



Application of graphene-based composites in environmental protection and its industrialization progress

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MEMS教育部重点实验室

Key Laboratory of MEMS of Ministry of Education, Southeast University, Nanjing, China



Outline

- **Background:**
- **Precisely monitoring surface structures**
- **Tailoring the surface structures**
- **Applications based on the surface effects**

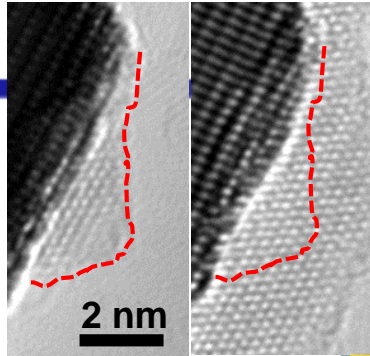


MEMS教育部重点实验室

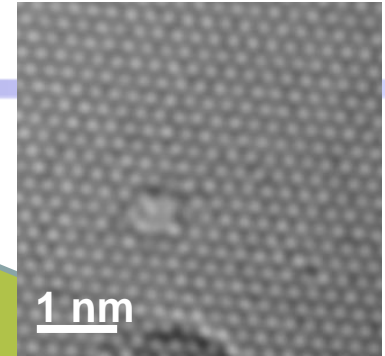
Key Laboratory of MEMS of Ministry of Education, Southeast University, Nanjing, China



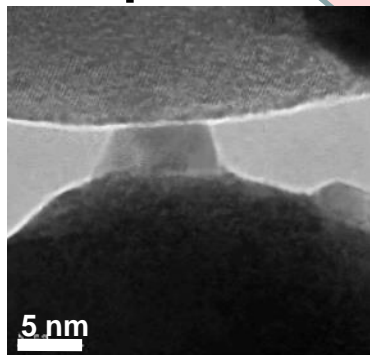
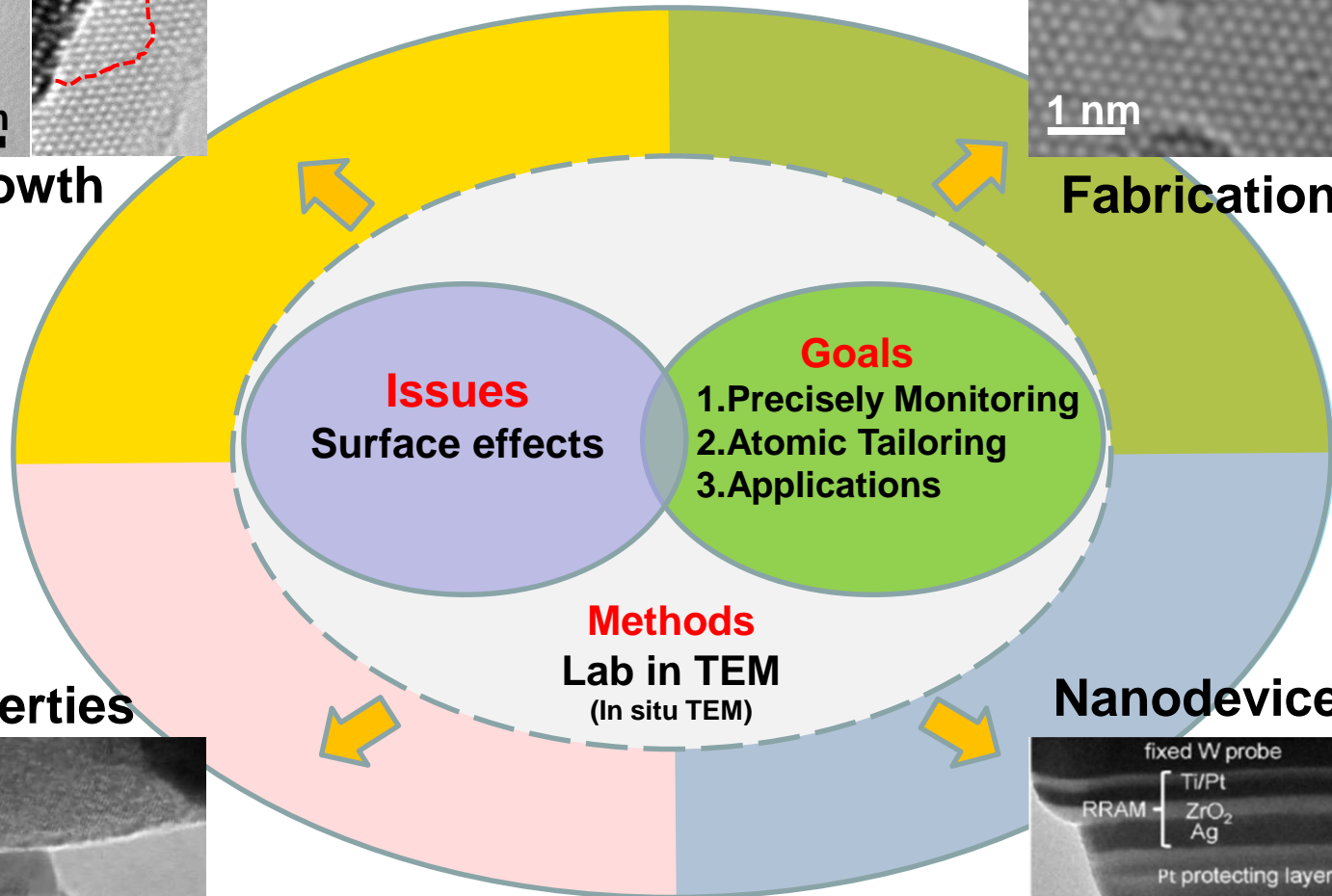
Background



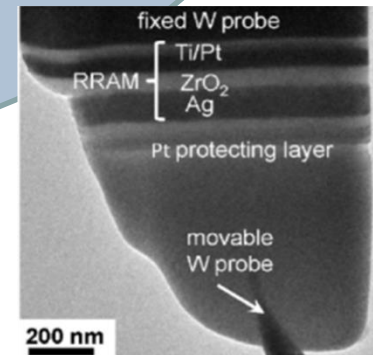
Growth



Fabrication

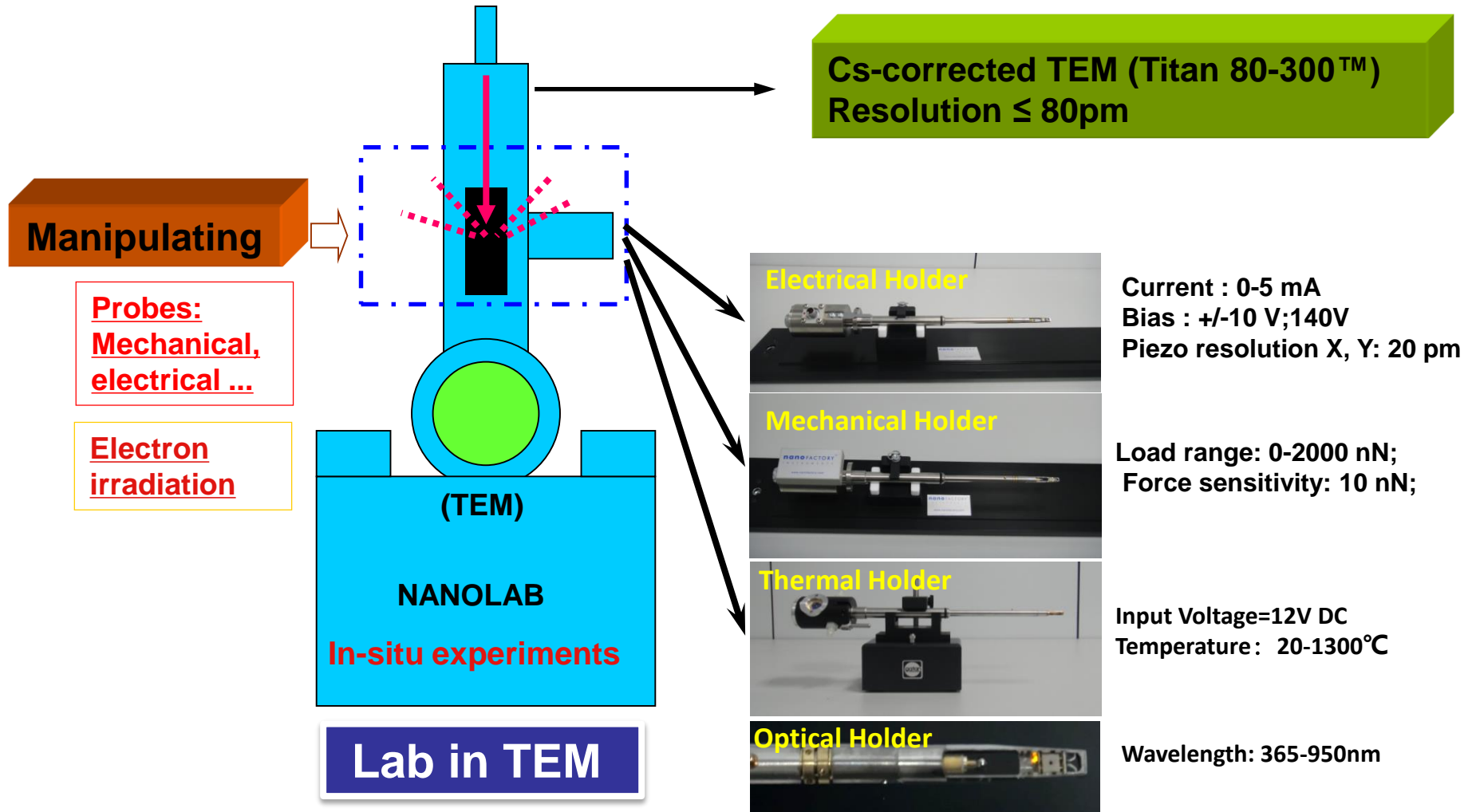


Properties



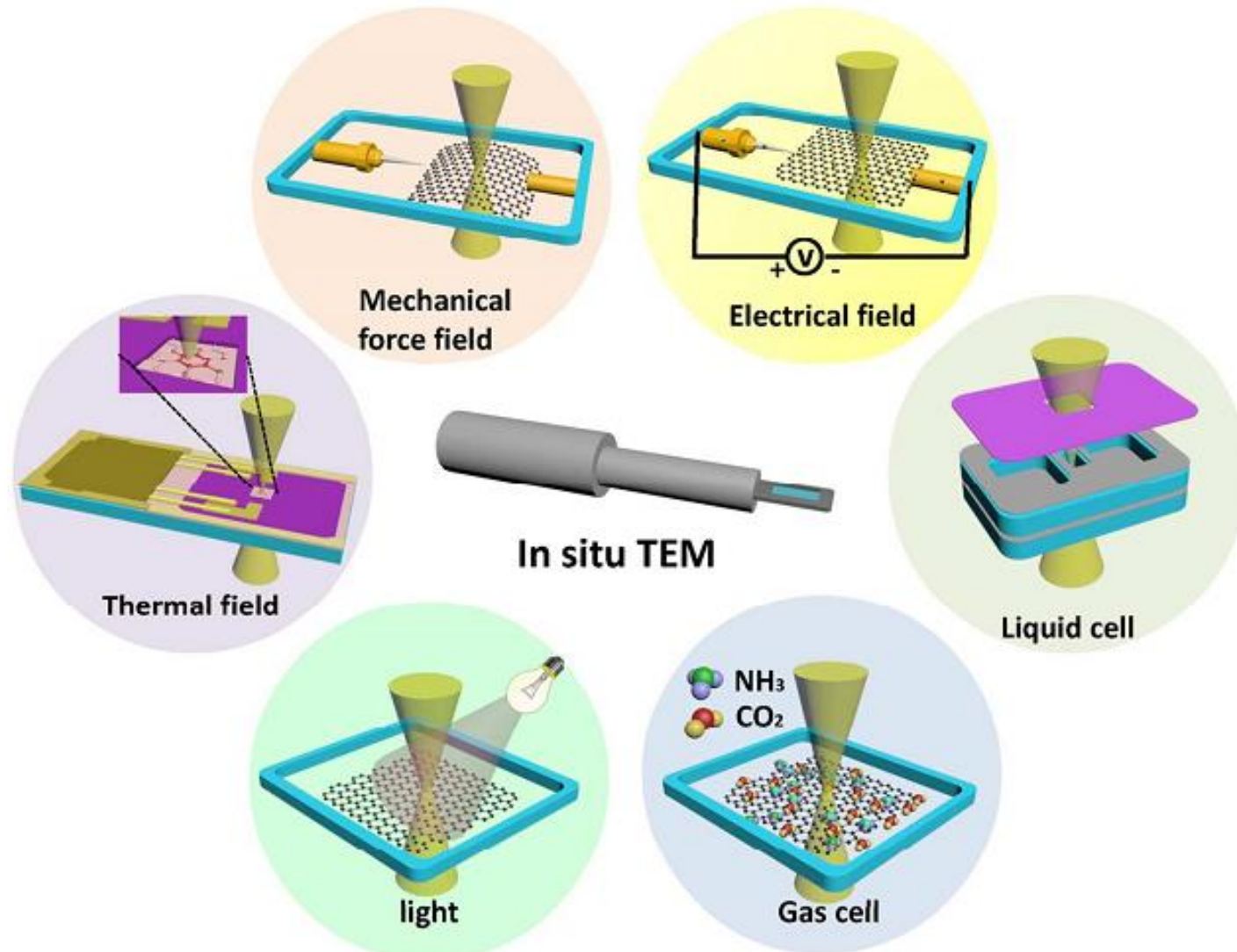
Nanodevice

How to set up a lab inside a TEM?



Imaging, manipulation and measurement... at atomic scale
Simultaneously?

A lab inside TEM



In situ TEM could simulate complicated environments (gas, liquid) with multiple stimuli (e.g., electrical, thermal field, light, and mechanical stress).

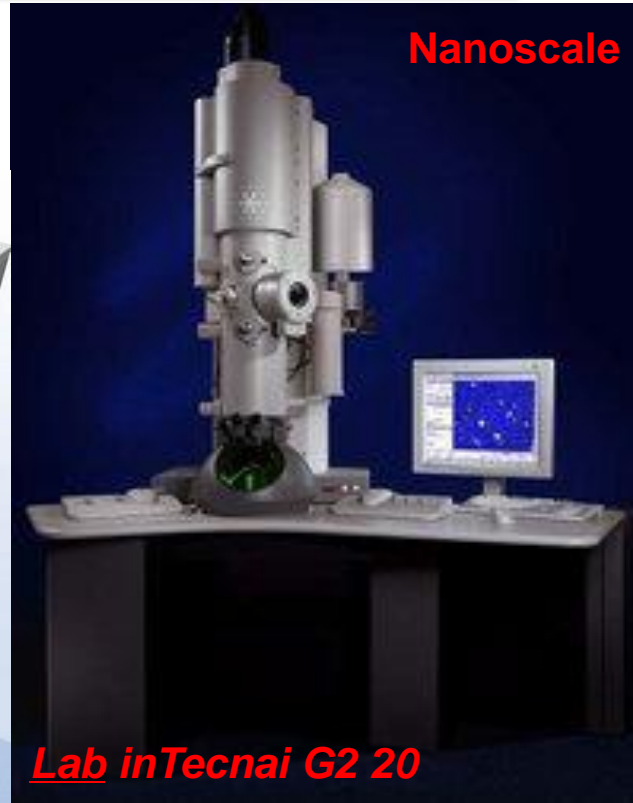
How to set up a lab inside a TEM

Multiscale dynamic characterization

Microscale



Nanoscale

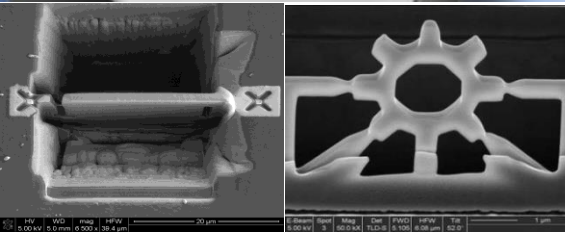


Picoscale



First Commercial Cs-corrected TEM in our lab

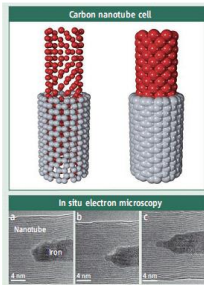
Basic (Nano, Pico) \longleftrightarrow Application (Micro)



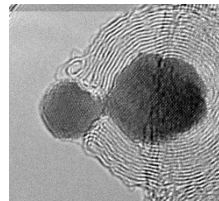
SEU-FEI Nano-Pico Center (Nanjing)

A lab inside a TEM

Development of **in-situ microscopy** in our group



Science 312, (2006)



PRL 101, (2008)

Property



Nature 528, (2015); *Science* 344, (2014); *Nature Mater.* (2014)

Device and Application

2006

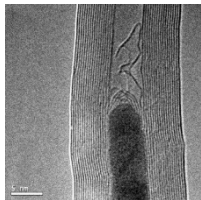
2008

2010

2012

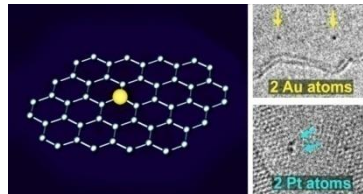
2014 ...

Dynamic
Characterization



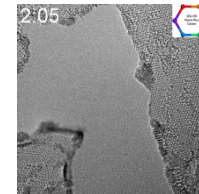
Nature Nanotech. 2, (2007)

In-situ growth



PRL 105, (2010)

Manipulation

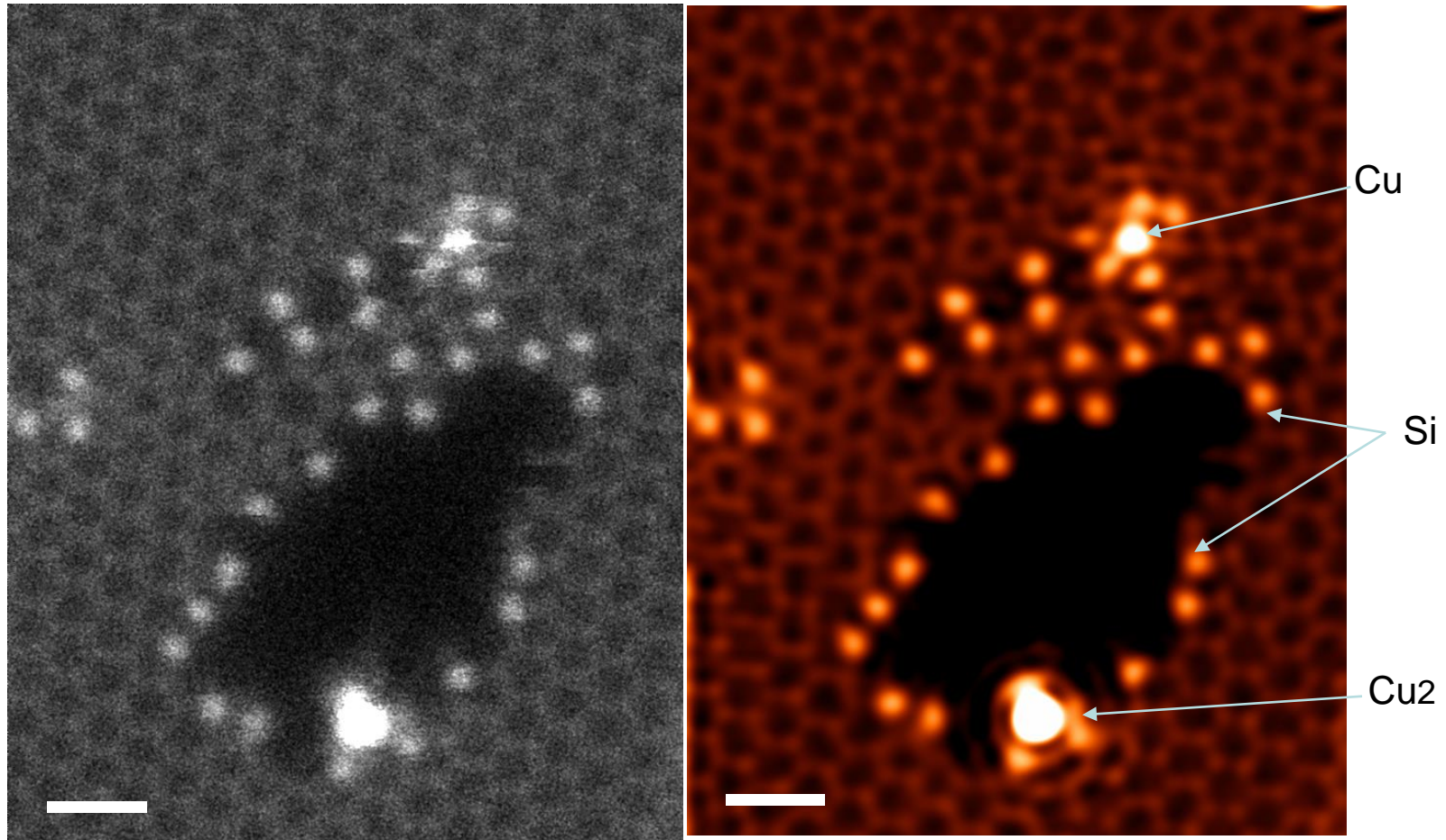


Nature Comm. 4, 1776 (2013);

