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Perspective

Exploiting Biological Systems: Toward Eco-Friendly and High-Efficiency Rechargeable Batteries

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To meet the ever-increasing energy demands and sustainability requirements, next-generation battery systems must provide superior energy densities while employing eco-friendly components. Transition metal oxide-based materials have served as important high-energy-density battery electrodes over the past few decades; however, their further development is challenging as we approach the theoretical limits arising from their crystal structures and constituting elements. Exploiting materials from biological systems, or bio-inspiration, offers an alternative strategy to overcome the conventional energy storage mechanism through the chemical diversity, highly efficient biochemistry, sustainability, and natural abundance provided by these materials. Here, we overview recent progress in biomimetic research focused on novel electrode material design for rechargeable batteries, exploiting redox-active molecules involved in the biometabolism and diverse bioderived materials with various morphologies. Successful demonstrations of energy storage using biomimetic materials that simultaneously exhibit outstanding performance and sustainability would provide insight toward the development of an eco-friendly and high-efficiency energy storage system.

Introduction

The growing markets for multi-functional portable electronics, electric vehicles, and large-scale energy storage systems have triggered a rapid increase in the demand for energy storage devices,[1,2] requiring the development of a next-generation rechargeable battery system that can provide a high energy density at reduced cost. Although lithium-ion batteries (LIBs) have successfully powered mobile electronic devices for the past few decades and intensive research has resulted in improvements in LIB technology, the current electrode chemistry based on lithium intercalation in transition metal oxides is reaching its theoretical limits, and further improvement of LIBs is not trivial.[3] To develop a new electrode material for LIBs that can overcome the heavy transition metal electrochemistry, instability of the host structure with the wide lithium compositional variation, and sluggish guest-ion diffusion kinetics, a "paradigm shift" in the design of electrode materials is required.

Living organisms, which have evolved over billions of years of natural selection, often exhibit efficient and optimized metabolic reactions that artificial devices can never achieve.[4,5] Moreover, their mechanisms are mostly based on earth-abundant, eco-friendly elements. The "reverse engineering" of such biological systems (e.g., important molecules in living organism, their product, or even themselves) or mimicking their reactions may thus offer inspiration for the development of next-generation

Context & Scale

Conventional battery electrodes, which mainly consist of heavy transition metal oxide materials, are believed to soon reach their limitations. In an effort to develop future battery electrodes, exploiting biological knowledge is considered a promising approach. Bio-organisms have evolved over a long period of time in the pursuit of optimal systems; thus, taking advantage of their functions including energy transduction reaction and morphological evolution can offer a new insight into the design of electrode materials for energy storage. While the exploration of biomimetic materials and their applications to energy storage is in its infancy, numerous materials remain to be investigated due to the diversity of biological systems. The discovery of new redox-active molecules can trigger the synthetic efforts of related organic electrodes with optimization processes, leading to a new group of active electrode materials beyond conventional electrodes. The exploration of new hierarchical structures in biosystems can inspire cost-effective and highly efficient electrode fabrication on the nano- and microscale. We believe that

energy storage devices. Because living organisms must convert, transport, and store energy to stay alive, their metabolism involves numerous energy transduction reactions.[6] In these metabolic reactions, energy is transported from one biocomplex to another via electron and ion transfer; these reactions are thus analogous to the electrochemical reactions occurring in rechargeable batteries where electrons and ions are transported between two electrodes during charge and discharge.[7] Central to the energy transduction reaction are biomolecules that are capable of carrying electrons via redox reactions. Their intrinsic redox capability enables the transport of electrons among stationed biocomplexes, where the oxidation and reduction of the mobile biomolecules mediate the energy flow.[8] Indeed, the energy flow proceeds over a life span of organisms, which are attributed to the various redox-active biomolecules with great reversibility. Considering that the basic criterion required for electrode materials in rechargeable batteries is the reversible redox capability, the biological system can offer an inspiration for selecting new redox-active materials for rechargeable batteries. While various types of redox-active biomolecules are found in nature, one can take advantage of their intrinsic redox reactions in designing novel active electrode materials for rechargeable batteries,[9] as schematically illustrated in the yellow box of Figure 1. In particular, biomolecules are usually composed of light and cost-effective elements such as carbon, hydrogen, oxygen, and nitrogen, implying the possibility of achieving a high gravimetric energy density for biomolecule-based electrode materials. Furthermore, molecular structures are potentially tunable; eliminating the redox-inactive parts in the molecule or functionalizing with other groups may enable optimization of the redox activity. The chemical tunability of these materials may thus offer flexibility of electrode design. Representative redox-active biomolecules, such as quinone and riboflavin derivatives, will be discussed in the next section.

The structural factors of the working electrode, including the surface area, morphology, spatial distribution of the active material, and the connectivity with the current collector, greatly affect the overall performance of battery systems and are becoming increasingly important for new types of energy storage systems such as lithium-air or lithium-sulfur batteries.[10] Ideally, micro- or nanostructural assembly of electrode components would enable fast electron/ion transport and effective utilization of active materials in the electrode, leading to a higher power and energy density; however, the realization of this micro-/nanostructuring is difficult because of the complicated fabrication processes and cost. The naturally grown hierarchical structure of biological systems can provide useful insight for building electrode structures. Various complex nano- and microstructures exist in nature by virtue of biological diversity that can scarcely be synthesized using conventional fabrication technology. In fabricating a complicated electrode architecture, such hierarchical biological structures can be used as a versatile building template. As depicted in the blue box of Figure 1, genetically modified bacteriophages, for example, can be used as self-assembling templates to prepare efficient electrode structures. In addition, the carbonization of nature-derived materials (e.g., leaves, spider webs) can result in an optimal carbon-based electrode with a high surface area and integral structure. In this Perspective, we introduce recent research focused on novel electrode design inspired or derived from the intrinsic redox reactions occurring in living organisms and on naturally grown hierarchical nanostructures for electrode optimization.

learning lessons from biological systems for advanced electrode materials and structures will offer a new perspective and accelerate the development of battery electrodes.

