

Previews

High-performance Na-S batteries enabled by a chemical and spatial dual-confinement strategy

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Sodium-sulfur (Na-S) batteries are promising for next-generation energy storage. Novel host materials with spatial and chemical dual-confinement functions for anchoring S are fabricated, which are incorporated in S cathodes. The Na-S batteries achieved a capacity retention of up to 97.64% after 1,000 cycles.

Rechargeable sodium-sulfur (Na-S) batteries are regarded as prospective substitutes for the commercial lithium-ion batteries because of their high theoretical specific capacity of 1,672 mAh g⁻¹ and low cost.¹ However, designing Na-S batteries with a high capacity and long lifespan for practical applications remains a challenge.² Three key factors are responsible for the inferior stability of Na-S batteries.^{3,4} First, the severe shuttling of soluble polysulfides (Na₂S_x, 4 ≤ x ≤ 6) reduces the cycle life and the energy efficiency to a large extent. A majority of the reported Na-S batteries failed to achieve high-capacity retention for over 100 cycles.³ Second, the slow conversion kinetics between the insulating S and Na₂S results in low S utilization and remains as a technical challenge. Finally, the volume variation of ~260% from S to Na₂S aggravates the cathode degradation.⁴ How to effectively address the above issues to develop long-lifespan S cathodes is crucial for achieving the high-performance Na-S batteries.

During the past decades, confining S within functionalized two- or three-dimensional (2D or 3D) carbon materials such as graphene, hollow nanospheres, carbon nanotubes, graphdiyne, and porous carbon nanofibers has gained much attention as it can simultaneously alleviate aforementioned issues.^{5–10} The

interaction between carbon host and S species plays an important role for improving the battery performance.⁵ Employing physical S-trapping strategies in carbon-based hosts can offer weak host-S interactions and postpone the S loss in a short period. In this regard, chemical S-trapping to carbon-based hosts is a good approach to avoid the polysulfide shuttling.^{8–10} Wang et al. represented an effective and facile strategy to achieve the long-term cycling for S cathodes by covalently bonding S species to the amino-functionalized reduced graphene oxide and realized a superior capacity retention of 80% for 350 cycles with high capacities at a high cycling rate of 4 C.⁸ Hu and co-workers anchored S on N-doped 2D carbon hosts via C–S_x–C bonds through vapor-infiltration treatment, showing the improved cycling stability of Na-S batteries.⁹ However, this kind of cathode cannot avoid the fracture of C–S bonds during the charging process when the Na⁺ reacts with S to form Na₂S, resulting in the loss of active S species. Therefore, precisely engineering S-host interactions to enable the steady capture of S during the charging-discharging process is crucial for achieving high-performance Na-S batteries.

Now, writing in *Proceedings of the National Academy of Sciences (PNAS)*, Jieshan Qiu and co-workers report a novel carbon-based host, where active sulfur

species were confined via chemical and spatial dual-confinement engineering. This strategy can effectively trap S species during the charging-discharging process for long-lifespan Na-S batteries.¹⁰ The N-doped carbon was made from coal tar pitch by pyrolysis at 600°C in a nitrogen gas (N₂) atmosphere with urea as a nitrogen (N) source and polystyrene microsphere as a template. The polycondensation of aromatic molecules was tuned via a coupling crosslinking method. The chemical structure of the pitch-derived carbon materials was regulated via *in-situ* doping of N atoms, which contributed to the chemical bonding sites for S active species. The S cathodes with tuned electronic structure help to promote the charge transfer between the carbon matrix and the active S species.

Specifically, an in-depth study of this strategy has been done to reveal the mechanism for extending the lifespan of Na-S batteries. As shown in Figure 1, during the carbonization process, S₈ molecules are gradually transformed to small S molecules (S₁ and S₂) that are spatially confined in the pores of carbon skeletons in forms of single-atomic sulfur or S₂ molecules, avoiding the formation of soluble polysulfides. The abundant as-built microporous structure not only provides physical adsorption for S but also accelerates the electrolyte penetration and facilitates the migration of Na⁺ ions and

