

## Review

# Catalytic Effects of Nanocage Heterostructures in Lithium-Sulfur Batteries

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## Abstract

With the increasing demand for high-energy-density energy storage systems in electric vehicles, smart grids, and portable electronic devices, the energy density of traditional lithium-ion batteries is approaching its theoretical limit. Lithium-sulfur (Li-S) batteries are regarded as strong candidates for next-generation high-performance energy storage systems due to their high theoretical energy density (2567 Wh kg<sup>-1</sup>), low cost, and environmental friendliness. However, the commercialization of Li-S batteries still faces key challenges such as the shuttle effect, sluggish reaction kinetics, volume expansion, and lithium anode corrosion. To address these issues, researchers have developed various functional materials and structural design strategies, among which heterostructures and nanocage host materials show significant advantages. This review systematically summarizes the basic principles, key problems, and solving strategies of lithium-sulfur (Li-S) batteries, focusing on the role of nanocage heterostructures in enhancing polysulfide adsorption, catalytic conversion, and structural stability, and outlines their future development path in high-energy-density Li-S batteries.

**Keywords:** lithium-sulfur batteries; nanocage structures; heterostructures; lithium polysulfides; electrocatalysis

## 1. Introduction

With the rapid development of modern industrial technology, fields such as electric vehicles, smart grids, artificial satellites, biomedical equipment, and power tools have put forward urgent demands for high-energy-density, high-power energy storage systems. Against the dual background of growing energy demand and prominent environmental issues, developing next-generation high-performance electronic devices and energy storage technologies has become a priority. Traditional lithium-ion battery systems, such as lithium iron phosphate and ternary lithium batteries, have achieved large-scale commercial application, but their theoretical energy density is gradually approaching the material limit. The practical energy density of ternary lithium batteries is generally maintained at 250–300 Wh kg<sup>-1</sup> [1–3], which makes it difficult to meet the requirement for energy density greater than 500 Wh kg<sup>-1</sup> in next-generation electric vehicles and portable electronic devices. Furthermore, issues such as performance degradation at extreme temperatures,



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charge/discharge rate limitations, and thermal runaway risks of lithium-ion batteries also restrict their further application in high-end fields [4,5].

In this context, Li-S batteries have attracted widespread attention due to their significant energy density advantage. The high energy density of Li-S batteries mainly stems from the extremely high theoretical specific capacity of its sulfur cathode ( $1675 \text{ mAh g}^{-1}$ ), far exceeding commercial cathode materials like lithium cobalt (Co) oxide ( $\sim 140 \text{ mAh g}^{-1}$ ) and lithium iron phosphate ( $\sim 170 \text{ mAh g}^{-1}$ ). Combined with the very high theoretical specific capacity ( $3860 \text{ mAh g}^{-1}$ ) and low electrochemical potential ( $-3.04 \text{ V}$ ) of the lithium metal anode, Li-S batteries can provide a theoretical energy density of about  $2567 \text{ Wh kg}^{-1}$  [6].

Because of the affect by factors such as electrolyte, conductive agents, and manufacturing process in battery commercialization, the practical energy density of Li-S batteries can reach  $400\text{--}600 \text{ Wh kg}^{-1}$ , significantly higher than existing commercial lithium-ion battery systems. Furthermore, sulfur, as an element abundant in the earth's crust, has advantages such as low cost, environmental friendliness, and non-toxicity, meeting the needs of sustainable development. The key to achieving high-performance Li-S batteries lies in the rational design and preparation of the sulfur cathode. Currently, most sulfur cathodes are prepared by the slurry casting method, and their performance is influenced by several key parameters, including the composition of the active material, the type and content of conductive agents and binders, sulfur loading, and the electrode's compaction density. Specifically, sulfur content and loading directly determine the battery's actual capacity; the reasonable selection of conductive agents is beneficial for electron transport, enhancing rate performance; the binder affects the structural integrity and cycling stability of the electrode; and the compaction density is closely related to electrolyte wettability, electrode structural stability, and sulfur utilization [7].

Although the Li-S batteries have significant theoretical advantages, several key issues still need to be resolved before being put into mass production. First, both  $\text{S}_8$  and the final discharge product  $\text{Li}_2\text{S}$  can be considered insoluble and non-conductive, which will lead to low conductivity of the electrode material, greatly affecting the electrochemical performance of the battery at high current densities. Second, the large volume changes during charging and discharging can lead to safety and mechanical stability issues. Due to the different densities of elemental S and the fully lithiated product  $\text{Li}_2\text{S}$ , the volume change of Li-S batteries can be as high as 75% when S is converted to  $\text{Li}_2\text{S}$ . This drastic volume change can cause mechanical damage to the electrode structure, accelerating battery performance degradation [8–10]. Finally, the notorious shuttle effect refers to the fact that lithium polysulfides (LiPSs) formed during charging and discharging are soluble in the electrolyte, so these intermediates shuttle between the cathode and anode and react with the electrode materials through chemical or electrochemical reactions. The accumulation of insoluble  $\text{Li}_2\text{S}/\text{Li}_2\text{S}_2$  on the cathode surface reduces the electrochemical reaction sites in the cathode, leading to capacity decay, causing lithium anode consumption and the formation of dead sulfur. Especially in the final stage of  $\text{Li}_2\text{S}_4$  conversion to  $\text{Li}_2\text{S}/\text{Li}_2\text{S}_2$ , there are significant kinetic barriers, manifested as increased overpotential and decreased energy conversion efficiency, ultimately leading to low Coulombic efficiency and stability [10–12].

The notorious shuttle effect triggers a series of chain problems: irreversible loss of cathode active material, deterioration of lithium anode surface morphology, formation of an unstable solid electrolyte interphase (SEI) film, and increased electrode interface resistance, manifested as accelerated battery capacity decay, decreased rate performance, reduced Coulombic efficiency, and shortened cycle life [10,11]. Moreover, the lithium metal anode continuously suffers from chemical corrosion by LiPSs. The side reactions between soluble LiPSs and metallic lithium not only cause irreversible capacity loss but also destroy the integrity of the SEI film, inducing aggravated growth of lithium dendrites [13–15]. During

cycling, the lithium anode surface gradually becomes loose and porous, and the increased specific surface area further accelerates side reactions, continuously consuming the limited lithium source and electrolyte [16]. When the electrolyte cannot effectively infiltrate all electrochemically active regions of the sulfur cathode, incomplete sulfur utilization occurs. This phenomenon of lithium anode failure triggered by LiPSs generated from the cathode is called “sulfur crosstalk”. It reveals that the performance degradation of Li-S batteries is a coupled process where the cathode and anode are interrelated and influence each other [17–19].

Researchers have developed various strategies to suppress the shuttle effect and enhance reaction kinetics. Among them, the introduction of functional separators and polar anchoring materials are two effective methods. Various materials such as graphene, porous carbon, transition metal oxides, phosphides, sulfides, and metal-organic frameworks (MOF) have been widely used to prepare functional separators [20]. These modified separators, by constructing a physical-chemical barrier between the cathode and the separator, can effectively block the migration of soluble LiPSs, thus inhibiting the shuttle effect to a certain extent. However, such separator modification strategies often focus on the static adsorption and interception of LiPSs, with limited effect on improving their conversion kinetics. The problem of low conversion rate of LiPSs has not been fundamentally solved, leading to low utilization of active material and rapid capacity decay. Therefore, developing new separator modification materials with both strong adsorption capacity and high catalytic activity, to achieve efficient capture and rapid conversion of LiPSs, appears crucial [21].

On the other hand, introducing polar anchoring materials such as transition metal oxides, sulfides, carbides, phosphides, and borides into the sulfur cathode is another mainstream strategy for constructing high-energy-density Li-S batteries [22]. These polar materials can immobilize LiPSs through strong chemical interactions, inhibiting their dissolution into the electrolyte. However, the root cause of the shuttle effect lies not only in the insufficient fixation on the cathode side but also in the dynamic migration of LiPSs in the electrolyte and their corrosion of the lithium anode. Therefore, although functional separators and polar anchoring materials alleviate the shuttle effect to some extent, they often struggle to simultaneously achieve efficient anchoring of LiPSs, rapid conversion, and effective protection of the lithium anode [23]. Especially under practical application conditions such as high sulfur loading and lean electrolyte, the limitations of the above strategies become more prominent. This urgently requires the development of a new material system that can comprehensively regulate polysulfide behavior and protect the lithium anode.

Using active catalysts to simultaneously achieve fixation and conversion of LiPSs still faces major challenges [24], as the efficacy primarily depends on several key factors, such as the binding affinity between the material and LiPSs, the number and dispersion of active sites, and the interfacial electron transfer rate [25]. In the pursuit of material systems with “adsorption-catalysis” synergistic effects, heterostructures materials have attracted extensive attention due to their flexible combination methods and excellent electrical properties. Heterostructures are usually composed of two or more different materials, generating synergistic effects at the interface through the unique physical and chemical properties of each component, achieving performance that single materials cannot reach. The heterojunction interface endows the material with excellent electronic conductivity, strong adsorption capacity for LiPSs, and efficient catalytic activity. In recent years, heterostructure design has been widely applied in key components such as sulfur hosts, functional interlayers, and modified separators, significantly improving the comprehensive performance of Li-S batteries [26].

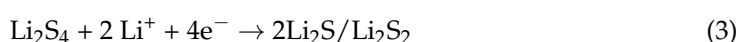
Traditional hollow structures (such as hollow spheres or hollow cubes) have obvious defects: their central cavity region cannot be effectively filled with sulfur, only the outer surface can participate in the adsorption and catalysis of LiPSs, leading to a large waste of space. At the practical application level, this structural limitation brings a series of problems: to achieve the same areal loading, hollow electrodes require greater thickness, leading to worsened electrical contact between the current collector and the active material, slow electron transport, and increased internal resistance of the battery [27]. If the electrode thickness is to be kept constant, the compression pressure during electrode preparation must be significantly increased for hollow materials. This may excessively reduce the gaps between host material particles, hindering electrolyte infiltration and ultimately leading to a sharp performance drop or even severe battery failure. Nanocage structures, a special type of hollow architecture form a porous surface morphology through secondary stacking, providing a large number of uniformly distributed active sites. Compared with traditional hollow sphere structures, the hollow space of nanocages is significantly reduced. This design retains the ability to resist electrode volume expansion while minimizing useless space, providing new ideas for electrode design of high-load Li-S batteries [28].

