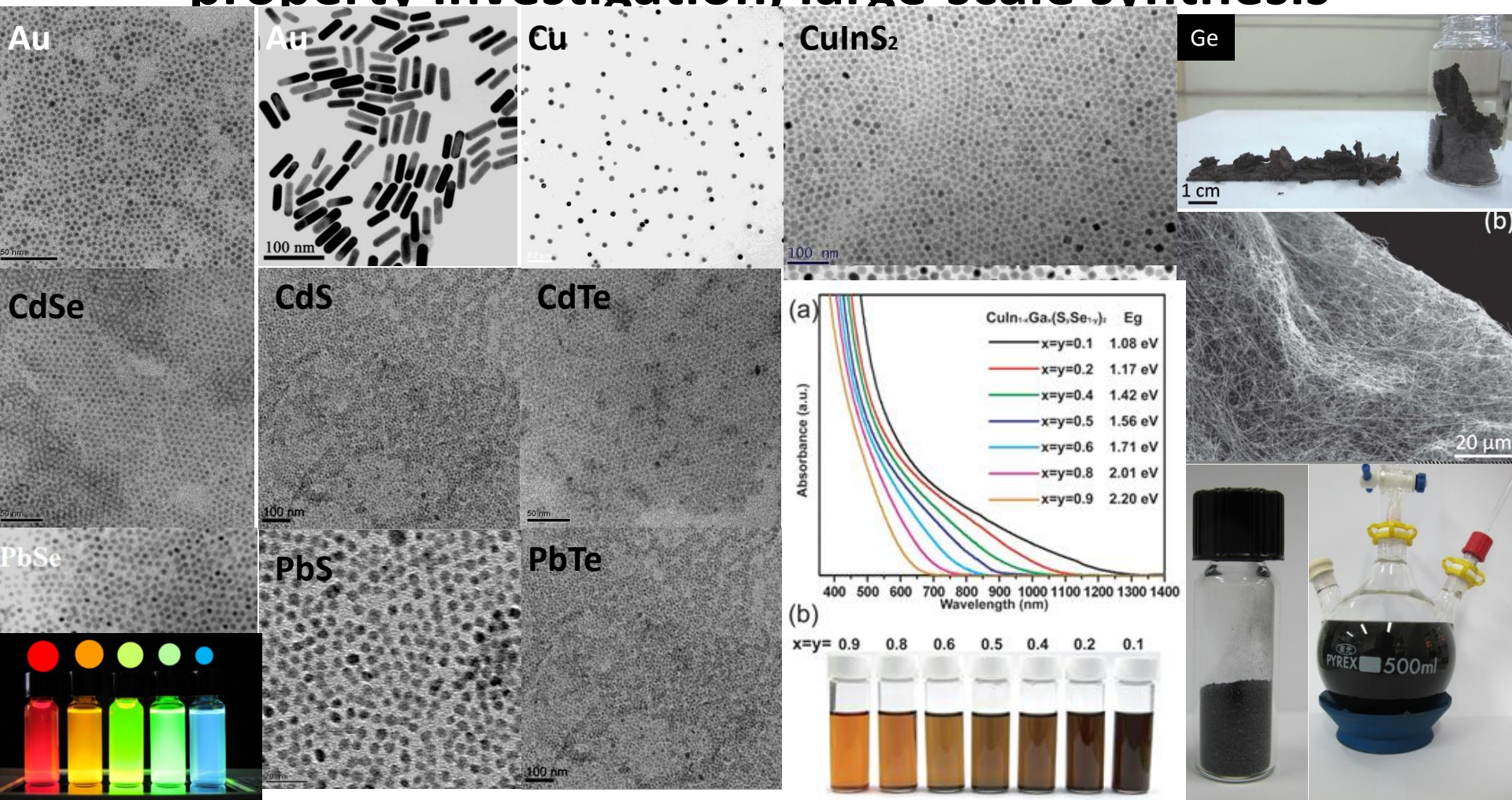


# High Specific Capacity Nanomaterials as Lithium ion battery anodes

Hsing-Yu Tuan (段興宇)

Professor, Department of Chemical Engineering, National Tsing Hua University,  
Taiwan, R.O.C.

# Nanomaterials: size, shape, composition, phase control property investigation, large-scale synthesis

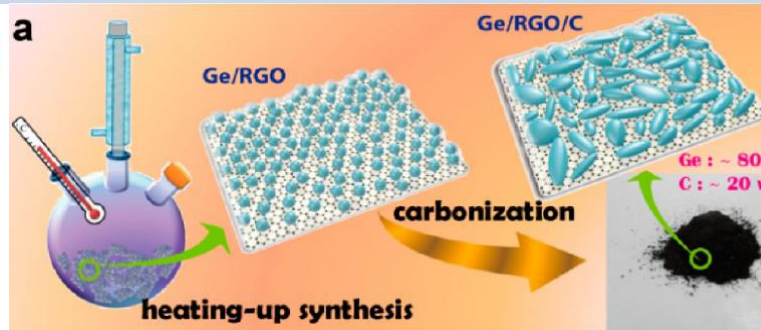
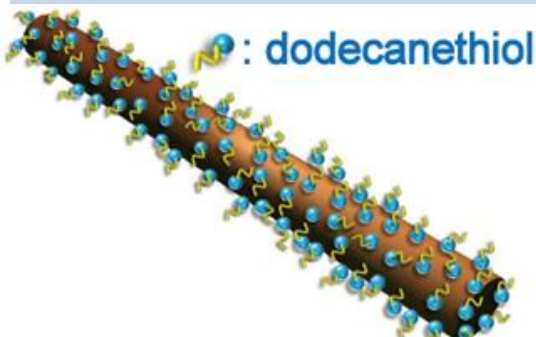


## Representative Publications of Nanomaterial Synthesis in Tuan research group

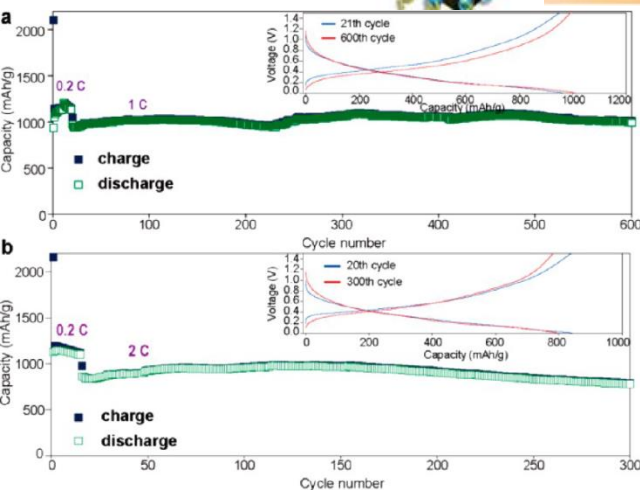
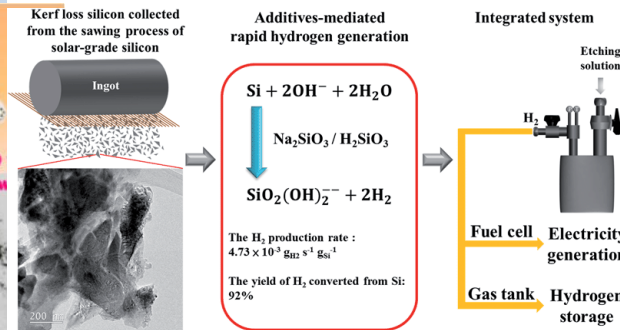
- |                                   |                                   |                                    |
|-----------------------------------|-----------------------------------|------------------------------------|
| Angew Chem.Int.2006, 45, 5184     | Chem. Mater., 2008, 20, 2306      | J. Phys. Chem. C, 2013, 117, 21955 |
| J. Am. Chem. Soc, 2008, 130, 8900 | Chem. Mater., 2008, 20, 1239      | Nanoscale, 2013, 5, 9875           |
| J. Am. Chem. Soc, 2008, 130, 5436 | Chem. Com., 2010, 46, 6105        | Nanoscale, 2012, 4, 4562           |
| J. Am. Chem. Soc, 2007, 129, 1733 | J. Phys. Chem. C, 2011, 115, 1592 | J. Mater. Chem., 2011, 21, 13793   |
| Nano Letters., 2005,5,681         | Cry. Growth. Des., 2010, 10, 4741 |                                    |

# Nanomaterials-based applications

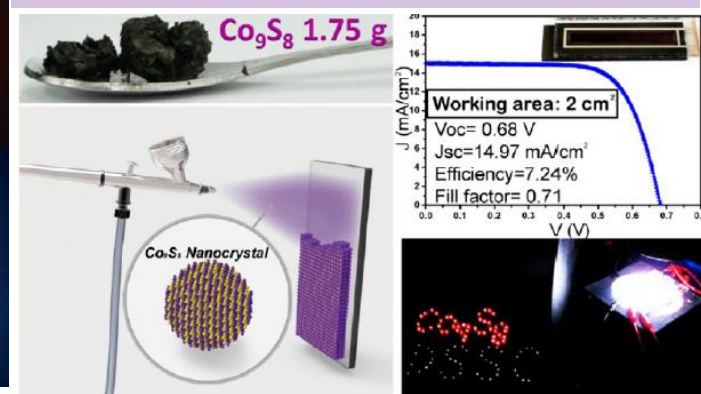
## High-capacity anode materials for lithium and sodium ion batteries



## Rapid hydrogen production



## Nanocrystal-based photovoltaic electrodes



## Representative Publications of Nanomaterial Applications in Tuan research group

Nano Letters, 2013, 13, 4036

Nano Letters, 2012, 12, 6372

Nano Letters, 2017, 17, 1240-1247

Energy&Environ. Science, 2011, 4, 4929

ACS Nano, 2016, accepted

ACS Nano, 2013, 7, 9443

ACS Nano, 2012, 6, 9932

ACS Nano, 2010, 4, 6278

ACS Nano, 2012, 6, 5710

Biomaterials, 2012, 33, 6559

Biomaterials, 2012, 33, 4108

Chem. Mater., 2015, 12, 4

Chem. Mater., 2014, 26, 2172

Chem. Mater., 2014, 26, 1785

J. Materi. Chem. A, 2017 in press

J. Mater. Chem. A, 2016, 4, 12921

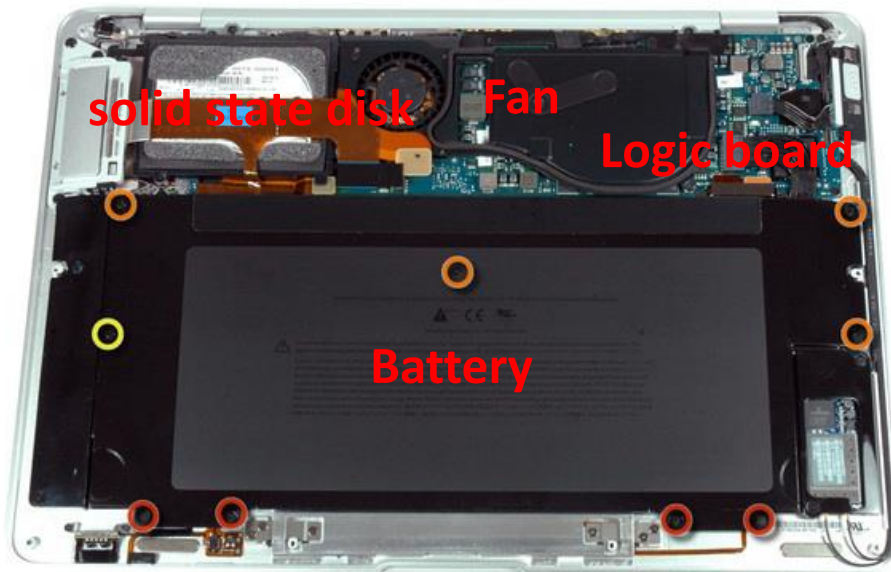
J. Mater. Chem., (cover story) 2012, 22, 2215

ACS AMI, 2016, 5, 5

ACS AMI, 2016, 12, 2

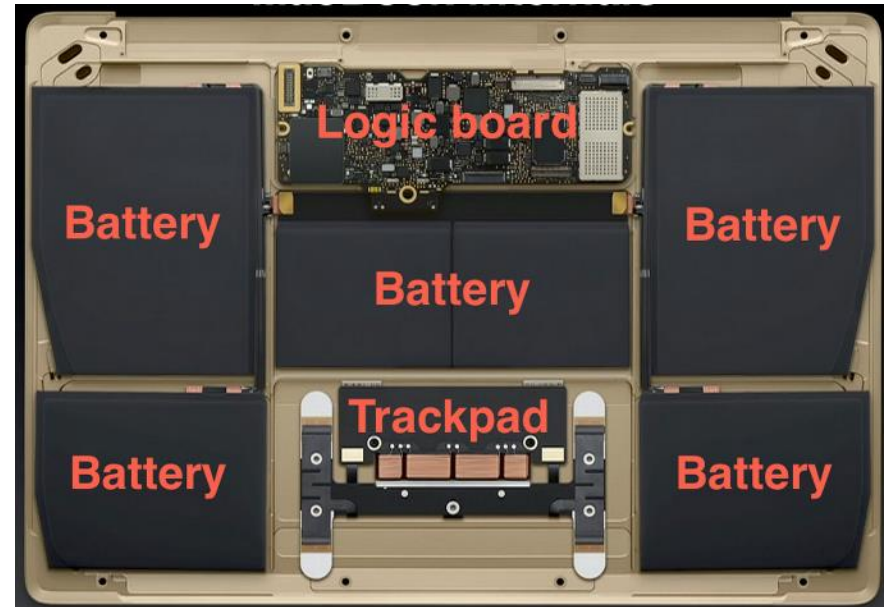
# Development of the lithium ion battery

Macbook Air 2008



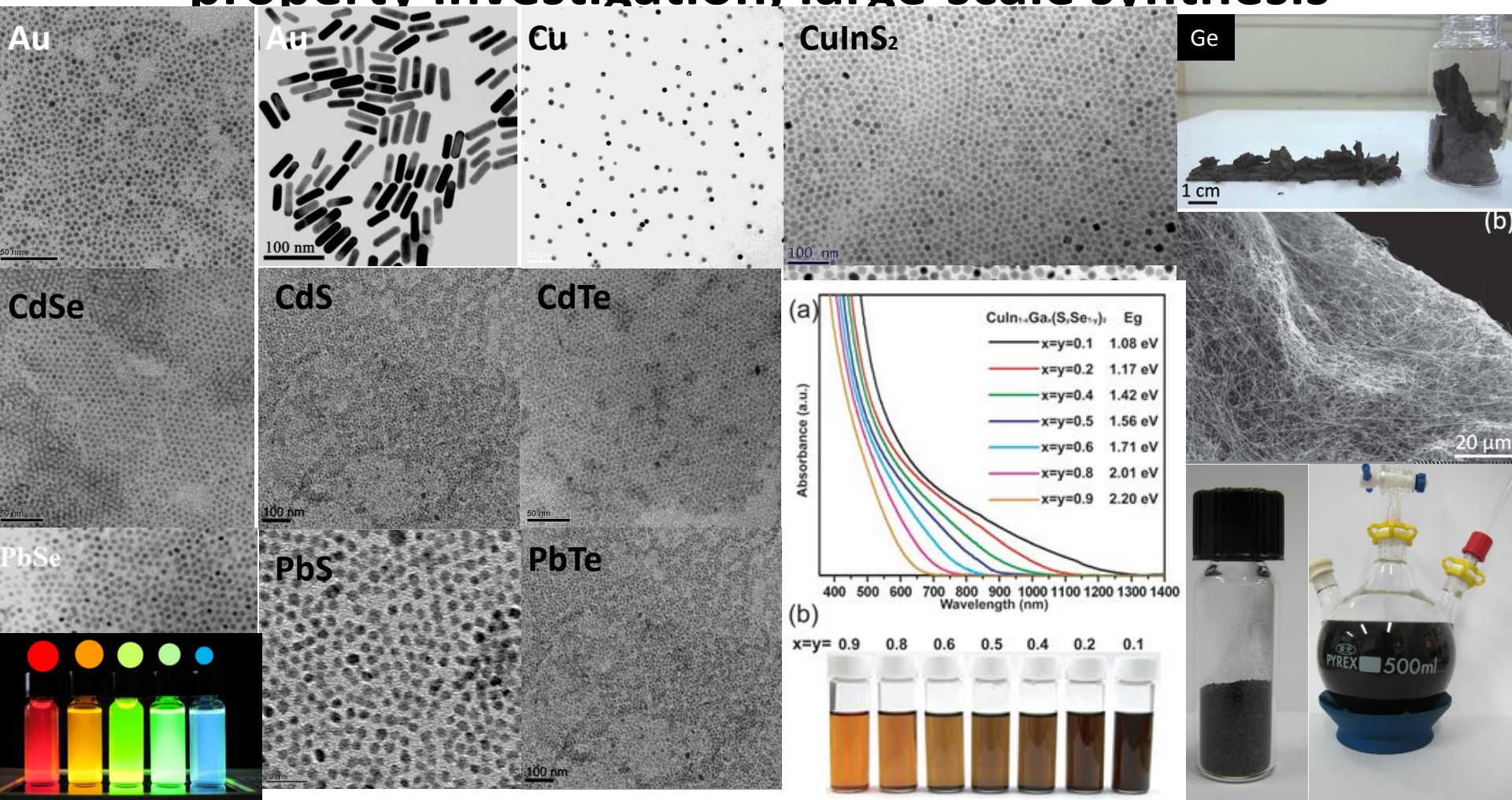
37 Wh lithium ion battery

New macbook 2015



39.7 Wh lithium ion battery

# Nanomaterials: size, shape, composition, phase control property investigation, large-scale synthesis



## Representative Publications of Nanomaterial Synthesis in Tuan research group

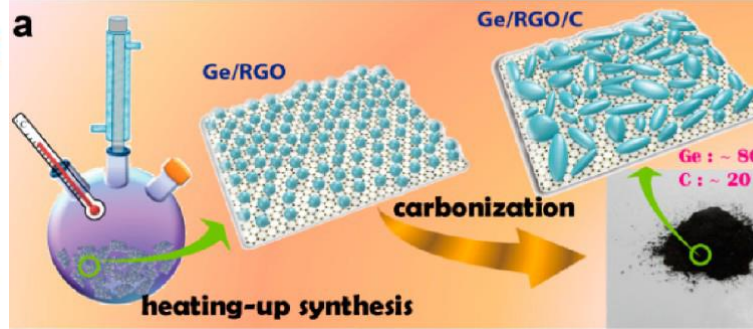
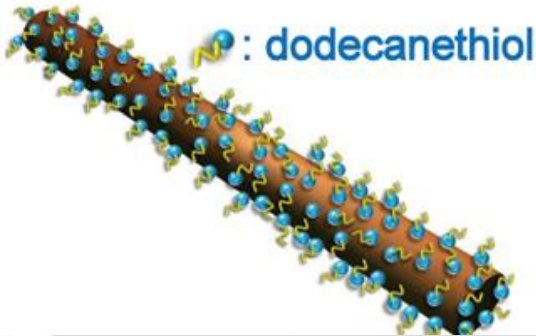
Angew Chem.Int.2006, 45, 5184  
 J. Am. Chem. Soc, 2008, 130, 8900  
 J. Am. Chem. Soc, 2008, 130, 5436  
 J. Am. Chem. Soc, 2007, 129, 1733  
 Nano Letters., 2005,5,681

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 Chem. Mater., 2008, 20, 1239  
 Chem. Com., 2010, 46, 6105  
 J. Phys. Chem. C, 2011, 115, 1592  
 Cry. Growth. Des., 2010, 10, 4741

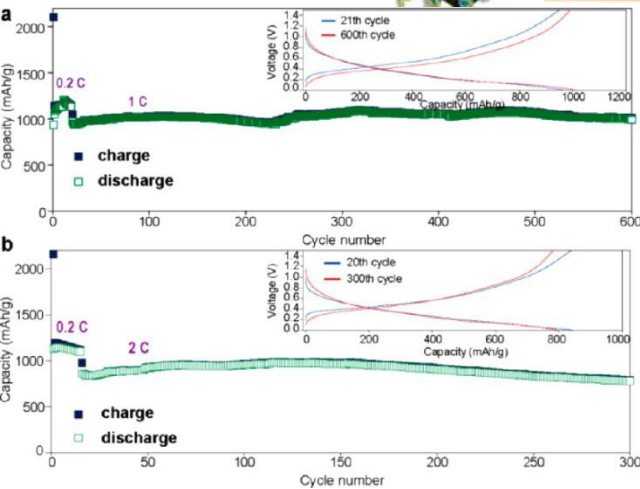
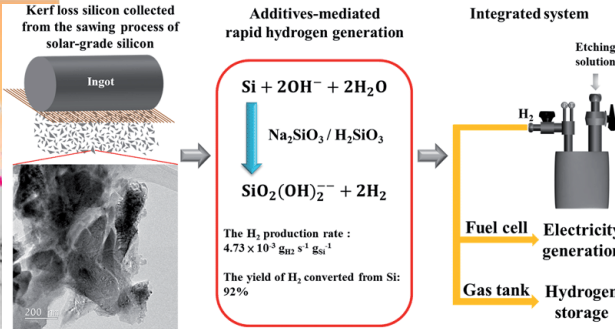
J. Phys. Chem. C, 2013, 117, 21955  
 Nanoscale, 2013, 5, 9875  
 Nanoscale, 2012, 4, 4562  
 J. Mater. Chem., 2011, 21, 13793

# Nanomaterials-based applications

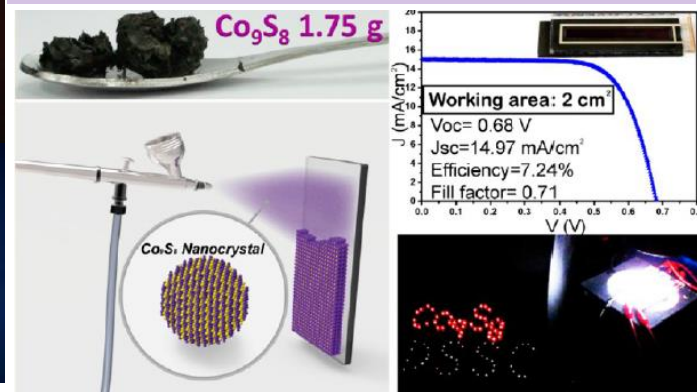
## High-capacity anode materials for lithium and sodium ion batteries



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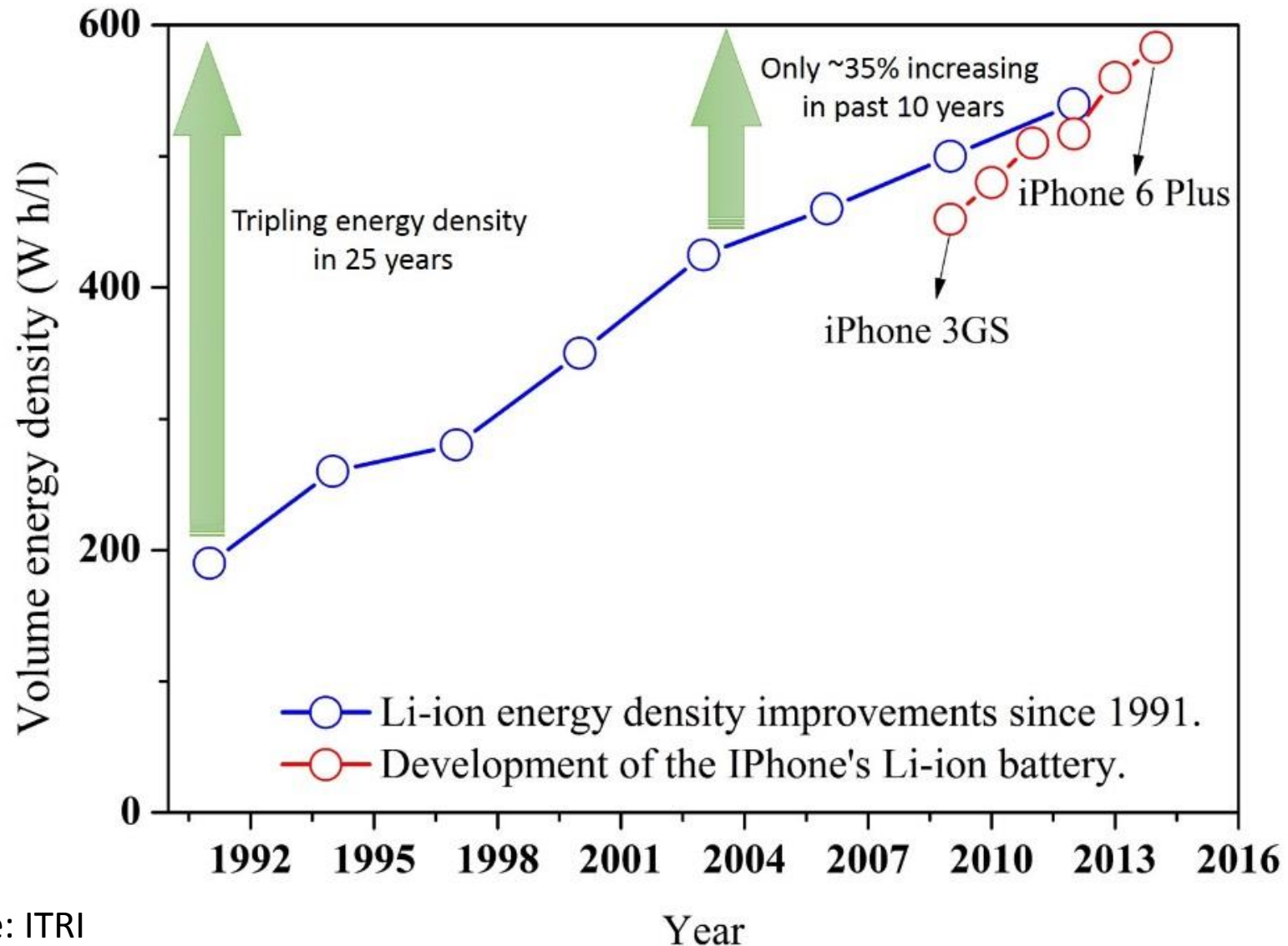
J. Mater. Chem. A, 2016, 4, 12921

J. Mater. Chem., (cover story) 2012, 22, 2215

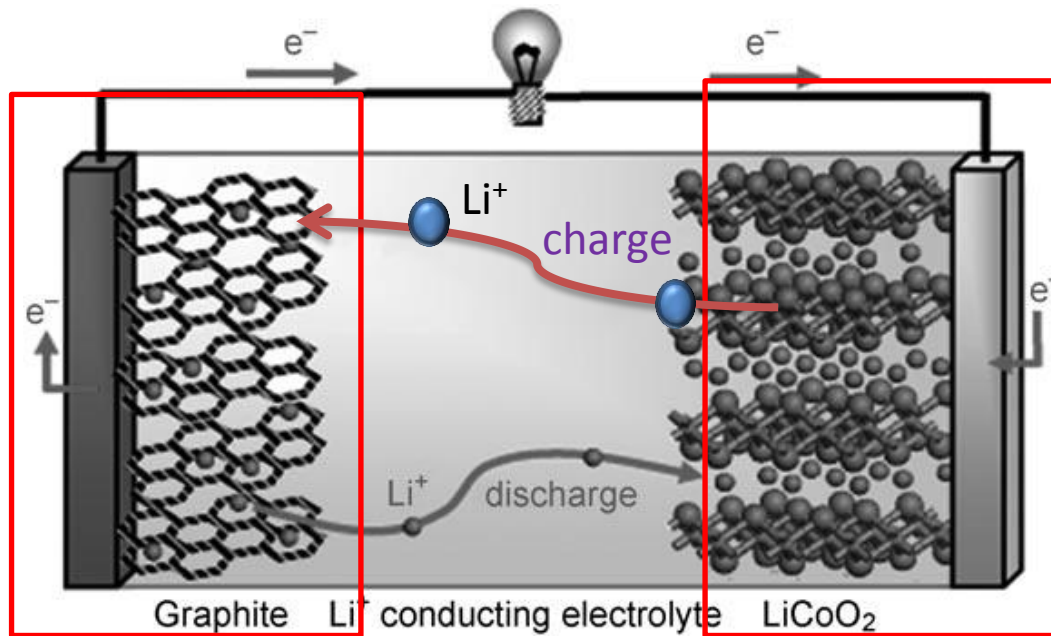
ACS AMI, 2016, 5, 5

ACS AMI, 2016, 12, 2

# Development trend of energy density of lithium ion batteries



# LIB: Mechanism and Anode Capacity



charge reaction :

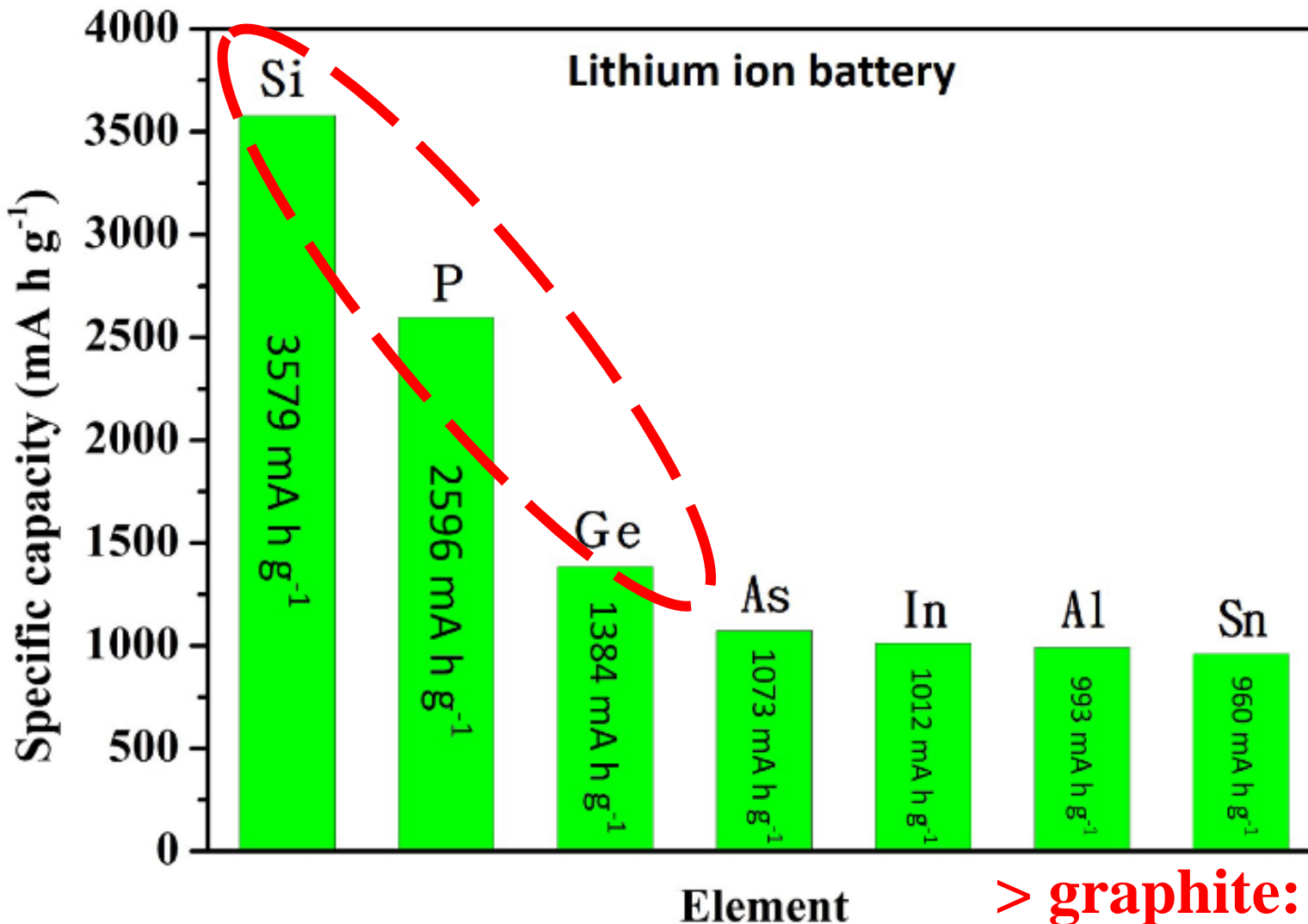


**Graphite capacity: only 372 mAh/g**



# Graphite alternative :lithium-alloy type materials

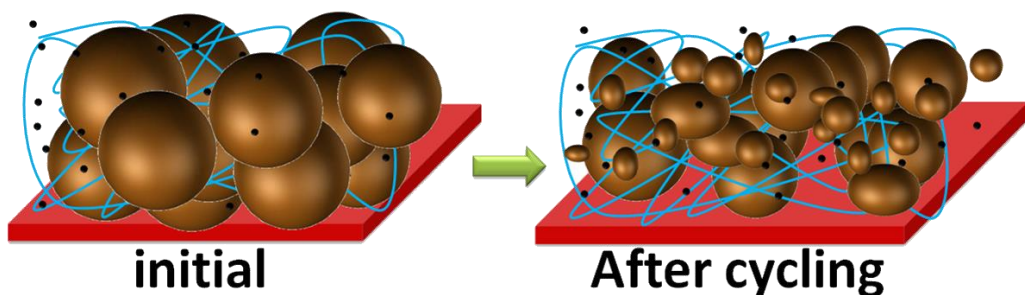
(a)



> graphite: 372 mAh/g

# Morphological Changes in high-capacity materials During Electrochemical Cycling

micro-size Ge/Si/P particle



~ 300 % volume change

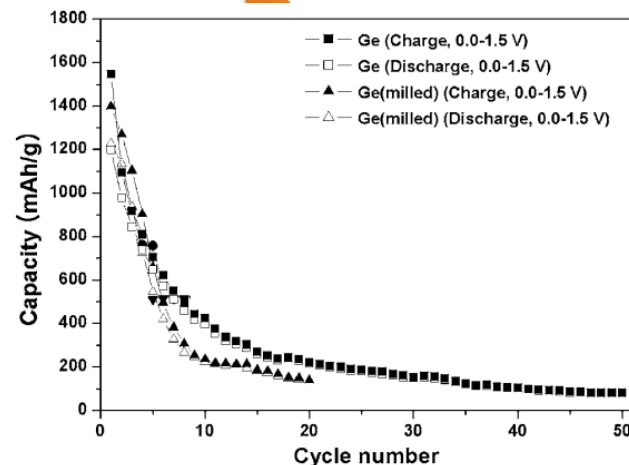
film



initial



capacity decline rapidly



Alloying-based anode materials suffers from pulverization while cycled

J. Electrochem. Soc., 2009, 106, A169

Yoon et al., Electrochem. Solid State Lett., 2008

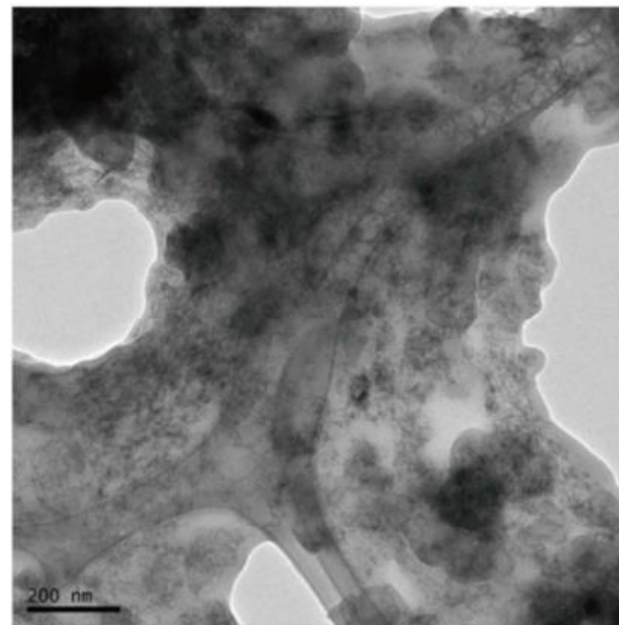
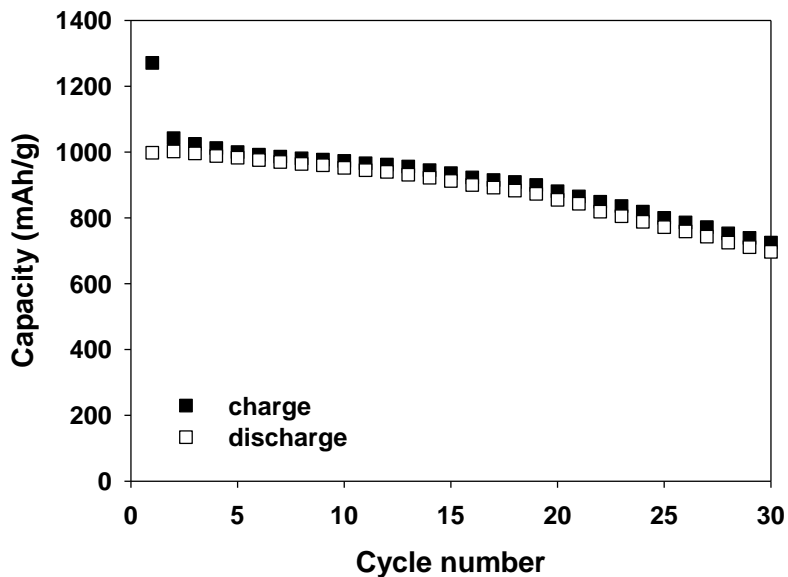
# Nanowires as LIB anodes



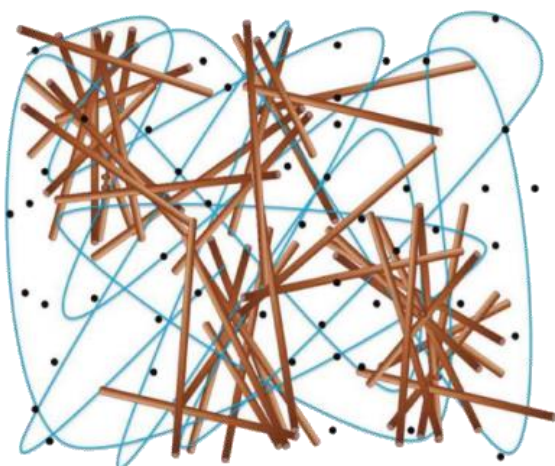
- Effectively accommodate the volume changes
- Tolerate relaxed mechanical strain
- Provide channels for
- Efficient electron transport

- Diameter: 1 to 100 nm
- High surface area
- Unique morphology
- Tunable surface chemistry
- Colloid solution

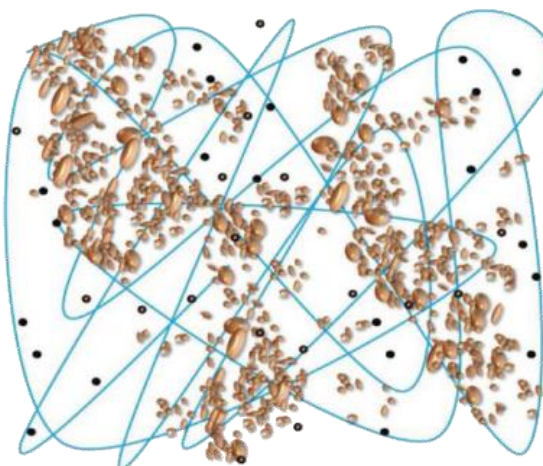
# Raw Ge nanowires for Lithium-Ion Batteries



TEM image of Ge nanowires after 30 cycles

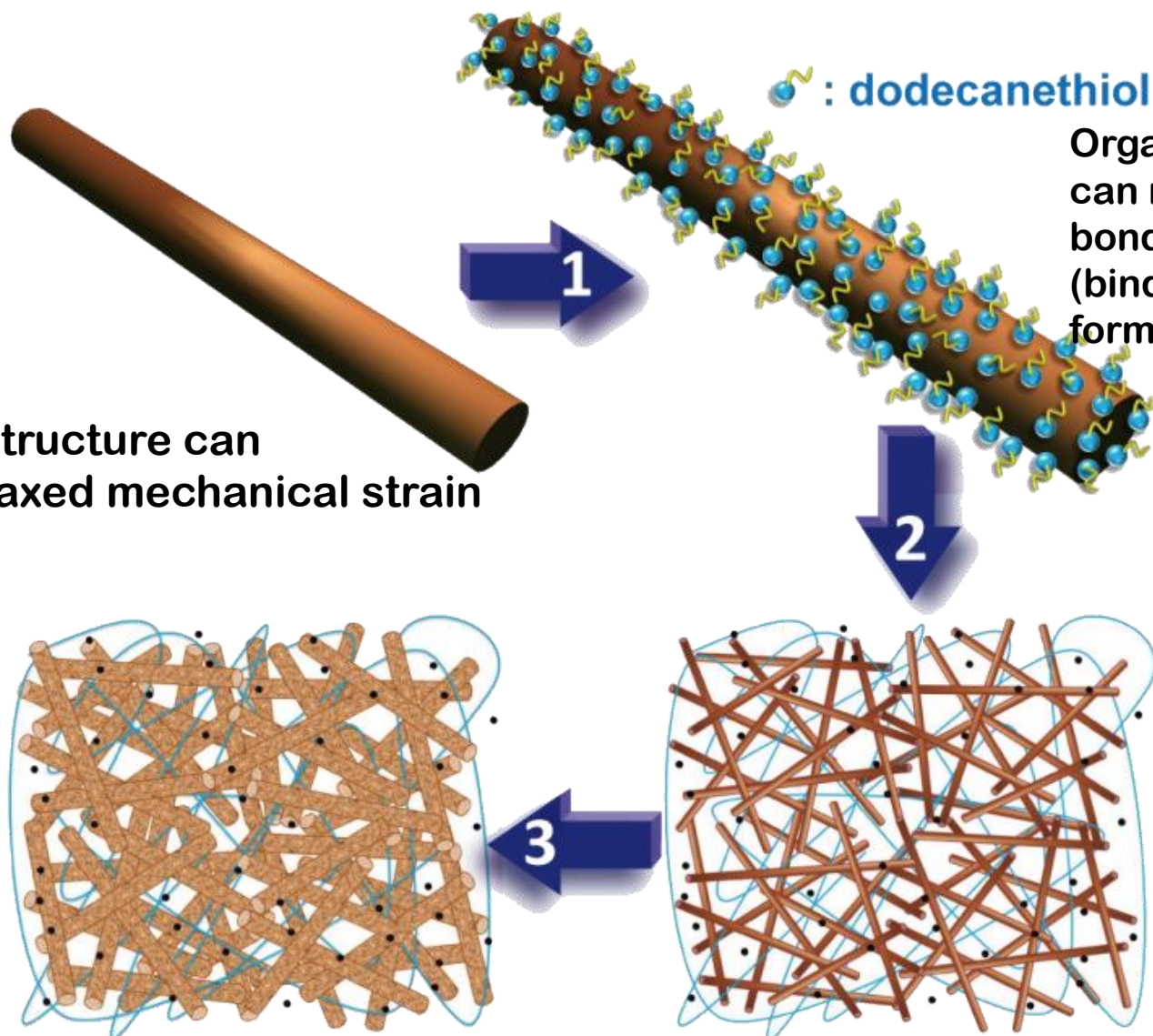


GeNW



Pulverization

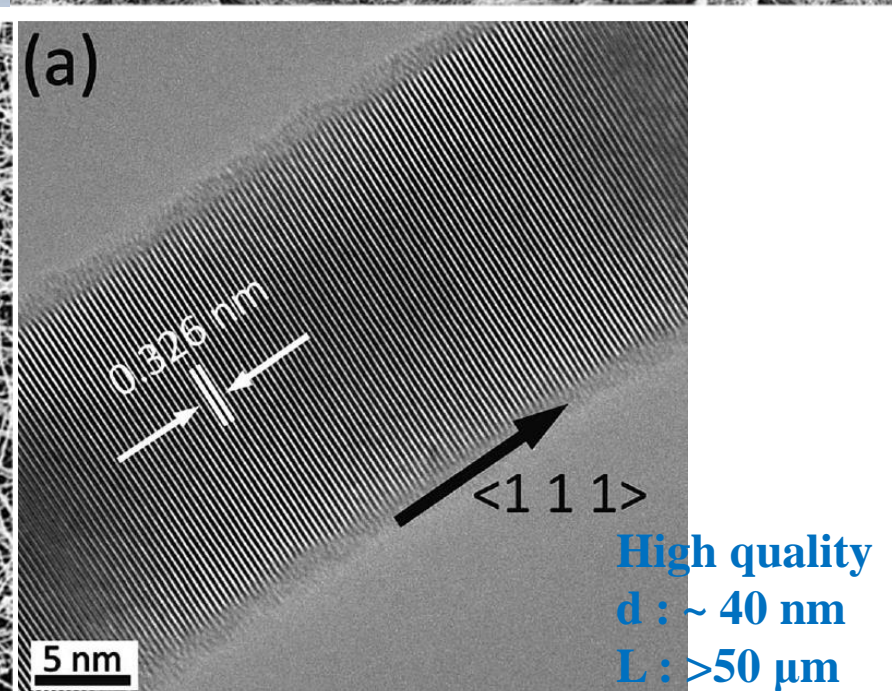
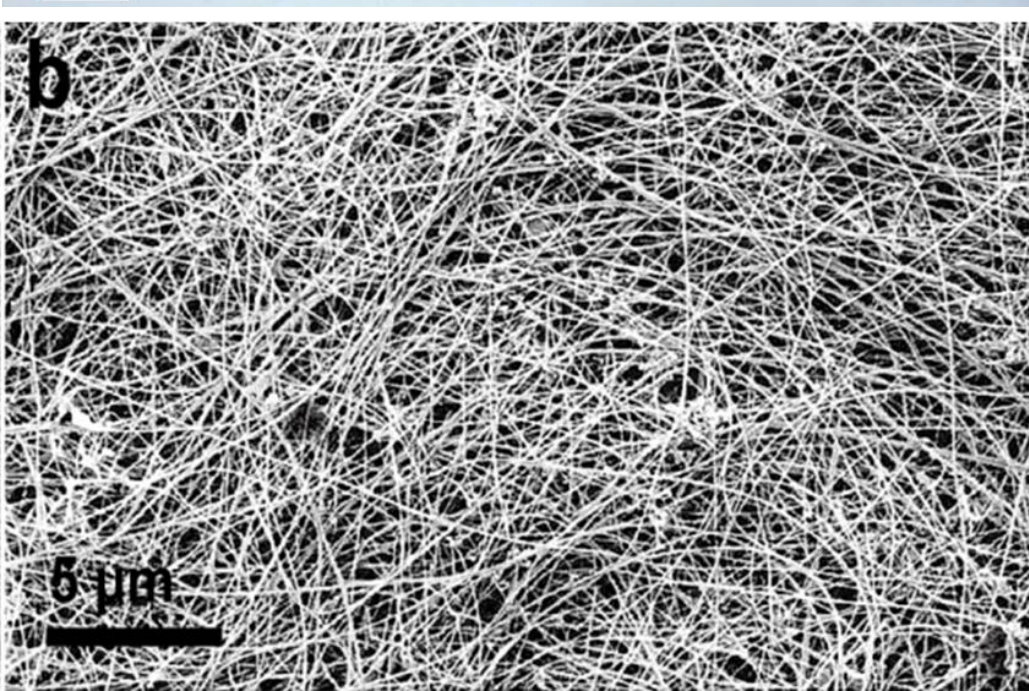
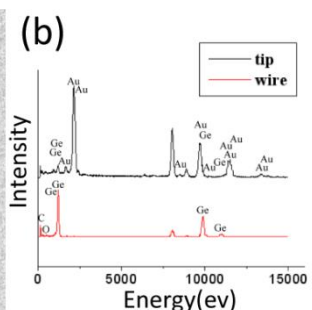
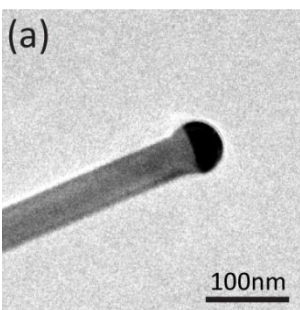
# Our approach: alkanethiol-passivated Ge nanowires as LIB anode



