Design of Sulfur Cathodes for High Energy Lithium-Sulfur Batteries

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Project ID
#ES230

Overview

Timeline

- Start: August 1, 2013
- End: July 31, 2016
- Percent complete: 90%

Budget

- Total project funding
  $900k from DOE
- Funding received in FY13
  $300k

Funding for FY14
  $300k

- Funding for FY15
  $300k

Barriers

Barriers of batteries

- High cost (A)
- Low energy density (C)
- Short battery life (E)

Targets: cost-effective and high-energy electrode materials and batteries

Partners

- Collaboration
  - BATT program PI's
  - SLAC: In-situ X-ray
  - Amprius Inc.
  - Beihang Univ, China
  - Zhejiang Univ of Technology, China

Project Objective and Relevance

Objective

- Develop lithium-sulfur batteries to power electric vehicles (HEV/PEV/EV) and decrease the high cost of batteries.

- Develop sulfur cathodes with high capacity and stability to generate high energy lithium-sulfur batteries with long cycle life.

- Design and fabricate novel nanostructured sulfur cathode with multifunctional coatings to overcome the materials challenges that lead to short battery life, including volume expansion, active material loss and low conductivity of sulfur cathode.

- Develop scalable low-cost methods for the synthesis of nanostructured sulfur cathode.

- Project contents are directly aimed at the listed barriers: high cost, low energy density and short battery life.

Milestones for FY15 and 16

Month/year	Milestones
1/2015	Demonstrate sulfur cathodes capped by layered metal disulfides; Demonstrate high areal capacity of 3 mAh/cm^2 under high mass-loading conditions (5.3 mg Li_2S/cm^2) (completed)
4/2015	Develop sulfur cathodes with high rate capability and volumetric energy density at high mass loading (completed)
7/2015	Identify the interaction mechanism between sulfur species and different types of oxides, and discover/select the optimal material to improve the capacity and cycling of sulfur cathode (completed)
1/2016	Demonstrate the balance of surface adsorption and diffusion of Li_2S_x species on nonconductive metal oxides (completed)
4/2016	Explore different metal sulfides through electrochemical test and postmortem analysis (on track)
7/2016	Give insight into the interaction mechanism between Li_2S_x species and metal sulfides through combined experiment-DFT computations (on track)

Approach/Strategy

Advanced nanostructured sulfur cathodes design and synthesis

1) Engineer empty space into sulfur cathode to solve the problem of electrode volume expansion.
2) Develop novel sulfur nanostructures with multi-functional coatings for the confinement of sulfur/lithium polysulfides to address the issues of active materials loss and low conductivity.
3) Develop/discover optimal nanostructured materials that can capture the polysulfide dissolved in the electrolyte.
4) Develop space efficiently packed nanostructured sulfur cathode to increase the volumetric energy density and rate capability.
5) Identify the interaction mechanism between sulfur species and different types of oxides/sulfides, and find the optimal material to improve the capacity and cycling of sulfur cathode.

Structure and property characterization

1)Ex-situ transmission electron microscopy
2)Ex-situ scanning electron microscopy
3)Inductively Coupled Plasma elemental analysis
4)In operando X-ray diffraction and transmission X-ray microscopy

Electrochemical testing

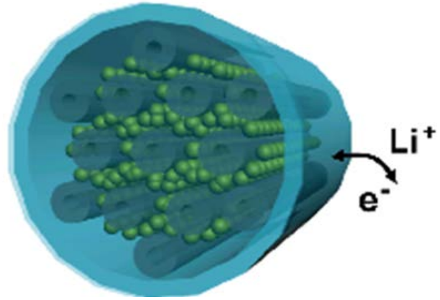
1) Coin cells and pouch cells
2) A set of electrochemical techniques

Previous Accomplishments on Sulfur Cathodes

Mesoporous carbon/S

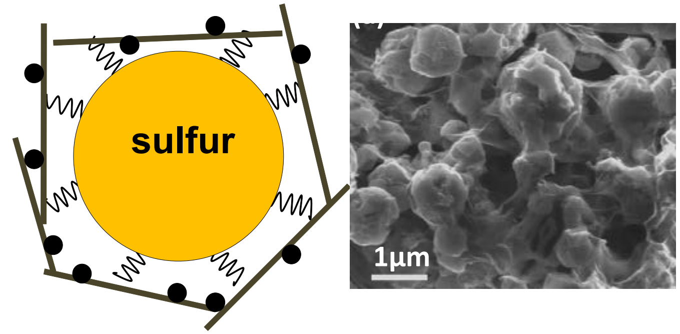
Nano Letters 10, 1486 (2010)

PEDOT/PSS-coated mesoporous carbon/S



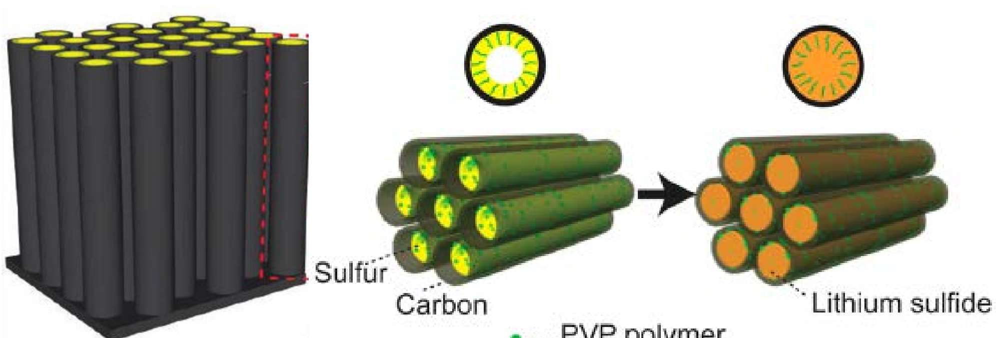
ACS Nano 5, 9187 (2011)

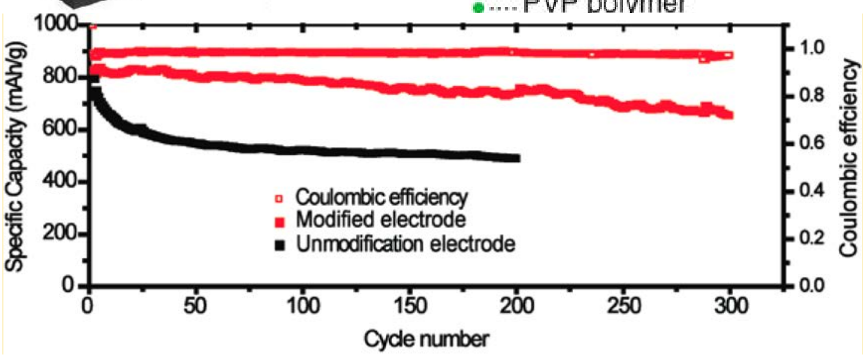
Graphene-coated S particles



Nano Letters 11, 2644 (2011)

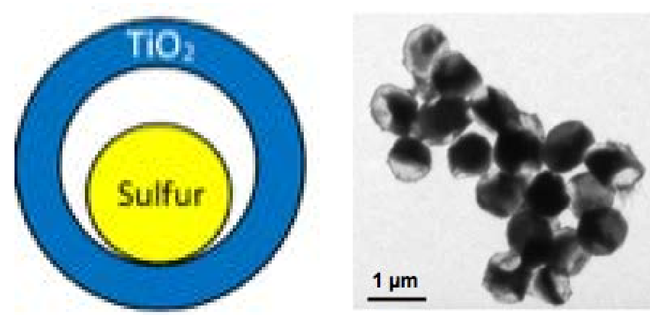
Hollow Carbon Fiber Encapsulated S

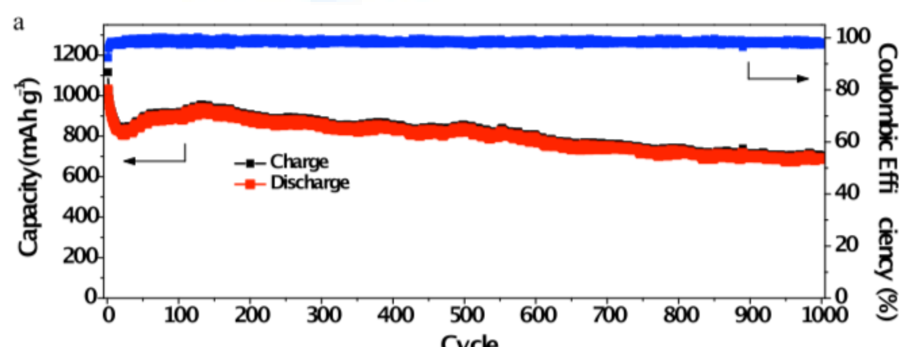




Nano Letters 11, 4462 (2011) *Nano Letters* 13, 1265 (2013)

Yolk-Shell S-TiO_2 Nanoparticles

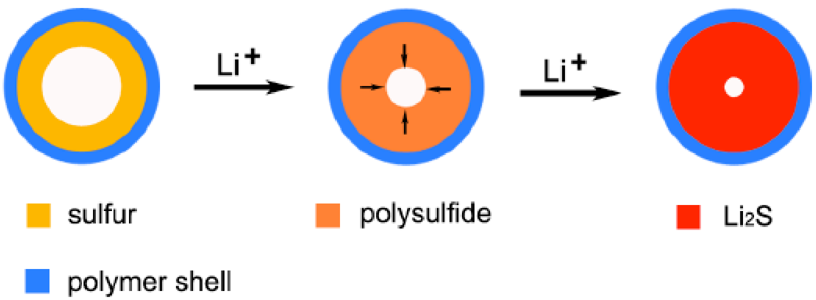


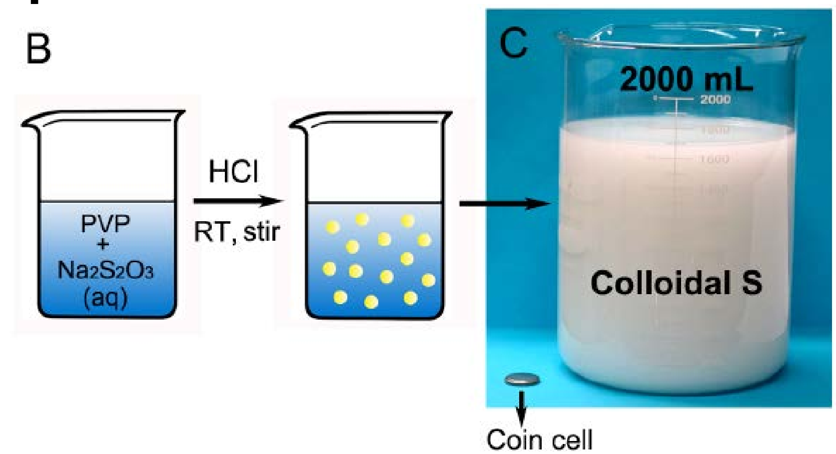


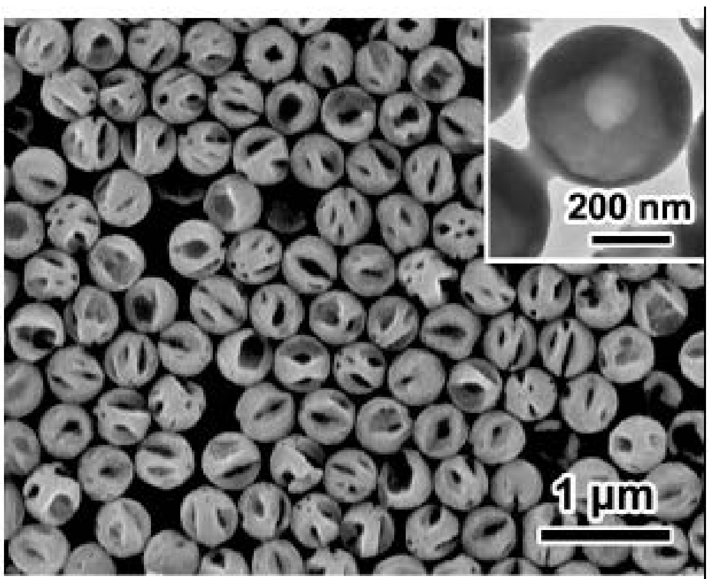
Nature Communication 4: 1331 (2013)