This article systematically analyzes the working principle and application prospects of nanocage heterostructures in Li-S batteries. Nanocage heterostructures, through their unique structural design and interface engineering, successfully achieve efficient management and conversion of LiPSs, providing new solutions for the practical application of Li-S batteries. Future research should further optimize the interface characteristics of heterojunctions, improve the utilization efficiency of active sites, and explore preparation methods more suitable for large-scale production, promoting the commercialization process of Li-S batteries technology. The literature reviewed in this work was collected from major scientific databases, including Web of Science and Google Scholar, which provide comprehensive coverage of peer-reviewed journals in materials science, electrochemistry, and energy storage. The search focused on publications from 2015 to 2025, with particular emphasis on studies reported in the past five years to reflect recent progress in Li-S batteries. Combinations of keywords such as “Li-S batteries”, “carbon nanocage”, “nanocage”, “heteroatom doping”, and “polysulfide adsorption” were used. Only peer-reviewed journal articles published in English were considered. Although this review does not aim to be a fully systematic review, the selected literature is representative and provides a comprehensive overview of recent theoretical and experimental advances in nanocage heterostructures for Li-S batteries. This study aims to provide a theoretical reference for the application of nanocage heterostructure materials in Li-S batteries and point out the direction for the further development of related materials.

## 2. Heterostructured Lithium-Sulfur Batteries

### 2.1. Principles of Lithium-Sulfur Batteries

Li-S batteries consist of a sulfur-containing cathode, a lithium metal anode, and a liquid or solid electrolyte and a separator. The working principle of Li-S batteries is that the sulfur cathode and lithium anode exchange ions through the electrolyte, undergoing reversible multi-step phase transitions and redox reactions while transferring electrons. The electrochemical involves complex multi-step phase transitions. As shown in Figure 1, the total reaction formula is  $S_8 + 16 Li \rightarrow 8 Li_2S$ . The specific stepwise discharge reaction formulas are [29]:



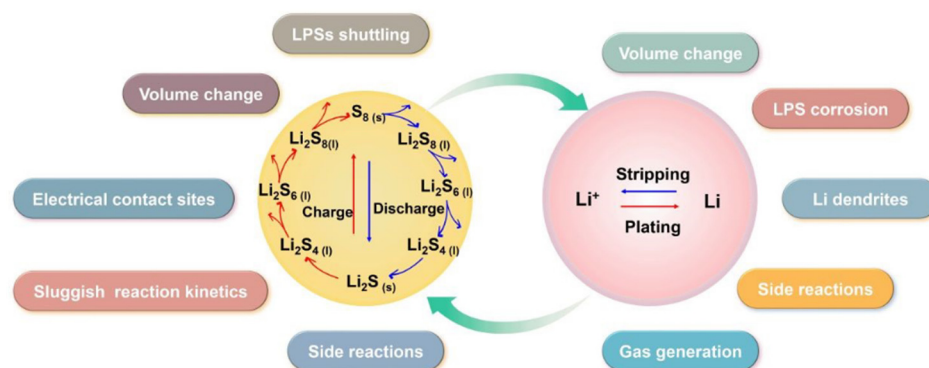


**Figure 1.** Operating principle of Li-S batteries [1].

The energy density of traditional lithium-ion batteries depends on the amount of  $\text{Li}^+$  that can be intercalated or inserted into the electrode, where the cathode material is usually lithium metal oxide (e.g.,  $\text{LiCoO}_2$  and  $\text{LiFePO}_4$ ). The ability of these oxides or phosphates to accommodate lithium is very limited, thus leading to low battery capacity. An important characteristic of Li-S batteries is the presence of the eight-atom molecule  $\text{S}_8$ , where each S atom in  $\text{S}_8$  can combine with two Li atoms. Therefore, the energy density of the sulfur cathode can be significantly increased [30]. During the discharge of Li-S batteries, metallic lithium at the anode undergoes an oxidation reaction, producing  $\text{Li}^+$  and electrons. The generated  $\text{Li}^+$  reach the cathode through the electrolyte, while electrons flow to the cathode through the external circuit, thus generating current; the sulfur cathode, after capturing electrons, reacts with  $\text{Li}^+$  to generate LiPSs.

The charging process is the reverse of the above reaction. Li-S batteries have two typical discharge plateau regions, one at about 2.3 V (high-voltage region) and one near 2.1 V (low-voltage region). These two plateaus are generated by the different states of sulfur during discharge. As shown in Figure 2, during the high-voltage plateau period, solid cyclic  $\text{S}_8$  opens and reacts with  $\text{Li}^+$ , gradually converting to soluble  $\text{Li}_2\text{S}_8$ , which is further reduced to  $\text{Li}_2\text{S}_6$  and  $\text{Li}_2\text{S}_4$ . This reaction process accounts for 25% of the theoretical total capacity, with a theoretical capacity of about  $418 \text{ mAh g}^{-1}$ . Meanwhile, under the low-voltage plateau, long-chain LiPSs are further reduced to insoluble  $\text{Li}_2\text{S}$  and  $\text{Li}_2\text{S}_2$ . This step provides  $1254 \text{ mAh g}^{-1}$  of theoretical capacity, accounting for 75% of the theoretical total capacity. The entire process involves complex phase changes from solid to liquid and back to solid [31]. As for the reversible charging process,  $\text{Li}_2\text{S}$  releases  $\text{Li}^+$  into the electrolyte and reconverts to LiPSs, then forming  $\text{S}_8$ . Different from the theoretical “stepwise” conversion mechanism of sulfur species, there is coexistence of  $\text{S}_8^{2-}$ ,  $\text{S}_6^{2-}$ ,  $\text{S}_4^{2-}$  dianions generated by electrochemical reduction and  $\text{S}_7^{2-}$ ,  $\text{S}_5^{2-}$ ,  $\text{S}_3^-$  anions generated by chemical reduction [10]. Although electrolyte access to the cathode region is necessary for proper diffusion of  $\text{Li}^+$ , the loss of LiPSs into the electrolyte is also a major problem [30].

## 2.2. Catalytic Effects of Heterostructures on Li-S Batteries

Since the stepwise reactions of Li-S batteries are complex multi-phase, multi-step reactions, catalysts are used to accelerate the overall reaction rate by promoting these stepwise reactions [32]. An ideal catalyst must exhibit moderate adsorption strength to ensure the facile desorption of products after the reaction is complete, thereby maintaining the catalytic cycle [33]. The performance of a catalyst is primarily determined by the number of active sites and structural stability. To increase the number of active sites, electrocatalytic materials are often designed with a high specific surface area. However, this can result in strong adsorption of  $\text{Li}_2\text{S}$ , leading to excessive accumulation of  $\text{Li}_2\text{S}$  during discharge and subsequently hindering the oxidation kinetics during charging. To address this, the

introduction of key structural features such as heterostructures can effectively enhance the bidirectional redox kinetics in Li-S batteries [34]. Compared with traditional homogeneous structures, heterostructures are composed of two or more materials with heterogeneous regions. Heterojunctions can combine the inherent properties of single functional materials that have high adsorption capacity or strong catalytic activity. Due to the unique physical/chemical properties of different materials, the interaction between heterogeneous regions can produce synergistic effects, thus exhibiting performance superior to that of single material. More importantly, the formation of heterojunctions will generate heterogeneous interfaces and induce new electronic structures and stress fields. This change may affect the substrate's anchoring ability for LiPSs, thereby improving adsorption/catalytic effects [35,36].

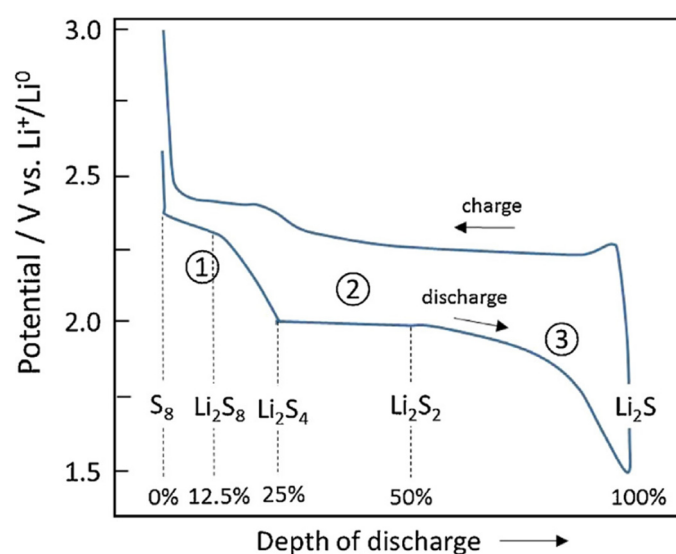


**Figure 2.** Discharge plateau of Li-S batteries [12].

Heterostructures enable the coupling of these heterogeneous regions to produce synergistic effects, giving the material high electronic conductivity and strong adsorption capability and catalytic activity toward LiPSs. Modulating the band structure of heterojunctions can accelerate the transport of both electrons and  $\text{Li}^+$  during the conversion of LiPSs [37]. The comprehensive performance of heterostructures exceeds that of simple materials mixtures, exhibiting advantages not possessed by homogeneous materials. Furthermore, the non-uniform distribution of internal charge in a heterojunction leads to the formation of a built-in electric field at the interface. This field not only promotes the transfer of charge carriers (e.g., electrons) but also enables strong anchoring of LiPSs, thereby facilitating their conversion into  $\text{Li}_2\text{S}/\text{Li}_2\text{S}_2$  on the interface [38]. The catalytic performance of heterostructures, together with the formation of Lewis acid/base induced by interfacial charge transfer, enhances the electrochemical performance of the material. Inspired by the high performance and strong catalytic performance of heterostructures, and the complex adsorption and catalytic steps involved in the Li-S batteries catalysis process, it is imperative to design an electrocatalyst with a geometric structure that contains an integrated adsorption-catalysis-desorption system, rather than focusing solely on one step [15,39]. For heterostructures, the problem becomes more complex due to the different crystal structures and chemical properties of the different components. Therefore, attention must be paid to the interface effects on the electrode when designing heterostructures. Interface effects can connect the electronic configurations of different catalysts, enhancing chemical adsorption and catalyst activity. The interface effect endows the heterojunction with unique physicochemical properties. The built-in electric field between the two phases

stabilizes the interface contact, promotes local charge polarization, accelerates  $\text{Li}^+$  diffusion and LiPSs conversion, and enhances the chemical adsorption of intermediate species [39]. Therefore, using heterogeneous catalysts can greatly improve the sulfur species utilization and redox kinetics of Li-S batteries [26]. An ideal heterostructure host for S encapsulation should meet the following characteristics: 1. Good electronic and ionic conductivity, providing unobstructed electron/ion pathways, allowing electrons/ $\text{Li}^+$  to easily access sulfur species; 2. Physical/chemical affinity with LiPSs, enabling favorable adsorption and desorption of LiPSs; 3. High catalytic activity to generate fast LiPSs conversion, such as  $\text{Li}_2\text{S}$  deposition and oxidation; 4. Large surface area for high S loading and  $\text{Li}_2\text{S}$  deposition; and 5. Light weight to achieve high energy density [40,41].

