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Barcelona (Spain)

Synthesis and Lithium Battery Applications of Few-layer Black Phosphorous (BP) Nanosheets

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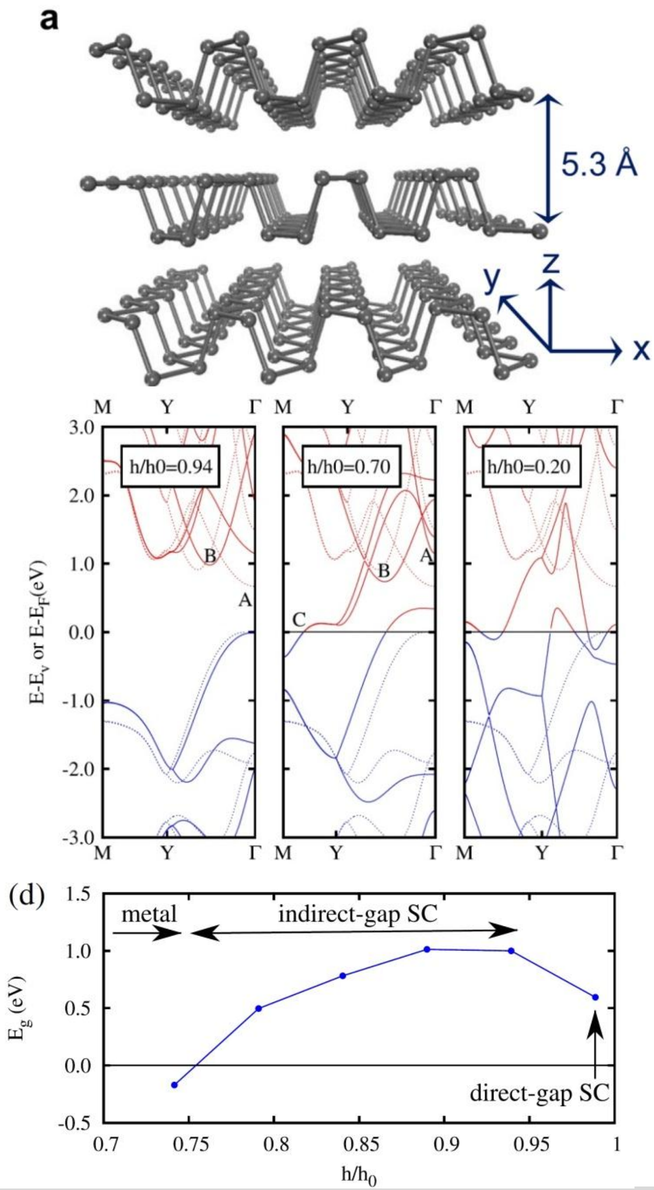
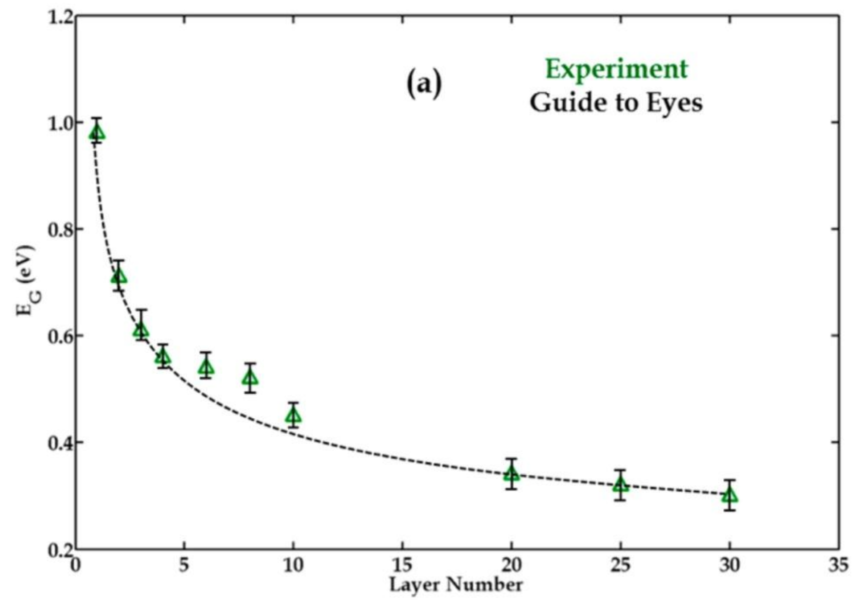
Outline

- Background
- Preparation of Few-layer BP Nanosheets
- Application for Lithium-ion Batteries
- Application for Lithium-sulfur Batteries
- Conclusions

