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Electronic Supplementary Information

Direct Growth of Porous Substrate on High-Quality Graphene via In-situ Phase Inversion of Polymeric Solution

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Materials and Methods
Figures. S1 to S5

Experimental

Graphene transfer

We purchase a high-quality CVD graphene sheet on a flat copper substrate from Hefei Vigon Material Technology Co., LTD. We prepare a

Polythehersulfone (PES) – N-Methyl-2-pyrrolidone (NMP) solution and take precautions to prevent exposure to humidity in air. This solution is cast onto the exposed graphene surface with resulting thickness of about 100 μm (the membrane thickness can be controlled by changing the solution drainage time after casting and before coagulation in water. In our process, we keep the CVD graphene upright for a certain time on top of paper towel to get rid of excess solution. The longer we allow the solution to flow down, the thinner the membrane is). Slide the coated graphene structure into tap water with PES solution side facing up, making a 30°angle with horizontal, at a constant speed and change water after 20 minutes. PES forms smooth surface during phase inversion process which is well suited for supporting graphene. Additionally, as an engineering polymer, PES has good chemistry/mechanical/thermal stability: it is tolerant of most of chemicals, can be used for a long term between 180-200°C and has excellent dimension thermal stability. It is widely used in membrane industry and known to be able to support high pressure. To simulate industry fabrication conditions, PES resin is sourced from Solvay group, TX, USA and tap water is used for coagulation. We float the graphene structure on persulfate ammonia until the copper substrate is fully etched. The resulting membrane needs to be properly stored in water below 60 °C, totally drying out or higher temperature causes the collapse of finger-like pores in supporting layer and cracks in graphene.

Characterizations

A well transferred graphene membrane appears grey while the polymer substrate is white. Big missing piece can be told from comparison of grey graphene and white substrate. This only happens when content of casting solution has changed (e.g. moisture dissolves in.) To examine quality of graphene transfer and fingerlike pore density, sample is sputter with 5 nm platinum and SEM is conducted at 5 KV for surface feature (Fig. 2a) and 10 KV for underlying structure. Graphene coverage area looks blur and whiter part is graphene covered PES and darker area is valid finger-like pore that underneath graphene. The crack/defect looks completely dark if no PES support or PES support will be exposed. The Raman spectroscopy is conducted for graphene on copper, graphene transferred to polymer and PES raw material at 532 nm and power 140 mW at maximum. Labspec 6 is used for analysis and baseline adjustment. AFM scanning is conducted on an Asylum-1 MFP-3D AFM System.

Etching of the CVD graphene on copper

Put a drop of persulfate ammonia (10g/100mL) on the CVD graphene on copper and keep for 0.5s, 1s, 2s and 3s, respectively, and quickly clean the graphene surface with DI water.

