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Unusual Na^+ Ion Intercalation/Deintercalation in Metal-Rich $Cu_{1.8}S$ for Na-Ion Batteries

Hyunjung Park,[†,‡] Jiseok Kwon,[‡] Heechae Choi,[§,||] Donghyeok Shin,[‡] Taeseup Song,[*,‡] and Xiong Wen David Lou[*,†]

[†]School of Chemical and Biomedical Engineering, Nanyang Technological University, 62 Nanyang Drive, Singapore 637459, Singapore

[‡]Department of Energy Engineering, Hanyang University, Seoul 133-791, Korea

[§]Center for Computational Science, Korea Institute of Science and Technology, Seoul 136-791, Korea

[||]Virtual Lab Inc., Hwarangno 14-gil 5, Seongbuk-gu, Seoul 02792, Korea

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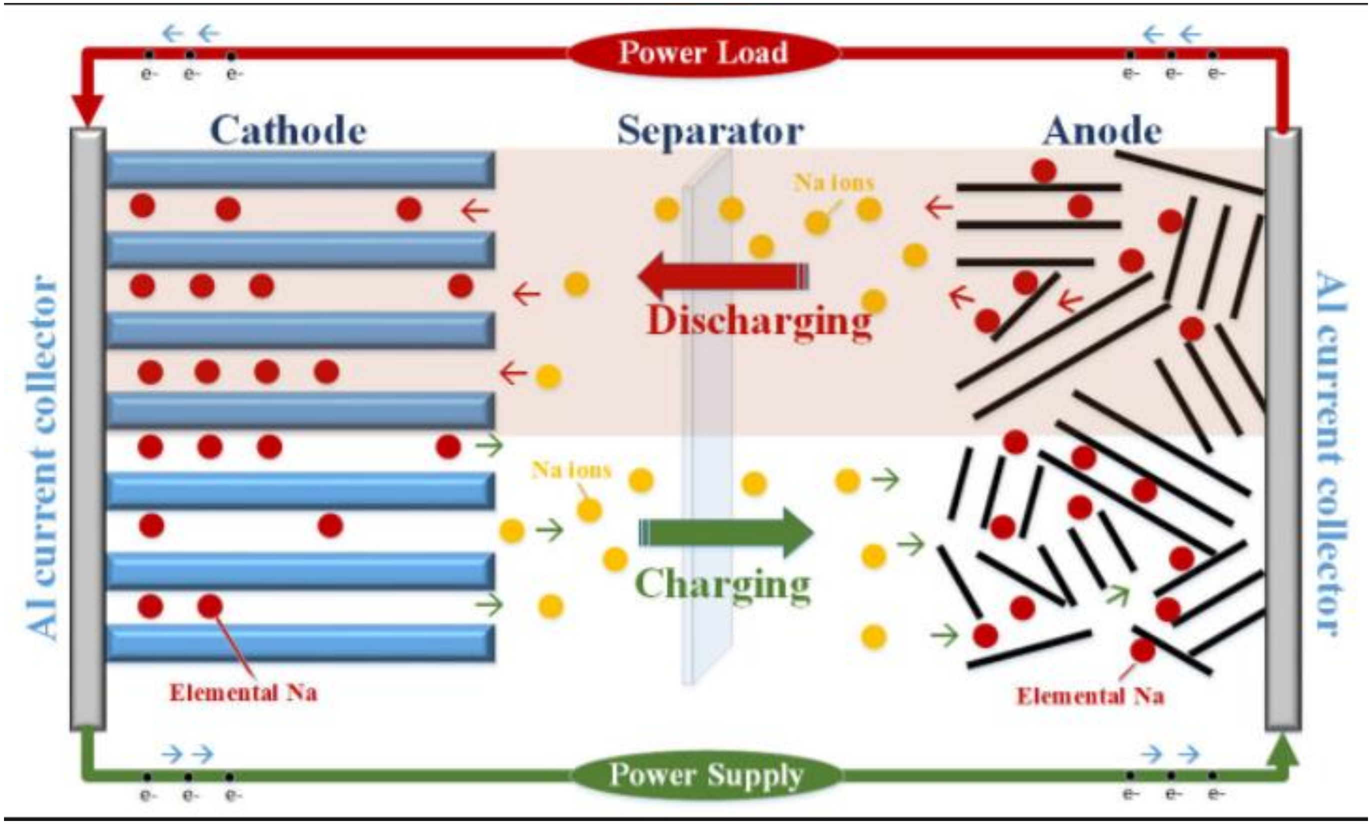
Na ion battery :



Important Issue about Na ion battery:

a) Electrode (cathode & anode) materials.

b) Suitable electrolyte.

1) Power output efficiency.
2) Longer life.
3) Cost & abundance.

