<u>2021 Virtual Annual UCFER Review Meeting</u>

Porous Silicon/Lignite-Derived Graphene Composite Anodes for Lithium-Ion Batteries

Project No. 04-UND-P2-15: Coal Beneficiation
Award No. DE-FE0026825/S000045-USDOE

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NETL collaborator: Christopher Matranga (NETL)
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10.05.2021

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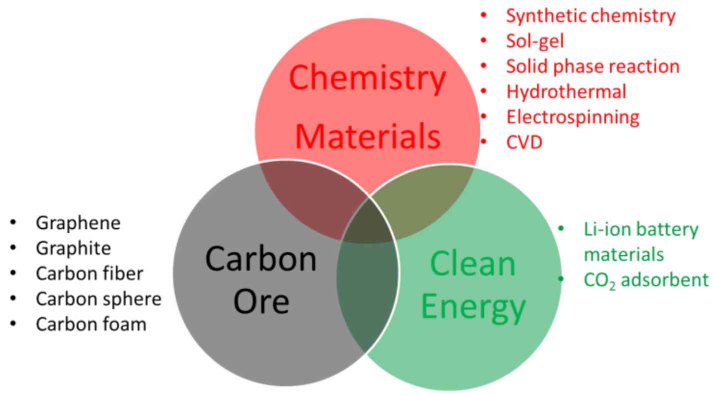
Outline

- Background-Lithium-ion Battery & Si Anode
- Project Goal and Objectives
- Proposed Technology and Current Progress
- Summary
- Q&A

Institute for Energy Studies (IES)

- Found in 2009
- One of eight units under CEM
- Mission: Energy Research-Education-Outreach
- Personnel (>25): Faculty, Engineers, and students
- Strong Industrial Collaboration
- Facilities
  - Materials Characterization Lab (MCL)
  - Bench and Pilot Facilities
  - Modeling and Simulation
- Degree Program
  - Energy Engineering Ph.D.
  - Energy Systems Engineering M.S. or M.Eng.



- **Use of fossil fuels in a carbon constrained environment / carbon management:**
  - Capture of CO_2 using sorbent materials
  - Novel combustion technologies
  - New products from coal
- **Recovery of valuable/critical materials:**
  - Recovery of **rare earth elements** from coal and coal by-products
  - Recovery of lithium, nickel and other valuable materials from oil field process waters
  - Rare earth value chain including recovering other critical materials
  - Co-producing graphene and rare earth elements from Leonardite and lignite
- **Building a renewable energy portfolio – moving beyond fossil fuel:**
  - Li-ion batteries (cathode/Anode material development, battery management systems)
  - Developing and integrating energy storage devices into the grid – chemical (battery); thermochemical (CLC), and others
  - Energy policy using system dynamic analysis
  - Geothermal energy development

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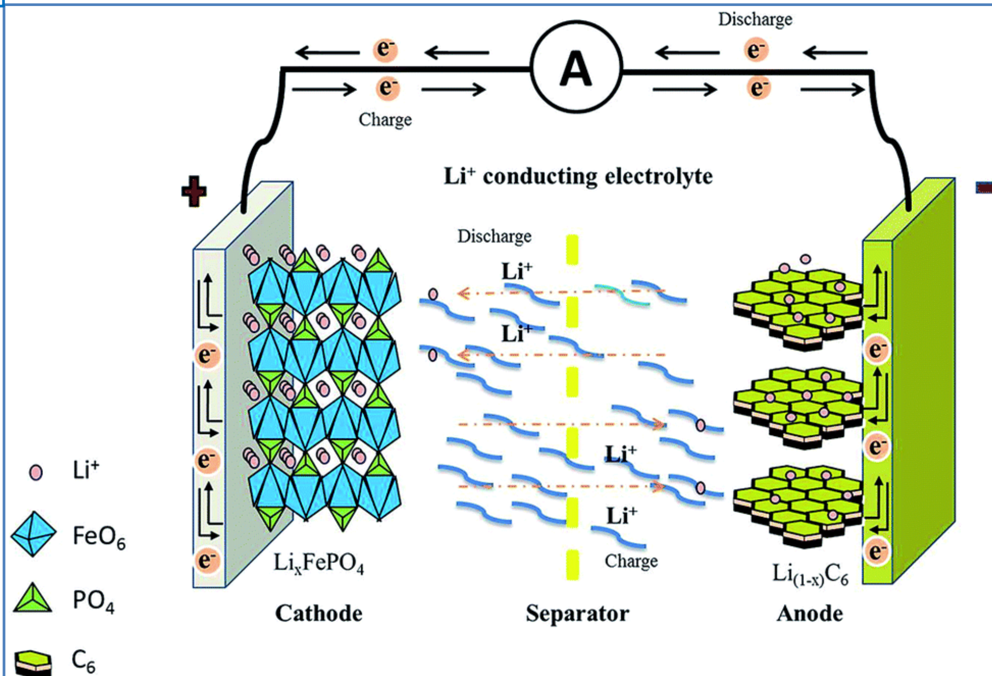
Lithium-Ion Battery (LIB)

Capacity

Cycle Life



Safety

Cost

Cathode (25%)
<u>Anode (10%)</u>
Separator (5%)
Electrolyte (10%)

~50% cost of LIB

Energy Environ. Sci., 2014,**7**, 3857-3886

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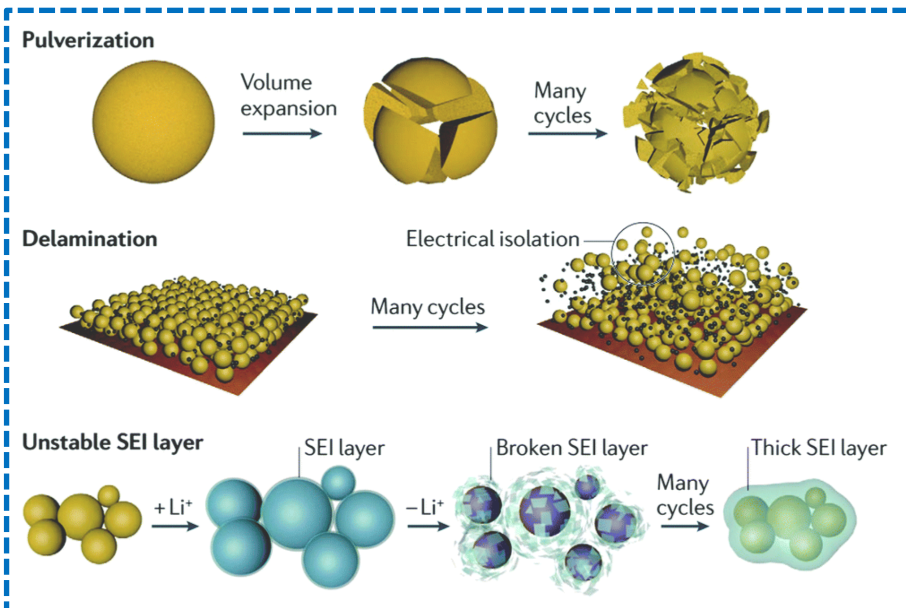
State of Problem: Graphite VS Si/Graphene Composite Anode

	Graphite	Si	SiO
Capacity	372 mAh/g	3600-4200 mAh/g	2600-3172 mAh/g
Cycle life (80% Retention)	>1000	<300	>500
Mechanism	$Li + 6C = LiC_6$	$15Li + 4Si = Li_{15}Si_4$ $22Li + 5Si = Li_{22}Si_5$	$(17+x)Li + 5SiO =$ $Li_{15}Si_4 + Li_2O + Li_xSiO_4$
Cost	\$10-15/kg	≥\$65/kg	~\$20-30/kg
Key Issues	Poor low-T performance & rate capability	Low conductivity, >300% volume change	Low conductivity, 100% volume change