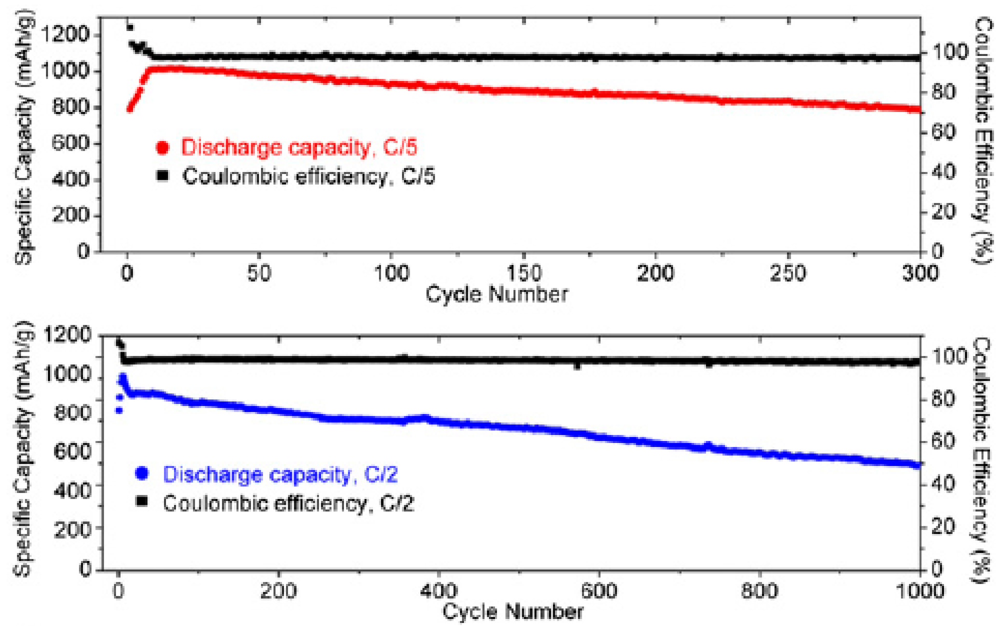
Accomplishment

Hollow S-Amphiphilic Polymer Nanoparticles





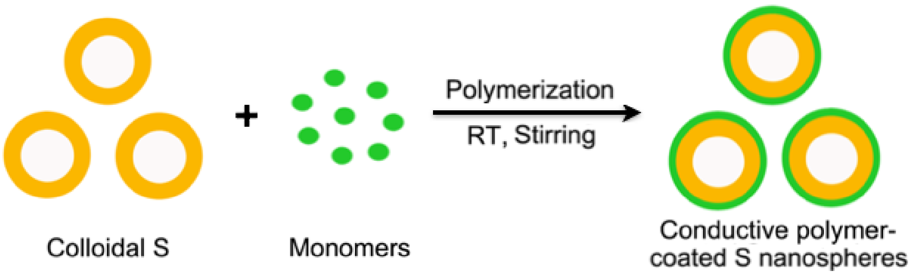


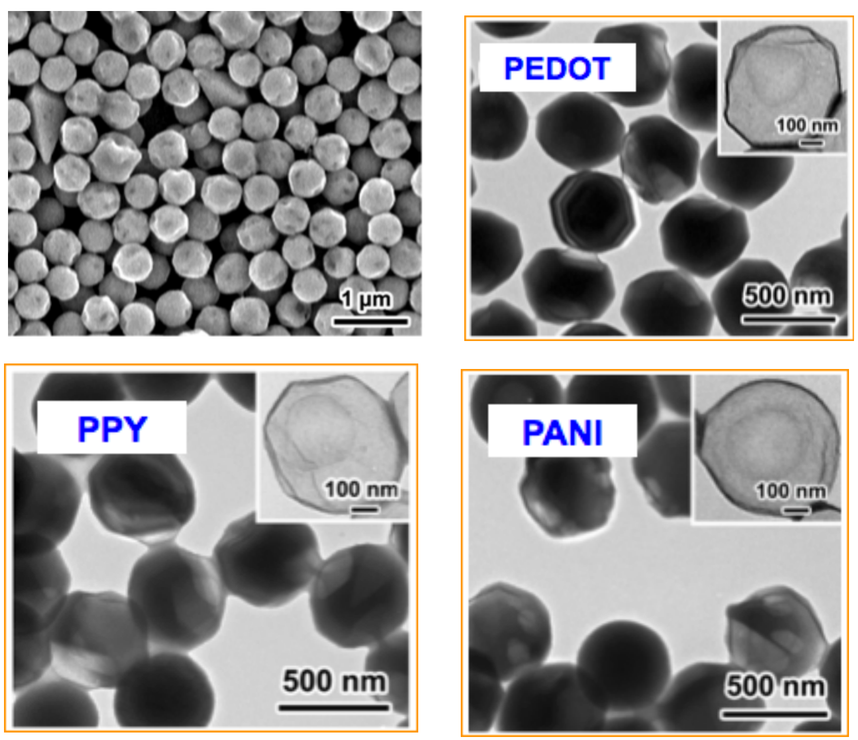


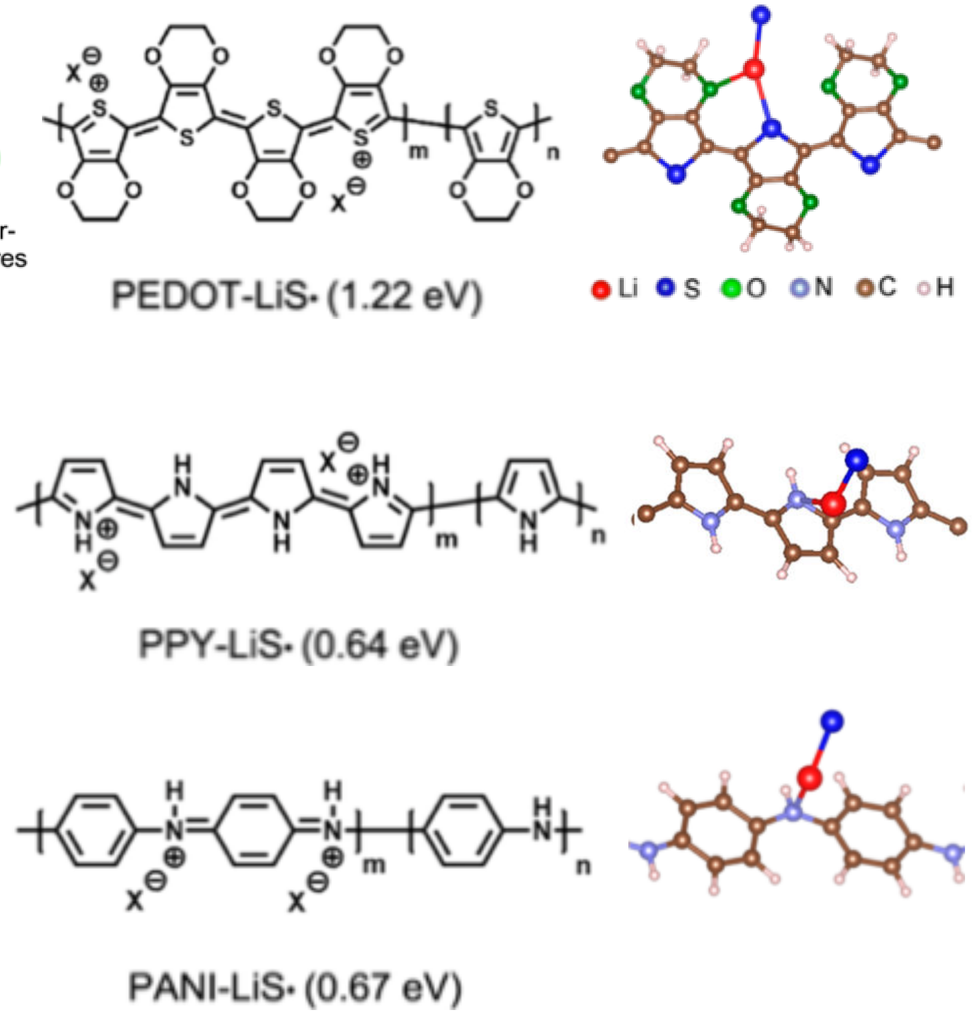
Cui group, *PNAS 110*, 7148 (2013)

Accomplishment

Conductive polymer-coated hollow sulfur cathodes
-Synthesis, morphology and simulation



