

Nanocarbon Networks for Advanced Rechargeable Lithium Batteries

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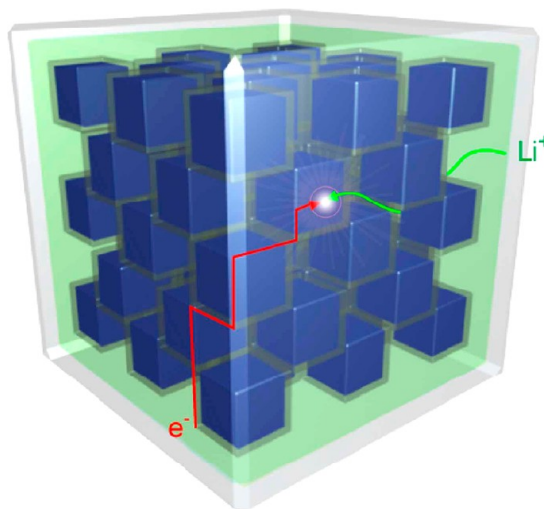
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CONSPECTUS

Carbon is one of the essential elements in energy storage. In rechargeable lithium batteries, researchers have considered many types of nanostructured carbons, such as carbon nanoparticles, carbon nanotubes, graphene, and nanoporous carbon, as anode materials and, especially, as key components for building advanced composite electrode materials. Nanocarbons can form efficient three-dimensional conducting networks that improve the performance of electrode materials suffering from the limited kinetics of lithium storage. Although the porous structure guarantees a fast migration of Li ions, the nanocarbon network can serve as an effective matrix for dispersing the active materials to prevent them from agglomerating. The nanocarbon network also affords an efficient electron pathway to provide better electrical contacts. Because of their structural stability and flexibility, nanocarbon networks can alleviate the stress and volume changes that occur in active materials during the Li insertion/extraction process. Through the elegant design of hierarchical electrode materials with nanocarbon networks, researchers can improve both the kinetic performance and the structural stability of the electrode material, which leads to optimal battery capacity, cycling stability, and rate capability.

This Account summarizes recent progress in the structural design, chemical synthesis, and characterization of the electrochemical properties of nanocarbon networks for Li-ion batteries. In such systems, storage occurs primarily in the non-carbon components, while carbon acts as the conductor and as the structural buffer. We emphasize representative nanocarbon networks including those that use carbon nanotubes and graphene. We discuss the role of carbon in enhancing the performance of various electrode materials in areas such as Li storage, Li ion and electron transport, and structural stability during cycling. We especially highlight the use of graphene to construct the carbon conducting network for alloy anodes, such as Si and Ge, to accelerate electron transport, alleviate volume change, and prevent the agglomeration of active nanoparticles. Finally, we describe the power of nanocarbon networks for the next generation rechargeable lithium batteries, including Li-S, Li-O₂, and Li-organic batteries, and provide insights into the design of ideal nanocarbon networks for these devices. In addition, we address the ways in which nanocarbon networks can expand the applications of rechargeable lithium batteries into the emerging fields of stationary energy storage and transportation.



1. Introduction

As an important type of secondary battery, lithium-ion batteries (LIBs) have quickly dominated the market for consumer electronics and become one of key technologies in the battery industry after their first release by Sony Company in the early 1990s.¹⁻⁴ Because of their distinct advantages in terms of high energy/power density, high

efficiency, long life, and pollution-free operation, LIBs are now expanding their applications into transportation and stationary fields.⁵⁻⁷ In addition, the emergence of new techniques in rechargeable lithium metal batteries (RLB), such as Li-S and Li-O₂ batteries, has brought great opportunities for the next-generation energy storage devices.⁷⁻⁹

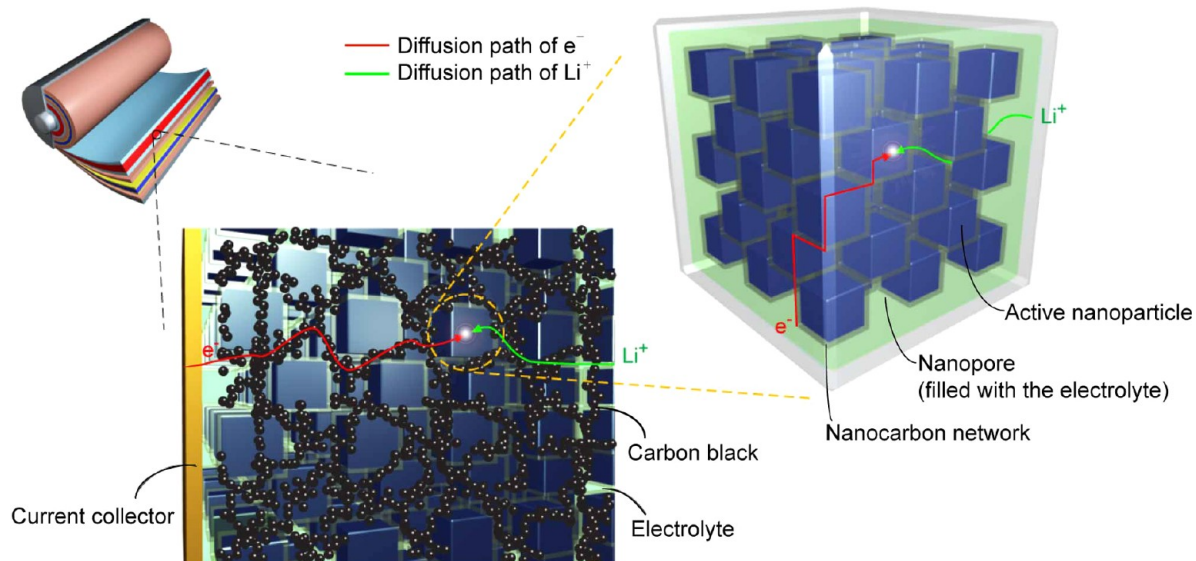


FIGURE 1. Design scheme of the hierarchically mixed conducting network in a LIB (left), in which the middle drawing gives the general view of the microscale conducting network (small black spheres represent the carbon black), and the right drawing gives the fine structure of an enlarged “building block” consisting of a nanocarbon network and ANPs.

Typically a LIB consists of an anode, a cathode, and a Li-ion conducting electrolyte-filled separator, which allows ion transfer but prohibits electron transport. The performance of LIB largely depends on the physical and chemical properties of its electrode materials. Therefore, intensive effort has been made to search for high-performance electrode materials to meet the kinetic and thermodynamic requirements for advanced LIBs.

In the development of better electrode materials, nanostructured materials have shown kinetic advantages over their micrometer-sized counterparts (usually showing low ionic diffusivities of ca. 10^{-8} – 10^{-15} $\text{cm}^2 \text{s}^{-1}$) due to a significantly shortened Li^+ diffusion pathway.^{4,10–12} Yet most nanomaterials still suffer from their naturally low electronic conductivities. An artificial three-dimensional (3D) conducting network provides a rational solution to improve the electronic conductivities of nanomaterials. Typically, such a network is constructed from microscaled building blocks, which are formed by nanosized subunits (Figure 1). Many materials with high electronic conductivities, such as RuO_2 , copper, and carbon,^{13–16} have been selected to construct the conducting networks, among which carbon is an appealing choice. Because of its low cost, high electronic conductivity, and favorable thermodynamic stability, carbon has widely served as a component material (e.g., graphite) and a functional additive (e.g., acetylene black) in LIBs.¹⁷ Porous carbons with properly designed 3D architectures have shown higher lithium storage capacities and better cycling and rate performances mainly due to their

fast Li^+ and e^- transport.^{18–22} Nanocarbon networks formed by different building blocks, such as carbon nanoparticle, carbon nanotube (CNT), graphene, and nanoporous carbon, have been employed to integrate with nanostructured electrode materials, and much improved performance has been obtained. The following sections will address these carbon networks by focusing on their functions in improving the performance of electrode materials.

