Facile fabrication of organic semiconductor/graphene microribbon heterojunction by self-assembly

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Materials and methods

Materials

3,7-bis(5-(2-ethylhexyl)thiophen-2-yl)dithieno[2,3-b:2',3'-e]pyrazine (BEHT-DTP) was synthesized by ourseleves[1]. The graphene water dispersion was purchased from Xiamen Knano Graphene Technology, Ltd.. The concentration of the graphene dispersion is 1mg/mL, the graphene sheets is about 0.1-5 μm in size and less than 1 nm in thickness (< 3 layers), and the oxygen content is less than 0.5%. The solvents used in the experiments were used without further purification. Deionized water was used in all experiments.

Characterization

Ultraviolet-visible absorption spectra were collected on a Hitachi U-3900H spectrophotometer. The fluorescence spectra were recorded by a Hitachi F7000 spectrophotometer. Raman spectra were obtained with a laser scanning Raman microscope (Raman-11, Nanophoton), excited by a laser of 532 nm, the Si peak at 520 cm^{-1} was used as a reference for wavenumber calibration. The optical microscopy

images were obtained by a PSM-1000 microscope. The TEM images and SAED were obtained by a JEM-2010 TEM with an accelerating voltage of 120 kV. AFM measurement was performed on a Nanoscope IIIa atomic force microscope in tapping mode. The electricity characteristics were carried out by Keithley 4200-SCS semiconductor characterization system connected to a Semishare SE-4 probe station in ambient environment. The simulated white light was provided by a tungsten light (~79.4 mW/cm^2) guided by a quartz fiber. The monochromatic light for external quantum efficiency (EQE) spectra measurement was provided by a Crowntech QEM24-S monochromator guided by a quartz fiber.

Preparation of BEHT-DTP microribbon

Before the drop-casting of BEHT-DTP/THF solution, the Si/SiO_2 substrates (14.8×14.8 mm) was cleaned by detergent and then sequentially ultrasonicated in deionized water and alcohol, followed by ultraviolet-ozone treatment for 15 min. Then, 50 μL of BEHT-DTP/THF was drop-casted onto a clean Si/SiO_2 substrate held in a beaker, and 1 mL THF was added into the beaker as "antisolvent" to slow down the evaporation speed of the solvent, and the antisolvent was kept from the Si/SiO_2 substrate. At last, the beaker was sealed by a parafilm with a small hole on it. After about 6 hours, with the evaporation of solvent, the self-assembly of microribbon was completed. For the preparation of BEHT-DTP microneedle, the "antisolvent" was removed and the beaker was kept open to allow the solvent evaporate quickly. For the TEM characterization, a copper grid was placed on the substrate and the microribbon

was self-assembly on it, then a copper grid with microribbon was obtained.

Preparation of BEHT-DTP/graphene heterostructure microribbon

The graphene dispersion was treated by ultrasonic for 10 min before using. Then 0.6 mL of the graphene water dispersion was dropped onto the substrate with BEHT-DTP microribbon (the substrate turned hydrophobic when covered by BEHT-DTP microribbon) to cover the entire substrate. Driven by π-π interaction, the graphene was adsorbed onto the surface of BEHT-DTP microribbon. After 10 min, the excess free graphene can be removed by rinsing the substrate with deionized water, followed by drying under a gentle stream of nitrogen.

Fabrication of photoconductive devices

The self-assembly process was the same as the above, except that the substrate was replaced by the Si/SiO_2 substrate with photolithography-defined gold electrodes array (50 nm thick) with a channel length of 5 μm. The substrates were cleaned according to the same process of fabrication of BEHT-DTP microribbon.

