Electronic Supplementary Material (ESI) for Nanoscale
This journal is © The Royal Society of Chemistry 2014

Supplementary information

Low temperature growth of graphene on Cu–Ni alloy nanofibers for stable, flexible electrodes

Zheng-Dong Liu,[a] Zong-You Yin,[bc]* Ze-Hui Du,[d] Yang Yang,[a] Min-Min Zhu,[b] Ling-Hai Xie,[a]* Wei Huang[a, e]*

[a] Center for Molecular Systems and Organic Devices (CMSOD), Key Laboratory for Organic Electronics & Information Displays (KLOEID), Institute of Advanced Materials (IAM), Nanjing University of Posts & Telecommunications, 9 Wenyuan Road, Nanjing 210046, China

[b] School of Materials Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798

[c] Institute of Materials Research and Engineering A*STAR (Agency for Science, Technology and Research) 3 Research Link, Singapore 117602 (Singapore)

[d] Temasek laboratories, Nanyang Technological University, Nanyang Drive, Singapore 637553

[e] Jiangsu–Singapore Joint Research Center for Organic/Bio– Electronics & Information Displays, Institute of Advanced Materials, Nanjing－Tech University, Nanjing 211816, China.

E–mail: iamlhxie@njupt.edu.cn(L.H. X.); iamwhuang@njupt.edu.cn(W.H.); zongyouy@gmail.com(Z.Y. Y.)

Experimental Section

Preparation of nanofibers (NFs) by using electrospinning method:

The Ni, Cu, and bimetal Cu–Ni NFs were prepared on common glass starts with the fabrication of electrospinning solution. In a typical procedure, 0.75 g of Poly(vinylpyrrolidone) (PVP) (Sigma–Aldrich, weight average molecular weight Mw = 1 300 000 g/mol) was dissolved in 8.0 ml of 2–methoxy–ethanol (2–MOE) (Sigma–Aldrich, 99.9%), followed by magnetic stirring for 4 h under room temperature to ensure the dissolution of PVP, after the polymer solution has been prepared, metal precursors were added to the solution and stirred for 2 h at room temperature to achieve a homogenous composite solution. Metal precursor 1.50 g nickel acetate ($NiAc_2$) was used to prepare Ni NFs, 1.50 g copper acetate ($CuAc_2$) was used to obtain Cu NFs, in order to prepare molar ratio of 2:1, 1:1, 1:2 Cu–Ni NFs, 1.00 g–0.49 g, 0.75 g–0.73 g, 0.50 g–0.97 g $CuAc_2$–$NiAc_2$ also were used as the metal sources. In the electrospinning procedure, a rotating collector was used to collect polymer NFs. The detail process was: glass was adhered to the rotating collector after the rotating collector surface has been covered with an aluminum foil, when applied 10 kV voltages with an electrode–to–collector distance of 10 cm at room temperature, the solution rate was 0.5 ml/h, and the rotating rate was 1000 r/min, aligned polymer NFs were collected on glass. After having collected some aligned polymer NFs on the glass, changed the glass crossing angle for 90 degrees, crossed arrays of composite NFs were collected on glass.

Thermogravimetric analysis (TGA) thermograms:

TGA thermograms of polymer NFs contain metal precursor $NiAc_2$–$CuAc_2$ is as follow: the dehydration of polymer–$NiAc_2$–$CuAc_2$ NFs that occurs first accounts for 10–12% mass loss and ceases at about 210 °C. This was followed by a weight–drop begins at 220 °C, which is attributed to the decomposition of PVP main chain. Then, a major weight loss begins at 350 °C and finish at about 450 °C, the main loss come from the decompose of $NiAc_2$–$CuAc_2$. According to the TGA thermograms, we set the decomposition temperature of the polymer–metal precursors NFs at 500 °C in order to decompose the metal precursors into metal oxide fully.