2. Carbon Nanoparticle Networks

Constructed by interconnected carbon nanoparticles, carbon nanoparticle networks are usually used for coating or accommodating active nanoparticles (ANPs).²³ Chemical vapor deposition (CVD) of small organic molecules (e.g., CH_4 and C_2H_2) is a favorable method to yield such carbon nanoparticle networks. Since the carbon CVD process mainly occurs at elevated temperatures, the generated carbon nanoparticles usually have a high graphitization degree and thereby an improved electronic conductivity. For example, through a simple annealing process, carbon black can organize itself into a multibranched substrate for loading of Si nanoparticles. The obtained Si–C composite then self-assembles into large porous Si–C spheres via a carbon CVD process, in which another carbon nanoparticle network is coated.²⁴ Both of the carbon nanoparticle networks are highly conductive, and the porous carbon sphere formed by these tiny building blocks serves as both an efficient conducting network for Li^+ and e^- and an elastic buffer with sufficient internal porosity to accommodate the

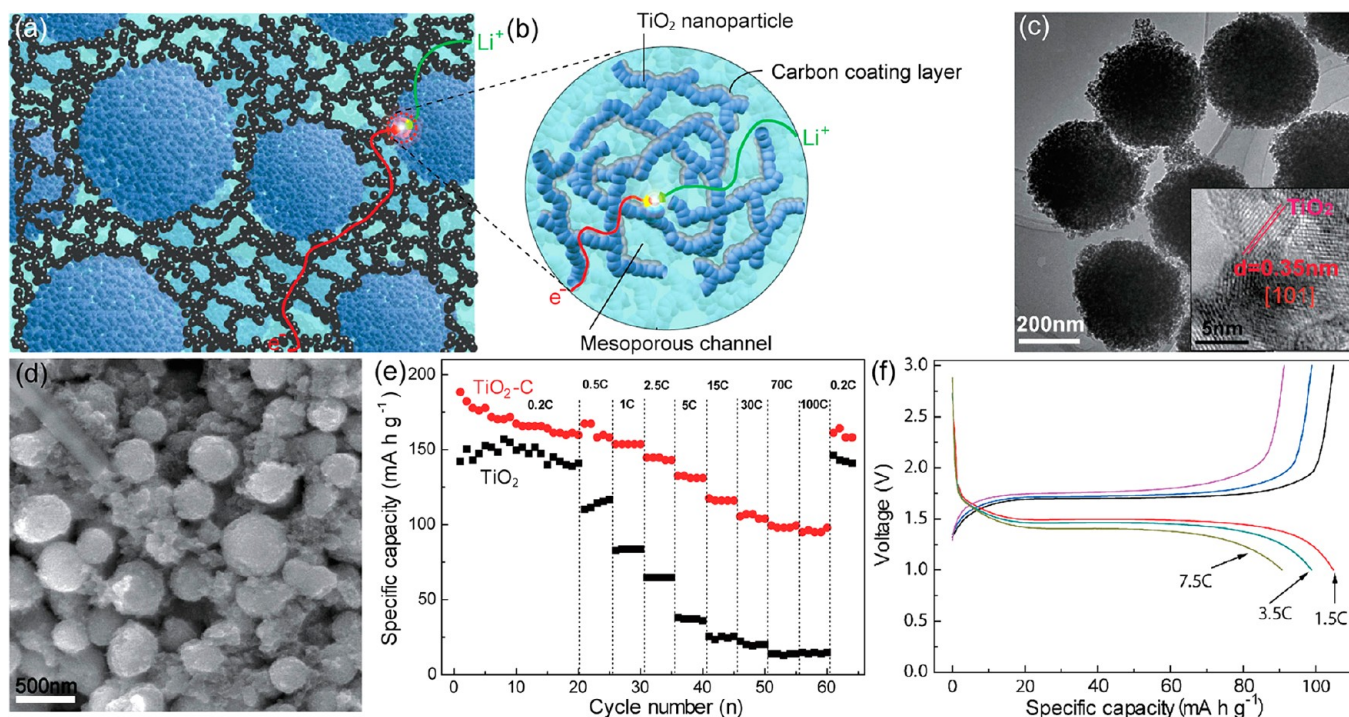


FIGURE 2. (a) General view of the conducting network formed by $\text{TiO}_2\text{-C}$ microspheres and carbon black, (b) partially enlarged view of mesoporous channels and nanocarbon network in a composite sphere, (c) TEM image of the $\text{TiO}_2\text{-C}$ spheres, in which the inset shows its high-resolution TEM image, (d) SEM image of the $\text{TiO}_2\text{-C}$ electrode after cycling, (e) Comparison of the rate capabilities between $\text{TiO}_2\text{-C}$ and TiO_2 mesospheres, (f) Galvanostatic discharge–charge curves of a $\text{TiO}_2\text{-C}/\text{LiFePO}_4\text{-C}$ cell between 1 and 3 V.

Si expansion. In this way, the Si–C composite exhibits remarkable cycling and rate performances.²⁴ The carbon CVD method is also applicable to LiFePO_4 and other polyanionic-type cathode materials with good thermal stabilities but poor electronic conductivities.²⁵ However, for the cathode materials of Li-containing metal oxides, the CVD method is not suitable due to the carbon reduction and grain growth problems at elevated temperatures. It still remains a challenge to develop an effective low-temperature carbon coating technique for these materials.

The hydrothermal reactions of various carbon sources (e.g., carbohydrates) provide another feasible route to obtain the carbon nanoparticle network. Compared with CVD, the hydrothermal method can achieve a homogeneous carbon coating at low temperatures, making it applicable for a wide range of materials. This approach has been proven effective in improving the performance of various transition metal oxides (MOs). For example, we have introduced a uniform carbon nanoparticle network into TiO_2 mesoporous spheres through a hydrothermal route (Figure 2c,d).²⁶ The carbon coating layer forms an efficient mixed conducting network with mesopores, so that fast and seamless transport of both electrons and Li^+ can be achieved (Figure 2a,b). The $\text{TiO}_2\text{-C}$ exhibits an advantage over bare mesoporous TiO_2 spheres

by holding a high capacity of 99 mA h g^{-1} at 100 C (Figure 2e). Moreover, a 1.5 V full cell assembled with the $\text{TiO}_2\text{-C}$ anode and the $\text{LiFePO}_4\text{-C}$ cathode can deliver a capacity greater than 90 mA h g^{-1} at 7.5 C^{26} (Figure 2f). The enhancement by the carbon nanoparticle network on the electrochemical performance of the $\text{TiO}_2\text{-C}$ mesoporous sphere is equivalent to that reported for RuO_2 ,¹³ suggesting the validity of the method. Moreover, in view of its universality, the simple hydrothermal approach to introduce nanocarbon coating network can also be extended to other MOs, such as SnO_2 and Fe_3O_4 .^{27,28}

3. Carbon Nanotube Networks

In the context of constructing carbon networks, the CNT is a favorable choice. In benefit of their unique wired morphology, fast e^- transmission rate, and robust structure, CNTs can easily form cross-linked conducting networks and serve as the conducting phase. However, simply mixing CNTs with ANPs is not optimal to yield the best result. One optimized method is to load ANPs onto CNTs to form a coaxial architecture, which then forms cross-linked conducting networks (Figure 3a,b). Many MO ANPs have been loaded onto the CNTs to obtain hybrid anode materials with enhanced performance.^{29–32} Especially, in the case of TiO_2 with good