Heterostructures have become very promising choices in photocatalytic hydrogen evolution [42], but heterostructures applied in Li-S batteries are different from hydrogen evolution heterostructures and need to additionally meet the following requirements: the host material needs to have the ability to carry sulfur, adapt to the volume change in the active material during battery cycling, and effectively suppress the shuttle effect [43]. At the same time, heterostructures designed for Li-S batteries catalysis have complex structures, so controlling the contact and interaction between different materials is very important. In Li-S Batteries, sulfur exhibits high electrochemical activity and requires a certain amount of conductive additives or matrix materials to prevent sulfur loss. In addition, the matrix material also helps to improve the mechanical strength of the electrode and the overall electrochemical performance. However, achieving uniform dispersion of sulfur and matrix materials in heterostructures is challenging. Therefore, optimizing the structure and morphology of heterostructures is necessary to achieve the desired electrochemical performance [26]. When the components are in close contact, charge redistribution occurs, modulating the electronic structure, and inducing the formation of a built-in electric field at the interface between the two components. This interesting phenomenon increases the number of adsorption sites and significantly affects the electrochemical behavior of heterostructure electrodes [44,45]. Furthermore, heterojunctions between nanocrystals with different band structures can induce an built-in electric field at their heterointerfaces to promote electron/ion transport and improve surface reaction kinetics [46].

By adjusting the chemical composition of heterostructures, various functional needs in different scenarios can be met. For example, materials designed as heterostructures can act as effective hosts for sulfur in the cathode. These materials help to significantly increase the adsorption of LiPSs, alleviate volume expansion, and promote uniform  $\text{Li}_2\text{S}$  deposition. For separators, heterostructures can improve ion transport rates and improve the shuttle effect. Meanwhile, for the anode, they can act as lithiophilic conductive scaffolds, enhance the uniformity of lithium deposition, and homogenize the current density on the electrode surface. Although heterostructure materials have sufficient advantages, there are still some shortcomings that need further improvement, including high manufacturing cost, unstable material structure, complex mechanisms, deactivation of active sites, and challenges in controlling size and dimensions [47].

### 2.3. Heterostructures Combined with Various Structures

Heterostructures can be used in combination with other structures, such as MOF, which have attracted great interest from researchers due to their highly ordered structure, tunable pore size, and abundant porosity. It is worth noting that these unique characteristics of MOF are consistent with the goal of reducing shuttle effect: MOF have a balanced pore size distribution and considerable specific surface area, which act as an effective barrier, physically hindering the shuttle effect. Structural design flexibility is one of the most significant advantages of MOF materials compared to other porous materials [48]. At

the same time, metals embedded in MOF, such as Ni and Co, exhibit significant catalytic activity, have a strong ability to accept electron pairs, and therefore can act as Lewis acids interacting with soluble LiPSs. Furthermore, some unique functional groups present in MOF, such as  $\text{-SO}_3\text{H}$  and  $\text{-NH}_2$ , play a crucial role in restricting the migration of LiPSs through electrostatic interactions. Therefore, more and more researchers have provided convincing evidence demonstrating the excellent performance of MOF integrated into separators in Li-S batteries [49]. Zhang et al. synthesized a MOF-derived MoC/WC@NC heterojunction as a bidirectional catalyst for LiPSs in high-performance Li-S batteries. After 1000 cycles at 1 C, the Coulombic efficiency remained above 99%, the capacity was  $589.1 \text{ mAh g}^{-1}$ , and the decay rate per cycle was only 0.062% [25]. Similarly, Wang et al. designed a two-dimensional MXene-MOF ( $\text{Ti}_3\text{C}_2\text{T}_x\text{-UIO-66-NH}_2$ ) composite material as a separator for the battery. Its initial discharge capacity at 0.1 C was  $1752.1 \text{ mAh g}^{-1}$ . At a high rate of 2 C, the decay rate per cycle of this MXene-MOF-based cell over 1000 cycles was 0.023% [50].

Besides MOF, there are many other heterostructures. For example, Huang designed a nitrogen-doped carbon (NC) based sulfur host coated with a small amount of transition metal telluride (TMT) catalyst [51]. Xiao prepared Ni/Ni<sub>3</sub>N heterojunction-modified hollow carbon nanotube (Ni/Ni<sub>3</sub>N-CNT) composites and used them as sulfur hosts [39]. Xiong designed MnS-MoS<sub>2</sub> p-n heterostructures showing the unique structure of MoS<sub>2</sub> nanosheets decorated with abundant MnS nanodots, which helps forming a strong built-in electric field at the two-phase interface [52]. At the same time, Meng et al. developed MoSe<sub>2</sub>@MCHS composites as a new functional reservoir for LiPSs with high chemical affinity, in which ultrathin MoSe<sub>2</sub> nanosheets with active edge sites were successfully grown on the inner and outer surfaces of hollow carbon spheres (MCHS) with mesoporous walls [53]. These precedents all illustrate the high performance of heterostructures and their advantage of being compatible with many different structures.

### 3. Nanocage Heterostructure Lithium-Sulfur Batteries

Hollow structures expose an extremely high active sites and are very suitable as battery hosts. However, common hollow structures such as hollow spheres or hollow cubes have some inherent defects because there is an obvious hollow space in the center of the morphology that sulfur cannot enter; therefore, only the outer surface of the material can absorb or catalyze LiPSs. This leads to a large amount of volume being wasted in terms of volume. The areal loading of active material must be considered for the practical application of Li-S batteries [54]. For the same areal loading, the thickness of hollow electrodes is much higher than that of other host materials. As the electrode thickness increases, the problem of poor electrical contact between the current collector and the active material is amplified, resulting slow electron transport and increased internal resistance of the battery. If the electrode thickness is expected to be the same, the pressure in the electrode preparation of hollow materials needs to be greatly increased, which will reduce the gaps between host material particles, thereby making it more difficult for the electrolyte to enter the active material and leading to a sharp drop in battery performance or even severe loss of battery function. The hollow host material enhances conductivity to increase capacity, while its porous structure confines polysulfide migration and buffers volume expansion, thereby effectively suppressing the shuttle effect and thus extending battery lifespan [55]. While retaining the hollow structure, minimizing the hollow space as much as possible is beneficial for building practical high-performance Li-S batteries. Therefore, thin nanocage structures with very small hollow spaces stand out among many structures. The small hollow space ensures that the nanocage structure can resist the volume expansion of the electrode, while also minimizing inactive space, which provides a feasible idea for

the electrode design of high-load Li-S batteries [56]. The well-developed hollow nanocage structure functions as an efficient electrolyte reservoir, thus ensuring uniform dispersion and high utilization of active sulfur [57]. Since nanocages are the secondary assembly of small nanosheets forming a porous surface morphology, this also provides a large number of uniformly distributed active sites for the electrode material [28]. The following will provide a detailed introduction of some nanocages with excellent structure and properties.

### 3.1. Co-Based Nanocages

Co atoms offer significant advantages in Li-S battery materials, primarily in enhancing electrical conductivity, improving sulfur utilization, optimizing reaction kinetics, and enhancing structural stability. Co is an excellent conductive material that effectively improves the electrical conductivity of the battery, enhancing the material's electron transport, thus performing better during high-power output and long cycling times. At the same time, Co atoms can form strong interactions with sulfur compounds, helping to suppress sulfur dissolution and loss, improving sulfur utilization efficiency, and enhancing specific capacity and cycling stability. In addition, Co provides catalytic active sites that promote electrochemical reactions in Li-S batteries, especially in sulfur reduction and oxidation reactions, increasing reaction rates and reducing impedance during charge and discharge, thereby improving charging and discharging efficiency. The introduction of Co also enhances the structural stability of electrode materials, preventing degradation due to volume expansion or structural changes during prolonged cycling.

Wan designed a novel hollow nanocage composite material  $\text{CoS}_2/\text{NiS}_2$  ( $\text{CoS}_2\text{-NiS}_2$ ) with a heterojunction interface [58]. In this composite, the Co catalyst is uniformly dispersed within the graphene matrix, and its strong physicochemical adsorption effectively suppresses shuttle effect. Furthermore, Co synergistically promotes the stepwise conversion processes: from soluble long-chain LiPSs to short-chain LiPSs, reduction in short-chain LiPSs to  $\text{Li}_2\text{S}$ , and oxidation of  $\text{Li}_2\text{S}$  back to sulfur, thereby enhancing the reaction kinetics during battery charge and discharge processes [59]. First, energy dispersive X-ray spectroscopy (EDX) showed that the elements Ni, Co, and S were uniformly distributed, indicating that the active sites on the nanocage were widely distributed. Second, electrochemical tests based on symmetric batteries [Figure 3a] and cyclic voltammetry (CV) tests [Figure 3b,c] showed that the current intensity, redox peaks, and electrochemical polarization of  $\text{CoS}_2\text{-NiS}_2$  were better than those of  $\text{CoS}_2$  and  $\text{NiS}_2$  alone, with higher reduction potentials (C1, C2), lower oxidation potential (A), and lower degree of polarization, indicating that  $\text{CoS}_2\text{-NiS}_2$  can effectively improve the conversion efficiency of LiPSs. Higher and sharper oxidation/reduction current peaks indicate improved charge/discharge reaction kinetics. Then, comparing the Tafel plots of  $\text{CoS}_2\text{-NiS}_2$ ,  $\text{NiS}_2$ , and  $\text{CoS}_2$  [Figure 3d–f], the  $\text{CoS}_2\text{-NiS}_2$  electrode had the lowest oxidation and reduction slopes, indicating its strongest catalytic ability for the fast redox conversion between soluble LiPSs and  $\text{Li}_2\text{S}/\text{Li}_2\text{S}_2$  in Li-S batteries.  $\text{Li}_2\text{S}$  deposition experiments using  $\text{Li}_2\text{S}_8$  as the active material [Figure 3g–i] showed that  $\text{CoS}_2\text{-NiS}_2$  had the strongest deposition capacity and the shortest peak current response time at a constant voltage of 2.05 V. This indicates that  $\text{CoS}_2\text{-NiS}_2$  can accelerate the conversion of LiPSs and the deposition of  $\text{Li}_2\text{S}$ . The battery prepared with  $\text{CoS}_2/\text{NiS}_2$  achieved a high initial specific capacity of  $1037.4 \text{ mAh g}^{-1}$  and a low decay rate of 0.047% per cycle. Despite the impressive performance, the study acknowledged that the long-term cycling stability of  $\text{CoS}_2\text{-NiS}_2$  at high current densities could be further optimized. Future studies may focus on enhancing the material's structural integrity and improving its performance under extreme cycling conditions.