Use NFs as the graphene growth templates:

After the polymer NFs have been prepared, they were dried at 80 °C in a vacuum condition for 4 h, and then heated at 500 °C under a heating rate of 5 °C/min for 2 h in an air atmosphere, therefore PVP was burned out and metal precursors were decomposed into metal oxide NFs. After that, reductive reaction was carried out in a hydrogen atmosphere at 400 °C for 2 hours with a flow rate of 100 standard cubic centimeters per minute (sccm), whereby pure Ni, Cu and molar ratio of 2:1, 1:1, 1:2 Cu–Ni alloy NFs were obtained on glass. Once NFs obtained on glass, the NFs were annealed in a 200 sccm H_2 flow at 700 °C for 5 min, and then moved the quartz tube from the furnace. After the temperature of graphene growth zone was cooled down to the desired temperature, moved the quartz tube into the furnace, use polystyrene (PS, Sigma – Aldrich, Mw = 300 000) as the solid carbon source, the solid precursor zone temperature was elevated up to 700 °C with the H_2 flow 100 sccm and Ar flow 150 sccm while maintaining the whole system under low pressure. Set up the graphene growth temperature at 450 °C, 500 °C, 550 °C, or 600 °C, growth time is 5 min, 10 min, 15 min, or 30 min, after graphene growth process finished, take out the quartz tube from the furnace and the samples were cooled down to room temperature quickly by natural cooling, and graphene–metal NFs were obtained on glass.

Oxidation and corrosion resistance of G–coated Cu–Ni NFs:

Two types of samples were used for oxidation resistance experiment, untreated 1:1 Cu–Ni alloy (designated as Cu–Ni) NFs and graphene coated Cu–Ni alloy (designated as G–coated Cu–Ni) NFs, graphene was growth directly on Cu–Ni NFs by using PS as a carbon precursor by CVD method at 600 °C for 10 min. Then these samples Cu–Ni and G–coated Cu–Ni were heated in laboratory air at 200°C for 4 hours, X–ray photoelectron spectroscopy (XPS) measurements of these samples were carried out before and after air oxidation.

Cyclic voltammetry (CV) was employed to study the corrosion resistance of G–coated Cu–Ni, the detail process was according to the reported method and used Cu–Ni, G–coated Cu–Ni as the subject samples.[S1] The CV measurement was performed in a three–electrode system, a platinum wire was used as a counter–electrode, an Ag/AgCl was used as a reference electrode, these samples were used as the working electrode, and sea water was used as electrolyte. The Cu–Ni and G–coated Cu–Ni growth on glass were laterally in the cell exposing the same sample area. Copper taper was attached to the NFs to make electrical contact. Once these samples were mounted onto the electrode cell, it was filled with sea water electrolyte. A Pt counter–electrode and Ag/AgCl reference electrode were immersed into the electrolyte.

Bending tests:

After Gr–Ni and G–coated Cu–Ni NFs films were prepared, these NFs films were transferred from glass to polyethylene terephthalate (PET), then two silver paints were painted on the end of the NFs films, after the silver dried out, two Cu films were adhered to the silver ends for resistance measurement. The NFs film on PET was bent until it reached a radius of curvature of about 8 mm, 7 mm, 6 mm, 5 mm, 4 mm, 3 mm and the resistance was measured by using two–probe method after the PET films were relaxed to the original shape (radius of curvature of about 10 mm). The flexibility test of the commercial indium tin oxide (ITO) on PET film was carried out use the same method.

The fabrication of electroluminescent device:

The electroluminescent devices (glass or PET/G–coated Cu–Ni NFs/ZnS:Cu phosphor/$BaTiO_3$/CNTs) were fabricated as follow: G–coated Cu–Ni NFs growth on glass can be directly used as the electrode to prepare rigid device, or transfer G–coated Cu–Ni NFs to PET to make flexible device which based on its good flexibility. On top of the conductive electrode, a layer of ZnS:Cu phosphor was coated through rod–coating method, after drying at 60 °C for 2 hours, coated with a layer of $BaTiO_3$ on ZnS:Cu phosphor via rod–coating method. A layer of multi–walled carbon nanotubes were coated onto the top of $BaTiO_3$ for top electrode.

