

REVIEW

NANOMATERIALS

Energy storage: The future enabled by nanomaterials

Ekaterina Pomerantseva^{1,2*}, Francesco Bonaccorso^{3,4*}, Xinliang Feng^{5,6*}, Yi Cui^{7*}, Yury Gogotsi^{1,2*}

Lithium-ion batteries, which power portable electronics, electric vehicles, and stationary storage, have been recognized with the 2019 Nobel Prize in chemistry. The development of nanomaterials and their related processing into electrodes and devices can improve the performance and/or development of the existing energy storage systems. We provide a perspective on recent progress in the application of nanomaterials in energy storage devices, such as supercapacitors and batteries. The versatility of nanomaterials can lead to power sources for portable, flexible, foldable, and distributable electronics; electric transportation; and grid-scale storage, as well as integration in living environments and biomedical systems. To overcome limitations of nanomaterials related to high reactivity and chemical instability caused by their high surface area, nanoparticles with different functionalities should be combined in smart architectures on nano- and microscale. The integration of nanomaterials into functional architectures and devices requires the development of advanced manufacturing approaches. We discuss successful strategies and outline a roadmap for the exploitation of nanomaterials for enabling future energy storage applications, such as powering distributed sensor networks and flexible and wearable electronics.

Energy usage is experiencing a large and fast shift toward electricity as the main power source. Reversible storage and release of electricity is an essential technology, driven by the needs of portable consumer electronics and medical devices, electric vehicles, and electric grids, as well as the emerging Internet of Things and wearable technologies. These applications and the need to store energy harvested by triboelectric and piezoelectric generators (e.g., from muscle movements), as well as solar panels, wind power generators, heat sources, and moving machinery, call for considerable improvement and diversification of energy storage technology. In this context, materials with nanometer-sized structural features and a large electrochemically active surface can change the paradigm for energy storage from within the electrode bulk to surface redox processes that occur orders of magnitude faster and allow a greatly improved power and cycle life (1–3). High electronic and ionic conductivities combined with intrinsic strength and flexibility of low-dimensional materials allow ultrathin, flexible, and structural energy storage solutions.

The short diffusion path can enable the use of nonflammable solid electrolytes, leading to safer batteries, and large or multivalent ions for more affordable grid-scale applications. In addition to active energy-storing nanomaterials, passive components can benefit from the use of nanomaterials as well. For example, ultrathin hexagonal boron nitride (*h*-BN) and metal oxide separators and graphene or two-dimensional (2D) transition-metal carbide (MXene) current collectors can decrease the size and weight of the batteries (4, 5). Today, we possess a large library of nanoparticles and nanostructured materials with a variety of compositions, electrochemical properties, and morphologies ranging from 0D nanoparticles and quantum dots (6, 7) to 1D nanowires, nanotubes, and nanobelts (8, 9), to 2D nanoflakes and nanosheets (10–13), and to 3D porous networks (14–17) (Fig. 1).

However, some of the challenges related to the reactivity of nanomaterials are due to their high specific surface area (SSA), which leads to parasitic, and often irreversible, reactions and strong interaction with electrolyte (1, 2); in addition, cost and manufacturability of nanomaterials make the battery community skeptical about their promise for practical applications. Although the number of studies of various phenomena related to the performance of nanomaterials in energy storage is increasing year by year, only a few of them—such as graphene sheets, carbon nanotubes (CNTs), carbon black, and silicon nanoparticles—are currently used in commercial devices, primarily as additives (18).

High-capacity conversion (sulfur and fluorides) and alloying (Si and Sn) materials undergo considerable structure changes and

large volume expansion and contraction (19, 20), which can cause mechanical and chemomechanical instability across the length scales of individual nanoparticles, electrodes, and full electrochemical cells (21, 22). Coatings with nanoscale thickness obtained via atomic or molecular layer deposition may be needed to suppress parasitic interfacial reactions, including the growth of metal dendrites, and/or form an artificial solid-electrolyte interphase (SEI) layer leading to the improved stability of electrochemical cells (23–27). Achieving future advancements in this research area will require broadening the compositional chemistry of interfacial layers and developing nanotechnology approaches that would allow for pinhole-free coating of 3D architectures with varying porosity. Advances in the development of autonomous microsystems and micro-devices call for smaller power sources. As a result, many of the future energy storage devices need to be just several microns or even tens of nanometers thick. Therefore, thin film electrode and electrolyte layers need to be grown or printed not only on flat chips but also on surfaces of various shapes, such as packaging materials, or created as wearable tattoos, requiring manufacturing processes which differ drastically from the current battery manufacturing practice.

This review takes a holistic approach to energy storage, considering battery materials that exhibit bulk redox reactions and supercapacitor materials that store charge owing to the surface processes together, because nanostructuring often leads to erasing boundaries between these two energy storage solutions. We explain how the variety of 0D, 1D, 2D, and 3D nanoscale materials available today can be used as building blocks to create functional energy-storing architectures and what fundamental and engineering problems need to be resolved to enable the distributed energy storage required by the technologies of the next decade.

