Toward Edge-Defined Holey Boron Nitride Nanosheets†,‡

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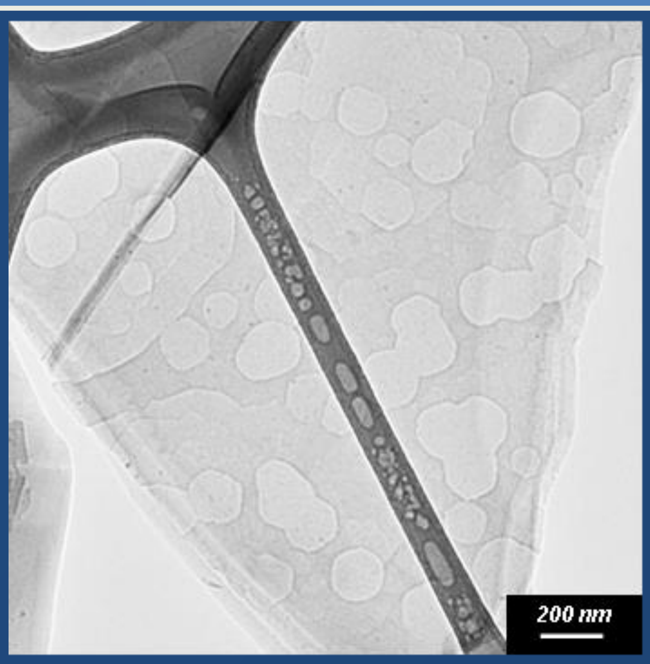
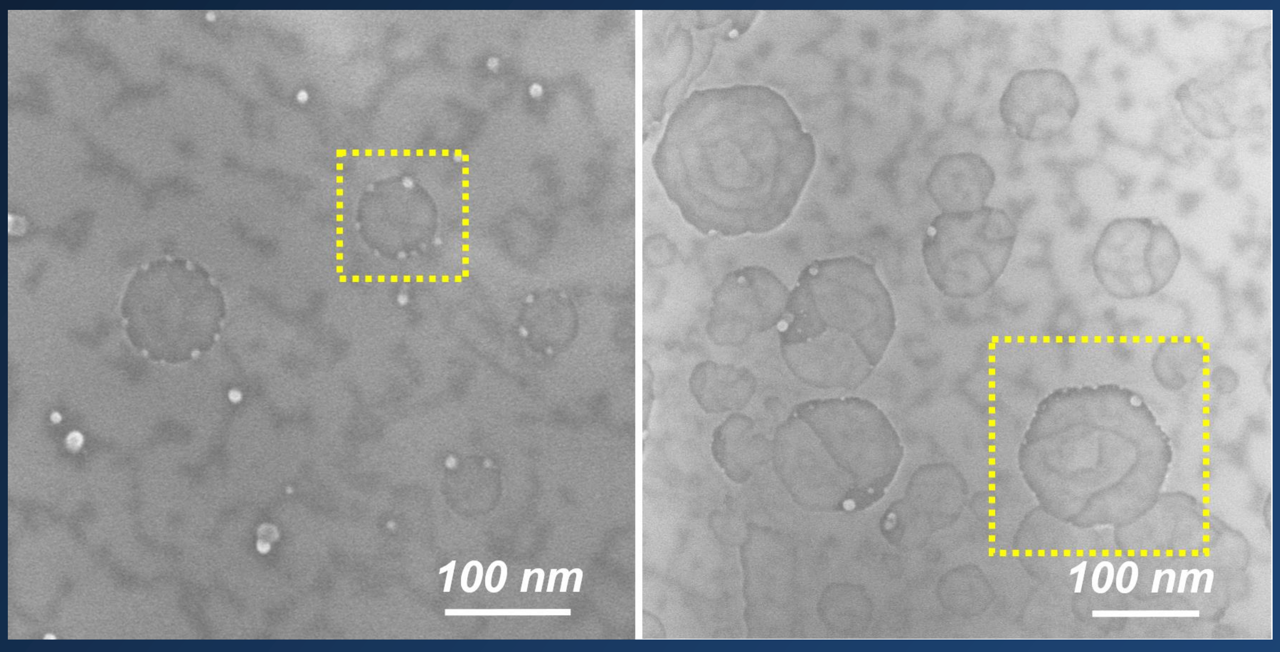
Introduction

