

Electronic Supplementary Information for Generating Electricity Using Graphene Nanodrums

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Synthesis of graphene: Our graphene samples were grown on copper foil (Alfa Aesar, item no.46365) using methane as the carbon source under ambient pressure by CVD, the schematic diagram of apparatus used was shown as Figure S1.¹ Prior to the growth of graphene, the copper foil needed pretreatment, which included: cleaning in acetate and acetone, electrochemical polishing and annealing.

The copper foil was put in a round quartz tube, which was inserted into the horizontal tube furnace (~ 32 mm inner diameter) served as sample growth chamber. A transition tube was used to link the air inlet end and the furnace, whose inner diameter was ~ 6 mm. Firstly, the mixture gas of H₂ and Ar was aerated into the quartz tube to drive air out when the temperature in the furnace was raising, H₂ was used for reduction of residual O₂. When the temperature in the furnace reached to ~1000 °C, heating was stopped, and CH₄ was begun to be aerated into the quartz tube. Carbon atoms were deposited on the copper foil through CH₄ decomposition under ambient pressure. At last, the furnace was cooled down to the common temperature.

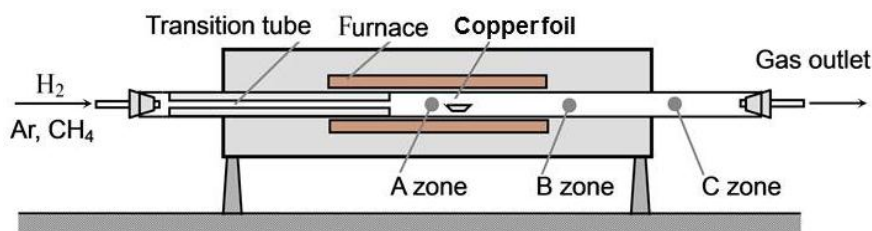


Figure S1. Schematic diagram of the apparatus used for synthesizing graphene on copper foil by CVD.

Fabrication of nanopore array and device: The SiO₂/Si substrate was sonicated in acetone, ethanol and DI water in turn; and then dried by a nitrogen flow. To fabricate the nanopores, firstly, a pattern of nanopore array in a photo mask is written by electron-beam lithography (E-beam). Secondly, the surface of SiO₂ substrate is coated with photoresist, and the photo mask is put onto the photoresist/SiO₂ for exposure. Thirdly, the photoresist is developed by MIBK³/IPA with ratio of 1:3 for 1 minute and then IPA for 1 minute. This step removes the parts of the photoresist that are exposed; as a result, the pattern is transferred on the photoresist. In the next step, the sample is etched vertically from above by ICP etcher, and the photoresist is developed like above. Finally, a 2-by-2-cm array of nanopores (diameter 1 μm, depth 200 nm) was patterned in SiO₂ epilayer (300-nm thickness) on a Si substrate.

The graphene/Cu was coated with PMMA solution, which was made by mixing PMMA (1 mL, MicroChem Corp. 950 PMMA A4, 4% in anisole) and anhydrous anisole (39 mL). The PMMA/graphene/Cu was put into the etchant (FeCl₃: HCl: H₂O in a wt/vol/vol ratio of 27 g: 50 mL: 50 mL) for 2 hours. The SiO₂/Si substrate with nanopore array was used to take up the PMMA/graphene sample from the solution. The PMMA/graphene/SiO₂/Si was then immersed in hot acetone for 30 minutes, the PMMA was removed. The graphene/SiO₂/Si sample was taken out and dried in the atmosphere.

Raman spectra of graphene: As shown in Figure S2, there are typical Raman spectra of graphene. From bottom to up, the intensity ratios of the G and 2D modes (I_{2D}/I_G) of the as-grown graphene show that the walls of graphene are mainly comprised of trilayer and 4-layer graphene sheets.²

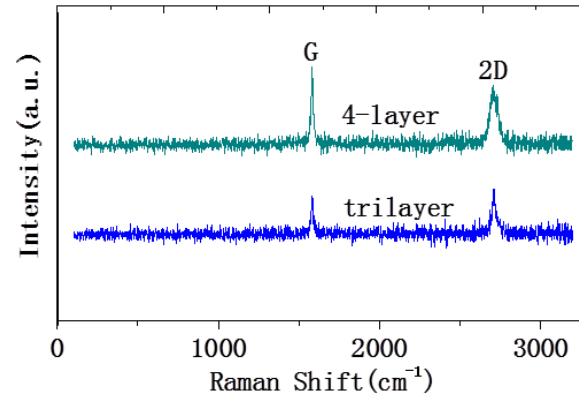


Figure S2. Raman spectra of graphene on the array of nanopores.