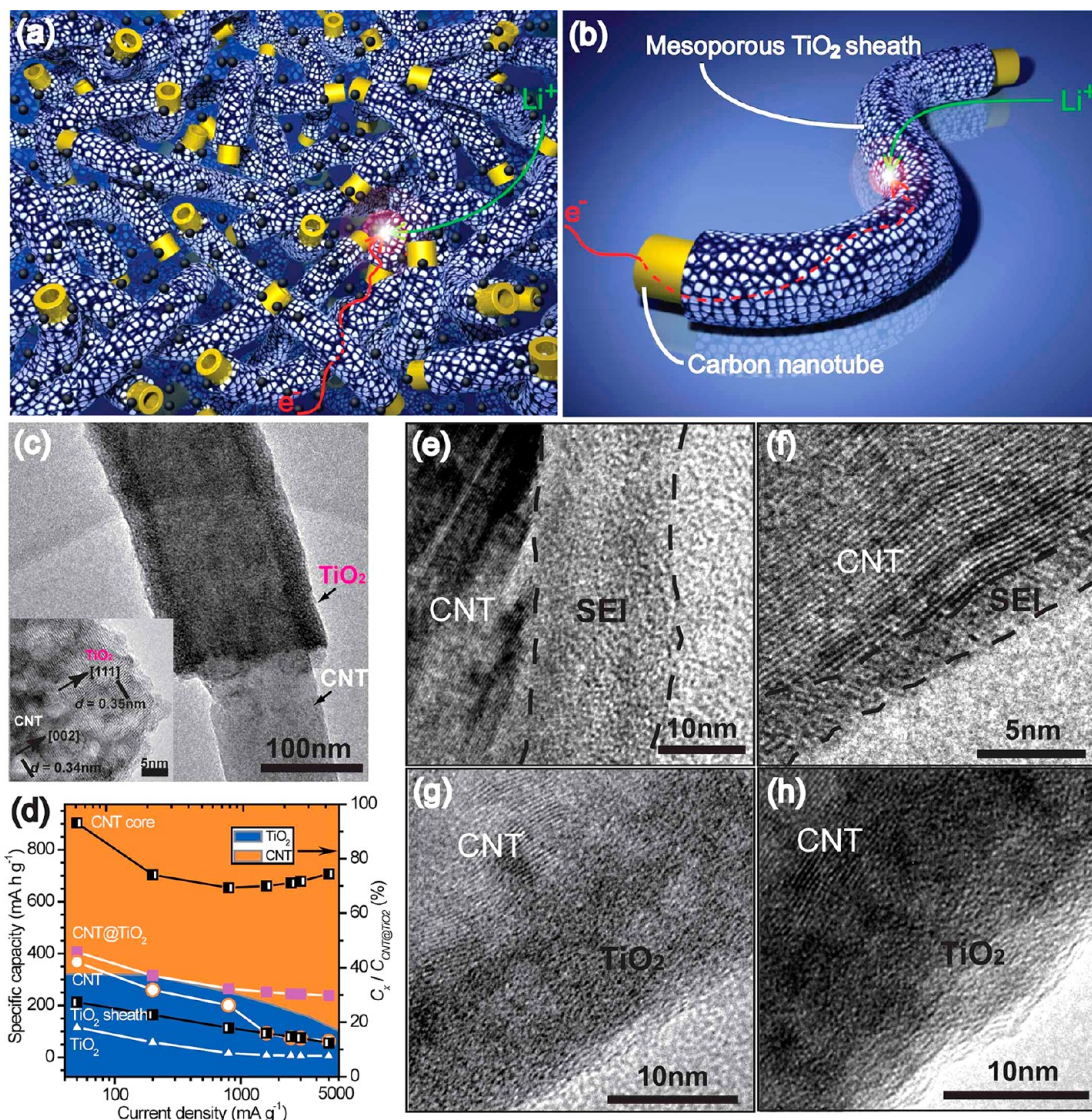


FIGURE 3. (a) General view of conducting network formed by coaxial nanocables and carbon black; (b) single nanocable with CNT core and mesoporous TiO_2 sheath; (c) TEM image of a $\text{CNT}@\text{TiO}_2$ nanocable, the inset shows the HRTEM image; (d) comparison of the rate performances among $\text{CNT}@\text{TiO}_2$, CNT, and TiO_2 sample, shaded areas indicate their capacity contributions; (e, f) TEM images of bare CNT in a fully lithiated state (e) and a fully delithiated state (f); (g, h) TEM images of $\text{CNT}@\text{TiO}_2$ nanocable in a fully lithiated state (g) and a fully delithiated state (h).

surface stability, synergistic effects are observed. We have fabricated $\text{CNT}@\text{TiO}_2$ core/porous-sheath coaxial nanocables by controlled hydrolysis of tetrabutyl titanate in the presence of CNTs (Figure 3c).³² The $\text{CNT}@\text{TiO}_2$ nanocables have several structural advantages toward efficient Li storage. On one hand, the CNT core with exposed ends provides sufficient e^- for the storage of Li in the TiO_2 sheath. On the other hand, the TiO_2 layer effectively prevents the formation of a thick and unstable solid electrolyte interphase (SEI) film on the surface of the CNT, and its porosity leads to an unperturbed Li^+ supply for the CNT core (Figure 3e–h).³² The synergistic effects of the two components lead to a composite material with high, fast, and stable lithium

storage. The coaxial nanocables can deliver a specific capacity of 244 mA h g^{-1} at an ultrahigh current density of 3000 mA g^{-1} , significantly higher than those of bare CNTs (74 mA h g^{-1}) or bare TiO_2 (almost no capacity) under the same conditions (Figure 3d).³²

For cathode materials, the content of CNTs should be low due to their negligible capacity contribution. The CNT network is especially suitable for cathode materials with good surface stabilities but poor electronic conductivities. However, there are few reports on using CNTs to improve the performance of cathode materials. The major limitation lies in the preparation method. While favorable coating of active particles onto CNTs is mainly obtained by wet chemistry,

most cathode materials are prepared by solid state reactions. With the development of solution-based synthetic techniques, the application of CNT networks into cathode materials may be available in the future.

4. Graphene Networks

Though graphene itself is not suitable for anodes due to its large initial irreversible capacity loss,^{18,33} it has been demonstrated to be a promising material for electrochemical supercapacitors.^{34,35} It is also widely used in constructing the conducting networks for LIBs because of its appealing features such as film-like structure, high electronic conductivity, excellent chemical stability, and large surface area.^{36,37} Generally, there are two ways to prepare the graphene–ANP (G-ANP) composites, namely, *in situ* growth of ANPs on graphene and the assembly of ANPs with graphene.

4.1. *In Situ* Growth of Active Nanoparticles on Graphene. The large surface area (theoretically $2600 \text{ m}^2 \text{ g}^{-1}$) of graphene makes it especially promising for loading ANPs. However, graphene itself is not suitable for *in situ* growth of ANPs due to a weak interaction between them. Therefore, most *in situ* growth of ANPs is first performed on graphene oxide (GO), followed by reduction of GO to produce G-ANPs. A solution method is usually adopted to grow MOs on graphene oxide, in which negatively charged GO sheets tend to trap positively charged metal ions for the *in situ* formation of MO ANPs on their surfaces. Under this direction, we have developed a two-step synthetic protocol to grow monodispersed SnO_2 nanoparticles onto single-layered graphene sheets.³⁸ The large surface area of graphene ensures a fine dispersion of SnO_2 nanoparticles on its surface without any agglomeration, and its flexibility relieves the volume changes upon cycling. Moreover, the graphene sheets with planar structure easily form an efficient 3D conducting network, allowing a high flux of Li^+ to pass through, while its high conductivity enables e^- to flow along the conductive plane to reach the ANPs for reaction with Li^+ (Figure 4). All these merits contribute to a high electrochemical activity and much enhanced kinetics for lithium storage. Other MO nanoparticles, such as TiO_2 and CuO , have also been supported on graphene sheets for improved capabilities.^{39,40} Currently, it is difficult to achieve the coadsorption and growth of two or more kinds of metal ions on GO. The *in situ* growth of cathode materials on graphene remains a challenge, and new techniques are highly desired.

