Electronic Supplementary Information

Highly Stable and Flexible Silver Nanowire-Graphene Hybrid Transparent Conducting Electrode for Emerging Optoelectronic Devices

Donghwa Lee,[‡a] Hyungjin Lee,[‡a] Yumi Ahn,[a] Youngjun Jeong,[a] Dae-Young Lee[b] and Youngu Lee*[a]

‡*These authors contributed equally to this work.*

**correspondence to : youngulee@dgist.ac.kr*

[a] Department of Energy Systems Engineering, Daegu Gyeongbuk Institute of Science and Technology (DGIST), 50-1 Sang-Ri, Hyeonpung-Myeon, Dalseong-Gun, Daegu, 711-873, Korea. Fax: +82-53-785-6414 ; Tel: +82-53-785-6409 ; E-mail: youngulee@dgist.ac.kr

[b] Display Research Center, Samsung Display, #95 Samsung 2-ro, Giheung-gu, Youngin-City, Gyeonggi-Do, 446-711, Korea.

Methods and Materials

Preparation of AgNW TCEs

Glass substrates were cleaned using acetone, deionized water, and isopropyl alcohol. They were treated with UV-ozone for 20 min to obtain a hydrophilic surface. Then, a AgNW ink (ClearOhm ink, Cambrios Technologies Corporation) was spin-coated onto the cleaned glass substrates. The spin-coated AgNW ink was then dried at 120 °C for 5 min to obtain a AgNW TCE on the substrates.

Synthesis of CVD-grown monolayer graphene

A graphene monolayer was synthesized by chemical vapor deposition (CVD) method using a copper foil (0.025mm thick, Alfa Aesar) as a metal catalyst. The copper foil was placed in a vacuum furnace with a quartz tube and heated to 1000 °C with hydrogen gas (8 ccm) at 1.3 x 10^{-1} Torr. The copper foil was annealed under same condition for 30 min to remove an oxide layer and other contaminants. Subsequently, the gas mixture of both hydrogen (8 sccm) and methane (24 sccm) was flowed for 30 min at 3.6 x 10^{-1} Torr. After the completion of the synthesis, the vacuum furnace was quickly cooled down to room temperature under hydrogen gas (8 sccm) to obtain a graphene monolayer grown on the copper foil.

Characterization of AgNW and AgNW/Graphene hybrid TCEs

The optical transmittance of AgNW and AgNW/Graphene hybrid TCEs was measured by using a UV/Vis/NIR spectrophotometer (CARY 5000 spectrophotometer, Agilent). The sheet resistance of both samples was measured by using a non-contact sheet resistance measurement instrument (EC-80, Napson). The nanostructure and surface images of both samples were recorded with a field emission scanning electron microscope (SU-8020, Hitachi). The Raman spectra of both smaples were measured by using a Raman spectrometer (Almega XR, Thermo scientific). The surface morphology of the AgNW and AgNW/Graphene hybrid TCEs was measured by using Atomic Force Microscope (NX10, Park systems).

Electrical connection test of AgNW and AgNW/Graphene hybrid TCEs

The electrical connection tests of AgNW and AgNW/Graphene hybrid TCEs were performed by measuring the sheet resistance values with a 4-point probe sheet resistance measurement instrument (MCP-T610, Mitsubishi Chemical).

Mechanical flexibility test of ITO/PEN and AgNW/Graphene/PEN TCEs

Mechanical flexibility tests of ITO/PEN and AgNW/Graphene/PEN TCEs were performed using a bending tester (ZBT-200, Z-tec). A ITO/PEN film (Rs = 15 Ω/sq) was purchased from Peccell technologies.

Fabrication of bulk heterojunction organic solar cells with a AgNW/Graphene hybrid TCE

