Selective Molecular Transport through Intrinsic Defects in a Single Layer of CVD Graphene

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Introduction

- Graphene, with its atomistic thickness, remarkable mechanical strength, and potential for size-selective transport through nanometer-scale holes in its lattice, is an ideal material for next generation membranes with high selectivity and permeability.

- Although impermeable in its pristine state, theoretical models predict that by the introduction of holes of controlled size, density, and functionalization, graphene membranes would outperform existing state-of-the-art membranes in gas-phase and liquid-phase separation processes.

- Experimental measurements of ionic and molecular transport through graphene membranes have so far been limited to microscopic areas. DNA translocation has been detected via measurement of ionic currents through single nanopores in suspended graphene, while graphene nanoballoon measurements have demonstrated the impermeability of pristine graphene to gases including helium.

- Much progress is required beyond the current status for exploiting the incredible potential of graphene to realize practical membranes, including advances in methods for fabricating large-area, nearly defect free graphene on porous supports, generating a high density of controlled nanoscale pores, and better understanding of the relationship between the pore structures and transport properties.

Introduction

- ❑ Here, they experimentally investigate the transport of ions and molecules across a single layer of large-area CVD graphene transferred to a porous polycarbonate track.

- ❑ They develop a procedure to transfer graphene ($\sim$25 mm^2) to the PCTE membrane and characterize the coverage of the transferred graphene using pressure-driven flow.

- ❑ They show that the CVD graphene contains a low frequency of intrinsic holes that permit the selective transport of molecules.

- ❑ The measured permeability is consistent with predictions of continuum theory.

Experimental section

Membrane fabrication:

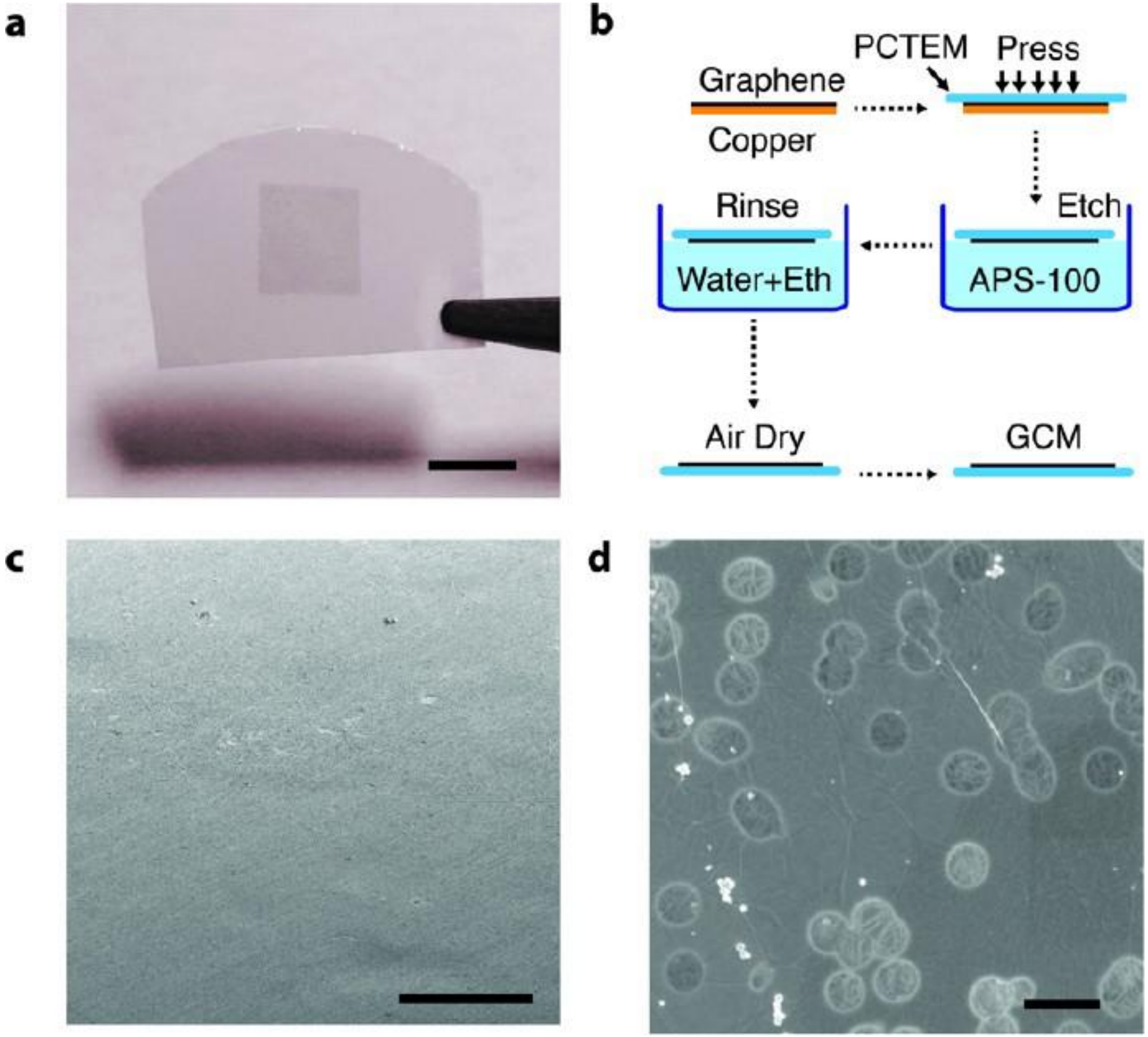
They used CVD graphene on copper, as it can be grown over large areas comprising primarily single layers.