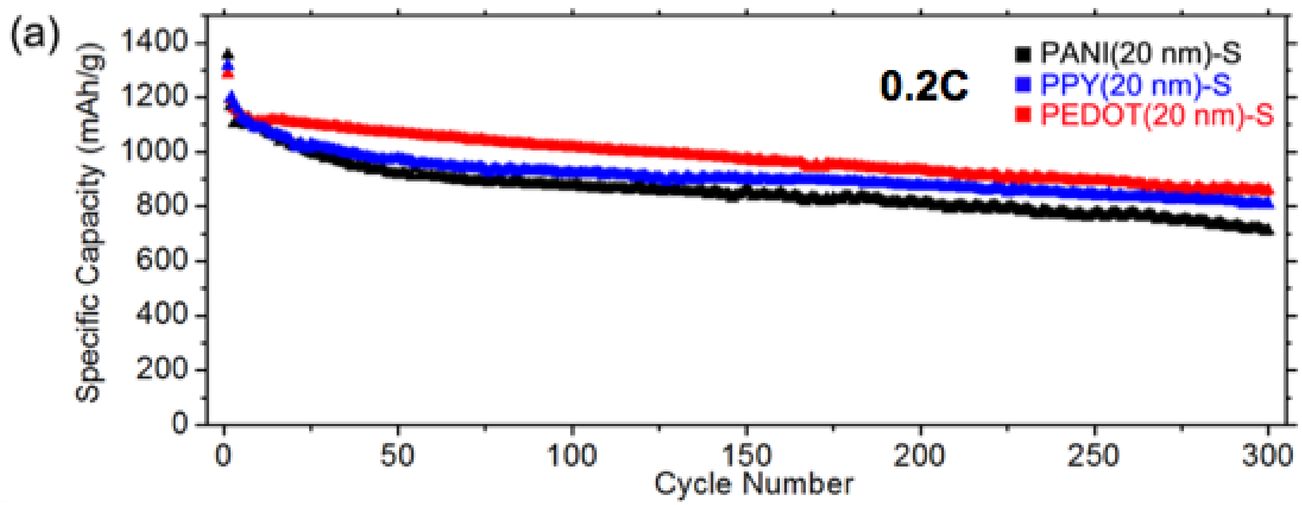


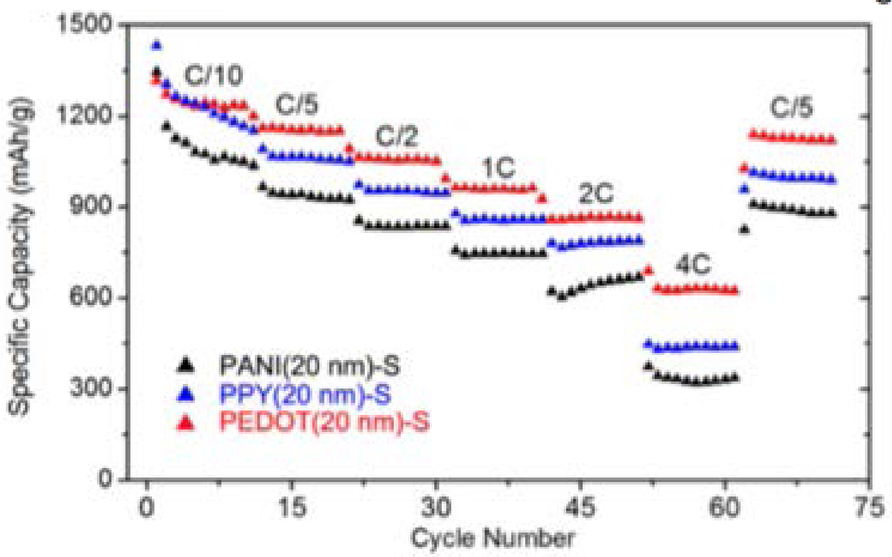


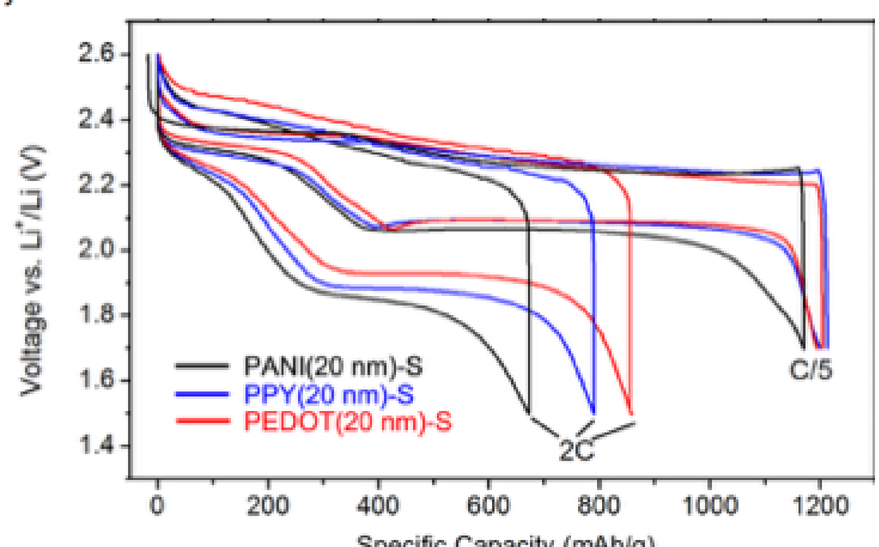
Cui group, *Nano Letters*, 13, 5534 (2013)

Accomplishment

Conductive polymer-coated hollow sulfur cathodes
-Battery performance: excellent rate capability



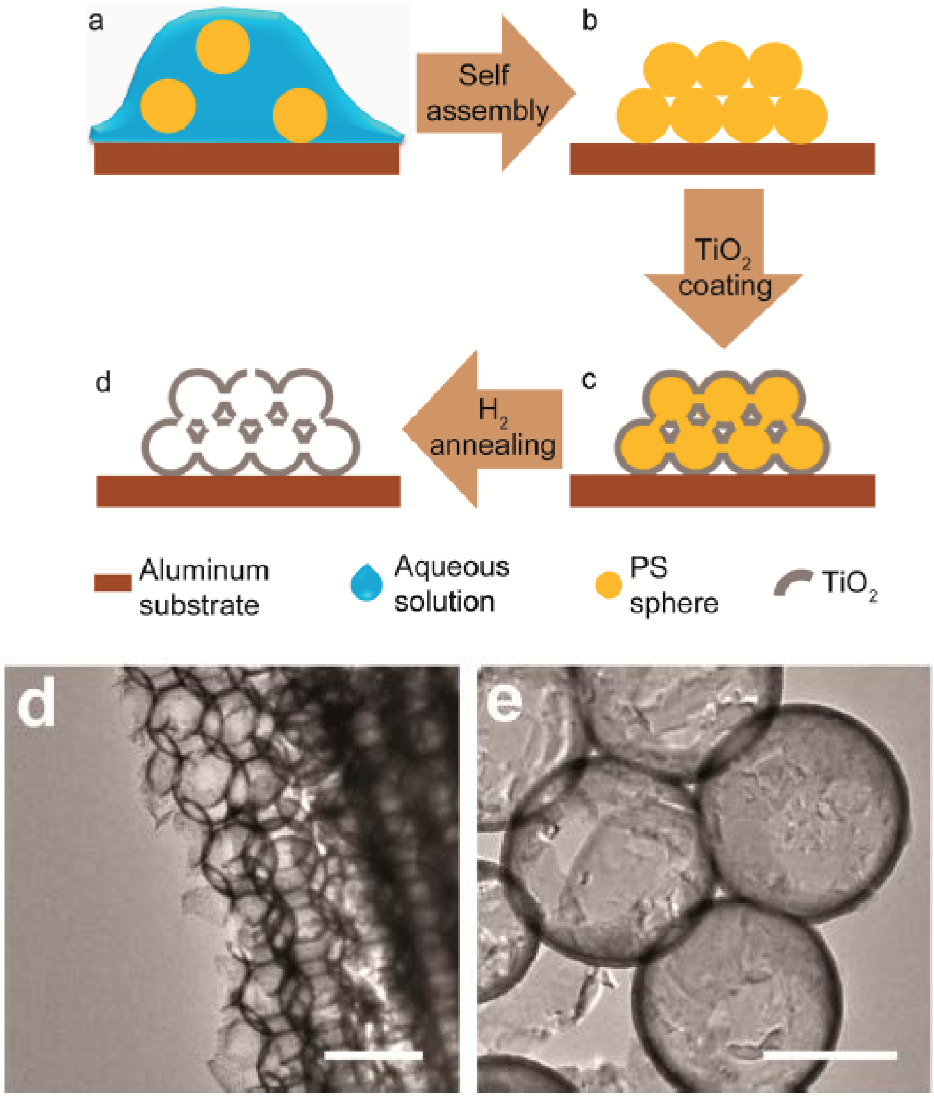


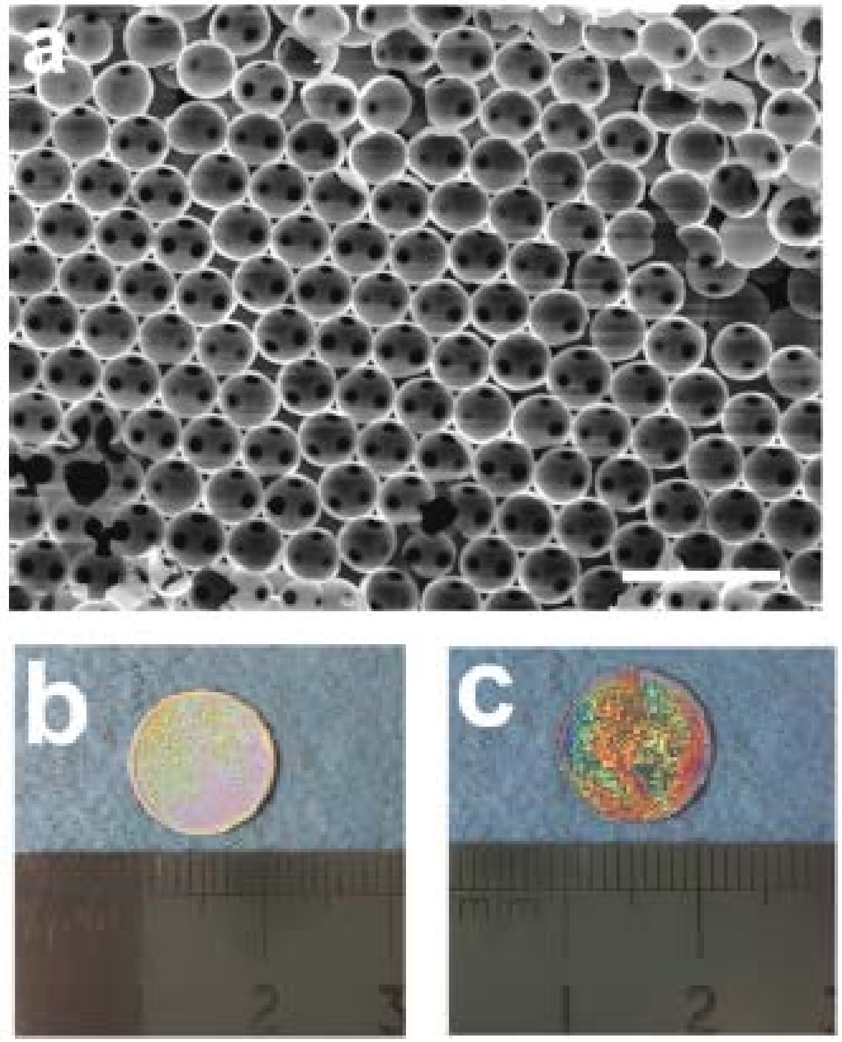


Cui group, *Nano Letters*,13, 5534 (2013)

Accomplishment

Hydrogen Reduced TiO_{2-x} Inverse Opal- synthesis and morphology

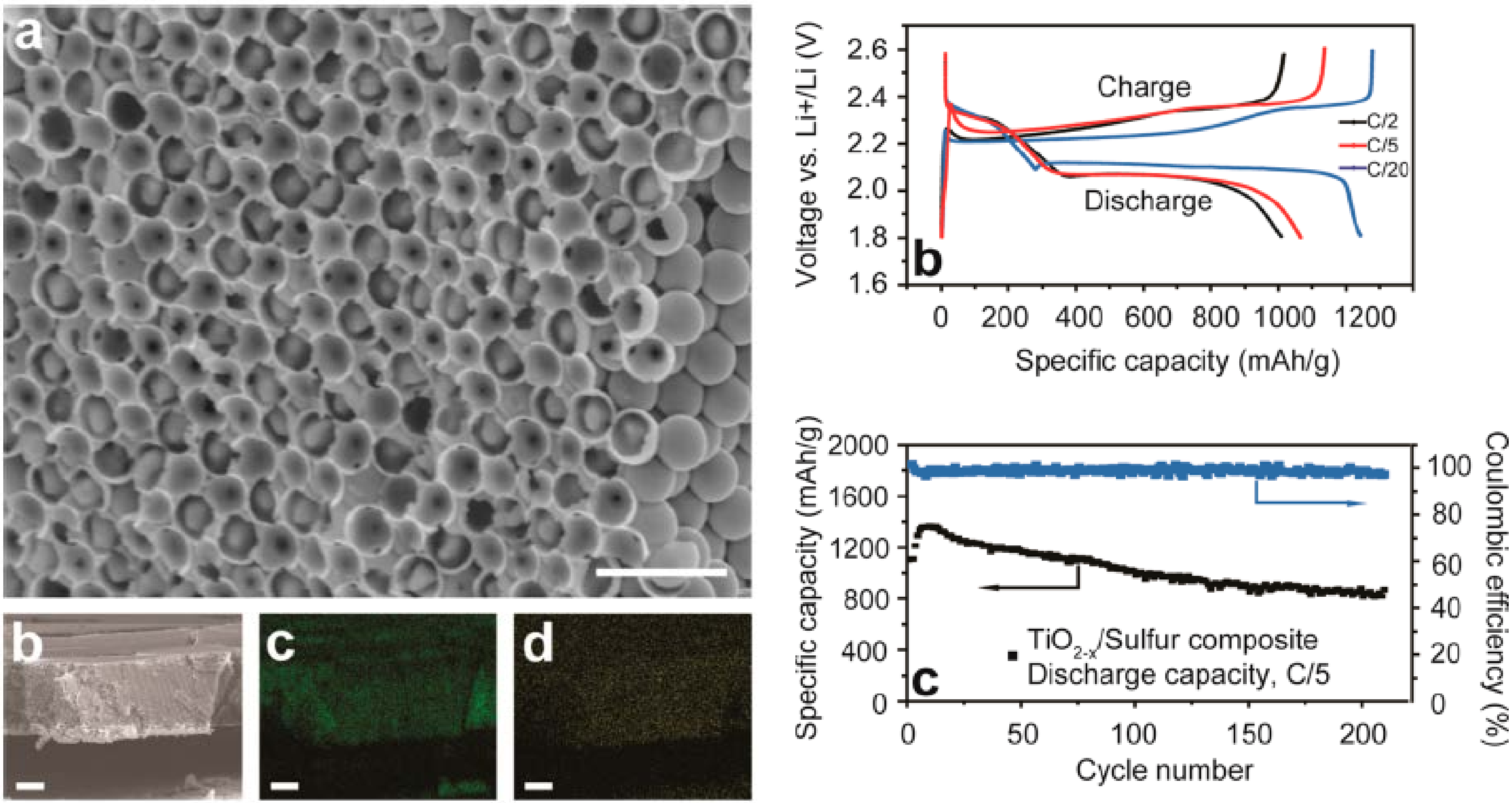




Cui group, *ACS Nano*, 8, 5249 (2014)

