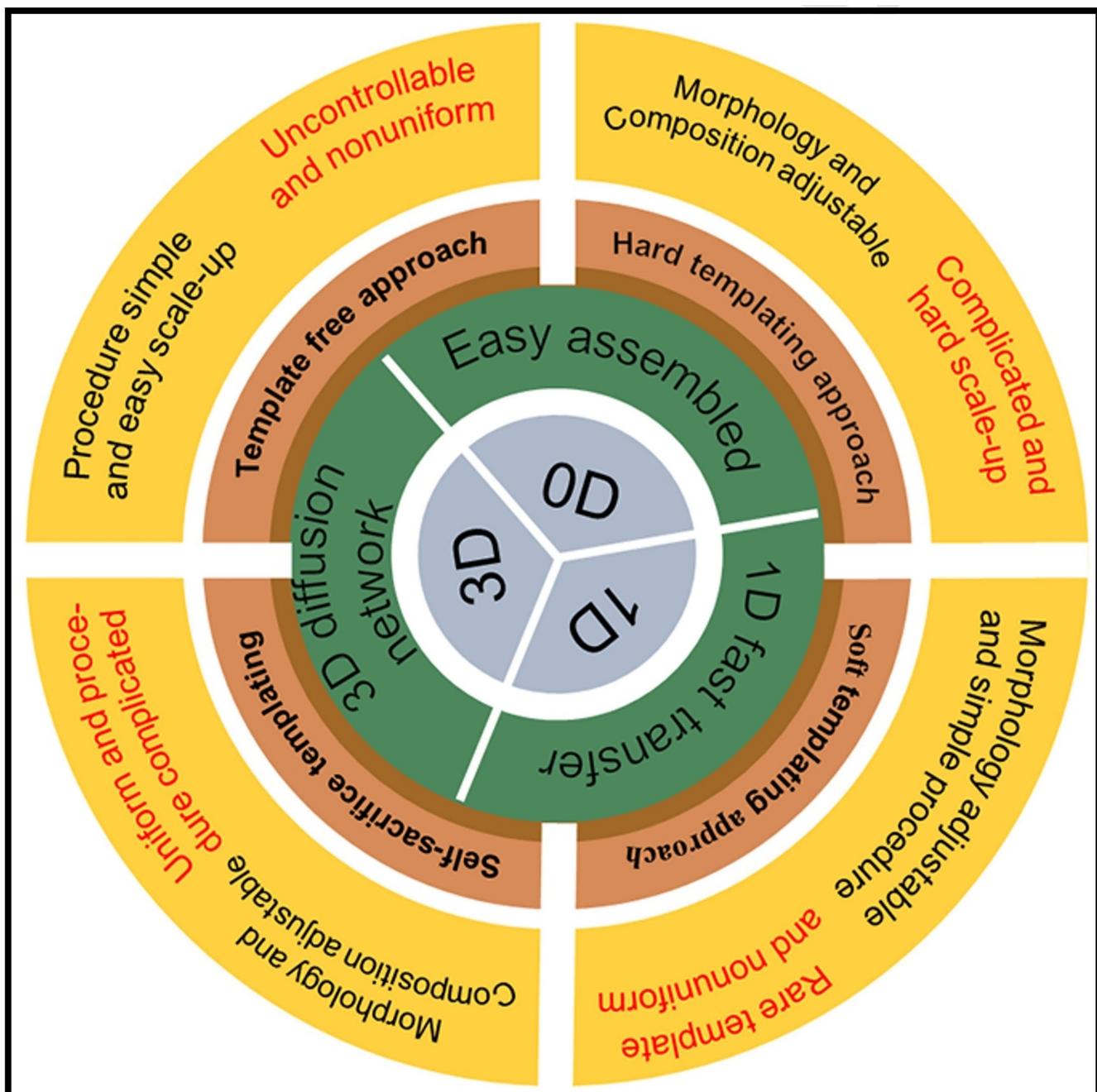


Advances in MoS₂ based Hollow Structural Materials for High-Performance Metal-Ion Batteries

Hui Zhang⁺^[a], Yashi Wang⁺^[a], Shilong Guo,^[a] Yiqing Hui,^[a] Hanyue Wei,^[a] Jianjun Song,^{*[b]} and Xiaoxian Zhao^{*[a]}



The construction of a hollow structure could promote the diffusion of electrons and ions to improve the electrochemical performance of MoS₂ based materials for metal-ion batteries. Herein, we summarize the preparation technique of MoS₂ hollow structural materials with different dimensions. The approaches to construct 0D hollow MoS₂ materials for electrodes of metal-ion batteries can be divided into the hard template approach, soft template approach, self-template approach, and template-free approach. Among them, the hard template approach and self-sacrifice template approach are controllable but complicated, the soft template approach and template-free approach are simple and scalable but not controllable. Furthermore, as the electrode material of metal-ion batteries

including lithium-ion battery, sodium-ion battery, potassium-ion battery or magnesium-ion battery, the 0D hollow structural MoS₂ based materials could improve the diffusion kinetics of ion and electron and restrict the stack of MoS₂. Furthermore, the 1D hollow MoS₂ can provide oriented electron diffusion along with the axial direction, and the 3D hollow MoS₂ can offer perforative pores for permeation of electrolytes and more active sites, which results in excellent rate capability and cycling stability. This paper could give inspiration for constructing MoS₂ hollow structural materials with different dimensions and provide a constructive suggestion for synthesizing hollow materials with excellent electrochemical performance.

1. Introduction

MoS₂, as a kind of two-dimensional (2D) transition metal sulfide, owns a unique 2D plane structure which is composed of Mo (+4) and S (-2) arranged by the covalent bonds as a sequence of S-Mo-S.^[1] Wherein, the adjacent 2D layers are stacked via Van der Waals' force.^[2] It has been attracting much attention in various fields, such as hydrogen evolution reaction,^[3] oxygen reduction reaction,^[4] magnetic anisotropies,^[5] biosensors,^[6] phototherapy,^[7] and so on, due to its unique structure and abundant resource. Especially, in the energy storage field, the MoS₂ exhibits extreme potential as electrode materials of metal-ion rechargeable batteries,^[8] such as Li⁺^[9,10] Na⁺^[11] K⁺^[12], even Zn²⁺^[13,14] and Mg²⁺^[15] and supercapacitor due to its enough layer space of 0.62 nm^[16] for hosting metal ions during charging/discharging process. Therefore, since it appears, the MoS₂ has been rising like a star in energy storage.

At the beginning of application on energy storage, the pure MoS₂ bulk was used as electrode materials due to its analogous structure to graphite^[17] with an indirect bandgap of ~1.2 eV,^[18] which facilitates faster ion transfer kinetic, enabling MoS₂ to be a kind of good electrode material.^[19] For example, a rheological phase reaction method was applied to prepare MoS₂,^[20] which exhibits good electrochemical performance. However, the development of pure MoS₂ bulk on energy storage is hindered due to its limited active sites for redox reactions and poor ion diffusion kinetics. Similar to the development history of graphite, compared to MoS₂ bulk, the single-layered MoS₂ can provide more active sites for redox reaction, shortened ion and electron diffusion path, which fosters excellent electrochemical performance.^[21,22] A facile liquid-phase exfoliation method was

used to exfoliate MoS₂ efficiently in 1-methyl-2-pyrrolidinone with a NaOH assistant.^[23] As anode of sodium battery, the materials shown outstanding cycling stability. But in fact, the exfoliated MoS₂ is easy to stack during preparing electrodes, which will lose active sites to failure-specific capacity, rate capability, and cycling stability.^[24,25]

Construction of nanostructure is an efficient approach to promote permeation of electrolytes from outer to inner,^[26] shorten diffusion path of ion and provide more active sites for redox reaction. Till now, various MoS₂ with different nanostructures, such as nanofiber,^[27] nanoflower,^[28,29] nanorod,^[30] nanoflake,^[31] and hierarchical microsphere,^[32] have been designed to overcome its disadvantage as slow ion diffusion kinetics and easy stack during circulation. So many kinds of techniques were adopted to synthesize nano-structural MoS₂, such as hydrothermal process,^[33] gas reaction between precursor of MoO₃ and sulfur or H₂S,^[34,35] solid-phase reaction by ball milling,^[36] chemical vapor deposition,^[37] and so on. It can be said that each method has its own point. Among various nanostructures, the hollow structure not only can provide more active sites for redox reactions, shorten the diffusion path of ions and electrons, but also can release the volume expansion and lattice stress due to its unique "breathable effect" to improve cycling stability and rate capability.^[38-41] What's more, designing hollow structural materials can constrain the stack of MoS₂ during the preparation of electrodes. Therefore, constructing a hollow structure is a reasonable strategy to improve the electrochemical performance of MoS₂ as materials for energy storage. As shown in Figure 1, from 2000 to 2021 the article about "MoS₂ hollow" and "energy" searched on the Web of Science is increased sharply. Compared to the preparation of other structural MoS₂, designing hollow structural MoS₂ is more difficult. However, many approaches were developed to synthesize MoS₂ with hollow structures as electrode materials of rechargeable batteries recently.