Their scalable, direct-transfer process relies on the conformability of a porous polymer substrate to adhere to the graphene (on copper) via a simple pressing process followed by etching of the copper.

The porous polymer supports the graphene during the copper-etching phase and also gives it sufficient mechanical robustness for further handling.

Before drying, the GCM was rinsed in an ethanol/water mixture to minimize mechanical stresses due to the receding meniscus.

Results and discussion



Results and discussion

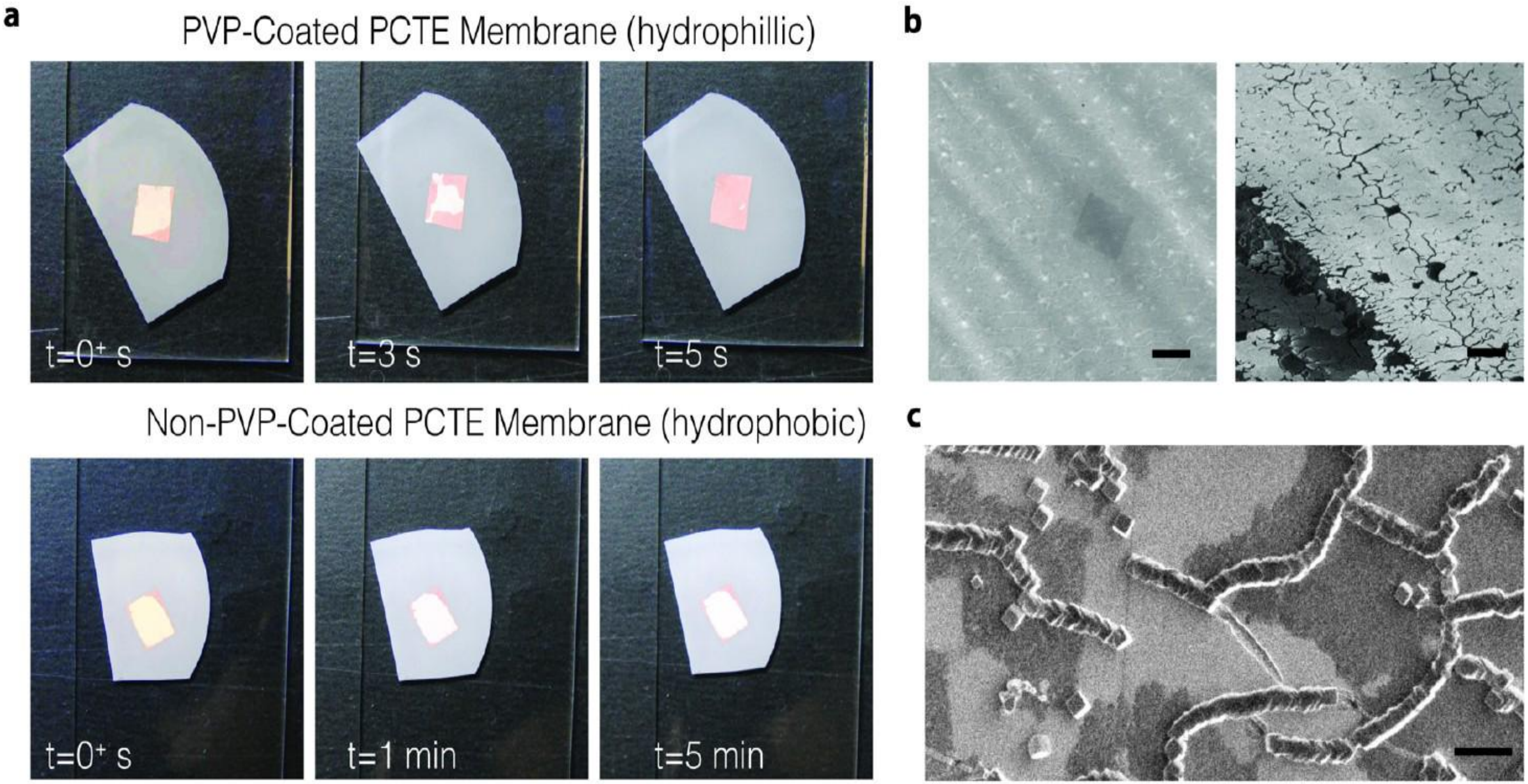
They found that the three primary factors that influence the quality of the transfer are the:

