Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Solution-Processed Flexible Transparent Conductors Based on Carbon Nanotubes and Silver Grids Hybrid

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Experimental section

Materials

The Ag-PET films were obtained from Cima NanoTech and used as received. The P2-SWNTs were purchased from Carbon Solutions and used as received. All other chemicals were purchased from Sigma and used as received. Deionized water (D. I. water) was used in all experiments.

Fabrication of SWNT-Ag-PET hybrid electrodes

10 mg P2-SWNTs were mixed with 10 mL of 1 mgmL^{-1} sodium cholate (SC) aqueous solution. The mixture was ultrasonicated using a 130-Watt Ultrasonic Processor (VCX130, Sonics & Materials, Inc., USA) for 1 hr (60% amplitude). The suspension was then centrifuged at 50,000 g for 1 hr. The top 80% supernatant was carefully removed and diluted 10-fold with 1% SC solution. The diluted solution was bath-sonicated for 10 min before use.

The as-received Cima Ag-PET film was covered with sacrificial thin PET layers, front (the side with Ag grid) and back (the side without Ag grid). The front sacrificial PET layer was removed before any surface treatment of the Ag network side of the film, while the back layer was kept in place during all processing steps to avoid any contamination to the back side. The back sacrificial layer was removed before characterization or use.

The front sacrificial plain PET layer on the Ag-PET was removed, and the Ag-PET films were exposed to Ar plasma for 60 s at 100W power. Then the films were immersed in 0.5 vol.% of (3-Aminopropyl)triethoxysilane (APTES) solution in ethanol for 45 min. The excess

APTES was rinsed away with ethanol. The films were rinsed with D.I. water and blown dry with compressed air. Then the APTES-treated Ag-PET films were immersed in the diluted SWNT dispersion for 1 h. After immersion, the hybrid films were rinsed with D.I. water and blown dry. The films were dried at 70°C overnight before characterization. The preparation of the control SWNT-PET samples followed the same procedure except that the plain PET film was purchased from Higashiyama Film (Singapore).

Fabrication of graphene-Ag-PET hybrid electrodes

Graphene was synthesized via an optimized atmospheric chemical vapor deposition (CVD) method. Copper foil (99.8%, 25 μm thick) was purchased from Alfa Aesar and cut into pieces of the desired size. The copper foil pieces were carefully rolled and transferred into a quartz tube with inner diameter of 22 mm. The tube was purged with 500 sccm Ar for 20 min, and then heated to 925 °C in a split tube furnace. 60 sccm H_2 was introduced during the heating process. The system was kept at 925°C for several minutes to reduce the surface oxidation of copper foils. Ar was cut off and 5 sccm CH_4 was introduced for 5 min while H_2 was kept at 60 sccm. After 5 min, during which graphene was grown, the CH_4 was cut off and Ar was introduced again in the cooling stage.

The synthesized graphene was transferred by an improved wet transfer process. While still on the copper foils, the graphene was protected by application of a sacrificial poly(methyl methacrylate) (PMMA) layer. The copper foils were then etched away with $Fe(NO_3)_3$ solution. After removal of the copper, the graphene films were rinsed with D.I. water several times and transferred onto Ag-PET films. The film (with its PMMA sacrifice layer) was exposed under UV light for 10 min to degrade the PMMA into methyl methacrylate monomers which were then removed with acetone.

Fabrication of met-SWNT-Ag-PET hybrid electrodes

99% met-SWNTs solution was purchased from NanoIntegris and diluted with D.I. water. The diluted solution was bath-sonicated for 10 min and vacuum filtered through 0.2 μm pore size PTFE membrane (diameter 47 mm). The met-SWNTs film on PTFE membrane was then washed with D.I. water and directly transferred onto Ag- PET film with a laminator at 130 ^oC.