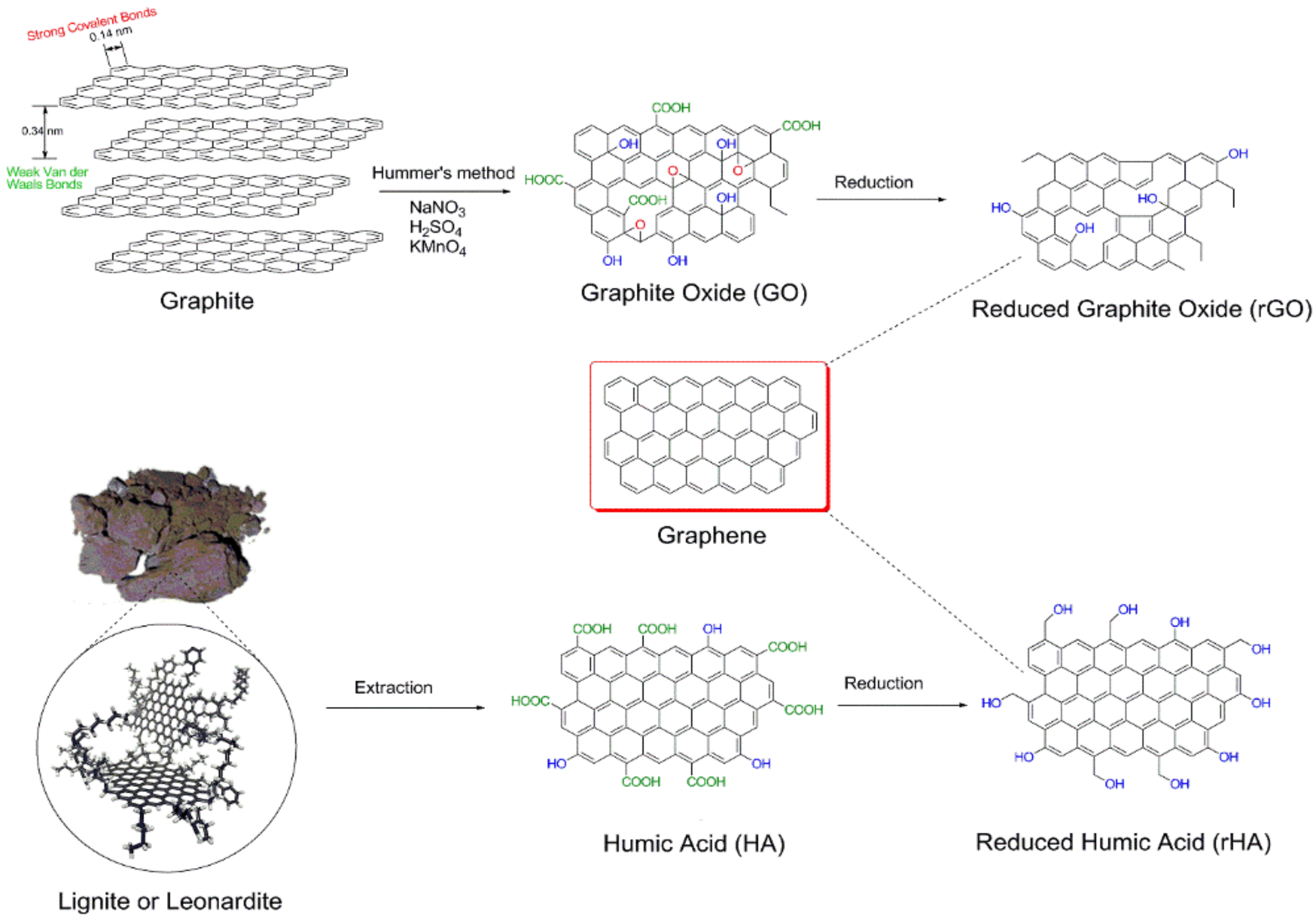


Mater. Chem. Front., 2017,**1**, 1691-1708

Solutions for Volume Change:
1) Nano-Si
2) Si-M alloy
3) Porous Si
4) SiO

Solutions for Low Conductivity:
Conductive coating:
(Carbon, MO_X, Graphene)

A Challenge: Mass Production of Graphene



Price in 2020:

Graphene

$100/kg
(low quality)
>$500/4'' disk
(high quality)

Graphite
$1000-2000/t

Leonardite
$220/t

Lignite
$22/t

North Dakota has the best leonardite in the world
(up to 86% humic acid dry and ash-free basis) !!

Powell, C. et al., *Curr. Opin. Colloid Interface Sci.* **2015**, 20, 362.

Hummers, W. S. et al, *JACS* **1958,** *80*, 1339.

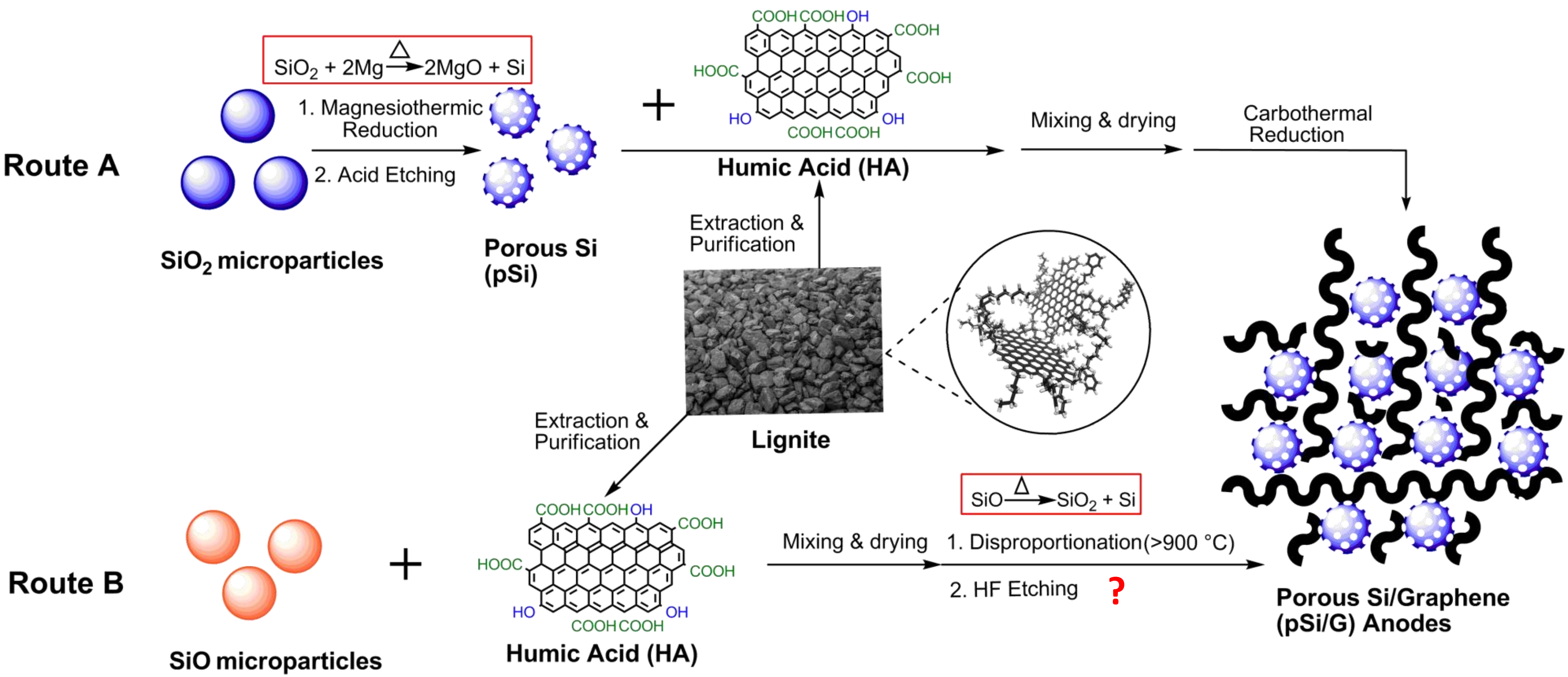
Project Goal and Objectives

Goal: **ND Lignite** → **Si/Graphene anodes for LIBs**

Battery Performance Objectives:

Performance Attribute	Performance Requirement	Reference Materials (S450-2A)
1st-cycle Specific Capacity (mAh/g)	1000	450
ICE (Initial Columbic Efficiency)	>80	80
Cycling Life (with 85% of capacity retention)	300	200
Cost ($/kg)	20	20-30