In this paper, we classified the preparation methods to construct hollow MoS₂ with different dimensions (0D, 1D and 3D) as electrode materials of metal ion rechargeable batteries^[8] including Li⁺, Na⁺, K⁺, Zn²⁺ and Mg²⁺, and supercapacitor. Especially, we classified the preparation methods including the hard templating approach, soft templating approach, self-

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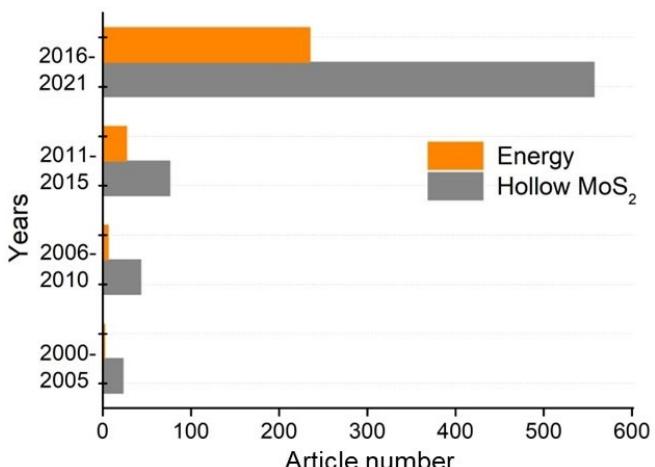


Figure 1. The number of articles from 2000 to 2021 on the topics of "MoS₂ hollow" and "energy", obtained by searching on the Web of Science.

sacrifice templating approach and template-free approach, and summed up their advantages. Additionally, the advantages of hollow MoS₂ with different dimensions (0D, 1D and 3D) structure on electrode materials of energy storage devices, such as supercapacitor, lithium-ion battery, sodium-ion battery, and so on were discussed in detail as well. We believe that this work can give an inspiration on designing hollow structural MoS₂ with different dimensions, and arise up a good effect on MoS₂ based hollow materials for electrode materials of rechargeable devices.

2. Construction of MoS₂ based Hollow Materials for Metal-Ion Battery

2.1. 0D Hollow structural MoS₂ particles

0D hollow structural MoS₂ particles as electrode materials of metal-ion battery not only can release the volume expansion during the charging/discharging process. Besides, the larger specific surface area and pore volume makes sure adequate contact area with electrolyte to provide more active sites for redox reactions and shortens the diffusion path of ion.^[42–45] Thus, the 0D hollow structural particles would contribute more ratio of capacitive contribution capacity corresponding to the surface-control process.^[46–49] Furthermore, as its unique structural feature, the theoretical contact area between 0D hollow structure particles during manufacturing electrode is only one spot as shown in Figure 2(a), which minimizes the loss of electrochemical active area to improve rate capability. Thus, the 0D hollow structural MoS₂ particles have got a lot of attention as anode materials for metal-ion batteries, which drive the development of various approaches to construct 0D hollow structural MoS₂ particles including hard templating approach, soft templating approach, self-sacrifice templating approach, and template-free approach.

2.2. Hard templating approach

As we know, the hard templating approach is a delicate method to fabricate 0D hollow structural particles with functional groups by employing various hard templates including polystyrene spheres,^[50] silica spheres,^[51] phenolic resin spheres,^[52] and Al₂O₃ particles.^[53] Meanwhile, the mesoporous silica was taken as the hard template due to its large channels, order mesopores, and to be easily removed.^[54] Especially, the sequential templating method was applied to construct metal oxide or metal sulfide with multi-shelled structures for



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Jianjun Song received his PhD from Yanshan University (Jan. 2017). During 2016–2017, he did research at University of Technology Sydney as a joint PhD student. In Apr. 2017, he joined the College of Physics, Qingdao University as an associate professor. His research interests focus on the design and construction of low-dimensional functional materials for energy storage.

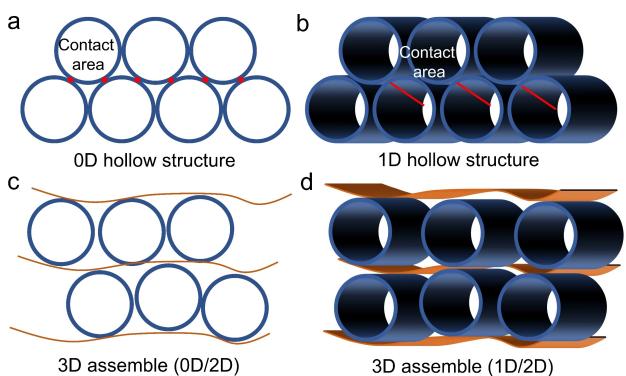


Figure 2. The contact area between the hollow structural materials with a) 0D, b) 1D or c, d) 3D during preparing electrode.

photocatalyst,^[55,56] drug carrier,^[57] and energy storage^[58] by Prof. Dan Wang. Besides, David Lou has done many works to construct hollow materials as electrode materials with the hard templating approach as well.^[59–61] It can be seen that the hard templating approach is a delicate, facile and controllable strategy to construct MoS₂ hollow materials with 0D structure for electrode materials of energy storage devices, such as lithium-ion battery, sodium-ion battery, potassium-ion cell, zinc-ion cell, magnesium-ion cell and even supercapacitor (Figure 3).

The hard templating method is very suitable to synthesize the 0D hollow structural MoS₂ particles due to its easy and controllable trait undoubtedly. For example, the hollow MoS₂/carbon spheres were synthesized by applying the silica sphere as hard template (Figure 4a).^[62] Interestingly, during this process, the polysaccharide layer formed by glucose interaction with molybdate on the surface of silicon sphere after annealing plays a spatial confinement role in driving MoS₂/polysaccharide sphere. Besides, the CeO₂ hollow sphere was taken as a supporting template to fabricate the MoS₂/CeO₂ hollow sphere (Figure 4b).^[63] Zhenyou Li prepared hierarchical C@MoS₂@C hollow spheres by using the MnCO₃ as hard templates, in which the MoS₂ was sandwiched by carbon layer derived from the polydopamine. At this process, for one thing, the polydopamine can prevent the template from being destroyed, at the same time, the polydopamine can confine the growth of MoS₂, which is the key to cast hierarchical C@MoS₂@C hollow sphere

(Figure 4c).^[64] Therefore, the hard templating approach has attracted much attention to constructing 0D hollow structural MoS₂ particles for photocatalyst, electrocatalyst, energy storage and so on.

Among them, as anode materials of lithium-ion battery the 0D hollow structural MoS₂ particles are extremely welcomed due to their unique structure feature, which minimizes the loss of electrochemical active area to improve rate capability.^[65] For example, Zhaorong Chang described a delicate approach to synthesize MoS₂ hollow nanocage with a diameter around 100 nm via a hard templating approach. The hollow structure spontaneously arising in the novel “close-edge” nanocages by taking the ammonia cation bubble as hard templates.^[66] What's more, as an anode material for lithium-ion batteries, the hierarchical MoS₂ hollow nanocages can release the expansion during circulation, thus such a highly desired structure offers remarkably reversible capacity and excellent rate capability.

Besides, the 0D hollow structural MoS₂ particles are more suitable for electrode materials of sodium ion battery which can release the bigger volume change during the charging/discharging process caused by the bigger volume of Na⁺ than Li⁺. Juexian Cao and his co-workers designed a kind of hierarchical hollow spheres composed of few-layered MoS₂@carbon nanosheets. Meanwhile, because the synergistic effect of ultrathin MoS₂ nanosheet, hollow space, and carbon coating layer could improve the Na⁺ diffusion kinetics and adjust the mechanical stability during the charging/discharging process. Therefore, as an anode material of sodium dual-ion batteries full cell, the MoS₂@N-C hollow spheres exhibit a high specific capacity of 45 mAhg⁻¹ at a current density of 2 Ag⁻¹ and show excellent cycling stability and rate capability.^[67] To sum up, the 0D hollow structural MoS₂ particles prepared by the hard templating approach have been applied to anode materials of the metal-ion storage system, which exhibit excellent performance due to its unique structure.

2.3. Soft templating approach

The soft templating approach is another popular method to construct 0D hollow structural MoS₂ particles, in which the micelle or vesicle plays a key role in regulating morphology. During this process, a variety of surfactants or copolymers are used as soft templates, wherein the 0D hollow structure including micelles, vesicles, or cylindrical at the interface of hydrophobic/hydrophilic can be formed.^[68,69] So many kinds of organic compounds, such as carbohydrates, polystyrene, or resorcinol formaldehyde, can be acted as soft templates.^[70–72] For example, Yusuke Yamauchi synthesized the hollow mesoporous silica by taking the cetyltrimethylammonium bromide and a kind of triblock copolymer as the dual soft template.^[73] Besides, both the surfactant and organic precursor can be converted to conductive carbon to promote the faster transfer of electrons, which is beneficial to the high-rate capability of electrode materials.

Among various soft templates, the cetyltrimethylammonium bromide (CTAB) as a cationic surfactant is the

Hard template	Soft template	Self-template	Free template
• Morphology adjustable	• Simple procedure	• Morphology adjustable	• Simple procedure
• Composition adjustable	• Morphology adjustable	• Composition adjustable	• Easy scale-up
• Complicated procedure	• Rare template	• Uniform	• Uncontrollable
• Hard scale-up	• Nonuniform	• Complicated procedure	• Nonuniform

Figure 3. The advantages and disadvantages of different methods on MoS₂ hollow structural materials synthesis.

