Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Supporting Information

Synthesis of Large-area Ultrathin Graphdiyne Films at the Air-Water Interface and Its Application in Memristors

Wanhui Li,[a] Jie Liu,[a] Yanxia Yu,[bc] Guangyuan Feng,[a] Yaru Song,[a] Qiu Liang,[a] Lei Liu,[a] Shengbin Lei*[a] and Wenping Hu*[a]

[a] Tianjin Key Laboratory of Molecular Optoelectronic Science, Department of Chemistry, School of Science & Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin University, Tianjin 300072, P. R. China

E-mail: Shengbin.lei@tju.edu.cn, huwp@tju.edu.cn

[b] Jiangxi University of Science and Technology, Ganzhou 341000, P. R. China

[c] MOE of the Key Laboratory of Bioinorganic and Synthetic Chemistry, The Key Lab of Low-carbon Chem and Energy Conservation of Guangdong Province, School of Chemistry, Sun Yat-Sen University, Guangzhou 510275, P. R. China

1. Experimental Details

Preparation of HEB:

Hexakis[(trimethylsilyl)ethynyl]benzene (HEB-TMS) was synthesized following the reported synthetic route.[1] TMS-HEB monomers (0.6 mg) were dissolved into 10 mL dichloromethane (CH_2Cl_2) solvent, then 20 μL tetrabutylammonium fluoride (1 M in tetrahydrofuran) was added into TMS-HEB solution. The solution was shaken for 10 min under an argon atmosphere to obtain HEB. The solution was immediately used for the synthesis of graphdiyne without further purification because of its instability.

Preparation of graphdiyne(GDY) thin films:

An aqueous solution (10 mL) of copper(Ⅱ) acetate (12 mg) and pyridine (16 μL) was poured into glass bottle with a diameter of 50 mm. Then the 100 μL HEB-CH_2Cl_2 solution synthesized by last step was dropped on the surface of aqueous solution. After quick evaporation of CH_2Cl_2, GDY thin films formed at the air-liquid interface after 16 h in dark at room temperature. Then the aqueous layer was replaced with HCl (1 mol/L) and deionized water three times respectively. The obtained thin films were transferred on the hydrophilic substrates and then set into pure CH_2Cl_2 solution 5 minutes to remove unreacted monomer.

GDY films are transferred on SiO_2 (300 nm)/Si substrates for next characterization. The SiO_2 wafer substrate was first cleaned by sonication in deionized water, acetone, and 2-proponol respectively, followed cleaning with oxygen plasma for 10 min.

Device fabrication:

Indium tin oxide (ITO) glasses were first cleaned by sonication sequentially in deionized water, acetone, and 2-proponol, followed by cleaning with oxygen plasma for about 10 min. The

prepared GDY thin films were transferred onto ITO and then immersed into pure CH_2Cl_2 solution for 5 minutes. The Ag or Au top electrode (TE) with a thickness of 50 nm was thermally deposited on the thin films with the help of a shadow masks, the area of electrode is 6.8×10^{-3} mm^2.

2. Characterization of materials:

Optical microscope images were taken by Nikon ECLIPSE Ci-POL polarized optical microscope with a blue filter. Tapping mode AFM was conducted with a Bruker Dimension Icon instrument. Raman spectroscopy was conducted on HORIBA LabRAM HR Evolution system with a laser excitation wavelength of 532 nm. The UV–vis absorption spectrum of GDY thin film was measured with a SHZMADZU UV-3600 Plus spectrophotometer. TEM and SAED measurements were carried out by a Tecnai G2 F20 S-TWIN. SEM images were measured by Hitachi SEM SU8010 Field Emission Scanning Electron Microscope (FESEM). X-ray photoelectron spectroscopy (XPS) spectrum was tested with Thermo Fisher Scientific ESCALAB 250Xi. The electric properties were measured using a micromanipulator 6150 probe station connected to a Keithley 4200-SCS.

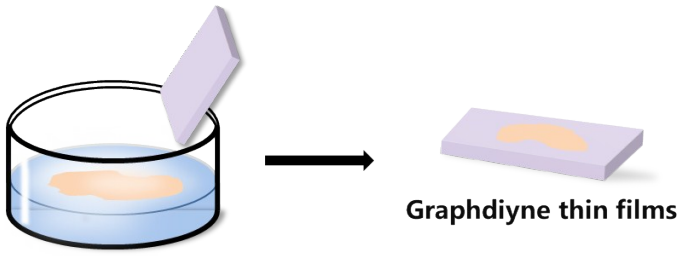

Figure S1 Transferring process of GDY thin films.