Advantages of BP





- Layer-dependent direct bandgap

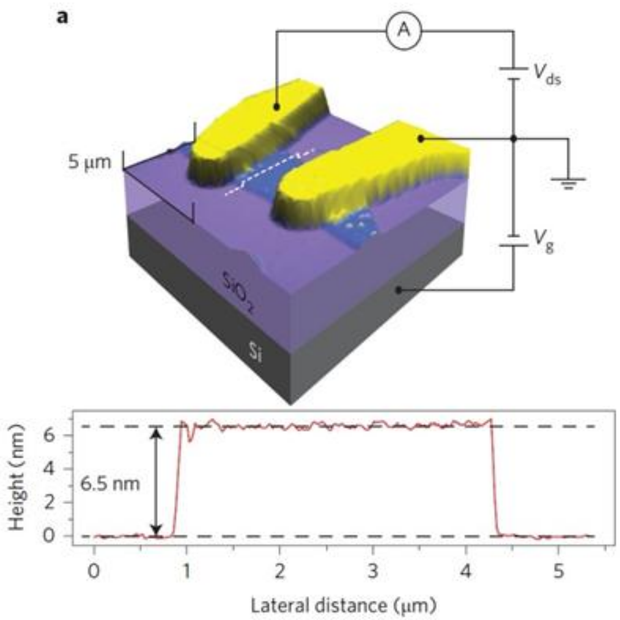
  Bulk to monolayer: 0.3 – 1.0 eV

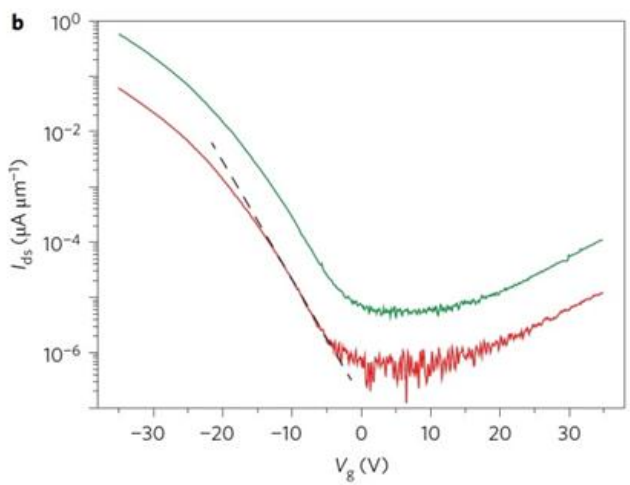
- Semiconductor-metal transition

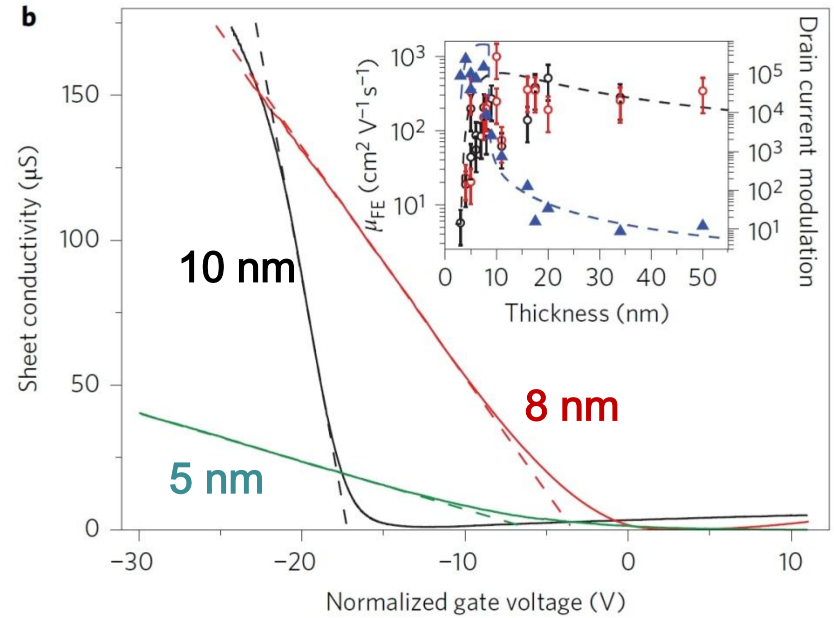
  Deformation-induced

A. S. Rodin et al., *Phy. Rev. Lett.* **2014**, 112, 17, 176801.
S. Das et al., *Nano Lett.* **2014**, 14, 10, 5733.

Advantages of BP







- High carrier mobility

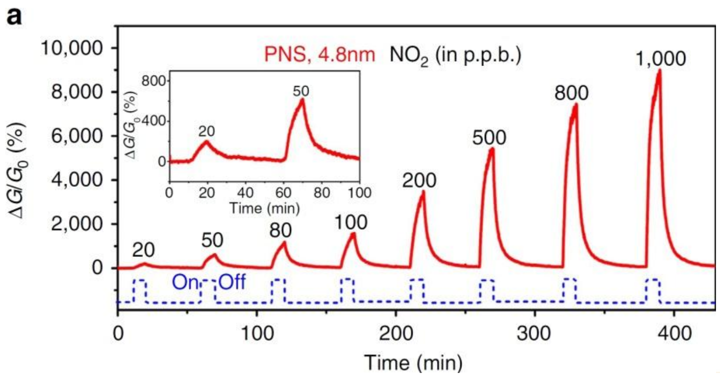
  ~1000 $cm^2 V^{-1}s^{-1}$

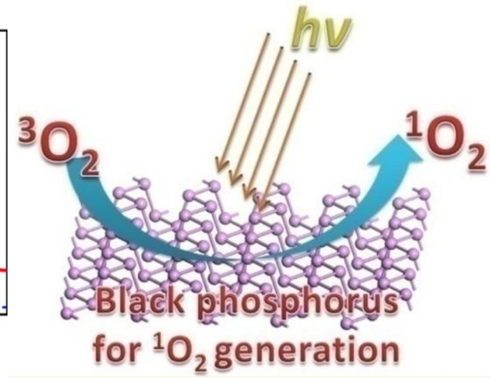
- High On/off Ratio

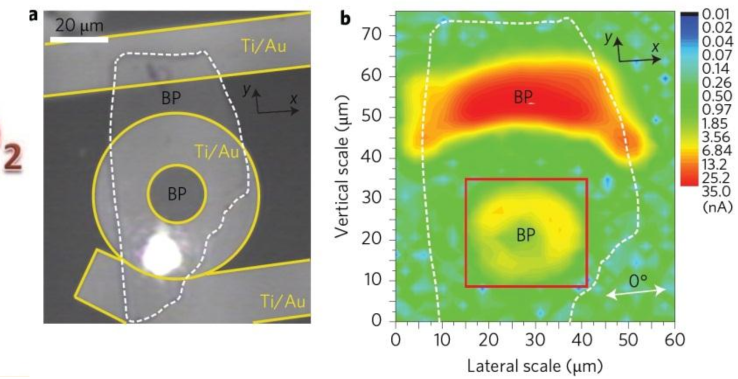
  ~10^5

L. K. Li et al., *Nat. Nanotechnol.* **2014**, 9, 5, 372.

Potential Applications of BP



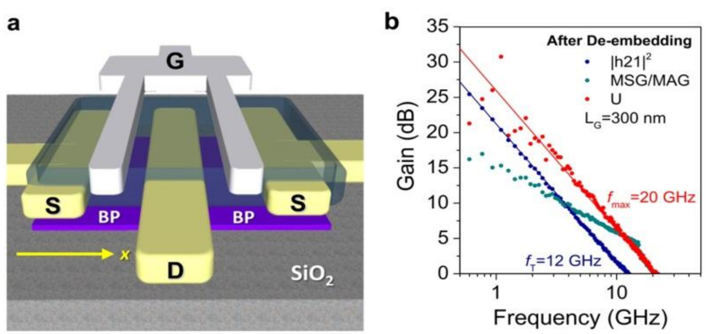


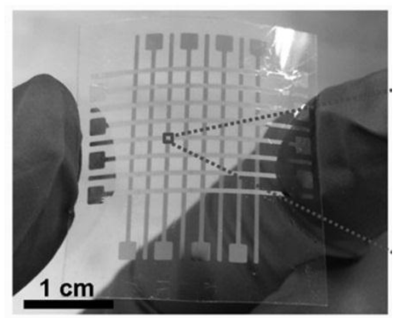


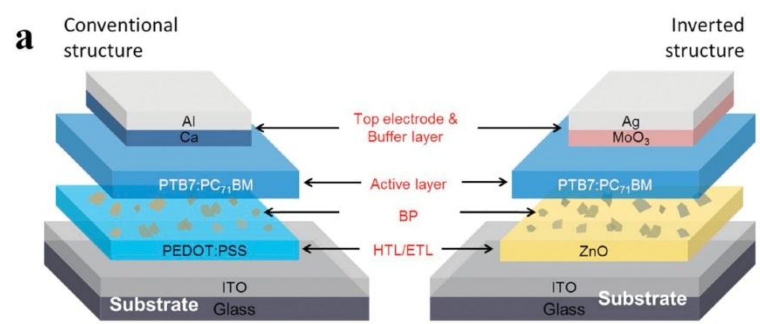
Gas sensor

Singlet oxygen generator

Photodetector







Radio-frequency transistors

Memory device

Organic photovoltaics

。。。。。。

S. M. Cui et al., *Nat. Commun.* **2015**, 6.
H. Wang et al., *J. Am. Chem. Soc.* **2015**, 137, 35, 11376.
S. H. Lin et al., *Adv. Funct. Mater.* **2016**, 26, 6, 864.
H. T. Yuan et al., *Nat. Nanotechnol.* ***2015***, 10, 8, 707.
W. Hang et al,. *Nano Lett.* **2014**, 14, 6424.
X. Zhang et al., *Angew. Chem. Int. Ed.* **2015**, 54, 1.

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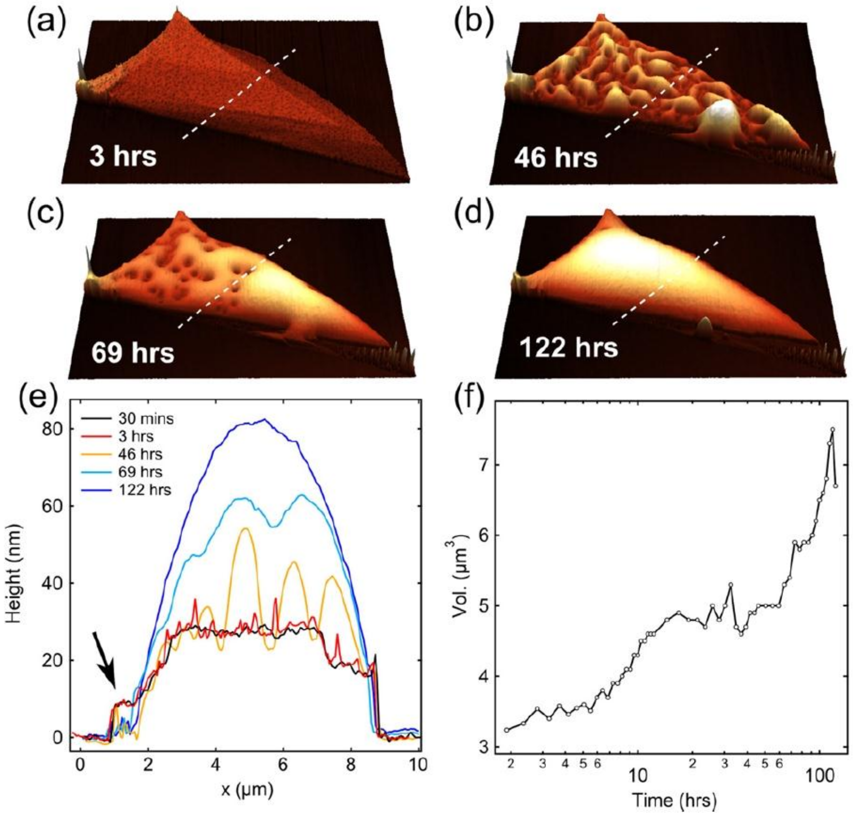
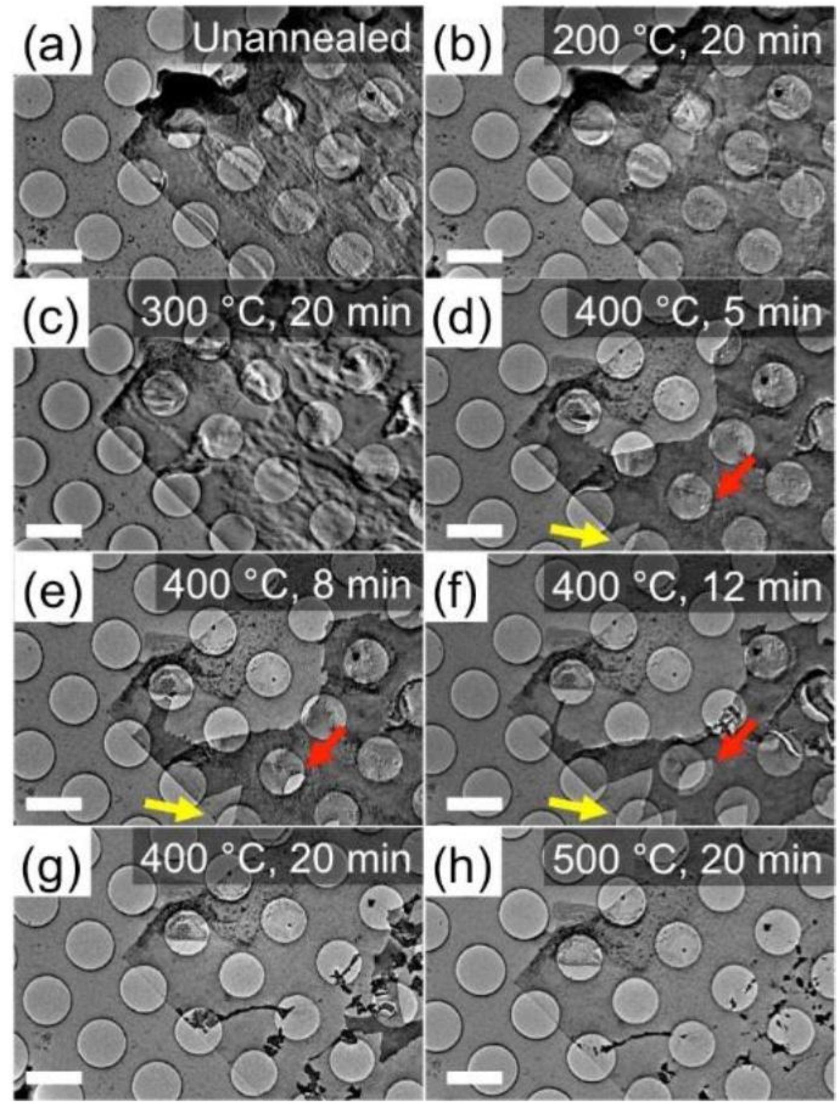
Disadvantages of BP





Bad stability !

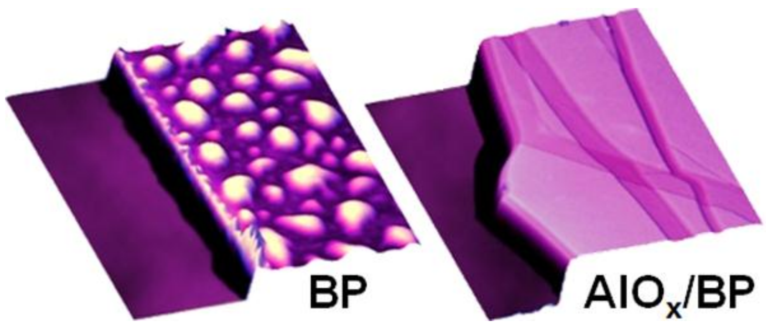
- Oxidized in air
- Decompose at ~400 ℃

J. O. Island et al., *2D Mater.* **2015**, 2, 011002.

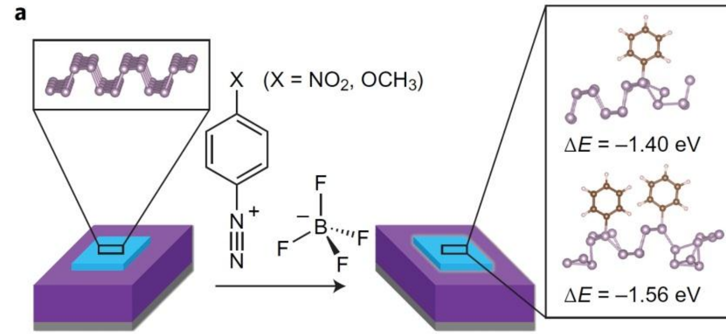
X. L. Liu et al., *J. Phys. Chem. L* **2015**, 6, 5, 773.