Organic surfactant can make a better bonding with PVdF (binder) to form good composites

Nanowire structure can tolerate relaxed mechanical strain

# Germanium nanowires for LIB applications





METTLER TOLEDO

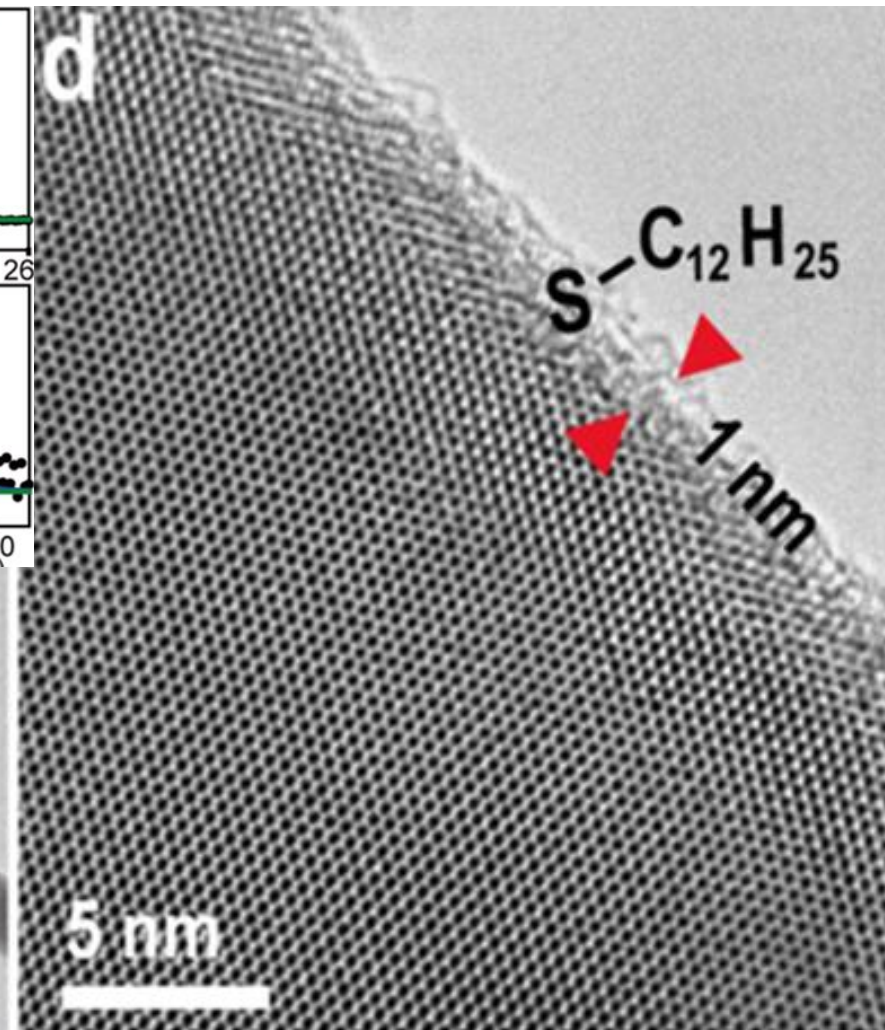
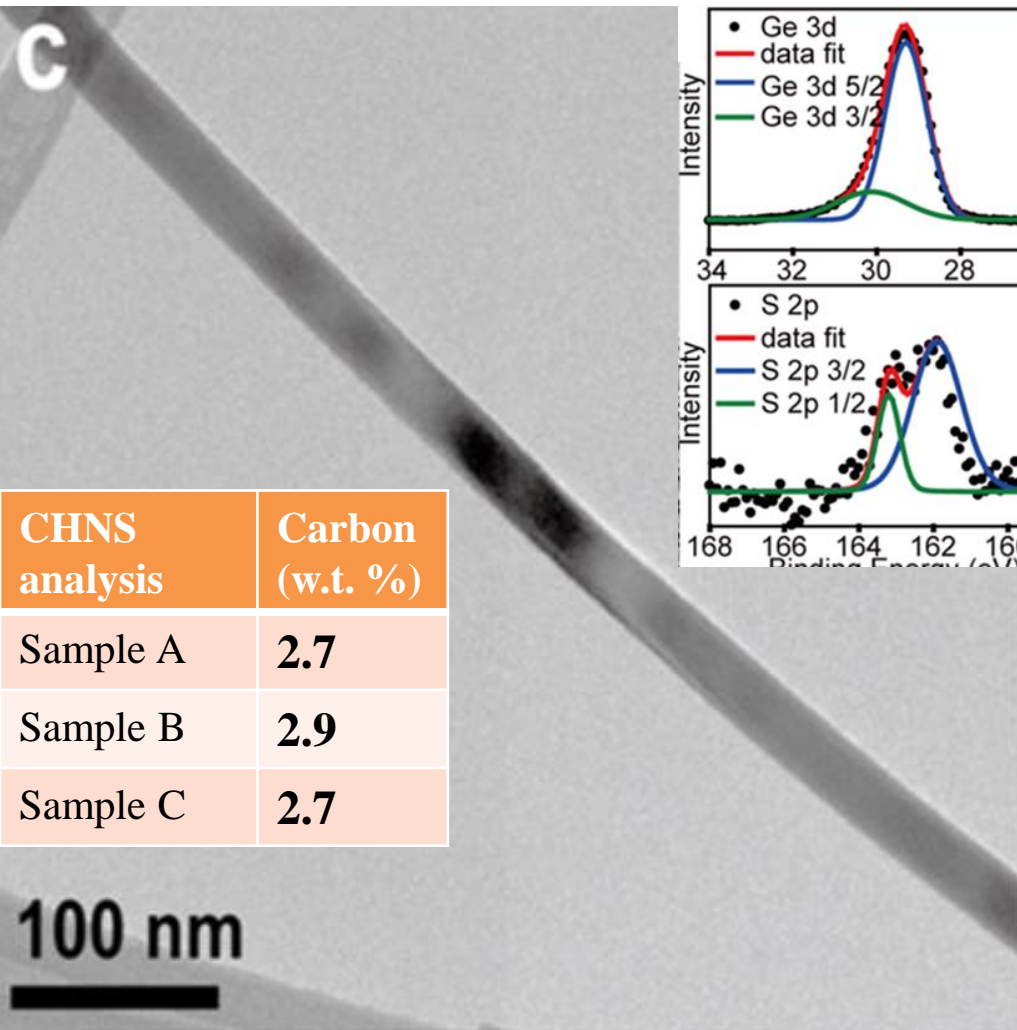
0.0885 g

→0/T←

g

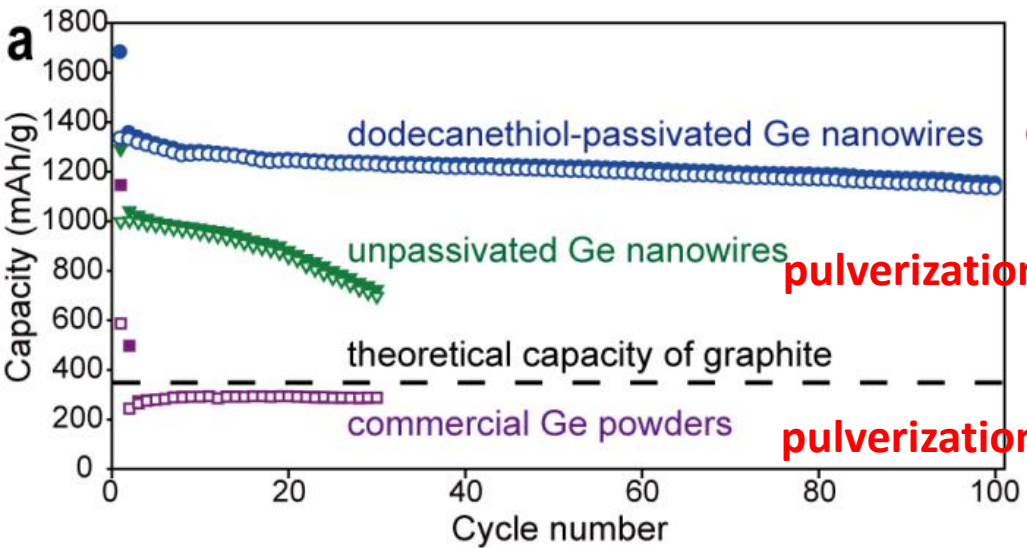
100

# Alkanethiol-passivated Ge nanowires





# Performance of Ge nanowire anode

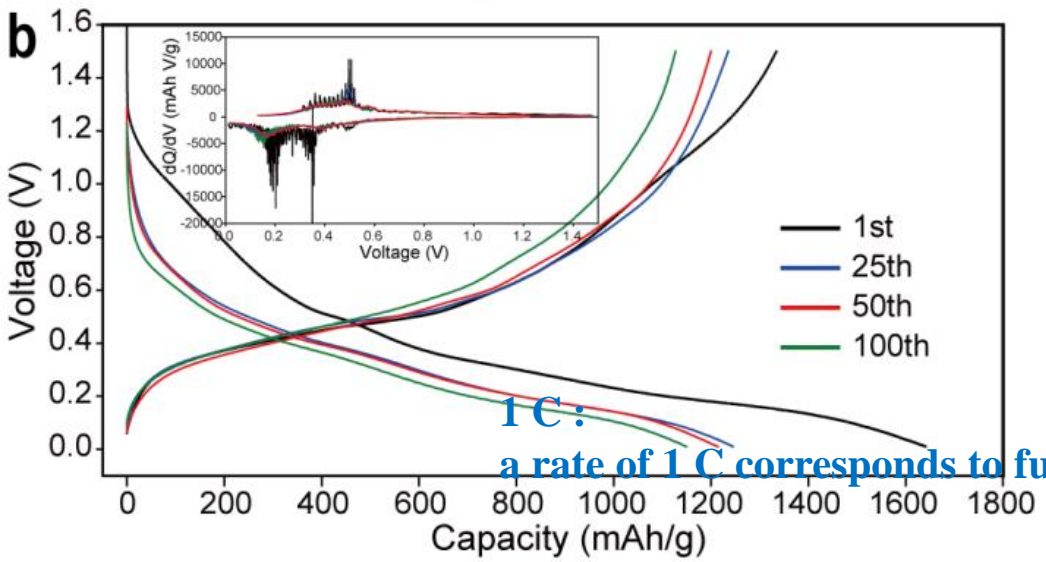


Good capacity retention

pulverization

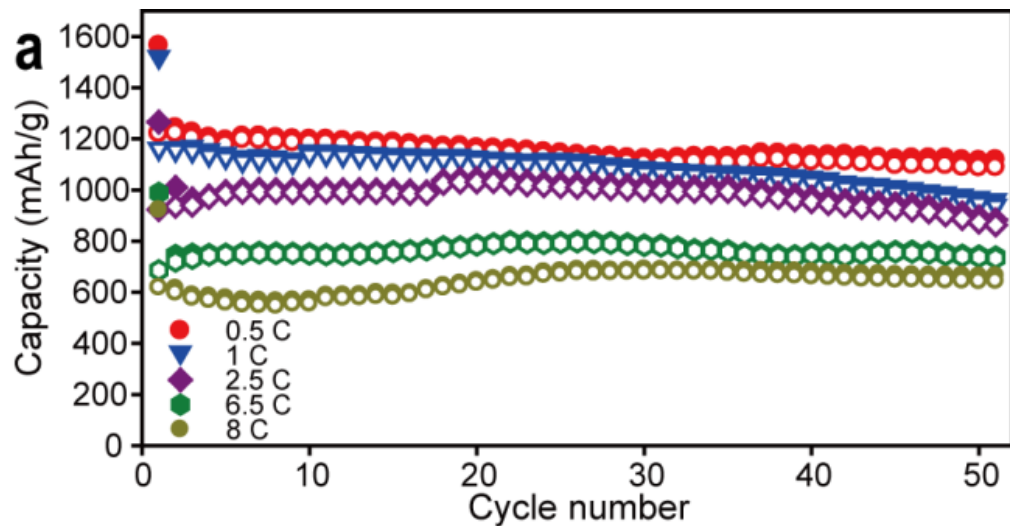
pulverization

1130 mAh/g  
(~3 times higher than graphite)

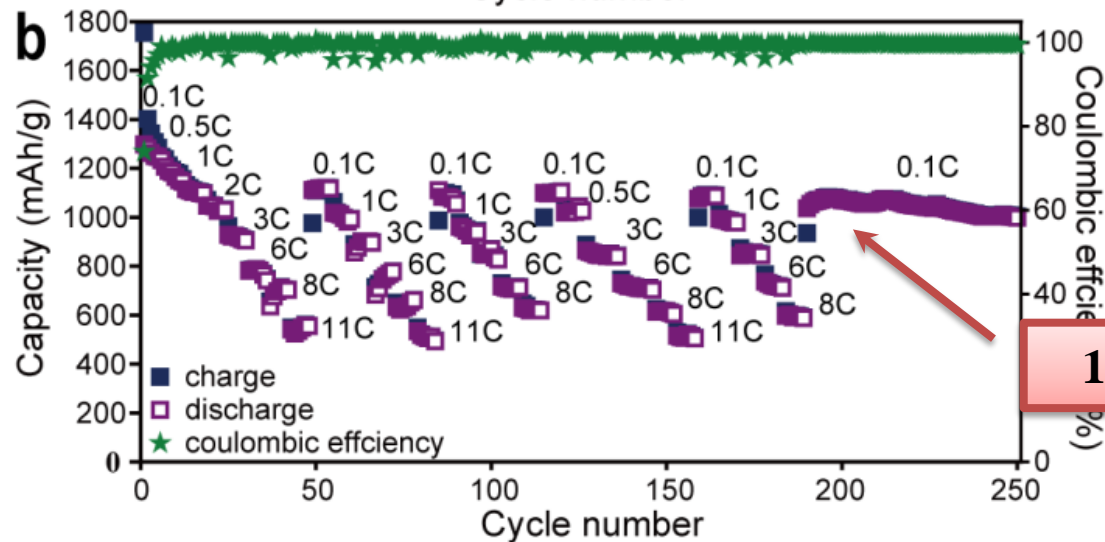


1 C: a rate of 1 C corresponds to full charge or discharge in 1 hour

# High-rate capability of Ge nanowire anode

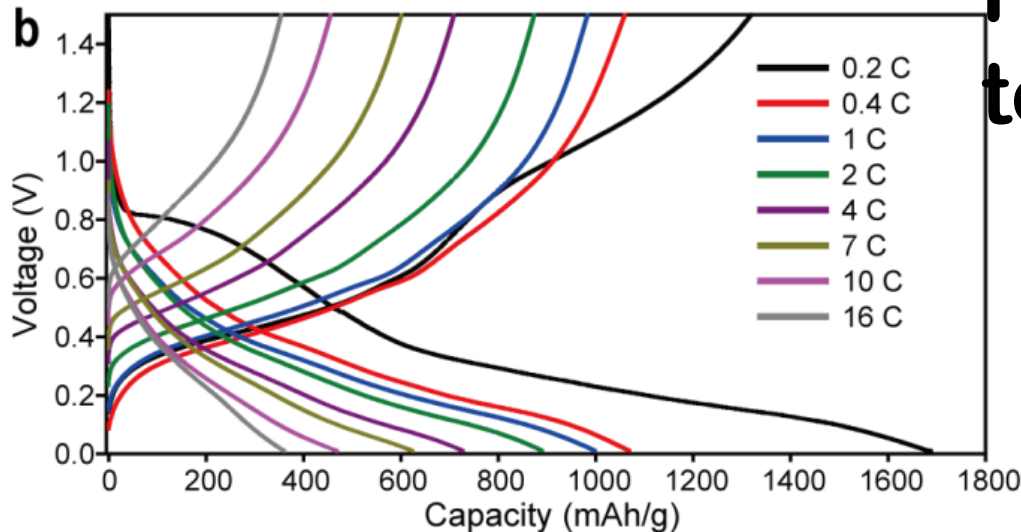
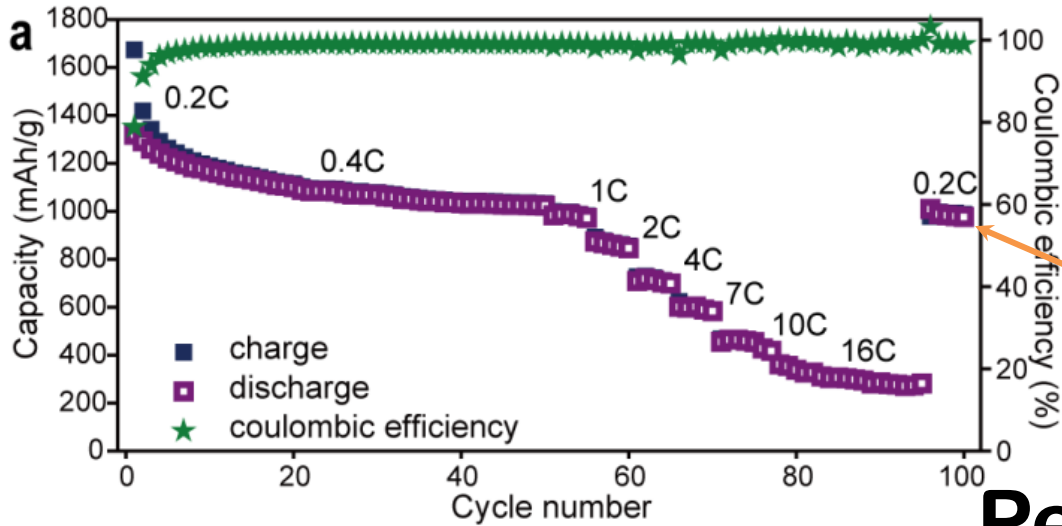


Current (rate)	Capacity (mAh/g)	Cycle number
0.1C	1130	100
0.5C	1090	50
2.5C	863	50
6C	733	50
8C	643	50



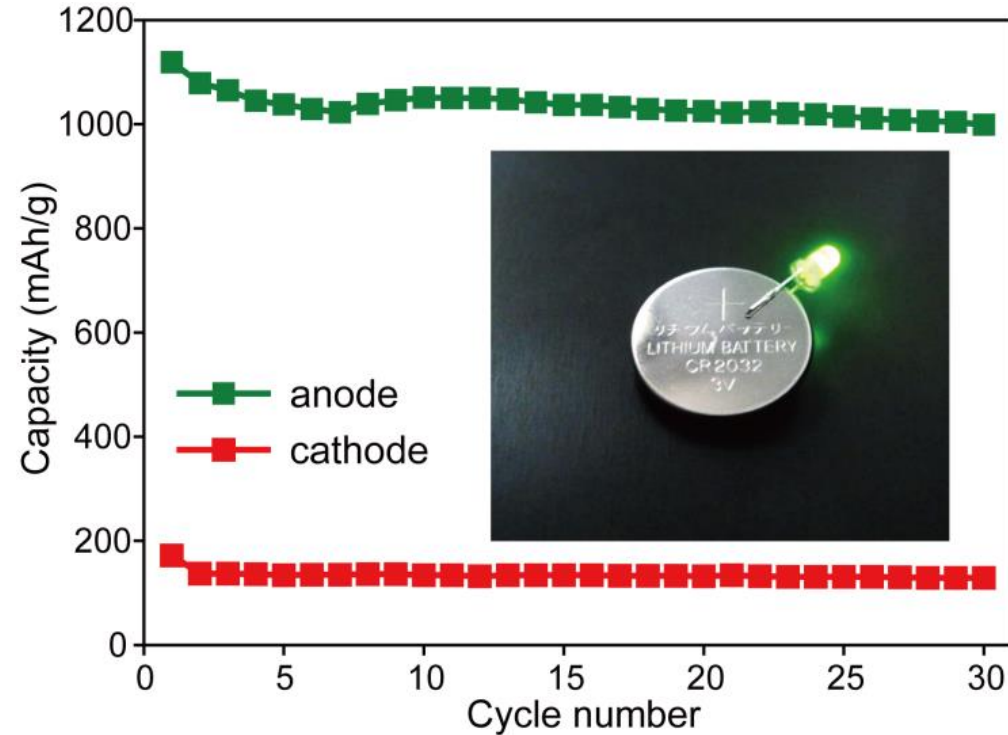
1000 mAh/g

# High-temperature performance (55 °C) of Ge nanoiwre anode



Performance similar to room temperature

# Performance of a Full Cell

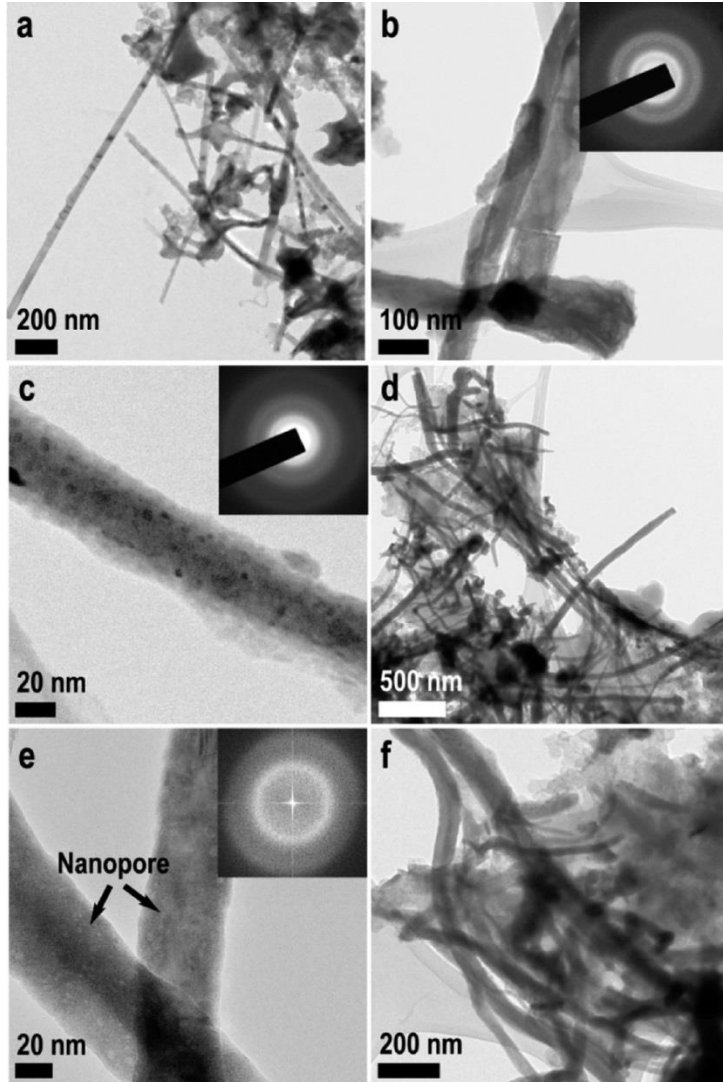


	anode	cathode
<b>Material</b>	GeNWs	LFP
<b>Loading</b>	~ 1 mg/cm <sup>2</sup>	~ 8 mg/cm <sup>2</sup>
<b>Capacity</b>	1100 mAh/g	140 mAh/g

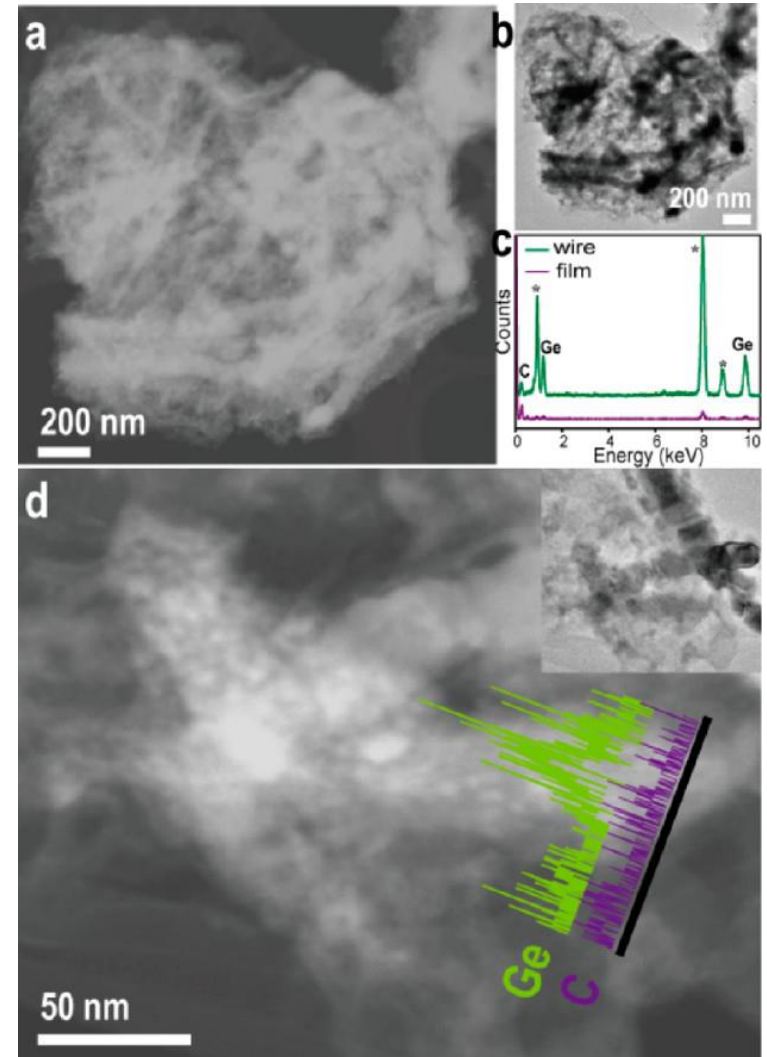
**Capacity versus cycle number of a coin full cell between 2.0 and 3.8 V with dodecanethiol-passivated Ge nanowire as the anode and LiFePO<sub>4</sub> as the cathode**

# Structure evolution of dodecanethiol-passivated Ge nanowires

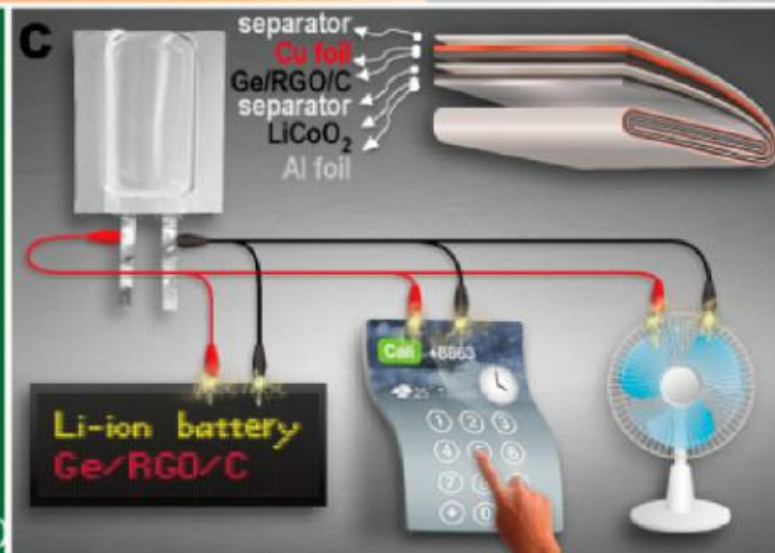
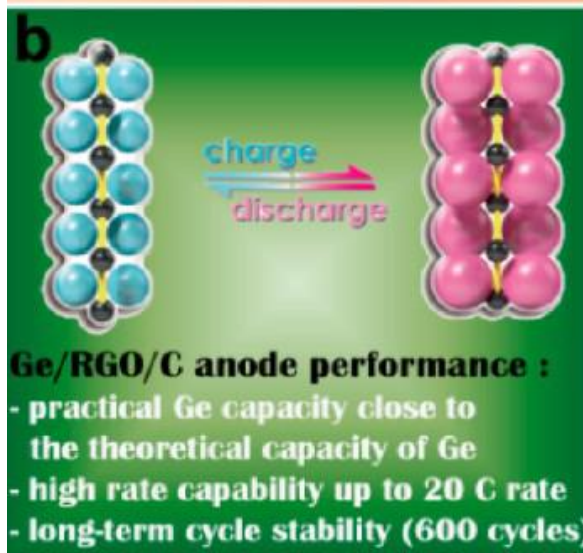
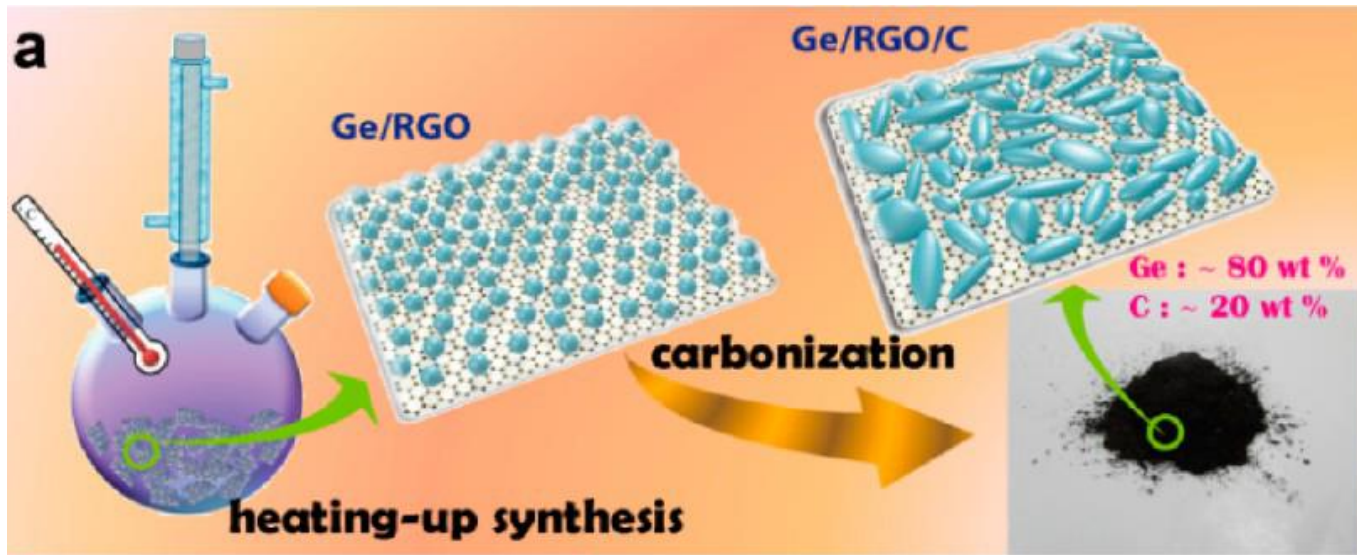
During lithiation/delithiation process



After 100 cycles at 0.1 C

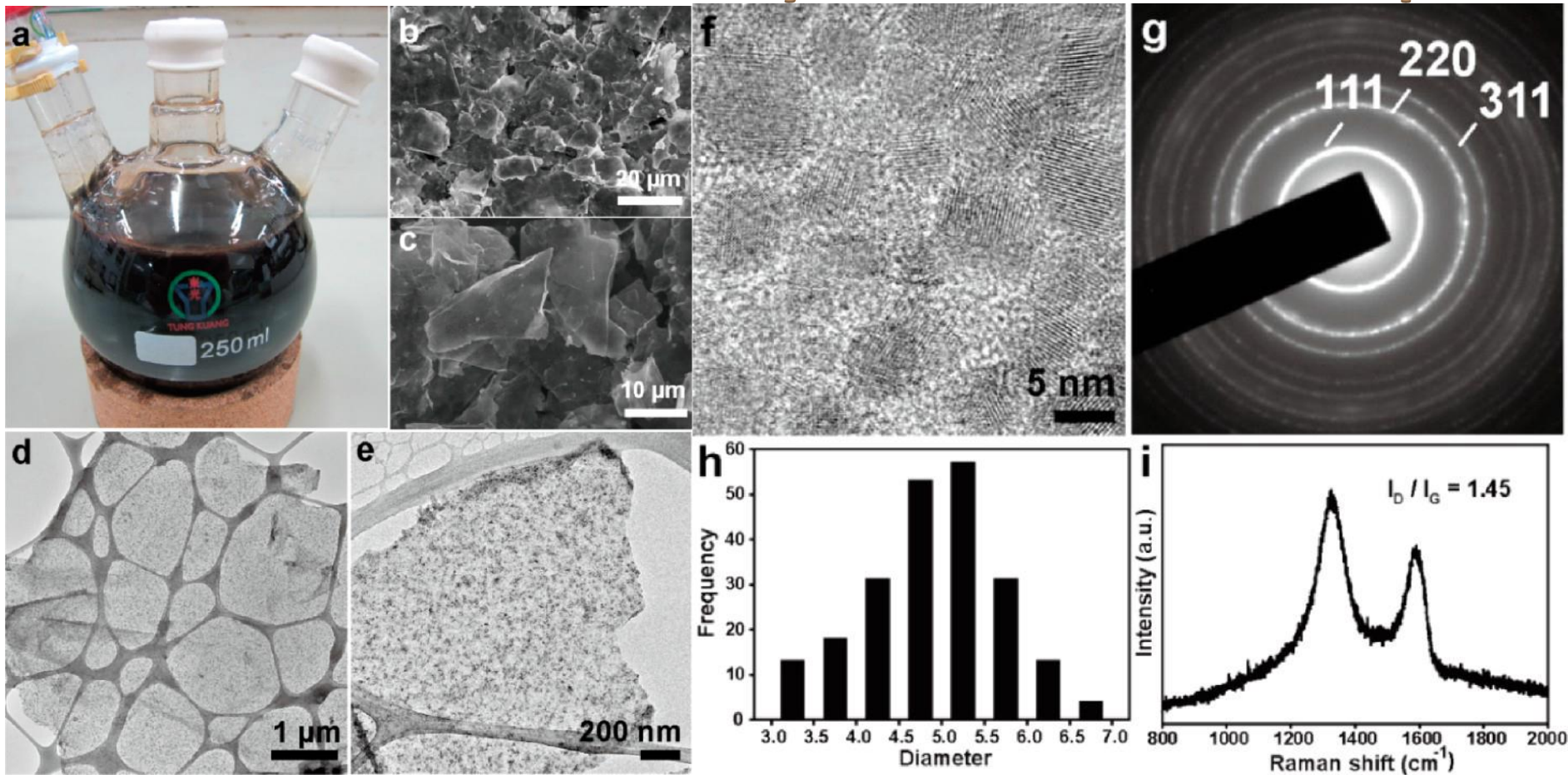


# Reduced Graphene Oxide as a supportive materials for performance improvement of high-capacity lithium ion materials



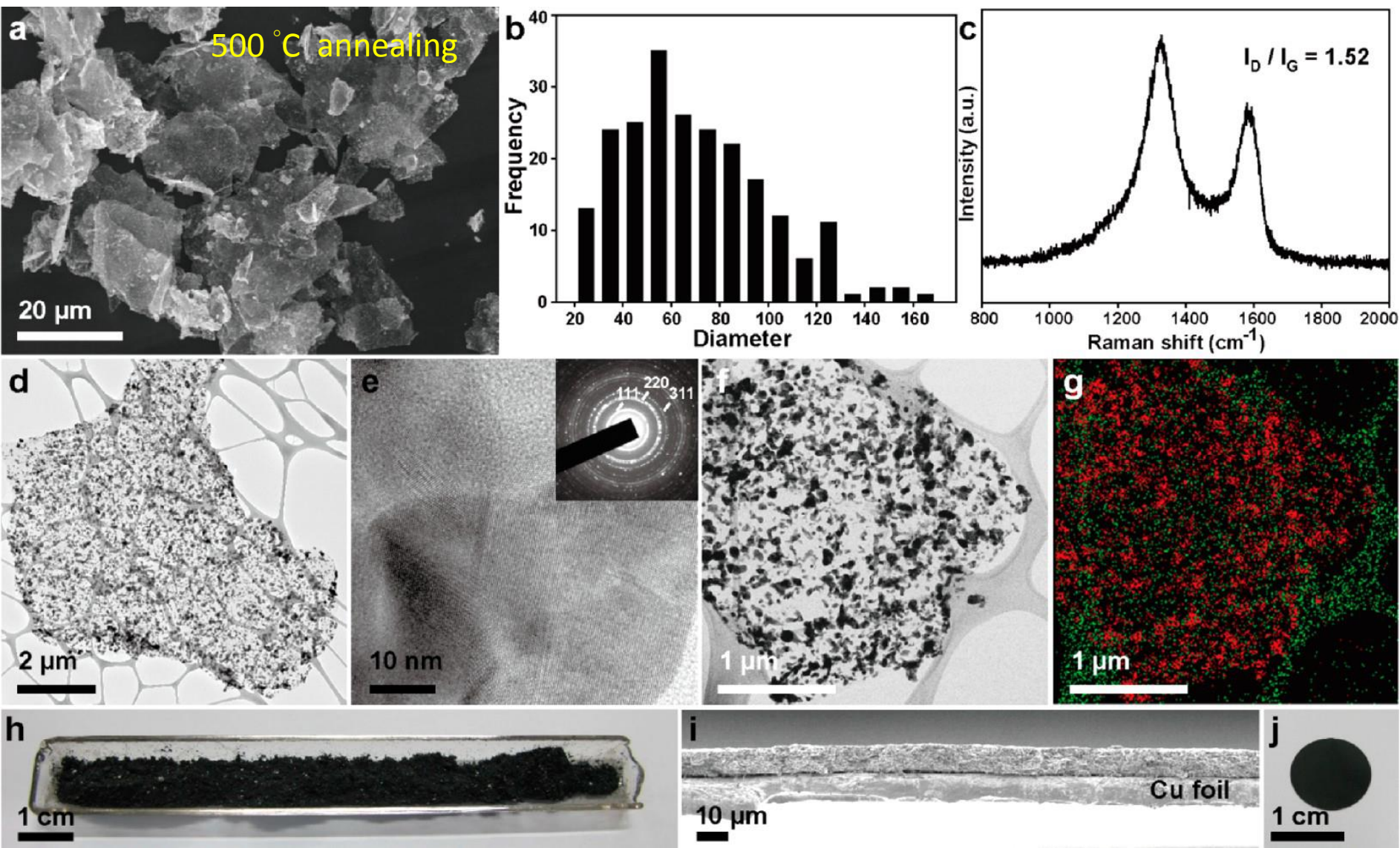
# Ge/RGO nanocomposites

Large-scale synthesis Crystalline & monodisperse



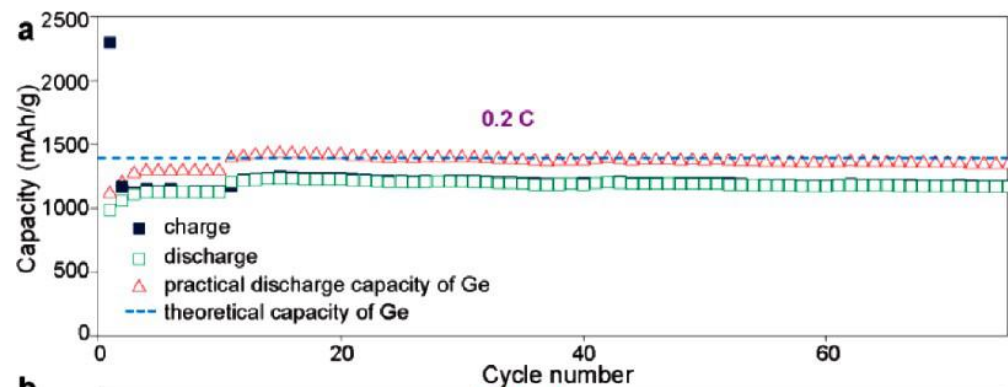
High-density coverage Small, uniform distribution

# Ge/RGO/C nanocomposites

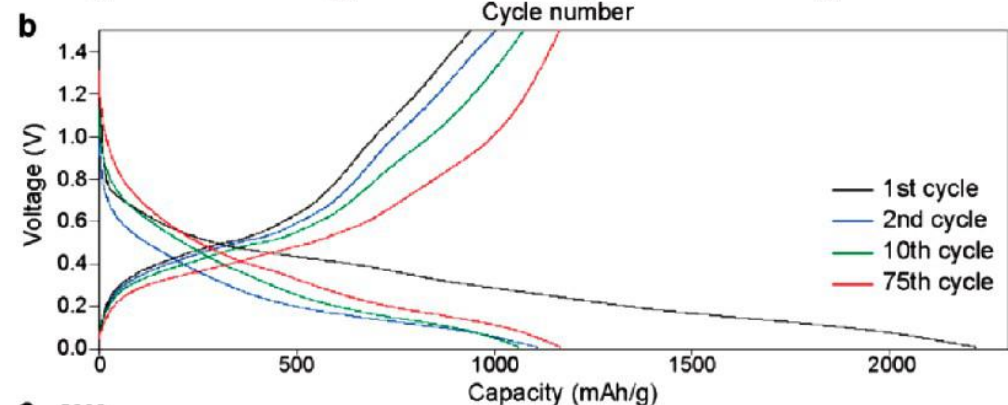




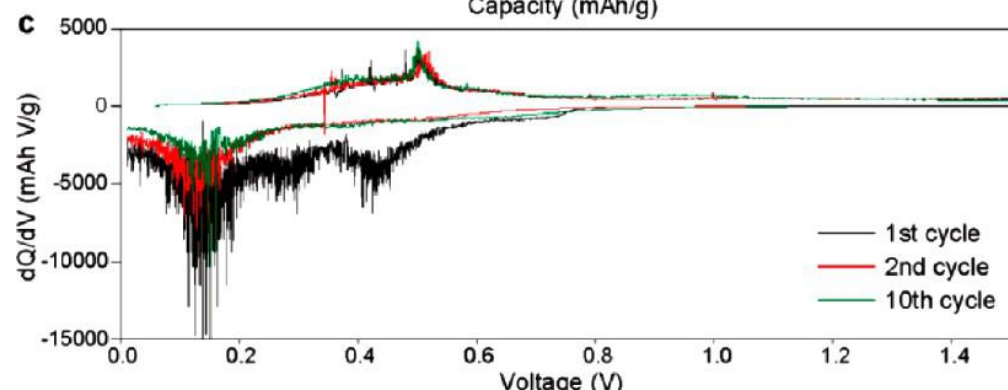
# LIB Performance of Ge/RGO/C



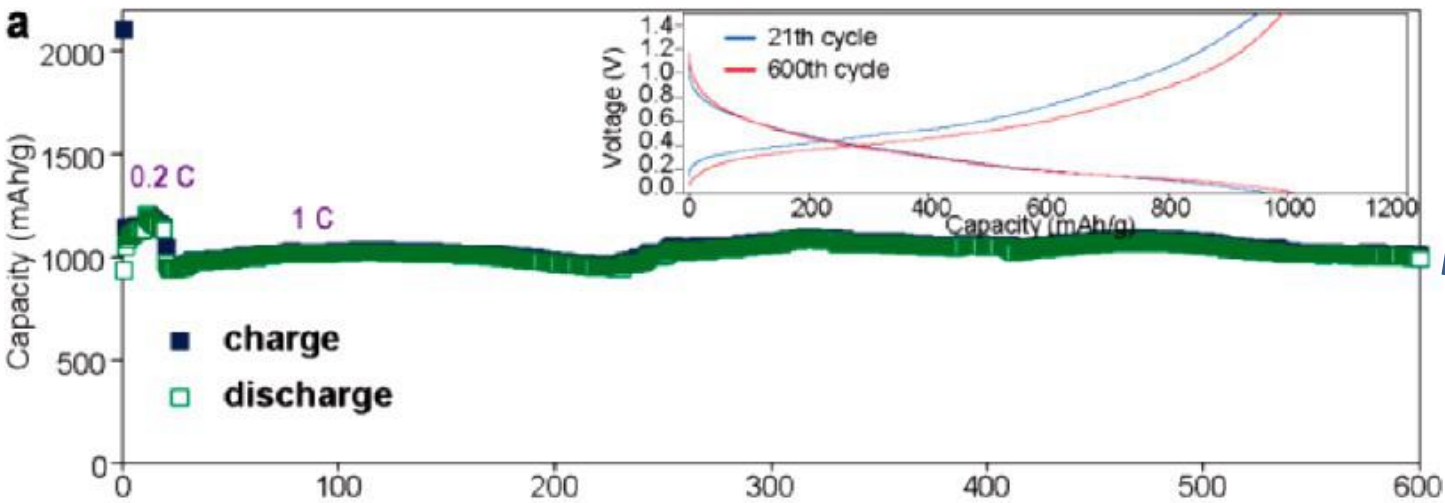
1332 mAh/g over 75 cycles  
~96% of theoretical capacity  
of germanium (1384 mAh/g)