Accomplishment

Hydrogen Reduced TiO_{2-x} Inverse Opal Sulfur- Battery performance



Cui group, *ACS Nano*, 8, 5249 (2014)

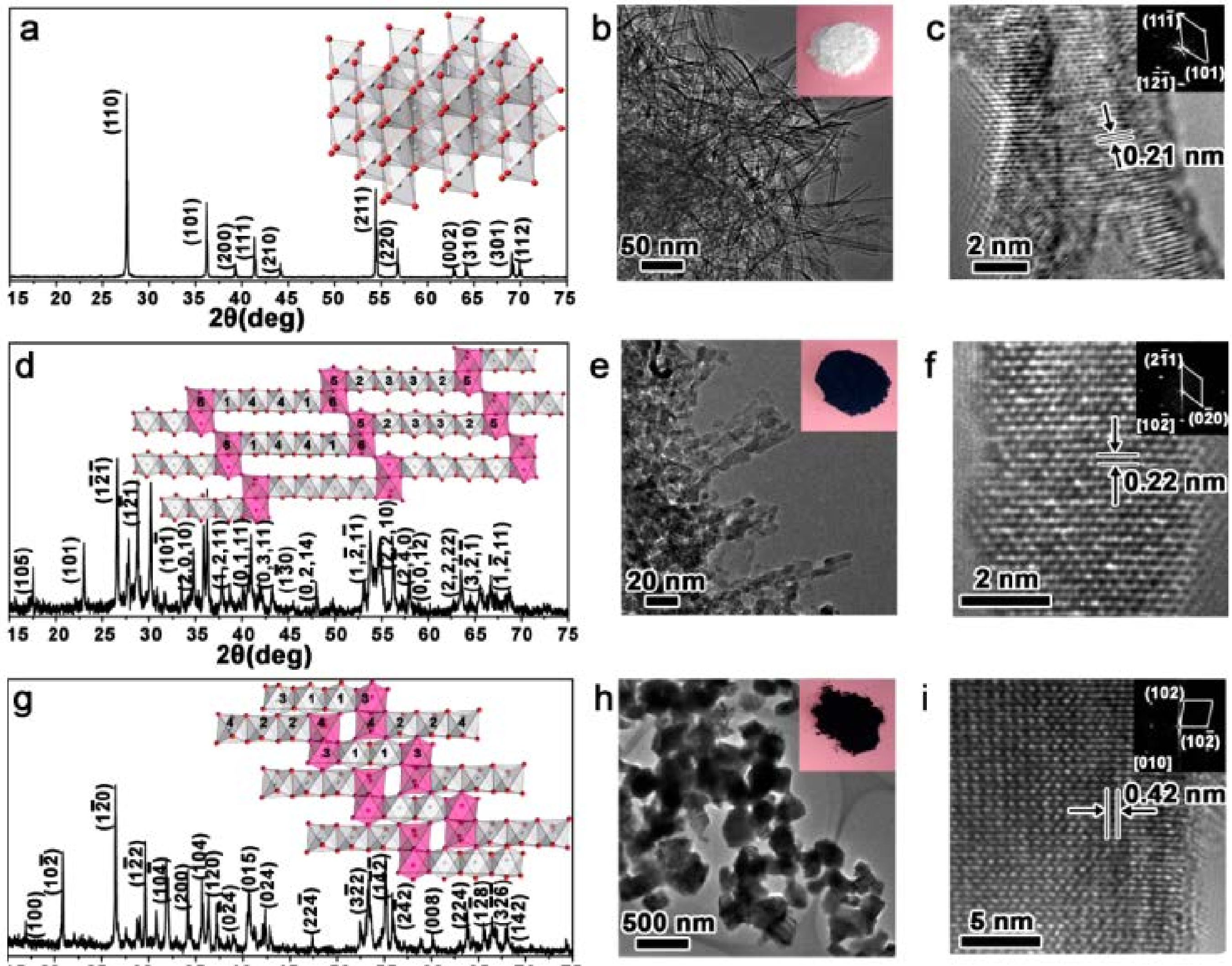
Accomplishment

Magnéli-Phase Ti_nO_{2n-1} Nanomaterials for S Cathodes

TiO_2

Ti_6O_{11}

Ti_4O_7

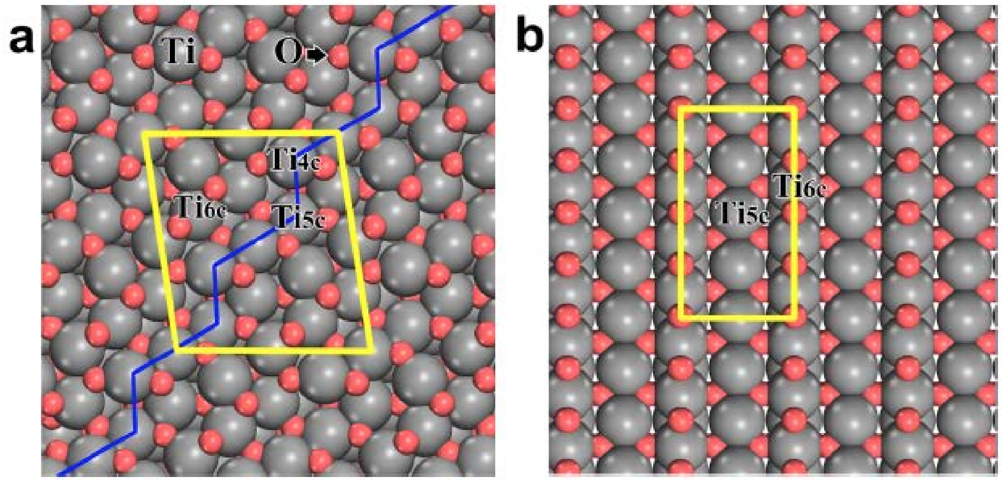


Cui group, *Nano Letters* 14, 5288 (2014)

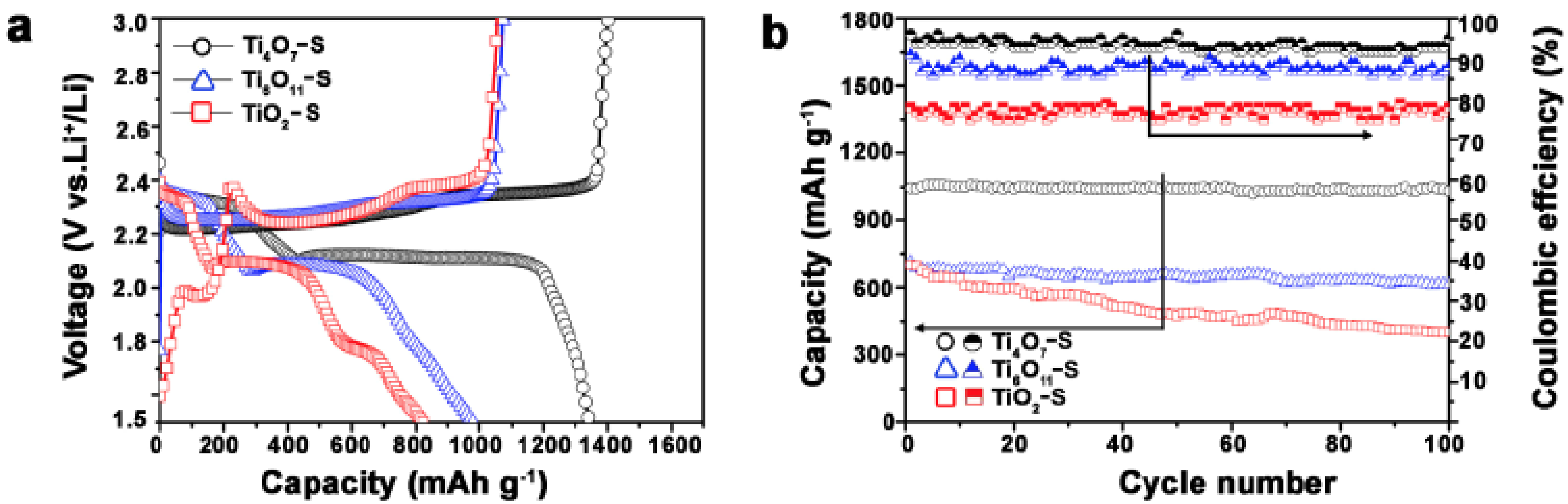
Accomplishment

Strong sulfur binding with conductive magnéli-phase Ti_4O_7 nanoparticles: Magnéli-Phase has high concentration of O vacancies

