Electronic Supplementary Material (ESI) for Nanoscale.

Supplementary Information

Wearable, Wireless Gas Sensors Using Highly Stretchable and Transparent Structures of Nanowires and Graphene

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Experimental Details

Preparation of silver nanowire (AgNW) films. AgNWs (average diameter of 35 ± 5 nm and average length of 25 ± 5 μm) dispersed in deionized water (3 mg mL^{-1}) were purchased from Nanopyxis Co. Ltd (Product name: AgNW ink (LOT No.: B 424-1)). AgNW solution was spin-coated for 30 sec with spin rates of 500 rpm. After spin-coating of AgNW suspensions on the target substrates, these samples were annealed at 90 °C and 150 °C for 90 sec subsequently to evaporate the solvent.

Graphene synthesis using CVD and transfer of graphene on the target substrate. A Cu foil (Alfa Aesar, item No.: 13382) on a quartz stage was placed on the center of quartz CVD chamber under low vacuum condition (10 mTorr). After loading, the furnace was heated up to 1000 °C under the flow of Ar (200 sccm) and H_2 (500 sccm). Under the flow of CH_4 (12 sccm) and H_2 (500 sccm), the graphene synthesis was carried out for 5 min, and then the furnace was cooled rapidly to room temperature with flowing Ar (500 sccm). A 200 nm thickness of poly(methyl methacrylate) (PMMA, Microchem Corp., 950 PMMA) was spun on the graphene sample which is synthesized on the Cu foil as a supporting layer. The metal foil was removed by floating on a diluted etching solution of $FeCl_3$: HCl: H_2O (1:1:20 vol.%). After etching process, the PMMA coated graphene layer was floated onto deionized water for rinsing. Subsequently, the sample was transferred onto the target substrate, and the PMMA layer was dissolved by acetone. Finally, the graphene transferred sample was dried in atmosphere for 4 hours.

Formation of AgNW-graphene hybrid structures. In this paper, the AgNW-graphene hybrid nanostructures were assembled in one approach, graphene on AgNW networks. For this approach, AgNW dispersions were coated on a target substrate as explained above. And then, the synthesized graphene layer was transferred onto the as-prepared AgNWs coated substrate.

Fabrication of back-gated field-effect transistor (FET) and functionalized gas sensor. On highly p-doped Si wafer with a 300 nm-thick thermal oxide layer, Cr/Au (3 nm/100 nm) electrodes were evaporated and patterned photolithographically for metal interconnects. On the wafer, AgNW films which serve as source and drain (S/D) were spun as described above, and patterned by photolithography, dry and wet etching processes. The etching processes of AgNWs includes dry etching process using oxygen reactive ion etching (RIE) plasma (50 W, 60 sccm, 240 sec) and wet etching in solution of H_3PO_4: $C_2H_4O_2$: $C_6H_4NO_5SNa$: H_2O (55:1:4:40 vol.%) for 10 sec. Subsequently, a graphene layer was transferred onto the sample and patterned by photolithography and oxygen RIE plasma (50 W, 60 sccm, 120 sec) to form both the hybrid structures for S/D and channel (width: 5 μm and length: 50 μm), simultaneously. And then, SU8 photoresist (PR) layer was patterned to open only channel regions to functionalize gas sensor. Finally, the samples were drop coated with 5 wt.% polypyrrole (PPy) aqueous solution (Sigma Aldrich) for 5 minutes and rinsed with DI water for functionalization of the graphene channel for gas sensing.

Preparation of samples for bending and stretching tests. For bending and stretching experiments, the substrates of sample are 2 μm-thick polyimide (PI) film that is spun using PI precursor (Poly(pyromellitic dianhydride-co-4,4'oxydianiline), Aldrich) and 100 μm-thick

polydimethylsiloxane (PDMS), respectively. On these films, AgNWs are patterned firstly, and the graphene layer covers the AgNW films and forms channel regions, simultaneously. The graphene layer is patterned photolithographically, subsequently.

Preparation of parylene films. Parylene is thermally evaporated. The furnace chamber of vaporizer is heated to ~650-690 °C. Then, the dimer of parylene is inserted into the vaporizer in the powder form and evaporated at ~120-175 °C. The dimer is converted to the substrate. After the process, the temperature is cooled to room temperature creating a parylene C film.

