Graphene Materials for High-Performance Li Storage

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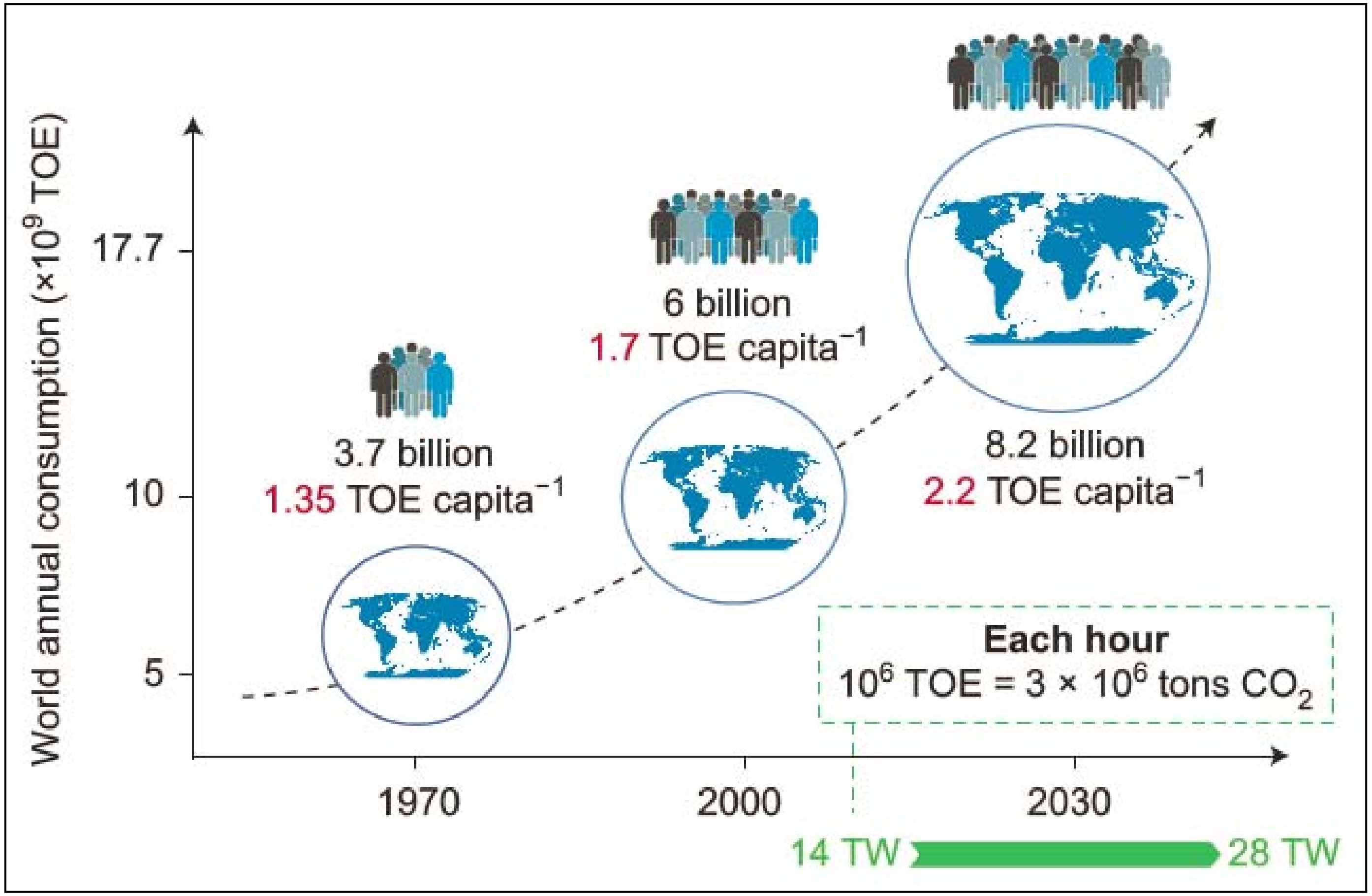
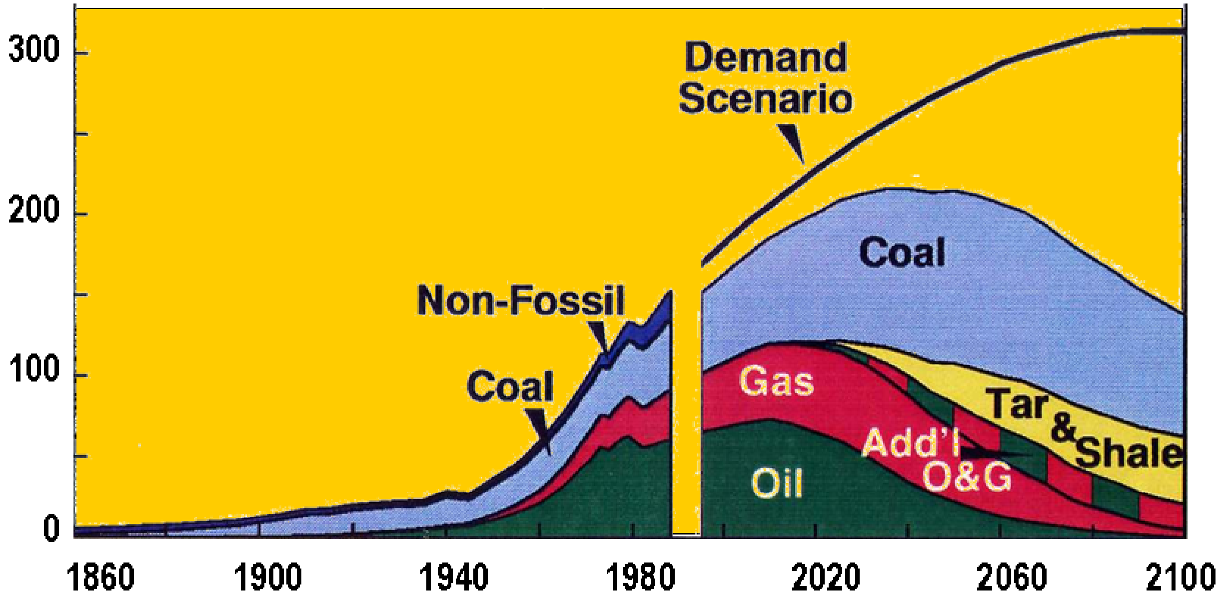
World's Energy Needs up to 2050

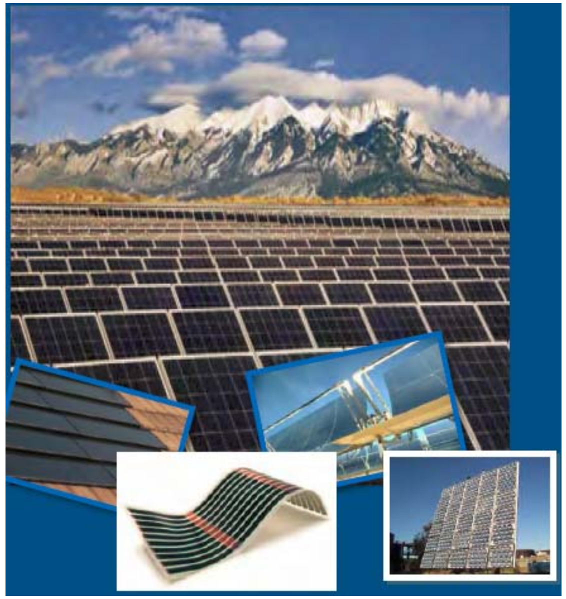


14 TW (2010) to 28 TW (2050)

D. Larcher & J. M. Tarascon, Nature Chem., DOI: 10.1038/NCHEM.2085, 17 Nov. 2014

World Energy Production





R. E. Smalley. 27th Illinois Junior Science & Humanities Symposium, Apr. 3(2005)

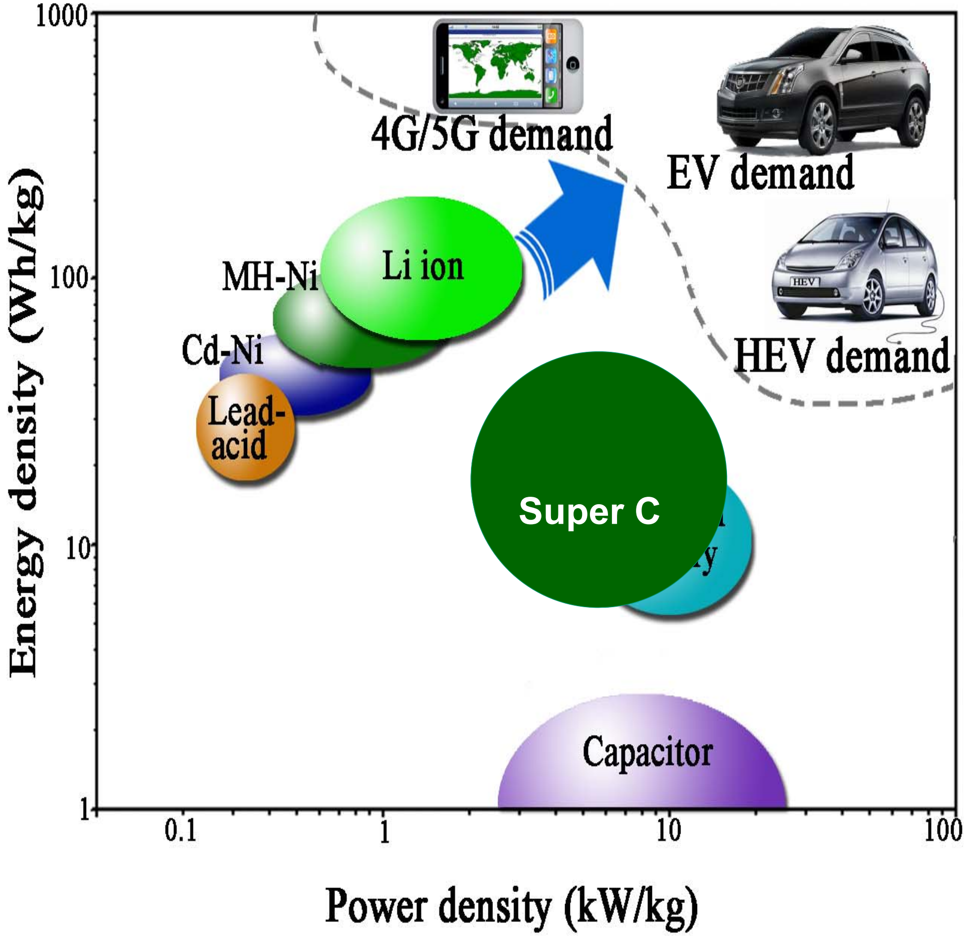
Stationary and Mobile Electric Energy Storage

IMR

Large scale electricity storage

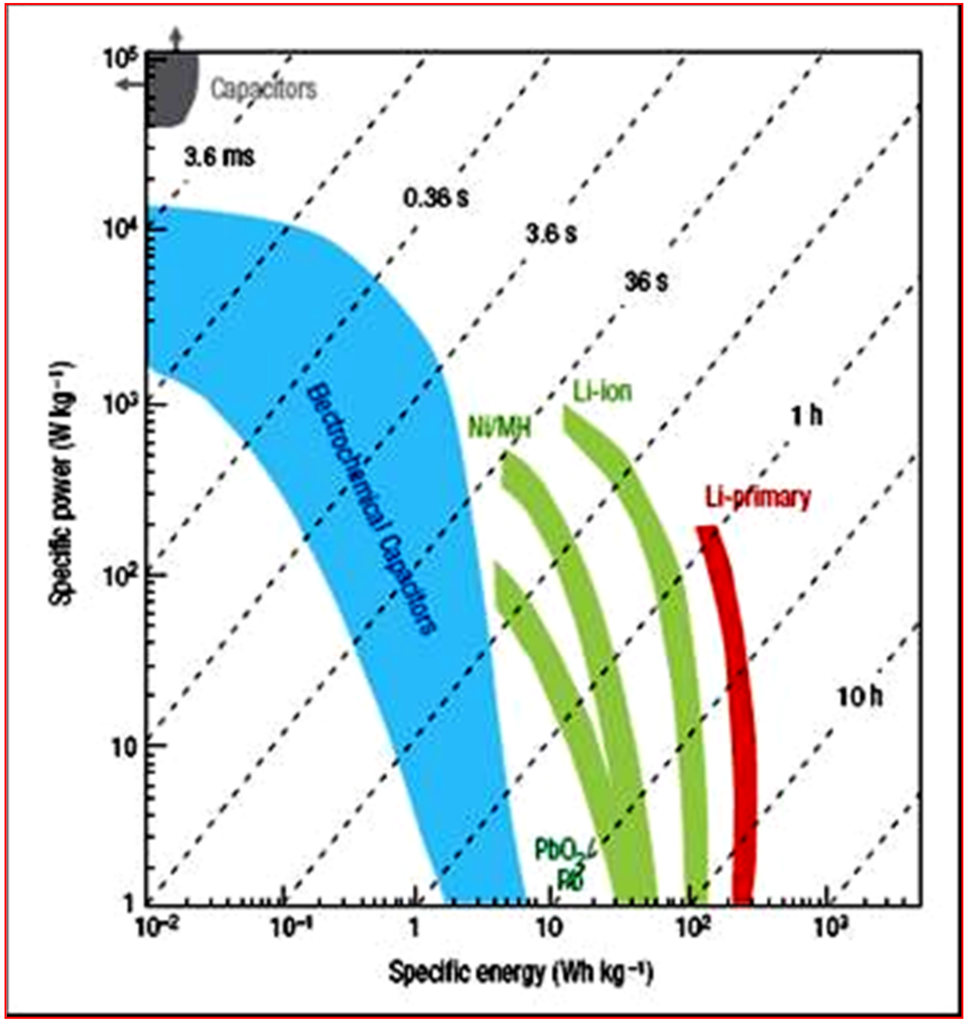
Electricity storage for EVs & MDs

Requirements for Mobile Electrical Energy Storage



- ***[Larger energy capacity]***
- ***[Higher power capability]***
- ***Higher reliability***
- ***Longer life***
- ***Wider temperature range***
- ***Better safety***

Challenge for electrical energy storage



Common Features:

Lower Energy Density

@ Higher Power Density

Materials development plays a key role!

Gogotsi Yet al., *Nature Mater 7(2008)45*

Strategies for R & D of EES Materials

- Nanostructuring
- Nano/micro combination
- Core-shell structuring
- Materials combination
- Hybridization
- Pore structure control
- Surface modification
- Configuration design
- New device design

⇒

Higher energy density

Higher power density

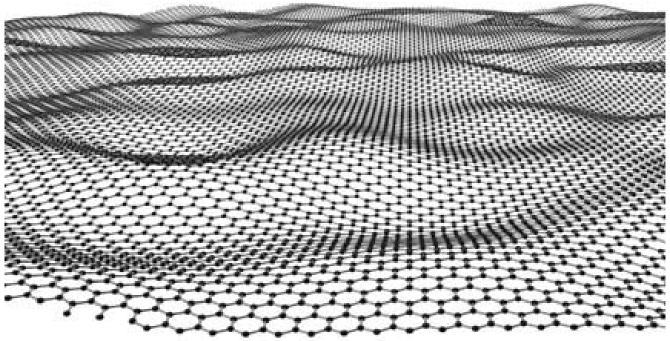
Higher reliability

Longer life

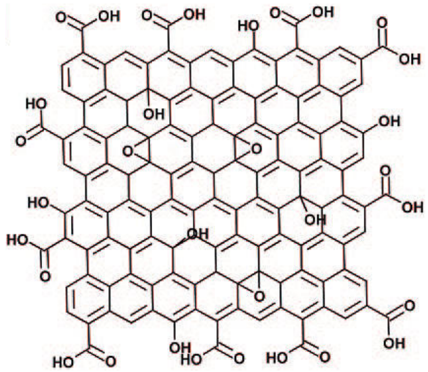
Lower cost

C Liu, F Li, LP Ma, HMC, Advanced materials for energy storage, *Adv. Mater., 22(2010)* E28-64.