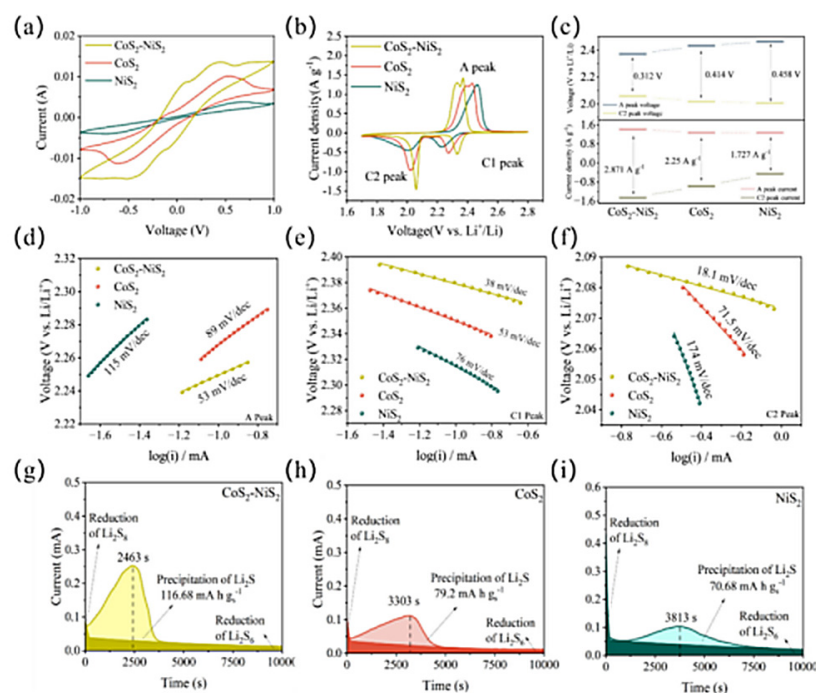


**Figure 3.** (a)  $\text{Li}_2\text{S}_6$  symmetric battery test diagram (b) Cyclic voltammetry (CV) test curves and corresponding (c) peak current density difference vs. voltage difference; (d–f) Tafel slopes for peaks A, C1, and C2; (g) Lithium sulfide deposition test for  $\text{CoS}_2\text{-NiS}_2$  (h)  $\text{CoS}_2$  (i)  $\text{NiS}_2$  [58].

As atoms belonging to the same group, oxygen and sulfur share many similarities, yet they also exhibit systematic differences. The study by Lu et al. explored the use of  $\text{CoO-Co}_4\text{N}$  hetero-nanocages as sulfur hosts for Li-S batteries [60]. The heterostructure was designed to combine the high polarity of  $\text{CoO}$  with the conductivity of  $\text{Co}_4\text{N}$  to enhance the redox kinetics and mitigate the polysulfide shuttle effect in Li-S batteries. The  $\text{CoO-Co}_4\text{N}$  nanocage-based sulfur host exhibited an initial discharge capacity of  $991 \text{ mAh g}^{-1}$  at  $0.5 \text{ C}$ , with a reversible capacity of  $662 \text{ mAh g}^{-1}$  after 350 cycles at  $1 \text{ C}$ . At higher current densities ( $2 \text{ C}$ ), the material provided  $737 \text{ mAh g}^{-1}$ , demonstrating excellent high-rate performance. Even with a high areal sulfur loading of  $3.0 \text{ mg/cm}^2$ , a capacity of  $713 \text{ mAh g}^{-1}$  was maintained after 100 cycles at  $0.2 \text{ C}$ . Lu demonstrated that  $\text{CoO-Co}_4\text{N}$  nanocages significantly enhanced polysulfide adsorption and redox kinetics in Li-S batteries. The heterostructure's combination of  $\text{CoO}$ 's strong adsorption properties and  $\text{Co}_4\text{N}$ 's high conductivity allowed for effective polysulfide trapping and conversion, leading to improved electrochemical performance, especially under high sulfur loading. Despite demonstrating excellent performance, the study also notes that there is room for improvement in the long-term cycling stability of  $\text{CoO-Co}_4\text{N}$  nanocages under high current densities. Enhancing the structural stability and electrical conductivity of this material under extreme cycling conditions remains necessary.

Regarding  $\text{CoO}$ , numerous studies exist. For example, Wu et al. focuses on the design and application of  $\text{CoO/NiO}$  heterostructure nanosheet assembled nanocages ( $\text{CoO/NiO@C-NC}$ ) as sulfur hosts for Li-S batteries [61]. The heterostructure was synthesized from  $\text{NiCo-Layered Double Hydroxides (LDH)}$  using  $\text{ZIF-67}$  as a template and used to modify separators in Li-S batteries to enhance the adsorption and redox kinetics of  $\text{LiPSs}$ . The Li-S batteries with  $\text{CoO/NiO@C-NC}$  modified separators demonstrated an initial discharge capacity of  $1176 \text{ mAh g}^{-1}$  at  $0.2 \text{ C}$ . After 500 cycles, the capacity retention was 78%. At higher current densities, the material exhibited  $738 \text{ mAh g}^{-1}$  at  $3 \text{ C}$  and a high areal capacity of  $5.8 \text{ mAh/cm}^2$  at a sulfur loading of  $5.87 \text{ mg/cm}^2$ . The  $\text{CoO/NiO@C-NC}$  composite enhanced the performance of Li-S batteries by improving the adsorption of  $\text{LiPSs}$ .

and facilitating their redox kinetics through both physical adsorption and electrocatalysis. CoO was found to accelerate the liquid–solid conversion, while NiO promoted the solid–liquid conversion, enhancing overall battery performance. Similar to CoO–Co<sub>4</sub>N, further optimization is required to improve the long-term cycling stability of CoO/NiO@C-NC at high current densities.

These three studies all explore the application of various types of nanocage heterostructure materials in Li-S batteries. Through the design of porous structures, heterogeneous interfaces, and the incorporation of multiple functional elements (e.g., CoS<sub>2</sub>, CoO, NiO, etc.), they effectively improve polysulfide adsorption, electrical conductivity, and reaction kinetics, thereby enhancing the cycling and rate performance of the batteries. However, despite their considerable potential, these materials still face challenges such as capacity fading at high current densities, poor long-term stability, and performance degradation under high sulfur loading. Future research needs to focus further on enhancing material stability, optimizing the structure of electrode materials, and addressing cycling degradation at high rates, in order to advance the practical application of these heterostructured materials in Li-S batteries.

In addition to the strategies demonstrated in the aforementioned studies, other studies have shown that doping carbon materials with heteroatoms or modifying carbon materials with metals is an effective method to enhance their polarity and catalytic activity. In addition, polar materials with hollow structures effectively confine LiPSs through physical and chemical fixation [62,63]. It is worth noting that composites composed of metals and carbon supports have been proven to perform excellently in the conversion process of LiPSs due to their high surface free energy and abundant adsorption/catalytic sites [64]. Compared with CoX, Co nanoparticles (NPs) exhibit strong adsorption and high catalytic activity, and their adsorption for LiPSs is much better than that of CoX (O, S, Se, P) [65]. Guo prepared Co/Co<sub>2</sub>P heterojunction nanoparticle-modified N, P, and S co-doped carbon nanocages (Co/Co<sub>2</sub>P-NPSC) for catalyzing LiPSs conversion [66,67]. Transition metal phosphides (TMPs), characterized by their strong polarity and abundant active sites, serve as ideal polysulfide inhibitors and catalytic mediators [68]. Studies have shown that constructing nanoparticles into heterojunction structures can effectively overcome the limitations of single-component materials and endow them with superior multifunctional properties [69]. The CV curves of the assembled symmetric battery [Figure 4] showed that the Co/Co<sub>2</sub>P-NPSC electrode had shorter deposition time and higher response current density than the Co-NPSC and Co<sub>2</sub>P-NPSC electrodes [70]. And the Co/Co<sub>2</sub>P-NPSC composite cathode exhibited an initial discharge capacity of 1291 mAh g<sup>−1</sup> at 0.1 C. After 500 cycles, it maintained a capacity of 465 mAh g<sup>−1</sup> with a decay rate of only 0.087% per cycle. The high rate performance at 1.0 C and low electrolyte-to-sulfur ratio (E/S) further underscores its superior performance, with a stable capacity of 880 mAh g<sup>−1</sup> at 0.1 C. Furthermore, as shown in Figure 5, Li<sub>2</sub>S in Co-NPSC and Co<sub>2</sub>P-NPSC presents a 2D deposition mode and a 3DP deposition mode, which will make Li<sub>2</sub>S tightly wrap the catalyst surface and lead to its passivation. Whereas in the Co/Co<sub>2</sub>P-NPSC host, it is a 3DI deposition mode. 3DP is dominated by surface-limited reactions, where precursors grow layer by layer on the external surface to form a dense and uniform coating, whereas 3DI relies on precursor diffusion into porous or low-density structures, enabling deposition within internal pores or frameworks and thereby enhancing the utilization of internal active sites. 3DI can improve the deposition efficiency of Li<sub>2</sub>S, avoiding surface passivation of the catalyst, and enhancing the host's adsorption and catalytic performance for LiPSs. Co/Co<sub>2</sub>P-NPSC material, with N, P, and S co-doping, significantly enhances the adsorption capacity and catalytic activity for LiPSs conversion. The Co/Co<sub>2</sub>P heterojunction facilitated rapid electron transfer and increased the catalytic efficiency for LiPSs, resulting in an

outstanding electrochemical performance. However, this material also has its drawbacks. Its outstanding performance cannot conceal the lack of long-term stability under high current densities and the complexity of its synthesis process.

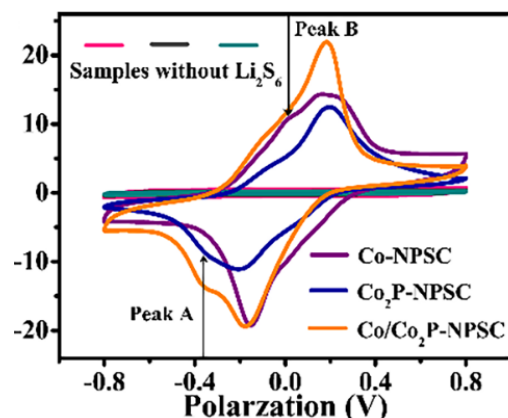


Figure 4. CV curves of three symmetric batteries [66].

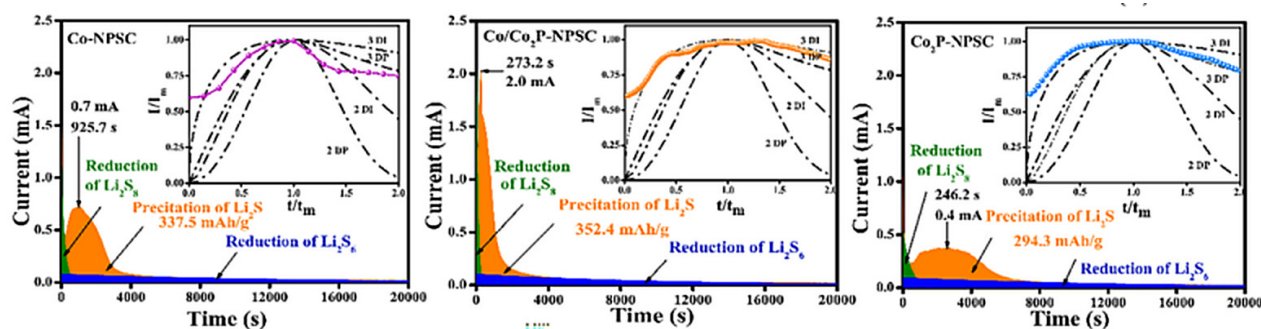


Figure 5.  $\text{Li}_2\text{S}$  nucleation curves and  $\text{Li}_2\text{S}$  electrodeposition models in three different hosts [66].