Background:

Batteries

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From Lithium-Ion to Sodium-Ion Batteries: Advantages, Challenges, and Surprises

*Prasant Kumar Nayak⁺, Liangtao Yang⁺, Wolfgang Brehm, and Philipp Adelhelm**

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Recent advances in inorganic 2D materials and their applications in lithium and sodium batteries

Le Shi and Tianshou Zhao*

Designing solid-liquid interphases for sodium batteries

Snehashis Choudhury[1], Shuya Wei[1], Yalcin Ozhabes[2], Deniz Gunceler[2], Michael J. Zachman[3], Zhengyuan Tu[4], Jung Hwan Shin[1], Pooja Nath[1], Akanksha Agrawal[1], Lena F. Kourkoutis[3,5], Tomas A. Arias[2] & Lynden A. Archer[1]

DOI: 10.1038/s41467-017-00742-x

Related in group:

- Our Electrodeposited Copper sulphide may be used as an active materials for Na ion battery.
- MoS_2 based materials can also be used as anode materials.
- Overall this paper brings an idea about electrochemical study of Na ion battery as well as electrode materials characteristic in different condition.

Introduction:

- **A key issue with Na-ion batteries is the development of active materials with stable electrochemical reversibility through the understanding of their sodium storage mechanism.**
- **Metal sulfides (M_xS_y , M = Co, Cu, Fe, Mo, Ni, Sn, W) have been extensively explored as negative electrode materials for rechargeable batteries because of its abundance, low cost, and environmental friendliness of Sulphur.**
- **Digenite ($Cu_{1.8}S$) with hollow octahedral structure were first time uses as an active anode materials for sodium ion battery.**
- **Based on crystallographic study of the $Cu_{1.8}S$ interstitial sites for Na ions are determined an essential role on structural stability and long term cycle life.**
- **To optimize sodium storage property two important parameters, such as the electrolyte and a wide voltage window (0.1-2.2 V) are thoroughly investigated.**
- **A detailed reaction mechanism is elucidated through X-ray diffraction and transmission electron microscopy (TEM) studies.**

Synthesis & Characterization:

