二维狄拉克材料的可控生长与光电性质研究

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北京大学 化学与分子工程学院

2013-09-26

致 谢

经 费： NSFC　国家重点基础研究发展计划（973）

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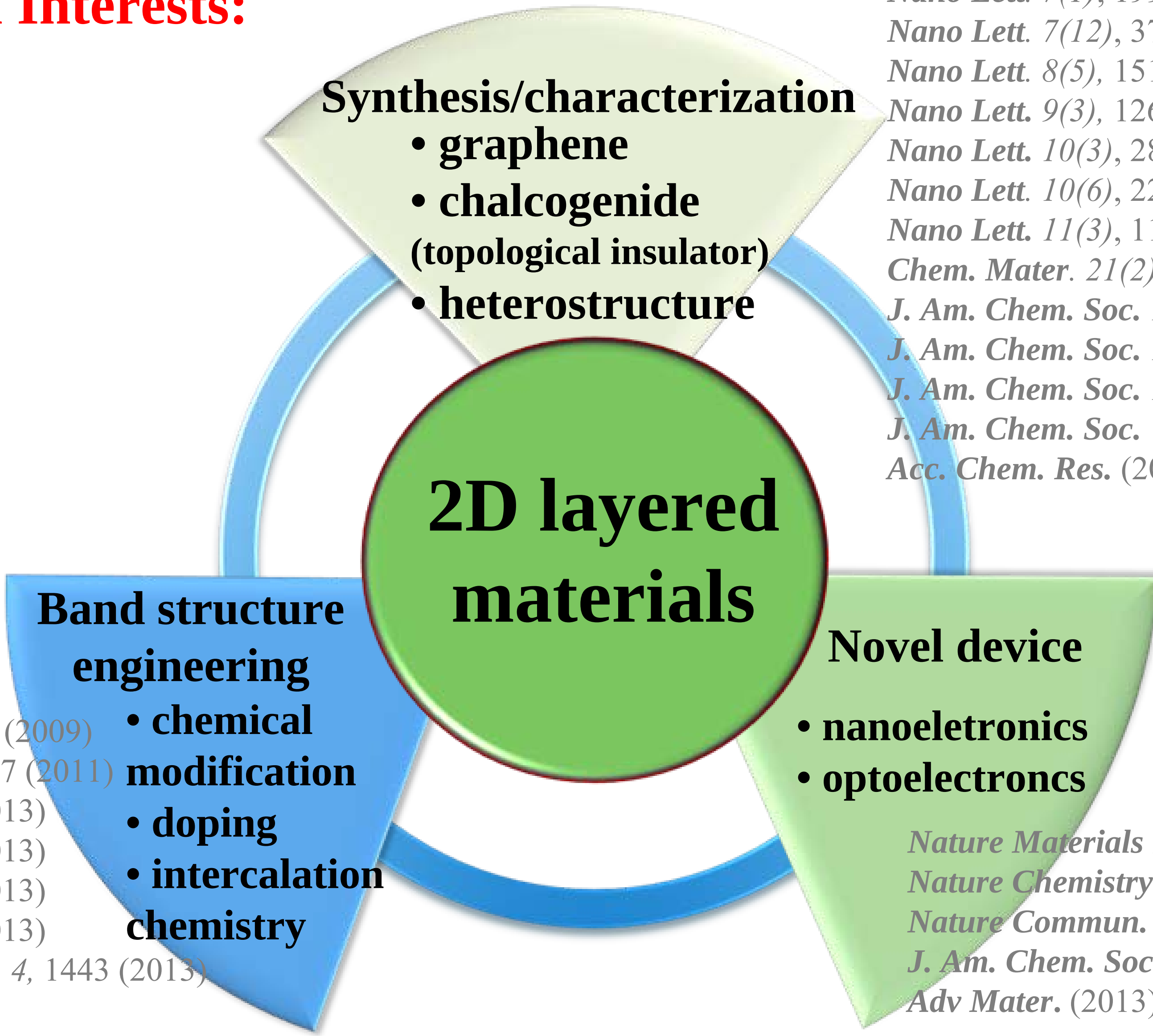
美国斯坦福大学
沈志勋 教授
张首晟 教授
崔 屹 副教授

Research Interests:



Nano Lett. *7(1)*, 199 (2007)
Nano Lett. *7(12)*, 3734 (2007)
Nano Lett. *8(5)*, 1511 (2008)
Nano Lett. *9(3)*, 1265 (2009)
Nano Lett. *10(3)*, 2870 (2010)
Nano Lett. *10(6)*, 2245 (2010)
Nano Lett. *11(3)*, 1106 (2011)
Chem. Mater. *21(2), 247* (2009)
J. Am. Chem. Soc. 129, 34 (2007)
J. Am. Chem. Soc. 131, 7973 (2009)
J. Am. Chem. Soc. 134, 6132 (2012)
J. Am. Chem. Soc. 135, 13274 (2013)
Acc. Chem. Res. (2013)

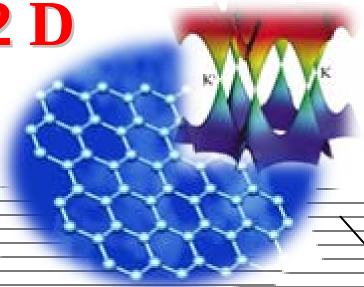
Nano Res. 2, 327 (2009)
ACS Nano 5, 5957 (2011)
Small 9, 1348 (2013)
Small 9, 1134 (2013)
Small 9, 1388 (2013)
Small 9, 1316 (2013)
Nature Commun. 4, 1443 (2013)

Nature Materials 9, 225 (2010)
Nature Chemistry 4, 281 (2012)
Nature Commun. 3, 1280 (2012)
J. Am. Chem. Soc. 135, 10926 (2013)
Adv Mater. (2013)

“Star Nanomaterials” in the last 30 years

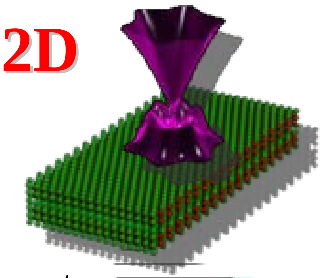
Dimensionality evolution

2 D



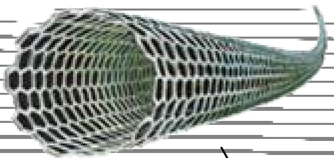
Graphene, 2004
(Manchester Univ.)
A. Geim, Science, 306, 666 (2004)

2D



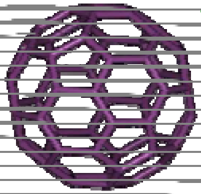
Topological insulator
Kane, PRL 95, 146802 (2005)
Zhang, Science 314,1757 (2006)
Moore, PRB 75, 121306 (2007)

1 D



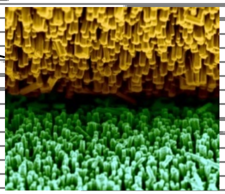
Carbon nanotube, 1991 (NEC)
S. Iijima, Nature, 354, 56 (1991)

0 D



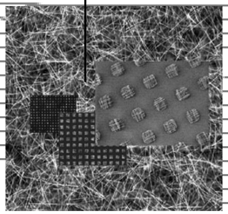
Fullerene, 1985 (Rice Univ.)
Kroto, Nature, 318, 162 (1985)

1 D

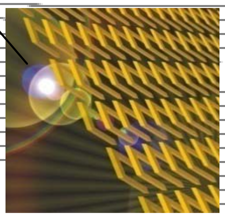


ZnO nanowire, 2001
Z. L. Wang, Science 291, 1947 (2001)

1 D

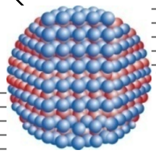


Si & Ge Nanowires,
C.M. Lieber, Science 279, 208 (1998)



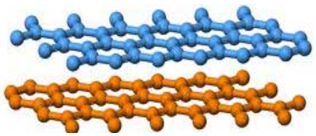
Metamaterial, 2000
(UCSD, USA)
D. R. Smith, PRL, 84, 418495 (2000)

0 D

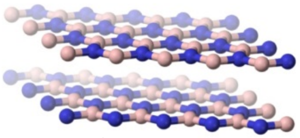


Quantum dot, 1981
(Vavilov State Opt. Ins.)
A. Ekimov, JETP Lett., 34, 345 (1981)

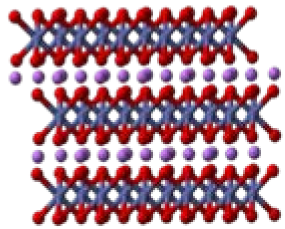
Two-Dimensional Crystal Family



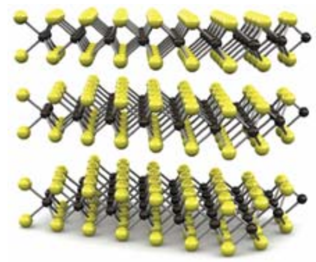
IV: graphene, Si, Ge



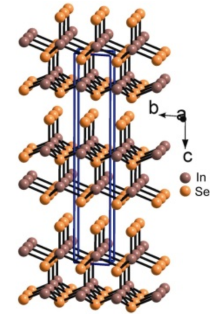
h-BN



transition metal oxide (TMO): MoO_3, $LiCoO_2$

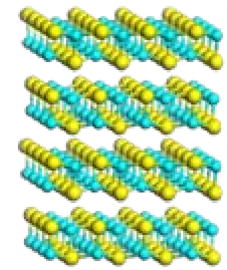


transition metal chalcogenides (TMC) MoS_2, WS_2 …



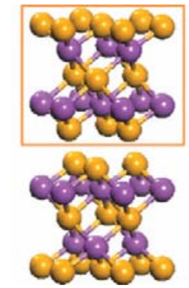
III-VI

In_2Se_3, GaSe



IV-VI

GeS, SnSe

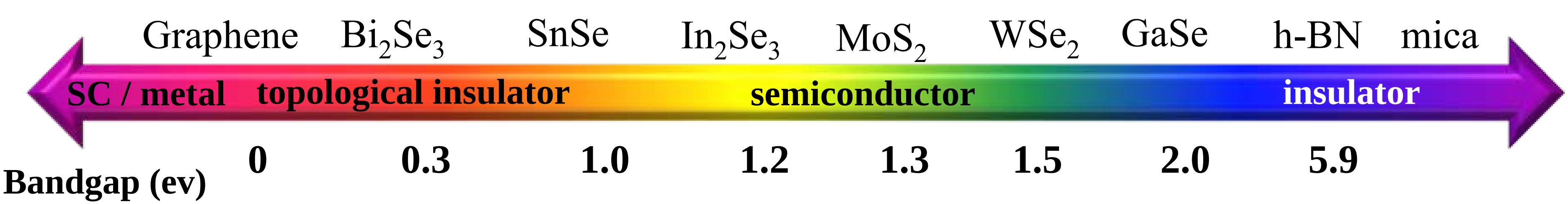


V-VI

Bi_2Se_3, Bi_2Te_3

topological insulator

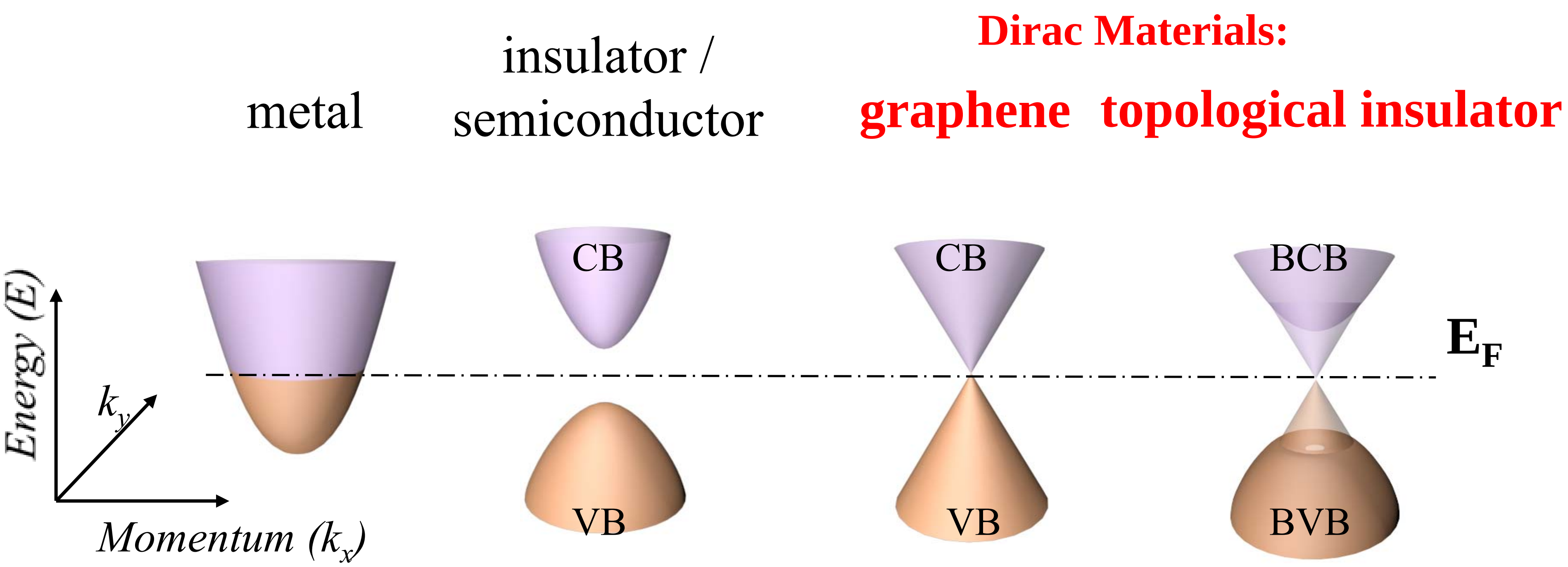
- **Layered and anisotropic structure; strong in-plane bonding; weak interlayer van der Waals bonding**
- **Large variety of electronic properties**



- **Properties of 2D crystals are very different from their 3D counterparts**

Electronic band structures

Dirac Materials:



$$E = \hbar^2 k^2 / 2m^*$$

$$E \propto k^2$$

Parabolic type band structure

$$E_{K(K')} = \pm \hbar v_F |k|$$

$$E \propto k$$

Dirac cone type:

linear energy-momentum "relativistic" dispersion described by the massless Dirac Hamiltonian

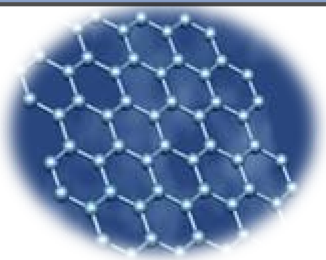
2D Dirac Materials

狄拉克材料（Dirac费米子系统）

Dirac锥形能带结构：能量-动量线性关系

Graphene

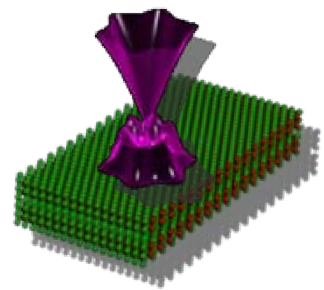
Layered structure | **Dirac cone**



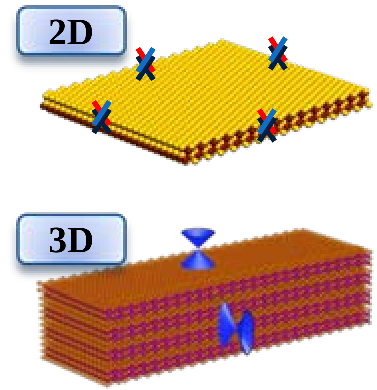
Geim, et al., *Science* 306, 666(2004)

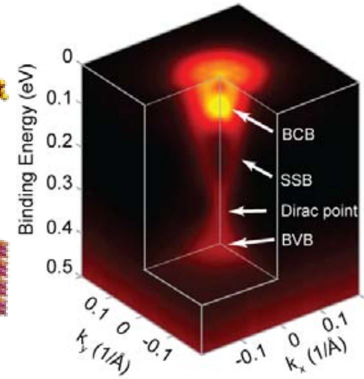
Topological insulator 拓扑绝缘体

Dirac cone | **Electrons live on the surfaces**



Bi_2Se_3, Bi_2Te_3, Sb_2Te_3





"Locking" of current & spin

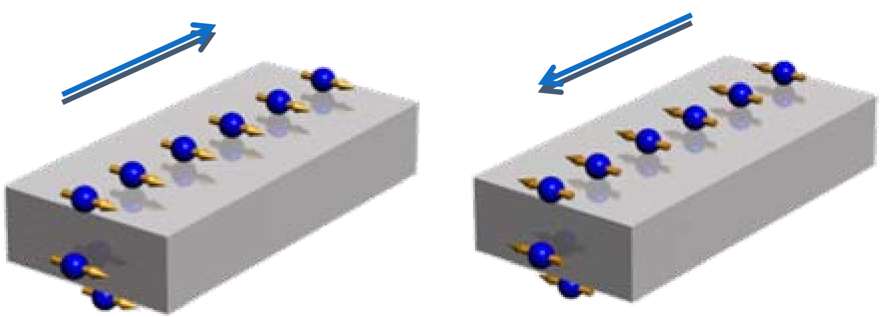
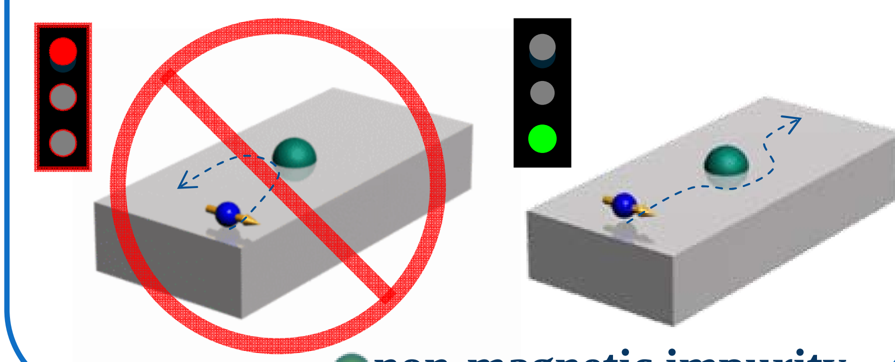


Image courtesy Y. L. Chen

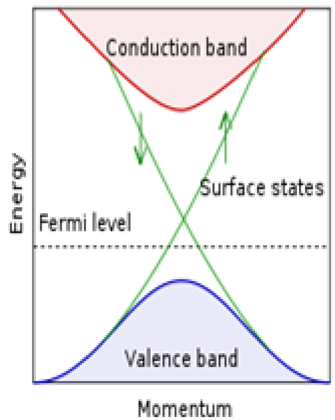
No back-scattering rule



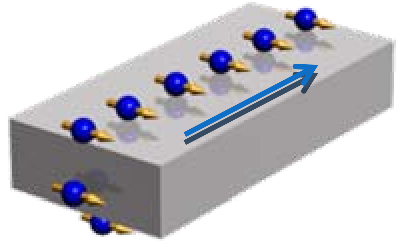
non-magnetic impurity

Robust, dissipationless spin currents

Topological Insulators and Their Applications



a new quantum material with insulating bulk and gapless Dirac surface state



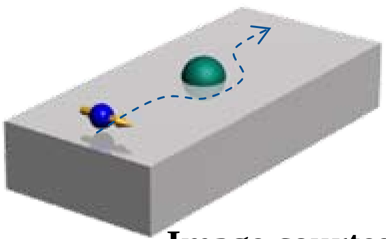
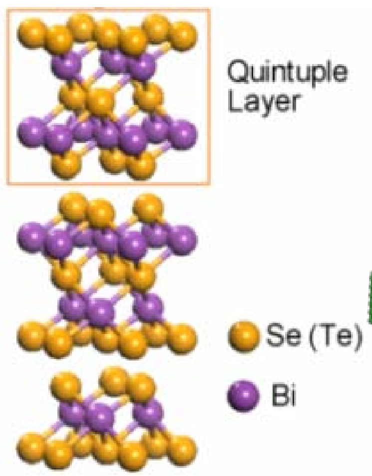
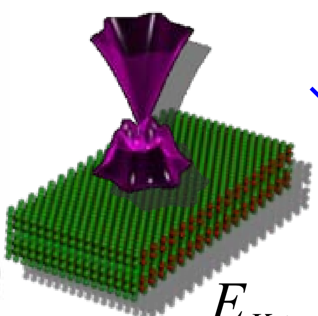


