Bacteria derived nanomaterials for lithium-based batteries

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Abstract

The increasing emphasis on environmental protection and the promotion of renewable energy sources has led to a growing demand for a mutually beneficial approach to efficiently convert pollutants, commonly perceived as 'trash,' into valuable energy-storage nanomaterials, considered as 'treasure'. Correspondingly, bacteria-derived carbon has garnered significant research attention owing to its inherent heteroatom dopants, distinctive nanostructures, and superior electrochemical properties, making it an excellent candidate as an electrode material for lithium-based batteries. More interestingly, a functional carbon-based nanocomposite can be obtained through harnessing the metabolic processes or biomineralization processes of bacteria to produce materials with desirable properties in a bio-assembly approach, thus achieving the convergent goal of engineering high-performance electrode structures while promoting sustainable development. In this mini review, we summarize the recent research on synthesis strategies of bacteria-derived carbon and nanocomposite materials that offer solutions to critical challenges encountered in lithium-ion and lithium-sulfur batteries. Their distinctive structures and properties, providing enhanced electrochemical performance, were further discussed. This review highlights the recent advancements in the convergent fields of microbiology and energy storage materials, offering new insights and inspiration for researching electrode materials obtained from sustainable and environmentally friendly alternatives.

Key words:

Battery; bacteria-derived carbon; bacteria-derived nanocomposite; biosynthesis of nanomaterials; biomineralization.

1. Introduction

As traditional intercalation-based lithium-ion batteries (LIBs) approach their theoretical energy capacity, there is a growing demand for new chemistry-based rechargeable battery technologies.[1] Considerable efforts have been dedicated to developing electrochemically active materials with high specific capacities, including the substitution of the graphite anode with materials like metal oxides, silicon, or even lithium metal itself, and replacing cathode intercalation materials with high-capacity materials such as sulfur. [2-4]

However, these electrode materials encounter several common challenges that impede their practical applications.[5,6] Unlike the intercalation chemistry in traditional LIBs, the charge storage mechanism in these new anode and cathode materials is based on chemical reactions. This leads to dramatic changes in the volumes of these materials, resulting in the loss of active materials and instability in the solid-electrolyte interphase (SEI). Moreover, their typical poor electronic and ionic conductivities significantly limit the reaction kinetics, and in some cases, these materials even dissolve in the electrolyte. All these factors pose significant challenges in harnessing these high-capacity materials for the next generation of batteries.

The opportunities and challenges are particularly prominent in lithium sulfur batteries (LSBs). LSBs use Li-metal as the anode and sulfur as the cathode material, storing energy through a reversible chemical conversion reaction between sulfur (S) and lithium sulfide (LiS_2). During discharge, lithium combines with S to form Li_2S, which then dissociates during charge. The theoretical capacity of sulfur cathodes (1675 mA h g^{-1}) is more than five times higher than that of traditional $LiCoO_2$ cathode materials used in LIBs. Furthermore, sulfur is abundant and considerably less costly than the cathode materials used in LIBs.[7]

However, the development of LSB technology faces formidable challenges. Sulfur and Li_2S are highly insulating, both electronically and ionically, and there is an 80% volume change between sulfur and Li_2S. An even more critical issue is the easy dissolution of intermittent lithium polysulfides (LiPSs) in the electrolyte and their subsequent shuttling between the cathode and the anode. This results in awful shuttle effect, further complicating the advancement of LSB technology[6,8].

To tackle these challenges, a conventional approach involves reducing the size of the electrochemically active materials and incorporating them into composite structures along with other substances[9,10]. Employing low-dimensional active materials enhances their contact with conductive additives, host materials, and electrolytes, thereby improving the electronic and ionic conductivity of the electrodes[11,12]. Decreasing the size of these materials also helps minimize volume changes during charging and discharging, ensuring the mechanical stability of the electrode[13,14]. In the formation of nanocomposites, the introduced substances can serve various functions, including enhancing the electronic and ionic conductivity of the electrodes, mitigating volume fluctuations, preventing electrode pulverization, and catalyzing redox reactions[15-19]. In the context of sulfur electrodes, host materials can act with polysulfides to restrict their dissolution and diffusion[20,21].

The utilization of a conductive and highly porous carbon material to host sulfur and sulfides has gained popularity in design[22,23]. However, this approach necessitates an excess of electrolyte to fill the carbon pores. This surplus electrolyte increases the ratio of electrolyte to sulfur (E/S) in the cathode, diminishing the overall energy density of the cell[24,25]. Moreover, carbon materials usually have poor affinity and wettability to the electrolyte, decreasing both the capacity and the rate capability.[26] This limitation becomes more significant in practical LSBs, which often operate with limited electrolyte. In such cases, the higher concentration of polysulfides increases the electrolyte viscosity, resulting in sluggish ionic transport due to low E/S ratios[27]. It is advantageous if these hosts also demonstrate robust interactions with sulfur and possess electrocatalytic activity.

Carbon-based materials have also garnered significant attention as anodes in energy storage systems due to their unique properties, high conductivity, and versatile structure[28]. Graphite, among these materials, is one of the most extensively studied and utilized carbon-based anode materials, particularly in LIBs. It offers good cycling stability and moderate capacity. However, it has limitations, including low lithium storage capacity and continuous capacity fade during prolonged cycling due to the formation of SEI layers.[29,30] In recent developments, well-designed nanostructured carbon materials are being explored.[31,32] Since carbon occupies a significant portion of bacteria biomass, bacteria could be an ideal source of nanostructured carbon for battery electrodes.

In nature, numerous biochemical processes occur intrinsically at the nanoscale. Bacteria, although not commonly associated with nanomanufacturing, function as sophisticated nanomachines to produce nanomaterials, which may outperform human-made counterparts. Therefore, bacterial-derived nanostructured carbon might provide an alternative option to human-made carbon materials, aiding in overcoming engineering challenges of battery electrodes.

Moreover, a variety of environmental bacteria play critical roles in the global cycle of various elements. Some of them could be used for biological conversion of pollutants into useful industrial nanomaterials. Such formed nanocomposites could be used for batteries with the merits of sustainable development and environmental protection. Notably, despite the complexity of these bacterial nanomachines, their rapid replication capabilities enable high-throughput production, expanding possibilities for mass production of nanotechnologies.

Exploring bacteria for producing nanomaterials used in new battery technology development holds significant potential for sustainable industrial development. Indeed, bacteria have been utilized in the construction of electrodes to enhance battery performance due to their unique morphology, structure, and functions[33,34].

In this focused review, we aim to provide an overview of the advancements made in exploiting bacteria for lithium-based battery technologies, including LIBs and LSBs. Based on the different approaches used to combine active materials with bacteria or bacteria-derived carbon, we categorize the research into three main areas based on how the nanostructured materials are produced: ex-situ assembly, metabolism-based in-situ assembly, and biomineralization-based in-situ assembly. Before delving into the synthesis methods, we summarize the unique properties of bacteria-derived carbon materials and the calcination process to convert bacteria mass into carbon. We also introduce the three methods to synthesize the nanostructured composites of carbon and active electrode materials.

It is noteworthy that bacterial cellulose has attracted intense interest for its potential use as functional battery separators[35], and carbonized bacterial cellulose has been explored as electrode scaffolds.[36,37] However, since bacteria themselves are not directly applied in these applications, they are not included in this focused mini review.

2. Bacteria-derived carbon and nanocomposite assembly

2.1. Properties of bacteria-derived carbon and the calcination process

Bacteria are composed of various structural elements, including a secreted capsule, cell wall, cell membrane, cytoplasm, and a circular chromosome, which together form a hierarchical microcapsule structure. The cytoplasm contains water and organic structural elements. Since bacteria possess a high carbon content, they are an excellent carbon source used to enhance the electronic conductivity of electrodes.[38]

Bacterial biomass is converted into carbon nanomaterials through controlled pyrolysis or calcination. In this process, organic components within the biomass undergo thermal degradation and vaporization, resulting in the formation of carbon-rich residues with porous interiors. These residues maintain a complex hierarchical structure inherited from the original biomass, characterized by a network of pores spanning multiple length scales[39,40].