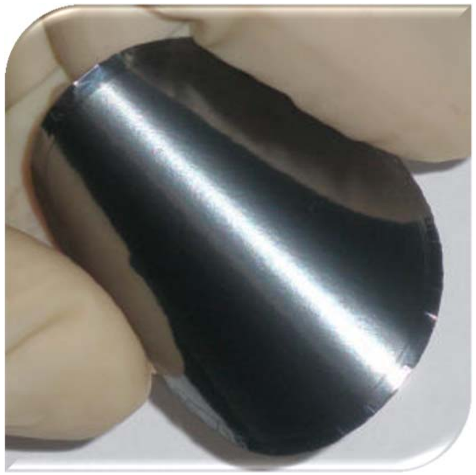
Graphene Materials



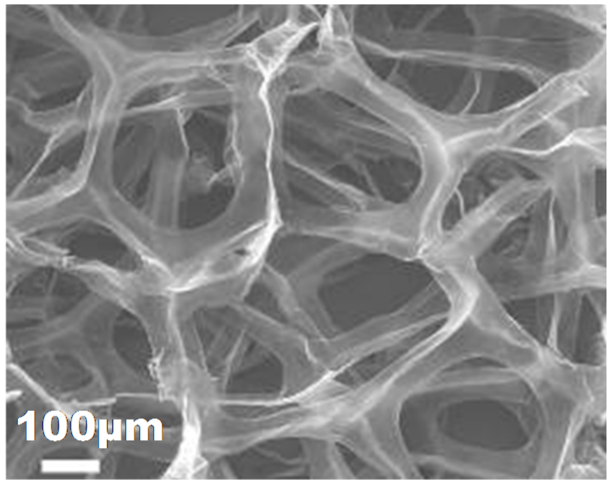
Graphene



Graphene Oxide



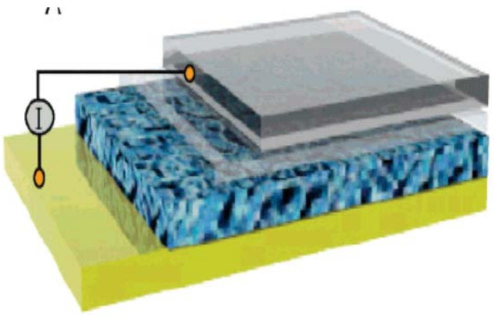
Graphene Membrane

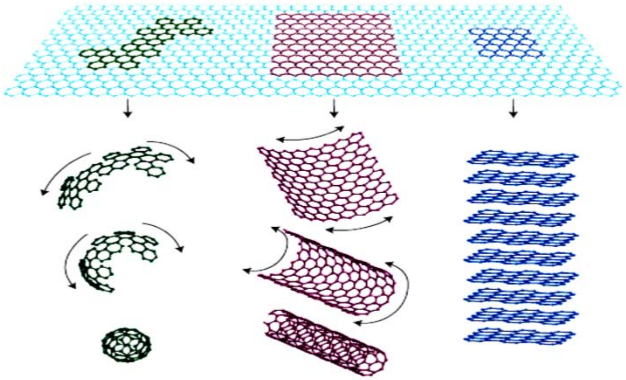


Graphene 3D structure

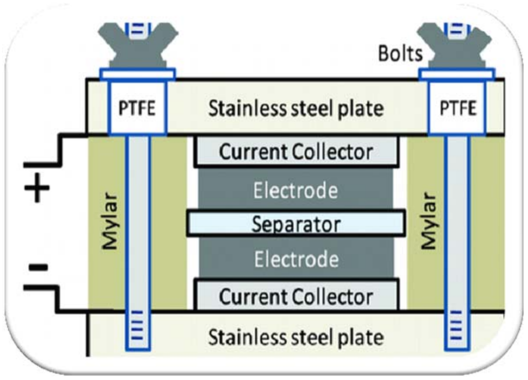
Advantages of graphene for EES

- ✓ High electric conductivity
- ✓ Flexible and transparent
- ✓ Rich porous structures
- ✓ Easy surface functionalization
- ✓ Facile fabrication of membranes, coatings and 3D structures





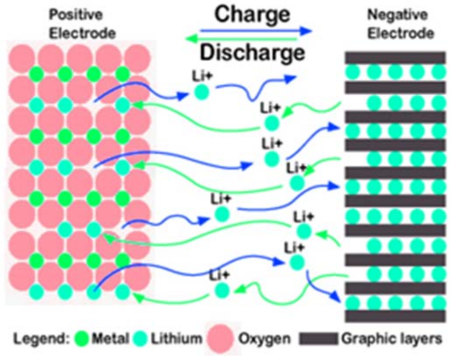
Geim AK, et al., *Nature Mater.* 6(2007) 83



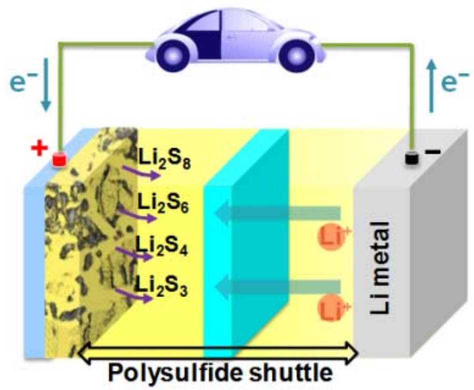
Toller MD, et al NanoLett. 8(2008)3498

Graphene can be a Core Component in energy storage devices

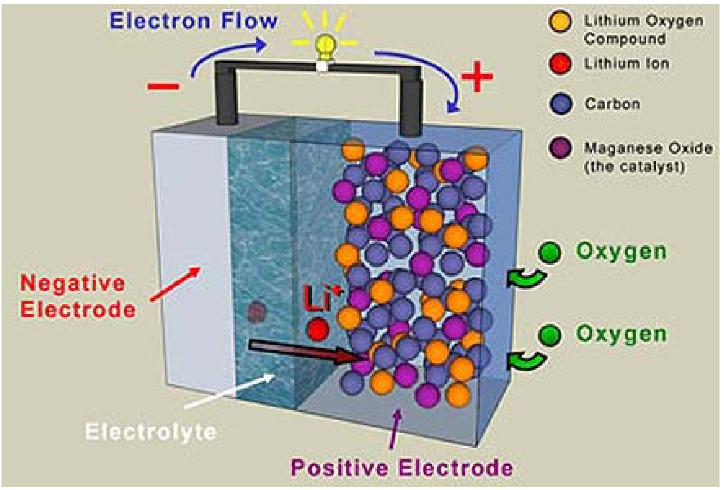
- Active substance
- Conducting network
- Catalysis
- Catalyst support
- Interface controller
- Substrate for composites



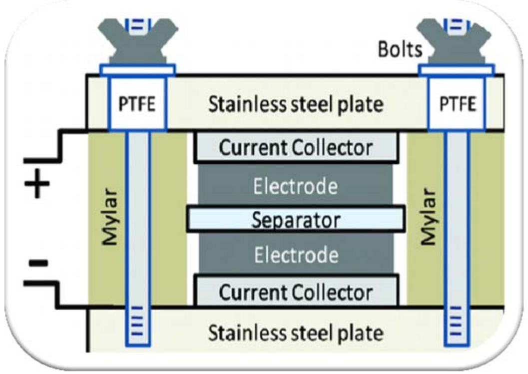
Li (Na, …) ion battery



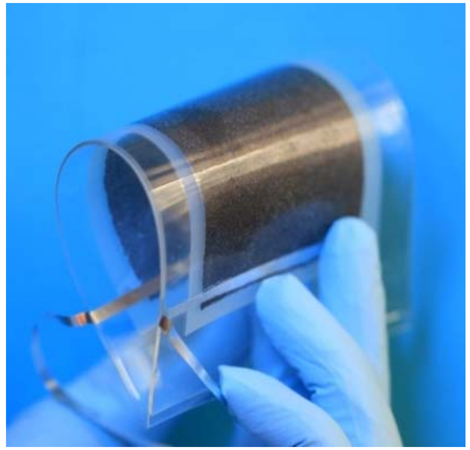
Li-S battery



Li-O2 battery

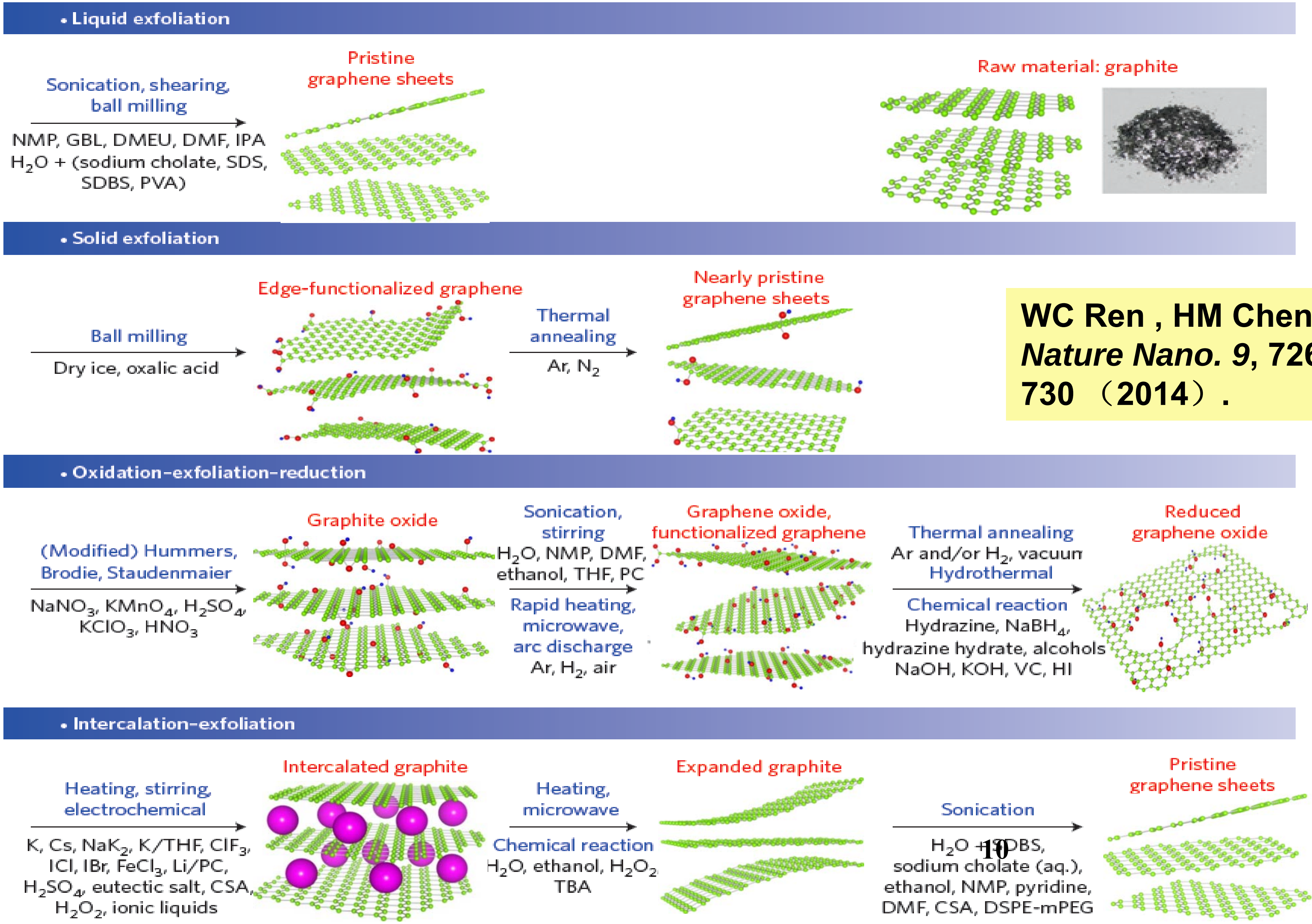


Supercapacitor



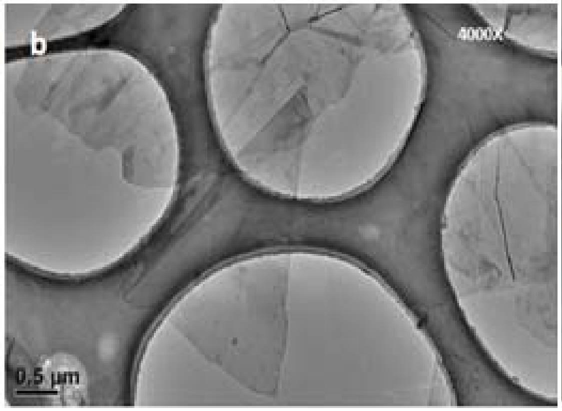
Flexible battery

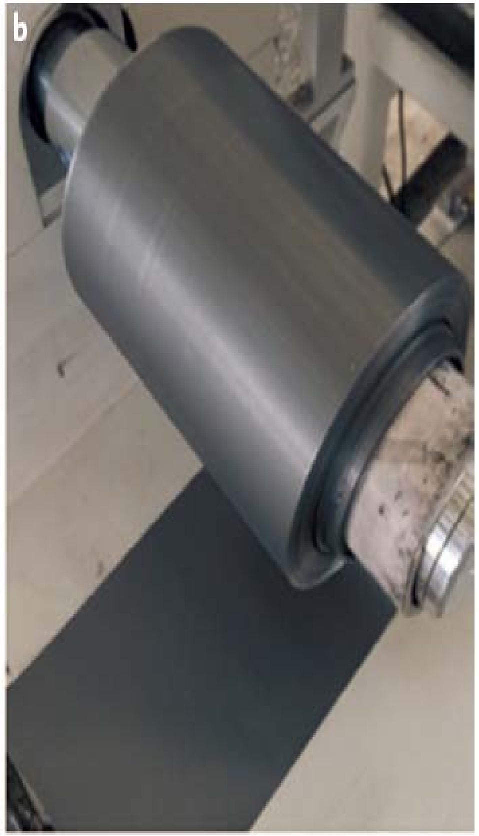
Synthesis of graphene sheets by chemical exfoliation of graphite



WC Ren , HM Cheng, *Nature Nano. 9*, 726-730 （2014）.

Large-Scale Production of High-Quality Graphene Materials

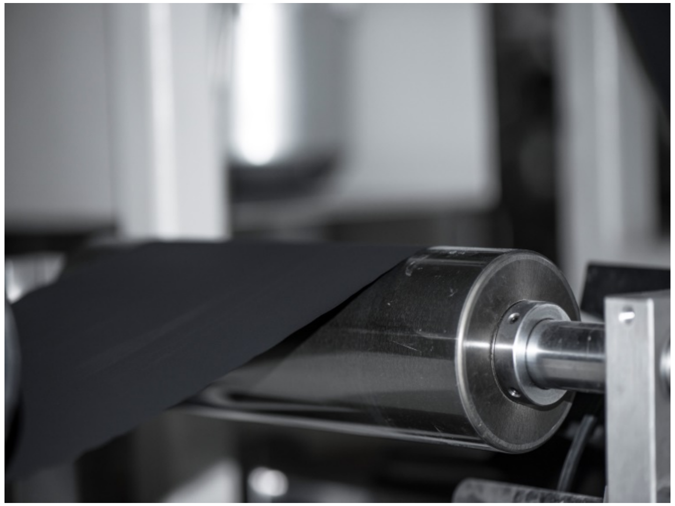


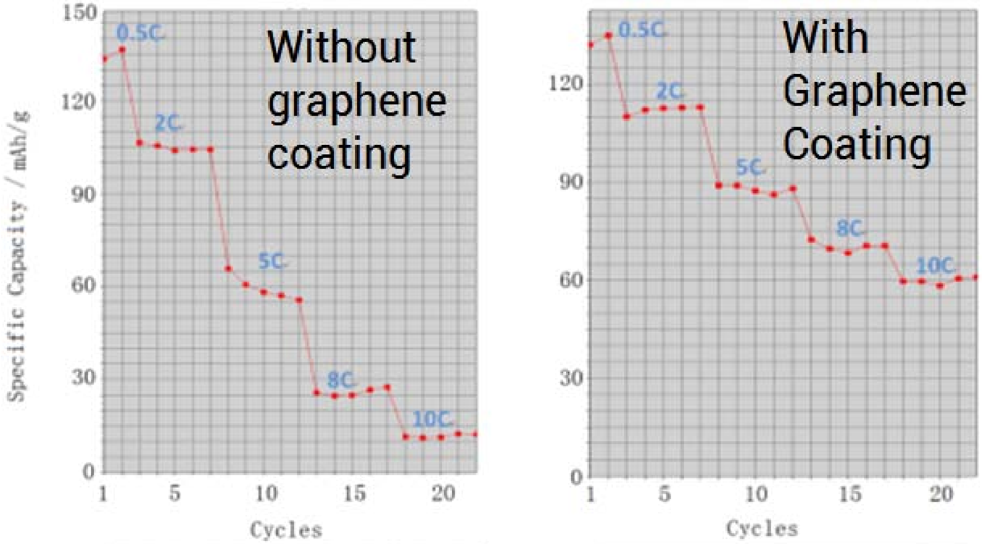


- **Prototype line: 1.5 T/year (2012); production line: 30 T/year (2016)**
  - **Number of layers: < 10; Size: 1-5 μm; Purity: >98wt%; Conductivity: ~1,000 S/cm**
- **Deyang Carbonene Technology Co., Ltd.**

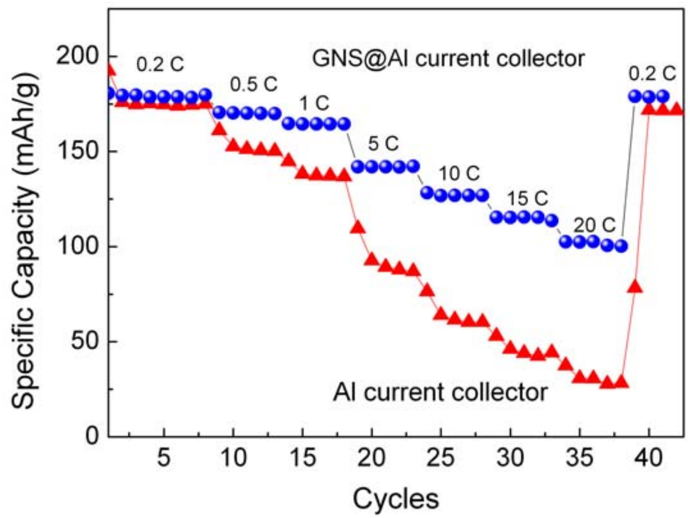
Patent: A new method to produce high-quality graphene, 201110282370.5.

