FIRST IN CHANGE

Engineered Flexible Conductive Barrier Films for Advanced Energy Devices

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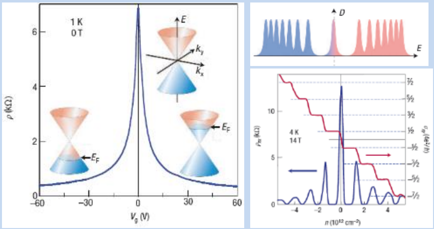
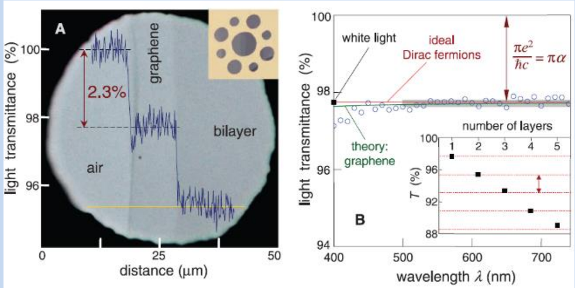
Graphene

1. Electrical properties
   - Ambipolar electric field effect
   - Ballistic transport (μ~200,000 cm^2/Vs)



K. Novoselov, Science 306, 666 (2004).

2. Optical properties
   - Absorption at 550 nm ~ 2.3 %



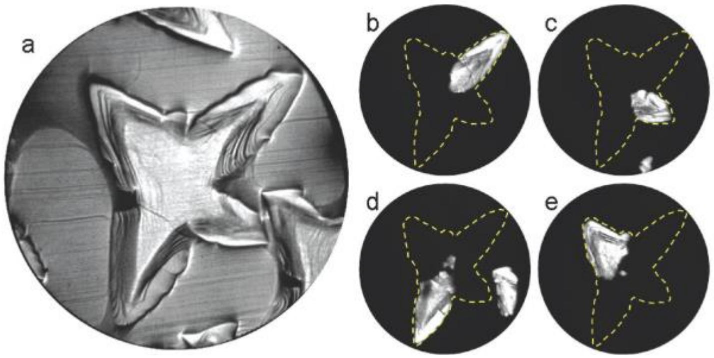
R. R. Nair, Science 320, 1308 (2008).

3. Impermeability
   - Impermeable to standard gases including He
   - The world’s thinnest membrane

These unique properties make graphene the most impermeable membrane for transparent and flexible energy devices

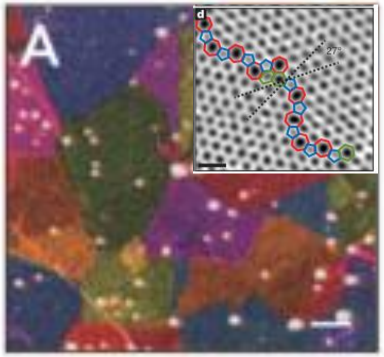
Defects in CVD-grown graphene

Intra-grain boundary



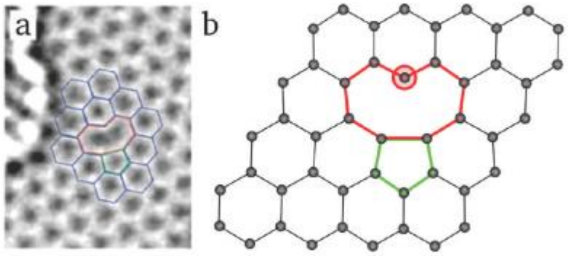
J. M. Wofford, Nano Lett. 10, 4890 (2010).