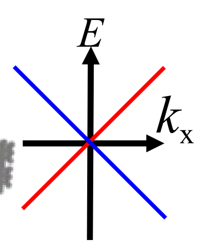
Image courtesy Y. L. Chen

“Locking” of current & spin **No back-scattering rule**

Robust, dissipationless spin current generated at surfaces







$$E_{K(K')} = \pm \eta v_F |k|$$

3D TI:
Bi_xSb_{1-x}
Bi_2Se_3, Bi_2Te_3, Sb_2Te_3
Bi_2Se_2Te, Bi_2SeTe_2 , $(Bi_xSb_{1-x})_2Te_3$
$TlBiTe_2$, $TlBiSe_2$, $TlBiS_2$, $TlSbTe_2$, $TlSbSe_2$
LuPtSb, LuPdBi, YPtBi, CePtBi, LaPtBi
… …

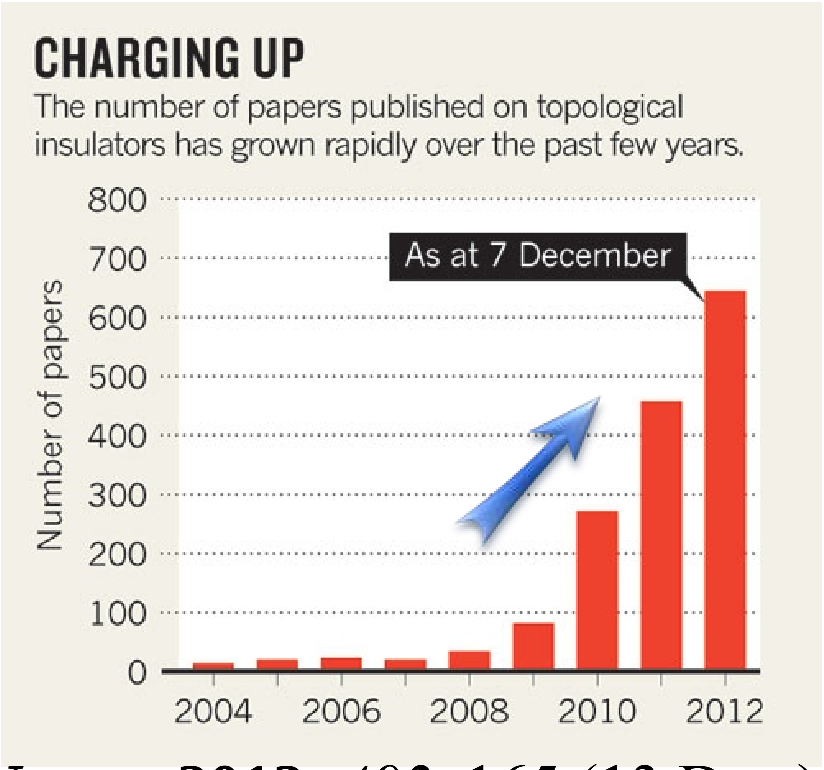
(layered crystal structure) **(Dirac band structure)**

Topological Insulators and Their Applications

- **Fundamental:** quantum anomalous Hall effect, Majorana fermions …
- **Applications:** information technology, energy, catalysis …

topological insulator: star material

Nature* 2010,** *466,** 15 July



***Nature* 2012,** *492*, 165 (13 Dec.)

2D Dirac Material — Calling all chemists

Nature Nanotechnology 3, 10 - 11 (2008)

GRAPHENE

Calling all chemists

Rod Ruoff
is in the Department of Mechanical Engineering, University of Texas at Austin, Austin, Texas 78712, USA.

nature chemistry PERSPECTIVE
PUBLISHED ONLINE: 24 OCTOBER 2011 | DOI: 10.1038/NCHEM.1171

Yi Cui*, Nature Chemistry 2011, 3, 845

Opportunities in chemistry and materials science for topological insulators and their nanostructures

TOPOLOGICAL INSULATORS

Chemists join in

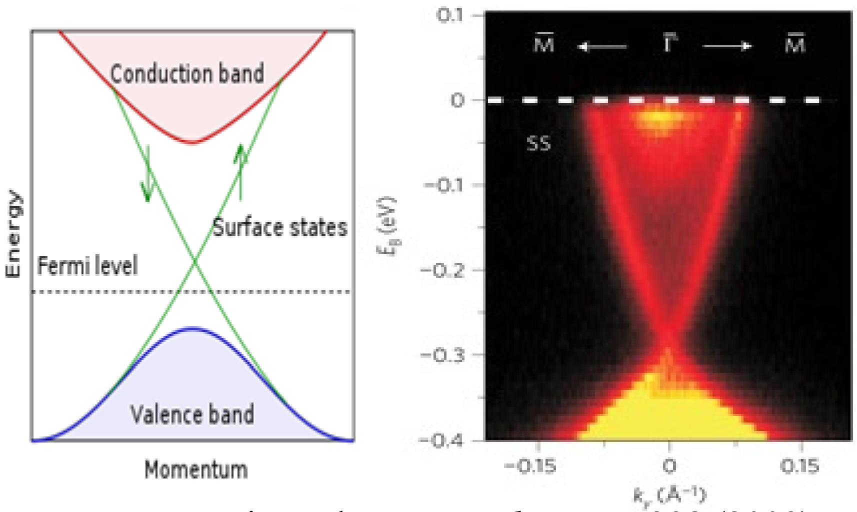
Topological insulators have generated much interest in condensed-matter physics. The synthesis and characterization of $Bi_{14}Rh_3I_9$, a so-called weak topological insulator, demonstrates that chemists also have much to offer to the field.

Robert J. Cava

Nature Materials | VOL 12 | MAY 2013

Our Approach to Study Topological Insulators

Bi_2Se_3 bulk single crystal



Y. Xia et al., *Nature Physics* 5, 398 (2009)

Surface states are overwhelmed by unwanted bulk carriers.

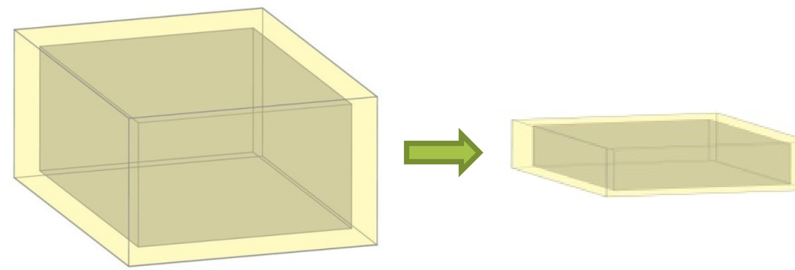
Issues:

- **Surface state vs. bulk state**
- **High-quality materials**
- **Transport**

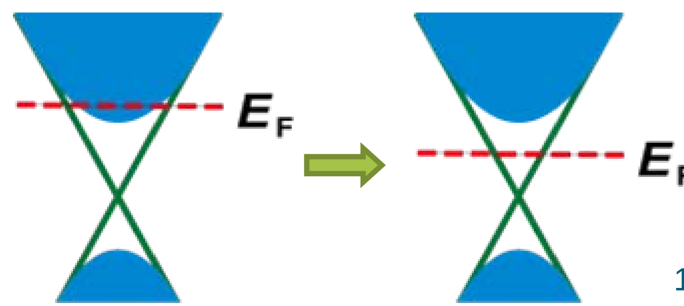
2D nanostructures

nanoribbon, nanoplate, nanosheet,…

- **Large surface-to-volume ratio**

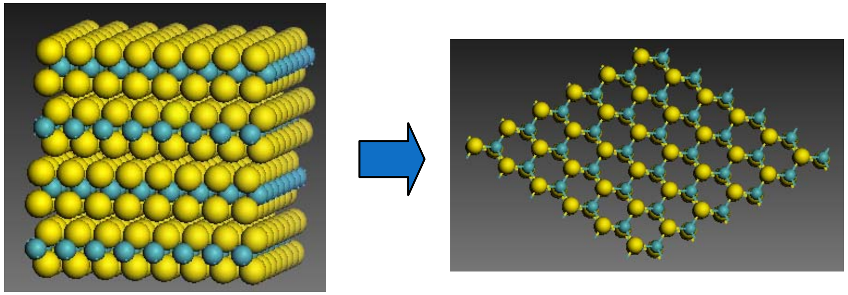


- **Excellent transport geometry**
- **Highly tunable chemical potential (doping, gating)**

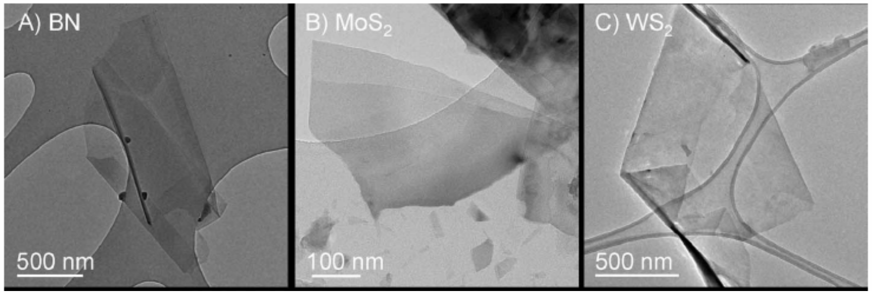


Production of 2D Layered Crystals

Top-down

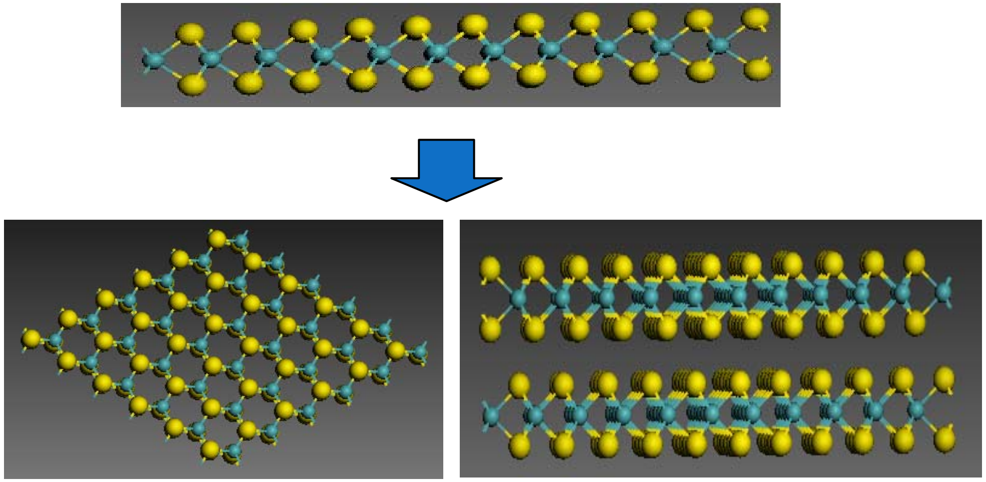


- **Micromechanical exfoliation**
- **Liquid-phase exfoliation**
(ultrasonic, ion/molecule insertion)

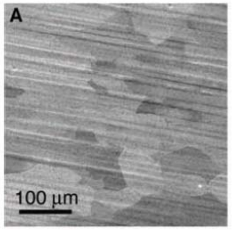


J. N. Coleman, et al. *Science* 331, 568 (2011)

Bottom-up

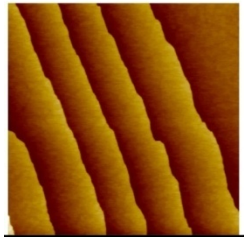


- **Liquid-phase synthesis**
- **Vapor-phase synthesis**



CVD of graphene

R. Ruoff, ***Science*** (2009)



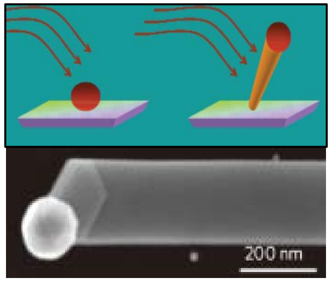
MBE of Bi_2Se_3

QK Xue, et al. ***Nat. Phys.*** **(**2010)

北京大学纳米化学研究中心
1993
PEKING UNIVERSITY
1898
Thermo
SCIENTIFIC

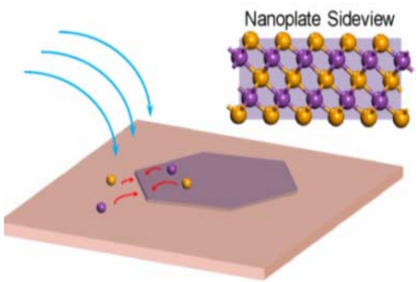
Dirac 2D Crystals and their novel optoelectronic devices

VLS growth:
TI nanoribbon



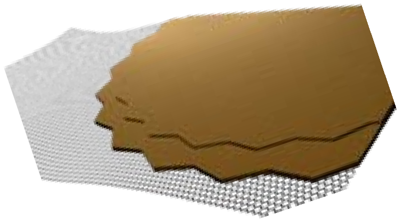
***arXiv:0908.3314* (2009)** ;
Nano Lett.* 2010, *10, 329

VS growth:
TI nanoplate



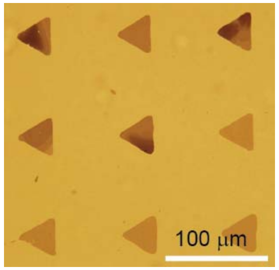
***Nano Lett.* 2010,** *10*, 2245

van der Waals epitaxy:
Nanosheet/thin film



***Nano Lett.* 2010**, *10*, 2870;
***Nano Lett.* 2011,** *11*, 1106

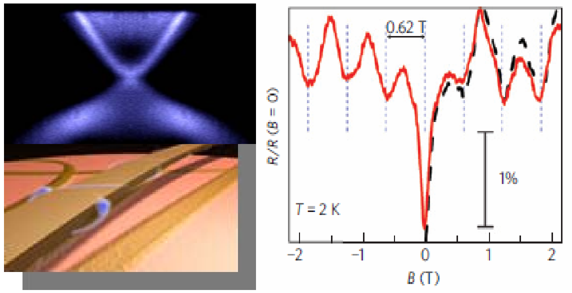
Selective-area VDWE:
2D ordered array



***JACS* 2012**, 134, 6132
***JACS* 2013**, 135, 13274

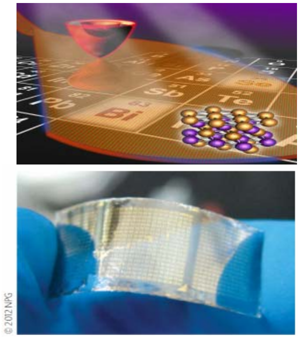
2009 **2010** **2011** **2012**

AB effect of surface state by quantum transport



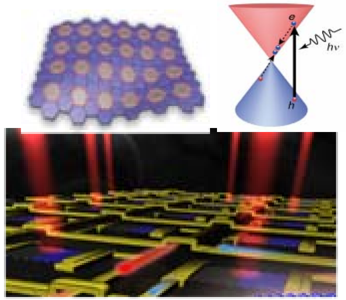
***Nature Mater.* 2010,** *9*, 225

TI nanostructure for flexible transparent electrode



***Nature Chem.* 2012**, *4*, 281
***Adv. Mater.* 2013**

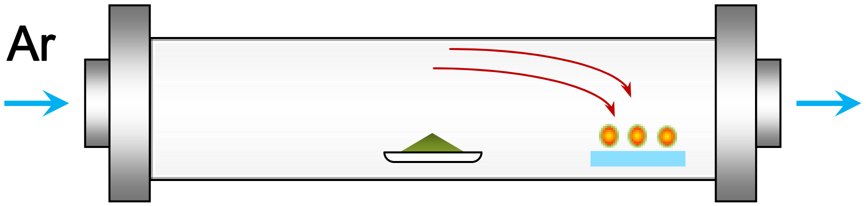
Dirac materials chemistry and PN juncton for optoelectronics



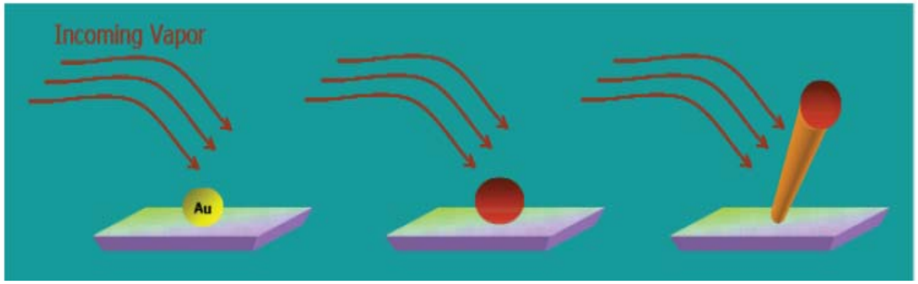
***Nature Comm.* 2012**, *3*, 1038
***Nature Comm.* 2013,** 4, 1443
***JACS* 2013,** *135,* 10926

Growth of 1D/2D Bi_2Se_3 Crystals

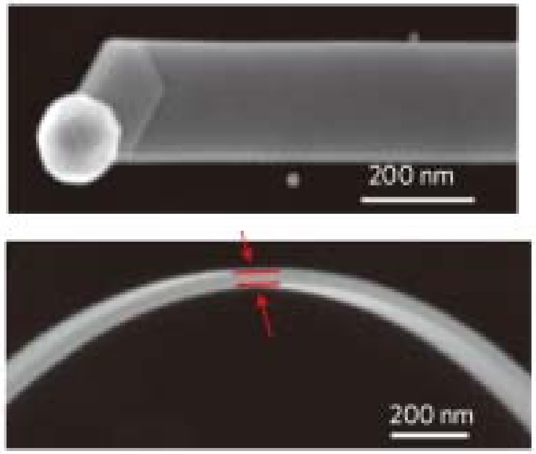
- **Vapor-liquid-solid (VLS) growth of nanoribbon**



vapor deposition system



Layered single-crystalline Bi_2Se_3 nanoribbons are synthesized via a gold-catalyzed vapor-liquid-solid growth.