Nanomaterials platform

Figure 1 shows the variety of available 0D to 3D nanomaterials (nanoscale building blocks). What emerges is the large family of carbon nanomaterials (Fig. 1, top row). Carbon is invaluable for energy storage owing to its properties, such as low specific weight and high abundance, coupled with the high electronic conductivity of graphitic carbons. Moreover, because of $sp/sp^2/sp^3$ hybridization, multiple carbon structures and morphologies are available. However, nanostructured carbons usually provide limited, if any, redox capacity and only after functionalization (28, 29). Therefore, they are usually used as a double-layer capacitor material, or as a conducting support backbone (28, 29), rather than as active material for energy storage devices.

¹A.J. Drexel Nanomaterials Institute, Drexel University, Philadelphia, PA 19104, USA. ²Department of Materials Science and Engineering, Drexel University, Philadelphia, PA 19104, USA. ³Graphene Labs, Istituto Italiano di Tecnologia, 16163 Genova, Italy. ⁴BeDimensional Spa, 16163 Genova, Italy. ⁵Center for Advancing Electronics Dresden (CFAED), Technische Universität Dresden, 01062 Dresden, Germany. ⁶Faculty of Chemistry and Food Chemistry, Technische Universität Dresden, 01062 Dresden, Germany. ⁷Department of Materials Science and Engineering, Stanford University, Stanford, CA 94305, USA.

*Corresponding author. Email: ep423@drexel.edu (E.P.); francesco.bonaccorso@iit.it (F.B.); xinliang.feng@tu-dresden.de (X.F.); yicui@stanford.edu (Y.C.); gogotsi@drexel.edu (Y.G.)

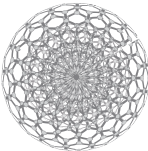
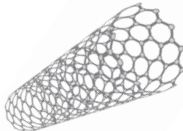
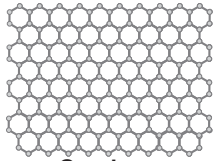
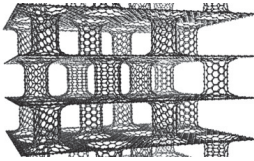
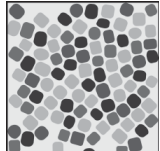
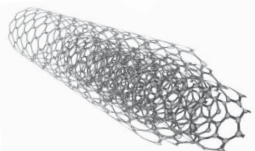
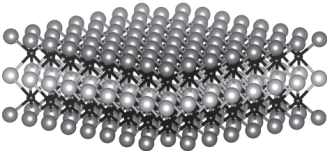
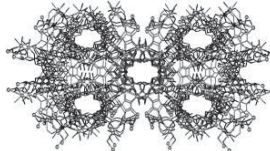
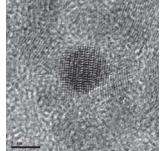
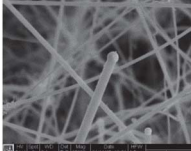
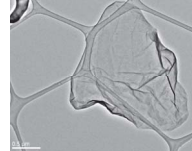
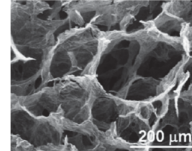
0D	1D	2D	3D
 Carbon Onion	 Single Wall Carbon Nanotube	 Graphene	 Pillared Graphene
 Nanoparticles	 Multiwall Nanotube	 Multielement 2D Compounds	 Metal-Organic Frameworks
 Quantum Dots	 Nanowires	 Nanoflakes	 Aerogels
Advantages			
Small in all dimensions Surfaces on all sites are accessible to electrolytes No bulk solid-state diffusion Can be integrated into multiple systems Can be used in stable inks for printing	Mechanical reliability Possibility to integrate with wearable devices Porous flexible freestanding films	Open 2D channels for ion transport; all surface is accessible enabling fast charge storage Compatible with flexible devices Small nanoflakes can be used in inks for printing	Can be used to create thick electrodes with large areal and volumetric storage properties
Limitations			
Agglomeration Do not densify and form only low density non-uniform structures Numerous points of contact lead to high resistance Poor chemical stability	Low packing density; cannot exhibit high volumetric performance Low yield and high cost of synthesis Diffusion pathways can be relatively long	Re-stacking Low out-of-plane electronic and ionic conductivity High cost of synthesis	Design Stability Manufacturing

Fig. 1. Overview of 0D, 1D, 2D, and 3D nanomaterials. An illustration of the chemical, structural, and morphological diversity of the available nanoscale building blocks that can be used to create complex functional architectures for next-generation energy storage devices with improved performance compared with the currently available ones. The advantages and challenges related to the application of each class of nanomaterials are summarized in the last two rows. [Metal organic frameworks, pillared graphene, quantum dots, and aerogels images reproduced with permission from (140–143), respectively; nanowires and nanoflakes images by Yayan Liu/Stanford University and Meng-Qiang Zhao/Drexel University, respectively.]