Supplemental figures

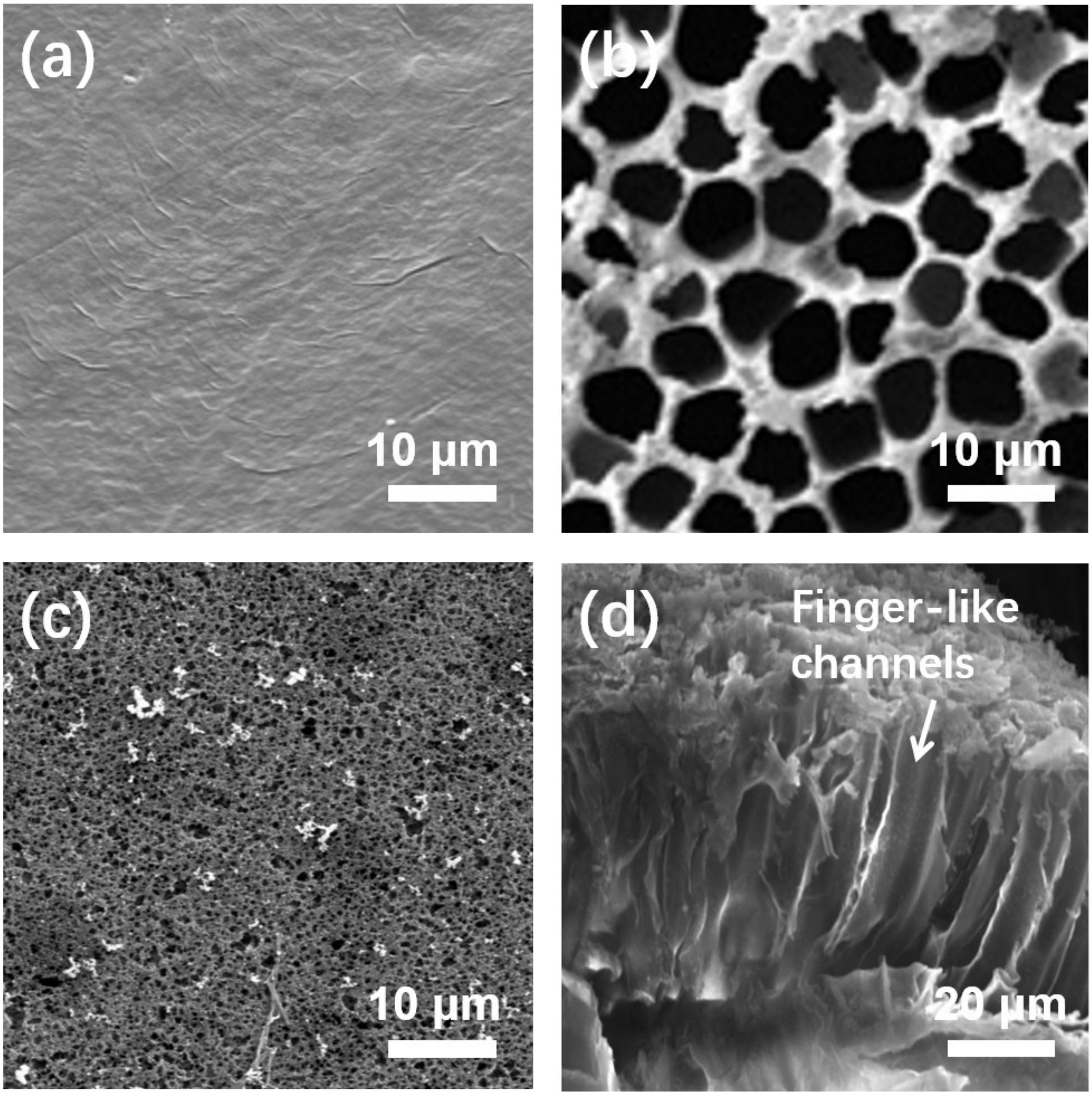


Fig. S1. The SEM images of morphologies of different layers of PES porous substrate via IP techniques. (a) The SEM image of the skin layer that formed within a few seconds after PES solution is immersed into water (scale bar is 10 μm). **(b)** The SEM image of membrane surface after removal of the skin layer (scale bar is 10 μm). **(c)** The SEM image of membrane surface (graphene side) after several seconds of oxygen plasma etching (scale bar is 10 μm). **(d)** Cross-section SEM image of the composite graphene membrane after removal of the skin layer reveals long fingerlike pores that span the membrane (scale bar is 20 μm).

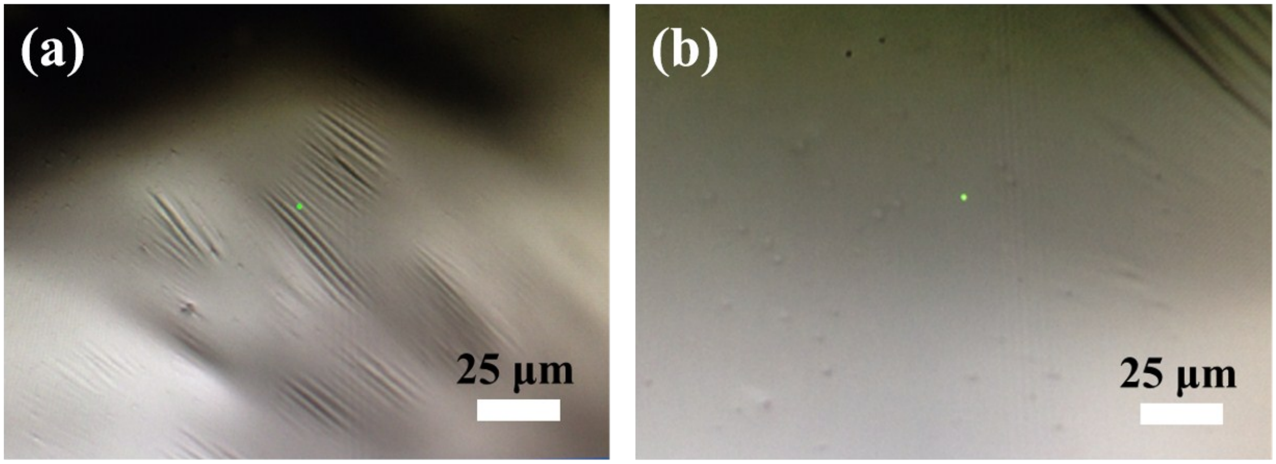


Fig. S2. The OM images of the surface of 5 nm platinum coated graphene composite membrane.