Nanofabrication

Precisely Monitoring surface

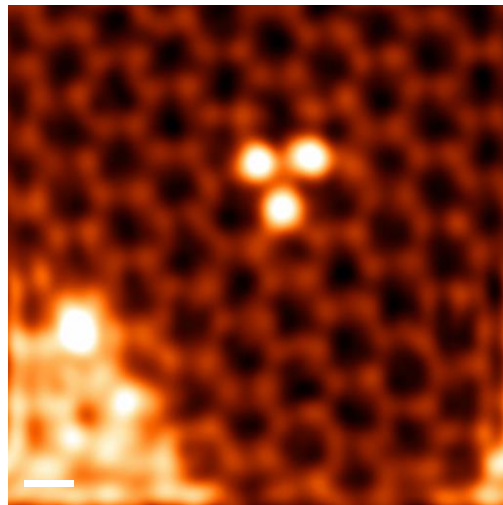
Si and Cu doping at graphene nanopore



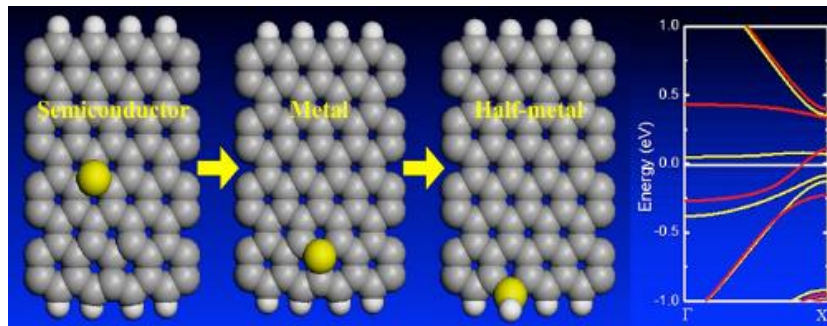
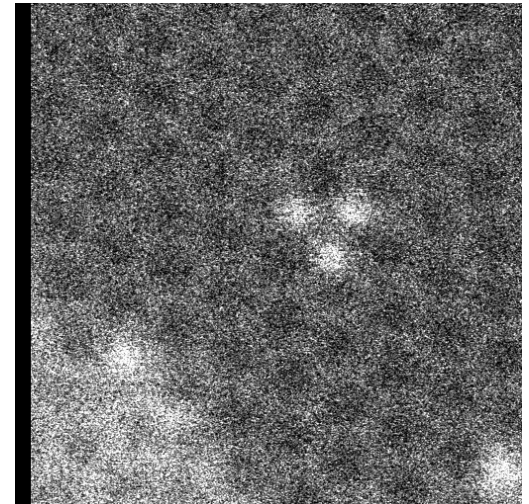
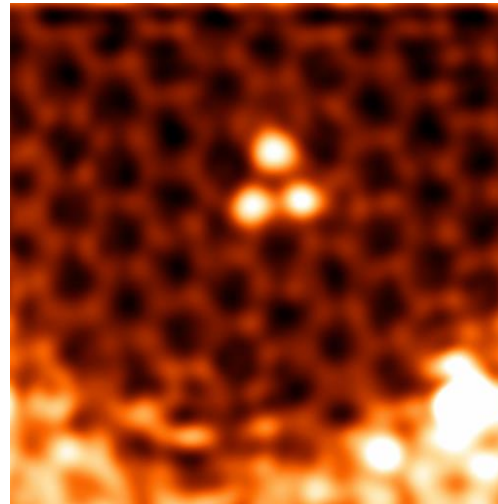
(left: original; right: processed)

Precisely Monitoring surface

Si trimer in monolayer graphene



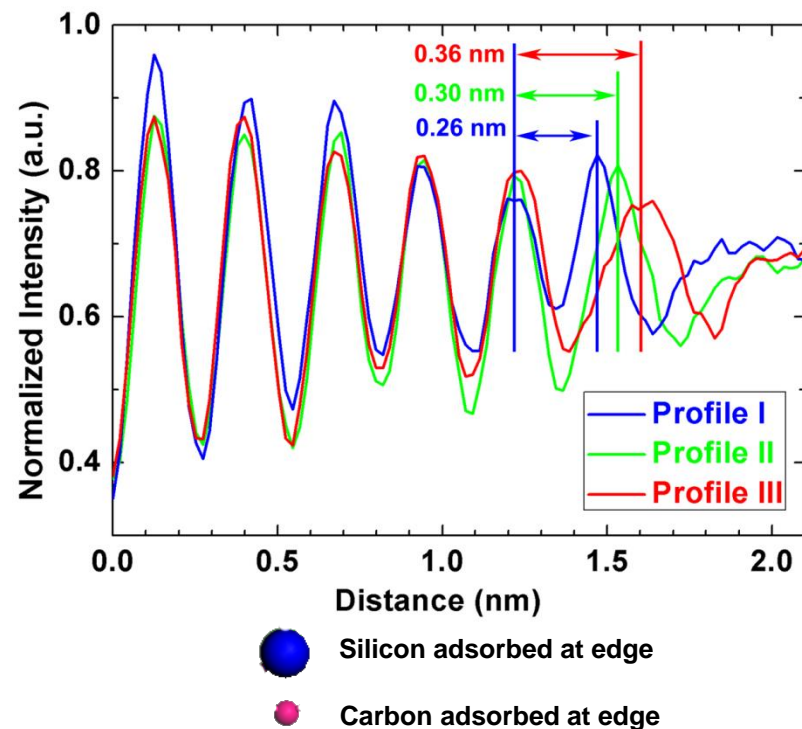
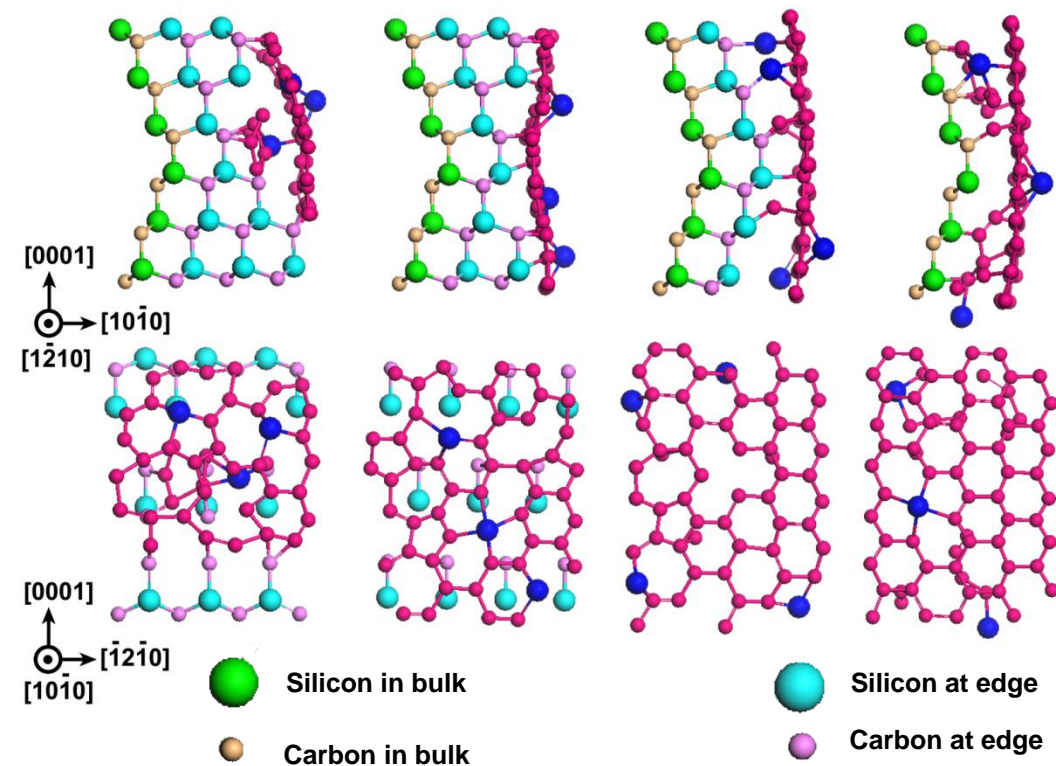
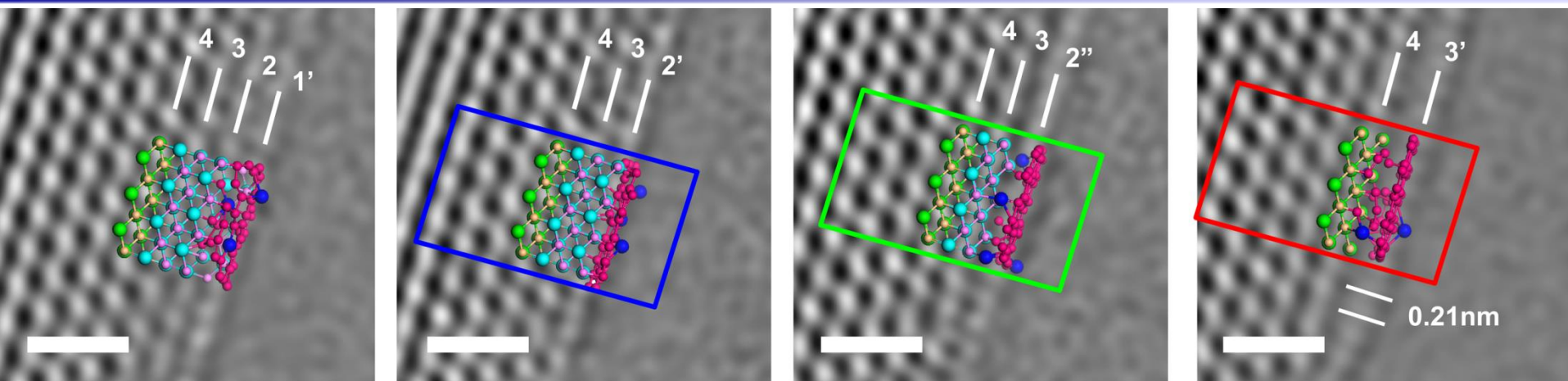
rotation