Stability of BP

Prevent oxidization

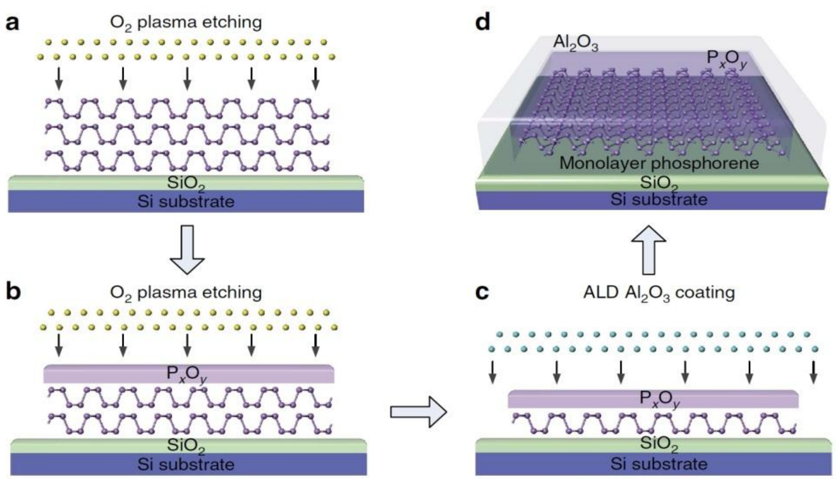


Surface coating

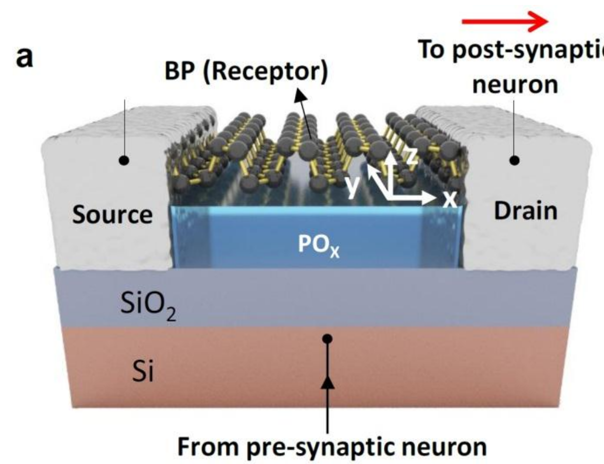


Surface modification

Utilize oxidization



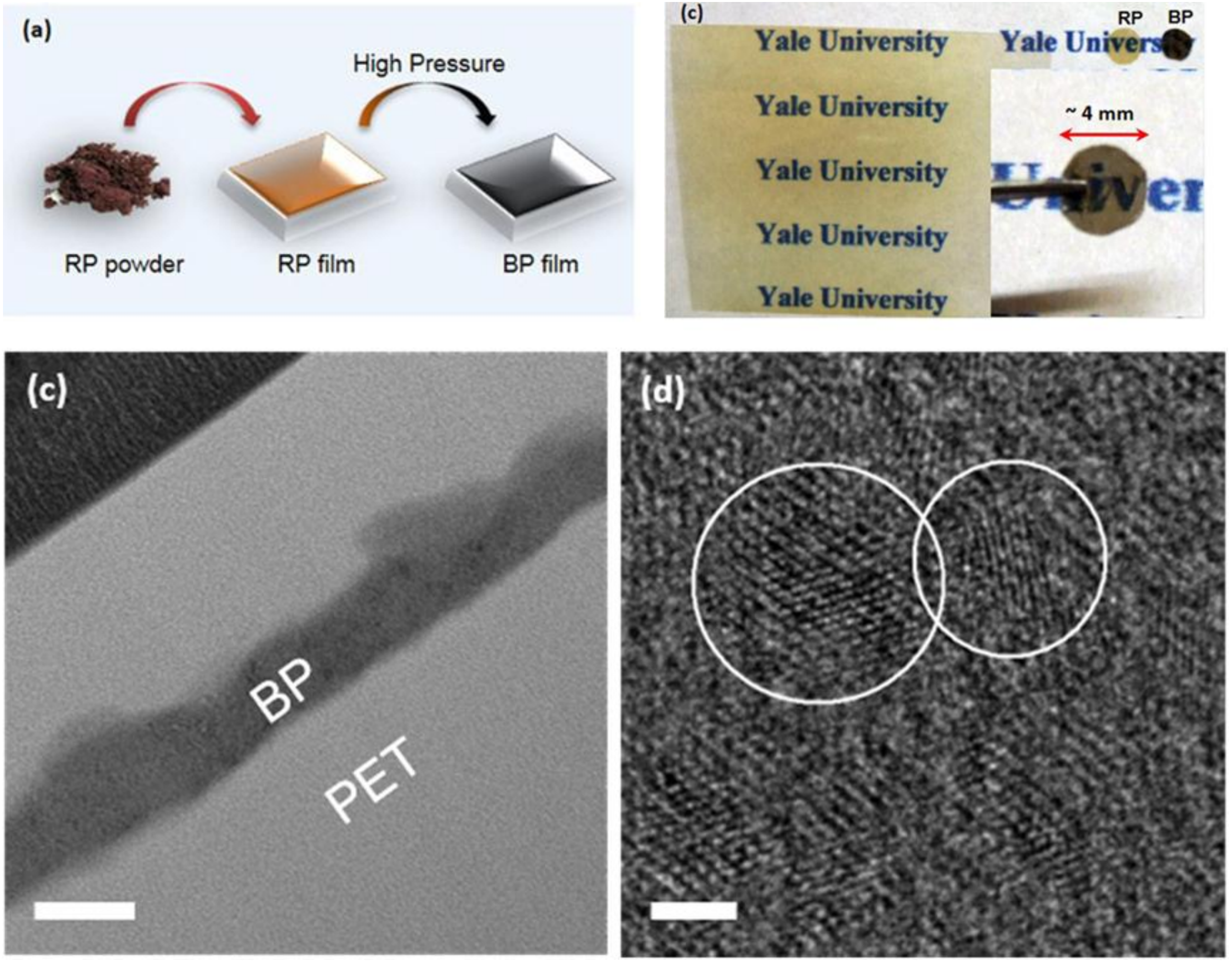
For single-layer BP



Neuromorphic synaptic device

J. D. Wood et al., *Nano Lett.* **2014**, 14, 12, 6964.
J. J. Pei et al., *Nat. Commun.* **2016**, 7, 10450.
C. R. Ryder et al., *Nat. Chem.* **2016**, 8, 597.
H. Tian et al., *Adv. Mater.* **2016**, 28, 25, 4991.

Synthesis of Few-layer BP Film



Thin BP film on PET

Problems:

- Very thick
  ~ 40 nm
- Not uniform
  rough surface
- Low quality
  polycrystalline

No effective way to obtain large-area, high-quality monolayer BP film !

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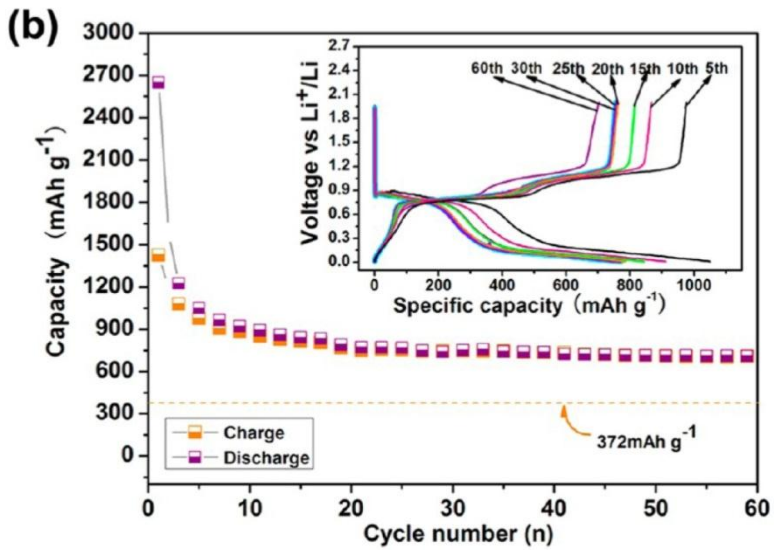
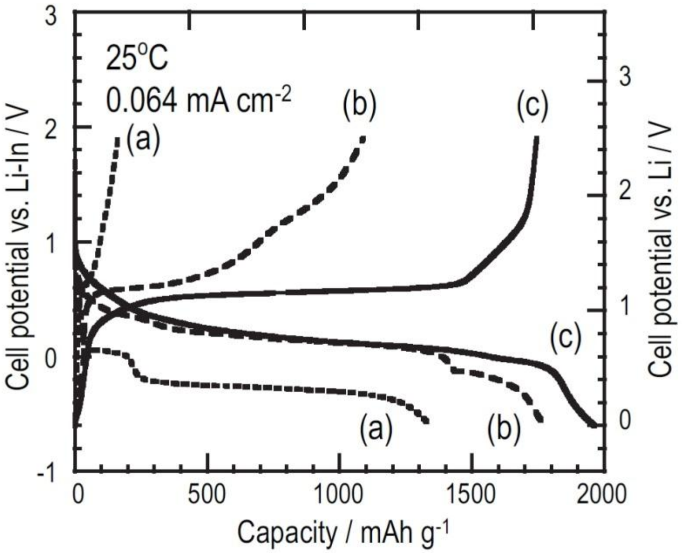
Another Way Out

Thick flakes, at 50 mA g^{-1}



Large powders, at 24 mA g^{-1}



Idea

- Low conductivity
- Severe volume expansion
- Small work current density
- Fast capacity decay

Materials	Specific capacity (mAh g^{-1})	Conductivity (S m^{-1})
Graphene	372	~10^8
BP	2596	~10^2
Si	4200	~10^{-4}

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L. Q. Sun et al., *J. Phys. Chem. C* **2012**, 116, 14772.
M. Nagao et al., *J. Power Sources* **2011**, 196, 6902.
C. M. Park et al., *Adv. Mater.* **2007**, *19*, 2465.