4.2. Assembly of Active Nanoparticles and Graphene. The soft and flexible nature of the graphene sheet makes it easy to wrap around ANPs to form a conducting network,

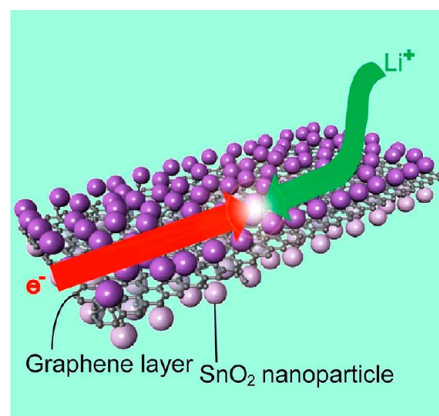


FIGURE 4. Schematic illustration showing a graphene sheet loaded with SnO_2 nanoparticles.

providing excellent electrical contact and leading to improved electrochemical performance of ANPs. Based on this idea, we have developed a novel assembly method, in which ANPs are directly combined with graphene to prepare the G-ANP composite. Compared with the *in situ* growth, this method is simple and general. However, several issues, including selection of appropriate dispersant for graphene, suitable interaction between graphene and ANPs, and prevention of phase separation, should be addressed. For example, in dealing with $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ (LNMC), a layered cathode material with good structural stability and relatively high energy density but poor kinetic properties, we have employed *N*-pyrrolidone as an efficient dispersant for both graphene and LNMC nanoparticles to prepare the LNMC/G composite cathode.⁴¹ Through a simple mixing procedure, a homogeneous LNMC/G composite is prepared, in which the graphene sheets uniformly wrap around the LNMC nanoparticles. With a hierarchical structure formed by the LNMC particles, graphene sheets, and carbon black, transportation of both Li^+ and e^- on the cathode are significantly enhanced, leading to a faster electrode reaction (Figure 5a). Consequently, remarkable improvements have been observed in both the charge transfer in the two-phase region and the apparent diffusion coefficient. This assembly technique is also applicable to anode materials. For example, much improved cycleability and rate capabilities have been achieved on the G- CuO composite.⁴⁰

The assembly technique can be extended to high-capacity alloy anodes (e.g., Sn, Ge, and Si),^{23,42,43} which are suffering from the pulverization problem due to their drastic volume variations (e.g., Si has a volume change of $>300\%$) during the alloying/dealloying process. Though the use of nanosized active material can reduce the deformation stress

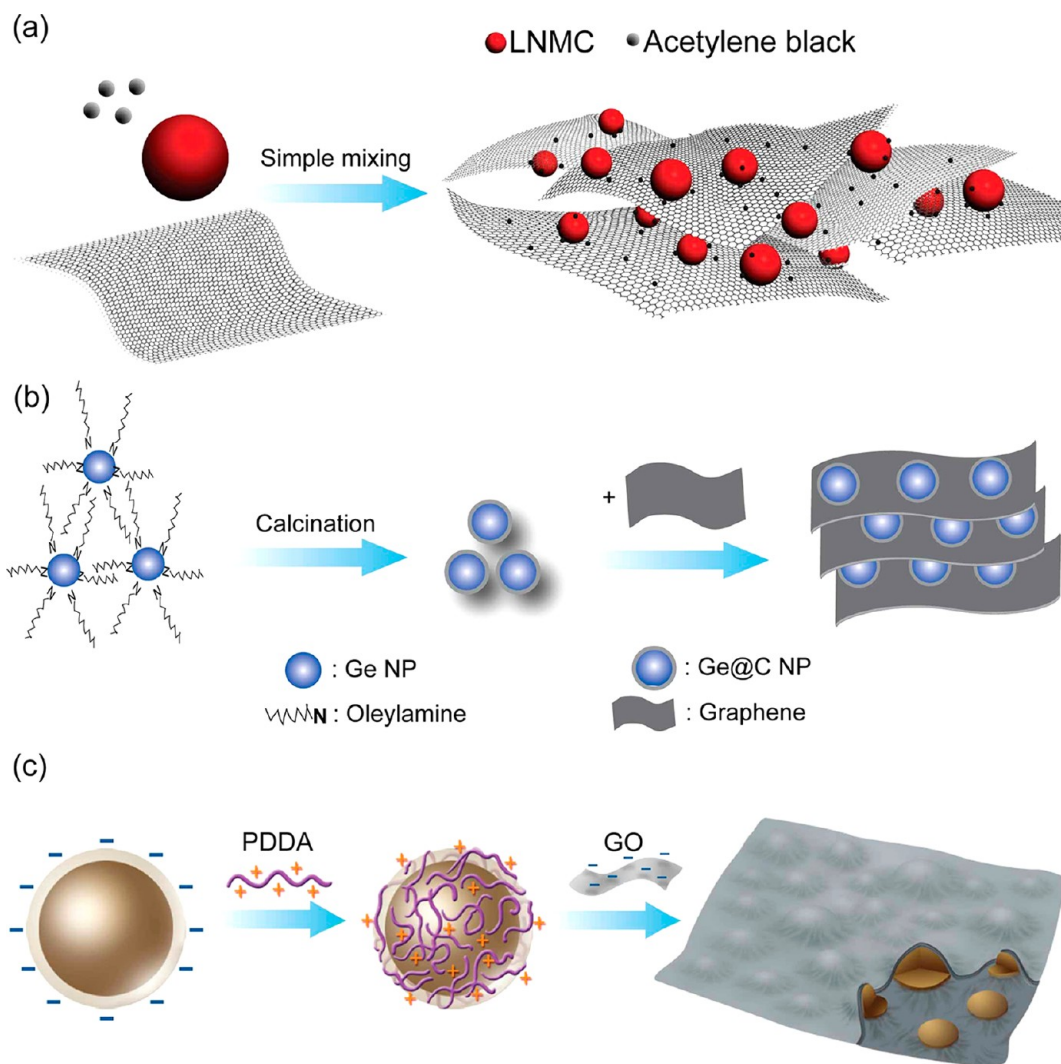


FIGURE 5. Assembly of ANPs and graphene to prepare the G-ANP composites: (a) preparation of LNM/C composite through a simple mixing route; (b) preparation of Ge@C/G composite; (c) preparation of Si-GO composite via electrostatic attraction.

to some extent, it also raises concerns on the agglomeration problem due to the unstable thermodynamics of ANPs. It causes difficulty for electrons to reach the center of the agglomerate. Graphene network offers an effective solution by dispersing the alloy ANPs, buffering the volume changes, and enabling a rapid electron transmission to each ANP. The strategy can be more effective when a core-shell structure is employed to replace the bare ANP. The power of this concept is demonstrated by the use of graphene network to disperse carbon-coated Ge nanoparticles (Figure 5b).⁴³ A double protection effect has been found on the obtained Ge@C/G composite, leading to both improved cycleability and high rate capability. Graphene and the carbon shell not only constitute a fast and continuous electron pathway but also serve as favorable buffers to accommodate the volume variation and dispersants to eliminate the agglomeration of Ge nanoparticles.

Another feasible method is to combine GO with ANPs first and then reduce GO leading to a well-dispersed G-ANPs composite. Based on this concept, we have inserted Si nanoparticles into GO sheets via a freeze-drying route to prepare the intermediate Si-GO composite. After further thermal treatment to reduce GO, the Si-G composite with a pod-like structure, in which Si nanoparticles are tightly wrapped by a few layers of graphene, is obtained.⁴⁴ The graphene coating ensures a good electrical contact with Si nanoparticles and an effective sponge to buffer the structural expansion/contraction, both of which contribute to an improved electrochemical performance. To achieve a better dispersion of Si nanoparticles, self-assembly through electrostatic attraction is proposed based on the negatively charged oxygen-containing groups (such as the hydroxyl and the carboxyl groups) on GO's surface and the negatively