Inter-grain boundary



A. W. Tsen, Science 336, 1143 (2012).

Point defects



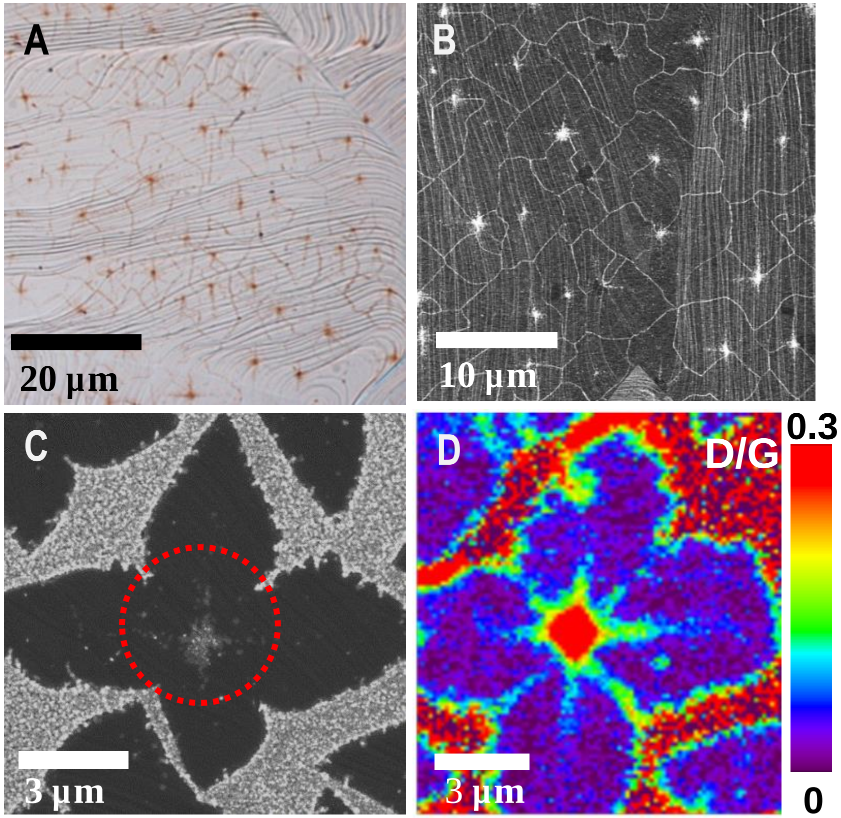
F. Banhart, ACS Nano 5, 26 (2011).

It is highly required to develop

➡ **a simple and feasible macroscopic investigation tool of graphene defects**

➡ **a novel method to block the nano-sized graphene defects.**

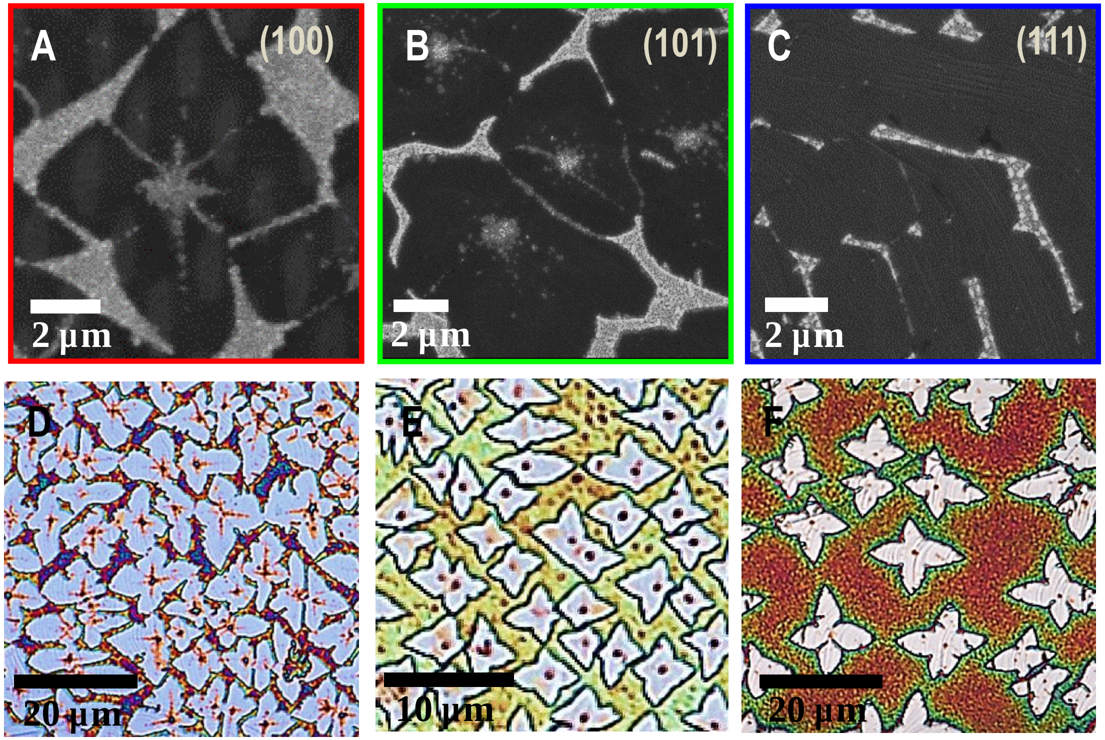
Facile method to characterize microscopic defect of graphene