The AgNW TCE for a cathode layer was prepared onto a glass substrate by spin-coating a AgNW ink at 1200 rpm. As for the AgNW/Graphene hybrid TCE, the CVD-grown monolayer graphene was dry-transferred onto the AgNW TCE. The AgNW/Graphene hybrid TCE was treated in an UV-ozone for 3 min and immediately spin-coated with a ZnO solution. The ZnO layer was formed by sol-gel method. The sol-gel derived ZnO was prepared by dissolving zinc acetate dehydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$, Aldrich, 1 g) and ethanolamine ($NH_2CH_2CH_2OH$, Aldrich, 0.28 g) in 2-methoxyethanol ($CH_3OCH_2CH_2OH$, Alfa aessar, 10 mL) under vigorous stirring for 24 hr in air. The ZnO coated AgNW/Graphene hybrid TCE was annealed on a hot plate for 1 hr at 200 °C in air. The thickness of the ZnO layer was approximately 150 nm. Poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C_{61}-butyric acid methyl ester ($PC_{60}BM$), which were blended in a weight ratio of 1:1, were dissolved in chlorobenzene. Then, the P3HT:$PC_{60}BM$ solution was spin-coated on top of the ZnO layer and dried for 60 min at 50 °C and then annealed for 10 min at 160 °C in a glove box to form an active layer with a thickness of 100 nm. Finally, an anode layer composed of a MoO_3 layer (10 nm) and an Ag layer (120 nm) was deposited by thermal evaporation with the shadow mask in a high vacuum thermal evaporator (<10^{-7} Torr). Therefore, we fabricated the inverted type organic solar cell devices with a AgNW-graphene hybrid transparent electrode / ZnO(150 nm) / P3HT:PCBM(100 nm) / MoO_3(10 nm) / Ag(120 nm) configuration.

Characterization of bulk heterojunction organic solar cells

The Current density - voltage (J-V) measurements of organic solar cell devices were performed by using Mcscience Inc. K-3300 under 100 mW cm^{-2} AM 1.5 G illuminations. All measurements were carried out under ambient conditions at room temperature.