1. Hydrophobicity of the substrate,

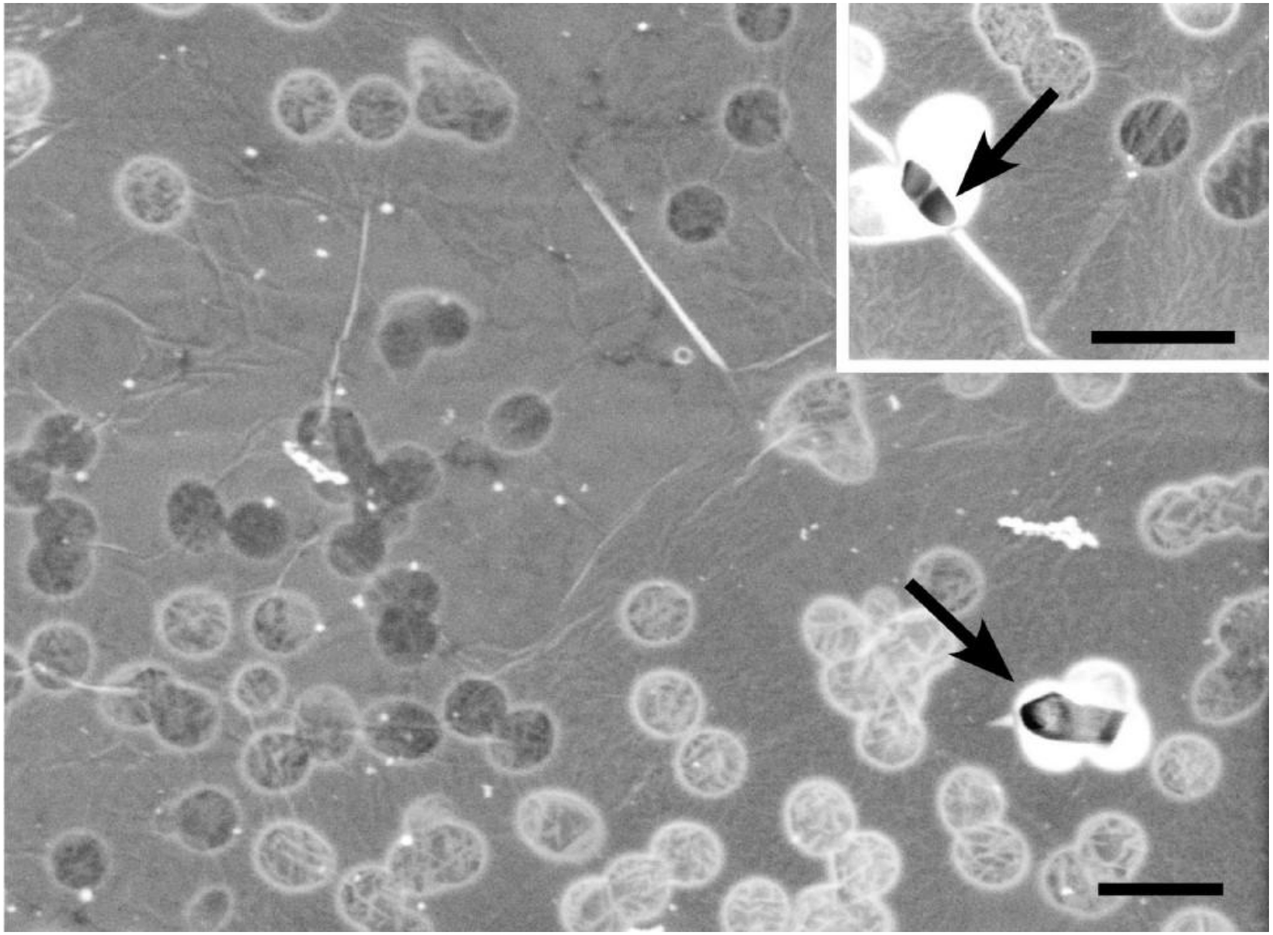
2. The surface roughness of the copper on which the graphene is grown, and