Ti_4O_7



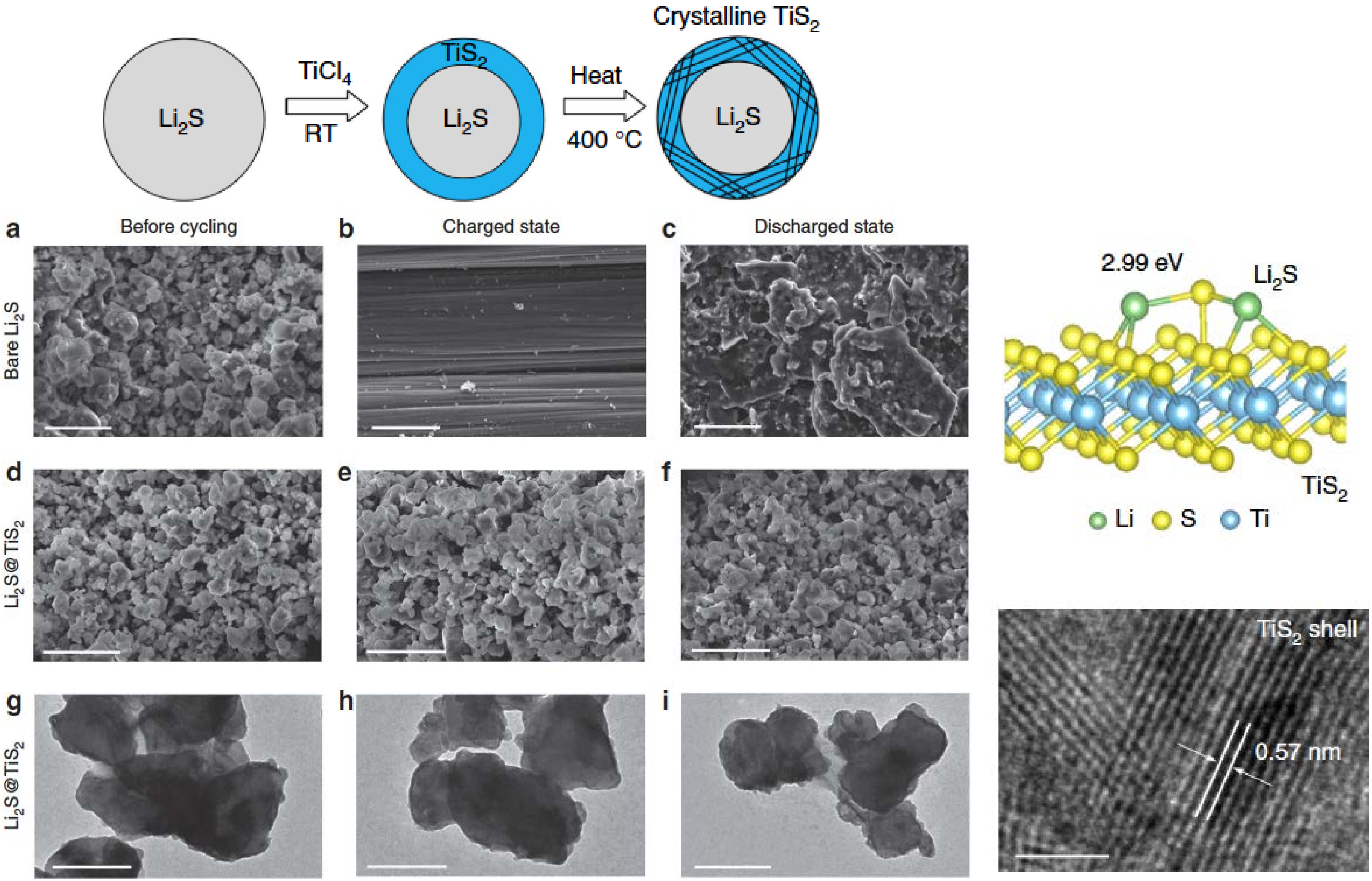
TiO_2



Cui group, *Nano Letters* 14, 5288 (2014)

Accomplishment

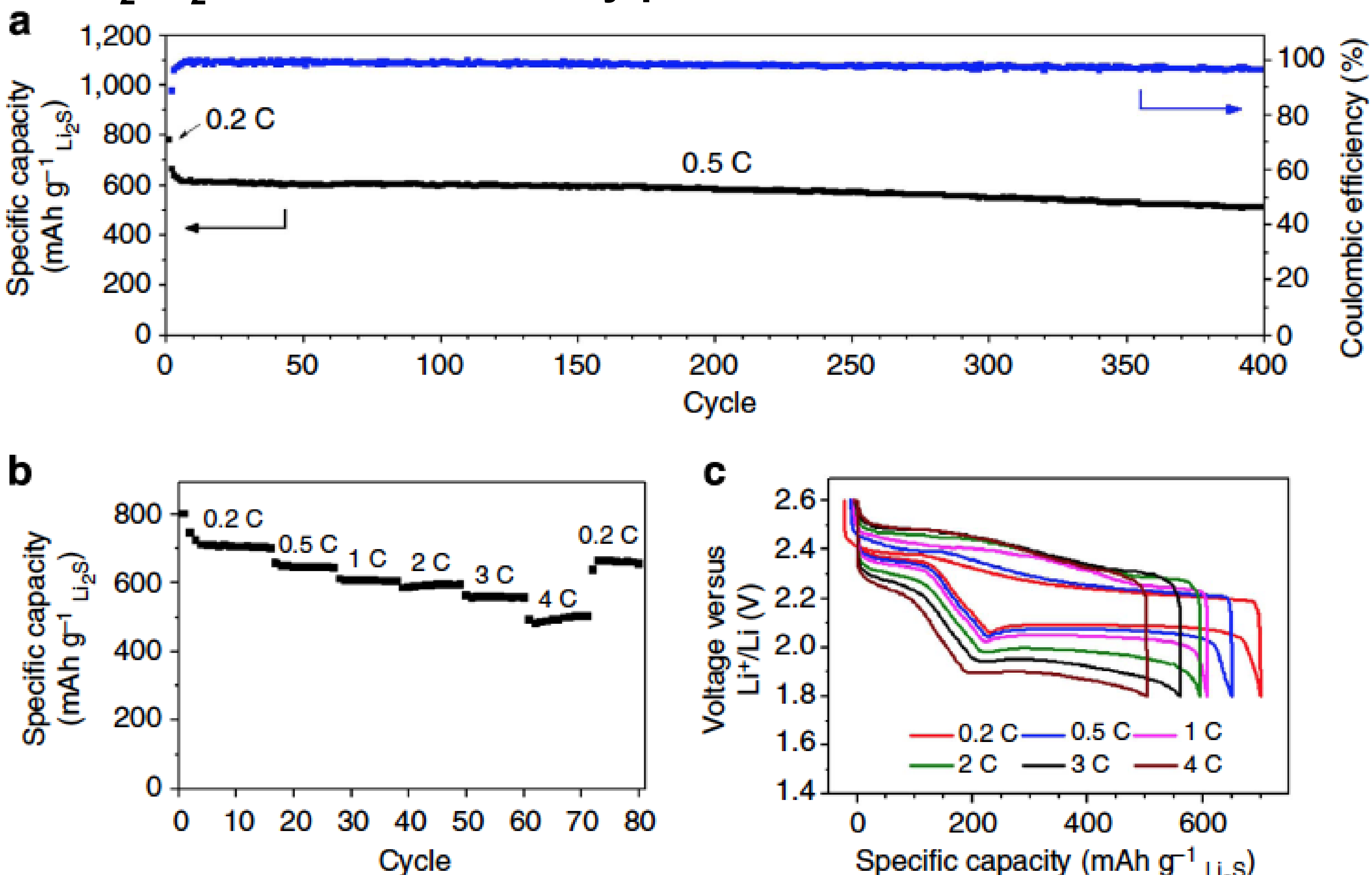
2D layered MS_2 for Effective Encapsulation of Li_2S Cathodes



Cui group, *Nature Communications* 5:5017 (2014)

Accomplishment

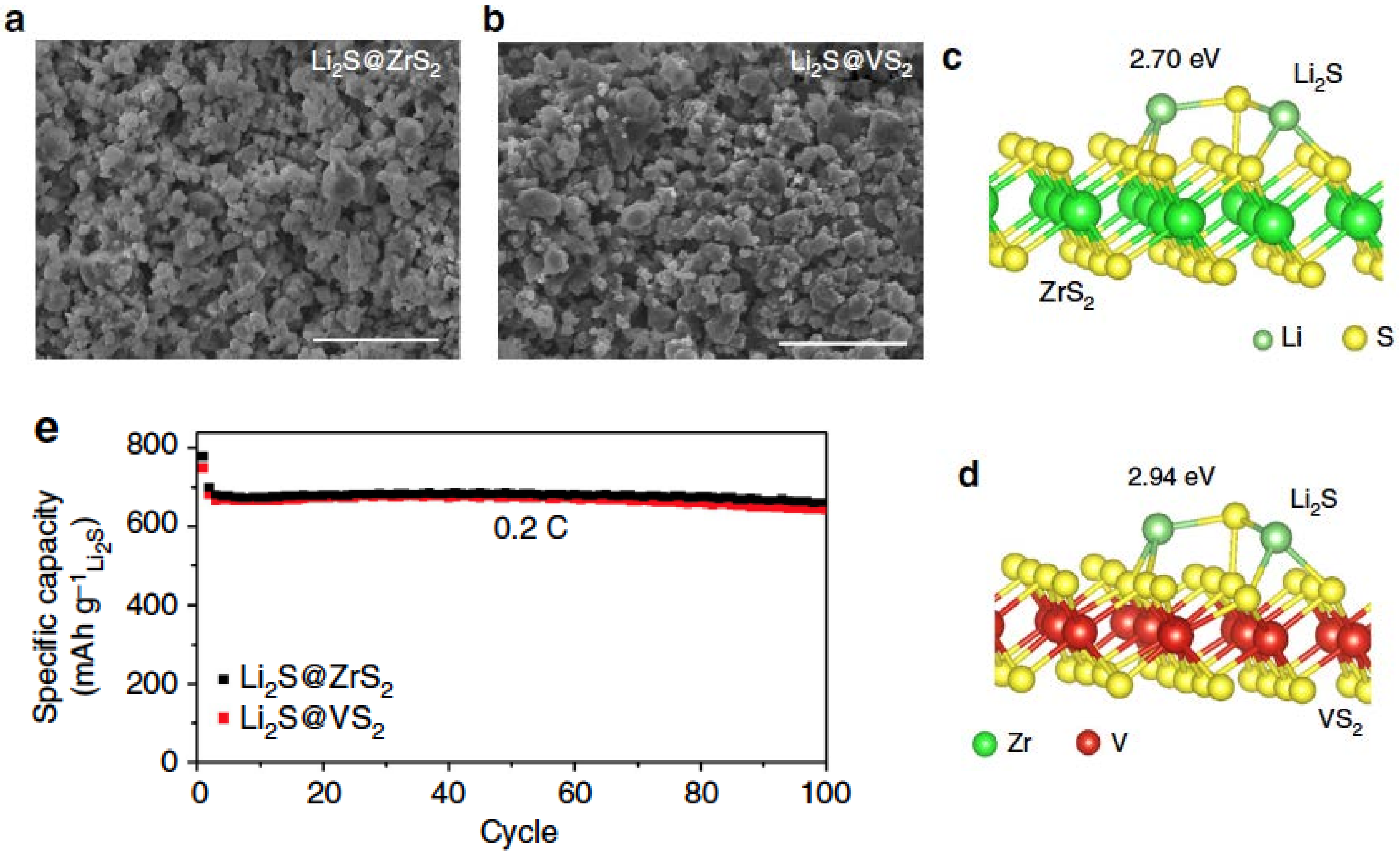
TiS_2-Li_2S Cathodes: battery performance



Cui group, *Nature Communications* 5:5017 (2014)