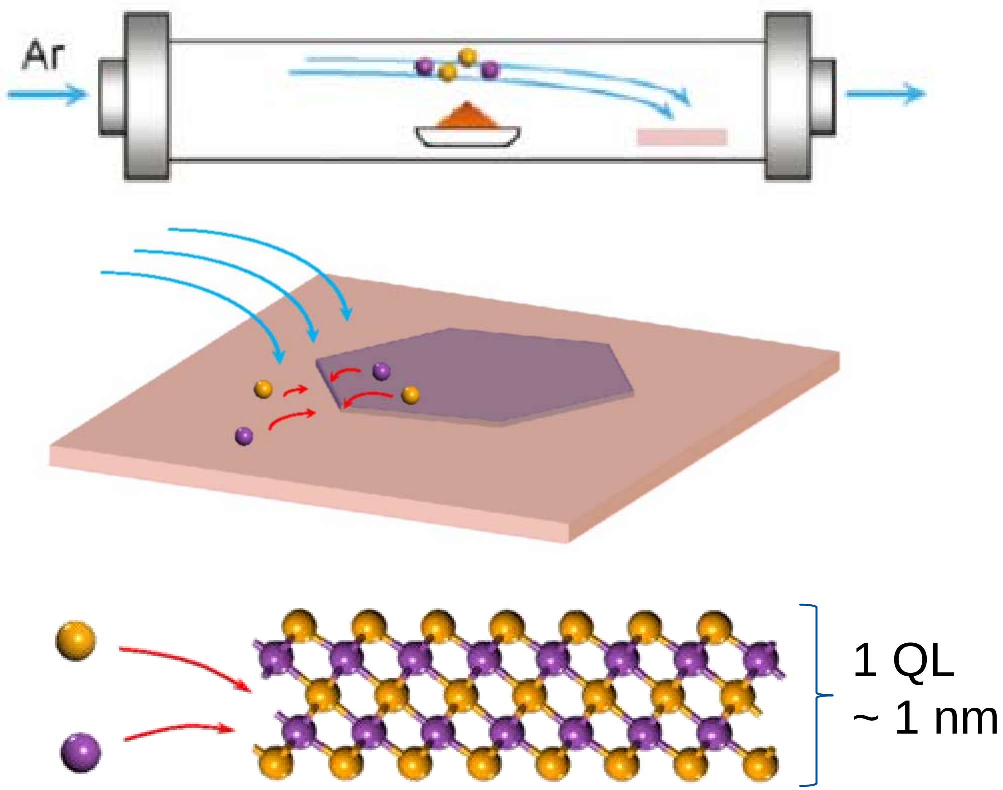


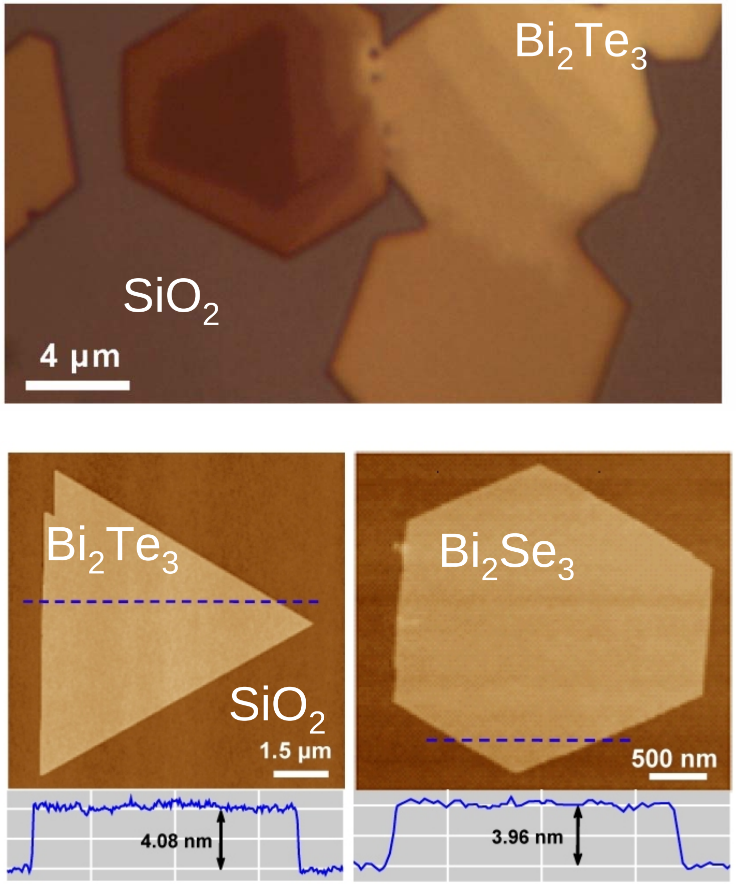
Thickness range: ~25 -100nm

H. Peng, K. Lai, Y. Cui, et al., arXiv:0908.3314 (**2009**)
Nature Materials 9, 225 (**2010**)

Growth of 2D Crystals

- Vapor-solid (VS) growth of nanoplate



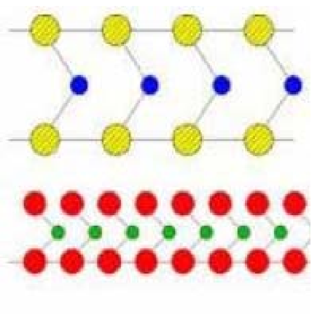


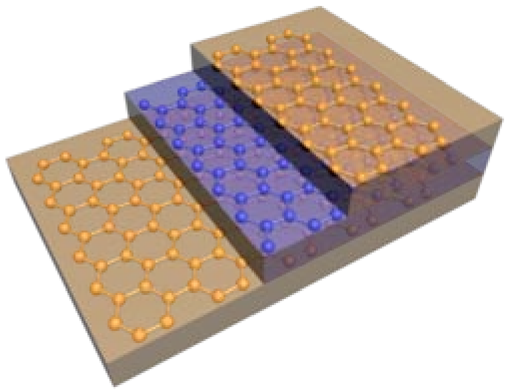
Thickness Range: ~3nm to 15 nm

D. Kong, W. Dang, H. Peng*, ZF Liu, Y. Cui*, et al, ***Nano Lett.*** *10*, 2245 (**2010**)

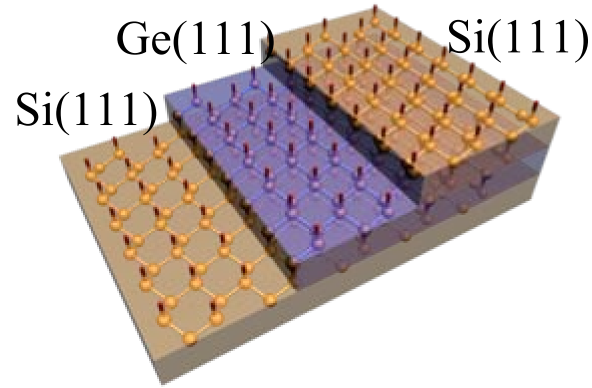
Controlled Growth of 2D Crystals

- **van der Waals (VDW) epitaxy**





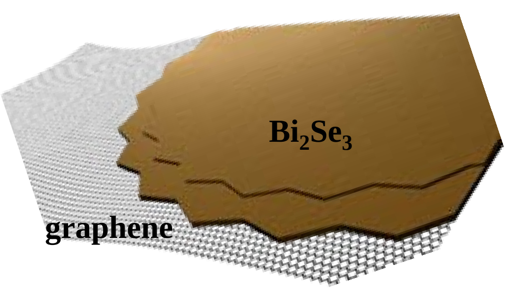
Conventional epitaxy

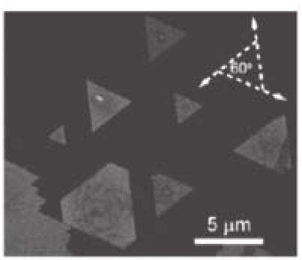


Koma, A. Thin Solid Films 216, 72 **(1992**)

Lattice matching condition is drastically relaxed

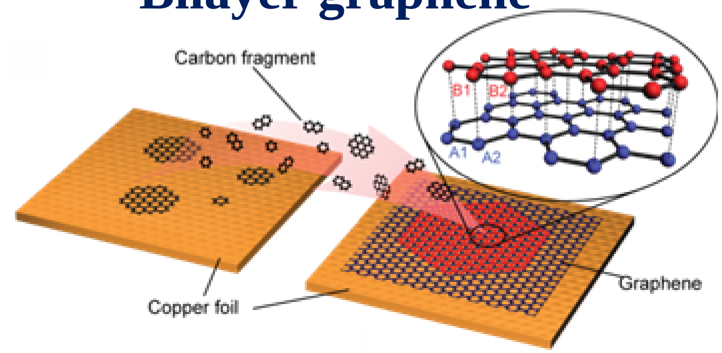
Bi_2X_3/graphene 2D structure





W. Dang, H. Peng, Z.F. Liu, et al.,
Nano Lett. *10*, 2870 **(2010)**
Also see QK Xue, et al. ***Nat. Phys.*** **(2010**)

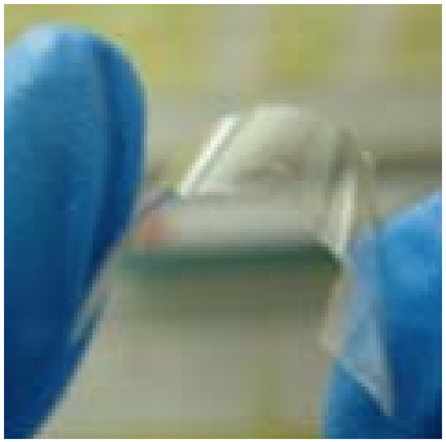
Bilayer graphene

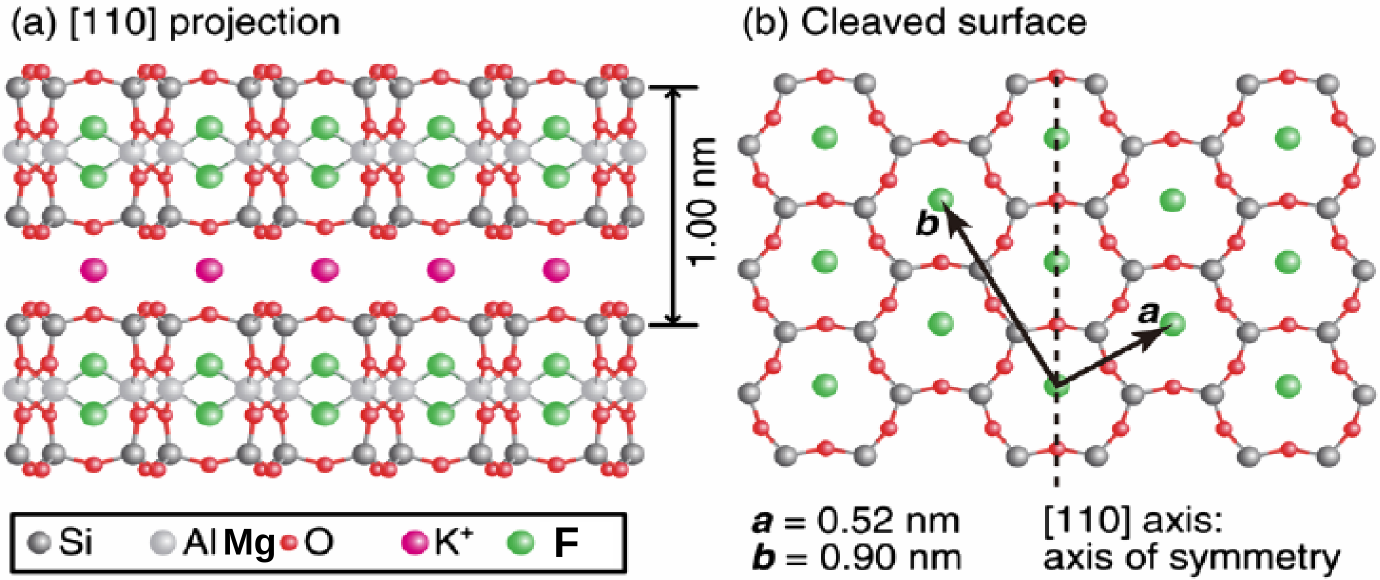


K. Yan. H. Peng, Z. F. Liu, et al.,
Nano Lett. *11*, 1106 **(2011)**

Graphene is a good VDW epitaxy substrate

VDW Epitaxy Substrate - Fluorophlogopite Mica





T. Fukuma, *Phys. Rev. Lett.* 104, 016101 (2010)
F. Tsui, *Phys. Rev. B* 47, 13648 (1993)

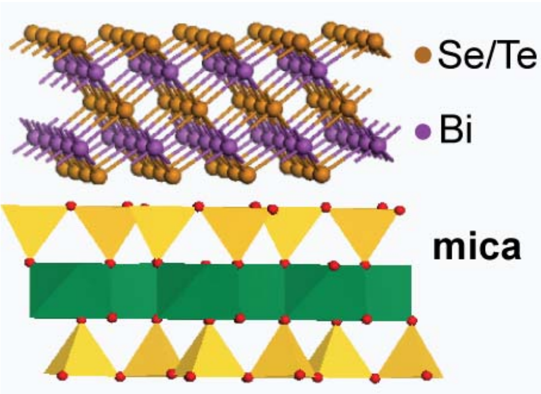
fluorophlogopite mica (氟晶云母)
(2D layered material)

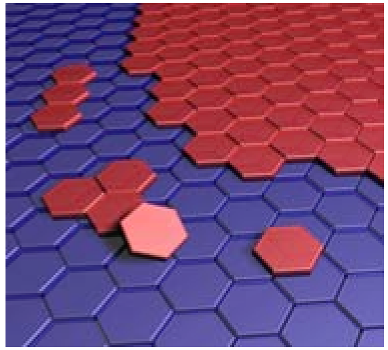
flat, stable, insulating, transparent, flexible

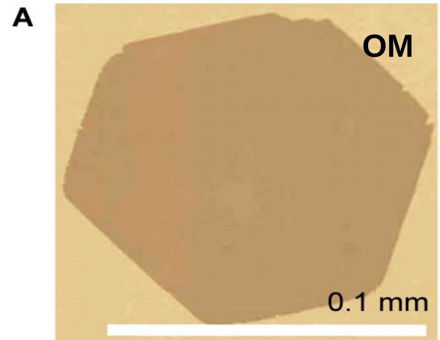
fluorophlogopite $2KMg_3(AlSi_3O_{10})F_2$
monoclinic structure C2/m space group
a =5.308 A, b =9.183 A, c =10.139 A, β= 100.07
pseudohexagonal Z_2O_5 sheets (Z=Si and Al)

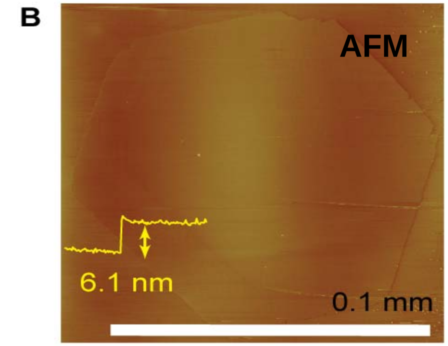
Excellent VDW epitaxy substrate

Position and orientation controlled growth

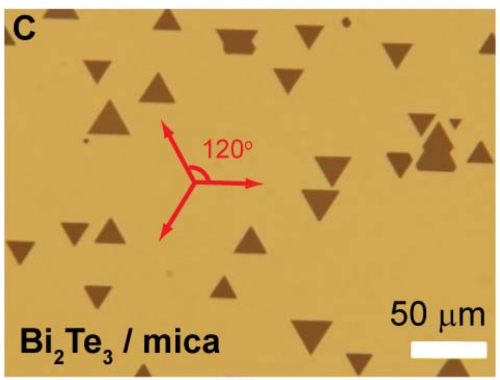


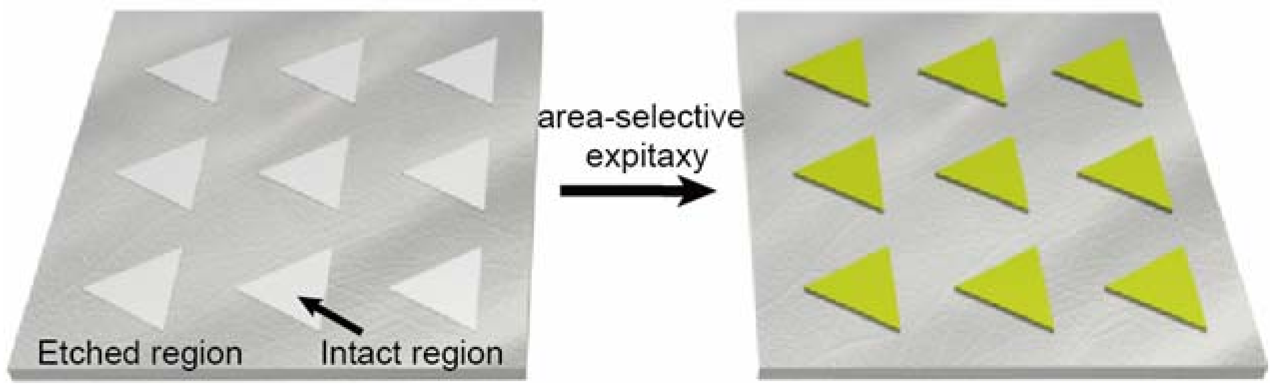






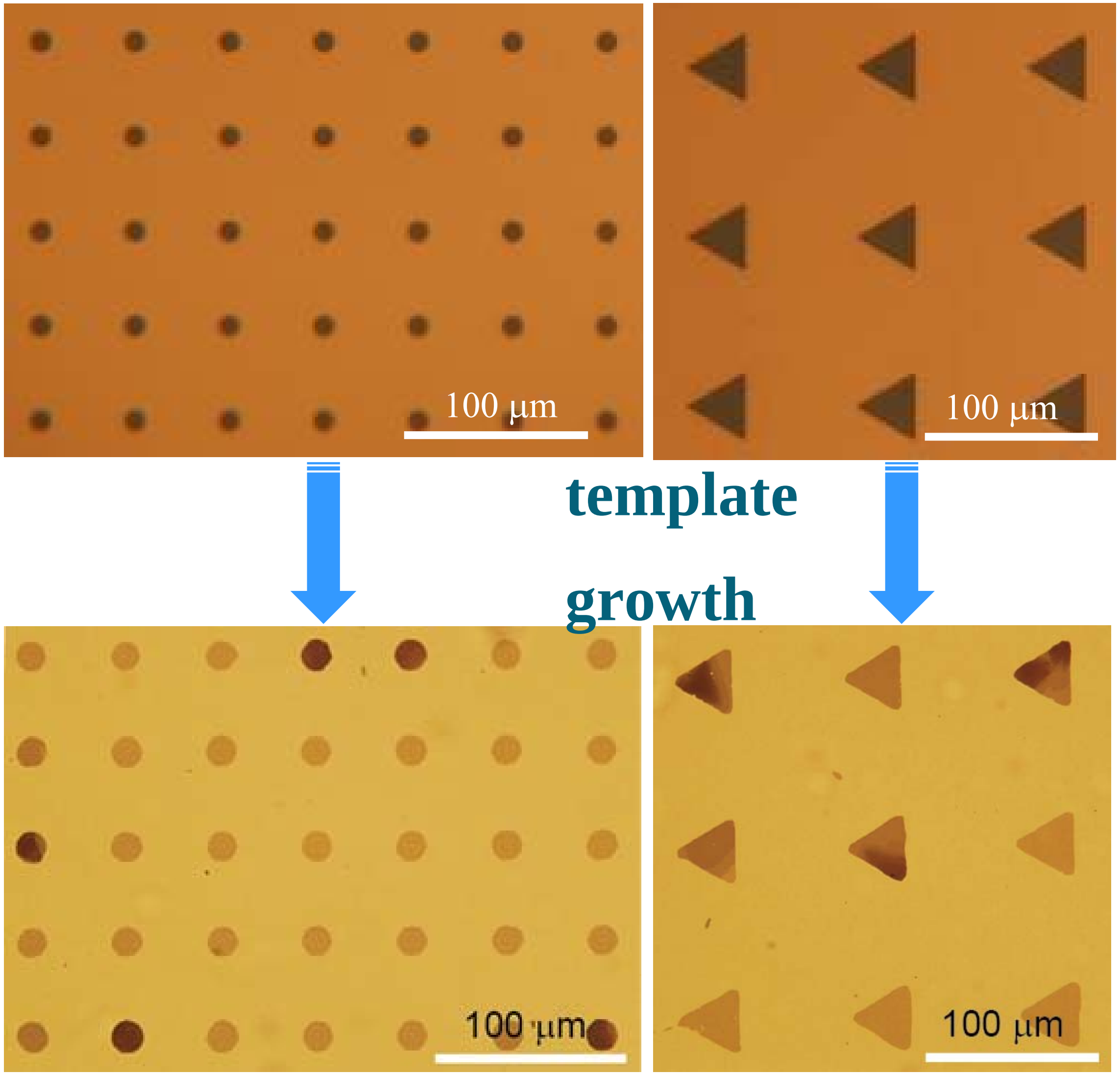
Epitaxy substrate– layered mica (cheap, flat, stable, insulating, transparent, flexible)