Active Electrode Materials Inspired from Redox-Active Biomolecules

Quinone and Its Derivatives

Quinone and its derivatives are some of the most intensively studied organic electrode materials inspired by biological systems.[11–14] They can be found in important

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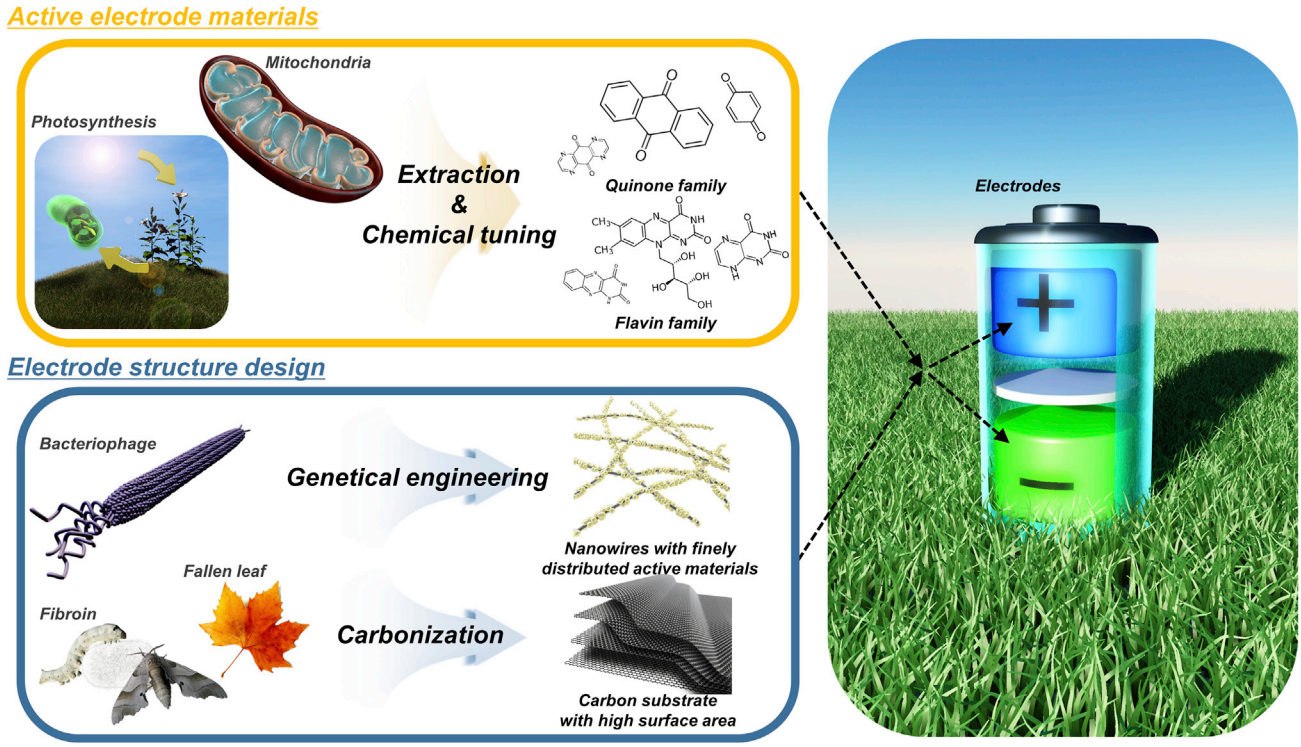

Figure 1. Schematics of Biologically Motivated Materials for Energy Storage Application

biometabolism processes in nature such as photosynthesis and respiration, serving as charge-mediating agents through redox reactions. For example, plastoquinone, one of the cofactors in photosystem II, carries electrons and protons in chloroplast through a redox reaction.[6] Ubiquinone (or coenzyme Q10) is also capable of mediating electrons and protons as one of the components in the electron transport chain reaction, which participates in the respiration reaction in mitochondria,[6] as shown in Figure 2A. Quinones are composed of aromatic compounds with an even number of -(CH)= groups substituted with -(C=O)- groups, accompanied by the rearrangement of double bonds, as illustrated in Figure 2B.[15] Because the redox center of quinones is a C=O double bond and there are two or more C=O bonds in quinones, multiple charges can be stored in a relatively compact structure, resulting in a high charge capacity. Moreover, quinone-based materials exhibit moderately high reduction potentials (>2 V versus Li/Li^+), which is attributed to the formation of an additional stable aromatic system upon reduction.[16] The resulting high gravimetric energy density (i.e., multiplication of capacity and potential) makes quinones attractive candidates for electrode materials compared with conventional intercalation-based electrode materials that contain heavy transition metal elements.

Various forms of quinone-based materials have been studied as electrode materials since the first introduction of quinones for secondary lithium-organic batteries in 1972.[11] One of the most important research directions concerning quinone derivatives has focused on the maximization of the energy density, i.e., increase of the capacity and redox potential. To achieve a high capacity, researchers have attempted to reduce the inactive part in the molecule. The simplest quinone derivative, 1,4-benzoquinone, can deliver a theoretical capacity of ~500 mAh g^{-1}. However, 1,4-benzoquinone easily sublimates in the standard state, which has hindered its practical use. To minimize the inactive part and simultaneously achieve a sufficiently

