Synthesis and OLED use of Graphene By CVD

Hui-Ming Cheng（成会明）

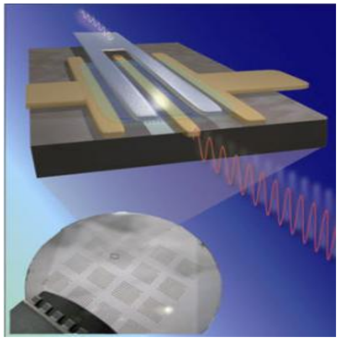
1. Shenyang National Laboratory for Materials Science, Institute of Metal Research, CAS, Shenyang, 110016, China
2. Tsinghua-Berkeley Shenzhen Institute, Shenzhen 518055, China

GRAPHENE'S SUPERLATIVES

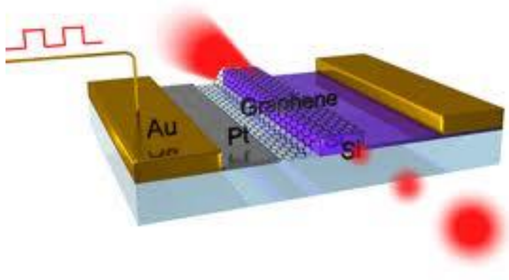
- thinnest known material in the universe
- strongest material ever measured (theoretical limit)
- stiffest known material (stiffer than diamond)
- most stretchable crystal (up to 20% elastically)
- most impermeable (even He atoms cannot squeeze through)
- recorded thermal conductivity (outperforming diamond)
- highest current density at room T
  (million times of those in copper)
- highest intrinsic mobility (100 times more than in Si)
- lightest charge carriers (zero rest mass)
- longest mean free path at room T (micron range)
- … … …

From A. Geim's Lecture at IMR CAS, 14 July 2009

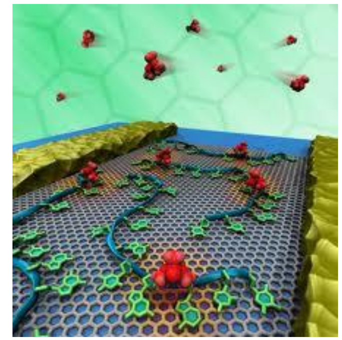
Potential Applications of Graphene and 2D Materials



Nanoelectronics

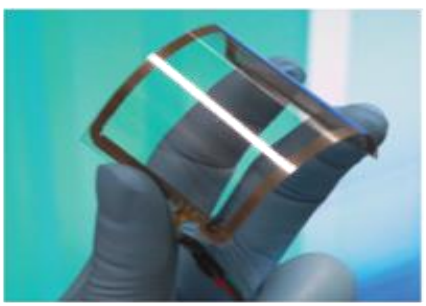


Light modulator

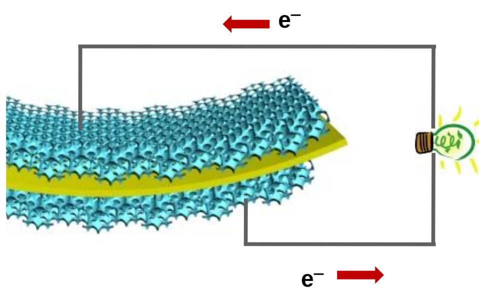


Sensors

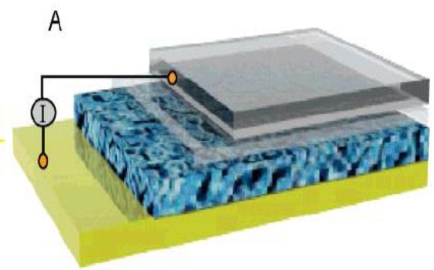
Composites



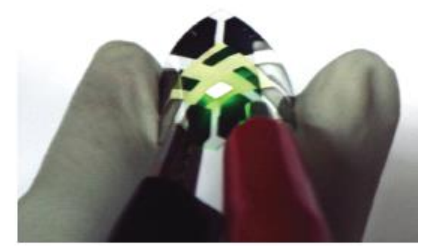
Flexible display



Energy storage



Solar cells



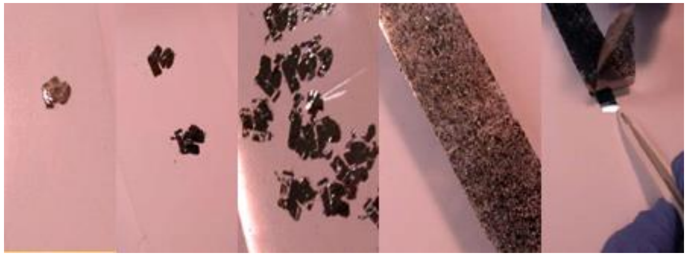
Flexible OLED

AK Geim et al., *Nature Mater.* 6 (2007) 183
HB Heersche et al., *Nature* 446 (2007) 56
F Schedin et al., *Nature Mater.* 6 (2007) 652
YM Lin, et al, Science 327 (2010) 662
M Liu, et al. Nature 474 (2011) 64.

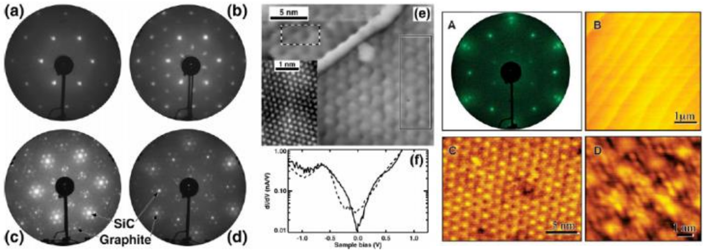
S Stankovich et al., *Nature* 442 (2006) 282
X Wang et al., *Nano Lett.* 8 (2008) 323
T Ramanathan et al., *Nature Nanotech*. 3 (2008) 327
S Bae et al., Nature Nanotechnol. 5 (2010) 574
TH Han et al., Nature Photonics 6 (2012) 105

Main Synthesis Methods

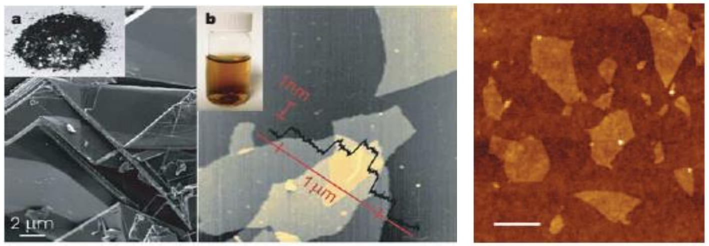
- **Mechanical cleavage**
  - **High quality**
  - **Low productivity and controllability**
- **Epitaxial growth**
  - **Large size**
  - **Low productivity and high cost**
  - **Inhomogeneous and difficult to transfer**
- **Chemical exfoliation**
  - **Mass production and low cost**
  - **Low controllability and quality**
- **Chemical vapor deposition**
  - **High quality and large size**
  - **Easy to pattern and transfer**
  - **Reasonable productivity**
- **Molecular assembly**
  - **Bottom up approach**
  - **Small size and Low productivity**



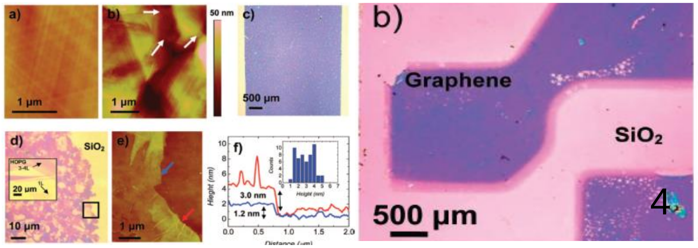
KS Novoselov et al., *Science* 306(2004) 666



C Berger et al., *J Phys Chem B 108* (2004) 19912

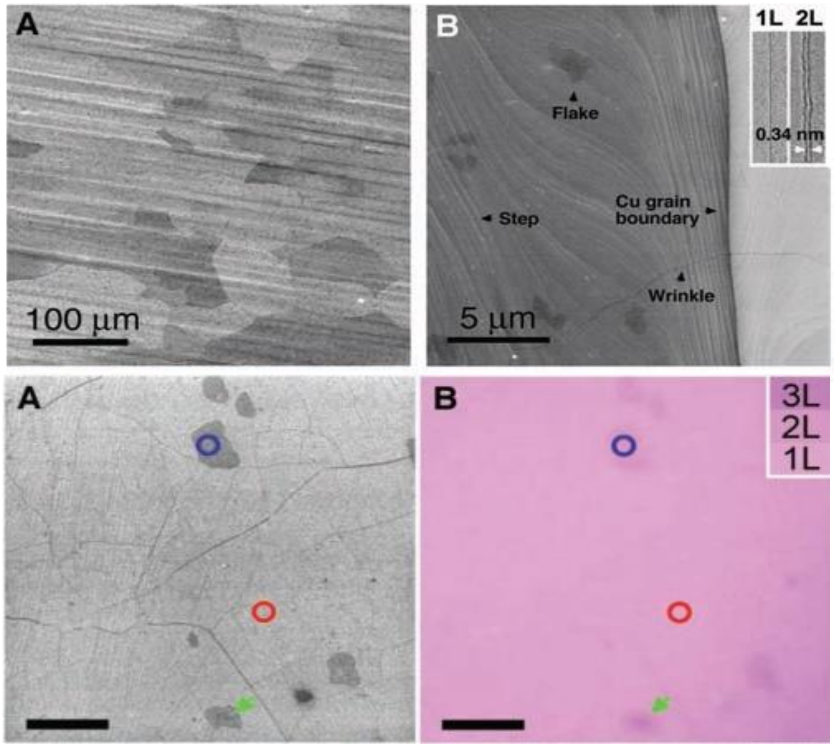


S Stankovich et al., *Nature* 442(2006) 282

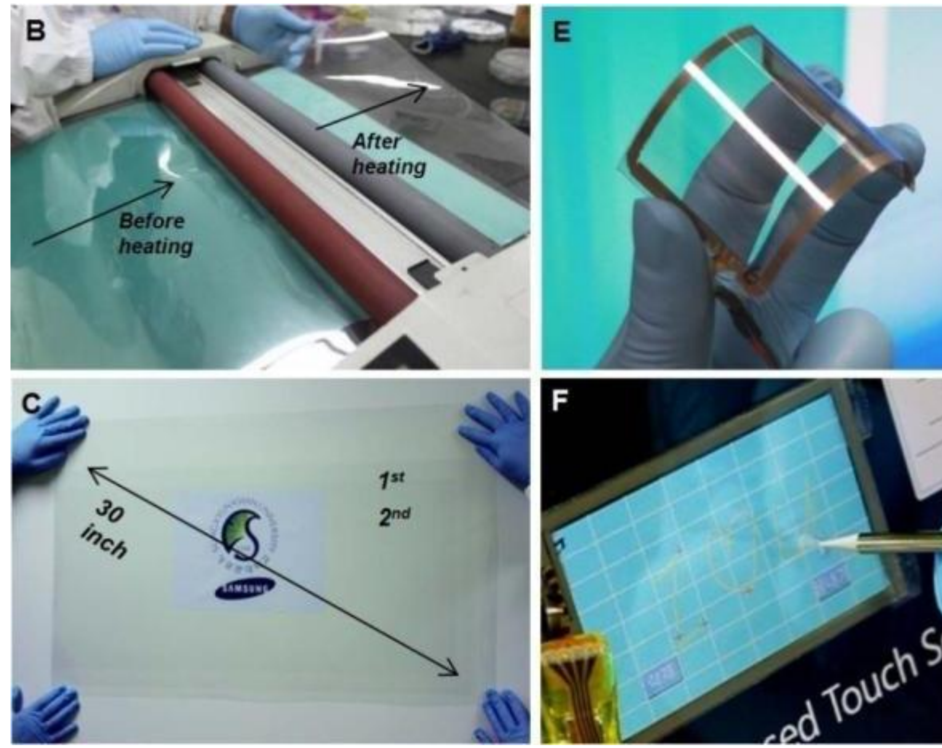


A Reina et al., *Nano Lett* 9 (2009) 30.

Low Pressure CVD
for Graphene Growth on Cu



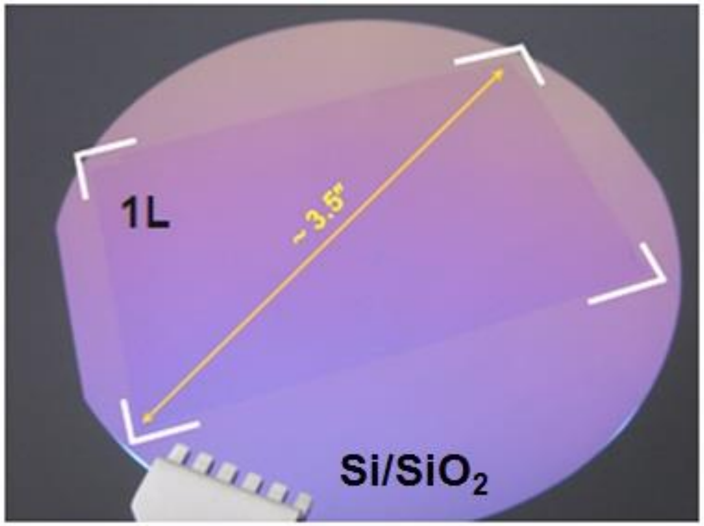
XS Li et al., *Science* 324 (2009) 1312.

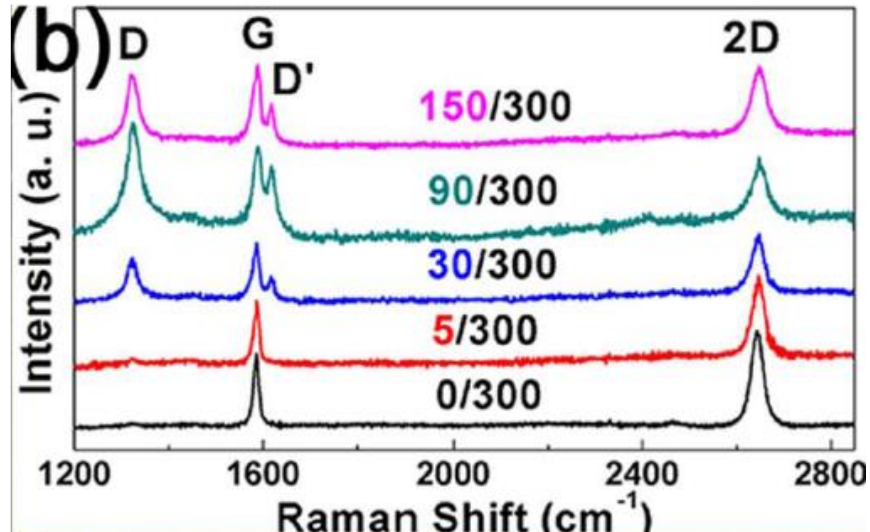


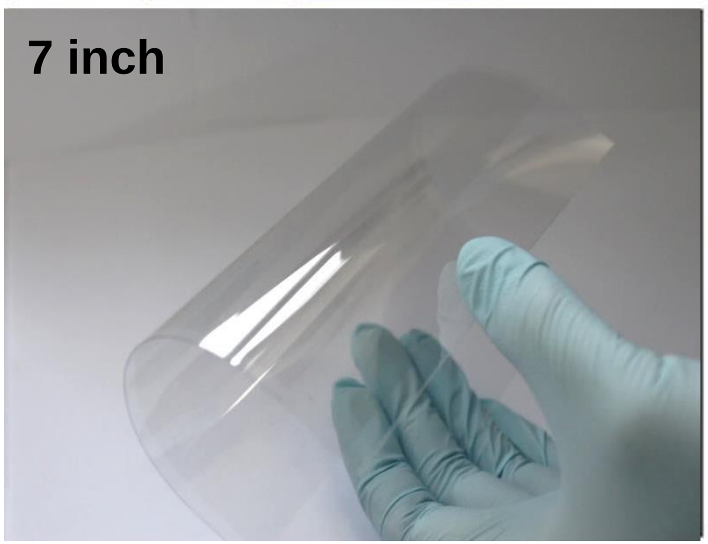
S Bae et al., *Nature Nanotechnol.* 5 (2010) 574.