The exception is graphite, which consists of an ordered stack of graphene layers and exhibits a specific capacity of 372 mA-hour g⁻¹ for lithium ion storage in between the layers (30). A more conventional approach to achieving high specific capacity is to exploit redox reactions in nanomaterials and thus utilize materials beyond carbons. High surface area of transition-metal compounds (oxides, sulfides, carbides, nitrides, etc.) and pure elements forming alloys with Li (Si, Ge, Sn, etc.) (31, 32) allow those reactions to occur without solid-

state diffusion limitations. More recently, highly crystalline conductive materials—such as metal organic frameworks (33–35), covalent organic frameworks (36), MXenes, and their composites, which form both 2D and 3D structures—have been used as electrodes for energy storage. They show promise to deliver high areal capacity owing to their high porosity, thus allowing the construction of thick electrodes (37). Organic nanomaterials, especially heteroatom-rich molecules and porous organic materials, not only can be directly used as

electrodes for energy storage but can also be used as precursors to develop carbon-rich materials for energy storage (38). In addition to chemical diversity, advances in nanomaterial synthesis enable control of morphological dimensionality, ranging from 0D to 3D nanostructures (Fig. 1), each of which has both advantages and limitations for energy storage applications. To benefit from their useful properties and alleviate shortcomings, redox-active 0D nanoparticles can be decorated on the surface of conductive 1D

and 2D materials with a double function—that is, preventing their aggregation and restacking—while at the same time contributing to charge storage. Examples of such structures are demonstrated by graphene-oxide (6, 39, 40) or MXene-oxide hybrids with enhanced energy storage capabilities enabled by the redox activity of oxide nanoparticles and the high electronic conductivity of graphene (41) or MXene (42). When produced as nanoscale particles, even typical battery materials can show pseudocapacitive behavior (pseudo-linear charge-discharge), as was demonstrated for 6-nm nanoparticles of LiCoO_2 (43) and will be discussed in detail later. The self-assembly of 0D nanoparticles into denser systems is possible if the particles are monodisperse, as shown by the assembly of oxide nanoparticles on dichalcogenide sheets into ordered structures (44). Another limitation of 0D nanoparticle electrodes is a low electrical conductivity, owing to the contact resistance created by each contact point. An electrode containing multiple nanoparticle contact points can be considered as many resistors in series. If nanoparticles are conductive, as in the case of carbon onions, this problem is mitigated, but for most less conductive materials, this represents a severe limitation. Even in the case of conducting particles, Schottky junctions can form (45). In addition, nanoparticles of certain material classes, such as dichalcogenides, are not very stable (46) and require protective treatment during both synthesis and handling. Many semiconductor and metal nanoparticles form a passivating coating layer on the surface (47), creating a barrier for the charge transport, which either requires a further annealing step or encapsulation.

A key feature of 1D structures relies on the possibility of forming highly conducting continuous networks, by assembling conducting 1D nanomaterials (e.g., CNTs and metallic nanowires) over a large area and thickness of the electrode, leading to fast electron transport (20). CNTs are already widely used as conductive additives in battery electrodes (20). Additionally, many of the 1D nanostructures, especially CNTs, provide high mechanical strength (e.g., Young's modulus of 0.6 TPa) (48), ensuring mechanical integrity of the electrodes (20). Unlike the 0D particles, 1D nanomaterials do not require a binder to produce flexible structures, a feature that is particularly attractive for wearable applications. Moreover, although 1D nanomaterials form bundles (49), they still produce porous electrodes enabling electrolyte penetration (20, 35). Porous free-standing membranes were formed using Al_2O_3 nanowires through direct transformation of bulk aluminum alloy into alkoxide nanowires, followed by heating in air (8). These membranes were used to produce ceramic separators for high-rate batteries, which

are less prone to catching fire (8). The empty space between 1D structures allows the design of zero-expansion electrodes, leading to increased lifetime and decreased mechanical, thermal, and resistive losses. This property is particularly important for alloying anodes, such as Si, Ge, or Sn, in accommodating volume changes associated with interaction with up to 4.4 Li^+ ions per atom (3). The downside of 1D nanostructures is their low packing density, which makes the design and realization of 1D nanomaterial-based electrodes with high volumetric performance challenging (3). A strategy to overcome this limitation could be combining 1D nanostructures with 0D nanoparticles, thereby filling gaps between the nanotubes or nanowires and increasing the volumetric performance. The large-scale production of 1D nanostructures is another challenge. 1D nanomaterials such as single-wall CNTs or silicon nanowires are difficult to produce in large quantities at low cost. Another limitation of 1D nanomaterials is their intrinsic structure-morphology relationship, which affects the electrochemical performances. For example, for tunnel manganese oxide nanowires (9, 50), the diffusion pathways are oriented along the length, not across the 1D nanowire, and can be relatively long, up to 100 μm .