Nitrogen (N), sulfur (S), and phosphorus (P) are vital nutrients for bacteria, and bacteria biomass also contains oxygen (O). Bacteria-derived carbon contains these elements as dopants. They modify the carbon's electronic properties, resulting in enhanced conductivity and a chemically polar surface. This polarity modification significantly enhances the electrode surface wettability towards electrolyte as well as its strong adsorption ability to polar LiPSs, hence inhibiting polysulfide shuttling[21,41,42]

The properties of bacteria-derived carbons are profoundly influenced by the calcination conditions. Factors such as temperature, heating rate, and duration of calcination determine the extent of thermal decomposition and carbonization. Higher calcination temperatures generally result in increased carbon content and improved structural ordering. However, excessive temperatures might lead to the loss of beneficial heteroatoms and reduction in surface area. The carbon yield depends on the calcination temperature and the bacterial strains. At 800ºC, the yield is between 60-20%.[43]

Guo et al. investigated the effect of pyrolysis temperatures ranging from 800 to 1000 ℃ on the morphology of heteroatoms doped carbon by carbonizing S. oneidensis MR-1 bacteria.[40] The resultant carbon products maintain the cylindrical shape of bacteria, but their surfaces become rough with irregular pores formed after pyrolysis under high temperatures. Heteroatoms, including N, P, S, and Fe, are distributed homogeneously on the carbon support. The study revealed that the diameter of pores on carbon surfaces becomes larger with increasing pyrolysis temperatures, while the specific surface areas also increase. Consequently, the resulting carbon materials exhibit a spectrum of oxygen reduction reaction catalytic properties contingent on the calcination parameters due to more available active sites exposed.

Optimal calcination conditions strike a balance between retaining the original biomass's beneficial characteristics and fostering the formation of a well-organized, conductive carbon matrix. Therefore, tailoring calcination conditions is a critical aspect of designing bacteria-derived carbons with optimal performance for energy storage applications.

2.2. Three methods to form nanocomposites

Carbon nanomaterials derived from bacteria are valuable, but for battery applications, they must form nanostructured composites with active electrode materials. Three methods can be applied to obtain these nanocomposites: ex-situ assembly, metabolism-based in-situ assembly, and biomineralization-based in-situ assembly.

- Ex-situ assembly

In this method, a selected bacterial strain is cultivated, and its biomass is then calcinated into heteroatom-doped porous carbon. Subsequently, the resulting carbon material is mixed with an active electrode material to form a nanocomposite as the electrode material. Although the biological processes in bacteria influence the nanostructure of the derived carbon, the assembly of nanocomposites is isolated from the biological process of bacteria. Hence, this method is named ex-situ assembly.

- Metabolism-based in-situ assembly.

Bacterial metabolism encompasses a series of chemical reactions that enable bacteria to extract energy from nutrients, grow, reproduce, and respond to their environments. The specific pathways and enzymes involved can vary based on bacterial species, nutrient availability, and environmental conditions. What's particularly intriguing about bacterial metabolism is that certain bacteria utilize industrial pollutants as their nutrients, generating electrochemically active materials. This transformation converts what we traditionally consider 'waste' into valuable resources.[44]

Cultivating these bacteria can occur under mild conditions with minimal energy consumption. Moreover, this process doesn't necessitate complex or costly toxic chemicals. Harnessing bacteria not only enhances battery performance but also offers significant cost benefits and environmental protection. This aligns with the overarching objective of developing high-performance electrode structures and promoting sustainable development.

Metabolism-based in-situ assembly of electrode nanocomposites involves directly utilizing bacterial metabolic pathways to generate electrochemically active materials. By engineering specific bacterial strains and their growth conditions, these metabolic processes can be harnessed to produce nanocomposites in-situ with desirable properties. It's worth noting that an additional step is required to convert the bacterial structure into the electrode nanocomposite.

- Biomineralization-based in-situ assembly.

In contrast to metabolism, biomineralization refers to the process in which bacteria influence the formation or precipitation of inorganic minerals, often as a byproduct of their metabolic activities. In synthesizing electrode materials for batteries, bacteria are employed to facilitate the growth and deposition of inorganic materials on their surfaces. This process enables the formation of composite materials with enhanced electrochemical performance. Bacteria's metabolic activity is utilized to promote the production of specific inorganic materials as needed.

What makes this approach particularly intriguing is that certain bacteria secrete polysaccharides and proteins on their surfaces, acting as binding ligands. These ligands are vital for the bacteria's colonization of host tissues. These surface binding anchors can be utilized for precursor nucleation, leading to the production of nanoscale metals, silicon, oxides, and other compounds. When combined with heteroatom-doped hierarchical porous carbon, these nanomaterials serve exceptionally well as electrode materials in batteries, ensuring high performance.

3. Ex-situ assembly

Ex-situ assembly involves integrating electrode active materials and ancillary components into bacteria-derived carbon nanostructures to create composites. The carbon nanostructure can be obtained by directly carbonizing bacteria biomass, or bacteria can be modified with other materials before carbonization, resulting in more intricate carbon nanostructures. Afterward, specific active materials are mixed with these bacteria-derived carbon nanostructures to form composites with enhanced electrochemical properties. This method is frequently employed in constructing sulfur cathodes for LSBs, where bacteria-derived carbon nanostructures serve as hosts for the active sulfur material, enhancing the overall performance of the electrodes.

Progress in LSB technology has faced challenging issues associated with the sulfur cathode, including the low electronic and ionic conductivities of elemental sulfur and Li_2S, significant volume changes of the sulfur electrode during charge/discharge cycles, and especially the shuttle problem of lithium polysulfides (LiPSs) when they are dissolved in the electrolyte.[45] To address these challenges, various carbon-based host materials have been developed to combine with sulfur, enhancing its electronic conductivity, mitigating volume changes, and simultaneously suppressing the dissolution and diffusion of LiPSs.

Bacteria-derived carbon nanostructures serve as ideal host materials for sulfur due to their enhanced conductivity, hierarchical pores, and polar surface. Notably, the presence of hetero-elements like N, O, P, and others in bacterial-derived carbon allows for strong interactions with LiPSs, effectively mitigating the shuttle effect. Elemental sulfur, owing to its low melting temperature, can be melted and diffused into bacteria-derived carbon nanostructures to form cathode materials. Alternatively, another approach involves infiltrating dissolved metal sulfide into bacteria, followed by carbonization of the bacteria and oxidation of the metal sulfide to elemental sulfur. These methods showcase the versatility and effectiveness of utilizing bacteria-derived carbon nanostructures in enhancing the performance of sulfur-based cathodes.

Li et al.[42] reported applying gram-positive bacteria *Bacillus subtilis* for the sulfur cathode design. *Bacillus subtilis* are capable of fixing N and P from their environmental nutrients and form a hierarchical structure. The rationale is to use N and P co-doped biological carbon as the sulfur host to enhance cathode conductivity, buffer volume expansion, and suppress the shuttling problem. After ball milling the mixture of bacteria biomass with sulfur particles and then calcining it at 500 °C, sulfur molecules break their eight-membered ring structure and establish C-S covalent bond with the bacteria-derived N, P co-doped carbon spheres. When applied as a sulfur electrode, the composite delivered a high reversible capacity up to 880 mAh

g^{-1} after 15,000 cycles with an ultra-low-capacity decay rate of 0.0024% per cycle. The superior stability was attributed to formation of covalent bonds between S and C and the strong adsorption between N, P co-doped carbon and LiPSs.

It is worth noting that in the above work, calcination at 500 °C is insufficient to convert biomass to highly conductive carbon. Higher calcination temperatures, although beneficial for carbon conductivity, result in a significantly reduced sulfur content in the formed composite. To overcome this paradox, Na_2S, with its much higher melting point, can be used as the sulfur precursor. In the work of Wang et al. [46] , *Bacillus subtilis* were first infiltrated with Na_2S solution. N, P co-doped carbon microspheres filled by sulfur nanoparticles (S@NPCS) with a sulfur content of 81.5% were then achieved by annealing the resulting composite (Na_2S/*Bacillus subtilis*) at 700 °C, followed by the oxidation of Na_2S to elemental sulfur (Fig. 1 (a)). The S@NPCS cathode exhibits exceptionally stable cycling performance (an ultralow capacity fading rate of 0.045% per cycle during 1,000 cycles at the current rate of 5 C), high specific capacity (1193.8 mAh g^{-1} at 0.5 C based on sulfur weight), and excellent rate capability. The superior performance was attributed to the high electronic conductivity of the bacteria-derived carbon, as well as the physical confinement and chemical binding of LiPSs resulting from the porous and N, P co-doped bacteria-derived carbon. These factors significantly suppress the shuttling of polysulfides.