"Holey" two-dimensional (2D) nanosheets with well-defined hole morphology and edge chemistry are highly desirable for applications such as energy storage, catalysis, sensing, transistors, and molecular transport/separation. For example, holey graphene is currently under extensive investigation for energy storage applications because of the improvement in ion transport due to through the thickness pathways provided by the holes. Without the holes, the 2D materials have significant limitations for such applications in which efficient ion transport is important. As part of an effort to apply this approach to other 2D nanomaterials, a method to etch geometrically defined pits or holes on the basal plane surface of hexagonal boron nitride (h-BN) nanosheets has been developed. The etching, conducted via heating in ambient air using metal nanoparticles as catalysts, was facile, controllable, and scalable. Starting h-BN layered crystals were etched and subsequently exfoliated into boron nitride nanosheets (BNNSs). The as-etched and exfoliated h-BN nanosheets possessed defined pit and hole shapes that were comprised of regulated nanostructures at the edges. The current findings are the first step toward the bulk preparation of holey BNNSs with defined holes and edges.



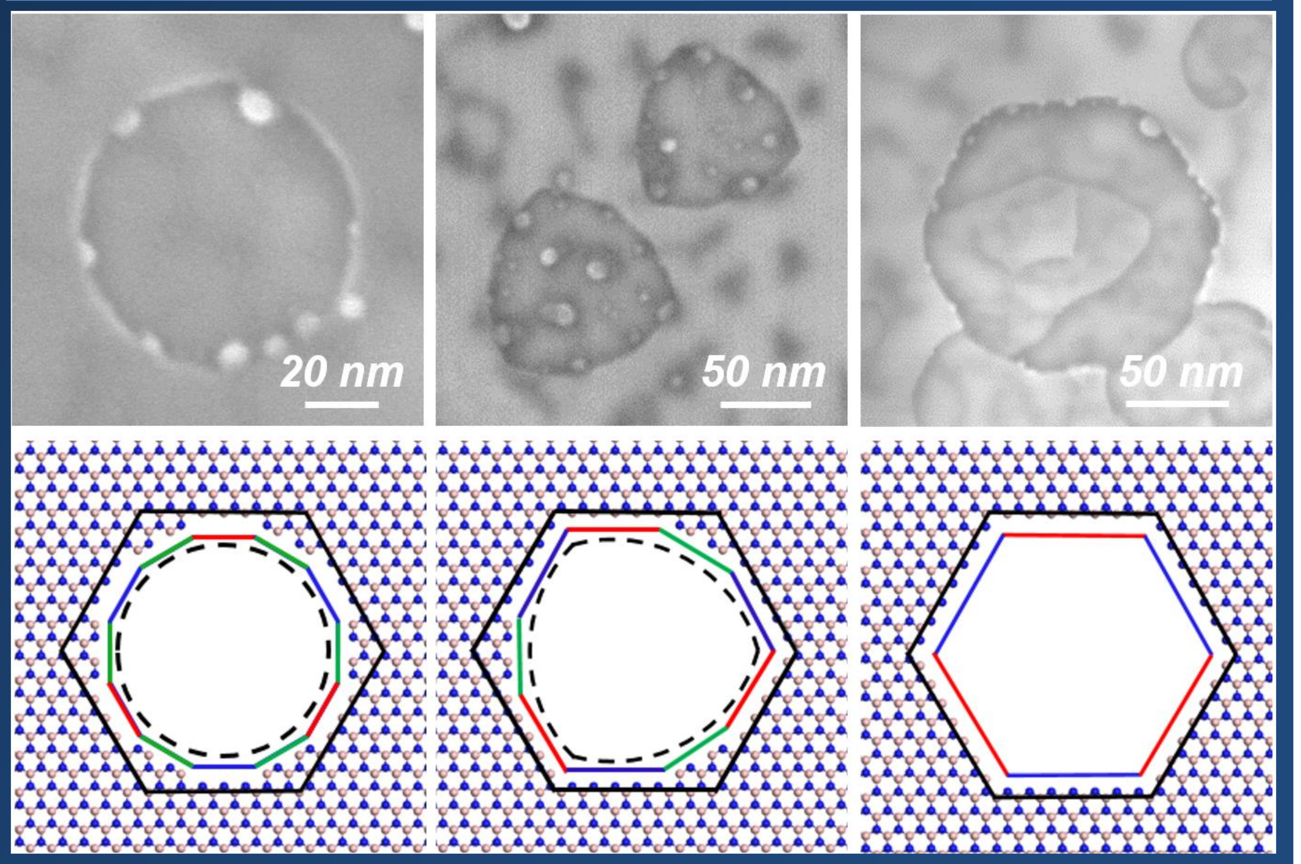
Ag-Catalyzed Etching of h-BN



Facile Etching Process:
- Step 1: Deposit Ag nanoparticles on h-BN
- Step 2: Heat Ag-h-BN in air at 800 °C for 3h