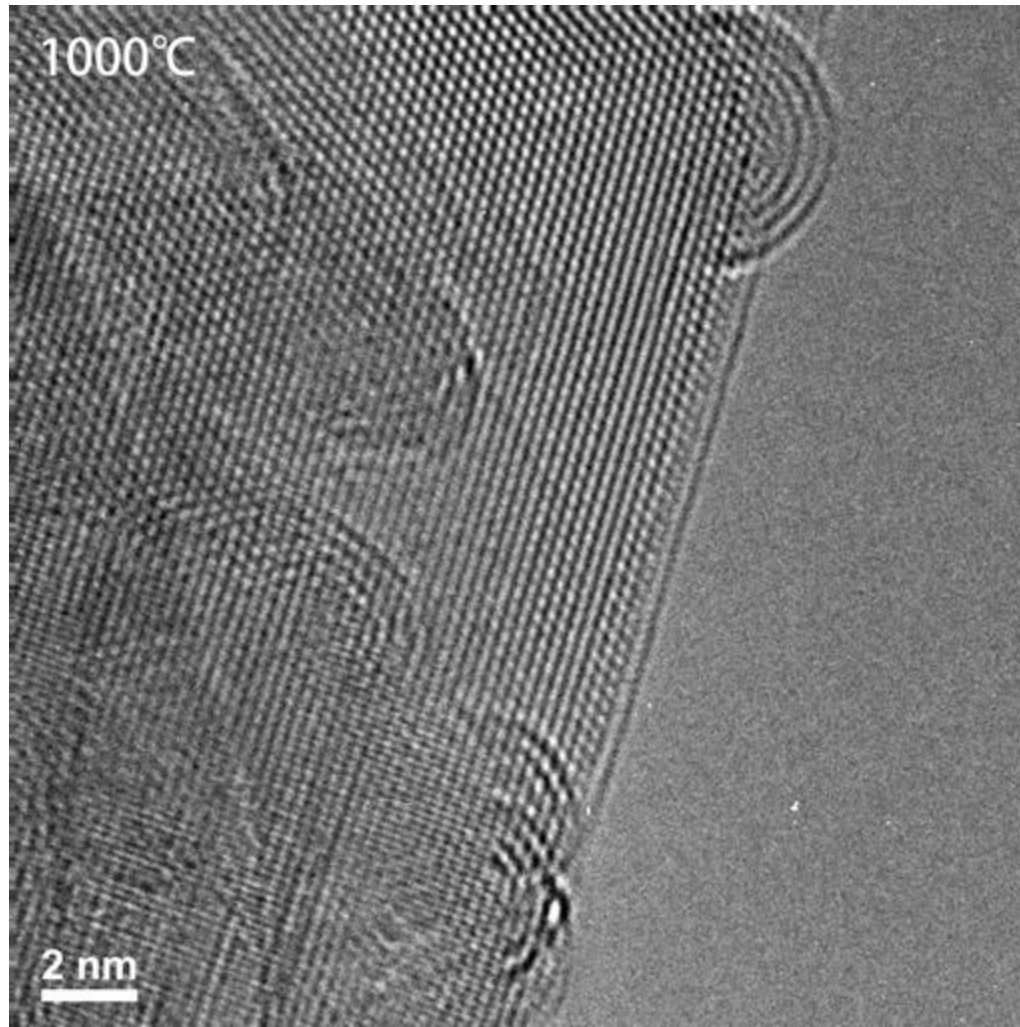
Speed: x20
Dynamic Characterization

Watching How Three-layer SiC Transforms to Monolayer Graphene

Unpublished results

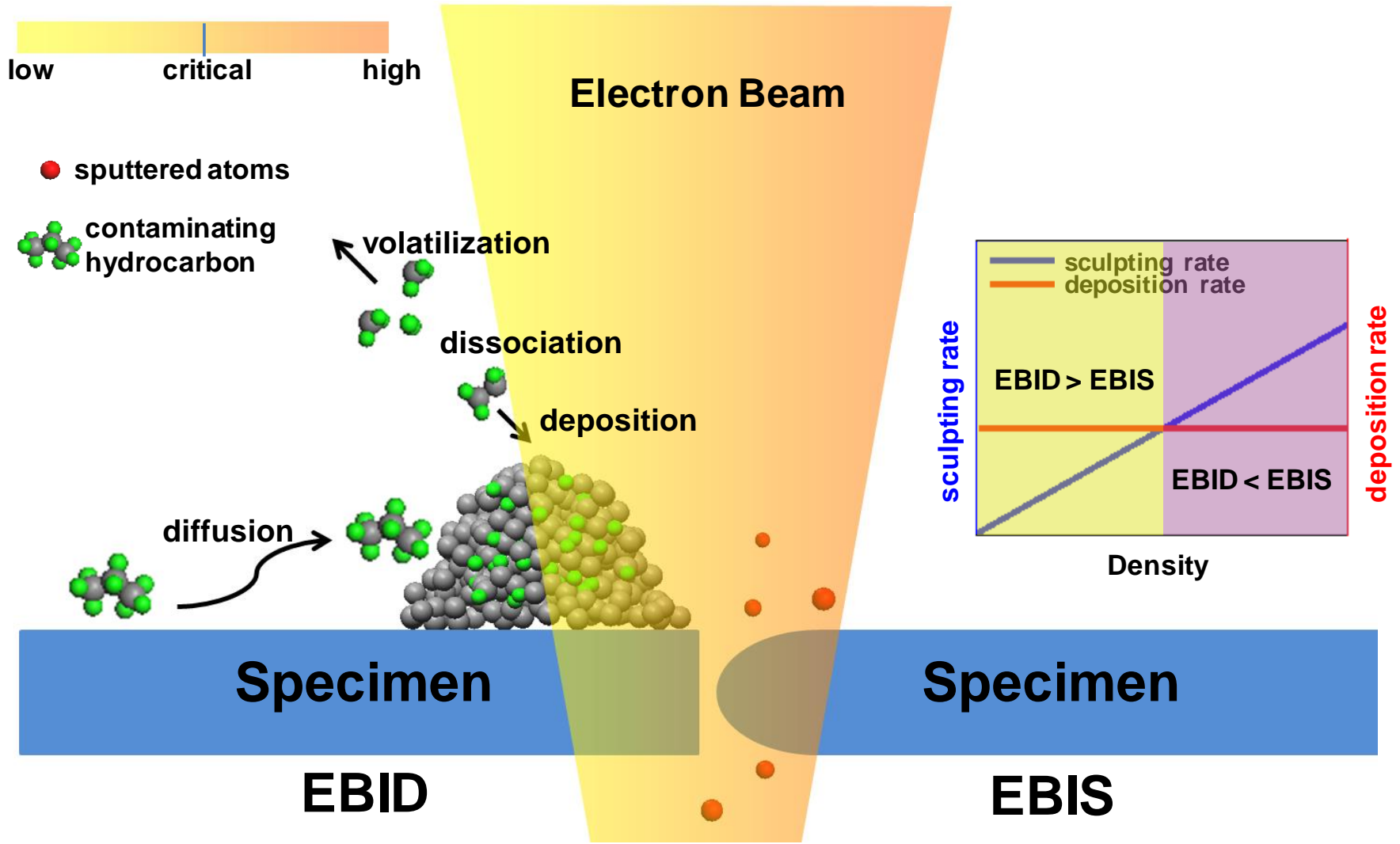


Graphene growth from SiC

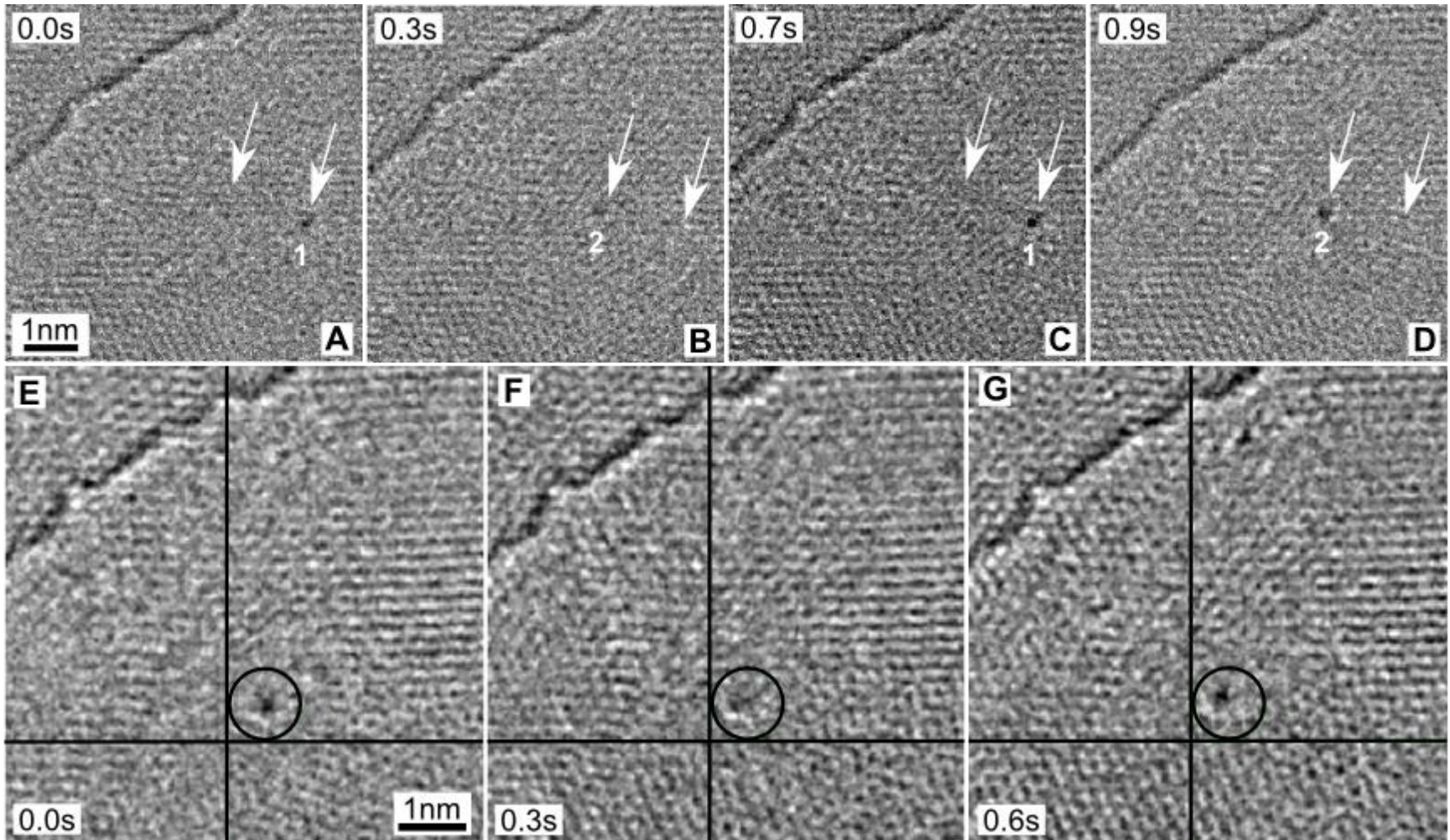


Unpublished results

◆ Tailoring structure: mechanism– by irradiation

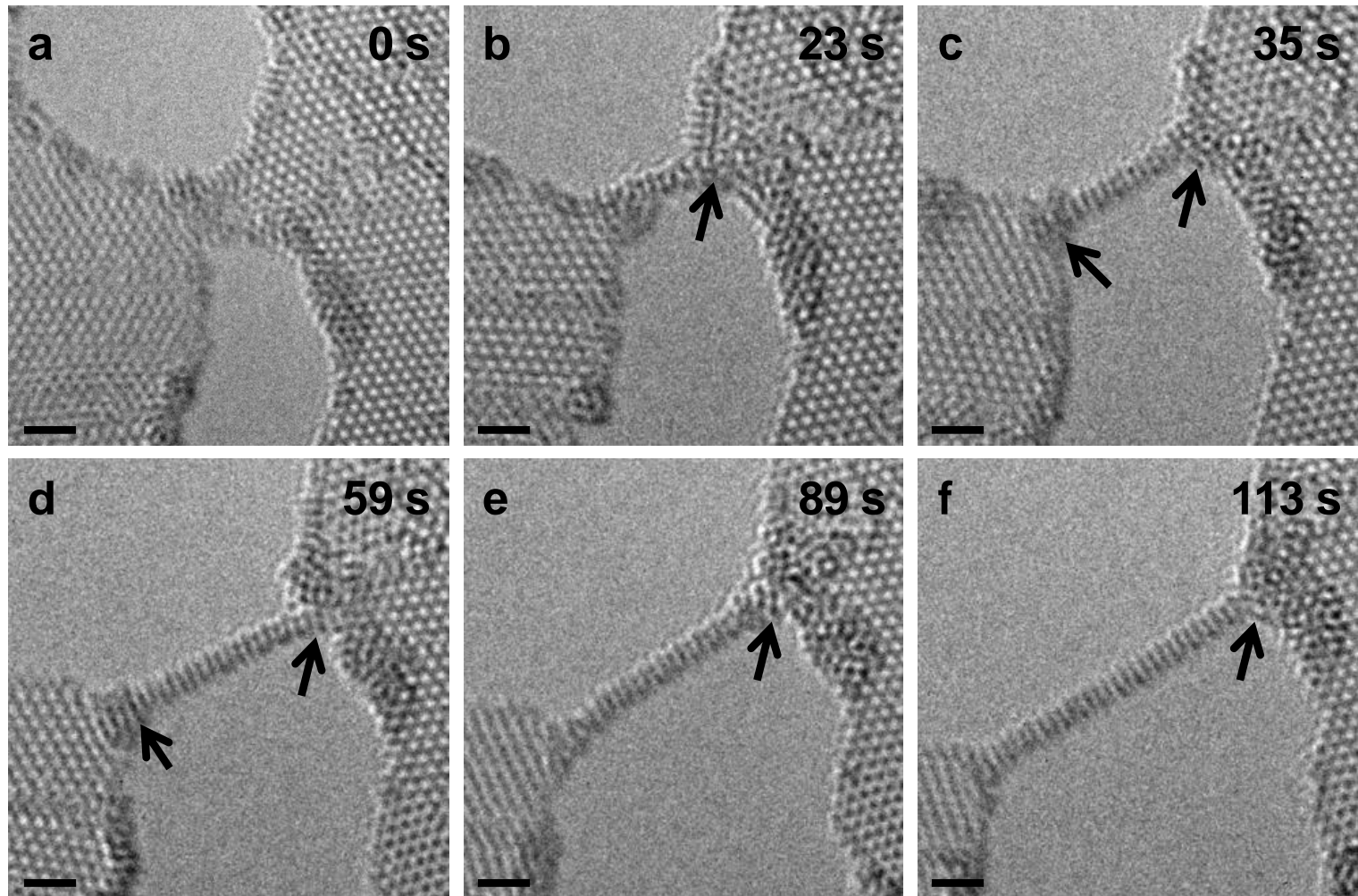


Tailoring structure: *sculpting*--create defects—manipulating atoms



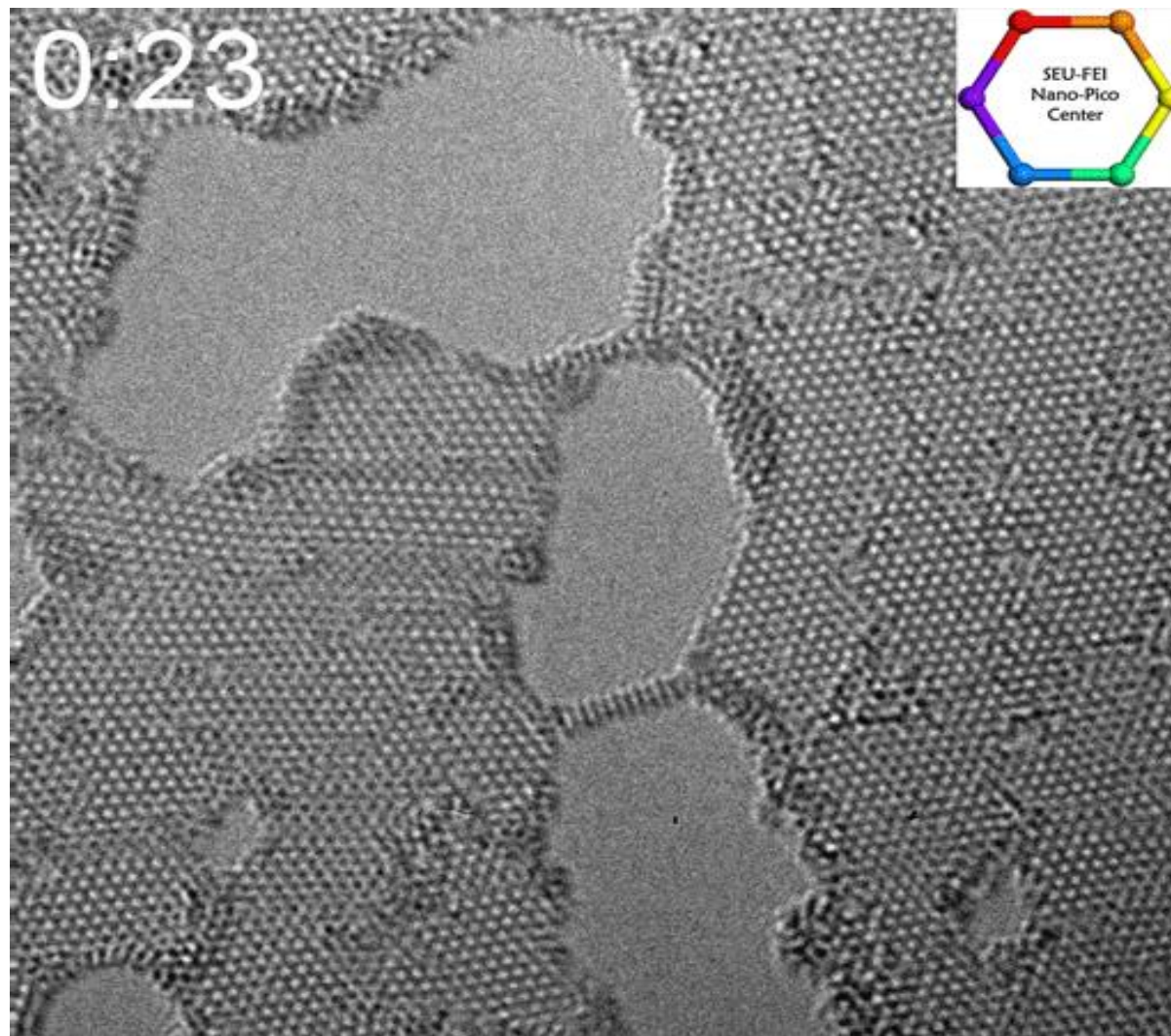
Migration and Trapping of metal atoms on graphene

Tailoring structure: mechanism--energy difference

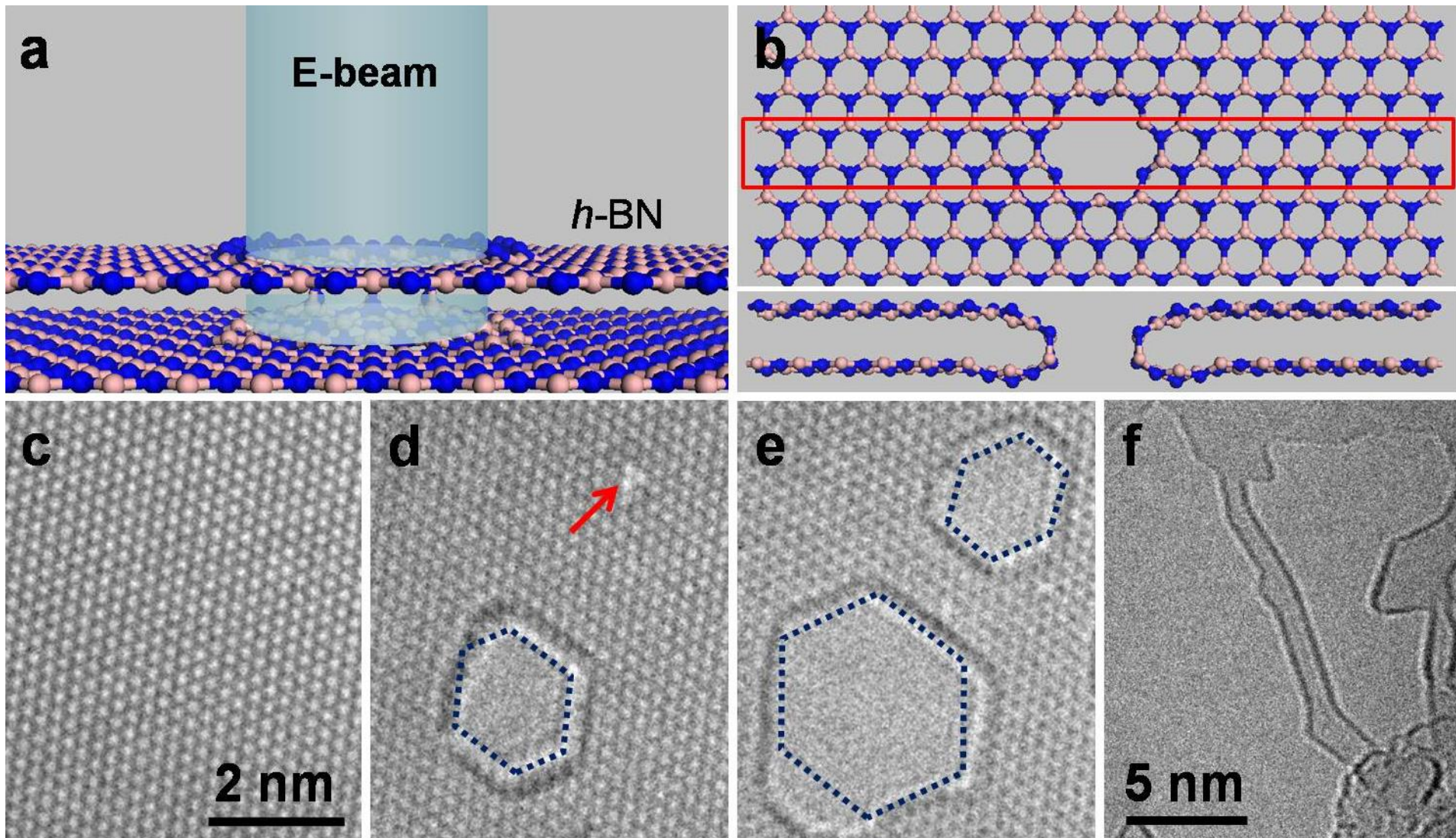


Possible **narrowest molybdenum sulfide nanoribbon**

Tailoring structures by energy difference

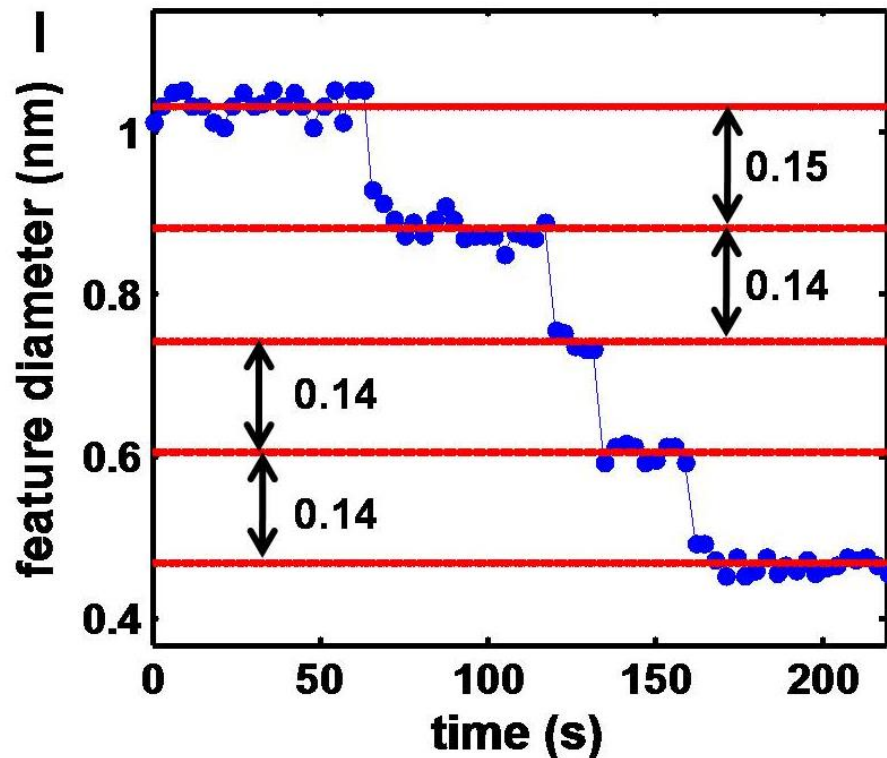
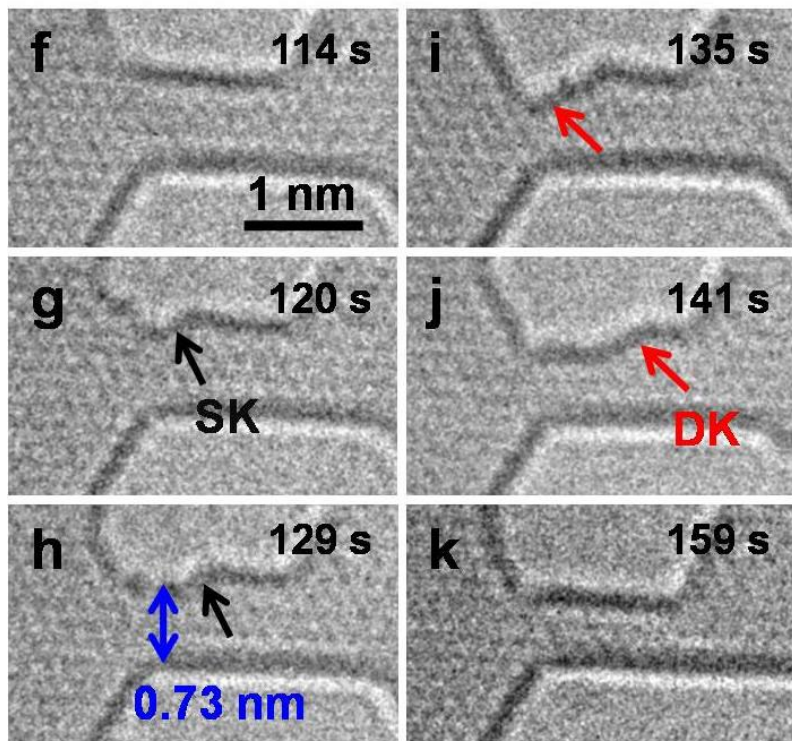
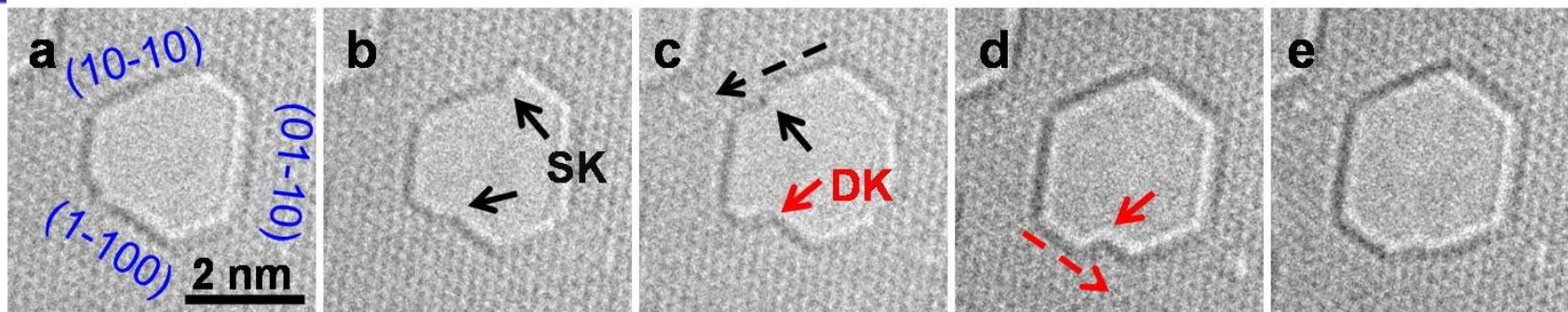


Nanofabrication at atomic scale



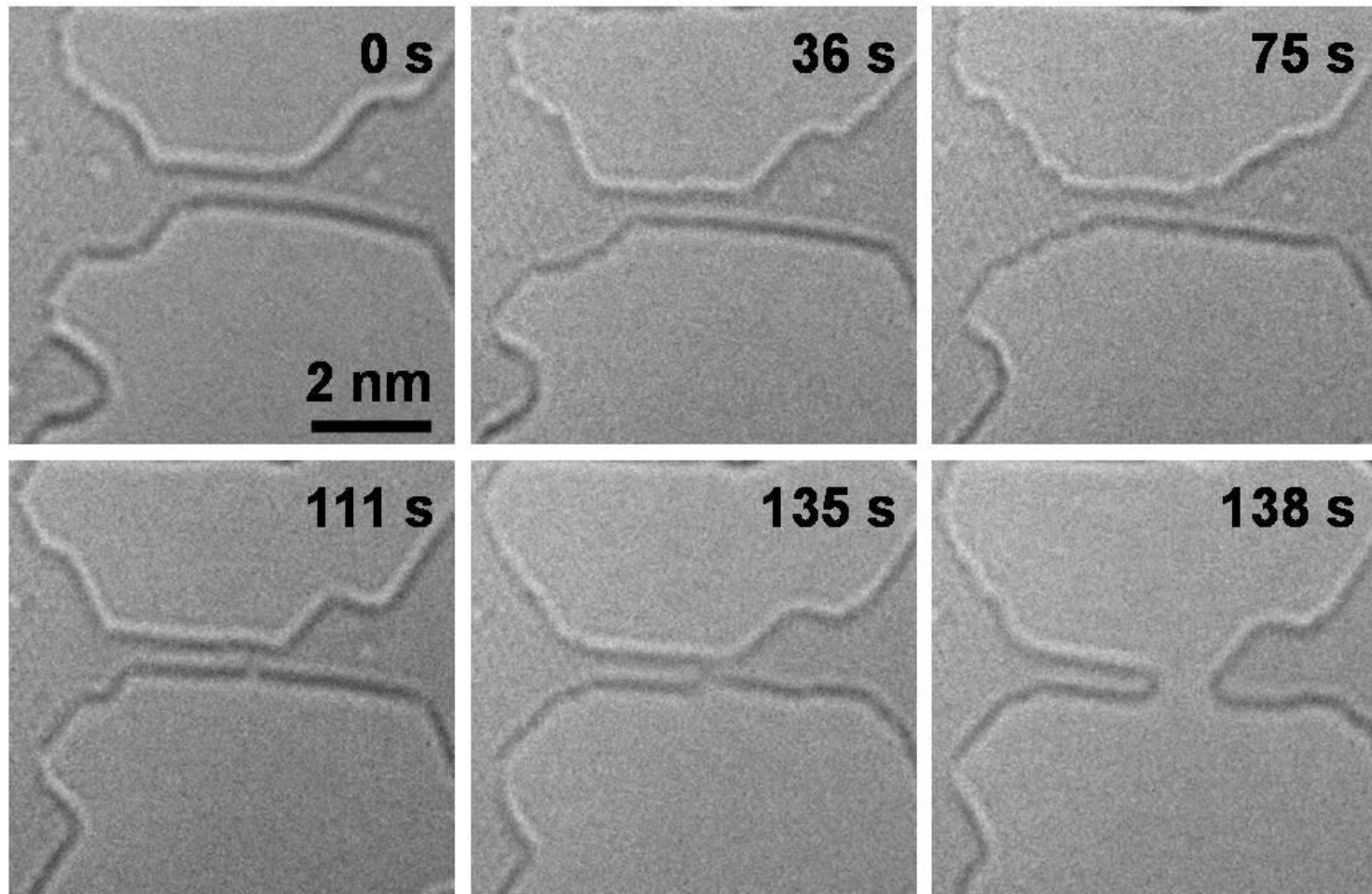
BN tubular structure from bilayer structures