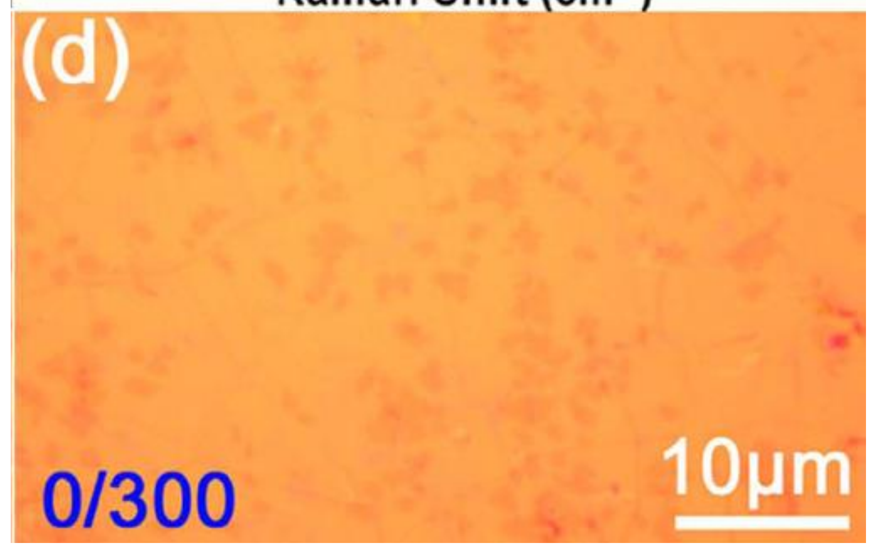
SYNL

Ambient Pressure CVD
for Graphene Growth on Cu







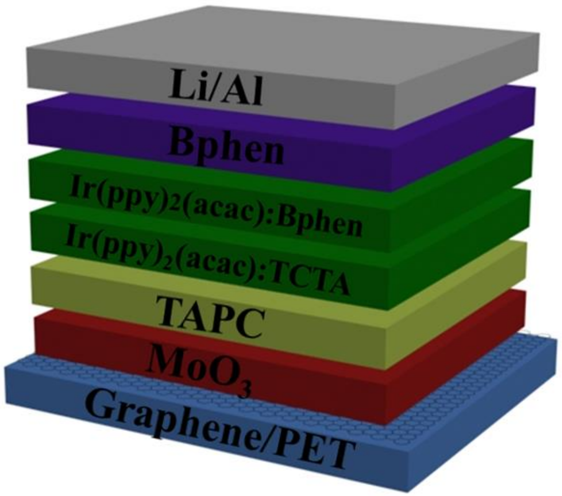


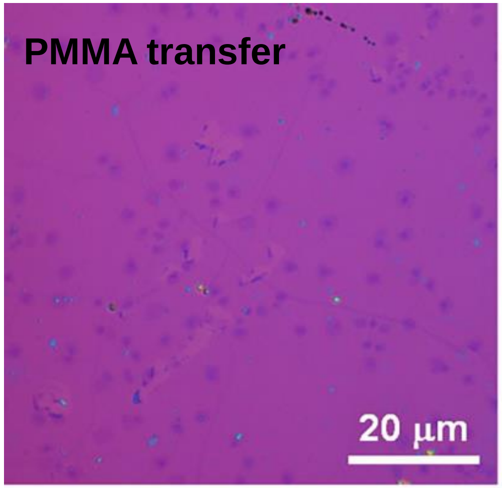
SYNL

Gao, Ren, Cheng, et al., *Appl Phys Lett* 97 (2010) 183109.

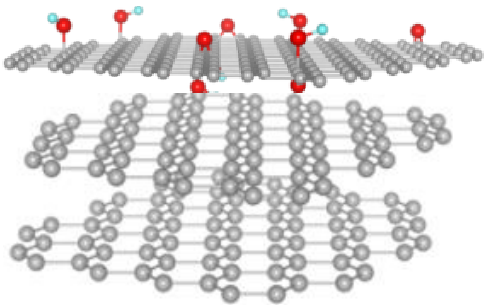
Challenges for OLED Application

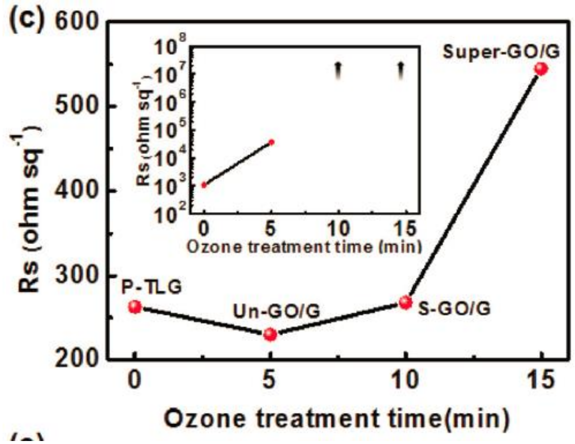
- **High resistance**
  - **Low current density**
- **Low work function (4.2-4.6 eV)**
  - **Large hole injection barrier**
- **Hydrophobic surface**
  - **Difficult to deposite hole injection layer**
- **Residues and big roughness**
  - **Electrical micro-shorts**

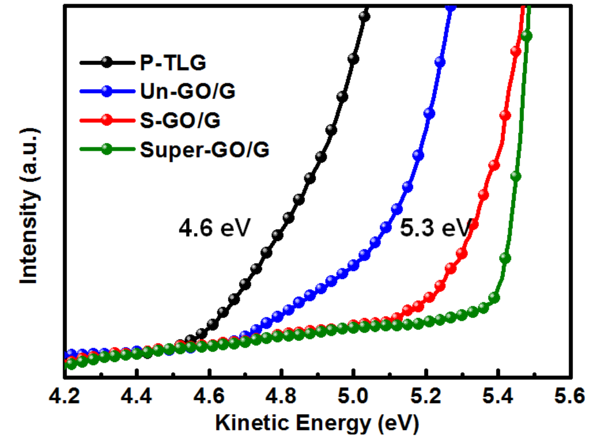


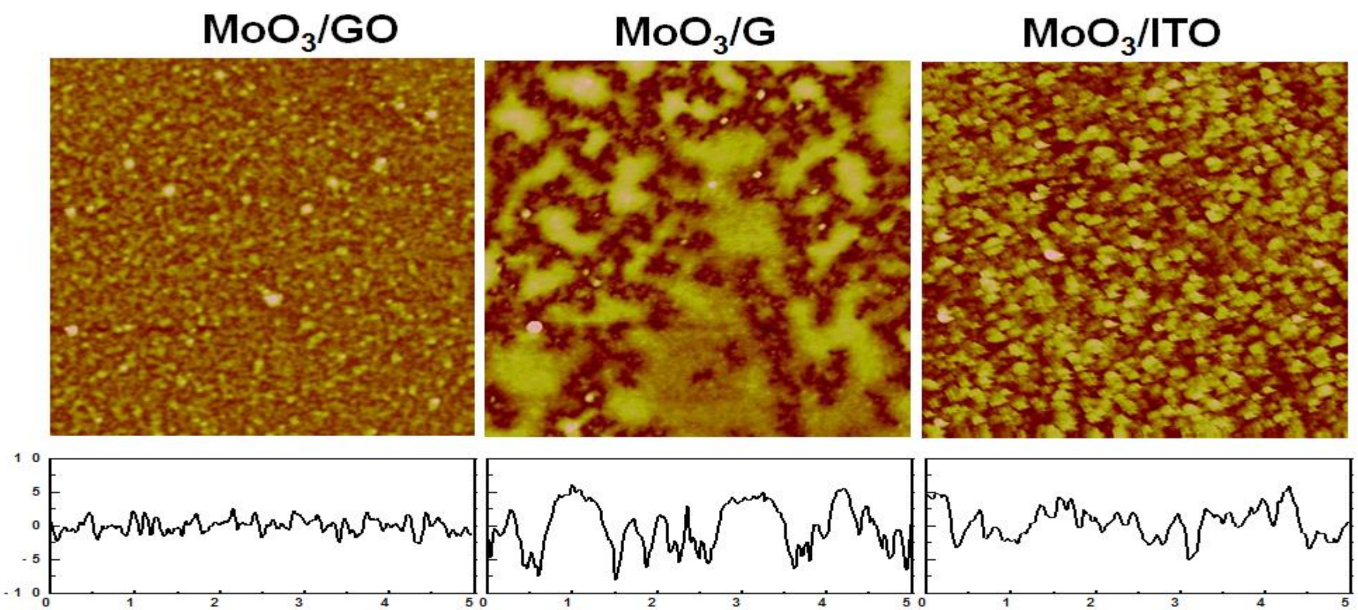


GO/G Vertical Heterostructure Anode



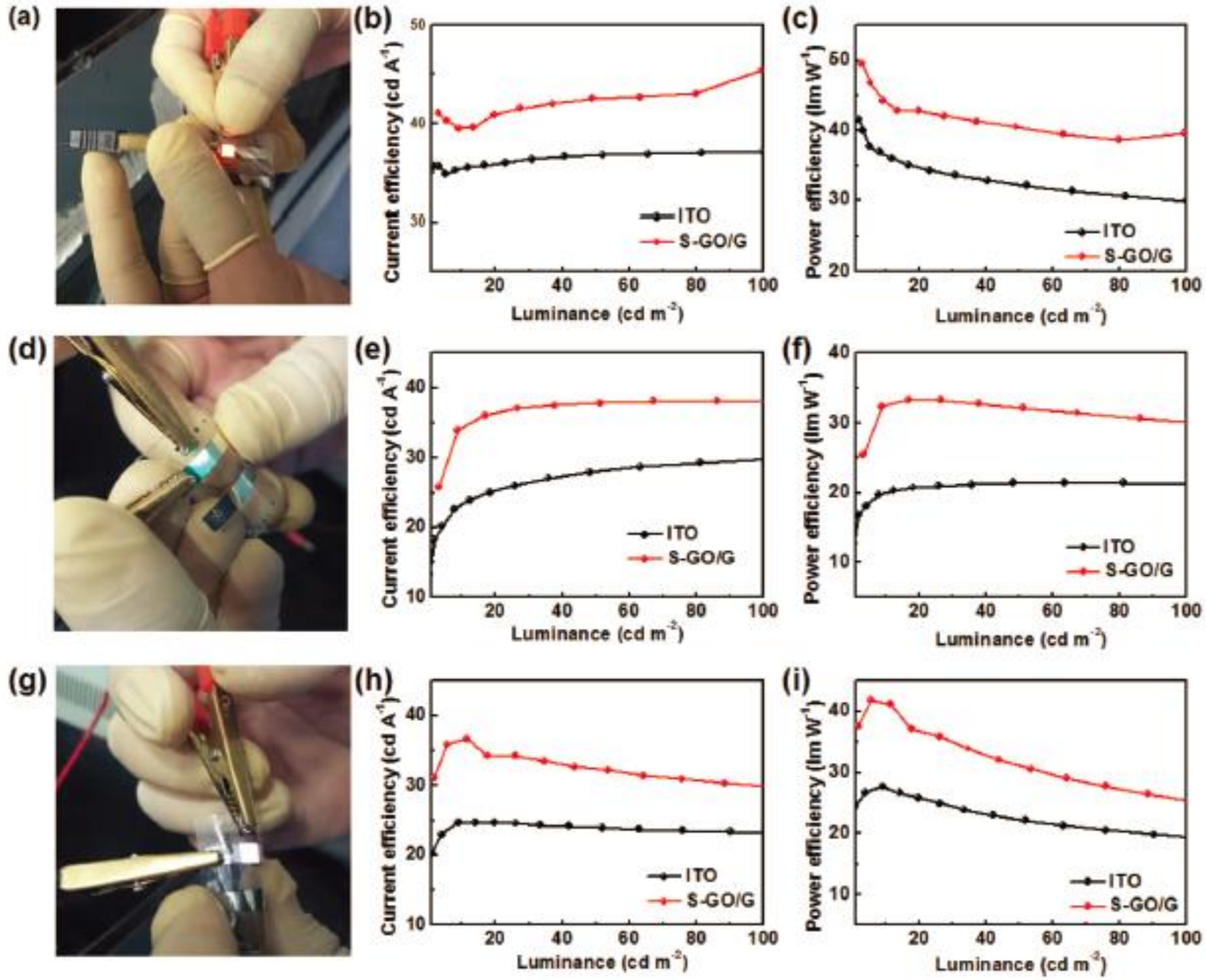






Jia, Du, Cheng, Ren et al., *Nanoscale 8*, 10714-10723 (2016)

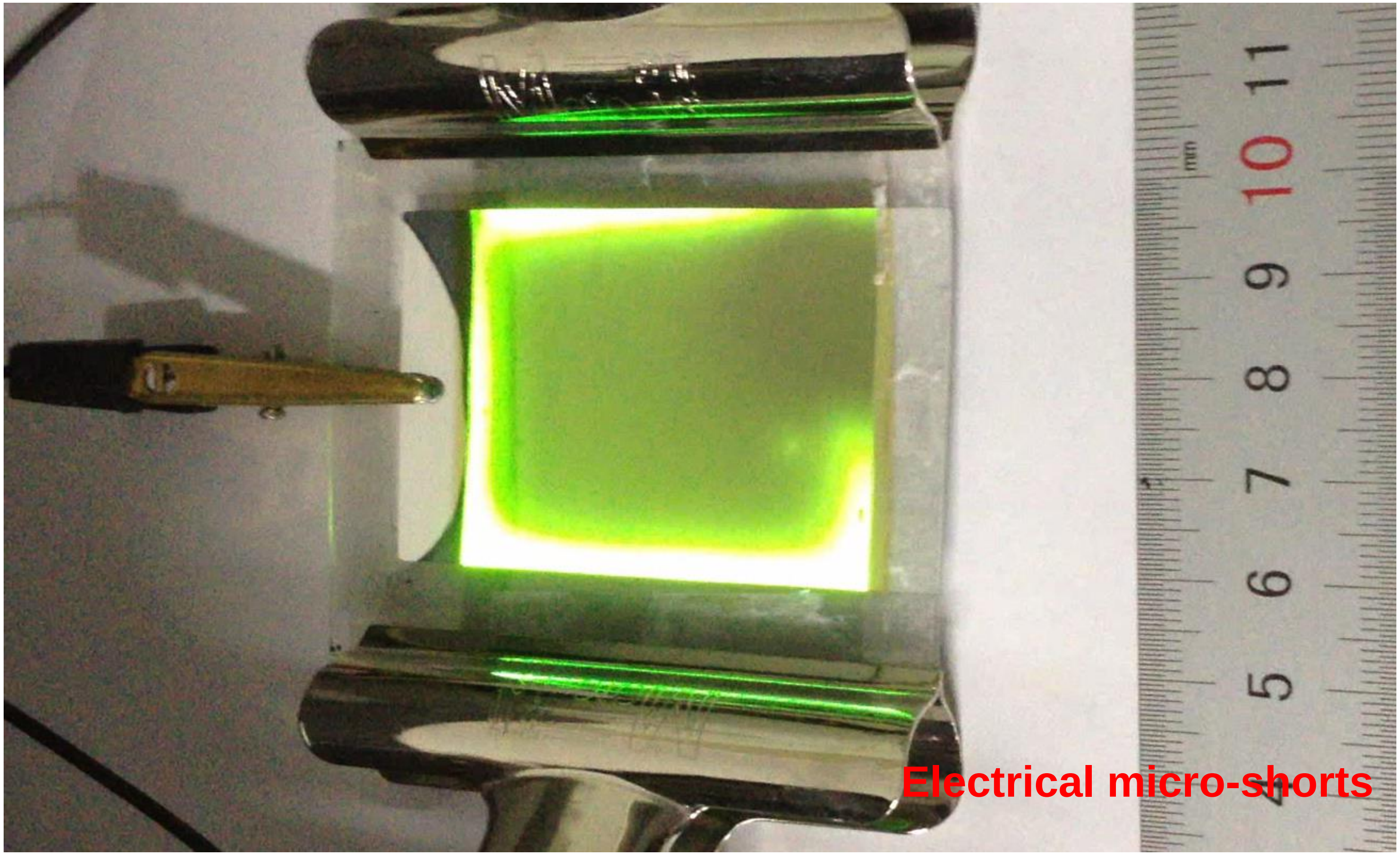
Current and power efficiency of small-size OLEDs