Etching Results:
- Pits of defined shapes (see below for enlargement)

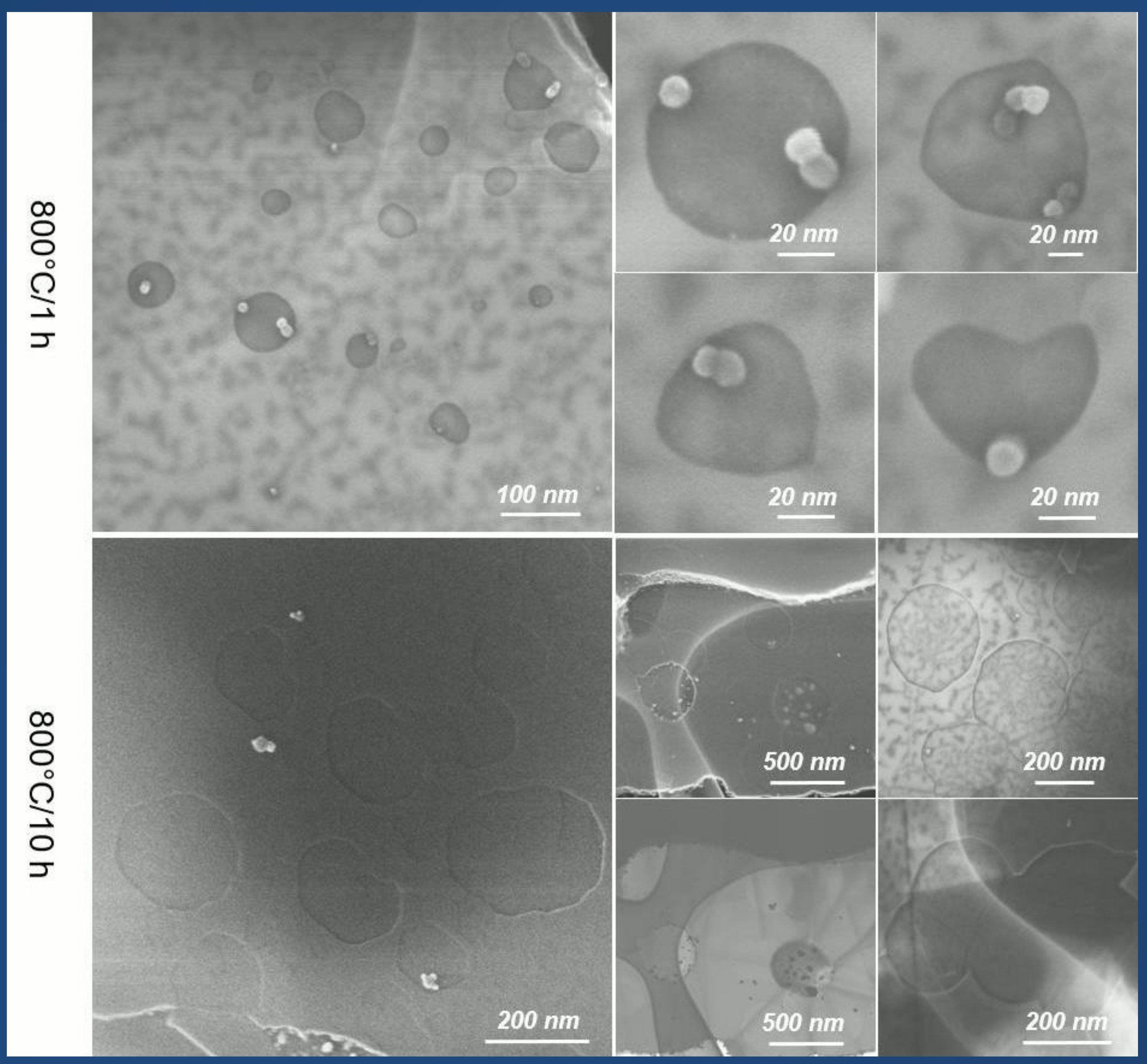
Pit Shapes & Structures



"Circles" (Dodecagons) | "Reuleaux Triangles" (Nonagons) | Hexagons

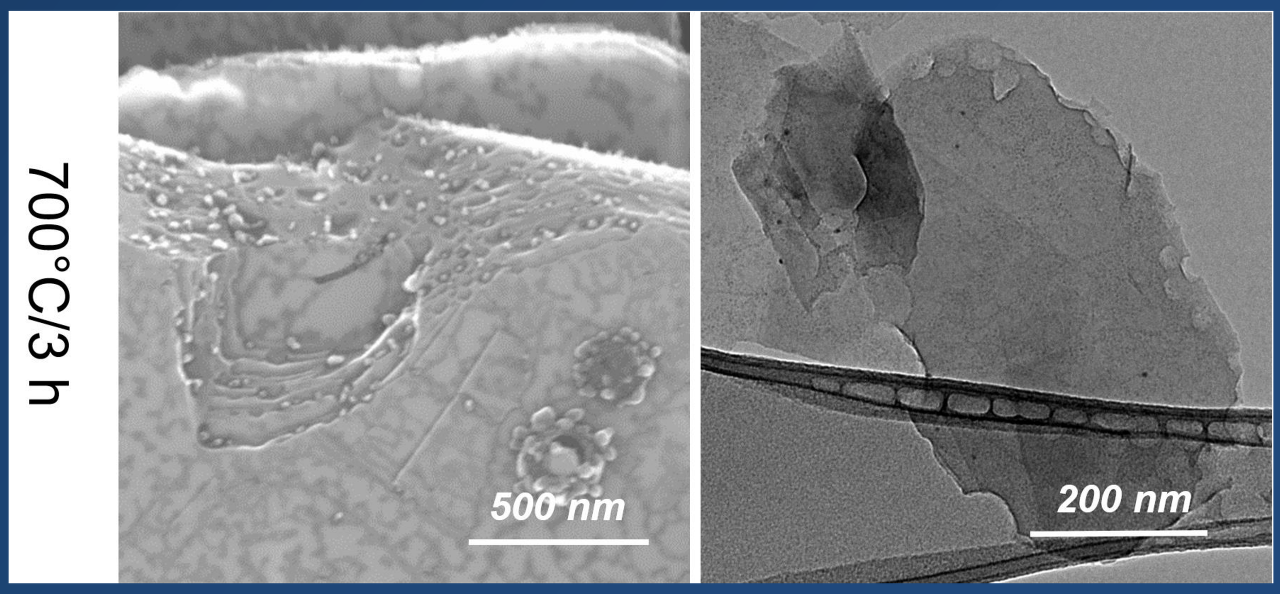