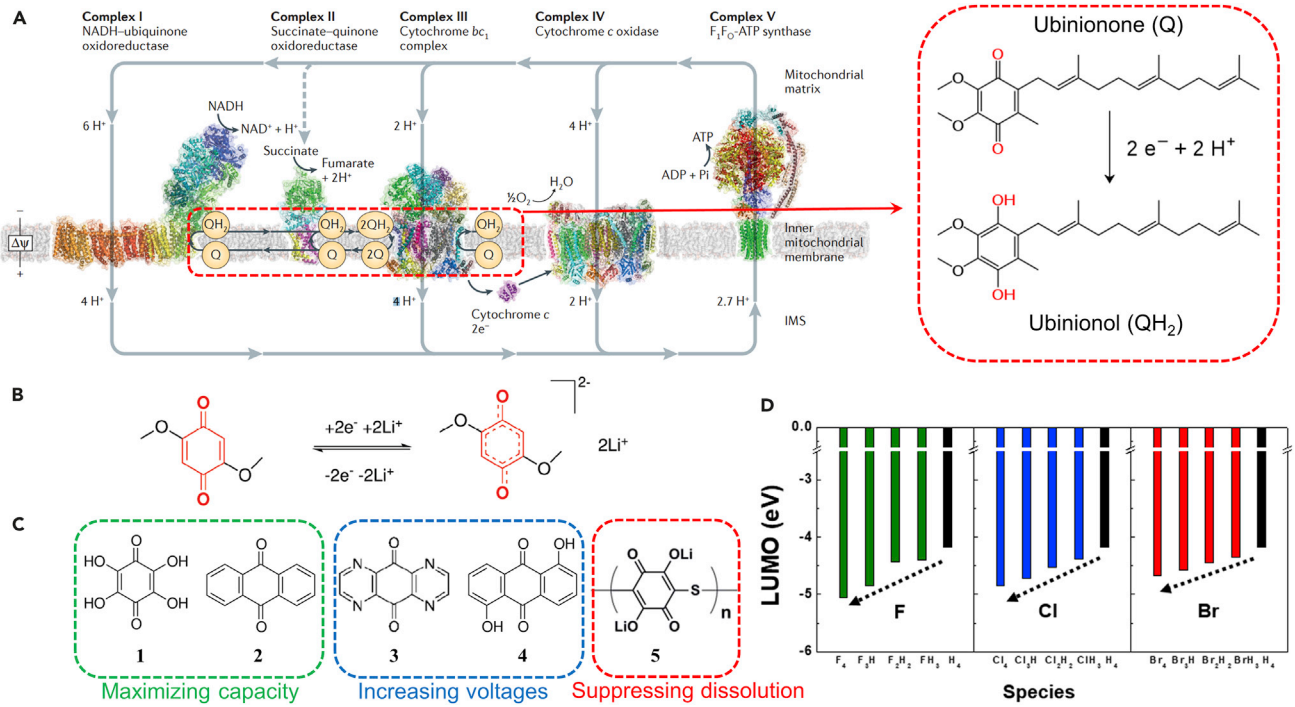

Figure 2. Origin, Redox Mechanism, and Chemical Tuning of Quinone-Based Electrode Materials

(A) Electron transport chain mechanism in mitochondria, where Q denotes ubiquinone, which mediates electrons and hydrogen ions between respiration complexes. Biochemical reaction mechanism of ubiquinone is depicted in red box. Reprinted from Sazanov,[9] with permission. Copyright 2015, Nature Publishing Group.

(B) Redox reaction mechanism of quinone derivatives.

(C) Quinone derivatives reported as electrode materials in the literature.

(D) Calculated LUMO level of halogen element substituted 1,4-benzoquinone. Lower LUMO level of a molecule generally implies higher reduction potential. Reprinted from Kim et al.,[17] with permission. Copyright 2015, American Chemical Society.

strong intermolecular force to prevent sublimation, quinone derivatives with 1–3 aromatic carbon rings and various functional groups have been intensively investigated. 2,3,5,6-tetrahydroxy-1,4-benzoquinone (**1** in Figure 2C), which has a theoretical capacity greater than 270 mAh g^{-1}, exhibits a practical capacity of ~200 mAh g^{-1} at a C/20 rate in a lithium cell, which is comparable with the capacities of conventional layered transition metal oxide electrodes.[18] 9,10-Anthraquinone (**2** in Figure 2C), with a theoretical capacity of ~250 mAh g^{-1}, can also deliver a high practical capacity of ~220 mAh g^{-1} at ~1C (300 mA g^{-1}) in a lithium cell based on a similar lithium reaction mechanism.[19]

Increasing the operation voltage (~2.3 V versus Li/Li^+ for the aforementioned quinones) was an important issue that needed to be resolved for further improvement of the energy density, considering the typical redox potential of transition metal oxide-based electrode materials (>~3 V Li/Li^+). One general strategy to enhance the redox potential of molecules is to engineer the neighboring redox-inactive part, e.g., substitution of the inactive part with electron-withdrawing groups.[17,20,21] Electron-withdrawing groups can attract the electrons from the electron cloud around the redox center (C=O double bond), requiring more energy to extract the electrons from the redox center itself, which consequently leads to an increase in the redox potential. Representative examples include 1,4,5,8-tetraaza-9,10-anthraquinone (1,4,5,8-TAAQ) and 1,5-dihydroxyanthraquinone (1,5-DHAQ) (**3** and **4**, respectively, in Figure 2C). In 1,4,5,8-TAAQ, the replacement of four carbon atoms

with nitrogen in the neighbor of the redox-active C=O bond in anthraquinone leads to a substantial increase of the redox potential by ~0.7 V, reaching 3 V versus Li/Li^+.[21] This increase was attributed to the presence of nitrogen, which has a strong electron-withdrawing nature compared with that of carbon, making the electron extraction from the neighboring C=O bond more difficult. A similar phenomenon was observed in 1,5-DHAQ with the substitution of two hydroxyl groups in anthraquinone, which also led to an increase of the average redox potential to 2.7 V versus Li/Li^+.[20] A more systematic study on the effect of substitution was performed by Kim et al., in which various substituting elements with different degrees of electron-withdrawing capability in quinone were investigated.[17] It was found that the redox potential of benzoquinone increased with increasing strength of the electron-withdrawing group from Br to Cl to F even when the same redox center of C=O was used, as shown in Figure 2D.

Despite the expected high energy density, quinone derivatives suffer from dissolution of the active materials in conventional organic-based electrolyte systems. A maximum cycle life of 50 cycles has been reported for the aforementioned quinone derivatives because of this severe dissolution problem.[17,19,21] To mitigate this issue, the design of quinone-carbon composites such as carbon nanotubes (CNTs) or mesoporous carbons (CMKs) was suggested.[17,19,22] The π-π attraction between the graphitic structure of carbon materials and the aromatic carbon ring of quinones enables their strong holding, suppressing the dissolution of the organic molecules. The quinone-carbon composite strategy successfully prolonged the cycle life of the cell, with retention of ~70% of the initial capacity after 50 cycles.[22] The polymerization of quinones has also been demonstrated to be an effective strategy to overcome the dissolution issue.[13,23,24] The polymerized dihydroxybenzoquinone (**5** in Figure 2C) was remarkably resistant to dissolution in a conventional organic electrolyte, which operated stably for up to 1,500 cycles with a capacity of >200 mAh g^{-1}.[24] Nevertheless, polymer electrodes generally exhibit lower redox potentials and poorer electronic conductivities than their monomer counterparts, an issue that remains to be resolved.[25]