SYNL

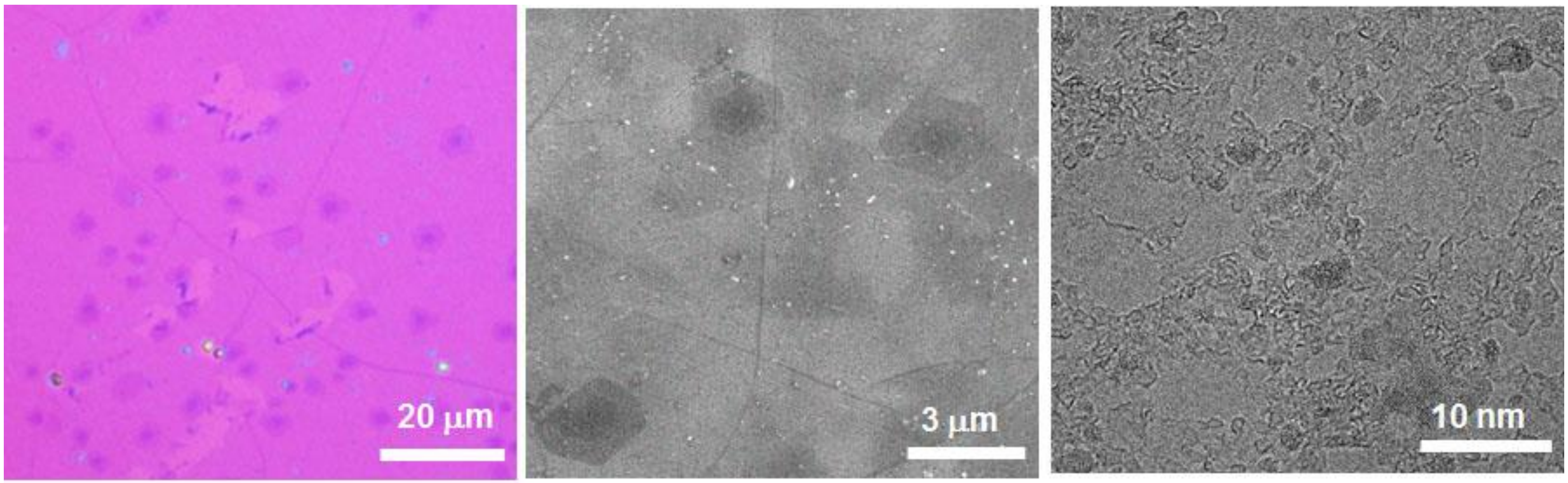
Jia, Du, Cheng, Ren et al., *Nanoscale 8*, 10714-10723 (2016)

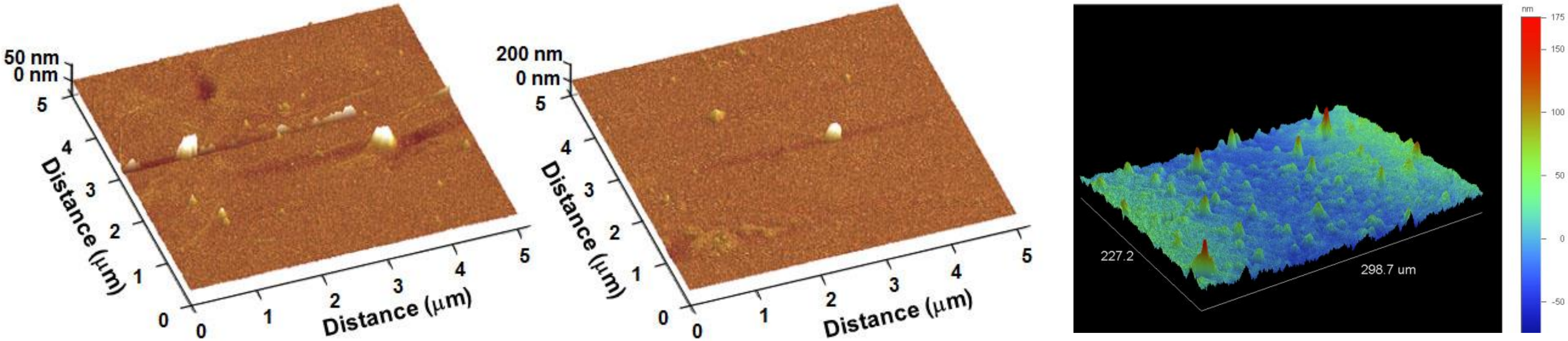
A 3 inch OLED with a Graphene Anode



Graphene with PMMA as a supporting layer

PMMA Graphene: Big Surface Roughness



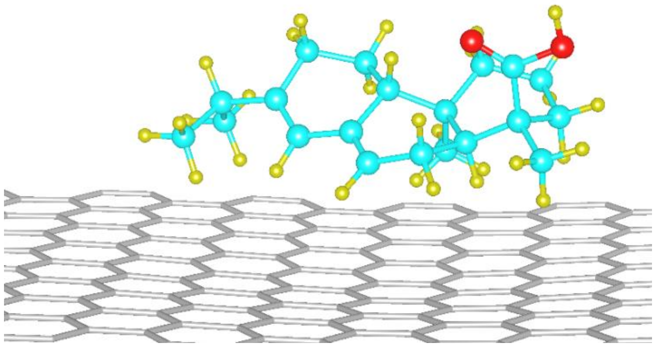


Requirements For Ideal Transfer Support

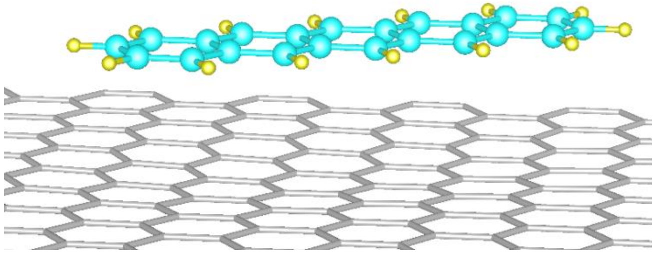
- **Good solubility in solvents**
  - **Allows the support layer to be easily dissolved in the commonly used chemical solvents**
- **Low $E_{ad.}$ with the graphene surface**
  - **beneficial for the separation of the polymeric support layer from the graphene surface**
- **Sufficient support strength**
  - **effectively prevent fragmentation or tearing of the graphene film during transfer**

SYNL

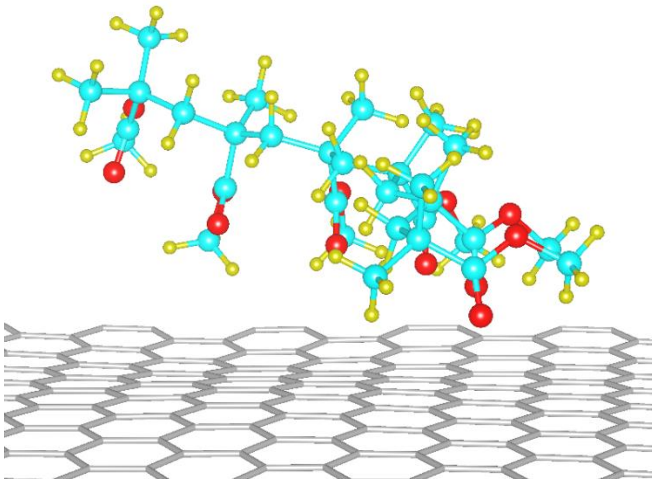
Adsorption Ability of Different Molecules



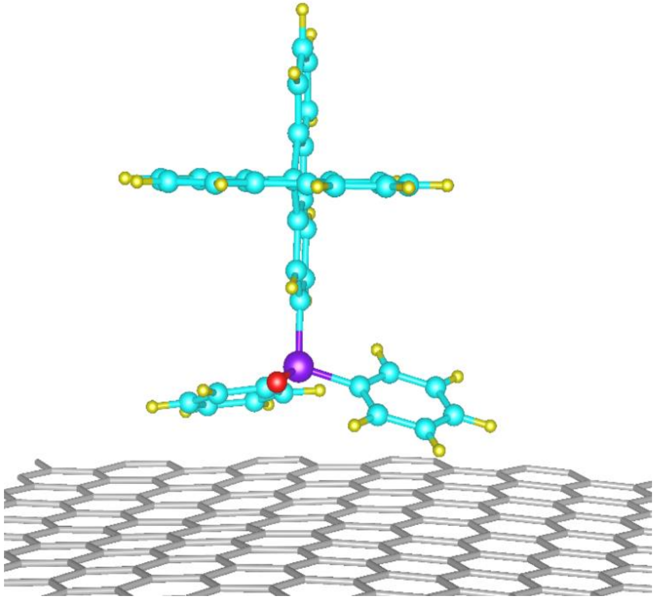
Rosin, $E_{ad.}$=1.04 eV



Pentacene, $E_{ad.}$=1.45 eV

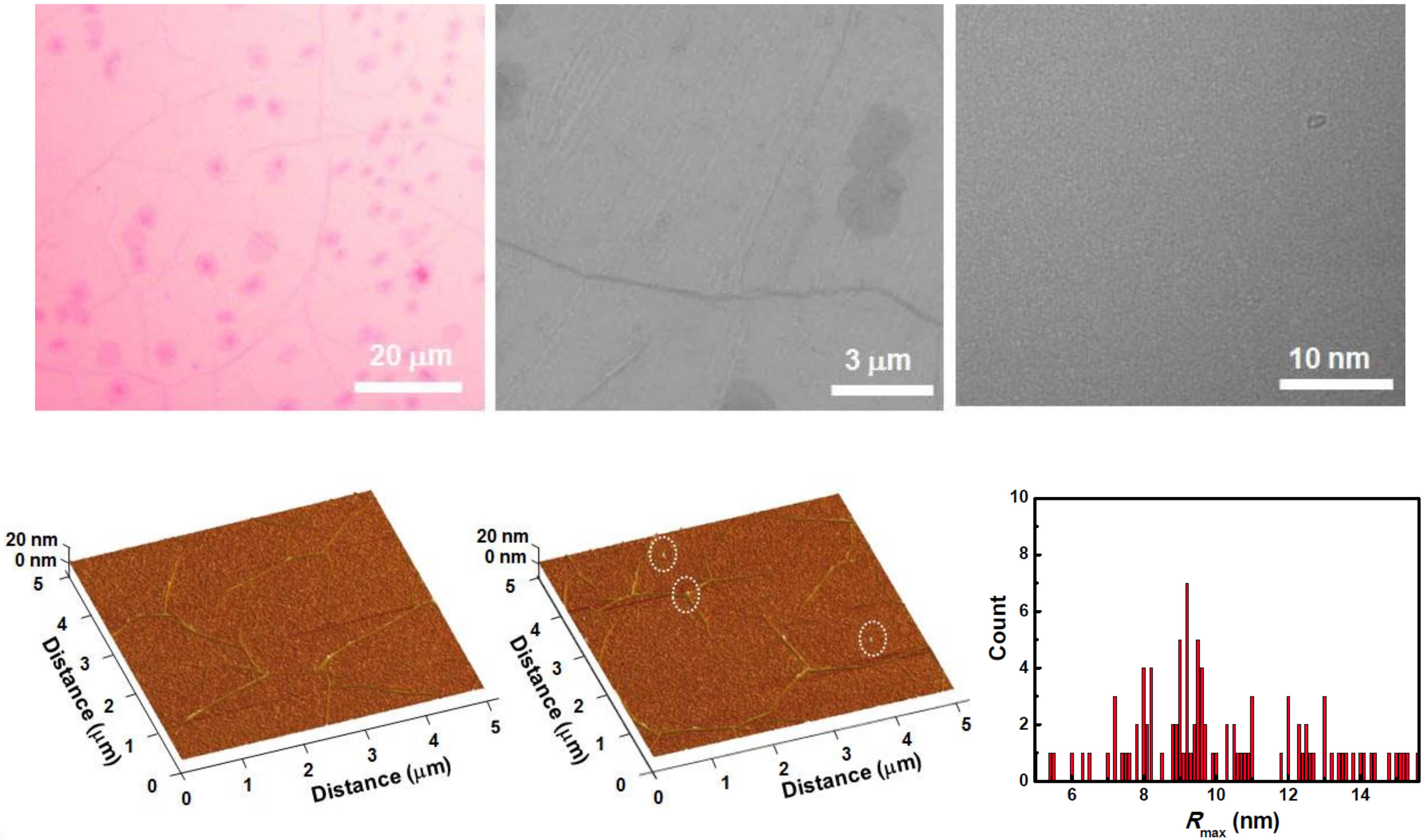


HMMA, $E_{ad.}$=1.45 eV



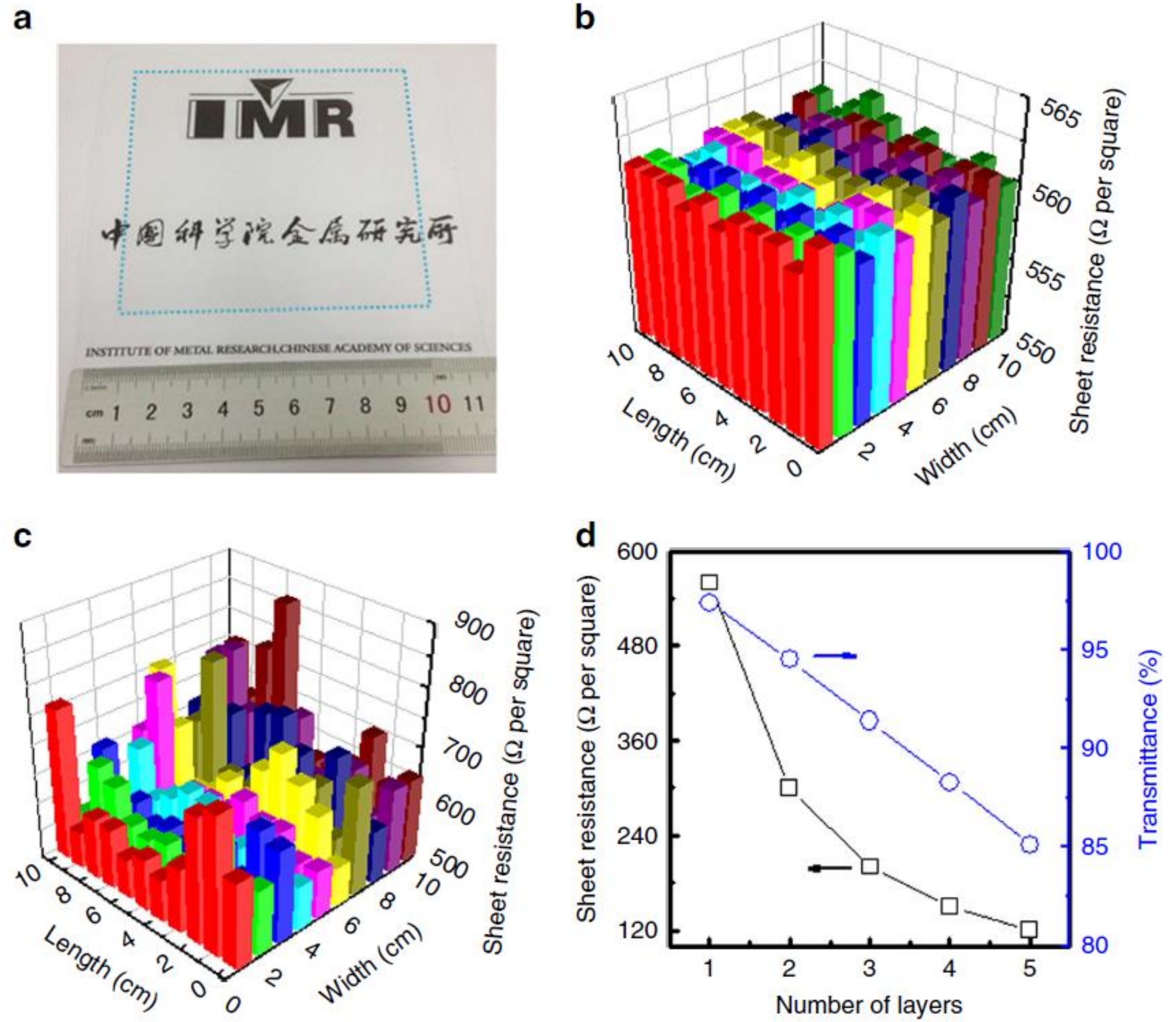
SPPO1, $E_{ad.}$=0.69 eV

Ultraclean and Smooth Graphene Films



Zhang, Du, Ma, Cheng, Ren et al., *Nature Commun* 8, 14560, 2017.

