

Supplementary Information for Architecture of Graphdiyne Nanoscale Films

Guoxing Li,^{a,b} Yuliang Li,^{*a} Huibiao Liu,^{*a} Yanbing Guo,^{a,b} Yongjun Li,^a and Daoben Zhu^a

^a CAS Key Laboratory of Organic Solids, Beijing National Laboratory for Molecular Sciences (BNLMS), Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, P. R. China.

E-mail: ylli@iccas.ac.cn(Y. L.), liuhb@iccas.ac.cn(H. L.)

^b Graduate School of Chinese Academy of Sciences, Beijing 100190, P. R. China

List of Contents

1. Materials and Methods

2. Measurements

3. Synthesis

Scheme S1: The synthetic route of graphdiyne films

4. X-ray (EDX) spectrum analysis for graphdiyne film

Fig. S1: The graphdiyn films: (a) The photograph, (b) EDX analysis

5. FT-IR spectrum of graphdiyne films

Fig. S2: FT-IR spectrum of graphdiyn films

6. Supplementary Reference

1. Materials and Methods

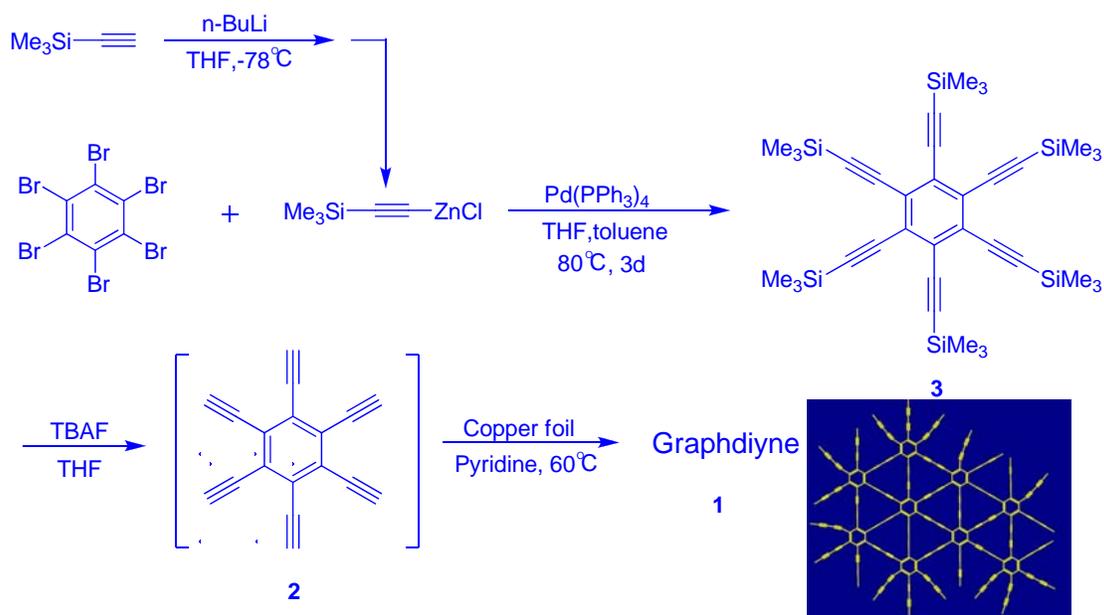
Unless otherwise stated, reagents and solvents were commercially obtained and used without further purification. Copper foils were pretreated by sonicating in 1M HCl and acetone and ethanol, sequentially, for 15 min, dried under a flow of argon, and used immediately for growing graphdiyne films.

2. Measurements

The morphologies and energy-dispersive X-ray (EDX) spectrum analysis of the graphdiyne films on copper substrates were observed on a JEOL JSM 4300F field-emission scanning electron microscope, at an accelerating voltage of 15 kV. Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) pattern measurements were conducted with JEOL 2010 transmission electron microscopes using an accelerating rate voltage of 120 keV. AFM observation was carried out using NanoScope IIIa-Phase Atomic Force Microscope. The XRD patterns are recorded with a Japan Rigaku D/max-2500 rotation anode x-ray diffractometer equipped with graohite-monochromatized Cu K α radiation ($\lambda=1.54178\text{\AA}$). The X-Ray photoelectron spectrometer (XPS) was collected on VG Scientific ESCALab220i-XL X-Ray photoelectron spectrometer, using Al K α radiation as the excitation sources. The banding energies obtained in the XPS analysis were corrected with reference to C1s (284.8eV). The Fourier Transform Infrared Spectrophotometer was recorded on a Bruker EQUINOX55 FT-IR spectrophotometer. Raman spectra were taken on a Renishaw-2000 Raman spectrometer at resolution of 2 cm^{-1} by using the 514.5 nm line of an Argon ion

laser as the excitation source. ^1H NMR and ^{13}C NMR spectra were obtained on a Bruker Avance DPS-400 spectrometer, respectively. The current-voltage (I-V) characteristics of graphdiyne films were measured with a Keithley Semiconductor Characterization System (SCS-4200) with a low current switching matrix. Al electrodes are grounded, voltage sweeps are applied on devices. All of electrical measurements were made under ambient conditions.