Riboflavin and Its Derivatives

Inspired by biological energy transduction in mitochondria, riboflavin (also known as vitamin B_2) has been considered a promising electrode material since its first utilization in an LIB system in 2013.[26] Flavin cofactors enable electron transport in the respiratory system, where ATP is produced when flavin adenine dinucleotide ($FADH_2$) simultaneously releases protons and electrons.[27] The oxidized flavin cofactors can be reversibly recycled in a reduction process (i.e., the uptake of protons and electrons) through the citric acid cycle of the mitochondria.[28] As schematically illustrated in Figure 3A, this biochemical energy transduction process involving flavin cofactors in the mitochondria is markedly analogous to the electrochemical reaction in rechargeable batteries in terms of the transport of electrons and charged ions. Based on this analogy, a lithium cell using riboflavin as the cathode active material was successfully demonstrated and delivered a reversible capacity of ~105 mAh g^{-1} with an average voltage of 2.5 V versus Li/Li^+.[26] The detailed redox mechanism was investigated using density functional theory calculations and several *ex situ* characterization techniques. As depicted in Figure 3B, Lee et al. observed that the flavin in the lithium cell undergoes a reversible two-step reaction involving two-electron reduction at the nitrogen atoms of the diazabutadiene motif.[26] The two sequential reductive reactions of the flavin molecule induce the formation of stable heterocyclic rings with lithium ions, which is consistent with the two high voltage plateaus of 2.4 and 2.6 V versus Li/Li^+ observed in the electrochemical profile.

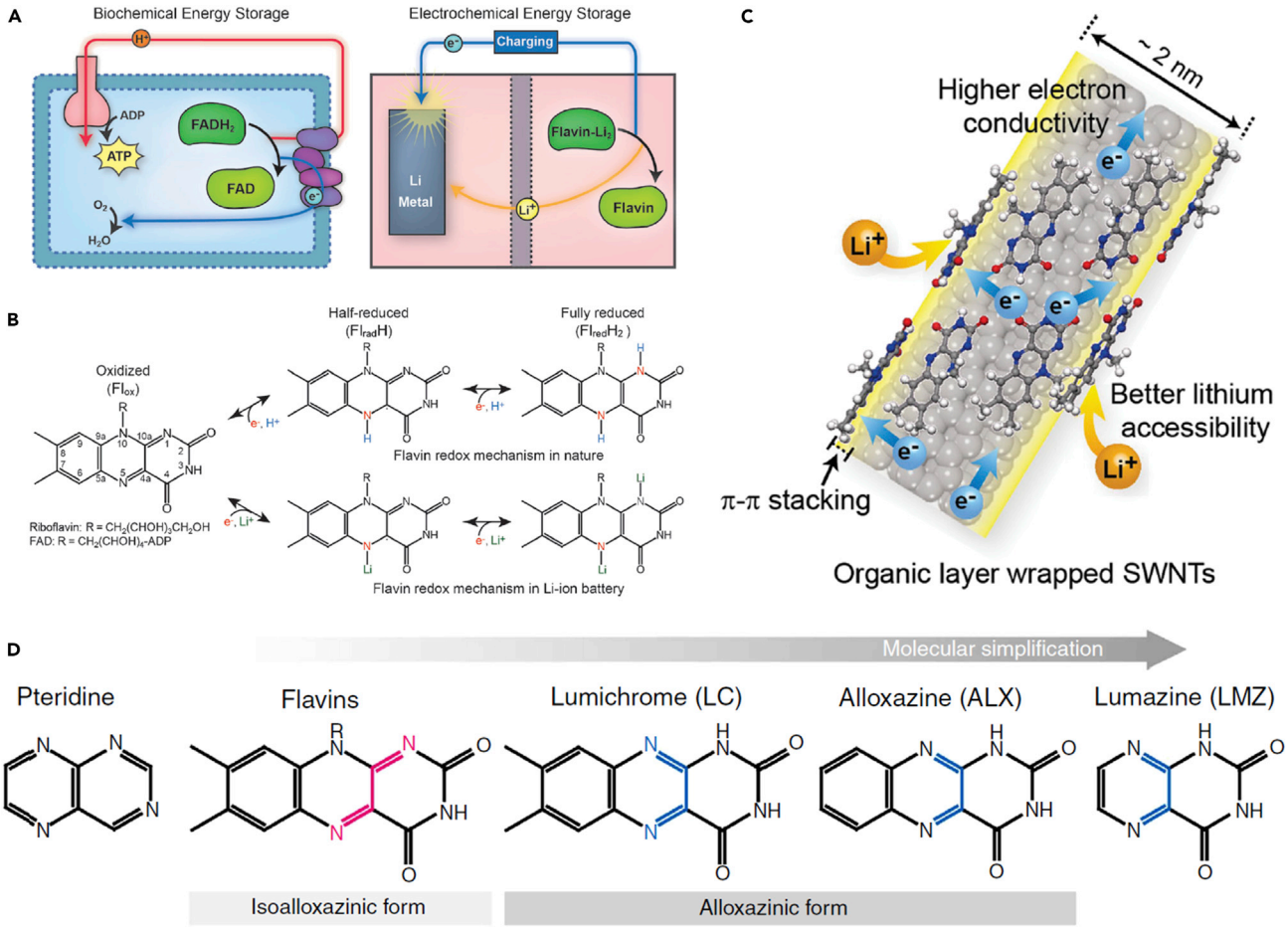

Figure 3. Flavin-Based Electrode Materials for Energy Storage Systems

(A) Illustration of energy conversion reaction in biochemical energy storage and electrochemical energy storage. Reprinted from Lee et al.,[26] with permission. Copyright 2013, Wiley.

(B) Redox mechanisms of flavin group in nature and Li-ion battery. Reprinted from Lee et al.,[26] with permission. Copyright 2013, Wiley.

(C) Nanohybridization of flavin molecules with SWNTs through π-π stacking. Reprinted from Lee et al.,[30] with permission. Copyright 2014, Wiley.