Accomplishment

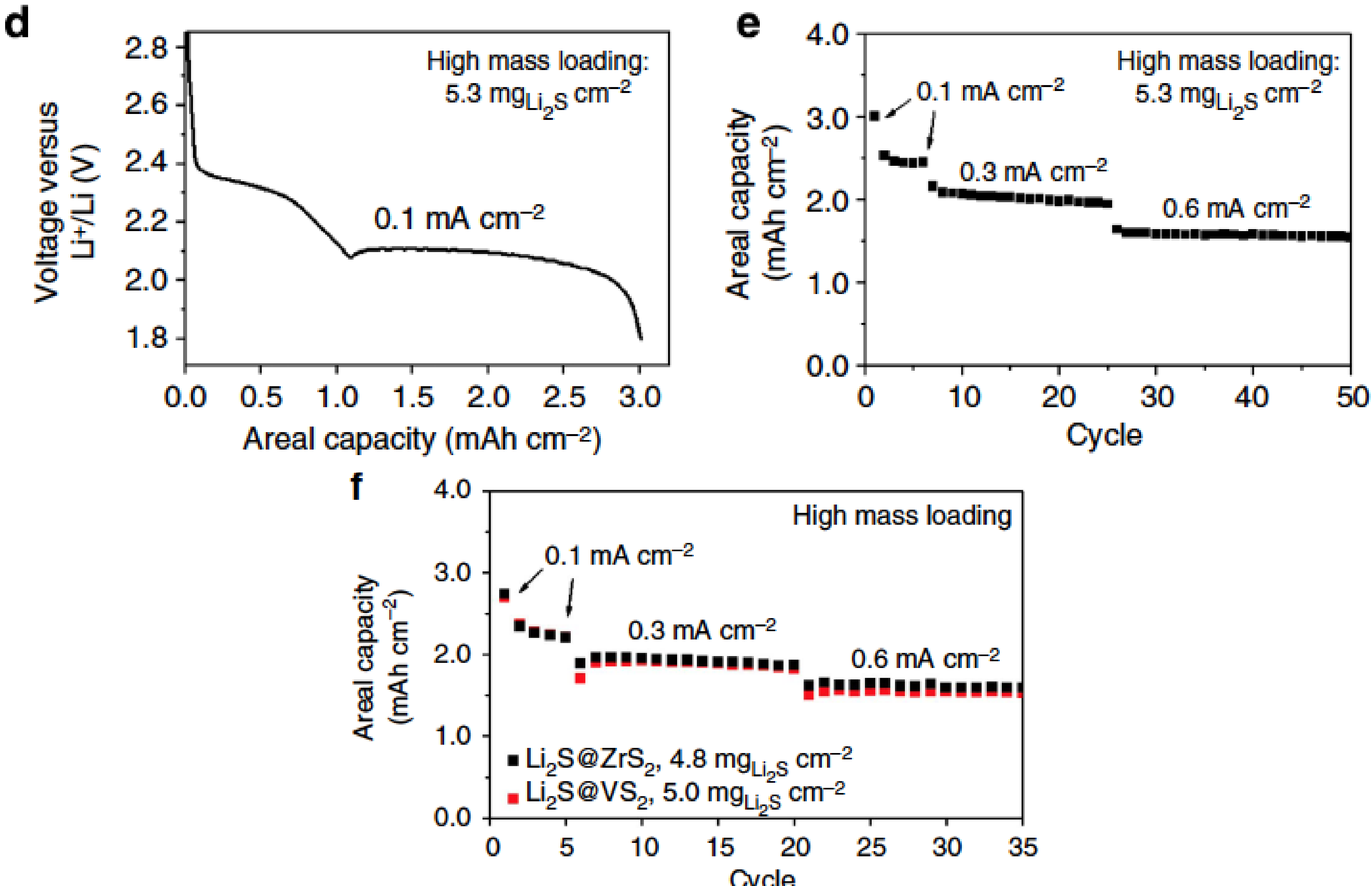
ZrS_2/VS_2-Li_2S Cathodes: morphology and battery performance



Cui group, *Nature Communications* 5:5017 (2014)

Accomplishment

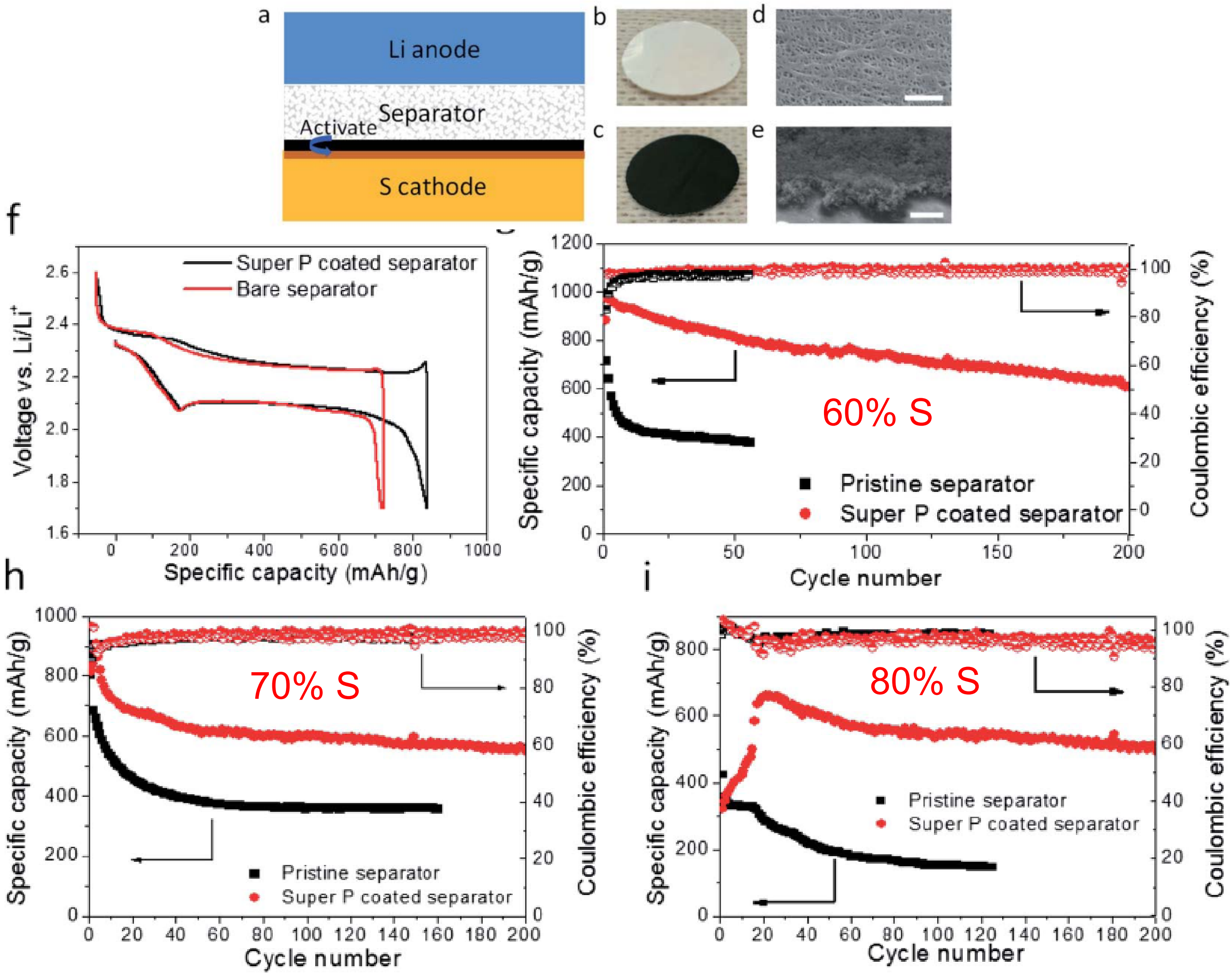
High Areal Capacity Loading of TiS_2/ZrS_2/VS_2-Li_2S Cathodes



Cui group, *Nature Communications* 5:5017 (2014)

Accomplishment

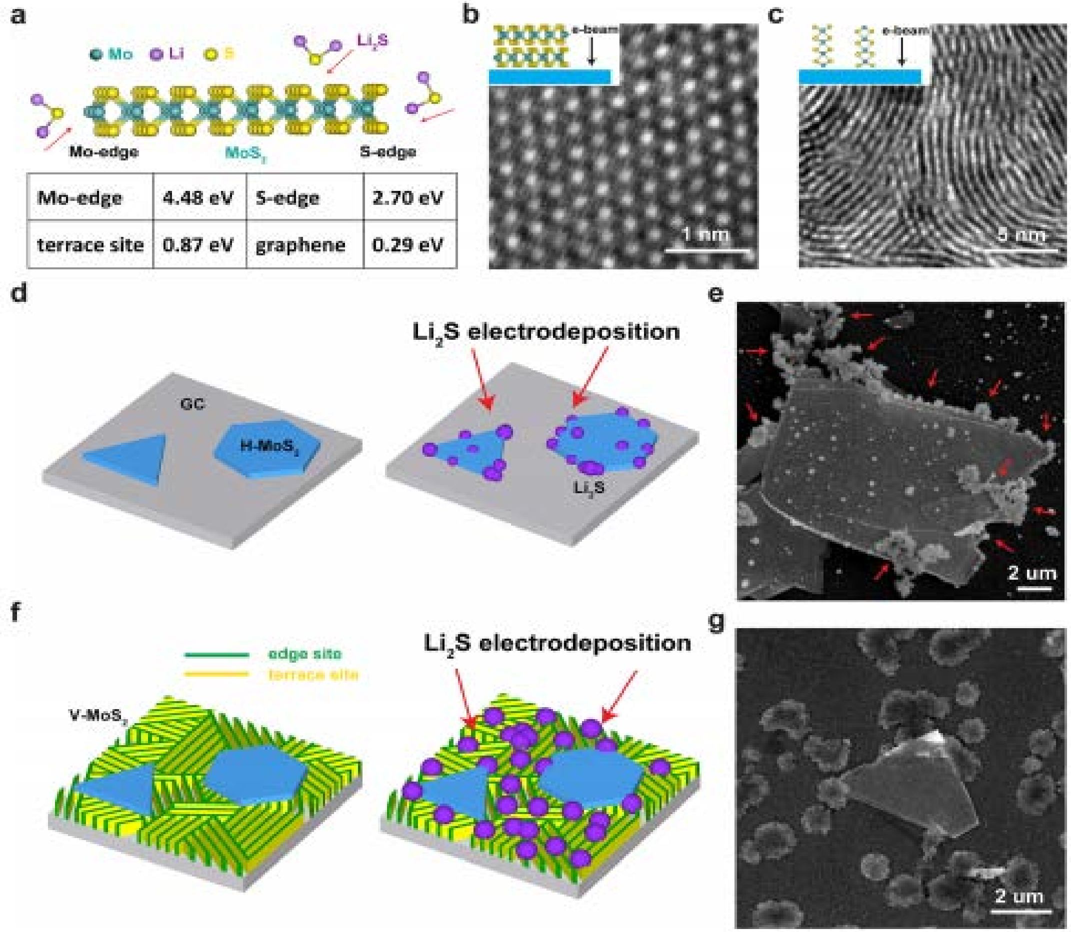
Improved Li-S batteries with a conductive coating on the separator
-Activate the sulfur cathode surface



Cui group, Energy & Environmental Science, 7, 3381 (2014)

Accomplishment

High electrochemical activity of edge sites in layered MoS_2 for high performance Li-S batteries



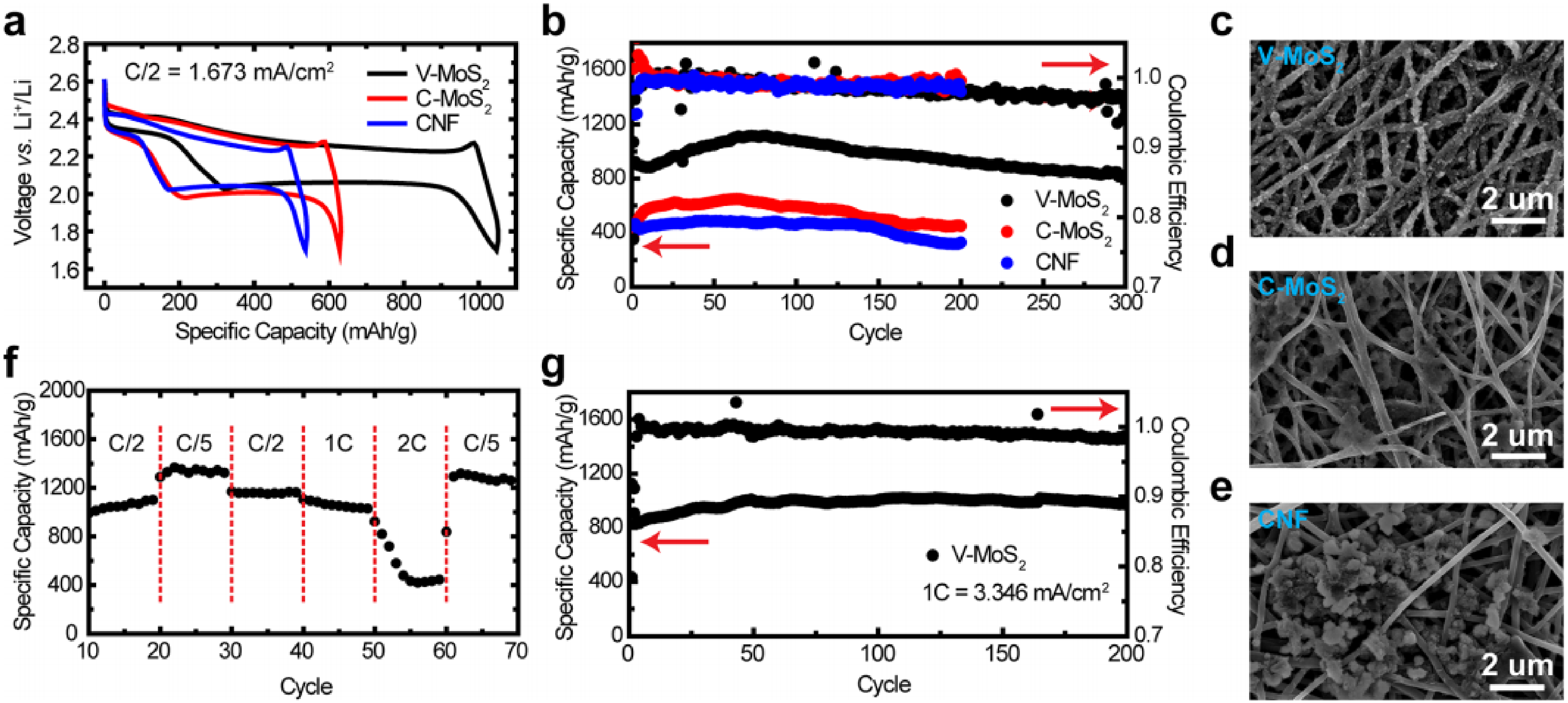
Mo-edge	4.48 eV	S-edge	2.70 eV
terrace site	0.87 eV	graphene	0.29 eV