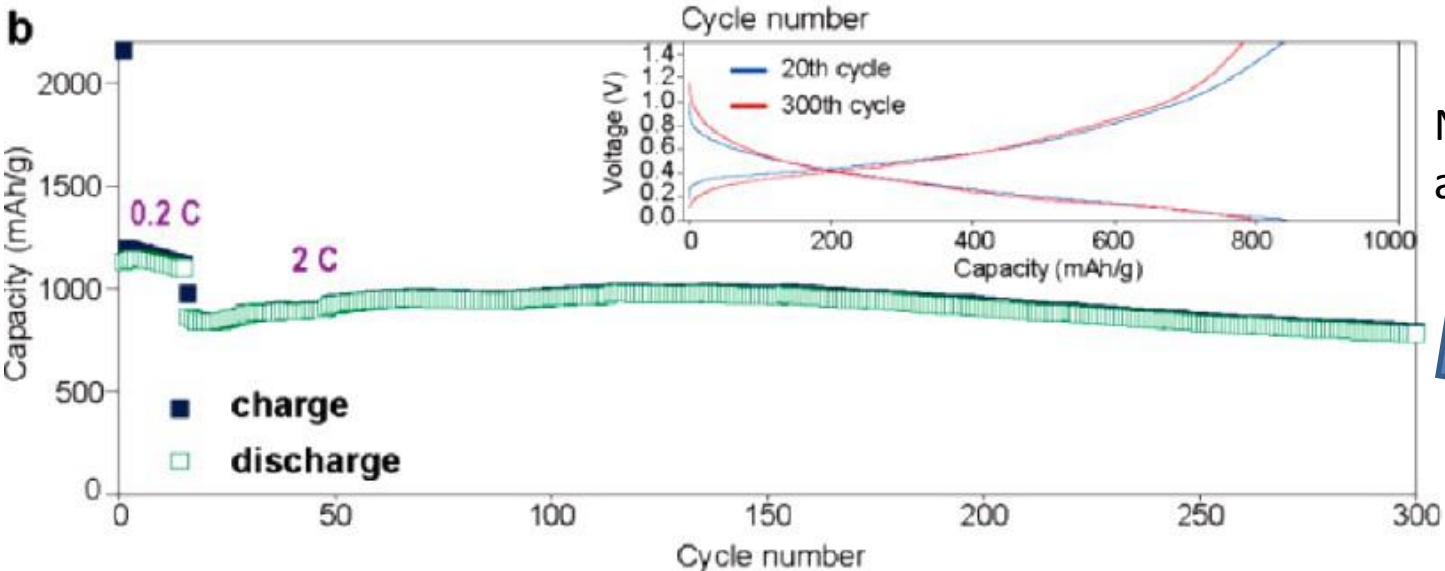
Very consistent electrochemical  
properties



# Cycling performance at 1C

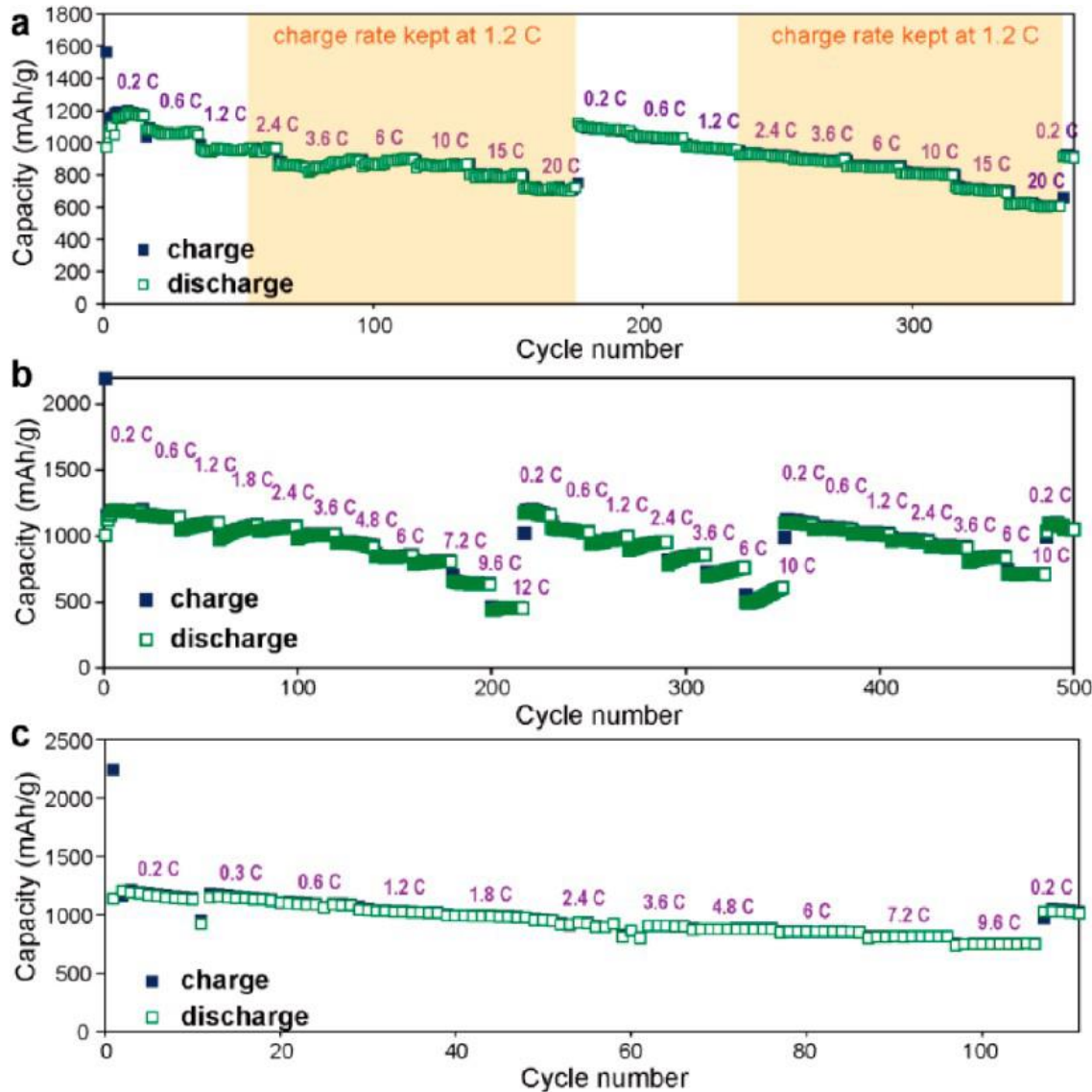


No capacity decay after 600 cycles at 1C

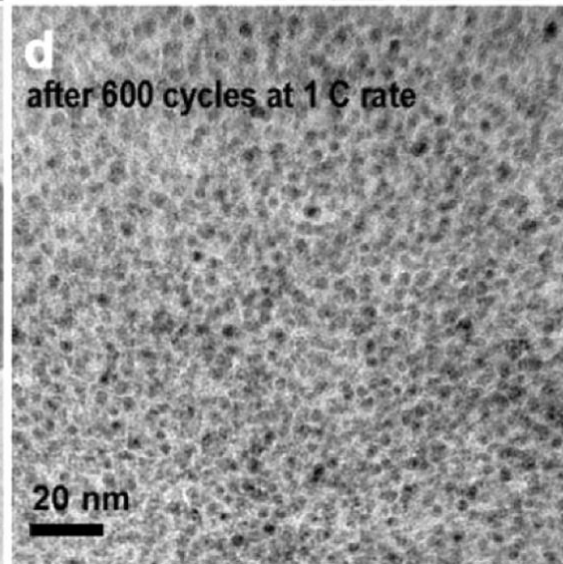
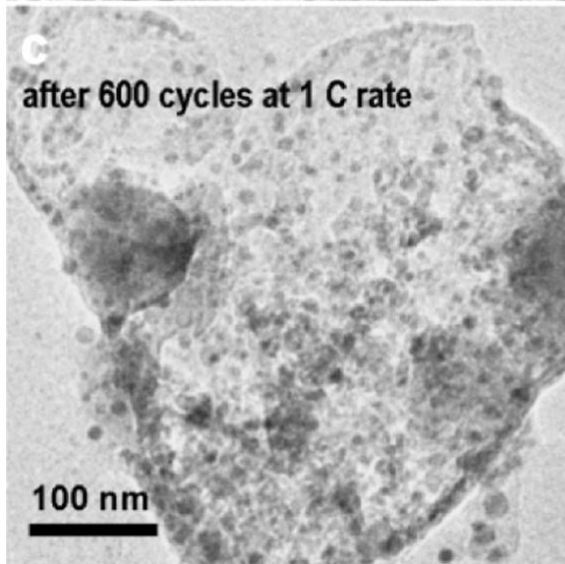
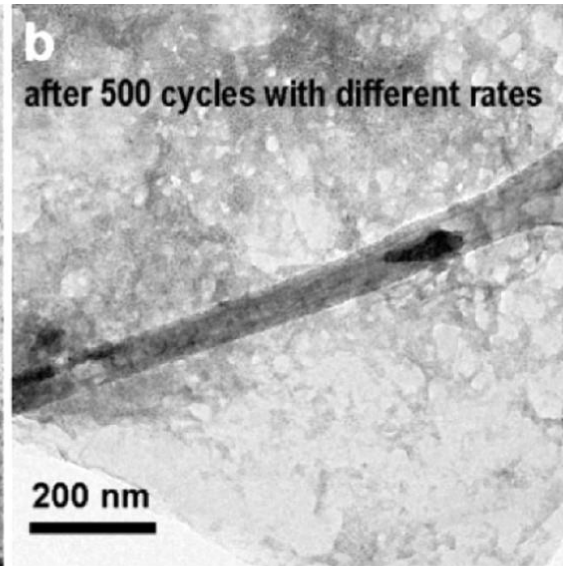
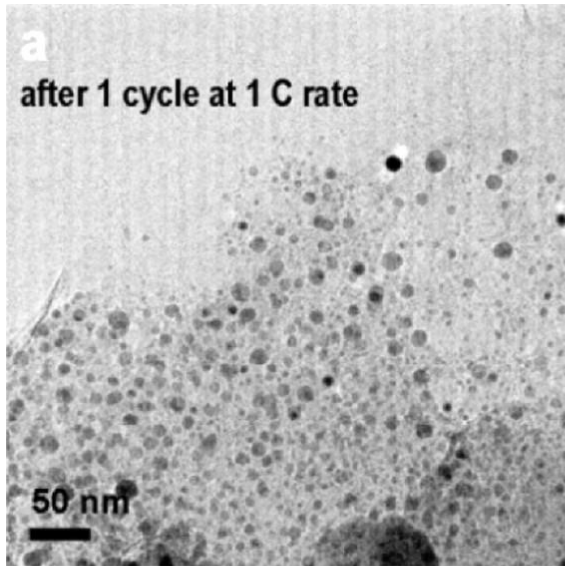


No capacity decay after 300 cycles at 2C

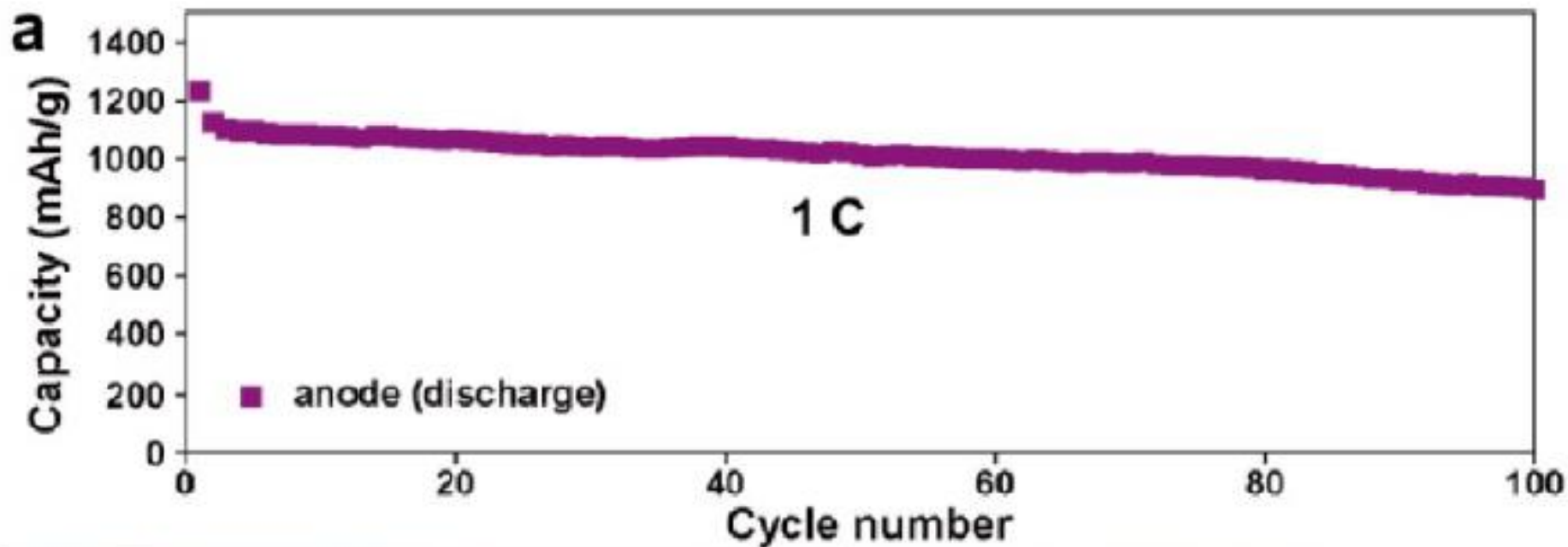
# Cycling performance at high rates



# Robust Ge/RGO/C nanocomposites



# Full cell performance



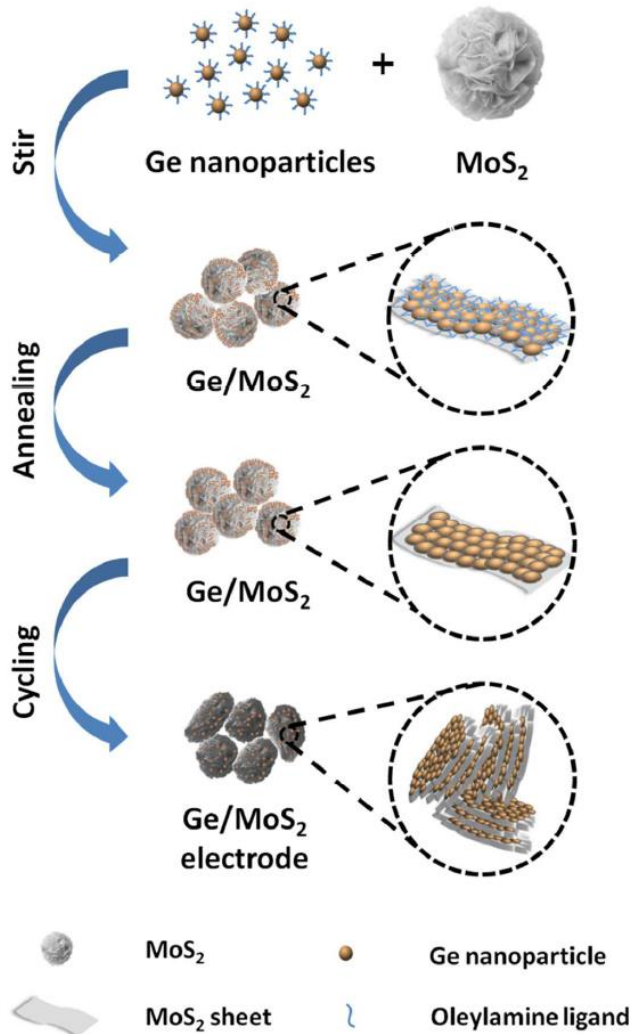
**Capacity versus cycle number of a full cell**

**between 2.5 and 4.2 V**

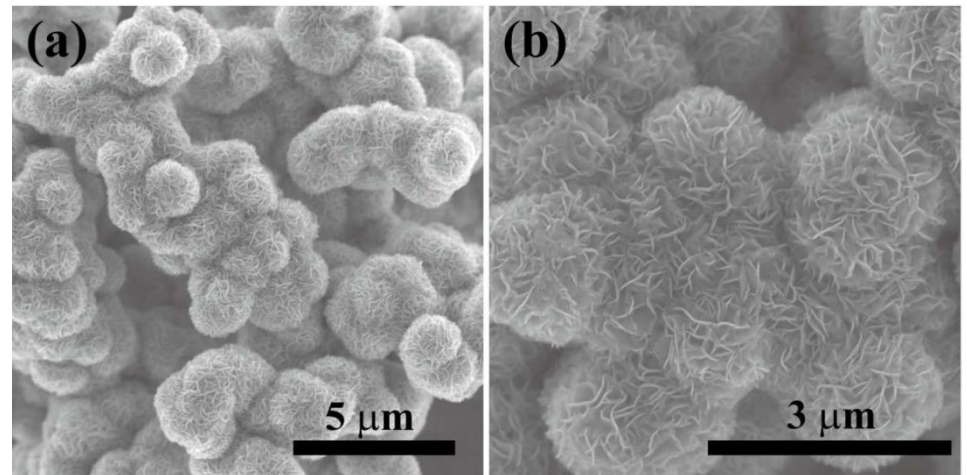
**Anode: Ge/RGO/C**

**Cathode: LiCoO<sub>2</sub>**

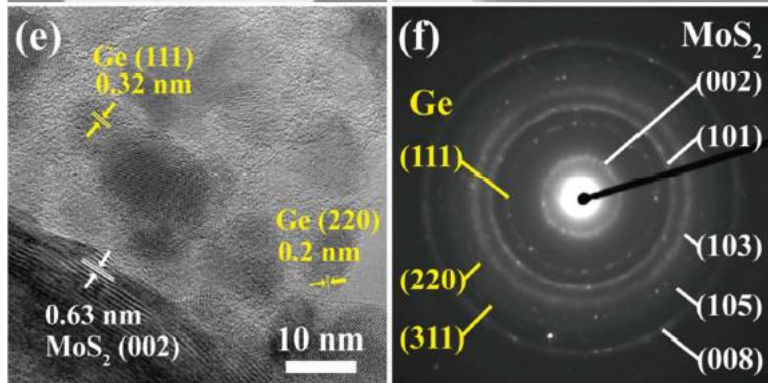
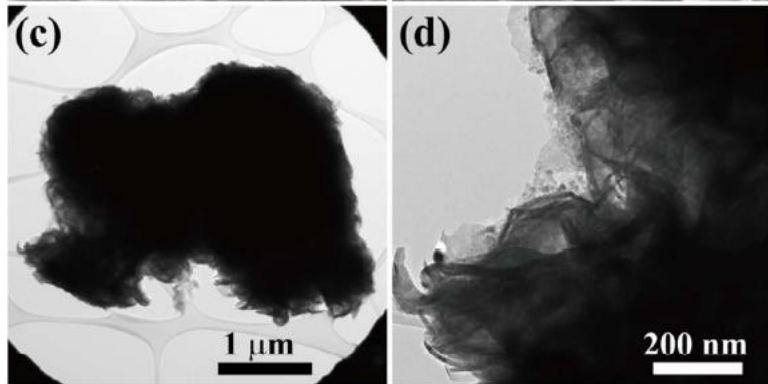
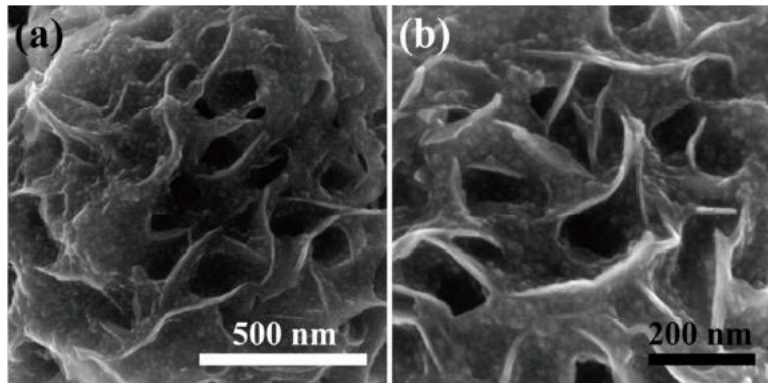
# MoS<sub>2</sub> nanoflower sheets as supportive materials for high-capacity anodes



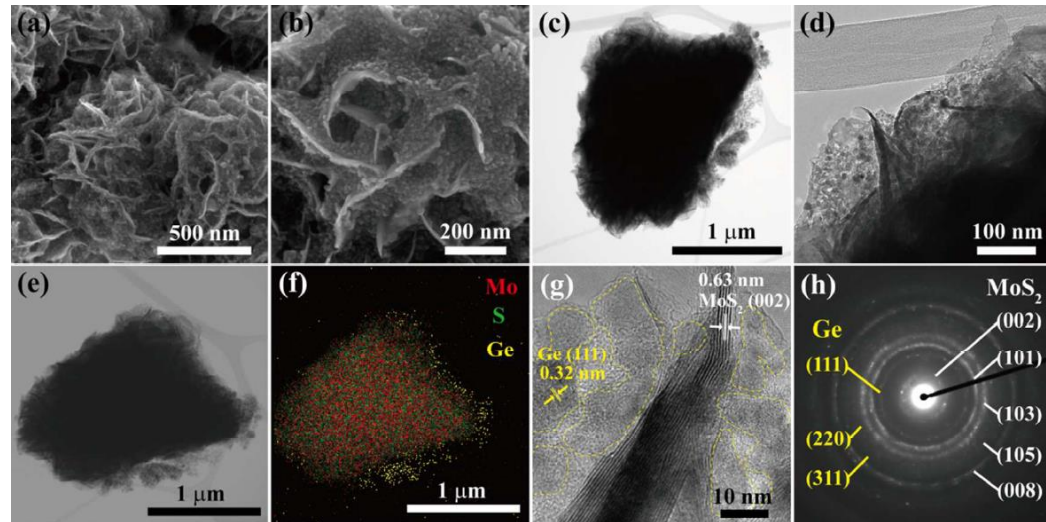
MoS<sub>2</sub> nanoflower sheets



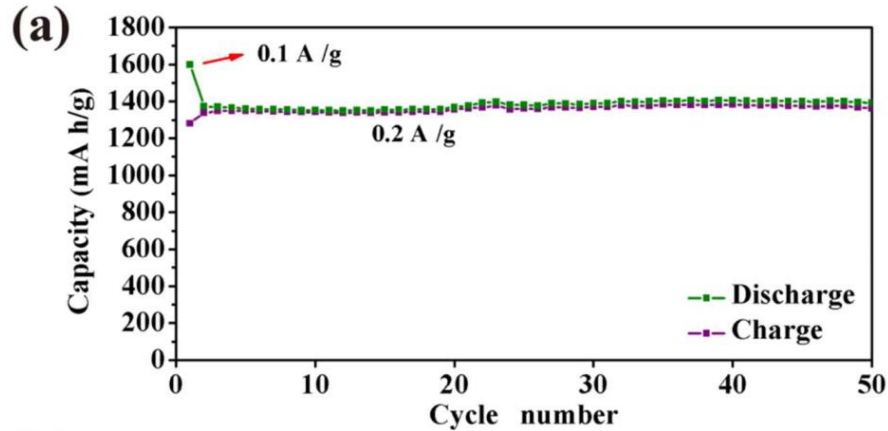
# Ge/MoS<sub>2</sub> and Ge/MoS<sub>2</sub>/C nanocomposite



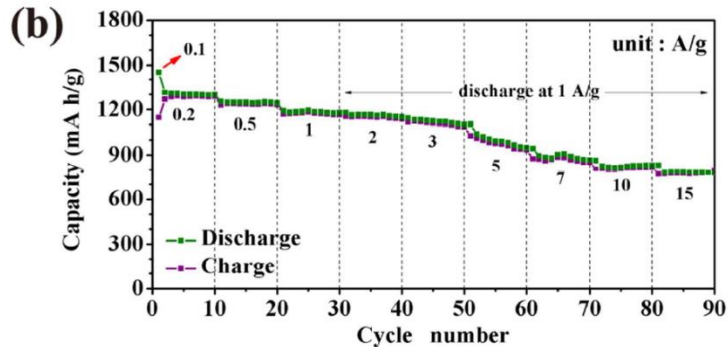
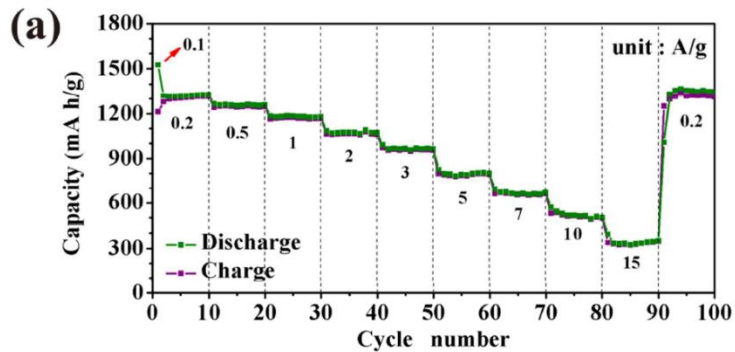
Annealing at 350 °C



# Performance of Ge/MoS<sub>2</sub> nanocomposites

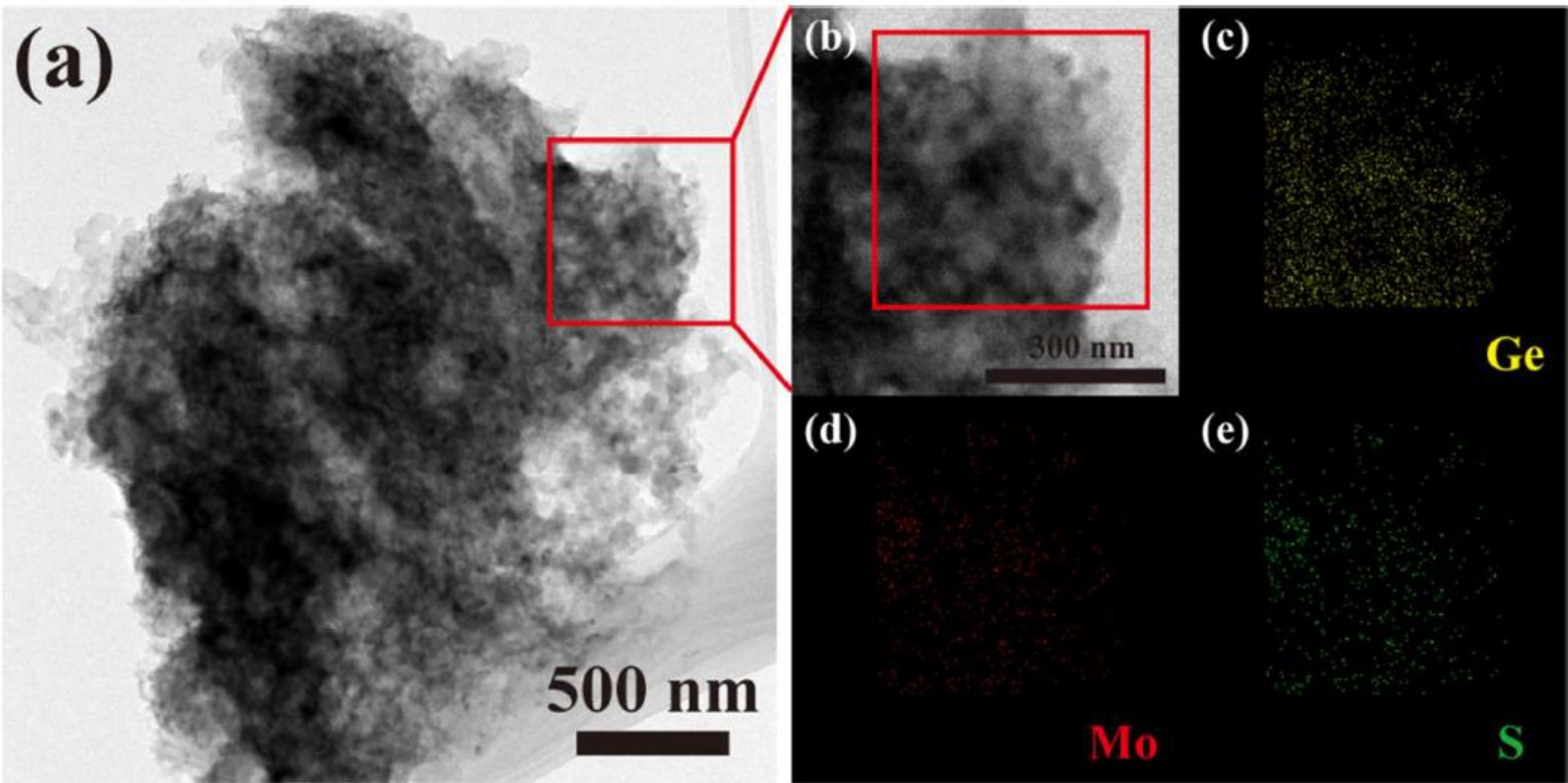


1362 mAh/g: ~98.4% of theoretical capacity of germanium (1384 mAh/g)

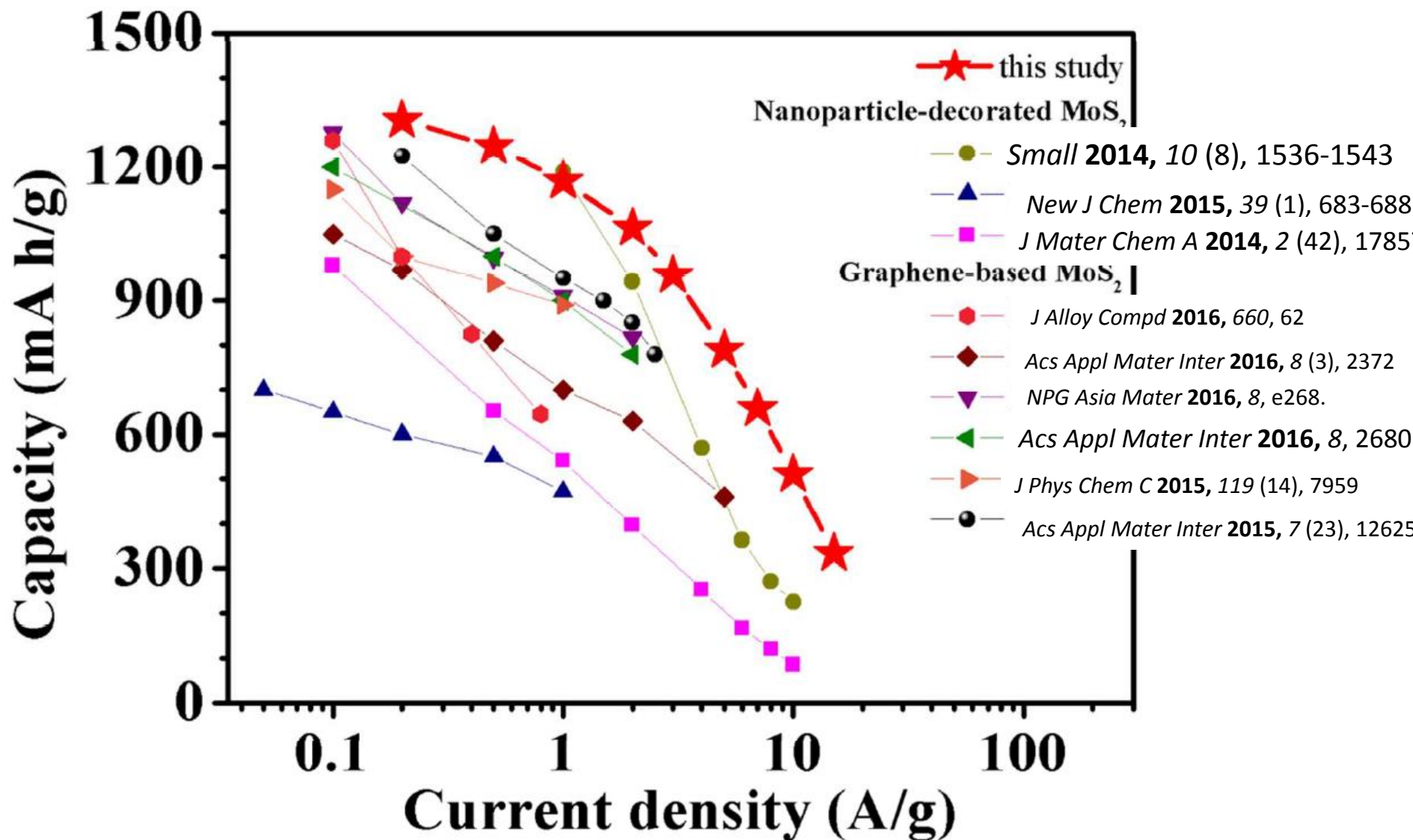




# Structure evolution of Ge/MoS<sub>2</sub> composites after cycling

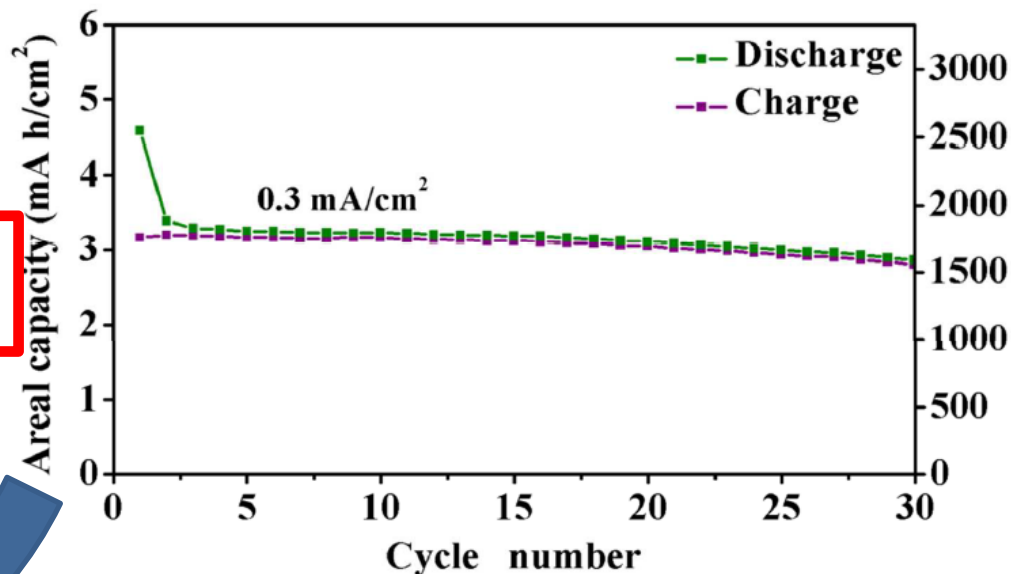


# Performance comparison with other work



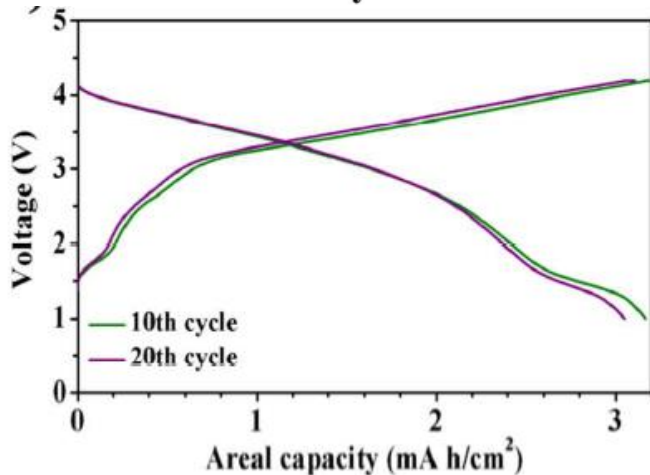
# Full cell with high-areal-volumetric capacity using Ge/MoS<sub>2</sub> as anode

(a)



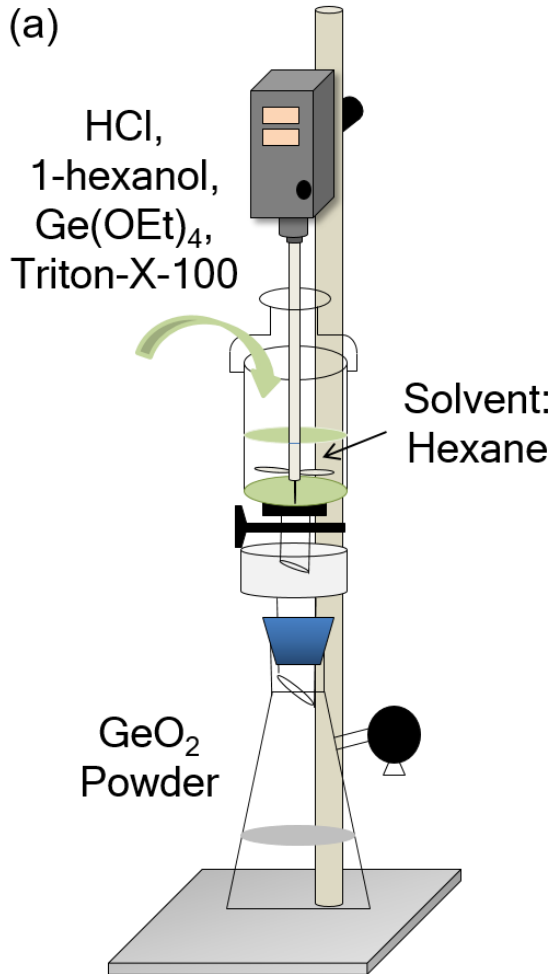
3 mA h/cm<sup>2</sup>  
Areal capacity

Volumetric capacity (mA h/cm<sup>3</sup>)



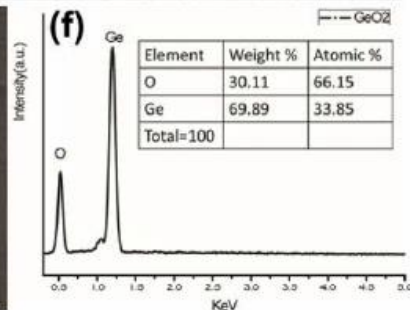
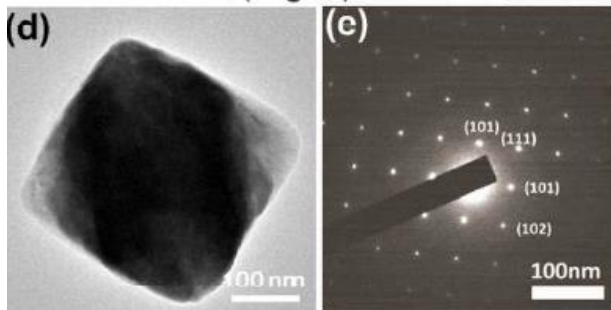
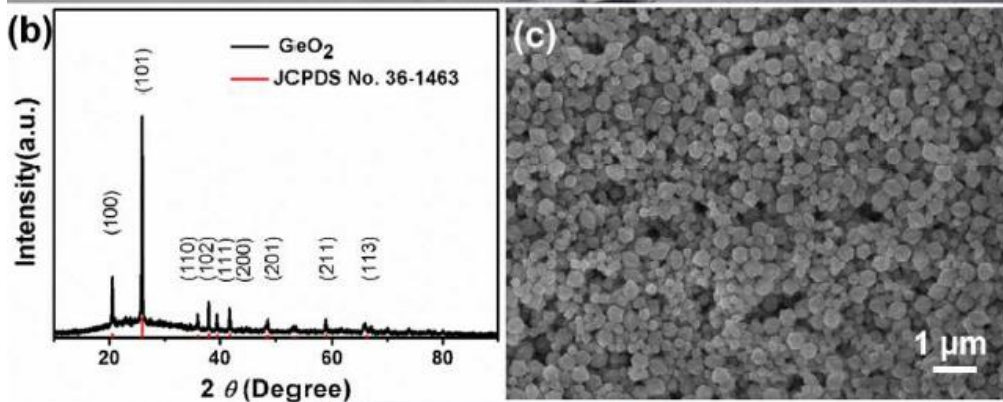
1700 mAh/cm<sup>3</sup>,  
several times higher than  
the commercial graphite  
(330-430 mAh/cm<sup>3</sup>).