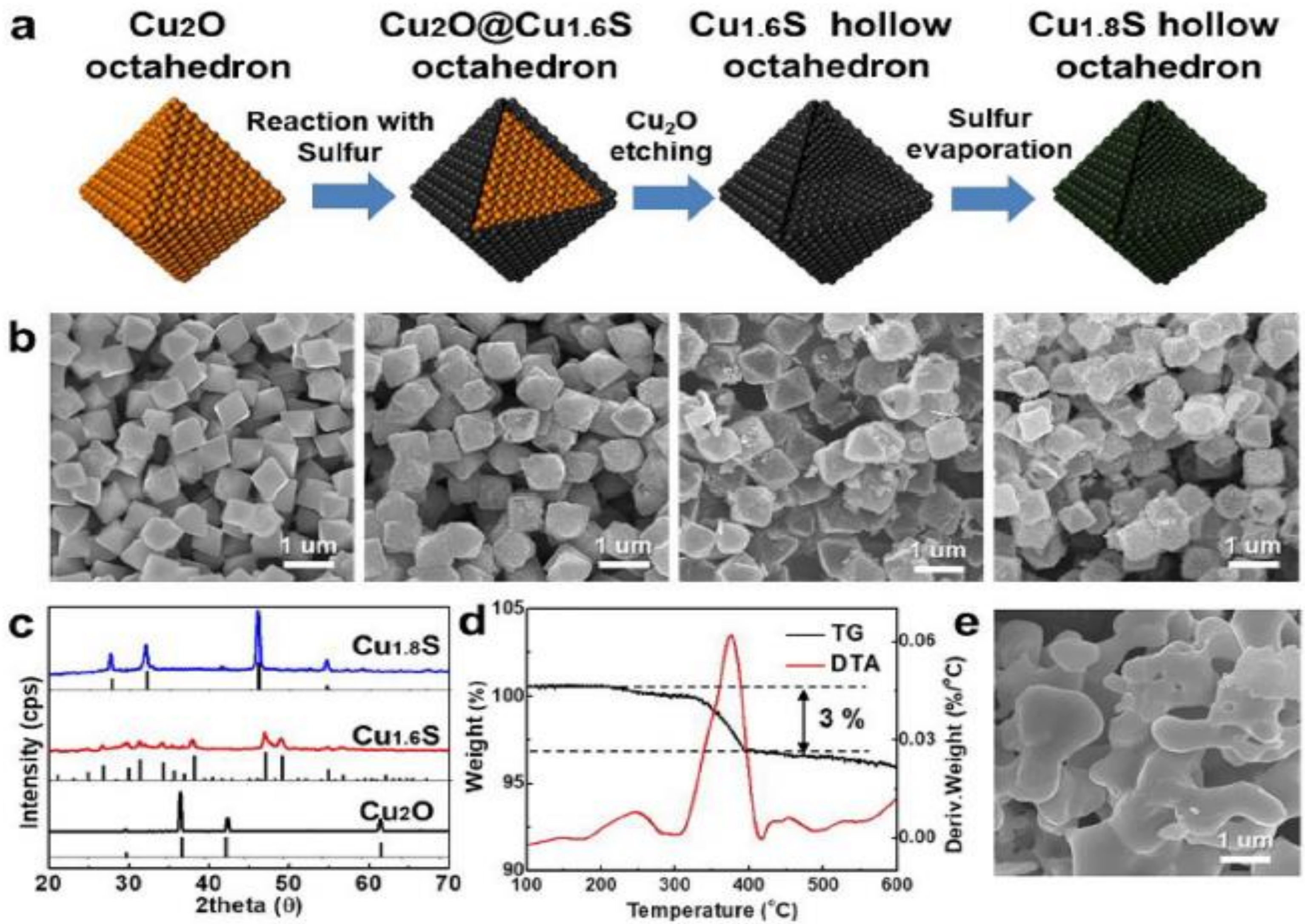


Figure 1. (a) Schematic illustration of the formation of $Cu_{1.8}S$ hollow octahedron. (b) Corresponding SEM images of as-prepared samples. (c) XRD patterns of as-prepared Cu_2O octahedral particles (black line), $Cu_{1.6}S$ hollow octahedral particles (red line), and $Cu_{1.8}S$ hollow octahedral particles (blue line). References are indexed below each pattern. (d) TG-DTA curve of $Cu_{1.6}S$ hollow octahedral particles in N_2 gas within the temperature range of 100−600 °C. (e) SEM image of as-prepared $Cu_{1.92}S/Cu_{1.94}S$ composite.

