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

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Outline

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

Issues
Surface effects

Goals
1. Precisely Monitoring
2. Atomic Tailoring
3. Applications

Methods
Lab in TEM
(In situ TEM)

Nanodevice

Growth

Fabrication

Properties

2 nm

1 nm

5 nm

fixed W probe
Tu/Pt
ZrO₂
Ag

Pt protecting layer
movable W probe

200 nm
How to set up a lab inside a TEM?

NANOLAB
In-situ experiments

Lab in TEM

Imaging, manipulation and measurement… at atomic scale
Simultaneously?

Manipulating

Probes: Mechanical, electrical ...

Electron irradiation

(TEM)

Electrical Holder

Current: 0-5 mA
Bias: +/-10 V; 140 V
Piezo resolution X, Y: 20 pm

Mechanical Holder

Load range: 0-2000 nN;
Force sensitivity: 10 nN;

Input Voltage=12 V DC
Temperature: 20-1300°C

Thermal Holder

Cs-corrected TEM (Titan 80-300™)
Resolution ≤ 80 pm

Optical Holder

Wavelength: 365-950 nm
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

Basic (Nano, Pico) ←→ Application (Micro)

Lab in Titan 80-300
First Commercial Cs-corrected TEM in our lab

Lab in dualbeam system

Lab in Tecnai G2 20

SEU-FEI Nano-Pico Center (Nanjing)
Development of in-situ microscopy in our group

**Property**

**Device and Application**

**Dynamic Characterization**
- *In-situ growth*
- *Manipulation*
- *Nanofabrication*

Precisely Monitoring surface

Si and Cu doping at graphene nanopore

(left: original; right: processed)
Precisely Monitoring surface

Si trimer in monolayer graphene

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Unpublished results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Unpublished results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

Electron Beam

sputtered atoms
contaminating hydrocarbon
volatilization
dissociation
deposition
diffusion

Specimen

EBID

EBIS

Density

EBID > EBIS
EBID < EBIS

sculpting rate
deposition rate

Tailoring structure: sculpting--create defects—manipulating atoms

Migration and Trapping of metal atoms on graphene

PRL 105, 196102 (2010)
Possible narrowest molybdenum sulfide nanoribbon
Tailoring structures by energy difference
Nanofabrication at atomic scale

BN tubular structure from bilayer structures

Adv. Funct. Mater. in press
Nanofabrication at atomic scale

Precisely thinning of the tubes: 0.14 nm

Adv. Funct. Mater. in press
BN tube with diameter of \( \sim 0.45 \text{ nm} \) is the smallest stable tube.

*Adv. Funct. Mater. in press*
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

2D Materials, in press
Tailoring structures - for new structure design -- deposition

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

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

Carbon 50, 2845(2012)

partially graphitized compact graphene structures
Tailoring structures - new structure design

Mechanical property of Graphic structures

Nice mechanical behavior of graphene-based structures

L. B. He/L. T. Sun et al., *Carbon* 50, 2845 (2012)
In situ property characterization -- for application

Porous graphene → Compact Graphene

Digital photographs
SEM images of surfaces
SEM images of cross-sections

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)


Scientific Reports 3, 2117 (2013)
In situ property characterization -- for application

Dynamic adsorption process

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

Joint Center between Southeast University and Jiangnan Graphene Research Institute

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Lab
Meeting room
Office
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)
High efficiency (J. Mater. Chem. A)
Compressible sponge
Continuous separation
Sorption for trace oil

First Patent


First-time Observed

Shape control
Structure control (Sci. Rep.)
Low cost Adv. Mater.; Small
Large scale sponge
Metal mesh combined
Separation for micro emulsion

40+ Patents: 201010607317.3, 201110312393.6, PCT/CN2012/078045 and others
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
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
Other application—graphene based filter materials

Product line for filter materials: 200000 m²/y
Application based surfaces--Anti smog mask
Application based surfaces--Anti smog mask

Anti amog masks
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 1 week)
Application based surfaces -- Anti smog mask

![Graph showing electrostatic potential vs breath time for different brands.](https://via.placeholder.com/150)
Application based surfaces--Anti smog mask

![Graph showing removal efficiency over breath time for different brands of anti-smog masks. The x-axis represents breath time in minutes, ranging from 0 to 120. The y-axis represents removal efficiency as a percentage, ranging from 75 to 95. Each brand is represented by a different symbol and color. The brands include Brand A (Japan), Brand B (U.K.), Brand C (South Korea), Brand D (USA), Brand E (USA), Brand F (Germany), Brand G (USA), and the authors' work.](image-url)
Application based surfaces--Anti smog mask

- 3M 9501
- 3M 9001v
- Uvex
- Honeywell
- Our product
- 伊藤良品
- 滴露
- 金佰利
Application based surfaces--Anti smog mask

TEM images of filter materials with graphene

ununiform distribution

uniform distribution
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
关于用于口罩的石墨烯毒性问题:

1. 目前没有迹象或任何目前仪器测试表明有毒性；
2. 不管有没有，尽量避免直接接触；
3. 压力吹风实验：用高于国家标准呼吸压力两个数量级的压力吹风3天3夜，未发现任何颗粒物掉落；
4. 尽量用最少量（每个约0.02g），比吃一顿烤肉里的石墨烯及无定形碳还少。
In situ property characterization — for application

Interface between the liquid and graphene?

Water  Oil

Selectivity, why?

Advanced Materials 25, 5916 (2013)
Interface between the liquid and graphene

Different liquids

Different surface structures

Liquid inside TEM
In situ property characterization -- for application

Growth of oil droplet

Unpublished results
**Summary**

**Issues**
- Surface effects

**Goals**
1. Monitoring
2. Tailoring
3. Application

**Methods**
- Lab in TEM

**Pico** → **Nano** → **Micro** → **Application**

**Potential applications**

- Growth Monitoring
- Structure Tailoring
- Novel Properties

**Potential applications**
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Group Members:

Neng Wan  Kuibo Yin  Feng Xu  Longbing He  Xing Wu  Binjie Wang  Xiao Xie
A happy graphene nanobear

Thanks for your attention