DTG curves of (a) Cu-Ni(3.5:1), (b) Cu-Ni(2.1:1), (c) Cu-Ni(1.6:1), (d) Cu-Ni(1:1.4), (e) Cu-Ni(1:2), and (f) Cu-Ni(1:3.3) NWs.

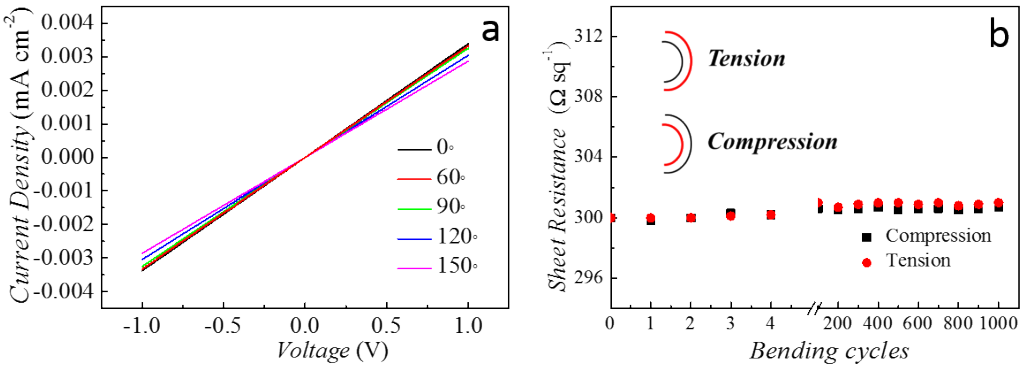

Fig. S5 Flexibility tests of Cu-Ni(1:1) TCFs. (a) I-V curves measured at 0-150° bending angles; (b) Resistance changing under continuous bending.

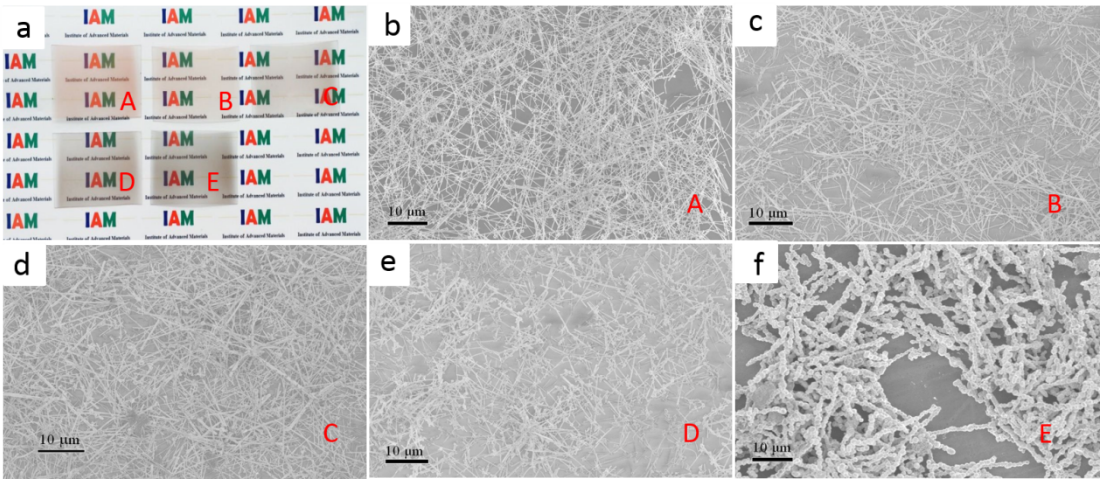

Fig. S6 (a) Photograph of Cu-Ni TCFs prepared using different Cu-Ni NWs. SEM images of (b) Cu-Ni(3.5:1), (c) Cu-Ni(2.1:1), (d) Cu-Ni(1:1), (e) Cu-Ni(1:2) and (f) Cu-Ni(1:3.3) TCFs.

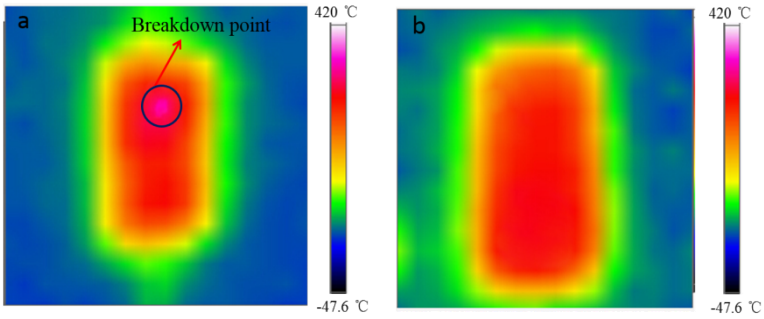

Fig. S7 Infrared thermal images of (a) Cu NW and (b) Cu-Ni NW heaters operated at 12 V.