Lei et al. adopted the same heterojunction structure,  $\text{Co}/\text{Co}_2\text{P}$ , as used by Guo, and presents a novel approach to create  $\text{Co}/\text{Co}_2\text{P}$  heterojunctions embedded in nitrogen-doped hollow graphitized carbon nanocages ( $\text{Co-NHGC}$ ) using in situ polymerization [71]. The  $\text{Co-NHGC}$  composite exhibited an initial specific capacity of  $1600 \text{ mAh g}^{-1}$  at  $0.1 \text{ C}$  and maintained 94.4% capacity retention after 500 cycles at  $1 \text{ C}$ . The material also demonstrated outstanding high-rate performance, with a capacity of  $850 \text{ mAh g}^{-1}$  at  $3 \text{ C}$ , making it suitable for high-power applications in Li-S batteries. The study demonstrated that the  $\text{Co-NHGC}$  composite effectively captures polysulfides and enhances sulfur conversion through a synergistic effect of the  $\text{Co}/\text{Co}_2\text{P}$  heterojunction and nitrogen doping. The hollow structure and high surface area of the material contribute to improved sulfur loading and mitigated volume expansion during cycling, leading to high capacity and excellent stability over extended cycles. Although the  $\text{Co-NHGC}$  material exhibits impressive performance at lower current densities, the capacity decay at higher current densities still requires improvement. Future work should focus on enhancing the stability of the  $\text{Co}/\text{Co}_2\text{P}$  heterojunction, especially in high-rate and long-cycle conditions.

This chapter reviewed five studies on the application of heterojunction nanocages and doped materials in lithium-sulfur (Li-S) batteries as Table 1 shown. Through the design of different types of nanocage materials and the introduction of doping elements (such as Co, N, P, S, etc.), significant improvements were achieved in the polysulfide adsorption ability, electrocatalytic performance, and reaction kinetics of the batteries, leading to enhanced capacity, rate performance, and cycling stability. The materials in these studies demonstrated effective solutions to the common issues of polysulfide shuttle effect and

reaction kinetics, providing diverse strategies and design approaches for improving battery performance. However, despite the promising results under low current densities and low sulfur loadings, capacity fading, cycling stability, and long-term performance remain significant challenges under high current density and high sulfur loading conditions. To drive the commercialization of these materials, future research needs to focus on: (1) enhancing material stability under high current densities, (2) optimizing performance under high sulfur loadings, and (3) addressing capacity degradation in long-term cycling. The following table summarizes the key material properties, performance characteristics, and challenges of the five studies discussed in this chapter:

**Table 1.** Comparison of material characteristics and performance across studies [58,60,61,66,71].

| Article                | Material Type                                                                         | Key Performance Features                                                                                                  | High Rate Performance | Capacity Retention (Long Cycling)      | Challenges and Future Directions                           |
|------------------------|---------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------|-----------------------|----------------------------------------|------------------------------------------------------------|
| Wan et al. (2025) [58] | CoS <sub>2</sub> -NiS <sub>2</sub> Heterojunction Nanocage                            | High capacity, excellent polysulfide adsorption ability<br>Excellent electrocatalytic activity and polysulfide conversion | Good                  | Good (under high sulfur loading)       | Capacity fading at high rate, long-term stability          |
| Lu et al. (2021) [60]  | CoO-Co <sub>4</sub> N Heterojunction Nanocage                                         | Efficient LiPS adsorption and conversion, excellent catalytic activity                                                    | Excellent             | Good capacity retention (at high rate) | Stability at high rate, capacity degradation               |
| Wu et al. (2022) [61]  | CoO/NiO Heterostructure Nanocage                                                      | Enhanced polysulfide conversion and reaction kinetics, good cycling stability                                             | Fair                  | High cycling stability                 | Long-term stability, especially at high current densities  |
| Guo et al. (2025) [66] | Co/Co <sub>2</sub> P Heterojunction Embedded in N, P, and S Co-doped Carbon Nanocages | Enhanced LiPS adsorption and conversion, excellent rate performance                                                       | Good                  | High capacity retention                | Cycling stability at high current density, capacity fading |
| Lei et al. (2020) [71] | Hollow Graphitized Carbon Nanocages Embedded with Cobalt Nanoparticles                |                                                                                                                           | Good                  | Good long-term stability               | Stability at high current density, structural optimization |

3.2. Co-Doped Carbon Nanocage Heterojunctions

Carbon-based materials are widely employed in sulfur cathodes due to their high electrical conductivity, ability to accommodate volume expansion, abundant availability, and facile fabrication [72]. Carbon nanomaterials usually refer to carbon with at least one dimension (1D) at the nanoscale. Due to their different sizes, degrees of graphitization, surface chemistry, and porosity, they have different uses in Li-S batteries. One-dimensional CNT have also been used in Li-S batteries, with excellent conductivity (102–106 S cm<sup>−1</sup>), high aspect ratio (up to 1.3 × 10<sup>8</sup>), and good mechanical/chemical stability. In addition, carbon nanofibers (CNFs) are another type of 1D nanocarbon, with feasible large-scale production, tunable porosity with a surface area of 20–2500 m<sup>2</sup>g<sup>−1</sup>, and adaptable conductivity in the range of 10<sup>−7</sup>–10<sup>3</sup> S cm<sup>−1</sup>, making them ideal as sulfur containers, current

collectors, and interlayers for Li-S batteries. Two-dimensional (2D) graphene, due to its excellent physical and chemical properties, including high conductivity of  $106 \text{ S cm}^{-1}$ , large specific surface area of  $2600 \text{ m}^2 \text{ g}^{-1}$ , and excellent mechanical strength and flexibility, is widely used as a conductive agents and scaffold for sulfur particles in Li-S batteries [73–75]. For example, Zhao et al. presents Co and N co-doped graphene sheets (Co,N-co-doped graphene) as a sulfur host material for Li-S batteries [59]. The material was designed to enhance the adsorption of LiPSs (LiPSs) and accelerate the electrochemical reaction kinetics in Li-S batteries. The Co,N-co-doped graphene composite achieved an initial discharge capacity of  $1255.7 \text{ mAh g}^{-1}$  at  $0.2 \text{ C}$ , maintaining a capacity of  $803 \text{ mAh g}^{-1}$  after 100 cycles with a retention rate of 64%. The material also exhibited excellent high-rate performance with  $704.6 \text{ mAh g}^{-1}$  at  $2 \text{ C}$ . They find that the Co,N-co-doped graphene sheet significantly enhanced the electrochemical performance of Li-S batteries by improving the adsorption of LiPSs and catalyzing the conversion reactions. The Co and N doping synergistically enhanced the lithium-ion conductivity and promoted the reaction kinetics, leading to excellent cycle stability and high rate performance. However, the long-term stability and high-rate performance of this material are not yet.

Porous carbon materials are widely used as host materials for sulfur cathodes due to their unique structural characteristics. Such materials have rich pore structures and large pore volumes, providing ideal conditions for their use as sulfur carriers. The porous structure and electronic conductivity of carbon materials are key factors determining their efficiency in utilizing LiPSs. These characteristics not only enable effective hosting of high-content sulfur active material but also buffer the approximately 80% volume change between sulfur and lithium sulfide during cycling, thereby maintaining the structural integrity of the electrode [76,77]. When sulfur is embedded in the pores of porous carbon, these pore structures can act as physical barriers, confining the active material to the cathode region. At the same time, the porous structure has good electrolyte wettability, which helps ion transport. Research shows that the surface chemical properties of porous materials also play a key role in inhibiting polysulfide diffusion. Suitable pore size distribution and pore volume are of great significance for achieving high sulfur utilization and stable performance [78]. Although porous carbon materials have the above advantages, they still have obvious shortcomings as sulfur hosts. High specific surface area carbon materials such as graphene, CNT, and carbon fibers can effectively load sulfur. Carbon materials are non-polar, while LiPSs are polar. The two only combine with weak physical adsorption [46,79]. To overcome this limitation, researchers have developed various improvement strategies. Heteroatom doping (such as nitrogen doping) has been proven to be an effective method to enhance the conductivity of carbon materials and their binding ability with LiPSs. By introducing heteroatoms, the electronic structure of carbon materials can be changed, enhancing the chemical bonding between them and LiPSs [80].

For example, Li et al. designed cobalt nanoparticles embedded in phosphorus and nitrogen co-doped hollow carbon nanocages (Co@PNC) as an efficient sulfur host and catalyst for Li-S batteries [81]. A schematic illustration of the synthesis process is presented in Figure 6. This work focuses on heteroatom co-doping to regulate the electronic structure of the carbon framework and strengthen metal-support interactions, enabling synergistic enhancement of polysulfide adsorption and catalytic conversion. The Co@PNC material is derived from a ZIF-8 template followed by polydopamine coating and two-step thermal treatment, resulting in hollow carbon nanocages with well-preserved internal cavities. During carbonization, Co precursors are in situ reduced to metallic Co nanoparticles ( $\sim 11 \text{ nm}$ ) uniformly embedded in the P,N co-doped carbon matrix. Notably, P doping increases defect density and effectively modulates the electronic interaction between Co nanoparticles and the carbon support, generating more catalytically favorable electronic states. Benefiting

from the above synergistic regulation, the Co@PNC/S cathode delivers stable cycling over 1000 cycles at 2 C with an ultralow capacity decay of 0.033% per cycle, and maintains high capacity even at a high sulfur loading of  $4.46 \text{ mg cm}^{-2}$ . Nevertheless, the electrochemical performance is sensitive to the doping strategy and thermal treatment conditions, as both P content and Co particle size distribution may influence long-term structural stability. Moreover, further optimization is still required under more practical conditions such as higher areal sulfur loading and lean electrolyte. This study demonstrates that rational P,N co-doping can effectively regulate the electronic structure of carbon nanocages and strengthen metal-support interactions, enabling synergistic optimization of polysulfide adsorption and conversion kinetics even without constructing explicit heterojunctions.