Other N-rich bacteria have also been explored to create sulfur and carbon composites. Considering the low melting point of sulfur and the fact that biomass-derived carbon with high electronic conductivity can typically be achieved only under high temperatures, the usual practice involves first obtaining bacteria-derived carbons at high calcination temperature and then infiltrating them with sulfur through melt diffusion..[47,48] After carbonizing yeasts (*Saccharomyces cerevisiae*) and microalgaes (*Schizochytrium sp.*), N-doped hollow porous carbon microspheres (NHPCM) were achieved, which showed a hollow sphere morphology (Fig. 1(b)-Fig. 1(c)). The scanning transmission electron microscopy (STEM) and energy dispersive X-ray spectroscopy (EDS) mapping results indicate that sulfur particles are distributed not only inside the hollow voids but also within the shell pores (Fig. 1(d)-Fig. 1(i)). As demonstrated in Fig. 1 (e), the interlayer spacing between two distorted lattice fringes slightly expands from 0.35 to 0.39 nm, suggesting that some low-molecular sulfur may have been embedded into the graphitic layers, forming a strong affinity with NHPCMs. These nanoparticles have a specific surface area and a pore volume as high as 721 m^2 g^{-1} and 0.86 cm^3 g^{-1}, respectively, whose porous structure provides electrochemically reactive sites and reservoir for sulfur species. The high nitrogen content (6.9 wt% to 9.1 wt%) in NHPCMs not only improves the carbon wettability by electrolyte, but also offers strong adsorption ability to LiPSs. Thus, the NHPCM/S delivered a reversible specific capacity of 1202 mAh g^{-1} and exhibited a capacity retention of 725 mAh g^{-1} over 400 cycles at 0.1 C with a capacity decay of 0.09 % per cycle, as well as an enhanced rate performance of 587 mAh g^{-1} at 2 C,[47] as shown in Fig. 1 (j) and (k).

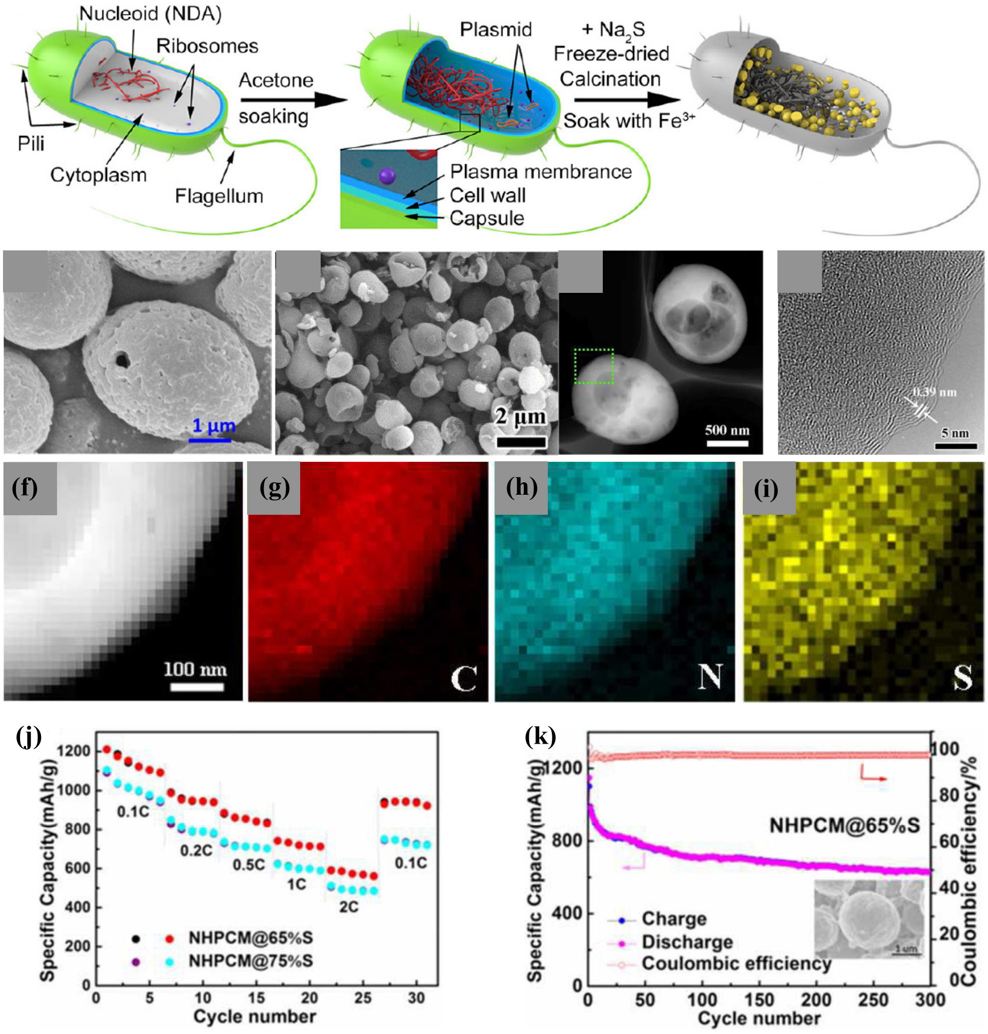


Fig. 1 (a) Schematic illustration of the synthesis process to S@NPCS. (b) SEM image of NHPCMs derived from *Saccharomyces cerevisiae*. (c) SEM image of NHPCMs derived from *Schizochytrium sp.* (d) STEM and (e) HRTEM images of NHPCM embedded with sulfur; (f) High magnification STEM image taken from the selected area in (d); (g-i) EDS mapping results of C, N and S. (j) rate and (k) cycling performance of LSBs based on NHPCM/S. Reproduced with permission from Ref. [46] for (a) ©2017 American Chemical Society, Ref.[47] for (b, j, k) ©2016 the Royal Society of Chemistry, and Ref.[48] for (c-i) ©2017 American Chemical Society.

To enhance the chemical adsorption of host materials to LiPSs further, a variety of polar inorganic nanoparticles are introduced into the bacteria-derived carbon microspheres or nanorods.[49,50] As illustrated in Fig. 2 (a), a core-shell structure (C@TiO_2) with a carbon core and a TiO_2 shell was developed to host sulfur. TiO_2 nanoparticles were nucleated on the surface of *staphylococcus aureus* (*S. aureus*), a round-shaped bacterium (Fig. 2 (b)), through the hydrolyzation of titanium tetraisopropoxide (TTIP) to achieve core-shell structured *S. aureus*@TiO_2 (Fig. 2 (c)). Then, a core-shell structure C@TiO_2 was realized by heating *S. aureus*@TiO_2 at 800 °C, as shown in Fig. 2 (d). Sulfur was infiltrated into C@TiO_2 through a melt diffusion method to achieve C@TiO_2/S (Fig. 2 (e)-(f)). When C@TiO_2/S was applied as sulfur electrode, the carbon core enhances the electronic conductivity of the sulfur electrode, while the TiO_2 shell serves as a barrier for the LiPSs diffusion outside due to the strong binding between TiO_2 and LiPSs. In addition, the void between the carbon core and the TiO_2 shell ameliorates the volume change of sulfur electrode during the charge/discharge process. It is worth noting that due to the different polarities of different sulfur species, host materials showing bipolar properties will synergistically enhance the electrochemical performance of LSBs.[21] In addition, the TiO_2 shell strengthens the mechanical integrity of the sphere structure, as the direct heat treatment of *S. aureus* powders would result in the morphological collapse of spherical *S. aureus*. As shown in Fig. 2 (l), the LSBs based on C@TiO_2/S demonstrates a low capacity decay rate of 0.016% per cycle at 1.5 A g^{-1} over 1500 cycles, showing a much better cycling stability than C/S.