Electrical characterization and dimethyl methylphosphonate (DMMP) detection measurements. Back-gate measurements were conducted with transfer (V_G-I_D) and output (V_D-I_D) characteristics using a probe station (Keithley 4200-SCS). The transfer curves are measured with the drain bias (V_D) of 0.05 V and gate bias (V_G) from -5 V to 50 V. In addition, the output curves are measured with the V_D from -0.1 V to 0.1 V and V_G of 0 V. For DMMP sensing, The DMMP vapor was injected through an aligned syringe to the PPy coated graphene using a syringe pump at room temperature and ambient conditions. The initial concentrations of DMMP were diluted with air to attain the concentrations.

Bluetooth based wireless sensing measurements. To connect between FET based graphene gas sensor and Bluetooth module, the Cu wire and silver paste are used. And then, the module is

connected with smartphone wirelessly. The wireless sensing is conducted at DMMP concentrations of 10 ppm.

Inductive antenna based wireless sensing measurements. When the antenna of sensor was located close to the reader, a current and voltage changed because of the inductive coupling. Commonly, the inductive changes are used to power to transmit data from sensor to the reader. The reader device was connected to the network analyzer (ROHDE&SCHWARZ, ZNB8) to measure the reflection coefficient (S11 parameter) at the resonant frequency. The wireless sensor was tested by the network analyzer at DMMP concentrations of 5 and 10 ppm.

Supporting Figurers

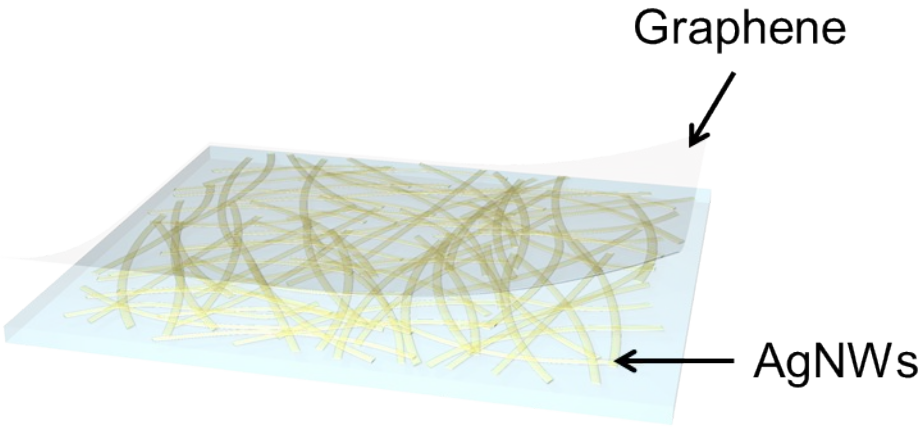

Figure S1. Schematic of AgNW-graphene hybrid nanostructures.

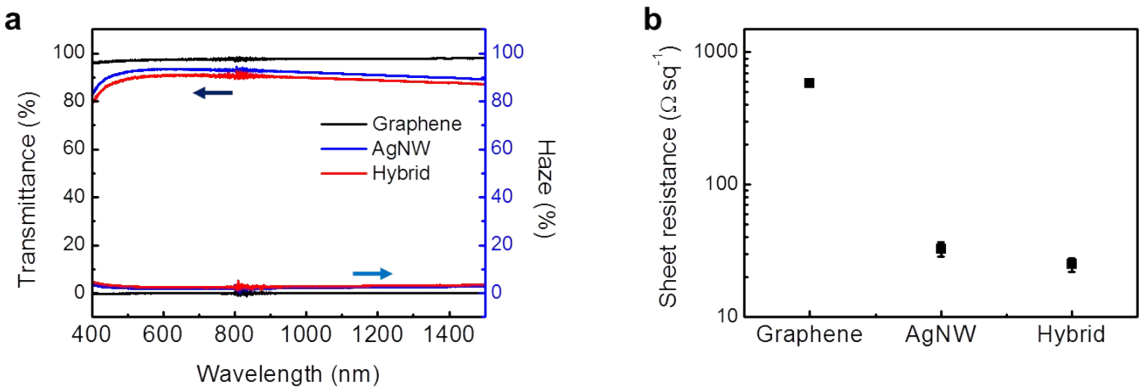

Figure S2. a) Optical transmittance spectra and haze data of graphene, AgNW, and their hybrid films where AgNW networks are formed with spin coating rate of 500 rpm. b) Plots of the sheet resistance for three materials.