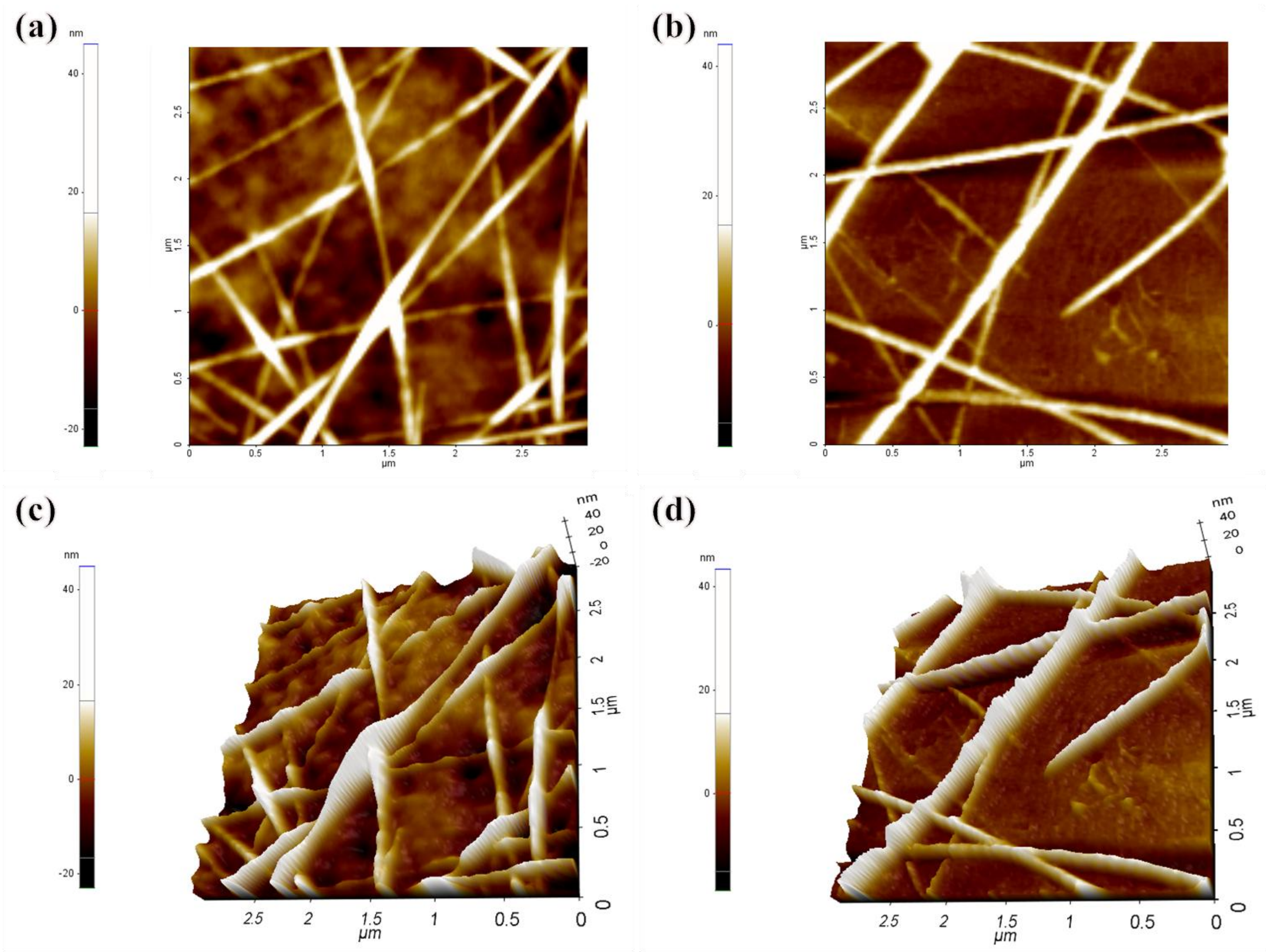

Fig. S1 AFM topographies of AgNW and AgNW/Graphene TCEs on glass substrate: 2D images of (a) AgNW and (b) AgNW/Graphene TCEs, 3D images of (c) AgNW and (d) AgNW/Graphene TCEs.

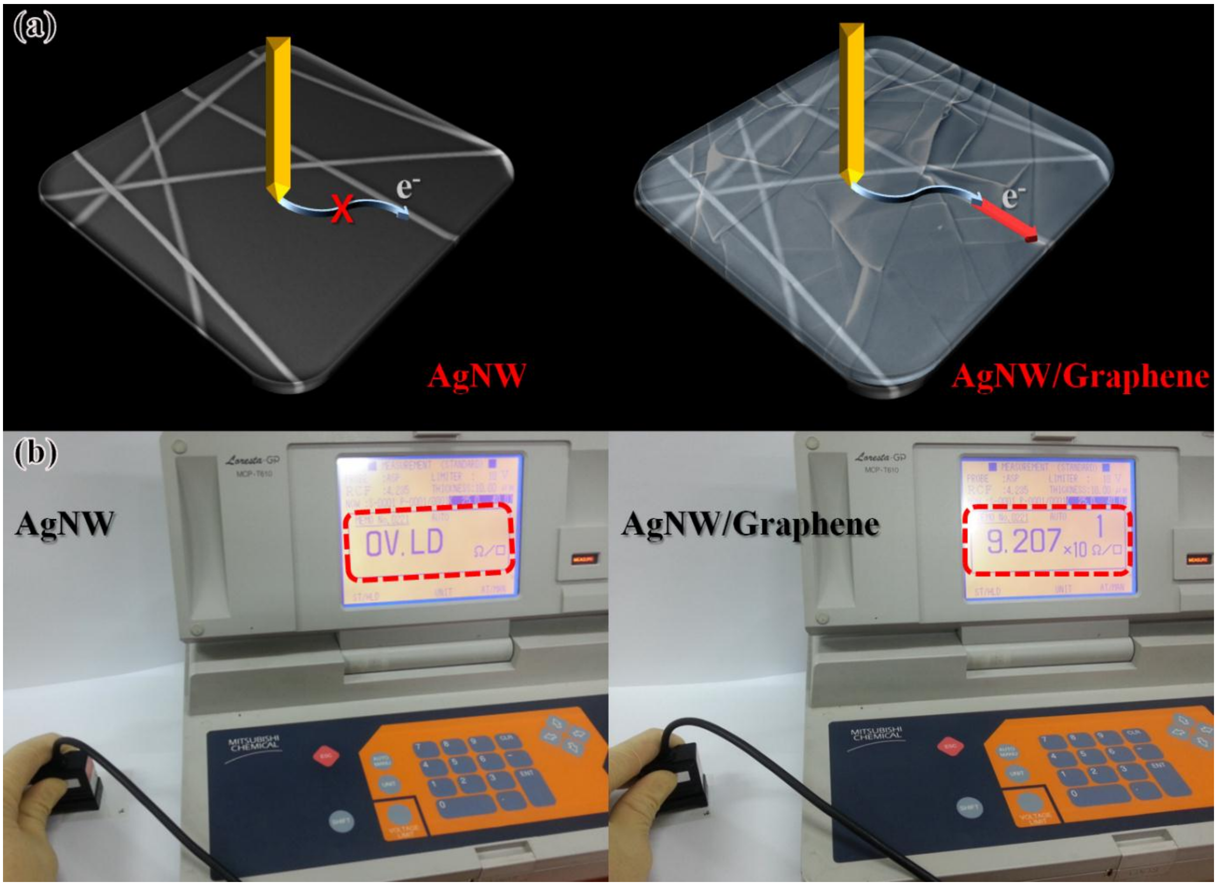

Fig. S2 (a) Schematic illustration showing the roles of the graphene layer in improving the electrical connection between the AgNW TCE and conductive probe. (b) Images of electrical connection test of AgNW and AgNW/Graphene hybrid TCEs using a four-point probe measurement system.