For 2D nanomaterials, their primary advantage is related to their intrinsic structure, that is, the entire 2D surface can be accessible to electrolyte ions, enabling fast charge storage (11, 42). Similar to 1D nanostructures, 2D sheets can form flexible electrodes without binders (51) or other additives, but they have the added value of achieving a much higher packing density and volumetric performance compared with the 1D counterparts. Although 2D sheets can be grown on some metal substrates, and progress is being made toward large-area single crystals (52), the large-scale bottom-up production of 2D materials is too expensive for the majority of energy storage applications, with the exception of small on-chip devices. By contrast, the direct liquid-phase exfoliation (LPE) of bulk layered crystals (53–55), wet chemical synthesis, and selective etching and dealloying (transformative synthesis) are much more relevant strategies for the scalable production and processing of 2D nanomaterials (56). The LPE process enables the formulation of inks of 2D materials in different solvents (10) for printing devices (10, 11). 2D structures can provide high electronic conductivity in-plane, but there might be low electronic conductivity and slow transport of ions in the out-of-plane direction (57, 58). Thus, the 2D morphology hinders the achievement of high (electro)chemical performance of thick planar electrodes with 2D sheets aligned along the surface of the current collector (37). In this respect, defect (pinhole) generation in 2D sheets would help, if it did not sacrifice

the intrinsic electronic and electrochemical properties. Moreover, restacking of 2D structures limits electrolyte penetration and ionic transport (57). Smart architectures should have sufficient porosity and enlarged interlayer distance, as well as vertical alignment of 2D sheets enabling fast electrolyte penetration, while still enabling dense packing of nanoflakes. Hybridization of 2D sheets with 0D and 1D nanomaterials can either minimize or completely eliminate the restacking issue. Preventing restacking is also important to boost the performance of catalytically active 2D materials in order to make their surface accessible to reagents and increase the number of reaction sites. Layered materials and pillared clays offer opportunities for a tailored nanodesign, including tunable interlayer spacing and modification of the interlayer chemistry often accompanied by improved stability, leading to their diverse applications as multifunctional catalysts (59). Efficient strategies demonstrated in the catalysis area can also be explored for energy storage application and vice versa.

Many 3D nanomaterials, such as carbon (graphene) aerogels (14) and metal organic frameworks (MOFs), are a result of the assembly process of nanoparticles. Few 3D nanomaterials have intrinsic nanoscale features (e.g., thin walls of porous templated or carbide-derived carbons); most of them are built by combining 0D, 1D, and 2D nanomaterials of the same kind (carbons). To produce thick electrodes (e.g., 100 to 200 μm) with large areal and volumetric storage properties, it is necessary to develop 3D architectures optimized for both ion and electron transport. These architectures would minimize the amount of passive materials in cells, such as current collectors and separators that occupy additional volume and add dead weight. Examples of 3D electrodes with porous architectures that enable advances in energy storage have already been reported in literature (60–62). Building on these approaches, as well as developing new ones, is important for moving closer to nanomaterials-enabled energy storage.

Despite exciting diversity, none of the available nanomaterials are perfect, and none of them can solve all the problems of the current energy storage technologies. Carbon materials offer high electrical conductivity and chemical stability but a limited charge-storage capability. Transition-metal oxides and redox-active organic materials can often offer much larger charge storage, but most of them have low electrical conductivity. The latter issue can be overcome by combining the aforementioned active materials in a physical mixture or a hybrid structure with carbon or other conducting materials (20). 2D transition-metal carbides, nitrides, and carbonitrides, classified as MXenes, possess high electronic and high ionic conductivities (42). However, for this

class of materials, cost, stability, and an understanding of the electrochemical mechanisms are still open issues. This field is rapidly growing, with more than 30 highly conductive materials available, of which Ti_3C_2 has already demonstrated exceptional values of capacitance in aqueous electrolytes and excellent performance at rates up to 1000 V s^{-1} (57). Overall, the availability of nanoscale building blocks is continuously increasing. This provides a portfolio of materials with properties not achievable with the conventional materials used for batteries and supercapacitors.

Fundamental processes governing energy storage

The fundamental processes that control electrochemical performance can be somewhat different from bulk battery materials. For example, the transport of ions in nanoscale systems typically occurs in confinement between or at the surfaces of electrode materials (Fig. 2A), as in supercapacitors with porous carbon electrodes (63), instead of the transport in bulk electrolyte and solid electrodes in conventional batteries. Examples of extreme confinement could be narrow 2D slit pores between 2D sheets or narrow 1D channels in the structure of tunnel oxides or nanotubes. Although an understanding of such transport properties is largely missing thus far, there are data that show anomalous fast transport of water in hydrophobic channels of CNTs (64) or fast transport of protons by the Grotthuss mechanism