Nanofabrication at atomic scale



Precisely thinning of the tubes: 0.14nm

Nanofabrication at atomic scale

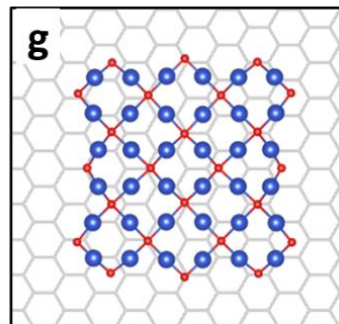
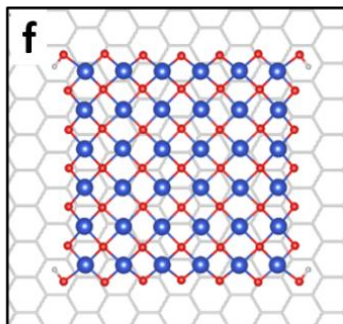
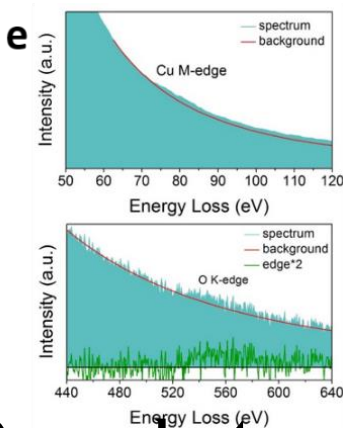
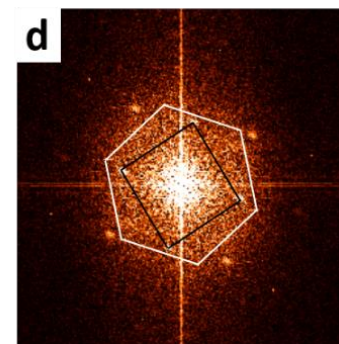
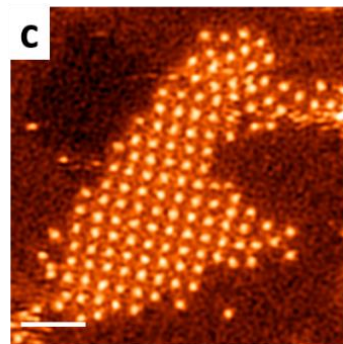
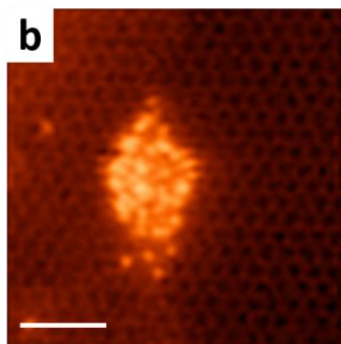
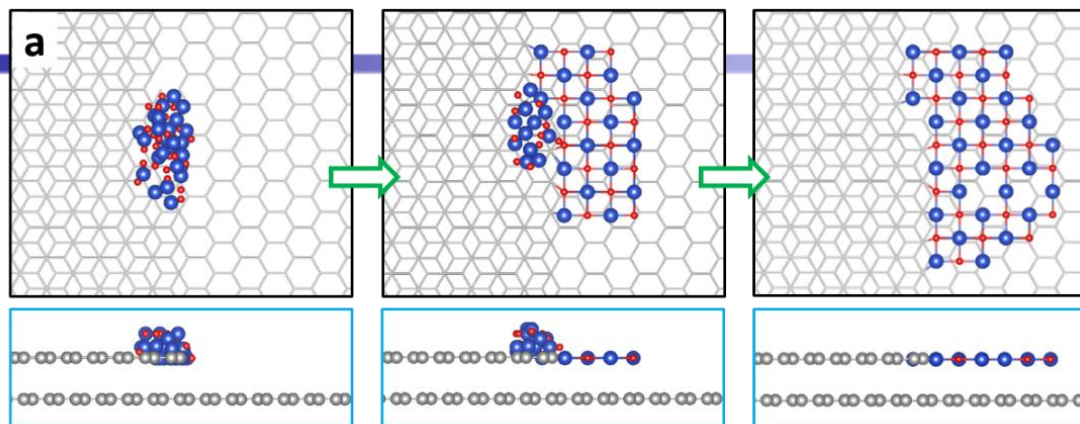


BN tube with diameter of ~ 0.45 nm is the smallest stable tube.

Nanofabrication at atomic scale: new 2D materials



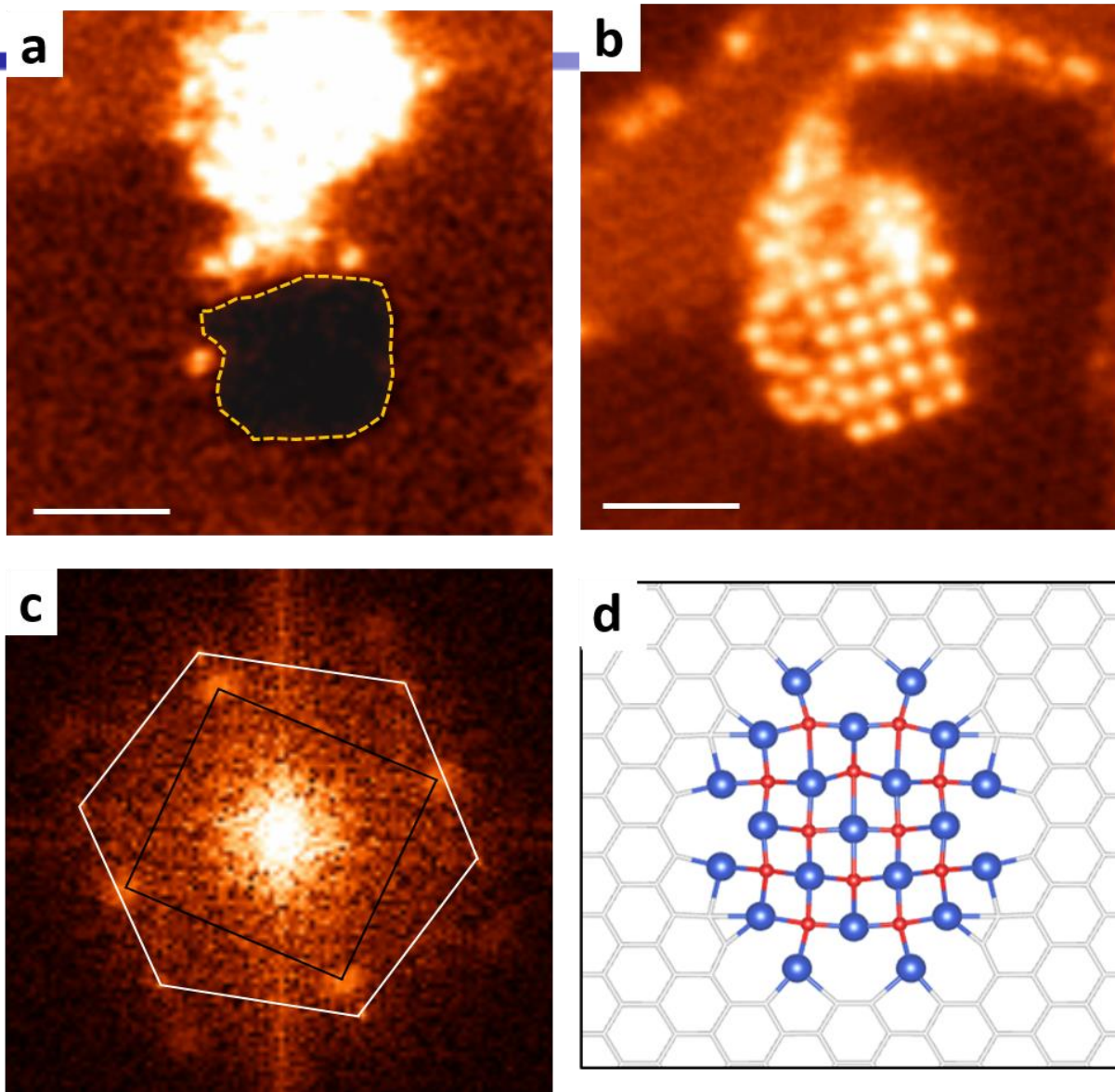
Kuibo Yin



Monolayer CuO nanosheets on a graphene substrate

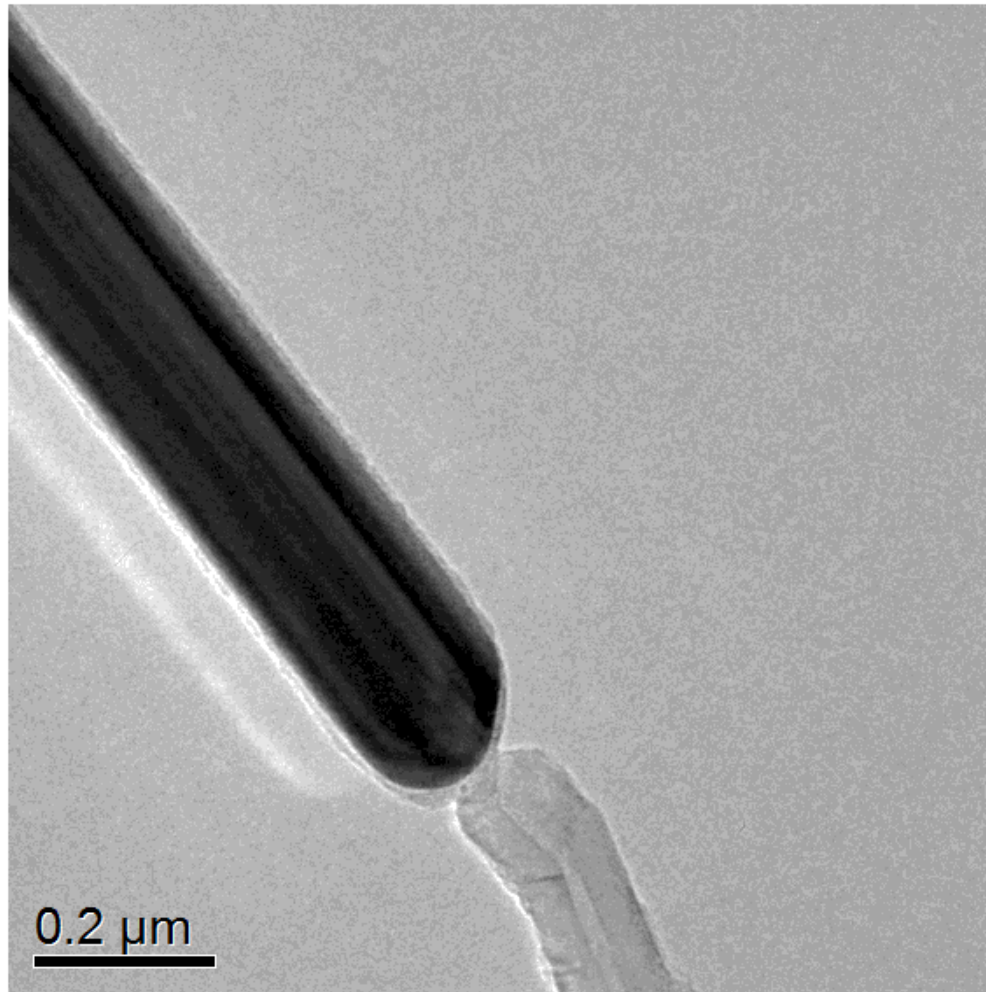
2D Materials, *in press*

Nanofabrication at atomic scale: new 2D materials



An unsupported monolayer CuO in a graphene pore

Tailoring structures -for new structure design--deposition



Acquisition date: 7/25/2011

Acquisition time: 9:46:16 PM

Exposure time: 0.1 s

Indicated Magnification: 9900.0

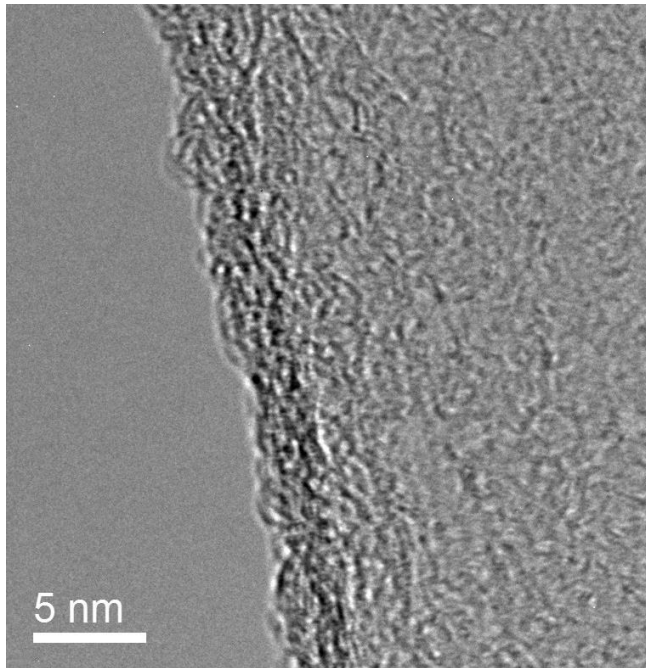
Investment casting of graphene-based structures

Joule heating can also drain away the silver to form graphitized single carbon nanotube with the STM-TEM platform

Carbon 50, 2845(2012)

Tailoring structures -for new structure design

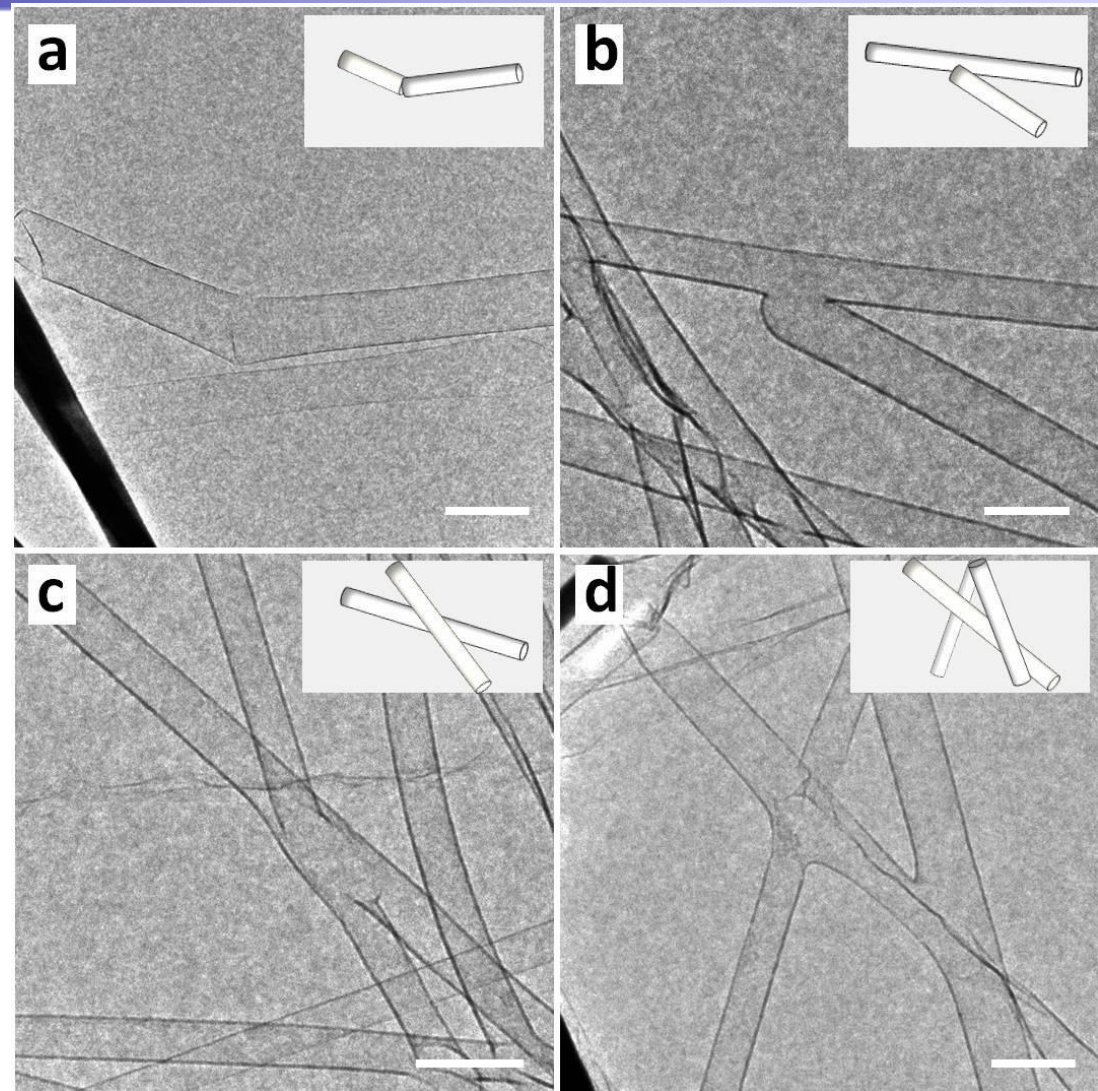
May find applications in nanofluidics, graphene-based devices



partially graphitized

compact graphene structures

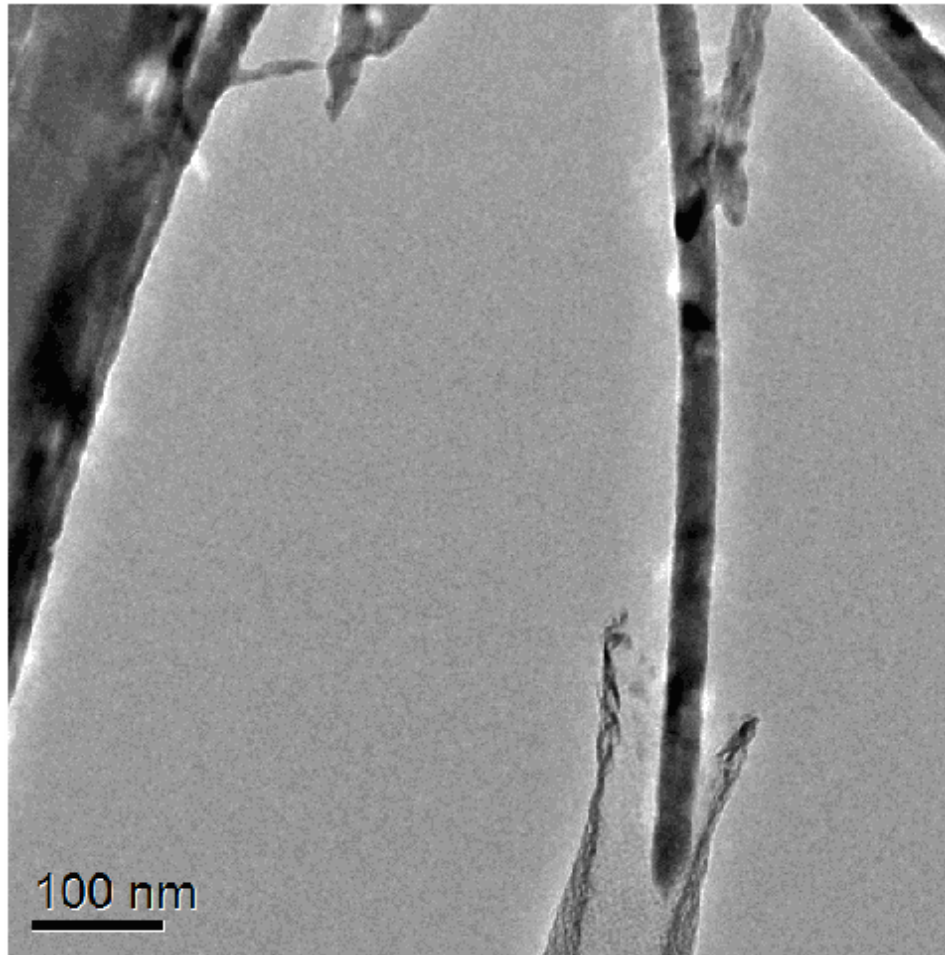
Carbon 50, 2845(2012)



(a) head-to-head connection. (b) A 'Y' shape connection. (c) A 'X' shape connection. (d) Complex connections.