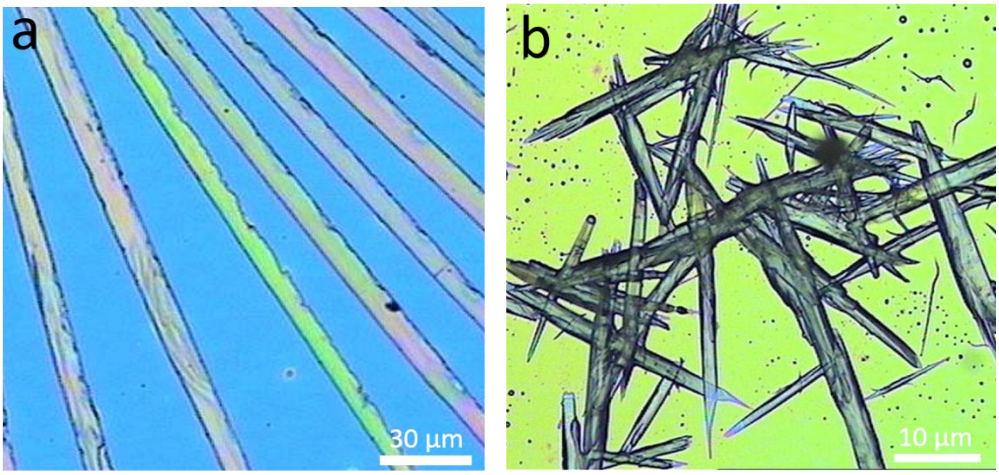

Fig. S1 The BEHT-DTP (a) microribbon fabricated in low evaporation rate (with antisolvent) and (b) microneedle fabricated in high evaporation rate (without antisolvent).

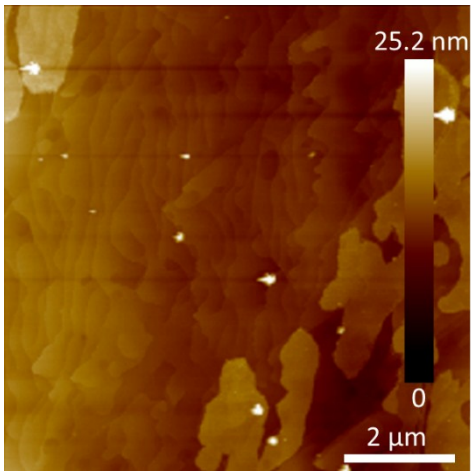

Fig. S2 The low magnification of the surface of the graphene coated BEHT-DTP microribbon.

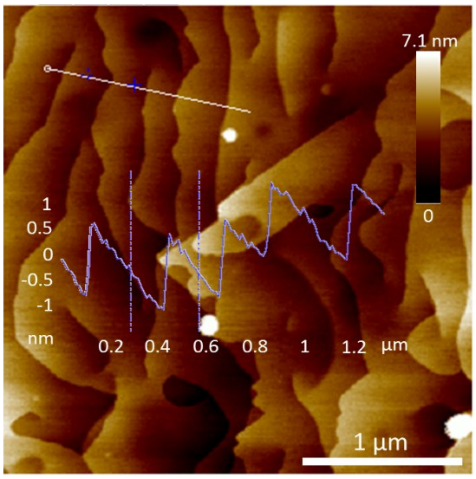

Fig. S3 The cross section profile along the white line at the surface of the assembled graphene sheets on the BEHT-DTP/graphene microribbon.

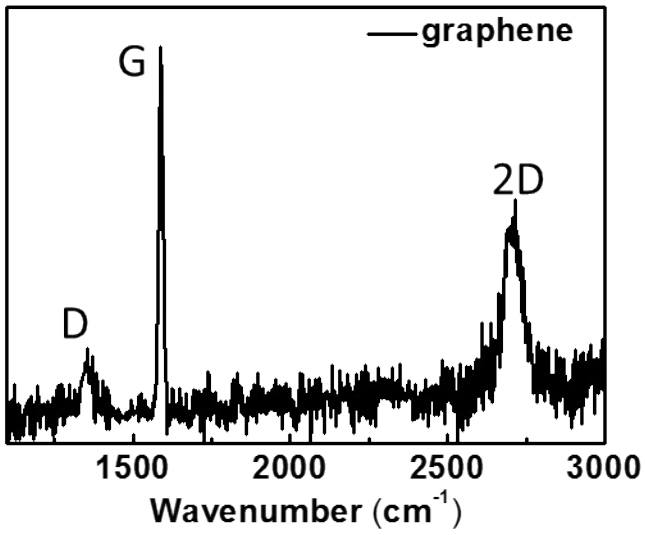

Fig.S4 The full Raman spectrum of the graphene with D, G and 2D bands.

References

1. J. Zhang, J. Wang, X. Xu, S. Chen, Q. Zhang, C. Yao, X. Zhuang, A. Pan and L. Li, *J Mater Chem C*, 2015, **3**, 5933-5939.