Our Approach to Synthesize Si/G Anode



Micro-sized Porous Si vs **Si Nanoparticles**

In-situ synthesis of graphene vs **Commercial graphene**

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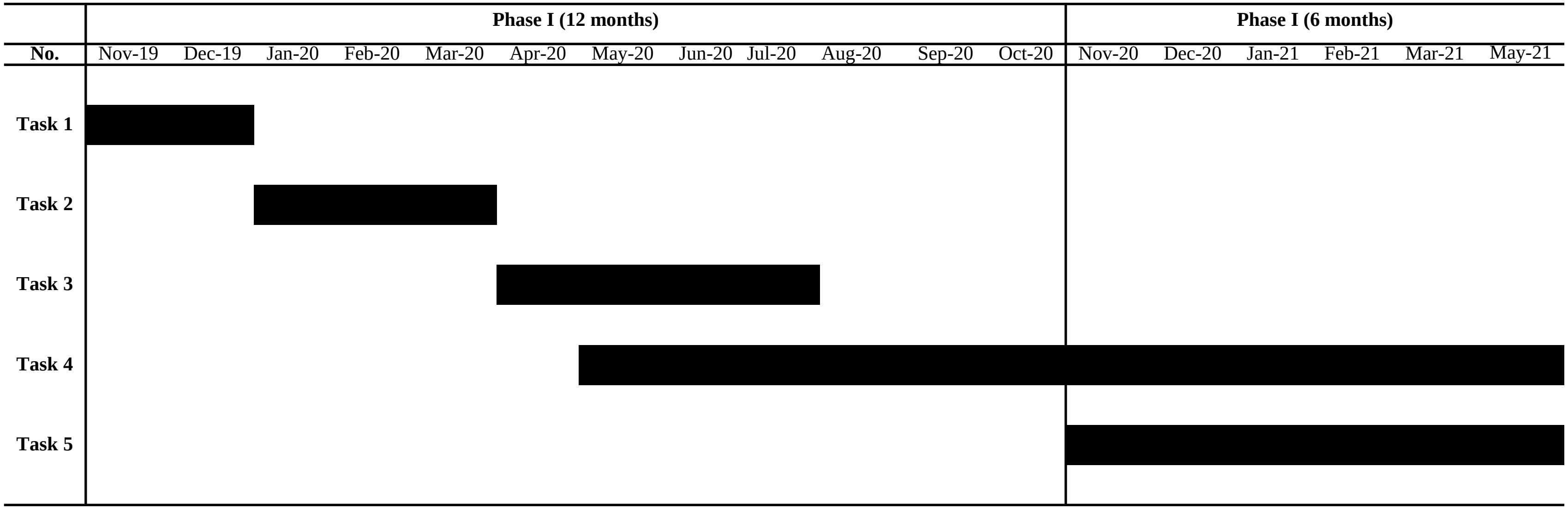
Plan of Work



<u>**A six month no-cost extension to October 30, 2021**</u>

Collaboration

Task 1, 2 and 5: Dr. Christopher Matranga at NETL **,** Materials characterization (Raman and XPS)

Task 2: Dr. Julia Zhao at UND chemistry department**,** Silica synthesis

Task 4: Dr. Yong Hou at Clean Republic LLC **,** battery performance test

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Current Progress

Task 1. Extraction of HA from lignite

- Established an optimal extraction & purification procedure at both lab-scale and bench-scale
- Produced a total 8 kg of crude humic acid (dry basis) at one batch
- Produced multiple batches of ~0.5 kg of high purity (>97%) of humic acid for bench-scale test in the **Task 5**

XRF Analysis Results

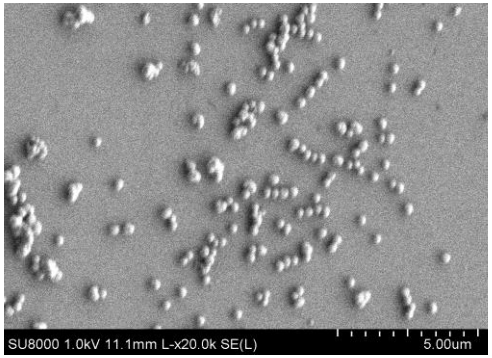
Composition (dry basis %)	***Raw Lignite***	***Crude HA***	**Purified HA at Lab-scale**	**Purified HA at Pilot-scale**
Na	--	8.59	--	0.55
Mg	0.27	0.04	--	--
Al	1.93	0.19	0.20	0.25
Si	3.89	0.17	0.26	0.38
S	1.08	1.47	1.66	1.62
Cl	0.01	6.79	0.02	0.01
K	0.17	0.04	0.03	0.04
Ca	0.64	0.12	0.02	0.06
Fe	1.77	1.81	0.14	0.15
Ba	0.19	–	--	--
Ash Content	15.87	15.58	2.46	3.22
Organic Matter	84.13	84.42	97.54	96.78
Yield (%)			28.9	26.6

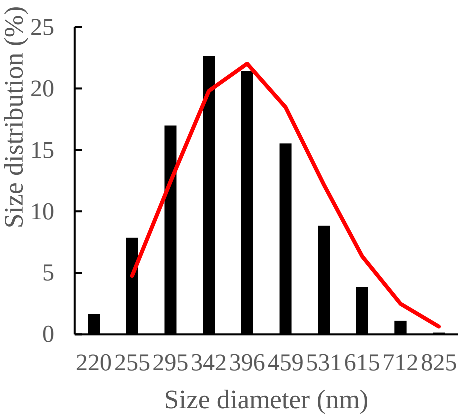
Current Progress

Task 2. Synthesis and Characterization of pSi via MR (Route A) (with Dr. Julia Zhao's group)

- **Stöber method**: solid spheres at a higher yield
- **Microemulsion**: desired **porous spheres** though at a lower yield
- A series of Silica particle with size from 100-1000 nm prepared by Microemulsion

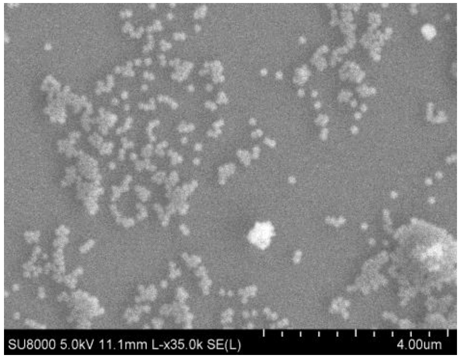
Stöber

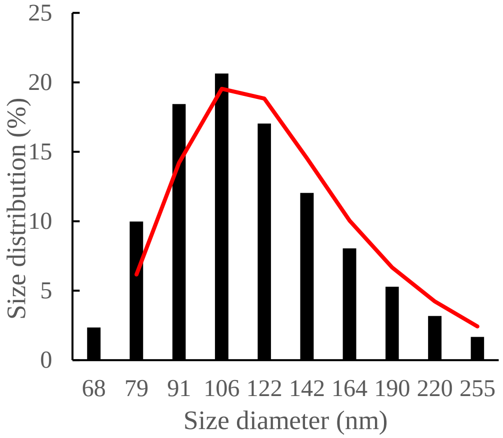




Yield **88%**

Microemulsion





Yield **44%**

Current Progress

Task 3: Synthesis and Characterization of pSi/G

Route A (SiO_2):

- A-1: MR reaction and then mixing with HA
- A-2: mixing with HA and then MR reaction

Route B (SiO) :

- Optimized three major factors: **particles size, humic acid feeding ratio**, **calcination temperature**
- Optimized two minor factors: **Humic acid purity** and **Electrode fabrication: binder & conductor**

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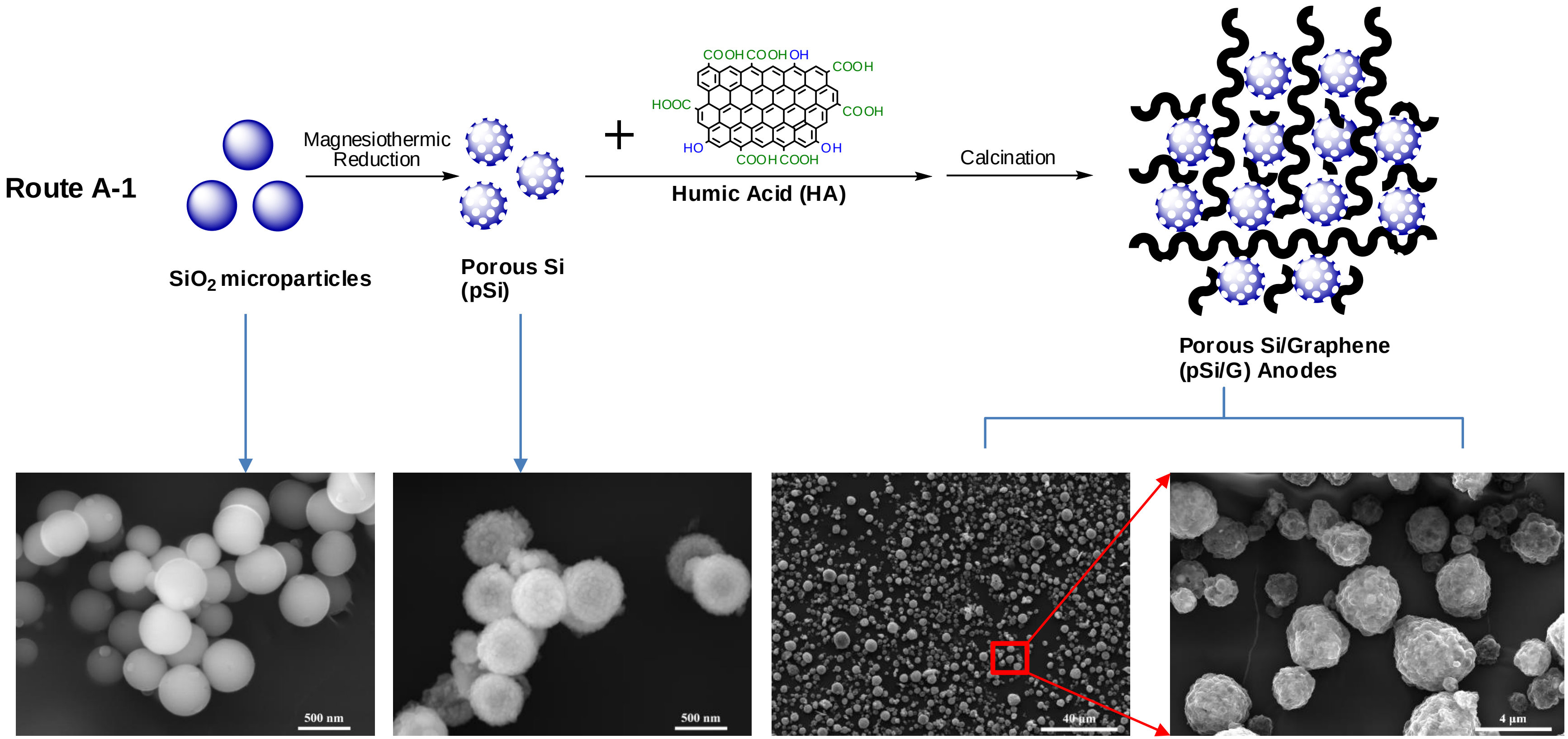
Characterization of pSi/G by Route A-1 (SiO_2)



- The SiO_2 precursor has particle size of 500 nm.
- After MR and acid etching, porous silicon pSi particles forms, and the spherical shape maintains
- After mixing with HA and calcination, secondary particle sizes ranging from 1-5 µm. The shape become less spherical but basically round-shape remains.