Electrochemical deposition of ZnO

ZnO nanosheets were electrodeposited on a PET/Ag/CNT substrate (1 cm × 2 cm) in a three-electrode cell with the PET/Ag/CNT as working electrode, a Pt plate as counter electrode, and a Ag/AgCl (sat. KCl) electrode as reference electrode. The electrolyte contained 50 mL of 0.05 M $ZnCl_2$ and 0.5 M KCl. The deposition was performed at –1.0 V for 1 h at room temperature.

Measurement of photocurrent

The photocurrent was measured on an electrochemical workstation (CHI660c, CH Instruments) with a three-electrode configuration. The as-prepared sample, Pt-wire electrode, and Ag/AgCl electrode were employed as the working, counter, and reference electrodes, respectively. The samples were illuminated by a Xenon-lamp light source (100 mW cm^{-2}) at the open circuit potential. 0.5 M Na_2SO_4 solution was used as the electrolyte.

Characterizations

The sheet resistance was measured with a Keithlink four-point probe station (probe spacing 1.6 mm, probe pin diameter 40.6μm.). Scanning electron microscopy (SEM) was performed using LEO 1550 Gemini field-emission scanning electron microanalyzer at an accelerating voltage of 5 kV. The ZnO-SWNT-Ag-PET sample was coated with Pt for 10 seconds under acurrent of 10 mA. All the other samples were scanned directly, without Pt coating. Raman spectroscopy was conducted using a Renishaw inVia Raman microscope with 514.5 nm (2.41

eV) laser wavelength in a backscattering configuration. UV-vis-NIR absorption spectra were measured using a Varian Cary 5000 UV-vis-NIR spectrophotometer. The substrate absorption for background subtraction was measured using a blank PET substrate. X-ray diffraction (XRD) patterns were recorded on a Bruker AXS D8 Advance, equipped with a Cu Kα photon source (40 kV, 20 mA, λ=0.15406 nm) scanned at the rate of 1.0^{o} min^{-1} over the range 32^{o}-80^{o} (2θ).

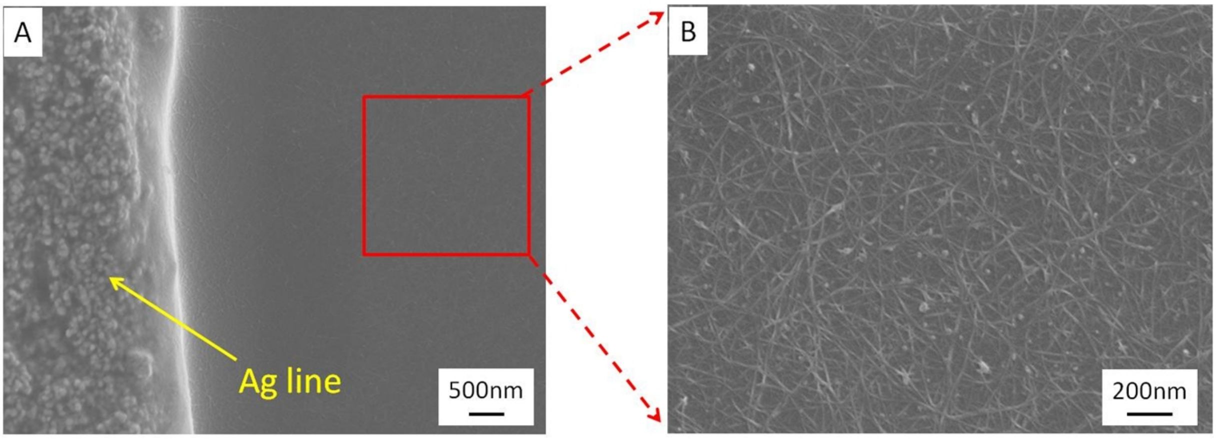

Figure S1. A) SEM image of SWNT network thin film on Ag-PET. B) High magnification SEM image of the SWNT network thin film in the empty area, marked with red square in A).