(D) Molecular simplification strategy of pteridine derivatives. Image obtained from Hong et al.[31]

Riboflavin-based biomolecules also easily dissolve in the electrolyte, leading to deterioration of the cycle stability. Several approaches to improve the cyclability have thus been attempted. Lee et al. demonstrated the effectiveness of anchoring flavin molecules (lumiflavins) using single-walled carbon nanotubes (SWNTs) in significantly suppressing the dissolution.[30] As illustrated in Figure 3C, flavin is immobilized to highly conductive scaffolds at the molecular level through π-π interactions between the flavin molecules and SWNTs, which results in a dramatic enhancement of the rate capability and cyclability. Strong π-π interactions can efficiently suppress the dissolution of flavin molecules in organic electrolytes, thereby resulting in stable capacity retention of approximately >99% for up to 100 cycles. Moreover, these organic nanohybrids could be operated even at an extremely high C-rate of 50C with a capacity of over 60% of the theoretical value. Polymerization has also been proved to be an effective strategy to reduce the dissolution issue of flavin molecules, as demonstrated in a quinone-based electrode.[29] A polymer electrode synthesized by inserting pendant flavin molecules into a poly(norbornene) backbone delivered a specific capacity of 125 mAh g^{-1}, which is higher than that of the riboflavin

monomer. Schon et al. observed that the dissolution of active materials was entirely suppressed in this system. Nevertheless, capacity fading was still observed, with ~50% of the initial capacity delivered after 50 cycles, which was attributed to the geometrical degradation.[29,32]

Enhancement of the energy density in flavin-based electrodes can be achieved through molecular tailoring based on a simplification strategy. While retaining the redox center of flavin, riboflavin molecules can be simplified into molecules such as lumichrome, alloxazine, and lumazine.[31] Figure 3D schematically demonstrates that the new tailored molecules still contain the redox-active diazabutadiene motif, whereas the inactive parts of the original riboflavin structure are systematically chopped off. Reduction of the molecular weight with the same redox center results in a higher energy density, with theoretical capacities of 250 and 327 mAh g^{-1} for alloxazine and lumazine, respectively. By adopting the nanohybrid strategy using a conductive CNT scaffold that suppresses the dissolution of alloxazine, the alloxazine/CNT hybrid electrode exhibited superior electrochemical performance with a specific capacity of 236 mAh g^{-1} at a 1C rate, which is 94% of the theoretical value, with >99% of the initial capacity retained after 200 cycles. Nevertheless, the use of smaller molecules such as lumazine is challenging because of their easier dissolution; only limited improvements with a CNT nanohybrid were possible because of the weaker π-π interactions arising from the small molecule size. This finding implies that trade-off relationships exist between the energy density and dissolution in the simplification strategy of flavin-based materials.

Recent studies have shown that flavin molecules can also be successfully introduced into a redox flow battery (RFB) system by taking advantage of the highly dissolvable nature of flavin.[33] Flavin molecules are known to be soluble in water; however, Lin et al. demonstrated that the solubility could be further increased by linking several substituents, such as a carboxylic acid group, to the flavin molecules to enhance the energy density of the RFB system. This system exhibited superior capacity retention of 99.98% per cycle and a high full cell voltage of 1.2 V, which is the maximum value in the electrochemical window of an aqueous system.

Other Redox-Active Materials from Bio-Inspiration

Several new redox-active biomolecules have recently been reported as electrodes for rechargeable batteries. For instance, humic acid, which is the major organic constituent in the biodegradation of dead plants under microbial metabolism, was utilized as an anode for LIBs.[34] A humic-acid-based electrode exhibited a redox potential of ~1.1 V versus Li/Li^+ and an initial capacity of ~500 mAh g^{-1}. It was proposed that the lithium incorporation in humic acid occurs on the carboxylate groups conjugated within the benzene ring. Additionally, Han et al. reported that unsaturated carbons of C_6 rings can also store lithium ions by absorption.[35] Recently, Kim et al. showed that melanin is electrochemically active with sodium and can be used as an anode for sodium-ion batteries.[36] Melanin is a natural pigment in human skin, hair, and eyes. The melanin-based electrode delivered a capacity of 80 mAh g^{-1} at an operation voltage of 1.9–2.2 V versus Na/Na^+ when combined with a silver nanowire substrate. Although humic acid and melanin exhibited interesting features, their electrochemical properties were not high compared with those of quinone and flavin derivatives, and their operation mechanisms should be further studied for their practical utilization.

Bioderived Design of Electrode Structure

In batteries and supercapacitors, the network of ionic and electronic diffusion paths and the surface area and porosity of an electrode play critical roles in amplifying the

electrode performance by fully utilizing the intrinsic properties of the active materials.[10] Constructing such an electrode with an optimal structure on both the micro- and nanoscale can be achieved with the aid of bioderived materials as templates or precursors. Exploiting nanosized bacteriophages (viruses) is considered a promising method for building nanostructured materials because they have inherent self-assembling capabilities by interacting with the environment or themselves. One of the remarkable features of viruses that makes them attractive toolkits is that the sequence of amino acids on a virus protein can be genetically engineered to possess an affinity toward certain molecules or ions. Functional groups in the genetically engineered amino acid can interact with the target species, which enables the self-construction of a nanostructure containing the material.[37–39]

M13 is one of the most widely explored viruses for synthesizing nanostructured electrodes.[39,40] The M13 virus contains approximately 2,800 copies of the coat protein (p8) stacked in a helical array on the body, with five copies of each minor protein (p3, p6, p7, and p9) at both ends of the virus. The functionalities of these proteins (i.e., the sequence of the amino acid unit in the proteins) can be genetically engineered to be bound to the targeted materials such as metal ions,[41,42] gold,[39,40] and carbon,[43] which can be used as the precursors of the active materials or conductive scaffolds.[43] An interesting structural feature of the M13 virus is that it has a high aspect ratio with a diameter of 6.5 nm and length of 880 nm, which is similar to the shape of nanowires (NWs). Because the homogeneous guided binding of precursors on the surface of the M13 virus leads to a fine distribution of active materials after synthesis, the M13 virus can be used as a versatile building template for NW-based and nanostructured electrodes containing various active materials.

Metal oxide and noble metal NWs have been synthesized using a genetically modified M13 virus for use as anodes for LIBs.[40,41] For instance, Co_3O_4 NWs were successfully synthesized with the M13 virus genetically engineered to have an amino acid sequence of tetraglutamate (EEEE-) at the N terminus of the coat protein (p8)[41] (Figure 4A). Carboxylic acid at the side chain of glutamate (E) binds to the positive cobalt ion, acting as a growth site of Co_3O_4 during synthesis. M13-derived Co_3O_4 NWs in a lithium cell exhibited an initial capacity of ~1,500 mAh g^{-1} with a reversible capacity of ~800 mAh g^{-1}, which surpassed that of a powder Co_3O_4-based electrode with an initial capacity of 1,300 mAh g^{-1} and a capacity of ~100 mAh g^{-1} after eight cycles. This improvement resulted from the effective assembly of the active material on the surface of the high-aspect-ratio NWs, which facilitated the transport of lithium ions and electrons.