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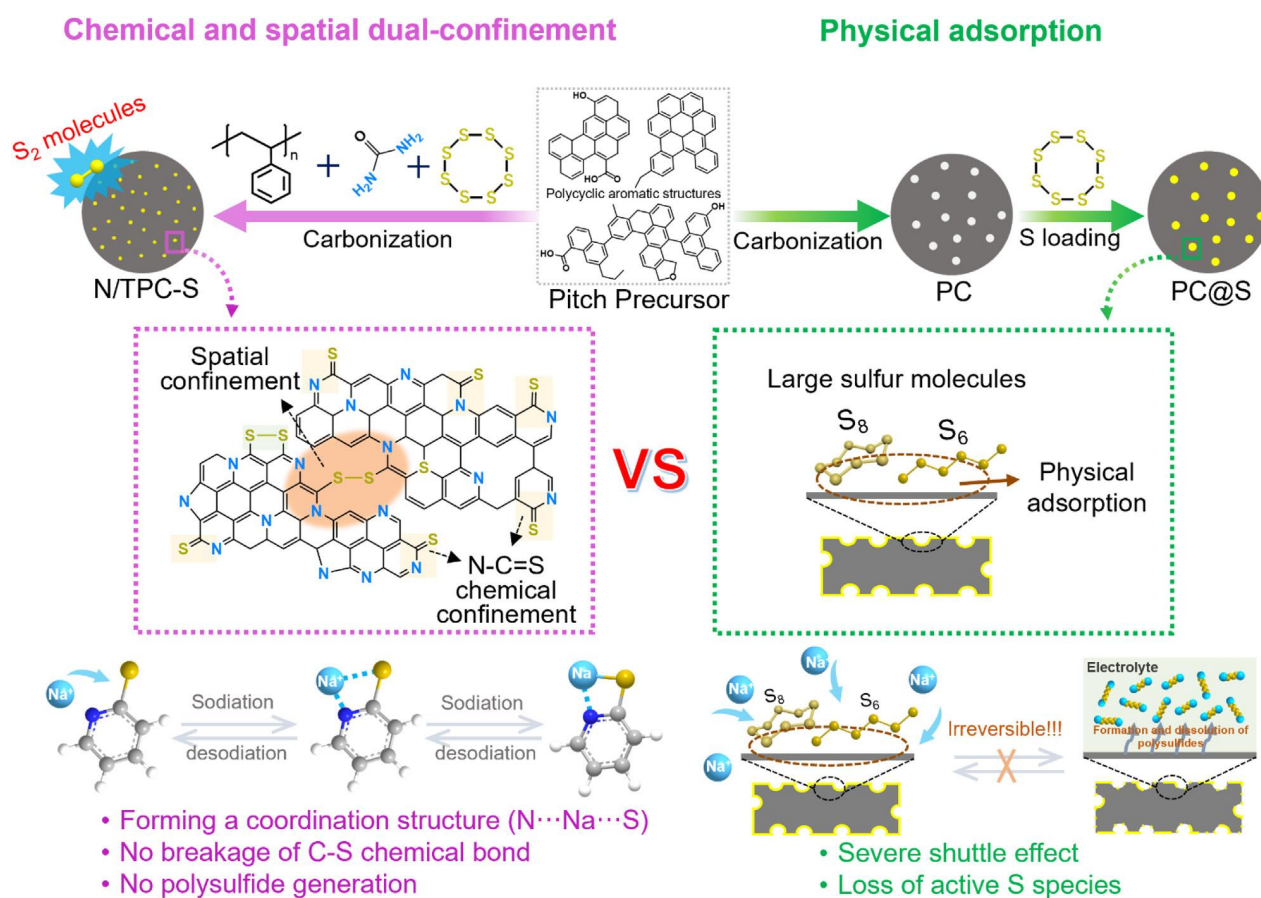


Figure 1. Design principles and synthetic processes of high-performance S cathodes

electrons. At the same time, the doped-N atoms in the carbon skeletons regulated the local electronic and chemical environments around carbon atoms to promote the formation of stable C-S and N-C=S bonds. The N-C=S bonds increased the adsorption capability of Na^+ and avoided the breakage of C-S bonds during insertion process of Na^+ by forming $N \cdots Na \cdots S$ coordination bonds in Na-S batteries. As a comparison, the pitch-derived carbon-loaded S (PC@S) synthesized by the conventional molten S-infusion method can only physically adsorb large S molecules (e.g., S_8 and S_6) at the surface and cannot avoid the loss of active S species during the charging/discharging process. The chemical and spatial dual-confinement strategy provides a new sight on fabricating ultra-stable and high-energy-density S cathodes and may shed a light on

the development of high-performance metal-S batteries.

Overall, Jieshan Qiu and co-workers presented a new strategy on the design and fabrication of a high-performance S host from a cheap aromatic precursor. The conversion mechanism between S and Na_2S was comprehensively explored. This work yielded new insights on the coal chemical industry and energy conversion and storage fields. The potential of coal-derived carbon materials via a concept of multi-dimensional carbon-material engineering has been demonstrated for large-scale fabrication of stable metal-S batteries. This strategy may be further extended to address the value-added utilization of other industrial byproducts such as petroleum pitch and the residual oil from direct coal liquefaction,

which were produced in a yearly scale of million tons. In this regard, the effect of morphology and chemical composition of the raw materials such as coal tar pitch needs to be further explored in terms of the controlled synthesis of multi-functional S-host materials. This remains a challenge, especially for the development of metal-S batteries and beyond.

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DECLARATION OF INTERESTS

The authors declare no competing interests.

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Breakthrough in scalable synthesis of metal telluride nanosheets

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Transition metal telluride (TMT) nanosheets are an important class of functional materials in condensed matter physics and energy-related fields. Recently in *Nature*, a novel solid lithiation and exfoliation strategy is reported for fast and scalable synthesis of various TMT nanosheets. This breakthrough will push the boundaries of TMT materials and beyond.

In the past two decades, the rise of graphene has promoted the rapid development of two-dimensional (2D) materials including metal chalcogenides. 2D transition metal telluride (TMT) nanosheets with atomic thickness, unique bandgaps, and physicochemical properties have great potential for use in superconductivity, energy storage and conversion, etc.¹ Nevertheless, the development of 2D TMT nanosheets is still far behind ex-

pectations simply because TMT nanosheets have only been prepared at a small scale and examined in model physical devices. As such, efficient and general synthesis methods of TMT nanosheets are highly required to further reveal unique properties of novel TMT nanosheets for various applications.

Top-down strategies are considered to be the most effective way to synthesize

atomically thin nanosheets since various high-quality bulk crystals can be prepared via a well-developed chemical vapor transport method. The key to a top-down strategy is making use of a strong external force to overcome the interlayer binding force between adjacent layers of TMT or weakening the binding force by intercalating guest ions/molecules to expand the interlayer spacing. Notably, the traditionally applied external forces (e.g., ultrasound, ball milling, and high shear force) greatly reduce the lateral size and/or quality of the nanosheets.² Additionally, the processes are

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