Besides TiO_2, Fe_2P nanoparticles were also introduced to decorate the bacteria-derived carbon nanorods, as shown in Fig. 2 (g).[50] Specifically, after *bacillus cereus*, a rod-shaped bacterium, added into the Fe-containing electroplating sludge leaching solution, the Fe^{3+} ions were either trapped on the bacteria wall by electrostatic interactions or gradually penetrated inside the bacteria. Through annealing Fe^{3+}/*bacillus cereus*, N, P co-doped carbon nanorods decorated with Fe_2P (NPC@Fe_2P) were achieved (Fig. 2 (h-k)). When NPC@Fe_2P was applied as the host materials, the sulfur electrode delivered a high specific capacity (1555.7 mAh g^{-1} at 0.1 C), appreciable rate capability (679.7 mAh g^{-1} at 10 C), and greatly enhanced cycling performance (761.9 mAh g^{-1} at 1.0 C after 500 cycles). This could be attributed to the high electronic conductivity resulting from the carbonized bacteria, the strong adhesion to LiPSs and the catalyzed Li_2S decomposition resulting from Fe_2P nanoparticles. The performance comparison between NPC/S and NPC@Fe_2P/S electrode further verifies the effects of the Fe_2P nanoparticles (Fig. 2 (m)). This work provides a strategy for direct biological recycling of iron metal from electroplating sludge using bacteria.

In this ex-situ assembly strategy, although a high percentage of sulfur could be embedded inside the nanopores of bacteria-derived carbon through sulfur melting and diffusion, it is unavoidable that some sulfur particles distribute outside the bacteria or the bacteria-derived carbon spheres. Consequently, the loss of active materials still occurs due to the detachment of sulfur particles, as well as the dissolution and diffusion of LiPSs.[6]

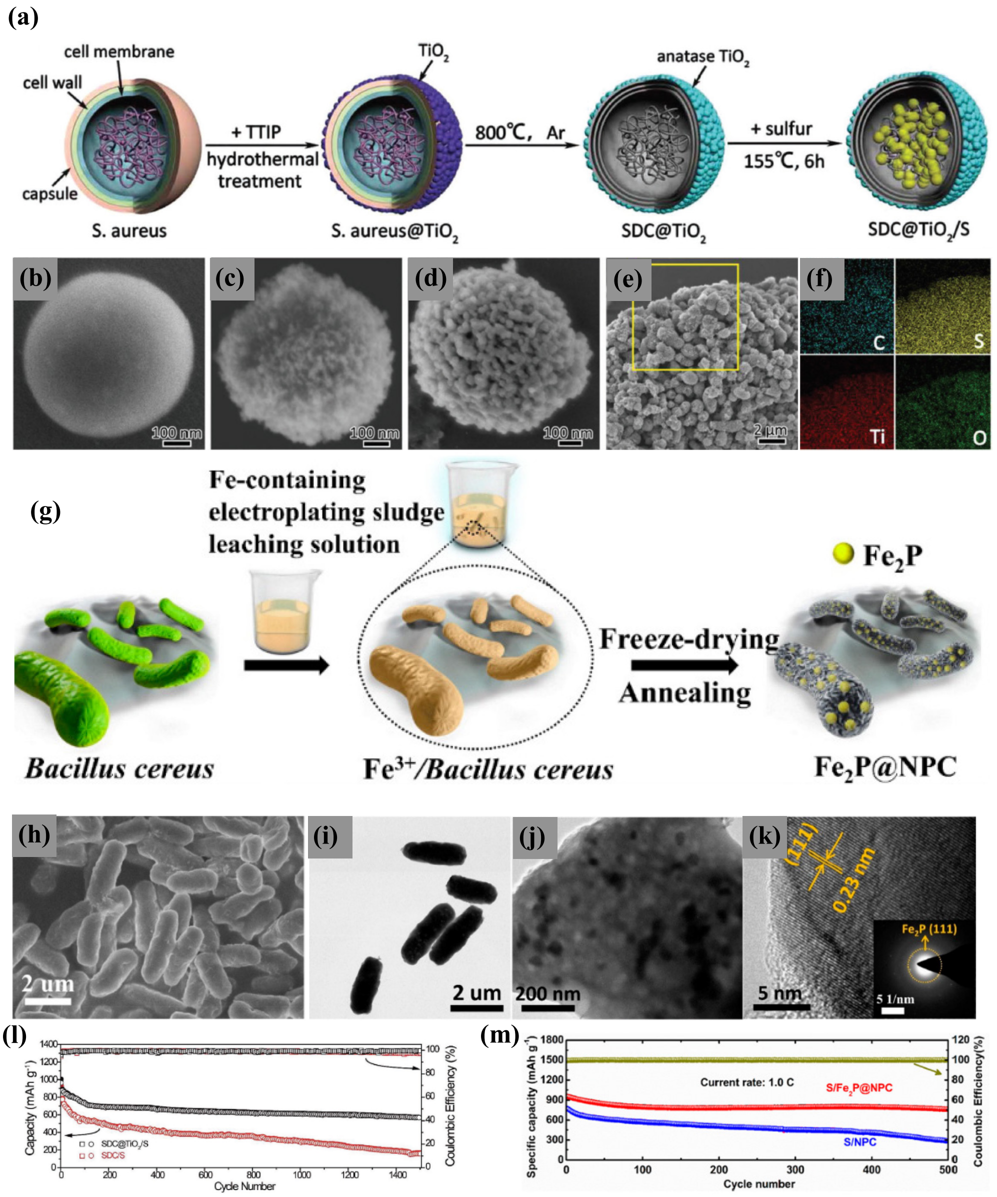


Fig. 2 (a) Schematic illustration of the synthetic procedure for the biomimetic microcapsule confined sulfur cathodes; SEM images of (b) *S. aureus*, (c) *S. aureus*@TiO_2, (d) SDC@TiO_2, and (e) SDC@TiO_2/S; (f) Elemental mapping of SDC@TiO_2/S. (g) Schematic illustration of the synthetic process of Fe_2P@NPC materials; (h) SEM, (i) TEM and (j-k) HRTEM images of Fe_2P@NPC. Cycling performance of LSBs based on (l) SDC/S and SDC@TiO_2/S, and (m) NPC/S and Fe_2P@NPC/S. Reproduced with permission from Ref. [49] for (a-f) ©2018 WILEY-VCH, Ref. [50] for (g-m) © 2022 American Chemical Society.

4. Metabolism-based in-situ assembly

Compared to the ex-situ assembly where biological processes in bacteria only provide a biomass structure to derive carbon, metabolism-based in-situ assembly represents a more advanced technology for composing bacteria or bacteria-derived carbon with active materials. It utilizes bacteria with a dual function: facilitating the biogenic preparation of active materials during bacterial respiration and providing a direct carbon source after calcination. More interestingly, some pollutants can serve as nutrient solutions to produce nanostructured materials in the metabolism process of bacteria, thus transforming 'trash' into 'treasure'.

Tellurium, Fe_2O_3, and Fe_3O_4 are three anode materials of LIBs with high theoretical specific capacity. However, due to their significant volume expansion, low electronic conductivity, and unstable SEI, these materials often experience rapid capacity fading during charge/discharge cycling and exhibit inferior rate capability. To address these issues, nano-sizing has been considered a solution to alleviate their volume variation during cycling and improve their electrochemical performance. Instead of employing conventional methods for nano-sizing, three types of bacteria have been explored to directly produce their nanostructures.

As an industrial waste, tellurite (TeO_3^{2-}) could be reduced to polycrystalline Te(0) nanorods by the dissimilatory metal reducing bacteria *Shewanella oneidensis MR-1*, as shown in Fig. 3(a).[51] Te nanorods were observed to be extracellular when Fe^{3+} was introduced into the culture solution (Fig. 3(b)), while they were found intracellularly in the absence of Fe^{3+} (Fig. 3(c)).