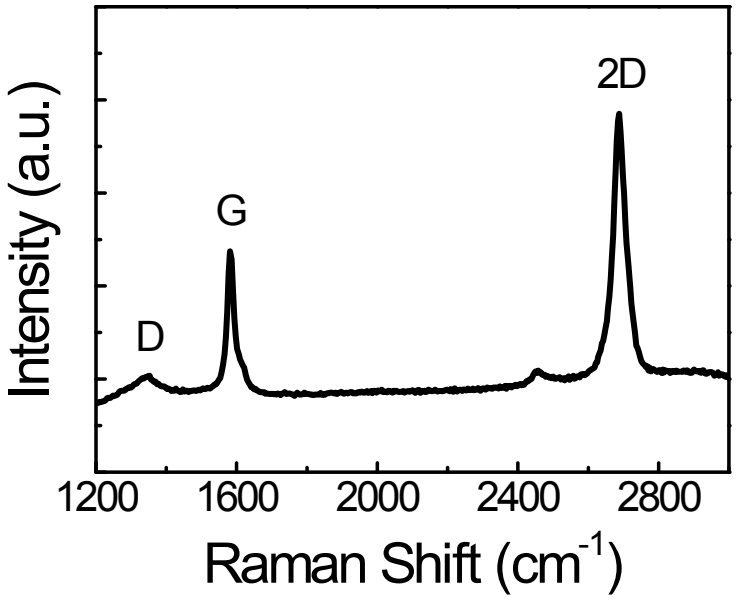

Figure S3. Raman spectrum of CVD-synthesized monolayer graphene transferred on a glass.

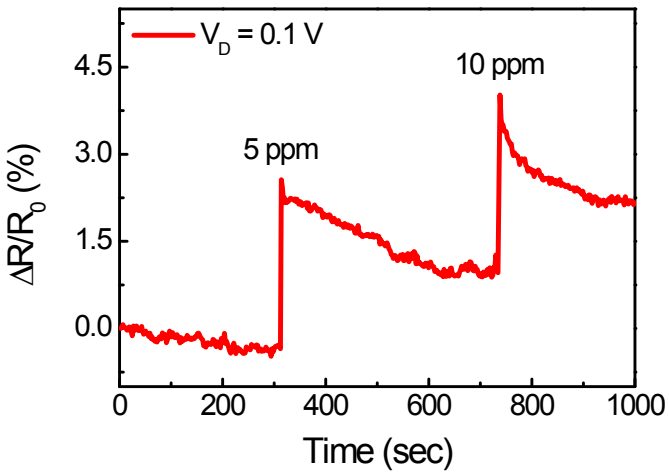

Figure S4. Real-time sensing of the graphene gas sensor without PPy-functionalization.

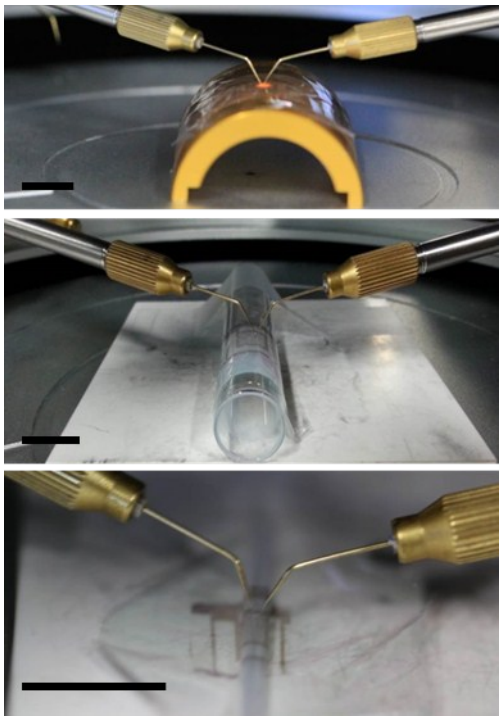

Figure S5. Photos of the AgNW-graphene hybrid FET arrays wrapped on various cylindrical supports with different radius of curvature. Scale bars, 1 cm.