A. Graphene Materials as Current Collector Coatings in LIBs



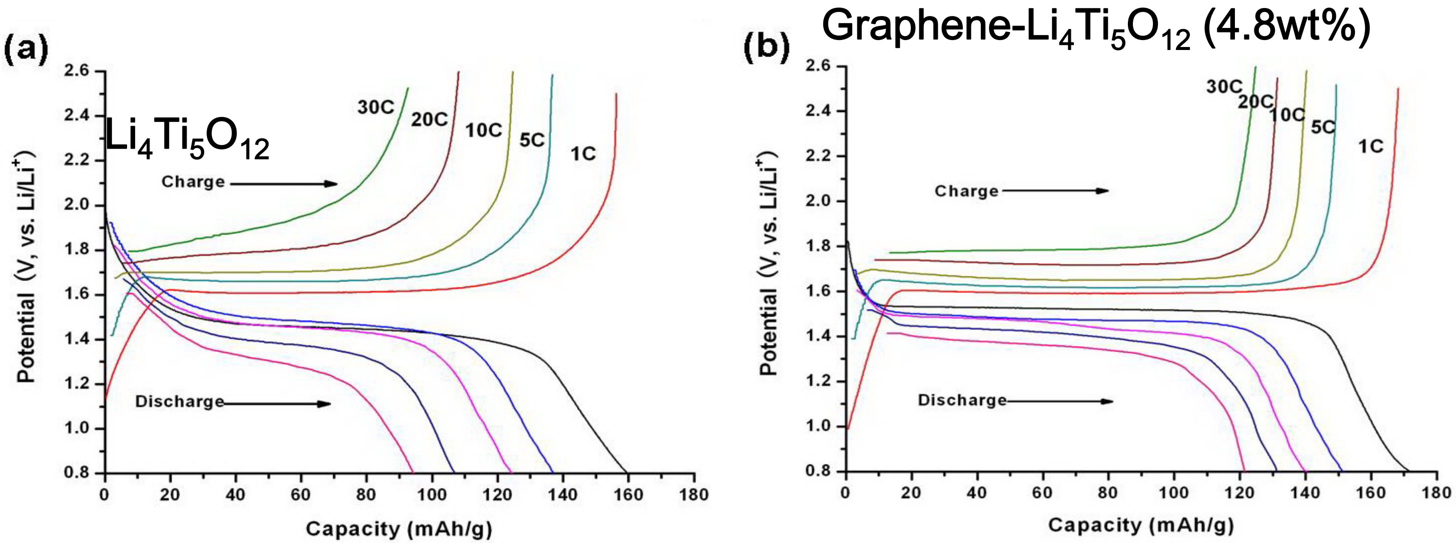


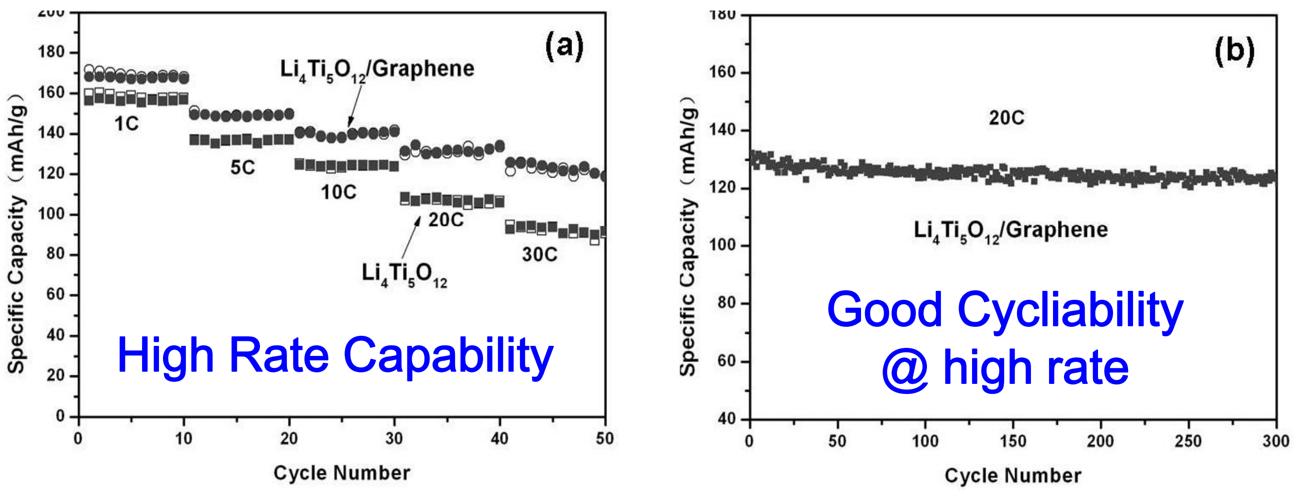
LFP materials



LTO materials

B. Graphene Materials as Conducting Additive for LIBs

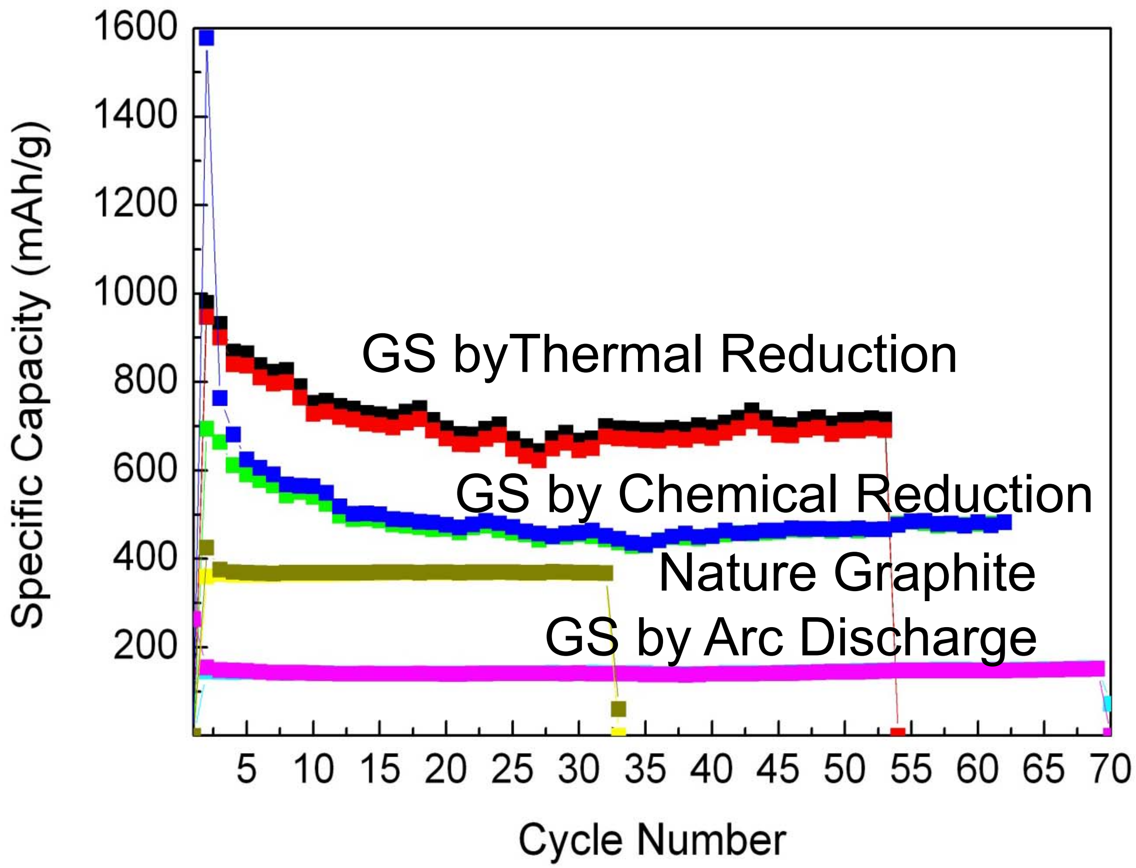




94.8%

Y Shi, et al., *J. Power Source*, 2011, 196, 8610

C. Graphene materials as anode materials？

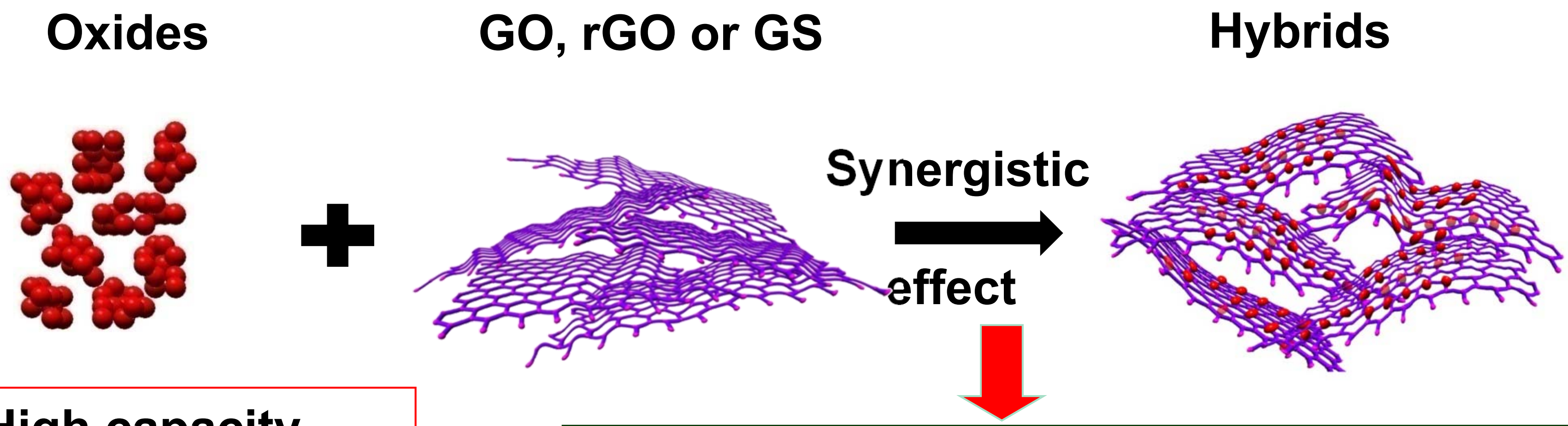


- **High irreversible capacity**
- **Low first Coulumbic efficiency**

High irreversible capacity:

- **High surface area**
- **Rich functional groups**
- **Many defects**
- **…**

D. Making Hybrids: Use Graphene as Electrode Materials for EES



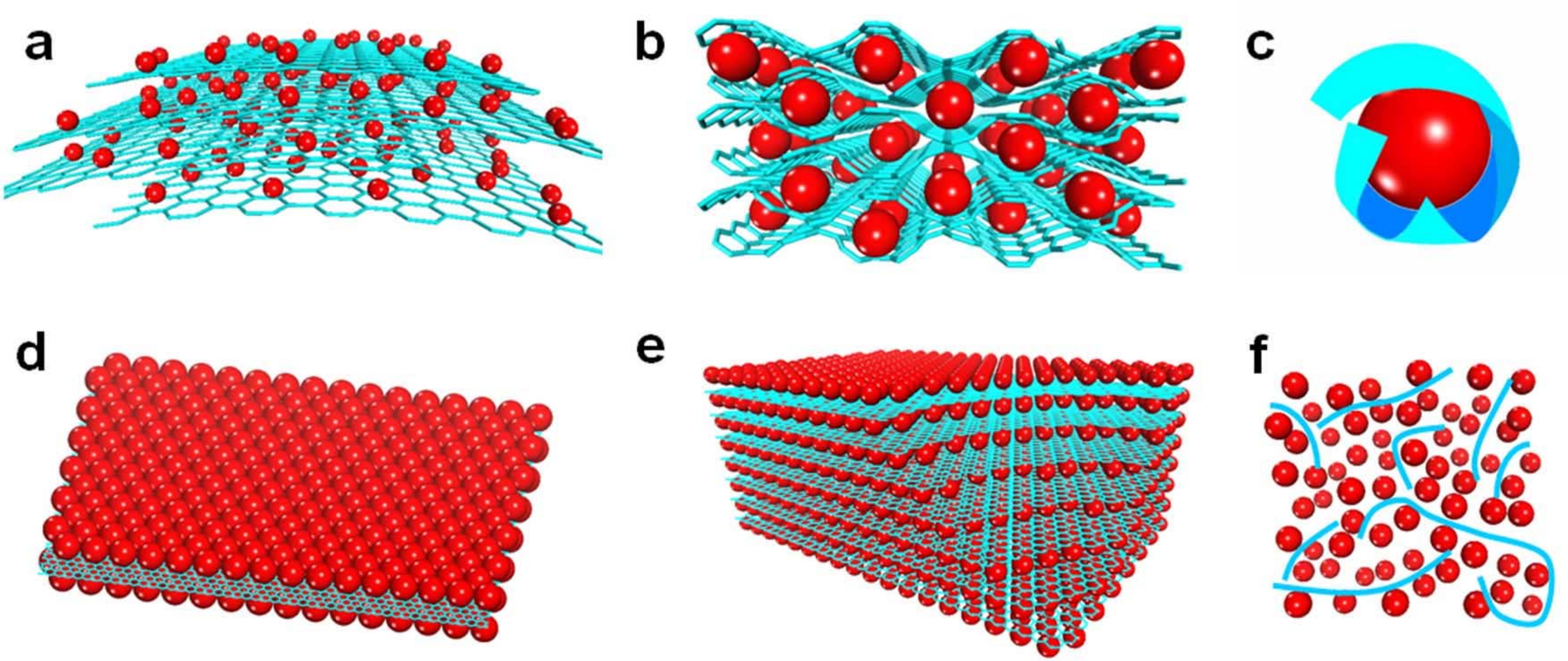
- High capacity
- High density

- Agglomeration
- Poor conductivity
- Big volume change

- Suppression of agglomeration, restacking, and volume change
- Formation and uniform dispersion of NPs
- Highly conductive and flexible network

- Large capacity/capacitance
- Enhanced cycling stability
- Good rate capability

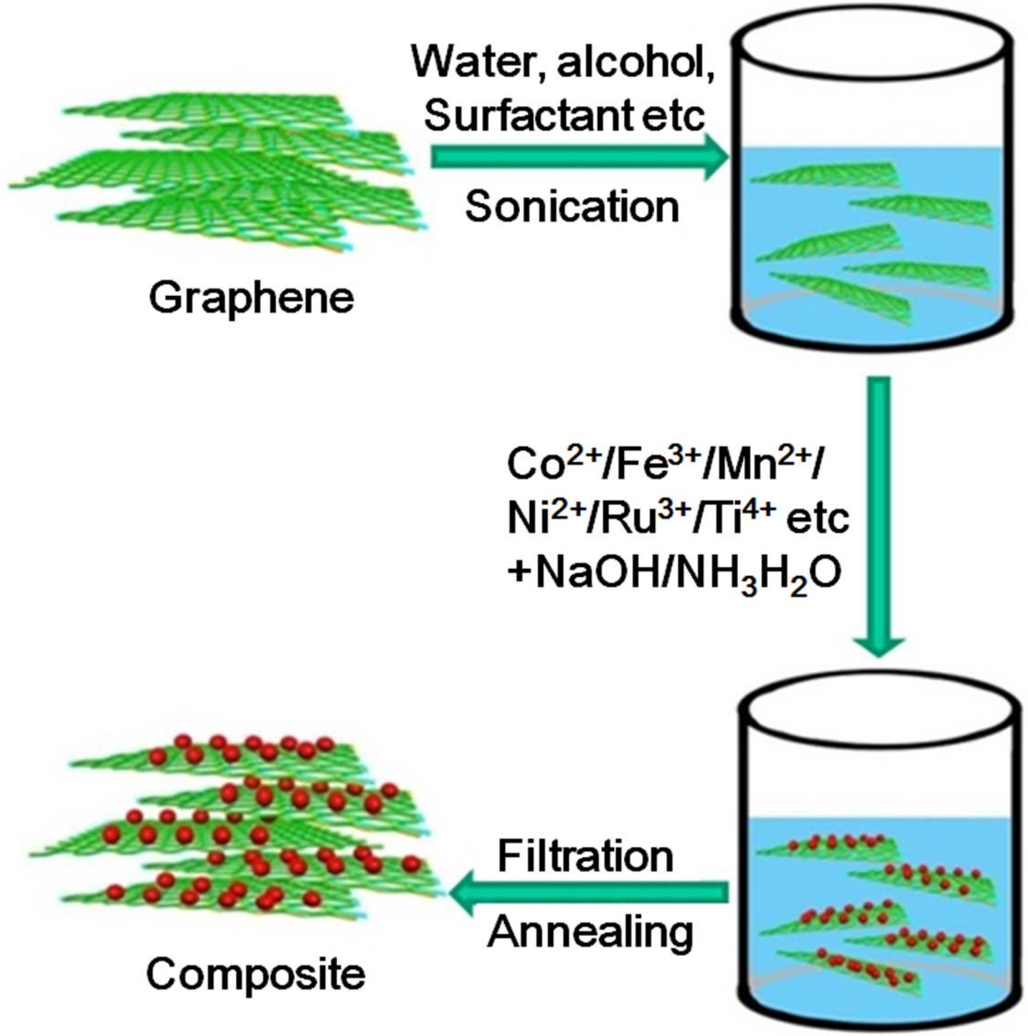
Structure of Graphene Hybrids



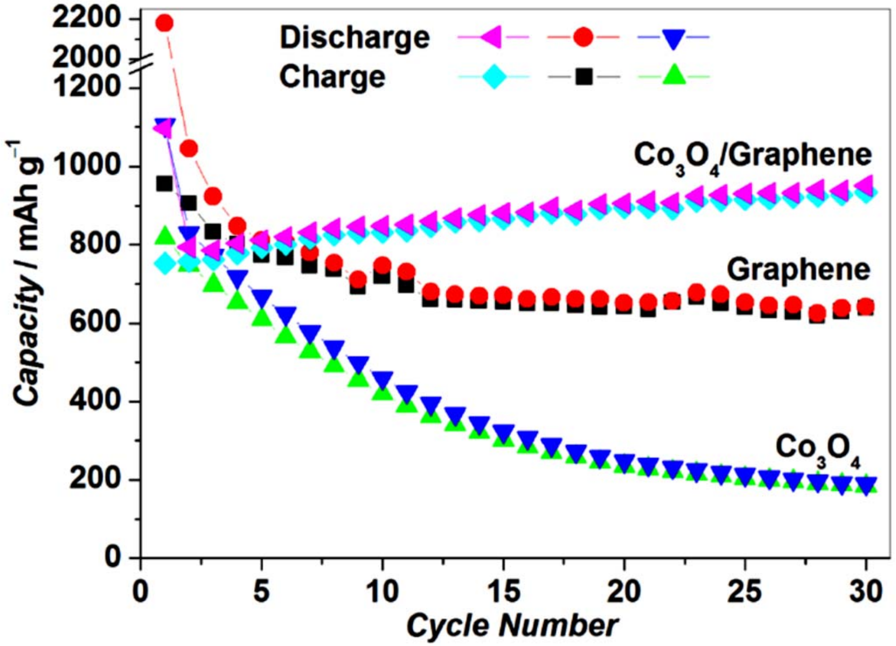
(a) Anchoring, (b) Wrapping, (c) Encapsulation, (d) Sandwich, (e) Layering, (f) Mixing

ZS Wu, et al., *Nano Energy* (invited review), 2012, 1, 107.