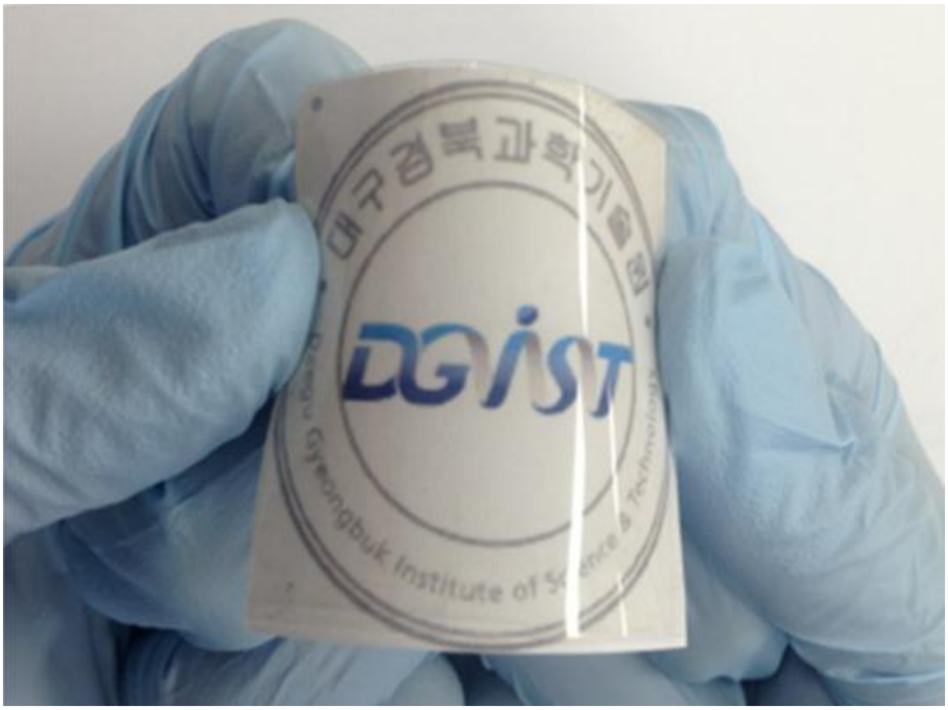

Fig. S3 A photograph of flexible AgNW/Graphene/PEN TCE.

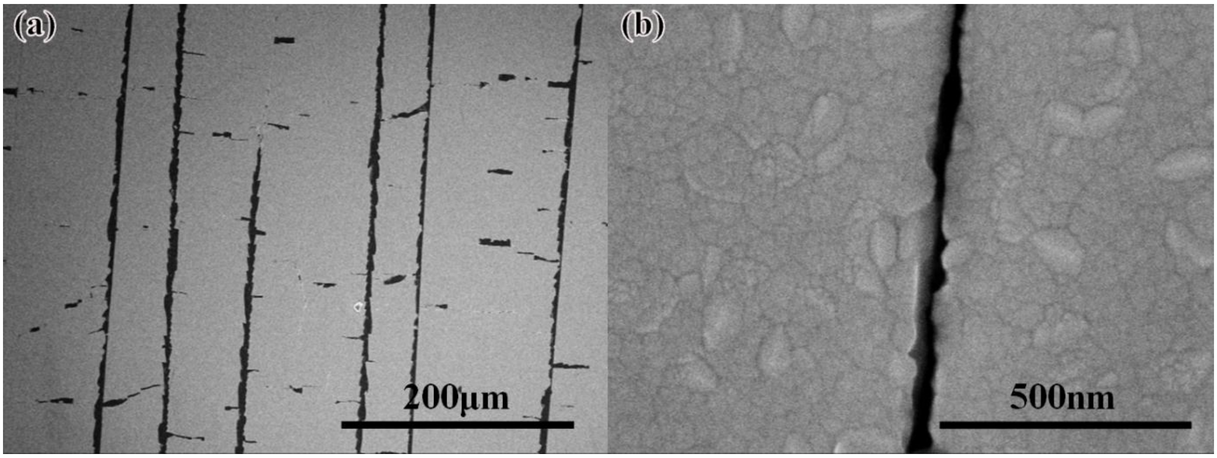

Fig. S4 The SEM images of ITO/PEN TCE after mechanical flexibility test.