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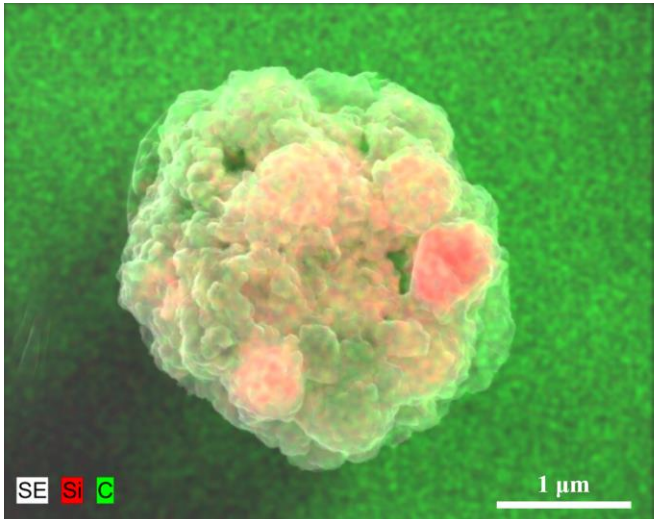
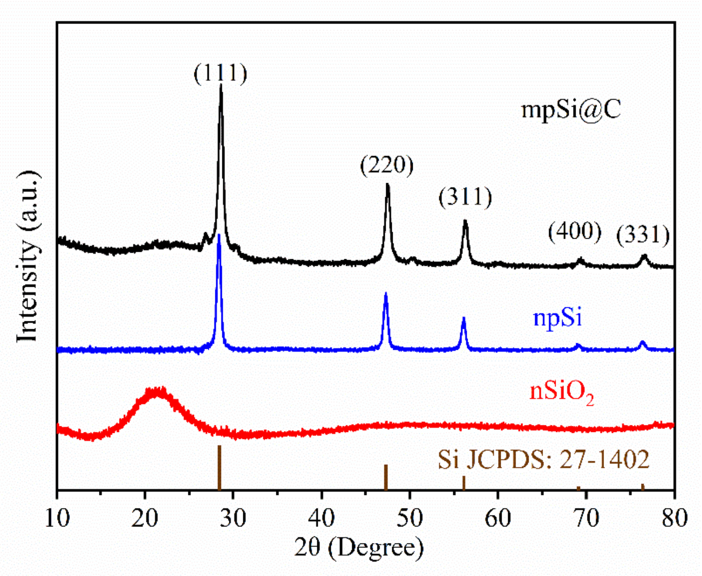
Characterization of pSi/G by Route A-1 (SiO_2)

EDX Si and C mapping

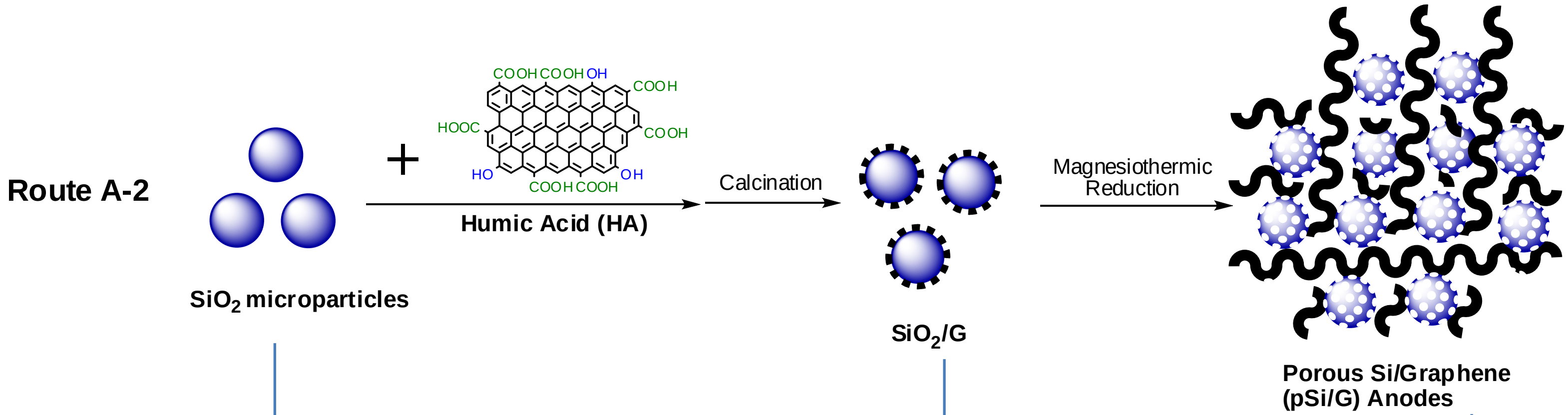


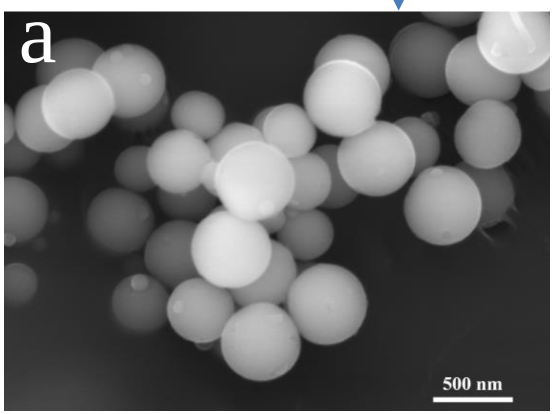
XRD



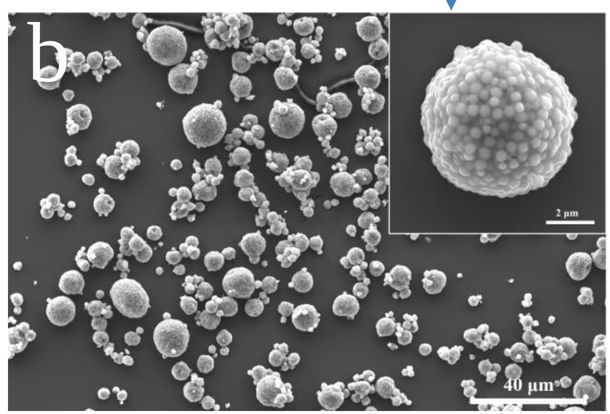
- An even carbon coating on the surface of Si particles
- Amorphous SiO_2 converted to high crystalline porous Si and final pSi@G anode

Characterization of pSi/G by Route A-2 (SiO_2)