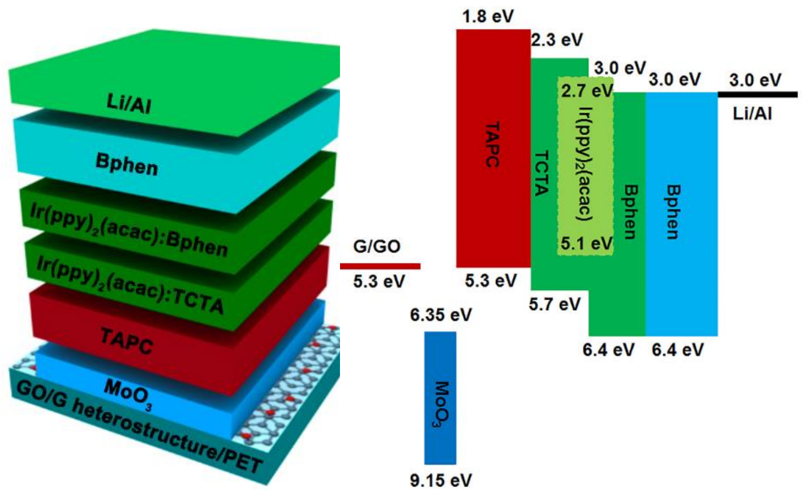
Uniform Graphene Films

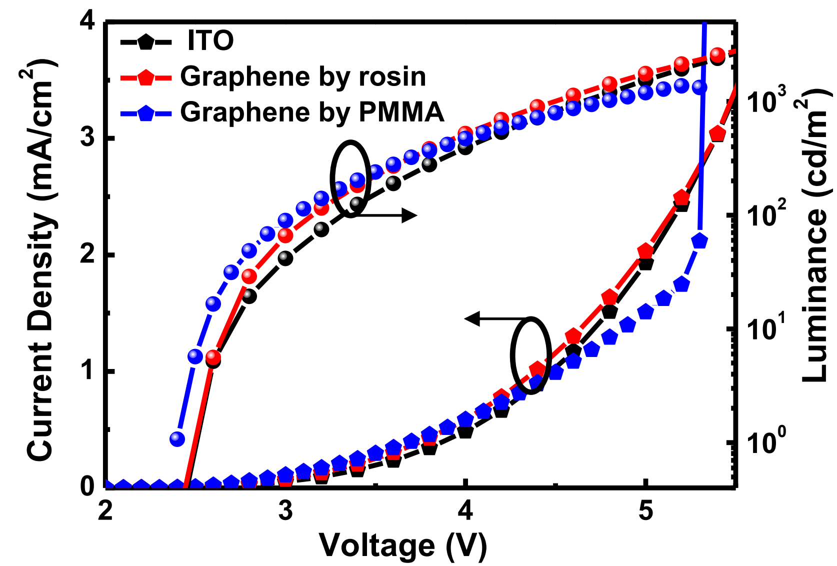


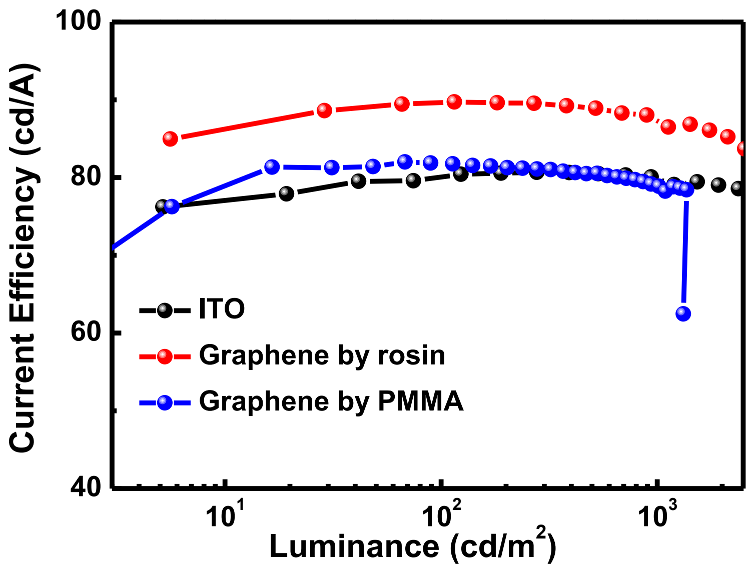
Very weak p doping

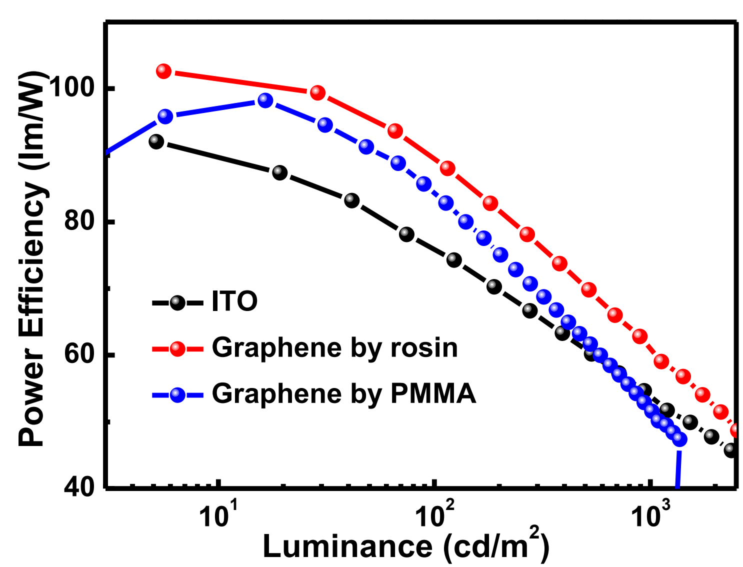
Zhang, Du, Ma, Cheng, Ren et al., *Nature Commun* 8, 14560, 2017.

OLED with Ultraclean Graphene



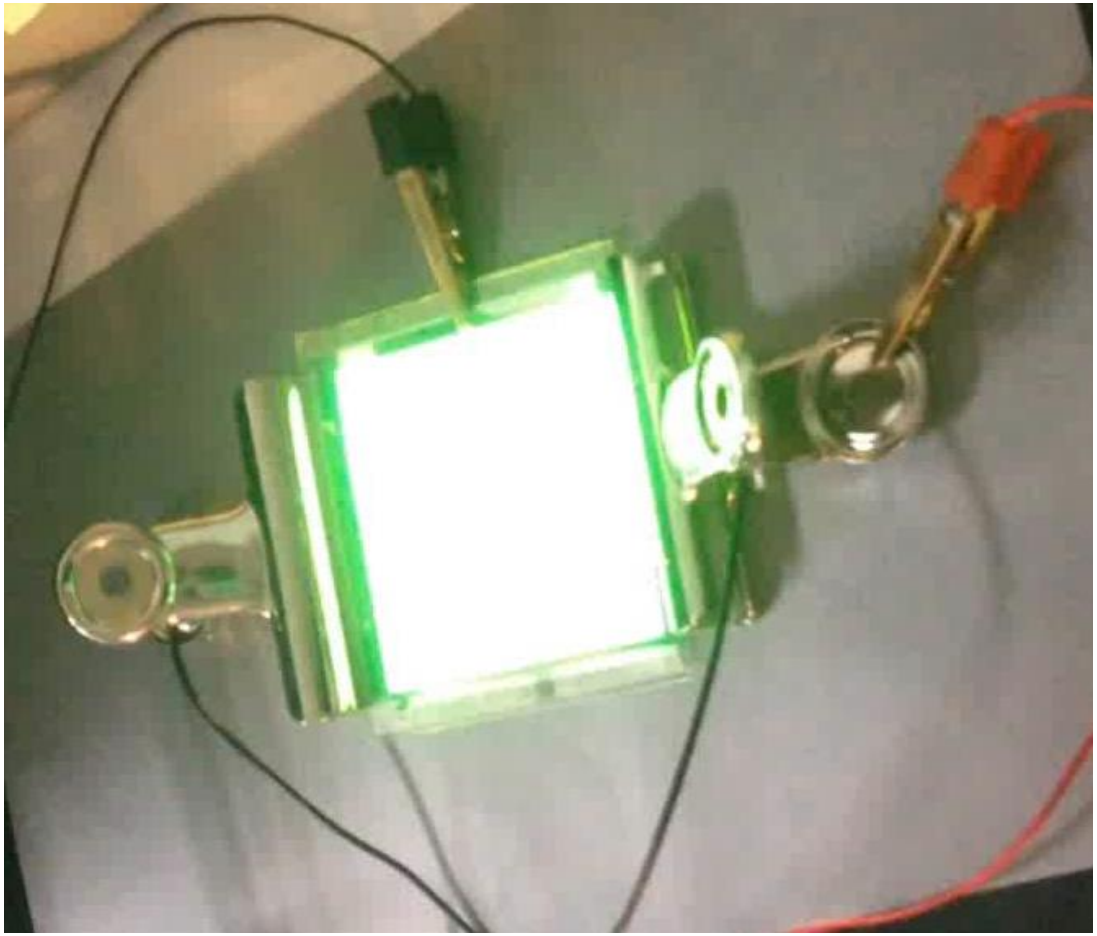






SYNL

4 inch Flexible OLED with Ultraclean Graphene Anode



In collaboration with Prof. Dongge Ma at CIAC, CAS

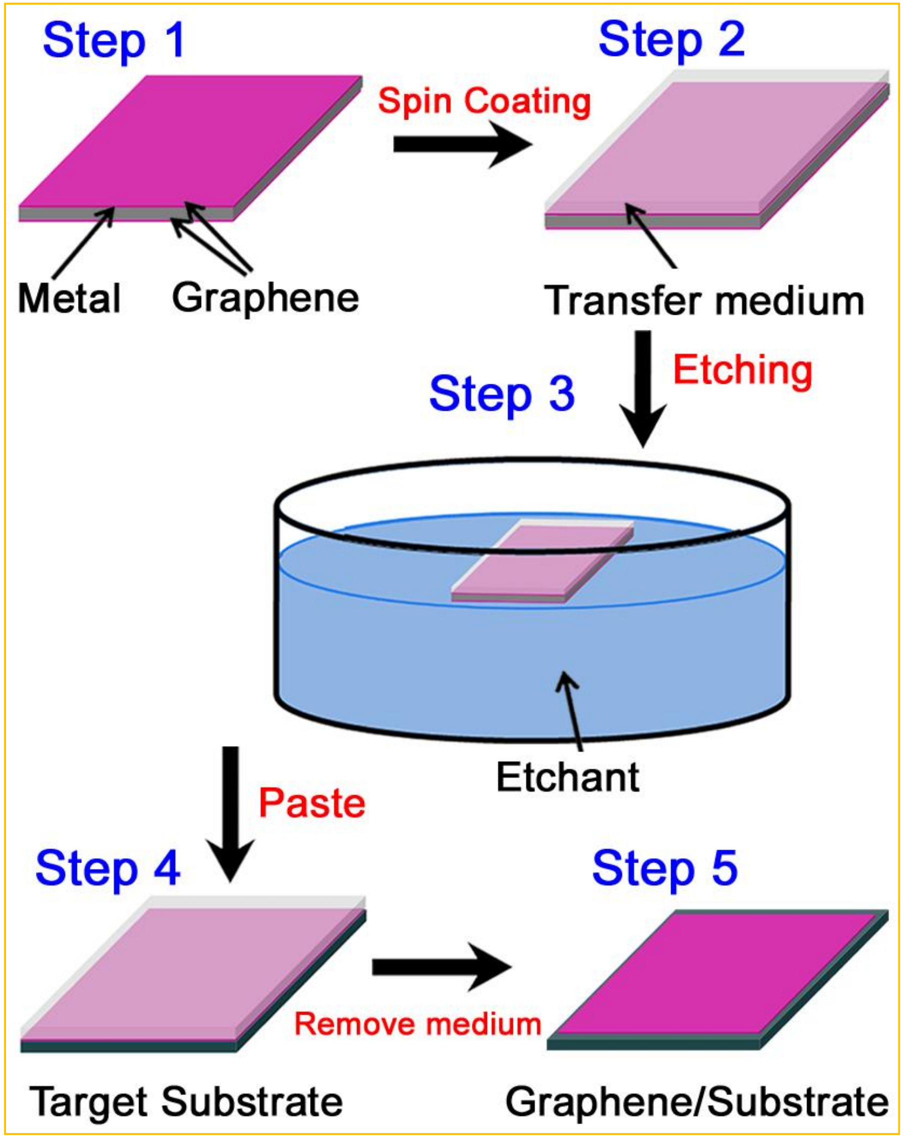
SYNL

Zhang, Du, Ma, Cheng, Ren et al., *Nature Commun* 8, 14560, 2017.

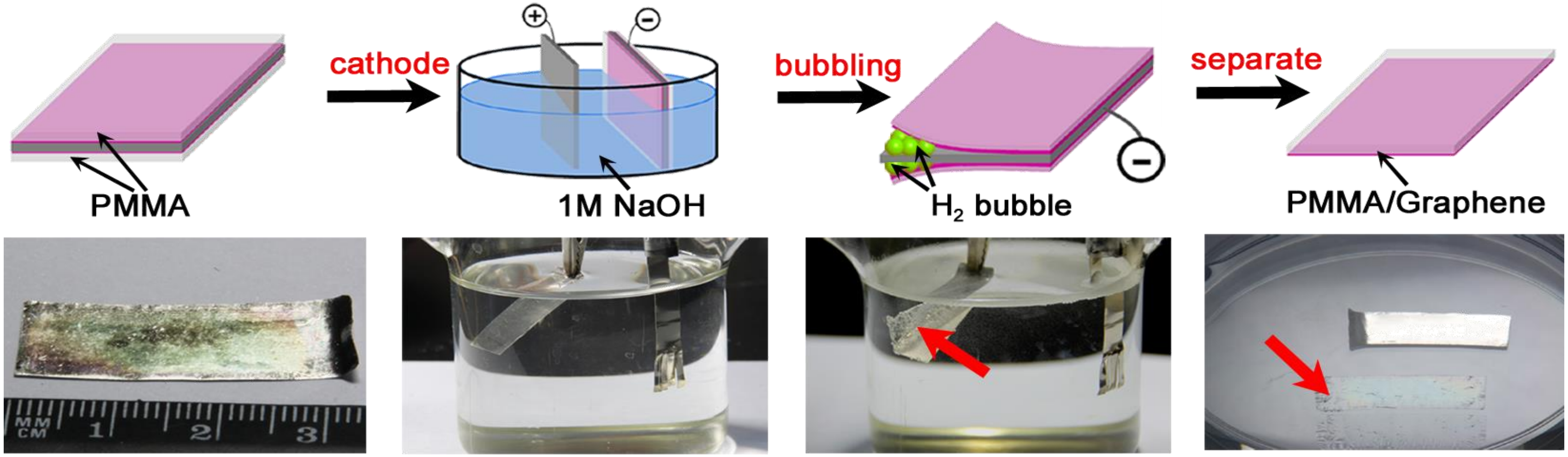
The Commonly Used Transfer Method

- Damage to the graphene
- Metal residues
- Environmental pollutions
- High cost

- Not suitable for chemically inert or noble metal substrates such as Pt because they are difficult to etch away completely or have a high cost



Nondestructive H_2 Bubbling Transfer method



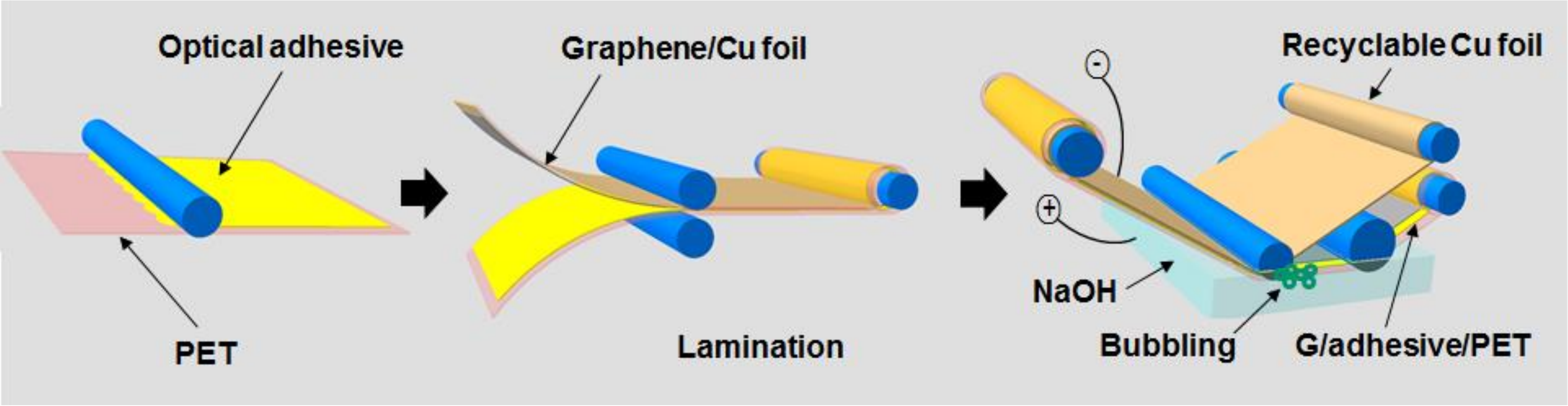
$$2\,H_2O\,(l) + 2\,e^- \rightarrow H_2\,(g) + 2\,OH^-\,(aq)$$

- **No damage on metal substrate**
- **Highly efficient, no pollutions**
- **Easy to scale up**
- **Suitable for transferring graphene grown on any metals**

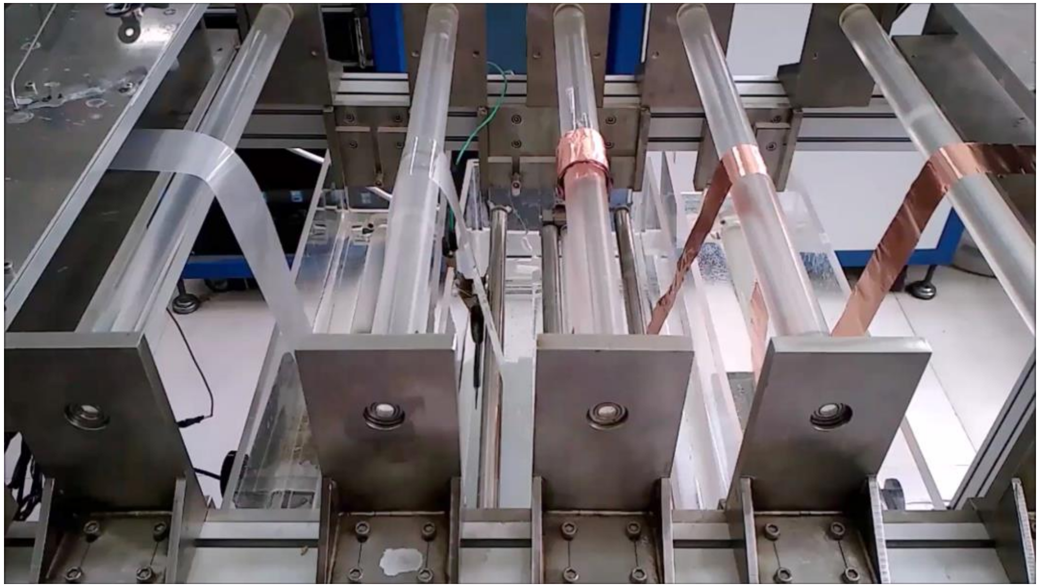
Gao, Ren, Cheng, et al., *Nature Commun* 3 (2012) 699.