3. The type of etchant used to remove the copper.

Results and discussion

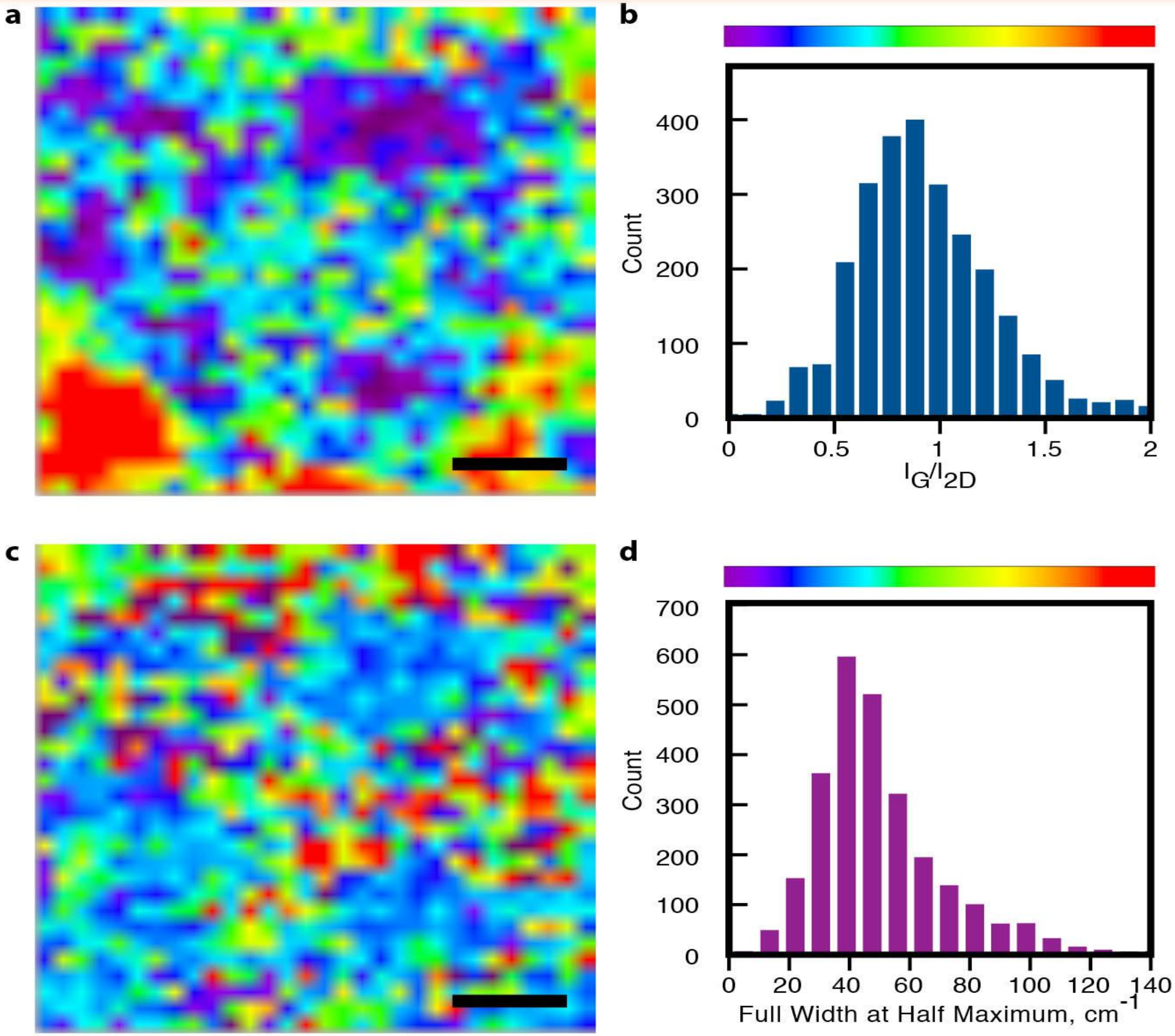


Results and discussion

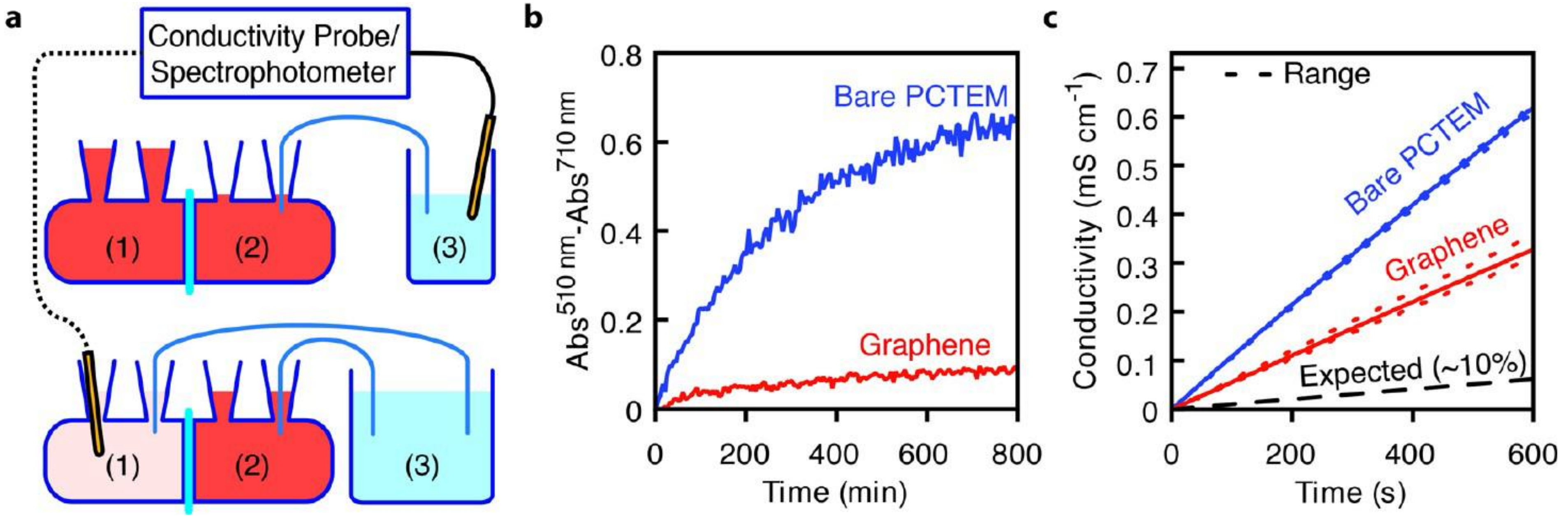


Uncovered single polycarbonate track etch membrane pores (indicated by arrows) and cracks (inset) were two types of defects commonly found in graphene after transfer. Analysis of similar images revealed typical graphene coverage to be 90-98%. Scale bars are 500 nm.