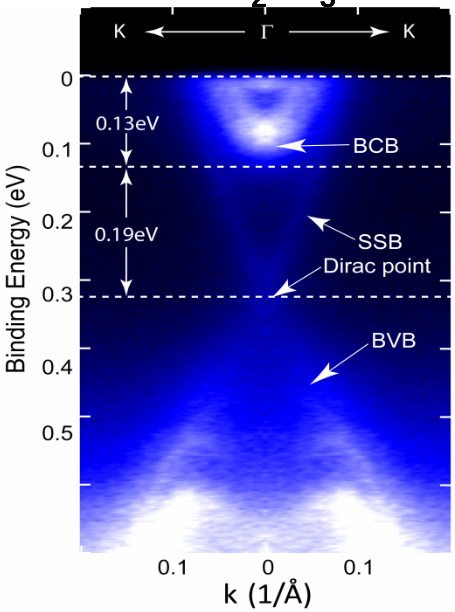
Li, Cao, Zheng, Chen, Peng*, Liu*, *et al., J. Am. Chem. Soc.* 2012, *134*, 6132. Highlight in *C&EN*

Position and orientation controlled growth of 2D Bi_2Se_3



template growth

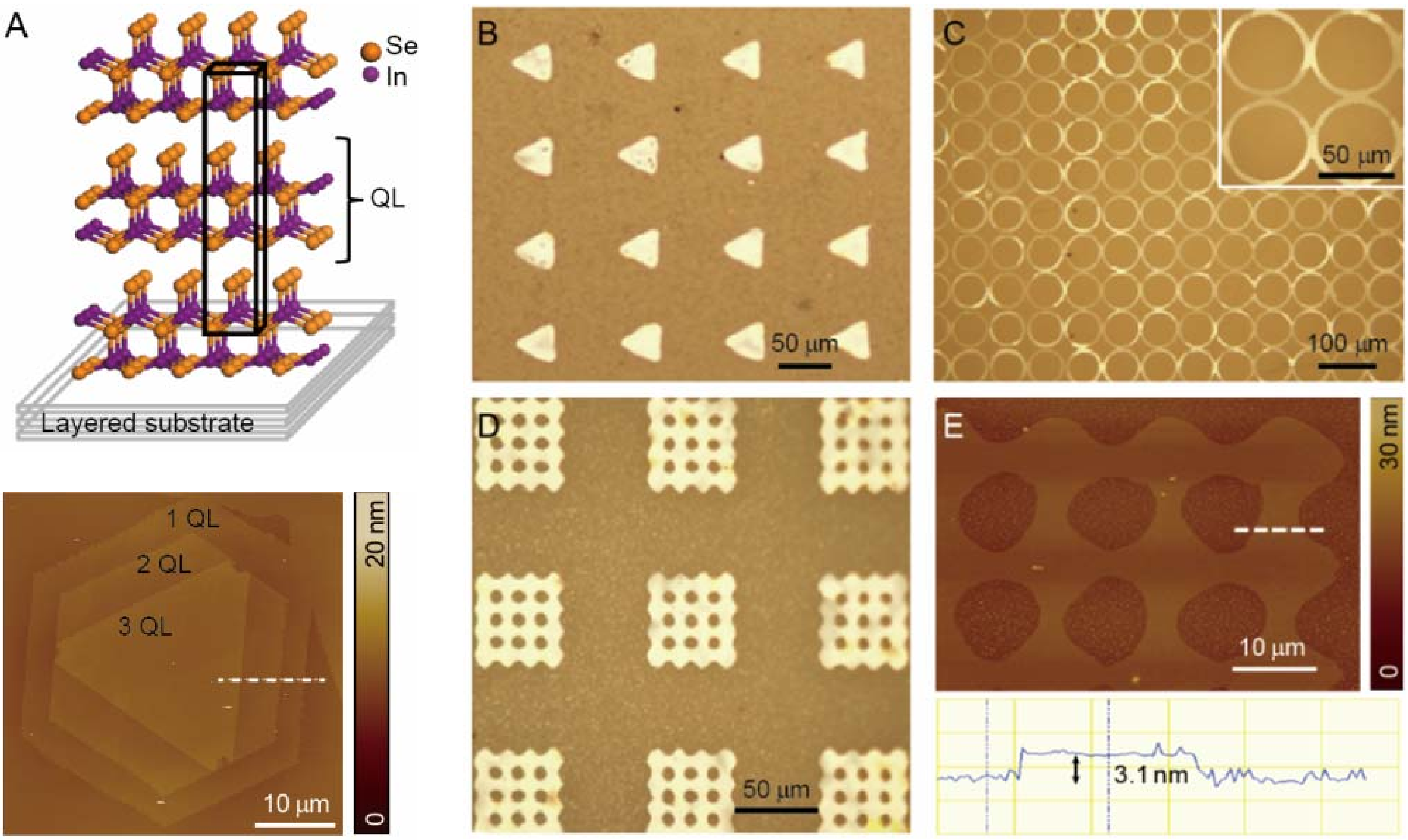
ARPES of Bi_2Se_3 nanosheet



By Dr. Yulin Chen

Li, Cao, Zheng, Chen, Peng*, Liu*, *et al., J. Am. Chem. Soc.* 2012, *134*, 6132. Highlight in *C&EN*

Position and orientation controlled growth of 2D In_2Se_3



Min Lin, Hailin Peng*, Z.F. Liu*， et al., *J. Am. Chem. Soc.* 2003, 135, 13274

Research Interests:

Nano Lett. *7(1)*, 199 (2007)
Nano Lett. *7(12)*, 3734 (2007)
Nano Lett. *8(5),* 1511 (2008)
Nano Lett. *9(3),* 1265 (2009)
Nano Lett. *10(3)*, 2870 (2010)
Nano Lett. *10(6)*, 2245 (2010)
Nano Lett. *11(3)*, 1106 (2011)
Chem. Mater. *21(2), 247* (2009)
J. Am. Chem. Soc. *129*, 34 (2007)
J. Am. Chem. Soc. *131*, 7973 (2009)
J. Am. Chem. Soc. *134*, 6132 (2012)
Acc. Chem. Res. (2013)

Synthesis/characterization

- graphene
- chalcogenide (topological insulator)
- heterostructure

2D layered materials

Band structure engineering

- chemical modification
- doping
- intercalation chemistry

Nano Res. *2*, 327 (2009)
ACS Nano *5*, 5957 (2011)
Small *9*, 1348 (2013)
Small 9, 1134 (2013)
Small 9, 1388 (2013)
Small 9, 1316 (2013)
Nature Commun. *4,* 1443 (2013)

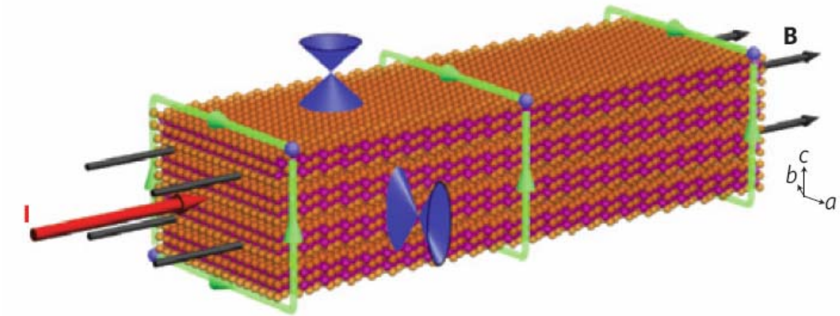
Novel device

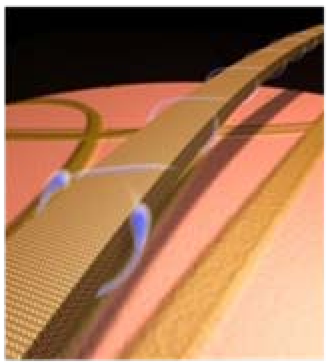
- nanoeletronics
- optoelectroncs

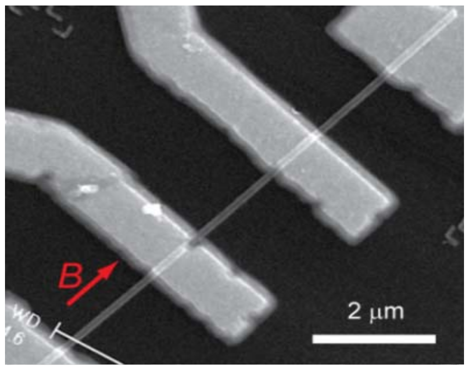
Nature Materials *9*, 225 (2010)
Nature Chemistry *4,* 281 (2012)
Nature Commun. *3, 1280* (2012)
J. Am. Chem. Soc. (2013)
Adv Mater. (2013)

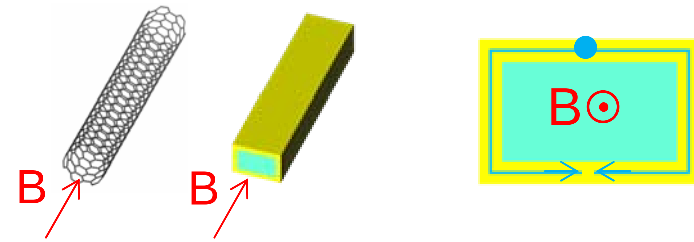
Transport from Surface States of TI (Bi_2Se_3) Nanoribbon

- **Periodic magnetoresistance osillations**
- **Well-known Aharonov-Bohm (AB) effects**
- **Fully coverage of 2D coherent electron state on the entire surface of topological insulator**

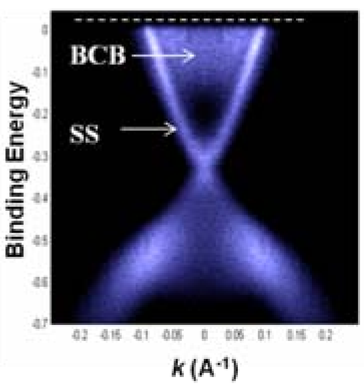


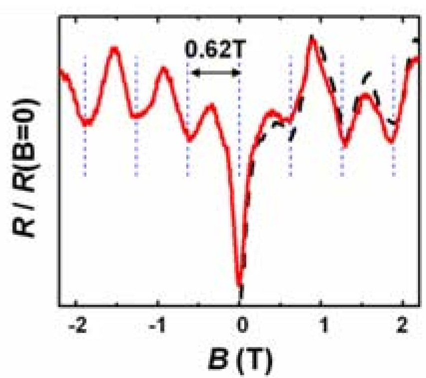






$$\Phi_0 = \Delta B \cdot S = h/e$$



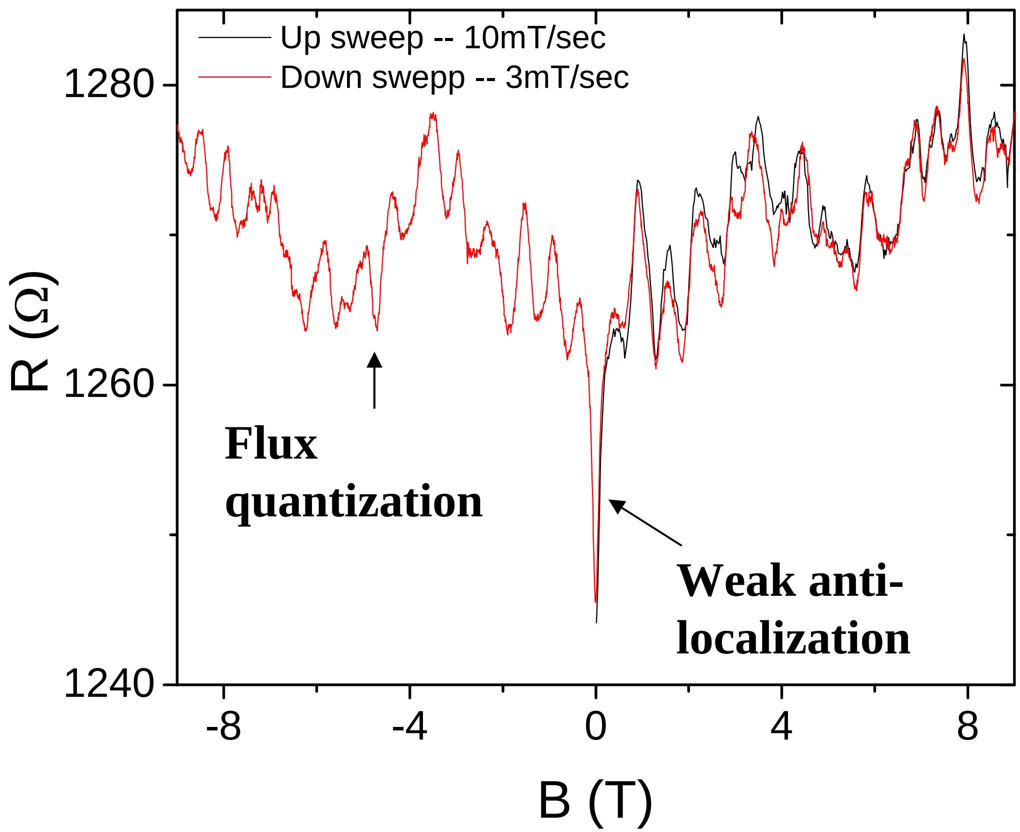


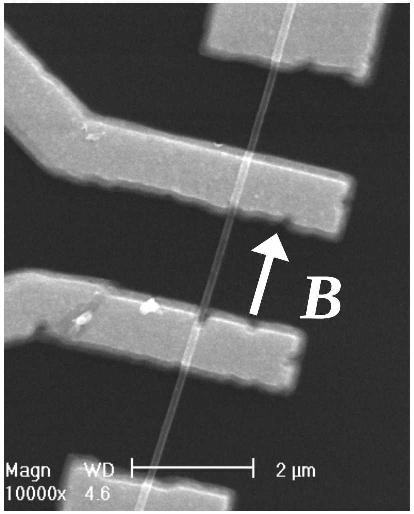
- AB effects observed in ring or tube-like geometry, such as mesoscopic conducting rings, hollow cylinders, tube-like 2DEGs, carbon nanotubes.
- The flux quantization results in an oscillation period of the external magnetic field ΔB. $\Delta B \cdot S = \Phi_0$, where $\Phi_0 = h/e$ is the flux quantum, S the enclosed cross section.

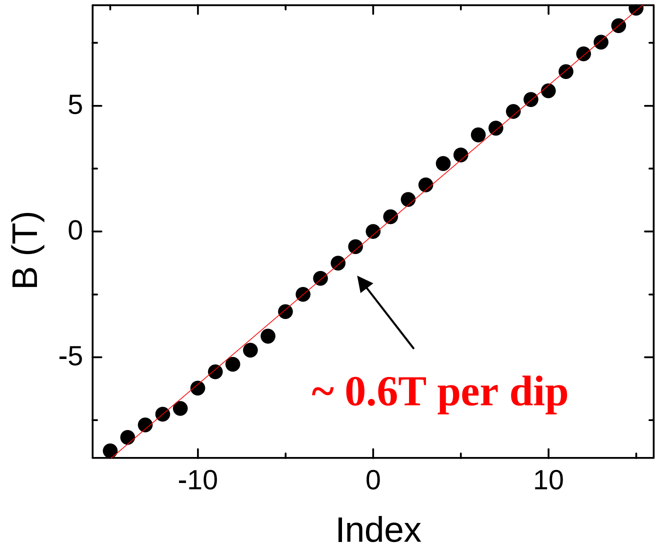
H. Peng, K. Lai, Y. Cui, *et al.*, ***Nature Materials*** **2010**, *9*, 225. **Times of citation > 200**

In-plane magnetoresistance in Bi_2Se_3 nanoribbons

Temperature: 2K



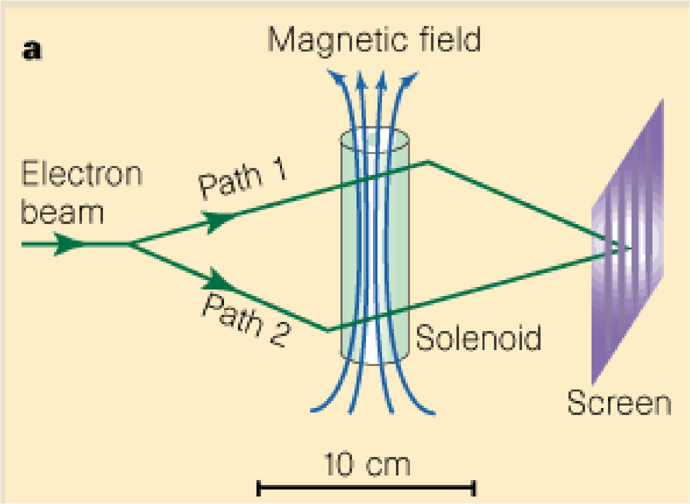




- Periodic magnetoresistance osillations;
- Well-known Aharonov-Bohm effects

H. Peng, K. Lai, D. Kong, S. Meister, Y. Chen, XL Qi, SC Zhang, ZX Shen, Y. Cui, ***Nature Materials*** 9, 225 **(2010)**

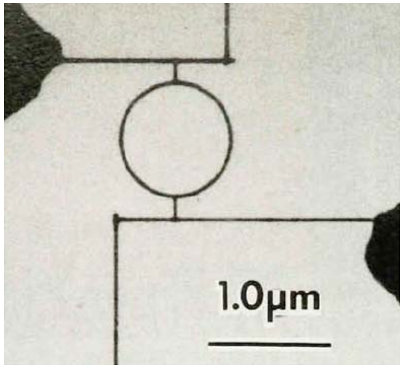
Aharonov-Bohm (AB) oscillations

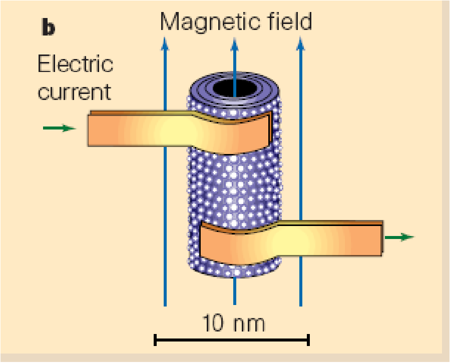


Aharonov-Bohm (AB) effects:
An electron beam, split into two alternative paths, can exhibit interference effects when the beams recombine.