Patents: ZL 201110154465.9; USA, EU, Japan, Korea Patents obtained.

Adhesive-Assisted R2R Bubbling Transfer

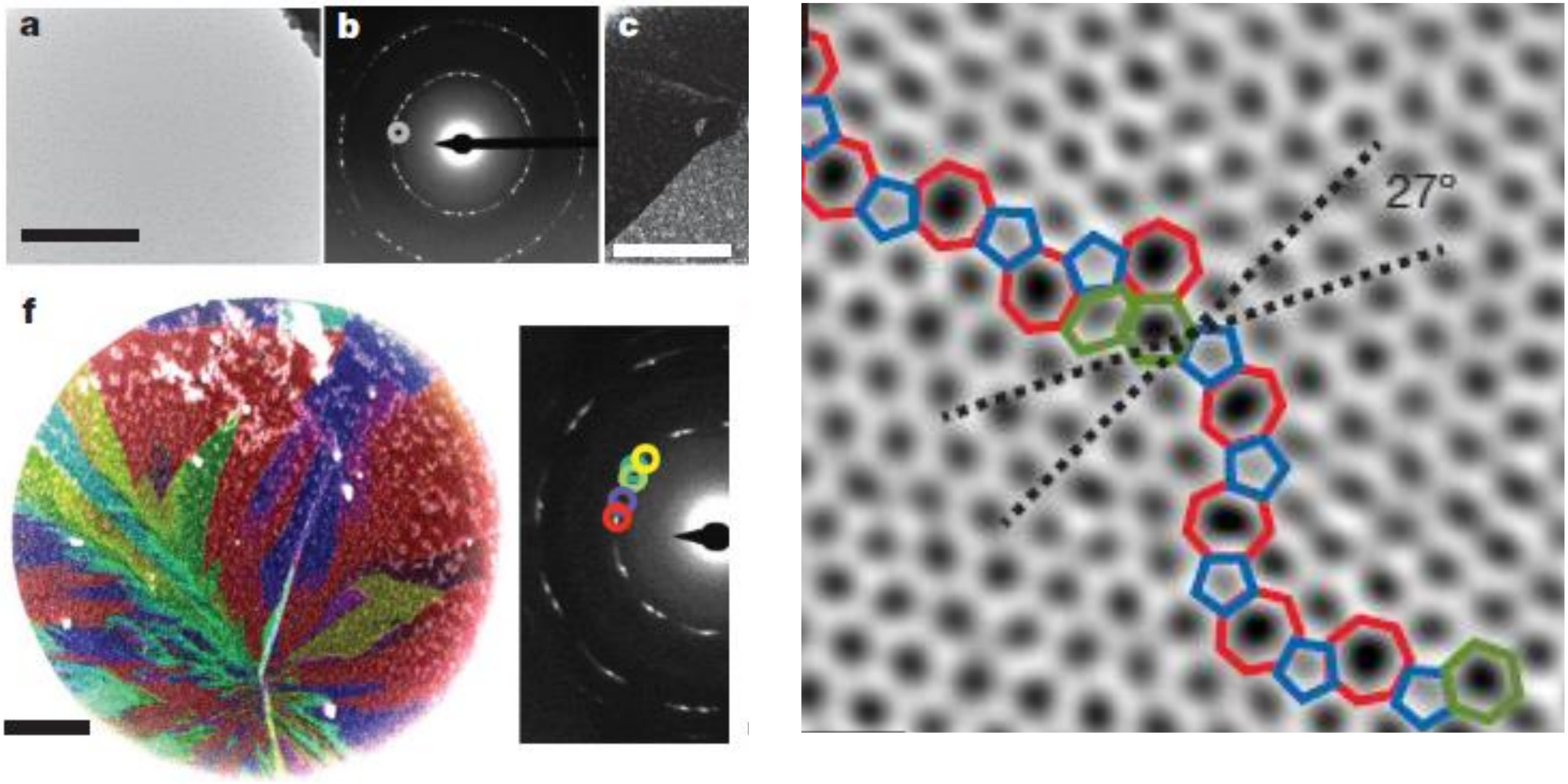


- Etchant-free
- No transfer media (PMMA, PDMS etc.)
- Low-cost
- Highly efficient
- Environment-friendly



LP Ma, et al, Patent filed, 2016

CVD Grown Graphene: Polycrystalline

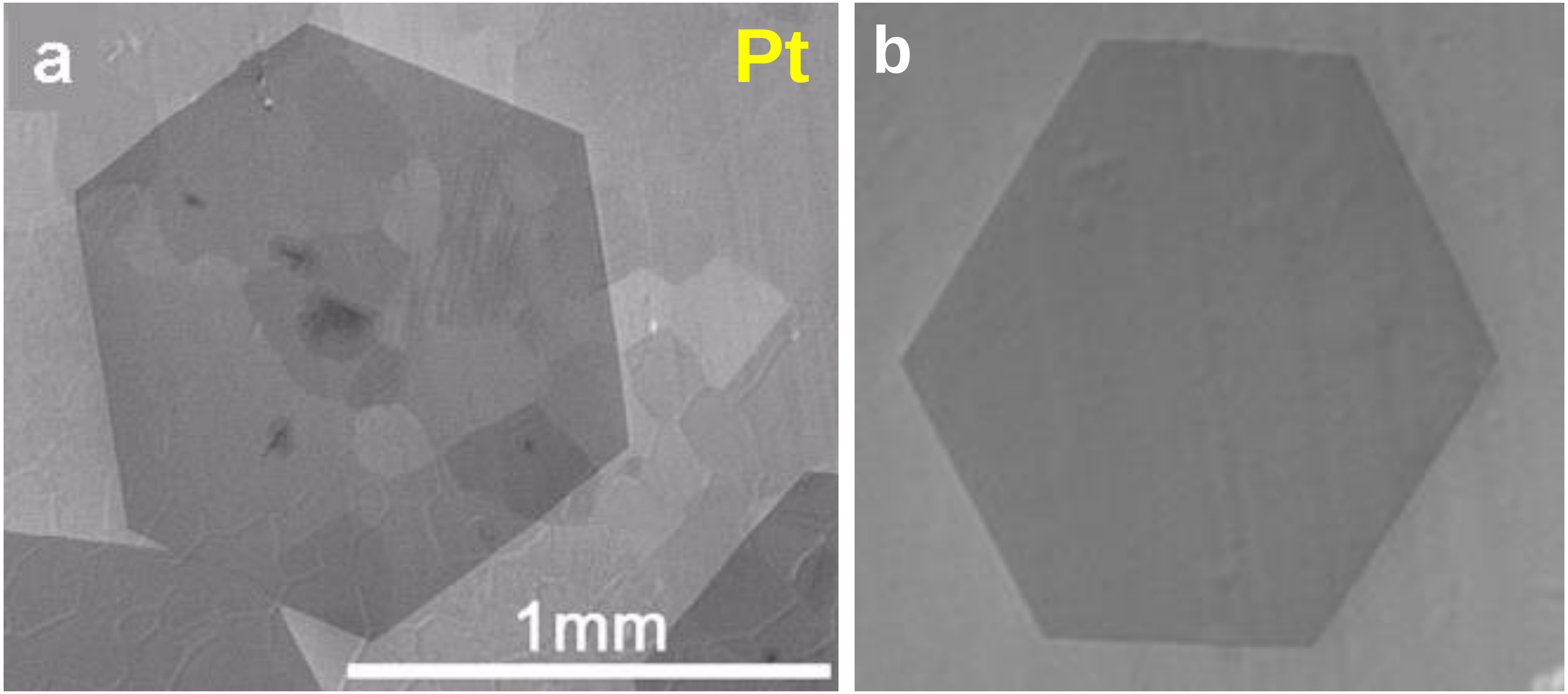


Scale bar: 500 nm

PY Huang et al., *Nature* 469 (2011) 389.

Growth of Single-Crystal Domains with Large Sizes by CVD

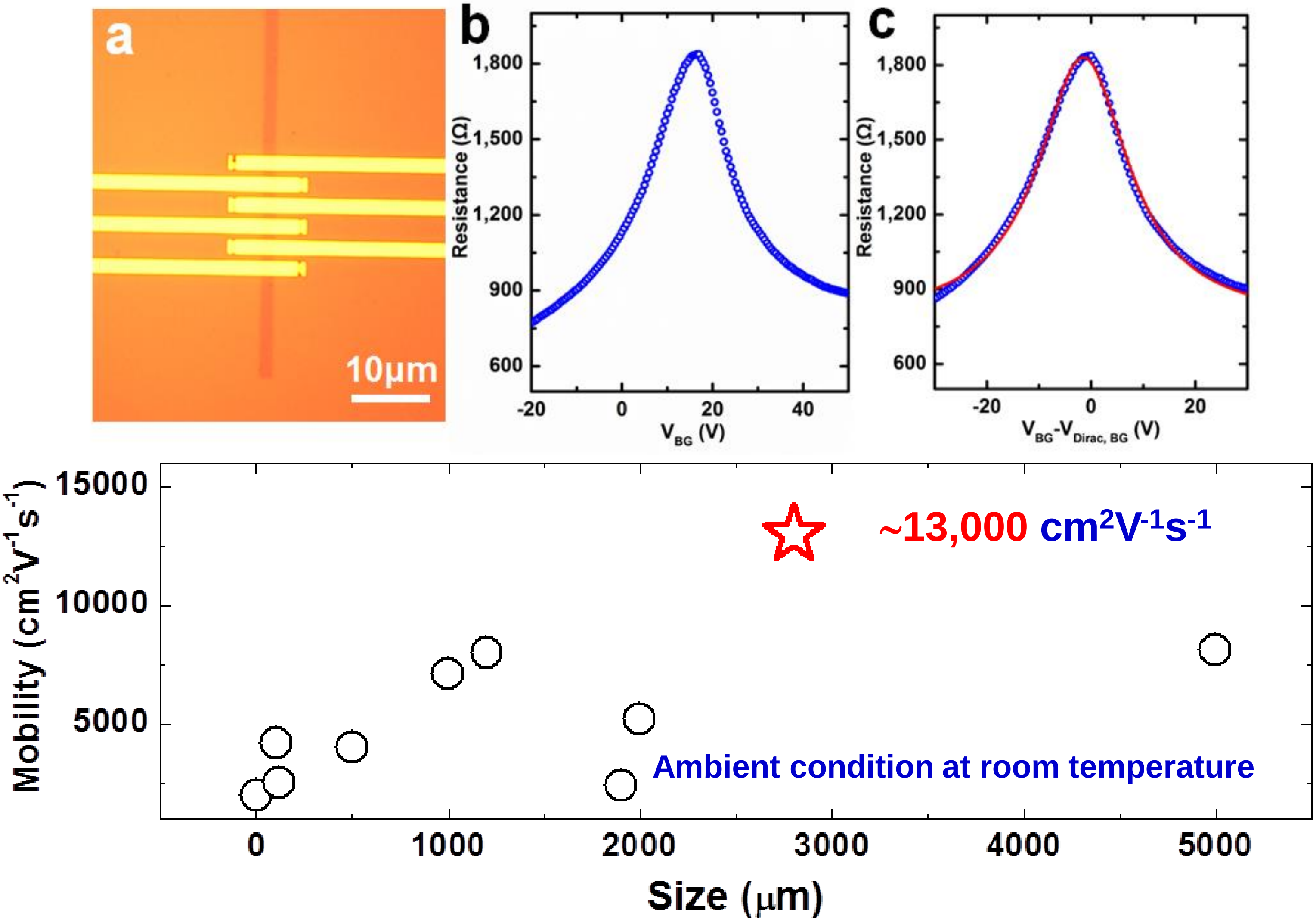
- **Very low flow rate ratio of CH_4/H_2**



Hexagonal shape; very smooth zigzag edges

Gao, Ren, Cheng, et al., *Nature Commun* 3 (2012) 699.