# GeO<sub>2</sub> (Germania) nanoparticles



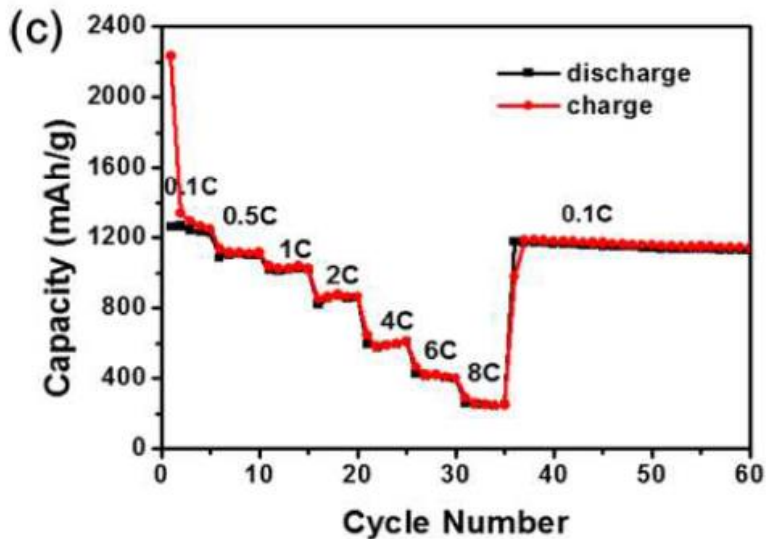
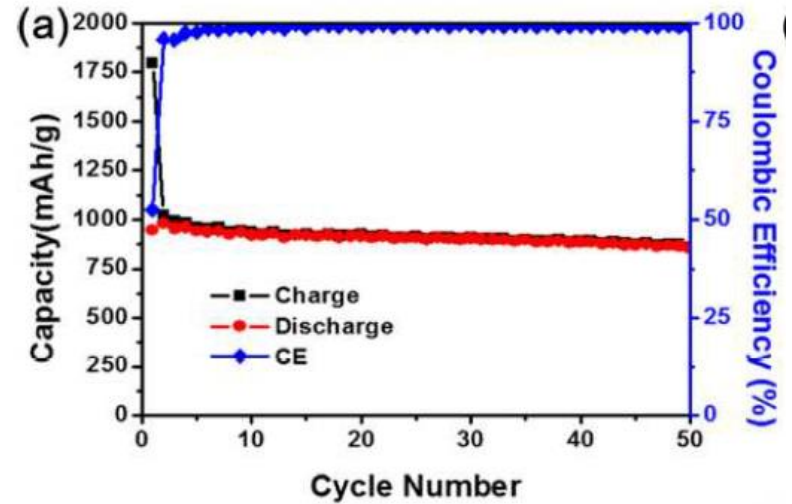
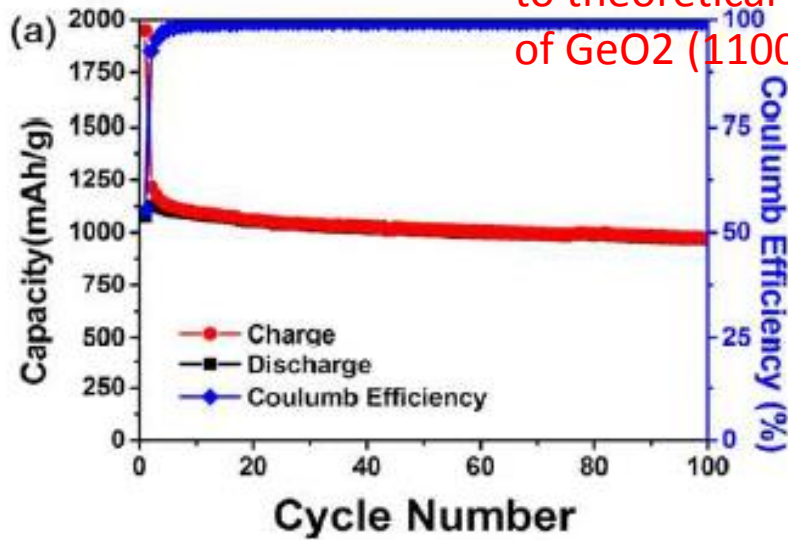
Germania is much less expensive than germanium  
Nearly 100 % yield and good crystallinity germanium oxide (GeO<sub>2</sub>) nanoparticles  
in a reverse micelle system at ambient temperature

# Nearly 100% yield, single crystallinity of germania nanoparticles

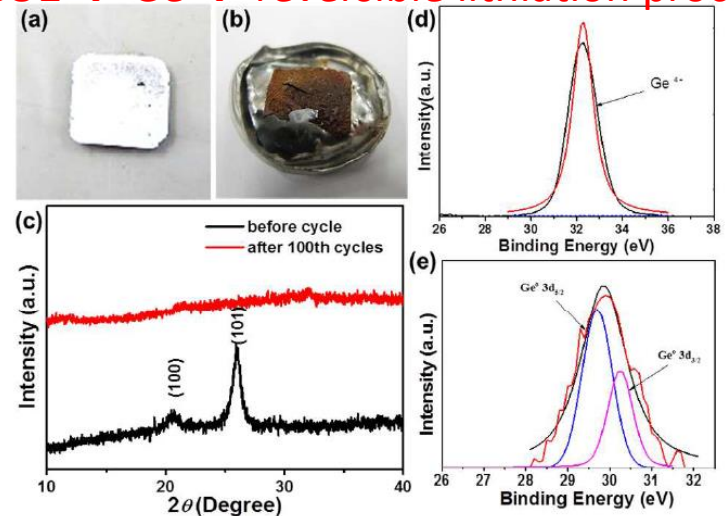


# GeO<sub>2</sub> anode performance

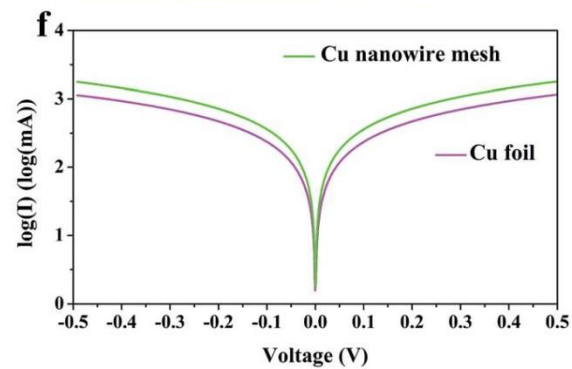
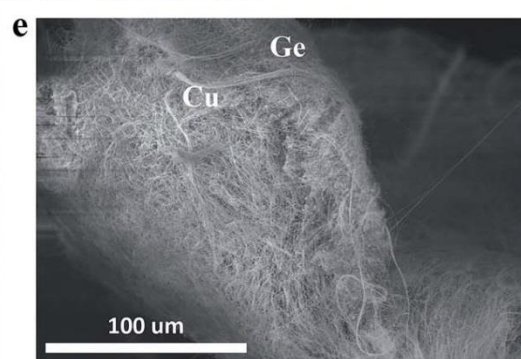
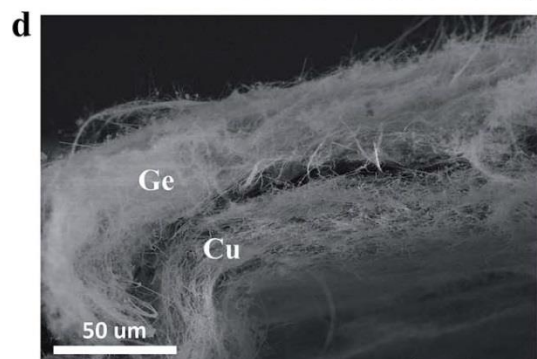
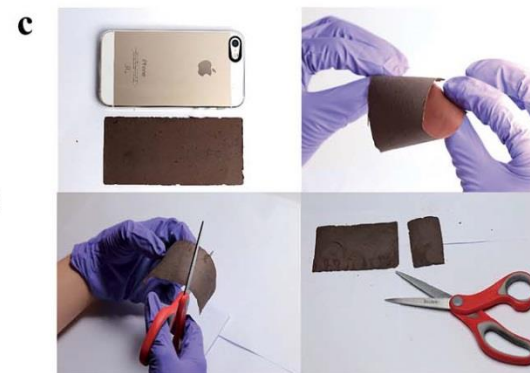
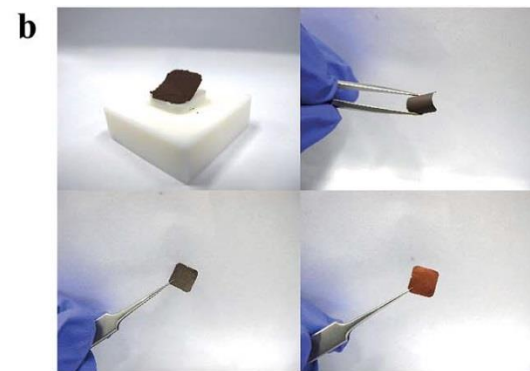
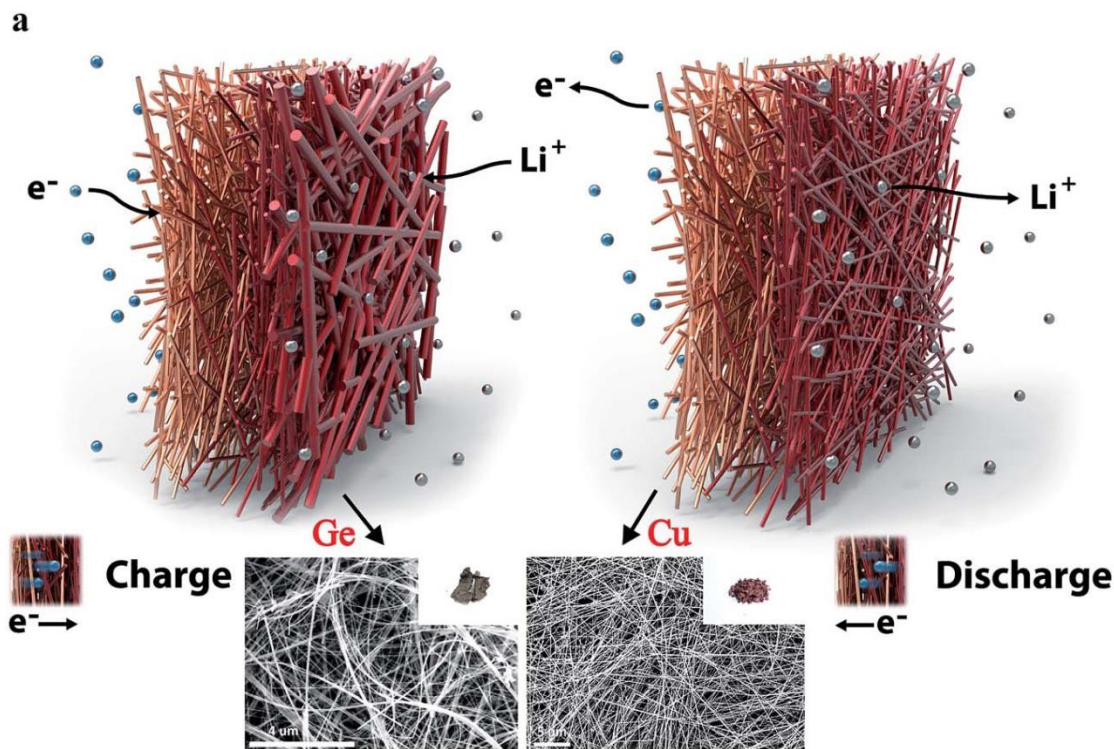
1100 mAh/g · 95.5%  
to theoretical capacity  
of GeO<sub>2</sub> (1100 mAh/g)



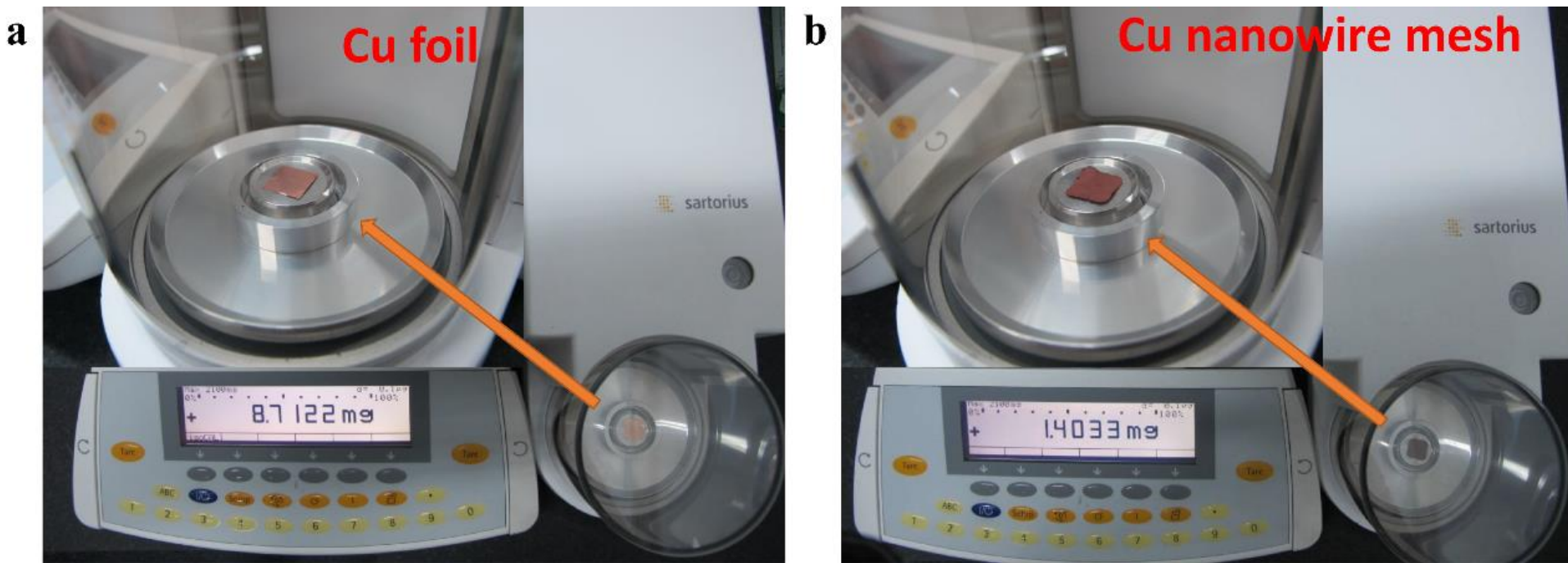
GeO<sub>2</sub> → Ge → reversible lithiation process



# A flexible all inorganic nanowire bilayer mesh as a high-performance lithium-ion battery anode



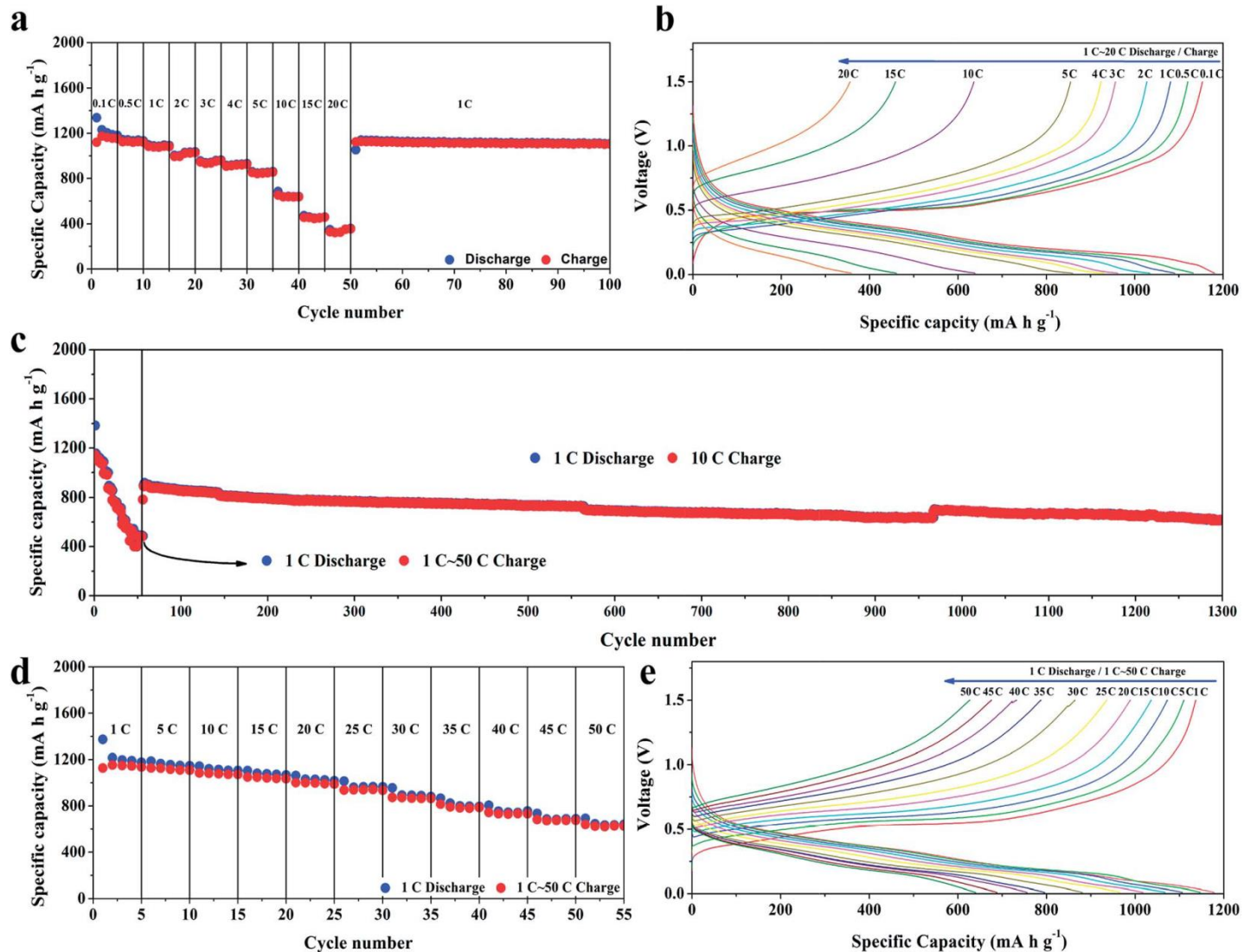
# Photographs of the mass of Cu foil and Cu nanowire mesh



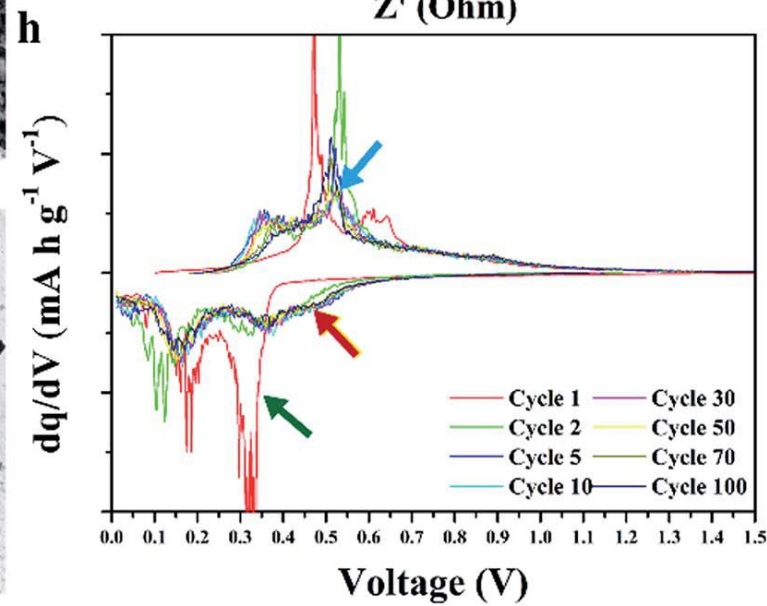
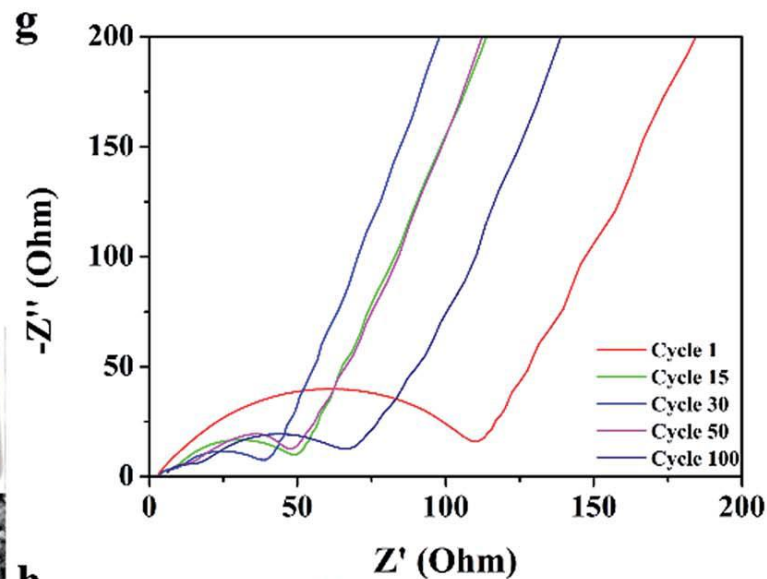
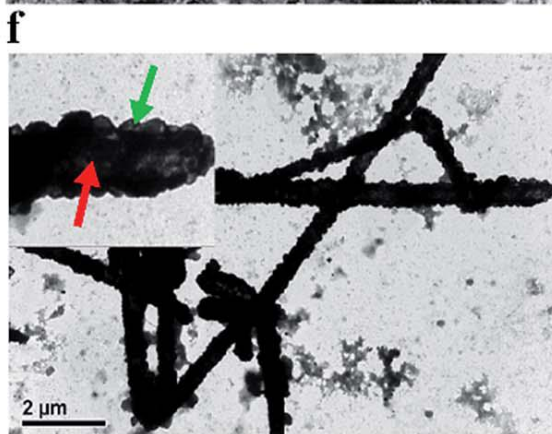
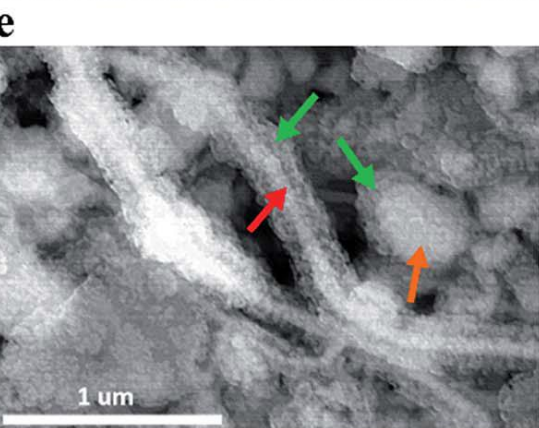
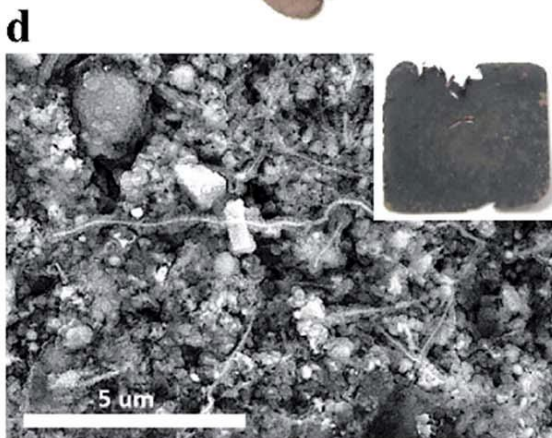
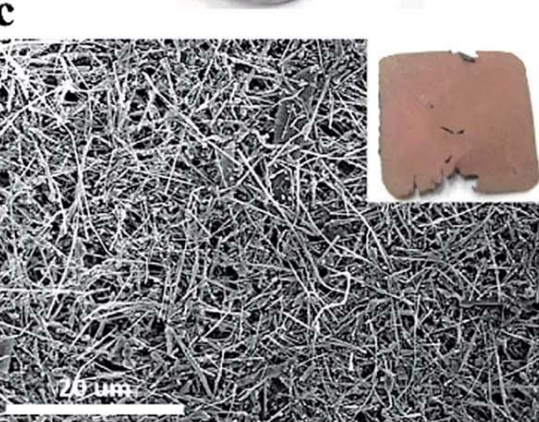
Cu nanowire mesh is only 16% of weight compared to Cu foil



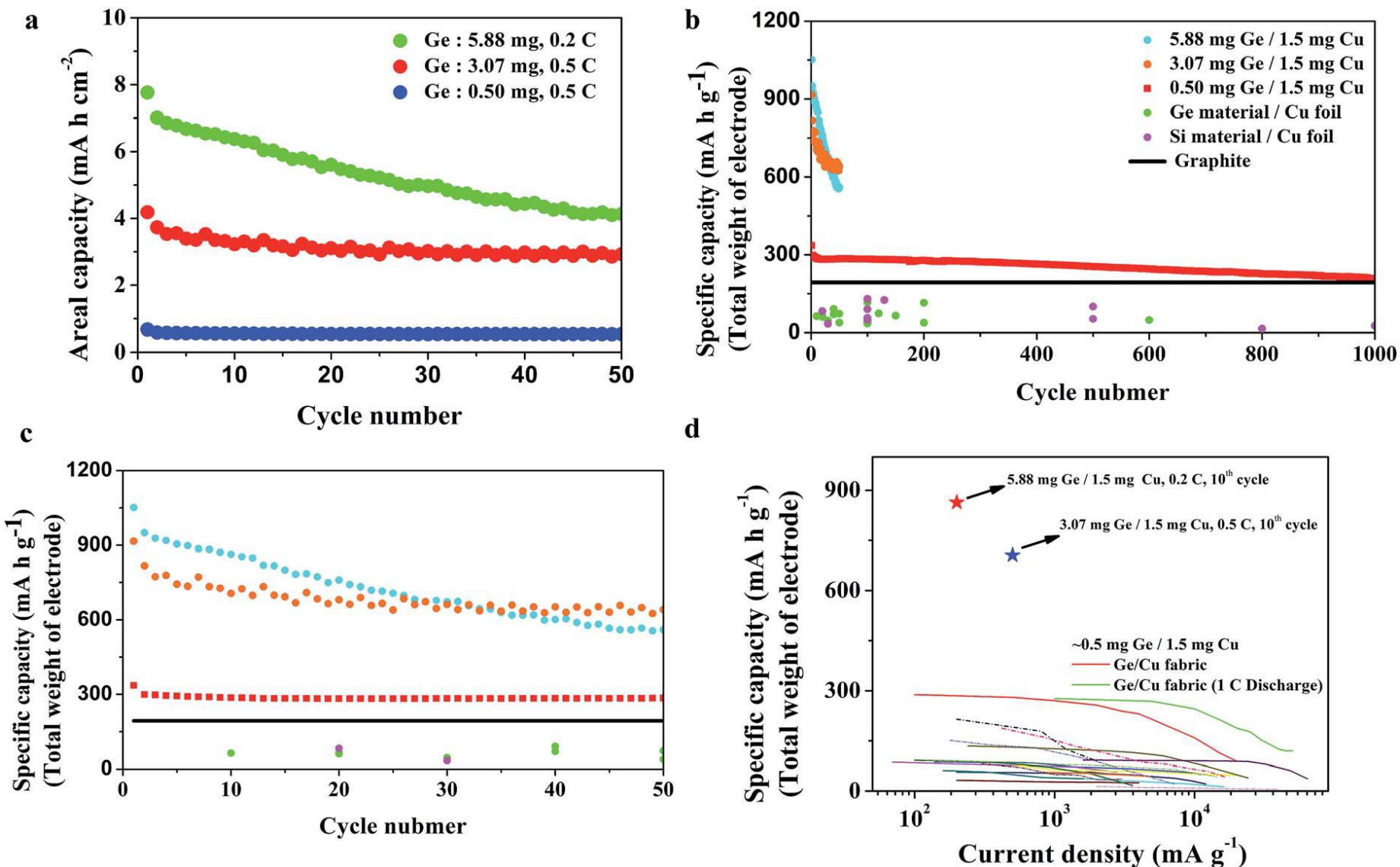
# Cycling performance of Ge/Cu nanowire fabric



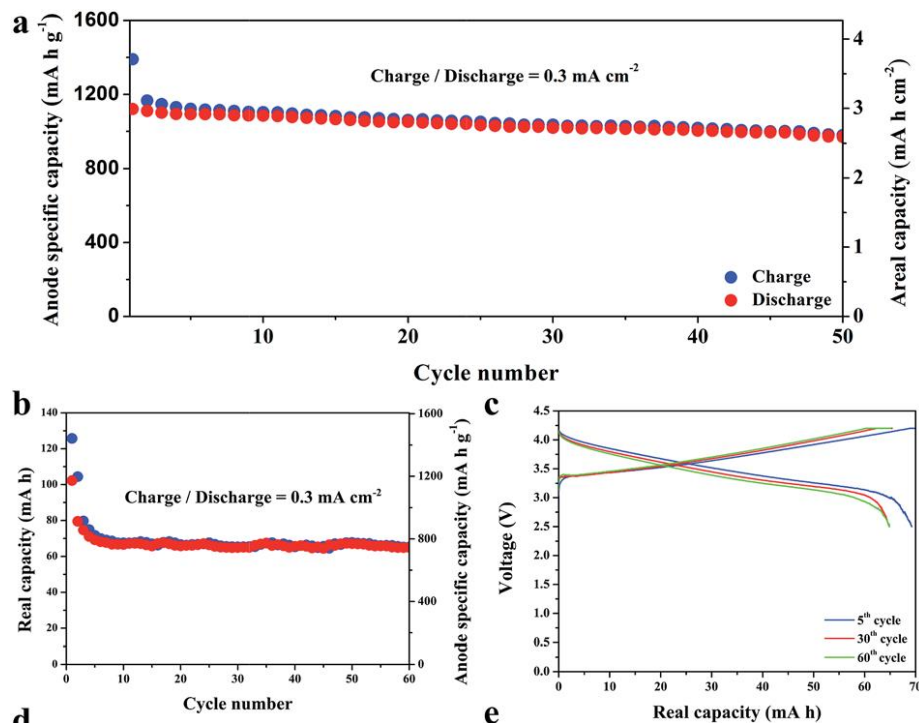
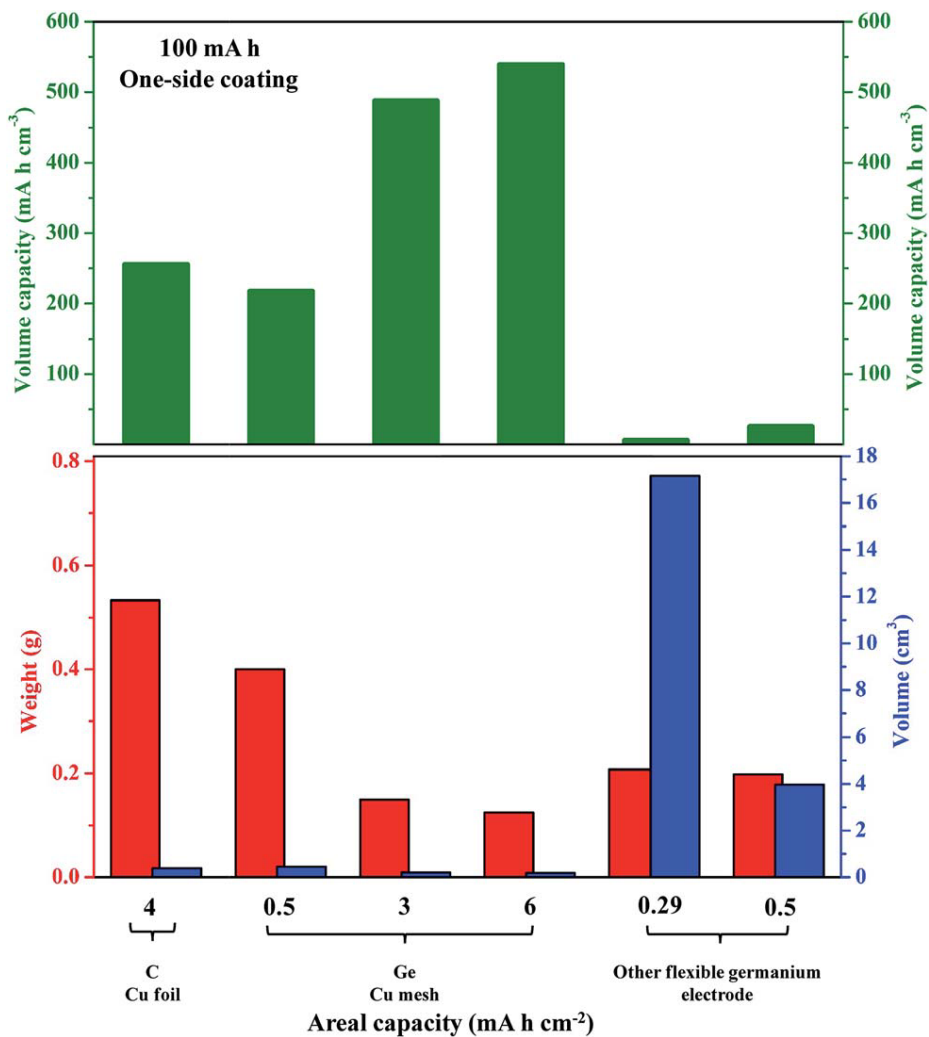
# Ge/Cu Nanowire fabric after cycling



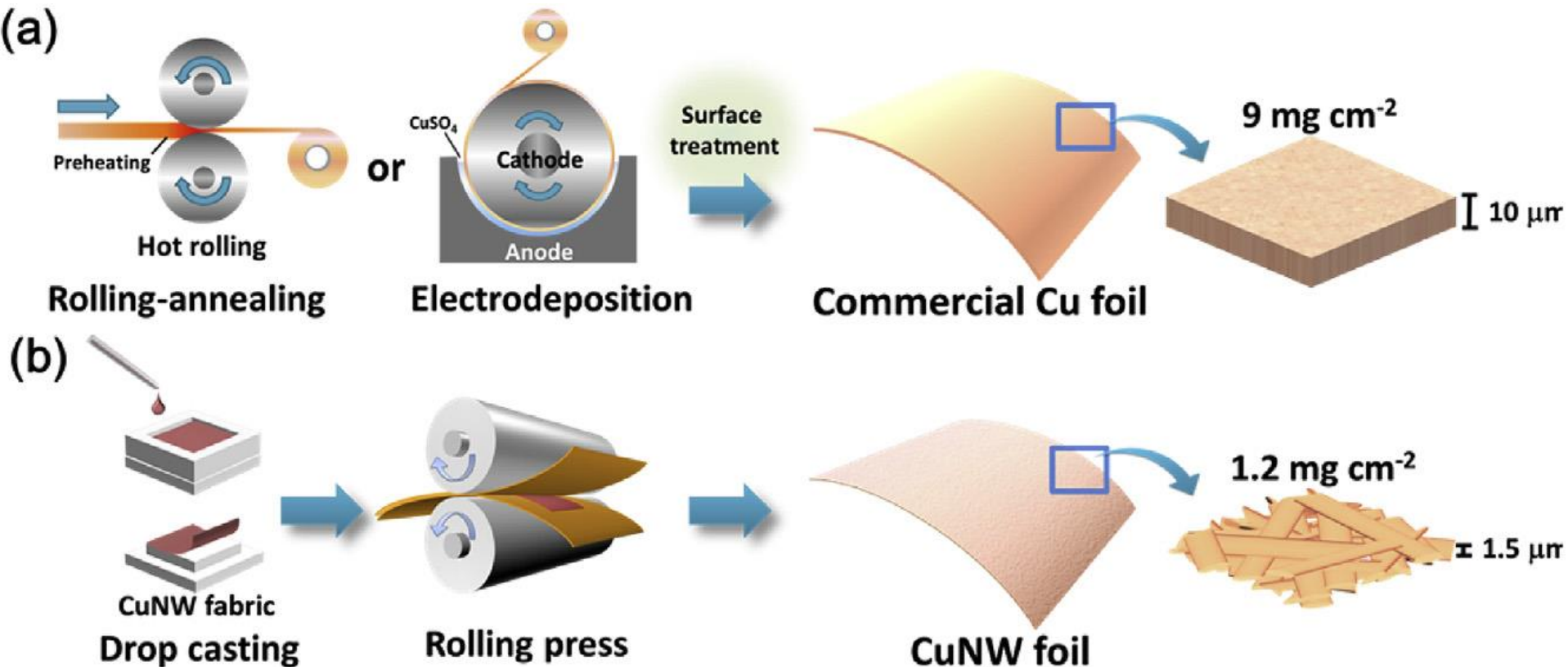
# Half-cell test at high loadings of active materials



# Theoretical Volumetric capacities and full cell demonstration

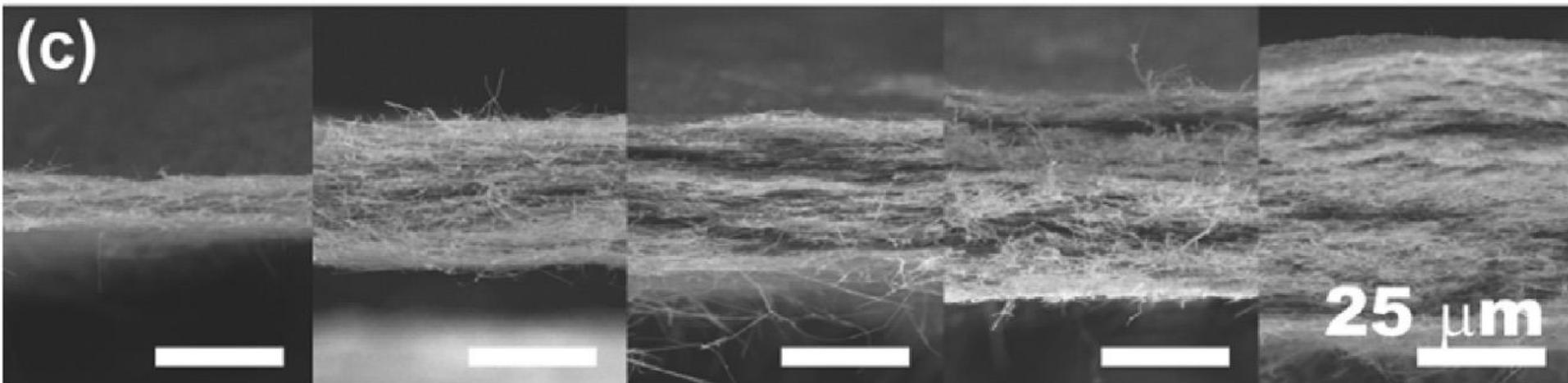
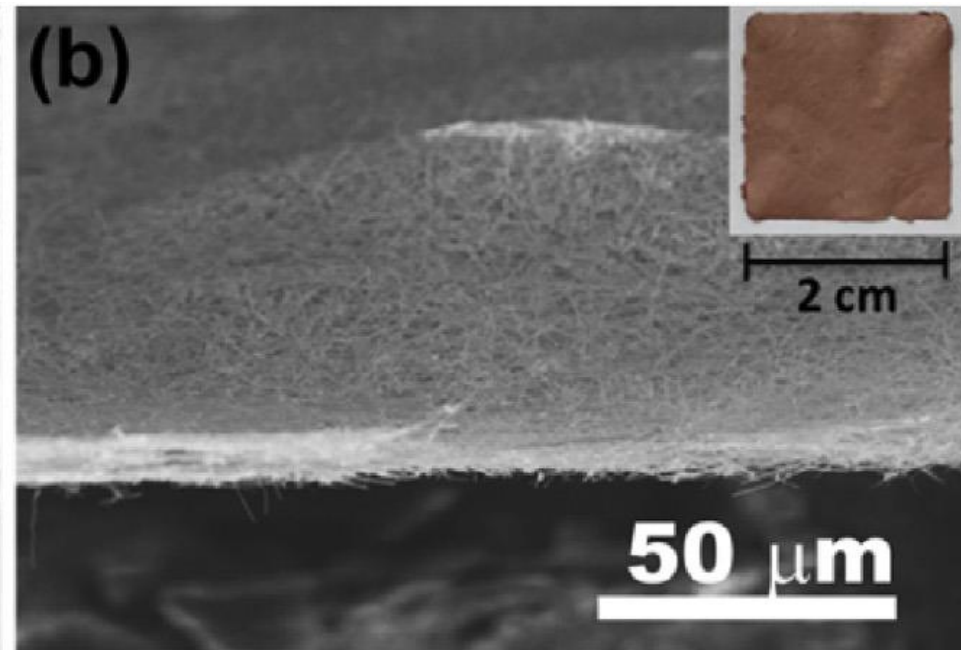
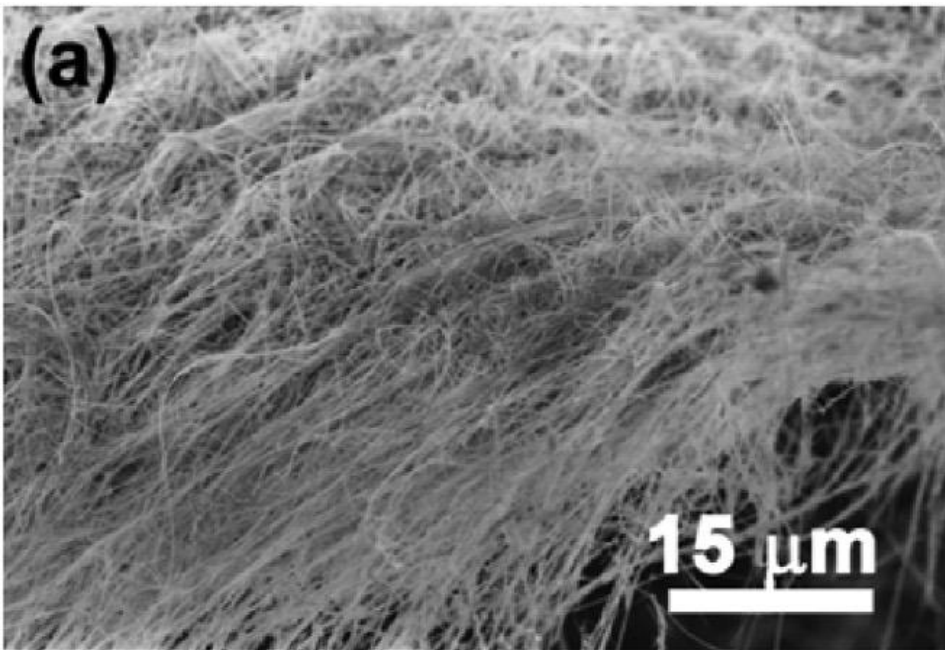


# High-performance lithium-ion batteries with 1.5 mm thin copper nanowire foil as a current collector

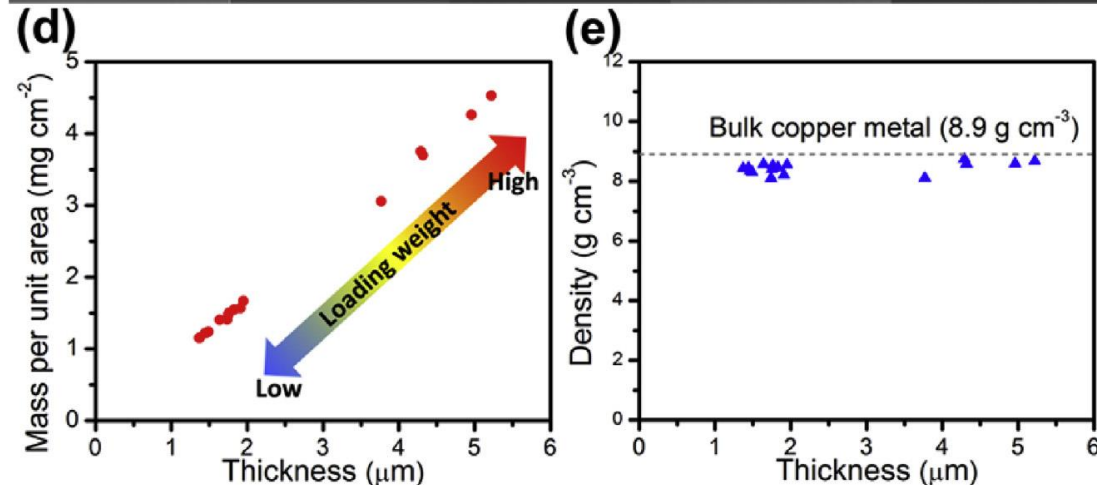
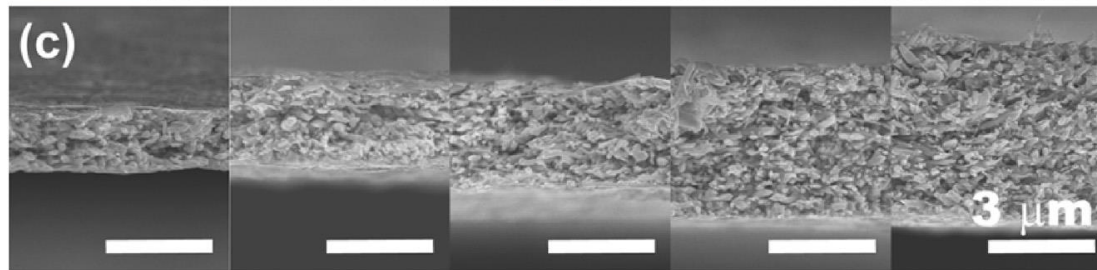
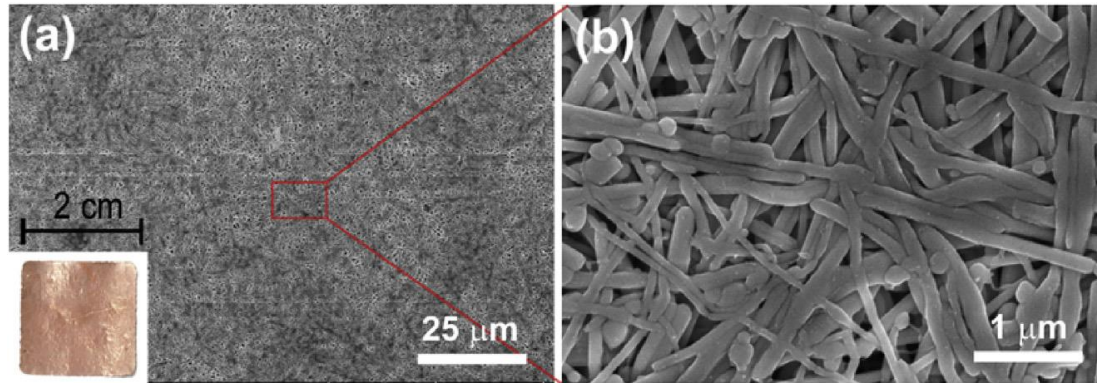


Schematic of the process of (a) conventional Cu foil fabrication process using rolling-annealing or electrodeposition methods and (b) CuNW foil fabrication process using a rolling press method.