To enhance the electronic conductivity of the composite, the Te nanorods/bacteria combination underwent thermal treatment in an inert atmosphere at high temperatures. As a result, the extracellular Te nanorods tended to aggregate and lost their nanorod structure (Fig. 3(d)). In contrast, the intracellular Te nanorods maintained their rod-like shape within the carbon matrix derived from bacterial cells (Fig. 3(e)). Additionally, while extracellular Te nanorods retained their polycrystalline nature, intracellular ones transformed into an amorphous phase. The tellurium encapsulated inside bacteria can be thermally affected by the amorphous carbon resulting from the thermal decomposition of organic bacteria. Carbon thermally diffuses into the amorphous Te phase, preventing the melted Te from undergoing reversible assembly and recrystallization during the cooling process. In contrast, the extracellular Te nanorods are relatively unaffected by bacterial thermal decomposition.

When applied as electrodes, *in situ* X-ray absorption fine structure and *in situ* wide-angle X-ray diffraction characterizations revealed distinct properties of carbonized extracellular and intracellular Te nanorods. Polycrystalline Te undergoes a phase transition to Li_2Te with Te_n^{2-} as intermediates, while amorphous Te exhibits a simple Li^+ accumulation around the Te element with only anionic redox reaction, thus mitigating volume expansion and enhancing lattice stabilization. Furthermore, carbon shells derived from bacterial cells provide an electronic pathway for intracellular Te nanorods. Therefore, intracellular Te nanorods demonstrate superior performance compared to extracellular Te nanorods.

However, due to tellurium's low melting point, the Te/bacteria composite was not subjected to a temperature high enough to achieve bacteria-derived carbon with high electronic conductivity. This limitation hampers the electrochemical performance of the Te electrode.

Acidithiobacillus ferrooxidans, a gram-negative bacterium, is able to gain energy via the oxidation of ferrous ions (Fe^{2+}) along with the consumption of protons (H^+) in acidic metallurgy sewage to produce insoluble ferric substances (Jarosite, $KFe_3(SO_4)_2(OH)_6$), as shown in Fig 3(h, i). The authors put forward a plausible process for the formation of $KFe_3(SO_4)_2(OH)_6$ as follows:

$$4\ Fe^{2+} + O_2 + H^+ \rightarrow 4\ Fe^{3+} + 2\ H_2O$$

$$K^+ + 5\ OH^- + 3\ Fe^{3+} + 2\ SO_4^{2-} + H_2O \rightarrow KFe_3(SO_4)_2(OH)_6 \downarrow + H^+$$

Single crystalline α-Fe_2O_3 nanorods, growing along the [110] direction, are obtained from Jarosite precursor through a straightforward heat treatment in air, as depicted in Fig. 3(j, k). The exposed (001) facets on the Fe_2O_3 nanostructures impart superior stable crystalline structure and high Li^+ diffusion coefficients to Fe_2O_3 anodes. These biometabolic α-Fe_2O_3 nanorods exhibit an outstanding stable capacity of 673.9 mA h g^{-1} at 100 mA g^{-1} over 200 cycles and demonstrate remarkable multi-rate capability that significantly outperforms the commercial counterpart.

Su *et al.* applied magnetotactic bacteria to achieve carbon encapsulated Fe_3O_4.[52] The bacteria *Magnetospirillum magneticum strain AMB-1* (ATCC 700264) was employed for producing bacterial magnetic nanoparticles (BMPs) with Fe_3O_4 nanocrystals enveloped by a lipid bilayer.[53] These BMPs exhibited an average particle size of 50 nm with a 4.1 nm thick bio-membrane coating, as illustrated in Fig. 3(l, m). By subjecting the BMPs to high-temperature treatment, nitrogen-doped carbon (NC) encapsulated Fe_3O_4 materials (Fe_3O_4@NC) were fabricated.[52] As shown in Fig. 3(n, o), the obtained core-shell Fe_3O_4@NC had a monodispersed size of around 50 nm covered with 1.6 nm thick C shell. The Fe_3O_4@NC electrodes retained a capacity of 860 mA h g^{-1} at a current density of 2 A g^{-1} after at least 1,000 charge-discharge cycles when testing against a lithium-metal anode.

It is crucial to emphasize that in the metabolic processes of bacteria aimed at converting pollutants into valuable battery electrode materials, these pollutants serve as a source of nutrients for the bacteria. Certain bacteria have the capability to utilize tellurium ions as electron acceptors during anaerobic respiration, thereby enhancing the microbial reduction of contaminants present in wastewater[54]. Similarly, some bacteria can employ Fe_2O_3 as electron donors in their metabolic reactions, promoting the reduction of contaminants. For instance, the combination of Fe_2O_3 nanomaterials with bacteria can be employed in bioreactors to augment the removal of phosphate from wastewater[55].

Moreover, certain bacteria can form interactions with Fe_3O_4 nanocrystals, facilitating both the degradation of pollutants and electron transfer. This is possible because Fe_3O_4 can function as both electron donors and acceptors. Bacteria are capable of utilizing Fe_3O_4 nanomaterials in redox reactions, thereby enabling the microbial reduction of pollutants while assisting in the subsequent oxidation of reduced species. This dual functionality allows for the simultaneous removal of pollutants and generation of energy[56].