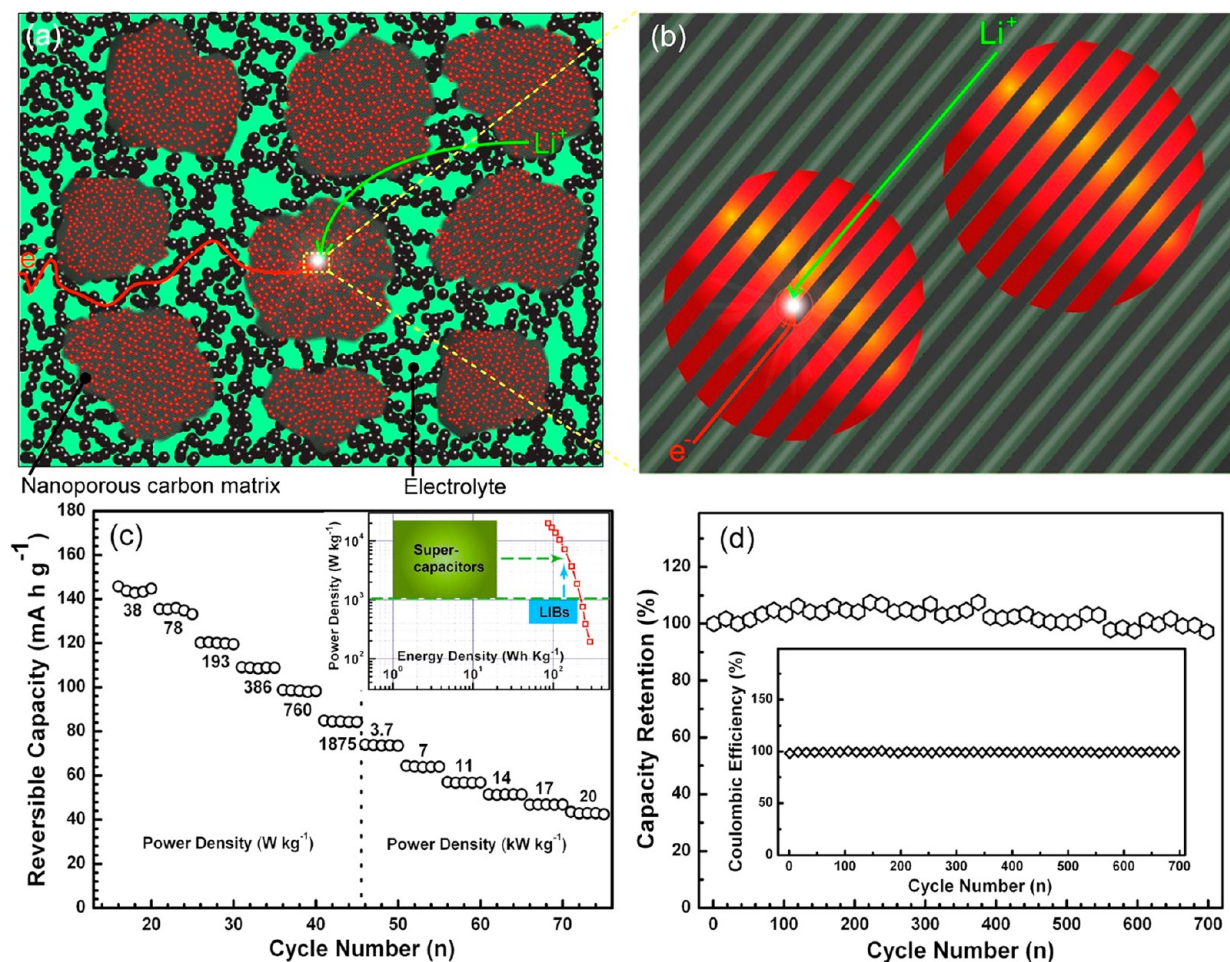


FIGURE 6. (a) General view and (b) partial enlarged view of hierarchically conducting network formed by LFP-NP@NPCM nanocomposites and carbon black. (c) The variation of reversible capacities of the composite along with the increase of the power density (the inset illustrates its compatibility for both LIBs and supercapacitors) and (d) the specific capacity and coulombic efficiency (inset) of the LFP-NP@NPCM nanocomposite at a charge–discharge rate of 1.5 C.

charged SiO_2 thin layer on the Si nanoparticles.⁴⁵ A positively charged polyelectrolyte, poly(diallyldimethylammonium chloride) (PDDA), is selected as a medium for the layer-by-layer assembly of GO and Si nanoparticles.⁴⁵ After the reduction of GO, a Si@G structure is obtained, in which an ultrathin graphene coating layer is tightly covering the outside of the Si nanoparticle (Figure 5c). Note that significant aggregation of Si nanoparticles commonly exists at high Si loading. To solve this problem, carbon nanoparticles could be added to effectively alleviate the aggregation of Si nanoparticles by separating them from each other and help graphene build efficient 3D conducting networks.⁴⁶ The obtained Si–C/G composite shows a much improved cycling performance (ca. 1521 mA h g^{-1} at 0.2 C after 200 cycles) and a favorable high-rate capability.⁴⁶ Considering the easy principles involved in the preparation and the highly versatile choices for electronic interaction, we

believe that these strategies can be easily extended to other electrode materials.

5. Nanoporous Carbon Networks

Nanoporous carbons prepared from the pyrolysis of polymers and carbohydrates will form interconnected nanochannels and electronically conductive walls, which are characteristically good conducting networks for both Li^+ and e^- . The use of nanoporous carbon networks leads to a facile and general design of electrode materials via dispersing ANPs into a nanoporous carbon matrix (NP@NPCM) (Figure 6a,b). One successful application is embedding LiFePO_4 nanoparticles in a nanoporous carbon matrix (LFP-NP@NPCM).¹⁶ With Pluronic F127, a block copolymer, as a nanopore-forming agent for obtaining the nanoporous carbon matrix (with mesopores of about 3.8 and 10 nm), the LFP-NP@NPCM nanocomposite with highly dispersed

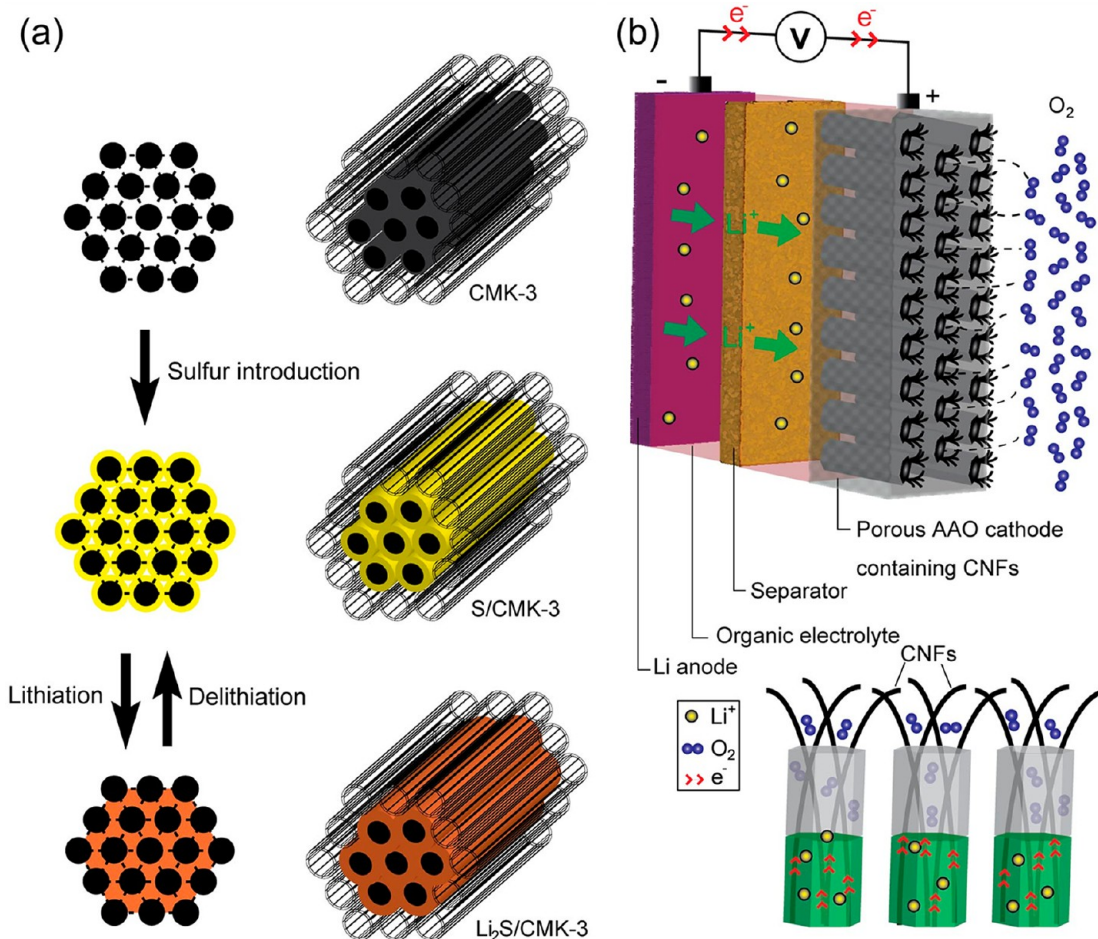


FIGURE 7. Nanocarbon networks for next-generation rechargeable lithium metal batteries: (a) CMK-3 mesoporous carbon substrate and its use in Li–S battery; (b) carbon nanofibers for porous cathode of Li–O₂ battery.