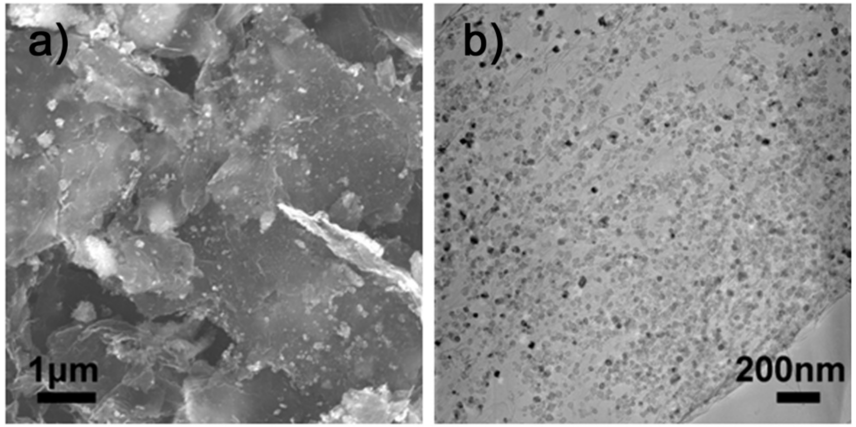
Wet Chemistry Synthesis of Graphene Hybrids

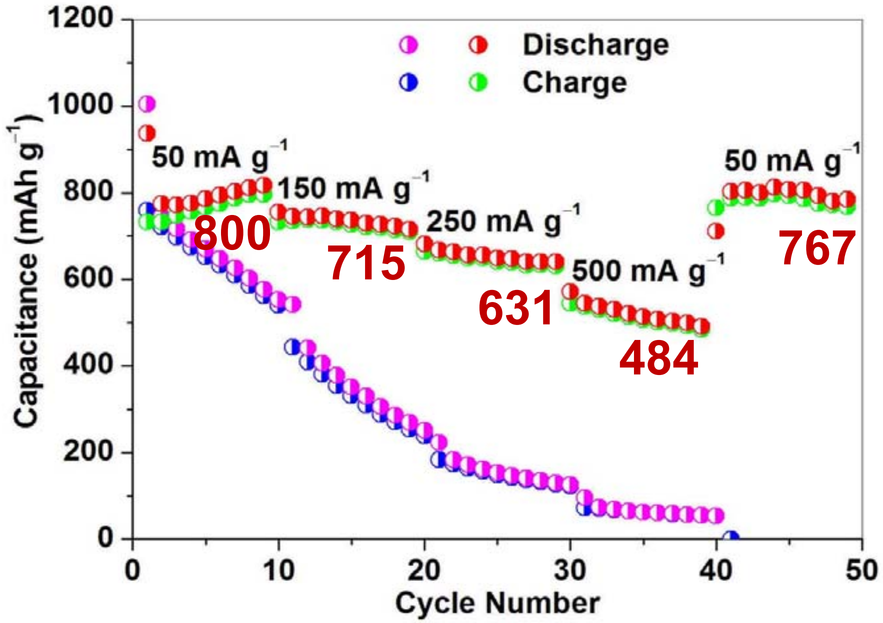


Anode for High Energy LIBs
-- Co_3O_4/rGO Hybrids (Anchoring)



High capacity + improved cyclability

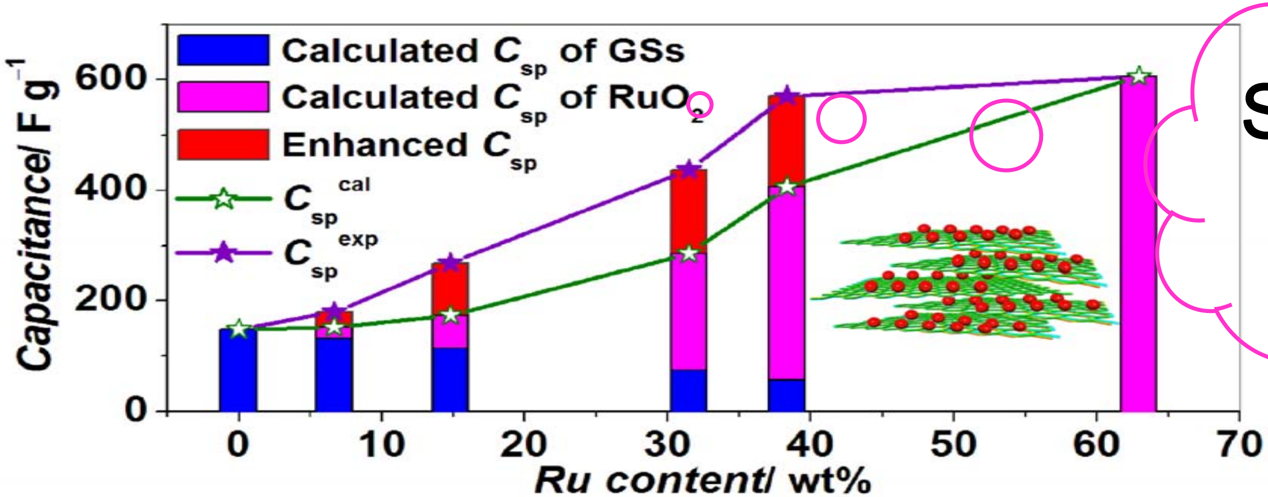


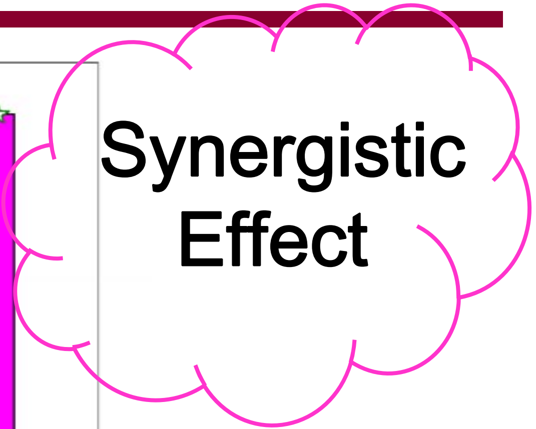


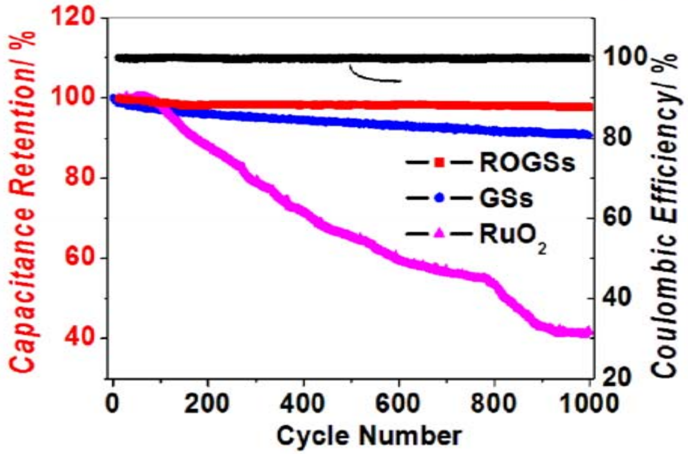
Improvement of rate performance

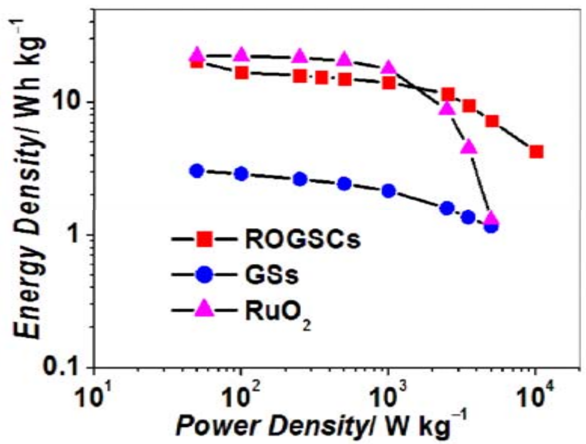
ZS Wu, et al. *ACS Nano*, 2010, 4, 3187.

Electrode for High-Energy ECs -RuO_2/rGO Symmetric ECs









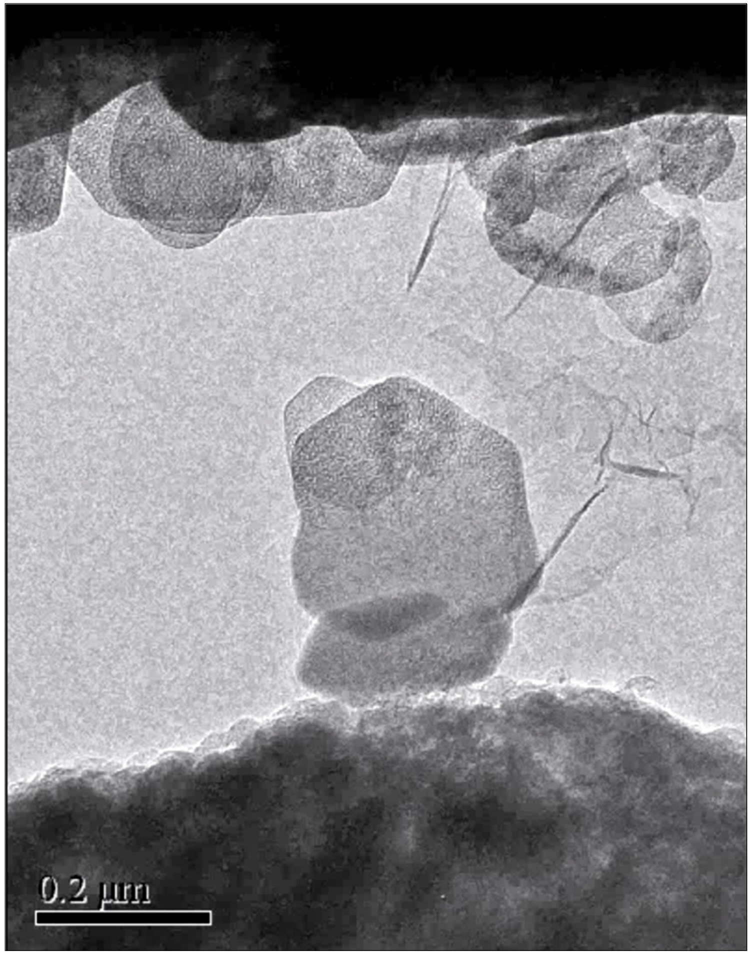
Better cyclic performance

Higher energy at high power

ZS Wu, et al., *Adv. Funct. Mater. 2010,* 20, 3595.

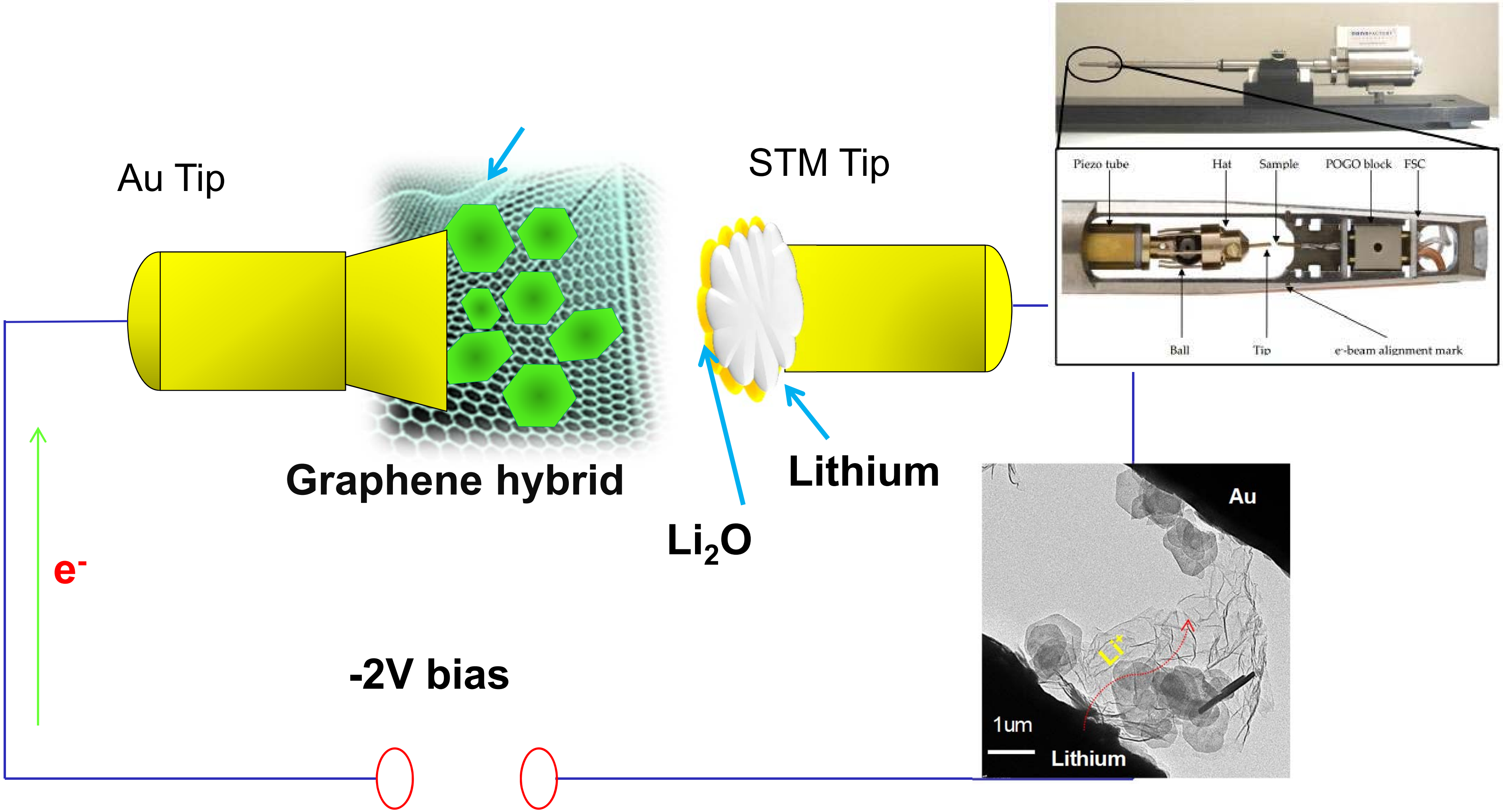
1+1>2

- **Macroscopic mechanism (*ex situ*)**
  - Formation of well-dispersed uniform oxide nanoparticles on graphene
  - Suppression of pulverization of oxide particles
  - Formation of a conductive network
  - Prevention of re-stacking of rGO
- **Microscopic mechanism (*in situ*)**
  - Increase of Li^{+} diffusion rate to improve reaction kinetics
  - Restriction of volume expansion