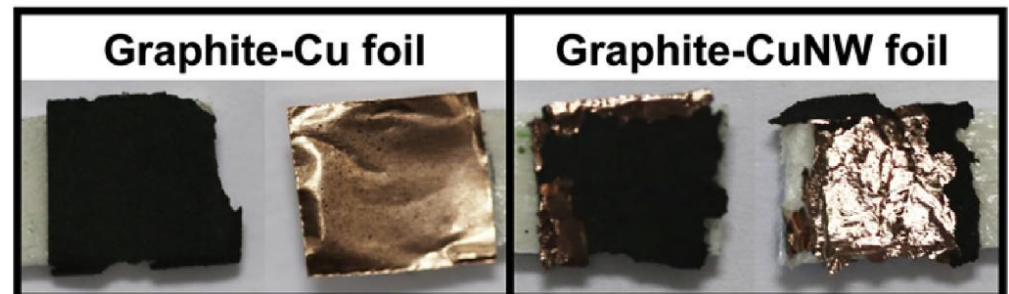
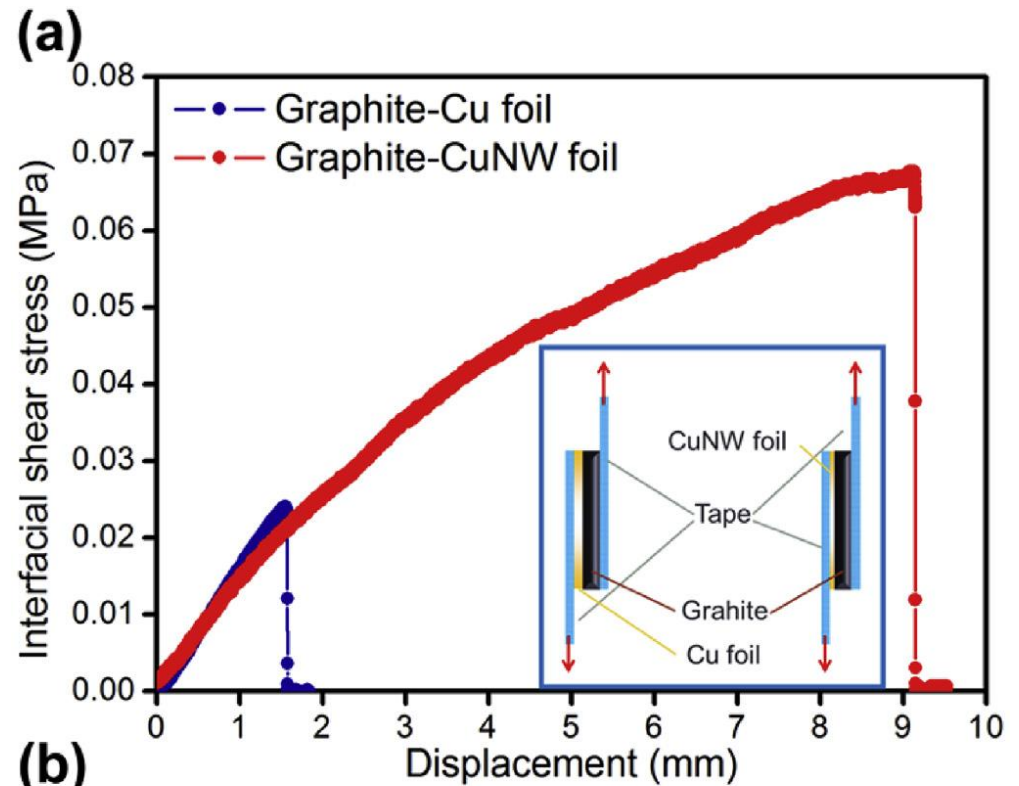
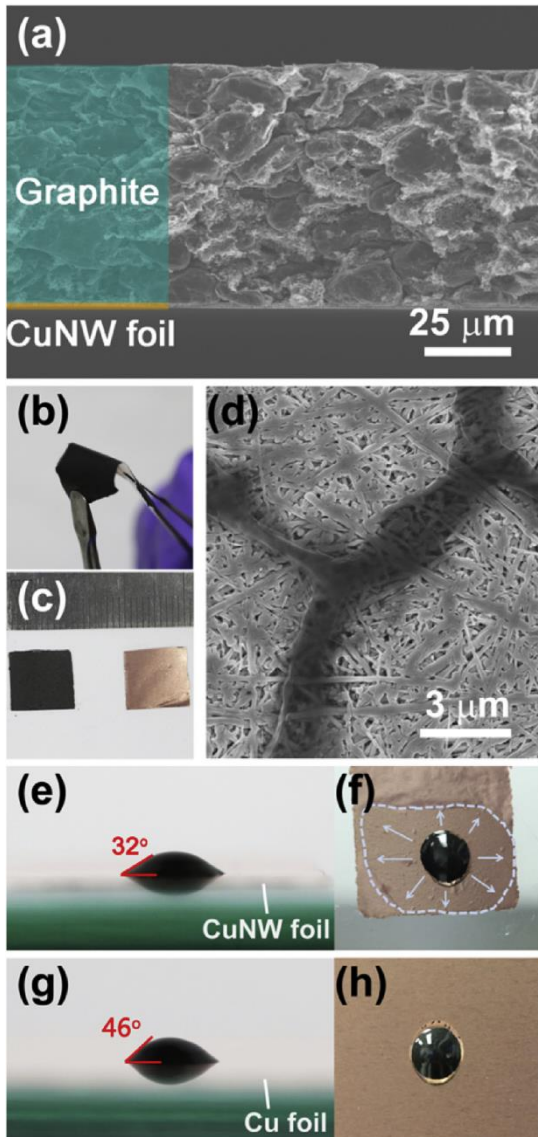
# Cu NW fabric with tunable thickness



# Cu NW foil and their density

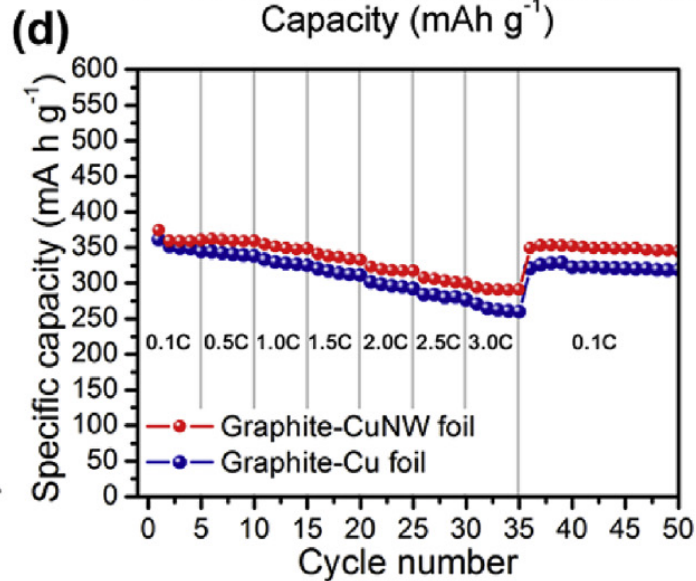
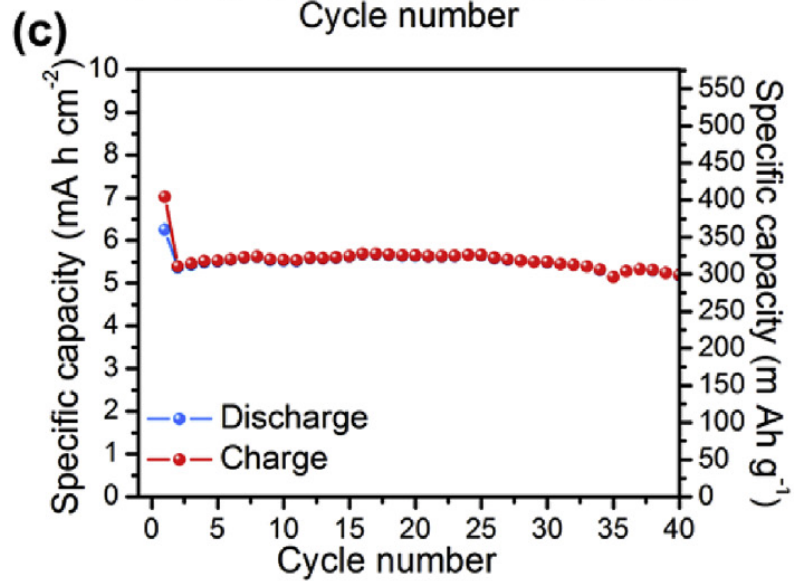
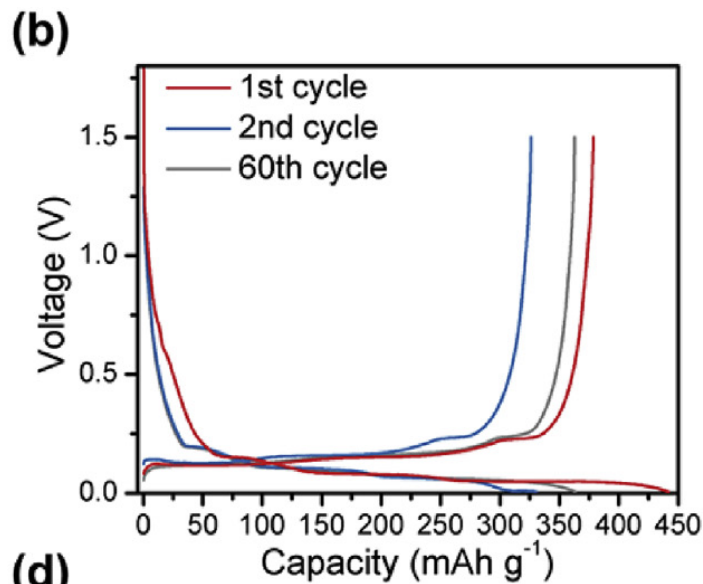
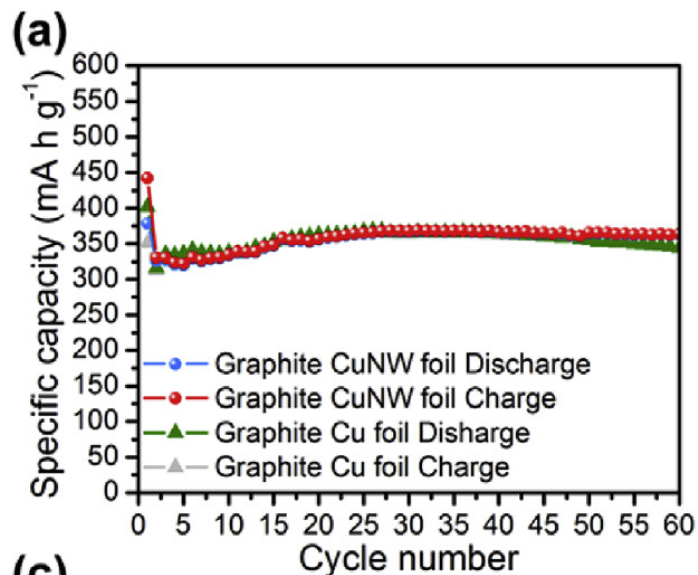


# Cu nanowire foil for LIB current collector

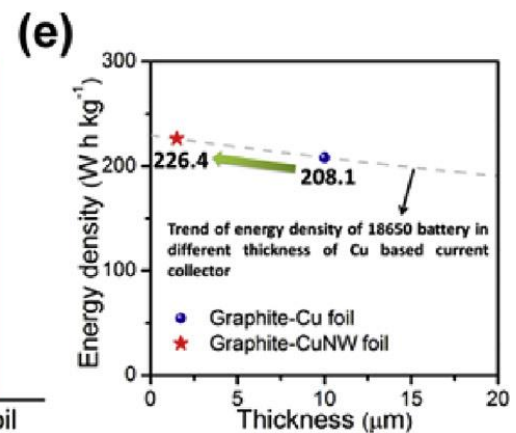
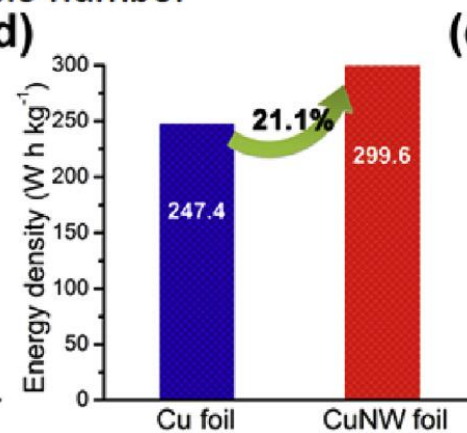
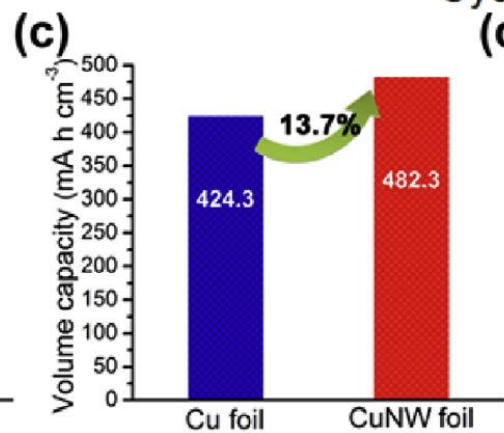
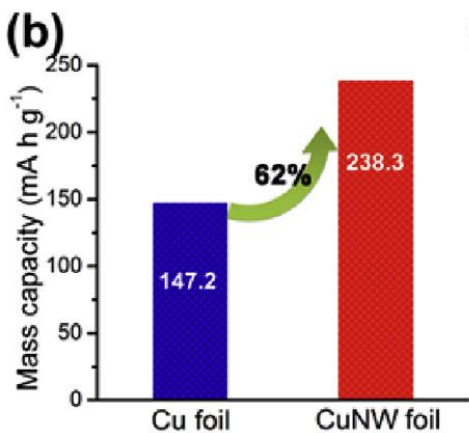
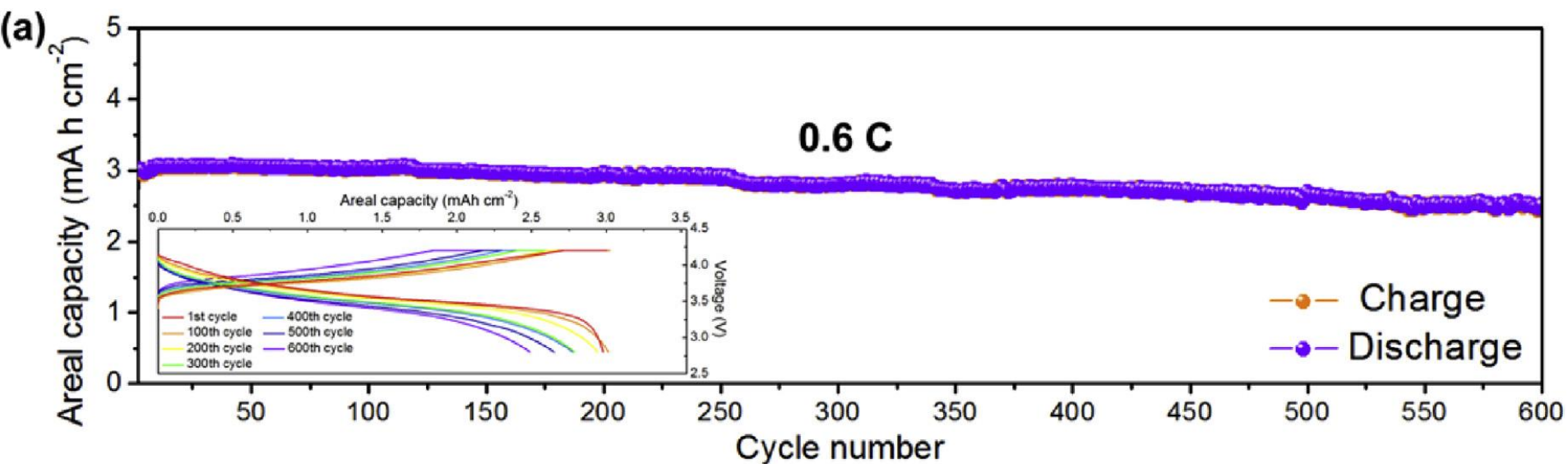




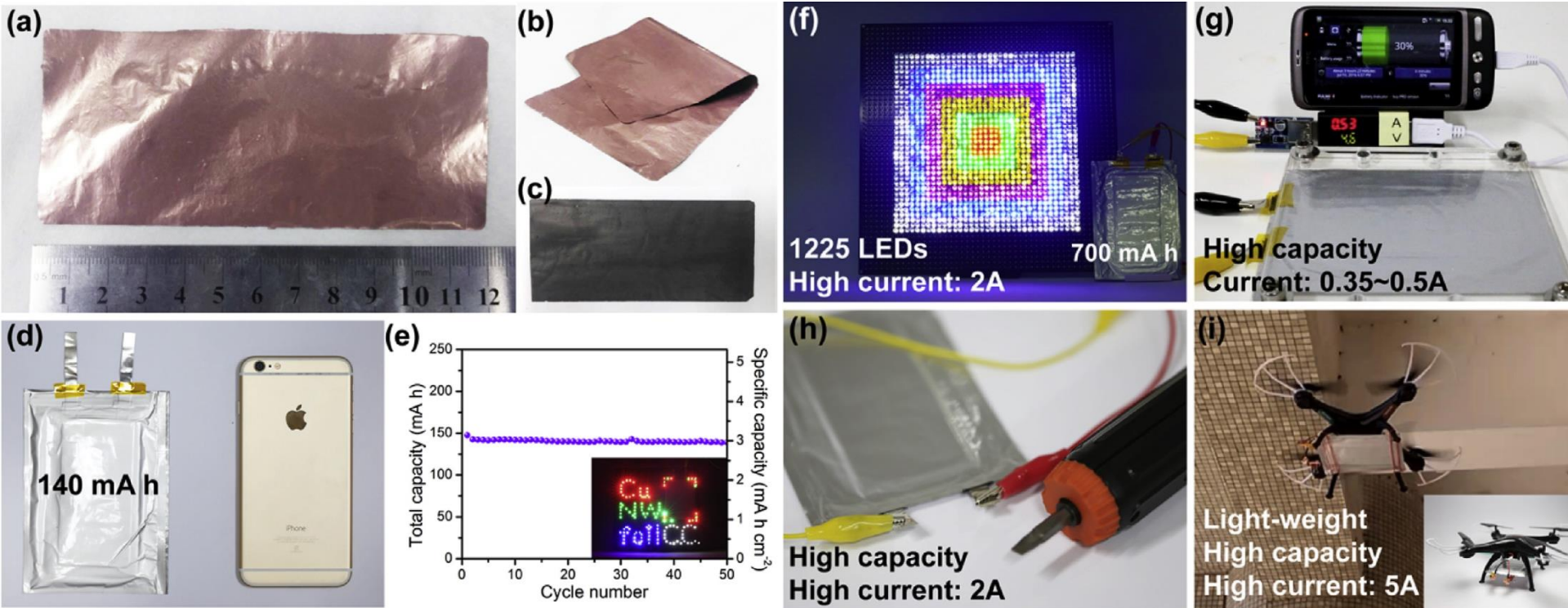
# Cycling performance of graphite-CuNW foil



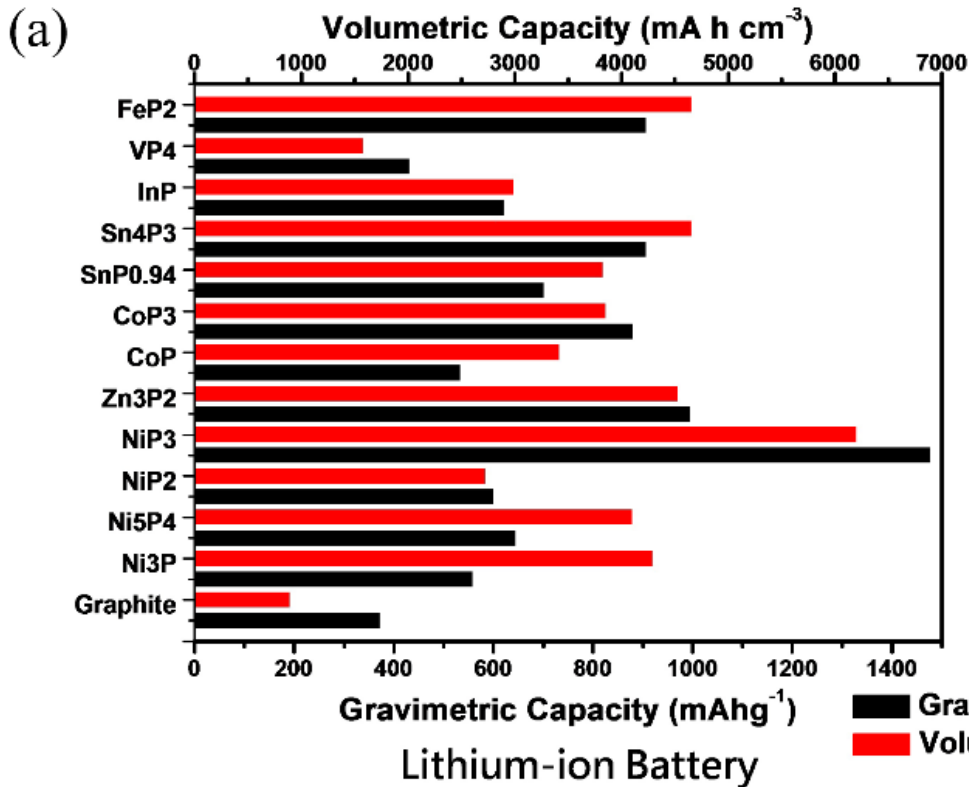
# Full cell performance of graphite-CuNW foil



# Pouch type full cells using graphite-CuNW foil anodes



# Metal phosphide as anodes for LIB



## Metal phosphide :

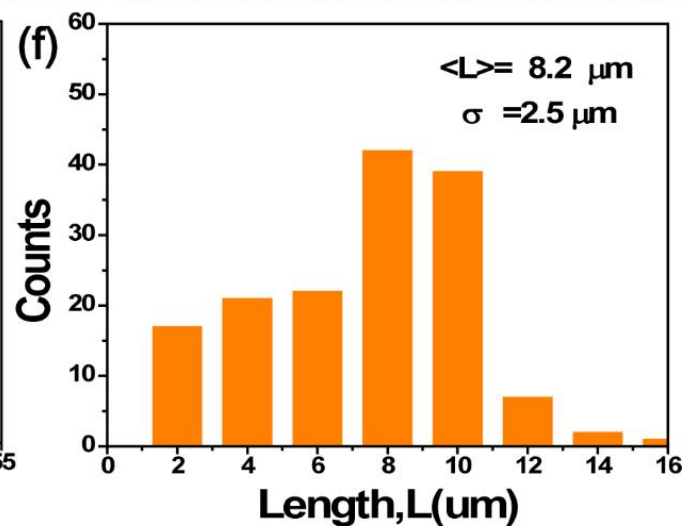
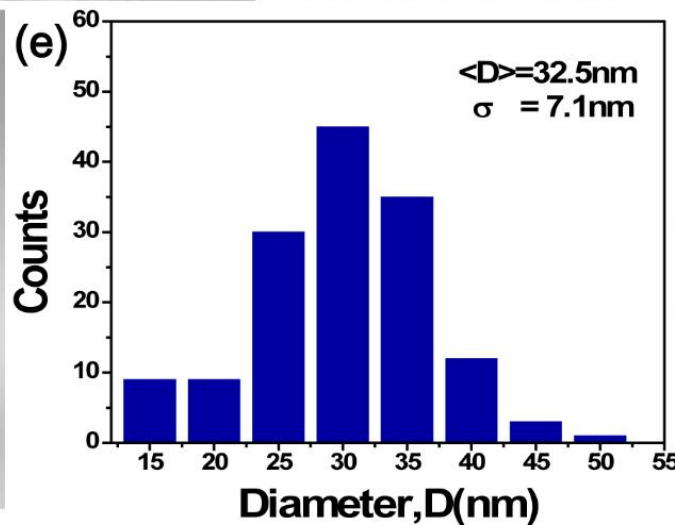
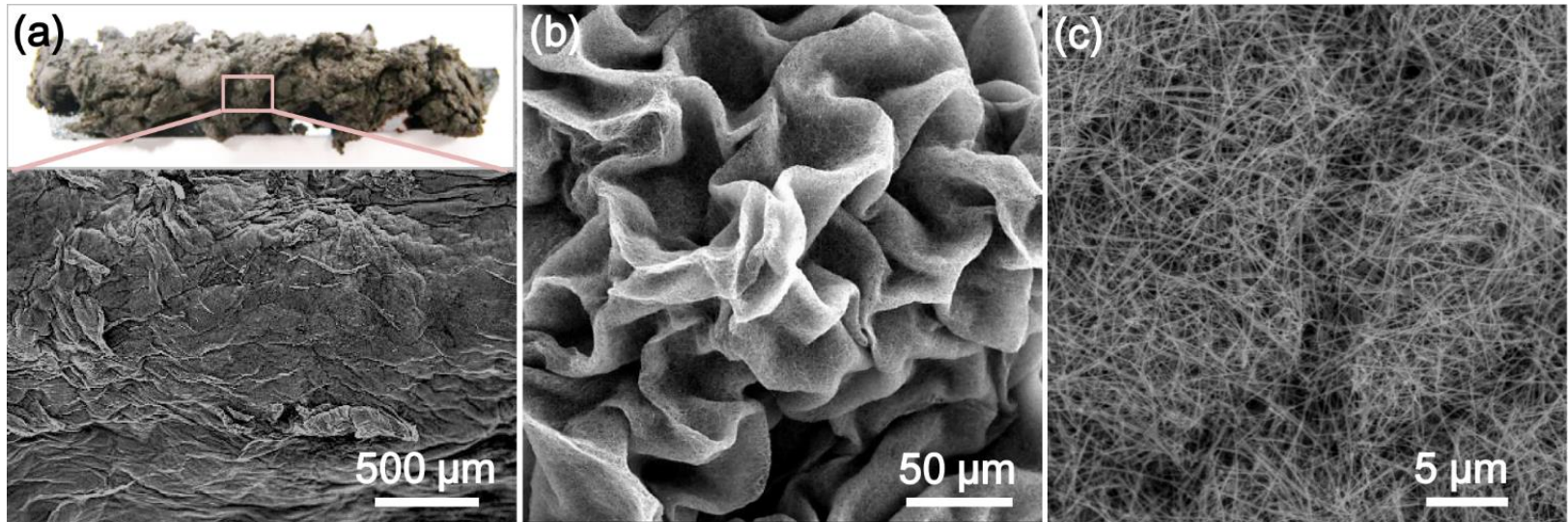
- High gravimetric capacities
- High volumetric capacities
- Smaller volume expansion
- Low polarization
- Avoid lithium plating during fast charging.

**P: 2596 mA h g<sup>-1</sup>**

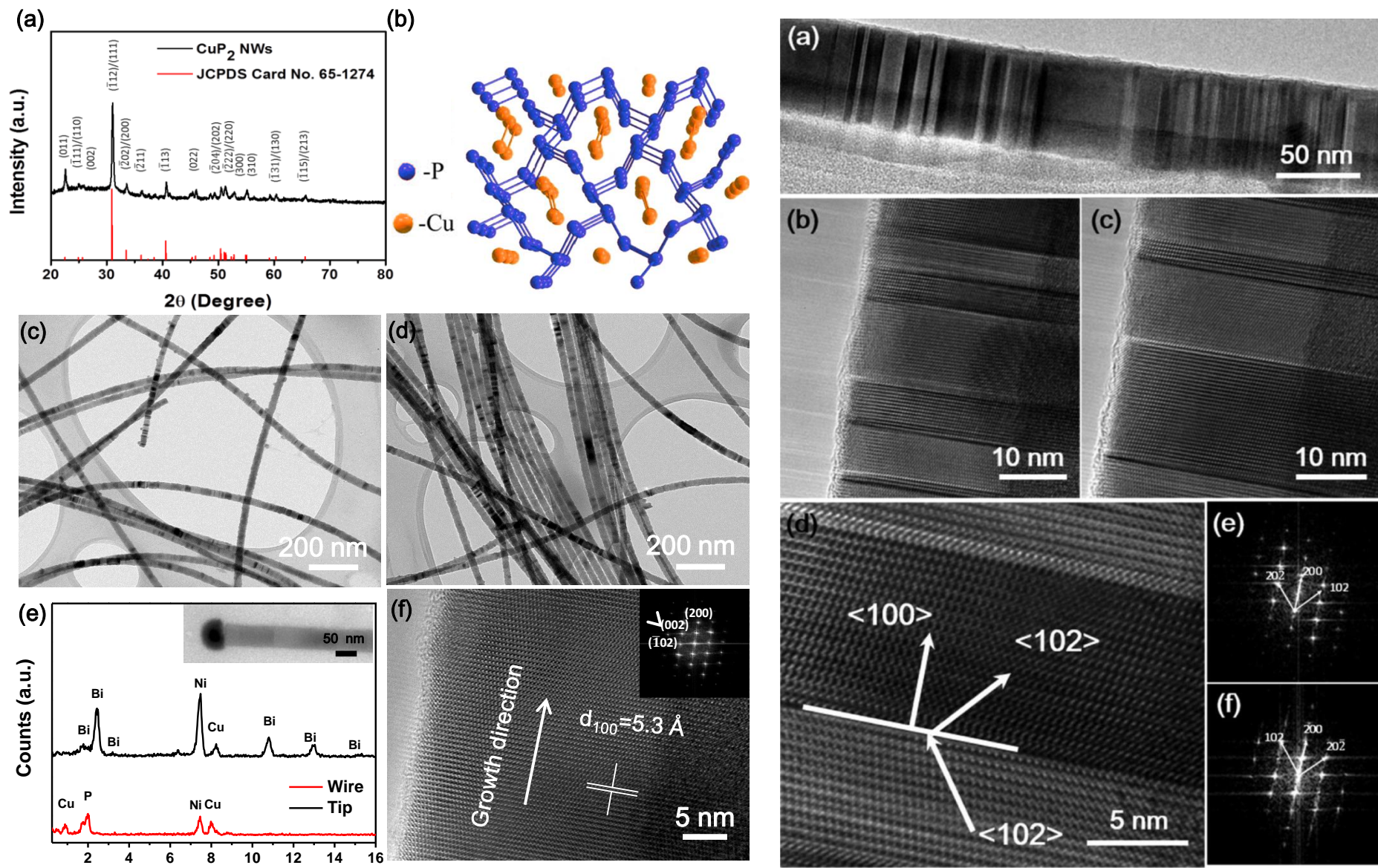
- Poor conductivity
- large volume expansion

**Goal: Synthesis of CuP<sub>2</sub> Nanowires and applied on Lithium ion Batteries**

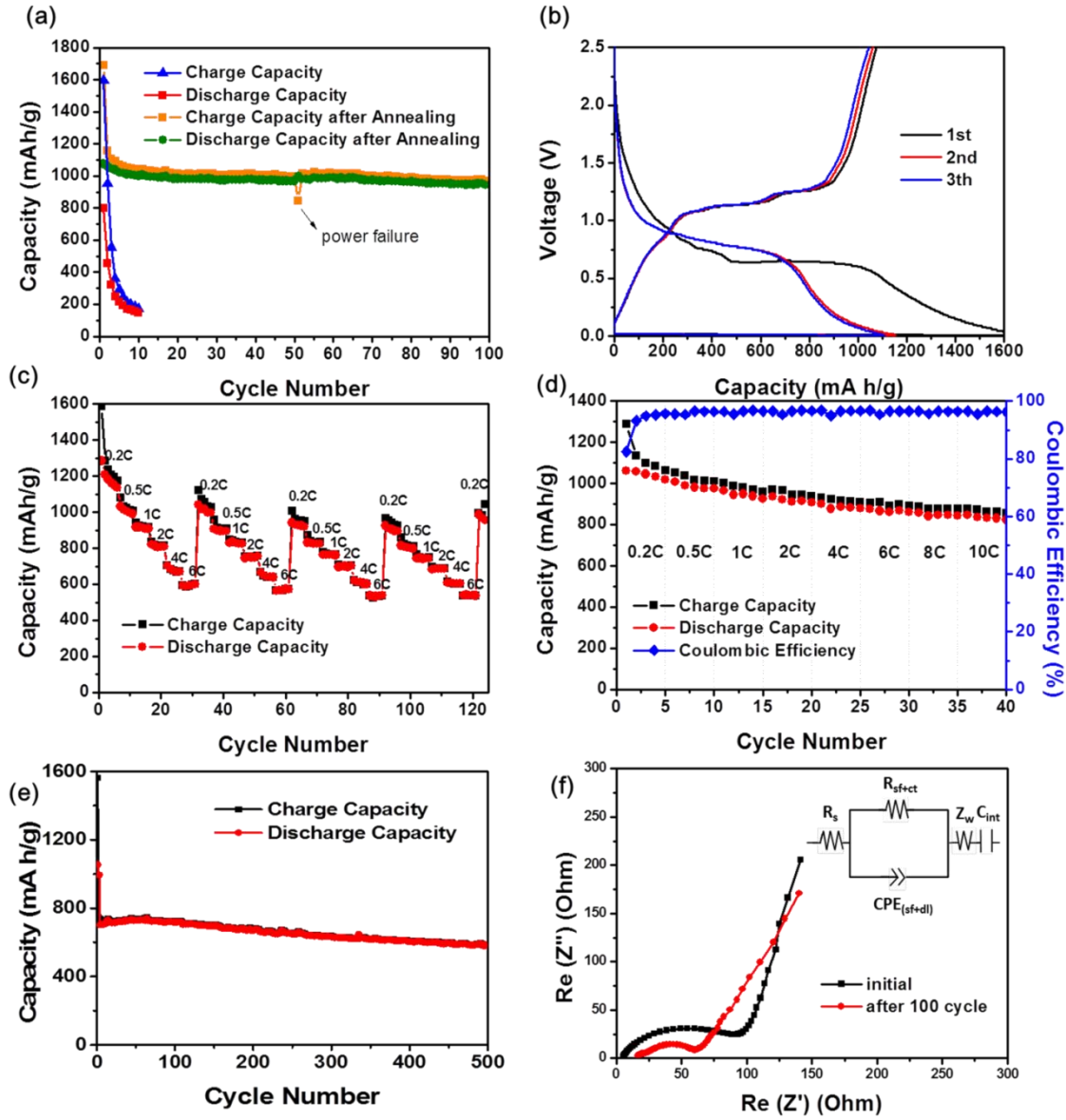
# CuP<sub>2</sub> nanowires seeded by Bi nanoparticles



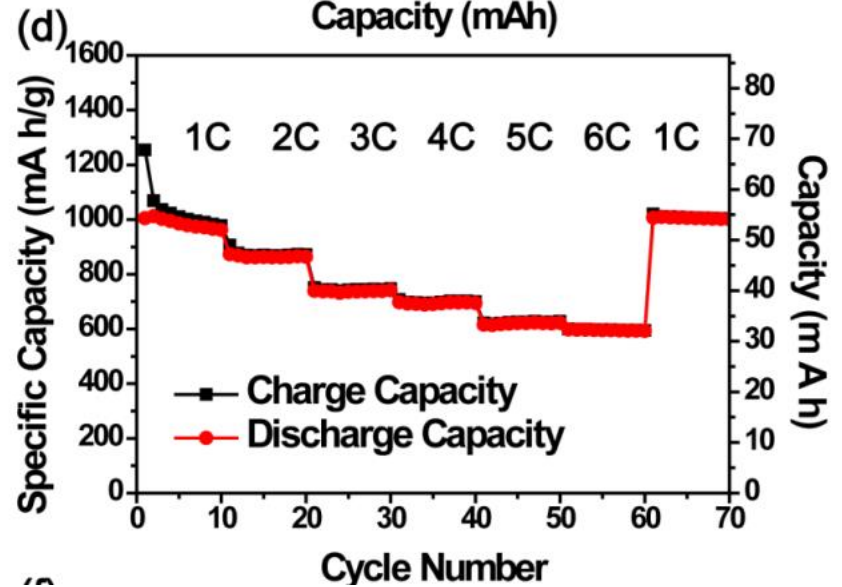
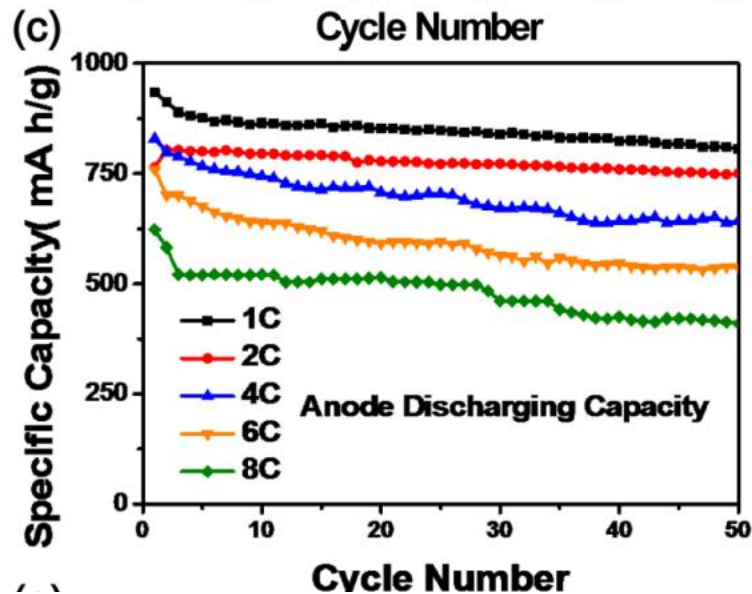
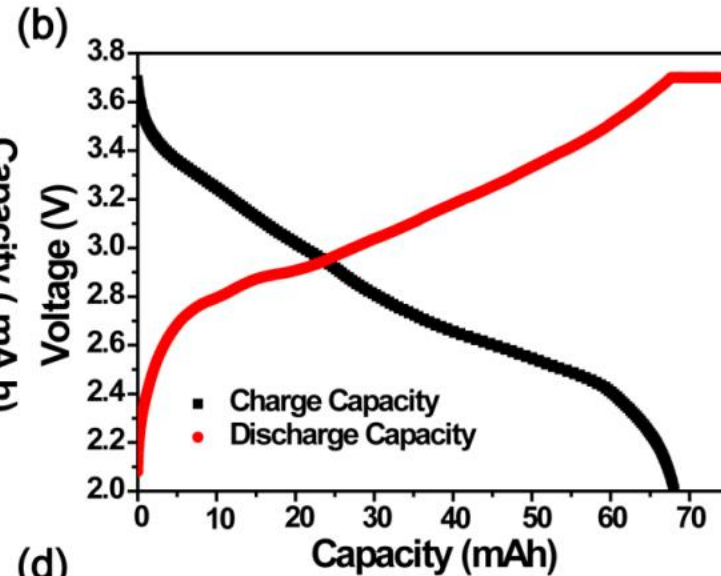
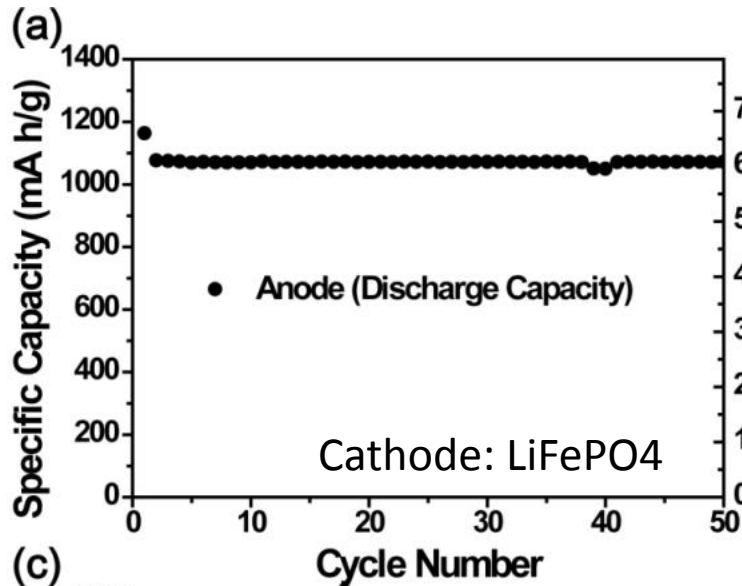
# CuP<sub>2</sub> nanowires seeded by Bi nanoparticles



# CuP<sub>2</sub> anode performance

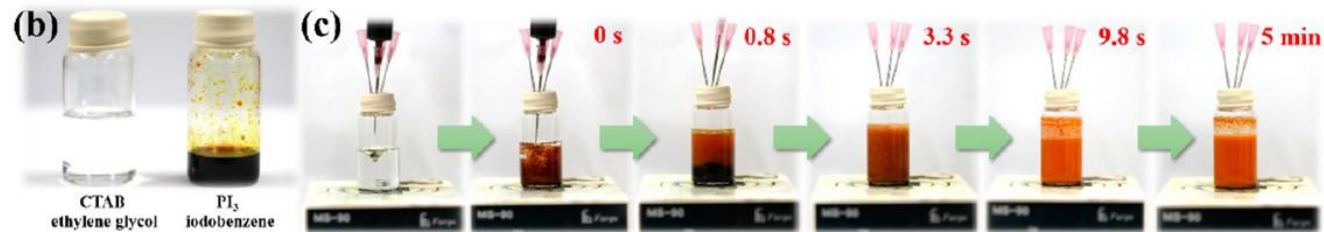
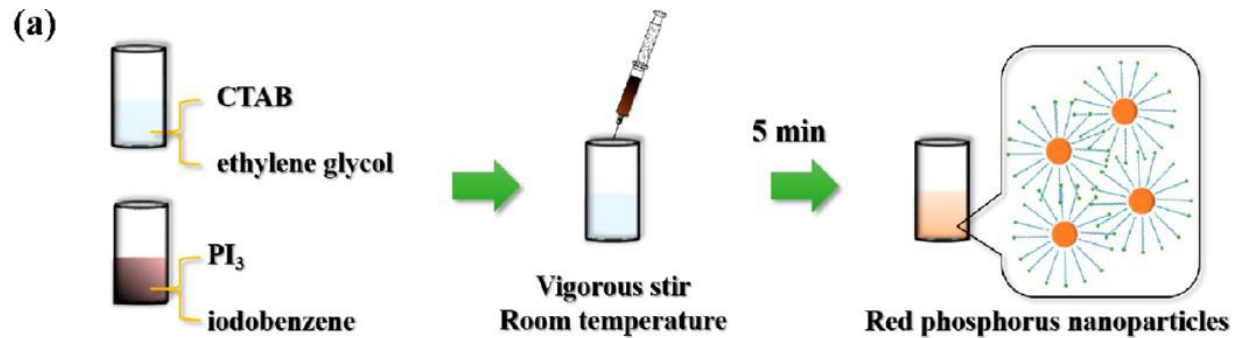