The flux quantization results in an oscillation period of the external magnetic field ΔB.
$\Delta B \cdot S = \Phi_0$, where $\Phi_0 = h/e$ is the flux quantum, S the enclosed cross section.

AB effects have been observed in mesoscopic conducting rings, hollow cylinders, and tube-like 2DEGs



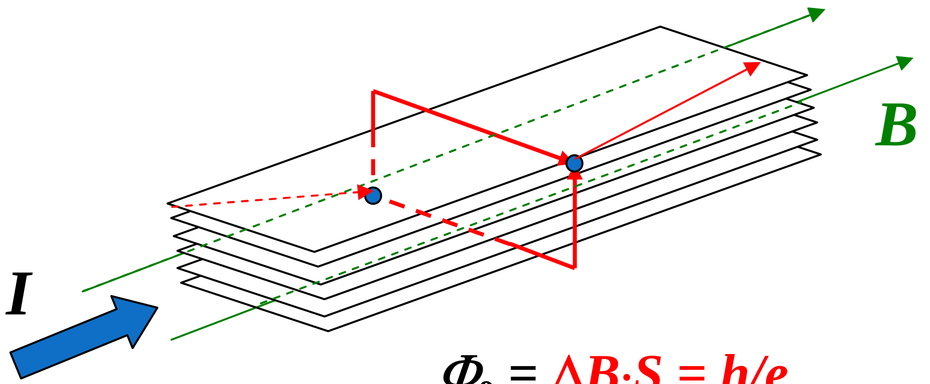


$$\Phi_0 = \Delta B \cdot S; \ \Phi_0 = h/e$$

Aharonov, Y. & Bohm, D. Phys. Rev. 115, 485 (1959)

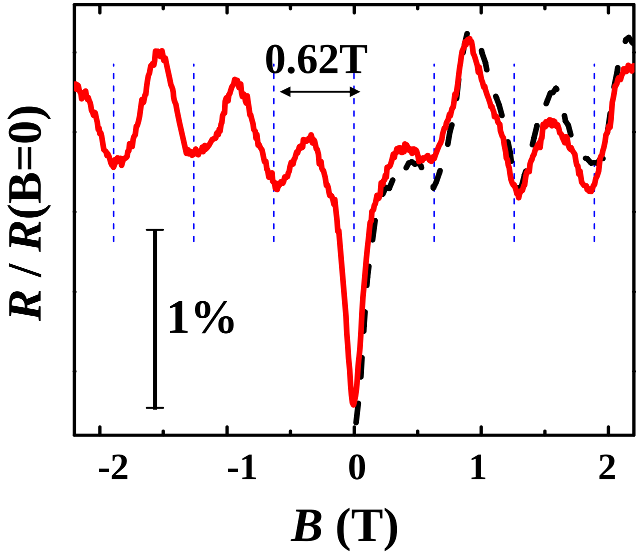
Bachtold, A. Nature 397, 673 (1999)

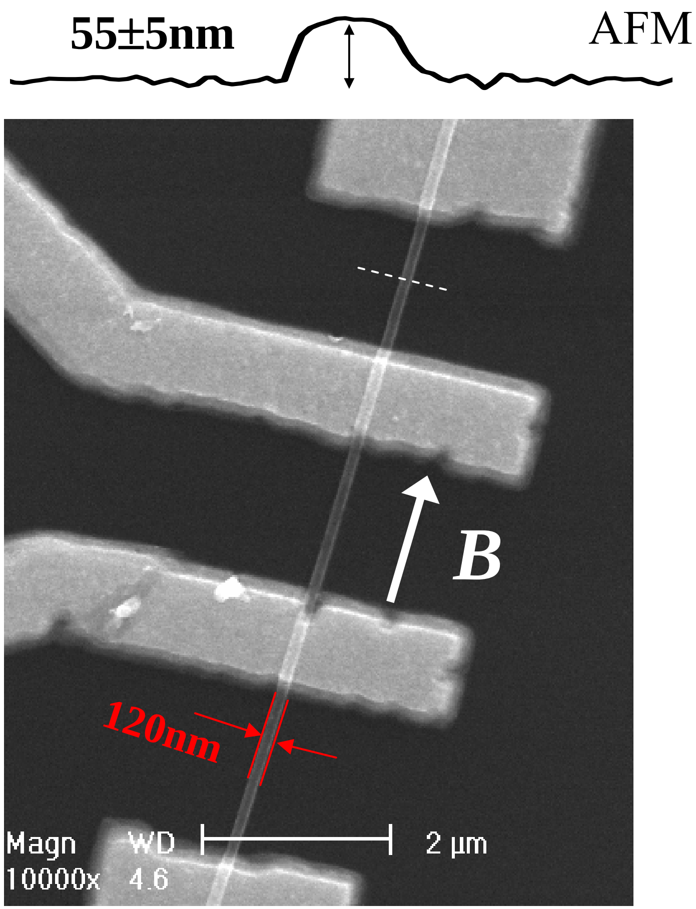
Aharonov-Bohm oscillation from surface states



$\Phi_0 = \Delta B \cdot S = h/e$

Expected AB period: $\Delta B = \Phi_0 / S = 0.63\text{T}$





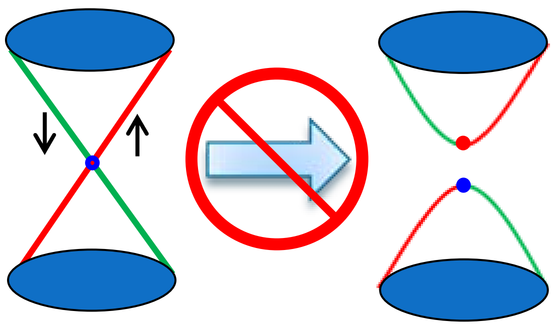
$S = w \cdot t = 6.6\times10^{-15}\ \text{m}^2$

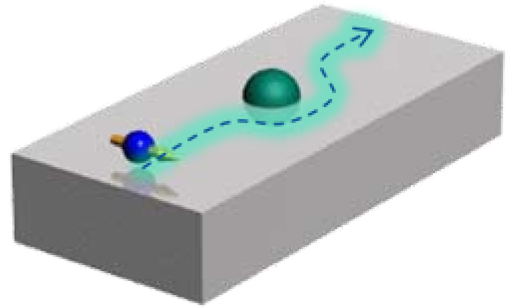
fully coverage of 2D coherent electron state on the entire surface

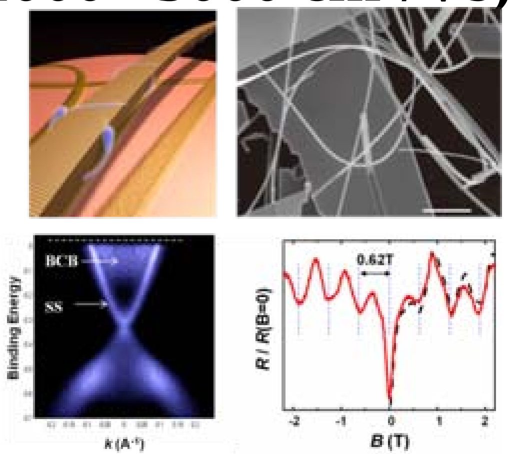
H. Peng, K. Lai, Y. Cui, et al., ***Nature Materials*** 9, 225 **(2010)**

Topological Insulator 2D Nanostructures for Flexible Transparent Electrodes

Metallic surface state: robust, high mobility (1000~ 5000 cm^2/Vs)

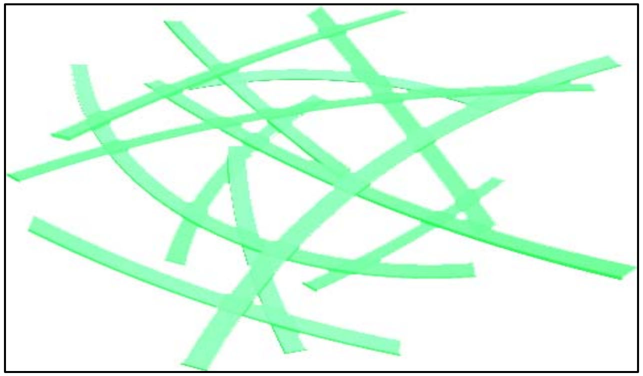




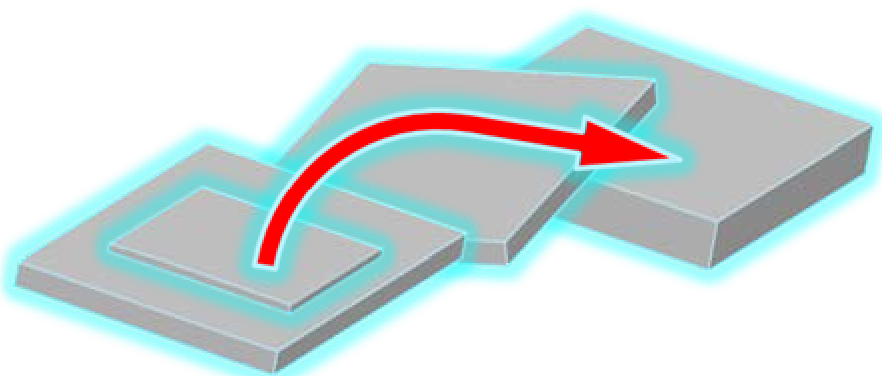


Metallic surface/edge state always occur at interface, boundary, edge

H. Peng, K. Lai, Y. Cui, et al., *Nature Materials* 9, 225 (2010).



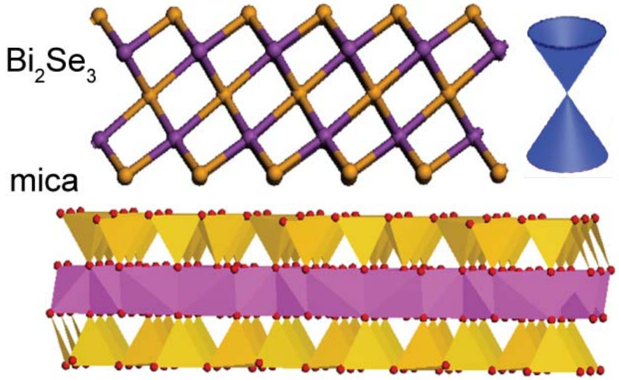
dissipationless interconnects for the conductive paths

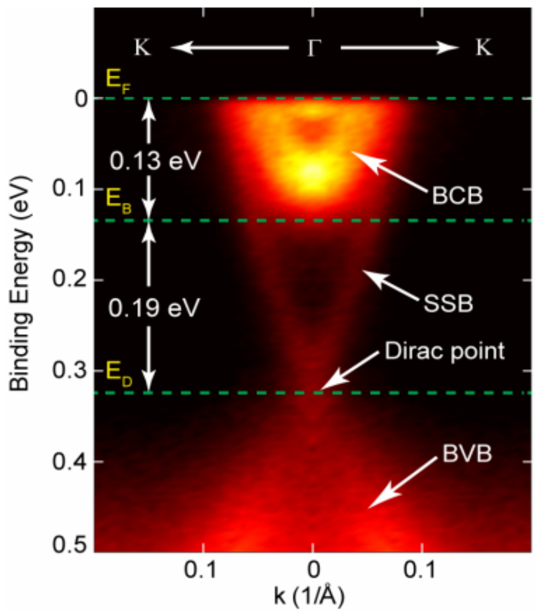


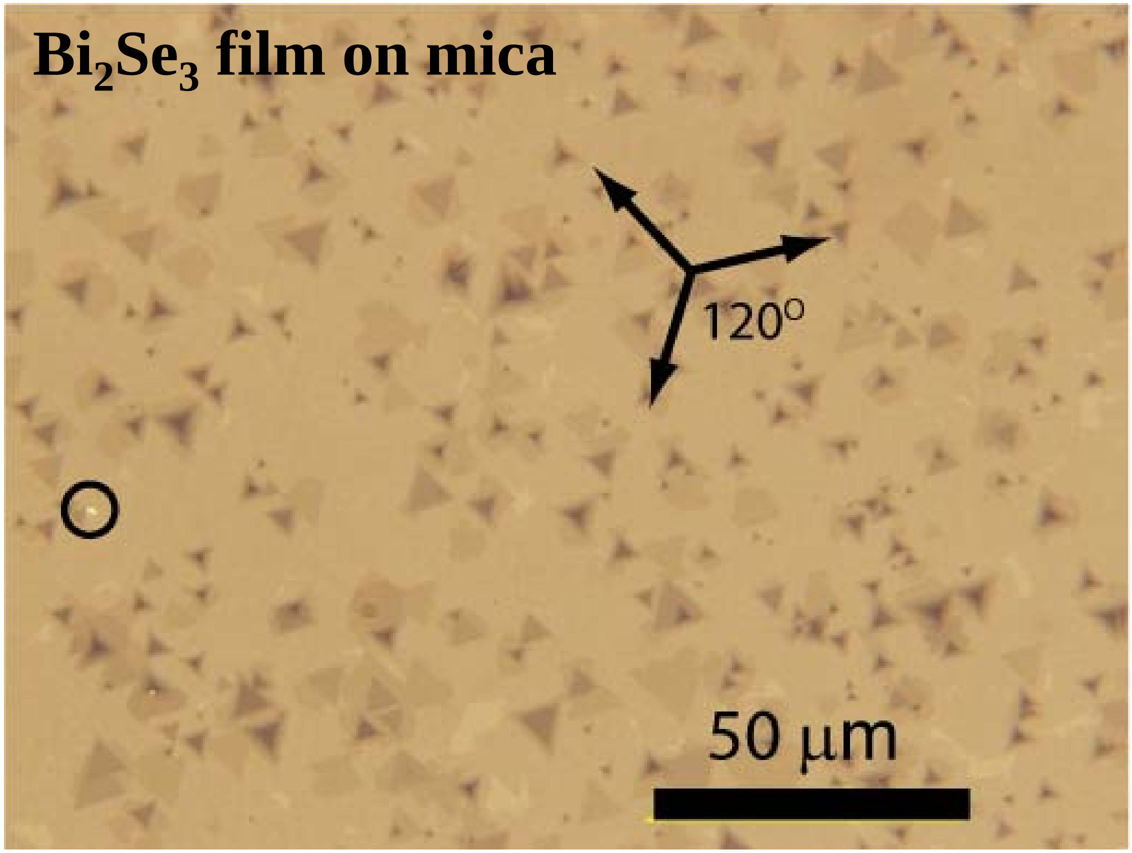
Transparent electrode

拓扑导电薄膜

Topological Insulator 2D Nanostructures for Flexible Transparent Electrodes

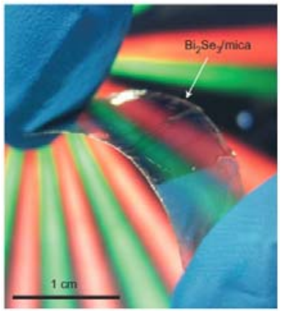


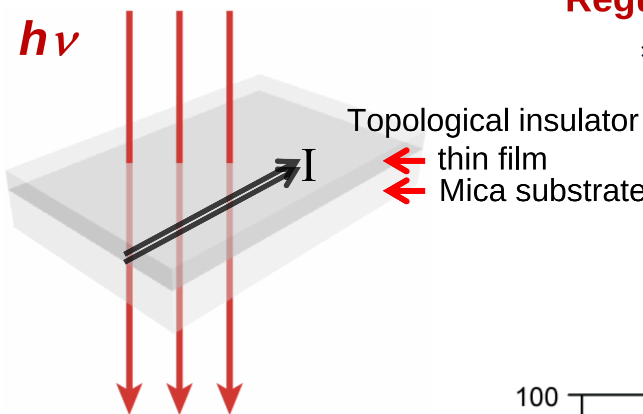


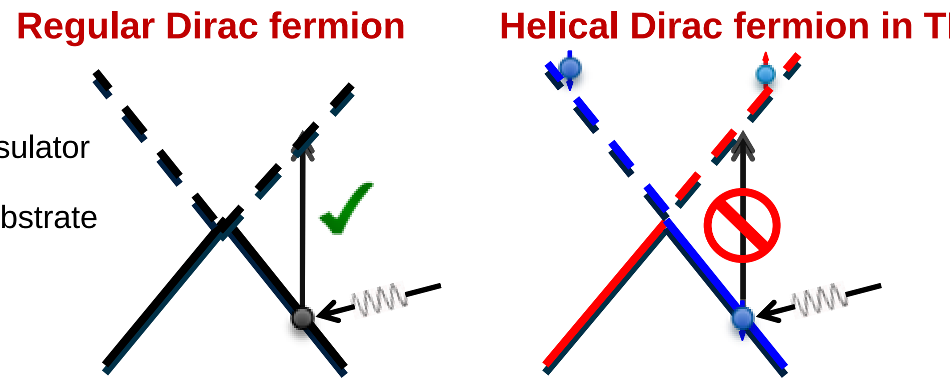


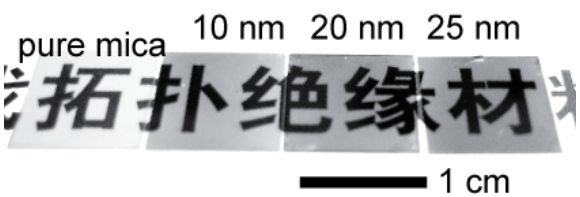
H. Peng*, et al., *Nature Chemistry 4*, 281 (2012)
highlight in *Nature Chemistry, Nature Photonics, PhysOrg.com,* etc.