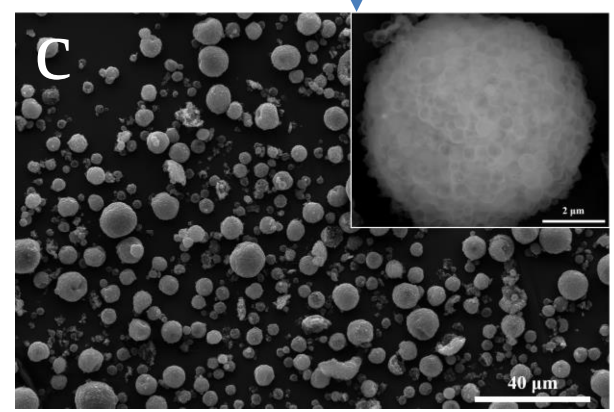




$nSiO_2$ precursor

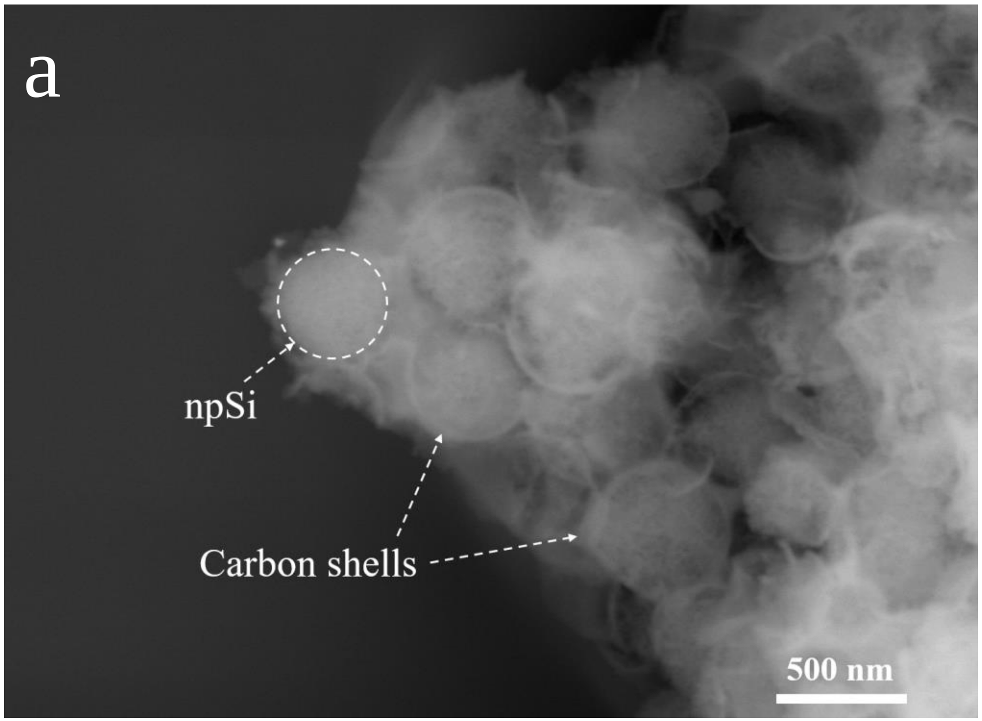


$mSiO_2$@G composite
After mixing with Humic acid and heat treatment

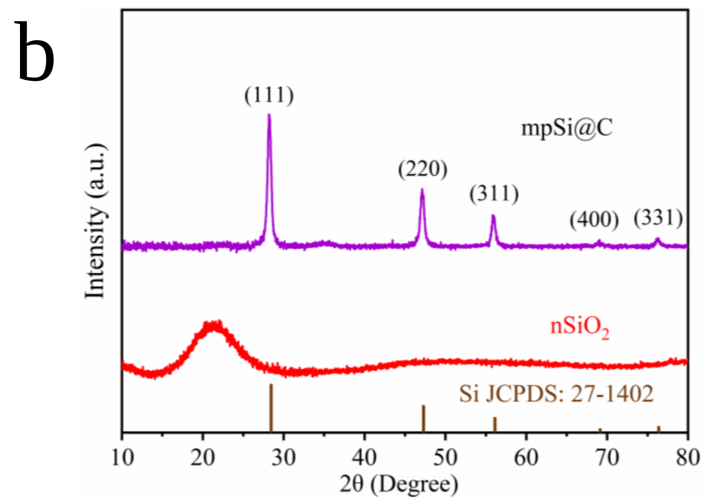


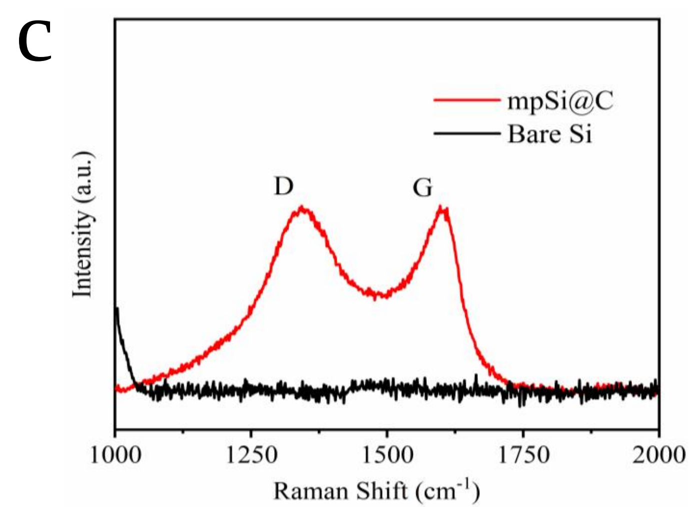
mpSi@G particles
After MR reaction and acid etching

Characterization of pSi/G by Route A-2 (SiO_2)

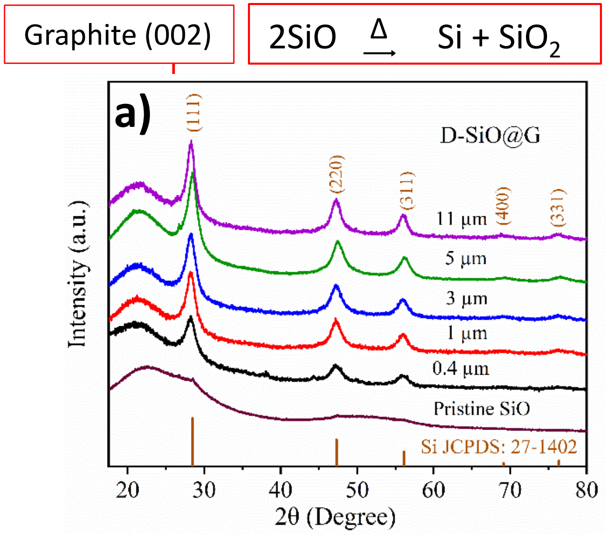


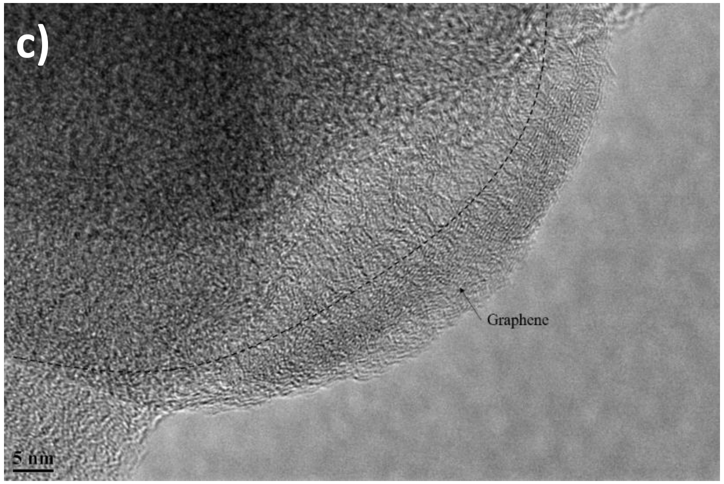
A broken mpSi@C particle

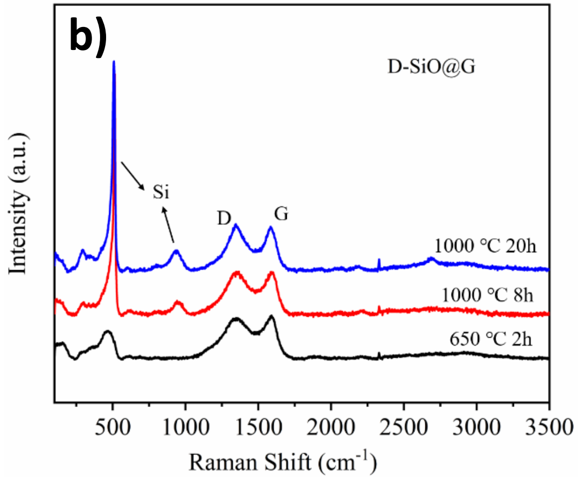




Characterization of D-SiO/G by Route B (SiO)







- **XRD pattern (a)**: Conversation of humic acid-to-graphene and disproportionation of SiO occur simultaneously
- **Raman spectrum (b):** characteristics of crystalline Si and graphene (G Band) were observed
- **TEM image (c):** Thickness of coating ~5 nm (15 layers of graphene)

(with Dr. Christopher Matranga @NETL)