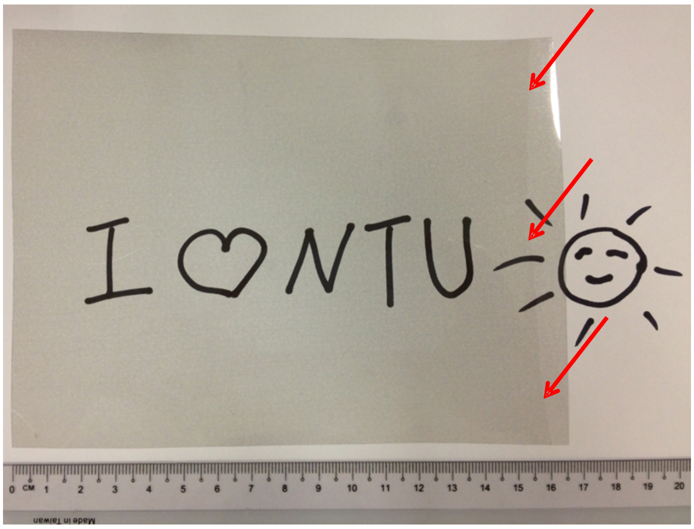

Figure S2. Gross visual appearance and transparency of SWNT-Ag-PET film (16cm ×12cm sample).The red arrows show the boundary between the regions with (left) / without (right) SWNT network thin film.

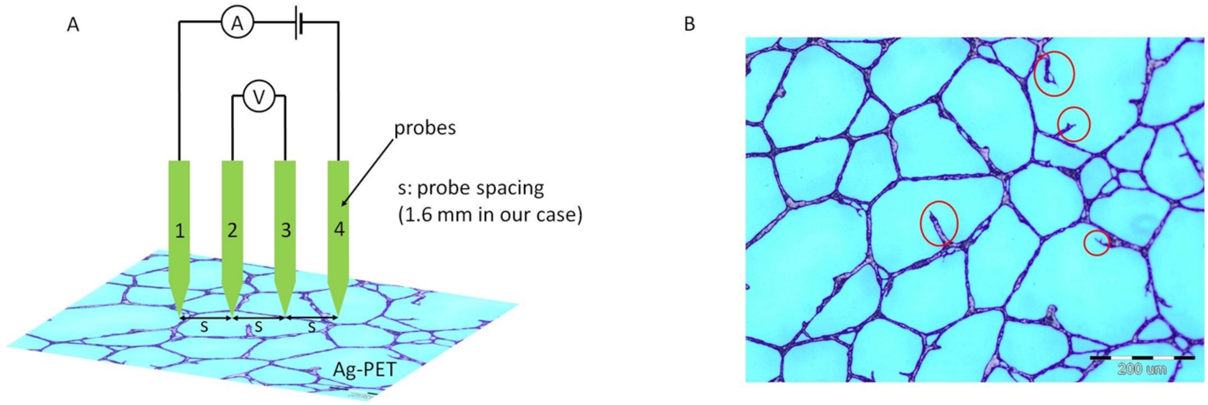

Figure S3. A) Schematic of the four-point probe configuration (not to scale).The probe spacing is 1.6 mm and the probe pin diameter is 40.6µm. B) Optical microscope image of the Ag-PET film. Some branches of the Ag-grids are highlighted in red circles.