between MXene nanosheets (65). The presence of confined water or electrolyte within nanochannels is known to facilitate the transport of ions (66), including large or multivalent ions, such as Mg^{2+} and Al^{3+} (67). Water or electrolyte confinement also allows the transport of complex ions—for example, AlCl_4^- or organic ions—which is challenging and/or cannot be achieved in conventional battery electrodes (68), at least not for the intercalation mechanism. In the case of nanomaterials, we can explore fast storage mechanisms, such as intercalation pseudocapacitance, which is a process determined as non-diffusion-limited insertion of ions into the active electrode material (69). Confined structural water can be beneficial to improving charge-transfer resistance, especially in the case of aqueous energy storage systems (70, 71). Moreover, it was shown that there was no detrimental effect on the performance of nonaqueous Li-ion cells over several hundreds of cycles when a small amount of water was added to the electrolyte (72). However, a considerable amount of water present in the electrode structure can be harmful to the device operation by causing parasitic reactions, which lead to irreversible chemical transformations of the device components (73). As of now, there is no clear understanding of how the kind of confinement or the amount of water in the material structure, the strength of bonds, crystallographic positions, and other parameters affect the electrochemical storage properties. A more in-depth study of these aspects

is important to gain knowledge of the role of confined water in charge storage properties of nanomaterials.

It is also necessary to study the transport of electrons, because for some low-dimensional materials—such as CNTs, graphene, or Nb_2C —quantum capacitance (74) can become a limiting factor. The quantum capacitance is linked with the variation of the density of states of the materials (i.e., the effect of band filling and band emptying), which modifies the capacitance, imitating a second capacitor in series (74). More severely, many nanomaterials, such as oxides, are poor electronic conductors, raising multiple questions. How can we wire them? How can we inject electrons? Can electrons tunnel through thin mono-, double-, or triple-layers of ions of electrolyte between the sheets? What are the rate-limiting factors?

Hybridization of dissimilar nanomaterials—that is, the combination of oxide nanoparticles and carbons—maximizes heterointerfaces at which new phenomena can occur, as schematically illustrated in Fig. 2B. As a result of different work functions of carbon (e.g., graphene, CNTs, or carbon onions) and oxide nanoparticles (e.g., MnO_2 or Nb_2O_5), electrons may be injected from the carbon into the oxide, increasing the electrical conductivity of the latter. Consequently, formation of holes in graphene leads to an increase in the number of charge carriers and its quantum capacitance. Faster ionic transport and different ion-insertion potentials have been reported for hybrid 2D materials (75), such as graphene and MoS_2 (76) and graphene and Ti_3C_2 compared with the individual components (77). Therefore, the synergistic effects between different nanomaterials can be achieved by combining materials with different properties.

One challenge is the avoidance of unwanted chemical reactions associated with the high SSA of nanomaterials, which reaches to more than $2000 \text{ m}^2 \text{ g}^{-1}$ for porous carbon and graphene and is between 100 and $1000 \text{ m}^2 \text{ g}^{-1}$ for most other nanomaterials, such as CNTs, dichalcogenides, or MXenes (42). High SSA favors chemical interactions and the formation of SEI-like structures, often resulting in a very large first-cycle irreversible capacity or parasitic reactions during cycling, limiting the device's lifetime (Fig. 2C). Therefore, reactions between nanoparticles and electrolyte during cycling need to be studied in depth to fully understand and control them. An effective strategy to solve this problem is to assemble small nanostructures into secondary particles—that is, aggregates or clusters—of larger dimensions. In these structures, the electrolyte only contacts the outer surface of the secondary particles, thus reducing the effective contact surface area without losing the advantages of nanoscale dimensions of electrode material. This has been seen in