Synthesis using the M13 virus can also be applied for the fabrication of a nanomixture cathode, enabling the construction of fully virus-built batteries.[43,45,46] The multi-functional M13 virus with two genetically engineered sites, the EEEE- amino acid sequence at p8 and amino acid sequence of N′-DMPRTTMSPPPR-C′ at the end protein (p3), was used to fabricate an amorphous $FePO_4$ NW–SWNT nanocomposite, which was used as a cathode in lithium-ion and sodium-ion batteries[43,45,46] (Figure 4B). The EEEE site of the coat protein of the M13 virus, which attracts Fe^{3+} ions, acted as a growth site for amorphous $FePO_4$, and the end protein (p3) with the N′-DMPRTTMSPPPR-C′ sequence could bind to the SWNTs. Using this multifunctional M13 virus, it was possible to construct a nanoscale network structure between the $FePO_4$ NWs and SWNTs. The $FePO_4$-CNT electrode displayed superior discharge capacity and rate capability, 170 mAh g^{-1} at C/10 and 130 mAh g^{-1} even at 10C.[43] The improved properties were attributed to the finely dispersed active materials ($FePO_4$), well-constructed electronic conducting path (SWNTs),

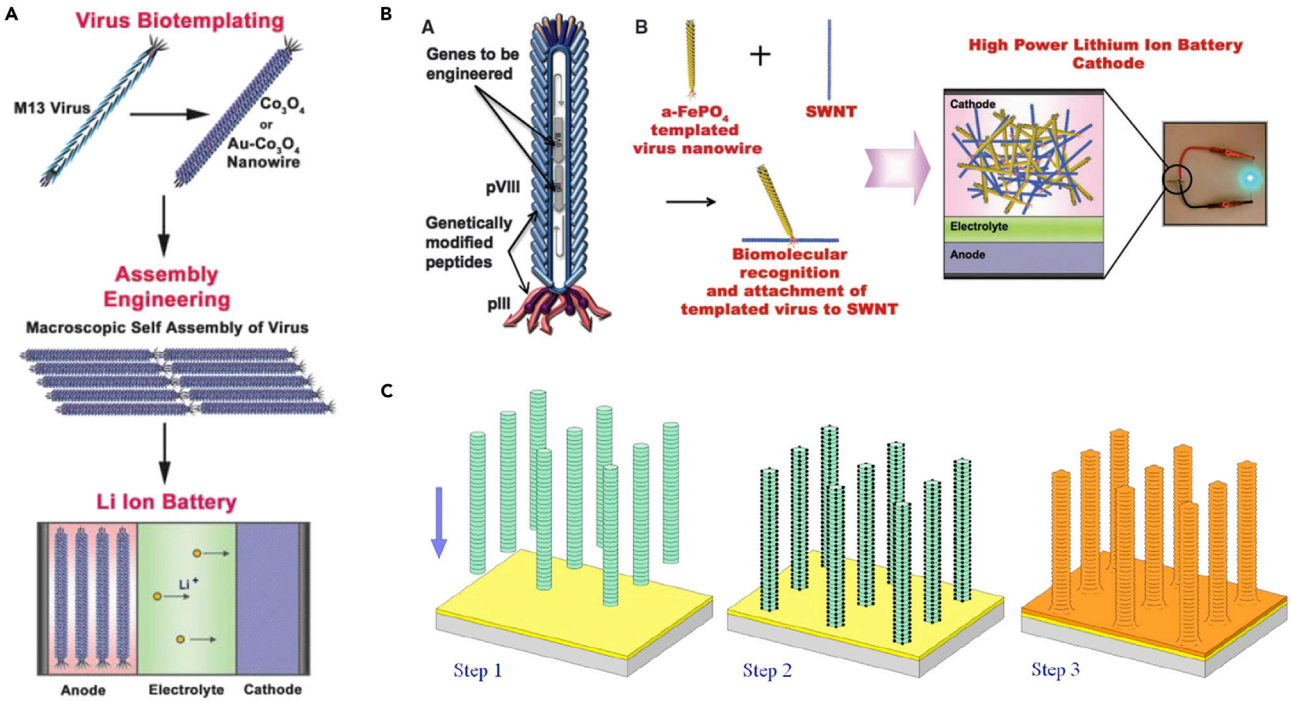

Figure 4. Schematics Showing Various Virus-Derived Nanostructures as Electrodes in Energy Storage Systems

(A) M13 virus coated with Co_3O_4 applied as a building block for an anode in Li-ion batteries. Reprinted from Nam et al.,[41] with permission. Copyright 2006, American Association for the Advancement of Science.

(B) Use of the multi-functional M13 virus, which is able to act as an $FePO_4$ growth site and binds to SWCNTs, as a passive template for a cathode in Li-ion batteries. Reprinted from Lee et al.,[43] with permission. Copyright 2009, American Association for the Advancement of Science.

(C) Use of TMV modified to have an affinity to the metal substrate to build a high-surface-area electrode with nanoforest structure. Reprinted from Gerasopoulos et al.,[51] with permission. Copyright 2008, IOP Publishing.

and reduced material dimensions (high-aspect-ratio NWs). Recently, nanostructures constructed by the M13 virus have also been utilized as air electrodes in Li-O_2 batteries.[47,48] MnO_x and Co_3O_4 NWs were fabricated as air electrodes using the M13 virus with the amino acid sequence of ADVYESALPDPAEAAFE and EEAE at p8, which had affinities to cobalt and manganese ions, respectively.[47,48] The advantage of the air electrodes made by M13 was their high surface areas with an effectively distributed solid catalyst, MnO_x or Co_3O_4, to maximize the reaction surface. In addition to simple NW-based structures, M13 virus-derived NWs where nanoparticles (NPs) are embedded inside have recently been reported, which has yet to be applied to a battery system.[49,50] NWs and NPs were designed to be composed of different materials in order to have multi-functionality. For instance, TiO_2 NWs containing Ag or Au NPs were synthesized by M13 virus for thin film solar cell application. In this system, the NW part accelerates the charge collection while the NP part facilitates the light harvesting.[50] Such an M13-derived nanocomposite electrode can also be a promising electrode material for energy storage systems, especially for Li-oxygen cells where multi-functional electrodes can play a significant role.