All possible microscopic topological defects of different origins can be observed by thermal annealing in air. (A) OM image of the Gr/Cu sample after annealing at 200 ^{o}C for 2hr in air, (B) SEM image of the Gr/Cu sample after annealing at 200 ^{o}C for 2hr in air, (C) SEM image of Gr islands grown on a Cu foil at 1000 ^{o}C after annealing at ~200 ^{o}C for 70 min in air, (D) A corresponding Raman D/G map images of the as-grown Gr islands transferred onto SiO_2/Si.

Using the thermal annealing in air, we can visualize various types of microscopic topological defects, such as nucleation point and grain boundaries.

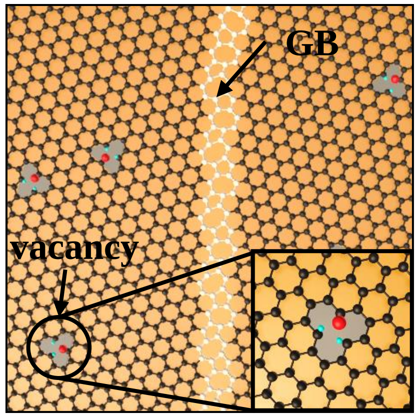
Facile method to characterize microscopic defect of graphene



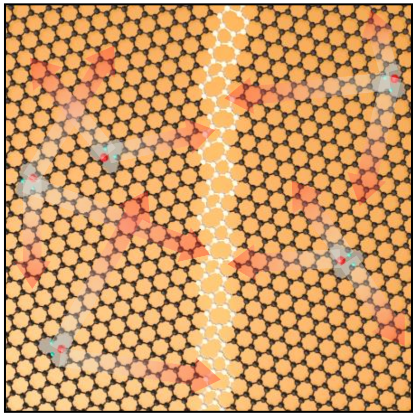
(A-C) Representative SEM images of the annealed Gr islands grown on Cu grains with an orientation of (A) (100), (B) (101), and (C) (111), (D-F) OM images of the Gr islands grown on Cu(100) grains after annealing at ~200 ºC for 120min under various CVD growth conditions.

The degree of structural deficiency was strongly dependent on the origins of the structural defects, the crystallographic orientation of underlying Cu grains, the growth conditions of graphene, and the kinetics of the graphene growth.

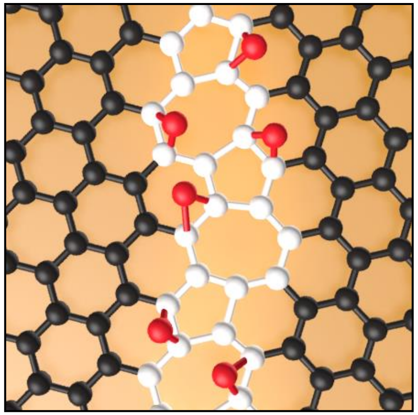
Mechanism of selective oxidation of Cu through a graphene barrier



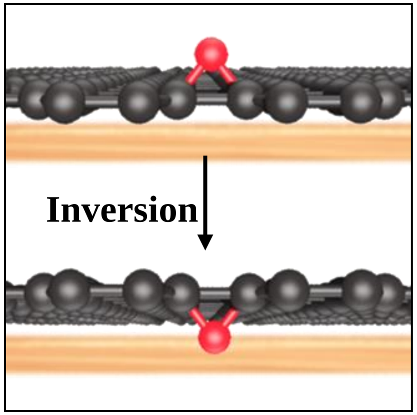
a. Dissociative chemisorption of H_2O molecules at intrinsic defects