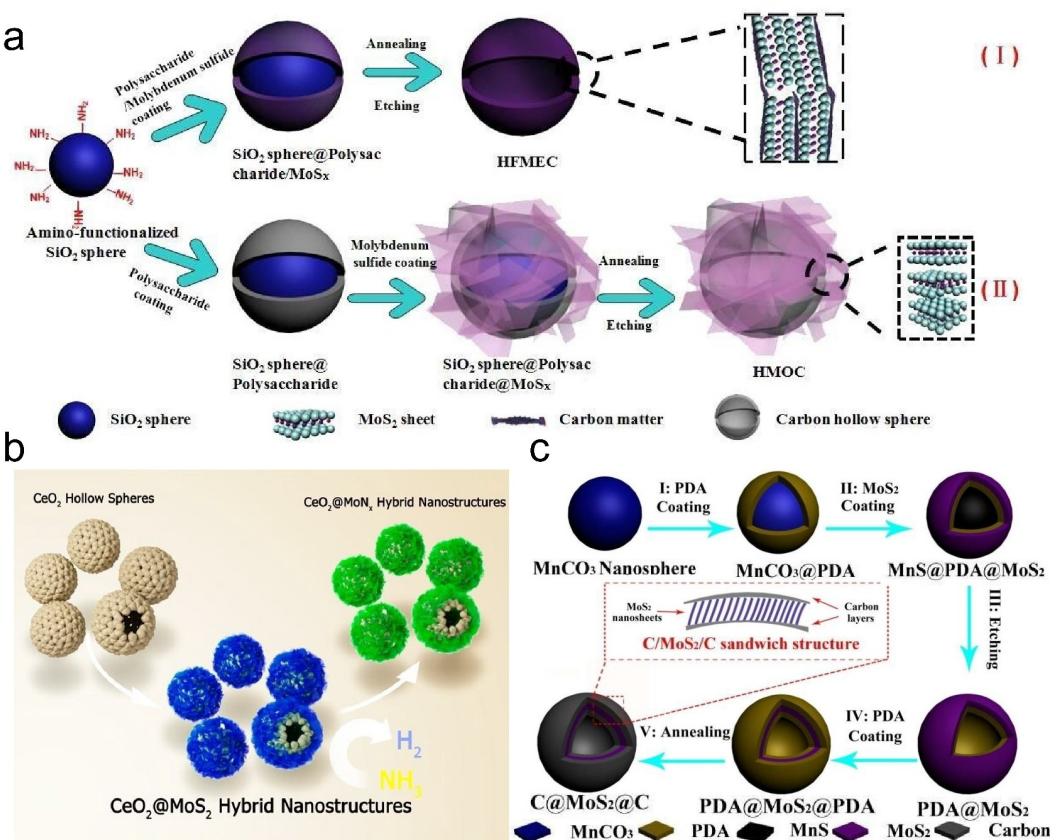


Figure 4. Construction of MoS₂ based hollow structural particles by using different hard templates. a) SiO₂ template. Reproduced with permission from Ref. [62]. Copyright (2016) Royal Society of Chemistry. b) CeO₂ template. Reproduced with permission from Ref. [63]. Copyright (2016) American Chemical Society. c) MnCO₃ template. Reproduced with permission from Ref. [64]. Copyright (2017) Royal Society of Chemistry.

most popular one for the construction of 0D hollow structural MoS₂ particles due to its low price and structural characteristics.^[74] Deliang Cui designed a novel sequential soft templating approach to synthesize the MoS₂ hollow spheres with an expanded interlayer at a high-pressure hydrothermal condition. During this process, the CTAB and MoS₂ monolayers were precipitated on the interface of CTAB micelles and water, which leads to the formation of the MoS₂/C hollow sphere composed of alternate MoS₂ monolayer and carbon layer after calcination as shown in Figure 5(a). Furthermore, as anode materials of lithium or sodium-ion batteries, the MoS₂/C hollow sphere could provide more contact area with electrolyte and void space to buffer volume change during circulation. And the alternate MoS₂ monolayer and carbon layer can promote faster diffusion of electrons and ions. Therefore, the MoS₂/C hollow sphere exhibited a high specific capacity of 401 mAh g⁻¹ at a current density of 200 mA g⁻¹ and excellent rate capability for sodium-ion battery, and a high specific capacity of 1025 mAh g⁻¹ at a current density of 1000 mA g⁻¹ for lithium-ion battery.^[75] Meanwhile, other organic compounds such as Pluronic F-127,^[76] pyrrolidone (PVP)^[77] (Figure 5b and c) or vapor^[78] can be taken as the soft template as well. For example, the 0D MoS₂/carbon hollow particles were synthesized by taking Pluronic F-127 as the softer template. Interestingly, the hollow particle was assembled by the MoS₂ nanosheet

vertically, which is suitable to improve the diffusion rate of a series of metal-ions (Li⁺, Na⁺, K⁺, Mg²⁺). Therefore, the 0D MoS₂/carbon hollow particles not only demonstrate an excellent lithium storage capability, but also sodium or potassium storage capability.^[79]

In summary, the soft-templating approach to construct 0D hollow structural MoS₂ via using micelle or vesicle as soft templates has become one of the most popular methods. The morphology of the product is controllable and its program is simple (Figure 3). However, it is difficult to control the particle size, morphology, and dispersity owing to the complexity of the sol-gel process.^[80]

2.4. Self-sacrifice templating approach

Recently, the self-sacrifice templating approach to construct 0D hollow structural particles has attracted much attention due to its controllable preparation process. Especially, taking the metal-organic frameworks (MOFs) as the sacrificial templates to fabricate porous or hollow structural metal oxide or metal sulfide for energy-related fields has been researched extensively in the domestic and overseas.^[81-83] For example, a 0D Co-Fe alloy/N-Carbon hollow particle was designed by taking MIL-101 and ZIF-67 as the dual self-template, which shows

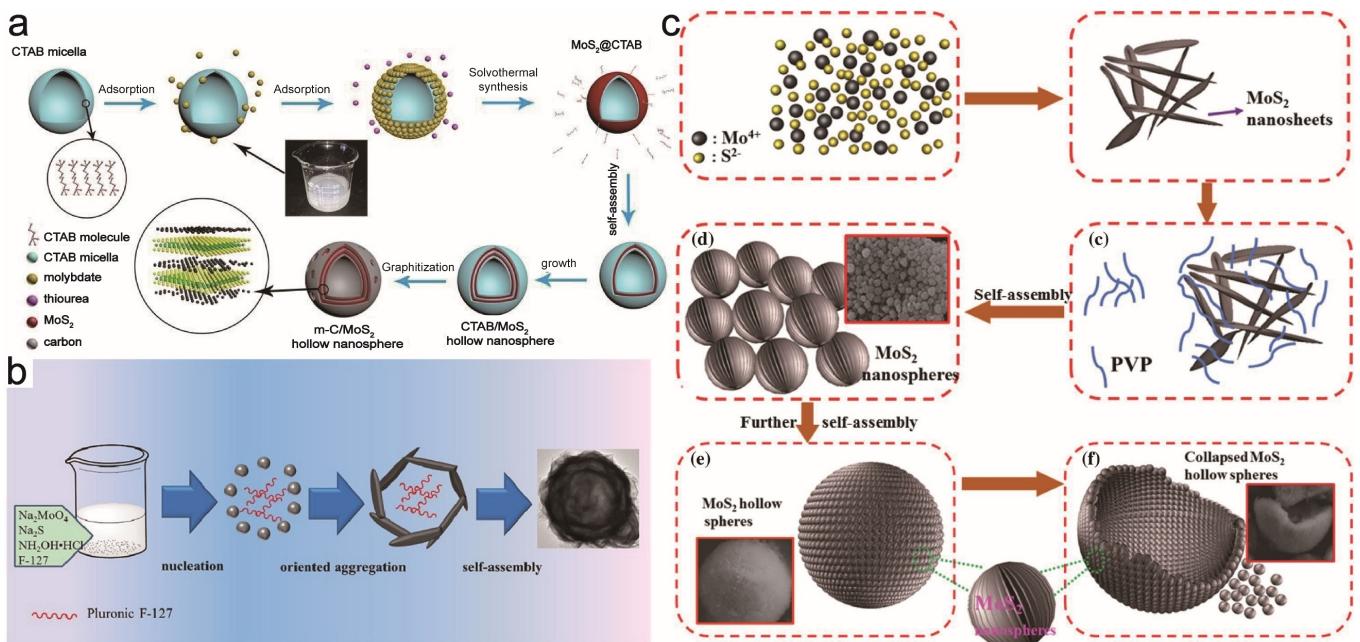


Figure 5. a) Construction of 0D hollow structural MoS₂ via using CTAB. Reproduced with permission from Ref. [75] Copyright (2018) Elsevier. b) Construction of 0D hollow structural flowerlike MoS₂ hollow microspheres via using Pluronic F-127 as soft template. Reproduced with permission from Ref. [76]. Copyright (2013) Elsevier. c) Construction of 0D hollow structural MoS₂ via using PVP as soft templates. Reproduced with permission from Ref. [77]. Copyright (2018) Springer.