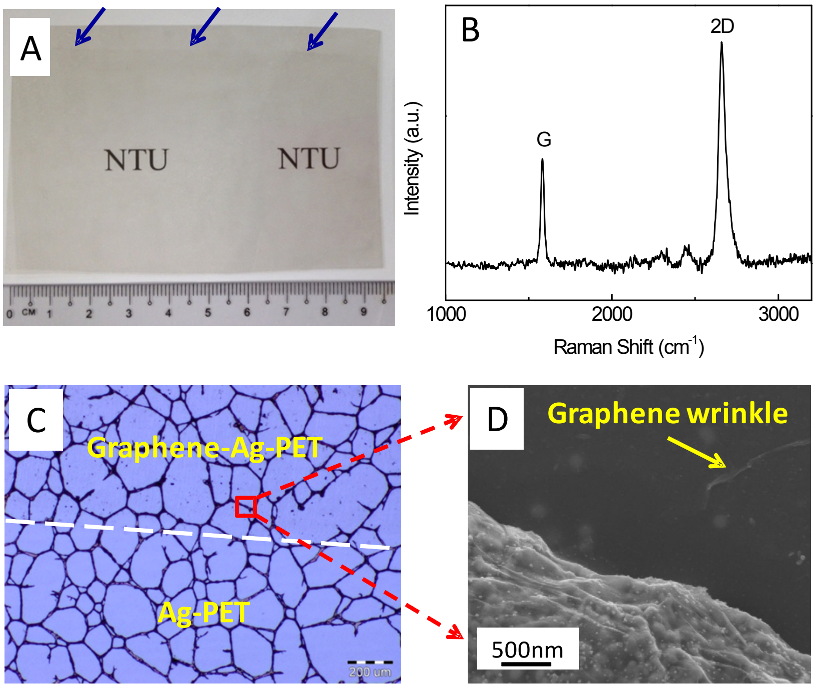

Figure S4. A) Visual appearance of graphene-Ag-PET hybrid film (9.5 cm × 5 cm sample). The blue arrows show the boundary between the regions with (bottom) /without (top) graphene. B) Raman spectrum of graphene used in this work. C) Optical microscope image of a graphene-Ag-PET film. Graphene covers the top part of the image, indicated by the white dashed line. D) SEM image of graphene-Ag-PET film in the red square of C).