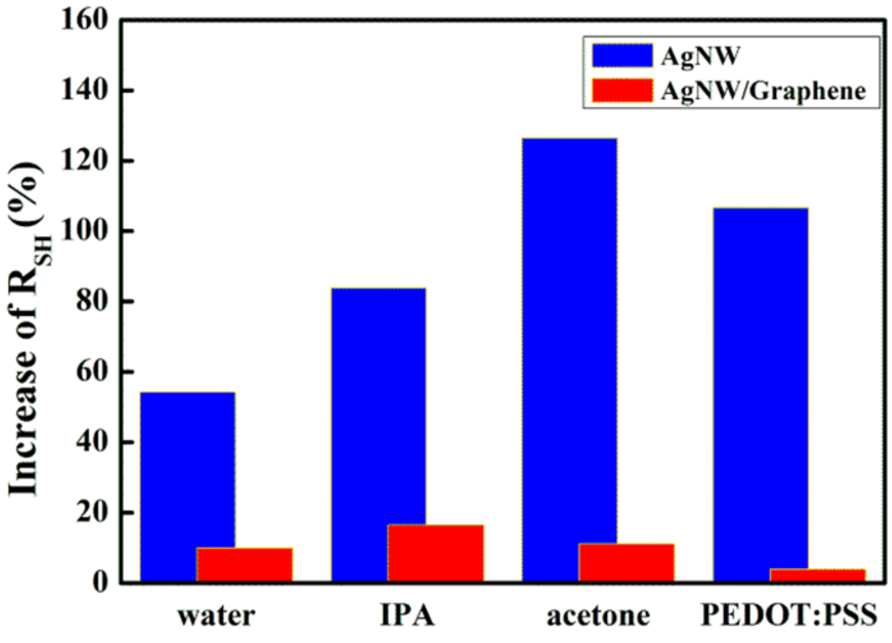

Fig. S5 The chemical stability test of AgNW and AgNW/Graphene hybrid TCEs measured by dipping into various solvents.

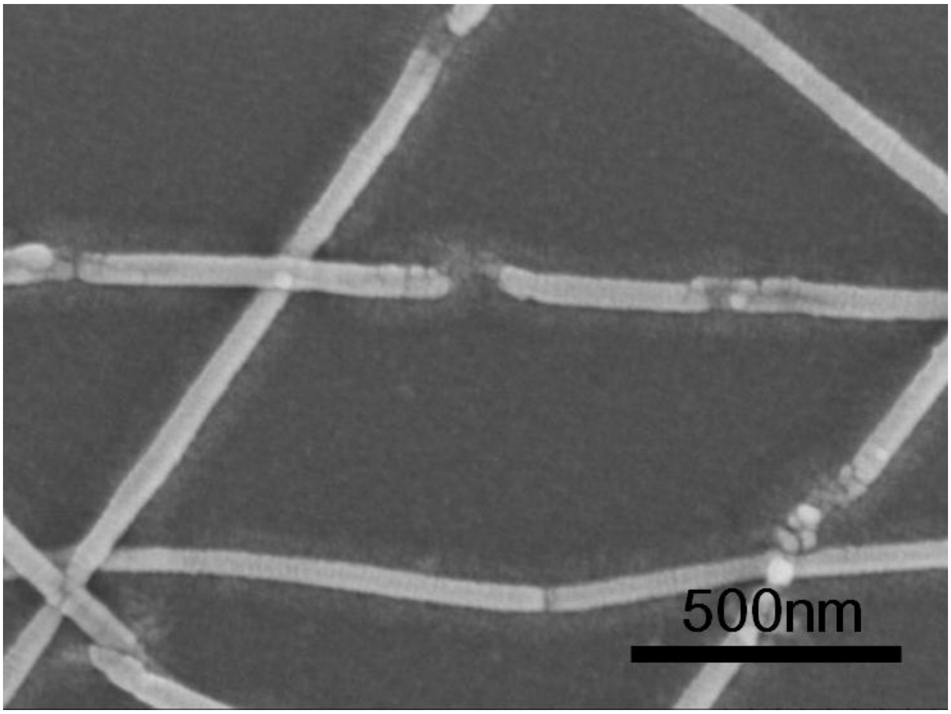

Fig. S6 A SEM image of the AgNW TCE etched by acidic PEDOT:PSS solution.