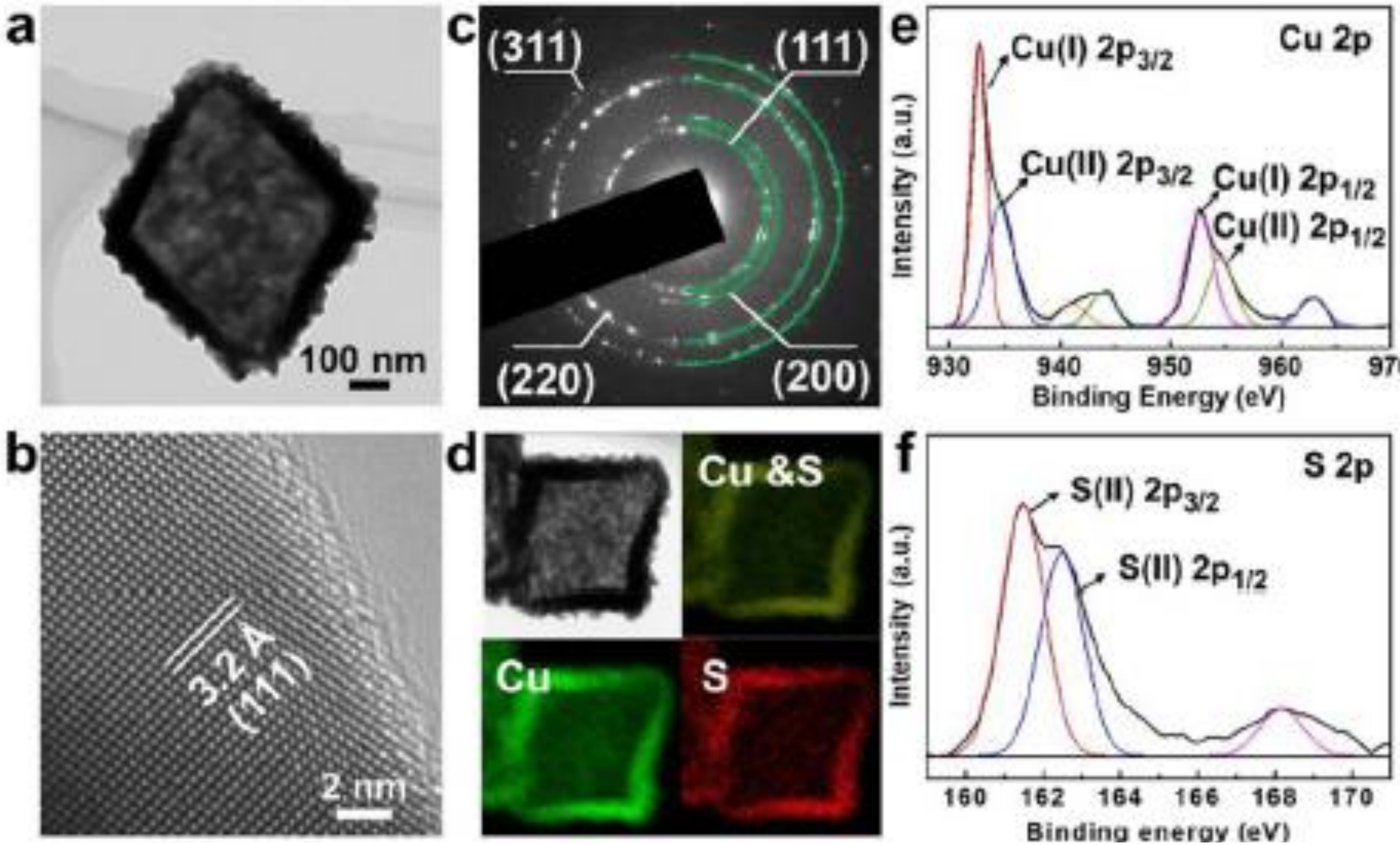
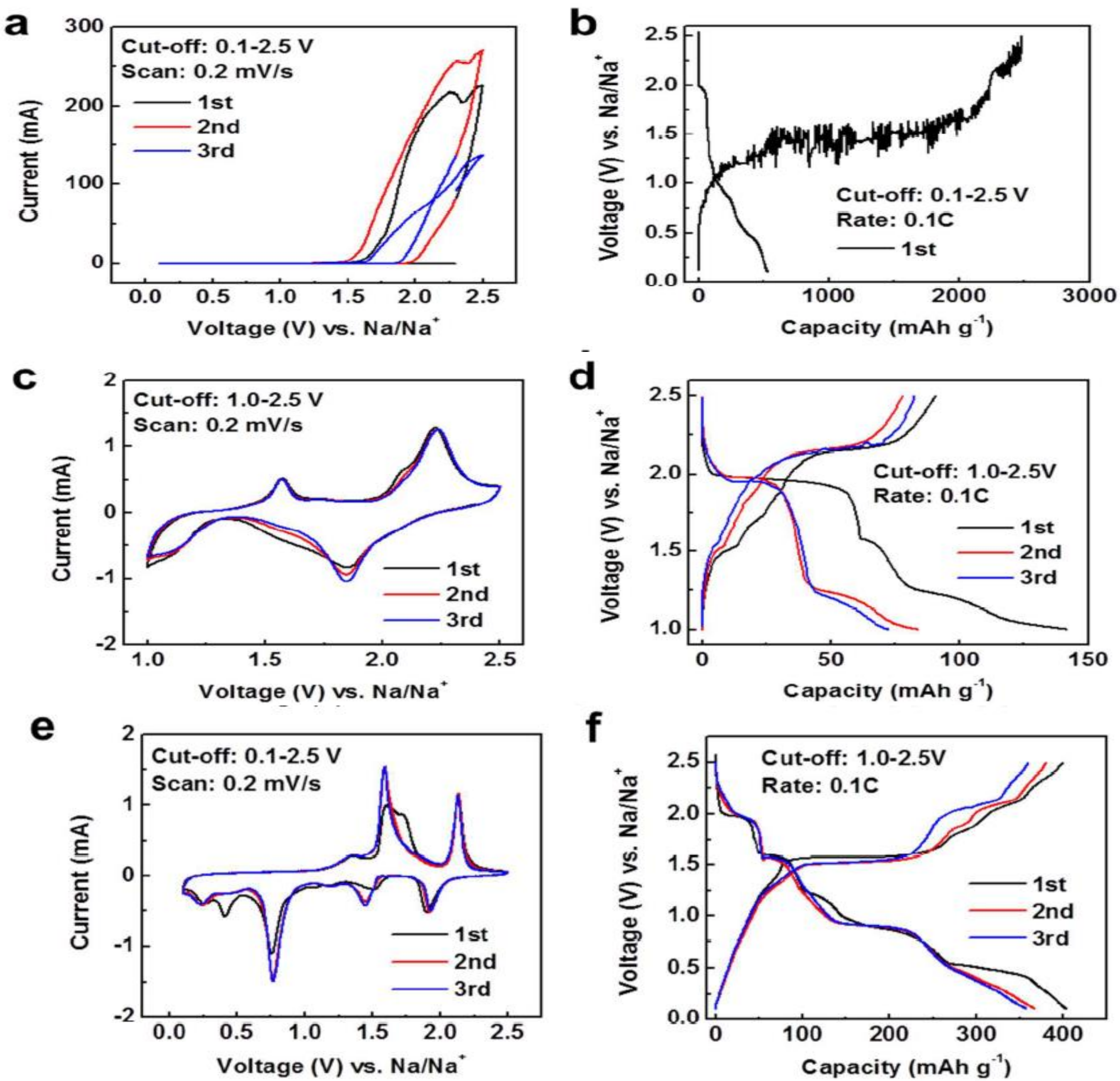


Figure 3. (a) Low-magnification and (b) high-magnification TEM images. (c) SAED patterns. (d) STEM image and EDX map for the Cu element (green) and the S element (red). XPS spectra of (e) Cu 2p and (f) S 2p.