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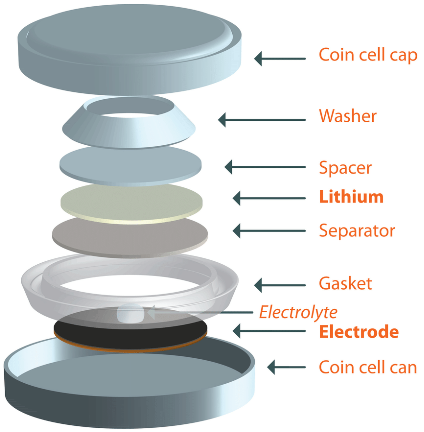
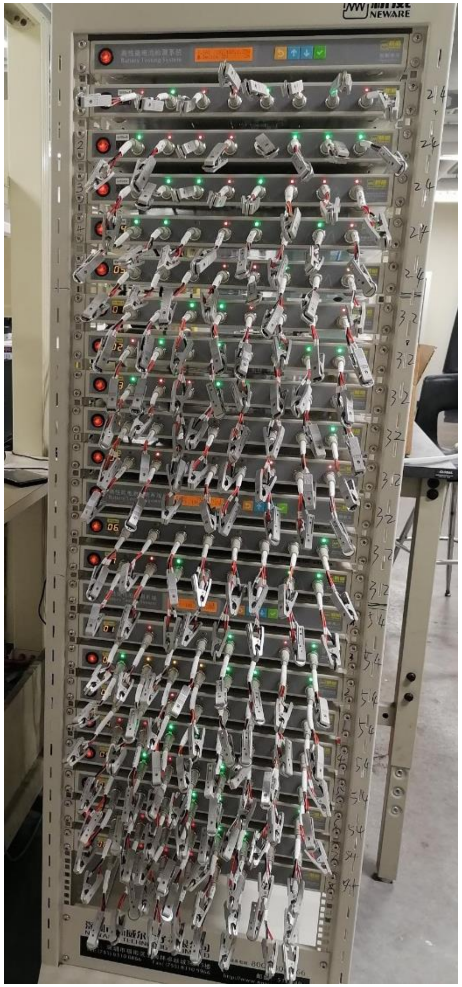
Current Progress

Task 4: Electrochemical Performance testing of the pSi/G anodes

- CR2032 Coin-type half cells made of pSi/G anodes were assembled

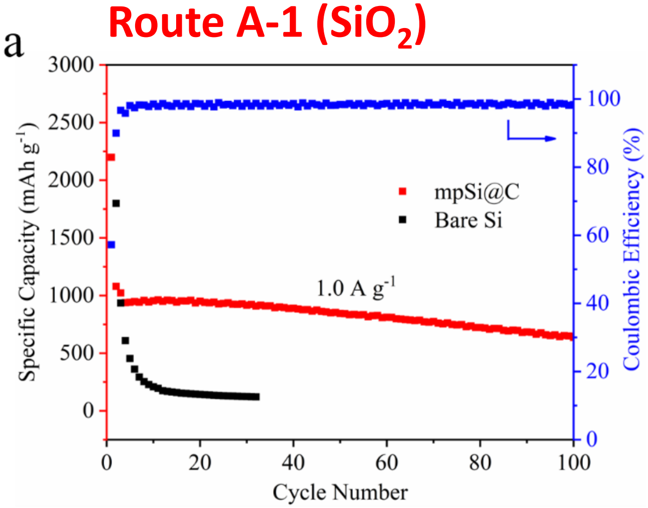
- Key Metrics
  - Specific capacity
  - ICE (initial coulombic efficiency)
  - Cycling performance



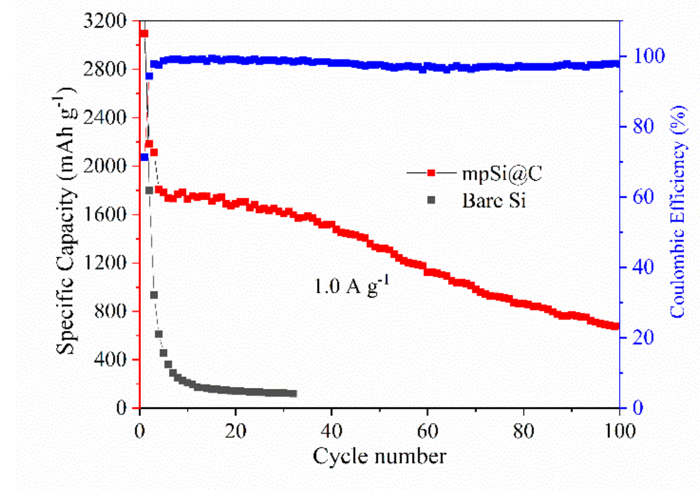


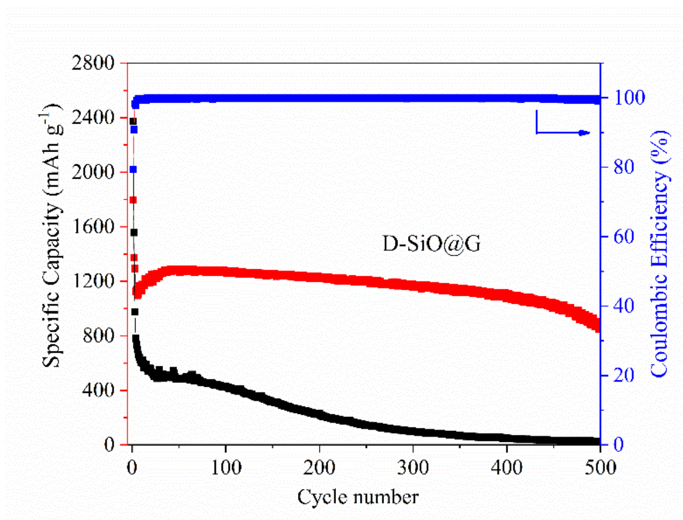
Battery Performance Comparison

Route A-1 (SiO_2)



Route A-2 (SiO_2)





Route B (SiO): the winner!

Batch	Initial Capacity	ICE	Capacity retention 85%
Route A-1	2200	57.2%	100
Route A-2	3094	71.3%	40
Route B	1796	79.3%	500

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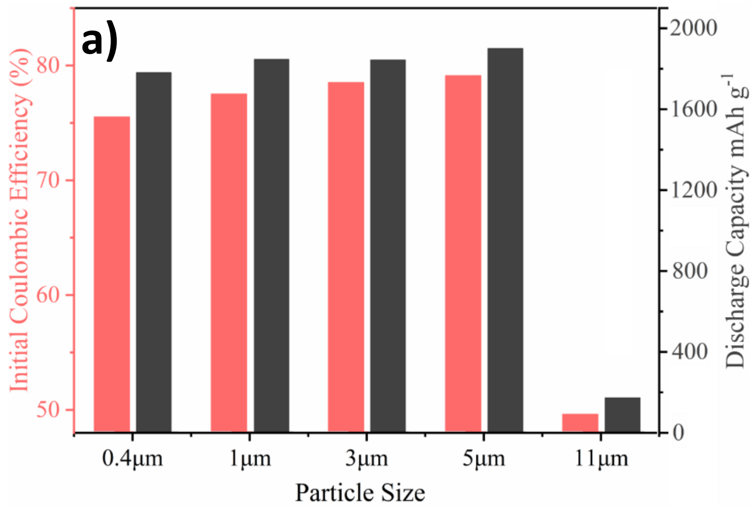
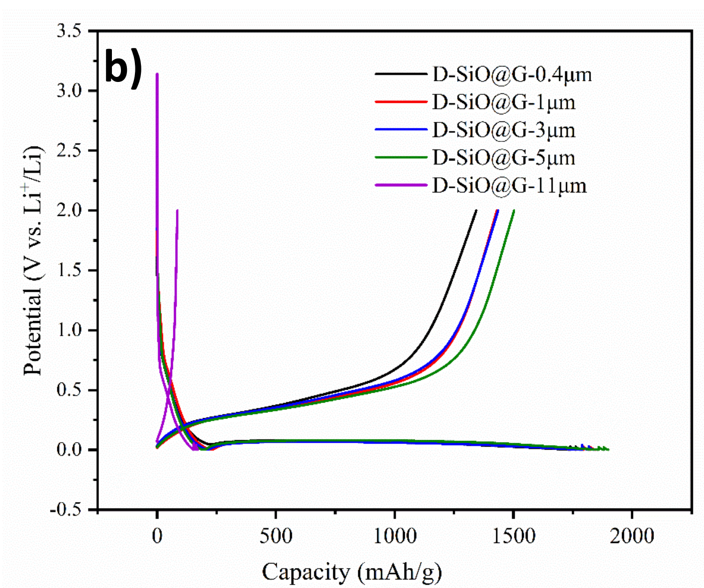
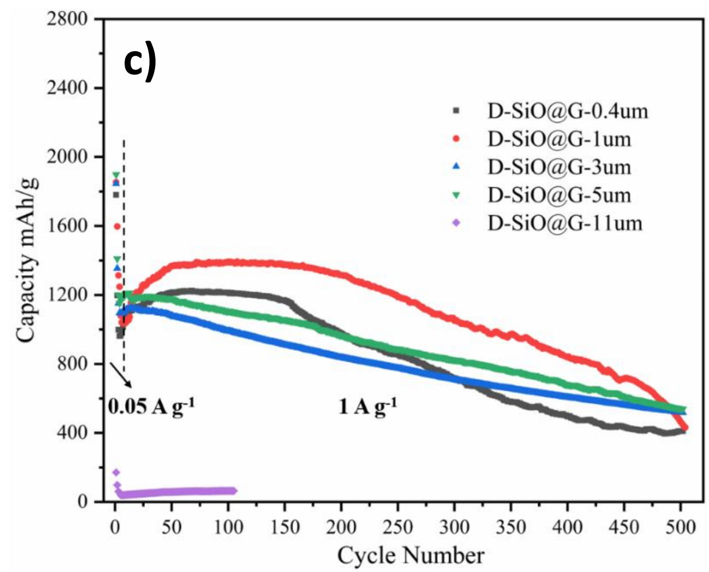
Impact of Particle Size on Battery Performance