LiFePO₄ nanoparticles (ca. 60–100 nm) was obtained by a facile sol–gel procedure and a subsequent solid state synthesis route. Owing to faster Li⁺ and e⁻ migrations, the LFP-NP@NPCM nanocomposite shows greatly enhanced power and rate capabilities. It exhibits a fast charge–discharge ability (ca. 16 s) similar to a supercapacitor, but with more energy density (87 vs 1–20 W h kg⁻¹ of typical supercapacitor) (Figure 6c). Due to the buffer effect of the nanoporous carbon, it also shows excellent cycling performance with a capacity loss of less than 3% after 700 cycles at 1.5 C (Figure 6d). Moreover, the nanoporous carbon networks are also expected to benefit the sulfur cathode and the oxygen cathode for the next generation Li–S and Li–O₂ batteries.

6. Nanocarbon Networks for Rechargeable Lithium Batteries: Toward Future Applications

Since domination of the electronics market by LIBs, new applications in other energy-related fields are coming,

especially the stationary energy storage (e.g., grid) and the transportation field.^{5,6} The grid application requires a large scale battery with cost-effective long lifespan, high safety, and easy maintenance. A LIB comprising a LiFePO₄ cathode and a Li₄Ti₅O₁₂ or TiO₂ anode is considered to be promising because both electrodes have excellent structure stabilities upon Li⁺ intercalation/deintercalation, which enables a long cycle life and favorable safety. However, its grid application is hindered by the sluggish e⁻ and Li⁺ transport in both electrodes. As discussed previously, the use of nanocarbon networks can facilitate the electrode kinetics and hence make the grid-oriented applications possible.^{16,26,32} Moreover, the excellent electronic conductivity of the nanocarbon network can promote the battery's response to a grid contingency. Its favorable thermal conductivity can help to improve the heat dissipation of the battery, which is beneficial to the thermal management of a battery pack.

For transportation applications including plug-in electric vehicles and hybrid electric vehicles, high-power LIBs are

highly desired. In this aspect, the use of nanocarbon networks in electrode materials has promised superior LIBs with high power densities due to their abilities in improving electrode kinetics. To run longer after each charge, electric vehicles need batteries with higher energy densities. The energy densities of traditional LIBs are limited by the low theoretical capacities of anode and cathode materials based on intercalation/deintercalation mechanisms. Recently, people have turned to lithium metal batteries, such as Li–S and Li–O₂ batteries, which have energy densities several times or even tens of times higher than the LIBs.^{2,7} However, many problems, such as large polarization, low capacity, and poor cycling performance, impede the practical uses of these batteries. The nanocarbon network with high electronic conductivity and elegantly designed porous structure may effectively solve the problems. For example, the utilization of porous carbon substrate for the sulfur cathode of Li–S battery offers a rational way to deal with the insulating problem of sulfur and the dissolution and shuttling problems of polysulfides (Li₂S_{*n*}, *n* = 4–8) in common liquid electrolytes during discharge/charge processes. The porous nanocarbon network not only can provide sufficient Li⁺ and e[−] for the electrochemical reaction between Li and S but also can prohibit the dissolution of polysulfides.⁴⁷ One successful demonstration is the combination of sulfur with a CMK-3

mesoporous carbon with ordered one-dimensional channels, which effectively improves the electroactivity of sulfur and prevents the dissolution of polysulfides (Figure 7a). As a result, the S/CMK-3 cathode exhibits a large specific capacity and favorable stability upon cycling.⁸ Macroporous and microporous carbon substrates have also been employed for the sulfur cathode.^{48,49} Though the former has a large space to accommodate more sulfur, the macropores have a weak effect in constraining polysulfides, and the loaded sulfur particles are big and show a low electroactivity.⁴⁸ The latter can yield a much improved electroactivity and cycling stability, yet the small pore volume makes it hard to achieve a sulfur loading of >50 wt % and limits its practicability.⁴⁹ In addition, extremely small micropores may block the free diffusion of Li⁺, increasing the polarization and lowering the utilization of sulfur. Therefore, nanocarbon networks with optimized pore structures are of great importance for such application and remain challenging.

Porous carbon is also a vital component of the oxygen cathode in Li–O₂ battery, and its pore structure fundamentally determines the performance of the oxygen cathode. An ideal porous carbon network for oxygen cathode should have high electronic conductivity and high triple phase boundary to enable fast diffusions of e[−], Li⁺, and O₂, as well as large void space to accommodate discharge products for

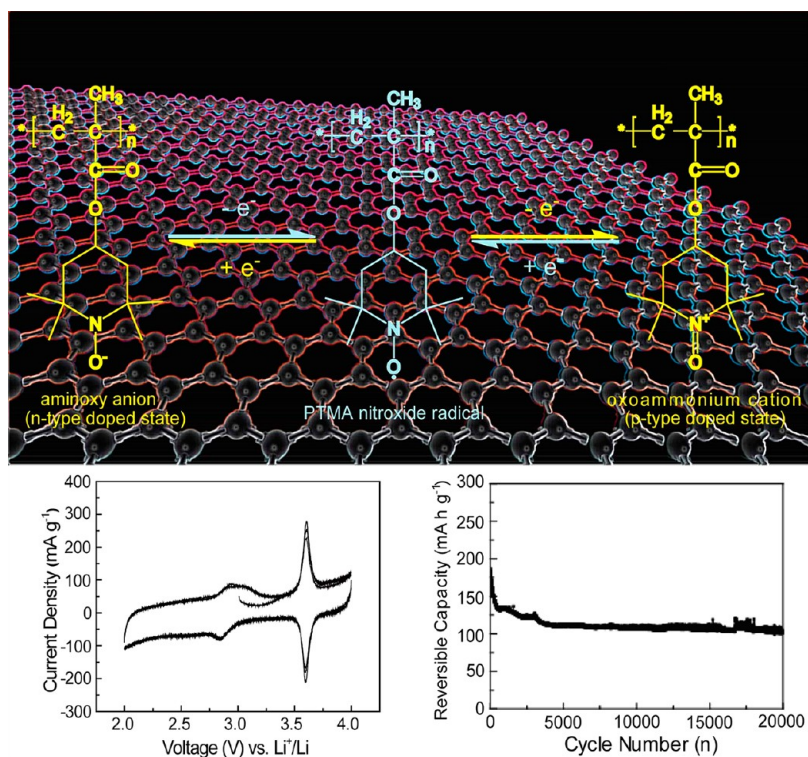


FIGURE 8. PTMA/graphene composite cathode and its electrochemical performance in a Li–organic battery.

a high capacity. Carbon nanofibers (CNFs) are promising in preparing the oxygen cathode.⁹ When grown on a ceramic porous substrate to prepare a binder-free oxygen cathode, a superior nanocarbon network is formed, in which electrons flow rapidly along the CNFs and the low carbon packing and porous structure enable fast diffusion of Li⁺ and O₂ in the cathode (Figure 7b). In this way, it achieves an efficient utilization of both the active carbon and the void volume. Graphene has also been used for the oxygen cathode due to its high electronic conductivity, large surface area, and good oxygen reduction catalytic ability. An oxygen cathode composed of heat-treated graphene exhibits both a high discharge voltage (near the oxygen cathode composed of 20 wt % Pt/carbon black) and a stable long-term cycling performance.⁵⁰

The Li–organic battery is another important prototype of future RLBs. The organic-based electrodes are light, flexible, eco-friendly, and easily processed.² However, most organic materials are insulative, resulting in low Li electroactivities and poor rate performances. For example, poly(2,2,6,6-tetramethyl-1-piperidinyloxy-4-yl methacrylate) (PTMA) is a radical polymer cathode material with high capacity (222 mA h g⁻¹ based on a two-electron redox reaction) but poor electroconductivity. However, after introducing a graphene network as the electronic conduction promoter, the prepared PTMA/graphene composite exhibits a high capacity approaching its theoretical value, an ultralong cycling life (up to 20 000 cycles), and a superior high rate capability (100 mA h g⁻¹ at 100 C) (Figure 8).⁵¹ The carbon conducting network opens a new window for turning those future batteries into realities.