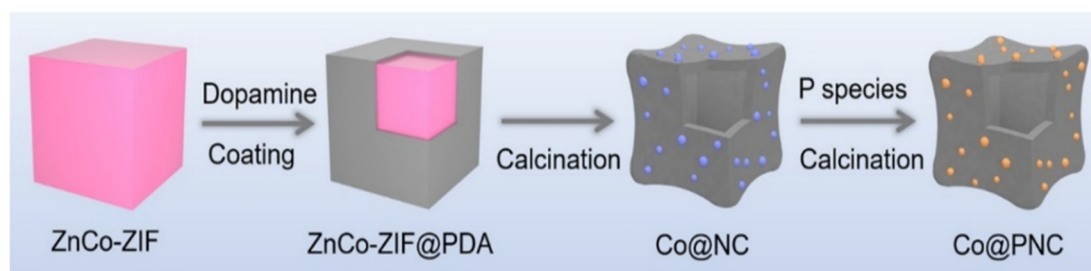


**Figure 6.** Schematic illustration of the formation process of Co@PNC [81].

In addition, introducing metal additives is another important strategy. Transition metal compounds (including oxides, phosphides, carbides, and chalcogenides) as polar catalytic additives show significant effects in sulfur cathodes. Among them, transition metal tellurides, although relatively less studied due to the low abundance and high cost of tellurium, have unique advantages. Taking  $\text{NiTe}_2$  as an example, its electrical conductivity is as high as  $1.15 \times 10^6 \text{ S m}^{-1}$ , much higher than its sulfide counterparts. At the same time, the metal ions (such as  $\text{Co}^{2+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Ni}^{2+}$ ) in TMTs form octahedral complexes with  $\text{Te}_2^{2-}$  in a low-spin state, and the metal 3d orbitals split into  $t_{2g}$  and  $e_g$  orbitals. This special electronic structure is conducive to promoting rapid charge transfer of the electrode and the conversion of LiPSs [51]. Guo et al. developed a FeCo alloy-modified, CNT-linked hollow carbon nanocage (FeCo-CHC) as an efficient sulfur host for Li-S batteries [82]. A schematic illustration of the synthesis process is presented in Figure 7. This work emphasizes the synergistic effect between alloy co-doping and carbon nanocage architecture. The hollow carbon nanocages provide physical confinement to suppress polysulfide diffusion, while the FeCo alloy modulates the surface electronic structure, enabling enhanced polysulfide adsorption and catalytic conversion. The material is derived from a Zn-based MOF precursor combined with melamine, yielding nitrogen-doped hollow carbon nanocages interconnected by CNT after pyrolysis. During carbonization, Fe and Co species are in situ reduced to form uniformly dispersed FeCo alloy nanoparticles embedded in the carbon matrix. By tuning the Fe/Co ratio, the authors demonstrate that excessive metallic Co or incomplete alloy formation deteriorates the nanocage structure, whereas FeCo-CHC-3, containing only FeCo alloy nanoparticles, achieves an optimal balance between structural integrity, conductivity, and active-site distribution. The performance enhancement of FeCo-CHC arises from the synergistic regulation enabled by alloy co-doping and hollow carbon nanocage architecture. On one hand, the Fe and Co alloy sites exhibit strong chemical affinity toward LiPSs through Fe-S and Co-S interactions, effectively anchoring soluble intermediates. On the other hand, alloying optimizes the surface electronic structure, reducing the energy barrier for the conversion of  $\text{Li}_2\text{S}_n$  to  $\text{Li}_2\text{S}/\text{Li}_2\text{S}_2$  and accelerating liquid-solid reaction kinetics. Meanwhile, the CNT-linked hollow carbon framework provides continuous pathways for electron and ion transport, allowing adsorption and catalytic conversion

to proceed in a coupled manner. Benefiting from these synergistic effects, the S@FeCo-CHC-3 cathode delivers stable cycling over 700 cycles at 1.0 C with a very low capacity decay rate. Nevertheless, the study also reveals that the electrochemical performance is highly sensitive to the Fe/Co ratio, and improper alloy composition may lead to metal aggregation or structural degradation. Moreover, further optimization is required to ensure long-term stability under higher sulfur loadings and more demanding operating conditions.

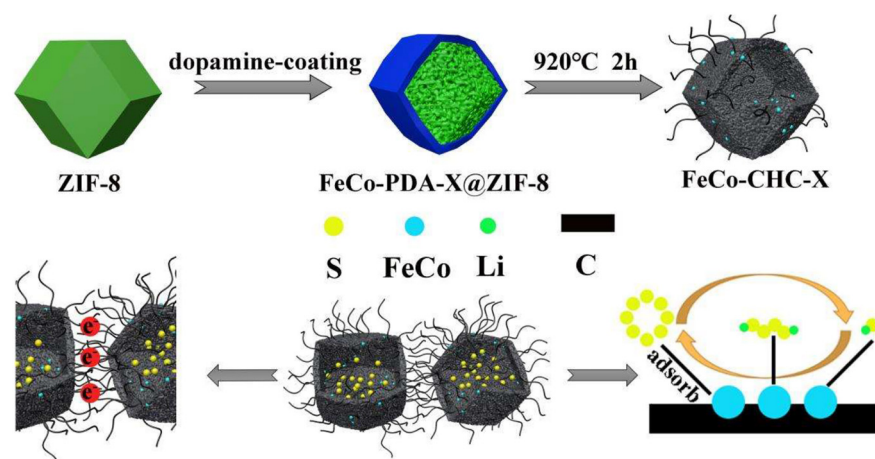


**Figure 7.** Schematic illustration of the formation process of FeCo-CHC-X hosts material [82].

Although the aforementioned studies demonstrate that co-doping strategies can effectively regulate the electronic structure and surface chemistry of carbon nanocages, thereby enhancing polysulfide adsorption and catalytic conversion when used as sulfur hosts, cathode-only modification is still insufficient to fully suppress polysulfide diffusion under high sulfur loading and long-term cycling conditions. This limitation has motivated researchers to reconsider the role of co-doped carbon nanocages from a cell-level perspective. Rather than serving solely as sulfur hosts, introducing co-doped carbon nanocages at the separator interface enables the construction of a functional interlayer, which provides an additional polysulfide regulation region without significantly increasing cathode complexity, thereby further strengthening the synergistic control of polysulfide migration and reaction kinetics.

Jin et al. proposed a strategy employing Co-N co-doped hollow carbon nanocages (Co-N-C) as a separator coating layer, rather than a conventional sulfur host design [83]. A schematic illustration of the synthesis process is presented in Figure 8. From a system-level perspective, this approach addresses the limitation of cathode-only modification under high sulfur loading conditions by introducing a functional interlayer as a secondary reaction interface. The coexistence of metallic Co active sites and N dopants enables synergistic regulation of polysulfide adsorption and catalytic conversion. The Co-N-C nanocages are derived from a ZIF-8@ZIF-67 dual-MOF precursor, which transforms into hollow carbon nanocages with pronounced internal cavities after high-temperature carbonization. The evaporation of Zn generates micro-/mesoporous interiors, while Co species are in situ reduced and uniformly distributed within the carbon shell. Meanwhile, highly graphitized CNT (CNTs) are epitaxially grown on the outer surface, forming a continuous conductive network. As a result, the Co-N-C structure integrates hollow confinement, abundant active sites, and rapid electron/ion transport pathways.

The regulation of polysulfide behavior by the Co-N-C coating layer arises from three synergistic effects: (1) N-doped carbon frameworks enhance surface polarity, enabling strong chemical adsorption of  $\text{Li}_2\text{S}_n$  via Lewis acid-base interactions; (2) metallic Co and Co- $\text{N}_x$  sites act as catalytic centers that accelerate the conversion between  $\text{Li}_2\text{S}_n$  and  $\text{Li}_2\text{S}/\text{Li}_2\text{S}_2$ ;

(3) the hollow nanocage architecture combined with an epitaxial CNT network establishes integrated pathways for electrons, ions, and reactants, allowing intercepted polysulfides to re-enter electrochemical reactions rather than being merely blocked. It should be noted that the system relies on high-temperature carbonization, and the long-term structural stability of Co nanoparticles warrants further investigation. Moreover, the adaptability of separator-coating strategies under lean electrolyte conditions and higher areal sulfur loadings remains to be systematically explored. This work highlights the dual functionality of Co-N co-doped hollow carbon nanocages in polysulfide interception and catalytic conversion from a separator-engineering perspective, offering valuable insights into the multifunctional application of co-doped carbon nanocages in Li-S batteries.



**Figure 8.** Schematic illustration of the formation process of Co-N-C nanocages [83].

In the aforementioned work, introducing Co-N co-doped hollow carbon nanocages as a functional separator coating has been demonstrated to effectively suppress shuttle effect while promoting reaction kinetics through combined physical blocking and catalytic effects. However, such systems mainly rely on polar sites induced by single heteroatom doping, leaving room for further optimization in balancing polysulfide adsorption strength and subsequent phase-transition kinetics. In this context, multi-heteroatom co-doping strategies have emerged as a promising approach to finely regulate the local electronic structure of carbon nanocages, thereby simultaneously enhancing chemical anchoring of polysulfides and catalyzing critical phase-transition processes.

Zheng et al. designed a Co-CoSe<sub>2</sub> nanoparticle-embedded N, Se dual-doped hollow carbon nanocage (Co-CoSe<sub>2</sub>@NSeC) and employed it as a functional separator coating to address the sluggish Li<sub>2</sub>S<sub>2</sub>-Li<sub>2</sub>S solid-solid conversion in Li-S batteries [84]. A schematic illustration of the synthesis process is presented in Figure 9. In this system, the hollow and porous carbon nanocage framework provides continuous pathways for electron and ion transport, while N and Se co-doping modulates the local electronic structure of the carbon skeleton, generating abundant polar active sites for enhanced chemical adsorption of polysulfides. Meanwhile, the embedded Co-CoSe<sub>2</sub> component offers high conductivity and catalytic interfaces, effectively lowering the energy barrier for the Li<sub>2</sub>S<sub>2</sub>-to-Li<sub>2</sub>S conversion. Both experimental and theoretical results demonstrate that the N, Se dual-doped carbon nanocages exhibit superior catalytic kinetics during both liquid-solid and solid-solid phase transitions compared with singly doped carbon materials, enabling stable electrochemical performance under high rate, long cycling, and high sulfur loading conditions. This work highlights the advantages of multi-heteroatom co-doping strategies in finely regulating polysulfide conversion pathways via carbon nanocage architectures.

This chapter systematically reviews recent advances in co-doped carbon nanocages for Li-S batteries as Table 2 shown, with an emphasis on how different co-doping strategies synergistically regulate the electronic structure and surface chemistry of carbon nanocages to improve polysulfide adsorption, conversion, and transport. Compared with singly doped or pristine carbon hosts, co-doping enables the introduction of multiple types of active sites into the carbon framework, allowing multiscale regulation of polysulfide behavior. Specifically, metal-metal or metal-nonmetal co-doping (e.g., FeCo or Co-N) effectively tunes the

electronic structure of metallic active centers, thereby accelerating polysulfide conversion kinetics, while nonmetal-nonmetal co-doping (e.g., N/P or N/Se) mainly enhances surface polarity and defect density of carbon nanocages, leading to stronger chemical anchoring of polysulfides. Meanwhile, the hollow architecture of carbon nanocages and their integration with conductive networks such as CNT provide efficient pathways for electron and ion transport, enabling effective coupling between adsorption and catalysis. Notably, co-doped carbon nanocages can function not only as sulfur hosts but also as functional interlayers at the separator interface, creating additional polysulfide-regulation regions within the cell. This extension from material design to cell-level architecture significantly broadens the application scope of co-doped carbon nanocages. Despite the encouraging progress, challenges remain, including sensitivity to dopant concentration, stability of active sites, and adaptability under practical conditions such as high sulfur loading and lean electrolyte. Future studies should focus on precise control of doping configurations, quantitative correlation between structure and phase-transition kinetics, and long-term stability evaluation under realistic operating conditions, to further advance the practical implementation of co-doped carbon nanocages in Li-S batteries.