Electrochemical performance:

Ethylene carbonate and dimethyl carbonate (EC:DEC,1:1,V/V)

Diethylene glycol dimethyl ether (diglyme)



Electrochemical performance:

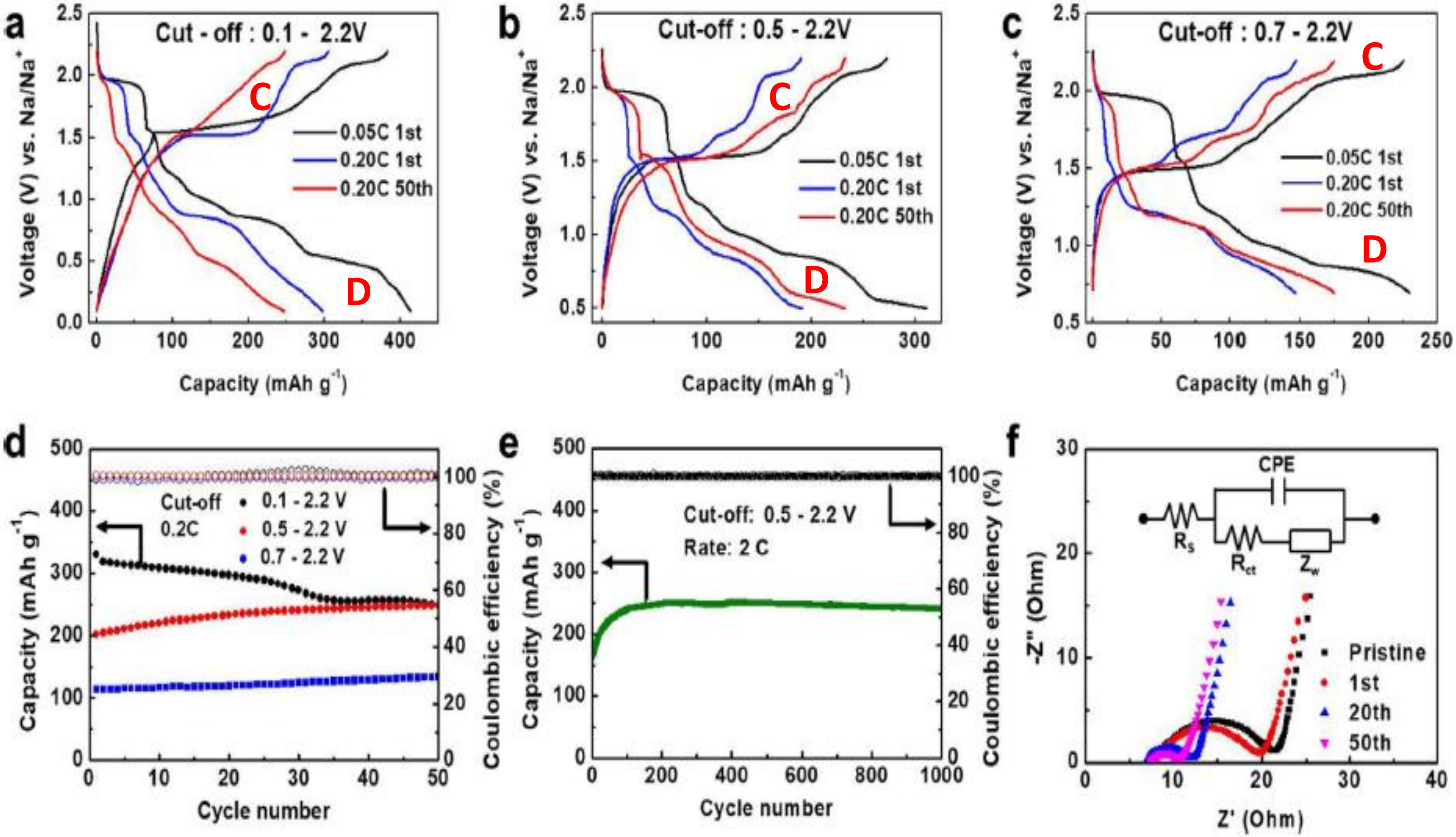


Figure 4. Voltage profiles of the first cycle at a current rate of 0.05C and the 1st/50th cycles at a current rate of 0.2C in the different voltage windows of (a) 0.1−2.2 V, (b) 0.5−2.2 V, and (c) 0.7−2.2 V versus Na/Na^+ (1C = 420 mA g^{-1}). (d) Cycle performance over 50 cycles at a current rate of 0.2C. (e) Long-term cycle performance at a current rate of 2C in the voltage window of 0.5−2.2 V versus Na/Na^+. (f) EIS spectra before and after cycling over the 1st/20th/50th. The inset shows an equivalent circuit of the $Na/Cu_{1.8}S$ electrode cell.