7. Conclusions and Outlook

Highly conductive carbon networks with elegantly designed nanoarchitectures are crucial in constructing electrode materials with superior performances for advanced RLBs. With the concept of a 3D hierarchical conducting network, both electronic conductivity and thermodynamic stability of the composite material can be improved, and sometimes a synergistic effect can be expected. Moreover, the strategy to improve the performance of the electrode material by the nanocarbon network is also effective for newly emerged battery systems including Li–S, Li–O₂, and Li–organic batteries toward future applications for grid and transportation. With the emergence of novel carbon materials, such as carbon nanohorn and graphdiyne, more nanocarbon networks are available for better electrode materials.

The strategies presented here are simple but very effective. Both anode and cathode materials can take advantage of these strategies to improve their performance. In view of the versatility and the facility of synthesis routes, they may also be extended to other electrode materials suffering from poor electronic conductivities. In addition, the other elements with favorable electronic conductivities, such as copper and silver,^{15,52} can also be good candidates to build similar networks for their applications in electrochemical energy storage devices (RLBs, sodium ion batteries, supercapacitors) with both high power and high energy densities.

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FOOTNOTES

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REFERENCES

- Maier, J. Nanoionics: Ion Transport and Electrochemical Storage in Confined Systems. *Nat. Mater.* **2005**, *4*, 805–815.
- Armand, M.; Tarascon, J.-M. Building Better Batteries. *Nature* **2008**, *451*, 652–657.
- Bruce, P. G.; Scrosati, B.; Tarascon, J.-M. Nanomaterials for Rechargeable Lithium Batteries. *Angew. Chem., Int. Ed.* **2008**, *47*, 2930–2946.