Tobacco mosaic virus (TMV) is another option for building virus-derived nanostructures. TMV has a nanorod-like shape with a length of 300 nm and outer/inner diameters of 18 and 4 nm, respectively.[51] It contains approximately 2,130 identical coat protein subunits stacked in a helix, which can also be genetically modified to form a desired amino acid sequence. The most widely used type of engineered TMV as a building template is that with a cysteine residue at the N terminus (TMV1cys). Thiol

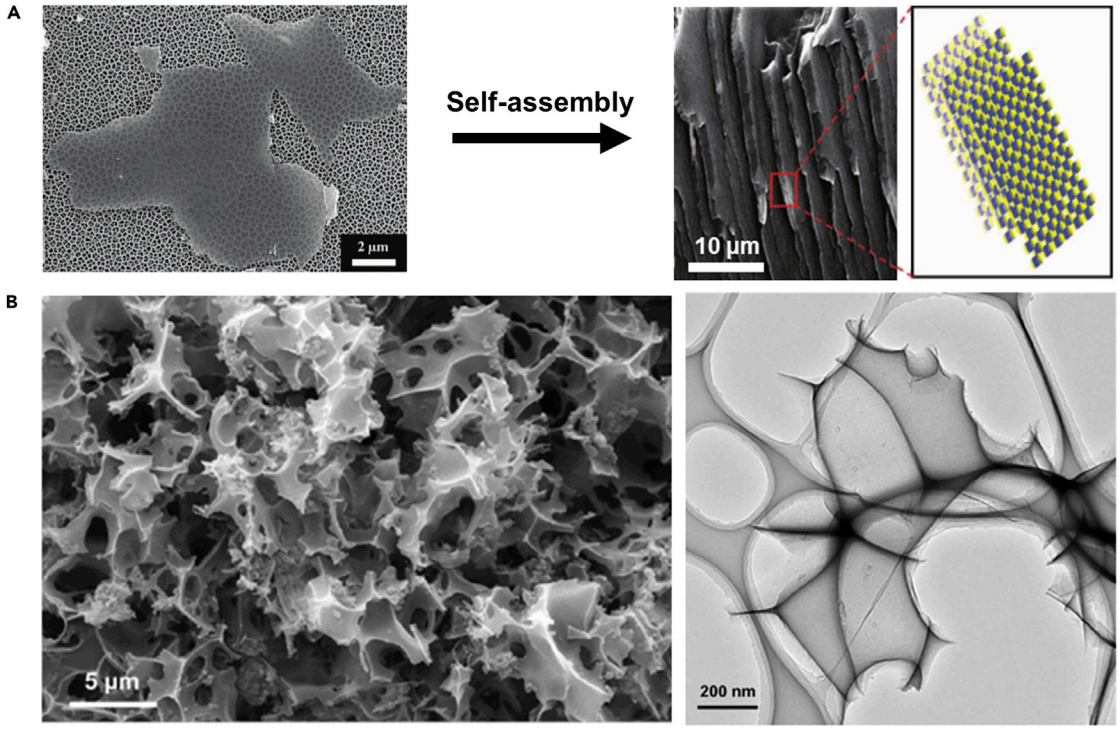

Figure 5. Nature-Derived Carbonaceous Materials as Electrodes for High-Performance Supercapacitors

(A) Morphology of *Bombyx mori* silk-fibroin-derived carbon electrode with lamellar-like layer structure. Reprinted from Yun et al.,[55] with permission. Copyright 2013, Wiley.

(B) Morphological characteristics of GL-AMPs produced from pyrolysis of fallen leaves. Reprinted from An et al.,[65] with permission. Copyright 2017, Elsevier.

interactions between the thiol group in cysteine and the metal substrate facilitate the attachment of the TMV nanorod on a metal substrate in a vertical array (Figure 4C). By coating various active materials such as Ni,[44] Si,[52] or oxides[53,54] on the metal-TMV composite, it is possible to construct nanoforest electrodes with high surface areas, which have been applied to Ni-Zn batteries and LIBs. For example, an $FePO_4$ nanoforest cathode exhibited a specific capacity of ~160 mAh g^{-1}, which is 3-fold higher than that of a conventional electrode with the same loading amount because of the enhanced electrochemical kinetics.[54]

Biologically derived materials, which are mainly composed of a carbon backbone, can be attractive precursors for carbon electrodes with specific nano- and micro-structures.[55–61] The pyrolysis of biologically derived materials such as leaves, silk worm fibroin, crops, and fruits can yield unique and useful micro- and nanostructures that cannot be easily synthesized using other methods. During the pyrolysis process with an activation agent, volatile components and moisture are removed and a porous carbon-based material is generally produced, which is advantageous for the electrodes of supercapacitors because of their high surface area and the feasible incorporation of heteroatoms from the various biomaterials.[55,62–64] Yun et al. fabricated carbon-based microporous nanoplates containing heteroatoms (H-CMNs) from silk fibroin, which is produced by the silkworm *Bombyx mori*.[55] As observed in Figure 5A, the derived material had a sheet-like lamellar structure assembled from nanoplates containing heteroatoms such as nitrogen and oxygen. Moreover, the surface area of the nanoplates (2,557.3 m^2 g^{-1}) was comparable with that of a sheet of pristine graphene. The use of H-CMNs as an electrode resulted in a specific

Table 1. Theoretical/Reversible Capacities and Average Voltages of Commercialized and Bio-Inspired Redox-Active Electrode Materials

	Conventional Electrode Materials[3]				Bio-Inspired Electrode Materials				
Materials	$LiCoO_2$	NCM[a]	$LiMn_2O_4$	$LiFePO_4$	2,3,5,6-tetrahydroxy-1,4-benzoquinone[18]	1,4,5,8-tetraaza-9,10-anthraquinone[21]	1,5-dihydroxy-anthraquinone[20]	alloxazine[32]	lumazine[32]
Theoretical/reversible specific capacity (mAh g^{-1}) (current rate)	274/148 (1C)	280/160 (C/20)	148/120 (C/10)	170/165 (C/100)	311/200 (C/20)	248/200 (C/5)	223/200 (C/10)	250/230 (C/5)	327/220 (C/6)
Average voltage (V versus Li/Li^+)	3.8	3.7	4.1	3.4	1.8	3.0	2.7	2.5	2.4

[a]NCM = $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$.

capacitance of 264 F g^{-1}, which was maintained even after 10,000 cycles with only 6.8% loss of the initial value at a current density of 2.5 A g^{-1} in 1 M H_2SO_4 electrolyte. Carbon materials derived from fallen leaves have also been suggested as electrode material candidates for supercapacitors (fallen-leaf-derived microporous pyropolymers; GL-AMPs). The GL-AMPs had random shapes and contained microscale debris, as observed in Figure 5B.[65] They exhibited a high specific surface area of ~1,348.4 m^2 g^{-1} with micropores smaller than 0.7 nm and a redox-active heteroatom content of approximately 13% of the total electrode. The GL-AMPs delivered high specific capacitances of ~731 F g^{-1} at a current density of 1 A g^{-1}.