Characterizations:

The scanning electron microscopy (SEM) images were recorded by using a field emission scanning electron microscope (JEOL, Model JSM–7600F) at 5.0 keV in the secondary electron mode. To identify the NFs components, powder X–ray diffraction (XRD, Shimadzu) analysis was carried out, theta/2–theta mode with the scan rate of 0.1°/min. The transmission electron microscopy (TEM, JEM–2010F) images were obtained with an accelerating voltage (AC) of 200 kV. Both brightness and electroluminescence spectra of devices were obtained with a spectroradiometer (spectra scan 655), the measurements were performed in a dark box at room temperature in air.

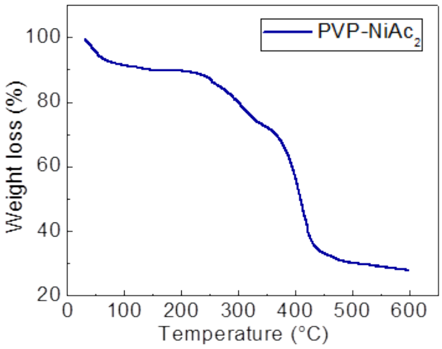

Fig. S1 Thermogravimetric analysis (TGA) thermograms of polymer NFs which contains metal precursor $NiAc_2$.

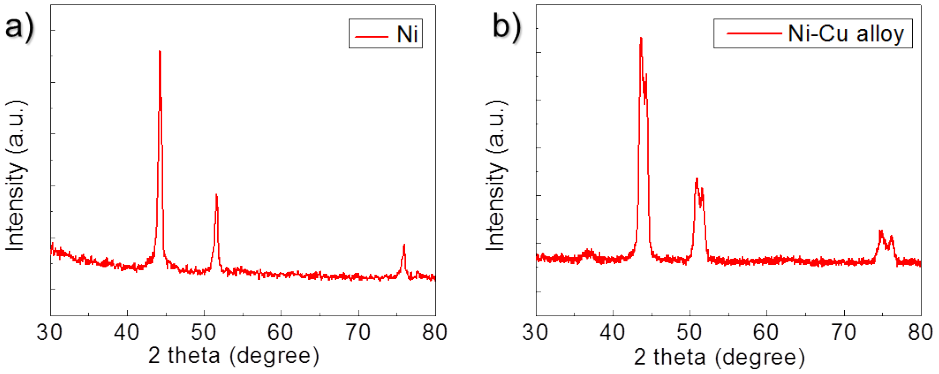

Fig. S2 XRD of (a) Ni NFs and (b) Cu–Ni alloy NFs.

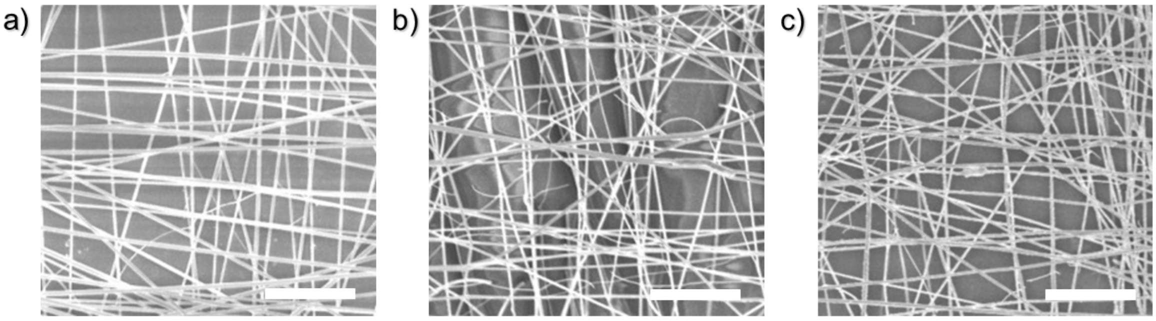

Fig. S3 FESEM images of a) polymer NFs contain metal precursors synthesized by electrospinning, b) metal oxide NFs, c) metal NFs. Scale bar = 5 μm.