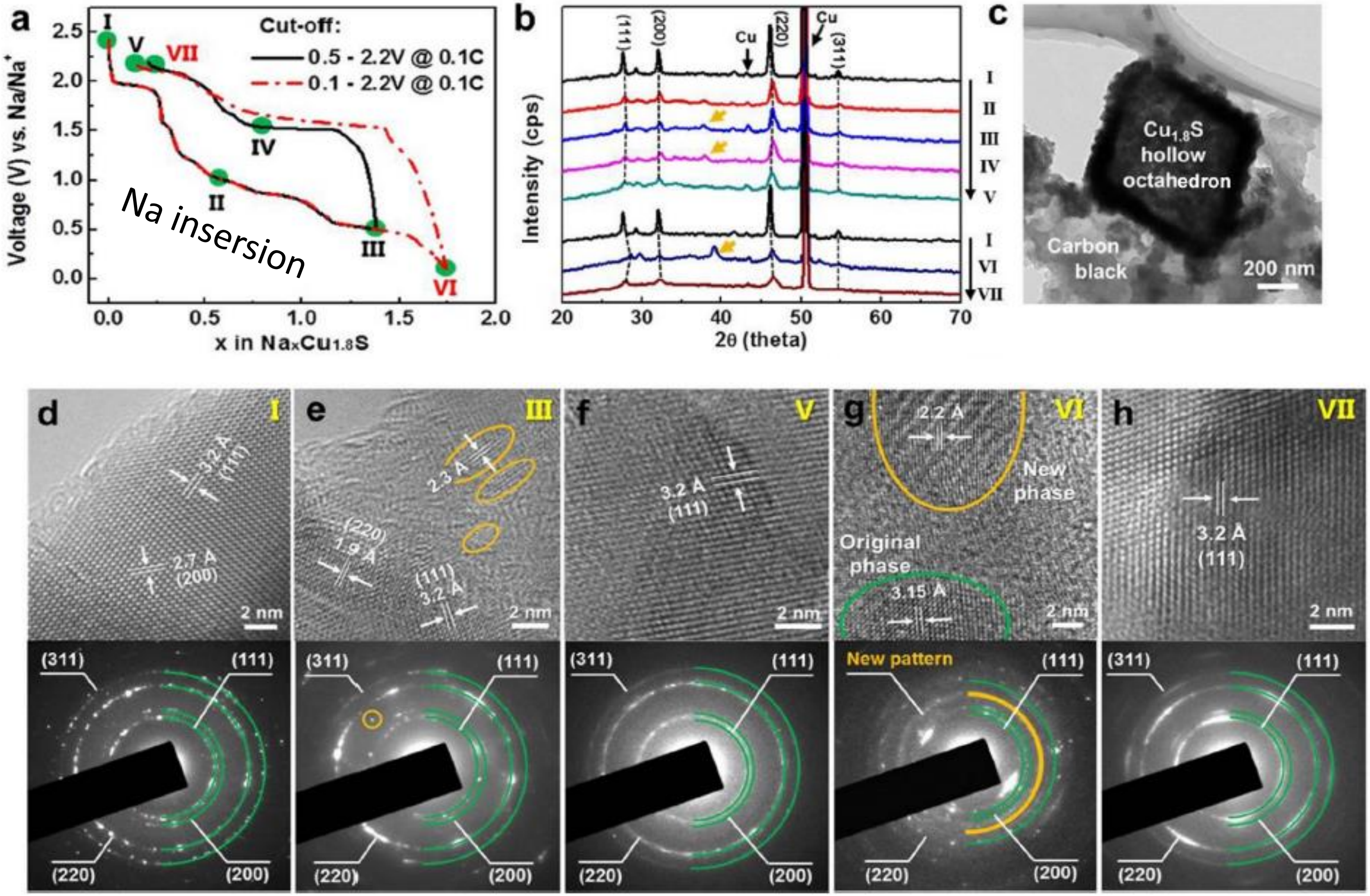


Figure 5. (a) Galvanostatic profile at a current rate of 0.1C in the potential window of 0.5/0.1−2.2 V versus Na/Na^+. (b) *Ex situ* XRD patterns obtained from the anode at each stage of I (pristine), II (discharge 1.0 V), III (discharge 0.5 V), IV (charge 1.5 V), V (charge 2.2 V), VI (discharge 0.1 V), and VII (charge 2.2 V). (c) Low-magnification TEM image of a $Cu_{1.8}S$ hollow octahedron after one cycle. (d−h) High-magnification TEM images and corresponding SAED patterns observed from the samples at I, III, V, VI, and VII stages.