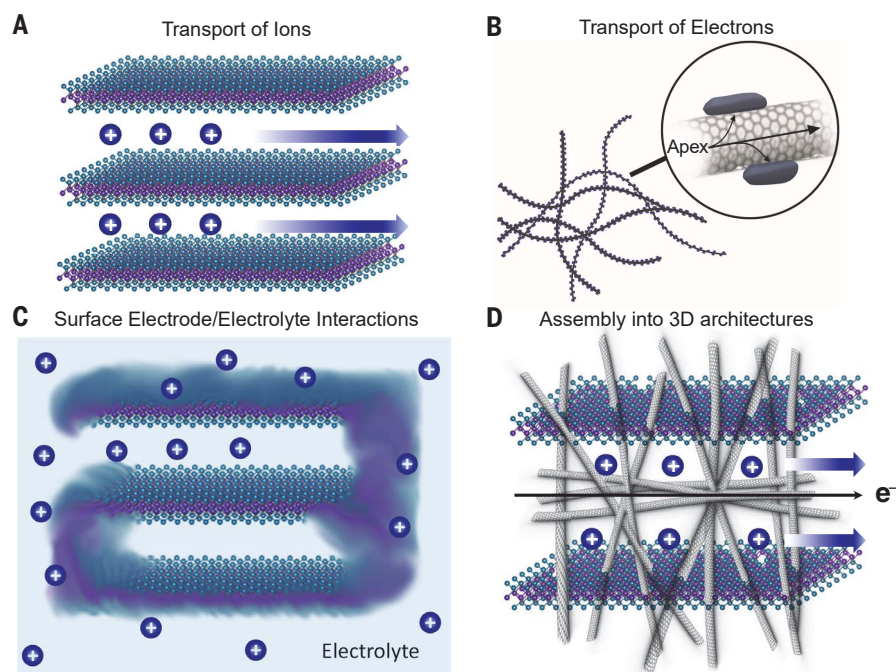


Fig. 2. Fundamental properties governing the performance of nanostructured materials for energy storage application. (A) Transport of ions. (B) Transport of electrons. (C) SEI formation and parasitic reactions between electrode and electrolyte. Blurry areas represent reaction products, such as SEI. (D) Connectivity and transport in 3D space.

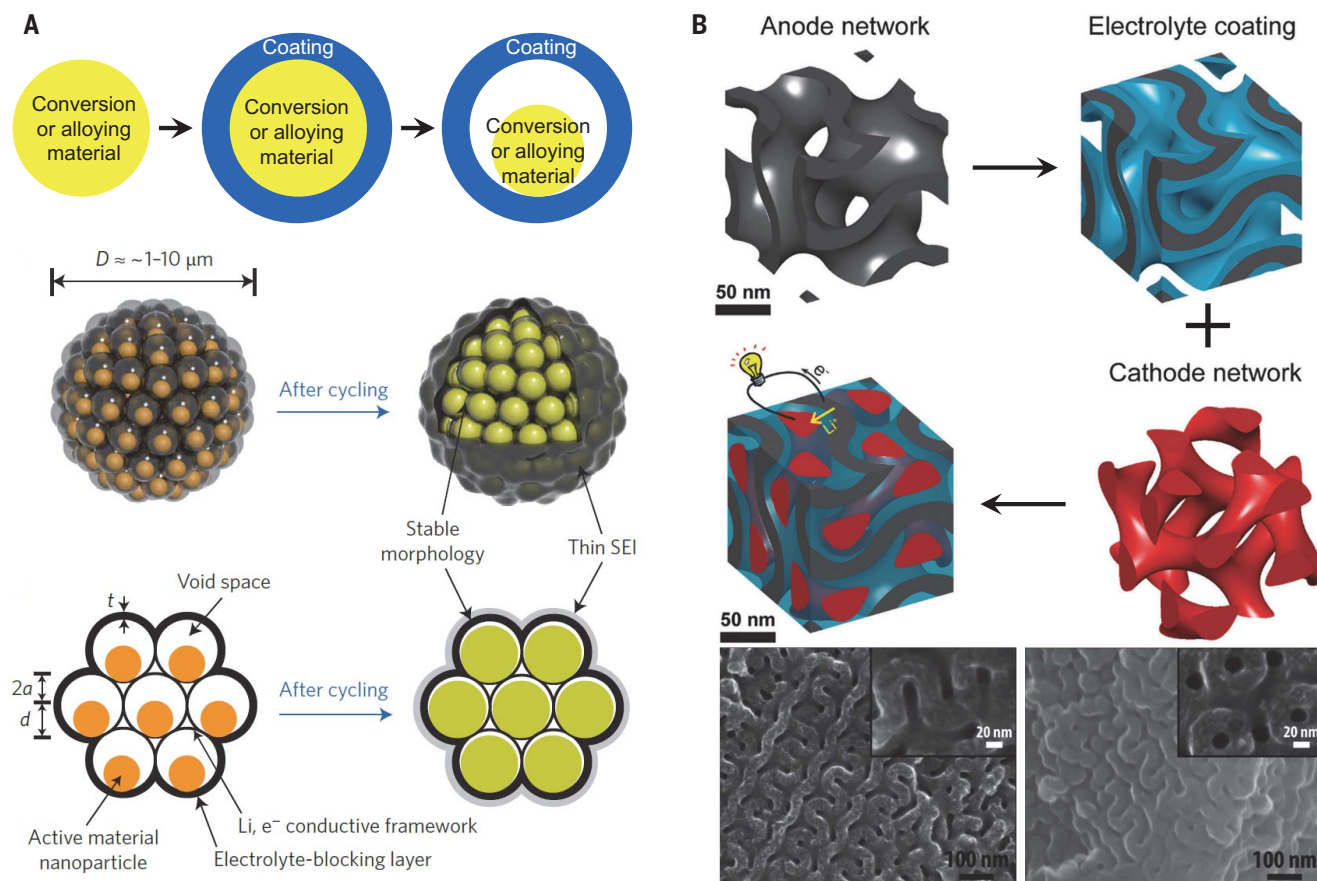


Fig. 3. Strategies developed to overcome performance limitations of nanomaterials in energy storage applications. (A) Nanoscale coatings on the surface of conversion and alloying electrode materials need to avoid mechanical instability caused by large-volume change and loss of the surface area as a result of agglomeration (78). D , diameter of pomegranate microparticle; t , thickness of the conducting framework; $2a$, void dimension; d , diameter of the active material primary particles. (B) Nanostructured 3D electrode architecture can be realized through a scalable block-copolymer self-assembly process (86). [Images adapted with permission from (78, 86)]

pomegranate-like Si nanoparticle-assembly anode materials (78) (Fig. 3A) and concentration-gradient LiNiMnCoO_2 cathode materials (79).