- 4 Guo, Y.-G.; Hu, J.-S.; Wan, L.-J. Nanostructured Materials for Electrochemical Energy Conversion and Storage Devices. *Adv. Mater.* **2008**, *20*, 2878–2887.
- 5 Dunn, B.; Kamath, H.; Tarascon, J.-M. Electrical Energy Storage for the Grid: A Battery of Choices. *Science* **2011**, *334*, 928–935.
- 6 Yang, Z.; Zhang, J.; Kintner-Meyer, M. C. W.; Lu, X.; Choi, D.; Lemmon, J.-P.; Liu, J. Electrochemical Energy Storage for Green Grid. *Chem. Rev.* **2011**, *111*, 3577–3613.
- 7 Bruce, P.-G.; Freunberger, S.-A.; Hardwick, L.-J.; Tarascon, J.-M. Li-O₂ and Li-S Batteries with High Energy Storage. *Nat. Mater.* **2012**, *11*, 19–29.
- 8 Ji, X.; Lee, K.-T.; Nazar, L.-F. A Highly Ordered Nanostructured Carbon-Sulphur Cathode for Lithium-Sulphur Batteries. *Nat. Mater.* **2009**, *8*, 500–506.
- 9 Mitchell, R. R.; Gallant, B. M.; Thompson, C. V.; Shao-Horn, Y. All-Carbon-Nanofiber Electrodes for High-Energy Rechargeable Li-O₂ Batteries. *Energy Environ. Sci.* **2011**, *4* (8), 2952–2958.
- 10 Cao, F.-F.; Guo, Y.-G.; Wan, L.-J. Better Lithium-Ion Batteries with Nanocable-Like Electrode Materials. *Energy Environ. Sci.* **2011**, *4*, 1634–1642.
- 11 Chen, J.; Cheng, F.-Y. Combination of Lightweight Elements and Nanostructured Materials for Batteries. *Acc. Chem. Res.* **2009**, *42*, 713–723.
- 12 Arico, A.-S.; Bruce, P.-G.; Scrosati, B.; Tarascon, J.-M.; van Schalkwijk, W. Nanostructured Materials for Advanced Energy Conversion and Storage Devices. *Nat. Mater.* **2005**, *4*, 366–377.
- 13 Guo, Y.-G.; Hu, Y.-S.; Sigle, W.; Maier, J. Superior Electrode Performance of Nanostructured Mesoporous TiO₂ (Anatase) through Efficient Hierarchical Mixed Conducting Networks. *Adv. Mater.* **2007**, *19*, 2087–2091.
- 14 Hu, Y.-S.; Guo, Y.-G.; Dominko, R.; Gaberscek, M.; Jamnik, J.; Maier, J. Improved Electrode Performance of Porous LiFePO₄ Using RuO₂ as an Oxidic Nanoscale Interconnect. *Adv. Mater.* **2007**, *19*, 1963–1966.
- 15 Cao, F.-F.; Deng, J.-W.; Xin, S.; Ji, H.-X.; Schmidt, O.-G.; Wan, L.-J.; Guo, Y.-G. Cu-Si Nanocable Arrays as High-Rate Anode Materials for Lithium-Ion Batteries. *Adv. Mater.* **2011**, *23*, 4415–4420.
- 16 Wu, X.-L.; Jiang, L.-Y.; Cao, F.-F.; Guo, Y.-G.; Wan, L.-J. LiFePO₄ Nanoparticles Embedded in a Nanoporous Carbon Matrix: Superior Cathode Material for Electrochemical Energy-Storage Devices. *Adv. Mater.* **2009**, *21*, 2710–2714.
- 17 Chen, Z.; Qin, Y.; Ren, Y.; Lu, W.; Orendorff, C.; Roth, E.-P.; Amine, K. Multi-scale Study of Thermal Stability of Lithiated Graphite. *Energy Environ. Sci.* **2011**, *4*, 4023–4030.
- 18 Kaskhedikar, N.-A.; Maier, J. Lithium Storage in Carbon Nanostructures. *Adv. Mater.* **2009**, *21*, 2664–2680.
- 19 Wu, X.-L.; Liu, Q.; Guo, Y.-G.; Song, W.-G. Superior Storage Performance of Carbon Nanosprings as Anode Materials for Lithium-Ion Batteries. *Electrochem. Commun.* **2009**, *11*, 1468–1471.
- 20 Wu, X.-L.; Chen, L.-L.; Xin, S.; Yin, Y.-X.; Guo, Y.-G.; Kong, Q.-S.; Xia, Y.-Z. Preparation and Li Storage Properties of Hierarchical Porous Carbon Fibers Derived from Alginate Acid. *ChemSusChem* **2010**, *3*, 703–707.
- 21 Guo, B.; Wang, X.; Fulvio, P.-F.; Chi, M.; Mahurin, S.-M.; Sun, X.-G.; Dai, S. Soft-Templated Mesoporous Carbon-Carbon Nanotube Composites for High Performance Lithium-Ion Batteries. *Adv. Mater.* **2011**, *23*, 4661–4666.
- 22 Li, H.; Wang, Z.-X.; Chen, L.-Q.; Huang, X.-J. Research on Advanced Materials for Li-Ion Batteries. *Adv. Mater.* **2009**, *21*, 4593–4607.
- 23 Yin, Y.-X.; Xin, S.; Wan, L.-J.; Li, C.-J.; Guo, Y.-G. Electro Spray Synthesis of Silicon/Carbon Nanoporous Microspheres as Improved Anode Materials for Lithium-Ion Batteries. *J. Phys. Chem. C* **2011**, *115*, 14148–14154.
- 24 Magasinski, A.; Dixon, P.; Hertzberg, B.; Kvit, A.; Ayala, J.; Yushin, G. High-Performance Lithium-Ion Anodes Using a Hierarchical Bottom-up Approach. *Nat. Mater.* **2010**, *9*, 353–358.
- 25 Su, J.; Wu, X.-L.; Yang, C.-P.; Lee, J.-S.; Kim, J.; Guo, Y.-G. Self-Assembled LiFePO₄/C Nano/Microspheres by Using Phytic Acid as Phosphorus Source. *J. Phys. Chem. C* **2012**, *116*, 5019–5024.
- 26 Cao, F.-F.; Wu, X.-L.; Xin, S.; Guo, Y.-G.; Wan, L.-J. Facile Synthesis of Mesoporous TiO₂-C Nanosphere as an Improved Anode Material for Superior High Rate 1.5 V Rechargeable Li Ion Batteries Containing LiFePO₄-C Cathode. *J. Phys. Chem. C* **2010**, *114*, 10308–10313.
- 27 Jiang, L.-Y.; Wu, X.-L.; Guo, Y.-G.; Wan, L.-J. SnO₂-Based Hierarchical Nanomicrostructures Facile Synthesis and Their Applications in Gas Sensors and Lithium-Ion Batteries. *J. Phys. Chem. C* **2009**, *113*, 14213–14219.
- 28 Cui, Z.-M.; Jiang, L.-Y.; Song, W.-G.; Guo, Y.-G. High-Yield Gas-Liquid Interfacial Synthesis of Highly Dispersed Fe₃O₄ Nanocrystals and Their Application in Lithium-Ion Batteries. *Chem. Mater.* **2009**, *21*, 1162–1166.
- 29 Wang, Z.; Luan, D.; Madhavi, S.; Hu, Y.; Lou, X.-W. Assembling Carbon-Coated α -Fe₂O₃ Hollow Nanohorns on the CNT Backbone for Superior Lithium Storage Capability. *Energy Environ. Sci.* **2012**, *5*, 5252–5256.
- 30 Sathiya, M.; Prakash, A.-S.; Ramesha, K.; Tarascon, J.-M.; Shukla, A.-K. V₂O₅-Anchored Carbon Nanotubes for Enhanced Electrochemical Energy Storage. *J. Am. Chem. Soc.* **2011**, *133*, 16291–16299.
- 31 Ding, S.; Chen, J.-S.; Lou, X.-W. One-Dimensional Hierarchical Structures Composed of Novel Metal Oxide Nanosheets on a Carbon Nanotube Backbone and Their Lithium-Storage Properties. *Adv. Funct. Mater.* **2011**, *21*, 4120–4125.
- 32 Cao, F.-F.; Guo, Y.-G.; Zheng, S.-F.; Wu, X.-L.; Jiang, L.-Y.; Bi, R.-R.; Wan, L.-J.; Maier, J. Symbiotic Coaxial Nanocables: Facile Synthesis and an Efficient and Elegant Morphological Solution to the Lithium Storage Problem. *Chem. Mater.* **2010**, *22*, 1908–1914.
- 33 Compton, O.-C.; Jain, B.; Dikin, D.-A.; Abouimrane, A.; Amine, K.; Nguyen, S.-T. Chemically Active Reduced Graphene Oxide with Tunable C/O Ratios. *ACS Nano* **2011**, *5*, 4380–4391.
- 34 Zhu, Y.; Murali, S.; Stoller, M.-D.; Ganesh, K.-J.; Cai, W.; Ferreira, P.-J.; Pirkle, A.; Wallace, R.-M.; Cychosz, K.-A.; Thommes, M.; Su, D.; Stach, E.-A.; Ruoff, R.-S. Carbon-Based Supercapacitors Produced by Activation of Graphene. *Science* **2011**, *332*, 1537–1541.
- 35 Zheng, G.; Hu, L.; Wu, H.; Xie, X.; Cui, Y. Paper Supercapacitors by a Solvent-Free Drawing Method. *Energy Environ. Sci.* **2011**, *4*, 3368–3373.
- 36 Wan, X.; Huang, Y.; Chen, Y. Focusing on Energy and Optoelectronic Applications: A Journey for Graphene and Graphene Oxide at Large Scale. *Acc. Chem. Res.* **2012**, *45*, 598–607.
- 37 Pummera, M. Graphene-based nanomaterials for energy storage. *Energy Environ. Sci.* **2011**, *4*, 668–674.
- 38 Zhang, L.-S.; Jiang, L.-Y.; Yan, H.-J.; Wang, W. D.; Wang, W.; Song, W.-G.; Guo, Y.-G.; Wan, L.-J. Mono Dispersed SnO₂ Nanoparticles on Both Sides of Single Layer Graphene Sheets As Anode Materials in Li-Ion Batteries. *J. Mater. Chem.* **2010**, *20*, 5462–5467.
- 39 Yang, S.; Feng, X.; Müllen, K. Sandwich-Like, Graphene-Based Titania Nanosheets with High Surface Area for Fast Lithium Storage. *Adv. Mater.* **2011**, *23*, 3575–3579.
- 40 Wang, B.; Wu, X.-L.; Shu, C.-Y.; Guo, Y.-G.; Wang, C.-R. Synthesis of CuO/Graphene Nanocomposite As a High-Performance Anode Material for Lithium-Ion Batteries. *J. Mater. Chem.* **2010**, *20*, 10661–10664.
- 41 Jiang, K.-C.; Xin, S.; Lee, J.-S.; Kim, J.; Xiao, X.-L.; Guo, Y.-G. Improved Kinetics of LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂ Cathode Material through Reduced Graphene Oxide Networks. *Phys. Chem. Chem. Phys.* **2012**, *14*, 2934–2939.
- 42 Lee, K.-T.; Jung, Y.-S.; Oh, S.-M. Synthesis of Tin-Encapsulated Spherical Hollow Carbon for Anode Material in Lithium Secondary Batteries. *J. Am. Chem. Soc.* **2003**, *125*, 5652–5653.
- 43 Xue, D.-J.; Xin, S.; Yan, Y.; Jiang, K.-C.; Yin, Y.-X.; Guo, Y.-G.; Wan, L.-J. Improving the Electrode Performance of Ge through Ge@C Core-Shell Nanoparticles and Graphene Networks. *J. Am. Chem. Soc.* **2012**, *134*, 2512–2515.
- 44 Zhou, X.; Yin, Y.-X.; Wan, L.-J.; Guo, Y.-G. Facile Synthesis of Silicon Nanoparticles Inserted into Graphene Sheets As Improved Anode Materials for Lithium-Ion Batteries. *Chem. Commun.* **2012**, *48*, 2198–2200.
- 45 Zhou, X.; Yin, Y.-X.; Wan, L.-J.; Guo, Y.-G. Self-Assembled Nanocomposite of Silicon Nanoparticles Encapsulated in Graphene through Electrostatic Attraction for Lithium-Ion Batteries. *Adv. Energy Mater.* **2012**, DOI: 10.1002/aenm.201200158.
- 46 Zhou, X.; Yin, Y.-X.; Cao, A.-M.; Wan, L.-J.; Guo, Y.-G. Efficient 3D Conducting Networks Built by Graphene Sheets and Carbon Nanoparticles for High-Performance Silicon Anode. *ACS Appl. Mater. Interfaces* **2012**, *4*, 2824–2828.
- 47 Ji, X.; Nazar, L.-F. Advances in Li-S batteries. *J. Mater. Chem.* **2010**, *20*, 9821–9826.
- 48 Zheng, G.; Yang, Y.; Cha, J.-J.; Hong, S.-S.; Cui, Y. Hollow Carbon Nanofiber-Encapsulated Sulfur Cathodes for High Specific Capacity Rechargeable Lithium Batteries. *Nano Lett.* **2011**, *11*, 4462–4467.
- 49 Elazari, R.; Salitra, G.; Garsuch, A.; Panchenko, A.; Aurbach, D. Sulfur-Impregnated Activated Carbon Fiber Cloth as a Binder-Free Cathode for Rechargeable Li-S Batteries. *Adv. Mater.* **2011**, *23*, 5641–5644.
- 50 Yoo, E.; Zhou, H. Li-Air Rechargeable Battery Based on Metal-free Graphene Nanosheet Catalysts. *ACS Nano* **2011**, *5*, 3020–3026.
- 51 Guo, W.; Yin, Y.-X.; Xin, S.; Guo, Y.-G.; Wan, L.-J. Superior radical polymer cathode material with a two-electron process redox reaction promoted by graphene. *Energy Environ. Sci.* **2012**, *5*, 5221–5225.
- 52 Cao, F.-F.; Xin, S.; Guo, Y.-G.; Wan, L.-J. Wet Chemical Synthesis of Cu/TiO₂ Nanocomposites with Integrated Nano-Current-Collectors As High-Rate Anode Materials in Lithium-Ion Batteries. *Phys. Chem. Chem. Phys.* **2011**, *13*, 2014–2020.