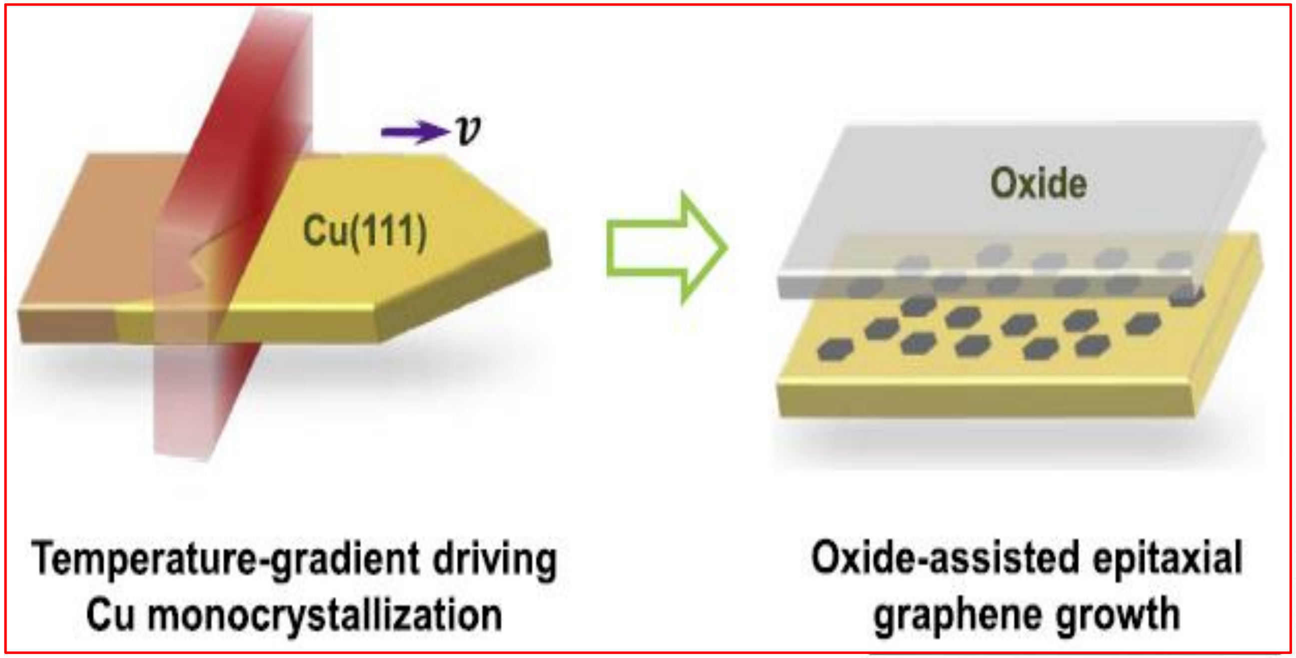
Electronic Performance



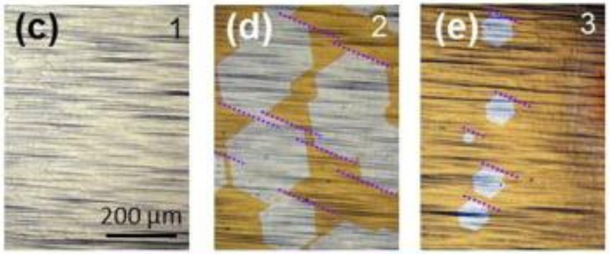
SYNL

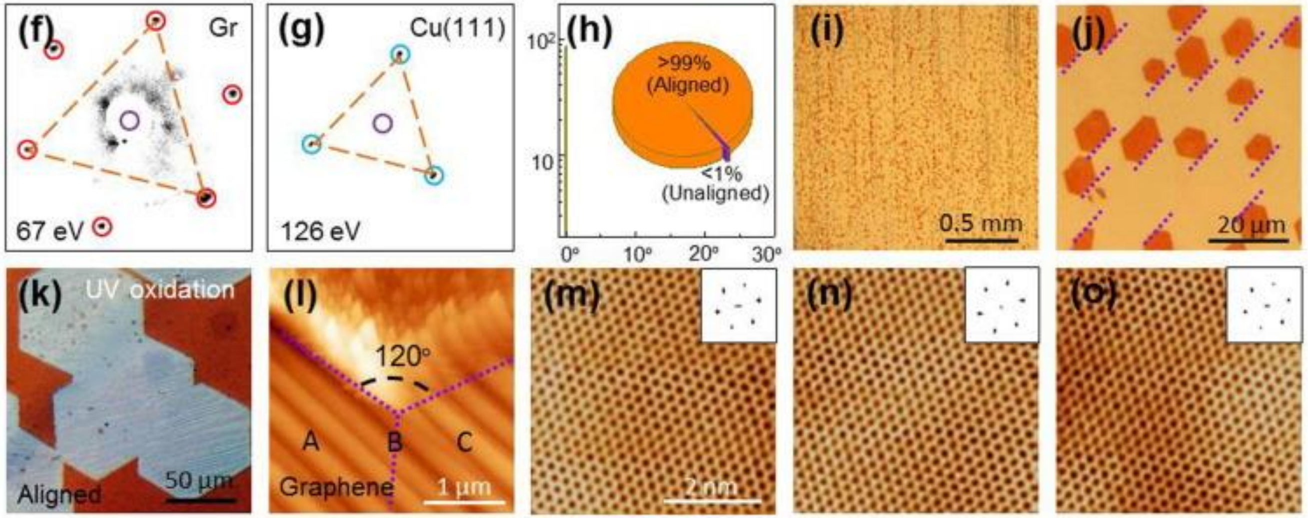
Ma, Ren, Cheng et al., *ACS Nano* 8, 12806-12813 (2014)

A meter-size single crystal Graphene film



Kaihui Liu, et al, *Science Bulletin* 62, 1074 (2017).





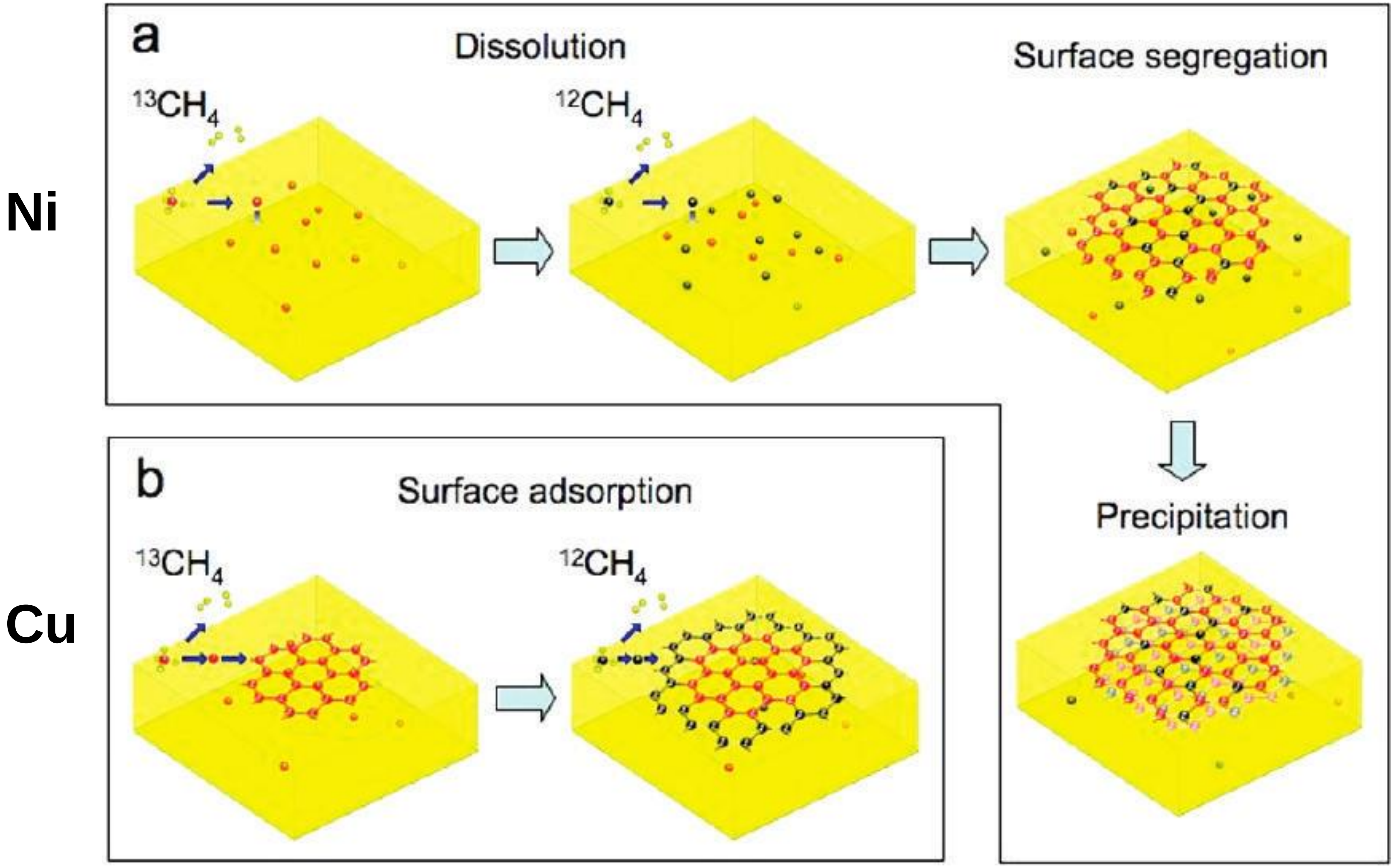
Graphene films with smaller grain size than the electron and phonon mean free paths (~a few hundreds of nanometers)

Influence of grain size on the electrical and thermal transport properties

Ma, Cheng, Ren et al., *Nature Commun.*, 8, 14486, 2017.

SYNL

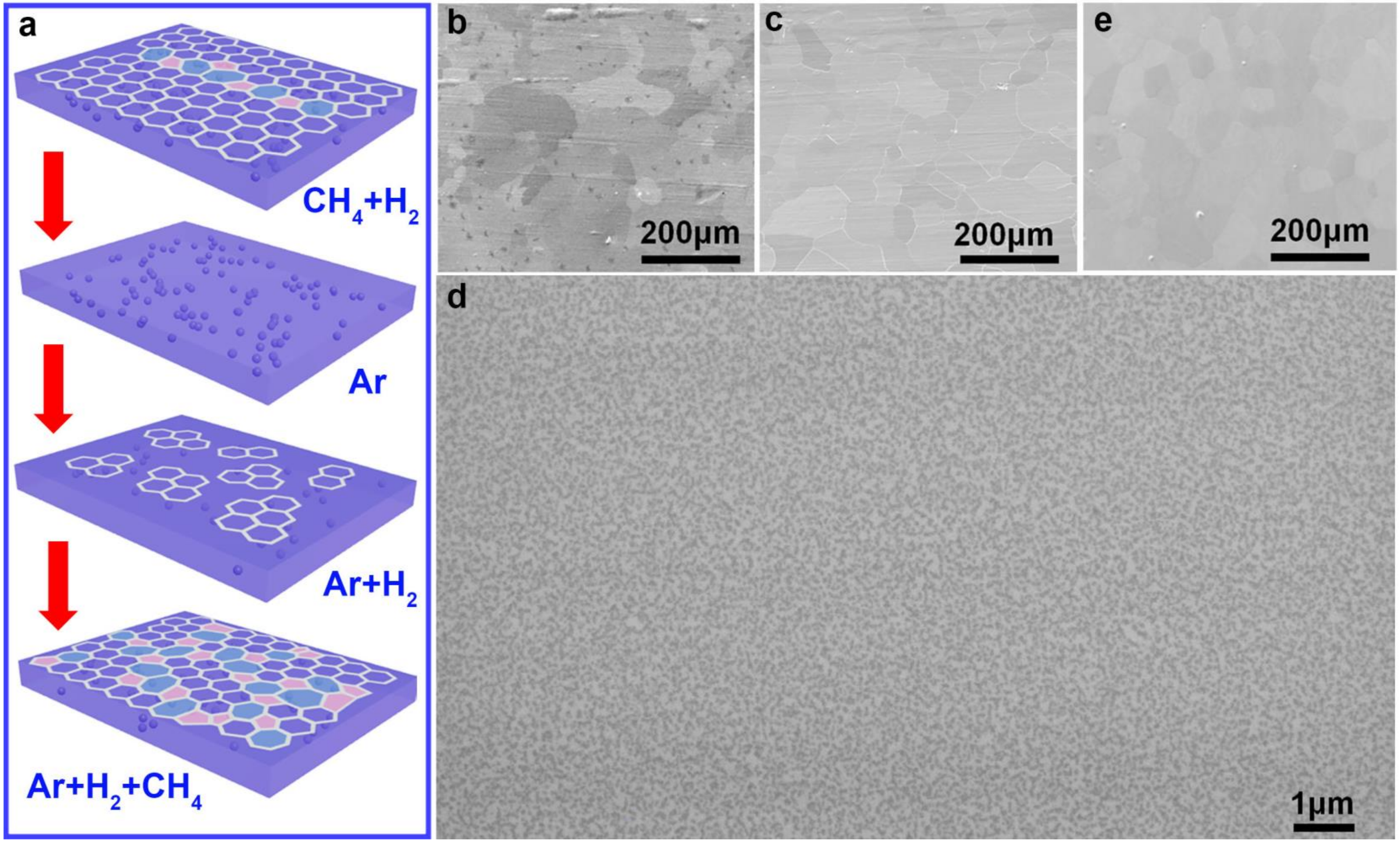
Graphene Growth on Cu and Ni



RS Ruoff et al., Nano Letters, 2009

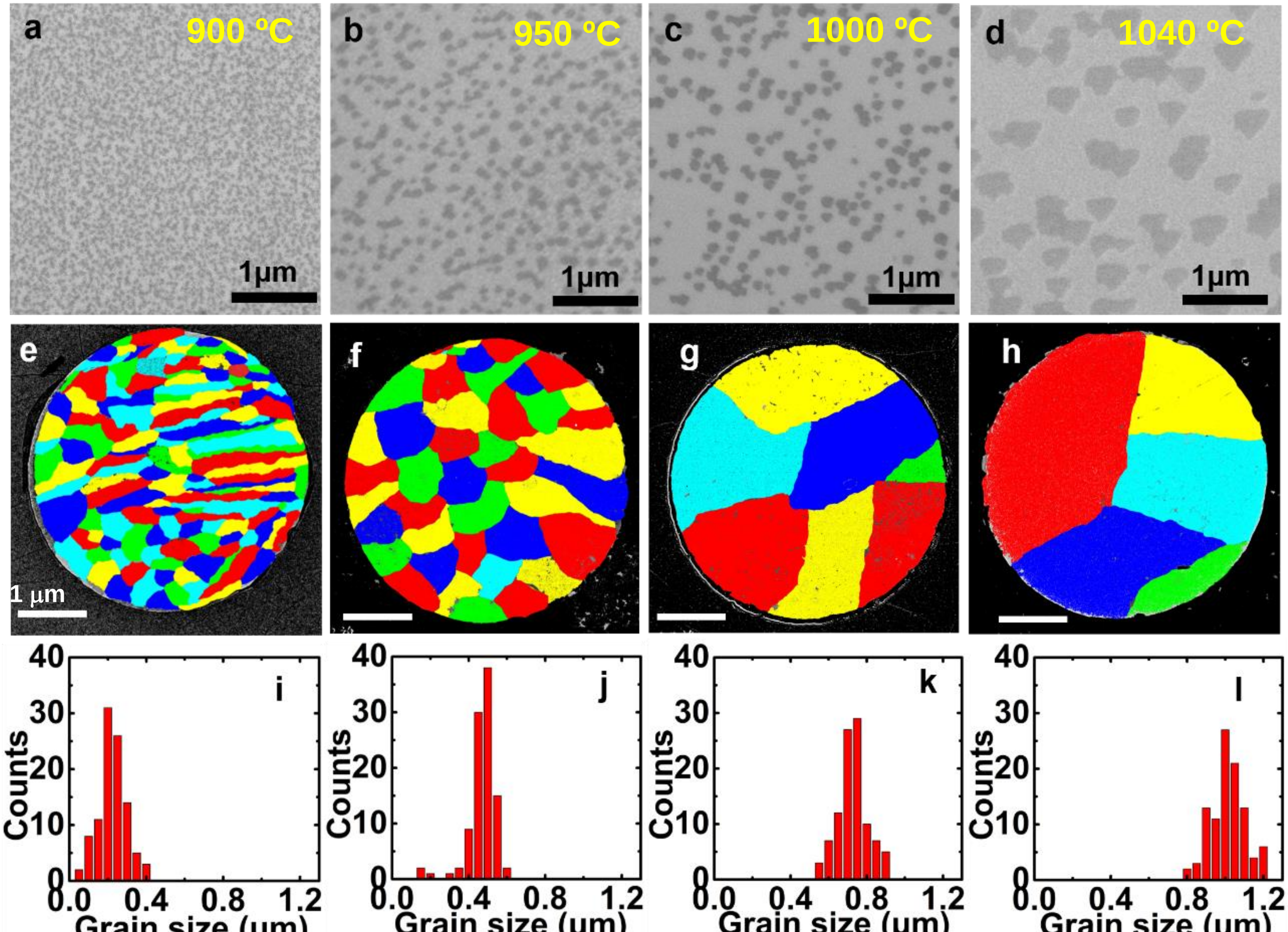
Absorption ↔ Segregation

Carbon solubility: Cu (0.008 wt.%) < Pt (0.07 wt.%) < Ni (0.3 wt.%)