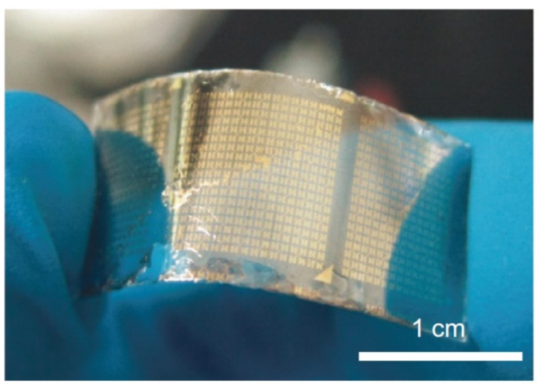
Transparent Electrodes - Transmittance

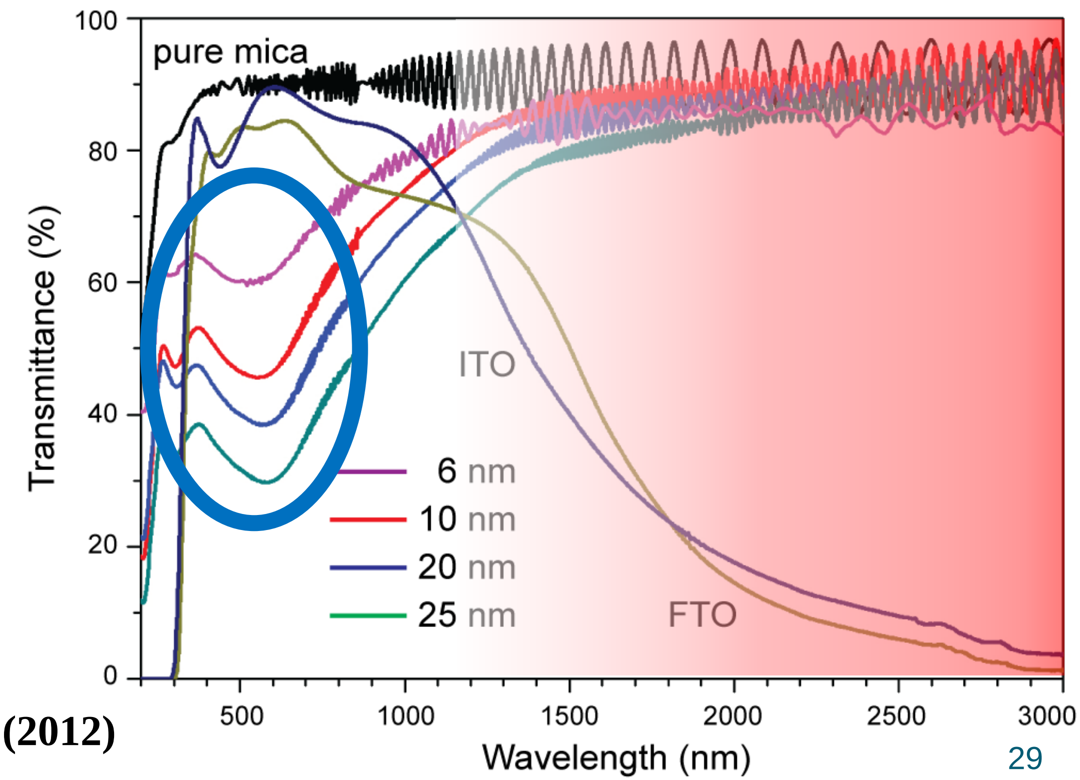






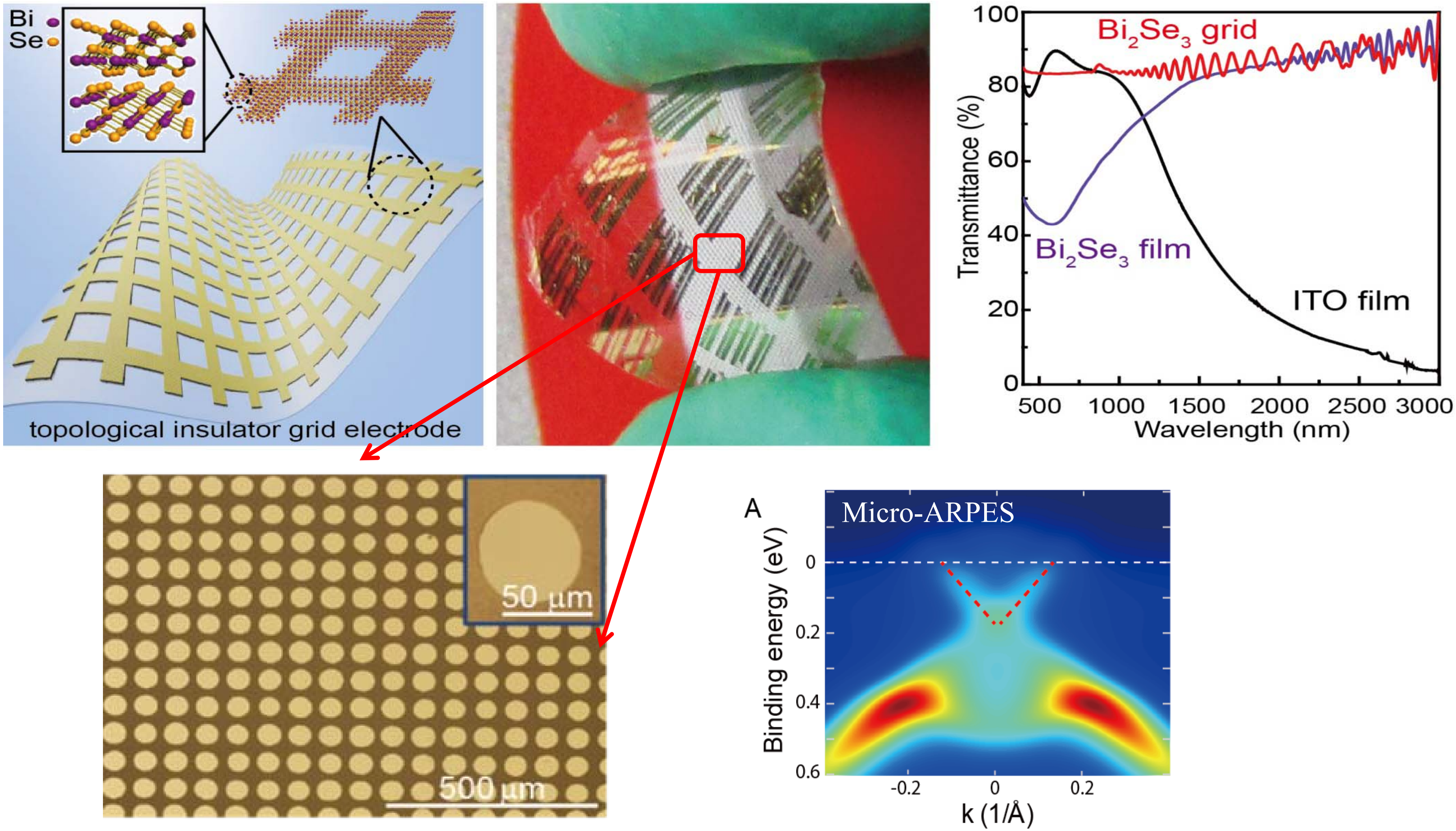






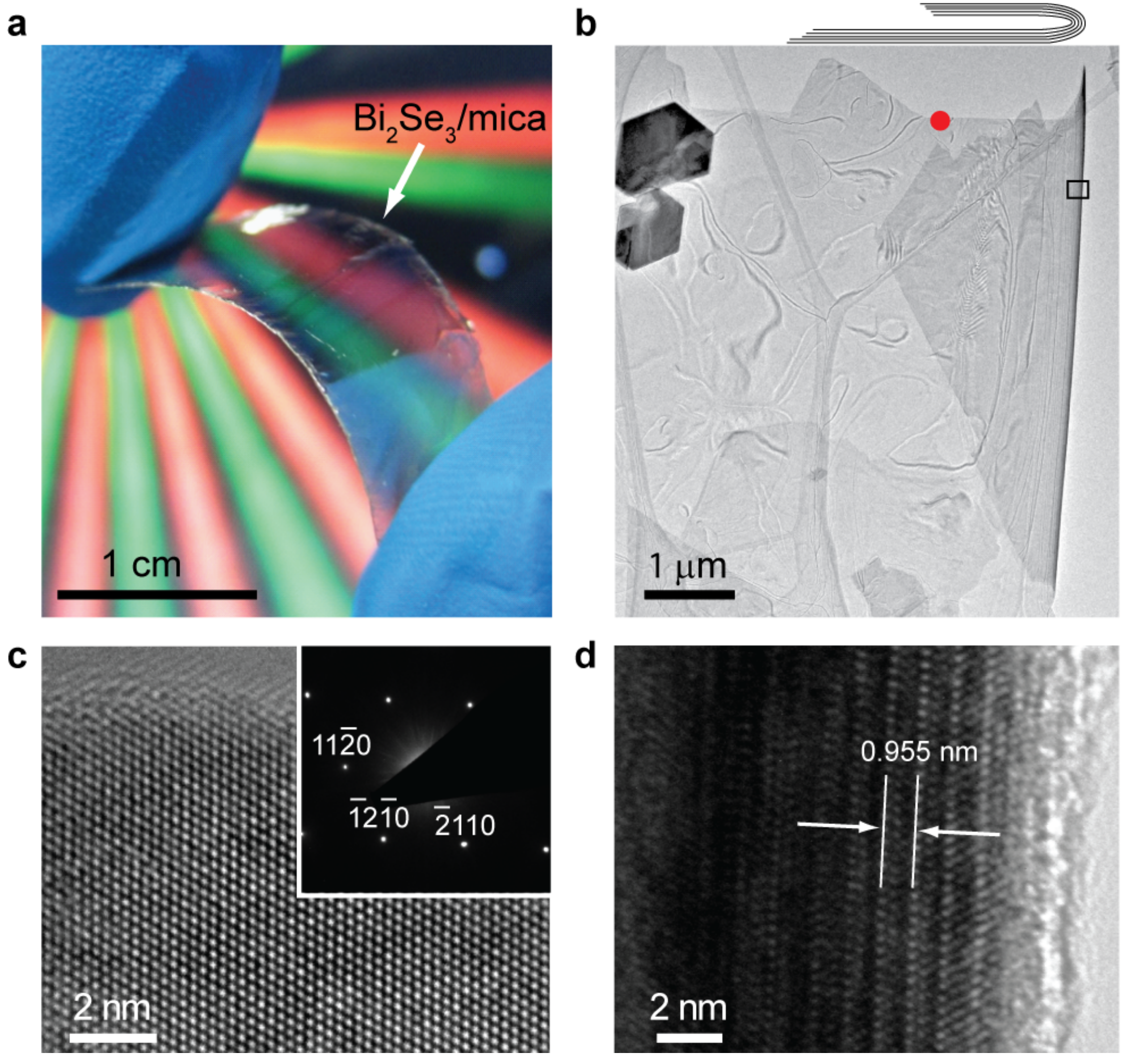
H Peng*, *et al.*, *Nature Chemistry 4*, 281 (2012)

Broadband Transparent Electrodes with 2D Grid



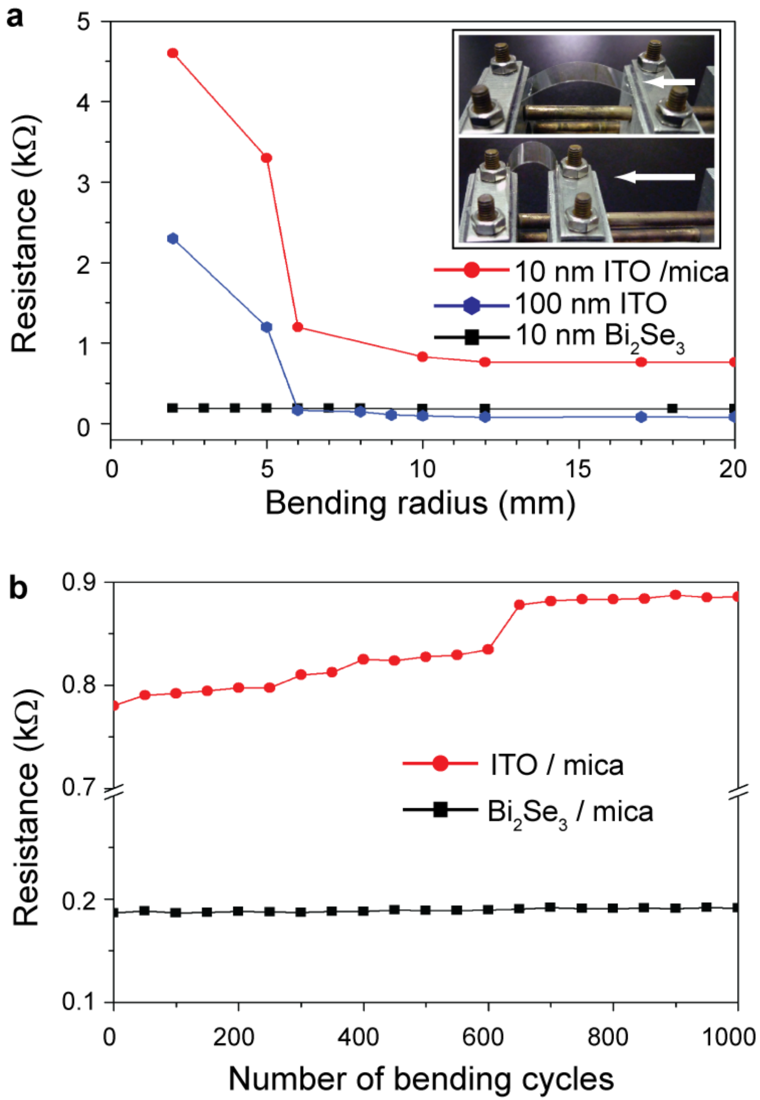
Yunfan Guo, Hailin Peng*, et al., ***Adv. Mater***. **2013,** in press

Transparent Electrodes - Flexibility



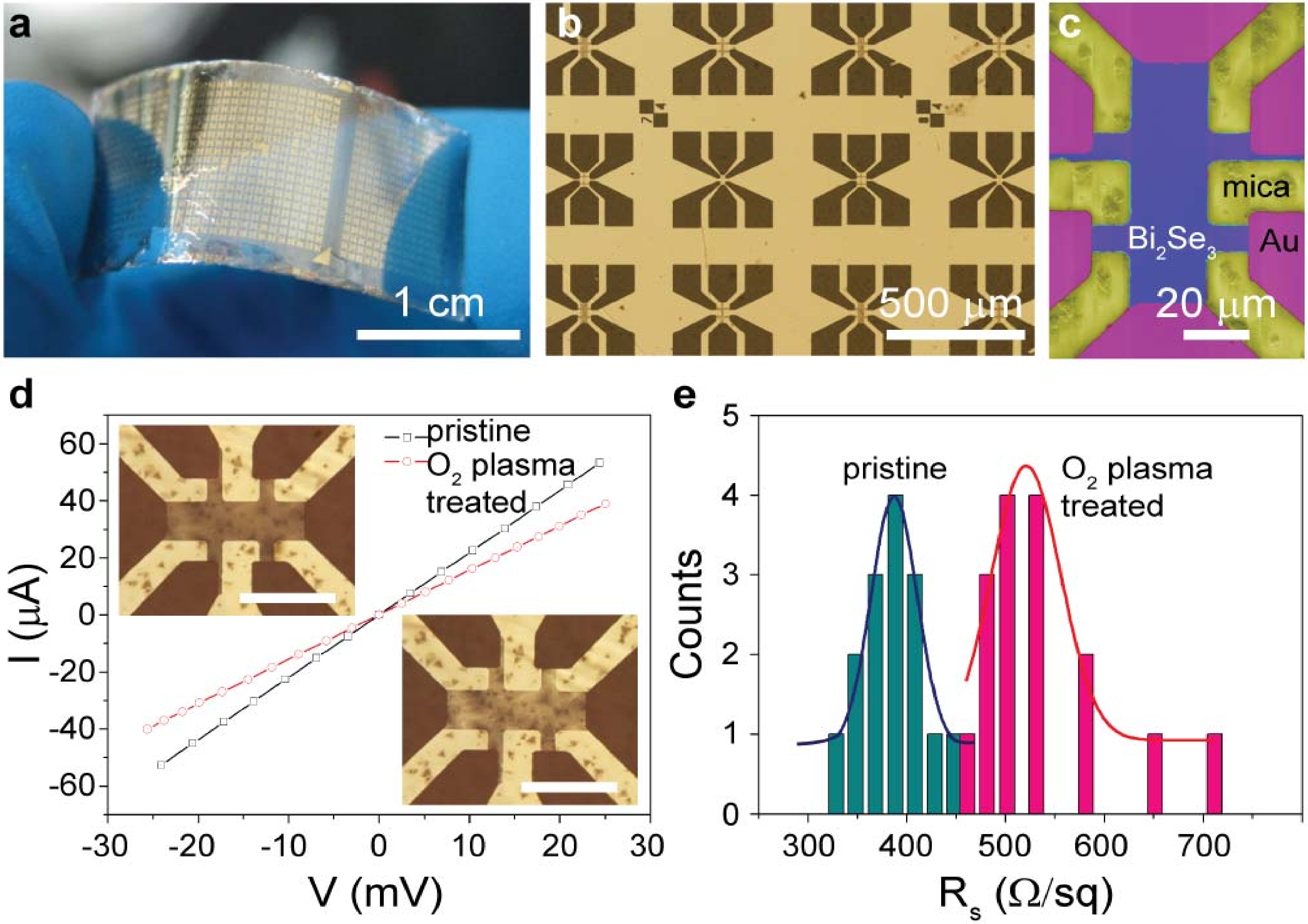
H Peng*, *et al.*, ***Nature Chemistry*** *4,* 281 (**2012**)
highlight in *Nature Chemistry, Nature Photonics, PhysOrg.com,* etc.

Transparent Electrodes - Flexibility



H Peng*, *et al.*, ***Nature Chemistry*** *4*, 281 (**2012**)
highlight in *Nature Chemistry, Nature Photonics, PhysOrg.com,* etc.

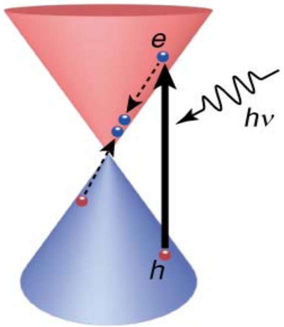
Transparent Electrodes – Robust Conduction



H. Peng*, *et al.*, ***Nature Chemistry*** **2012**, *4*, 281

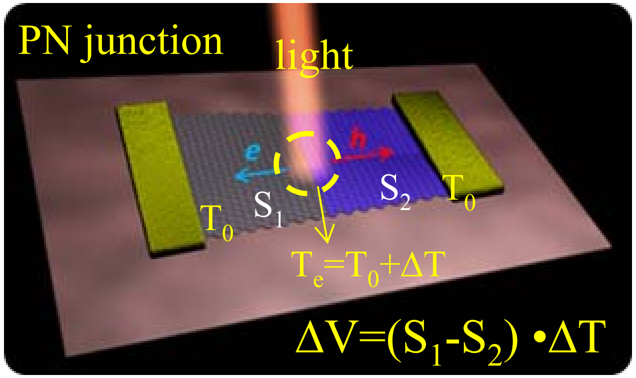
Optoelectronic properties of graphene p-n junction

The thinnest p-n junction



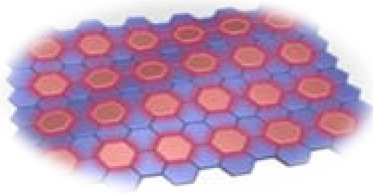
- ◆ Ultrahigh carrier mobility
- ◆ Broadband absorption
- ◆ Hot-carrier multiplication
- ◆ Weak electron-phonon coupling
- ◆ Tunable thermopower
- ◆ Photo-thermoelectric effect