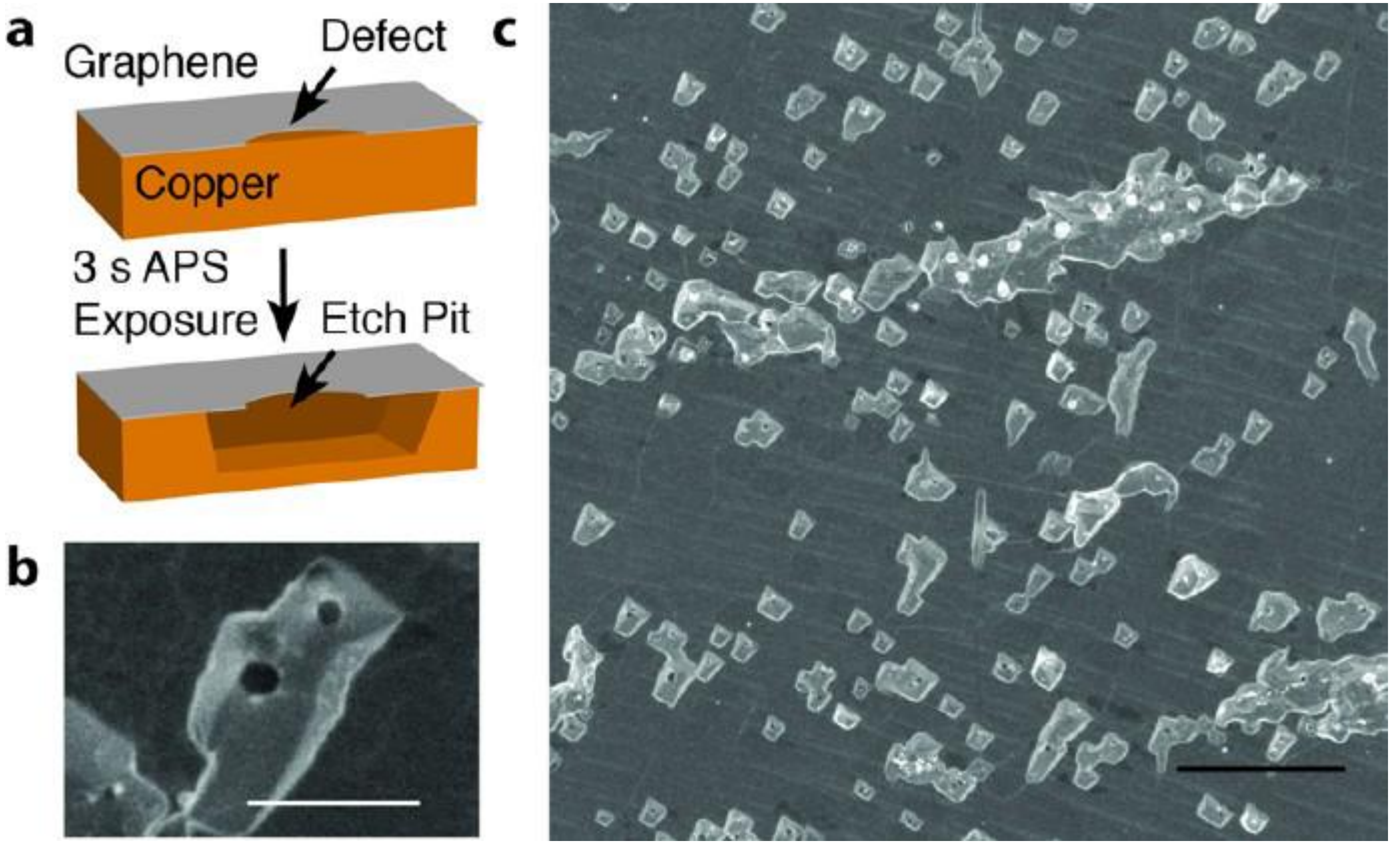
Characterization of graphene



Results and discussion

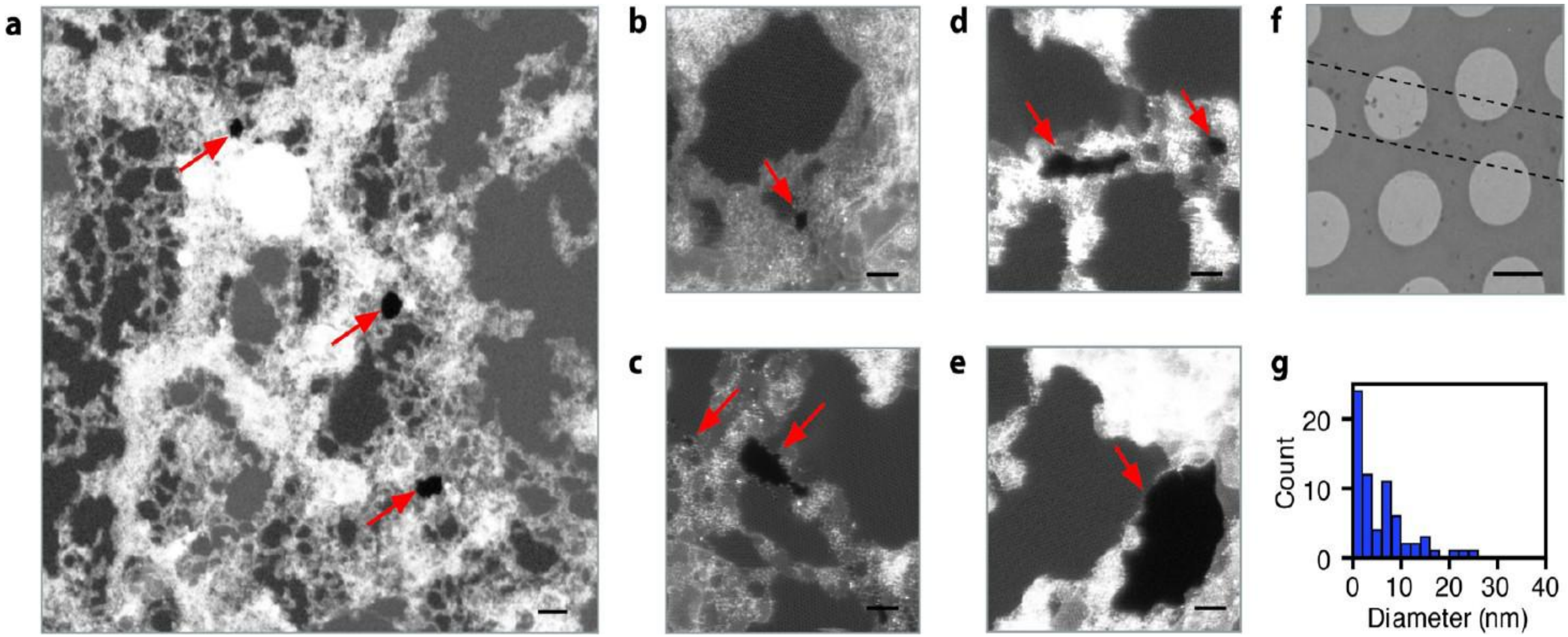


Results and discussion