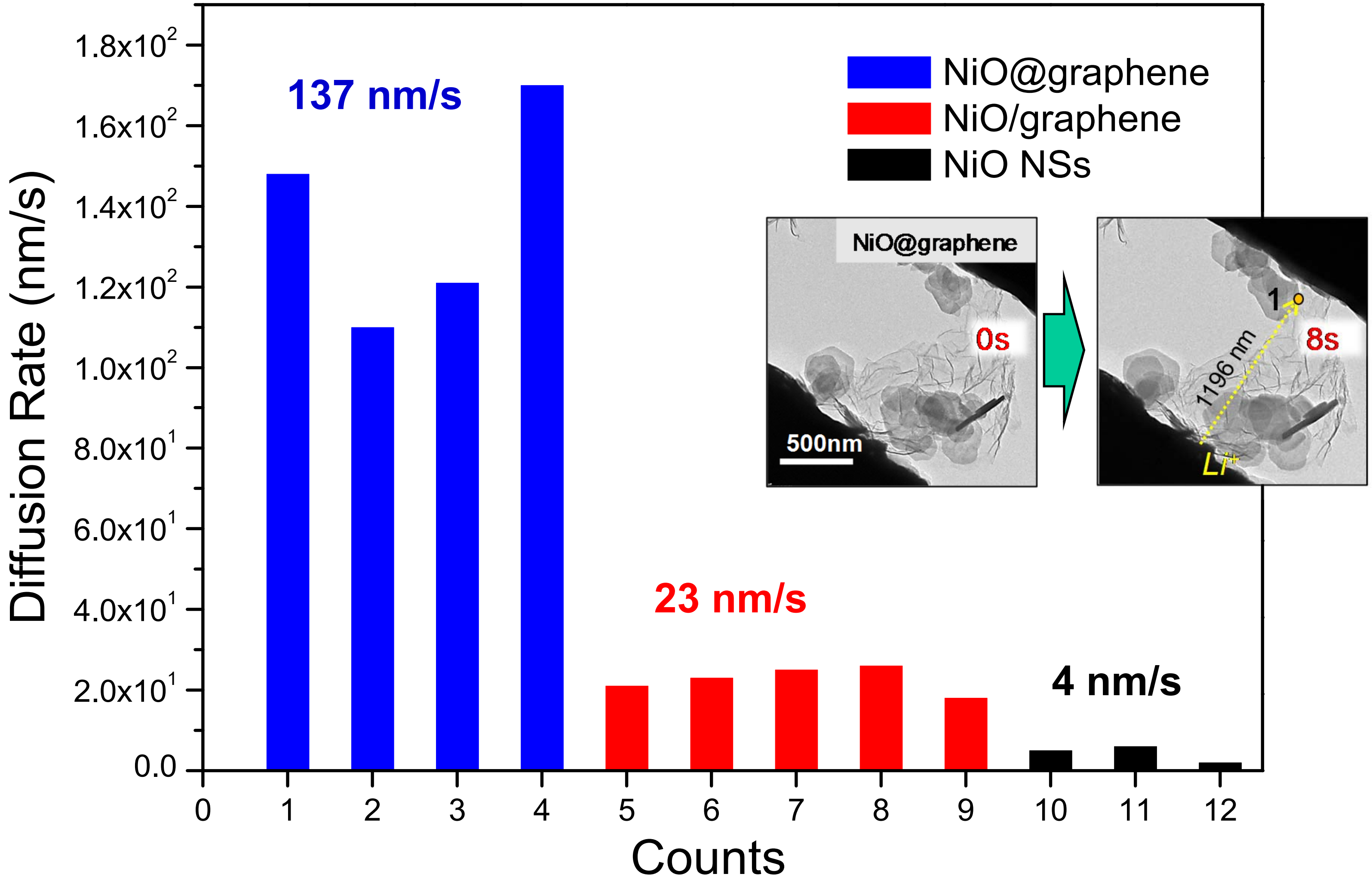
XY Shan, et al. *J Mater Chem A,* 2014, 2, 17808.

In Situ Studies on the Role of Graphene Materials

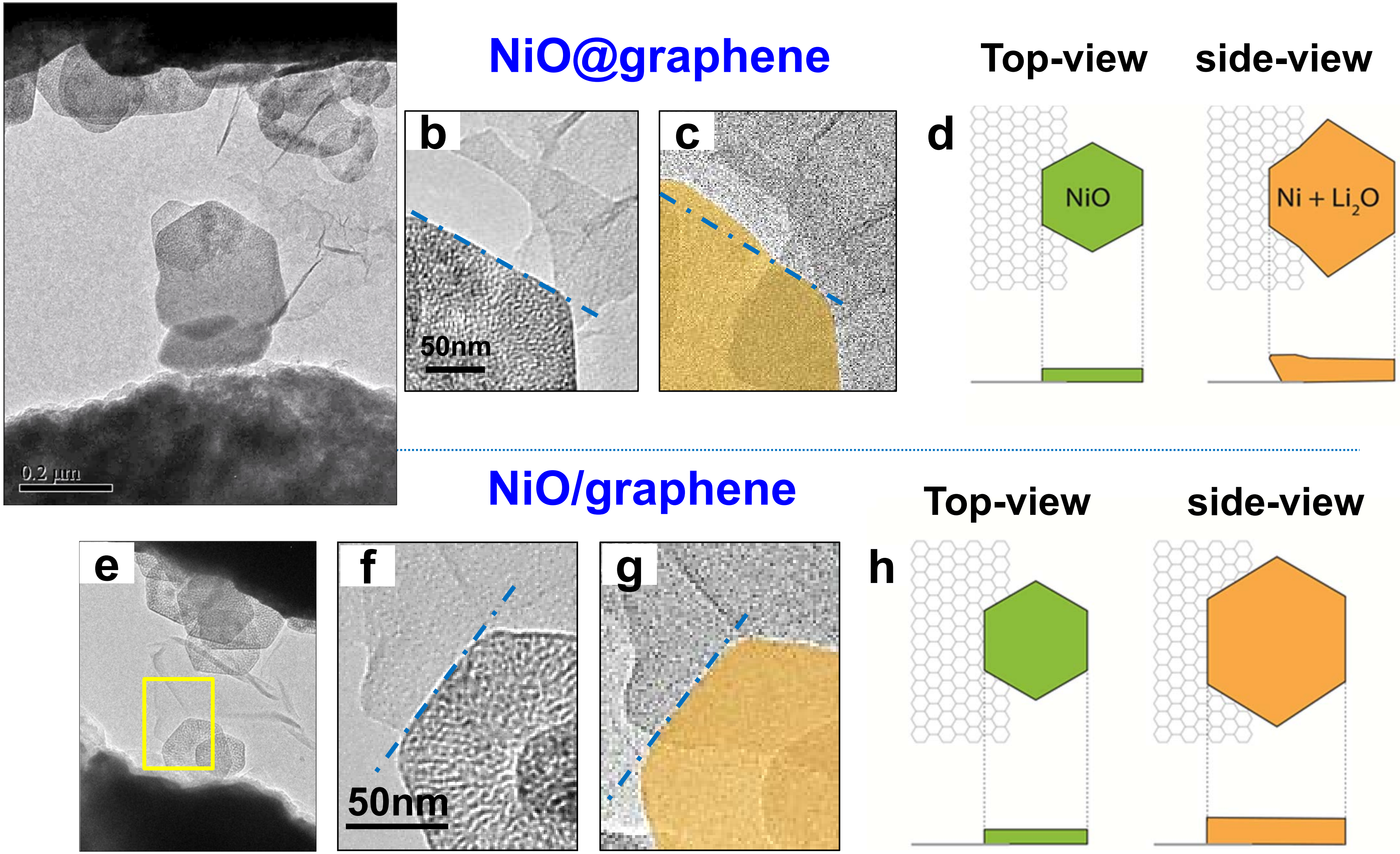


XY Shan, et al. *J Mater Chem A*, 2014, 2, 17808

Role 1: Increasing Li^+ Diffusion Rate/ Improving Li^+ Reaction Kinetics



Role 2: Interfacial Expansion-Restriction Effect



Graphene's Role in LIBs

- Increase of the *Li*$^+$ diffusion rate
- Improvement of the *Li*$^+$ reaction kinetics

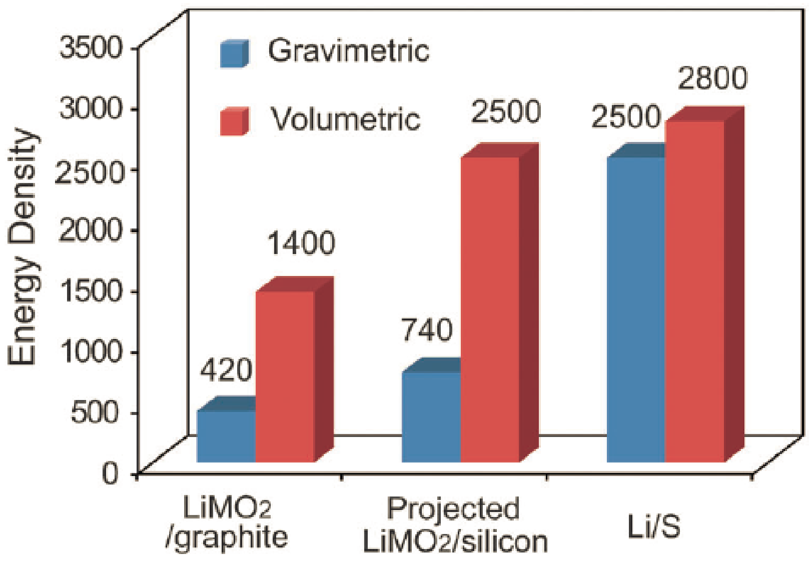
→ High power dens

- Interfacial expansion restriction

→ Superior cyclin performance

→ Excellent Lithium storage

Comparison of Li-S batteries with LIBs



Chem Soc Rev

REVIEW ARTICLE

Nanostructured sulfur cathodes†

Yuan Yang,[a] Guangyuan Zheng[b] and Yi Cui*[ac]

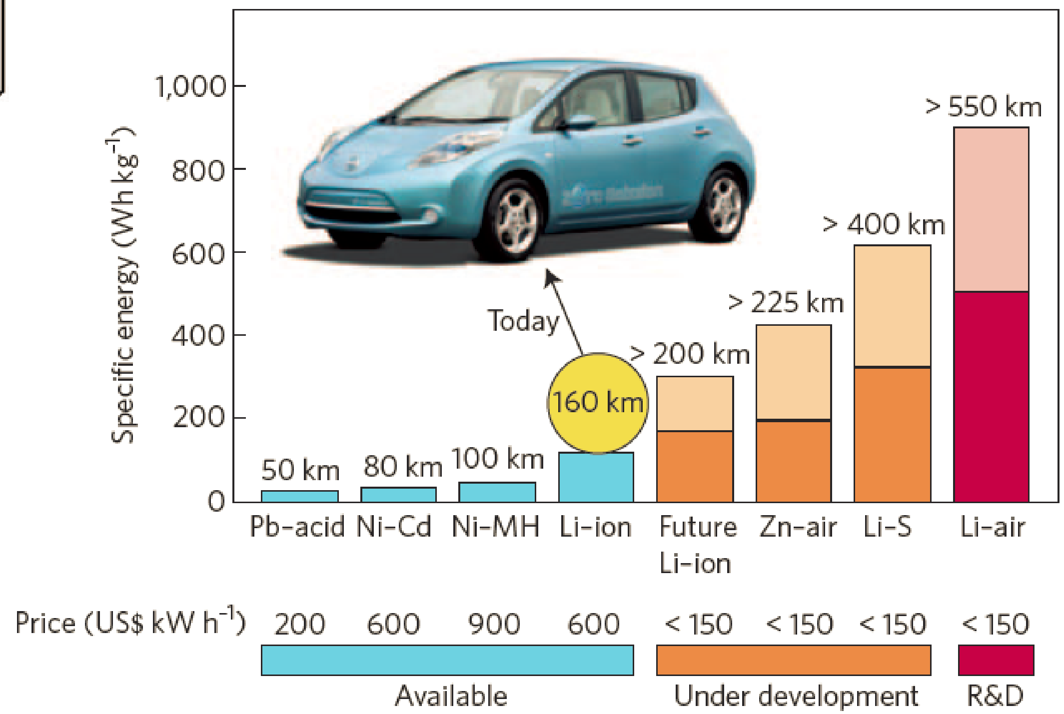
Cite this: *Chem. Soc. Rev.*, 2013, **42**, 3018

nature materials | REVIEW ARTICLE

PUBLISHED ONLINE: 15 DECEMBER 2011 | DOI: 10.1038/NMAT3191

Li–O_2 and Li–S batteries with high energy storage

Peter G. Bruce[1*], Stefan A. Freunberger[1], Laurence J. Hardwick[1†] and Jean-Marie Tarascon[2]



E. Li-S batteries

- **Advantages**

✓ **High capacity**

2567 Wh/kg@S Vs 420 Wh/kg@LI

✓ **Cheap, rich, Environment friendly**

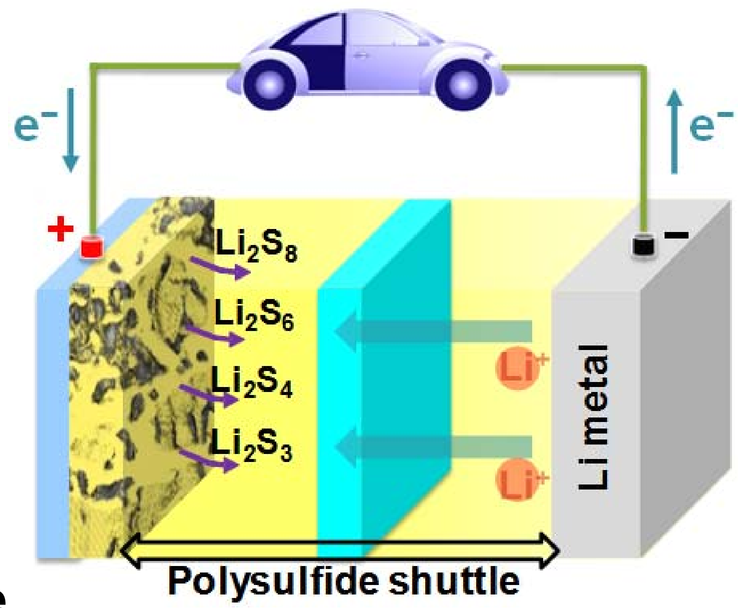
- **Problems**

➢ **Fast capacity fading**

➢ **Poor cyclibility**

- **Reasons**

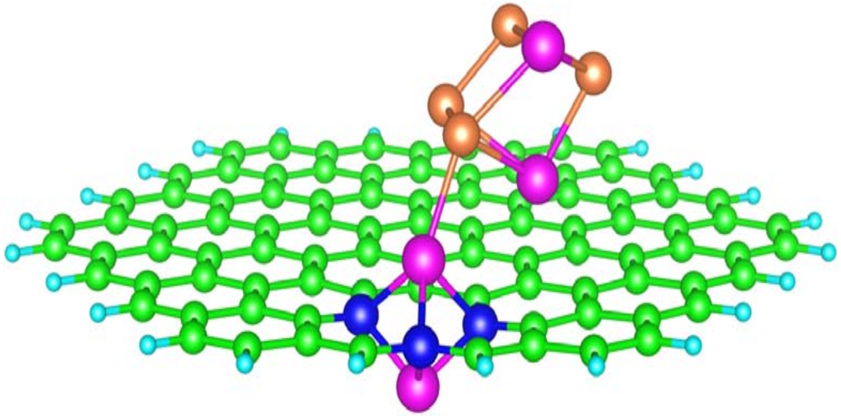
- **Insulating**
- **Shuttle effect of polysulfides**
- **Volume change during charge/discharge**



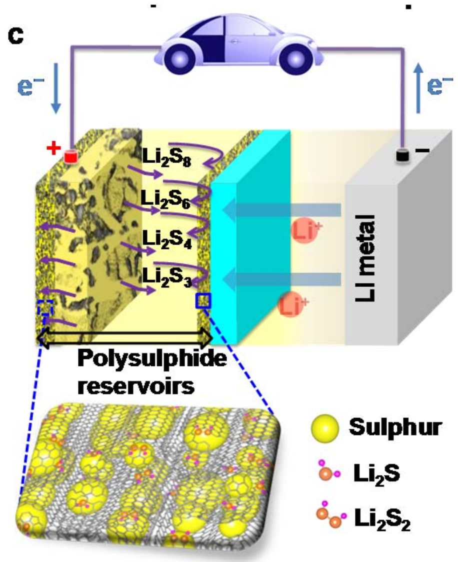
Graphene in Li-S Batteries

- ✓ **Hybrid Materials**
  - ➢ **Confinement** (*ACS Nano* 2013)
  - ➢ **Chemical bonding (O&N)** (*Nano Energy*, 2016; *Nature Commun* 2017)
- ✓ **Integrated Cathode**
  - ➢ **Double layer** (*Adv Mater* 2014)
  - ➢ **Single layer** (*Adv Mater* 2015)
  - ➢ **All-in-one** (*Nano Energy 2015; Adv Mater 2016*)
  - ➢ **GO + 3D GF** (*Adv Mater 2016*)