Photo-thermoelectric effect



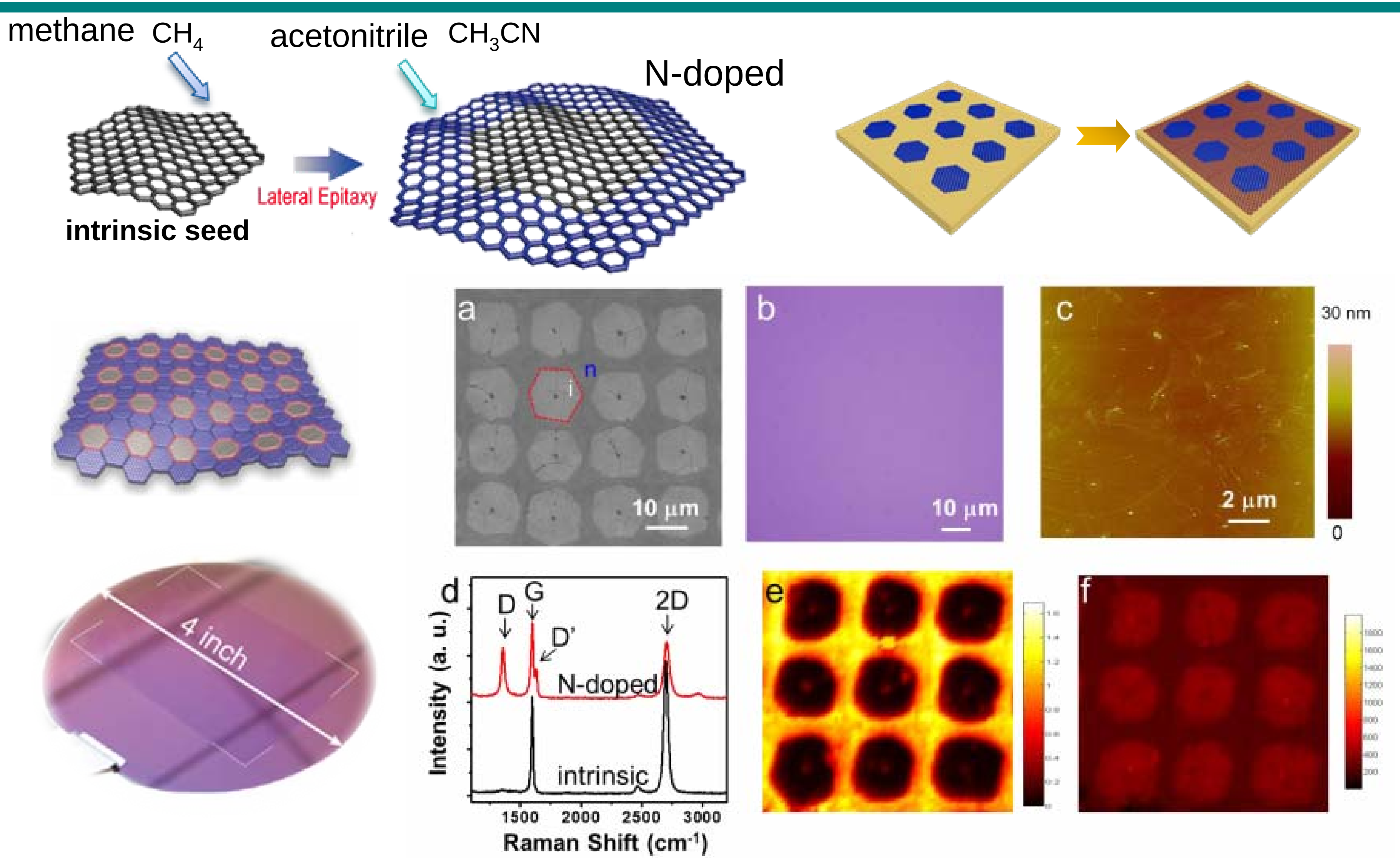
Potential applications in optoelectronic devices

- broadband and ultrafast photodetector
- high-efficiency photoelectric conversion



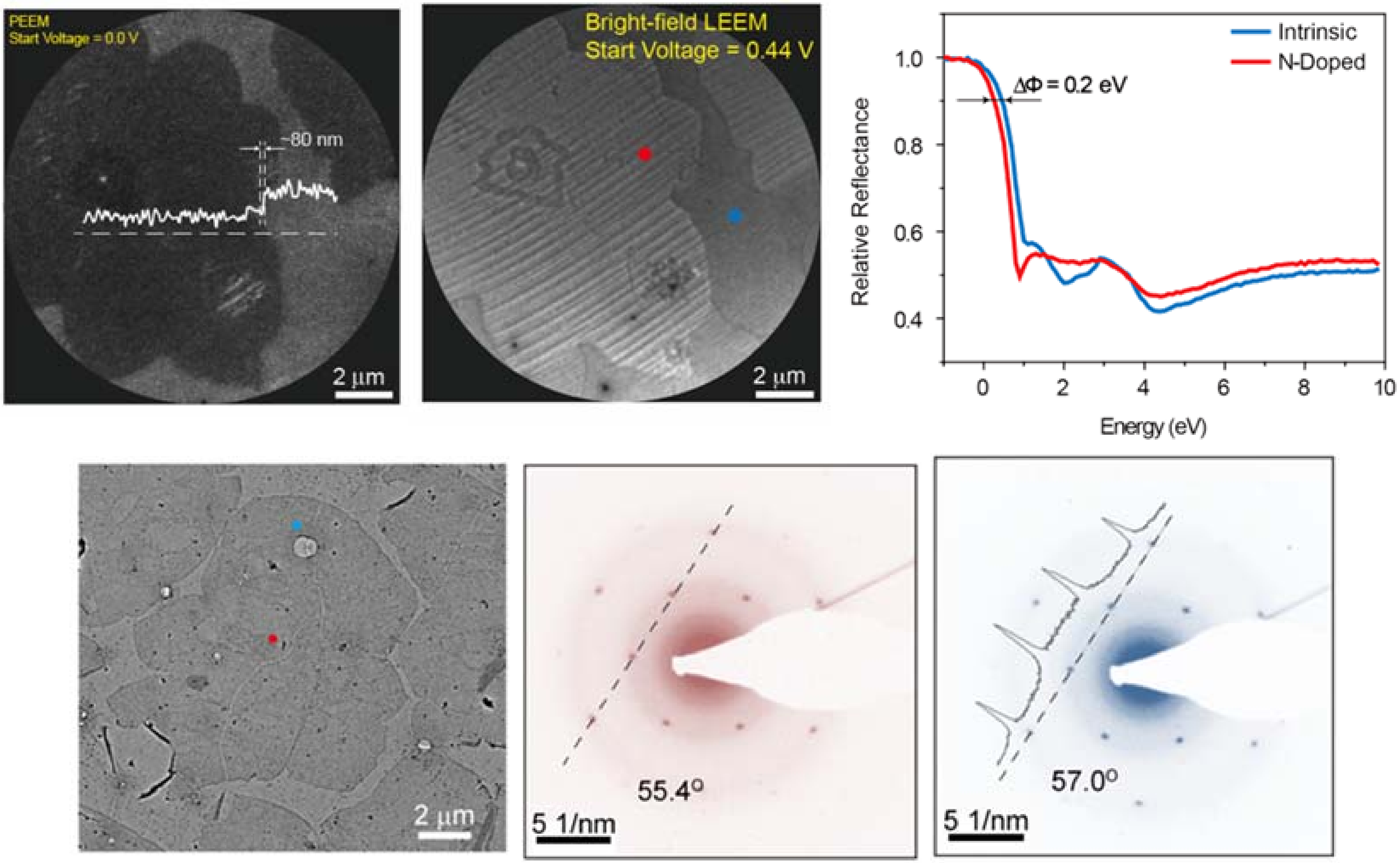
Synthesis of graphene p-n junction is challenging

Modulation-doped growth of mosaic graphene p-n junctions



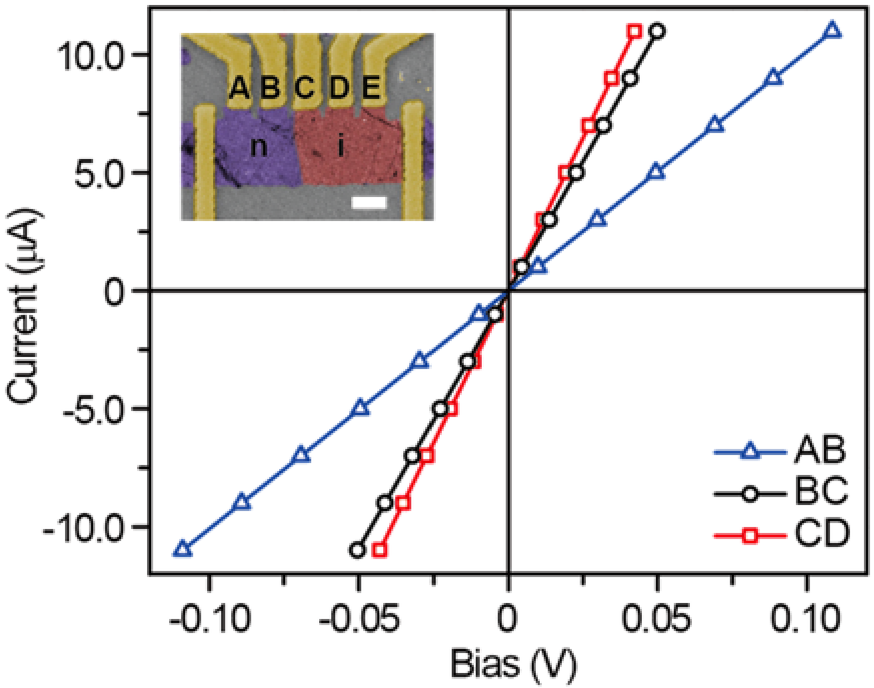
Yan, Wu, Peng*, Jin, Fu, Bao, Liu*, ***Nature Communications*** **2012,** *3,* 1280

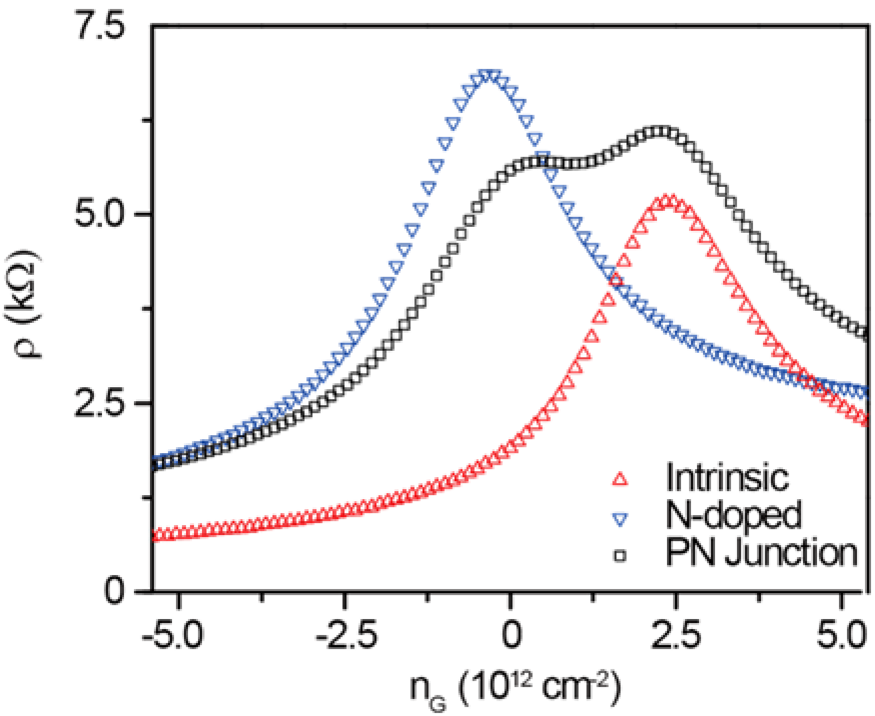
Characterizations of mosaic graphene p-n junctions



Yan, Wu, Peng*, Jin, Fu, Bao, Liu*, ***Nature Communications* 2012,** *3,* 1280

Transport of single crystal graphene p-n junction



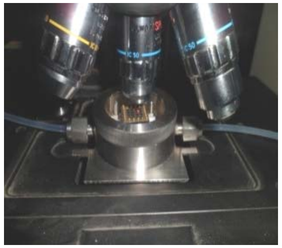


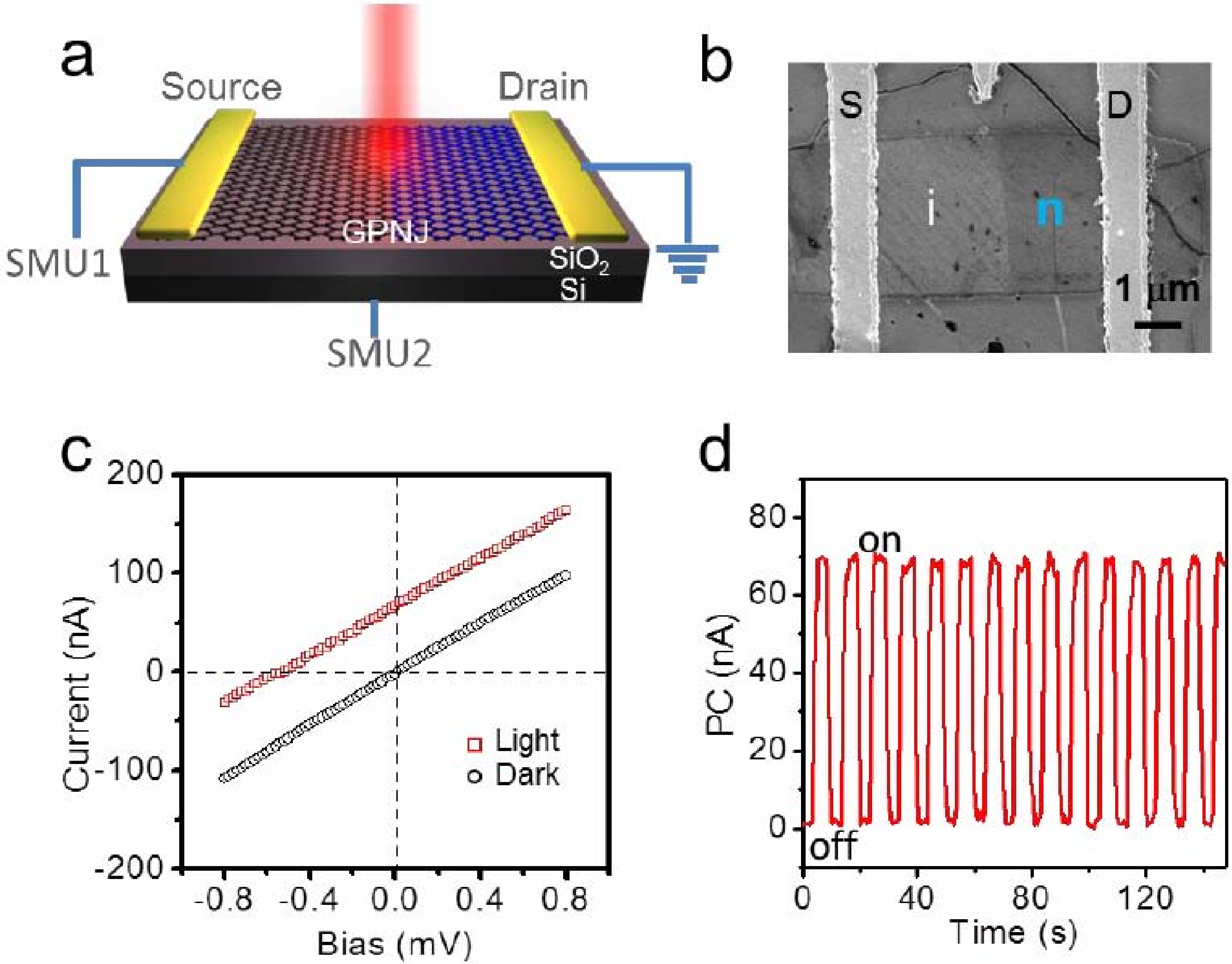
mobility of intrinsic graphene: 5000 cm^2 V^{-1} s^{-1}

mobility of N-doped graphene: 2500 cm^2 V^{-1} s^{-1}

Yan, Wu, Peng*, Jin, Fu, Bao, Liu*, ***Nature Communications*** **2012,** *3,* 1280