zigzag: B or N, N or B
armchair

Progressive Etching I: Time Dependence

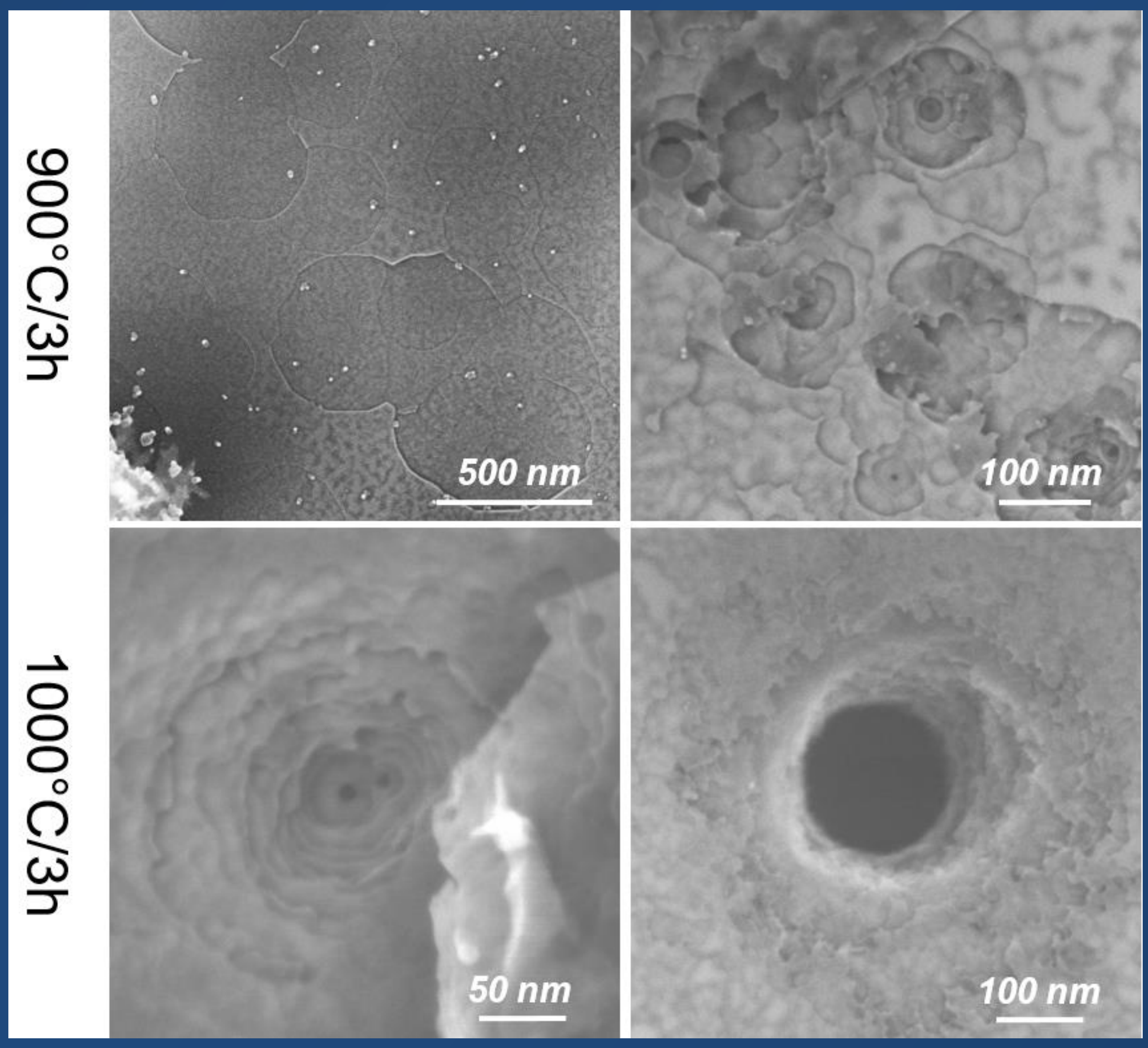


- 800 °C/1h: smaller pit sizes; irregular shapes
- 800 °C/10 h: larger pit sizes; polygonal shapes