Shuttle Impeding

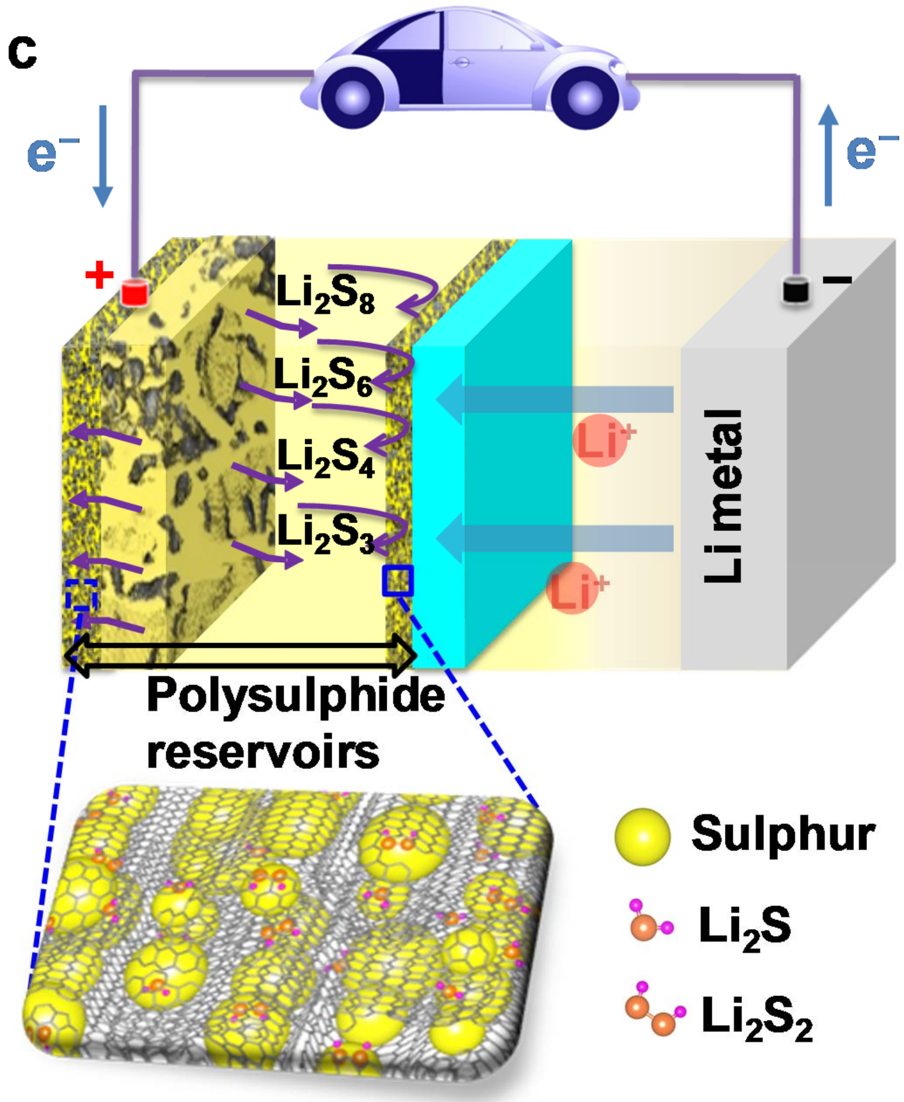


Shuttle Retarding; Conductive



Goal: "Double High" - Loading & Content

Design of a sandwich structure



- Improve adhesion
- Lower internal impendence & polarization;
- Act as a site for the retention of ions;
- Adsorb and trap polysulfides
- Increase surface area

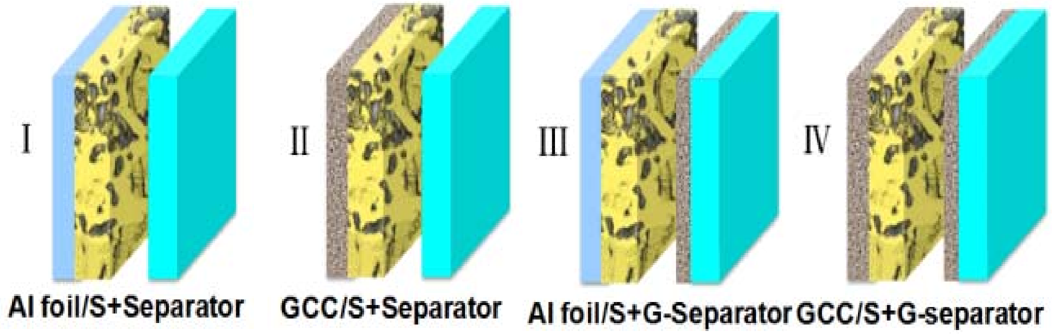
- **Polysulphides are blocked in cathode and re-used during cycling.**

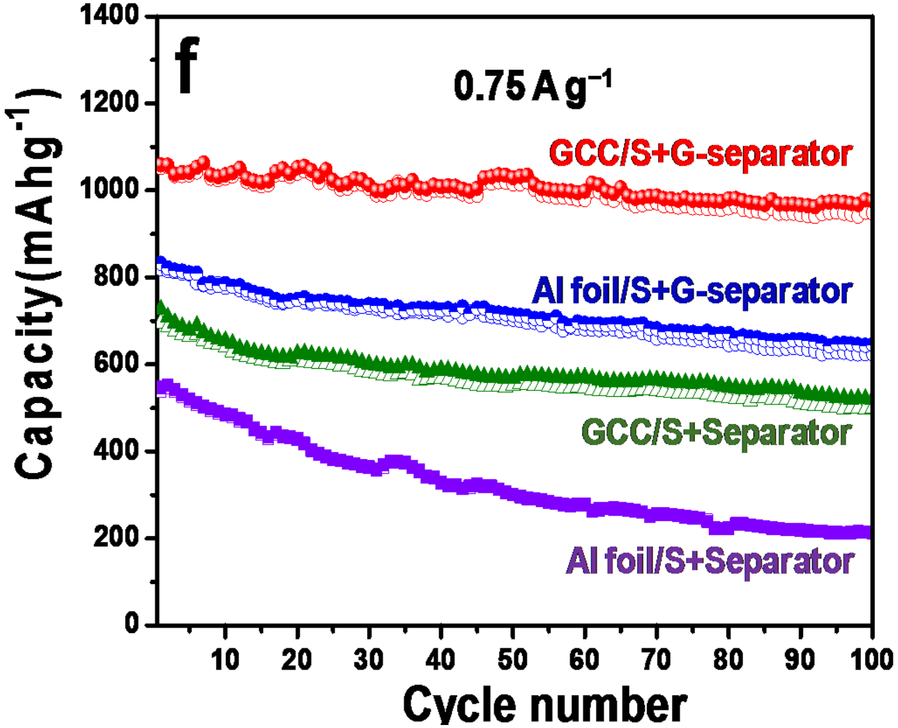
GM Zhou, et al, *Adv Mater*, 2014, 26, 625

Electrochemical performance

Graphene current collecotr

Polymer separator (up) and graphene-coated polymer separator (bottom)





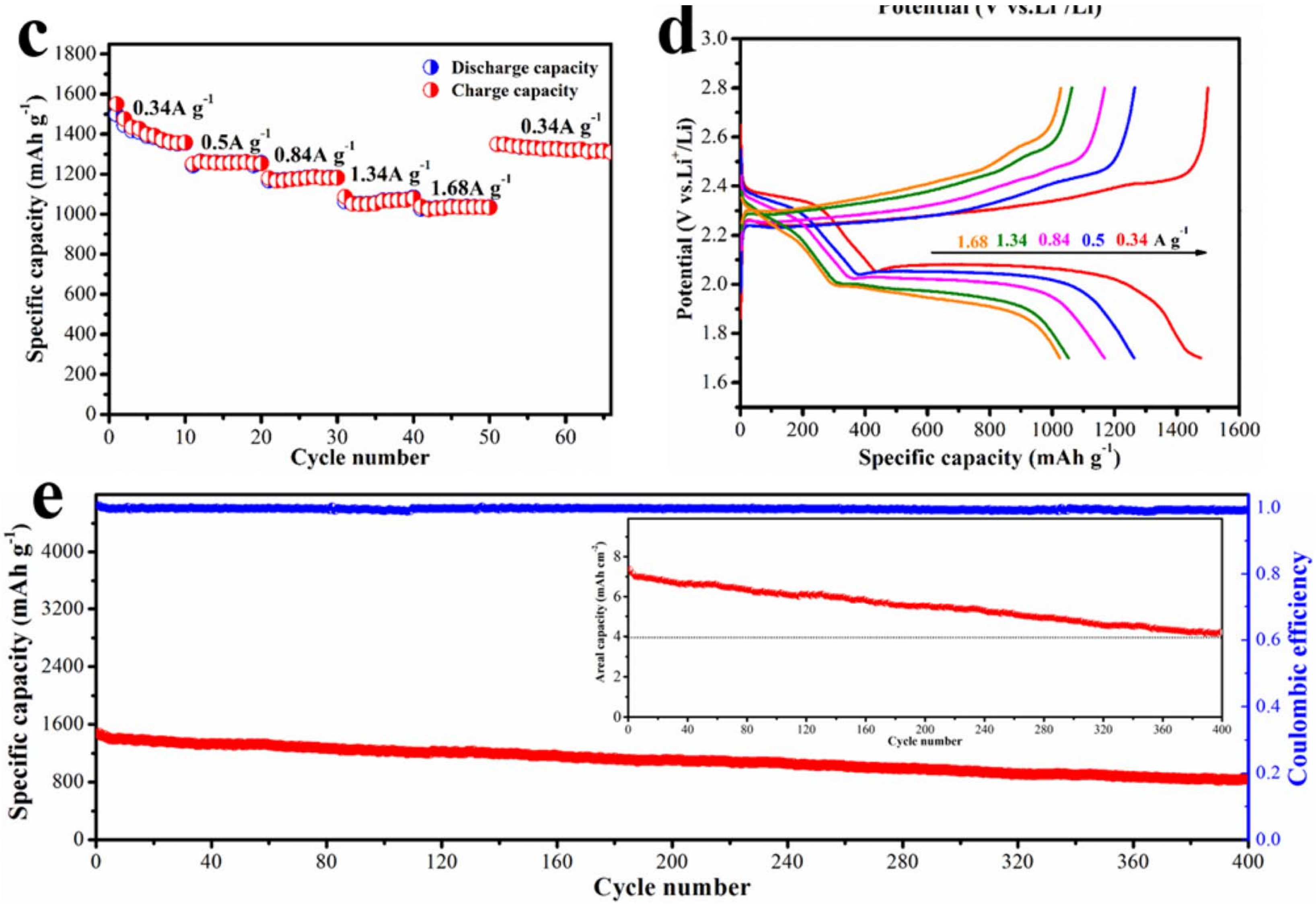
Design of an all-graphene S cathode

POG: Partially oxygenated graphene
HCG: Highly conductive graphene
HPG: Highly porous graphene

S content: 80 et%
S loading: 5 mg/cm2

RP Fang, et al, *ACS Nano,* 2016, DOI: 0.1021/acsnano.6b04019

Electrochemical performance



Improvement of areal capacity

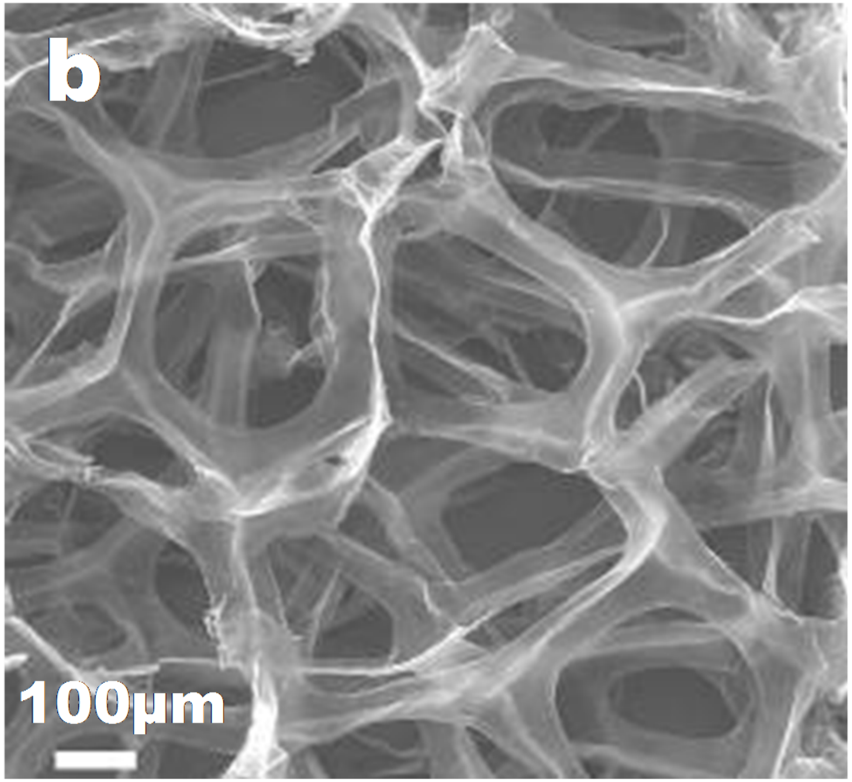
Material [Reference]	S percentage of material /electrode	Sulfur loading or thickness of cathode	Cycle performance, 1C=1.675A/g	Surface capacity/ mAh cm^{-2}
CNT@S[1]	53% /45%	0.42mg cm^{-2}/ 10~15μm	1C, 1000 cycles, 1053~535mAh g^{-1}	**0.2~0.4**
PVP-encapsulated S nanosphere[2]	70.4%,/--	1mg cm^{-2}/21.3μm	0.5C, 1000 cycles, 990~535mAh g^{-1}	**0.5~1**
Sulphur–TiO_2 yolk–shell nanoarchitecture[3]	71%/53%	0.4~0.6mg cm^{-2}/--	0.5C 1000 cycles, 1030~690mAh g^{-1}	**0.4~0.6**
S@C NW[4]	80.85%/--	1mg cm^{-2}/--	2C, 1000 cycles, 1138~863mAh g^{-1}	**0.8~1.1**
CTAB -S– GO[5]	80%/56%	0.8 mg cm^{-2}/--	1C 1500 cycles, 740~440 mAh g^{-1}	**0.3~0.6**
DTG/S nanocomposites[6]	64%/-	0.8~1.1 mg cm^{-2}/- -	5C, 200 cycles, 1200~832 mAh g^{-1}	**0.6~1.3**
GCC/S+G-separator[7]	70%/--	2~2.8mg cm^{-2} /20~30μm	0.9C, 300 cycles, 1052~ 680mAh g^{-1}	**1.4~2.9**
S–Pani yolk–shell structure[8]	58%/46.4%	2mg cm^{-2}/ --	2C, 200 cycles, 1100~765 mAh g^{-1}	**1.5~2.2**
Mesoporous carbon-sulfur (MCS)[9]	50%/40%	--/--	1C 400 cycles, 900~800 mAh g^{-1}	
PD-coated FLSNS[10]	83%/66%	<1.2mg cm^{-2} / 20μm	0.6C 500 cycles, 715~640 mAh g^{-1}	**<0.8**
PD- coated RGO/S[11]	74%/56%	<1mg cm^{-2}	0.6C 800 cycles, 715~530 mAh g^{-1}	**<0.72**
Amphiphilic surface-modified hollow CNF-S composite[12]	--	~1mg cm^{-2}	0.5C 300cycles 828~660 mAh g^{-1}	**0.6~0.8**
CFC/S	66%	6.7mg cm^{-2} / ~150μm	0.3mA/cm^{2} 50 cycles, 1100 mAh g^{-1}	**>7.0**

"Double Low" Issues

- **Low sulfur loading**
  - **typically <2 mg cm^{-2}**
- **Low sulfur content**
  - **typically <70 wt%**

- **Low areal capacity**
- **Low energy density**

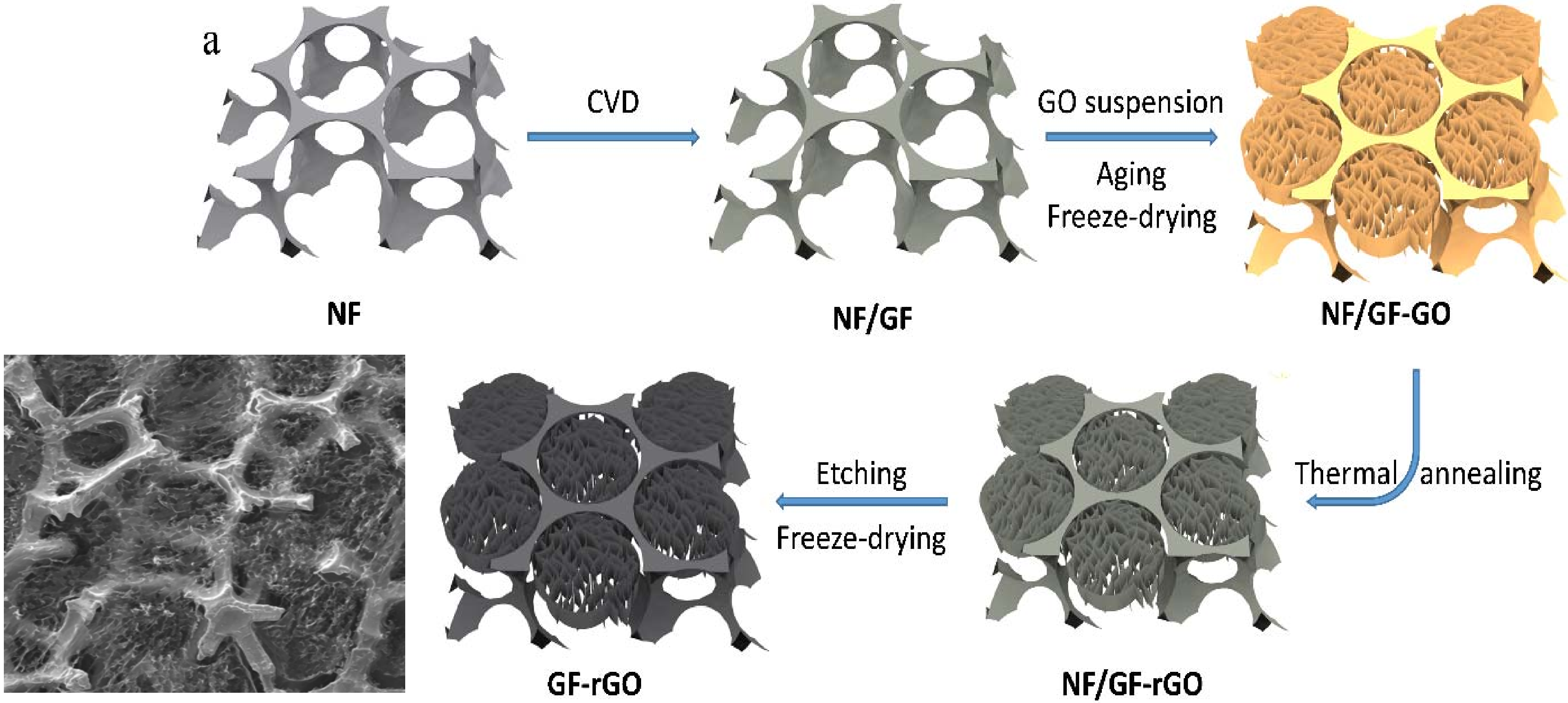
Free Standing Graphene Foam (GF)