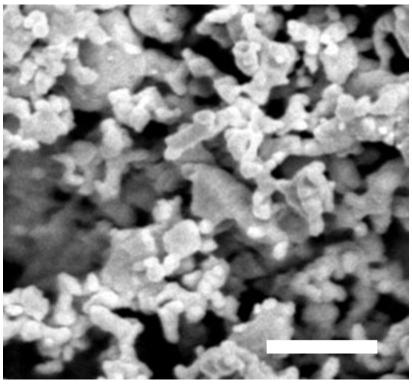

Fig. S4 Cu NFs after growing graphene at 450 °C for 30 min. Scale bar = 5 μm.

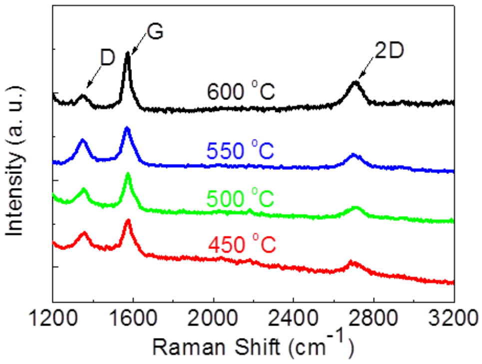

Fig. S5 Raman spectrum (under 488 nm excitation) of graphene growth on Ni NFs at 450 °C, 500 °C, 550 °C and 600 °C for 30 min, respectively.

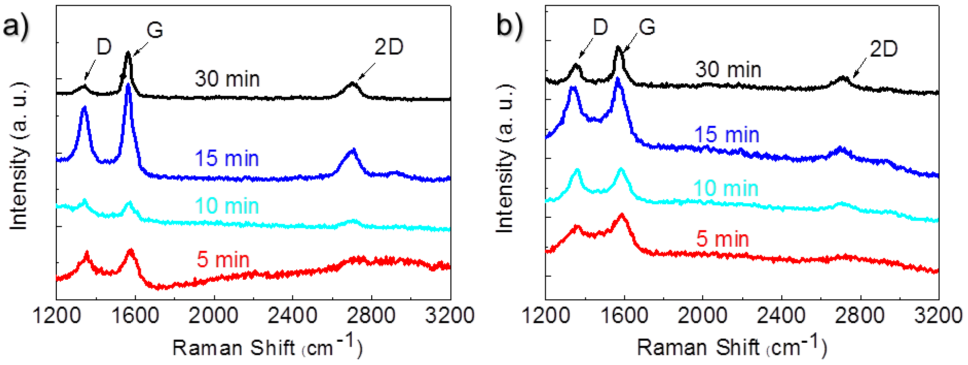

Fig. S6 Raman spectrum (under 488 nm excitation) of graphene grown on a) Ni NFs and b) 1:1 Cu–Ni alloy NFs at 600 °C for 5 min, 10 min, 15 min and 30 min, respectively.

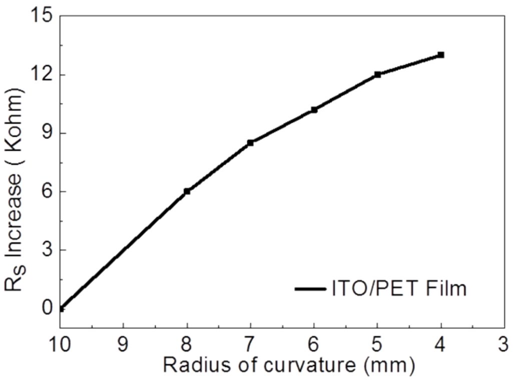

Fig. S7 The resistance increase of ITO/PET film after bending to different radius of curvature.