**Table 2.** Summary of co-doped carbon nanocages for Li-S batteries [81–84].

| Material System            | Co-Doping Type                                                                                       | Structural Features of Carbon Nanocages             | Application Position    | Main Regulation Mechanism                                                                                                             | Representative Advantages                                  |
|----------------------------|------------------------------------------------------------------------------------------------------|-----------------------------------------------------|-------------------------|---------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------|
| FeCo-CHC                   | Fe-Co (metal-metal)                                                                                  | Hollow carbon nanocages interconnected by CNTs      | Sulfur host (cathode)   | Alloy-induced electronic structure modulation, synergistic polysulfide adsorption and catalysis                                       | Enhanced reaction kinetics and long-term cycling stability |
| Co@PNC                     | P-N (nonmetal-nonmetal) with Co nanoparticles   Hollow carbon nanocages                              | Hollow carbon nanocages                             | Sulfur host (cathode)   | Increased surface polarity and strengthened metal-support interaction, accelerated $\text{Li}_2\text{S}$ nucleation and decomposition | Improved sulfur utilization and phase-transition kinetics  |
| Co-N-C                     | Co-N (metal-nonmetal)                                                                                | Hollow carbon nanocages with epitaxially grown CNTs | Separator coating layer | Polysulfide interception and catalytic reconversion at the interlayer                                                                 | Stable cycling under high sulfur loading                   |
| Co-CoSe <sub>2</sub> @NSeC | N-Se (nonmetal-nonmetal) with Co/CoSe <sub>2</sub> Embedded in N, P, and S Co-doped Carbon Nanocages | Hollow and porous carbon nanocages                  | Separator coating layer | Catalysis of solid-solid phase transition and fine regulation of polysulfide conversion pathways                                      | Enhanced rate capability and prolonged cycling life        |

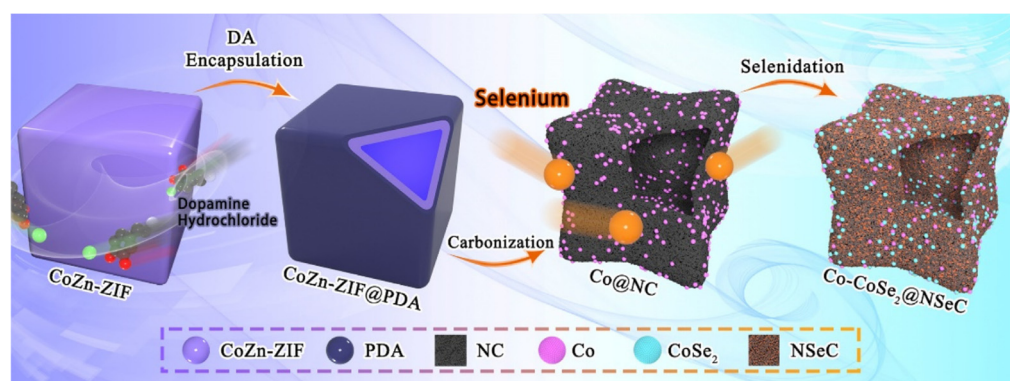


**Figure 9.** Schematic illustration of the formation process of Co@NC and the Co-CoSe<sub>2</sub>@NSeC [84].

### 3.3. Double-Shelled Nanocage

Despite the significant progress achieved through heterostructure engineering and co-doping strategies in enhancing polysulfide adsorption and conversion kinetics, single-shelled nanocage architectures still suffer from intrinsic limitations arising from multifunctional coupling during practical electrochemical operation. In Li-S batteries, sulfur cathode materials are required to simultaneously provide strong polysulfide anchoring, fast electron/ion transport, sufficient structural stability, and effective accommodation of volume changes. Integrating all these functions within a single shell often leads to mutual trade-offs among different performance requirements. Against this background, double- and multi-shelled hollow nanocage architectures have emerged as a promising structural design strategy. By introducing multiple functional layers along the radial direction, these architectures enable spatial separation and synergistic regulation of distinct functionalities. Typically, the inner shell is responsible for chemical adsorption and/or catalytic conversion of polysulfides, while the outer shell mainly serves as a conductive framework, a physical barrier to polysulfide diffusion, and a stabilizing layer for structural integrity. Such hierarchical designs effectively alleviate the difficulty of balancing adsorption, catalysis, and transport within single-shelled structures without excessively increasing material complexity. In a broader sense, double-shelled nanocages can be regarded as hierarchical heterostructures, where distinct functional shells form radial heterointerfaces enabling synergistic regulation of adsorption, catalysis, and mass transport.

Moreover, compared with single-shelled nanostructures, double- and multi-shelled nanocages exhibit superior structural robustness during repeated electrochemical cycling. The inter-shell voids provide sufficient buffer space to accommodate the volume expansion of sulfur species and extend the diffusion pathways of polysulfides, thereby further suppressing the shuttle effect. In recent years, the incorporation of functional components such as metal oxides, sulfides, and carbon layers into double-shelled architectures has gradually established a structure-engineering-centered design paradigm for advanced Li-S battery materials. Based on these considerations, this chapter focuses on the design principles and functional mechanisms of double- and multi-shelled nanocage architectures. By systematically reviewing representative studies, the division of labor and synergistic effects between different shells in regulating polysulfide adsorption, catalytic conversion, and mass transport are discussed, highlighting the unique advantages and remaining challenges of double-shelled nanocages in Li-S batteries.

Cao et al. reported an early exploration of double-shelled hollow architectures using SnO<sub>2</sub>@C nanocages, highlighting the role of shell-level functional division in Li-S batteries [85]. A schematic illustration of the synthesis process is presented in Figure 10. The structure consists of an inner SnO<sub>2</sub> shell and an outer carbon shell, forming a representative radially layered hierarchical heterostructure. The polar SnO<sub>2</sub> inner shell exhibits strong

chemical affinity toward LiPSs, while the outer carbon shell mainly serves as a conductive framework and a physical barrier to suppress polysulfide diffusion. The functional disparity between the inner and outer shells endows the structure with early characteristics of a “functional heterojunction”. Although no pronounced charge redistribution or built-in electric field was reported at the  $\text{SnO}_2/\text{C}$  interface, this work clearly demonstrates that introducing radially separated functional layers can effectively mitigate the trade-off between adsorption and conductivity in single-shelled architectures, providing a foundational structural concept for subsequent double-shelled heterostructures.

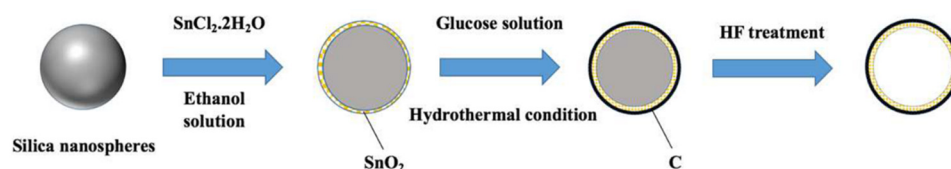


**Figure 10.** Schematic illustration of the formation process of hollow  $\text{SnO}_2@\text{C}$  nanospheres [85].

Building upon early double-shelled architectures, Hu et al. further incorporated compositional heterojunctions into a double-shelled nanocage system by constructing a hollow structure composed of an inner NiO shell, a  $\text{NiCo}_2\text{O}_4$  intermediate shell, and an outer carbon layer [86]. A schematic illustration of the synthesis process is presented in Figure 11. This architecture simultaneously realizes clear radial functional separation and a well-defined oxide heterojunction interface between NiO and  $\text{NiCo}_2\text{O}_4$ , representing a typical example of nanocages integrating both structural and compositional heterojunctions. From a functional perspective, the polar NiO inner shell provides strong polysulfide anchoring capability, while the spinel  $\text{NiCo}_2\text{O}_4$  shell offers improved electrical conductivity and catalytic activity toward polysulfide conversion. The outer carbon shell further facilitates electron transport and enhances structural robustness. More importantly, the NiO/ $\text{NiCo}_2\text{O}_4$  heterointerface contributes to interfacial charge redistribution, which promotes directional migration and accelerated conversion of polysulfides across the shell layers. This work demonstrates that double-shelled nanocages are not merely physical compartmentalization units but can also serve as effective platforms for hosting compositional heterojunctions. By introducing heterointerfaces between distinct shell layers, synergistic regulation of polysulfide adsorption, conversion, and transport can be achieved at the nanoscale, leading to enhanced reaction kinetics in Li-S batteries.

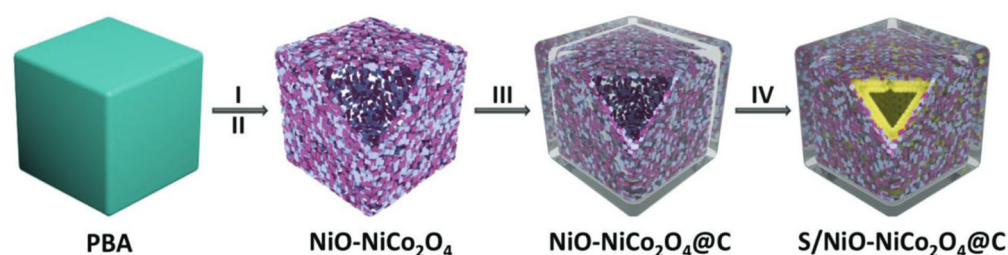


**Figure 11.** Schematic illustration of the formation process of the synthesis [86].

Beyond sulfur cathode chemistry, Deivendran et al. extended the design concept of double-shelled heterostructures to  $\text{Li}_2\text{S}$  cathodes by constructing a hierarchical hollow architecture composed of an N-doped  $\text{Co}_3\text{O}_4$  inner shell and an outer rGONR/CNT conductive network [87]. A schematic illustration of the synthesis process is presented in Figure 12. This system forms a representative radial structural heterointerface, where the inner shell is responsible for  $\text{Li}_2\text{S}$  activation and catalytic conversion, while the outer shell provides continuous and efficient electron transport pathways. In  $\text{Li}_2\text{S}$ -based systems,

sluggish solid-solid phase-transition kinetics are widely recognized as a major performance-limiting factor. The N-doped  $\text{Co}_3\text{O}_4$  inner shell introduces abundant defects and polar sites, effectively lowering the oxidation energy barrier of  $\text{Li}_2\text{S}$ . Meanwhile, the three-dimensional conductive network formed by rGONR/CNT significantly enhances electron transport, ensuring full utilization of the catalytic interfaces. Notably, the double-shelled architecture not only decouples catalytic and transport functions but also accommodates volume variations through inter-shell voids, thereby preserving structural integrity. This work demonstrates that double-shelled nanoporous heterostructures are not confined to sulfur cathodes and can also play a critical role in regulating  $\text{Li}_2\text{S}$  activation and phase-transition kinetics, further broadening their applicability in Li-S batteries.