Synthesis of Bulk BP

Comparison of Present Methods

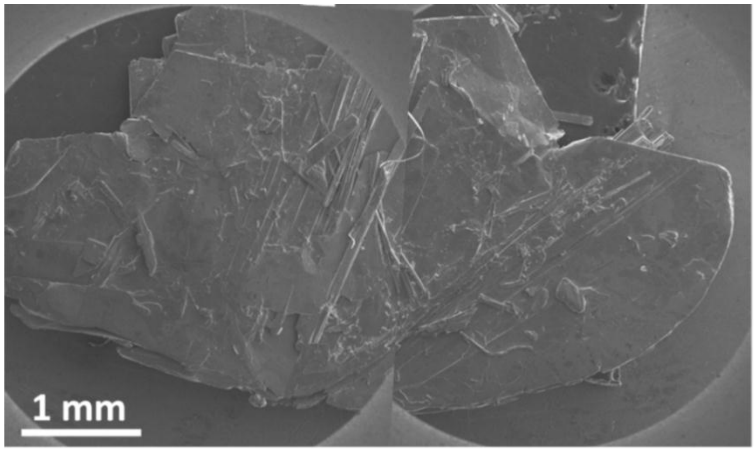
Methods	High Temp. high Press.	Bi/Hg catalyst	HEMM	Sono-chemistry	Gas-phase transformation
Raw materials	white P	white P Hg/Bi	red P	red P	red P, SnI_4, AuSn
Conditions	p >10000 atm	normal pressure	ambient Ar	sonication	vacuum
Size	mm-scale	5x0.1x0.07 mm^2	nm-scale	tens of um	cm-scale
Time	tens of min	tens of hours	tens of hours	several hours	several hours
Quality	high	low	low	high	very high

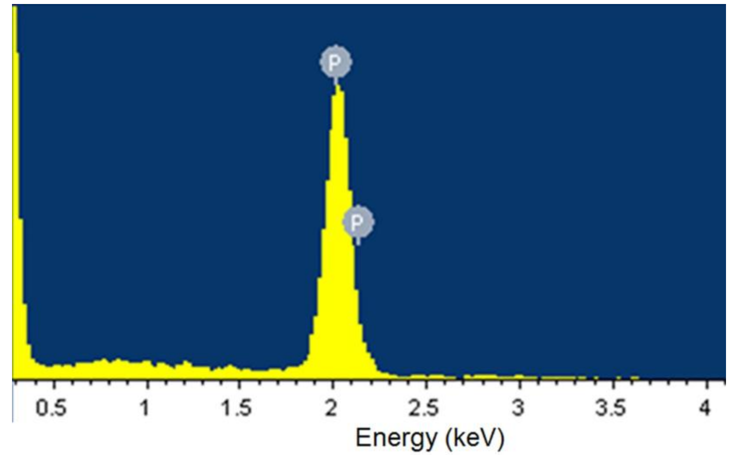
Toxic chemicals Complex apparatuses

Small size Time-consuming

Y. Maruyama et al., *Physica B+C* **1981**, 105, 1, 9.
P. W. Bridgman, *J. Am. Chem. Soc.* **1914**, 36, 7, 1344.
S. H. Aldave et al., *2D Mater.* **2016**, 3, 014007.
T. Nilges et al., *J. Solid State Chem.* **2008**, 181, 1707.

Characterization of Bulk BP

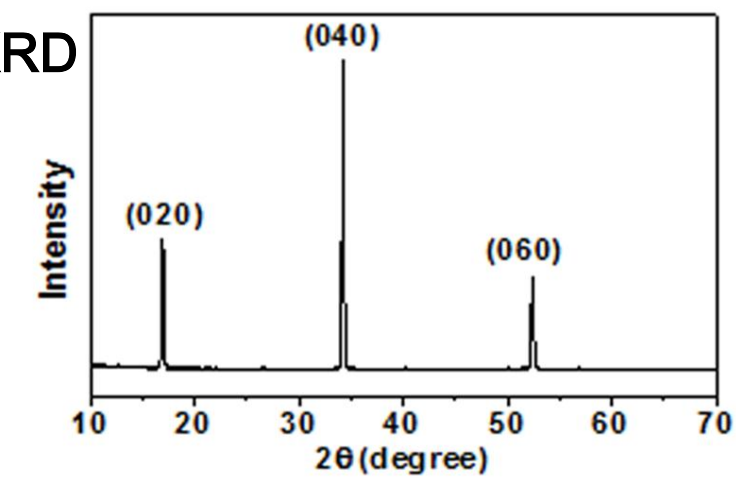


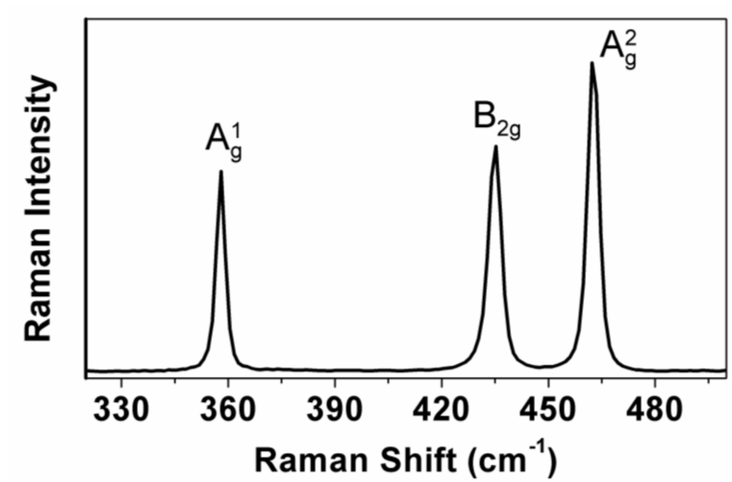


Large size

High purity

XRD





Raman

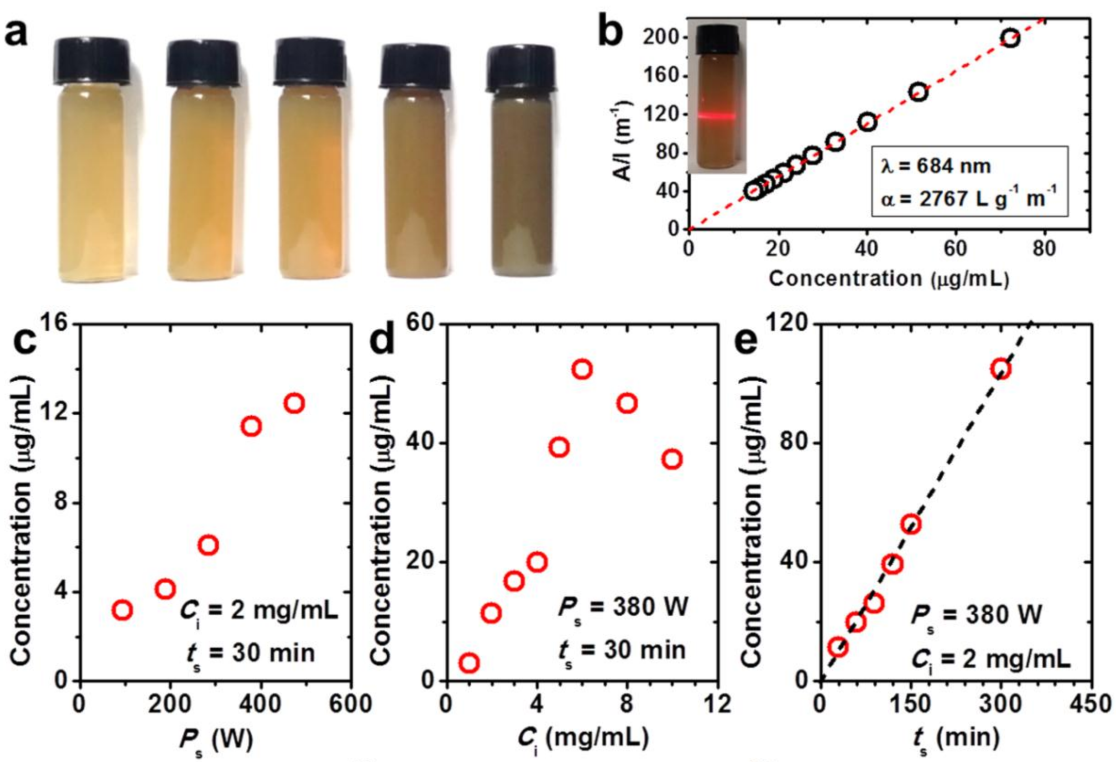
High-crystallinity

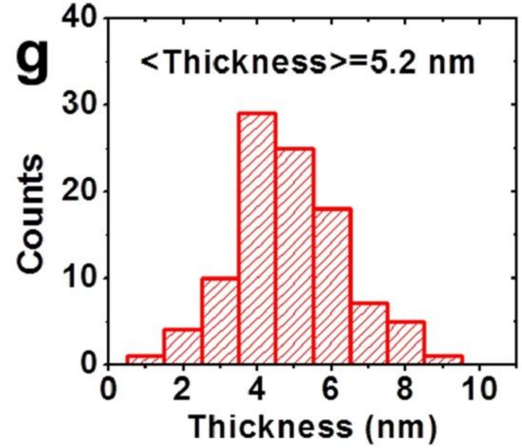
L. Chen et al. *Adv. Mater.* **2016**, *28*, 510.

Exfoliation of Few-layer BP Nanosheets

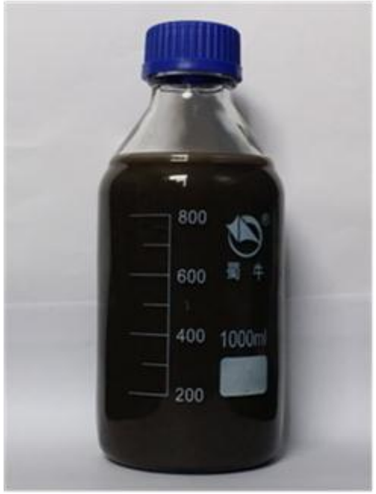
Solvent	NMP	DMSO	CHP	DMF	H_2O
b. p. (℃)	204	189	154	153	100

Systematic sonication





Scaling up



J. R. Brent et al., *Chem. Commun.* **2014**, *50*, 13338.
P. Yasaei et al., *Adv. Mater.* **2015**, *27*, 1887.
D. Hanlon et al., *Nat. Commun.* **2015**, 6, 8563.