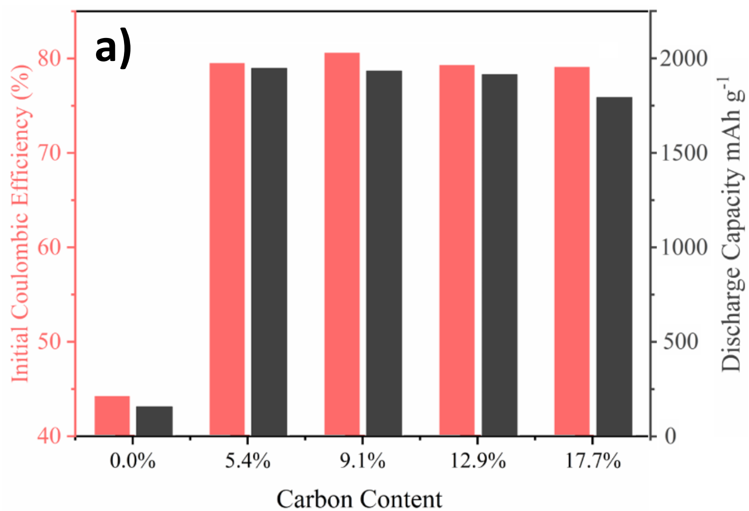
$$(17+x)Li + 5SiO \longrightarrow \underbrace{Li_{15}Si_4}_{\text{Reversible}} + \underbrace{Li_2O + Li_xSiO_4}_{\text{Irreversible}}$$

- 11 μm sample has very low ICE and capacity and poor cycling performance because of the poor conductivity
- 5 μm has the best overall battery performance

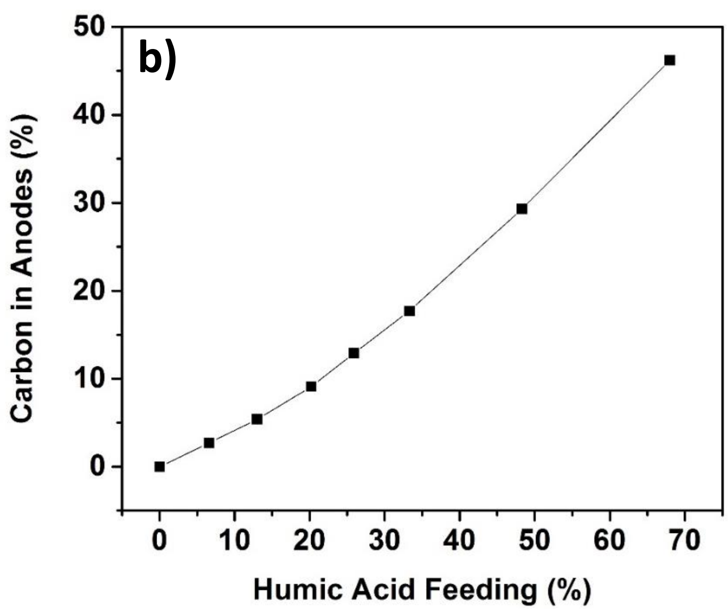


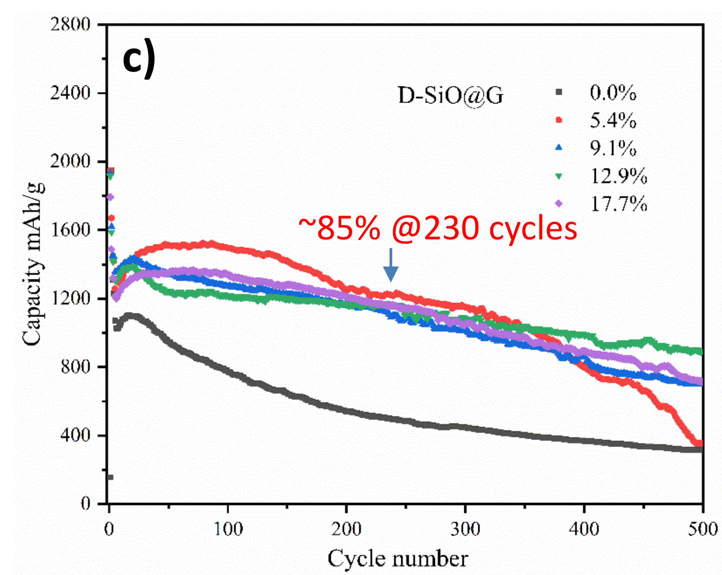


Impact of Humic Acid Feeding Ratio on Battery Performance



- **Graph (a)**: compared with pristine SiO (0.0%C), a graphene coating can significantly improve the ICE and capacity.
- **Graph (b):** the residual carbon in anodes is proportional to humic acid feeding. About 50% humic acid becomes carbon.
- **Graph (c):** the 12.9% C sample (20% humic acid) has the best cycling life.





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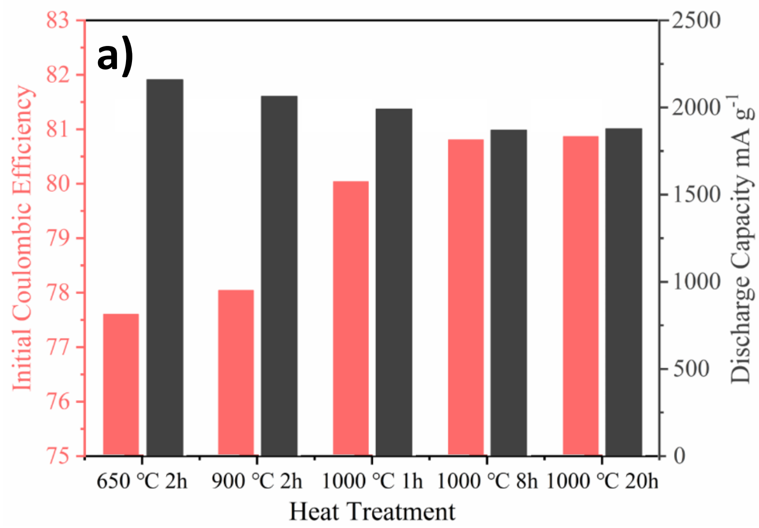
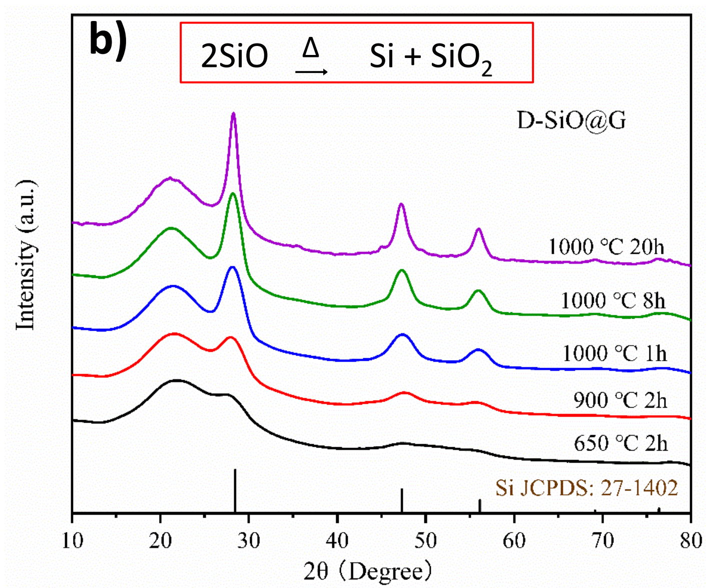
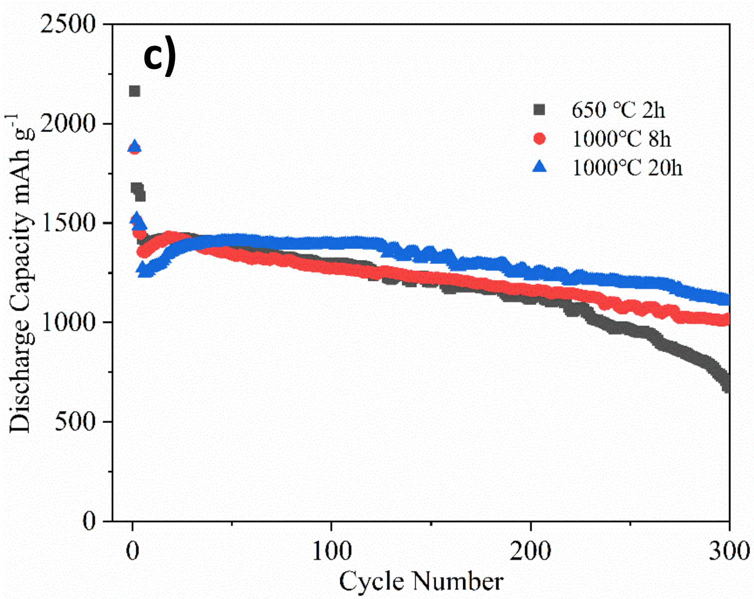
Impact of Calcination Temperature on Battery Performance



- **Graph (a):** higher T and longer time lead to higher ICE but slightly decreased capacity
- **Graph (b):** XRD shows higher T and longer time promoted the disproportionation reaction
- **Graph (c):** the sample at 1000°C for 8h has the best cycling performance.