3. Synthesis



Scheme S1: The synthetic route of graphdiyne films

Hexakis[(trimethylsilyl)ethynyl]benzene(3)¹

To a three-necked flask, 1.1040 g (2.00 mmol) of hexabromobenzene, 500 mg (0.400 mmol) of $\text{Pd}(\text{PPh}_3)_4$, 25 ml of toluene, and a solution of 20.0 mmol of [(trimethylsilyl)ethynyl]zinc chloride in 40 ml of THF prepared by literature method were added in this order. The mixture was stirred under a nitrogen atmosphere at 80°C (oil

bath temp.) for 3 days. After 20 ml of 1 N HCl was added, the reaction mixture was extracted with ethyl acetate. The combined organic layer was washed with brine and dried over anhydrous MgSO₄. The solvent was evaporated and the residue was then purified by column chromatography (silica gel, hexane : dichloromethane = 17 : 3) to yield 910 mg (69.6%) of hexakis[(trimethylsilyl)ethynyl] benzene(3) as pale yellow solid. ¹H NMR (400 MHz, CD₃Cl): δ=0.36 (s, -Si(CH₃)₃). ¹³C NMR (400 MHz, CD₃Cl): δ=128.2, 105.2, 101.2, 0.017.

Graphdiyne(1)

To a solution of 43.6 mg (0.066 mmol) **3** in 15 ml THF was added 0.4 ml TBAF (1 M in THF, 0.4 mmol) and stirred at 8 °C for 10 min. The solution was then diluted with ethyl acetate and washed with brine and dried with anhydrous Na₂SO₄. The solvent was removed in vacuo and the deprotected material (9.08mg, 62%) was rediluted with 25 ml pyridine and added slowly over 24 h to a solution of copper foils in 50ml pyridine at 60 °C. Then the mixture was stirred under a nitrogen atmosphere at 60 °C for 2 days. Upon completion copper foils were washed with acetone and DMF in turn and a black film was obtained on the copper foil.

4. X-ray (EDX) spectrum analysis for graphdiyne film

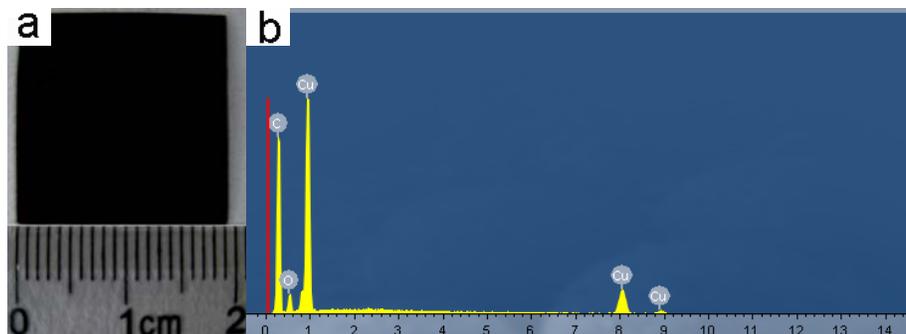


Fig. S1. The graphdiyne films: (a) The photograph, (b) EDX analysis

5. FT-IR spectrum of graphdiyne films

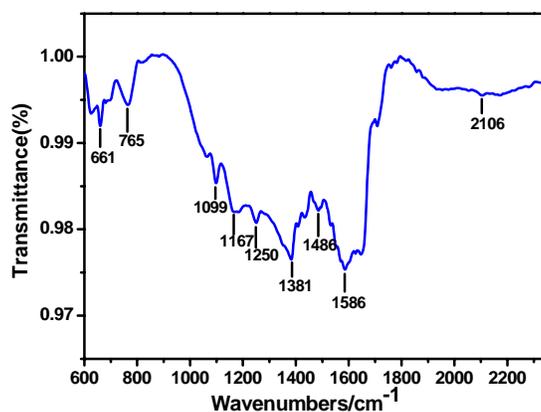


Fig. S2. FT-IR spectrum of graphdiyne films

Fig. S2 shows Fourier transform infrared spectroscopy (FT-IR) spectrum of as-grown graphdiyne film on copper foil. The bands located at 1450 cm^{-1} , 1587 cm^{-1} are assigned to the skeletal vibrations of aromatic ring, and the band of 2100 cm^{-1} is the typical $\text{C}\equiv\text{C}$ stretching vibration the intensity of which is a slight weak because of the molecular

perfectly symmetry².

6. Supplementary References

1. S. Motohiro, I. Akiko, I. Kayo and T. Yoshito, *Org. Lett.*, 2001, **3**, 2419.
2. R. Dembinski, T. Bartik, B. Bartik, M. Jaeger and J. A. Gladysz, *J. Am. Chem. Soc.*, 2000, **122**, 810.