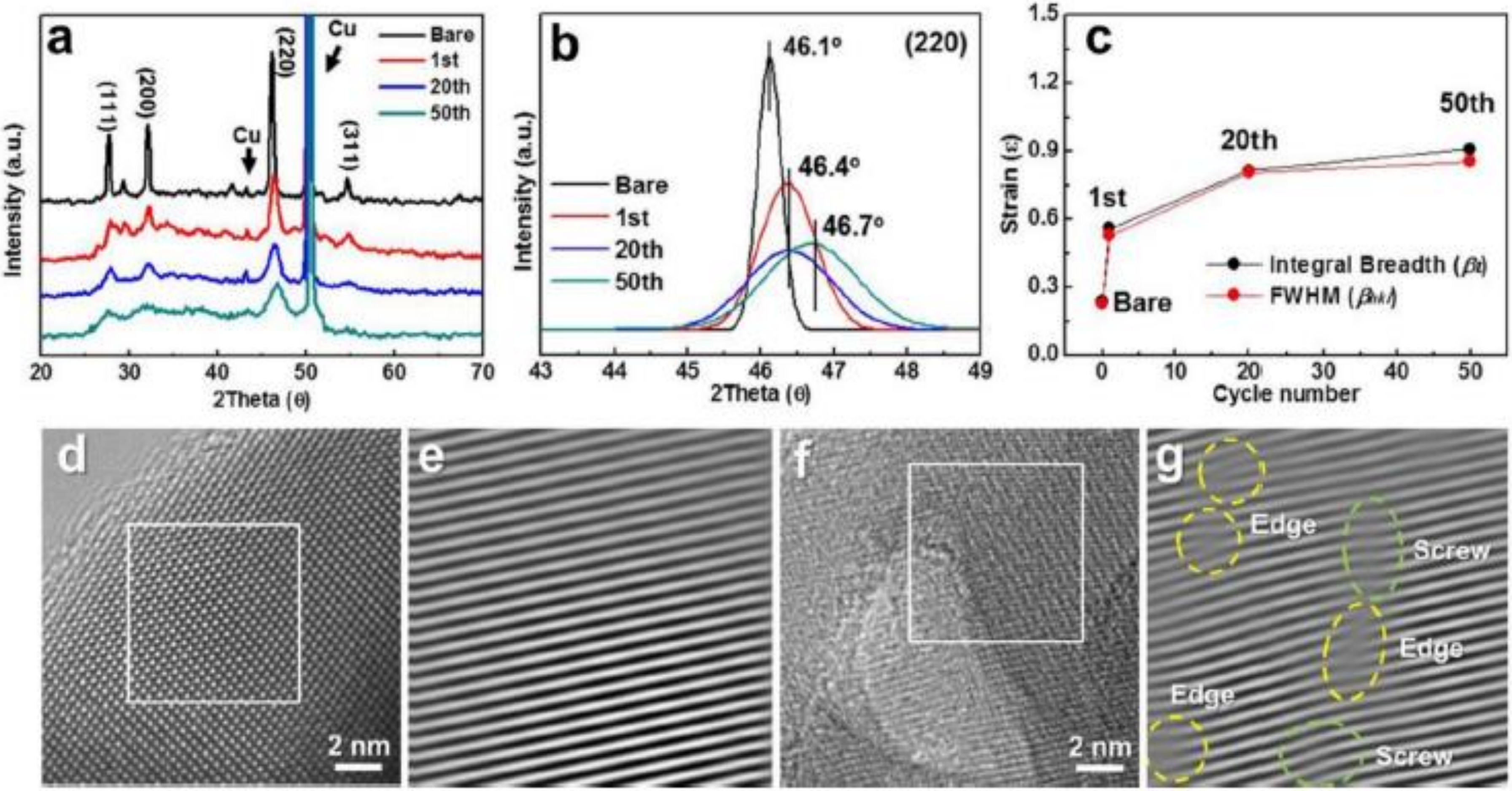


Figure 6. (a) *Ex situ* XRD patterns of the samples after cycling in the potential range of 0.5−2.2 V versus Na/Na^+. (b) Gaussian profile fitting of (220) peaks normalized with minimum values. (c) Cycle number−Strain plot. HRTEM and inverse fast Fourier transformation (IFFT) images of (d,e) pristine and (f,g) after one cycle.