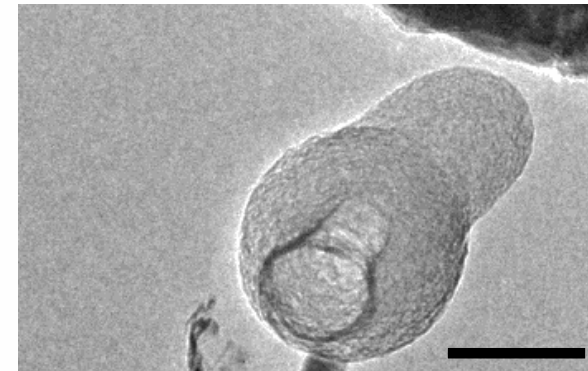
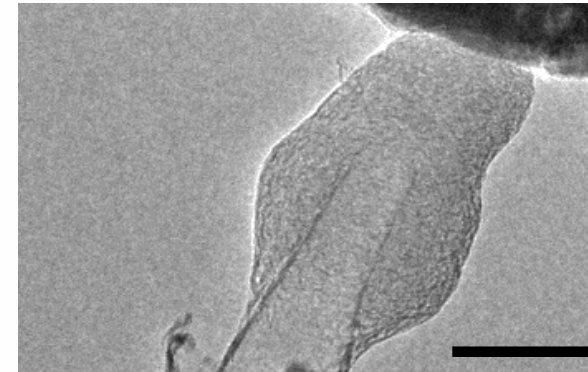
Tailoring structures - new structure design

Mechanical property of Graphene structures



Exposure time: 0.2 s

New Software from Gatan



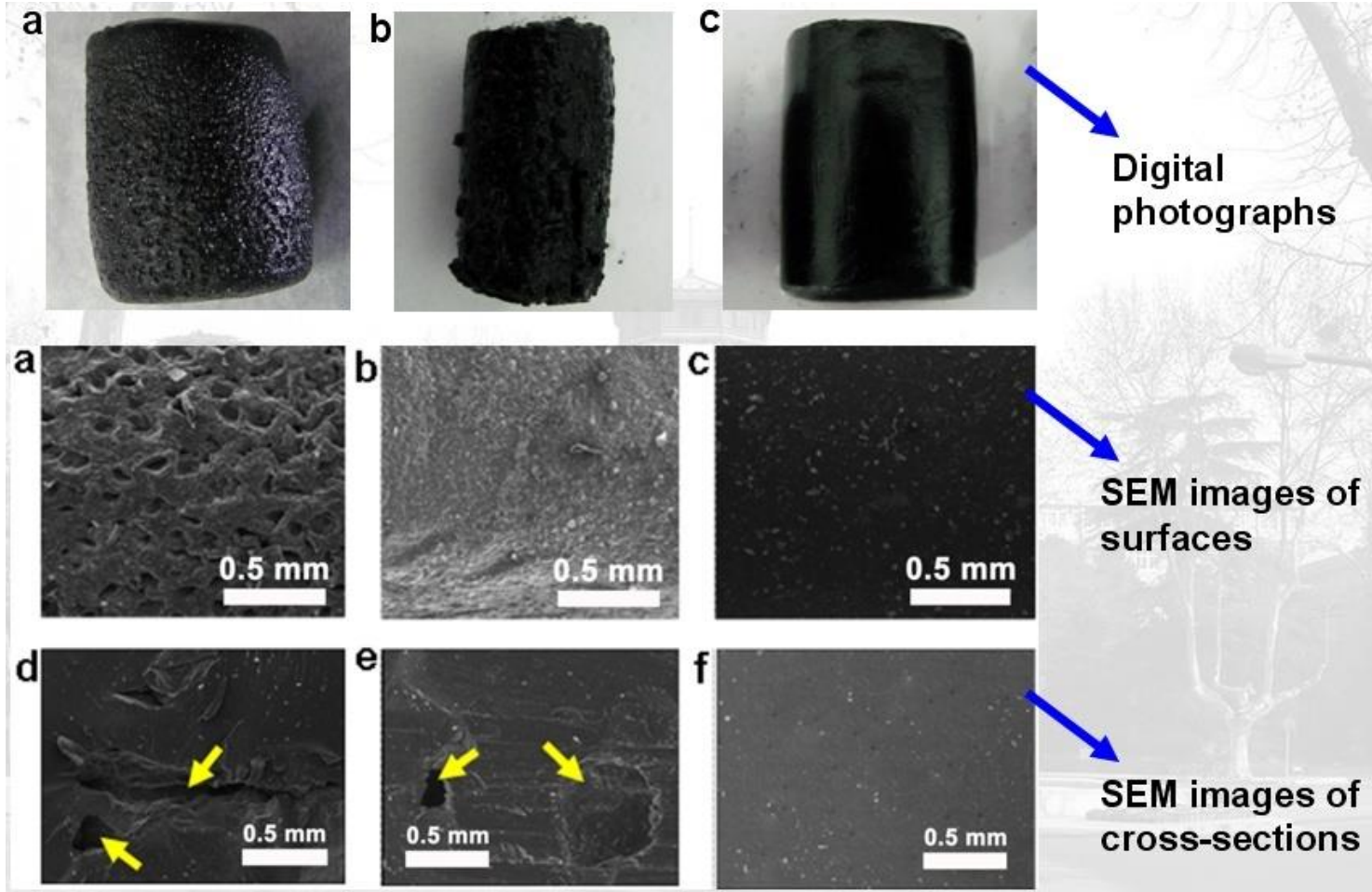
Nice mechanical behavior of graphene-based structures

In situ property characterization --for application

Porous graphene



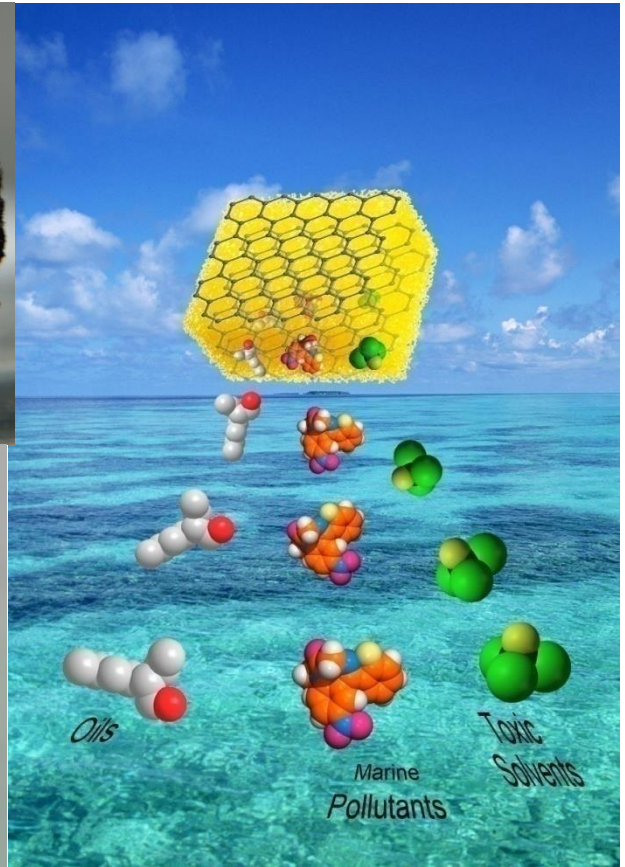
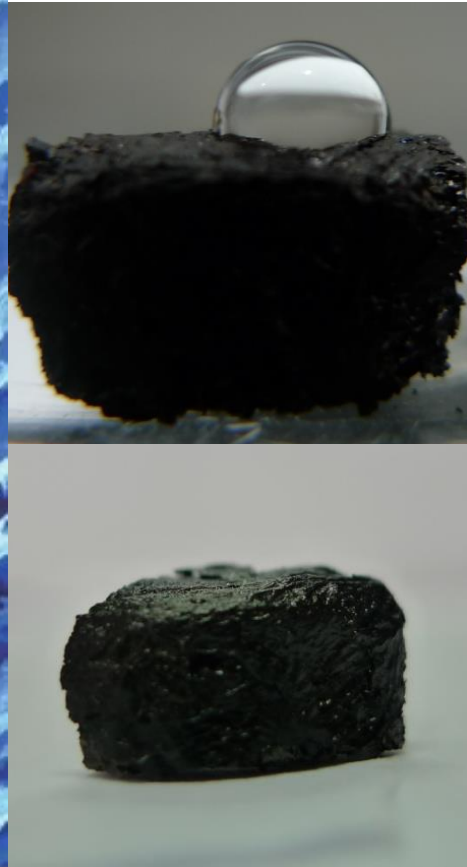
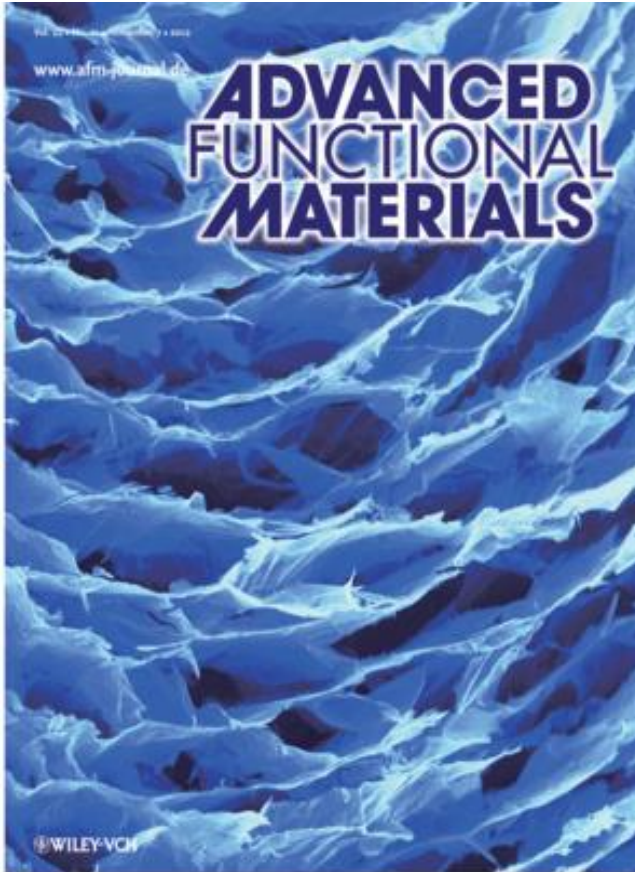
Compact Graphene



Tailoring 3D graphene structures

In situ property characterization --for application

Spongy graphene (SG) as a highly efficient and recyclable sorbent for oils and organic solvents (first time report)



Adv. Funct. Mater. **22**, 4421 (2012) Cover article

Superhydrophobic property

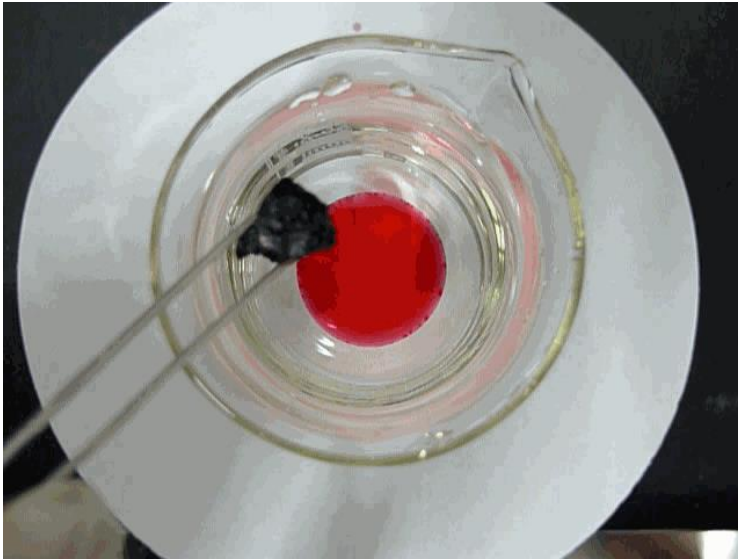
Scientific Reports **3**, 2117 (2013)

In situ property characterization --for application

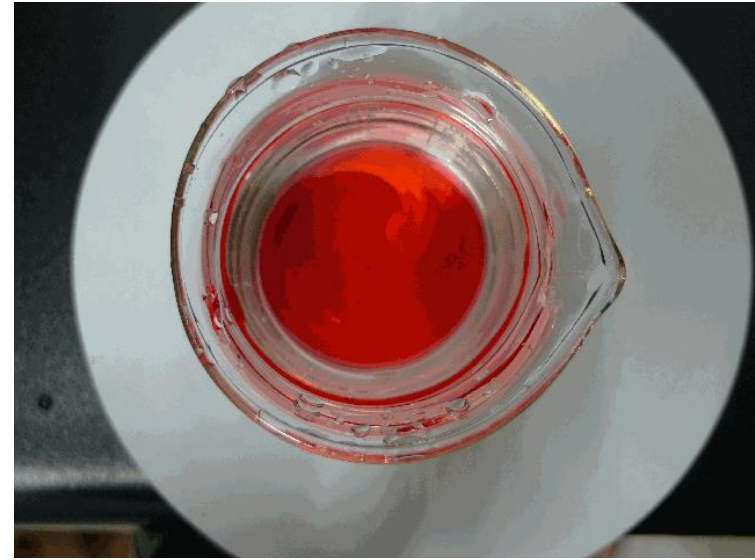
Dynamic adsorption process

Superhydrophobic property

oil on artificial seawater



Toluene on artificial seawater



Absorb: Petroleum products and fats + toxic solvents (toluene and chloroform)
(absorb up to 800 times its own weight)

SEU-JGRI Joint Center for Advanced Carbon Materials



Litao Sun



Chunxiang Xu



Xinli Guo



Z. X. Shi



Jinlan Wang



Zhenhua Ni

Principal Investigators



Joint Center between Southeast University and Jiangnan Graphene Research Institute

In situ property characterization --for application

Dynamic adsorption process

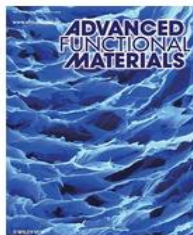


highly efficient and recyclable

Research History- Spongy graphene as sorbent for oils/organic solvents

Progress of the environmental application in our group

First Paper published
(AFM2012, Cover)

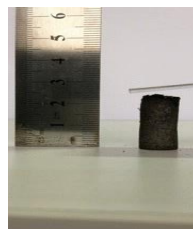


First Patent

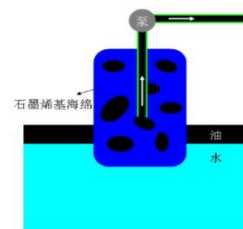
High efficiency
(J. Mater. Chem. A)



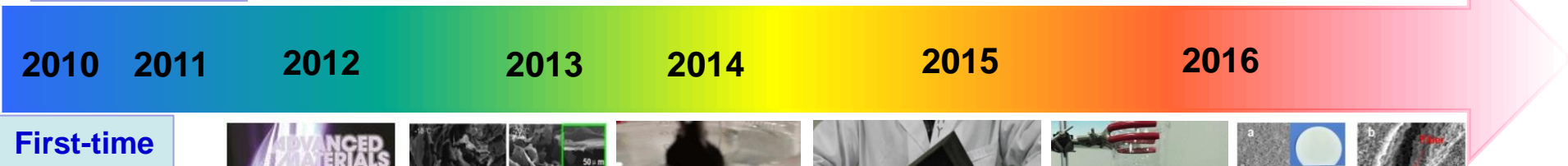
Compressible sponge



Continuous separation

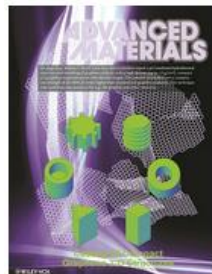


Sorption for trace oil

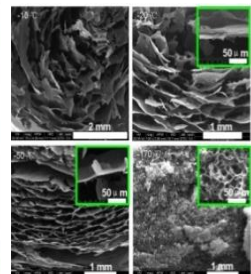


2010 2011 2012 2013 2014 2015 2016

First-time Observed



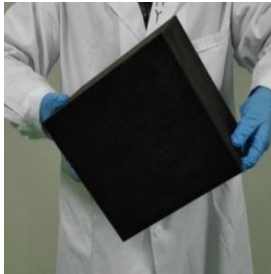
Shape control



Structure control
(Sci. Rep.)



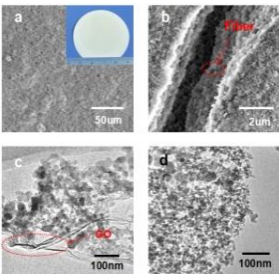
Low cost
Adv. Mater.;
Small



Large scale sponge

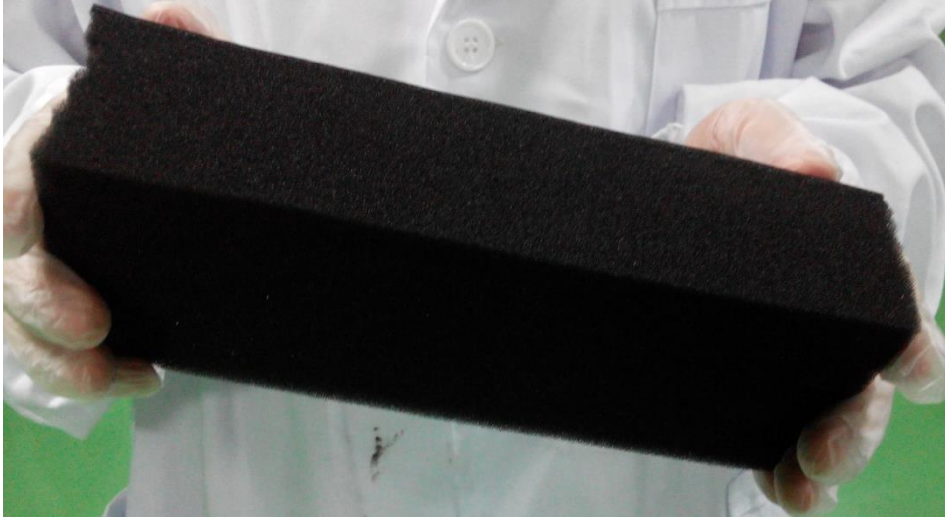


Metal mesh combined



Separation for micro emulsion

Industrialization progress: **graphene based sponge**

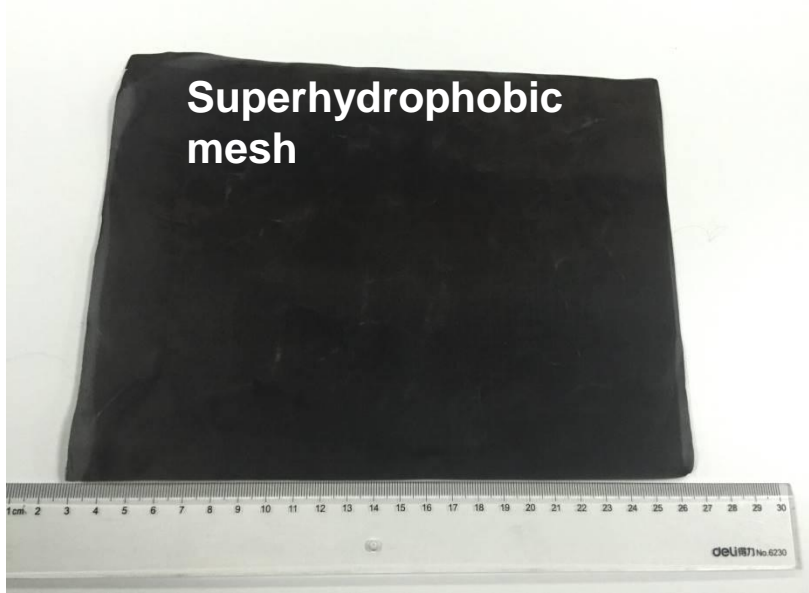


- ◆ Large-scale production
- ◆ Low cost
- ◆ High sorption capacity
- ◆ Good recyclability