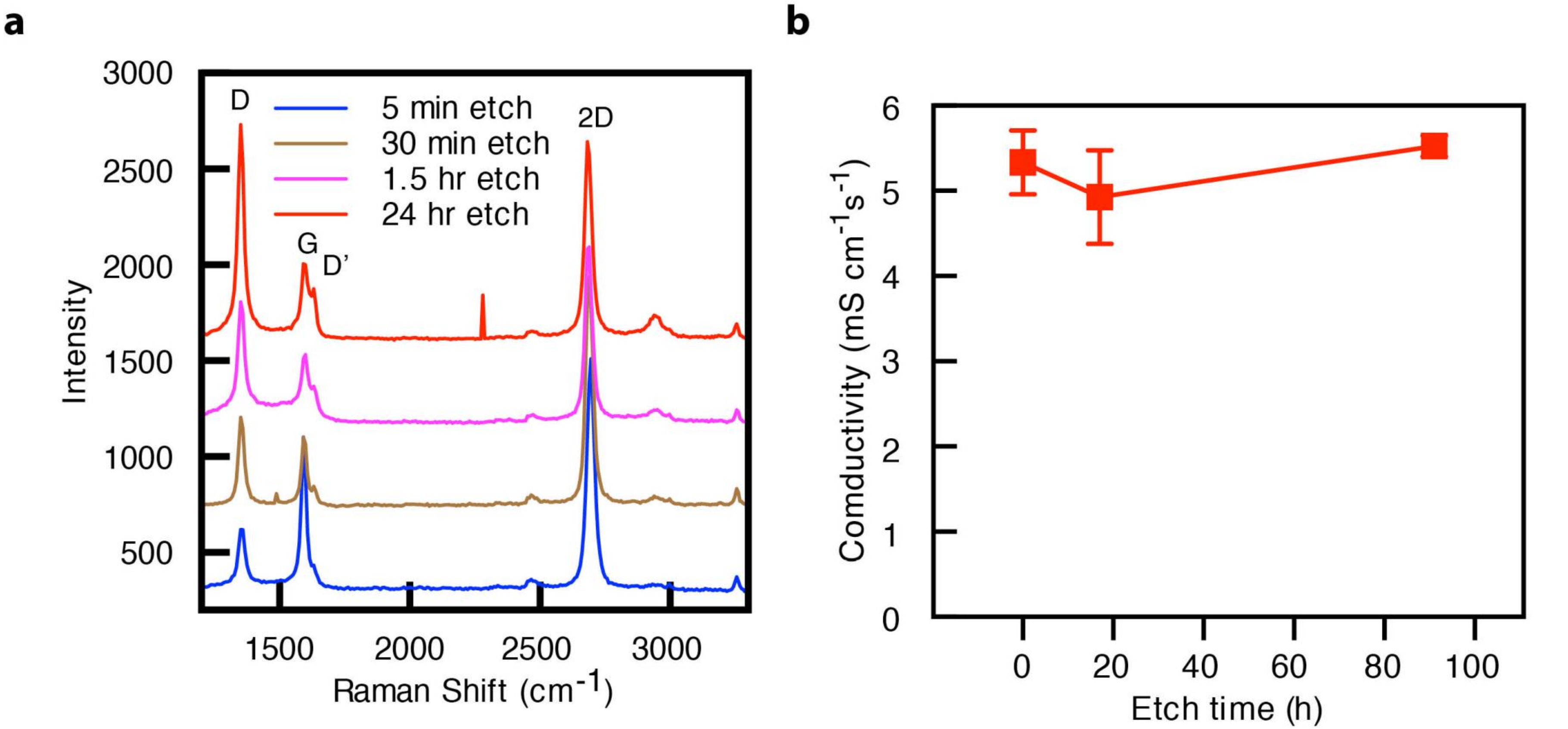
Results and discussion

Characterization of nanometer-scale pores in graphene by STEM medium-angle annular dark field (MAADF).