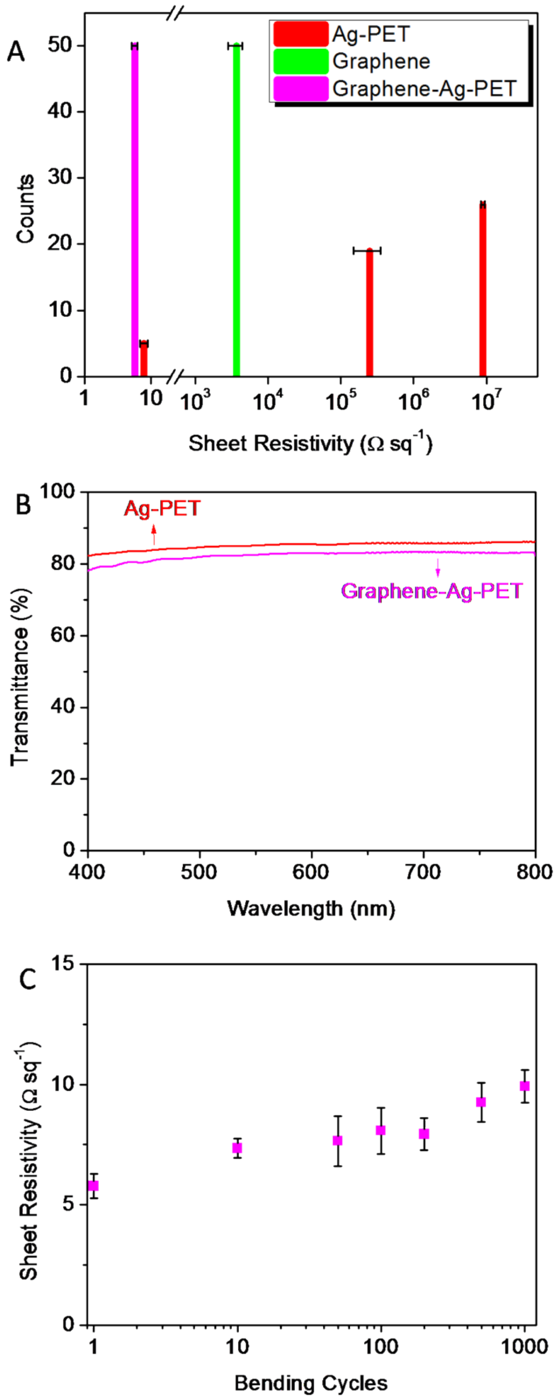

Figure S5. A) Sheet resistance of Ag-PET film (red), CVD-grown graphene (green), and graphene-Ag-PET film (magenta). 50 points were measured for each sample. B) Transmittance of Ag-PET film without (red curve) and with (magenta curve) graphene. C) Flexibility test of the graphene-Ag-PET film. The plot shows the sheet resistivity of the graphene-Ag-PET film, as a function of bending cycles, up to 1000 cycles.

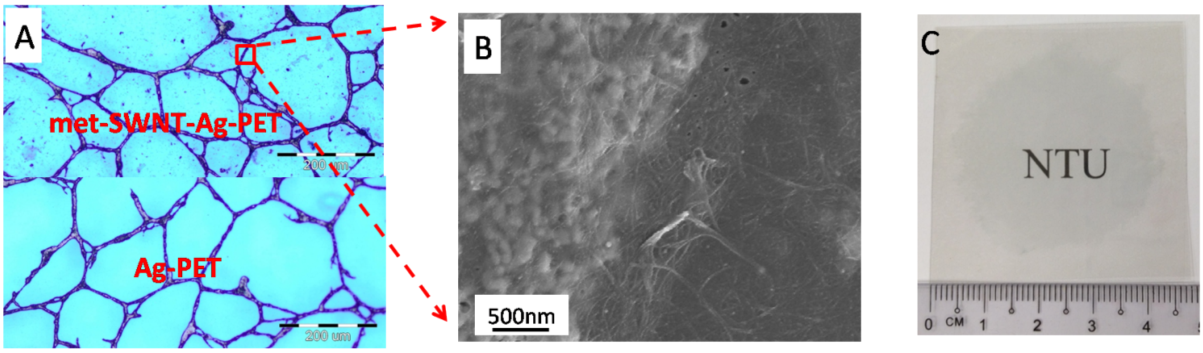

Figure S6. A) Optical microscopy image of Ag-PET with (top) and without (bottom) thin film of met-SWNTs network. B)A SEM image of met-SWNTs-Ag-PET hybrid film in the red square of A). C) Visual appearance of a met-SWNTs-Ag-PET film. The met-SWNTs film was prepared by vacuum filtration on PTFE membrane (47 mm diameter) and then transferred onto the Ag-PET film.