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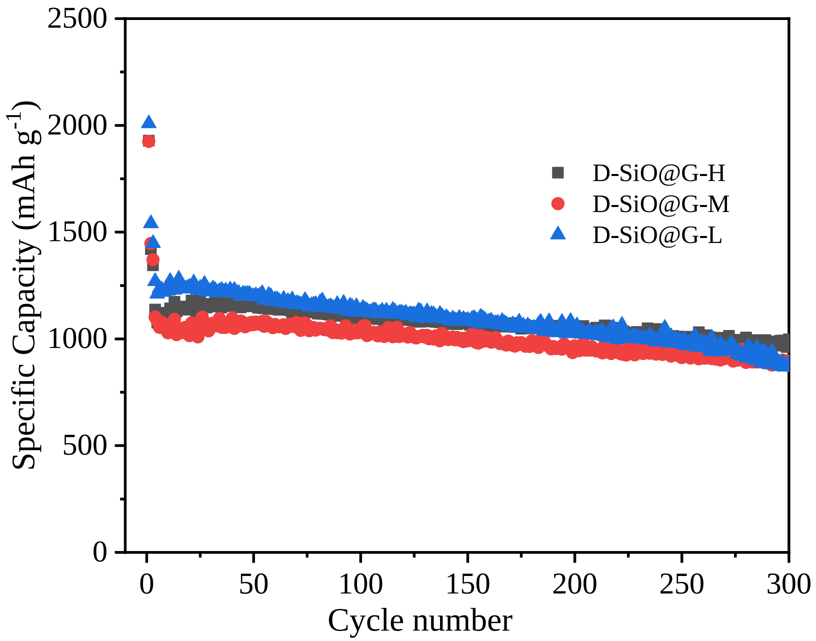
Impact of Humic acid Purity on Battery Performance



HA	Ash Content %	Initial Capacity	ICE
D-SiO@G-H	5.7	1928.2	78.6%
D-SiO@G-M	2.0	1924.5	79.1%
D-SiO@G-L	1.2	2008.6	79.0%

- The low ash sample has slightly better battery performance
- The overall impact of humic impact in the testing range (Feeding 20%) is NOT significant
- Avoid purification steps has significant economic advantage

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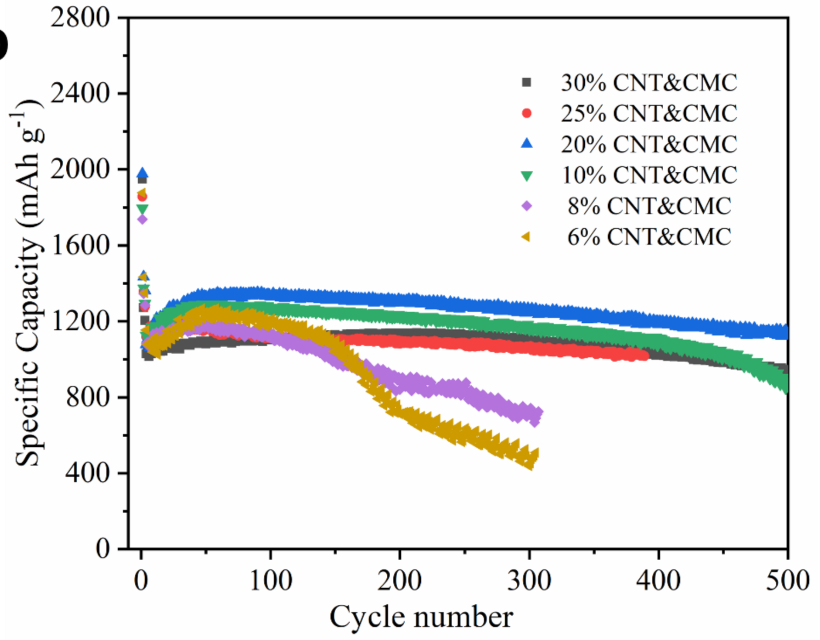
Impact of Electrode Fabrication : Binder and Conductor

a

CNT&CMC content	Initial Coloumbic Efficiency (%)
30%	70.12
25%	74.30
20%	77.82
10%	79.60
8%	80.20
6%	80.65

b



- Conductor/Binder pairs: CB/PAA, CB/PVDF, CNT/CMC, etc
- CNT/CMC pair is the best because of linear CNT contact
- **10% CNT/CMC** in electrode shows a good balance of ICE and cycle life

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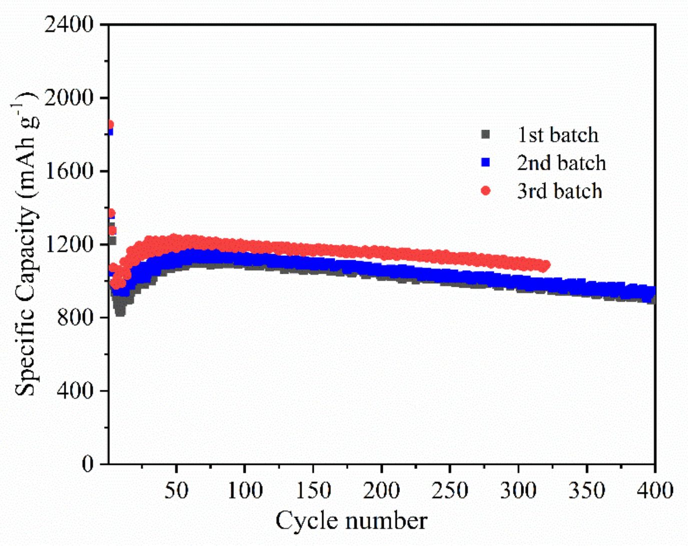
Task 5: Scaling Up the Optimal Procedure

- Bench-scale testing (Kg-level)
- Scale up by >20X
- The initial capacities decrease by about 2-5%, ICE by 1.0% and capacity retention by <5%



Batch	Initial Capacity	ICE	Capacity retention 85%
1st	1832	78.3%	>400
2nd	1817	78.4%	>400
3rd	1854	78.5%	Ongoing
VS Lab-scale Sample	2-5%	1%	<5%

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Summary

- The pSi/G anode produced by Route B (SiO) meets the objectives

Performance Attribute	Performance Requirement	Reference Materials (S450-2A)	1st year Performance	End of the Project
1st-cycle Specific Capacity (mAh/g)	1000	450	1500	**1800**
ICE (Initial Columbic Efficiency)	>80	80	79	**79**
Cycling Life (with 85% of capacity retention)	**300**	200	**230**	**500**

- Successful scale up by > 20X to 0.3kg/batch level and easily scalable further
- Journal Article: "In Situ Synthesis of Graphene-Coated Silicon Monoxide Anodes from Coal-Derived Humic Acid for High-Performance Lithium-Ion Batteries". *Advanced Functional Materials* **2021,** *31* (32), 2101645.
- Conference Presentation and Paper: "Facile Synthesis of Micrometer-sized Hierarchical Porous Si@C Anodes for High-Performance Lithium-Ion Batteries". *The 45th International Technical Conference on Clean Energy*, Virtual, July 26-29, 2021.
- Patent: Hou, X.; Xu, S. "Battery Materials and Fabrication Methods". USA 62/706,191, August 4, 2020.
- Commercialization: a private company interested in licensing this technology and sponsored us $250,000 to further develop the technology into a market-ready product.

Acknowledgement

- **Sponsors**
  - DOE UCFER program
  - Clean Republic LLC

- **Collaborators**
  - Dr. Christopher Matranga (NETL)
  - Dr. Congjun Wang (NETL)
  - Dr. Michael Mann (UND IES)
  - Dr. Julia Zhao (UND chemistry Department)
  - Dr. Yong Hou (Clean Republic LLC)

- **Students**
  - Shuai Xu
  - Andrew Dockter
  - Xin Zhang
  - Di Sun

NATIONAL ENERGY TECHNOLOGY LABORATORY

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