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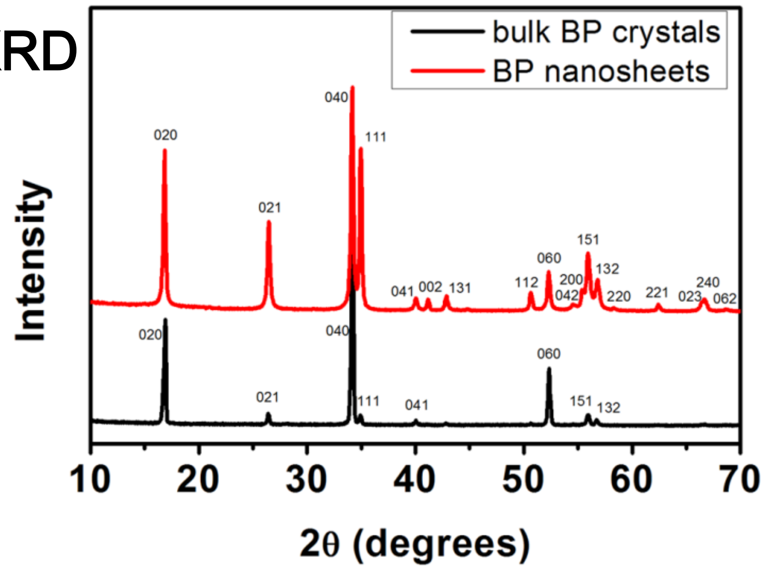
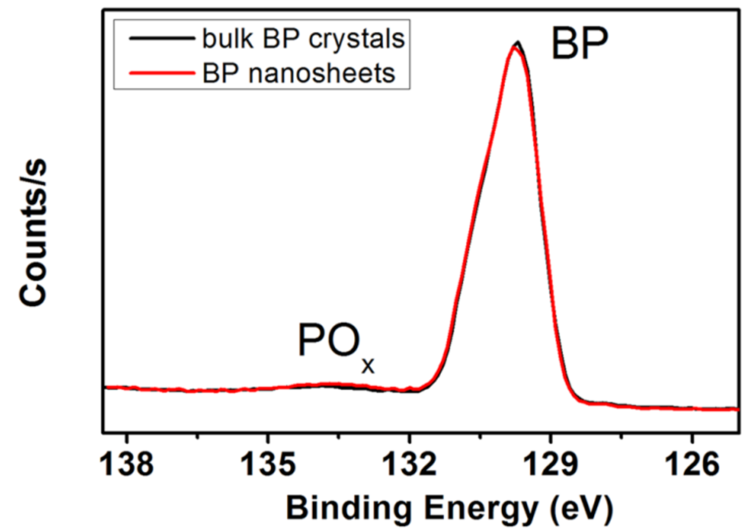
Quality of Few-layer BP Nanosheets

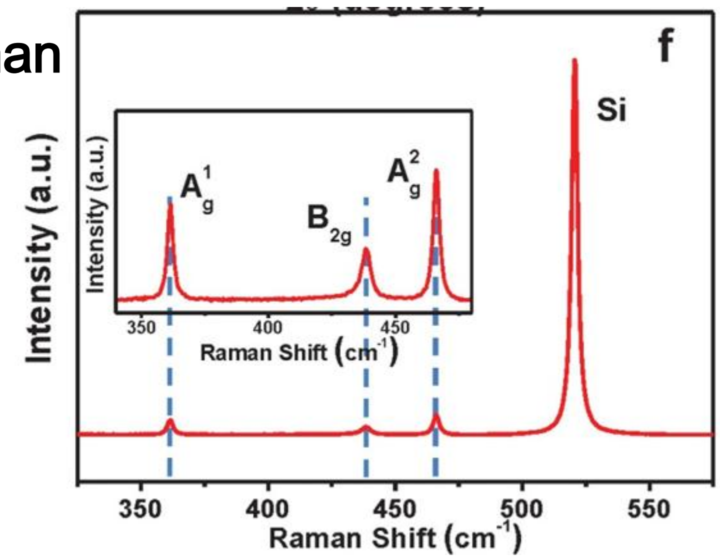
XRD



XPS



Raman



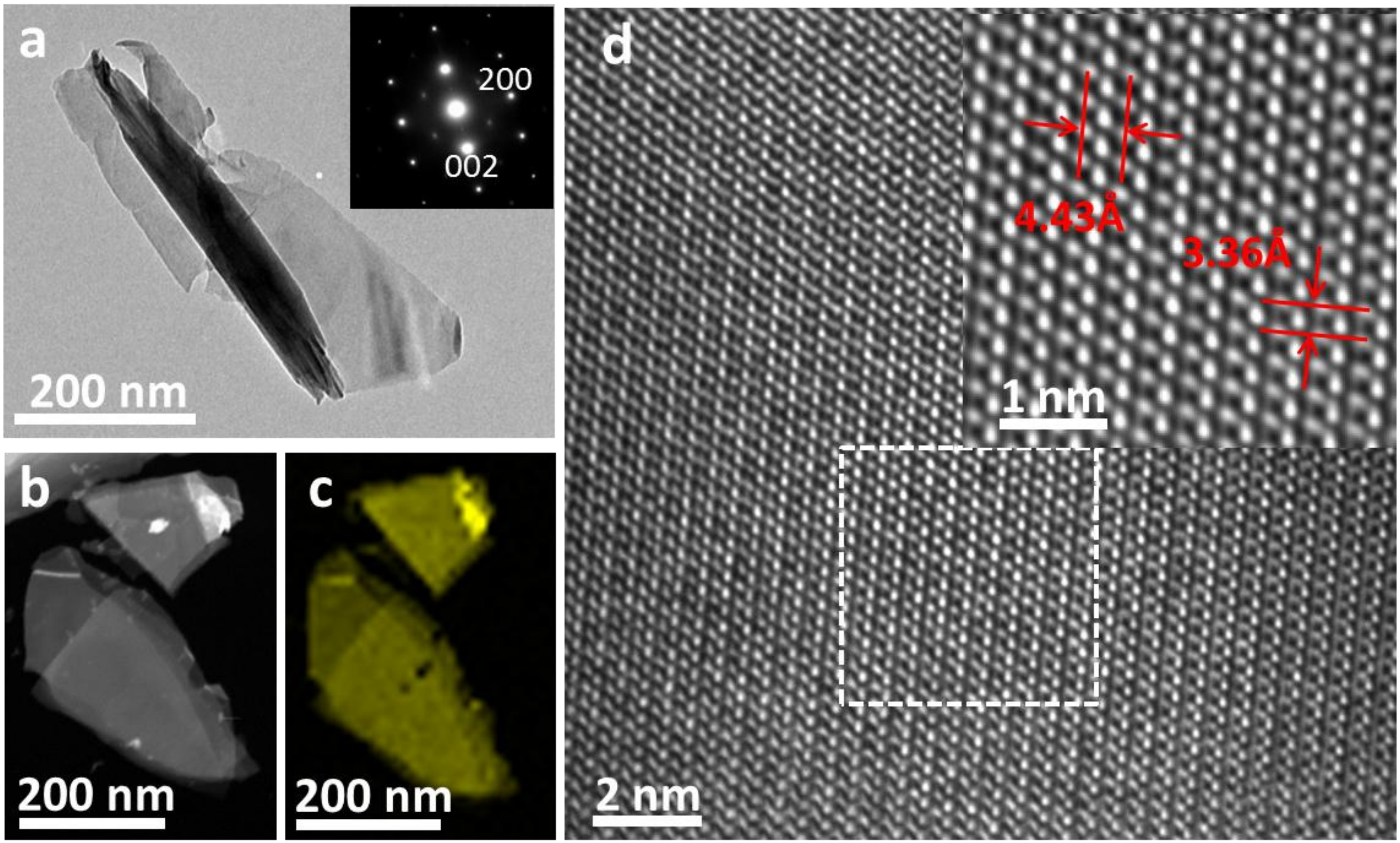
Evidences

XRD: only more new peaks appear, no new phases introduced

Raman: A_g^1/A_g^2 > 0.6, pristine BP

XPS: almost no oxides exist

Structure of Few-layer BP Nanosheets



High-quality, clean surface

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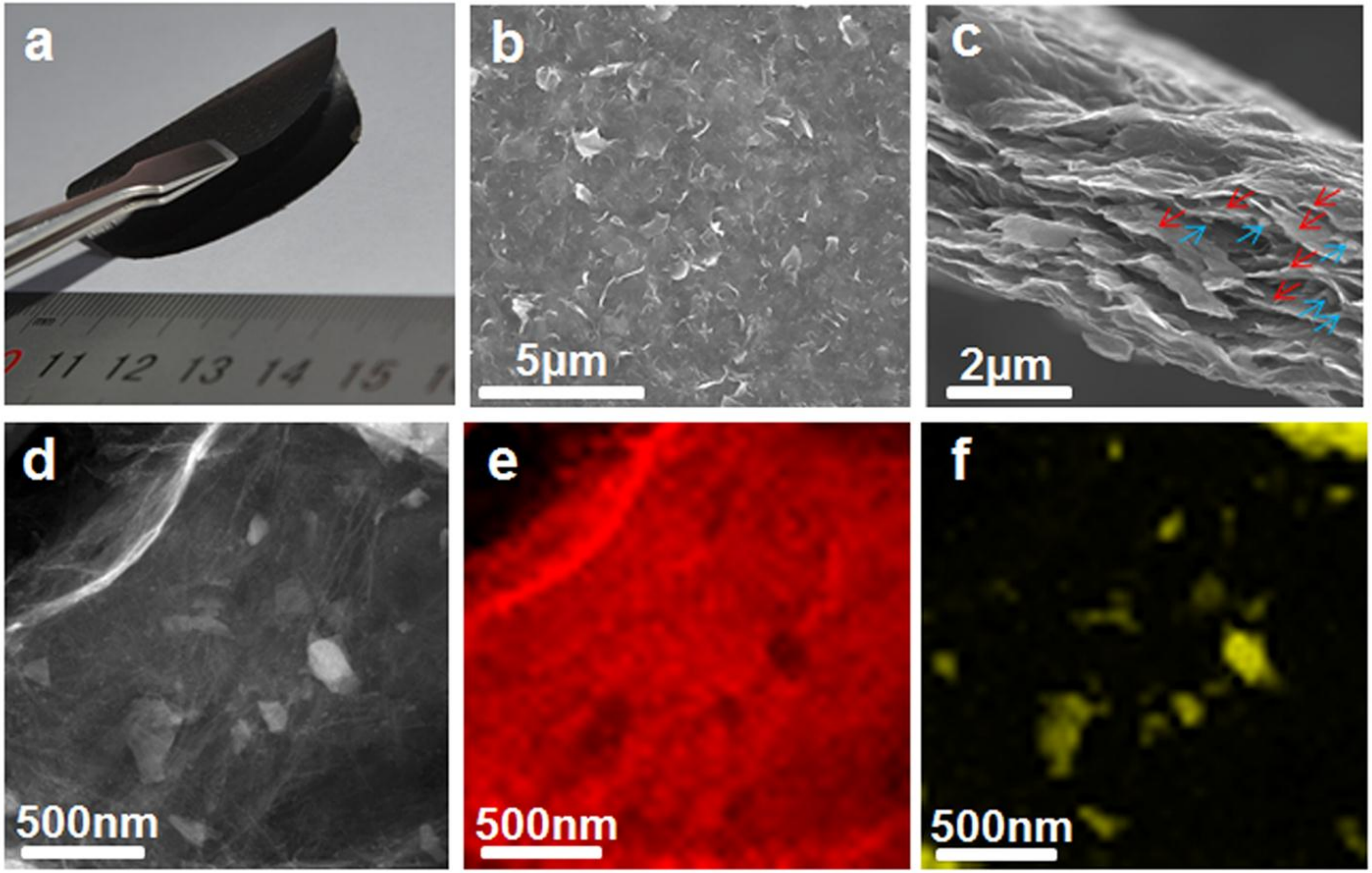
BP-G Hybrid Paper Electrode