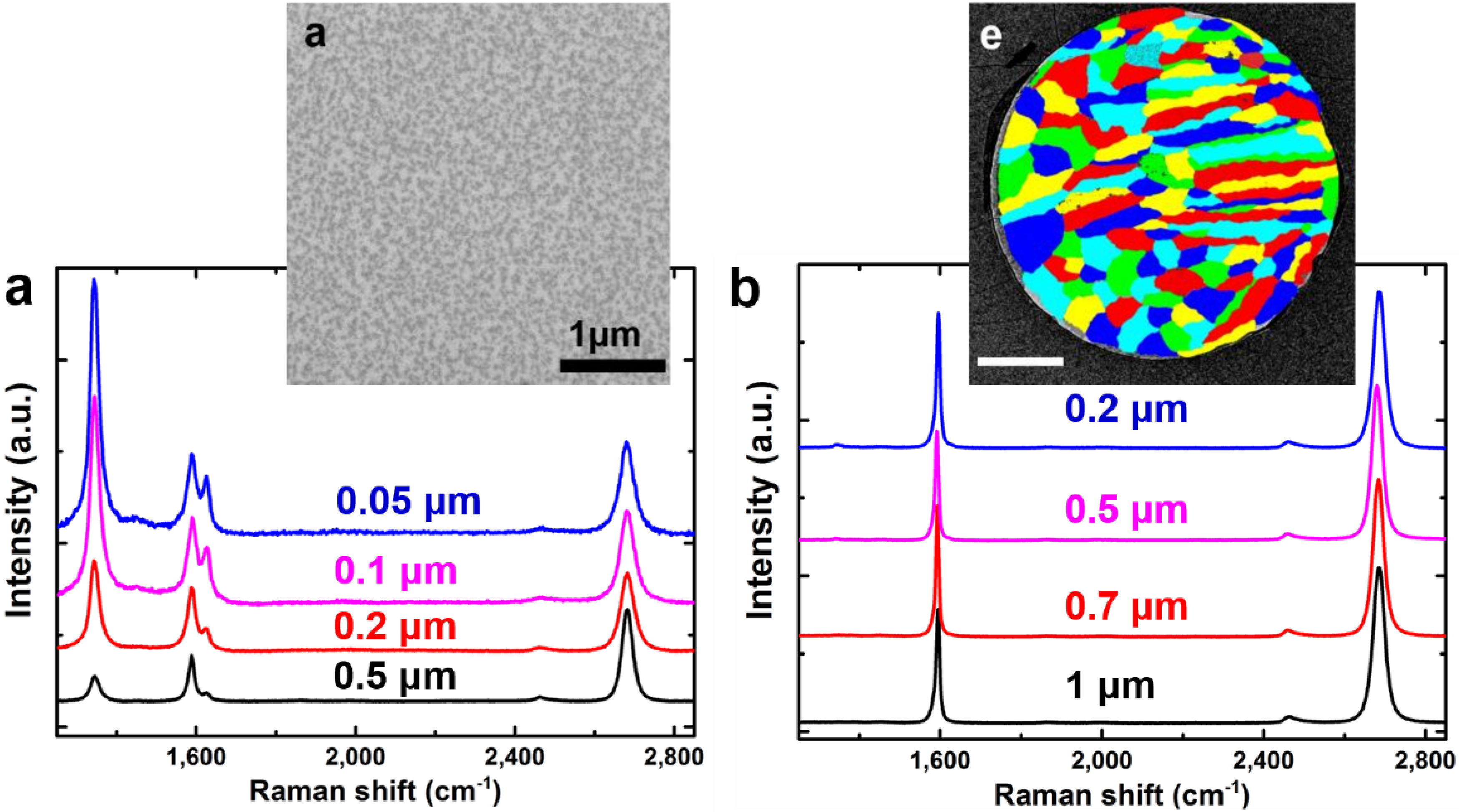


Surface growth + segregation + surface growth

Tunable Uniform Grain Size with the Segregation T

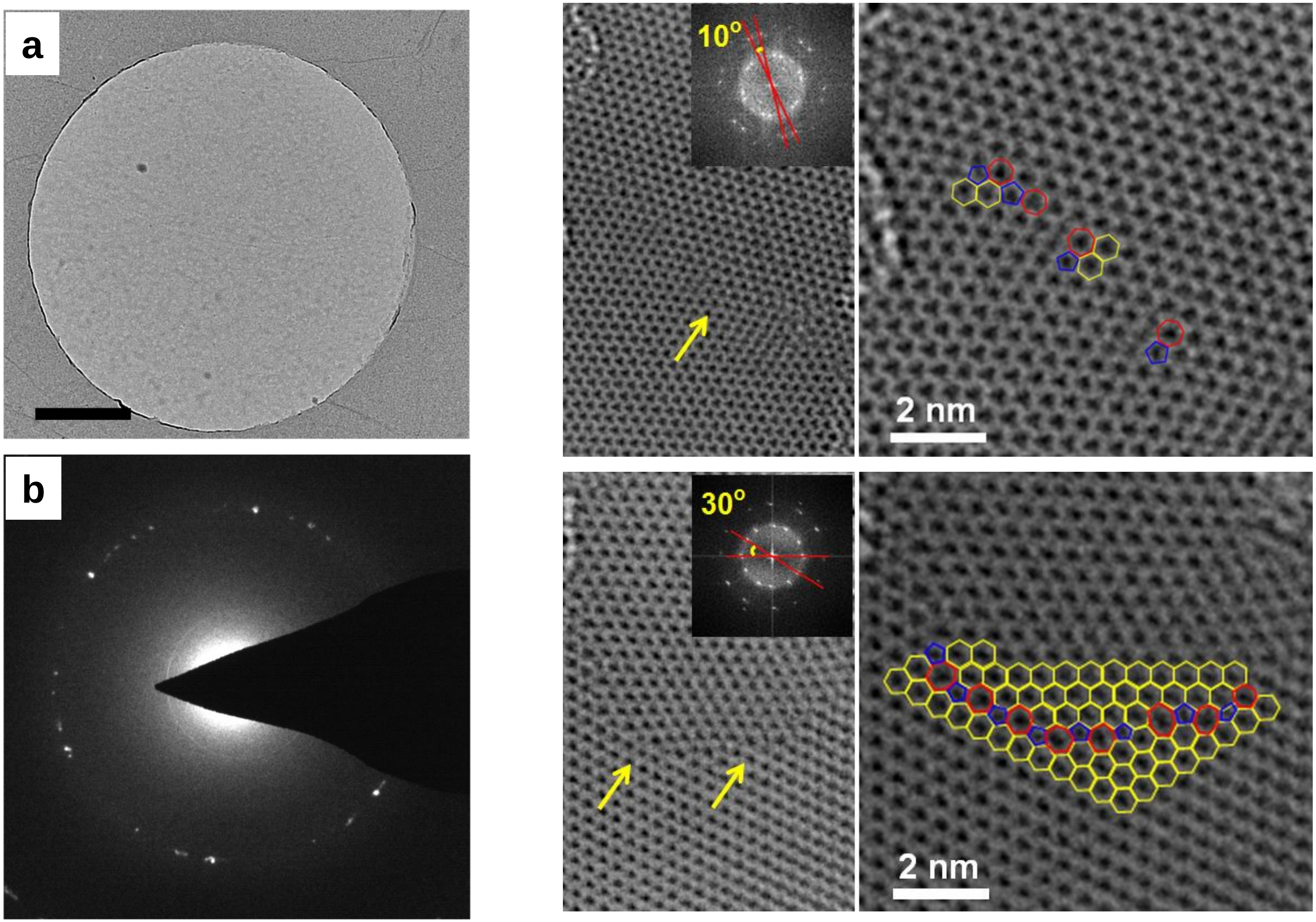


Well-Stitched Graphene Grains

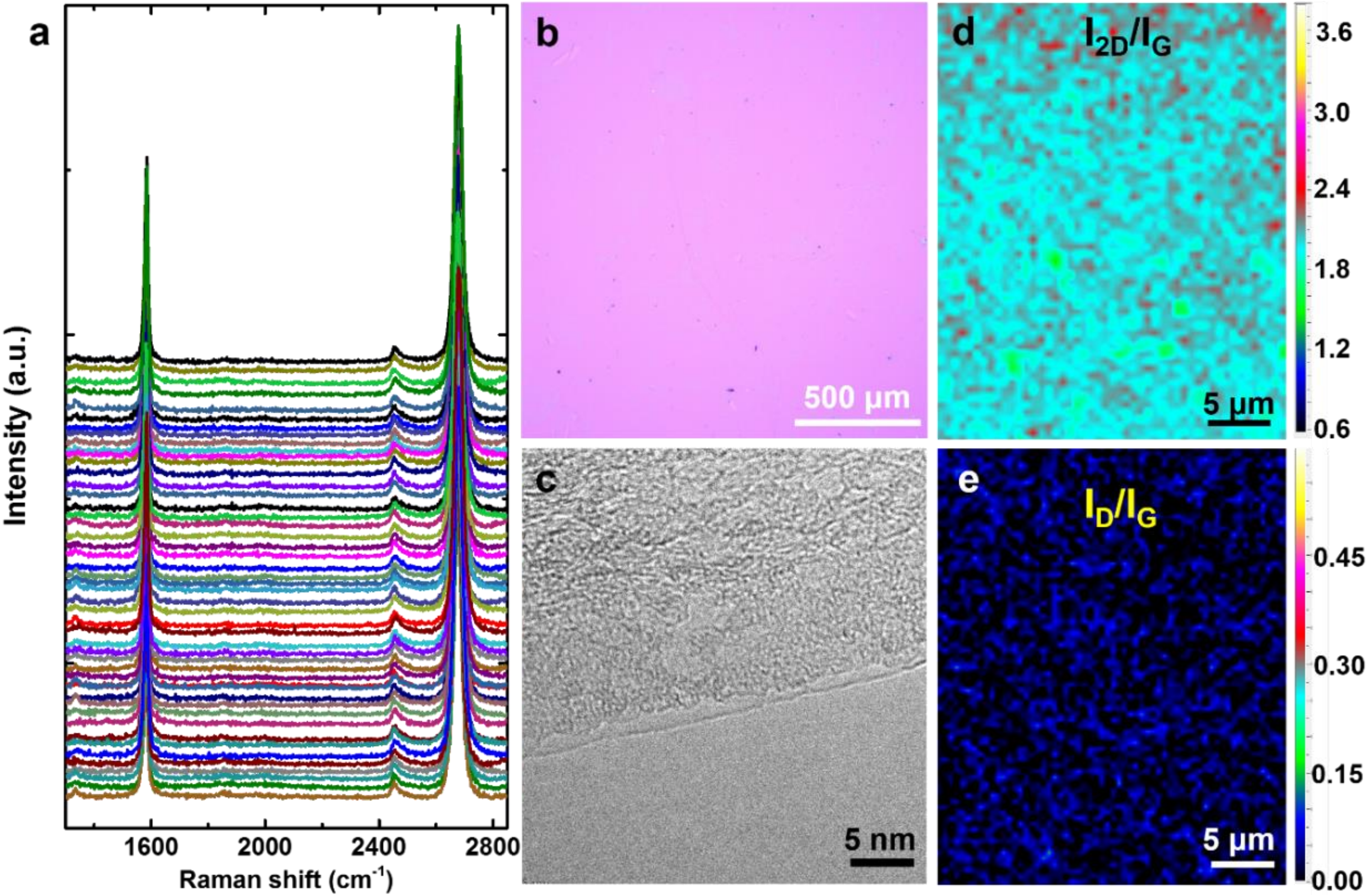


SYNL

Well-Stitched Graphene Grains

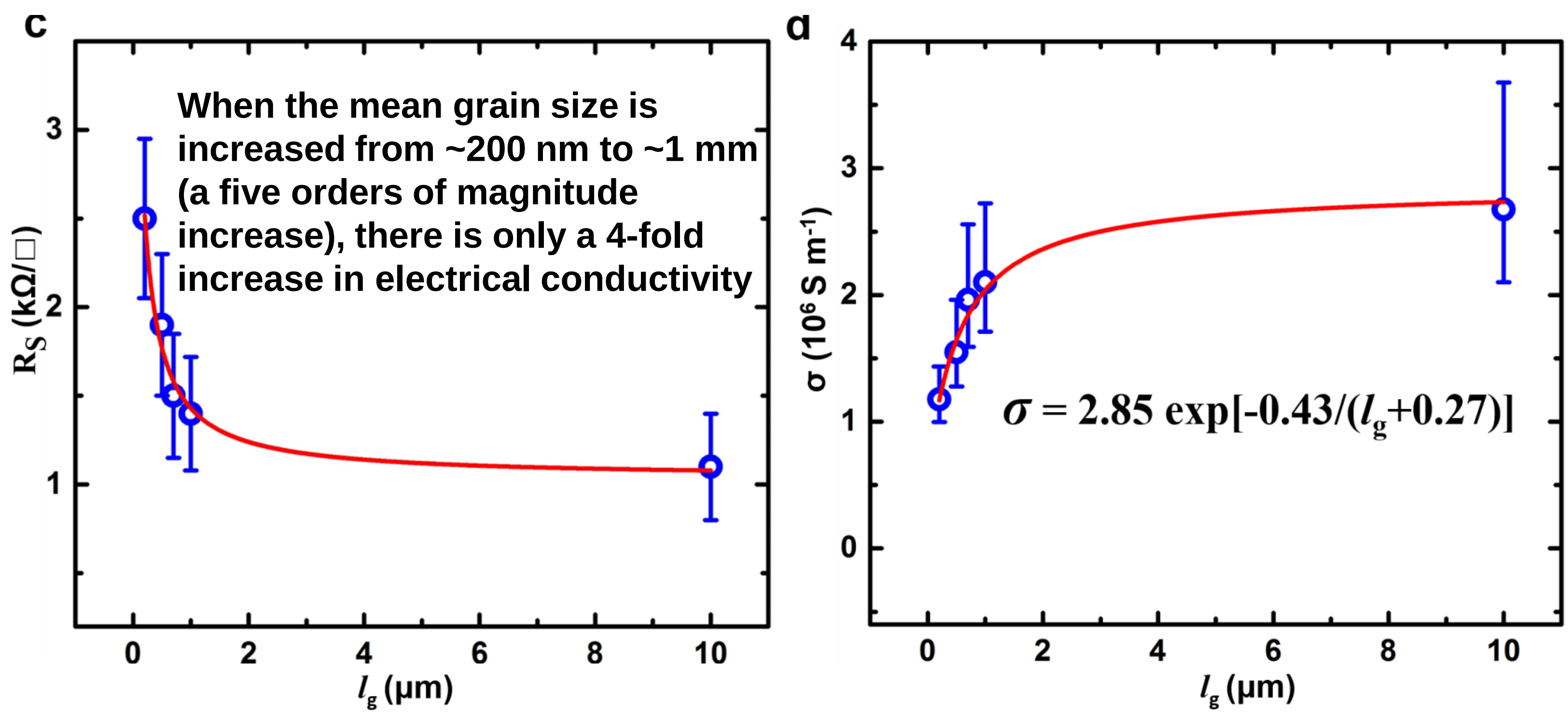


Uniform High-Quality Monolayer



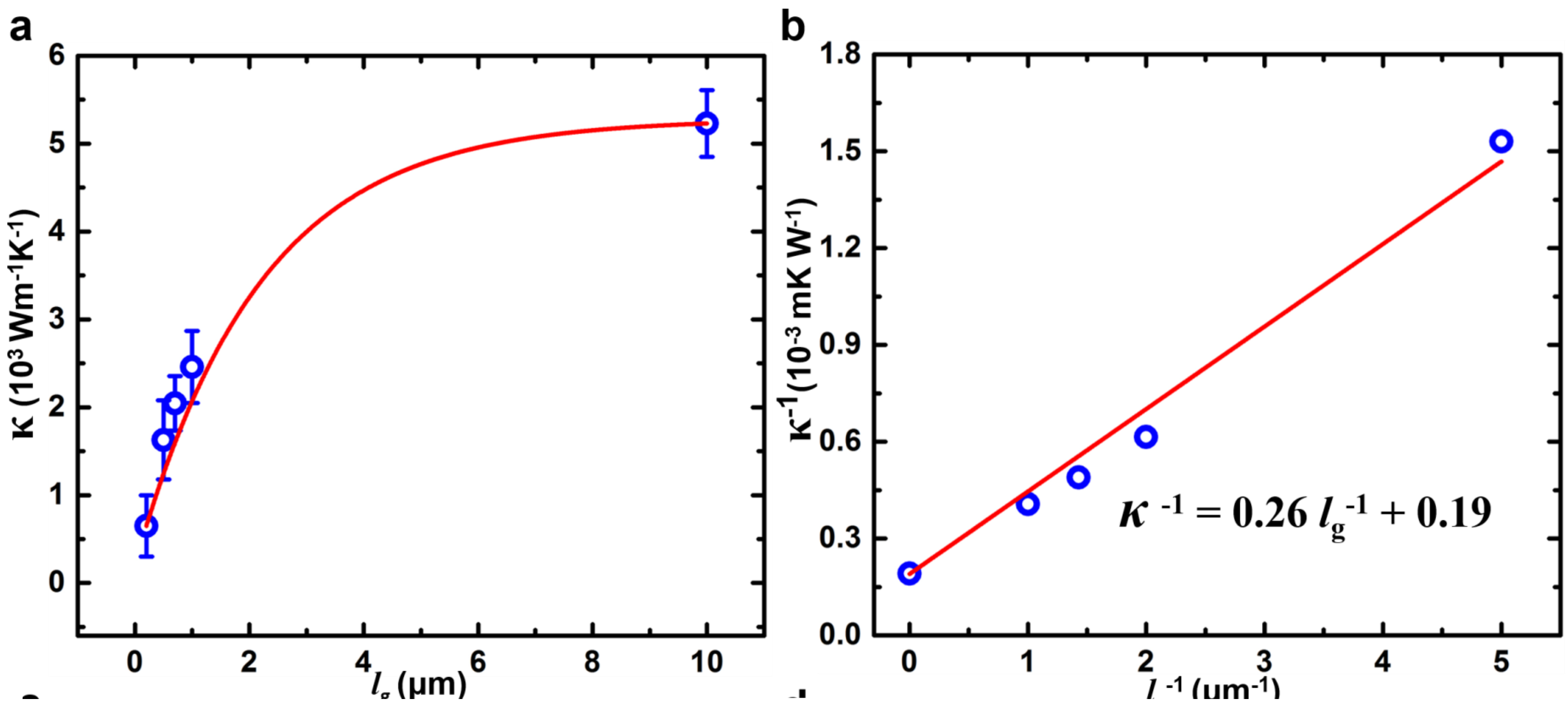
SYNL

Influence on Electrical Transport



- $\sigma = \sigma_0 \exp\{-Ea/[RT(l_g+c)]\}$ modified Arrhenius equation
  - Conductivity within in grain: $\sigma_0 \approx 2.85 \times 10^6$ S m^{-1}
  - Transport gap: $Ea \approx 0.01$ eV; GB resistivity: 0.3 kΩ.μm
  - 1 nm: ~5.8×10^5 S m^{-1}, ~10 times decrease

Influence on Thermal Transport



- $\kappa^{-1} = \kappa_g^{-1} + (l_g G)^{-1}$ kinetic theory of phonon transport
  - Boundary conductance, ~3.8×10^9 $Wm^{-2}K^{-1}$
  - 1 nm: ~3.8 $Wm^{-1}K^{-1}$, ~1,400 times decrease

Ma, Cheng, Ren et al., *Nature Commun.*, 8, 14486, 2017.