impressive electrocatalytic oxygen reduction capability.^[84] The Fe₃O₄/FeS/Carbon heterostructure flake was constructed via using MIL-88b(Fe) as a self-sacrifice template, wherein the morphology and composition can be adjusted by controlling the adding mass of citric acid and calcination temperature.^[85] Undoubtedly, the self-sacrifice templating approach is more suitable to construct 0D hollow structural MoS₂ particles, because the nanostructure can be adjusted by the morphology of the self-template.^[86]

Actually, in the energy storage field, many researchers put their attention on synthesizing the 0D hollow structural MoS₂

particles by self-sacrifice templating approach as anode materials of metal-ion batteries (Figure 6a).^[87] Firstly, in the early years, the 0D hollow structural MoS₂ particles were used for lithium-ion batteries, which reflects the effective influence on diffusion kinetics and volume expansion. For example, the self-sacrifice templating approach by taking ZIF-8 as the template for synthesis of 0D ZnS@MoS₂ hollow polyhedrons particles composed of inner ZnS hollow shell and outer MoS₂ nanosheet arrays were designed as shown in Figure 6(b).^[88] The hollow structure can provide more active sites for a redox reaction to shorten the transfer path of Li⁺ ion.^[89] Thus, as

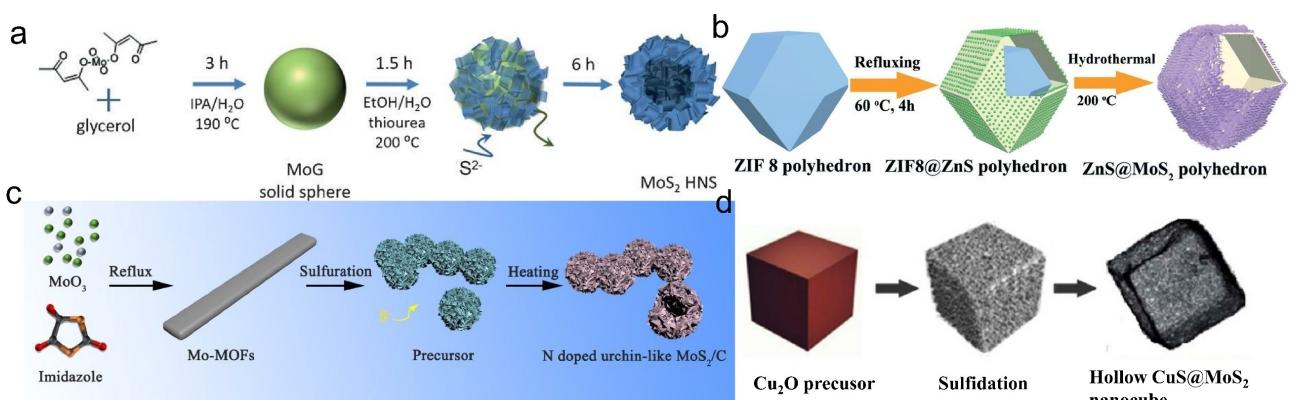


Figure 6. The self-sacrifice templating approach to construct 0D hollow structural particles. a) Mo-glycerate (MoG) solid spheres were firstly formed by a solvothermal process, and then sulfurized by thiourea at 200 °C to obtain the MoS₂ hollow nanospheres (HNS). Reproduced with permission from Ref. [87]. Copyright (2016) Wiley-VCH. b) ZnS@MoS₂ hollow polyhedrons were prepared by the refluxing-solvothermal method using the metal organic framework ZIF-8 as a template and raw material. Reproduced with permission from Ref. [88]. Copyright (2018) Royal Society of Chemistry. c) The synthesis of nitrogen doped MoS₂/C hollow structures with expanded interlayers by sulfuration of Mo-MOFs. Reproduced with permission from Ref. [91]. Copyright (2017) Elsevier. d) Hollow CuS@MoS₂ were synthesized using Cu₂O as precursor. Reproduced with permission from Ref. [90]. Copyright (2017) Elsevier.

anode of lithium-ion battery, the 0D ZnS@MoS_2 hollow polyhedrons particles displayed a high specific capacity of $1346.3 \text{ mAh g}^{-1}$ at a current density of 0.2 A g^{-1} and brilliant cycling and rate capability. Except for MOF, the Cu_2O was also used as the self-sacrifice template to synthesize the 0D hollow structural MoS_2 particles for anode materials of metal-ion battery as shown in Figure 6(d). Hong Guo created a hollow CuS@MoS_2 heterostructure microcube by applying the Cu_2O nanocube as the self-sacrifice template based on the redox reaction between Cu_2O , ammonium molybdate, and sulfur.^[90] This unique $\text{Cu}_2\text{O}@\text{MoS}_2$ hollow polyhedrons heterostructure could promote the permeation of electrolytes to increase the contact area between electrolyte and electrode materials, as well as the releasing effect on volume expansion. It leads to the materials delivered a high capacity of 912 mAh g^{-1} at a current density of 0.5 A g^{-1} after long cycling, and especially the excellent rate performance at different current densities. Besides, so many works focus on applying the 0D hollow structural MoS_2 particles by a self-sacrifice templating approach to anode materials of sodium-ion battery, which belongs to the metal-ion batteries as well. Yangsheng Cai reported a nitrogen-doped urchin-like MoS_2/C hollow nano-spherical structure, which demonstrated excellent electrochemical performance as an anode electrode of sodium ion battery. The superior performance could be attributed to the combination of carbon and nitrogen making the material have high conductivity (Figure 6c).^[91] Anqiang Pan synthesized the Mo-MOFs firstly, then taking the Mo-MOFs as the self-sacrifice template to prepare the hollow MoS_2/C sphere after a sulphuration treatment. In the materials, abundant hard carbon derived from glucose and organic ligand was formed, which could promote the transfer rate of electrons. The unique hierarchical structure not only can shorten the diffusion path of Na^+ , but also accommodate volume expansion during the charging/discharging process, which leads to a high reversible specific capacity (972 mAh g^{-1} at a current density of 0.1 A g^{-1}), outstanding cycling stability (a specific capacity of 128 mAh g^{-1} was retained after 5000 cycles at a current density of 2 A g^{-1}) and good rate capability.^[92] The 0D hollow structural MoS_2 particles obtained by the self-template approach also was made as to the electrode materials of the supercapacitor. For example, Ziqiang Zhu constructed a $\text{MoS}_2/\text{Co}_3\text{S}_4$ heterostructure hollow octahedron by using ZIF-67 as the self-sacrifice template, which shows a higher specific capacitance of 1369 F g^{-1} at 1 A g^{-1} and 83% capacity was retained after 10,000 cycles as an electrode for supercapacitors.^[93]

Anyway, because of the advantages of controllable morphology of product and introduction of conductive carbon derived from the organic ligand, the self-sacrifice templating approach to construct 0D hollow structural MoS_2 particles with abundant active sites for redox reaction and hollow space to release volume expansion is very popular in the energy storage field such as lithium-ion battery, sodium-ion battery, and other metal-ion batteries. However, the disadvantage of the complicated manufacturing process restricts its further development on scalable preparation of nano 0D hollow MoS_2 materials (Figure 3).

2.5. Template free approach

The processes to prepare hollow structural materials by template approach are usually complicated, time-consuming and high cost. However, different from templating approach, the template is not essential to construct hollow structural materials.^[94] Thereby, compared with a templating method, removing the template process is not needed for the template-free approach, which leads to simpler and scalable manufacturing technology,^[95] and extensive application in designing 0D hollow structural particles. For example, Dan Wang introduced a kind of simple and scalable template free hydrothermal approach to prepare hollow $\text{a-Fe}_2\text{O}_3$ spheres with different phase compositions.^[96]

For generating 0D hollow structural MoS_2 particles, various routes with different synthesis mechanisms such as nanoscale Kirkendall effect, oriented assemble under the action of the guiding agent, and Ostwald ripening.^[97–99] For example, the $\text{CdS/MoS}_2/\text{graphene}$ hollow spheres can be constructed by using cysteine as the guiding agent, which exhibits high efficiency photocatalysts for hydrogen evolution.^[100] Ziqiang Zhu designed a novel MoS_2 micro-hollow sphere coated by the nano hollow MoS_2 spheres by a simple one-step hydrothermal approach, wherein the formation mechanism was confirmed to be Ostwald ripening based on the experiment by interrupting the reaction at different times.^[101] Many scientists applied the 0D hollow structural MoS_2 particles to electrode materials of metal-ion batteries by the template-free approach. A delicate one-step template-free hydrothermal approach was achieved to synthesize the hollow MoS_2/C spheres. According to the characterization of XRD, SEM, and TEM, the phase composition and inner hollow structure can be confirmed. Furthermore, as electrode materials of the lithium-ion battery, a high reversible specific capacity of 1147 mAh g^{-1} at a current density of 0.1 A g^{-1} , excellent cycling stability, and rate performance were achieved due to its unique hollow structure.^[102]

Undoubtedly, the template-free approach to construct 0D hollow structural MoS_2 particles is the simple and scalable one, of which templates don't need to be removed. Therefore, the template-free approach has captured the researcher's attention on scalable preparation of 0D hollow structural MoS_2 particles. However, the morphology of the product is not controllable which limits its further development (Figure 3).