Progressive Etching II: Temperature Dependence

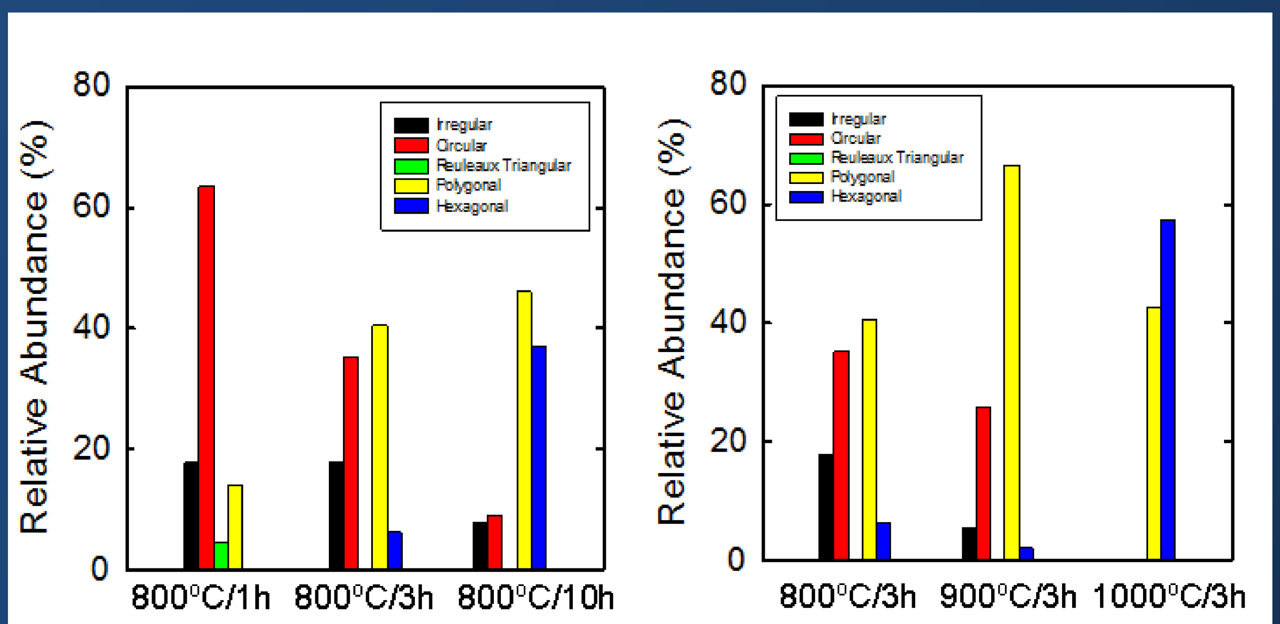


- 700 °C/3h: predominant sheet-edge etching



- 900-1000 °C/10h: larger sizes; through-thickness
- Rough edges due to oxidized boron build-up can be removed by nitric acid treatment for defined shapes