Finally, assembly into interconnected 3D electrode architectures with different length scales (from nanometers to microscale) can provide electronic and ionic conductivity in three dimensions. This requires pore engineering (80) and controllable assembly of different classes of nanomaterials (Fig. 2D). A goal is to generate a self-assembled 3D bicontinuous nanoarchitecture consisting of electrochemically active material with rapid ion and electron transport pathways (81). For building truly 3D architectures that integrate anode, cathode, and electrolyte together, which shortens the ionic diffusion length compared with conventional electrodes, the interdigitated types of electrode configurations have been proposed (82), although their experimental realization at a large scale is still challenging. A true 3D architecture was demonstrated using layer-by-layer self-assembly of interdigitated thin films on the surface of an open-cell aerogel substrate and other examples (83–85). An alter-

native strategy relies on the infiltration of a 3D scaffold that has a macroporous structure—for example, aerogel, graphene, or CNTs—with nanoparticles of active material. However, this approach has a number of limitations, such as limited volumetric performance. Fundamentally, it is necessary to learn how to build 3D architectures by self-assembly during electrode manufacturing. Relatively little has been done in this direction, but there are already encouraging demonstrations of truly integrated 3D electrodes (86) (Fig. 3B). Electrochemical or vapor-phase deposition of a separator and a counter electrode on a meso- or macroporous scaffold is promising as well.

Advances and phenomena enabled by nanomaterials in energy storage

Nanostructuring often enables the use of conventional materials that cannot be used in the microcrystalline state as either cathodes or anodes. Classical examples are alloying anodes—such as silicon, germanium, or tin—that experience large structure and volume changes during cycling (31, 32). Bulk silicon, which has a

theoretical capacity of up to $3579 \text{ mA}\cdot\text{hour g}^{-1}$, considering $\text{Li}_{15}\text{Si}_4$ formation, cannot work as stand-alone anode in a Li-ion battery. The life cycle of silicon-based anodes is limited by the pulverization of the active material, which is determined by the volume swelling of silicon upon lithiation (up to 400 volume %) and subsequent shrinkage upon delithiation (87). However, reducing the particle size below $\sim 150 \text{ nm}$ (3) limits the electrode cracking upon the insertion of Li^+ ions, which mitigates the anode mechanical failure (Fig. 4A). There have been designs proposed to overcome the issues of large volume expansion and mechanical failure, including the use of nanowires (1, 8), nanotubes (88), graphene flakes (19), hollow spheres, and core-shell and yolk-shell structures (89). To build a stable SEI for nanomaterials with large volume change, the concept of nanoscale double-walled hollowed structures was demonstrated. In this structure, the outer wall confines the expansion of the inner wall toward the hollow space inside and therefore generates a static outer surface for stable SEI formation (31).