# Full cell performance

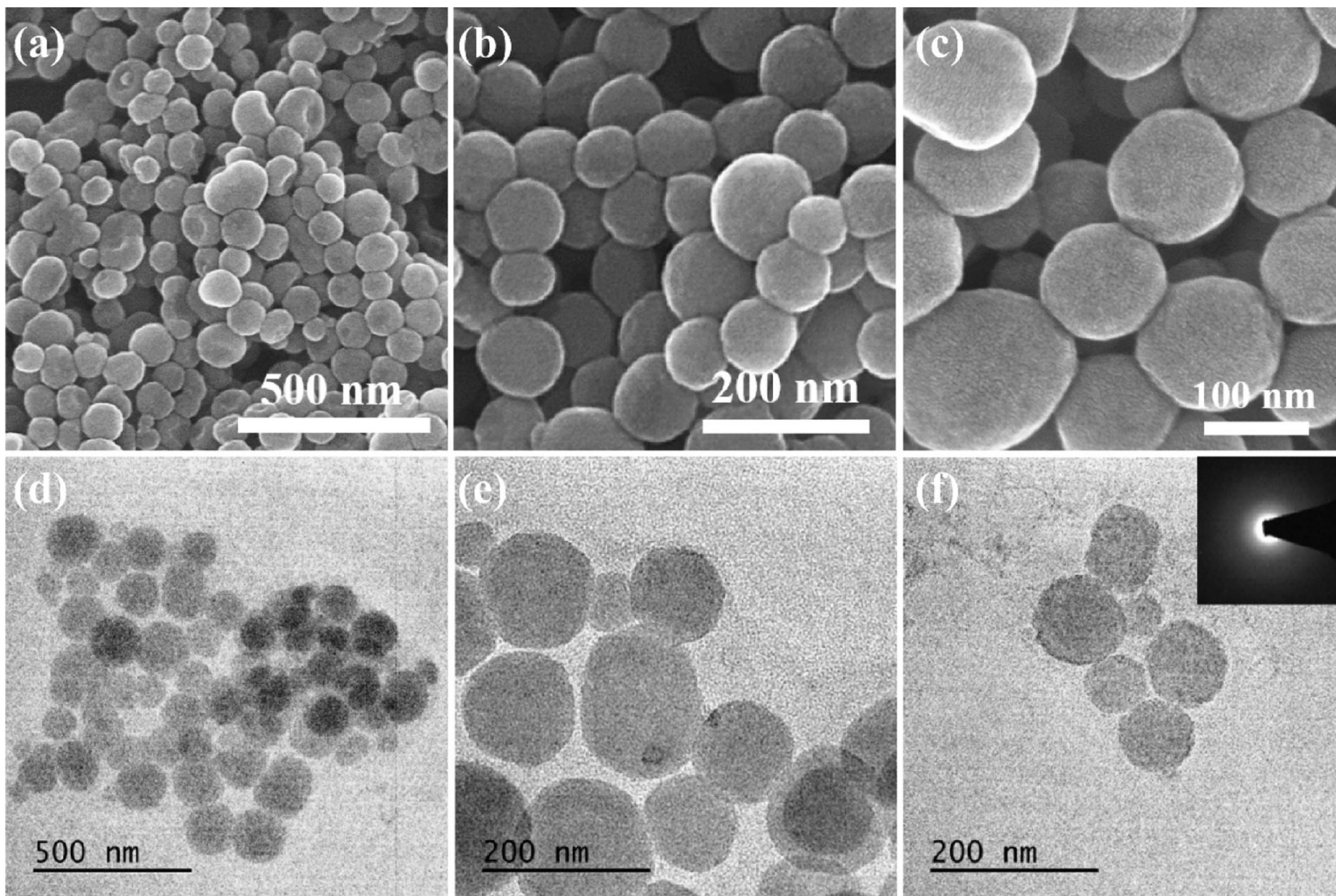




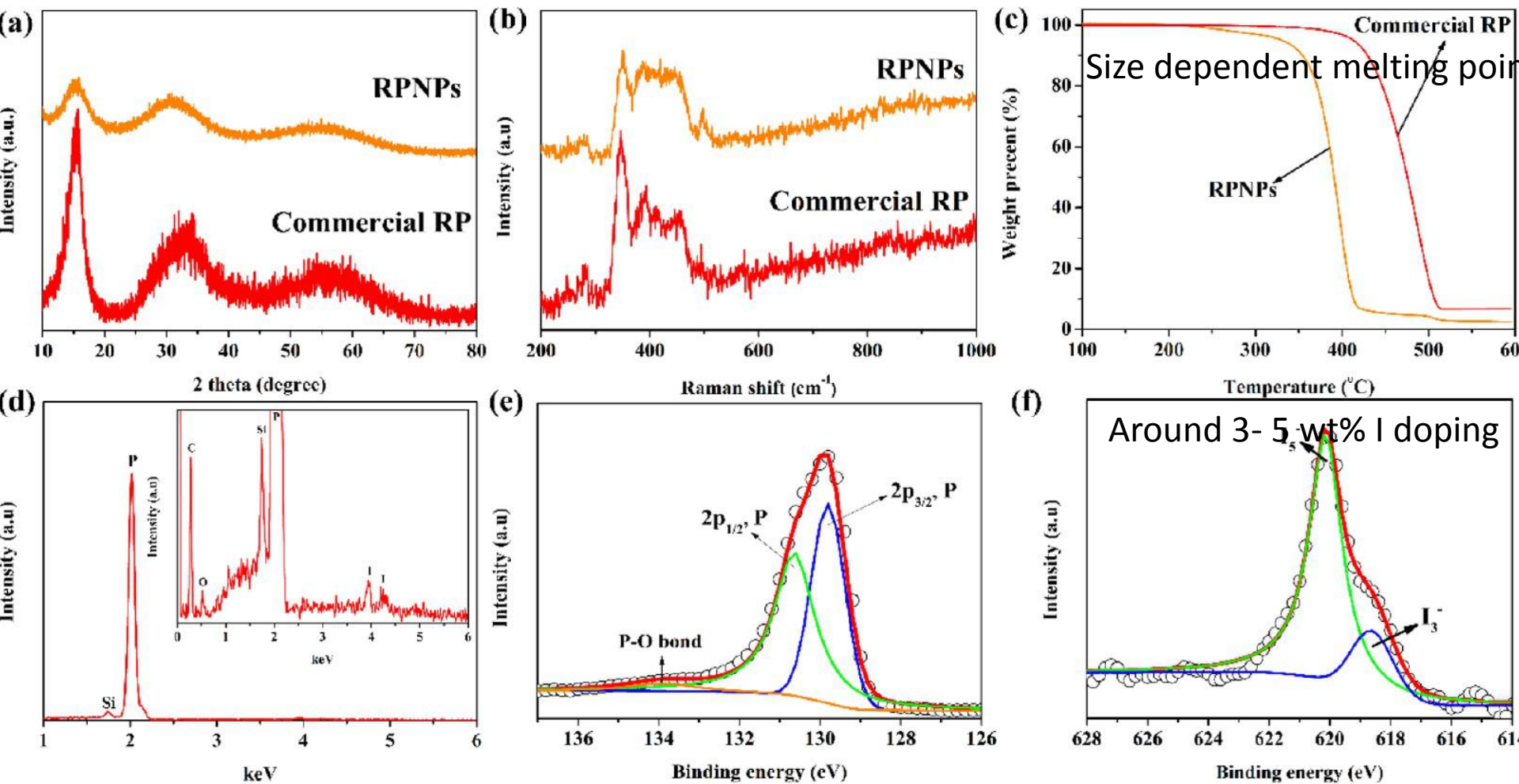
# Red phosphorus Nanoparticles (RPNPs)



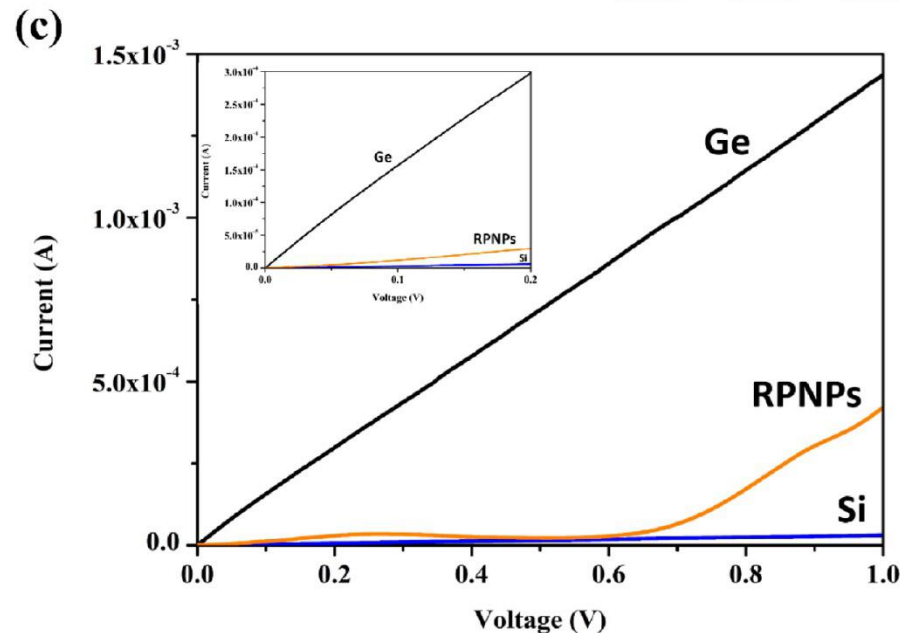
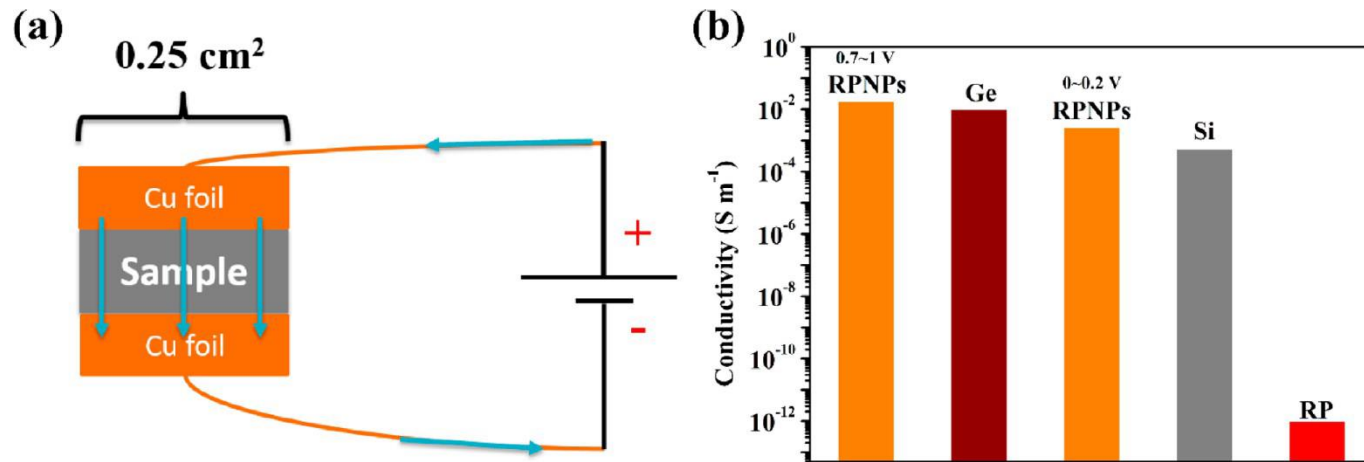
# Morphology of RPNPs



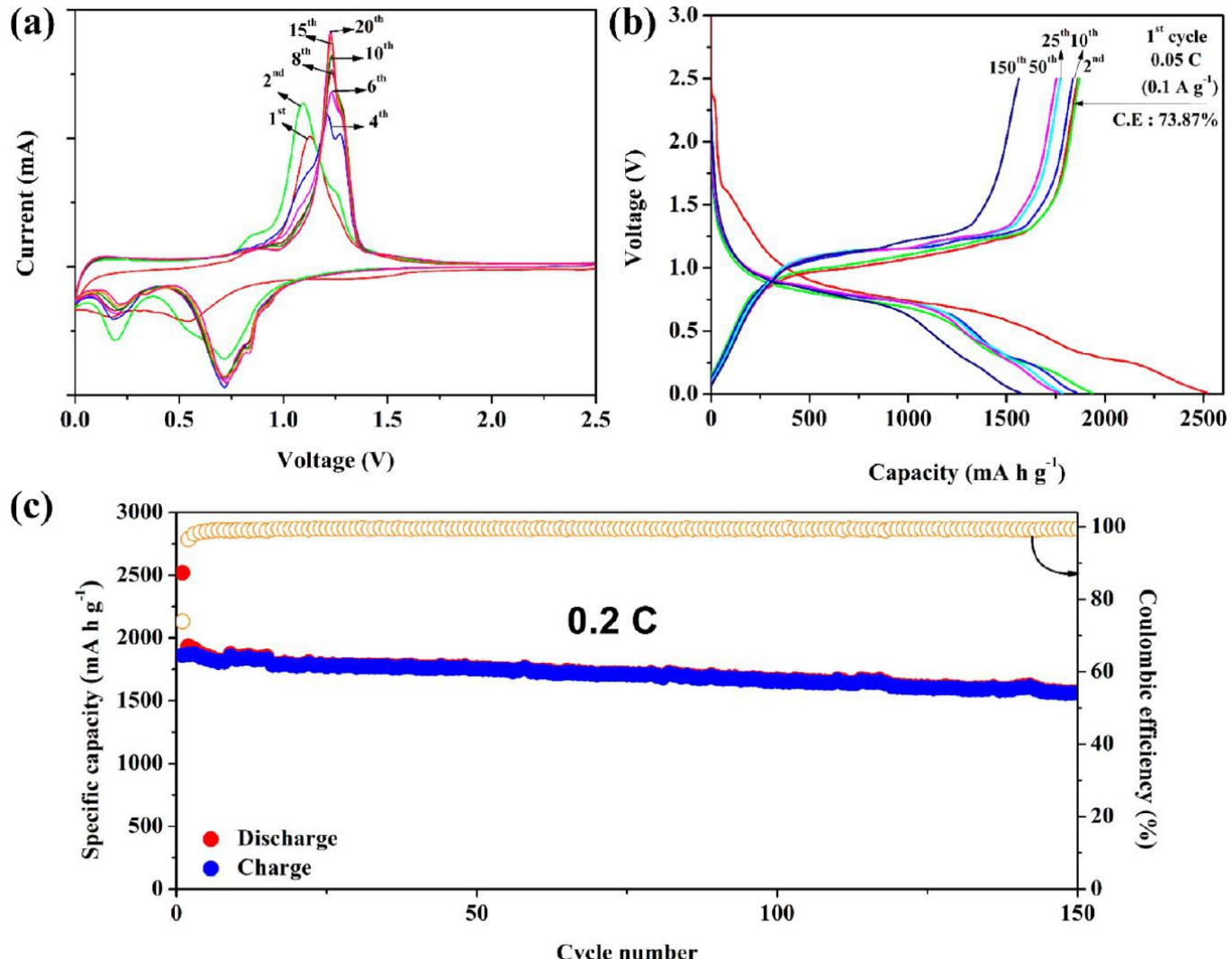
# Characterization of RPNP : size dependent and Iodine doping



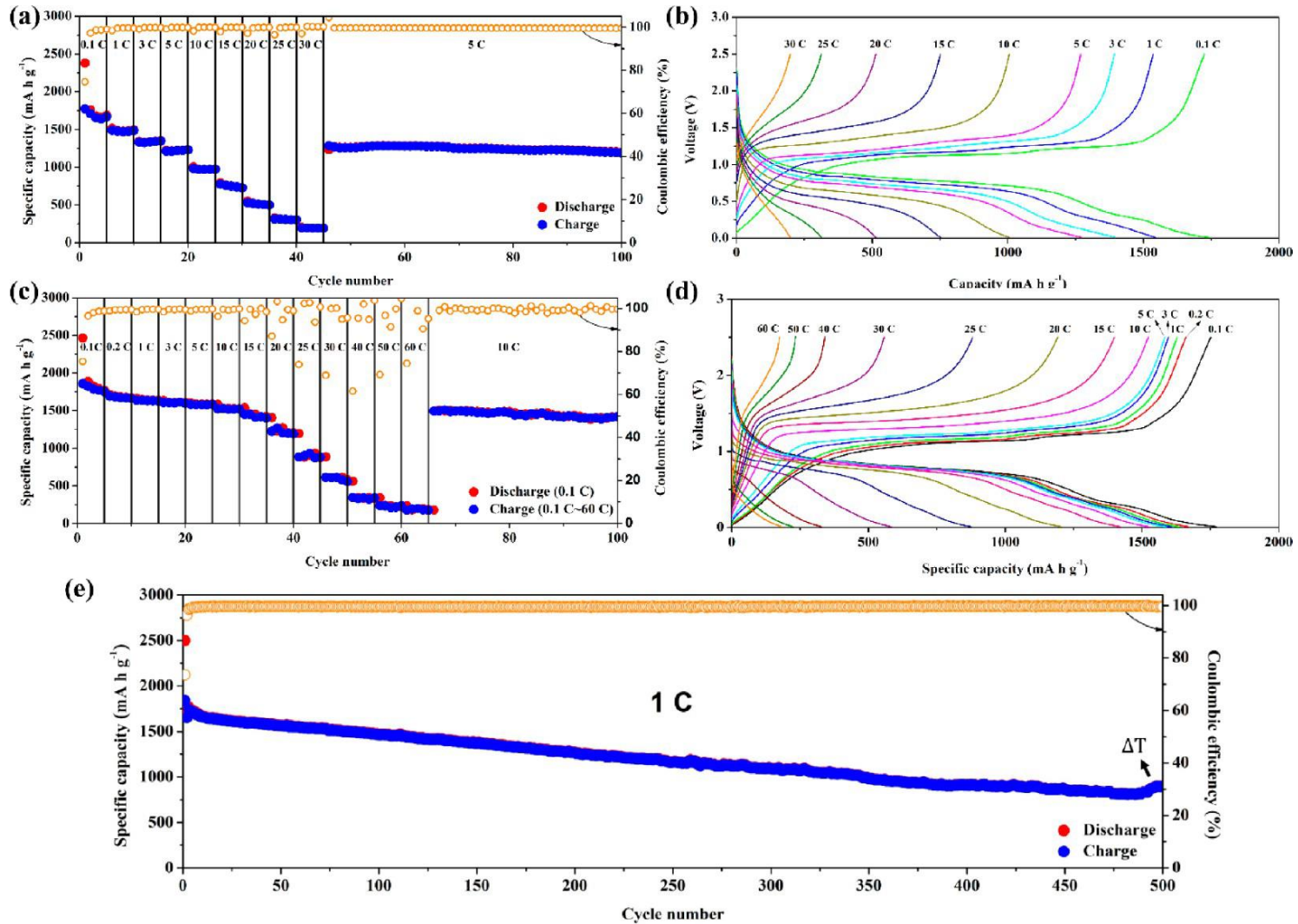
# Significantly improved conductivity



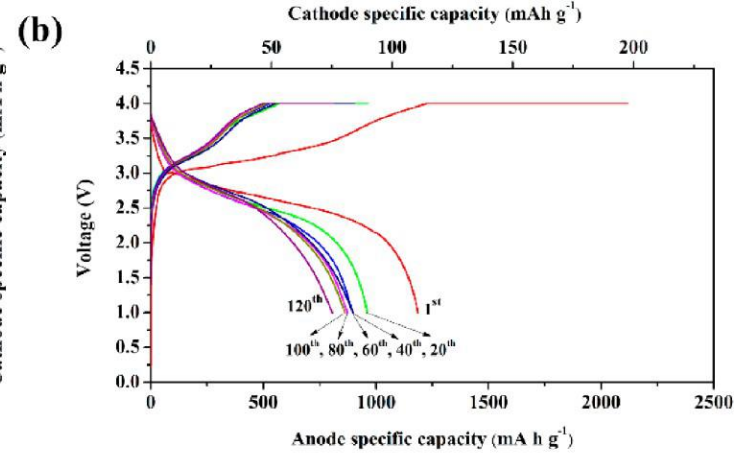
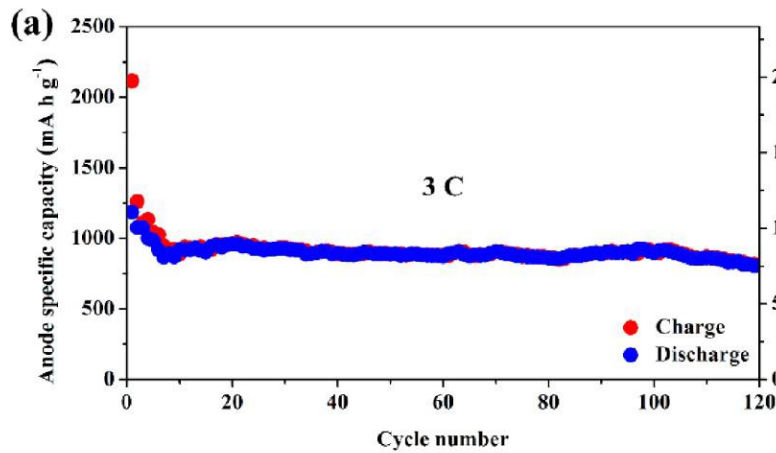
# Half-Cell battery test



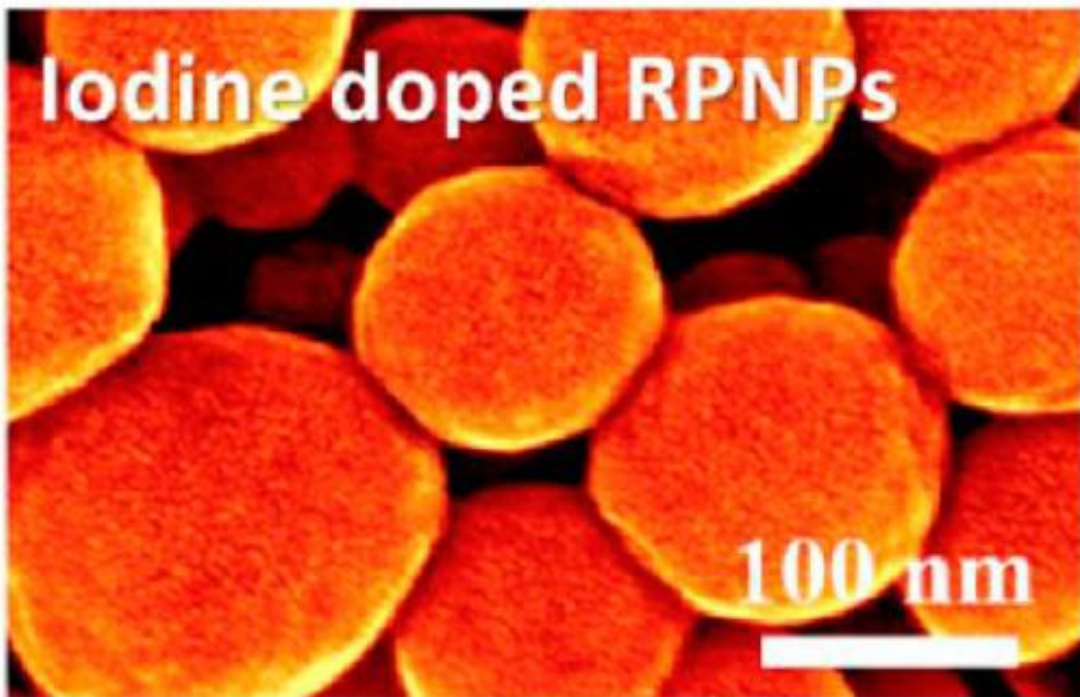
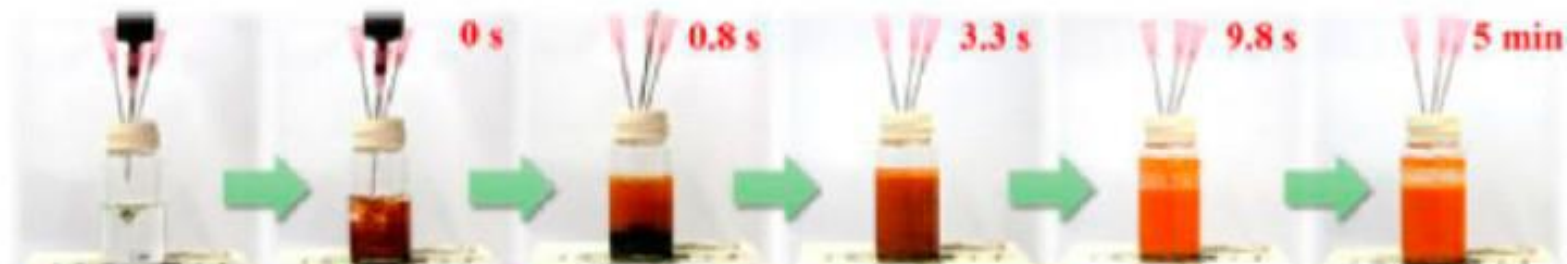
# Half-cell battery test



# Full cell tests

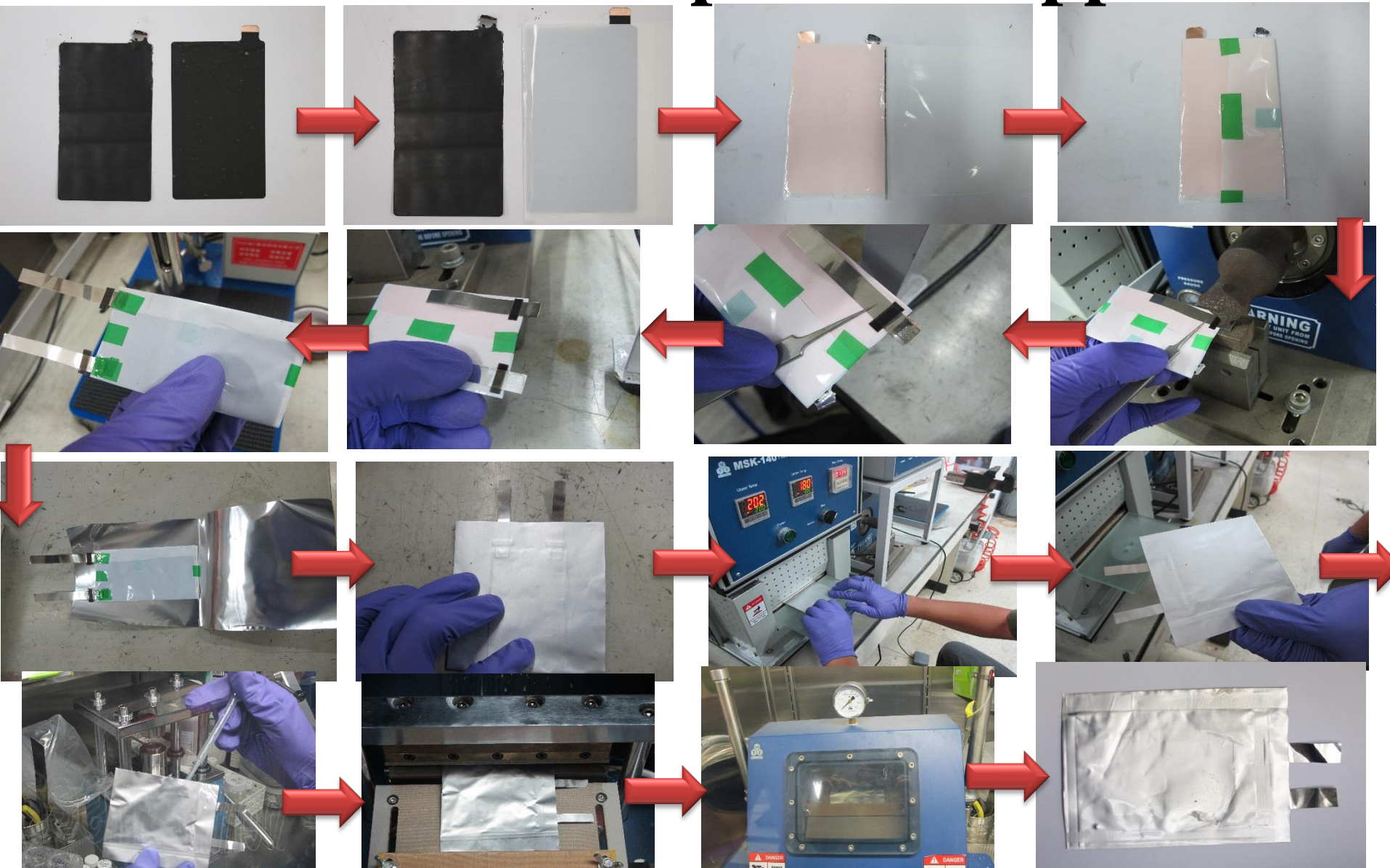


# C&EN News: Phosphorus boosts lithium-ion battery charge capacity





# Pouch type full cells as proof-of-concept demonstration for practical applications

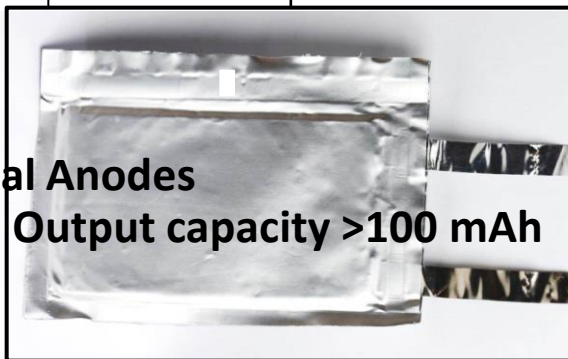




Mobile phone

Mini 4D car

High specific capacity Nanomaterial Anodes  
Ge、Ge/RGO、Ge/MoS2、  
GeO2、CuP2、silicon/graphite

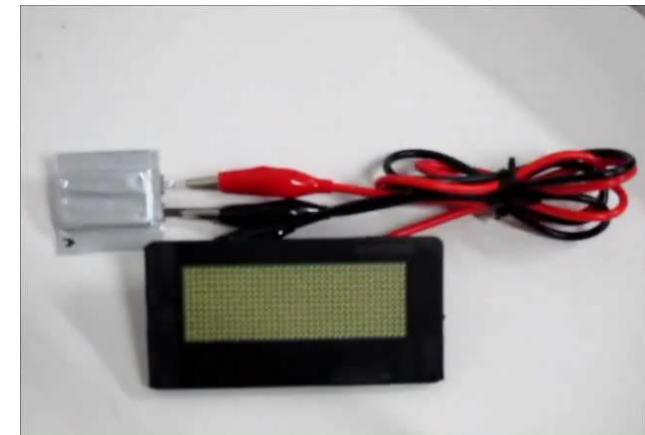
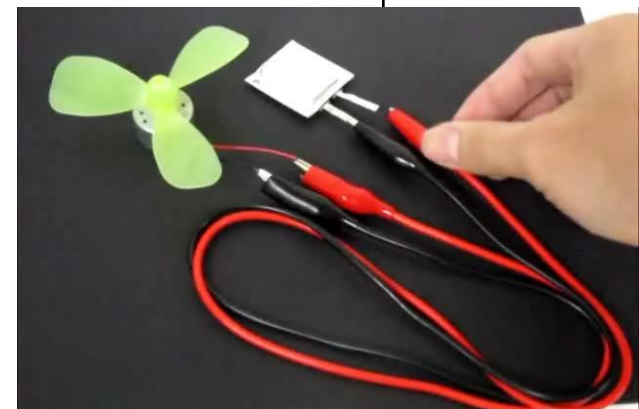


Output capacity >100 mAh

LED Lighting

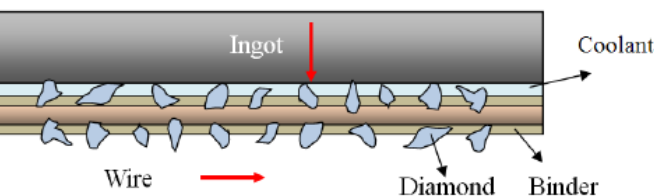
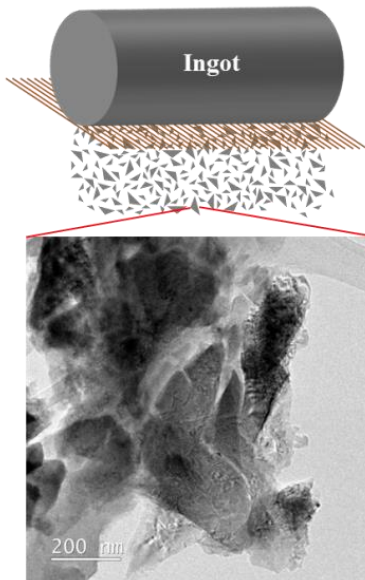
fan

marquee



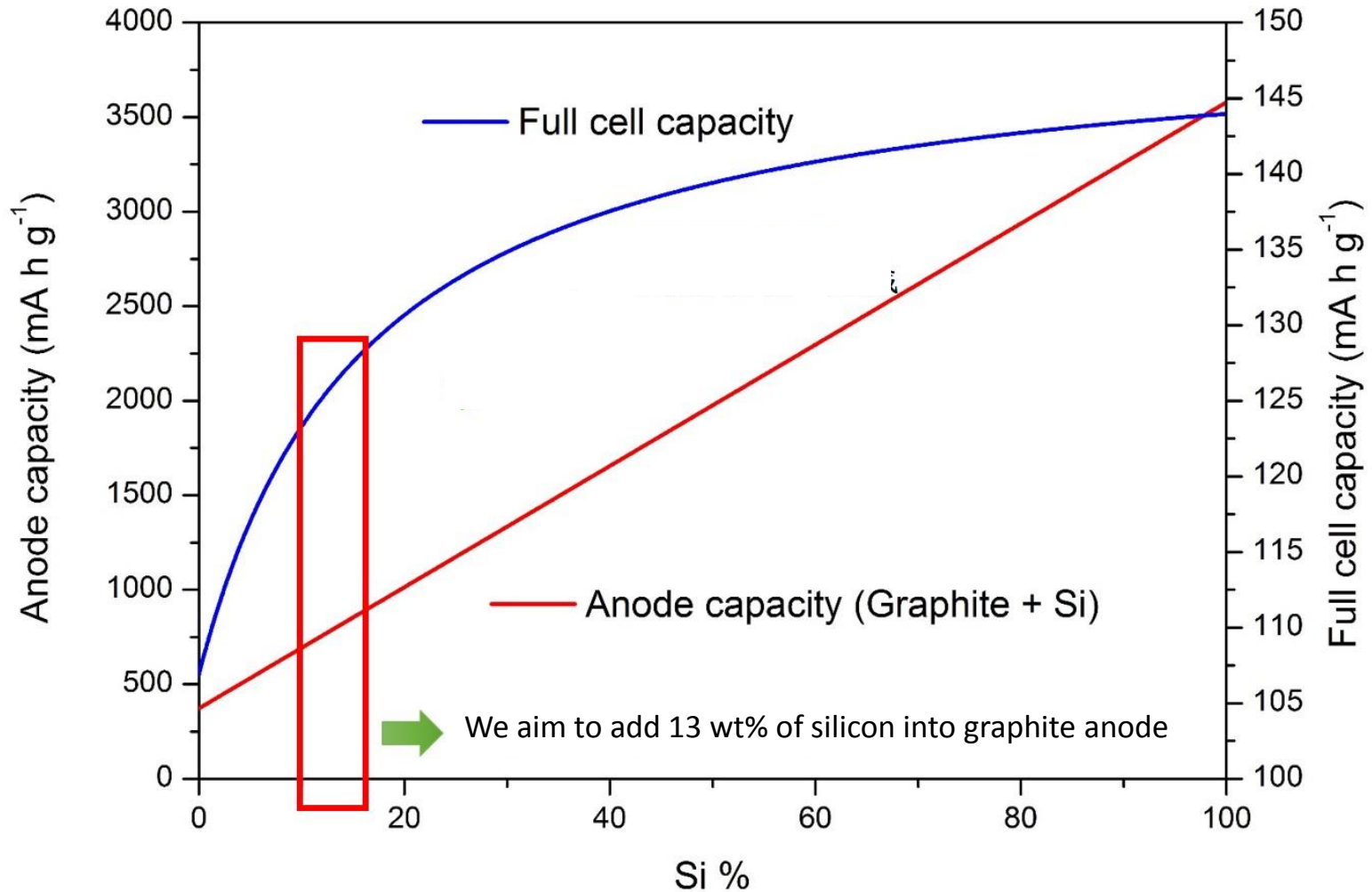
# Nanoscale kerf loss Si :A top-down approach to make high-capacity nanomaterials

Kerf loss silicon collected from the sawing process of solar-grade silicon



- Nanoscale kerf loss silicon
- Low cost (1 USD / kg)
- A solar cell wafer company can produce ~1000 MT/Y
- Sufficient supply : annual consumption of polysilicon: 157000 tons with 20% growth rate

# The capacity influence of Si addition into graphite anode full



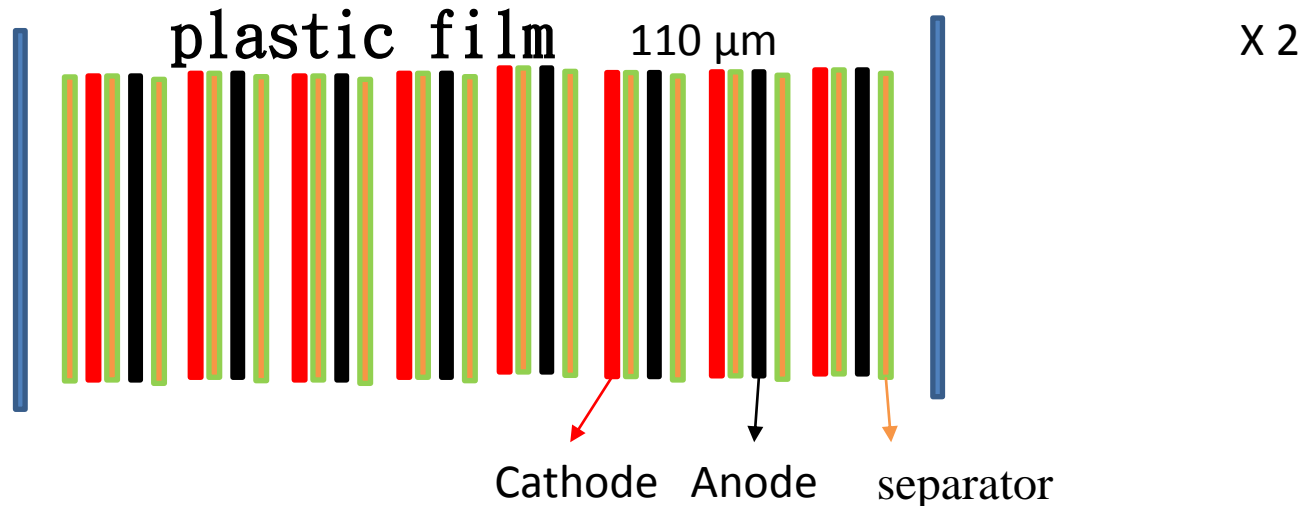
# Proposed battery components with volumetric capacity higher than 600 mAh/cm<sup>3</sup>

**Cathode : Li(NiCoMn)O<sub>2</sub>** Double-sided coating 135 μm X 8

**Anode : Si/graphite or MCMB** double-sided coating 110 μm X 8

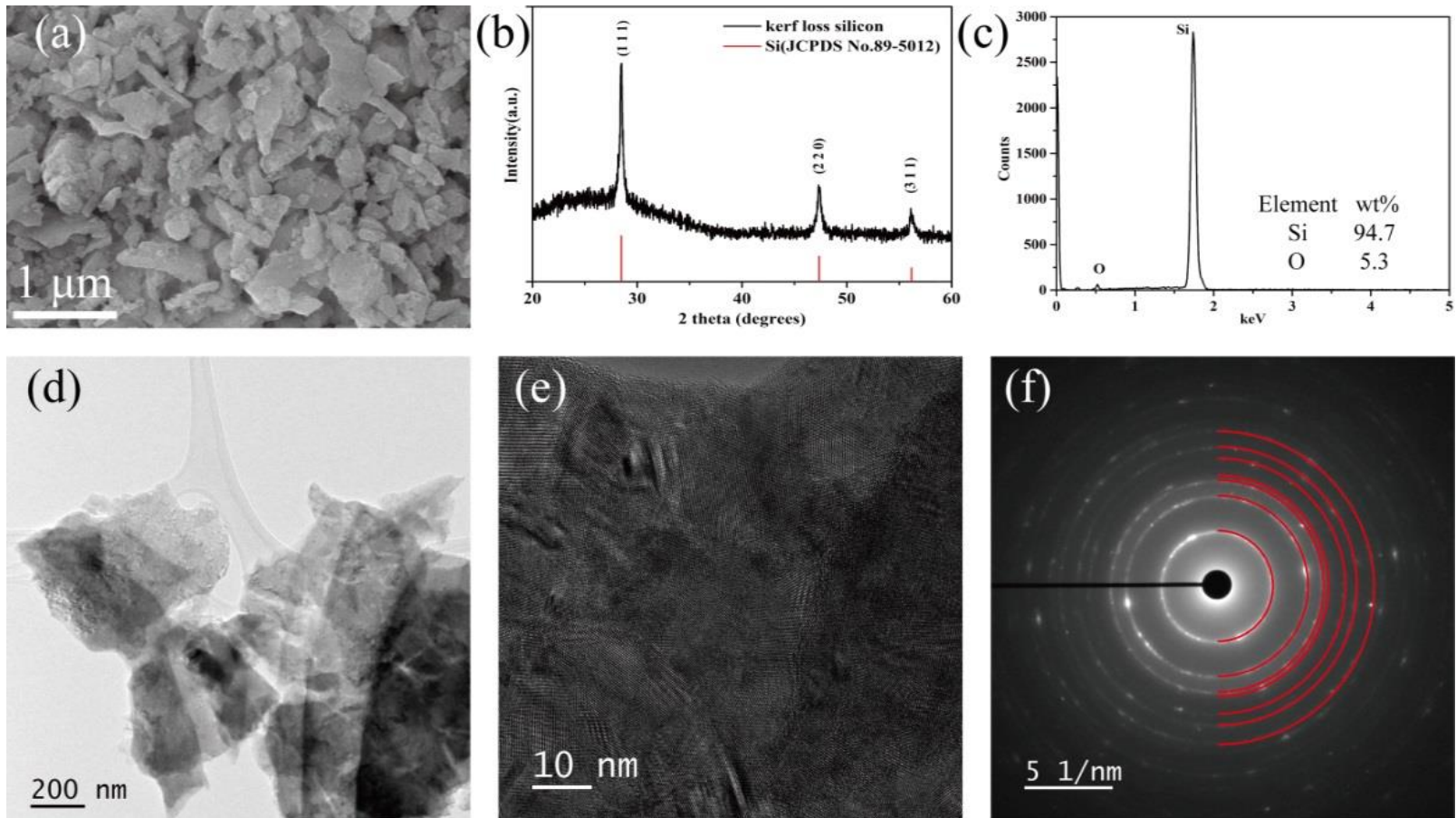
Areal capacity 3.2 mA h/cm<sup>2</sup>

single layer 25 μm X17



**Cell volume 100 x 50 x 2.605 mm 2350 mA h @3.45 V**

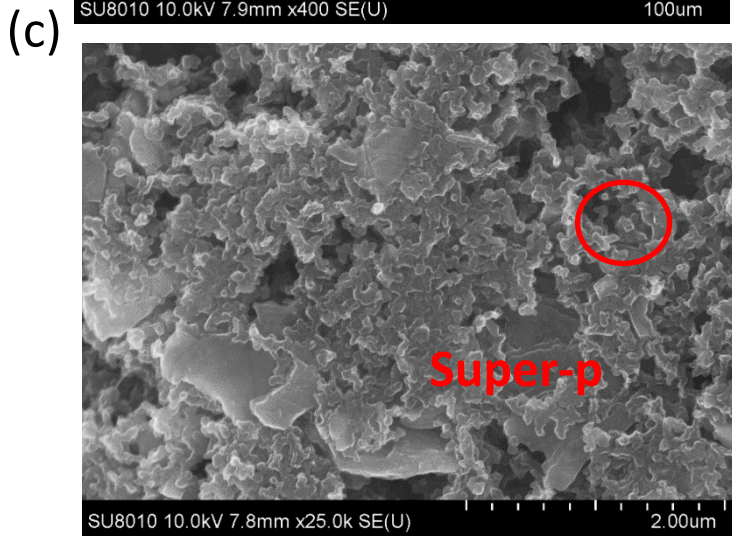
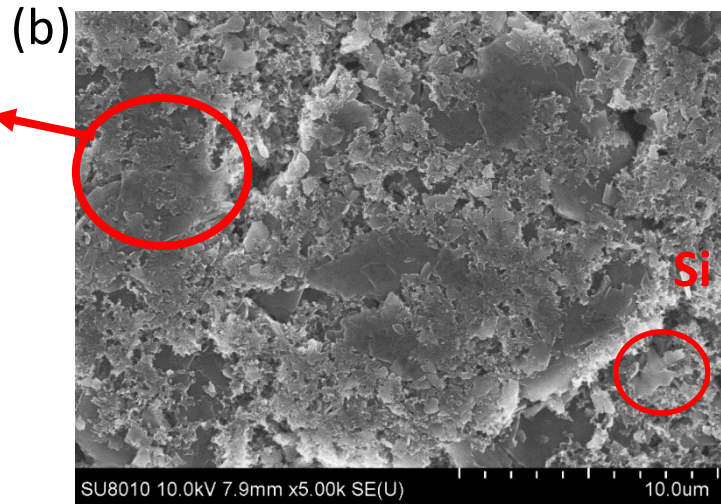
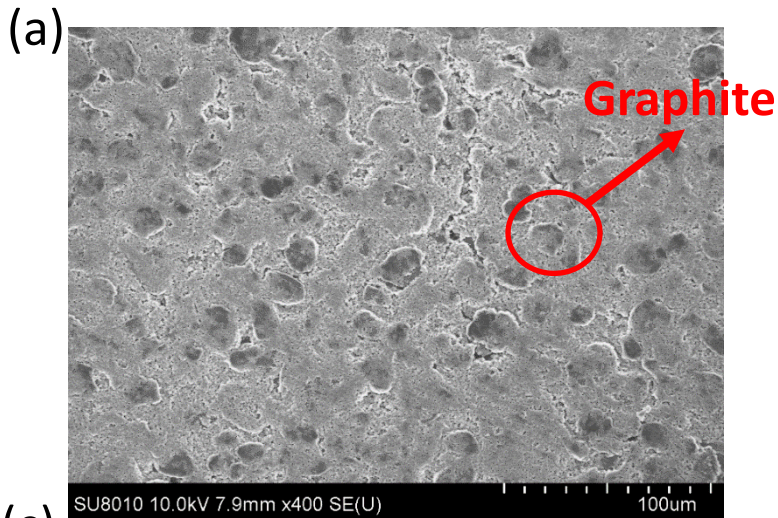
# Characterization of kerf loss silicon



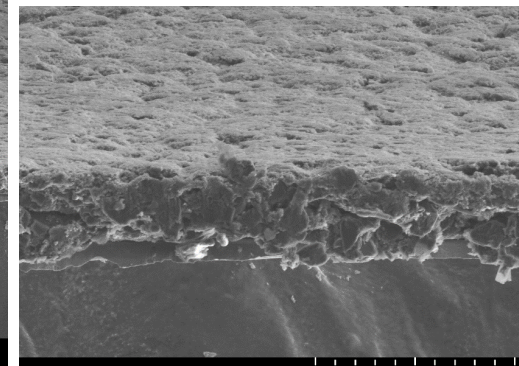
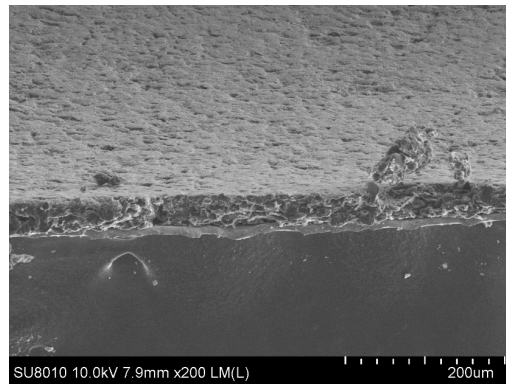
- Average size around 300-600 nm
- Slightly oxidized
- Polycrystalline
- No other metal impurity