Growth of 3-Dimensional Graphene Frameworks by CVD

Chen, Ren, HMC*, et al., *Nature Mater* 10 (2011) 424

SYNL

Bulk Growth of Graphene by CVD

IMR

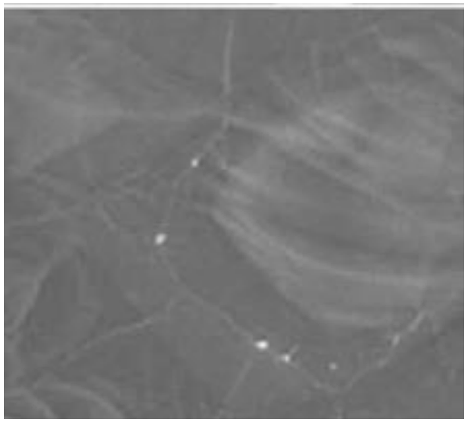
- **Flat metal substrates**
  - **2D graphene films (good for TCFs, devices,…)**
  - **Low yield**

- **Bulk growth of graphene by CVD?**
  - **Bulk applications (composites, energy storage, …)**
  - **2D growth→3D growth**

The Substrate is key !

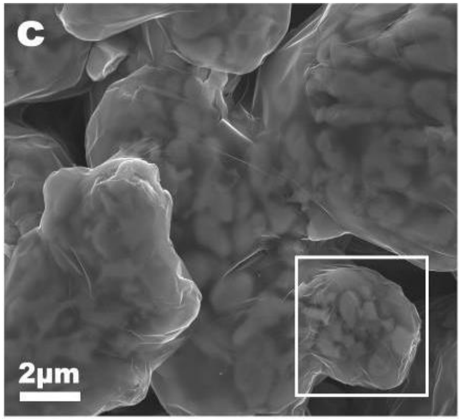
SYNL

How to obtain graphene with unique structure and in a large scale by CVD?



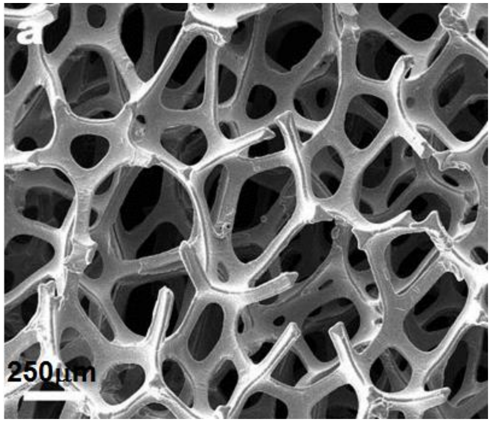
Metal foil
(plane)

Appl Phys Lett 97 (2010) 183109



Metal Particles
(curved surface)

Carbon 48 (2010) 3543



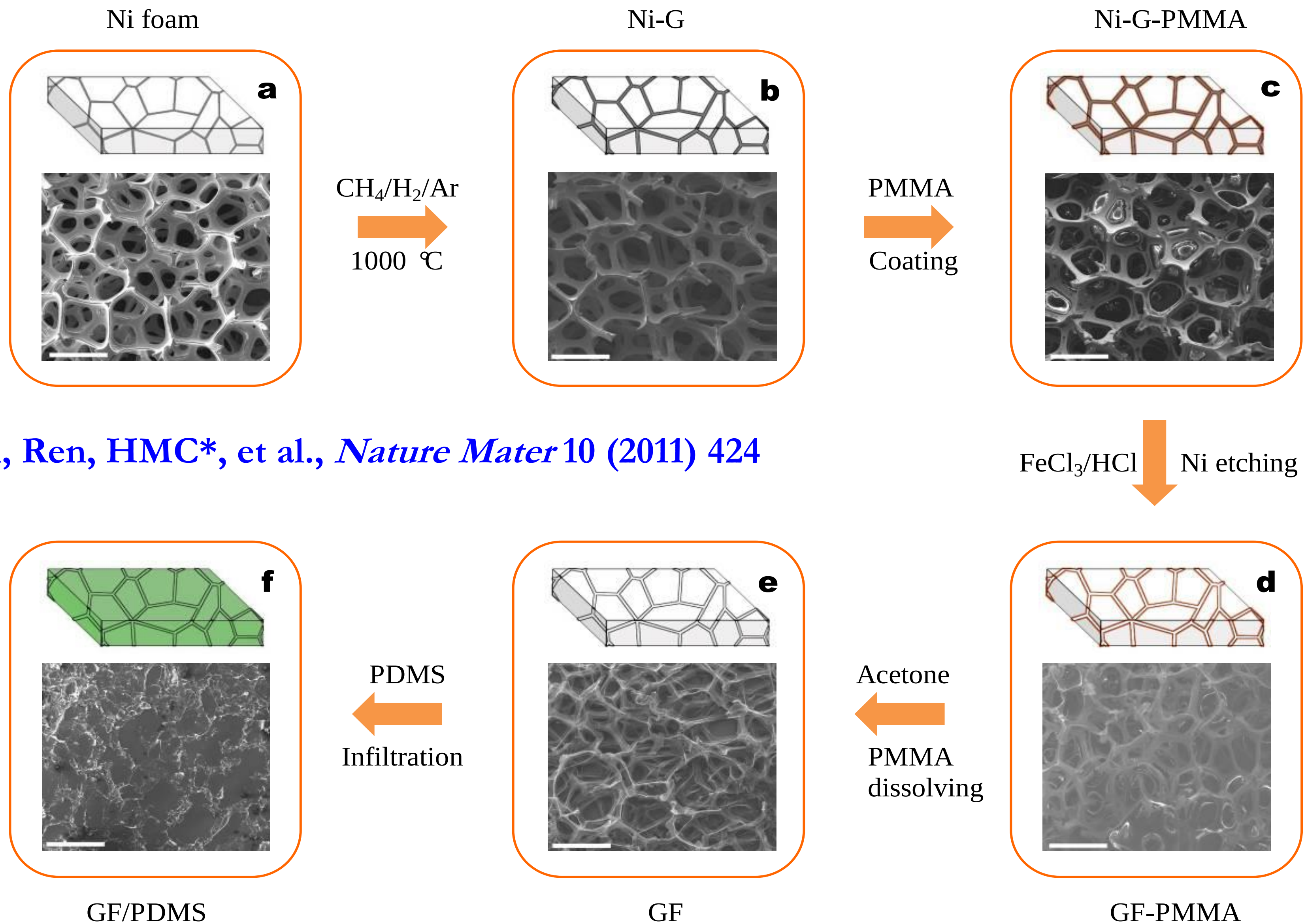
Metal foam
(plane+curved surface)

Nature Mater 10 (2011) 424

- **Metal Foams**
  - **Plane+curved surface → 3D interconnected**
  - **High surface area → growth in a large scale**

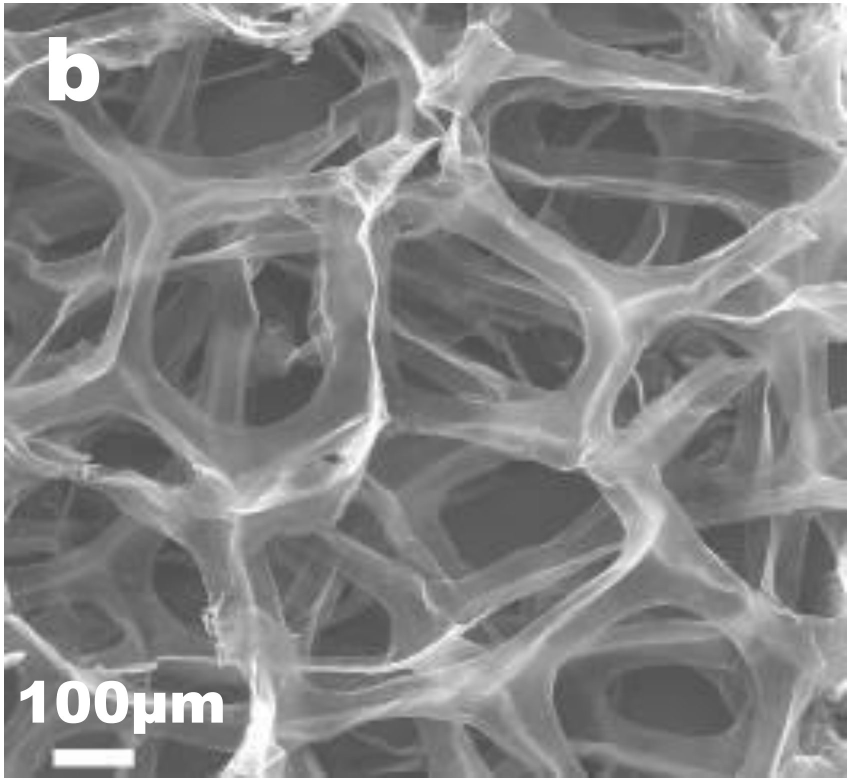
SYNL

Procedure for Synthesis of a GF



Chen, Ren, HMC*, et al., *Nature Mater* 10 (2011) 424

Free Standing Graphene Foam

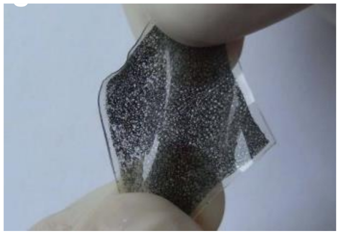


- Ultra-low density: ~5 mg/cm^3, very light aerogel
- A very high porosity: ~99.7%
- Specific surface area: ~900 m^2/g

Chen, Ren, HMC*, et al., *Nature Mater* 10 (2011) 424

Potential Applications of GFs

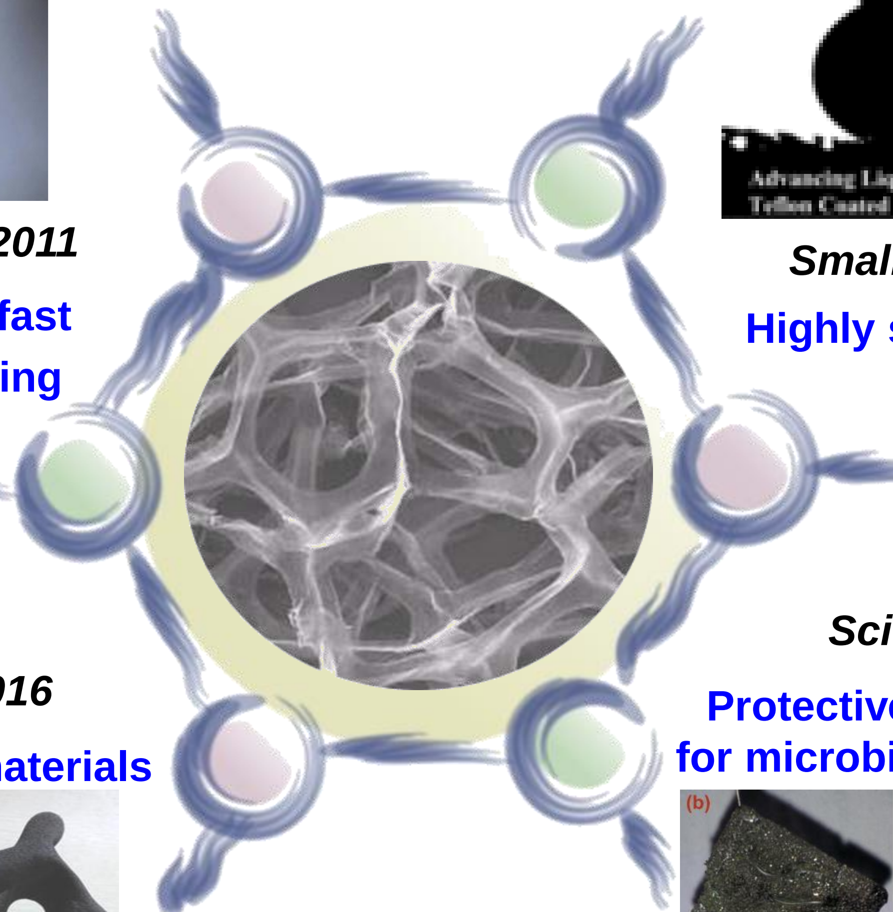
Elastic conductors



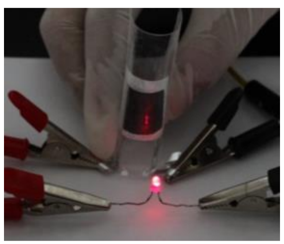
Nature Mater, 2011

Superhydrophobic materials

Small, 2013

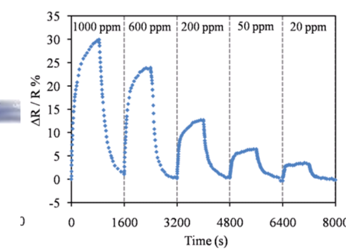


Flexible Batteries with fast charging and discharging



PNAS 2012; Adv Mater 2016

Highly sensitive gas sensors

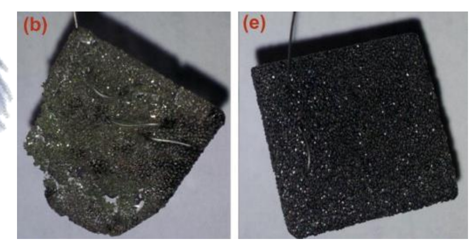


Scientific Reports, 2011

Lightweight EMI materials

Adv Mater, 2013

Protective coatings for microbial corrosion



Carbon, 2013

SYNL

Summary

- **CVD on metals is a powerful approach to grow graphene**
  - Good controllability
  - Large area
  - Different grain sizes
  - High quality
  - Possible applications in flexible devices such as OLED

Acknowledgment

- Prof. Wencai Ren
- Prof. Feng Li
- Prof. Jinhong Du
- Dr. Laipeng Ma
- Dr. Songfeng Pei
- Dr. Dongming Sun
- Dr. Lichang Yin
- Dr. Zhikun Zhang

- Prof. Ning Kang @ Peking Univ
- Prof. Lianmao Peng @ Peking Univ
- Prof. Feng Ding @ Polytech Univ, Hong Kong

Prof. Xiuliang Ma @ IMR, CAS

Prof. Xinhe Bao & Qiang Fu @ DICP, CAS

- Dr. Zhong-Shuai Wu (Chem exfoliation)
- Dr. Libo Gao (CVD Graphene)
- Dr. Teng Ma (G mechanism)
- Dr. Zongping Chen (3D graphene)
- Dr. Chuan Xu (2D TMCs)
- Dr. Yang Gao (2D TMDs)
- Dr. Guangmin Zhou (Li-S batteries)
- Dr. Zhibo Liu (TEM)
- Mr. Long Chen (2D TMCs)
- Mr. Shuai Jia (OLEDs)

SYNL

Acknowledgement

- 国家自然科学基金委员会 National Natural Science Foundation of China
- 中华人民共和国科学技术部 Ministry of Science and Technology of the People´s Republic of China
- 中国科学院 CHINESE ACADEMY OF SCIENCES
- **Deyang Jinghua New Carbon Co.**

Thank you very much

for your kind attention!