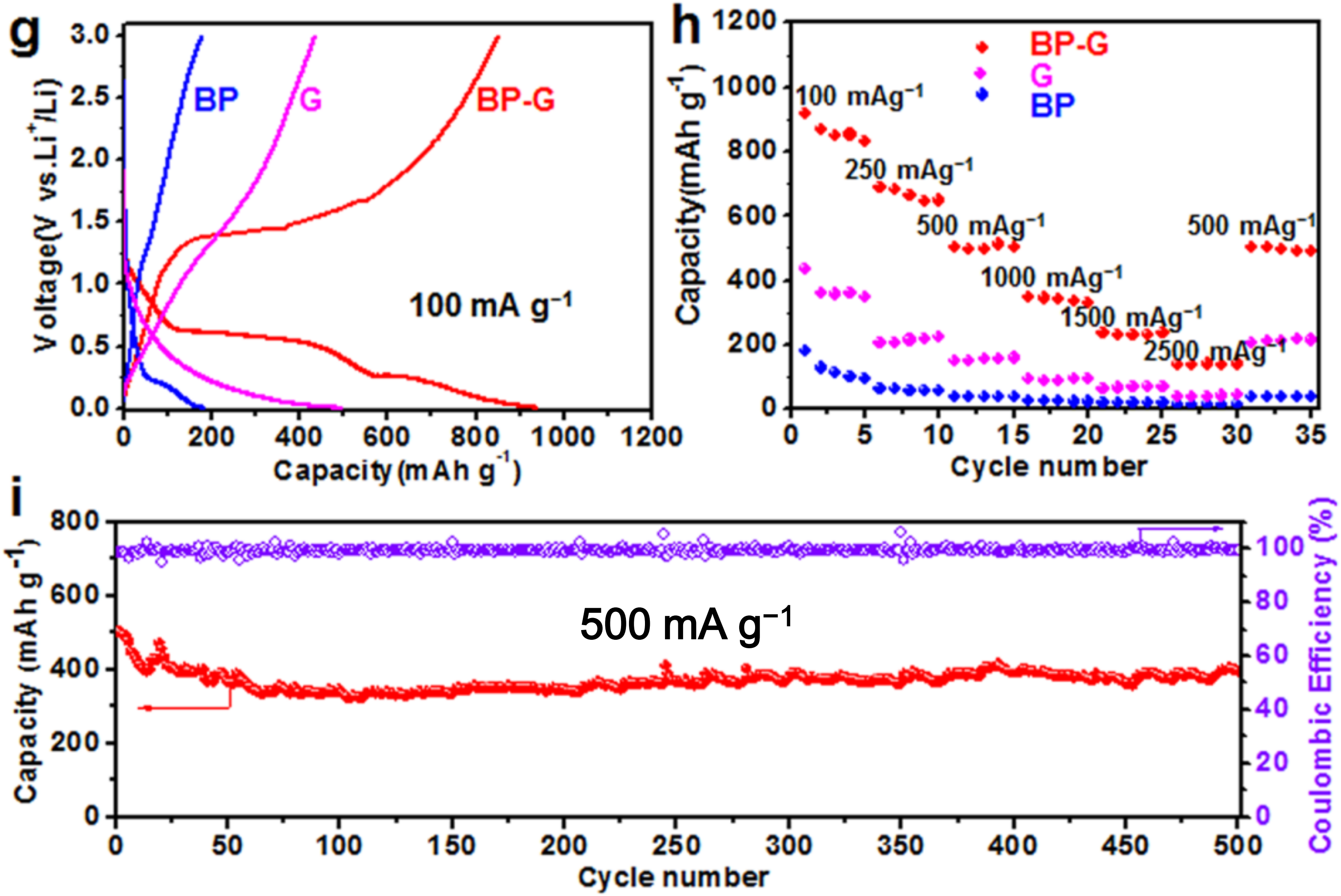


G : BP = 20 : 80 wt%

High flexibility

BP nanosheets wrapped by G flakes, effectively confining the expansion of BP nanosheets during charge/discharge cycles.

Electrochemical Behaviors



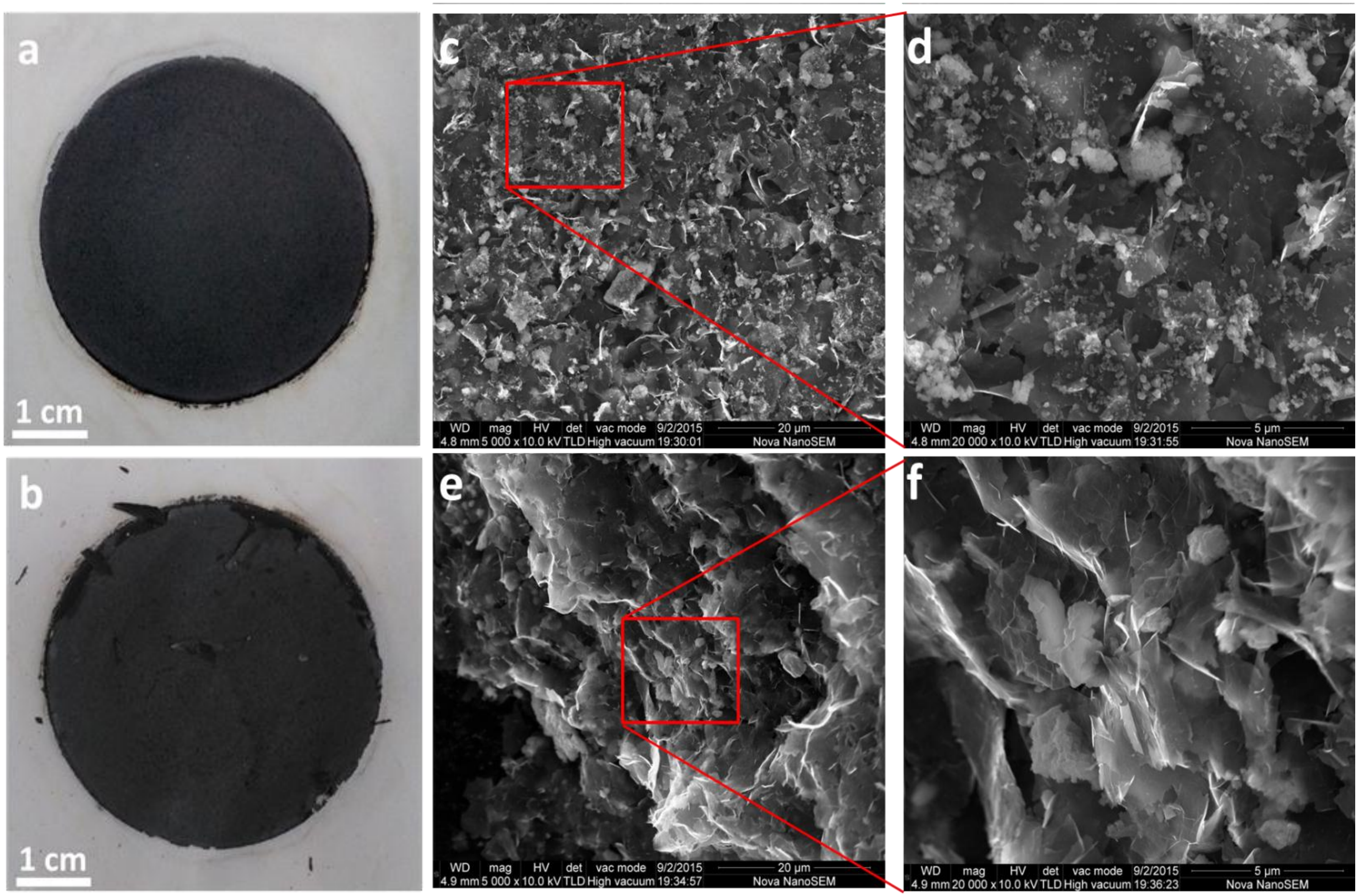
Lower overpotential

Better rate capability

Higher specific capacity

402 mAh g^{-1} after 500 cycles

BP Nanoparticle-G Hybrid Electrode



Top-view

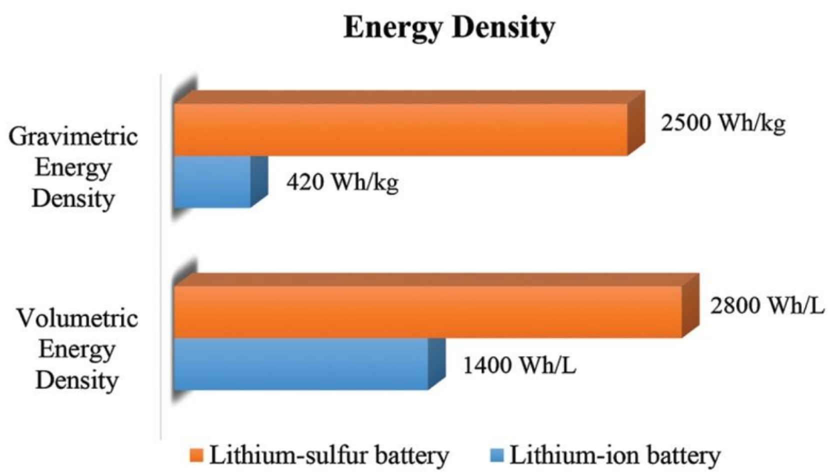
Cross-section

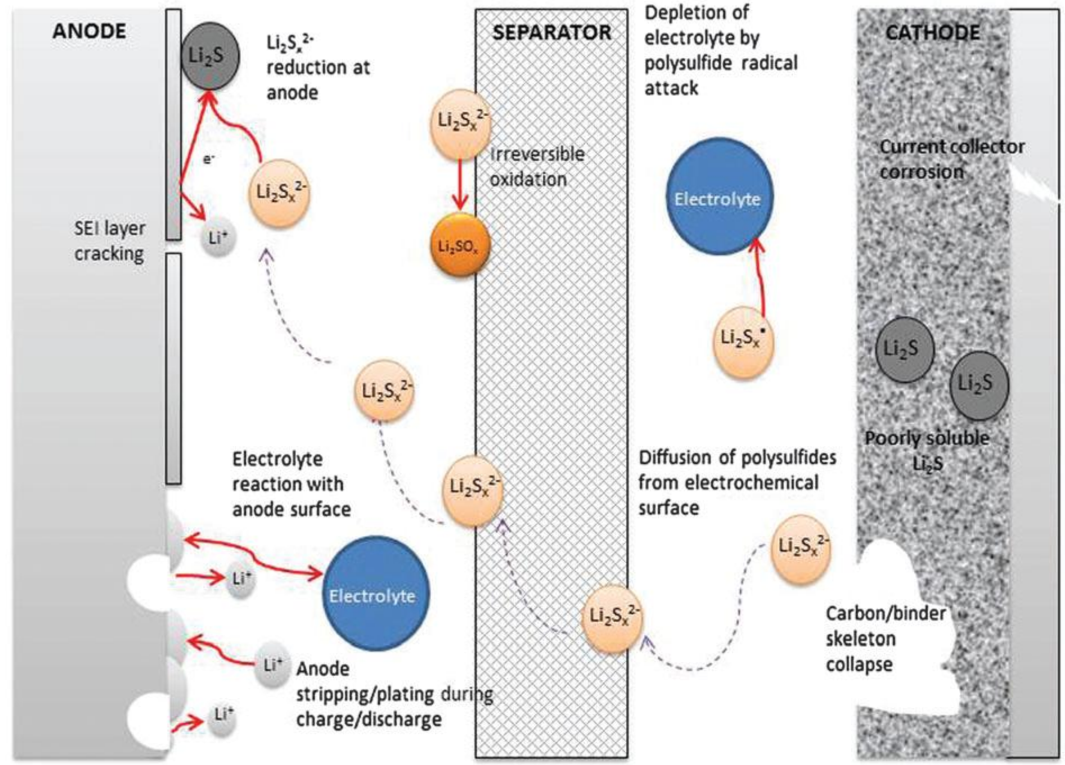
G : BP = 20 : 80 wt%

Broken when peeling off

Agglomeration of BP nanoparticles leads to weak interaction with G flakes, impossible for performance test