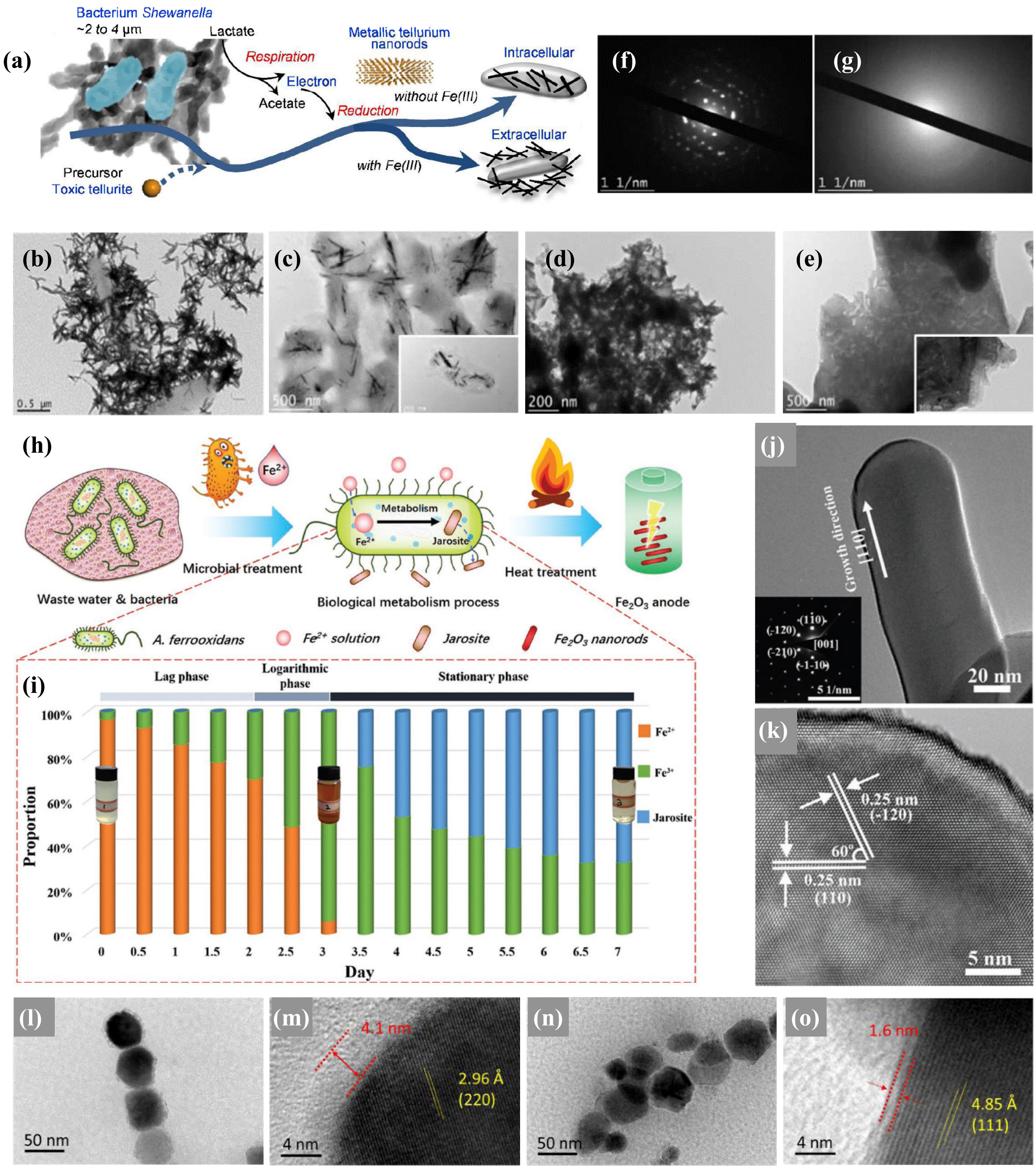


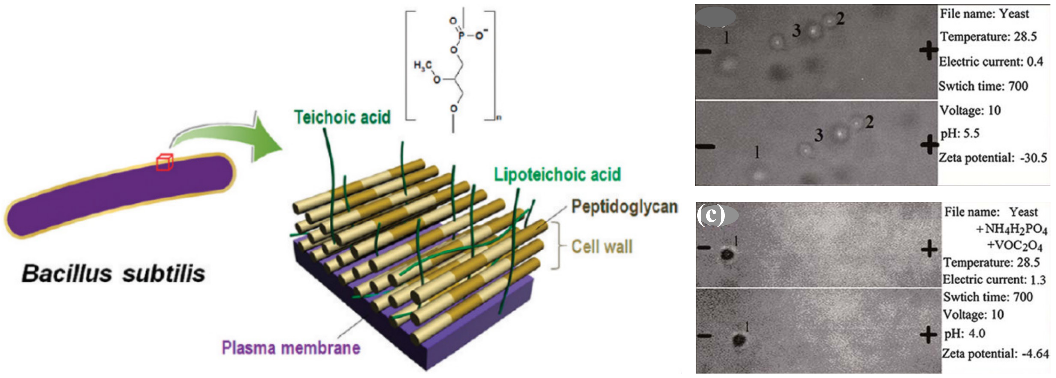
Fig. 3. (a) A schematic illustrating the process of TeO_3^{2-} reduced to Te(0) by *S. oneidensis MR-1*.[51] TEM images of extracellular Te nanorods (b) and intracellular Te nanorods (c) produced by *S. oneidensis MR-1*. TEM images of extracellular Te nanorods (d and f) and intracellular Te nanorods (e and g) produced by *S. oneidensis MR-1* after high temperature treatment. (h) A schematic illustrating the biological metabolism synthesis process and Li storage application of Fe_2O_3 nanorods. (i) The concentration variation histogram of Fe^{2+}/Fe^{3+} and metabolic products in 9K medium. (j) TEM and (k) HRTEM images of Fe_2O_3 nanorods. TEM and

HRTEM images of BMPs before (l-m) and after (n-o) high temperature treatment. Reproduced with permission from Ref. [51] for (a-g) © 2015 the Royal Society of Chemistry, Ref. [44] for (h-k) © 2019 the Royal Society of Chemistry, Ref. [52] for (l-o) © 2019 Wiley-VCH.

5. Biomineralization-based in-situ assembly

Biomineralization function of bacteria qualifies them as nanomachines to assemble nanostructures in-situ.

Due to the presence of multiple peptidoglycan sacculus layers consisting of polymeric chains of teichoic acid and teichuronic acid, bacteria exhibit a negatively charged surface, as depicted in Fig. 4(a). For instance, the Bacillus subtilis suspension demonstrates a negative zeta potential of -46 mV, indicating its strong negative charge, which allows bacteria to attract metal ions effectively.[57,58] In contrast, yeast cells initially possess a zeta potential of -30.5 mV. However, after adsorbing cations, their surfaces retain excess negative charges, resulting in a zeta potential changes to -4.64 mV, as shown in Fig. 4(b)-(c).[59]



File name: Yeast
Temperature: 28.5
Electric current: 0.4
Swtich time: 700
Voltage: 10
pH: 5.5
Zeta potential: -30.5

File name: Yeast $+NH_4H_2PO_4$ $+VOC_2O_4$
Temperature: 28.5
Electric current: 1.3
Swtich time: 700
Voltage: 10
pH: 4.0
Zeta potential: -4.64

Fig. 4. (a) A schematic illustrating the cell wall of Bacillus subtilis. Micro electrophoresis of purified yeast cells (b) and yeast cells after contact interaction with the cations. Reproduced with permission from the publishers. Reproduced with permission from Ref. [57] for (a) © 2010

American Chemical Society, and Ref. [59] for (b,c) © 2012 the Royal Society of Chemistry.

With their ability of attracting metal ions, bacteria can serve as an effective template to synthesize nanomaterials. By selecting *bacillus subtilis*, *micrococcus lylae*, or *Escherichia coli* as templates, a variety of electrochemically active nanomaterials have been developed (Fig. 5(a)-(g)), such as Co_2O_3 hollow nanorods,[57] MnO_2 hollow nanorods,[60] SnO_2 hollow nanorods,[33] Fe_3O_4 hollow microspheres and core-shell structured C@Fe_3O_4 microspheres,[61] core-shell structured C@Fe_3O_4 nanorods.[62] Specifically, bacteria are dispersed in solutions containing metal ions. The metal ions are subsequently adsorbed onto the cell wall and then chemically converted into a metal oxide film coating on the bacteria. The thickness of the metal oxide shell can be easily controlled by synthetic conditions, particularly the concentrations of the cations. As a result, the morphology of the bacteria is replicated by metal oxide. For example, when selecting rod-shaped bacteria such as *Escherichia coli* and *Bacillus subtilis* as templates, rod-shaped metal oxide nanostructures are achieved. In contrast, using spherical bacteria like *Micrococcus lylae* leads to the formation of spherical metal oxide nanostructures. When bacteria coated with metal oxides are subjected to calcination in the presence of air, the bacteria are removed, leaving behind hollow metal oxide structures. Conversely, calcination in an inert atmosphere converts the bacteria into carbon, resulting in a core-shell structure with a carbon core and a metal oxide shell. Since the carbon core enhances the electronic conductivity of the electrode, the core-shell structure exhibits superior performance compared to the hollow metal oxide structure.[61]

Elemental Si nanostructures have also been synthesized through biomineralization.[63]

Micrococcus bacteria are dispersed in a solution containing tetraethyl orthosilicate (TEOS). With the addition of NH_4OH and the resulting hydrolysis of TEOS, silica is coated on the bacteria. Through magnesiothermic reduction, the silica shell is converted to a porous hollow Si shell. Additionally, during high temperature treatment, the bacteria transform to amorphous carbon in the porous hollow Si spheres, improving the electronic conductivity of Si. The Si hollow spheres have a large specific surface area and a high pore volume of 314 $m^2\ g^{-1}$ and 0.927 $cm^3\ g^{-1}$, respectively, which helps buffer large volume changes during lithiation and delithiation and improve their contact with the electrolyte and conductive additives. Thus, the achieved Si hollow spheres demonstrate better performance than commercial Si nanopowder, as shown in Fig. 5(h).

Metal pyrophosphates and lithium metal phosphates have been synthesized through biomineralization. Yang et al. developed a strategy to synthesize $Mn_2P_2O_7$@carbon microstructures with a $Mn_2P_2O_7$ yolk and a carbon shell, as shown in Fig. 5(i)-(k).[64] Specifically, the *Gram-positive Bacillus Subtilis* (*GPBBS*) bacteria adsorb the metallic ions (Mn^{2+}) via their bacterial walls and retain them in their interior. The Mn^{2+} ions combine with the phosphorous organic compounds present in the bacteria to form multiple MnH_2PO_4 nanoparticles in each cell. After annealing under an inert atmosphere, these MnH_2PO_4 nanoparticles and the bacterial wall transform into $Mn_2P_2O_7$ nanoparticles encapsulated inside the same carbon shell. The yolk-shell structure with internal void space alleviates the volume expansion of the electrode during the charge/discharge process. The carbon shells act as an ideal barrier, limiting most solid–electrolyte interphase formation on the surface of the carbon films. Upon further blending with reduced graphene oxide, the anode exhibited high capacities, long cycle-life, and excellent rate performance.