In summary, the structural parameters of MoS_2 in different dimensions will endow them with different characteristics, thus making different effects on electrochemical performance. By integrating the above methods, we found that the hollow 0D MoS_2 structure shows superior electrochemical performance when it is applied to the energy storage field. Based on the large specific surface area and pore volume, stable structure and easy assembled of 0D hollow MoS_2 , usually a fantastic rate capability and cycling stability are achieved. IF- MoS_2 hollow nanocage structure synthesized by Zhaorong Chang demonstrated superior cycle stability and excellent rate performance as an electrode of lithium-ion batteries. After 100 cycles at a current density of 100 mAh g^{-1} , the reversible capacity remained as high as $1043.7 \text{ mAh g}^{-1}$ (Figure 7a). In addition,

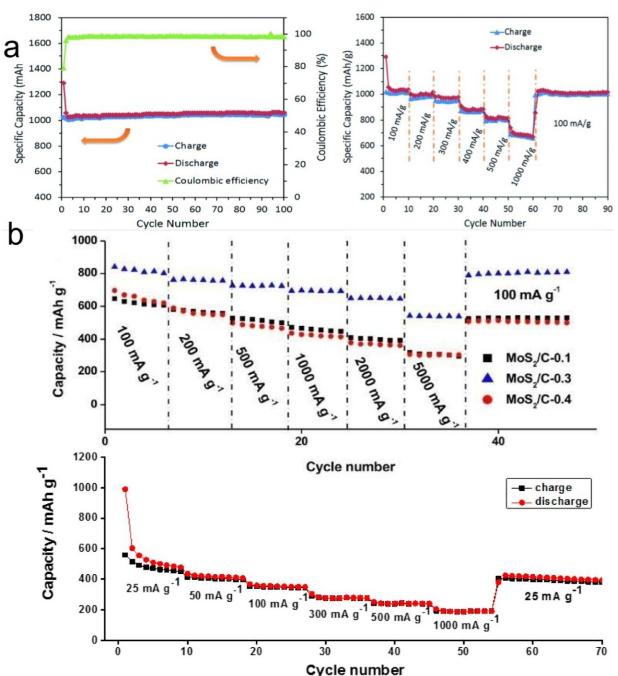


Figure 7. Electrochemical properties of 1D MoS₂ based hollow structure for metal-ion batteries. a) Cycling behavior of the IF–MoS₂ nanocage electrode at a current density of 100 mAh g⁻¹ and the rate performance of the IF–MoS₂ nanocage electrode at various current densities in lithium-ion cells. Reproduced from Ref. [66]. Copyright (2016) The Author(s). Published by the Royal Society of Chemistry. b) The rate performance of the materials in lithium-ion and Na-ion cells. Reproduced with permission from Ref. [79]. Copyright (2018) Royal Society of Chemistry.

when the current densities were 100, 200, 300, 400, 500 and 1000 mA g⁻¹, the specific capacities of the hollow IF–MoS₂ nanocages were 1008, 987, 945, 862, 796 and 680 mAh g⁻¹, respectively. This excellent performance is ascribed to the large cavity inside the hollow nanocage structure which alleviates volume expansion during charging and discharging.^[66] Moreover, Tianyu Yang created a porous graded 0-D MoS₂/C nanocomposites highlighting the huge development potential and good prospects in energy storage. It can deliver a specific capacity of 800 mAh g⁻¹ at a current density of 100 mA g⁻¹, and maintains a specific capacity of 540 mAh g⁻¹ even at a high current density of 5 A g⁻¹ as anode of the lithium-ion battery, demonstrating the excellent rate performance. In addition, 0-D MoS₂/C nanocomposites also show high ion storage capacity in Na⁺ and K⁺ storage. The superior electrochemical properties are ascribed to the superior structural of 0-D MoS₂/C nanocomposites as shown in Figure 7(b).^[79]

2.6. 1D hollow structural MoS₂ materials

Same to the 0D hollow structural MoS₂ particles, the construction of 1D hollow structural MoS₂ materials such as nanofiber,^[103] nanotube,^[104] and nanorod could reduce particle size and significantly increase the contacting area between material and electrolyte, which promotes more active sites and effectively shortens the diffusion path of ion and electron,^[105–108]

thus to improve ion diffusion kinetics. So many researchers focus their work on the study of 1D hollow structural MoS₂ materials for the anode of metal-ion batteries. Especially, the MoS₂ nanotube not only has the inner hollow space to release volume expansion as the 0D hollow structural MoS₂ particles but also the directed electron diffusion along with the axial direction, which could improve the mechanical stability and electron transport rate of MoS₂.^[109] Besides, the largest contact area between 1D MoS₂ hollow structural materials is only a line at the axial direction as shown in Figure 2(b), which decreases the loss of electrochemical active area during preparing the electrode and facilitates diffusion of electrons between MoS₂ nanotube. Therefore, the rate capability and cycling stability of MoS₂ as cathode of metal-ion battery can be improved effectively.

At the beginning of discovering the 1D hollow MoS₂ nanotube applied in energy storage field is anode material of lithium-ion battery.^[110] Combining the high specific capacity of MoS₂ (over 1000 mAh g⁻¹) with the unique nanotube structure, the 1D hollow MoS₂ nanotube exhibits outstanding electrochemical performance.^[111] For example, Hongli Zhu synthesized a novel MoS₂ nanotube composited of metallic MoS₂ nanosheets via a delicate scalable hydrothermal approach as shown in Figure 8(a). As all we know, the conductivity of metallic MoS₂ is higher than 2H MoS₂. Meanwhile, the open porous hollow nanotube structure promotes the permeation of electrolytes and diffusion of Li⁺ from the electrolyte to materials. Furthermore, the stack of MoS₂ can be avoided. Thus, as anode materials of lithium ion battery, the 1D metallic MoS₂ nanotube delivered a high reversible specific capacity of 1100 mAh g⁻¹ at 5 A g⁻¹, and 589 mAh g⁻¹ remained at an ultra-high current density of 20 A g⁻¹ as shown in Figure 9(a).^[112] A kind of sandwich-like structural nanotube assembled by TiO₂, carbon and MoS₂ was designed by David Lou originally. The ultrathin MoS₂ nanosheets were arranged on the surface of nitrogen-doped carbon, and the inner shell is TiO₂ coating layer shown in Figure 8(b). The delicate strategy could decrease the diffusion path of Li⁺, increase the conductivity of materials and release volume expansion, which leads to high specific capacity, excellent cycling stability, and rate capability.^[113]

Applied to anode materials for other kinds of metal-ion batteries, 1D hollow MoS₂ nanotube also can demonstrate a brilliant electrochemical performance, such as sodium-ion battery,^[114,115] potassium-ion cell,^[116] magnesium-ion battery,^[117] and so on. For example, a hierarchical Mn-doped MoS₂ nanotube with an expanded interlayer space due to the doping of Mn, a thickness of 20 nm and diameter of 100–200 nm was synthesized by the delicate solvothermal approach (Figure 8c). The 1D hollow MoS₂ nanotube structure with hierarchical surfaces could provide more active sites for Na⁺ insertion/extraction and hollow space for volume expansion. Thereby, a high reversible capacity of 441 mAh g⁻¹ at 100 mAh g⁻¹ was obtained, and still a specific capacity of 160 mAh g⁻¹ at 1 A g⁻¹ remained after 1000 cycles.^[118] Potassium-ion batteries are a new kind of secondary battery, which has attracted much attention from researchers due to their low cost, abundant source. The energy storage mechanism of potassium-ion