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

ZP Chen, et al., *Nature Mater* 2011, 10, 424

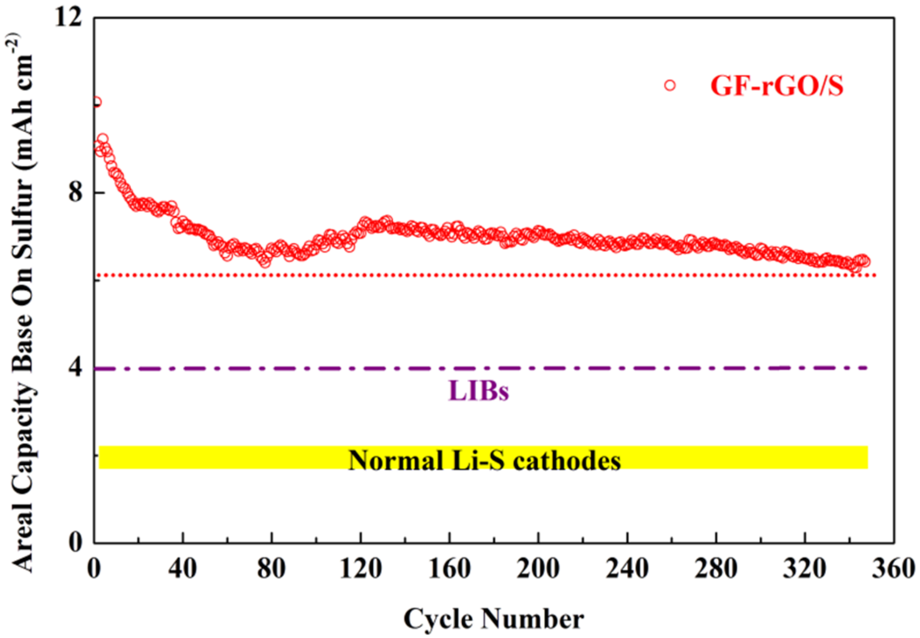
Graphene Foam-rGO
3D Nested Hierarchical Network

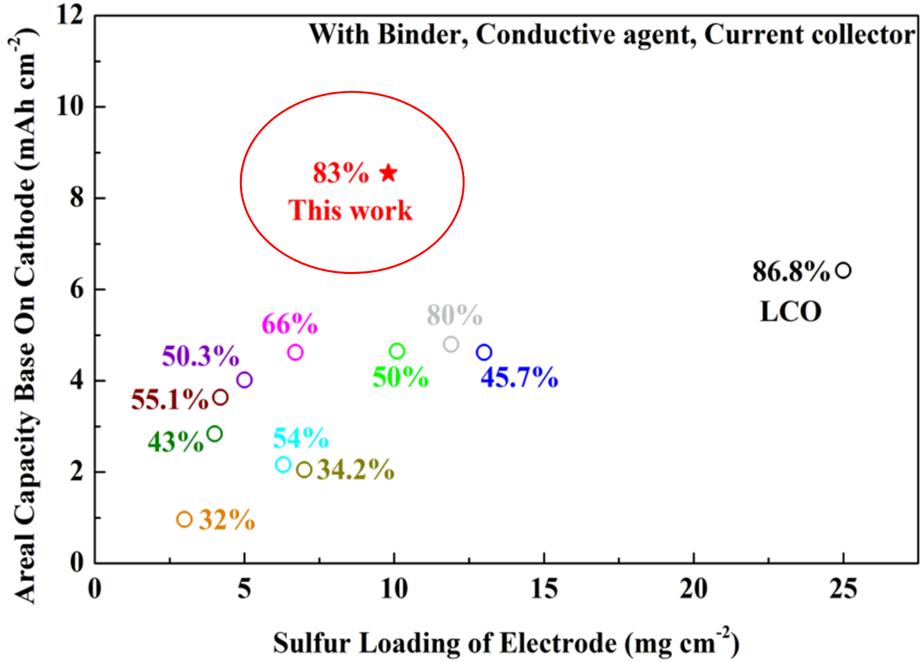


- **GF-rGO:** **high porosity and specific surface area; 3D networks**
- **GF:** **highly conductive network**
- **rGO:** **anchoring sulfur nanoparticles via functional groups**

Areal Capacity Comparison

- **Sulfur loading: 14.4 mg cm^{-2}; Sulfur content: 89.4 wt%**





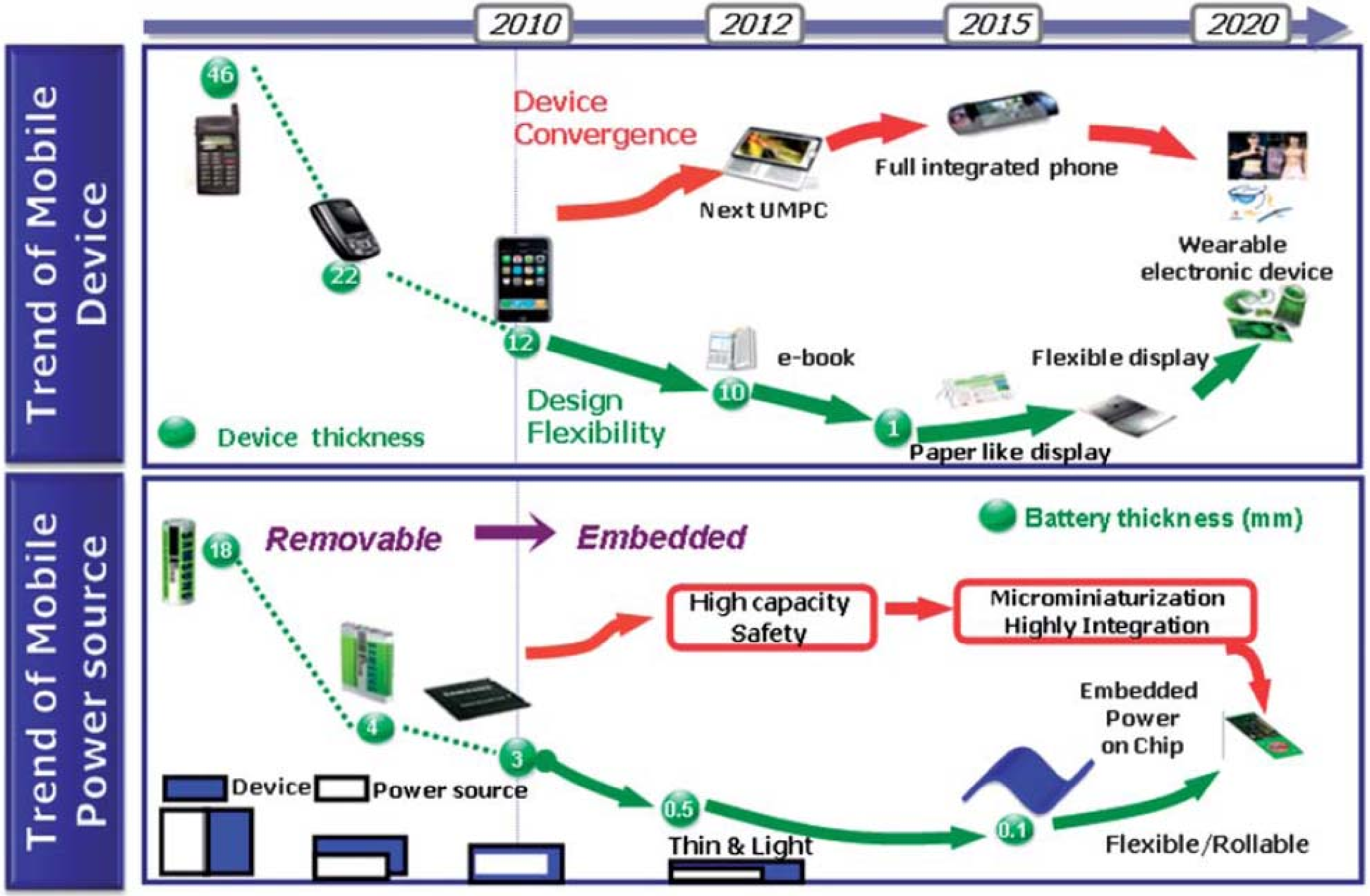
- **High sulfur loading and high sulfur content**
- **High areal capacity, good rate capability and cycling stability**

GJ Hu, et al, *Adv. Mater.* 28, 1063 (2016).

Graphene —

A Promising Material for Flexible and Smart Energy Storage

Trend of mobile devices & power sources

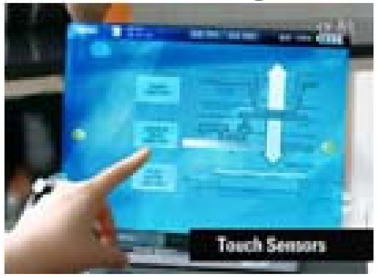


Heavy & Thick & Stiff ⟶ Light & Thin & Flexible

Jeong G, et al, *Energy Environ. Sci.*, 2011, 4, 1986

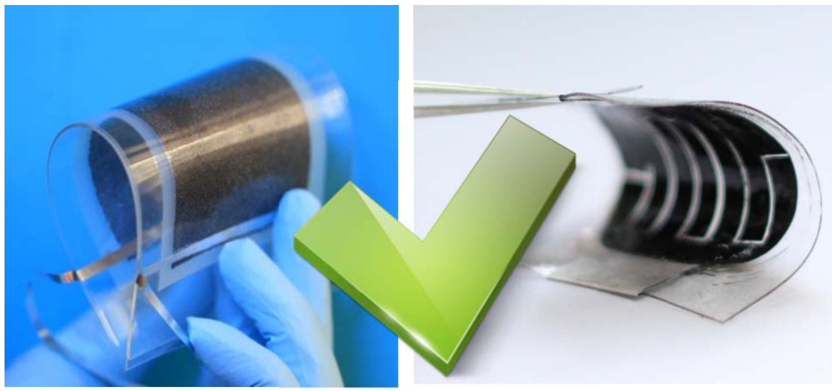
Nokia Humanform

Samsung



Power for Flexible Devices

Stiff & bulky

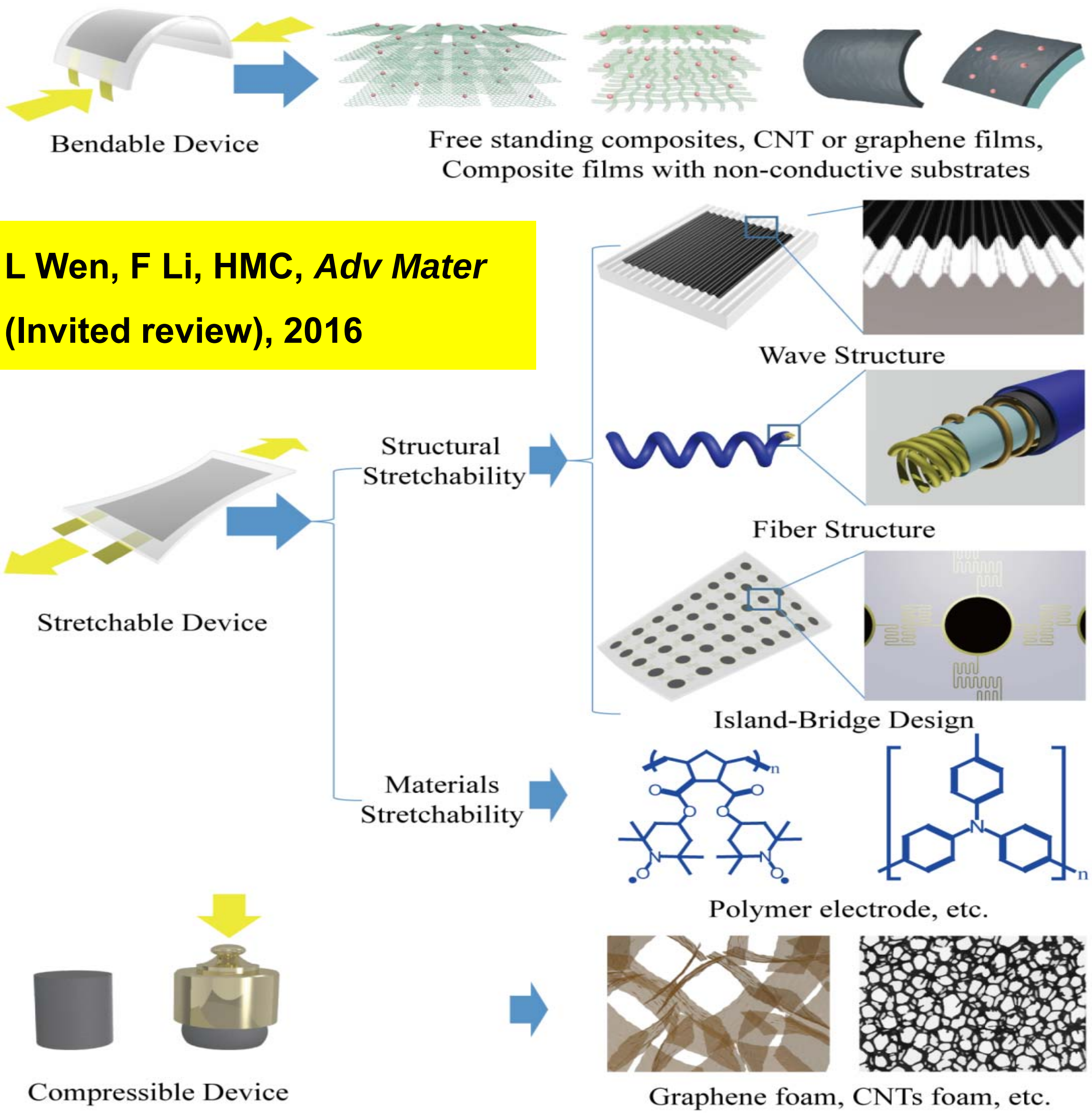


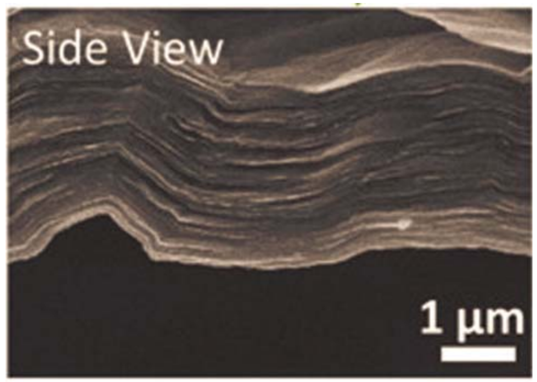
Light, thin & flexible

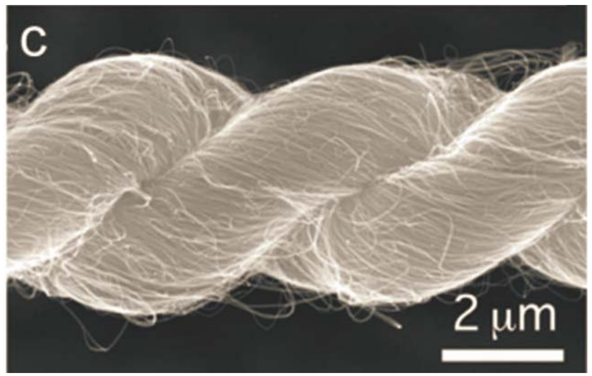
- **Integratible with electronic devices**
- **High capacity per area & mass**
- **Superior mechanical flexibility**
- **Vital component: Free-standing flexible electrodes**