Na insertion mechanism: DFT and crystallographic study.

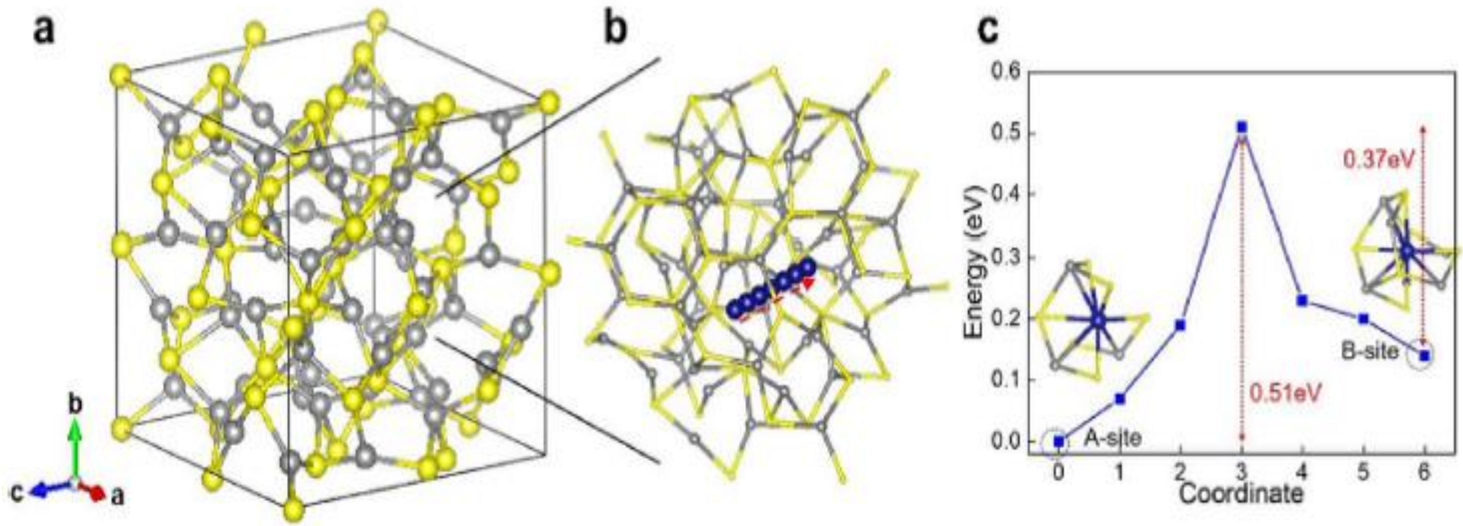
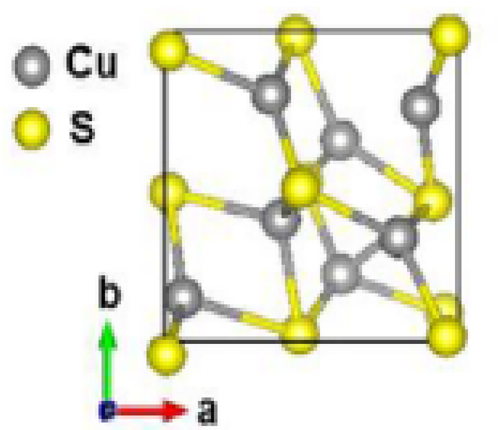


Figure 7. (a) 2 × 2 × 2 unit cell scheme of digenite $Cu_{1.8}S$. (b) Scheme of Na^+ ion migration path inside the $Cu_{1.8}S$ unit cell. (c) Calculated energy barrier of Na^+ ion diffusion. The gray, yellow, and deep blue spheres indicate Cu, S, and Na atoms, respectively.



- 8 Td. sites, 13 Oh. Sites are available for Na ion insertion.
- Cu atoms are close to tetrahedral sites, Na ion more likely to octahedral sites. So that 6 S atom surrounded by one Na atom.

Conclusion:

- Digenite ($Cu_{1.8}S$) was studied as a anode materials for sodium ion battery.
- An wide range of potential window (0.1 to 2.2 V) and electrolyte performance were optimized for $Cu_{1.8}S$ hollow anode.
- $Cu_{1.8}S$ anode electrode shows a reversible charge capacity of 250mAhgm^{-1} and a high Coulombic efficiency of 100% over 1000 cycles at a high rate of 2C in a potential range of 0.5-2.2 V versus Na/Na^{+} without irreversible phase transformation and structural collapse.
- This finding of Cu1.8S can give a way to develop new intercalation materials, and enhanced sodium storage properties can be achieved by engineering size and geometry, and doping of foreign materials.