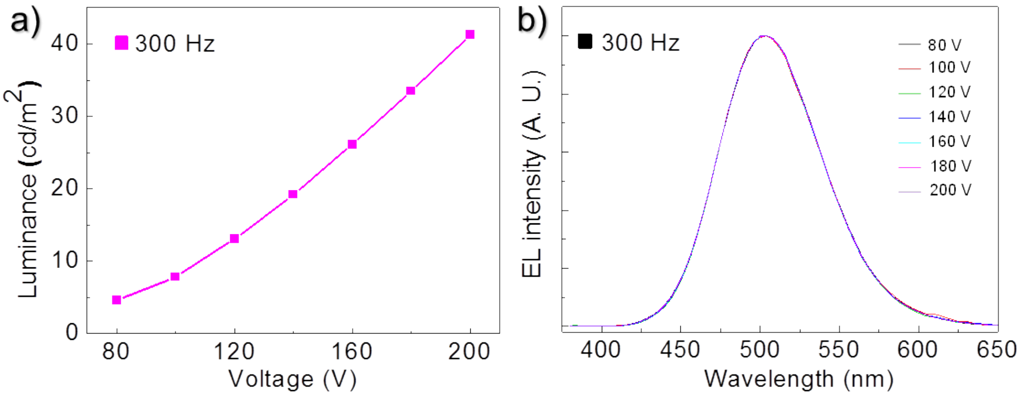

Fig. S8 a) Brightness versus AC voltage plot of the rigid AC device at a frequency of 300 Hz. b) EL spectra versus AC voltage plot of the rigid AC device at a frequency of 300 Hz.

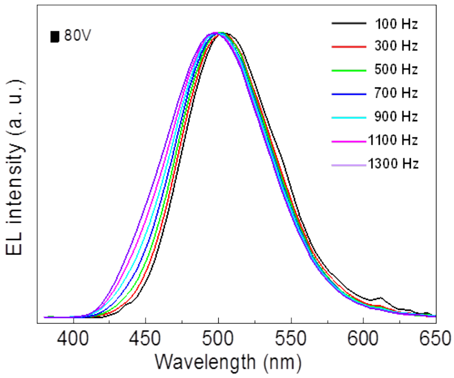

Fig. S9 EL spectra versus AC voltage plot of the rigid AC device at a voltage of 80V.

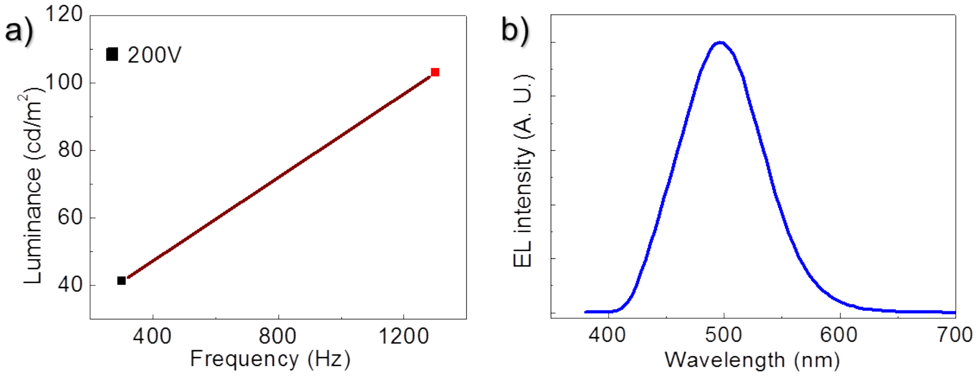

Fig. S10 a) Brightness and frequency plot of the rigid AC device at a driving voltage of 200 V. b) EL spectra of rigid AC device at a driving AC voltage of 200 V and frequency of 1300 Hz.

References

S1 D. Prasai, J. C. Tuberquia, R. R. Harl, G. K. Jennings and K. I. Bolotin, *ACS Nano*, 2012, **6**, 1102.