Application for Lithium-sulfur Battery





- Higher energy density
- Abundant resources

- Low conductivity
- Polysulfide "shuttle effect"

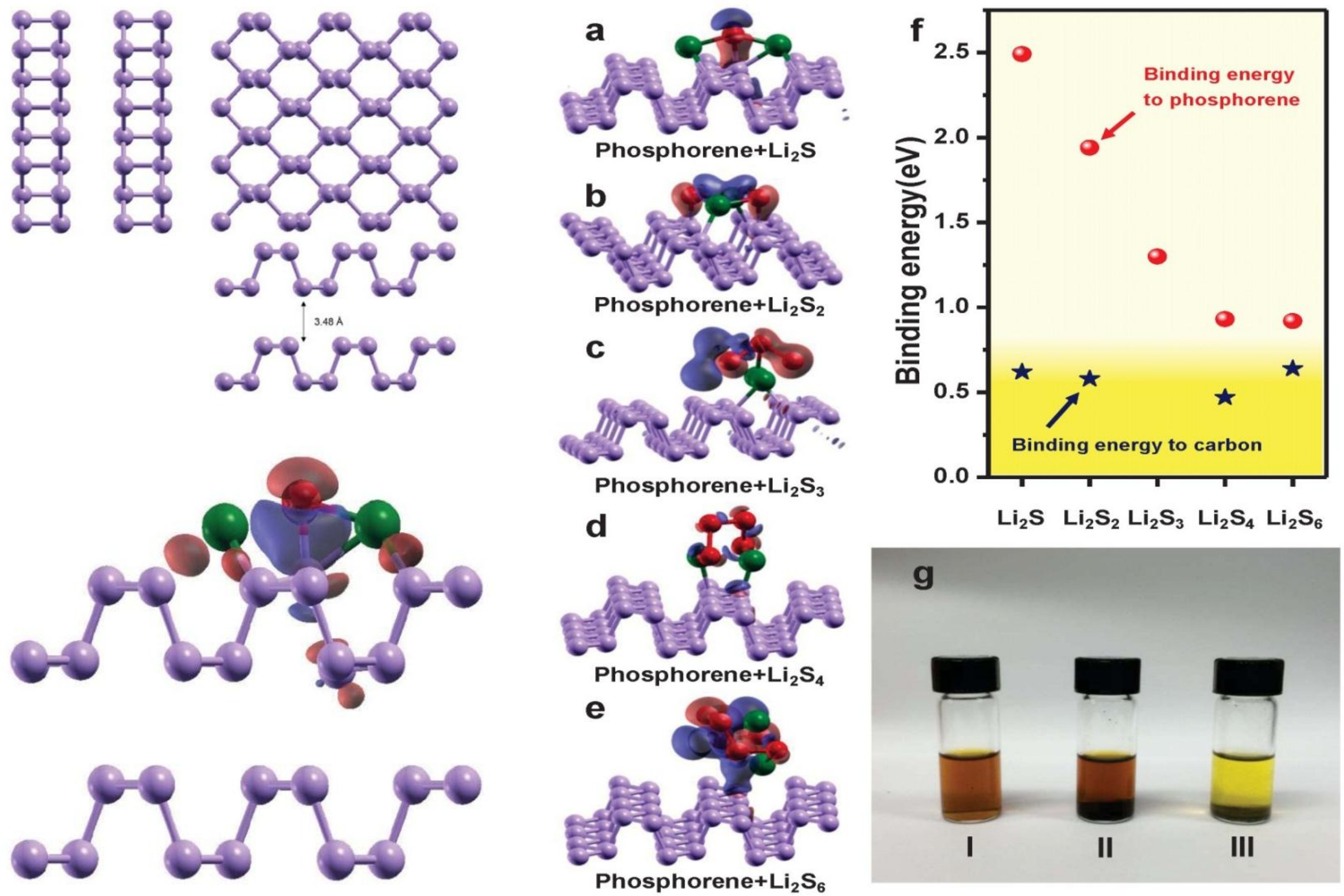
Performance related

- Growth of Li dendrites
- Volume expansion

Safety related

M. Wild et al., *Energy Environ. Sci.*, **2015**, 8, 3477.
Z. W. Seh et al., *Chem. Soc. Rev.*, **2016**, 45, 5605.

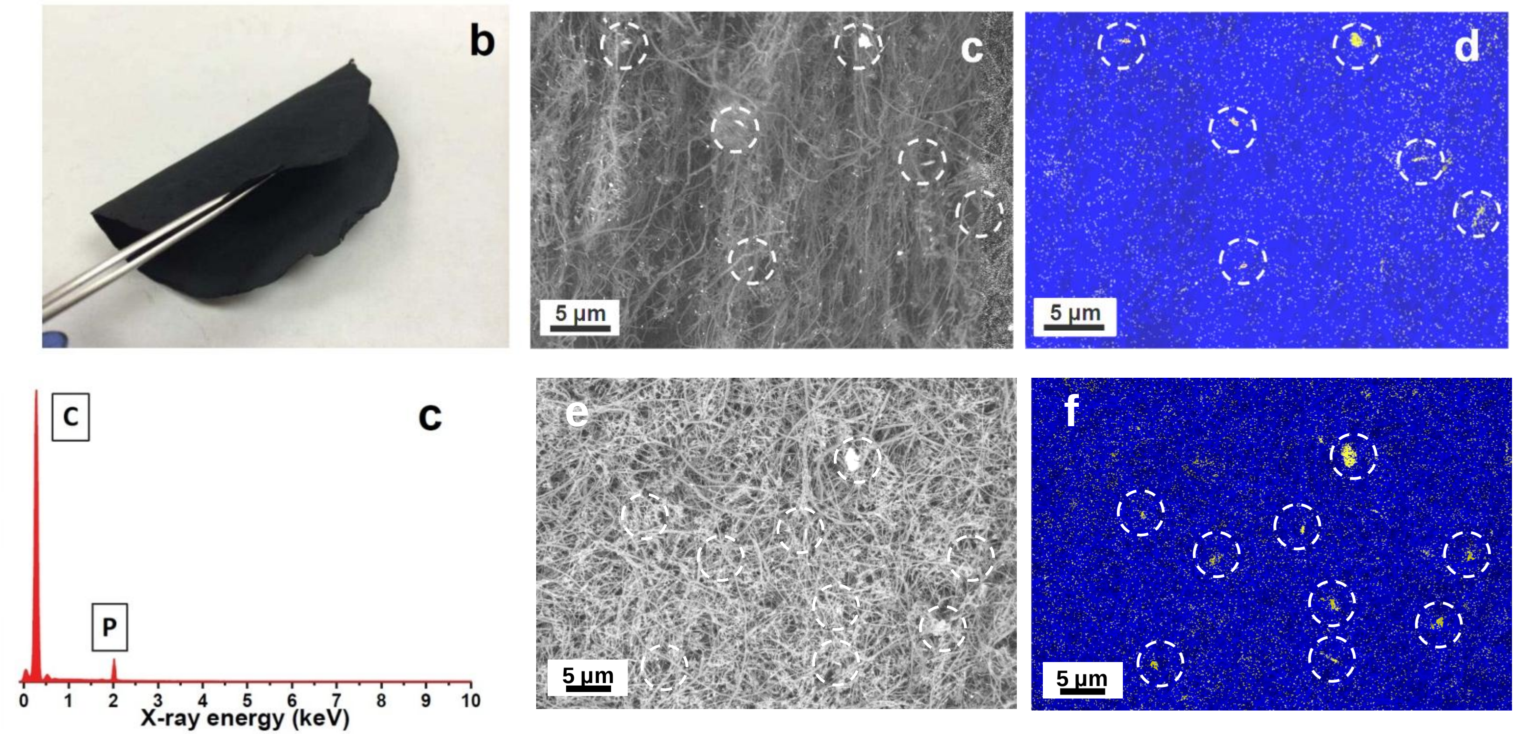
Density Functional Theory Calculation



FLP nanosheets act as polysulfide immobilizer,

reducing loss of capacity and keeping integrity of structure

FLP-CNF Electrode



Cross-section

Inner part

CNF: carbon nanofiber **FLP: few-layer phosphorene**

FLP : CNF ~15 : 85 wt% highly flexible

FLP nanosheets uniformly distributed in CNF matrix

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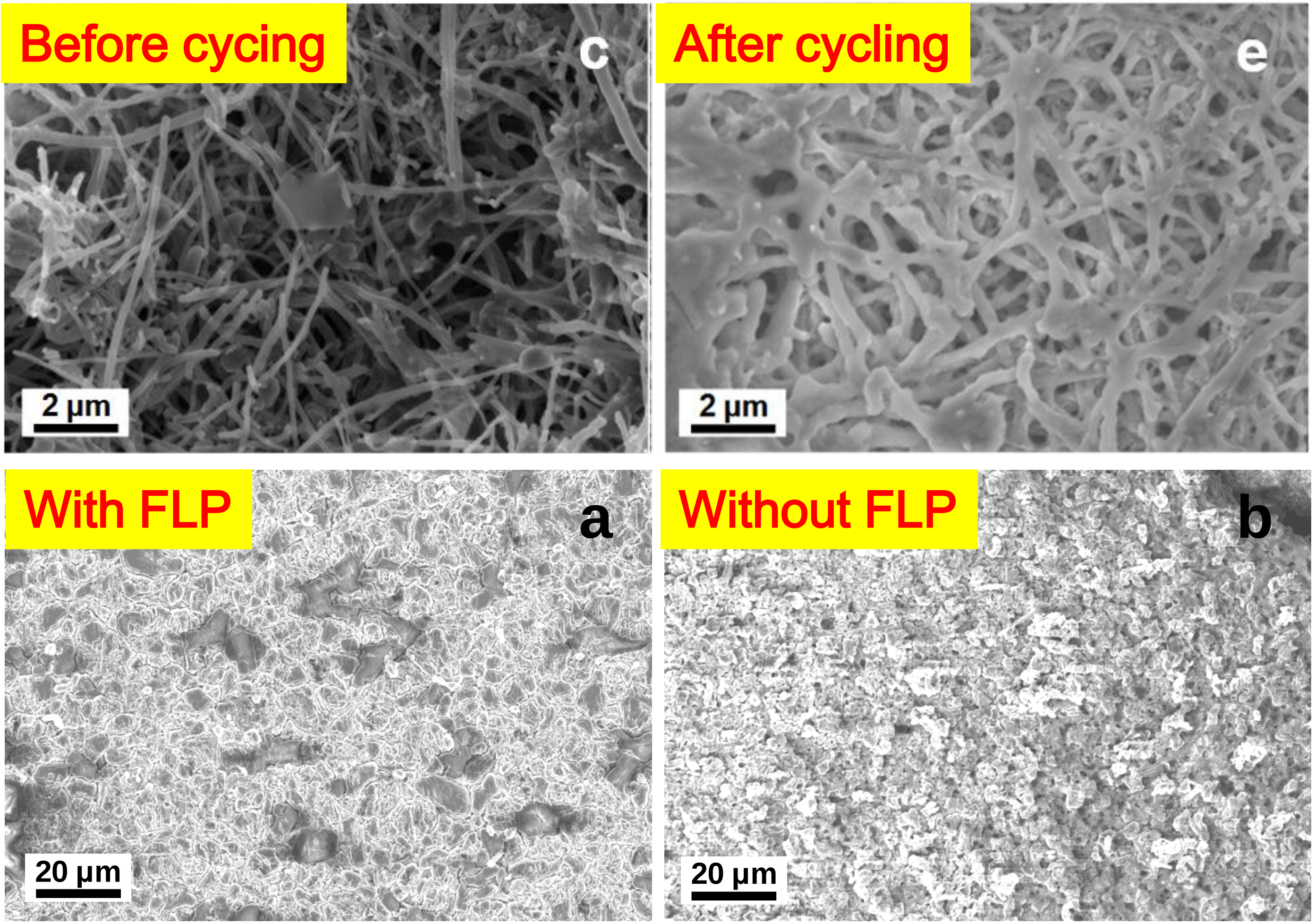
L. Li, L. Chen et al. *Adv. Mater.* **2016**, DOI: 10.1002/adma.201602734.

Morphology of Electrodes



Cathode

Anode

Cathode with FLP fasten polysulfide

Anode in battery with FLP nanosheets keep intact