Leveraging the electrostatic interaction between yeast cells and cations, mesoporous $Li_3V_2(PO_4)_3$/C microspheres have been synthesized.[59] Vanadium ions (V^{3+}), Li^+, and PO_4^{3-} are successively adsorbed and coated on and into the yeast cells. Subsequently, crystalline $Li_3V_2(PO_4)_3$ and amorphous carbon are formed through high-temperature treatment. Initially, the chemically formed $Li_3V_2(PO_4)_3$ is uniformly distributed inside the bacterial bodies. During high-temperature treatment, the growth in the size of $Li_3V_2(PO_4)_3$ can be effectively suppressed, enhancing electron and lithium-ion conductivity.

In some cases, the production of electrochemically active materials involves both metabolism and biomineralization processes, as depicted in Fig. 5(l).[65] Previously, the recombinant *E. coli* strain was shown to accumulate excess phosphate through the overexpression of polyphosphate kinase (PPK) in the cell. The PPK enzyme catalyzes excess phosphate into polyphosphate (polyP) while maintaining the overall cytoplasmic phosphate concentration constant. When PPK enzymes are in excess, bacteria cells absorb phosphate from their environment, accumulating them as polyP granules. This function is not limited to *E. coli*; *Acinetobacter* and *Actinobacter* also exhibit this capability. The phosphate-rich recombinant *E. coli* cells were further treated with acidic solutions containing Fe^{3+} or Mn^{2+}. High-energy phosphoanhydride bonds found between phosphate units in polyP molecules are readily broken down under acidic conditions, releasing phosphates. The Fe-PO_4 or Mn-PO_4 complex is achieved through the combination of Fe^{3+} or Mn^{2+} and PO_4^{2+}. Upon adding lithium salt and high temperature treatment, the bacteria cell bodies transformed into a carbon film with a thickness of 3–5 nm. This carbon film provided a conductive carbon matrix dispersing the

$LiFePO_4$ and $LiMnPO_4$ nanoparticles (20 nm), preventing their aggregation into larger particles at high temperatures, as shown in Fig. 5(m)-(o). Both carbon coating and particle size tailoring contributed to better electrochemical performance of LIB. Even under 10 C, a stable discharge capacity of 75 mA h g^{-1} could still be achieved.

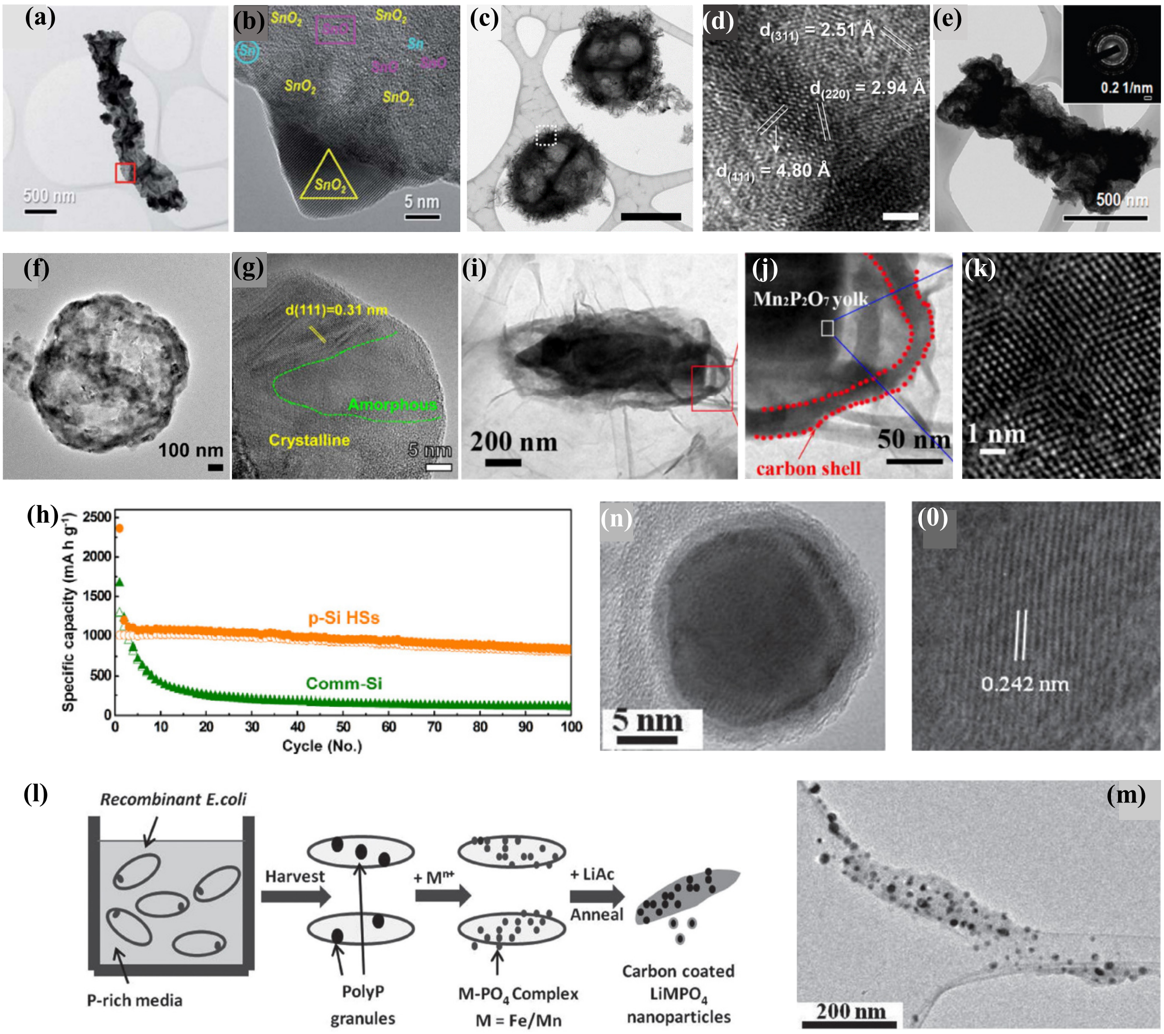


Fig. 5. (a) TEM and (b) HR-TEM images of SnO_2 nanorods. (c) TEM and (d) HR-TEM images of Fe_3O_4 hollow nanospheres. (e) TEM image of Co_3O_4 nanorods. The inset shows its SAED pattern. (f) TEM and (g) HR-TEM images of Si hollow spheres. (h) The comparison of cycling performance between Si hollow spheres and commercial Si powder. (i) and (j) TEM images of

the yolk-shell structured $Mn_2P_2O_7$@C, and (k) HR-TEM image of $Mn_2P_2O_7$. (l) A schematic showing the production process of electrochemically active materials combining metabolism and biomineralization. (m) TEM and (n) HR-TEM image of carbon coated $LiFePO_4$ nanoparticles.[65] (o) HR-TEM image of $LiFePO_4$.[65] Reproduced with permission from Ref. [33] for (a,b) © 2012 Wiley-VCH, Ref. [61] for (c,d) © 2012 European Chemical Societies Publishing, Ref. [57] for (e) © 2012 American Chemical Society , Ref. [63] for (f-h) © 2017 Elsevier, Ref. [64] for (i-k) ©2016 American Chemical Society, and Ref.[65] for (l-o) ©2015 Wiley-VCH.