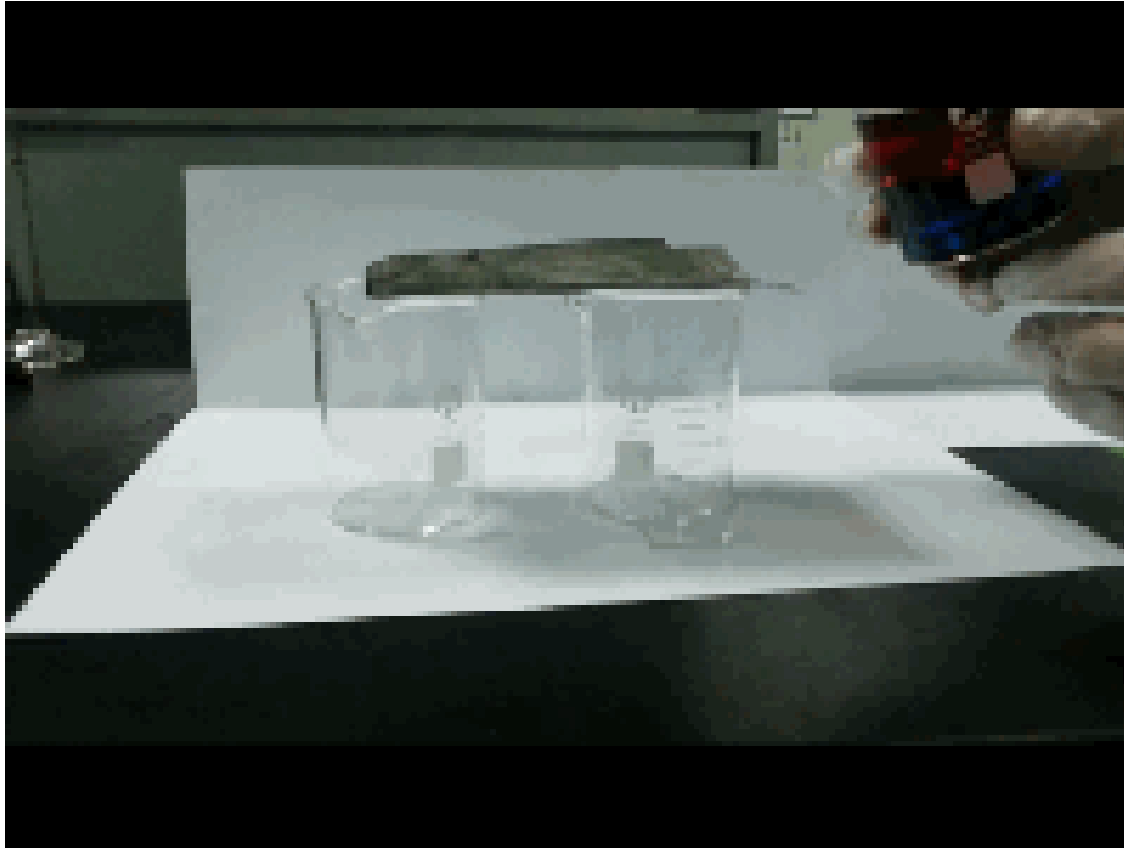
Continuous separation



Industrialization progress: separation mesh



Application based surfaces



Graphene-based film for separating the oil and water

Industrialization progress: separation mesh



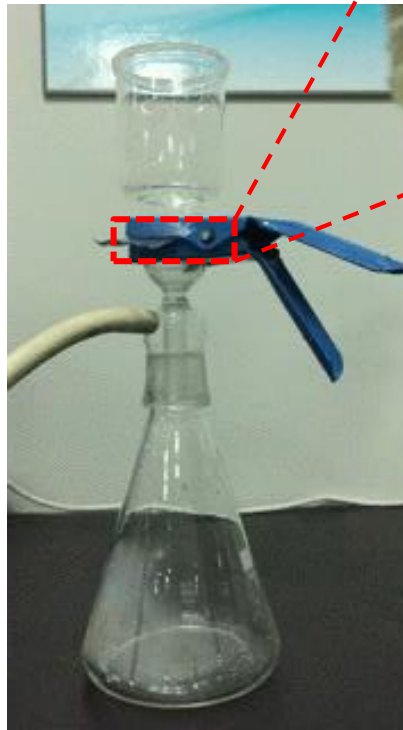
**Superhydrophobic
and superoleophilic**



**Superhydrophilic
and superoleophobic**

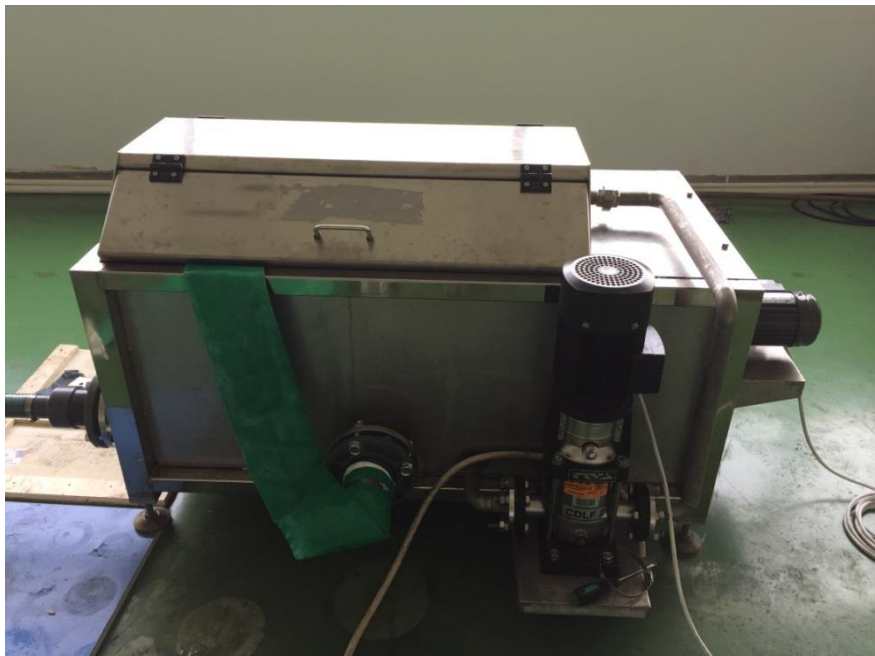
Red: oil; blue: water

Industrialization progress: separation mesh

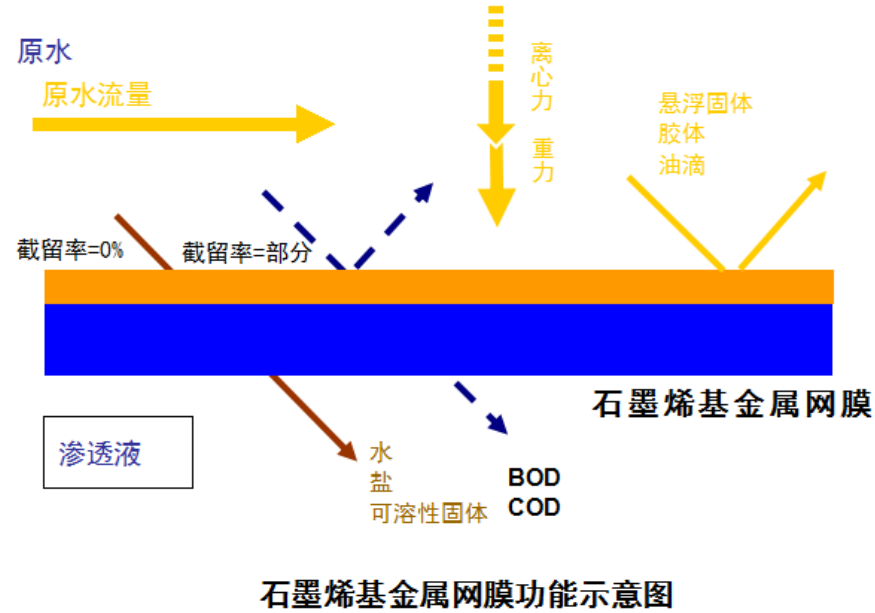


blue green algae
过滤蓝藻

Application based surfaces



Equipment for separate oil, water and solid particles



Equipment for separate oil, water and solid particles



Equipment for separate oil, water and solid particles



APPLICATIONS



常州市政府景观河，
10000t/d



泸州 20000t/d

惠州 52000t/d



Industrialization progress: separation mesh



Building product line for separation metal mesh 10000 m²/y

APPLICATIONS



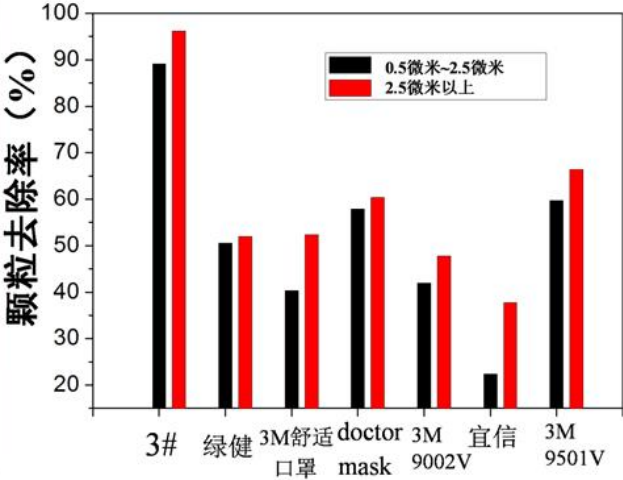
Other application – graphene based filter materials



Filter materials



Gauze mask sample



Comparison

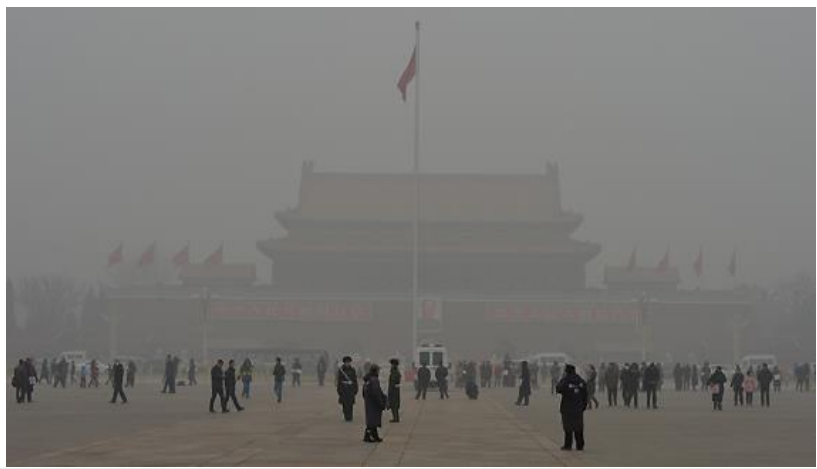
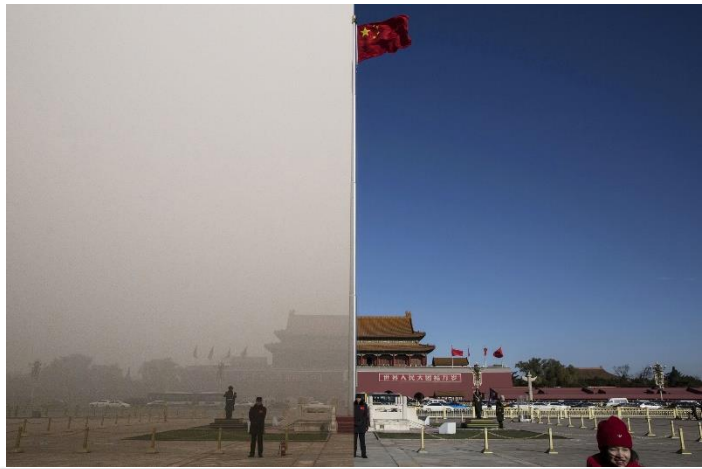


Other application—**graphene based filter materials**



Product line for filter materials: 200000 m²/y

Application based surfaces--Anti smog mask



The Central Business District, Beijing



WITHOUT SMOG



WITH SMOG

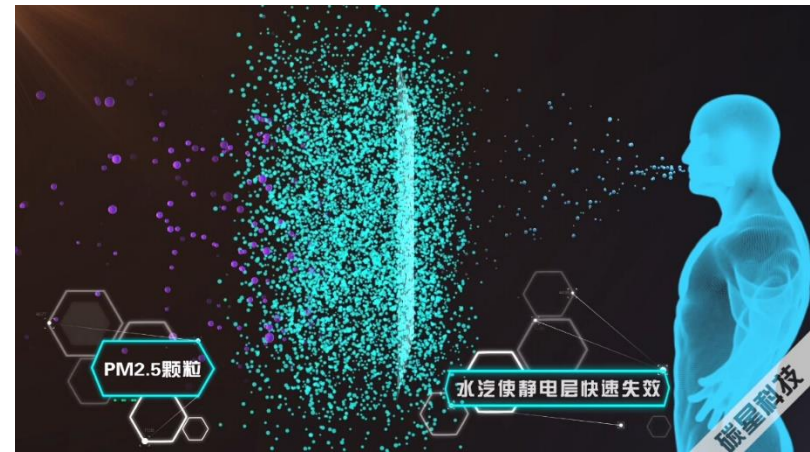
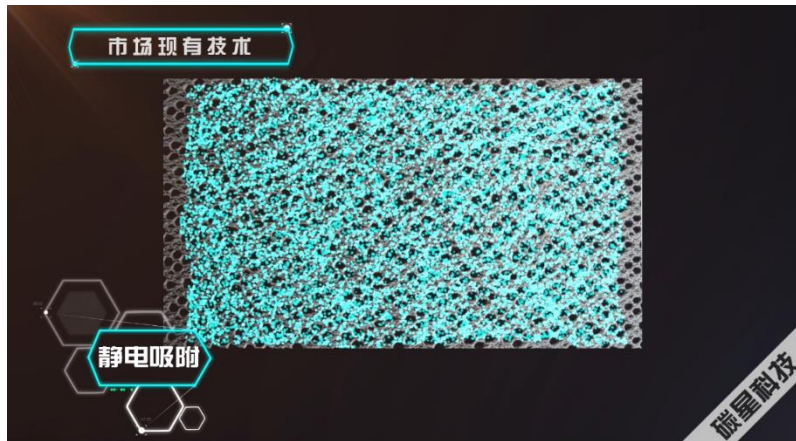
Application based surfaces--Anti smog mask



Anti amog masks

Application based surfaces--Anti smog mask

Anti smog mask: current technology

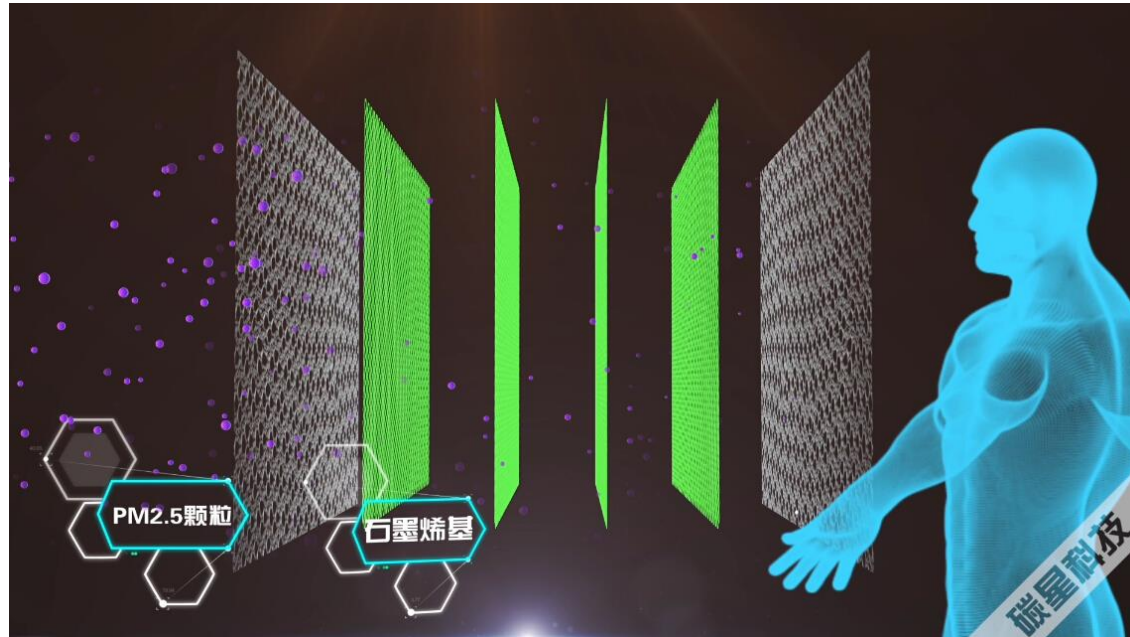


Mechanism: block big particles + adsorb small particles
(Melt-blown Nonwoven Fabric) (electrostatic charges)

Problem: disappear of electrostatic charges
under moisture condition or meet vapor (short-time available:<1h)

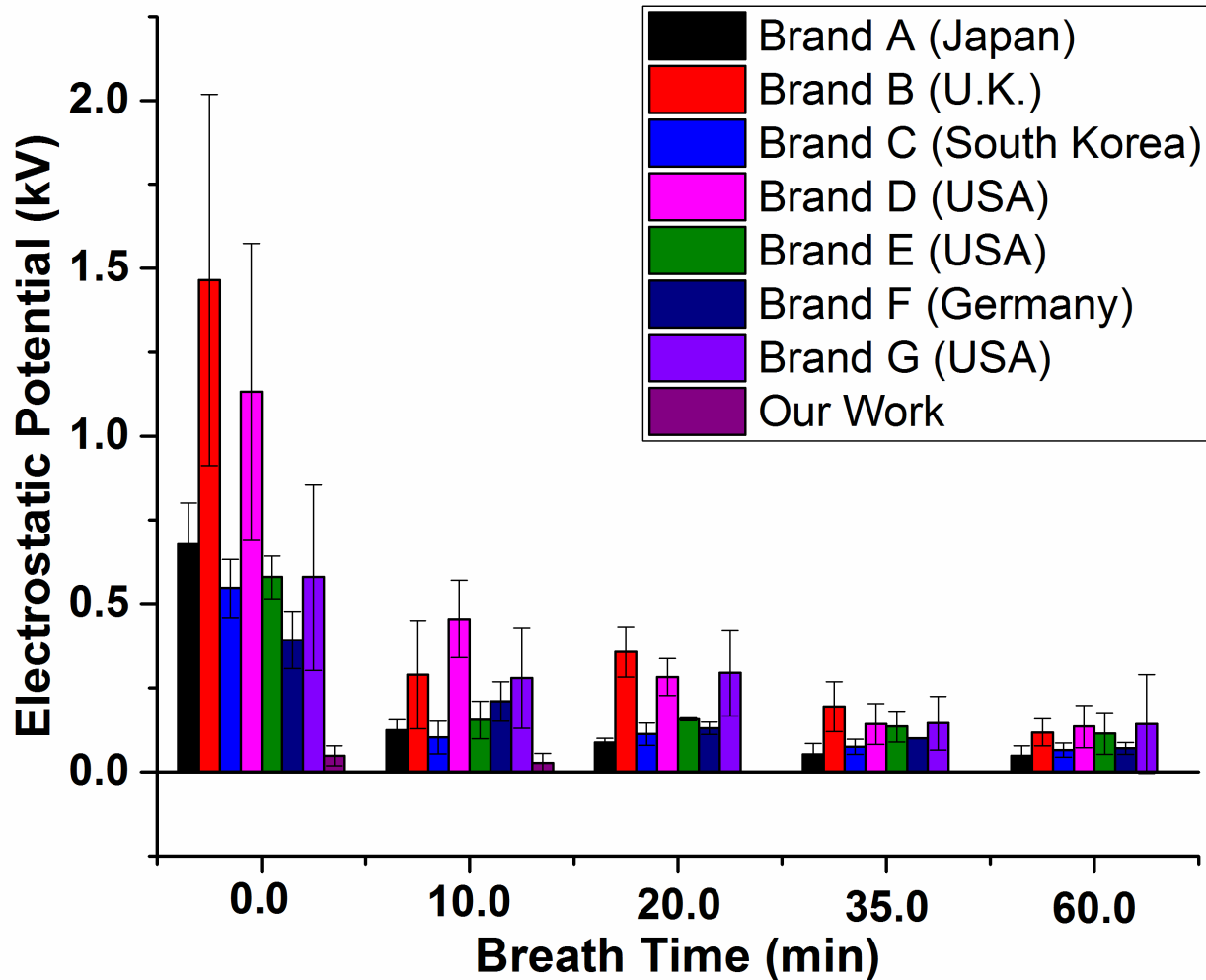
Application based surfaces--Anti smog mask