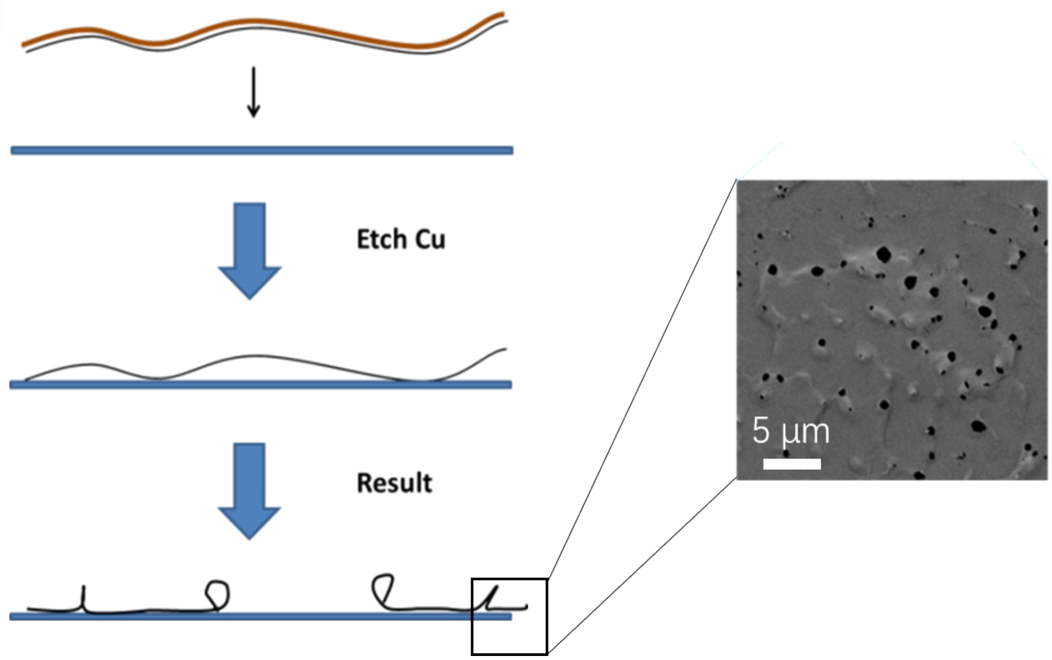
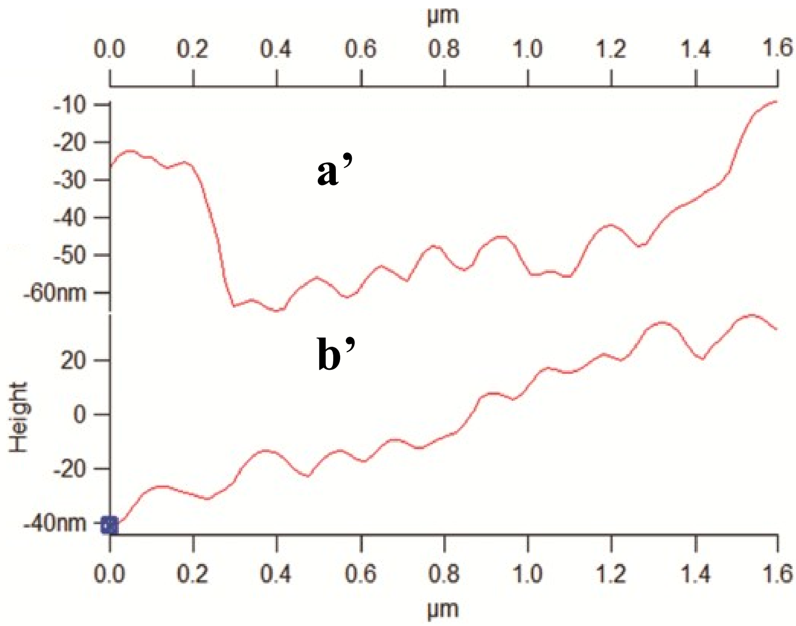


Fig. S3. The hypothesis of defect generation in graphene during solid phase to solid phase transfer techniques such as the ET process, and the SEM image of the resulting graphene membrane.