6. Discussion

Nanocomposites assembled by bacterial nanomachines have emerged as a potential solution to address challenges in the next generation of batteries, offering several key merits:

1) A hierarchical structure of porous carbon: The intricate organization of bacterial cells gives rise to a hierarchical pore structure, facilitating a well-defined ion diffusion pathway. This structure reduces diffusion limitations, enabling faster charge/discharge kinetics.[66] Additionally, the mesoporous/microporous structure helps alleviate strain caused by volume changes during cycling, promoting extended cycling stability. The microporous structure physically confines dissolved LiPSs, reducing the loss of active materials.[67]
2) Heteroatom doping in carbon: Heteroatoms originating from bacterial biomass modify the electronic properties of the carbon material. This modification results in enhanced conductivity and a chemically polar surface, improving the electrochemical performance and stability of the electrodes.[68]

3) Uniformly dispersed active nanomaterials in the carbon host: Metabolism- and biomineralization-based biosynthesis methods enable the impregnation of metal ions into living bacteria during culture, while the growth of nanoparticles is thermally driven at elevated temperatures during calcination, in which bacteria are converted into porous carbon, facilitating the uniform distribution of metal cations in the precursor to obtain highly dispersed nanomaterials. For instance, Kang et al. utilized a cost-effective, non-pathogenic bacterial precursor easily harvested by collecting Escherichia coli in an iron/nickel ion-enriched liquid medium. This precursor was then directly calcinated, resulting in highly dispersed nano-catalysts named BC-FeNi. The bacterial precursor served as a carbon source, carbonized into highly-stable mesoporous graphitized carbon, and embedded with FiNi alloy nano-catalysts to generate the GC-FeNi nanocomposite with high FeNi dispersion.[69]
4) Easy replication of nanostructures: Maintaining bacterial culturing factors within a reasonable range ensures that the biological processes in bacteria can precisely synthesize or replicate their nanostructures. When the calcination process is well controlled, the final nanocomposites for battery electrodes can be easily replicated, ensuring their consistency.
5) Environmentally benign manufacturing. Utilizing nonharmful bacterial strains to produce nanomaterials is inherently environmentally friendly. Additionally, bacteria possess a natural decontamination function, transforming contaminants into valuable resources, thereby contributing to a sustainable and eco-friendly manufacturing process.

Among the three methods reviewed, ex-situ assembly relies on bacterial biomass to supply the carbon source, and formation of active electrode nanocomposites is performed after bacterial growth. In contrast, the two in-situ methods, metabolism- and biomineralization-based, create nanostructures during bacterial growth.

Metabolism and biomineralization are both biological processes occurring within bacteria, yet they serve distinct roles and operate through different mechanisms. In terms of similarity, both metabolism and biomineralization are both biologically mediated methods involving biological processes that initiate and control the synthesis of nanomaterials. These processes can lead to the creation of complex and precisely controlled nanomaterial structures with well-defined morphologies and properties. Additionally, both methods can be guided or influenced by templates provided by biological systems, such as proteins, peptides, or cellular structures. These templates play a role in shaping specific nanomaterial forms and arrangements.

However, these two approaches significantly differ in their mechanisms and functional roles. Metabolism utilizes cellular enzymatic reactions for controlled synthesis, while biomineralization involves the interaction of bacteria with mineral components to create intricate structures.

Using metabolism and biomineralization to synthesize bacteria-derived nanomaterials indeed holds great potential, but there are associated limitations. Biological processes are highly complex and can be influenced by a variety of factors. Achieving precise control and consistency in the synthesis of nanomaterials through metabolism and biomineralization can be challenging due to the inherent variability in bacteria. Therefore, selectively guiding the metabolism and biomineralization toward producing the desired nanomaterials while avoiding byproducts and impurities can be difficult. Additionally, metabolism occurs continuously and is necessary for the immediate survival and daily activities of the bacteria, whereas biomineralization requires extended periods to form complex mineralized structures, making it relatively time-consuming.

Below is a comparative table providing a concise overview of the advantages and challenges associated with the three methods of bacteria-based nanomaterial synthesis for batteries.

Table 1 Comparison of the advantages and challenges of the three synthesis methods

Method	Ex-situ assembly	Metabolism-based in-situ assembly	Biomineralization-based in-situ assembly
Advantages	• Inherent heteroatom doped carbon • Hierarchical porous carbon structure	• Inherent heteroatom doped carbon • Hierarchical porous carbon structure • Bio-assembly of nanomaterials within bacteria to form functionalized nanocomposites • Precise nanocomposite structure control • Decontamination function	• Inherent heteroatom doped carbon • Hierarchical porous carbon structure • Bio-assembly of nanomaterials within bacteria to form functionalized nanocomposites • Precise nanocomposite structure control • Tunable sizes and shapes and tailored materials properties
Disadvantages Or Challenges	• Bacteria only provide carbon source and nanocomposites are created in a separated process • Limited	• Complicated biological process • Limited active material options	• Complicated biological process • Low yields and time-consuming

	nanocomposite structure control • Limited active materials loading		

7. **Conclusion and Prospect**

In this mini-review, we have presented an overview of the recent advancements in utilizing bacteria-derived materials for lithium-ion and lithium-sulfur batteries. These materials were categorized into three main groups based on their synthesis methods: ex-situ assembly, metabolism-based in-situ assembly, and biomineralization-based in-situ assembly. Bacteria-derived carbon has shown promise in modifying carbon surface polarity, confining polar polysulfides, and enhancing the performance and lifespan of LSBs. In-situ bio-assembled nanostructures in the metabolic and biomineralization processes of bacteria have demonstrated their superior performance in LIBs.

However, it is crucial to recognize that bacteria-derived carbon and its nanocomposites for battery applications are still at an early developing stage. Challenges must be addressed to fully unlock their potential. These challenges encompass:

- Appropriate selection and utilization of bacteria: Choosing different types of bacteria with unique characteristics, morphologies, and composites is essential. They also should have high carbon yield.

- Compatibility and phase control: Ensuring the compatibility of the target active materials with the bacteria and precisely controlling the phase formation of desired active materials during the biomineralization process is critical.
- Choice of Functional Compounds: Selecting functional compounds with large theoretical capacities, excellent catalytic properties, good physicochemical stability, and high compatibility with the bacteria matrix is crucial.
- Efficiency and Scalability: Improving the efficiency and scalability of the synthesis process to make them commercially viable. This involves investigating various approaches to optimize bacteria culture and electrode nanofabrication.
- Advanced Characterization Techniques: While the nanostructure and morphology of these bacteria-derived carbon materials and their impact on electrochemical performance have been partly understood through traditional characterization methods, more advanced techniques are needed. In situ methods, integrated with theoretical calculations, in situ TEM analysis, and synchrotron radiation technology, can provide valuable insights into the unique biomineralization process of metal nanoparticles and compounds.

To address the aforementioned challenges, we propose corresponding solutions and outline possible directions and opportunities for the future:

- Isolating and characterizing bacteria species: Researchers can focus on isolating and characterizing bacteria species with a high affinity for specific metals and compounds beneficial for battery materials. This involves screening and optimizing conditions for bacteria growth and metal uptake. Genetic engineering techniques can be employed to enhance bacteria-metal interactions.

- Designing active materials: Active materials with surface chemistries promoting interaction with bacteria can be designed. Coating strategies or surface modifications can ensure compatibility and control over biomineralization processes.
- Investigating functional compounds: Exploration and investigation of functional compounds that enhance the electrochemical properties of bacteria-derived carbon are crucial. This involves a combination of experimental screening and computational methods. High-throughput screening methods can be developed to rapidly identify functional compounds and predict their properties when coupled with bacteria-derived carbon.
- Optimizing bacteria culture conditions: Optimizing bacteria culture conditions is an effective approach to improve the efficiency of the biological process and achieve scalability for practical applications. Additionally, bioengineering methods can enhance bacteria's mineralization capabilities and ensure precise control and consistency over material synthesis.
- Developing new in-situ techniques: Developing and employing new in-situ techniques combined with multi-modal imaging can help study biological evolutionary processes at high spatial and temporal resolution. This approach is valuable for gaining real-time insights and revealing mechanisms of phase transitions and structural changes.

Additionally, future research should also explore potential directions and opportunities beyond LIBs and LSBs. This includes investigating applications of bacteria-derived nanomaterials in other metals such as Na, K, Zn based batteries, metal-O_2 batteries, supercapacitors, or other energy storage devices.

Indeed, despite numerous challenges, bacteria-derived carbon and its composites, especially those obtained through harvesting carbon sources and contaminants from environments, offer an alternative route to clean and sustainable battery manufacturing in a cost-effective manner. Unlocking the full potential of these materials in energy storage applications requires further studies of bacteria strains, culture conditions, and nanofabrication methods.

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Declaration of generative AI and AI-assisted technologies in the writing process

During revision of the submitted manuscript, the authors used ChatGPT 3.5 in order to improve language and readability. After using this tool, the authors reviewed and edited the content as needed and take full responsibility for the content of the publication.

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