Photocurrent generation of graphene p-n junction

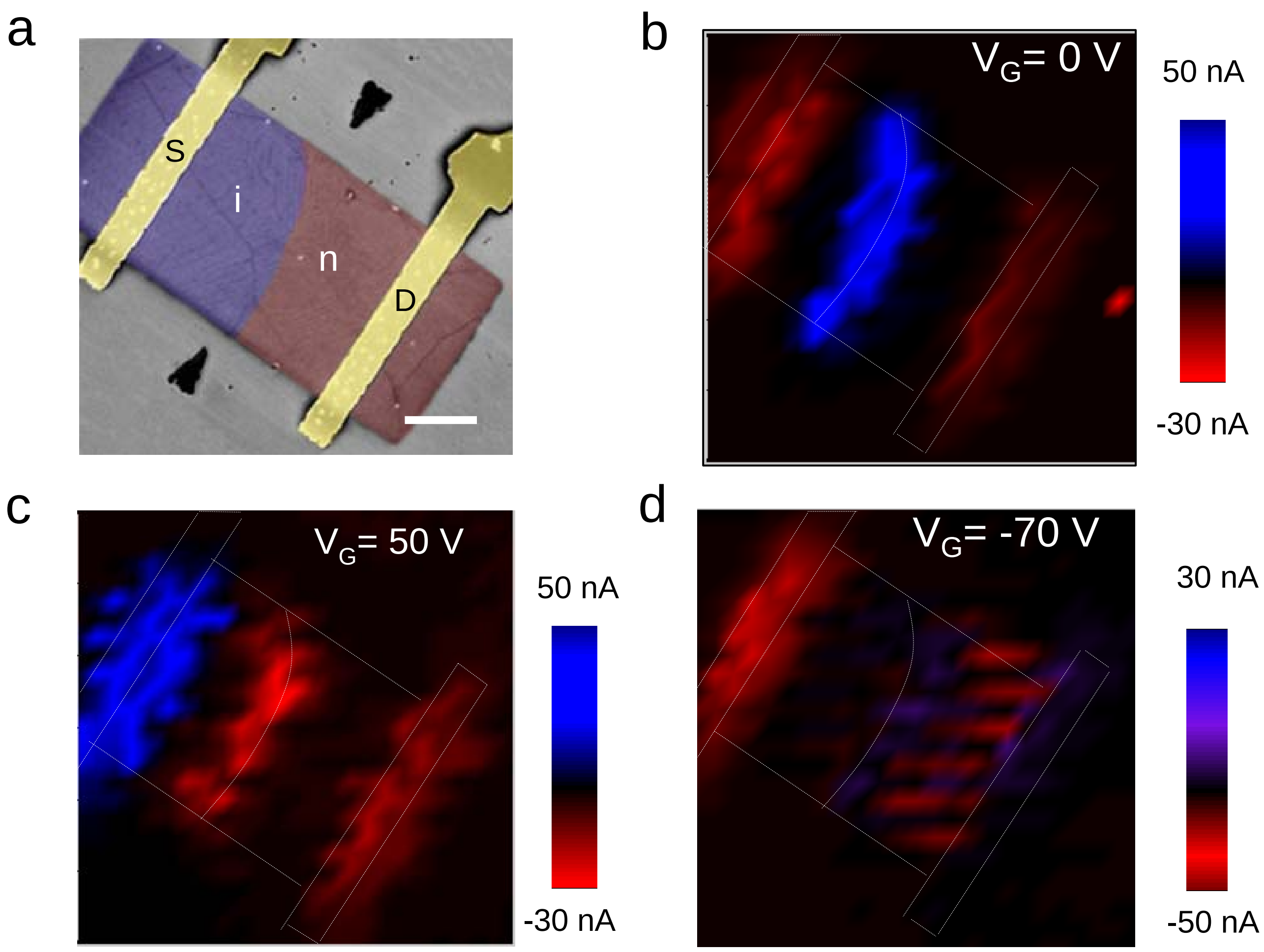




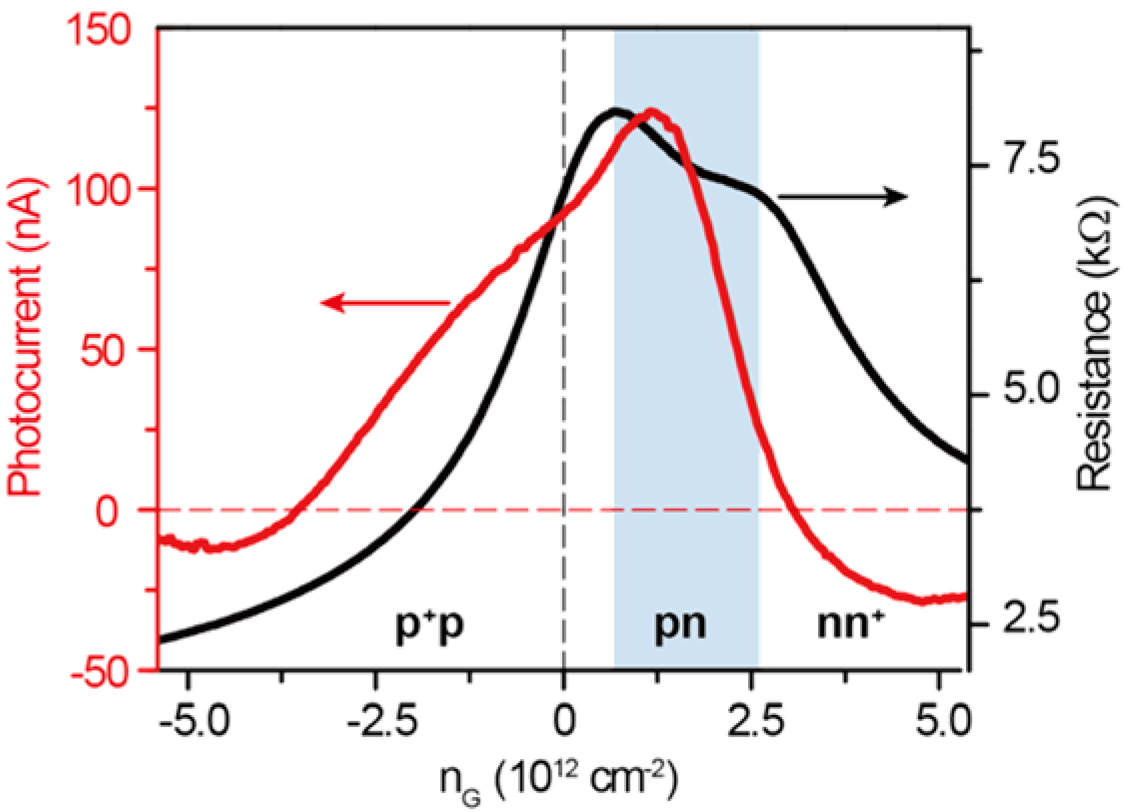
Photoresponse: 0.14 mA·W^{-1}

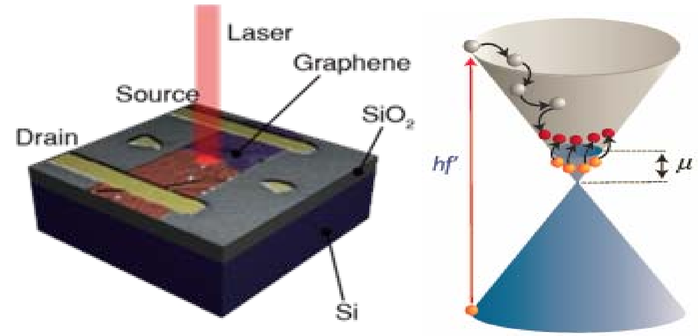
Yan, Wu, Peng*, Jin, Fu, Bao, Liu*, ***Nature Communications*** **2012,** *3,* 1280

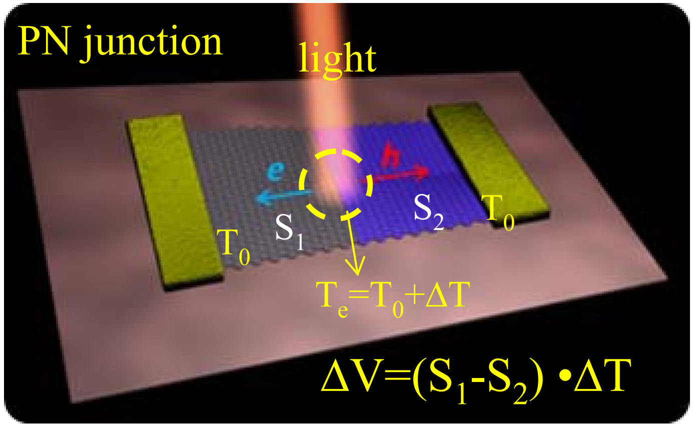
Photocurrent maps at different gate bias



Photoelectric measurement and transfer of p–n junction at different gate bias







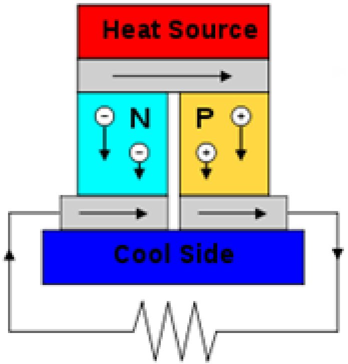


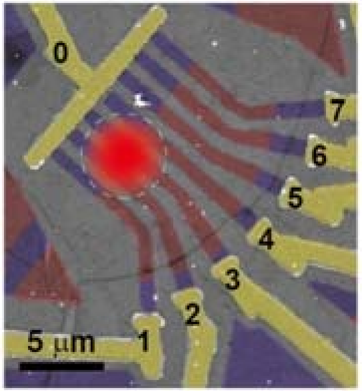
Photo-thermoelectric effect

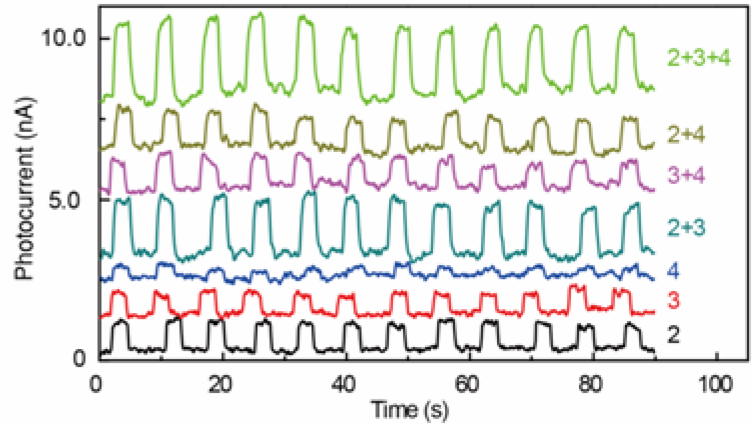
(See Pablo Jarillo-Herrero, ***Science*** **2011**, 4, 648)

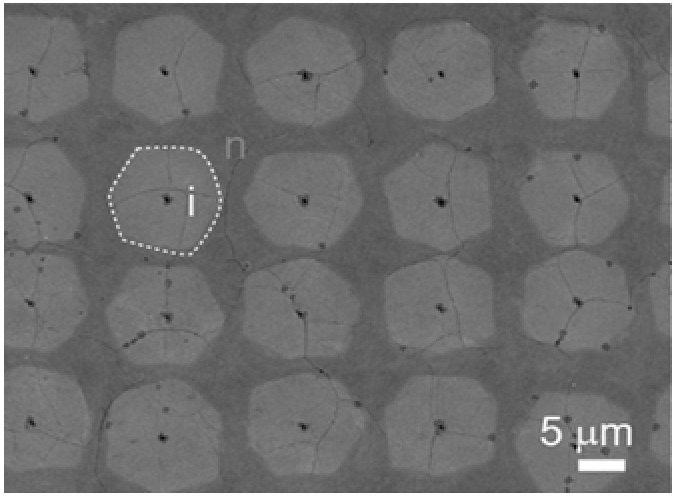
Yan, Wu, Peng*, Jin, Fu, Bao, Liu*, ***Nature Communications*** **2012,** *3,* 1280

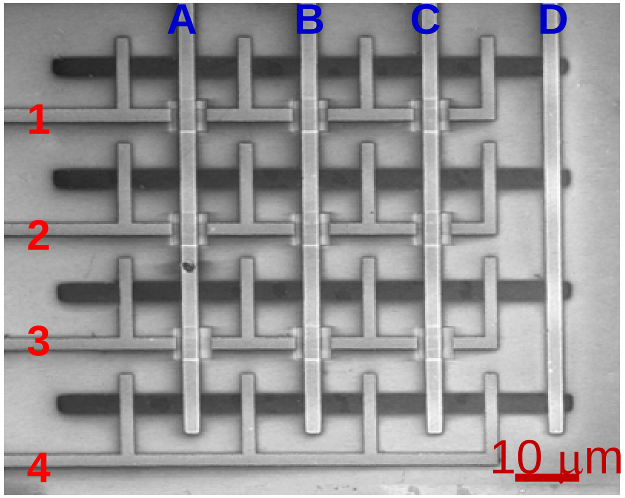
Photoresponses of individual channels and their additions

integration of multiple graphene photodetector channels





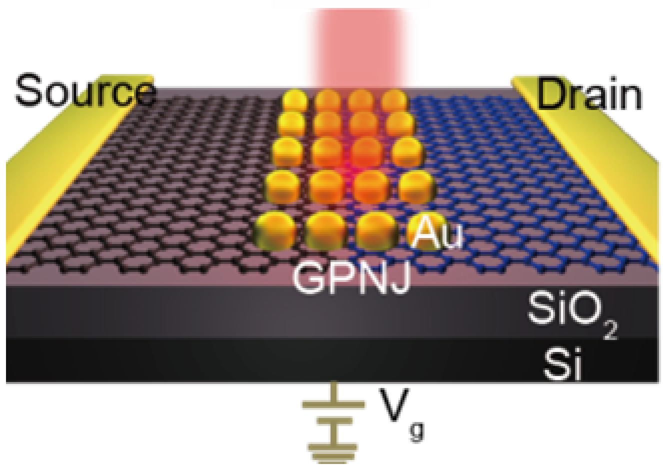


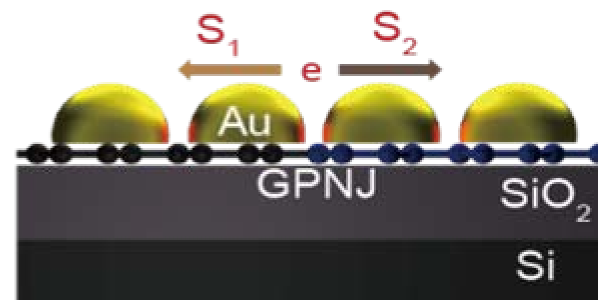


cooperative photodetection

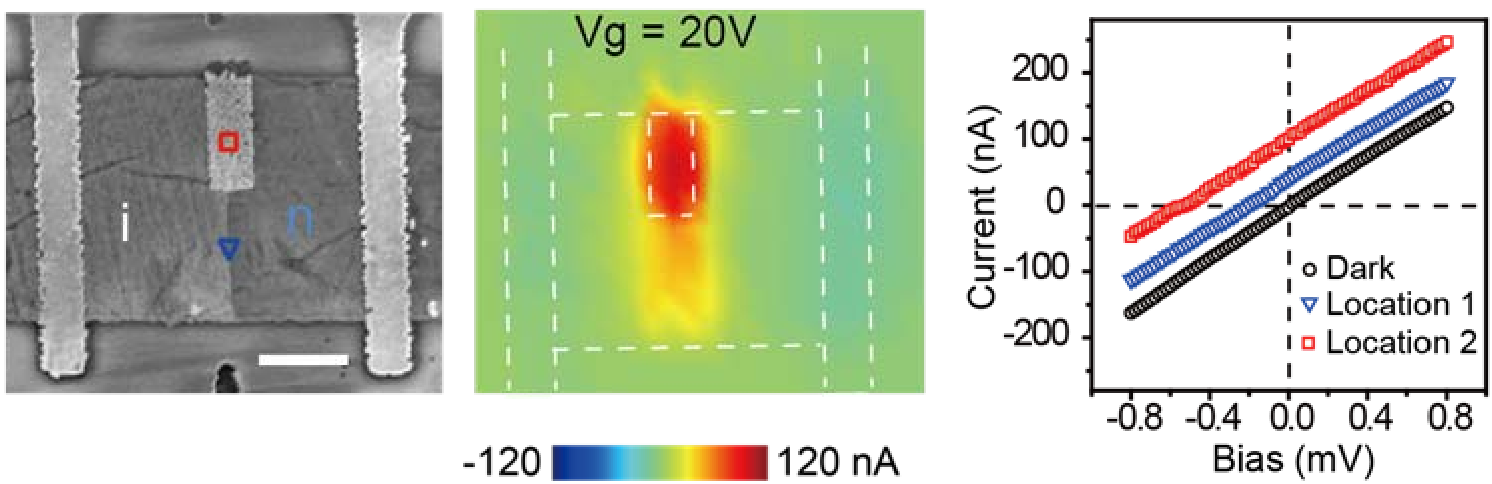
Yan, Wu, Peng*, Jin, Fu, Bao, Liu*, ***Nature Communications*** **2012,** *3,* 1280

Plasmon enhanced photo-thermoelectric conversion at graphene p-n junction





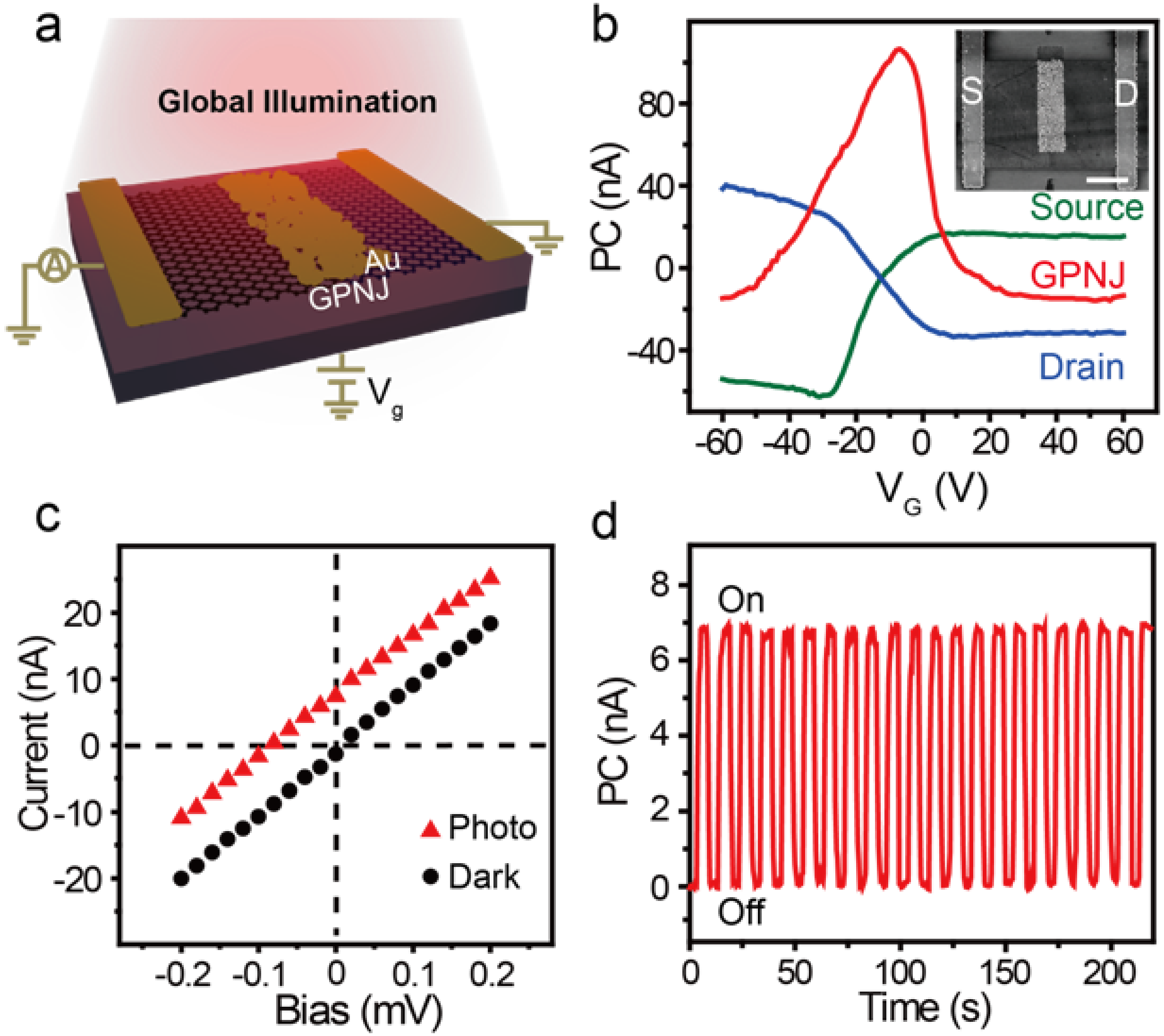
Plasmon enhanced PTE conversion



Enhancement factor: 4

Di Wu, Hailin Peng*, Zhongfan Liu*, et al., *J. Am. Chem. Soc*. 2013, *135,* 10926.

Global light photodetection via plasmonic enhancement of photothermoelectric conversion



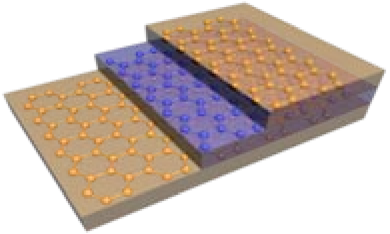
Di Wu, Hailin Peng*, Zhongfan Liu*, et al., *J. Am. Chem. Soc*. 2013, *135,* 10926.

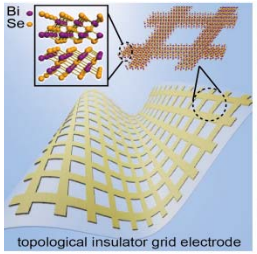
Summary

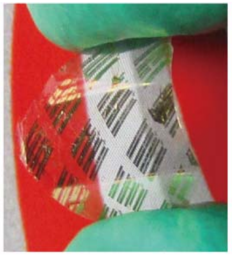
1. **Material synthesis: vapor-liquid-solid, vapor-solid, and van der Waals epitaxy strategy** were employed for the growth of 2D crystals, including nanoplate array with controlled orientation, thickness, and placement.

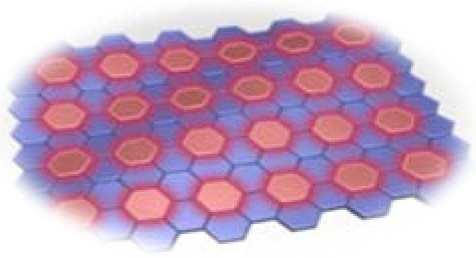
2. **Near-infrared transparent flexible electrodes** based on few-layer topological-insulator Bi_2Se_3 nanostructures was demonstrated for the first time. In addition, we present the realization of **broadband transparent electrodes** with 2D grids of topological insulator.

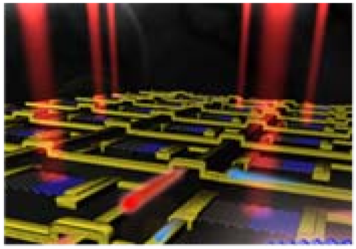
3. **Modulation doped graphene** was grown via a large-scale CVD process. Pronounced photocurrent was observed in CVD hybrid graphene with p-n junctions.











Thank you for your attention

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