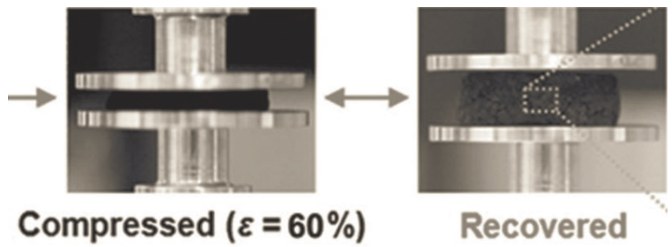
Classification of flexible devices

L Wen, F Li, HMC, *Adv Mater* (Invited review), 2016

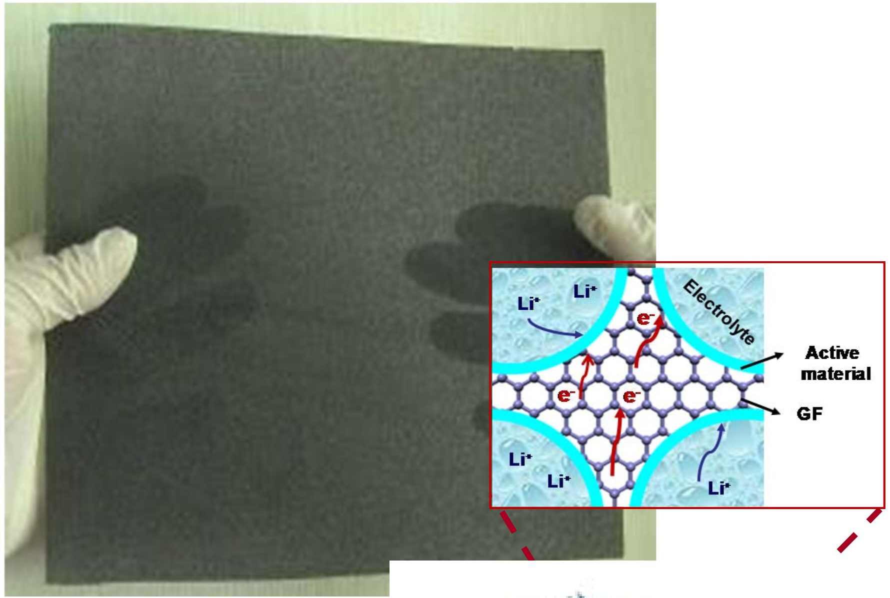






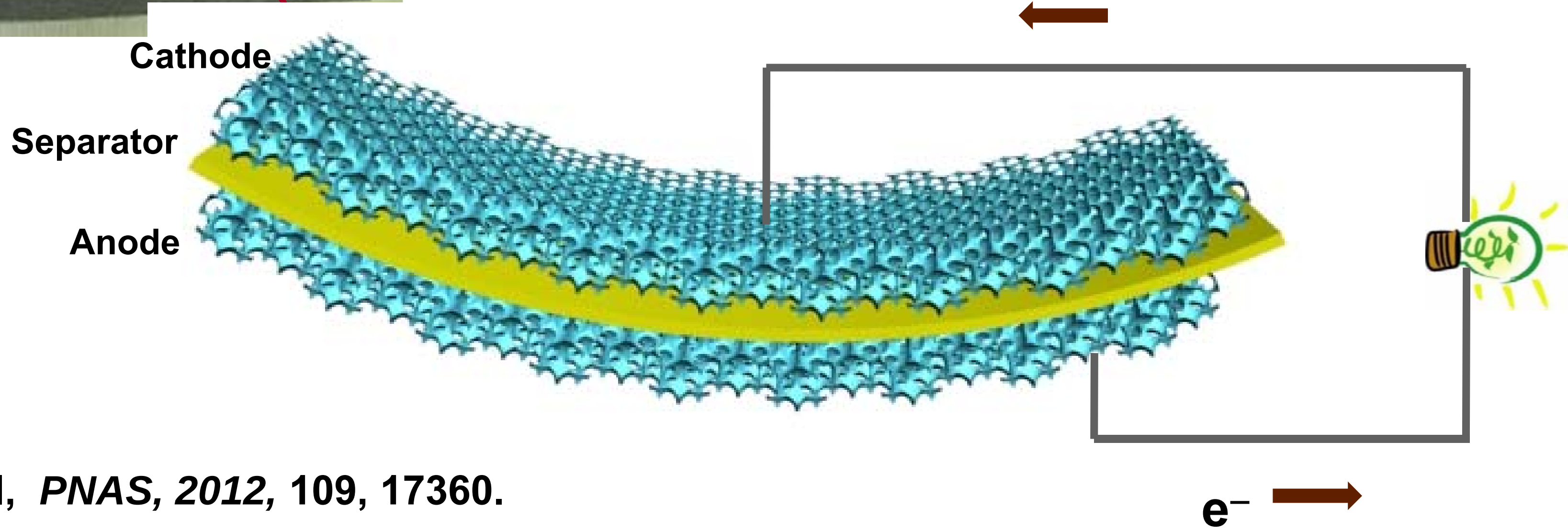


Graphene Foam-based flexible LIBs



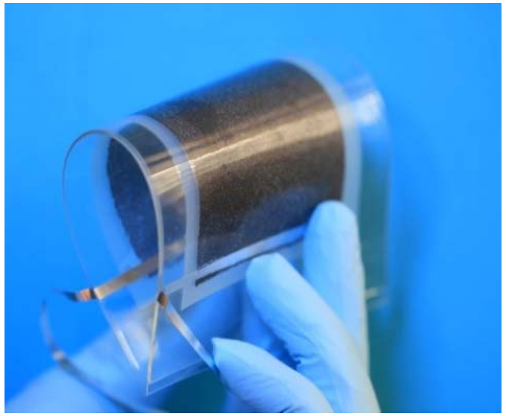
- Sufficiently light
- Flexible and integrated
- Highly conductive

- Binder-free
- Conducting additive-free
- Metal current collector-free
- Strong contact and binding



N Li, et al, *PNAS, 2012,* 109, 17360.

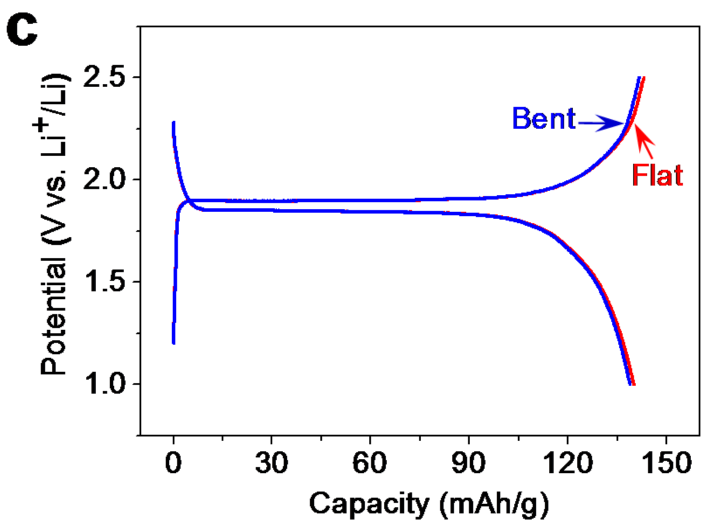
Performance of A GF-based Flexible LIB

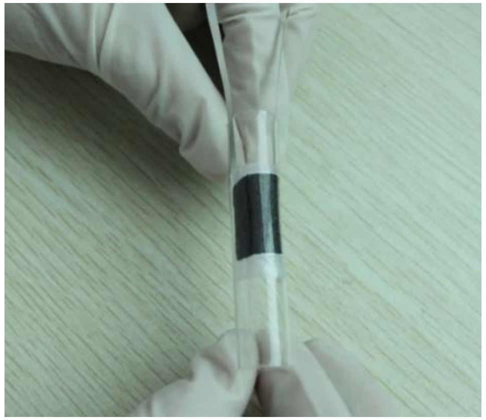


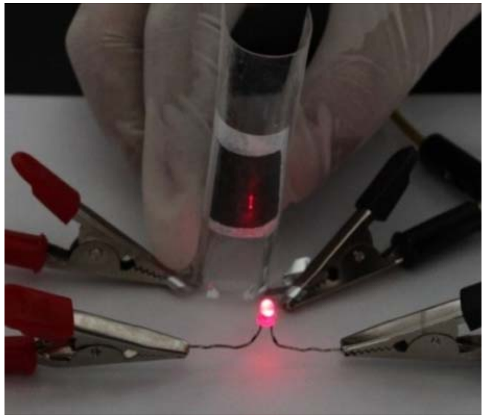
Voltage: 1.9 V

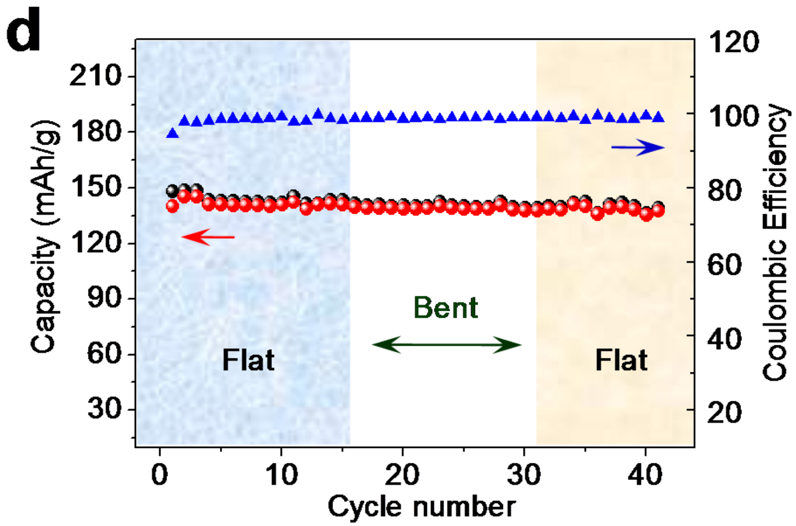
Capacity (Cell):

137 mAh/g (0.2C)





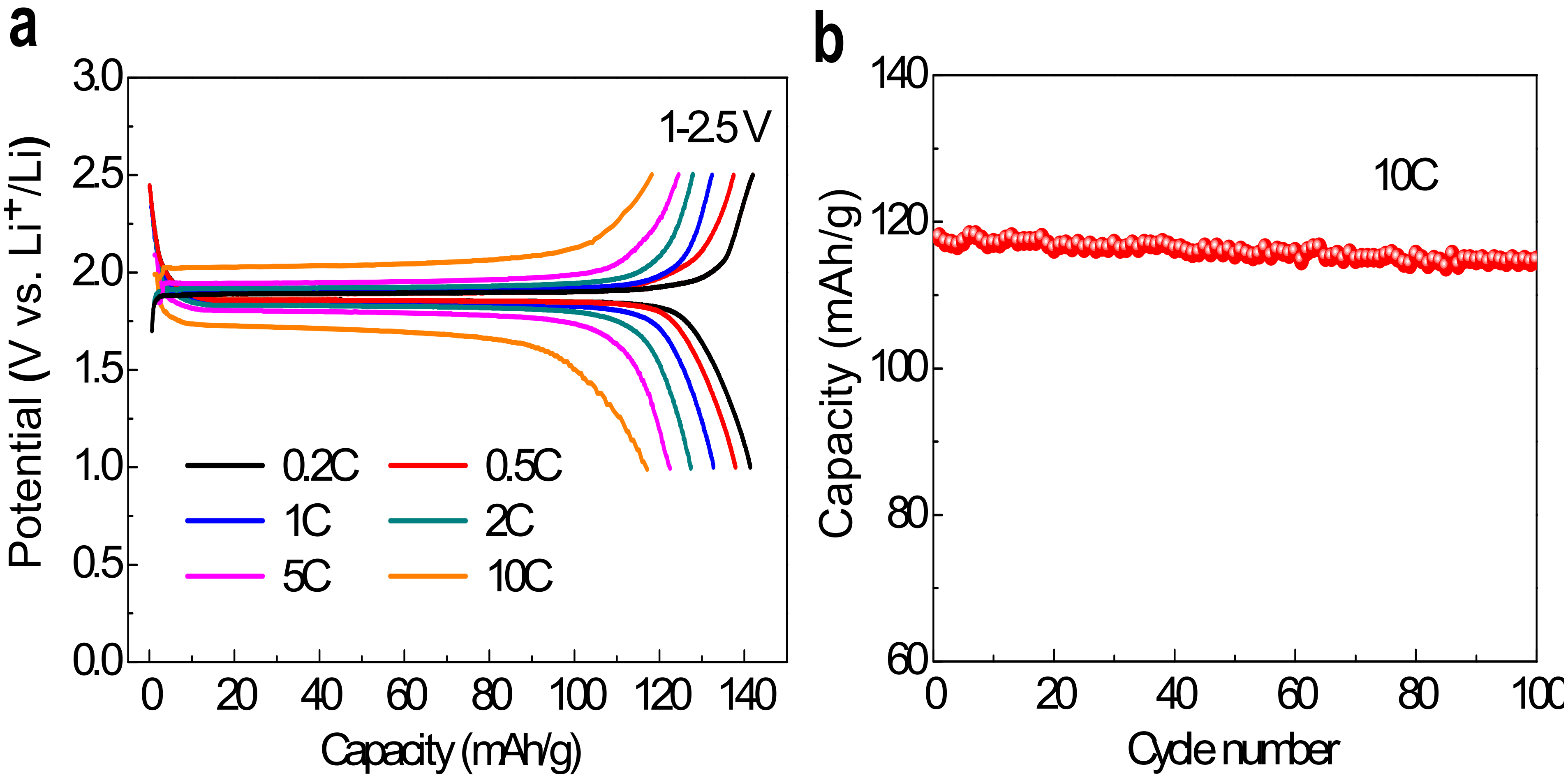




No metal current collector;

No binder; No additive!

Performance of A GF-based Flexible LIB



High rate performance. Fully charged in 6 minutes.

Summary

- **Various uses of graphenematerials in Li storage.**
  - **LIBs;**
  - **Li-S;**
  - **flexible devices;**
  - **Etc**
- **Different functions of graphene-based materials in Li storage.**
  - **Conductive network;**
  - **Buffer and protection layer;**
  - **Matrix;**
  - **Current collector**

Challenges and Perspective

- Challenges of graphene-based materials in Li storage.
  - Customer-tailoring of graphene materials;
  - Control of quality
  - Design of composition, structure and configuration;
  - Improvement of first Coulumbic efficiency;
  - Control of SEI formation;
  - Enhancement of cyclic performance;
  - Lowering of cost;
  - Understanding of the mechanisms;
  - Etc.
- Great potential of graphene-based materials for Li storage.

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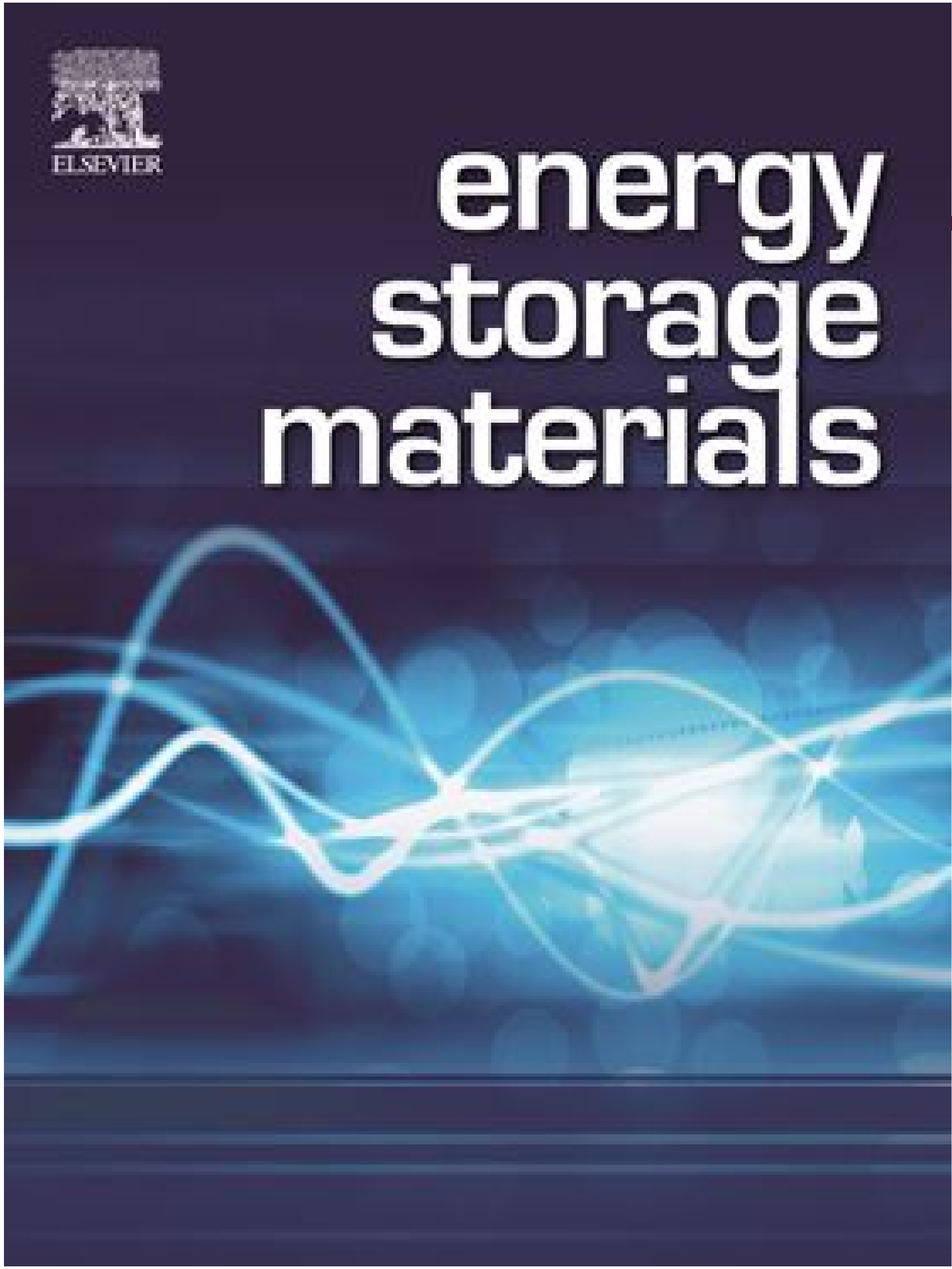

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