AFM images of individual graphene nanodrum: As shown in Figure S3, there are the noncontact AFM images of individual graphene nanodrum at 50°C, 75°C, 100°C and 125°C, respectively. With the rise of the temperature, the graphene membrane upheaves continuously; and the image becomes blurrier.

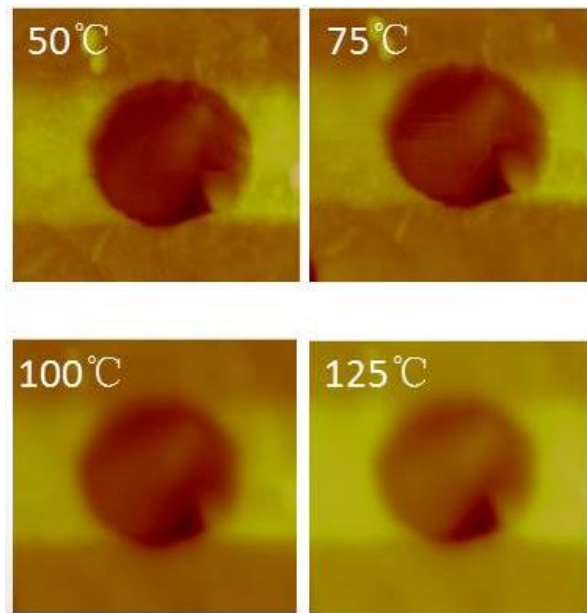


Figure S3. AFM images of individual graphene nanodrum at 50°C, 75°C, 100°C and 125°C, respectively.

Anisotropic Coverage of Graphene on Individual Nanopore: As shown in Figure S4, there are the AFM images of three individual graphene nanodrum. It is found that there are some anisotropic coverages, as indicated by the arrows.

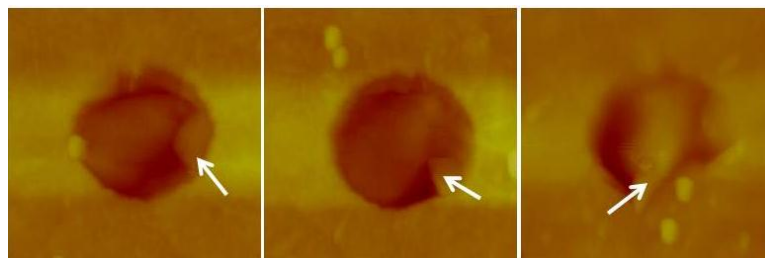


Figure S4. Anisotropic Coverage of Graphene on Individual Nanopore.

Temperatures of two electrodes: The temperatures at the two electrodes were measured using a sensitive temperature testing device (K-type Chromel Alumel Thermocouple) when the temperature of the heating stage was 200 °C. As shown in the figure below, the temperatures of two electrodes are measured within 50 s. It can be seen that there is no stable temperature difference between the two electrodes.

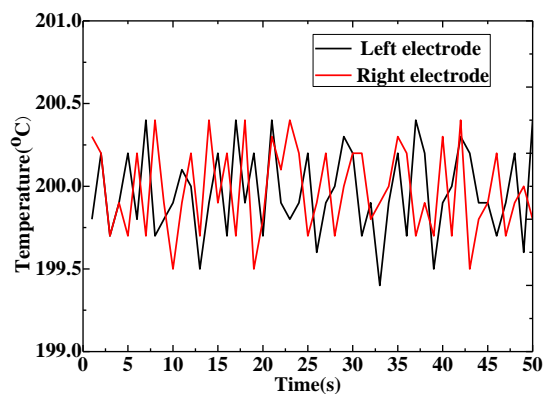


Figure S5. Temperatures of two electrodes when the heating stage is 200 °C.

Voltage measurements: The electrical conductivity and voltage signal between two electrodes of the device were measured in real time using a semiconductor characterization system called Keithley 4200-SCS (voltage resolution $\sim 1 \mu\text{V}$).

References

1. Z. P. Chen, W. C. Ren, L. B. Gao, B. L. Liu, S. F. Pei, H. M. Cheng, *Nat. Mater.* 2011, **10**, 424-428.
2. L. M. Malard, M. A. Pimenta, G. Dresselhaus, M. S. Dresselhaus, *Phys. Rep.* 2009, **473**, 51-87.