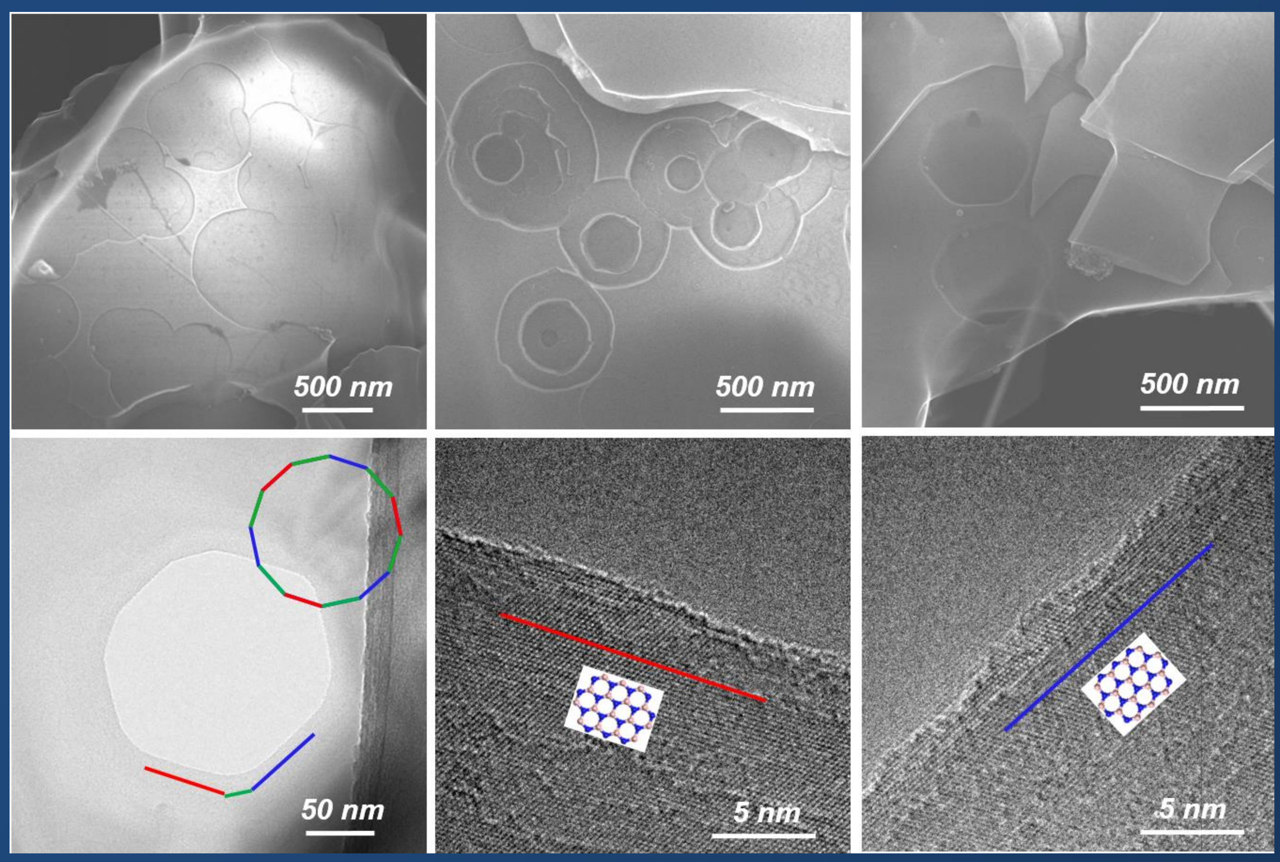
Evolution of Pit/Hole Shapes



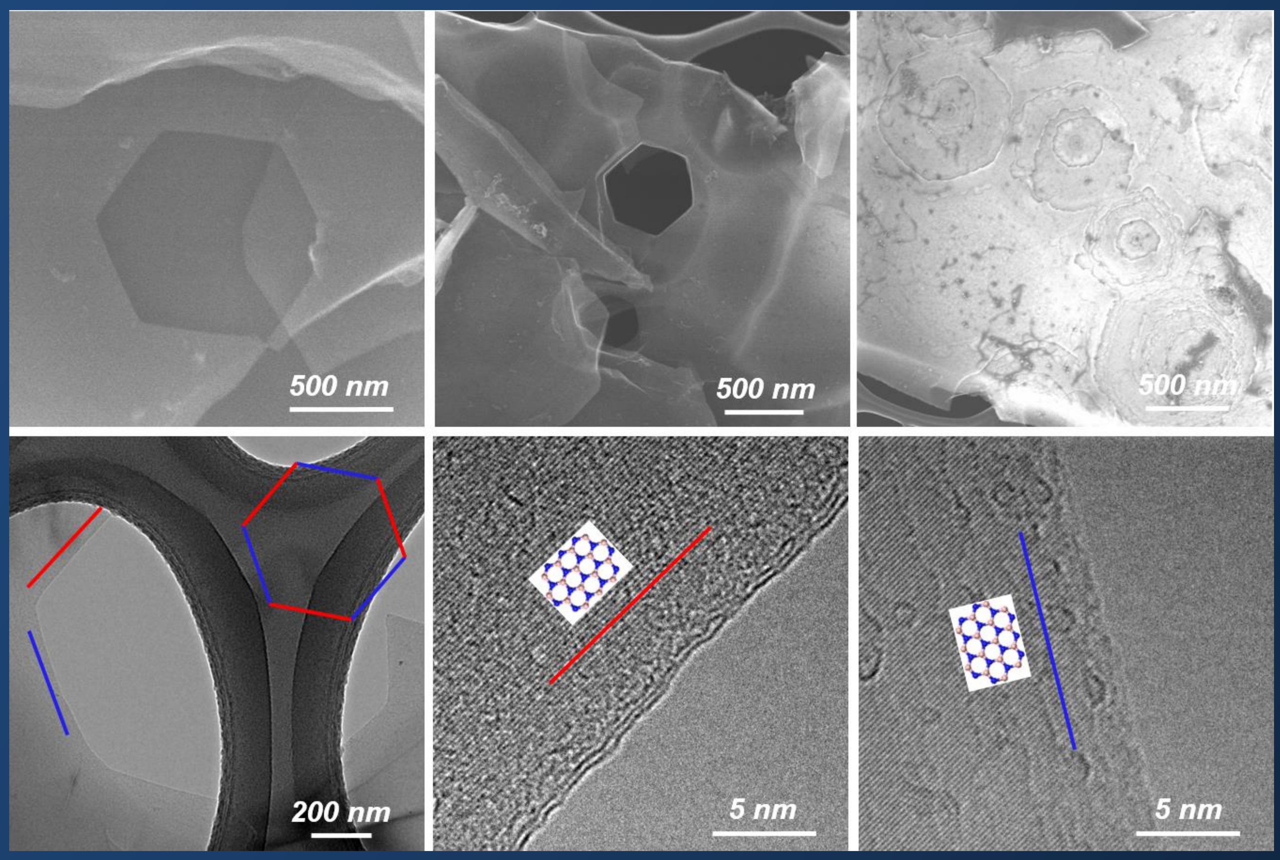
- Higher temperature and/or longer time both promotes the formation of more defined, hexagon-like pits and holes

Purified, Etched h-BN/BNNSs

- **Purification** (i.e. removal of Ag catalysts & oxidized boron) was achieved using diluted nitric acid
- Etched **BNNSs** were obtained via simple solvent exfoliation methods