Summary and Outlook

Biomimetic electrode materials are a promising option for next-generation battery systems that offer improved eco-friendliness and sustainability over the current transition metal-based electrochemistry. While the conventional transition metal-based electrode materials are now reaching their limits in the performance and abundance and meeting requirements for the next-generation battery systems is more challenging, life on this planet found its way by using relatively simple elements to achieve sophisticated functions with high efficiencies. The interesting feature of those redox-active biomolecules is that they show redox activity with great reversibility by the assembly of simple elements into a sophisticated superstructure. In addition, they can be potentially tuned for use as high-performance electrode materials for rechargeable batteries. Therefore, several types of organic electrode materials inspired by biosystems have been reported; quinone derivatives especially have been intensively studied from the onset because of their high redox potentials and large capacities. The natural abundance and chemical diversity of quinone derivatives have made them promising candidates for cost-effective and high-capacity battery electrodes; nevertheless, further efforts are needed to simultaneously achieve a high operating voltage/energy density and stable cyclability. Riboflavin in mitochondria has also provided great intuition to many researchers because of its well-studied redox mechanism and remarkable battery performance, with a voltage and specific capacity comparable with those of conventional electrode materials. The use of flavin derivatives as battery electrodes has not yet been extensively studied; however, approaches such as substituting new functional groups and particle morphology control are expected to further improve their electrochemical performance. The performances of bio-inspired redox-active materials are summarized in Table 1, in comparison with the commercial transition metal oxide electrode materials.[3,17,18,20,31]

Table 2. BET Surface Areas and Specific Capacitances of Bioderived Carbon Electrodes Compared with Conventional Carbon Electrodes

	Conventional Carbon Electrode		Bioderived Carbon Electrode	
Materials	activated MWCNT[66]	reduced graphene[67]	H-CMNs from fibroin[55]	GL-AMPs from fallen leaf[65]
BET surface area ($m^2\ g^{-1}$)	1,035	2,620[a]	2,557	1,348
Specific capacitance[b] ($F\ g^{-1}$)	90	205	264	731

[a]Theoretical value for single-layer graphene.
[b]Aqueous media.

In addition to using biomimetic materials as redox-active parts, novel nanostructuring of biomaterials can be used to maximize electrode performance. By optimizing the structural characteristics of electrodes such as the assembly of the active materials and conductive agent, the electrochemical performances can be substantially enhanced. Viruses with self-assembly capability such as M13 and TMV have been exploited as templates to build well-constructed electrode nanostructures. By using a high-aspect-ratio virus that is genetically modified to have affinity to the target species, it is possible to induce homogeneous self-growth of the active material on the modified site of the virus or to build a well-connected network with electron-conducting media such as CNTs or conductive metal. Such a structure with a homogeneous distribution of the active material, reduced dimension (high aspect ratio), high surface area, and well-connected conducting paths results in improvements in the capacity and rate capability of batteries by promoting the diffusion of guest ions and electrons. This strategy can be further extended to construct electrodes containing materials that have not been fully utilized because of their low conductivity.

As most bio-organic compounds intrinsically contain high carbon contents, the pyrolysis of biomaterials can yield various types of carbon materials with unique nanostructures. Exploiting these new carbon structures has resulted in highly efficient electrode performance in several energy storage systems such as supercapacitors and batteries, in which carbon materials play an important role. Moreover, pyrolytic carbon materials derived from biological systems often contain a significant amount of heteroatoms depending on their bioprecursors, which sometimes leads to unexpected performance enhancement. The exploration of these findings requires fundamental studies on the effect of doping on an atomistic level. Numerous types of carbon materials that can be produced from the vast diversity of biospecies, mimicking the natural textures using carbon materials, are expected to provide an unexplored opportunity not only for enhancing electrode performance for energy storage applications but also in other fields for which controlling the micro- and nanostructure is important. The performances of bioderived carbon electrode materials are summarized in Table 2, in comparison with commercial materials.[55,65–67]

Bio-organisms have evolved over a long period in the pursuit of optimal systems; thus, examining their functions, including their energy transduction reactions, and morphological evolution can offer new insight into the design of electrode materials for energy storage. While the utilization of biomimetic materials and their applications to energy storage is in its infancy, numerous materials remain to be investigated by virtue of the diversity of biological systems. Therefore, it is worthwhile to explore a number of reactions occurring in biosystems such as antioxidant systems and photosynthesis, or the growing new field of biosensing that takes advantage

of redox reactions, to discover possible new candidates as electrode active materials. The discovery of new redox-active molecules can trigger synthetic efforts for related organic electrodes with optimization processes, leading to a new group of active electrode materials beyond quinone and flavin derivatives. Simultaneously, strategies for the further enhancement of the electrochemical performance, such as chemical modification and particle morphology control, should be developed and applied to the biomolecules. The exploration of new hierarchical structure in biosystems can inspire cost-effective and highly efficient electrode fabrication on the nano- and microscale. The successful demonstration of an energy storage system that is simultaneously equipped with biocompatibility and outstanding performance inspired from nature would result in its widespread use in applications ranging from small-scale bio-implant devices to large-scale energy storage systems.

AUTHOR CONTRIBUTIONS

B.L., Y.K., and G.K. examined literature and wrote the quinone section, riboflavin section, and virus section, respectively. S.L., K. Ku, and J.K. wrote the carbonaceous section. K. Kang conceived the original idea and supervised all writing. All authors discussed and contributed to preparing the manuscript.

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