Functionalized graphene-based anti-smog mask

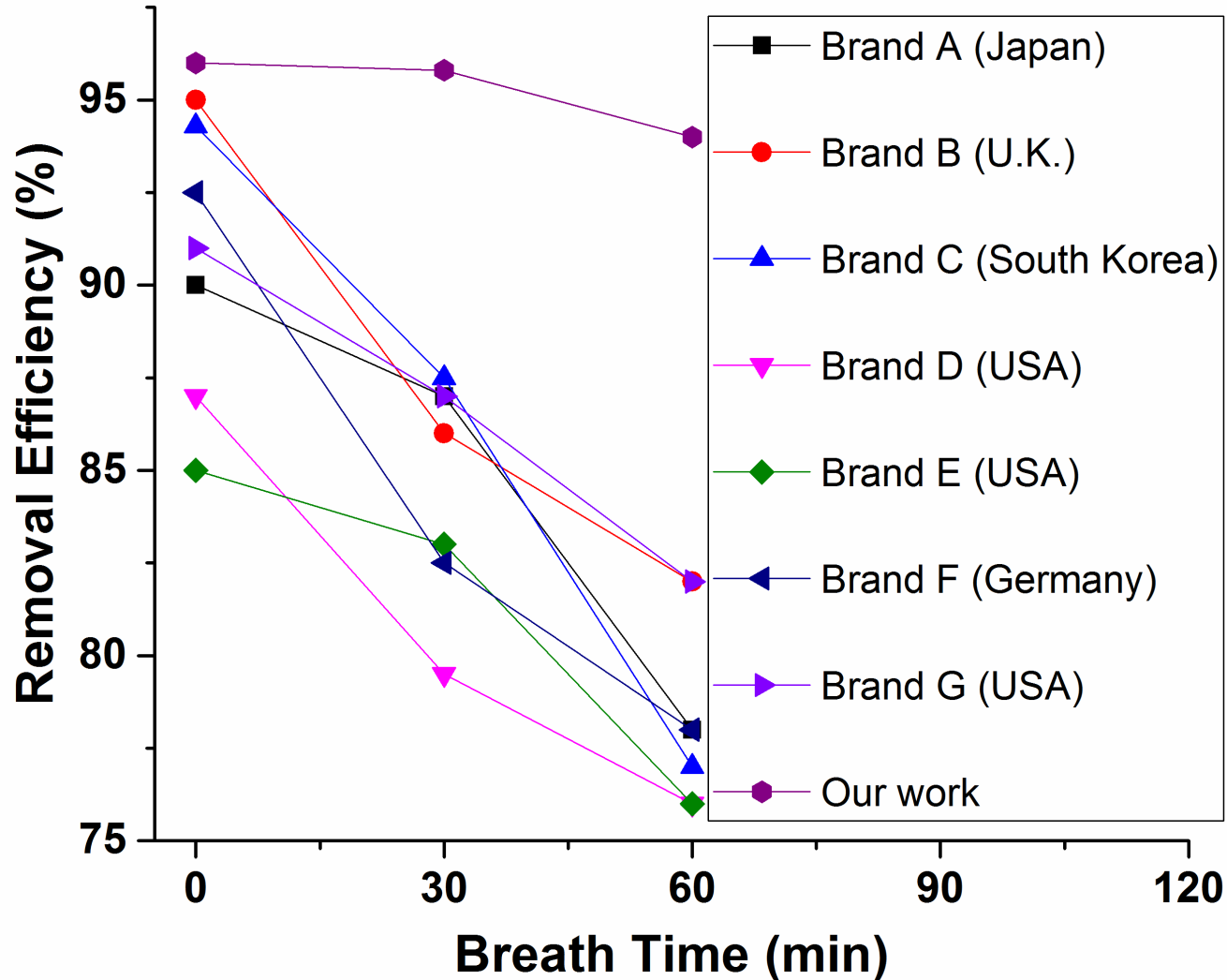


Advantage: large surface area of functionalized graphene with many defects (adsorption property for small particles)
(long-time available: around 1week)

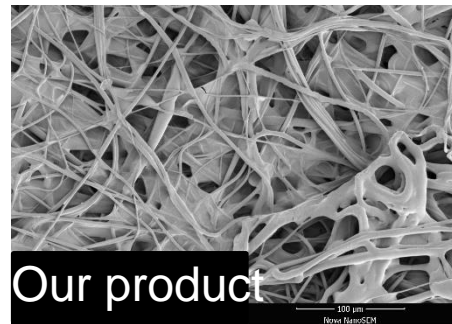
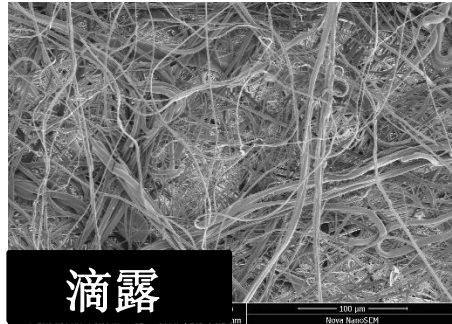
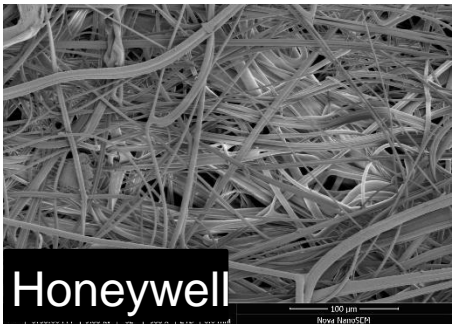
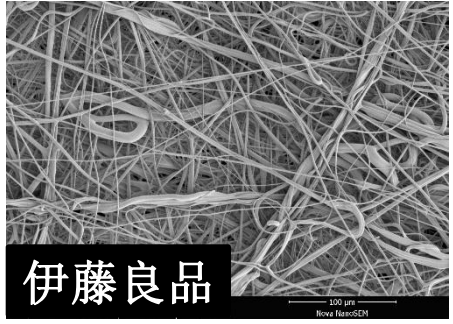
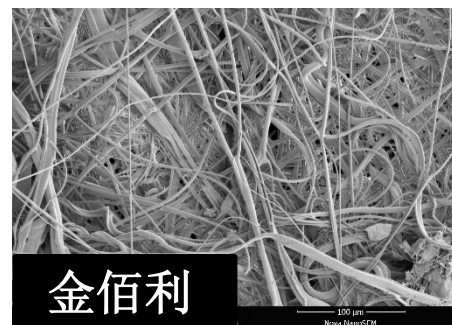
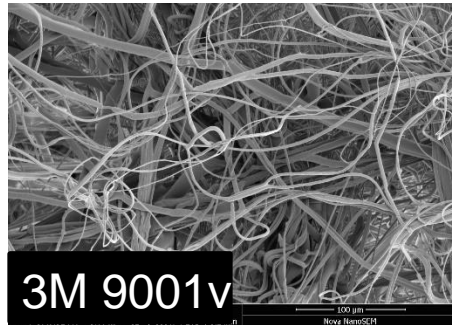
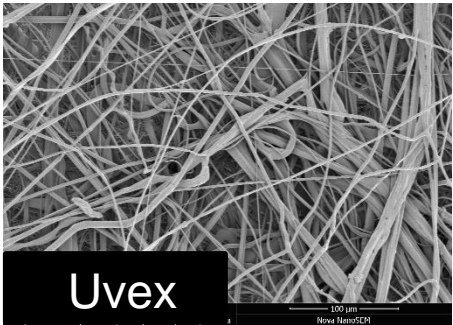
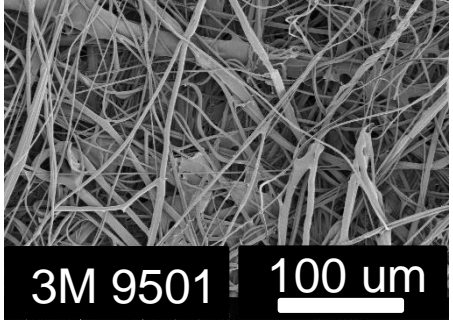
Application based surfaces--Anti smog mask



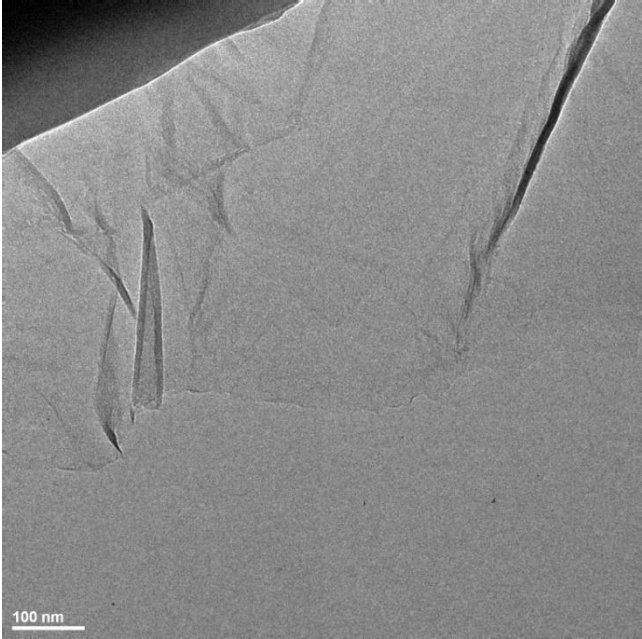
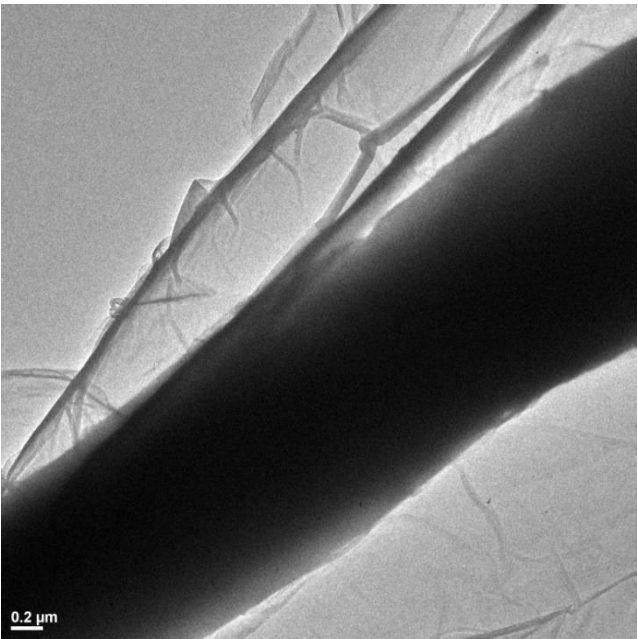
Application based surfaces--Anti smog mask



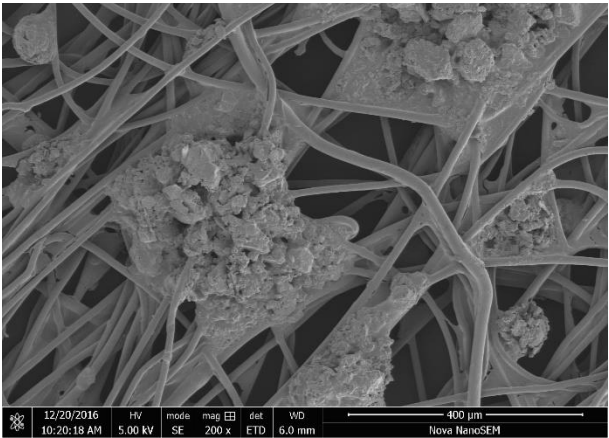
Application based surfaces--Anti smog mask



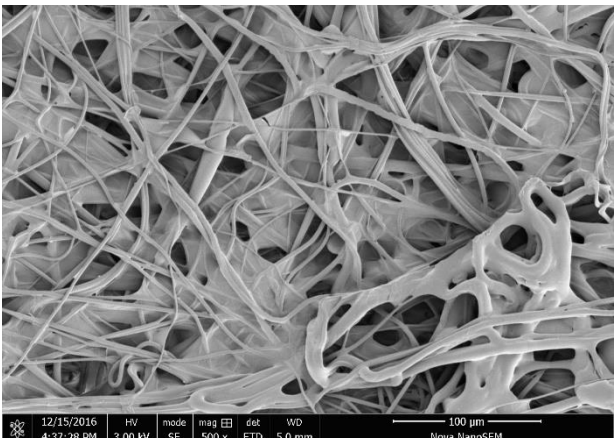
Application based surfaces--Anti smog mask



TEM images of filter materials with graphene

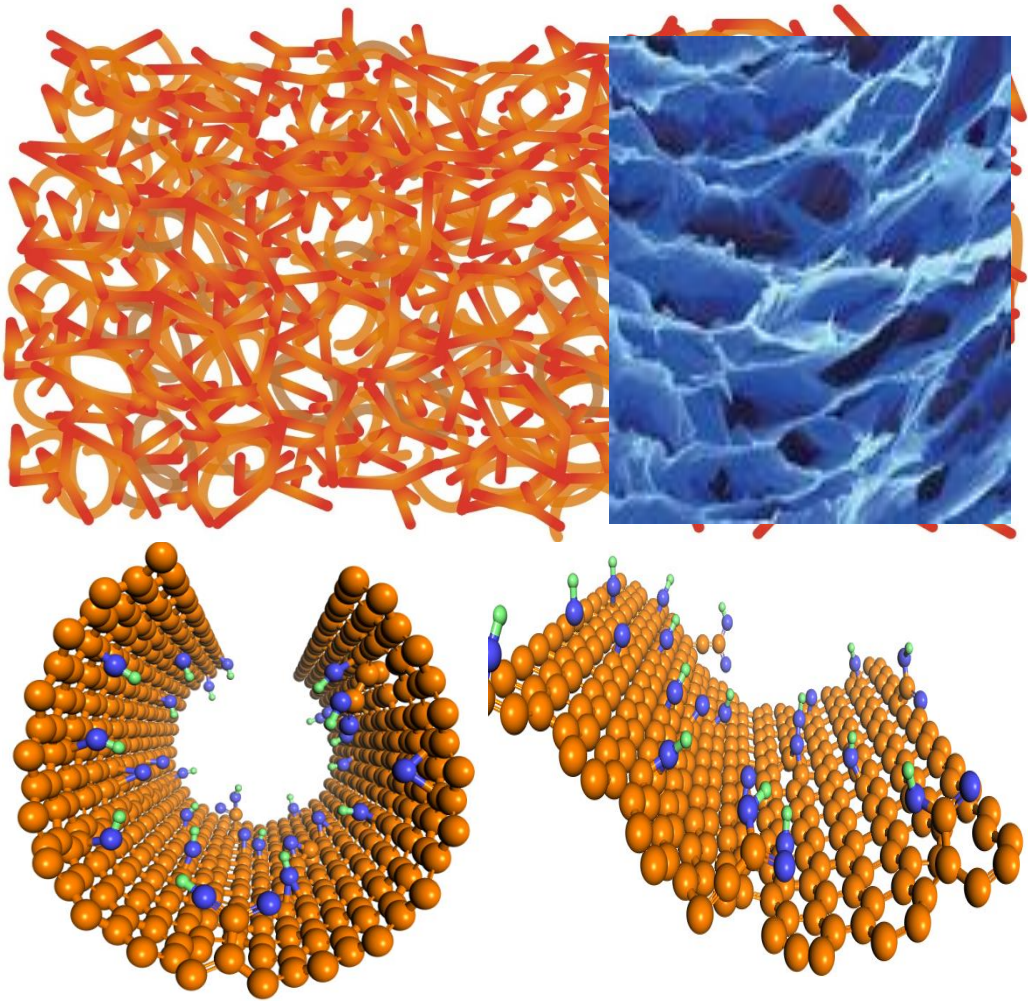


ununiform distribution

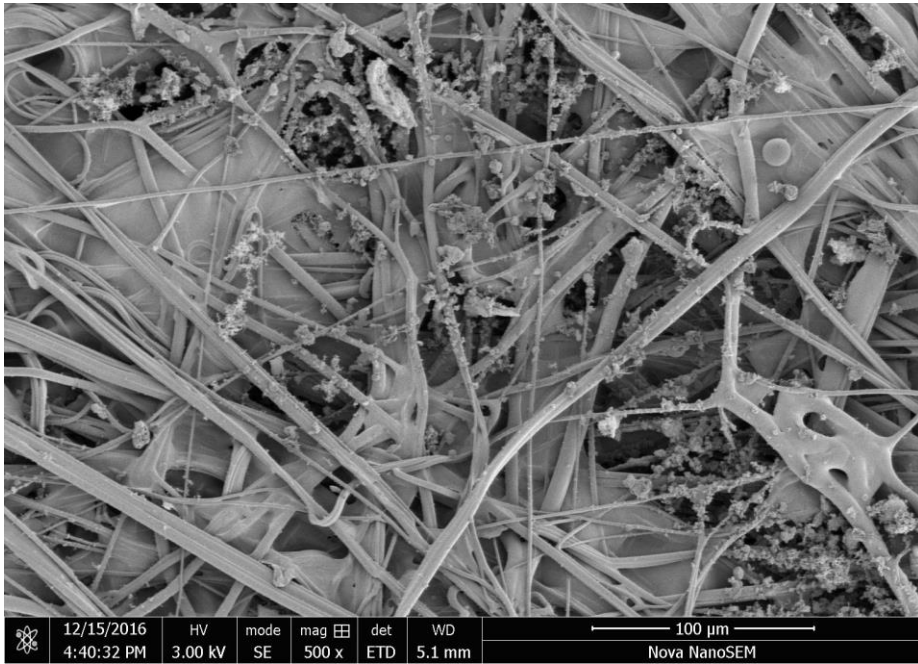


uniform distribution

Application based surfaces--Anti smog mask

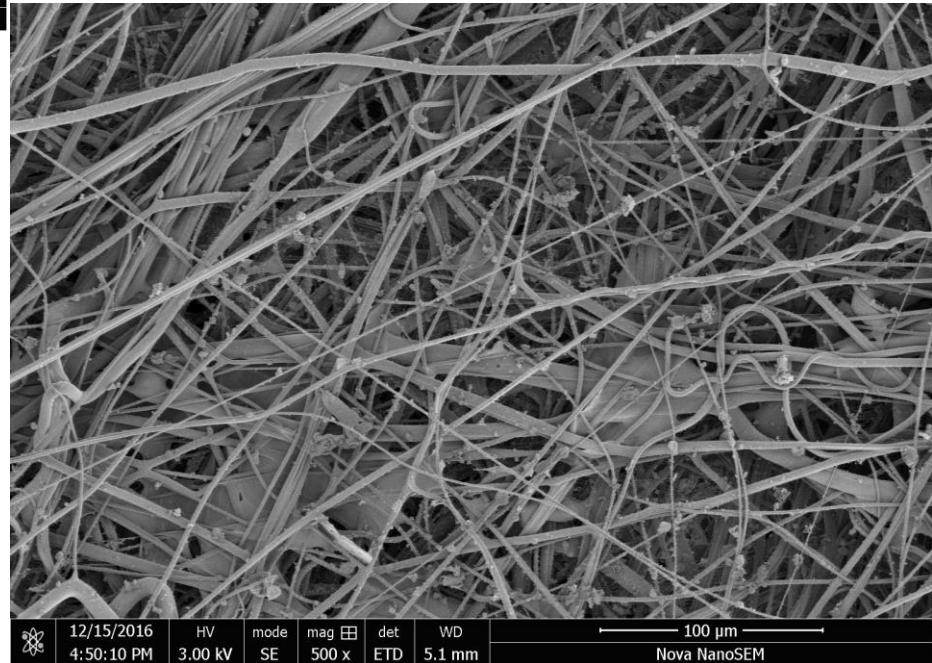


Functionalized graphene-based mask for fog and haze/smog

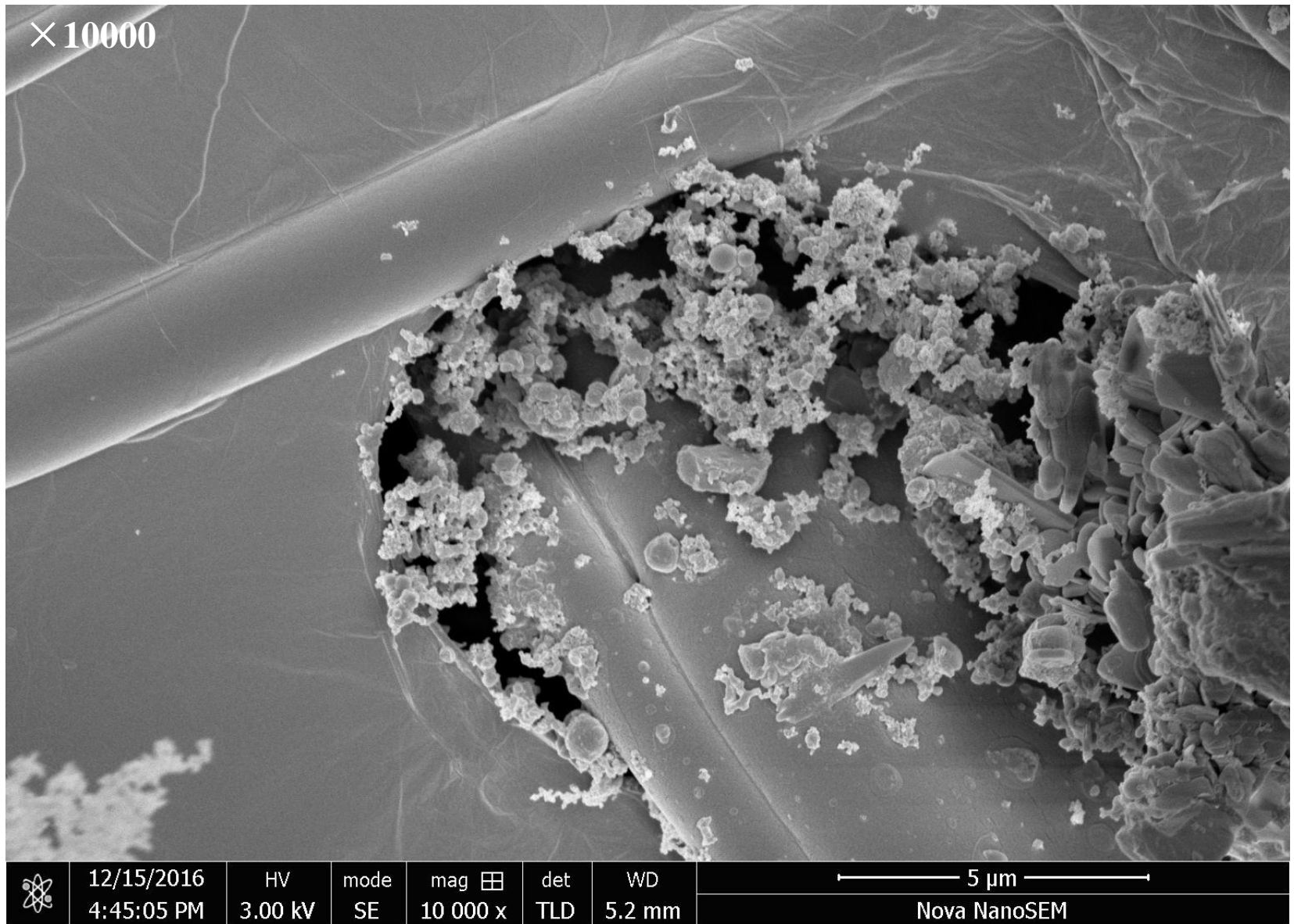


Used after 2h
Filter materials with graphene

Used after 15h
Filter materials without graphene



Used after 2h
Filter materials with graphene





MA[®]
MAKING AIR

ADVANCED TECHNOLOGY
COMFORTABLE FIT
BREATH FREELY
BLOCK EFFECTIVELY



无纺布保护层
石墨烯基过滤层
无纺布外层

2只装

石墨烯基
防霾口罩

3D
立体舒适

环保
时尚

360°
全方位贴合肌肤无缝环保

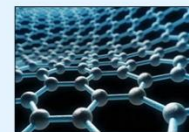
PM2.5抗菌口罩
有效阻隔各种粉尘

MA[®]