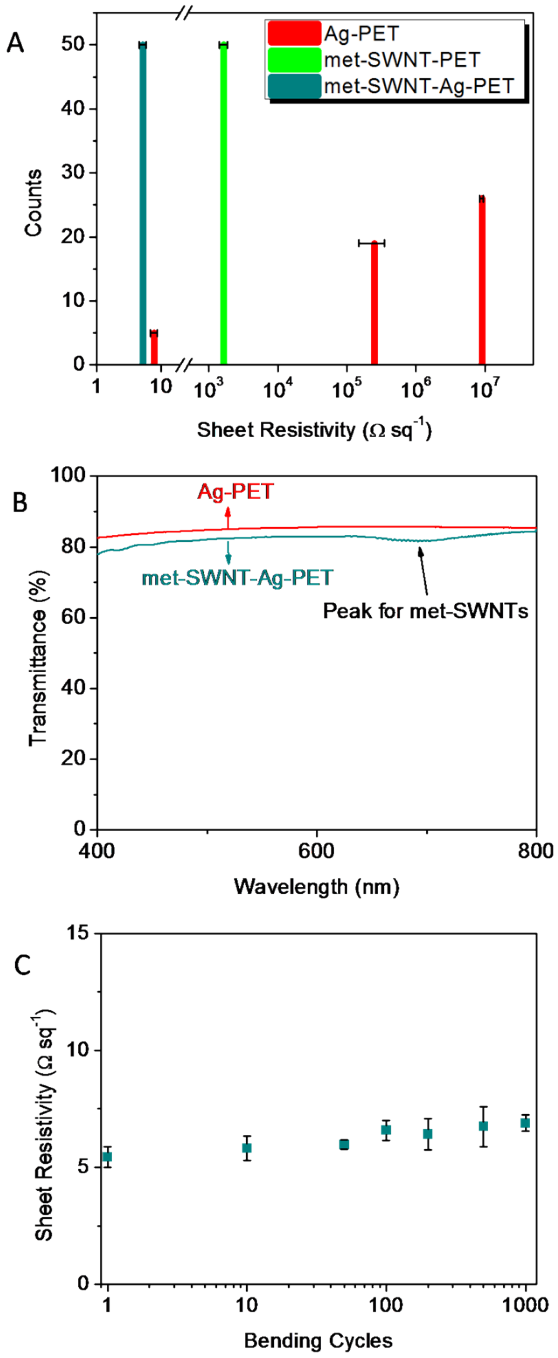

Figure S7. A) Sheet resistance of Ag-PET film (red), met-SWNTs network (green) and met-SWNTs-Ag-PET film (dark cyan). 50 points were measured for each sample. B) Transmittance of Ag-PET film without (red curve) and with (dark cyan curve) met-SWNT network thin film. The absorbance peak between ~600-800 nm is attributed to the M11 transitions of met-SWNTs. C) Flexibility test of the met-SWNT-Ag-PET film. The plot shows the sheet resistivity of the met-SWNT-Ag-PET film, as a function of bending cycles, up to 1000 cycles.