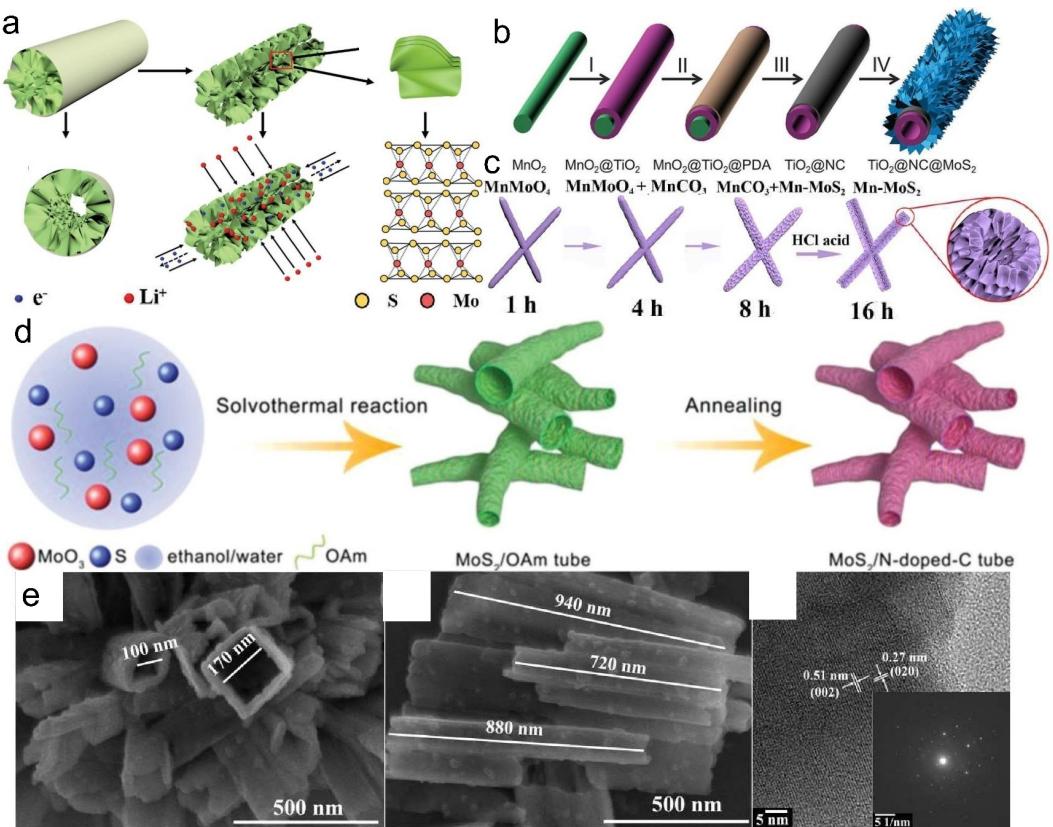


Figure 8. The construction of 1D MoS_2 based nanotube for metal-ion batteries. a) Schematic representation of metallic MoS_2 nanotube as anode for lithium-ion battery. Reproduced with permission from Ref. [112]. Copyright (2018) Wiley-VCH. b) The synthesis process of $\text{TiO}_2@\text{NC}@ \text{MoS}_2$ tubular nanostructures as anode for lithium-ion battery. Reproduced with permission from Ref. [113]. Copyright (2017) Wiley-VCH. c) The synthesis process of $\text{Mn}-\text{MoS}_2$ nanotubes as anode for Sodium-ion battery. Reproduced with permission from Ref. [118]. Copyright (2018) Royal Society of Chemistry. d) The synthesis process of MoS_2/N -doped-C as anode for Potassium-ion battery. Reproduced with permission from Ref. [119]. Copyright (2018) Wiley-VCH. e) The SEM images of Cu_2MoS_4 nanotubes which was used in magnesium-ion battery. Reproduced with permission from Ref. [120]. Copyright (2020) Wiley-VCH.

battery is similar to sodium-ion battery, the 1D hollow MoS_2 nanotube can be used as the electrode materials of potassium-ion battery as well due to its larger interlayer space for reversible storing K^+ . Wei Wang designed a bamboo-like MoS_2/N -carbon hollow nanotube with expanded interlayer space as shown in Figure 8(d). As anode materials of potassium-ion batteries, the expanded interlayer of MoS_2 could provide a friendly environment for storing K^+ reversibly. Meanwhile, bamboo-like MoS_2/N -Carbon hollow nanotube owns inner hollow space along with the axial direction, it will release the larger volume expansion compared to the sodium-ion battery due to larger volume of K^+ than Na^+ , which results in good mechanical stability. As a result, the bamboo-like MoS_2/N -Carbon hollow nanotube delivered a higher reversible specific capacity, excellent cycling stability, and outstanding rate performance.^[119] Electrode materials of magnesium ion batteries with a huge challenge is another important application of 1D MoS_2 based nanotube. A kind of Cu_2MoS_4 square nanotube with a side length of 170 nm and an axial length around 900 nm is achieved by a one-pot hydrothermal approach as shown in Figure 8(e), which demonstrates a super high reversible specific capacity of 390.5 mAh g^{-1} at a current density of 20 mA g^{-1} .^[120] Finally, the 1D hollow MoS_2 nanotube caught the researcher's eye in the dual-ion battery system due

to its appropriate interlayer for Na^+ insertion/extraction. Yongbing Tang for the first time applied the penne-Like MoS_2/C Carbon to electrode materials for dual ion batteries, which exhibit a specific capacity of 65 mAh g^{-1} at a current density of 2 C with a wide voltage window from 1.0 V to 4.0 V.

Same to 0D MoS_2 hollow structural particles, the 1D MoS_2 hollow structure is another favorable competitor in the energy storage field with its unique feature, such as an orientation diffusion to improve rate capability and inner hollow space for releasing volume expansion along with the axial direction. Meanwhile, the assembly technique of 1D MoS_2 hollow materials could restrict the stack of MoS_2 and provide channels for the permeation of electrolyte, which results in more electrochemical active area for energy storage. That's why the 1D MoS_2 hollow materials deliver an excellent electrochemical performance.

Based on the characteristics of 1D hollow structure MoS_2 nanomaterials, such as large contact area with electrolyte, more active sites and superior ion diffusion kinetics, it has been widely used as anode materials for metal-ion batteries by researchers. As above mention, David Lou reported a three-layer $\text{TiO}_2@\text{carbon}@ \text{MoS}_2$ layered nanotube structure as anode material for lithium-ion batteries. As shown in Figure 9(b), the $\text{TiO}_2@\text{NC}@ \text{MoS}_2$ electrode can maintain a high reversible

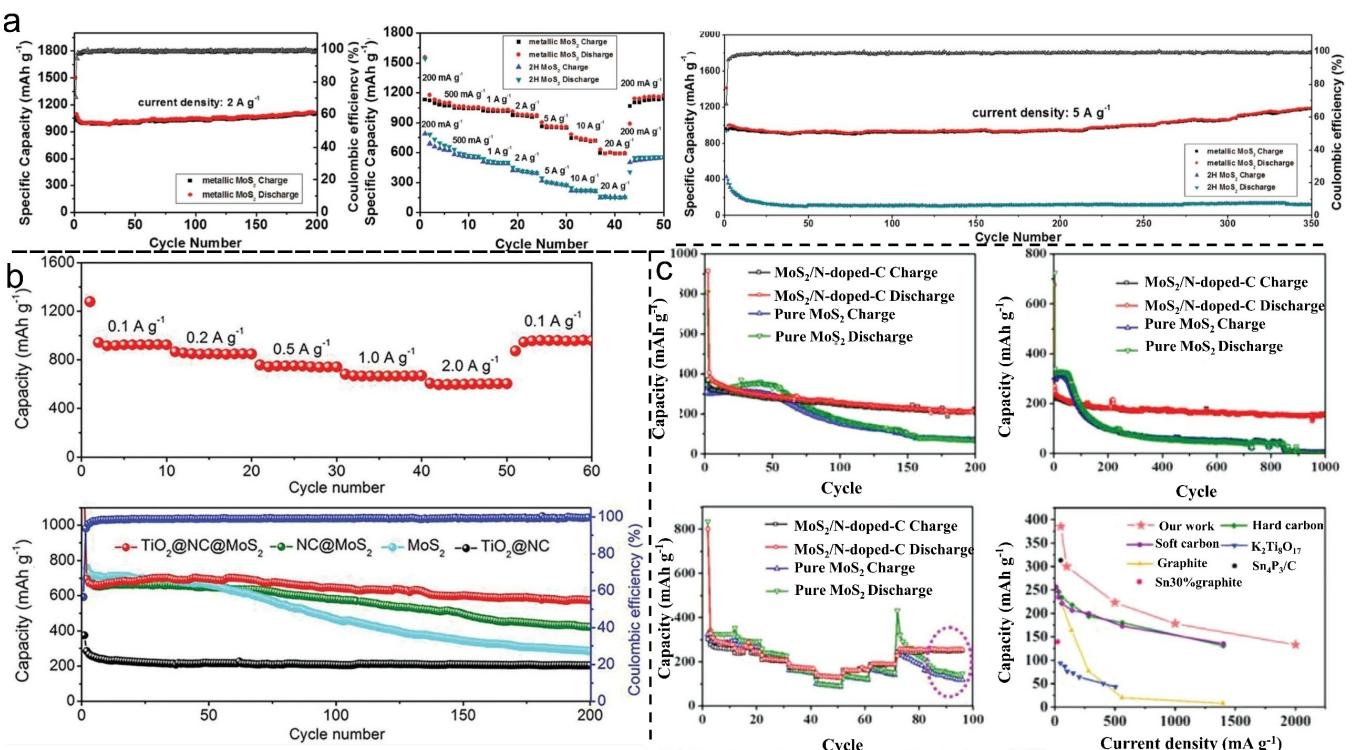


Figure 9. Electrochemical performance of 1D MoS₂ based hollow structure for metal-ion batteries. a) cycling performance at a current density of 2 A g⁻¹, rate performance at different current densities and cycling performance at a current density of 5 A g⁻¹ of metallic MoS₂ nanotube as anode for lithium-ion battery. Reproduced with permission from Ref. [112]. Copyright (2018) Wiley-VCH. b) Rate performance at various current densities and cycling performance at a current density of 1.0 A g⁻¹ of annealed TiO₂@NC@MoS₂ tubular as anode for lithium-ion battery. Reproduced with permission from Ref. [113]. Copyright (2017) Wiley-VCH. c) The cycling performances of pure MoS₂ and MoS₂/N-doped-C tube at a current density of 100 and 500 mAh g⁻¹, rate capability and the comparison between the MoS₂/N-doped-C and other reported anodes as electrode for potassium-ion battery. Reproduced with permission from Ref. [119]. Copyright (2018) Wiley-VCH.