μm
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
-10
-20
-30
-40
-50
-60nm
a’
b’
20
0
-20
-40nm
Height
μm

Fig. S4. Measurement of wavy graphene composite membrane surface by AFM.

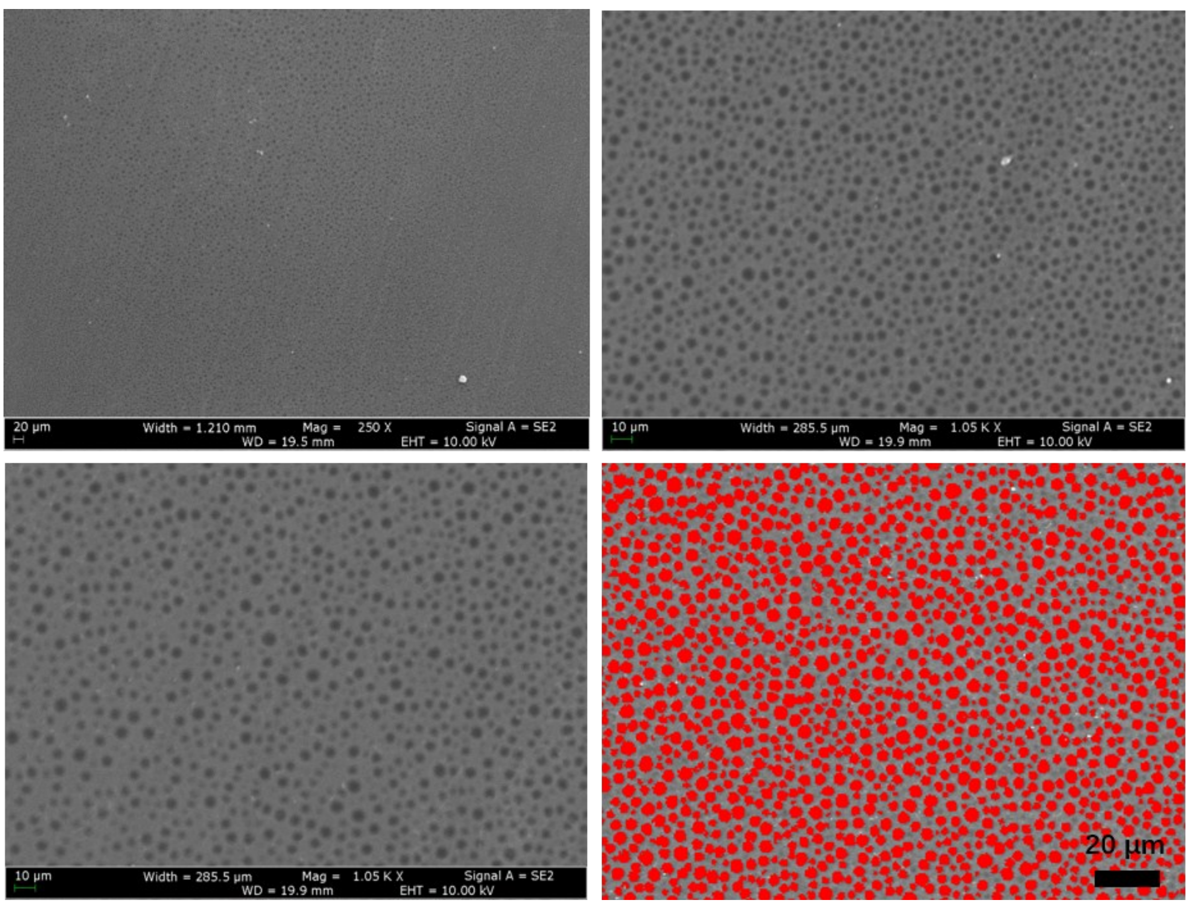


Fig. S5. A SEM images of graphene composite membrane in the form of panorama **(a)**, two SEM images of graphene composite membrane in different location **(b)** **(c)** and void space calculation using Imagepro plus **(d)**.