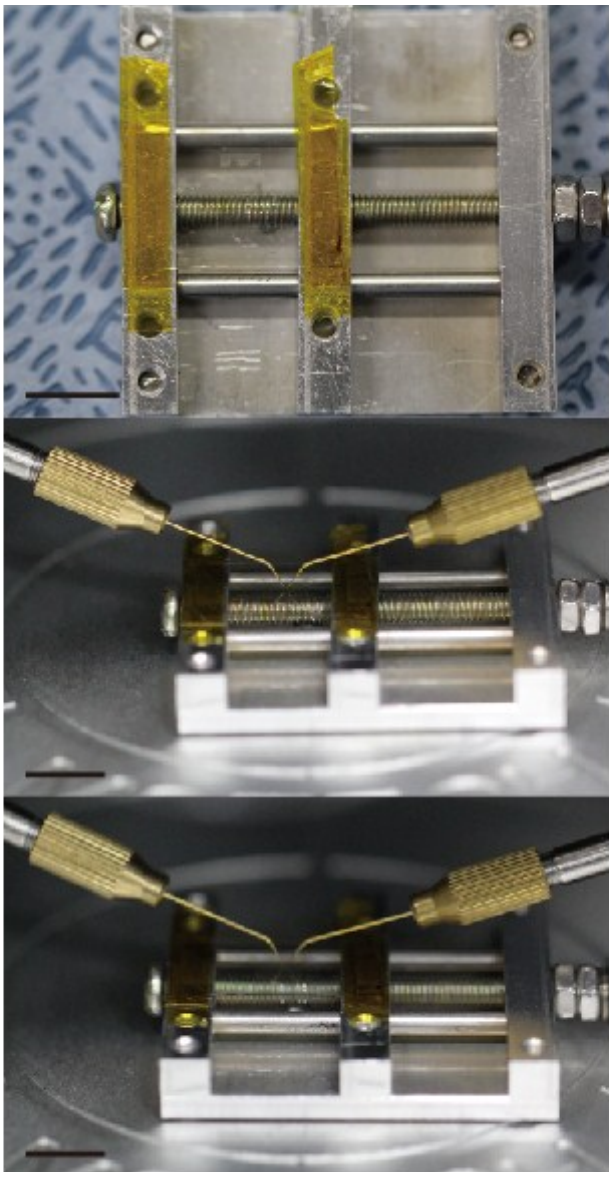

Figure S6. Photographs of AgNW-graphene hybrid FET arrays on stages for the stretching tests. Scale bars, 1 cm.

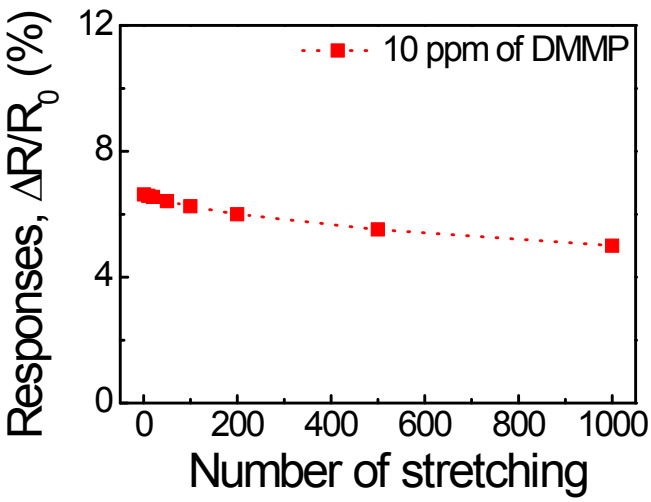

Figure S7. Sensing responses as a function of repeated strain (tensile strain: 5%)

Captions of Supplementary Movie

Supplementary Movie S1. Real-time and wireless sensing of sensors integrated with Bluetooth module.