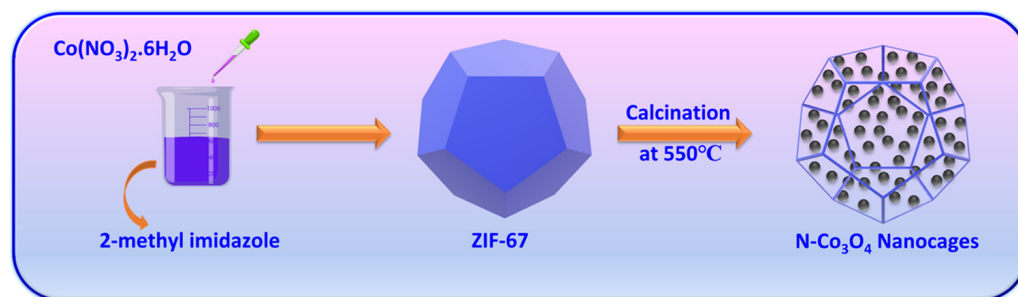


**Figure 12.** Schematic illustration of the formation process of an N- $\text{Co}_3\text{O}_4$  Nanocage Powder via ZIF-67 [87].

In a more advanced evolution of double-shelled nanocages, Zhou et al. constructed  $\text{ZnS}@\text{CoS}_2$  double-shelled hollow nanocages, in which compositional heterojunctions are tightly coupled with radial structural heterointerfaces to achieve more efficient polysulfide regulation [88]. A schematic illustration of the synthesis process is presented in Figure 13. In this system, a well-defined sulfide heterojunction is formed between the inner ZnS shell and the outer  $\text{CoS}_2$  shell, and the confinement of the double-shelled architecture induces a pronounced built-in electric field across the heterointerface. From a functional perspective, the ZnS inner shell exhibits strong chemical affinity toward polysulfides, whereas the  $\text{CoS}_2$  outer shell provides high electrical conductivity and catalytic activity. More importantly, the built-in electric field at the ZnS/ $\text{CoS}_2$  interface drives directional migration of electrons and ionic species across the shell layers, thereby accelerating stepwise polysulfide conversion and suppressing their random diffusion into the electrolyte. The porous double-shelled structure further extends polysulfide diffusion pathways, enabling synergistic coupling between electric-field regulation and spatial confinement. This work represents an advanced form of double-shelled nanoporous heterojunctions, marking a transition from simple functional layering to interface-driven reaction pathway regulation, and highlights the potential of rational shell engineering for precise control of polysulfide chemistry at the nanoscale.

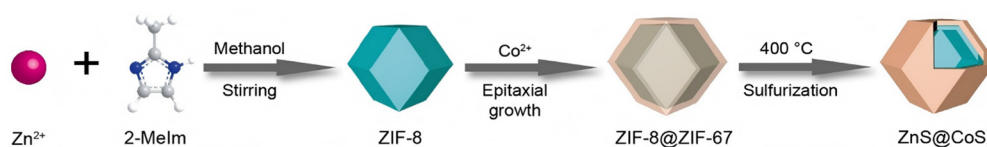


**Figure 13.** Schematic illustration of the formation process of  $\text{ZnS}@\text{CoS}_2$  nanocages [88].

This chapter systematically reviews recent advances in double- and multi-shelled nanocage heterojunctions for Li-S batteries [Table 3], with a particular focus on how radially arranged shell architectures enable spatial separation and interfacial synergy among different functional components within nanocages. Compared with single-shelled nanocages,

double-shelled nanocage heterojunctions provide a more rational structural platform to simultaneously realize polysulfide adsorption, catalytic conversion, and efficient charge transport. From an evolutionary perspective, early  $\text{SnO}_2@\text{C}$  double-shelled nanocages primarily relied on the functional contrast between polar inner shells and conductive outer shells to suppress polysulfide diffusion. Subsequently, systems such as  $\text{NiO-NiCo}_2\text{O}_4$  introduced compositional heterojunction interfaces into double-shelled nanocage frameworks, enabling synergistic interfacial charge regulation and significantly enhanced polysulfide conversion kinetics. Building upon these developments, nanocage heterojunctions were further extended to  $\text{Li}_2\text{S}$  cathode chemistry, where solid-solid phase-transition processes could be effectively regulated. More recent studies have demonstrated that constructing built-in electric fields within sulfide-based double-shelled nanocages allows directional regulation of polysulfide reaction pathways, representing an advanced stage in the evolution of nanocage heterojunctions from simple functional separation to interface-driven reaction control. Overall, double- and multi-shelled nanocage heterojunctions offer a structure-engineering-centered strategy for advanced Li-S batteries. Nevertheless, challenges remain, including synthetic complexity, precise control over shell thickness and mass distribution, and long-term stability under practical conditions such as high sulfur loading and lean electrolyte. Future efforts should focus on quantitative tuning of interfacial properties, structural robustness of nanocages, and their applicability under realistic operating conditions.

**Table 3.** Double-/multi-shelled nanoporous heterojunction nanocages for Li-S batteries [85–88].

| Nanocage Heterojunction System             | Heterojunction Nature                                                           | Nanocage Shell Architecture                                                              | Functional Role of Each Shell                                                                                        | Interfacial Regulation Mechanism                                          | Key Structural Merit                                                      |
|--------------------------------------------|---------------------------------------------------------------------------------|------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------|---------------------------------------------------------------------------|
| $\text{SnO}_2@\text{C}$                    | Structural nanocage heterojunction                                              | Inner $\text{SnO}_2$ shell/outer carbon shell                                            | shell $\text{SnO}_2$ : polysulfide adsorption; carbon: conductivity and diffusion barrier                            | Radial functional separation within nanocage                              | Proof-of-concept for function decoupling in nanocages                     |
| $\text{NiO-NiCo}_2\text{O}_4@\text{C}$     | Structural + compositional nanocage heterojunction                              | Inner $\text{NiO}$ shell/intermediate $\text{NiCo}_2\text{O}_4$ shell/outer carbon layer | $\text{NiO}$ : chemical anchoring; $\text{NiCo}_2\text{O}_4$ : catalytic conversion; carbon: transport and stability | Charge redistribution across oxide heterointerface inside nanocage        | Synergistic coupling of nanocage architecture and chemical heterojunction |
| $\text{N-Co}_3\text{O}_4/\text{rGONR-CNT}$ | Structural nanocage heterojunction                                              | Inner $\text{N-Co}_3\text{O}_4$ shell/outer conductive network                           | Inner shell: $\text{Li}_2\text{S}$ activation; outer network: fast electron transport                                | Radial separation of catalytic and transport functions                    | Extension of nanocage heterojunctions to $\text{Li}_2\text{S}$ chemistry  |
| $\text{ZnS@CoS}_2$                         | Structural + compositional nanocage heterojunction with built-in electric field | Inner $\text{ZnS}$ shell/outer $\text{CoS}_2$ shell                                      | $\text{ZnS}$ : strong polysulfide affinity; $\text{CoS}_2$ : conductivity and catalysis                              | Built-in electric field driving directional charge/intermediate migration | Advanced reaction-pathway regulation within nanocages                     |

#### 4. Conclusions

Lithium-sulfur (Li-S) batteries are widely regarded as one of the most promising next-generation energy storage systems owing to their ultrahigh theoretical energy density,

cost-effective sulfur cathodes, and environmental friendliness. However, their practical implementation is still fundamentally constrained by a series of interrelated challenges, including the notorious shuttle effect, sluggish sulfur redox kinetics, severe volume expansion during cycling, and instability of the lithium metal anode. To address these issues, this review systematically summarizes recent advances in nanocage heterostructures for Li-S batteries, with a particular focus on how structural confinement and heterojunction interface engineering synergistically regulate polysulfide adsorption, conversion, and transport. Compared with conventional hollow structures, nanocage architectures effectively minimize inactive internal voids while preserving sufficient space to buffer volume expansion, thereby offering a more practical structural framework for high-loading sulfur cathodes. More importantly, the introduction of heterojunctions within nanocage architectures enables a transition from passive polysulfide interception to active interfacial regulation. Heterojunction interfaces induce charge redistribution and built-in electric fields, which not only enhance the chemical affinity toward LiPSs but also significantly accelerate their stepwise conversion kinetics. Representative systems discussed in this review—including metal sulfide, oxide, phosphide, and alloy-based nanocage heterostructures—demonstrate that rationally designed interfaces can simultaneously improve sulfur utilization, rate capability, and long-term cycling stability.

In addition, this review highlights the functional diversification of nanocage heterostructures at the device level. Beyond serving as sulfur hosts, nanocage-based heterostructures have been successfully employed as functional interlayers or separator coatings, creating additional polysulfide regulation regions within the cell. Such system-level design strategies further strengthen the suppression of polysulfide migration while maintaining efficient redox kinetics, especially under high sulfur loading conditions. Despite the encouraging progress, several challenges remain before nanocage heterostructures can be practically implemented. These include the complexity and scalability of current synthesis routes, the long-term stability of heterojunction interfaces under harsh cycling conditions, and the lack of systematic evaluation under realistic operating parameters such as high areal sulfur loading and lean electrolyte. Addressing these challenges will be critical for bridging the gap between laboratory demonstrations and practical Li-S battery applications. Overall, nanocage heterostructures represent a highly effective material design paradigm that integrates structural engineering with interfacial chemistry. Continued efforts in rational interface design, scalable synthesis, and full-cell-level optimization are expected to further advance the development of high-energy-density and long-lifespan Li-S batteries.

## 5. Outlook and Perspectives

Although nanocage heterostructures have demonstrated significant potential in regulating polysulfide chemistry, several key issues should be carefully addressed in future studies. First, scalable and controllable synthesis remains a major challenge. Most reported nanocage heterostructures rely on multistep templating, high-temperature pyrolysis, or complex post-treatment processes, which may limit large-scale production. Developing simplified, low-cost, and reproducible synthesis strategies is essential for practical applications. Second, interfacial stability under realistic operating conditions requires further investigation. Many heterojunction effects are demonstrated under relatively mild conditions, whereas long-term stability under high sulfur loading, lean electrolyte, and high current density remains insufficiently explored. Third, dynamic mechanistic understanding of polysulfide conversion within nanocage heterostructures is still limited. Advanced in situ and operando characterization techniques, combined with theoretical modeling, are necessary to clarify how interfacial electric fields and charge redistribution influence multistep sulfur redox reactions. Finally, system-level integration should be emphasized.

The effectiveness of nanocage heterostructures must be evaluated in conjunction with lithium anode protection strategies, electrolyte optimization, and full-cell configurations to truly assess their practical value. Addressing these challenges will not only deepen fundamental understanding but also accelerate the translation of nanocage heterostructures from laboratory research to real-world Li-S battery technologies.

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