- Lithium sulfide (Li_2S) nanoparticles decorates along the edges of the MoS_2 nanosheet versus terrace, confirming the strong binding energies between Li_2S and the edge sites.

Cui group, Nano Letters 14, 7138 (2014)

Accomplishment

MoS_2 based Cathodes: battery performance and morphology

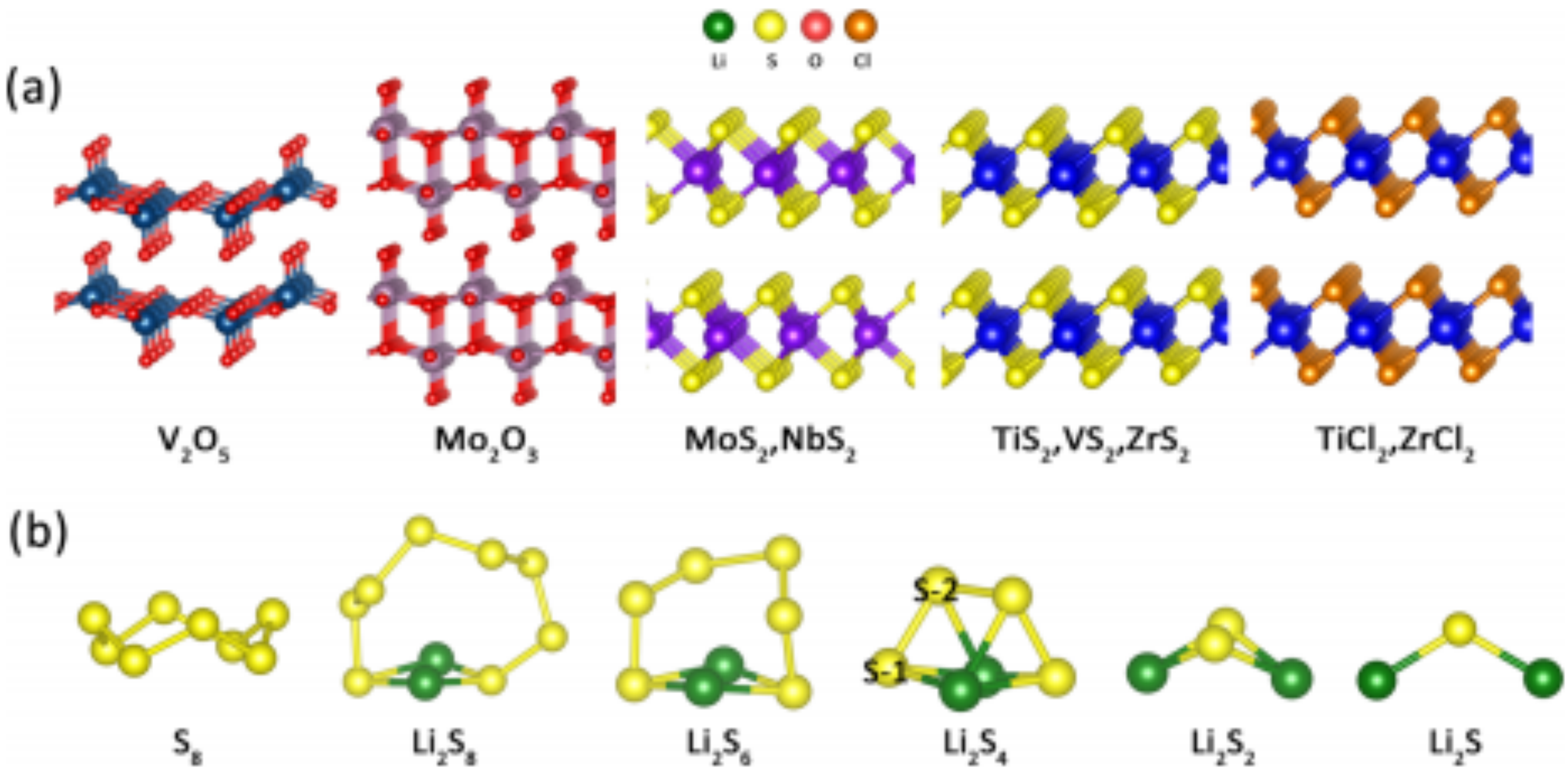


- ➢MoS_2 edge sites have much higher electrochemical selectivity and activity than its terrace surface, which provides important guidance to the battery electrode materials design.
- ➢The outstanding performance of the high rate testing benefits from the facile electrochemical deposition of S species on the V-MoS_2 edge terminated surface.

Cui group, Nano Letters 14, 7138 (2014)

Accomplishment

Atomic structure of layered materials that are used as anchoring materials

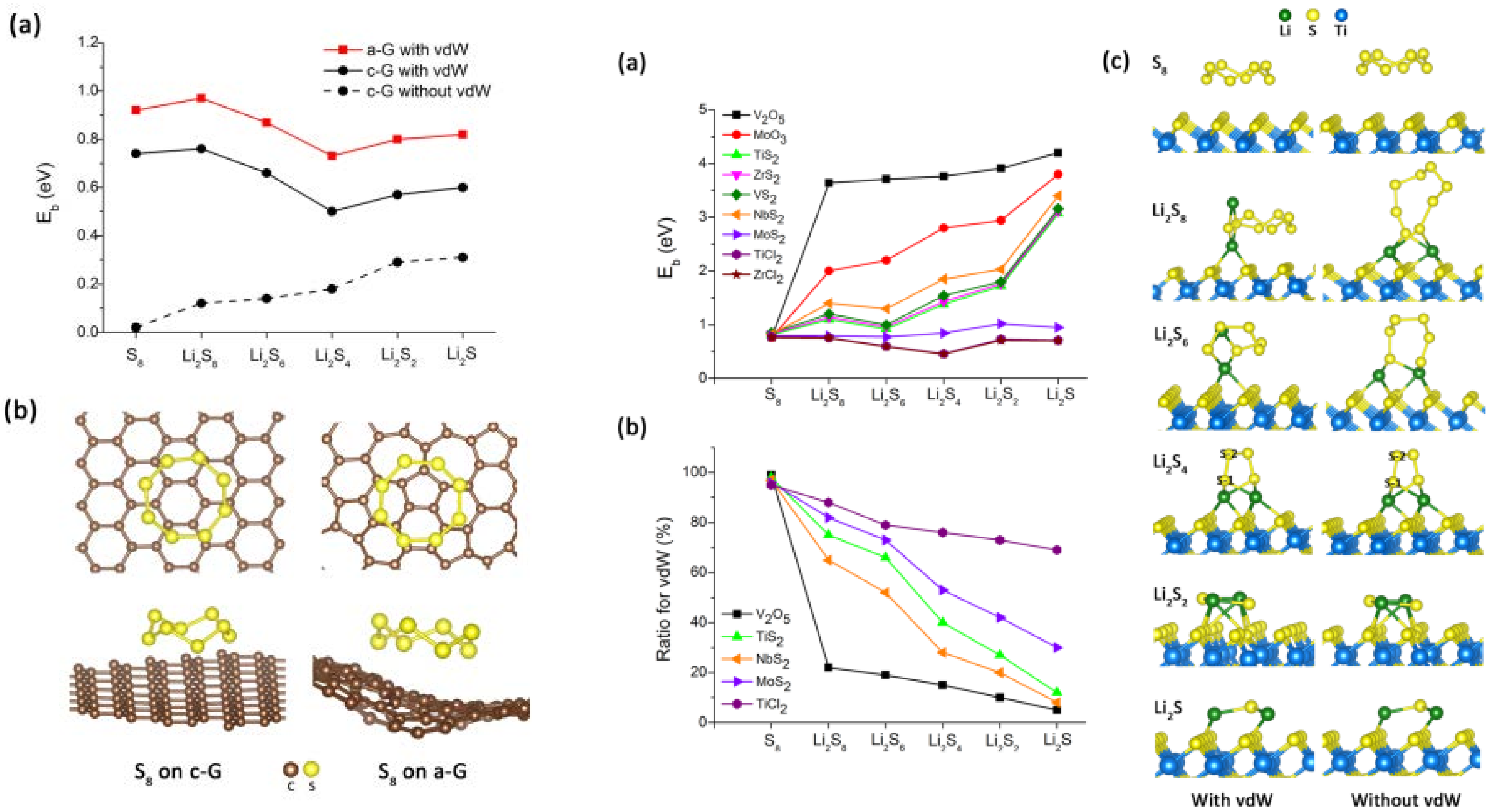


Molecule configurations for Li-S composites at various lithiation stages, from unlithated S_8 to Li_2S_2

Cui group, Nano Letters 15, 3780 (2015)

Accomplishment

On the basis of the computation, moderate anchor materials are the best choices for battery electrode.