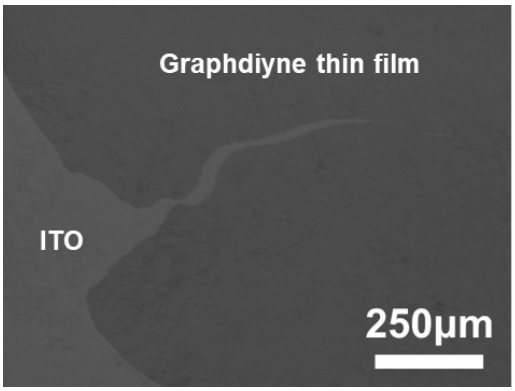

Figure S2 Low resolution SEM images of GDY ultrathin films on ITO/glass substrate.

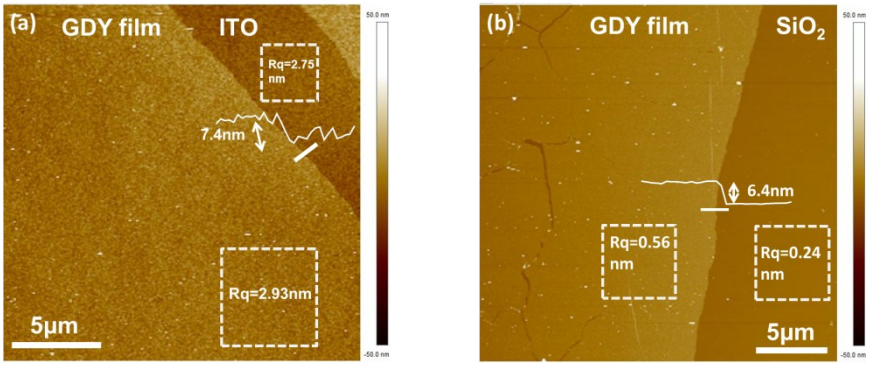

Figure S3 (a) and (b) AFM images of GDY film transferred on ITO and SiO_2 (300 nm)/Si substrates and cross-sectional analysis**.**

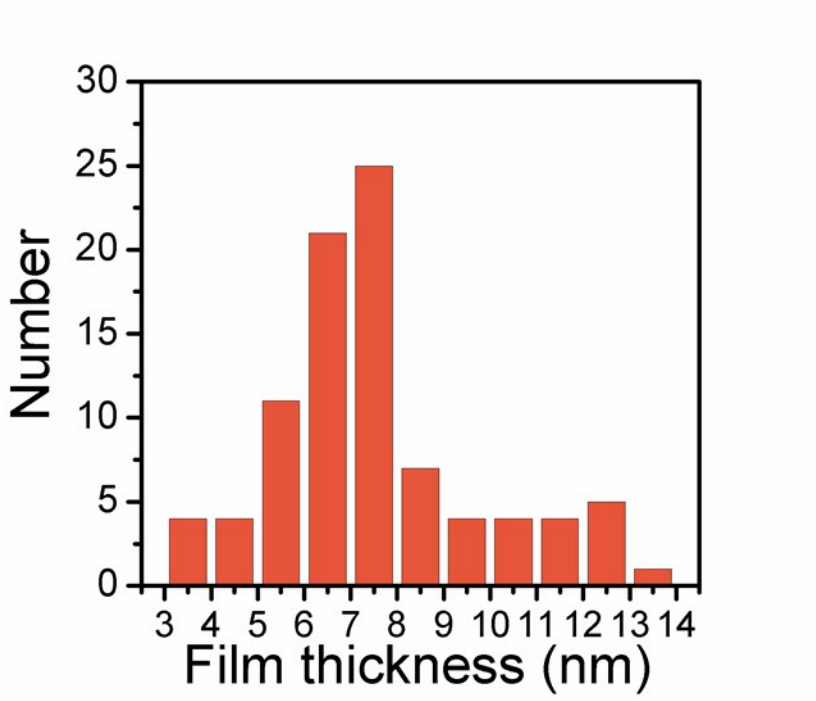

Figure S4 AFM thickness histogram of GDY films transferred on SiO_2 (300 nm)/Si.