Element	Concentration. (ppb)
Si	1000000
P	440
Ca	370
B	190

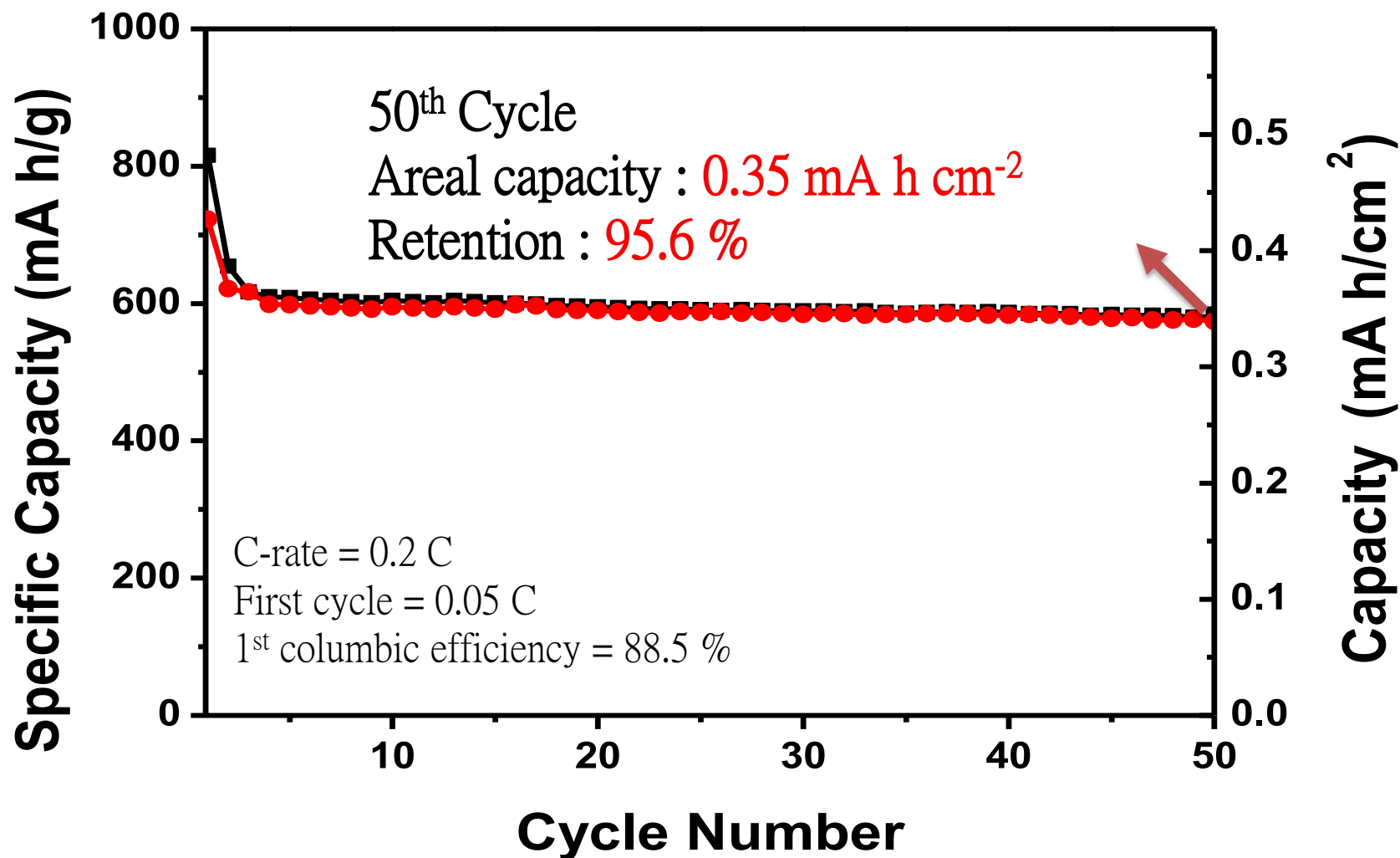
# Coated film of Si/Graphite



- Graphite : 15~30 µm, Si : average size 600 nm  
Super-p : 42~66 nm



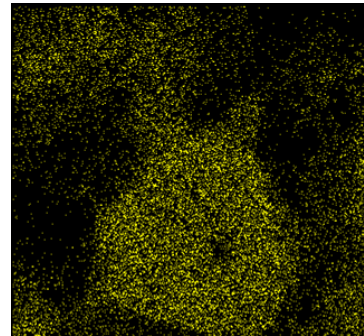
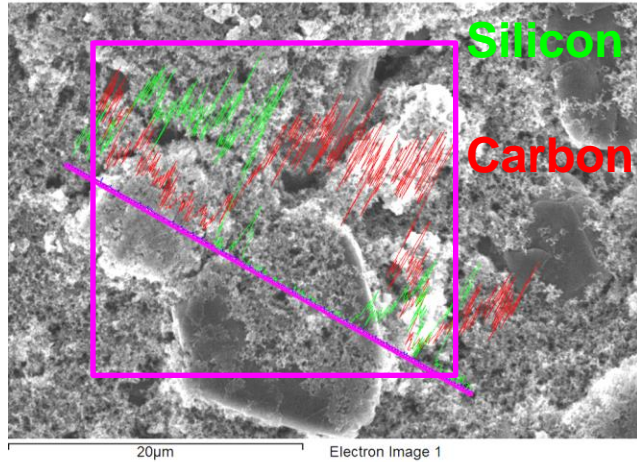
# Half-cell performance of Si/graphite anode



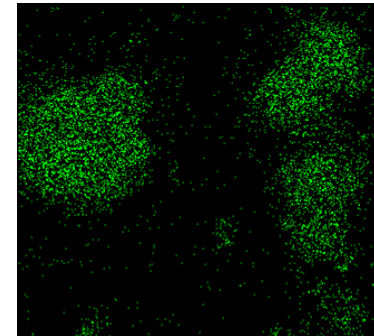


# Electrode Appearance-Front view

Before cycle

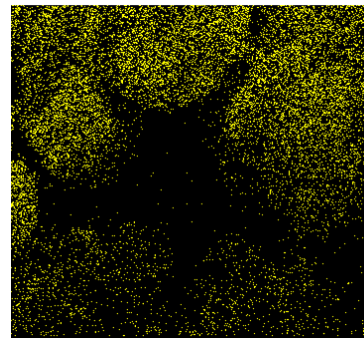
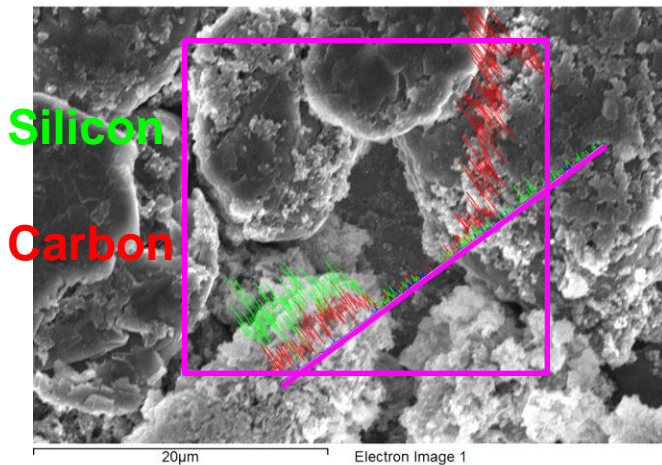


Carbon

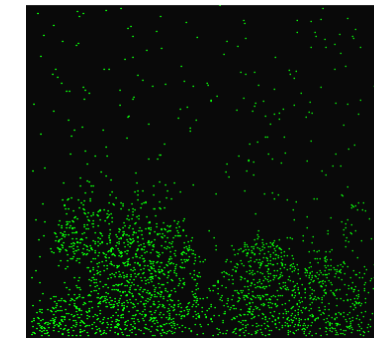


Silicon

After 100 cycles



Carbon

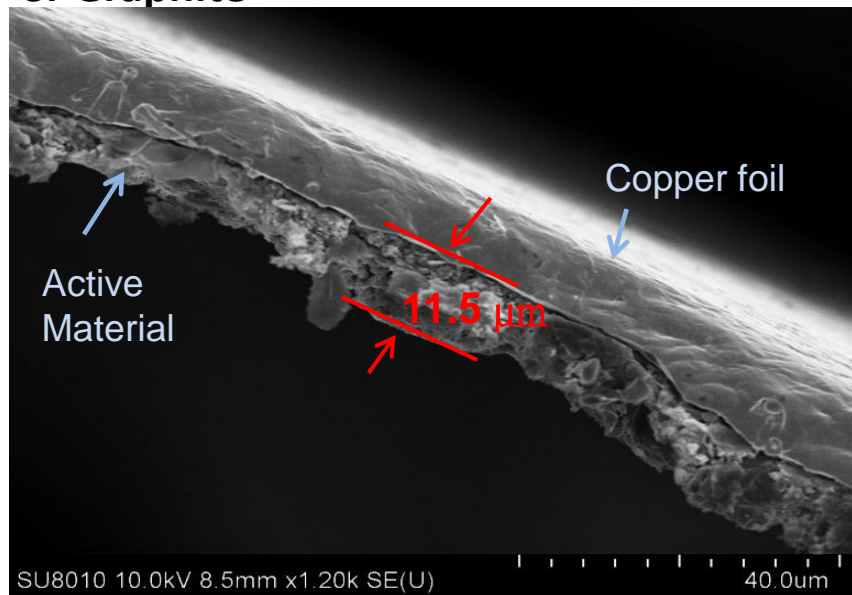


Silicon

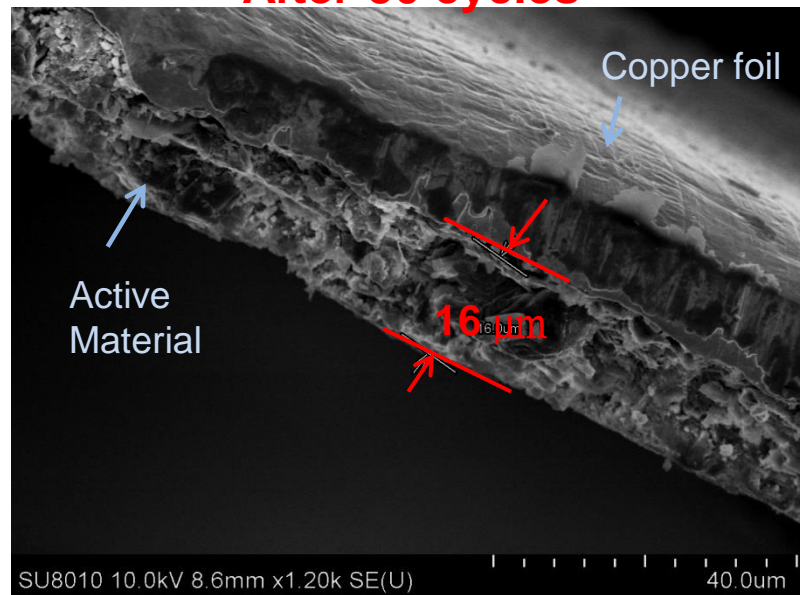
# Electrode Appearance-Side view

Si-Graphite

Before reaction



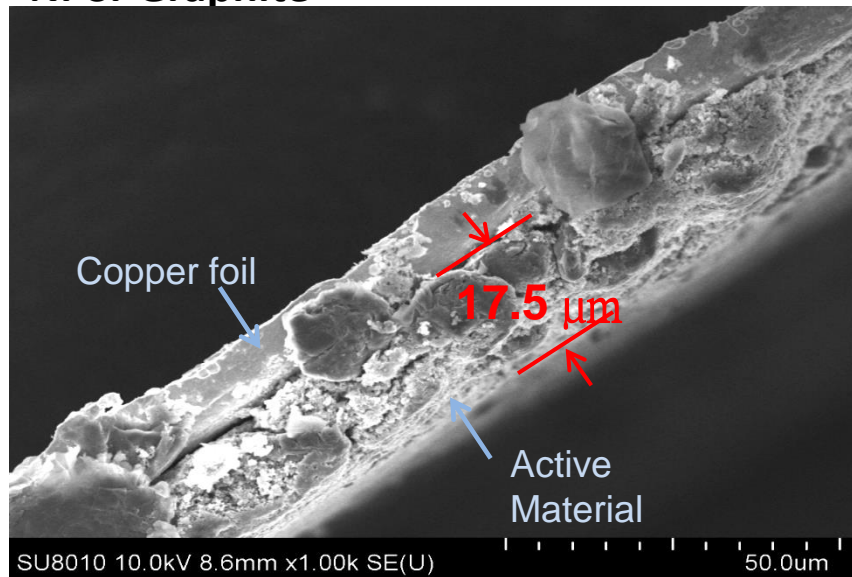
After 50 cycles



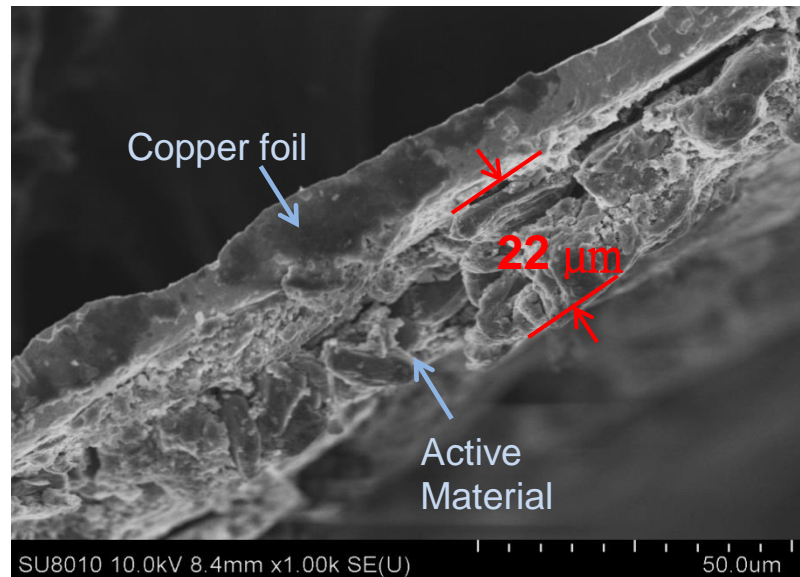
~40%

Ni-Si-Graphite

Before reaction

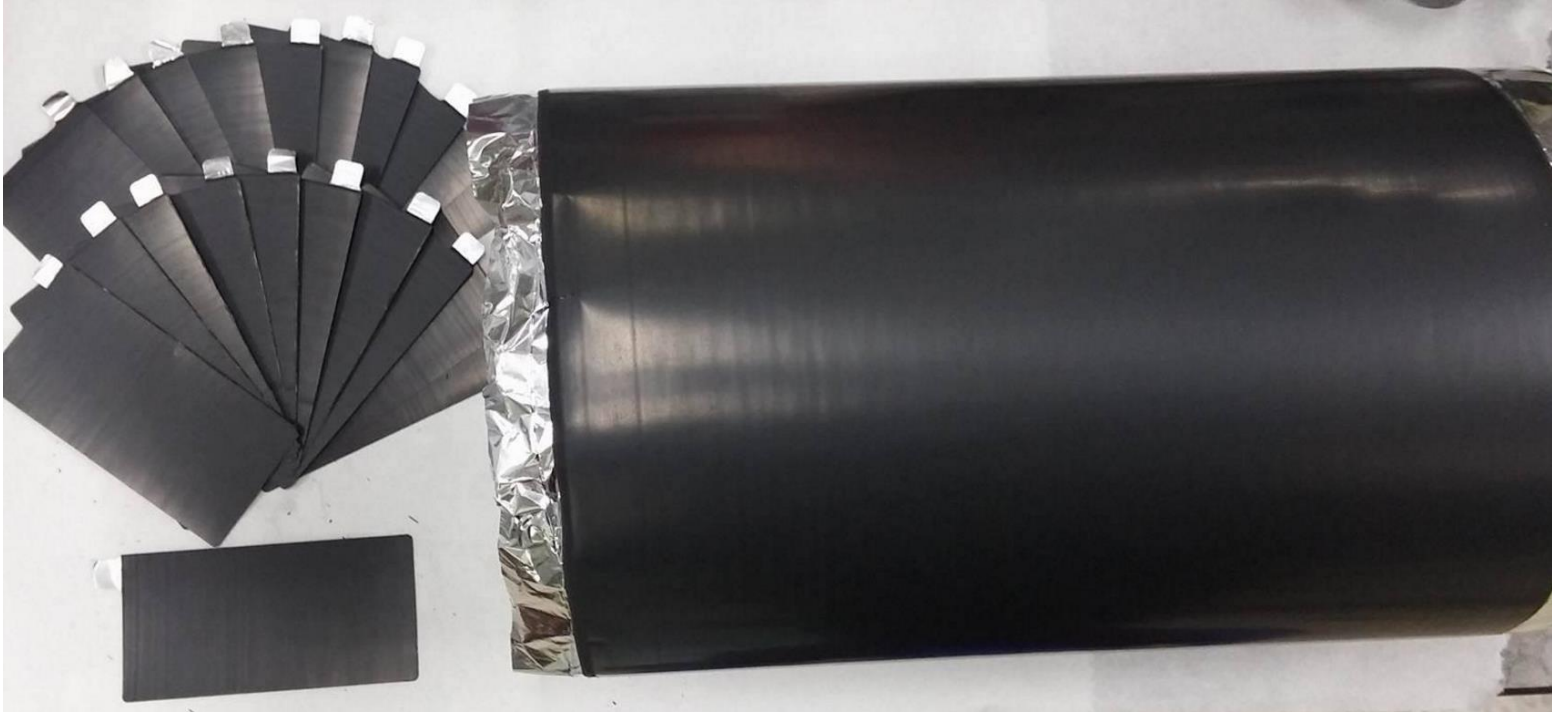


After 100 cycles



~25%

# Positive electrode



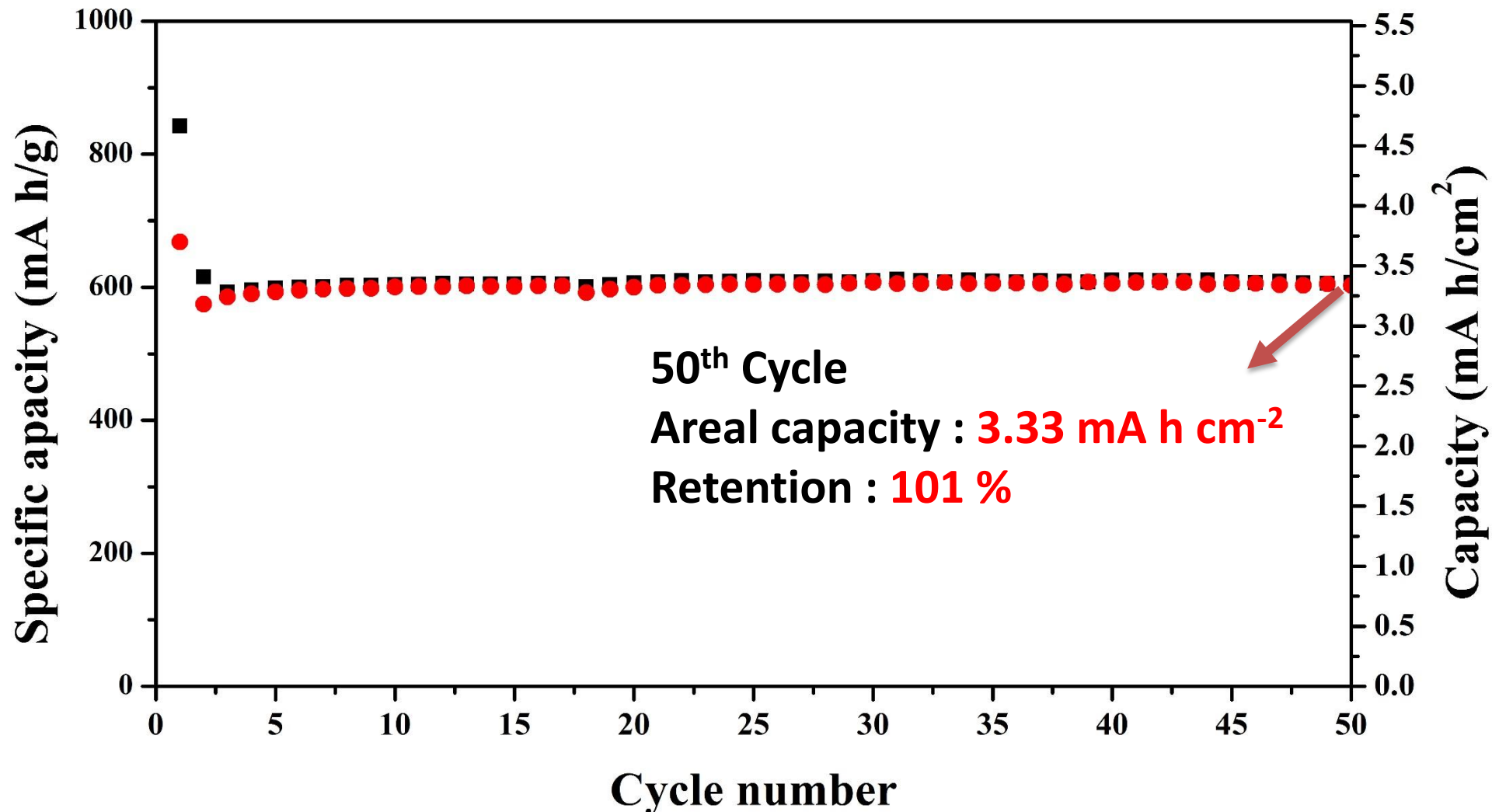
Li(NiCoMn)O<sub>2</sub> (NCM) :

Theoretical capacity : ~160 mA h/g), 4.2V

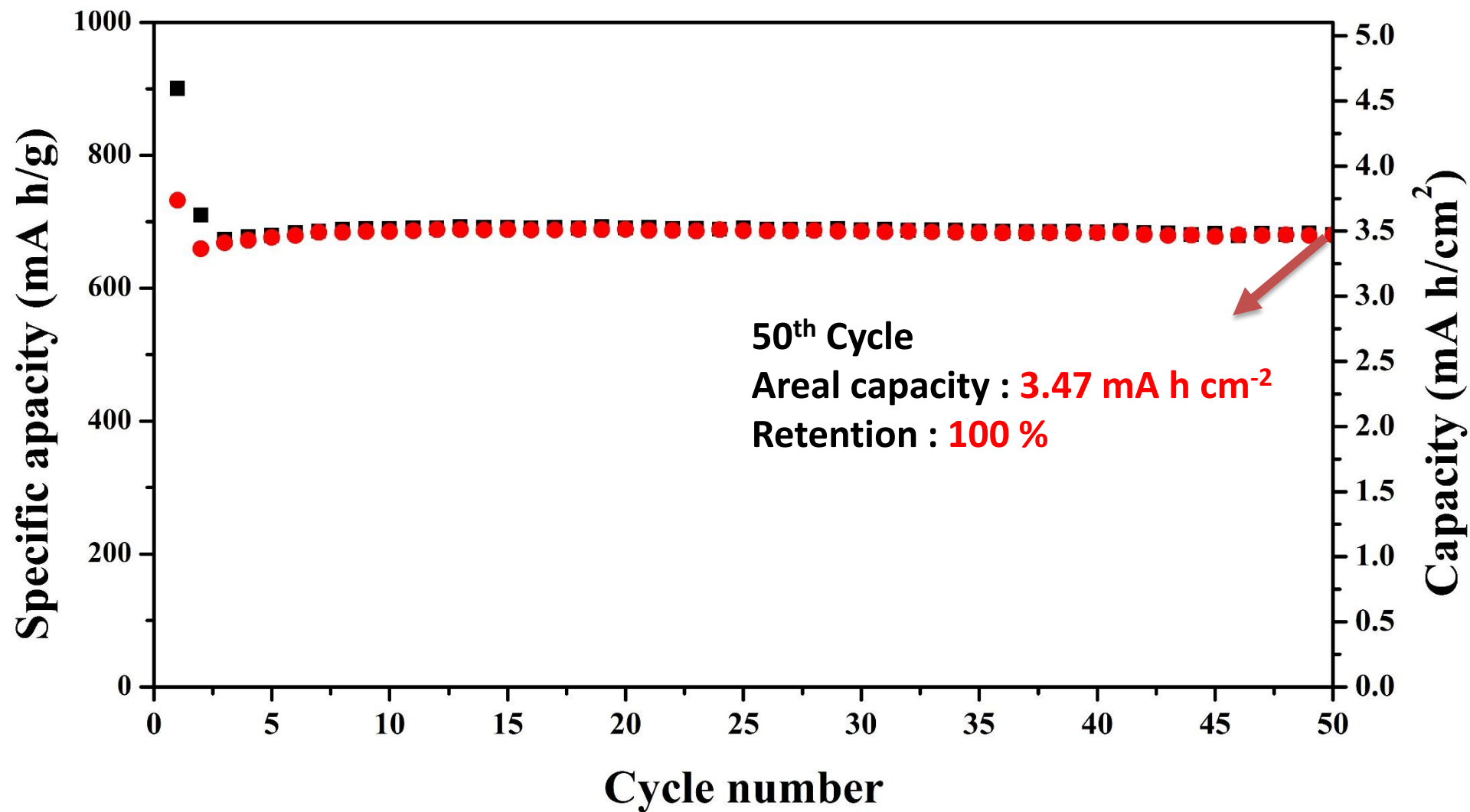
Operation range: 4.4V~4.5V(4.4V ~192 mA h/g)

Areal capacity :3.6 mA h cm<sup>-2</sup> ◦

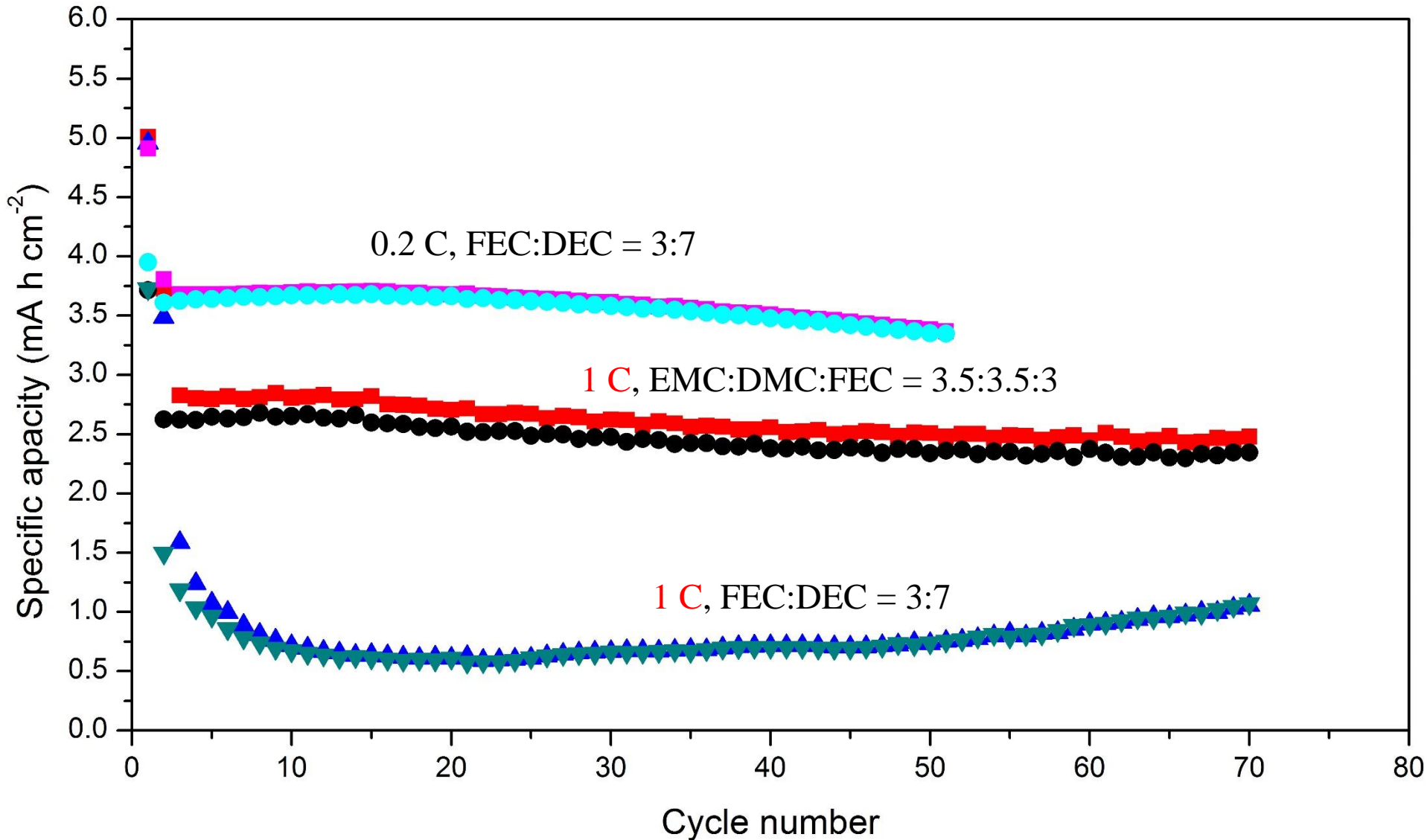
# Full cell: Si/Graphite-NCM



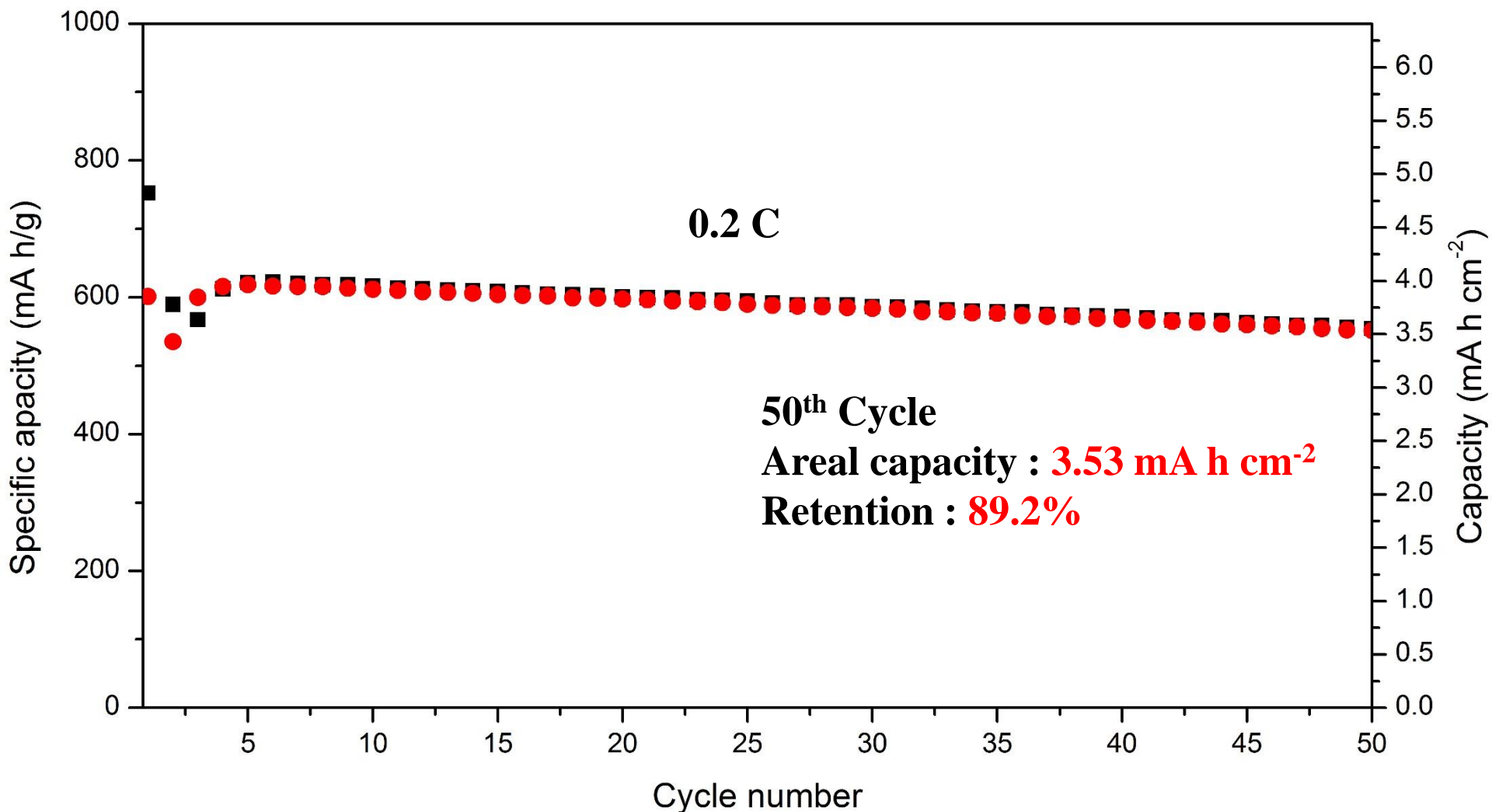
# Full cell : Si/MCMB-NCM



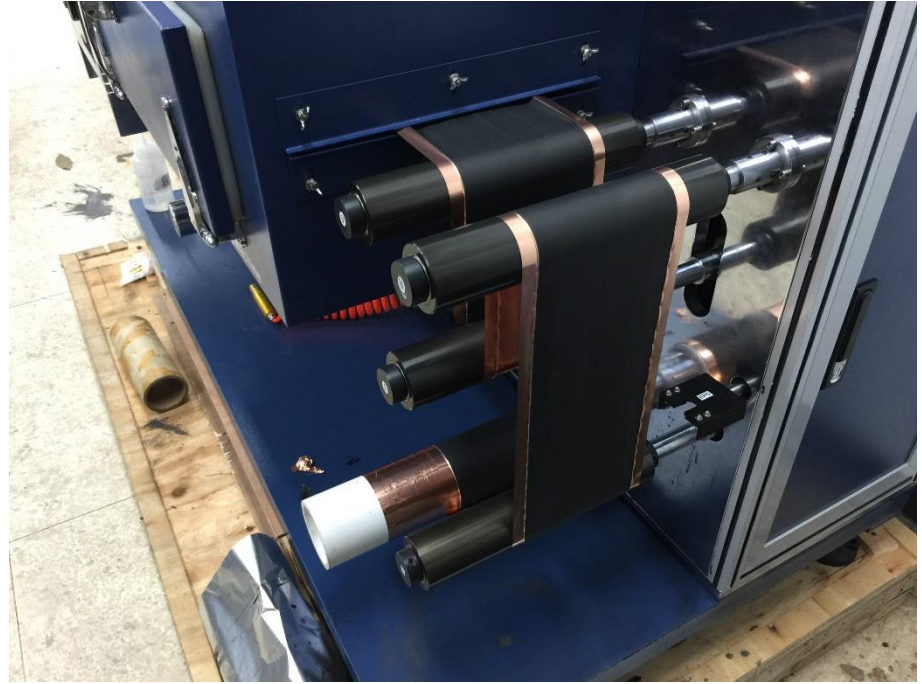
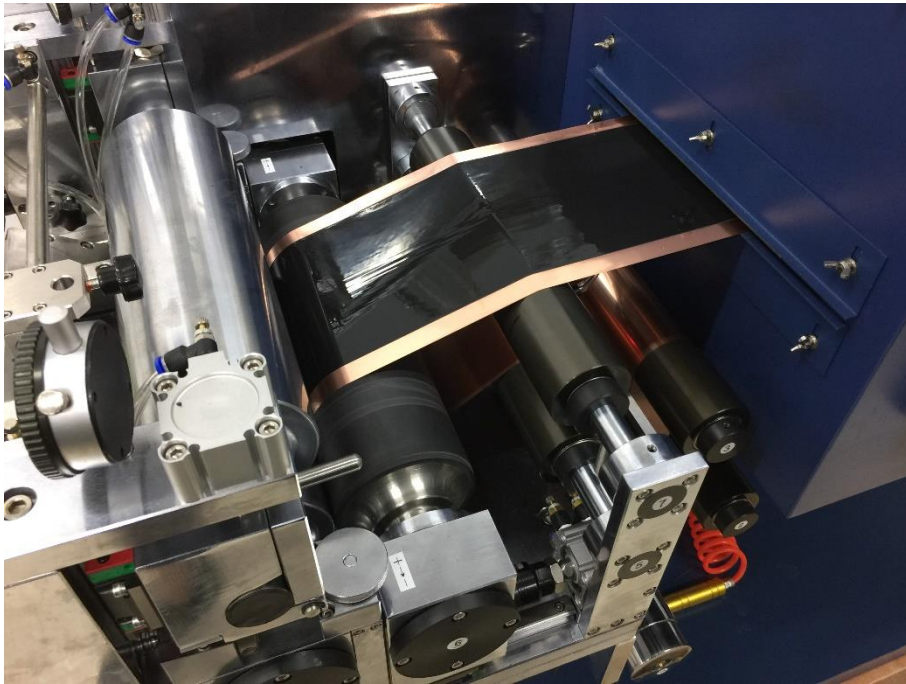
# The effect of electrolyte on battery performance



# Pouch-type full cell: Si/Graphite -NCM



# Double sided coating of active materials





# Power bank preparation



## Charge (4.3V)

Second cycle charge capacity: 2731 mA h

Average charge voltage : 3.90 V

Areal capacity : 3.03 mA h cm<sup>-2</sup>

thickness : 3.435 mm

**Volumetric energy density : 620.1 Wh l<sup>-1</sup>**

## Discharge 2.5V

Second cycle charge capacity 2703 mA h

Average charge voltage : 3.50 V

Areal capacity : 3.00 mA h cm<sup>-2</sup>

thickness : 3.069 mm

**Volumetric energy density : 616.5 Wh l<sup>-1</sup>**

# Conclusion

## Coin half cell

Parameters of Slurry, coating, rolling

First cycle coulombic efficiency : 88.5%

Areal capacity retention: 95.6 %

## Coin Full cell

Areal capacity:  $3.33 \text{ mA h cm}^{-2}$

Areal capacity retention: 101 %

## Pouch-type cell: Single layer

Areal capacity:  $3.53 \text{ mA h cm}^{-2}$

Areal capacity retention: 90%  
50th cycle

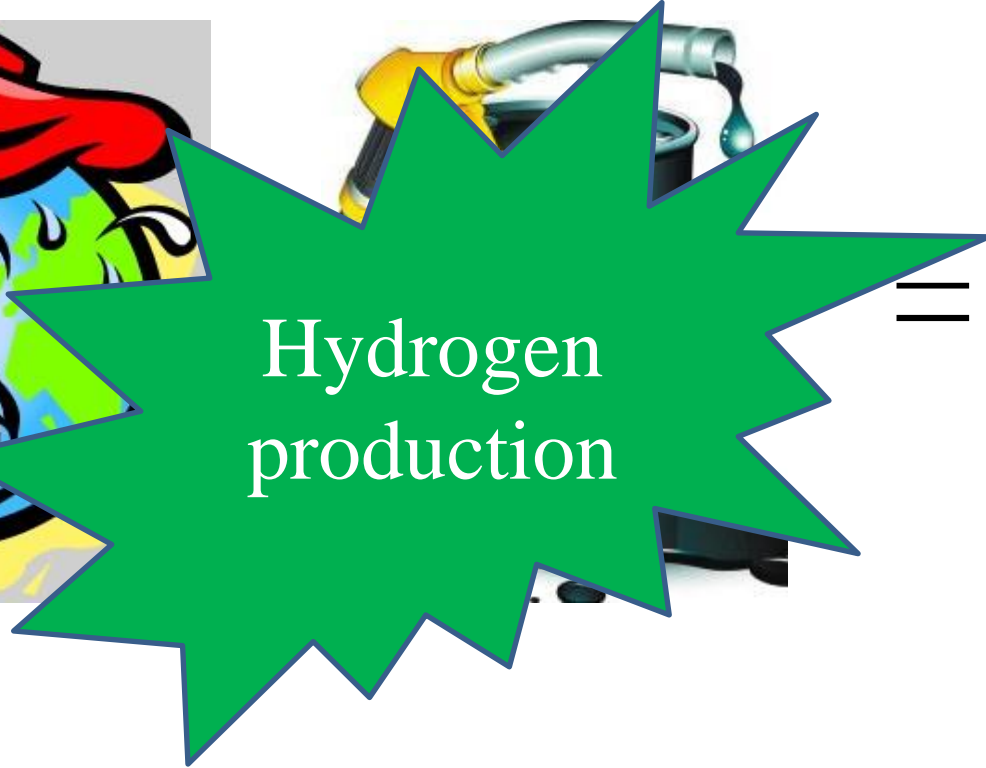
## Pouch-type Cell: multiple layer

1. Continuous coating technique
2. Cell capacity >2300 mAh
3. Volumetric capacity >600 mAh/cm<sup>3</sup>

# Introduction

Greenhouse effect

Limited fossil oil reserves



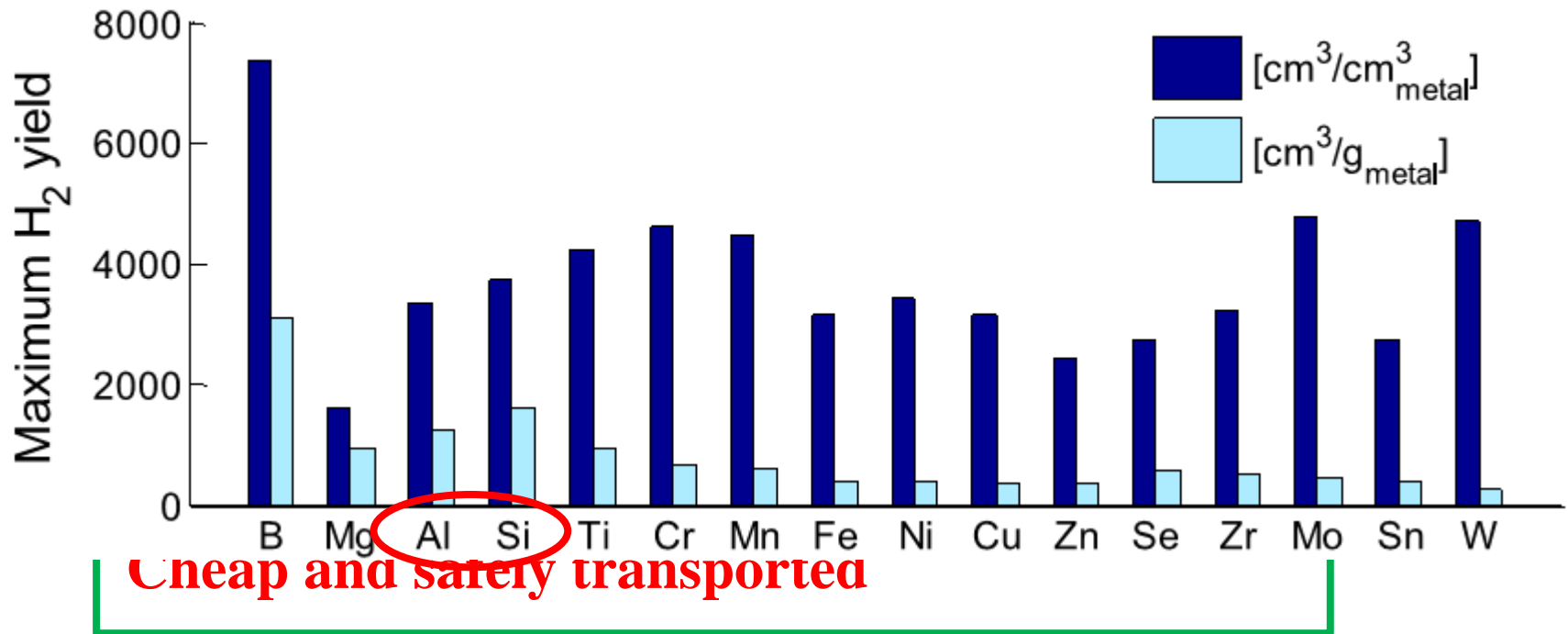
Develop  
alternative  
clean  
energy

- high heat value of 141.79 MJ/kg
- Benign emission after combustion

# Hydrogen Production Method

## Chemical process

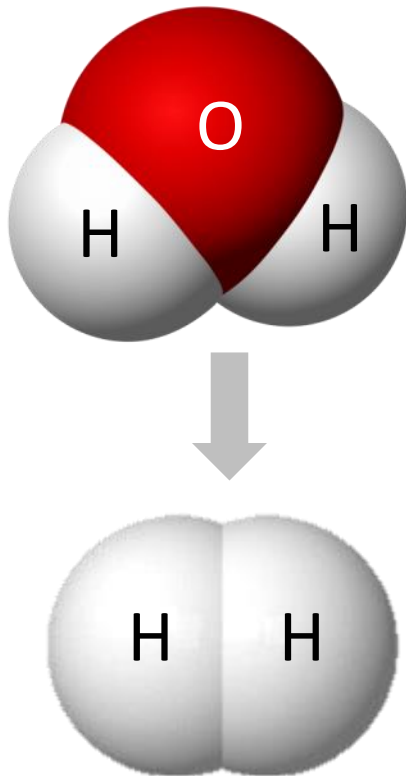
- **Metal-hydride (e.g.  $\text{NaBH}_4$  and  $\text{MgH}_2$ )**