specific capacity of 590 mAh g⁻¹ after 200 cycles at a current density of 1 A g⁻¹. What's more impressive, the specific capacity was recovered when the current density switched back to 0.1 A g⁻¹. Such an excellent properties can be attributed to the three-layered hierarchical nanotubes. This ingenious design significantly reduces the diffusion path of lithium ions and enhances the conductivity of the electrode.^[113] X. H. Qu developed a bamboo-like MoS₂/N–carbon hollow nanotube, which was applied to promote potassium ion diffusion. Owing to its large layer spacing and internal space and the additional attraction of potassium ions at the interface, the structural integrity and higher charge transfer rate during the cycle were guaranteed. Remarkably, after 200 cycles at a current density of 100 mA g⁻¹, the MoS₂/N–Carbon hollow nanotube delivered a capacity of 212 mAh g⁻¹. After 1000 cycles at a high current density of 500 mA g⁻¹, the capacity retention rate was 74%, showing excellent cycle stability (Figure 9c). At the same time, different to other materials the MoS₂/N–Carbon hollow nanotube demonstrated a remarkable rate capability.^[119]

2.7. 3D MoS₂ hollow structural materials

The application of 3D MoS₂ hollow structural materials is more extensive than 2D structural MoS₂ in the energy storage field.

That's because the unique 3D hollow structure can restrict the aggregation, which will remain the superior intrinsic characteristic of MoS₂ sheet such as larger specific surface area, optics, or electricity property.^[121–123] Meanwhile, the porous hollow structure can release the volume expansion during the charging or discharging process to enhance mechanical stability. Furthermore, the pores throughout the whole bulk of materials can provide a three-dimensional channel for the permeation of electrolyte to increase the contact area, which results in more electrochemical active area as shown in Figure 2(c and d).^[124] Therefore, the cycling stability and rate performance are improved.

As anode of lithium-ion battery, the 3D MoS₂ based hollow structural materials can shorten the diffusion path of Li⁺ and mitigate volume changes during the delithiation and lithiation process, which could improve the specific capacity, cycling stability, and rate capability.^[125] For example, a novel 3D ordered porous MoS₂/C material was constructed by using carbon cloth as substrate, PS sphere as the template. In the materials, the ordered pores throughout the MoS₂ layer coated on the surface of carbon substrate are formed after calcination as shown in Figure 10(a), which promotes electrolyte permeation to shorten the diffusion path of Li⁺. The carbon cloth substrate can provide a conductive net for rapid electron transfer. Thereby, as a flexible electrode, the 3D ordered porous

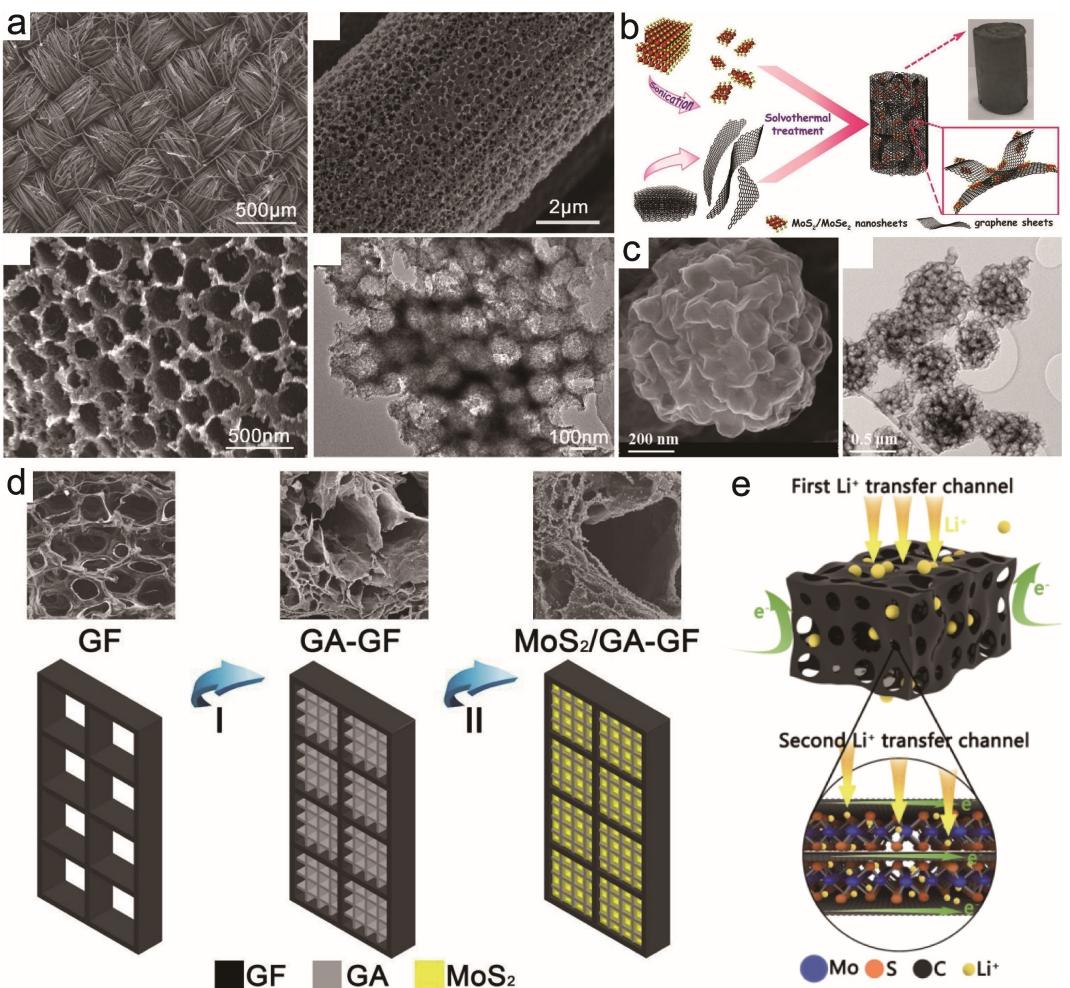


Figure 10. The construction of 3D MoS₂ based hollow structure for metal-ion batteries. a) SEM images and TEM images at different magnification of the MoS₂@C/CC electrode. Reproduced with permission from Ref. [126]. Copyright (2017) Wiley-VCH. b) The synthesis process to prepare MoS₂/MoSe₂-graphene hybrid aerogel. Reproduced with permission from Ref. [123]. Copyright (2015) Royal Society of Chemistry. c) FE-SEM images and TEM images of the 3D MoS₂-graphene composite microspheres. Reproduced with permission from Ref. [129]. Copyright (2015) Wiley-VCH. d) The construction process of the MoS₂/GA-GF hybrid. Reproduced with permission from Ref. [128]. Copyright (2018) Royal Society of Chemistry. e) The transport pathway of Li ions and electrons in the defect-rich 3DR MoS₂/C. Reproduced with permission from Ref. [127]. Copyright (2020) Wiley-VCH.

MoS₂/C exhibited a high reversible specific capacity of 3.428 mAh cm⁻² at a current density of 0.1 mA cm⁻² and stable capacity.^[126] Xuefeng Song designed a 3D porous hollow MoS₂/carbon composite, which exhibits excellent electrochemical performance as anode material of lithium-ion batteries due to its unique 3D hollow structure (Figure 10e).^[127] During the construction of 3D MoS₂ hollow structural materials, usually, the carbon materials such as graphene are used as the skeleton to support the MoS₂, as well as to increase the conductivity of materials. Applying the graphene foam as the support, Shichao Zhang fabricated a 3D MoS₂/graphene foam with multi-channel for the diffusion of Li⁺ via hydrothermal approach as shown in Figure 10(d). The hollow porous structure can provide a channel for permeation of electrolyte, and graphene aerogel can offer a channel for the transfer of electrons, which is beneficial to excellent electrochemical performance.^[128] The graphene also can be taken as a support to construct 3D MoS₂ hollow structural materials for the electrode of sodium-ion

batteries. For example, the 3D hollow porous MoS₂/graphene microspheres composed of uniform nanospheres were synthesized by spray pyrolysis as shown in Figure 10(c).^[129] In the materials, there is so much hollow space for releasing volume expansion. Meanwhile, the pores on the surface and the holes in the bulk make sure the electrolyte goes into the inner of material and provide more active sites for redox reaction, which leads to a high specific capacity of 797 mAh g⁻¹ at 200 mA g⁻¹ and still 322 mAh g⁻¹ was retained after 600 cycles at 1.5 Ag⁻¹.