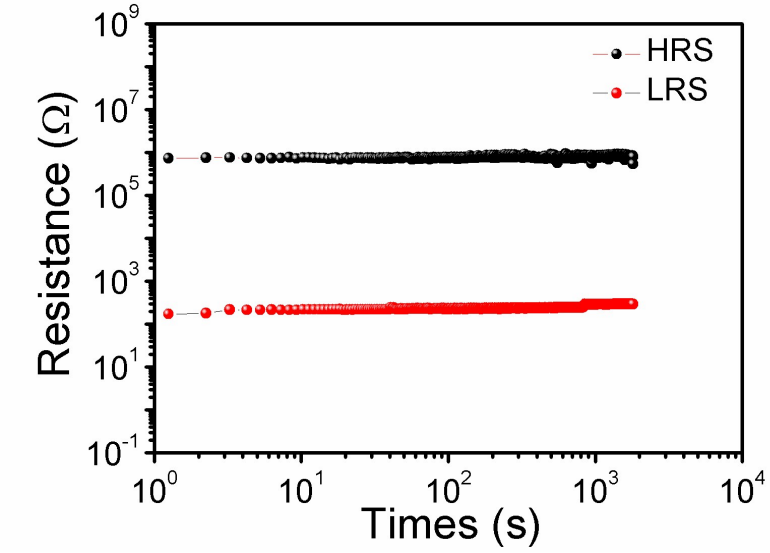

Figure S5 Retention time of the Ag/GDY film/ITO device in the "ON" and "OFF" states at reading voltage of 0.1 V.

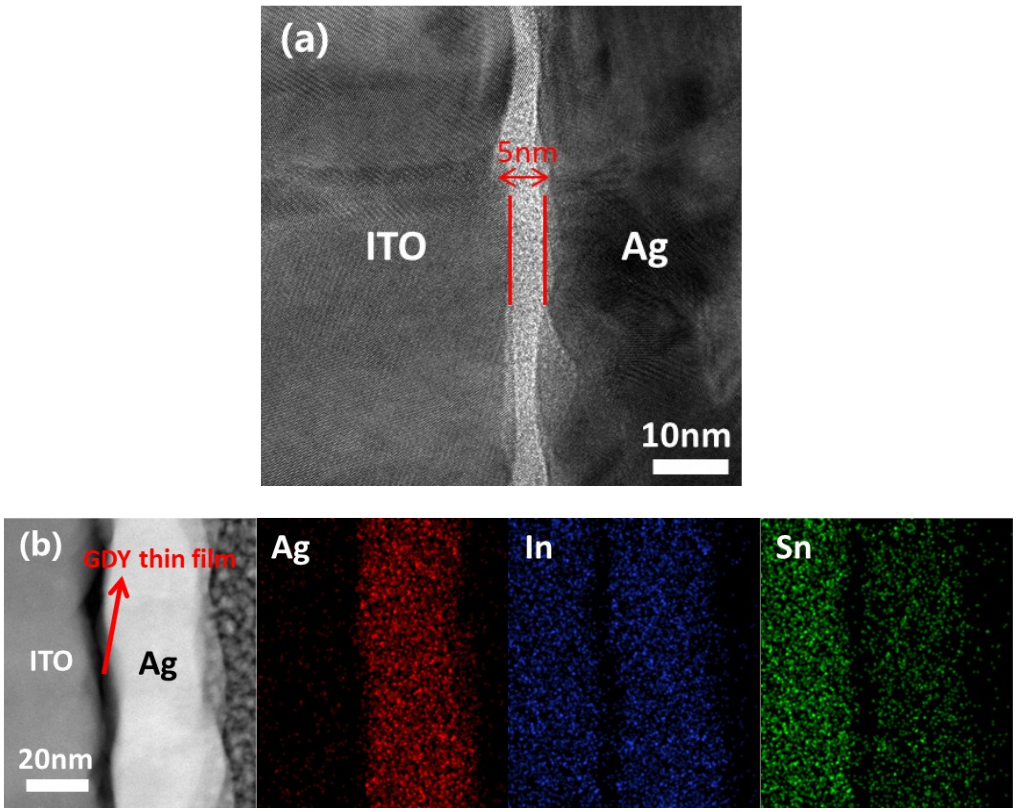

Figure S6 TEM images of Ag/GDY film/ITO memory cell before switching ON. (a) Cross section TEM images of the device. (b) EDS elemental mapping of the device.

References:

1. G. Li, Y. Li, H. Liu, Y. Guo, Y. Li and D. Zhu, *Chem. Commun.,* 2010, **46**, 3256-8.