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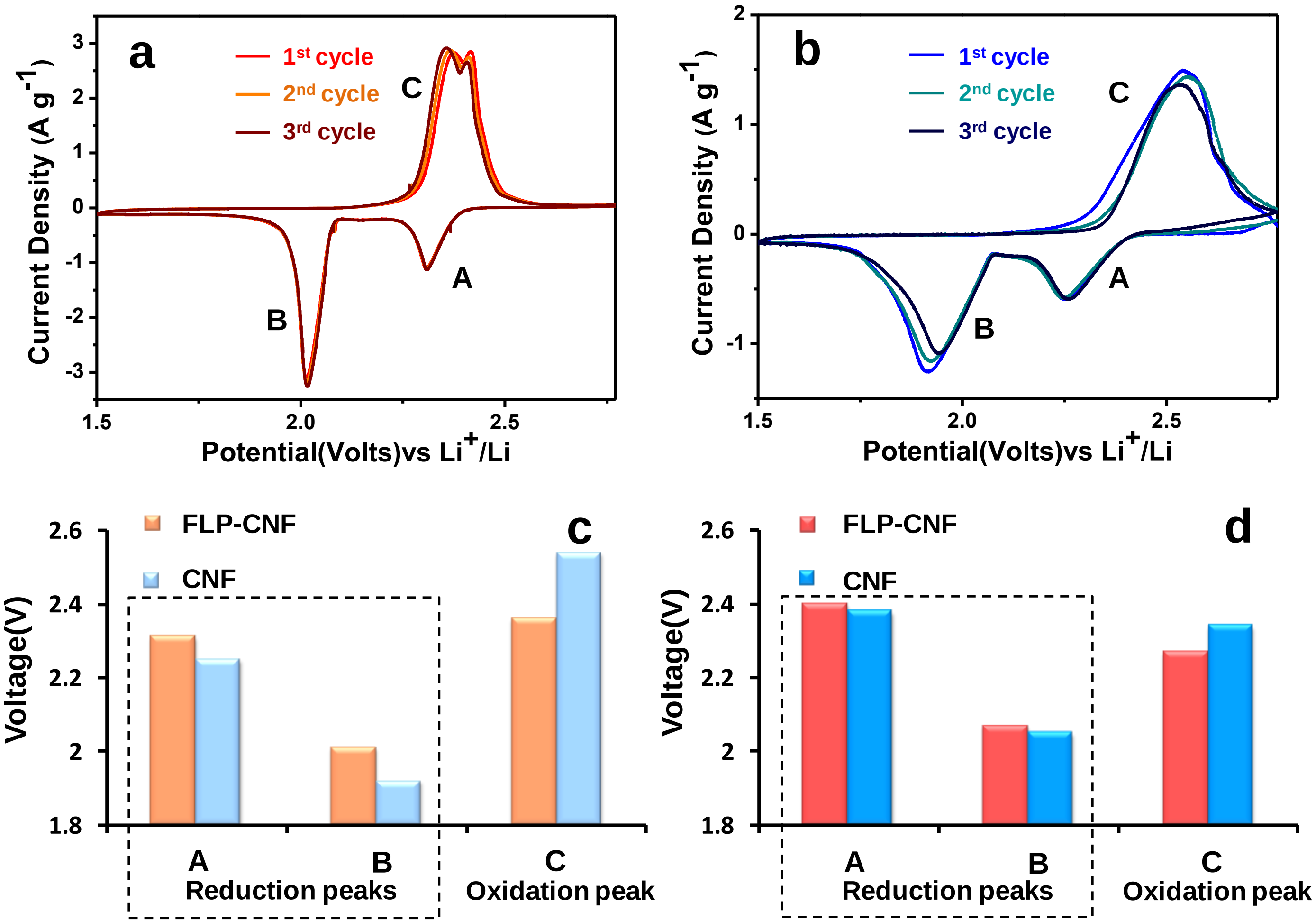
Cyclic Voltammetry (CV)

FLP-CNF

CNF



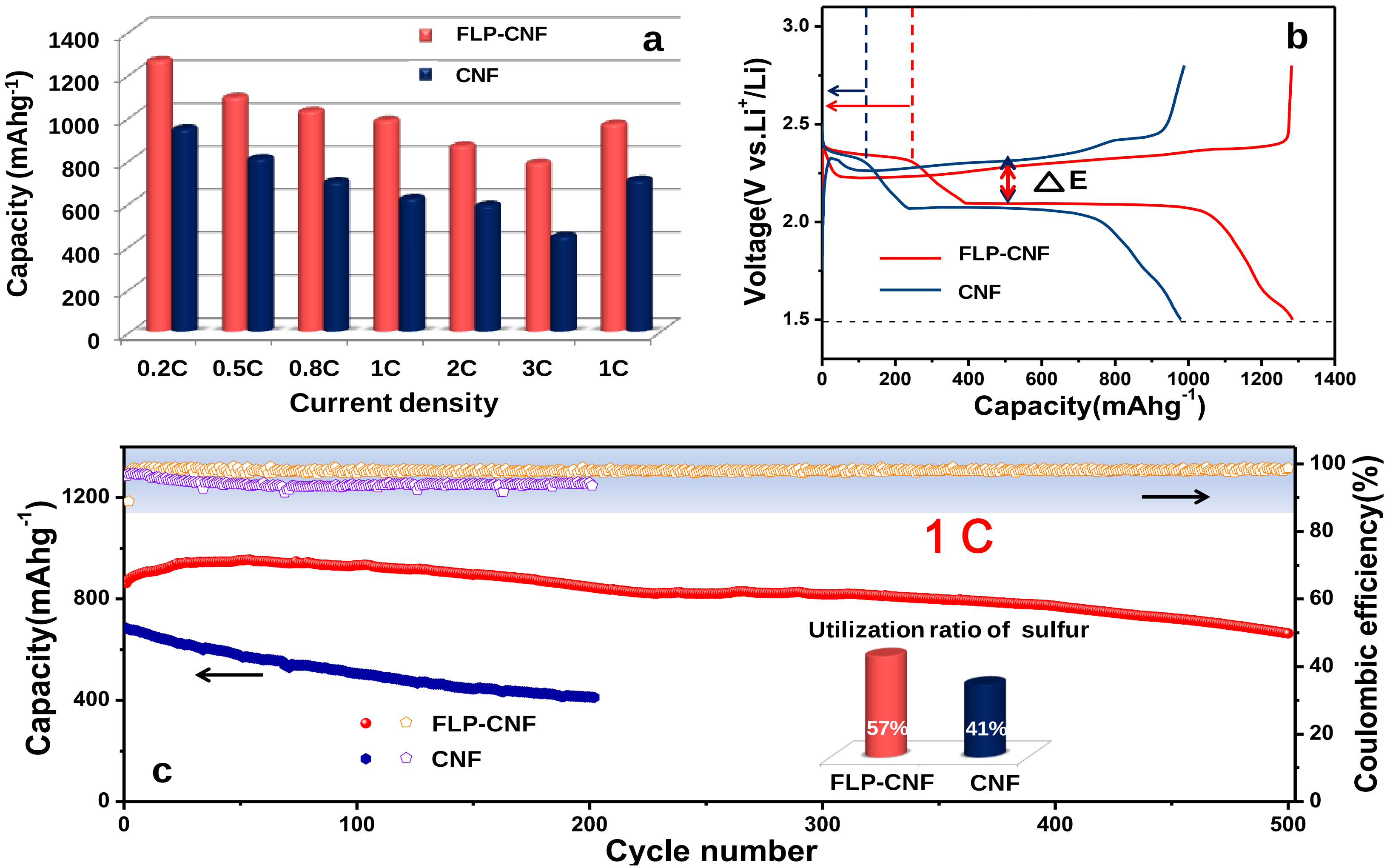
peak potentials

onset potentials

FLP nanosheets act as catalyst, accelerating reaction

Higher reduction peak and lower oxidation peak potentials

Galvanostatic Charge/discharge Tests



Promoted specific capacity

Better rate capability

After 500 cycles, 660 mAh g^{-1} remains, coulumbic efficiency ~98%

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Conclusions

- High-quality few-Layer BP nanosheets have been prepared by exfoliation in water
- Using of graphene in BP-G hybrid paper promoted the conductivity of electrode and confined expansion of BP
- Adding small amount of BP into CNF electrode greatly improves overall performance due to the catalyst effect and its role as polysulfide immobilizer

Acknowledgment

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- **Prof. Nikhil Koratkar**
- **Ms. Lu Li**

Mechanical, Aerospace, and Nuclear Engineering

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Thank you for your attention !