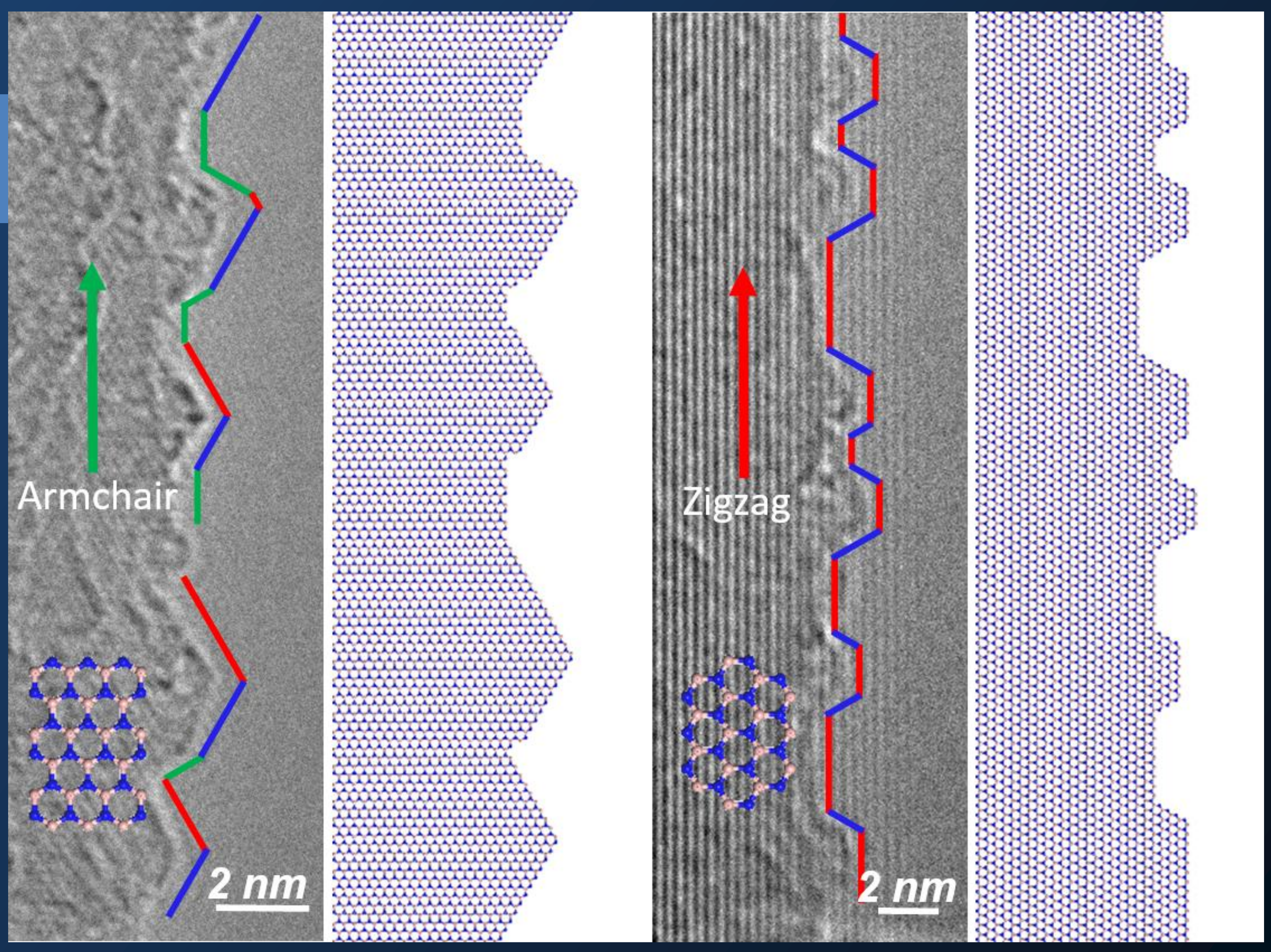


- 900 °C/3h: predominantly dodecagons/polygons



- 1000 °C/3h: predominantly zigzag-edged hexagons

Edge Chirality Preference



Most edges were zigzag!
- Armchair-oriented edges: triangle-like tips = **zigzag**
- Zigzag-oriented edges: hexagon-like tips = **zigzag**

†Majority of this work has been published in the open access journal *Scientific Reports* (*Sci. Rep.* **2015**, *5*, 14510).
‡**Acknowledgements**: The authors thank experimental assistance by Dr. Xiaogang Han and Prof. Liangbing Hu (U. Maryland, College Park), Dr. W. Cao and Prof. H. Elsayed-Ali (Applied Research Center, Old Dominion U.), and C. Chamberlain (NASA Langley Research Center). Y. Liao was supported by a fellowship awarded via Institute for Functional Nanomaterials (IFN) at University of Puerto Rico. Y. Lin acknowledges the financial support by National Institute of Aerospace. Z. Chen acknowledges the support by Department of Defense and NASA.

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