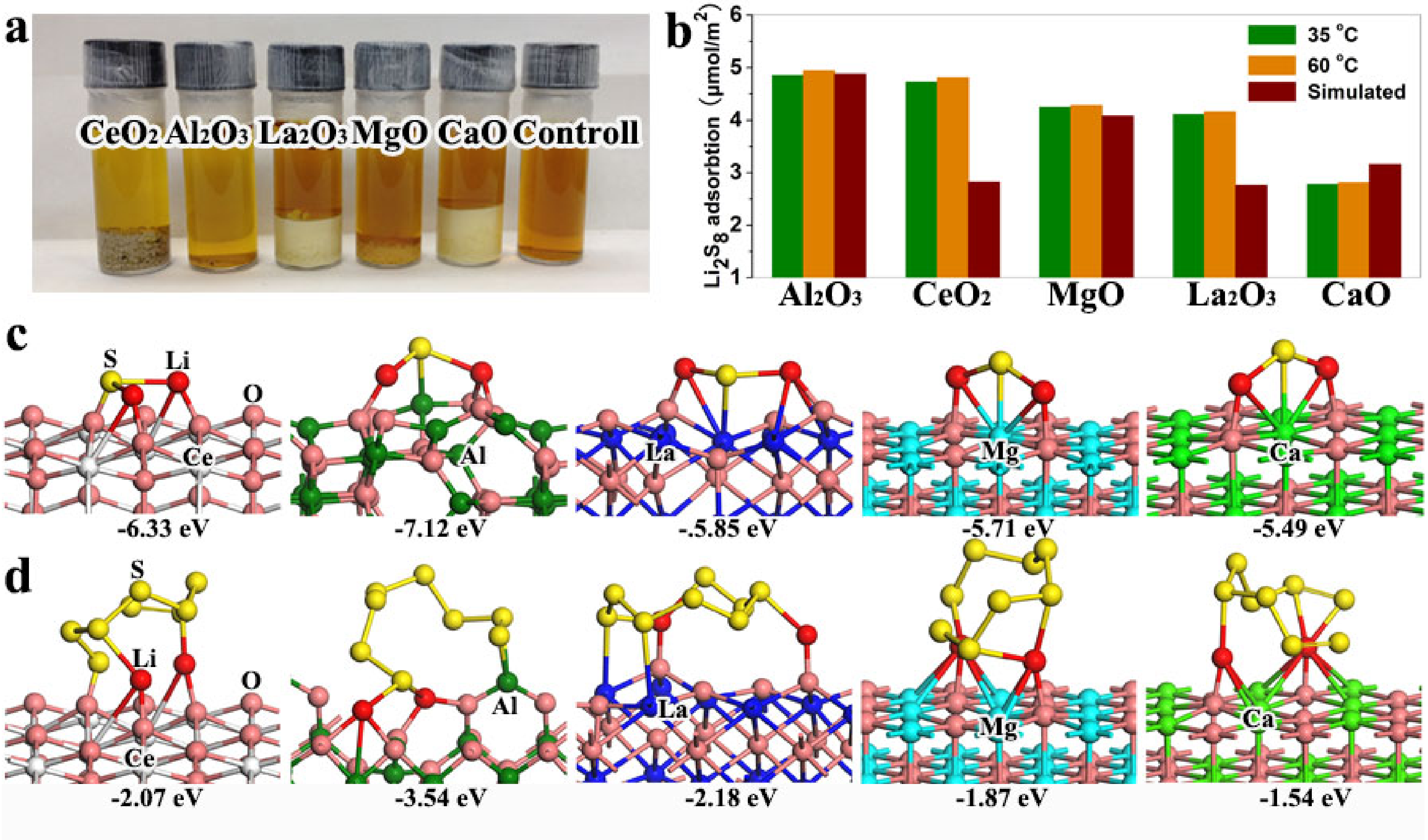


- ➢**The anchoring is accompanied by the softening of Li-S bonds, too strong binding can induce the destruction of Li_2S_n species.**
- ➢**Graphene cannot firmly adhere Li_2S_n species due to the weak interaction.**

Cui group, Nano Letters 15, 3780 (2015)

Accomplishment

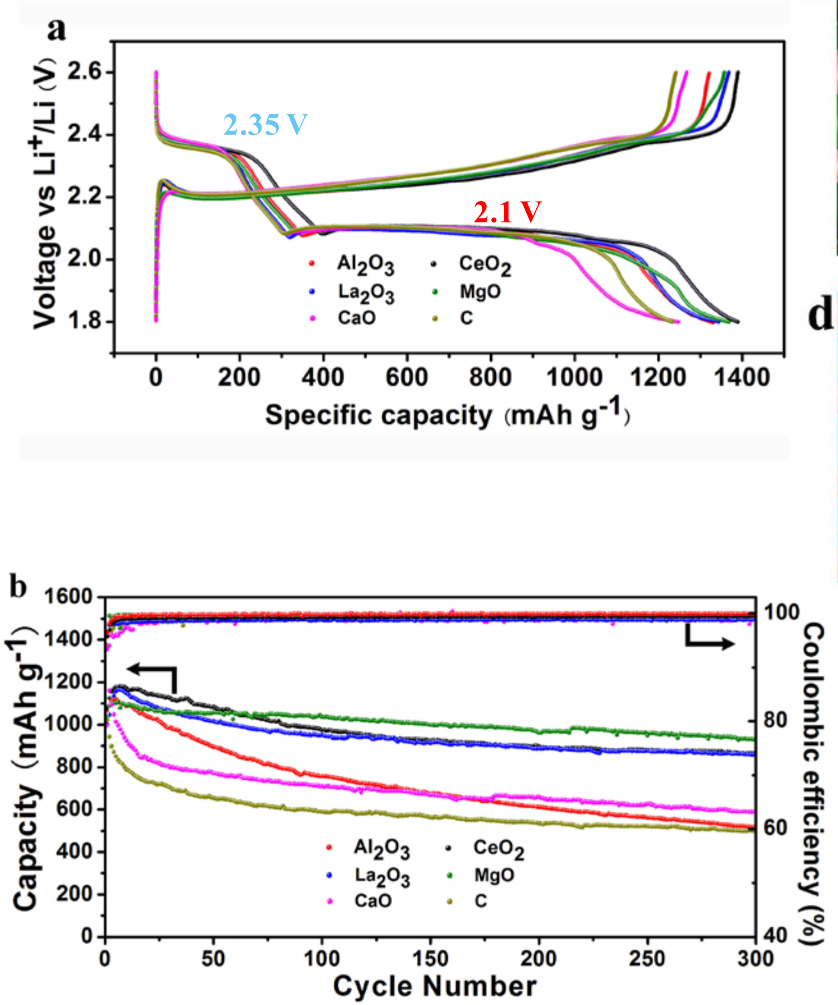
Polysulfide capture on the surface of metal oxides is monolayered chemisorption confirmed by combined experiment-DFT computations

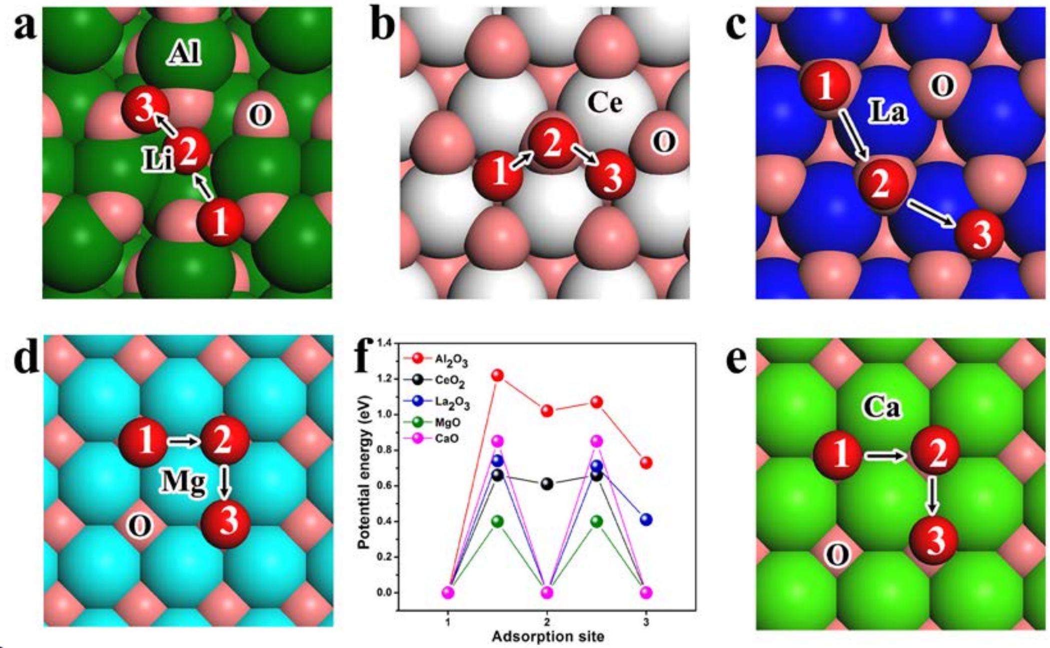


Cui group, Nature Communications, (2016), in press

Accomplishment

Oxide selection criterion: balance optimization between sulphides adsorption and diffusion on the metal oxides surface





➢ Lithium sulphide species can strongly adsorb, however, difficult to diffuse on Al_2O_3

➢MgO with suitable adsorption energies of lithium sulphur species and small diffusion barriers of Li

➢CeO_2(111) and La_2O_3(001) surfaces with similar diffusion barrier of 0.66 eV have the similar cycling performance.

Cui group, Nature Communications, (2016), in press

Responses to Previous Year Reviewers' Comments

Overall review comment: The project is innovative and productive and has a good future plan.

Review suggestions to improve:
Suggestion: There are many good nano-architectures demonstrated. The reviewers suggest to focus on one and do a thorough study.
Response: At this moment, none of the architectures can provide the perfect encapsulation of polysulfide yet having the desirable parameters all met. We will focus on the most promising architecture once we realize all the materials design principles within the same one.

Suggestion: Reviewers suggest to study the effect of electrolyte as well.
Response: We indeed to started to study the electrolyte effect in conjunction with nano-architecture. For example, we found the cooperative effect of polysulfide and $LiNO_3$ to suppress Li metal dendrite formation.

Suggestion: Reviewers suggest to increase the volumetric energy density
Response: This is an excellent suggestion to improve sulfur cathode. We have been carried out studies relevant to it by increasing active materials percentage and try to calendar the electrodes.

Suggestion: Reviewers suggest to keep focusing on suppressing the polysulfide dissolution
Response: We agree with reviewers and have indeed been focusing on understanding the trapping of polysulfide and designing strategies of solving it.

Collaboration and Coordination

SLAC: In-situ X-ray, Prof. Mike Toney

Beihang University, China:
Ab initio simulations, Prof. Qianfan Zhang

Zhejiang University of Technology, China:
Development of conductive magnéli-phase Ti_4O_7 nanoparticles, Prof. Wenhui Zhang, Prof. Xinyong Tao

Companies: Amprius Inc.

Remaining Challenges and Barriers

- It is difficult to maintain high capacity and excellent cycling stability of lithium-sulfur batteries while increasing the mass loading of active sulfur in the cathode.

- It is challenging to improve the rate capability (performance of battery at high current densities) of lithium-sulfur batteries.

- It is difficult to fully prevent all the active sulfur species from diffusing into the electrolyte.

- The volumetric energy density of lithium-sulfur batteries needs to be further increased.

- The lithium dendrites grown on the lithium metal surface is a concern for the safety of lithium-sulfur batteries that use lithium metal as anodes.

Summary

- **Objective and Relevance:** The goal of this project is to develop stable and high capacity sulfur cathodes from the perspective of nanomaterials design to enable high energy lithium-sulfur batteries to power electric vehicles, highly relevant to the VT Program goal.
- **Approach/Strategy:** This project combines advanced nanomaterials synthesis, characterization, battery assembly and testing, and guided by theoretical calculations, which have been demonstrated to be highly effective.
- **Technical Accomplishments and Progress:** This project has produced many significant results, meeting milestones. They include identifying the key issues in lithium-sulfur batteries, using rational materials design, synthesizing and testing, and developing scalable and low-cost methods. The results have been published in top peer-reviewed scientific journals. The PI has received numerous invitations to speak in national and international conferences.
- **Collaborations and Coordination:** The PI has established a number of highly effective collaborations.
- **Proposed Future Work:** Rational and exciting future has been planned.

Proposed Future Work

- To understand the interaction between sulfur/sulfide species and different metals sulfides, and select the optimal materials to re-capture the active sulfur species diffused in the electrolyte.
- To develop space efficiently packed nanostructured sulfur cathode to increase the volumetric energy density.
- To improve the interparticle contact and conductivity of sulfur nanostructures to increase the kinetics and thus improve the rate capability.
- To test sulfur cathodes with high areal mass loading up to 5 mg/cm^2 at high current densities.
- To develop approaches to prevent the lithium dendrites growth on lithium metal anodes in lithium-sulfur batteries
- To combine lithium sulfide cathodes with non-lithium anodes, such as silicon, to assemble full batteries to eliminate the safety concern of using lithium metal.