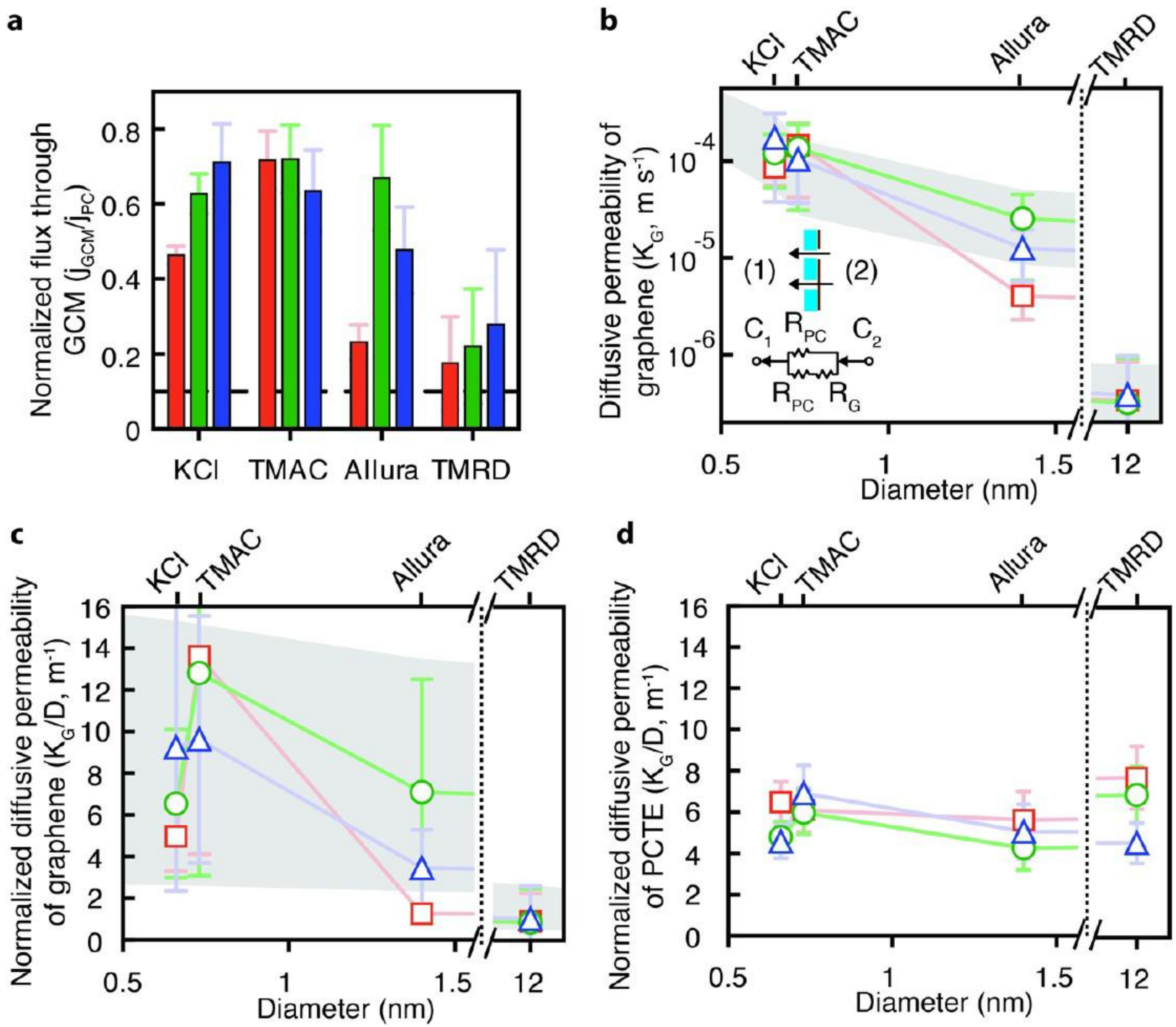
(a) Low density of pores can be seen in the graphene lattice, as indicated by red arrows. Scale bar is 10 nm. (be) Representative images of pores that vary in size from 1 to 15 nmin diameter. Scale bars are 2 nm. (f) A higher concentration of pores exists in the region between the dashed lines. Scale bar is 1 µm. (g) Distribution of pore sizes imaged in STEM suggests~83% of holes in lattice are less than 10 nm in diameter.

Results and discussion



a, Raman shift of graphene for APS-100 etch times of 5 min, 30 min, 1.5 h and 24 h. Increasing D-band and D'-band suggest APS-100 may modify graphene lattice. b, Diffusive transport rate of KCl through graphene membrane for etch times of 0 h, 17 h, and 91 h. Lack of substantial transport increase suggests that APS-100 does not increase intrinsic hole size.

Results and discussion



Summary and conclusion

In this work, they fabricated membranes comprising a single sheet of CVD graphene on a porous support and developed methods to measure the transport properties of graphene.

The understanding of the origins of the permeability of graphene and the measurement techniques developed in this study will aid the design of future graphene membranes for various applications and may also provide insights into the behavior of graphene as barrier films.

This study shows that these defects occur at a fairly low frequency, and they can only speculate that they occur due to defects in the copper itself or deposition and growth of particulates on the copper.

The work promises to reveal interesting transport properties for applications in gas separations, water purification, and biomedicine.

Thank you