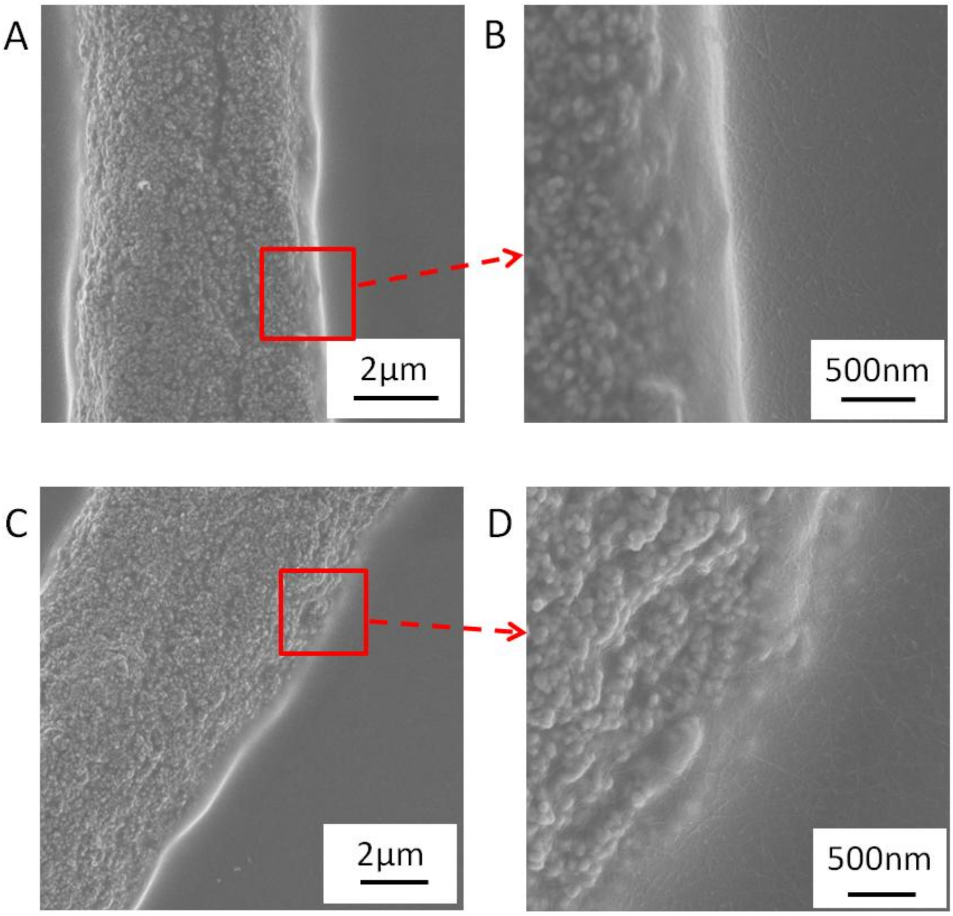

Figure S8. A) SEM image of SWNT-Ag-PET hybrid film before bendability test. B)* High magnification SEM image of pre-bending SWNT-Ag-PET hybrid film, marked with red square in A). C) SEM image of SWNT-Ag-PET hybrid film after bendability test (1000 cycles), showing no machenical degradation of Ag nanoparticles or thin film of SWNT network after 1000 cycles of bendability test. D) High magnification SEM image of pre-bending SWNT-Ag-PET hybrid film, marked with red square in C).

* Figure S8-B is the same figure as Figure 1F.

Table S1. Sheet resistance and transmittance of SWNT-Ag hybrid hybrid electrode (No. 1) graphene-Ag hybrid electrode (No. 2) and met-SWNT-Ag hybrid (No. 3) compared to commercial transparent electrode materials and previous research results (No. 4-18).

No.	**Product**	**Substrate**	**Sheet Resistance (Transmittance)**[a)]	σ_{DC}/σ_{Op}
1	SWNT-Ag hybrid (this work)	PET	5.8±1.1 Ω sq^{-1} (83.7%)	349
2	graphene-Ag hybrid (this work)	PET	5.6±0.6 Ω sq^{-1} (82.3%)	329
3	met-SWNT-Ag hybrid (this work)	PET	6.1±0.4 Ω sq^{-1} (82.0%)	296
4	ITO	glass	30-80 Ω sq^{-1} (90%)	44-116
5	PEDOT/PSS[1]	glass/PET	100 Ω sq^{-1} (91%)	39
6	SWNTs[2]	PET	60 Ω sq^{-1} (90%)	58
7	graphene[3]	glass	350 Ω sq^{-1} (90%)	10
8	graphene/SWNTs[4]	glass	280 Ω sq^{-1} (86%)	9
9	Cu nanofibers[5][b)]	glass	12 Ω sq^{-1} (80%)	133
10	Ag nanowires[6]	PET	13 Ω sq^{-1} (85%)	171
11	graphene[7] (doped by $AuCl_3$)	glass	150 Ω sq^{-1} (87%)	17
12	graphene[8] (doped by $AuCl_3$)	PET	54 Ω sq^{-1} (85%)	41
13	graphene[9] (doped by HNO_3)	PET	30 Ω sq^{-1} (90%)	116
14	Cu grid-Ni thin film hybrid[10]	fused silica	6.5 Ω sq^{-1} (75%)	187
15	Cu-Ti bilayer thin film[11]	fused silica	16 Ω sq^{-1} (86%)[c)]	150
16	graphene-Au grid[d)] hybrid[12]	glass	4±1 Ω sq^{-1} (79%) / 20±4 Ω sq^{-1} (91%)	377/195
17	graphene-Al grid[e)] hybrid[12]	PET	18±9 Ω sq^{-1} (79%) / 60±15 Ω sq^{-1} (91%)	84/65
18	graphene-Cu grid[e)] hybrid[12]	PET	8±3 Ω sq^{-1} (79%) / 30±6 Ω sq^{-1} (91%)	188/130

[a)] Transmittance of all the electrodes (except No. 15[c)]) was measured at 550 nm (substrate absorption substracted). [b)] Copper nanofibers were prepared by electrospinning. [c)] Transmittance at 630 nm. [d)] The metal grids were prepared by sputtering. [e)] The metal grids were prepared by thermal evaporation.

References

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