PM2.5
石墨烯基防霾口罩

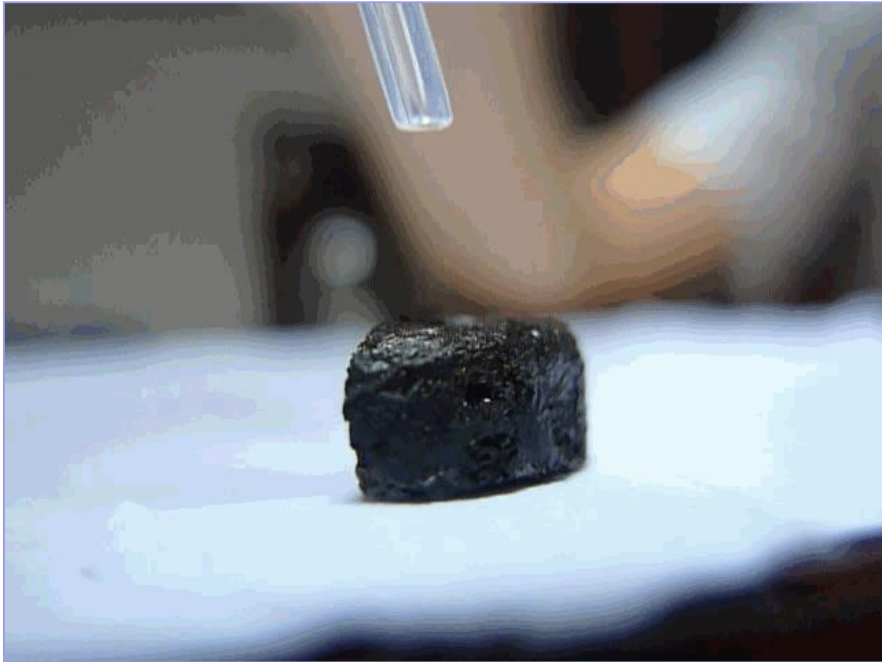
解决传统静电除霾口罩易失效问题
实现长时高效除霾

过滤效果 > 97%



In situ property characterization --for application

Interface between the liquid and graphene?



Water

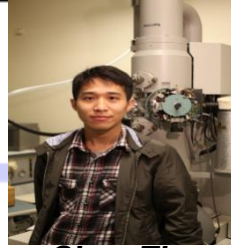


Oil

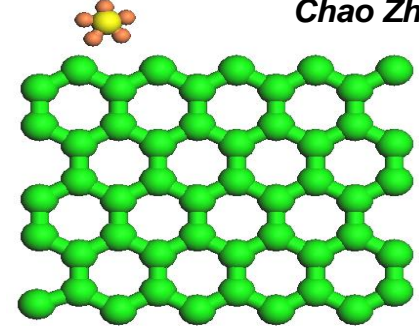
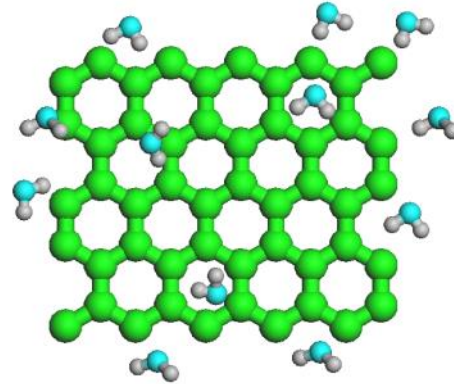
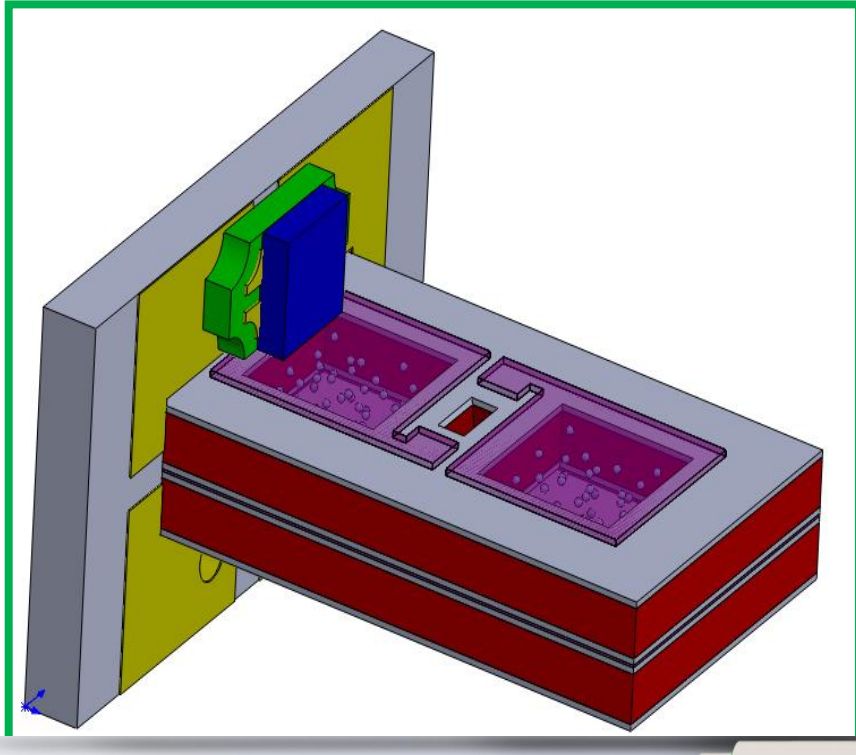
Selectivity, why?

Nature: Scientific Reports 3, 2117 (2013)
Advanced Materials 25, 5916 (2013)

Interface between the liquid and graphene

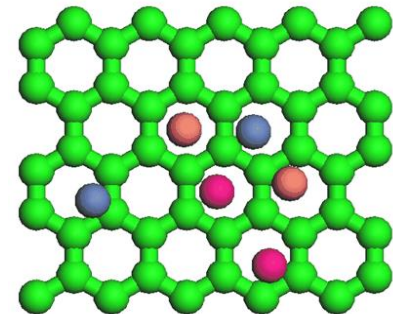
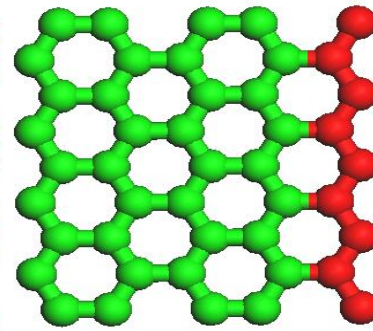
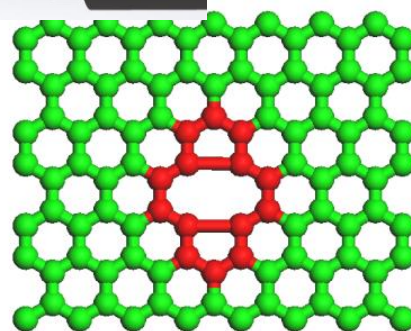


Chao Zhu



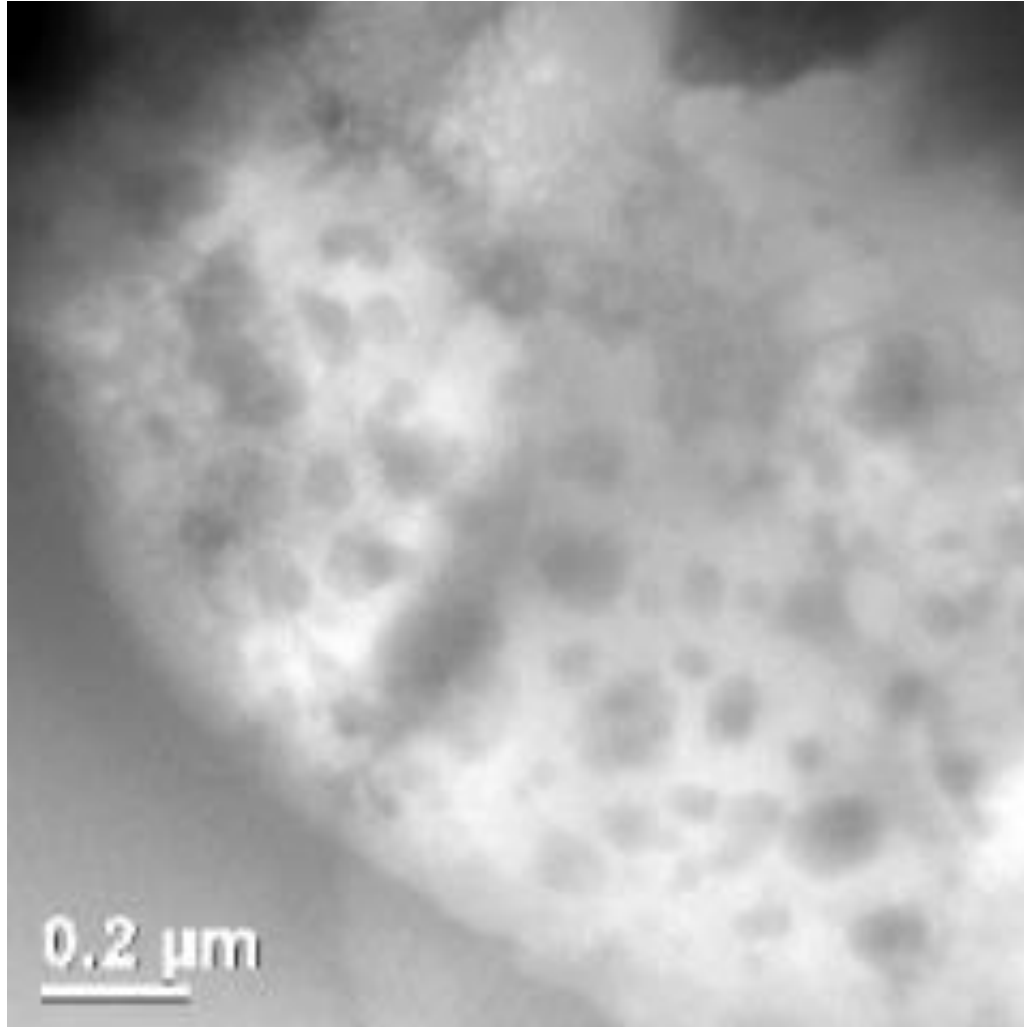
Different liquids

Different surface structures



Liquid inside TEM

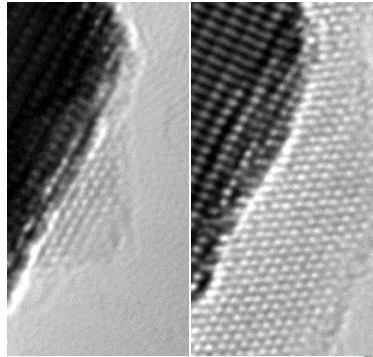
In situ property characterization --for application



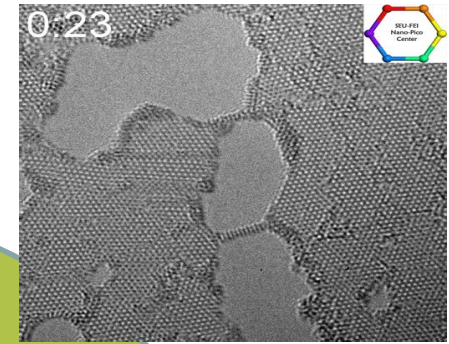
Growth of oil droplet

Unpublished results

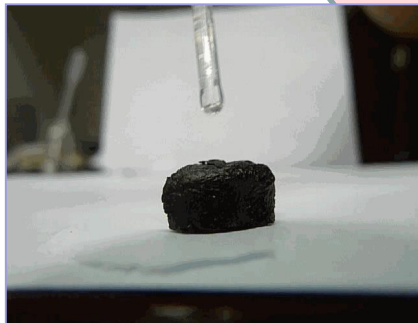
Summary



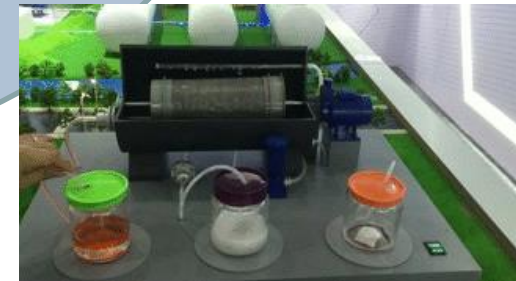
Growth Monitoring



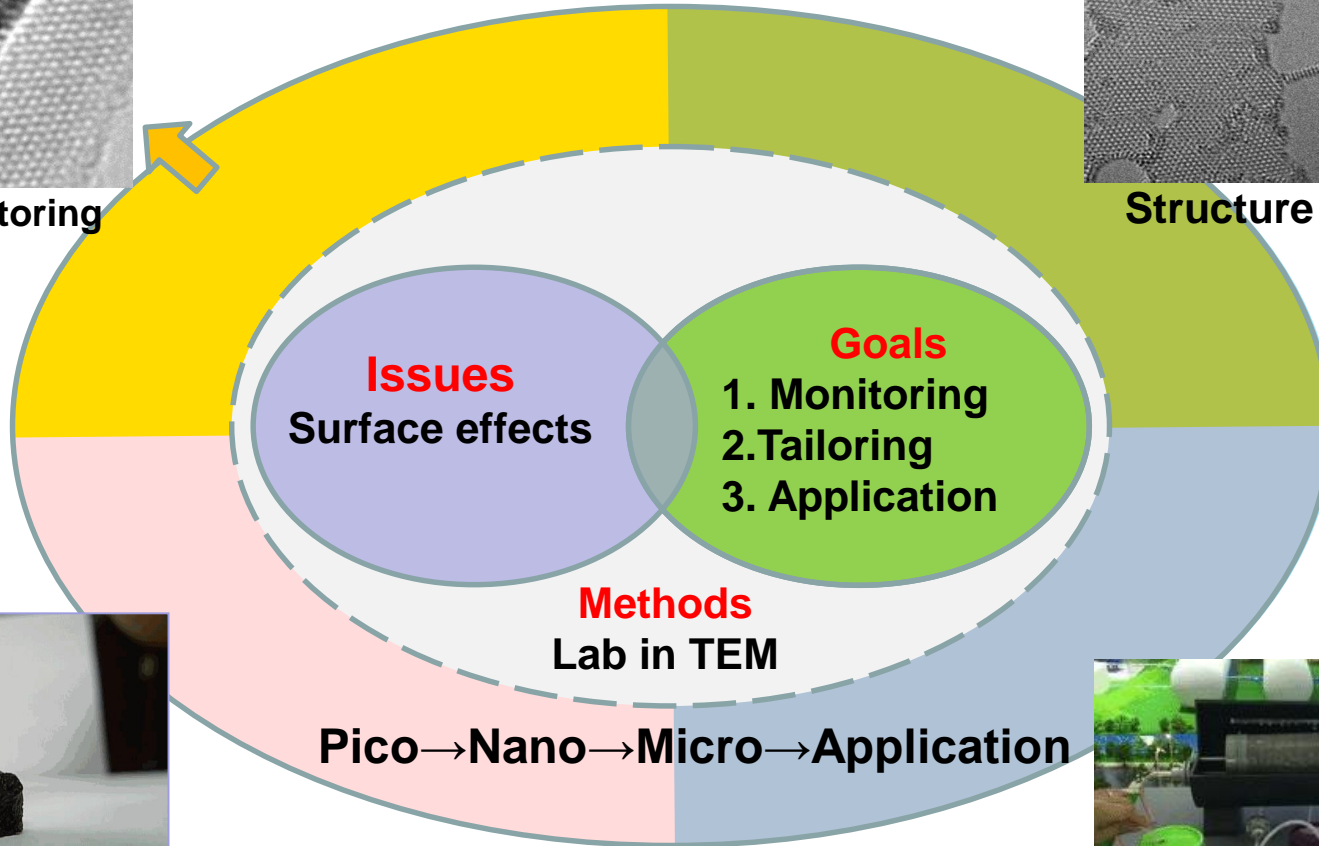
Structure Tailoring



Novel Properties



Potential applications





Acknowledgement

Collaborators

International: F. Banhart, M. Terrones, Rod Ruoff, A. Krashennnikov, P. M. Ajayan, Harold Kroto...
National: Z Zhang, DP Yu, XH Bao, M Liu, XR Wang, WL Gou, CH Jin, JL Wang, ZH Ni, J Li...

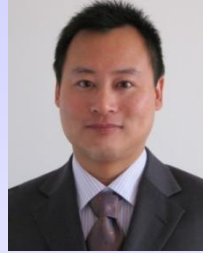
Group Members:



Neng Wan



Kuibo Yin



Feng Xu



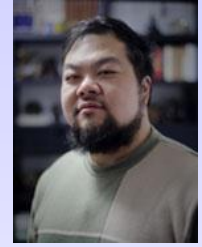
Longbing He



Xing Wu



Binjie Wang



Xiao Xie

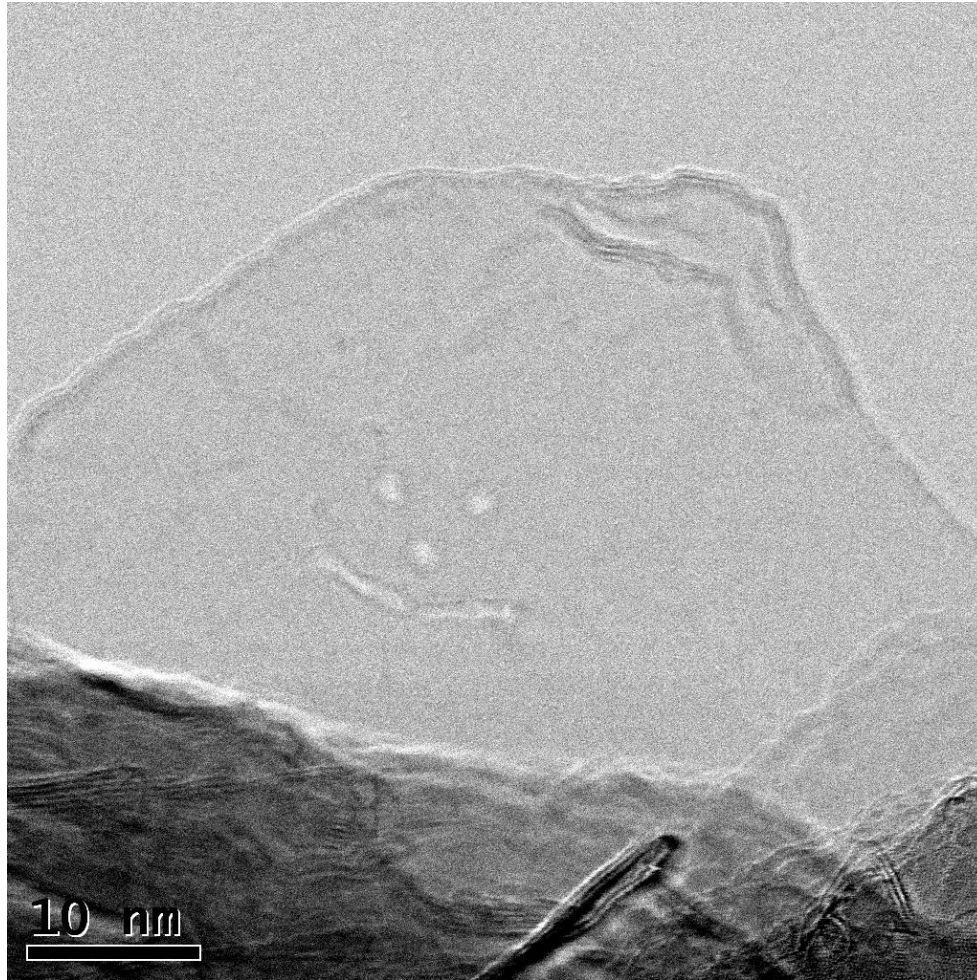


MEMS教育部重点实验室

Key Laboratory of MEMS of Ministry of Education, Southeast University, Nanjing, China



Thanks for your attention



A happy graphene nanobear