b. Migration of dissociated O adatoms on a Gr/Cu surface

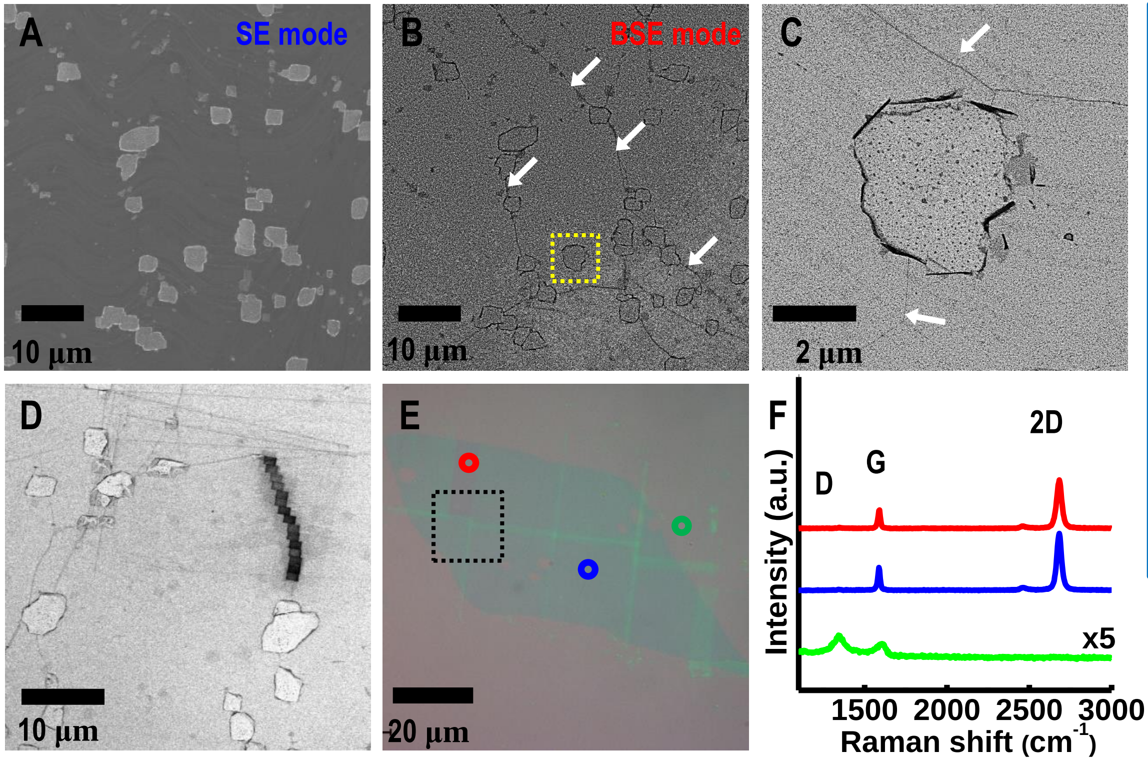


c. Accumulation of O atoms at GBs of graphene grains



d. Inversion of O atoms with an attachment of facilitators at SW defect

Enhancing impermeability using EBIC



Water permeable CVD-Gr grown on a Cu foil through a lot of Gr defects. (A-B) A representative SEM image of the Gr/Cu surface after etching by an aqueous HCl solution for 10 min in SE (A) and BSE (B) mode. (C) A magnified SEM image taken from the yellow-dotted square in B. In b and c, white arrows indicate the Gr wrinkles. (D) A typical SEM image of a Gr surface selectively stacked by EBIC layer after etching in aqueous HCl solution. (E-F) An optical microscopy image (E) and Raman spectra (F) obtain from red, blue, and green circles in (E).

The graphene layer stacked by EBIC shows the enhanced impermeability to water.

Conclusions

- **We have demonstrated facile, large-area characterization technique of observing all possible microscopic graphene defects that can be prepared by annealing at 200 °C in ambient air.**

- **Our approach can, in principle, be used to discern the degree of structural deficiencies of graphene defects with different origins by using Cu oxidation features.**

- **We have develop an effective passivation method of various graphene defects using an electron beam induced carbon in macro-scale. This relatively simple method opens up new possibilities for flexible, transparent, and conductive water impermeable layer.**

Thank You