Owing to the structural advantages of 3D materials, the excellent cycle stability and rate performance are obtained. For example, Xuefeng Song designed a 3D porous hollow MoS₂/carbon composite as an anode material for lithium-ion batteries. The three-dimensional conductive interconnecting carbon network improved the interparticle conductivity while maintaining the structural stability. At a current density of 0.1 Ag⁻¹, it exhibited a high reversible specific capacity of 1163 mAh g⁻¹ after 100 cycles, still remaining 800 mAh g⁻¹ at a

high current density of 5 A g^{-1} , showing high rate performance (Figure 11a).^[127] In addition, the three-dimensional MoS₂/dual-channel graphene framework (MoS₂/GA-GF) hybrid structure synthesized by Shichao Zhang has shown high initial capacity, excellent rate performance, and long-cycle stability when used as anode materials for lithium-ion batteries. This special two-channel structure composed of graphene foam and graphene aerogel can effectively improve electron transport and ion diffusion, thus improving the electron and Li⁺ transport kinetics. For its superior electrochemical properties provide important safeguards. As shown in Figure 11(b), MoS₂/GA-GF exhibited an initial specific capacity of 1404 mAh g^{-1} at a current density of 0.2 A g^{-1} . Additionally, a specific capacity of 843 mAh g^{-1} was maintained after 500 cycles at 1 A g^{-1} , and a specific capacity of 593 mAh g^{-1} was maintained at a high current density of 5 A g^{-1} .^[128] Yunchan Kang reported a 3D hollow porous MoS₂/graphene microsphere, which demonstrated the excellent performance as shown in Figure 11(c). The capacity retention rate after 600 cycles is 84% at the current density of 1.5 A g^{-1} . The excellent electrochemical properties can be ascribed to the reduction of layered MoS₂ stacked reduces the Na⁺ insertion barrier, the 3D structure of porous graphene microspheres enhances the Na⁺ storage perform-

ance, and the hollow structure inside the spheres also alleviates the volume expansion.^[129]

The pores on the surface and holes in the bulk of 3D MoS₂ hollow structural materials offer multi-channel for permeation of electrolyte to promote the diffusion of electron and ion, which will improve rate capability. Meanwhile, the abundant inner space can release the volume expansion to increase the mechanical stability of materials, which improves the cycling stability. However, usually the synthesis of 3D MoS₂ hollow structural materials needs to construct the carbon skeleton, which results in the manufacture being complicated.

By summarizing the electrochemical properties of 0D and 3D structure MoS₂, it can be found that both of these two structures demonstrated excellent electrochemical properties. Compared with the 3D structure, the 0D structure minimizes the loss of electrochemical active area, improves the rate ability and is easier to assemble. Compared with the 1D structure, the 3D structure builds a 3D diffusion network. Therefore, the cyclic stability and rate performance of 3D structure can be improved. The different structures have different characteristics and show excellent electrochemical performance.

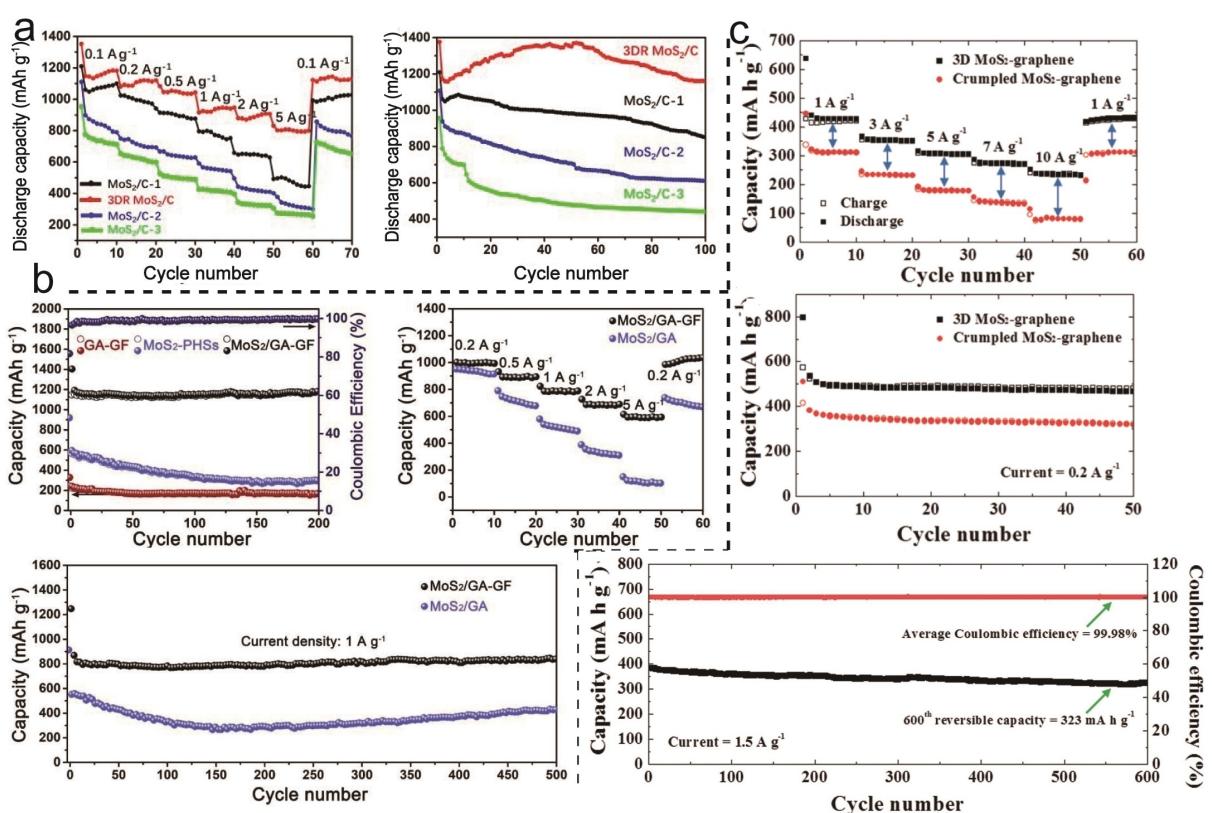


Figure 11. Electrochemical performance of 3D MoS₂ based hollow structure for metal-ion batteries. a) Rate capability and cycling performance at a current density of 100 mA g^{-1} of MoS₂/C-1, 3DR MoS₂/C, MoS₂/C-2, and MoS₂/C-3 as anode for lithium-ion battery. Reproduced with permission from Ref. [127]. Copyright (2020) Wiley-VCH. b) Cycling performance of MoS₂/GA-GF, MoS₂-PHSs, and GA-GF at a current density of 0.2 A g^{-1} , rate capability of MoS₂/GA-GF and MoS₂/GA at different current densities and long-term cycling performance of the MoS₂/GA-GF and MoS₂/GA electrodes at a current density of 1 A g^{-1} . Reproduced with permission from Ref. [128]. Copyright (2018) Royal Society of Chemistry. c) High rate performance, cycling performance at a current density of 0.2 A g^{-1} and long-term cycling properties at a current density of 1.5 A g^{-1} of the 3D MoS₂-graphene composite microspheres. Reproduced with permission from Ref. [129]. Copyright (2015) Wiley-VCH.

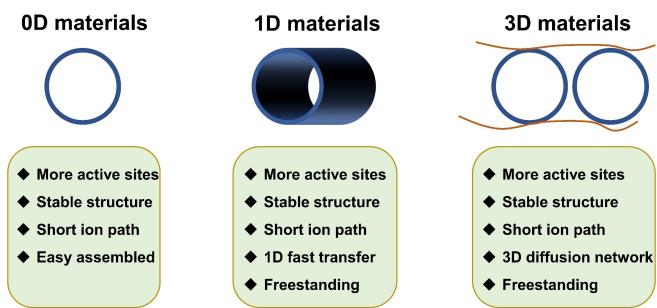


Figure 12. The effects of different dimensions of MoS₂ on electrochemical performance were compared.

3. Conclusion

MoS₂ as a kind of two-dimensional transition metal sulfide owns a unique 2D plane structure for intercalation/deintercalation of metal-ions with high specific capacity. However, its disadvantages such as low diffusion kinetics of ions, poor conductivity, and easy stacking during preparing the electrode limit further development. In this work, we summarize the construction technique of MoS₂ hollow structural materials with different dimensions, which could improve the diffusion kinetics of ion and electron and restrict the stack of MoS₂. The approach to constructing 0D MoS₂ hollow materials for the electrode of metal ion battery can be divided into the hard template approach, soft template approach, self-template approach and template-free approach. Among them, the hard template approach and self-sacrifice template approach are controllable but complicated, the soft templated approach and template-free approach are simple and scalable but not controllable. The selection of the method should be decided according to the circumstances. Besides the advantages of 0D MoS₂ hollow structural materials discussed previously, the 1D MoS₂ hollow structural materials can provide oriented electron diffusion along with the axial direction, and the 3D MoS₂ hollow structural materials can offer perforative pores for permeation of electrolyte and more active sites (Figure 12). This paper could give inspiration for constructing MoS₂ hollow structural materials with different dimensions, and provide a constructive suggestion for synthesizing hollow materials with excellent electrochemical performance.

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Conflict of Interest

The authors declare that there is no conflict of interest regarding the publication of this article.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: hollow structure · lithium-ion battery · magnesium-ion battery · metal-ion battery · molybdenum disulfide · sodium-ion battery

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