# Hydrogen Economy

## Characteristics of H<sub>2</sub>

- ❑ Heating value (142 MJ/kg)
- ❑ Benign end production (i.e. H<sub>2</sub>O)
- ❑ Extremely low density (0.081 kg/m<sup>3</sup>)

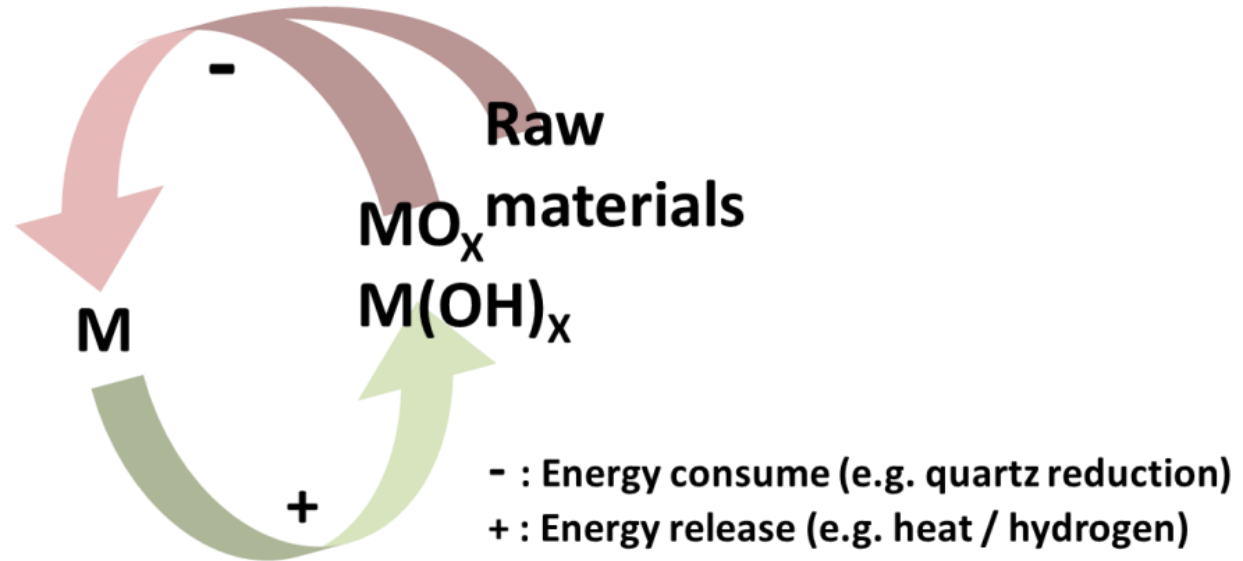


## H<sub>2</sub> production method

- ❑ Fossil fuel reforming : CO, CO<sub>2</sub> emit
- ❑ Electrolysis : Energy intensive
- ❑ **Chemical process : Safe Transportation**
- ❑ Photocatalysis : small-scale
- ❑ Fermentative : small-scale

# Metal-Water reaction

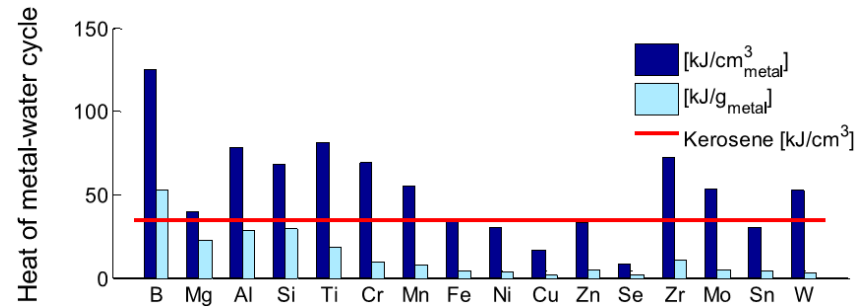
## *Silicon versus Aluminum*



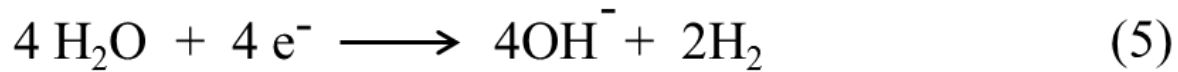
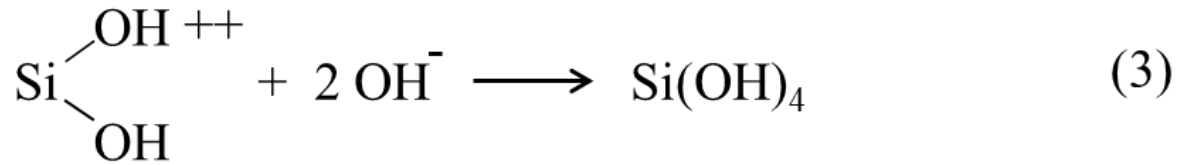
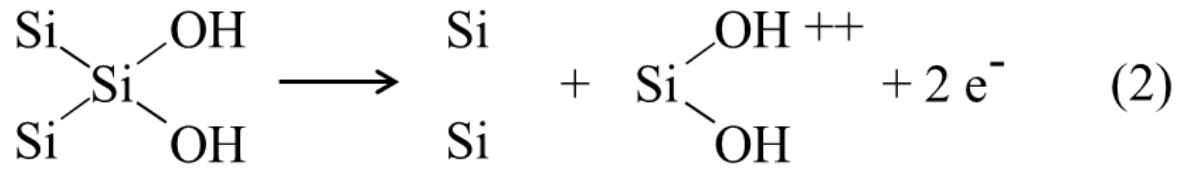
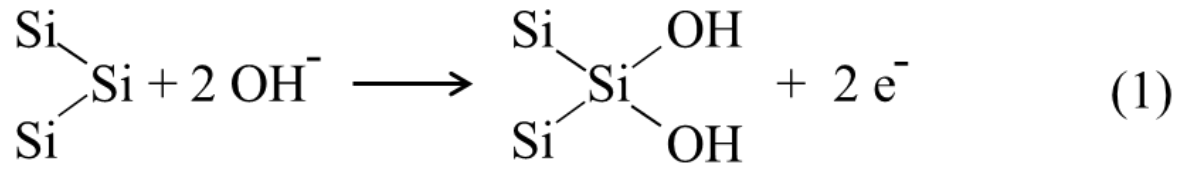
Type of metals	Energy release <sup>1</sup> (MJ kg <sup>-1</sup> )	Price (USD Kg <sup>-1</sup> )	Abundance in earth crust (wt%)
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Si	33	2	27.7
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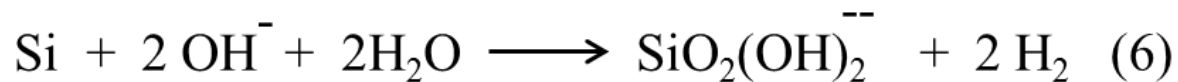
Al	31	2	8.2
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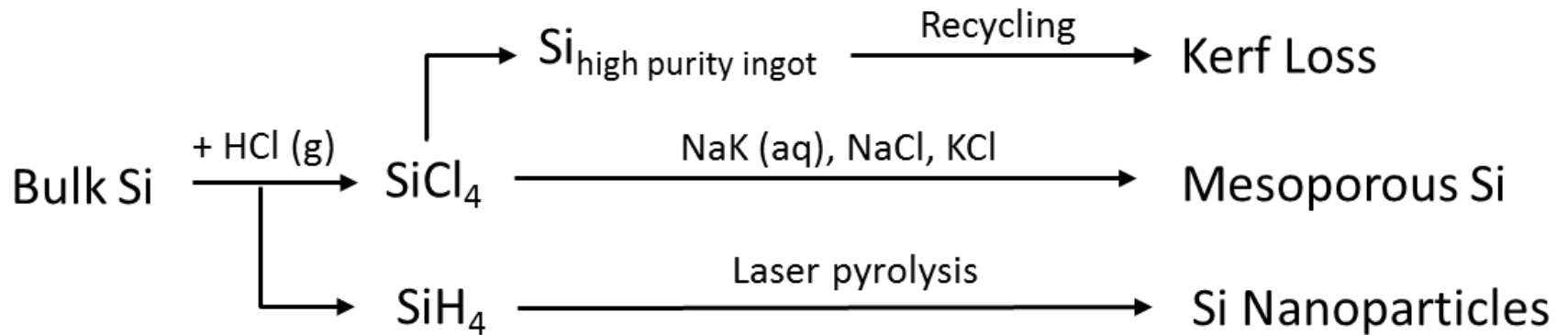
<sup>1</sup>Total energy of metal-water reaction heat and hydrogen released from it.



Overall reaction :

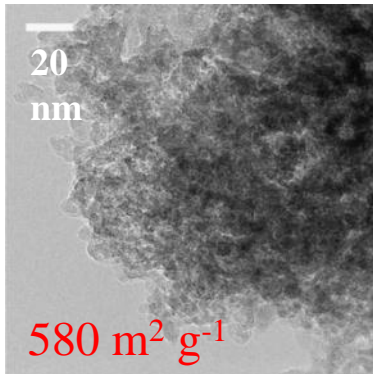


# Scheme Diagram of using kerf loss as energy carrier





# Mesoporous Si

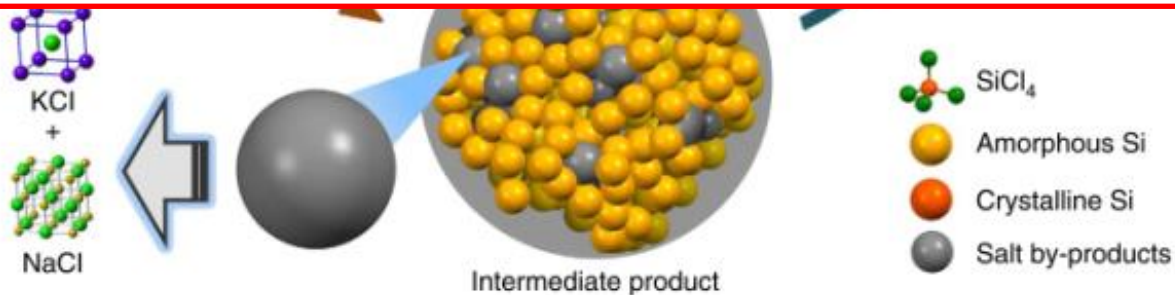


## Advantages

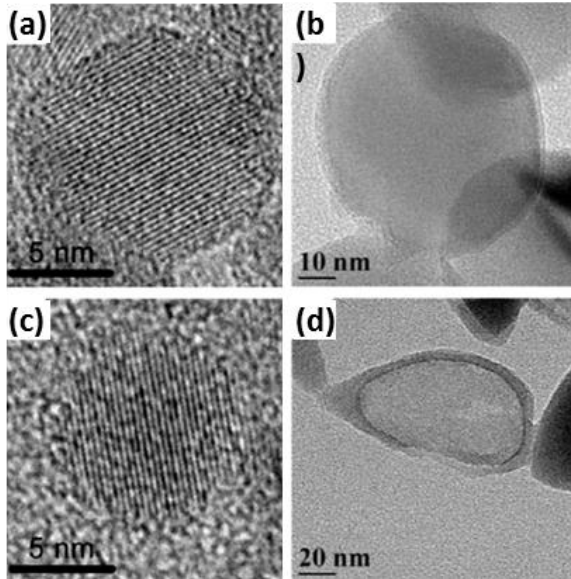
- ❑ High specific surface area :  $580 \text{ m}^2 \text{ g}^{-1}$
- ❑ Hydrogen production rate ( $9.5 \times 10^{-2} \text{ g}_{\text{H}_2} \text{ s}^{-1} \text{ g}_{\text{Si}}^{-1}$ )
- ❑ Yield (90%)

## Disadvantages

- ❑ Highly active NaK was used
- ❑ Toxic  $\text{SiCl}_4$  was used



# Si Nanoparticles



## Process description:

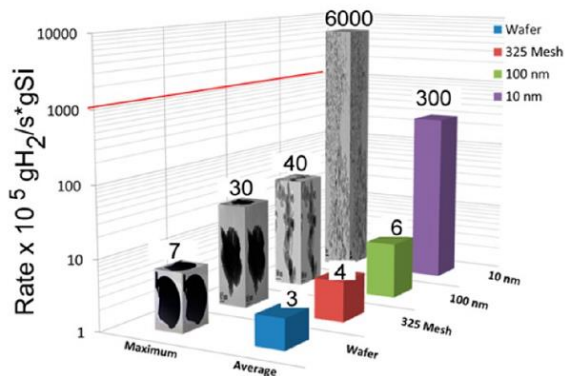
Laser-driven chemical reaction using  $\text{SiH}_4$  to generate hydrogen-bonded Si nanoparticles.

## Advantages

- ❑ Hydrogen production rate ( $6.0 \times 10^{-2} \text{ g}_{\text{H}_2} \text{ s}^{-1} \text{ g}_{\text{Si}}^{-1}$ )
- ❑ Yield (129%)

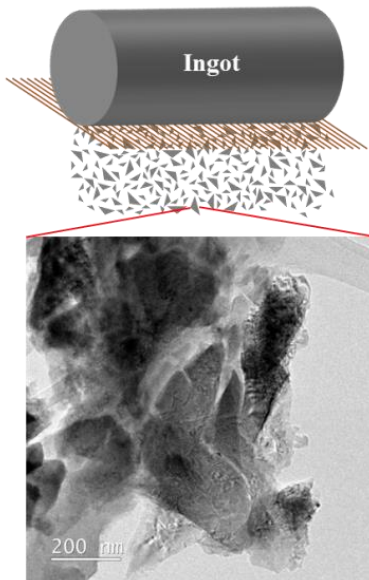
## Disadvantages

- ❑ Flammable  $\text{SiH}_4$  was used
- ❑  $\text{CO}_2$  laser beam (Heating rate  $10^5 \text{ K/ sec}$ )



# Motivation

Kerf loss silicon collected  
from the sawing process of  
solar-grade silicon



- Micro-sized kerf loss silicon
- Additives-mediated
- Low cost (1 USD / kg)
- Environmental-friendly process

# Time-resolved small-scale hydrogen production set-up

Constant temperature



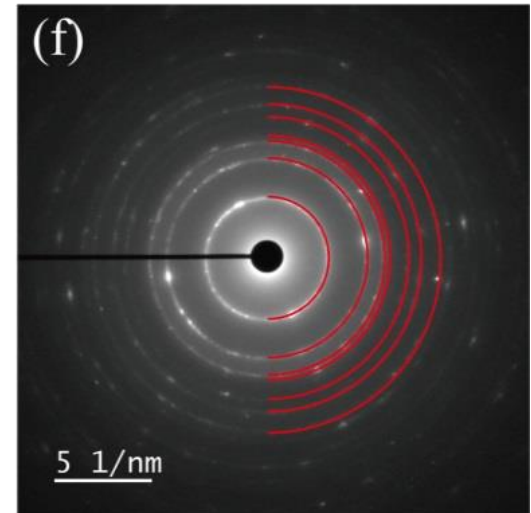
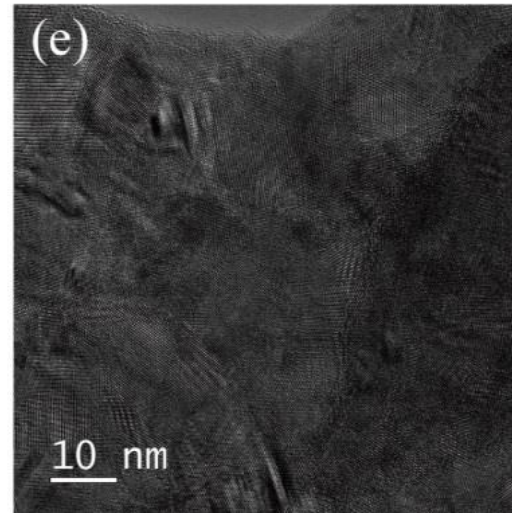
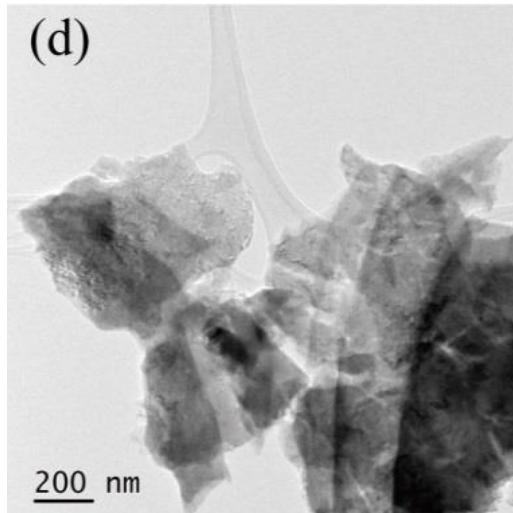
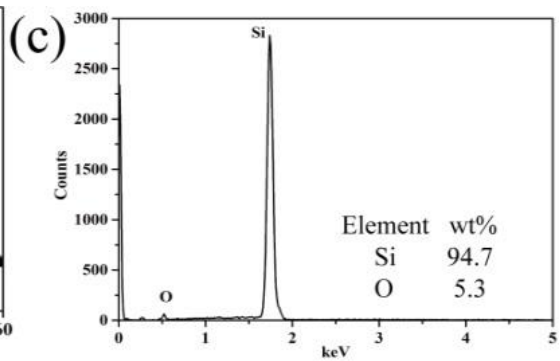
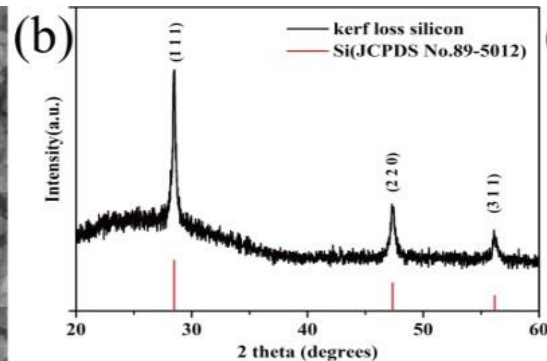
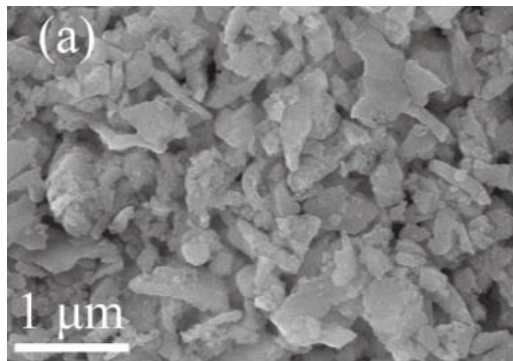
Volumetric calculation for small scale (70ml) hydrogen production



Remove water vapor



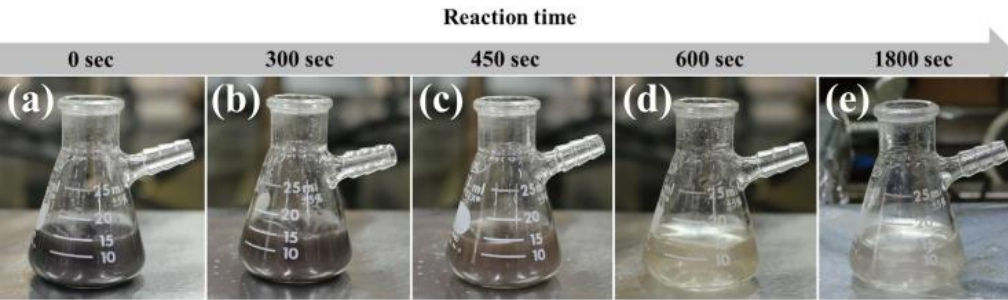
# Characterization of kerf loss silicon



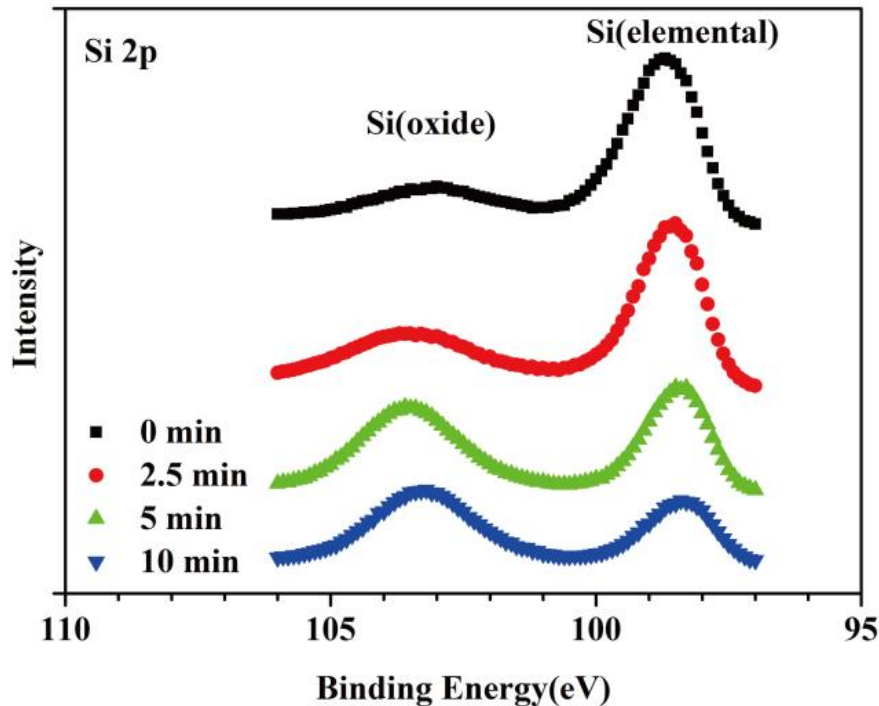
- Average size around 0.5  $\mu\text{m}$
- Slightly oxidized
- Polycrystalline
- No other metal impurity

Element	Concentration. (ppb)
Si	1000000
P	440
Ca	370
B	190

# Real-time observation



(f)



- As reaction time went by, the color of etching solution became lighter gradually.
- The oxide peak at 103.3 eV became relatively strong as reaction time proceeded, indicating the concentration of silicate increased.

# Hydrogen Production Video



$$P_i V_i = n_i RT \quad \& \quad P_f V_f = n_f RT$$

$$\Rightarrow (P_i + \Delta P)(V_i + \Delta V) = (n_i + \Delta n)RT$$

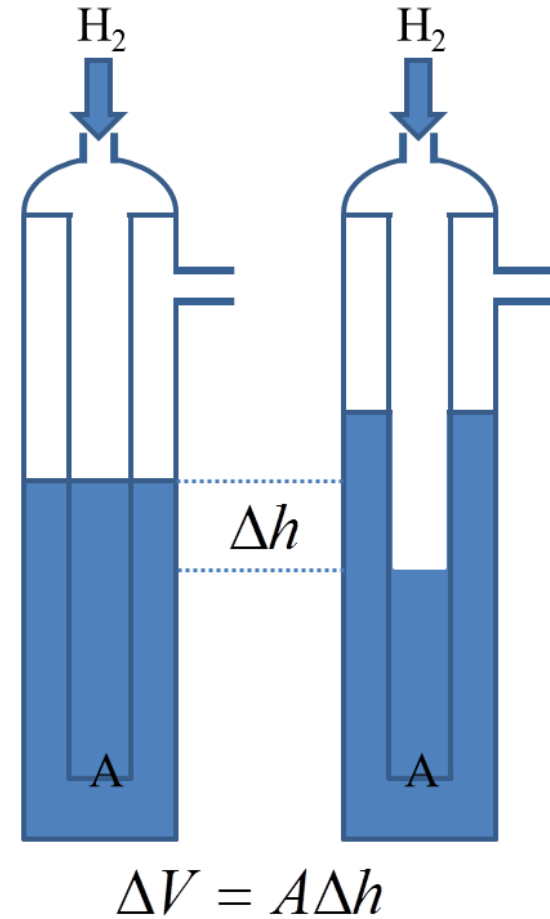
$$\Rightarrow P_i \left( 1 + \frac{\Delta P}{P_i} \right) (V_i + \Delta V) = (n_i + \Delta n)RT$$

$$\Rightarrow P_i (V_i + \Delta V) = (n_i + \Delta n)RT$$

$$\Rightarrow P_i V_i + P_i \Delta V = n_i RT + \Delta n RT$$

$$\Rightarrow P_i \Delta V = \Delta n RT$$

$$\Rightarrow n_{H_2} = \Delta n = \frac{P_i \Delta V}{RT} = \frac{P_i A \Delta h}{RT}$$



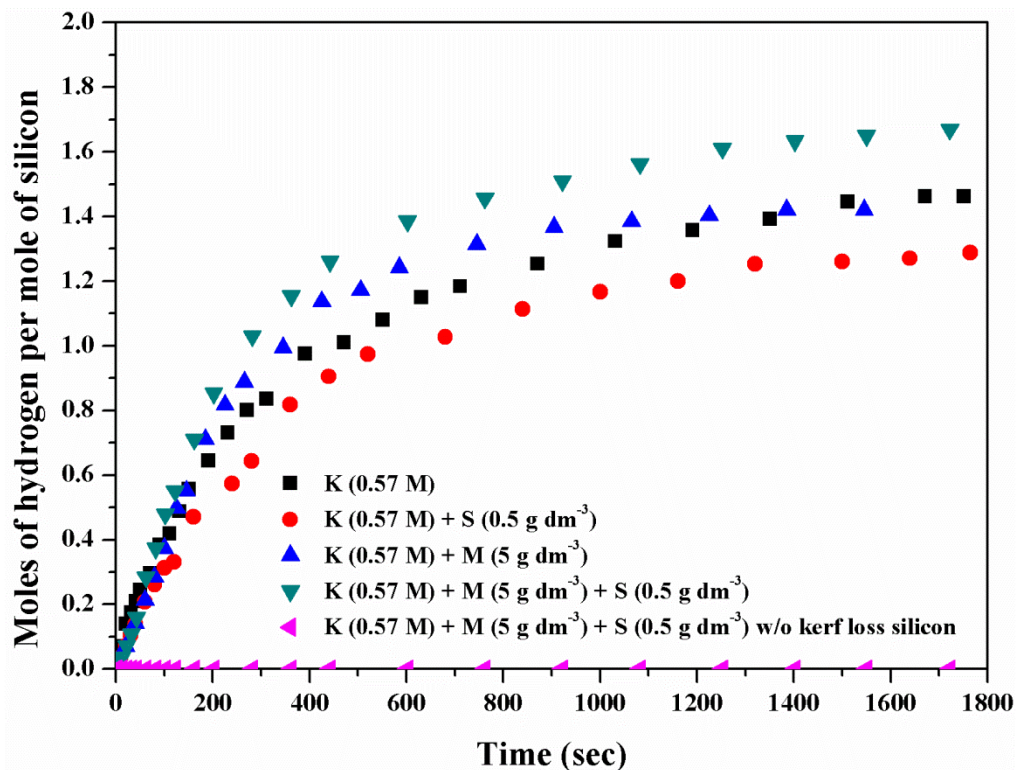


# Ideal gas and real gas

- Table 2 Density table of real gas and ideal gas regarding hydrogen

P ( atm )	T ( K )	density( ideal gas, kg m <sup>-3</sup> )	density( NIST, kg m <sup>-3</sup> )	deviation percentage( % )
1	273	0.089990	0.089934	0.063
1	283	0.086811	0.086758	0.061
1	293	0.083848	0.083798	0.059
1	303	0.081080	0.081033	0.059
1	313	0.078490	0.078445	0.057
1	323	0.076060	0.076017	0.057
1	333	0.073776	0.073735	0.056
1	343	0.071625	0.071586	0.055
1	353	0.069596	0.069559	0.053
1	363	0.067679	0.067644	0.051
1	373	0.065864	0.065831	0.051

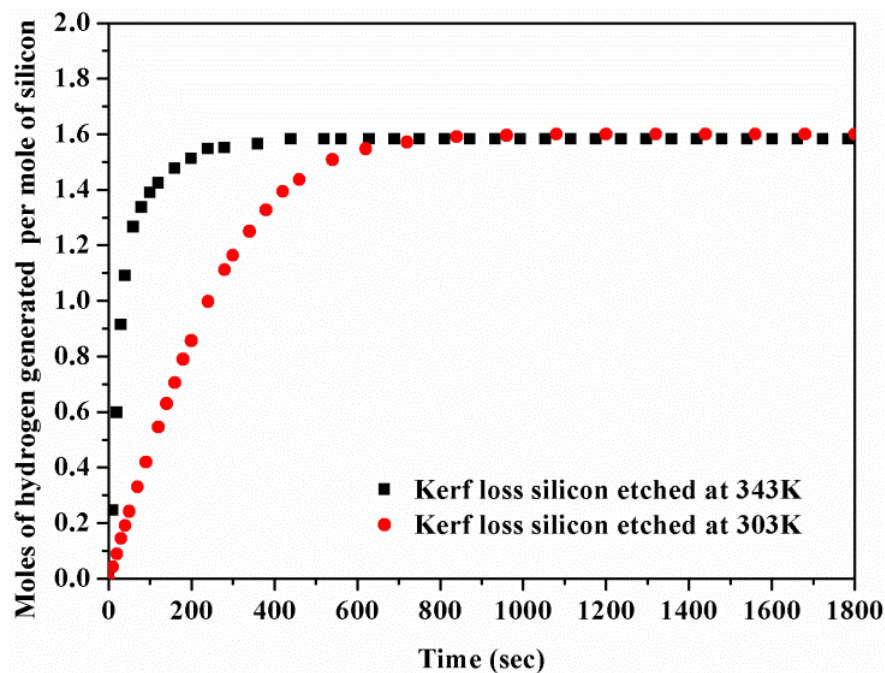
# Effects of $\text{Na}_2\text{SiO}_3$ and $\text{H}_2\text{SiO}_3$ on the base-catalyzed etching of kerf loss silicon at 303 K



Additives	Hydrogen production rate , $\text{g}(\text{H}_2) \text{ s}^{-1} \text{ g}^{-1}(\text{Si})$	Yield (%)
K (0.57 M)	$6.0 \times 10^{-5}$	73
K (0.57 M) + S ( $0.5 \text{ g dm}^{-3}$ )	$6.3 \times 10^{-5}$	64
K (0.57 M) + M ( $5 \text{ g dm}^{-3}$ )	$6.8 \times 10^{-5}$	71
K (0.57 M) + M ( $5 \text{ g dm}^{-3}$ ) + S ( $0.5 \text{ g dm}^{-3}$ )	$7.4 \times 10^{-5}$	83
K (0.57 M) + M ( $5 \text{ g dm}^{-3}$ ) + S ( $0.5 \text{ g dm}^{-3}$ ) w/o kerf loss silicon	0	0



# Effects of reaction temperature on the base-catalyzed etching of kerf loss silicon



	Hydrogen production rate , $\text{g}(\text{H}_2) \text{ s}^{-1} \text{ g}^{-1}(\text{Si})$	Yield (%)
K (0.57 M) + M (5 $\text{g dm}^{-3}$ ) + S (0.5 $\text{g dm}^{-3}$ ) at 303 K	$1.1 \times 10^{-4}$	79
K (0.57 M) + M (5 $\text{g dm}^{-3}$ ) + S (0.5 $\text{g dm}^{-3}$ ) at 343 K	$2.6 \times 10^{-4}$	78

# Result and Discussion

## Small scale – Optimal quantity of additives

– : low level    + : High level

No. of experiments	K	M	S
1	-	-	-
2	-	+	-
3	+	-	-
4	+	+	-
5	-	-	+
6	-	+	+
7	+	-	+
8	+	+	+

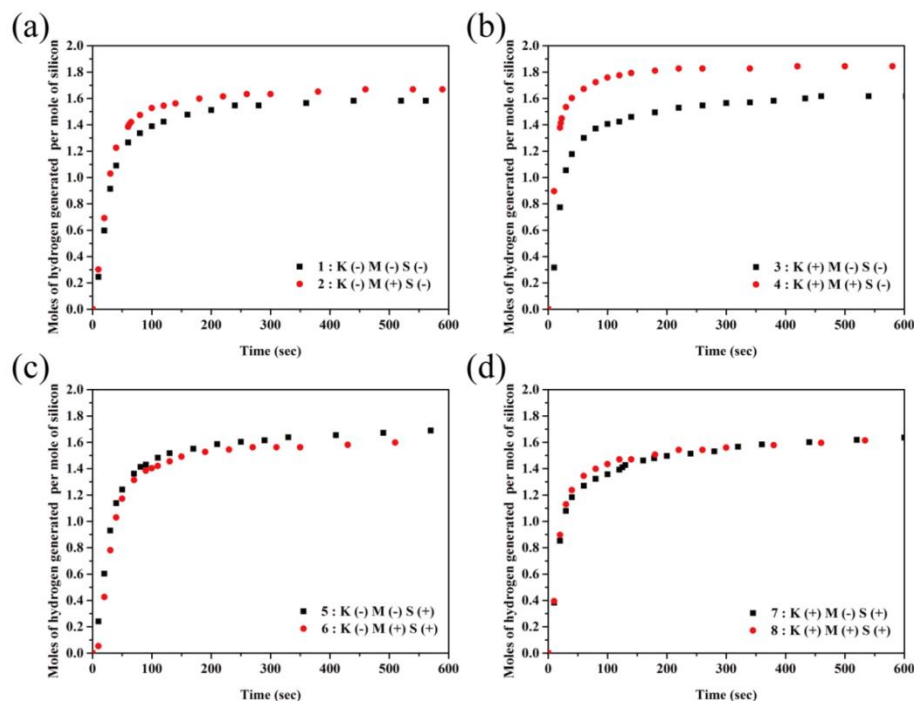
### Abbreviation

K: Potassium hydroxide (KOH)

M: Sodium metasilicate ( $\text{Na}_2\text{SiO}_3$ )

S: Silicic acid ( $\text{H}_2\text{SiO}_3$ )

# Different compositions of additives at 343K



No. of experiment	Composition of additives	70% conversion rate , $\text{g}(\text{H}_2) \text{ s}^{-1} \text{ g}^{-1}(\text{Si})$	Yield (%)
1	K (0.57 M) + M (5 $\text{g dm}^{-3}$ ) + S (0.5 $\text{g dm}^{-3}$ )	$9.88 \times 10^{-4}$	79
2	K (0.57 M) + M (40 $\text{g dm}^{-3}$ ) + S (0.5 $\text{g dm}^{-3}$ )	$1.61 \times 10^{-3}$	83
3	K (2.14 M) + M (5 $\text{g dm}^{-3}$ ) + S (0.5 $\text{g dm}^{-3}$ )	$1.00 \times 10^{-3}$	81
4	K (2.14 M) + M (40 $\text{g dm}^{-3}$ ) + S (0.5 $\text{g dm}^{-3}$ )	$4.72 \times 10^{-3}$	92
5	K (0.57 M) + M (5 $\text{g dm}^{-3}$ ) + S (4 $\text{g dm}^{-3}$ )	$1.24 \times 10^{-3}$	84
6	K (0.57 M) + M (40 $\text{g dm}^{-3}$ ) + S (4 $\text{g dm}^{-3}$ )	$9.99 \times 10^{-4}$	80
7	K (2.14 M) + M (5 $\text{g dm}^{-3}$ ) + S (4 $\text{g dm}^{-3}$ )	$8.03 \times 10^{-4}$	82
8	K (2.14 M) + M (40 $\text{g dm}^{-3}$ ) + S (4 $\text{g dm}^{-3}$ )	$1.24 \times 10^{-3}$	81

163%

472%

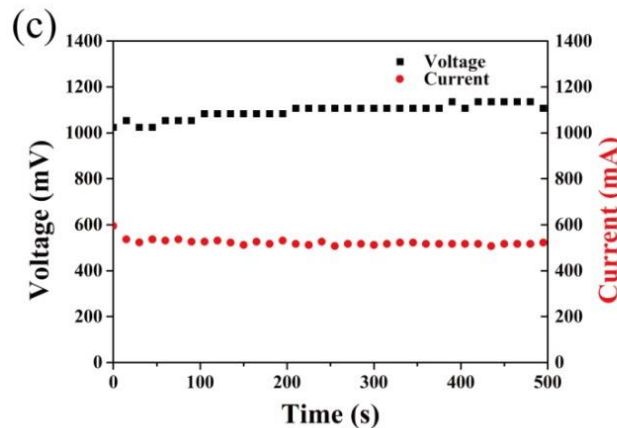
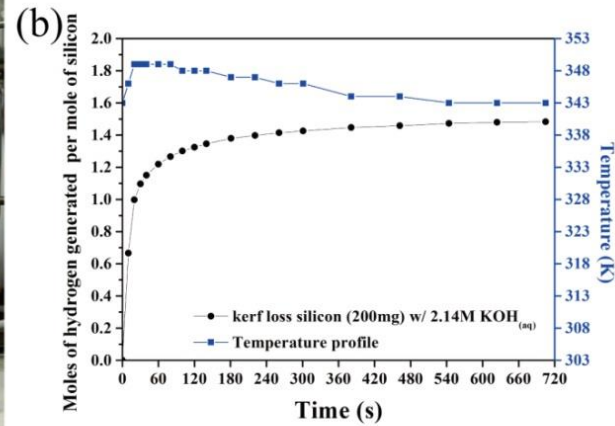
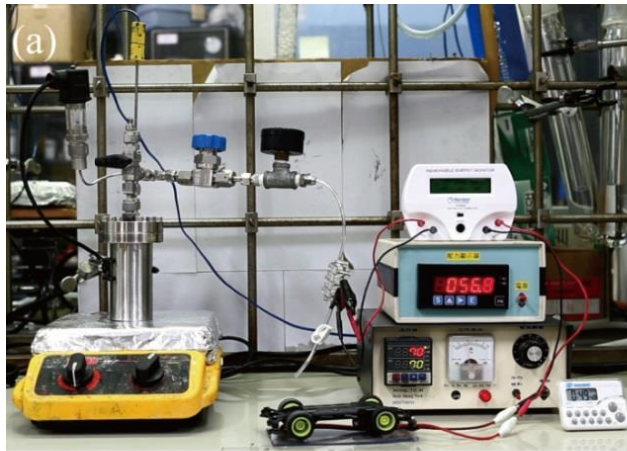
125%

80%

# Different hydrogen production methods.

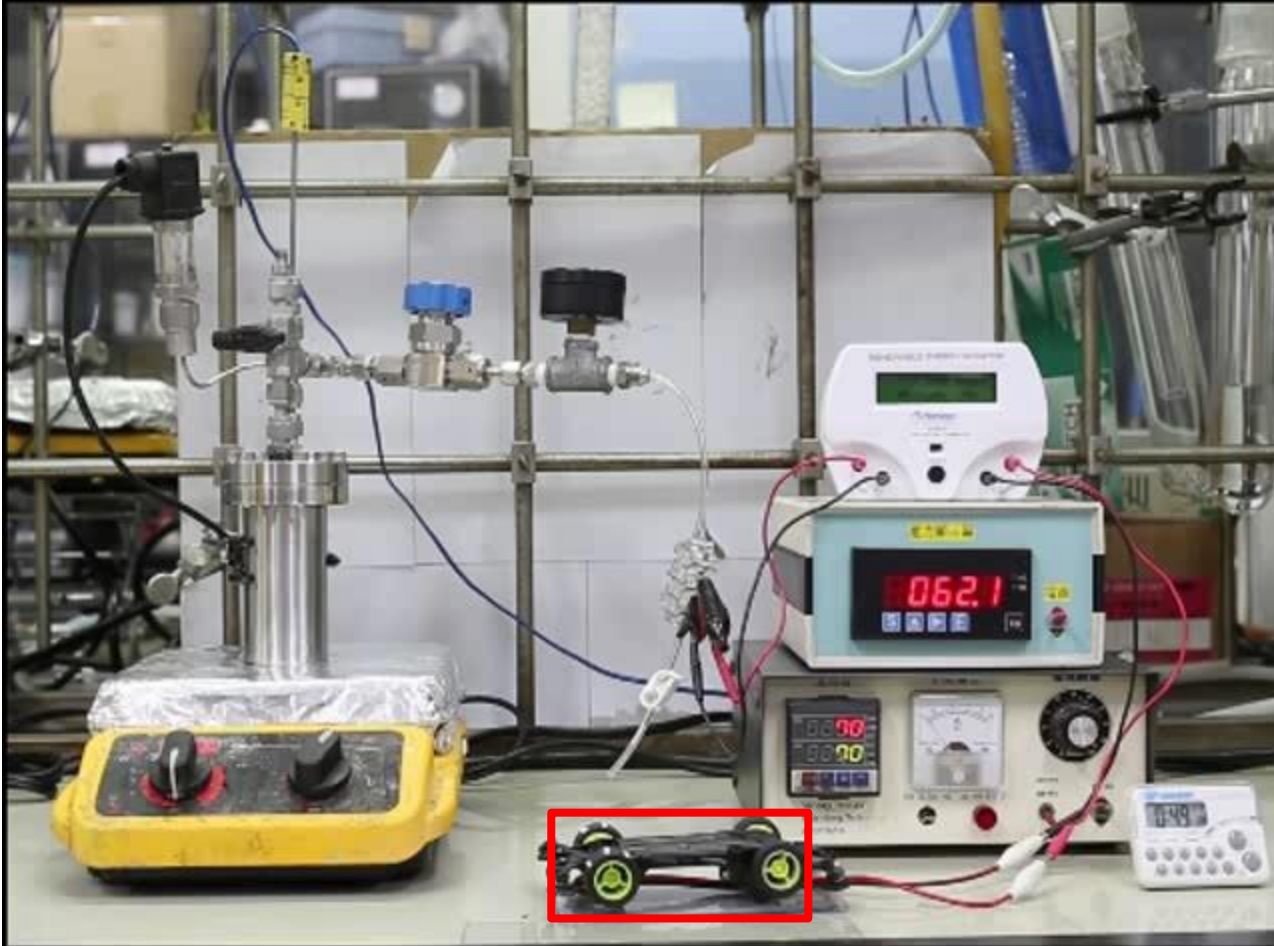
Type	Catalyst	Temp. ( K )	Rate ( $\text{g}_{\text{H}_2} \text{s}^{-1} \text{g}_{\text{Si}}^{-1}$ )	Ref
Etching of Si	KOH	343	$4.72 \times 10^{-3}$	This work
Etching of Si	NaOH	N/A	$9.33 \times 10^{-9} (\text{g}_{\text{H}_2} \text{s}^{-1})$	26
Etching of Si	NaOH	373	$2.03 \times 10^{-4}$	27
Etching of Si	$\text{NH}_3$	333	$6.48 \times 10^{-5}$	28
Etching of Si	NaOH	353	$5.56 \times 10^{-4}$	29
Etching of Si	KOH	R. T.	$1.48 \times 10^{-4}$	30
Electrochemical	SiNWs/FeP	N/A	$9.85 \times 10^{-9} (\text{g}_{\text{H}_2} \text{s}^{-1})$	31
Photoelectrochemical	$\text{TiO}_2/\text{RGO}/\text{Cu}_2\text{O}$	N/A	$9.92 \times 10^{-10} (\text{g}_{\text{H}_2} \text{s}^{-1})$	32
Photocatalytic	Si	298	$1.89 \times 10^{-7}$	34
Ethanol Steam Reforming	Meso- $\chi$ LaNiAl	873	N/A	37
Fermentative	Microbes	303	N/A	39

# Demonstration



- In coordinate with a fuel cell converting the supplied hydrogen to electricity
- Connected to a gas tank for hydrogen storage

# Demonstration

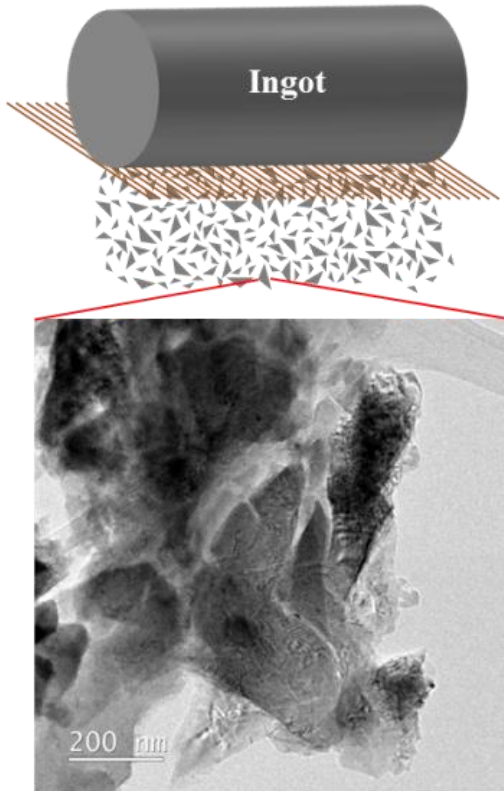


- Enough to keep a small electric vehicle in motion for minutes.

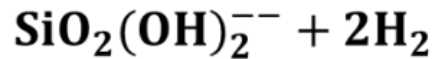
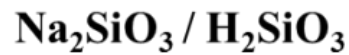


# Conclusions

Kerf loss silicon collected from the sawing process of solar-grade silicon



Additives-mediated rapid hydrogen generation



The  $\text{H}_2$  production rate :  
 $4.73 \times 10^{-3} \text{ g}_{\text{H}_2} \text{ s}^{-1} \text{ g}_{\text{Si}}^{-1}$

The yield of  $\text{H}_2$  converted from Si:  
92%

Integrated system