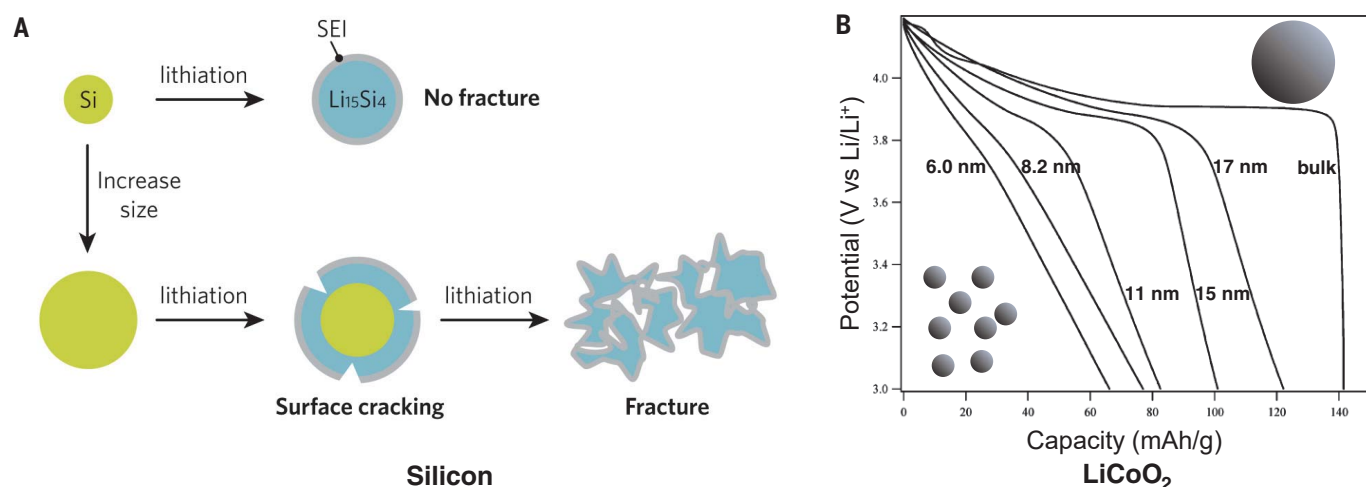


Fig. 4. Effect of nanostructuring on the electrochemical performance of energy storage materials in Li-ion batteries. (A) Schematic showing the effect of particle size on the lithiation of silicon anode material (144). (B) Effect of grain size on the galvanostatic discharge curve of LiCoO_2 cathode material (43). [Images adapted with permission from (43, 144)]

A large family of conversion materials—such as oxides, sulfides, and fluorides—offer potential for storing a large amount of charge, but they have poor cyclability coupled with phase transformation and large volume change (90). Benefits of nanostructures have been fully demonstrated on these materials as well (20). For example, through a conversion reaction, lithiation and sodiation of FeF_2 electrodes generate a composite material consisting of ultrafine (1 to 4 nm) Fe nanoparticles, which are further fused into a continuous conductive network, and a fluoride phase. Metal nanoparticle networks in the resulting structures enable fast electron transport during further cycling (91, 92). A similar effect is observed during lithiation of a $\text{Ag}_2\text{VO}_2\text{PO}_4$ cathode (93). High rate capability demonstrated by this material is attributed to the 15,000-fold increase in electronic conductivity associated with in situ formation of Ag nanoparticles during electrochemical reduction of $\text{Ag}_2\text{VO}_2\text{PO}_4$ (93). The sulfur cathode is another important example (94). Sulfur has a high theoretical capacity of $1673 \text{ mA}\cdot\text{hour g}^{-1}$ and offers a high theoretical specific energy of $2500 \text{ W}\cdot\text{hour kg}^{-1}$ for Li-S batteries. However, sulfur cathodes have three critical problems: (i) dissolution of lithium or sodium polysulfides into the organic electrolyte and their shuttling across the separator, (ii) lack of the electronic and ionic conductivity of sulfur and lithium sulfide resulting in poor utilization of active material, and (iii) large (80%) volume expansion of sulfur upon lithiation. The nanomaterials approach represents the most powerful solution to the aforementioned problems (89, 95). Thin layers of 2D materials, such as MXene (42), or electrospun carbon nanofibers (96) at the separator on the cathode side can serve as barriers for polysulfide transfer across the

separator. Encapsulation of sulfur in mesoporous carbon or MXene (95), S- TiO_2 yolk-shell structures (89), hollow sulfur spheres, and amphiphilic binding of sulfur and lithium sulfide species by oxide and nitrides offer solutions. In the case of metal-S batteries, nanomaterials with strong affinity to Li-polysulfides, such as carbides and nitrides of transition metals with high metallic conductivity (97), are preferred for building a scaffold for sulfur. The same materials with nanofiber or nanosheet morphology can be used for coating separators to prevent polysulfide shuttle. Another type of nanomaterial in the form of 0D or 2D particles or porous scaffolds can be used to prevent Li dendrite growth on the anode side (98, 99). Such battery architecture highlights the importance of the use of nanomaterials in all the battery components but also requires a holistic approach toward selecting nanomaterials that can perform different functions within an energy storage device. This area of research is currently under active investigation, and specific material solutions are yet to be found for each individual energy storage system. Nevertheless, MXenes and graphene have already shown promise in all the three key aforementioned battery components.

The continued pursuit of high-energy density battery chemistries, such as Li-S, recently revived considerable interest in Li metal anodes. Li metal has the theoretical specific capacity of $3860 \text{ mA}\cdot\text{hour g}^{-1}$ and the lowest potential as an anode, which maximizes the specific energy. However, Li metal has a long list of problems, including extremely high chemical reactivity and large volume changes during Li metal plating and stripping, which create phenomenological problems of Li metal dendrites and mossy Li formation, instability of SEI, low coulombic efficiency, battery short-

ing, and fire hazard (100). The interfacial stability was recently improved with additives or coatings of nanodiamonds, *h*-BN, and other nanomaterials (4, 101). The issue of large volume change can be addressed by designing host materials to house Li metal plating and stripping, including hollow carbon nanospheres, graphene oxide, MXene, and polymer nanofiber scaffolds (102).

Many conventional cathode materials, such as LiFePO_4 or LiCoO_2 , when downsized to the nanometer scale, can provide faster energy storage compared with the bulk counterparts (43). However, the energy storage mechanism changes, with the surface redox reaction becoming a dominant process. Large surface area creates a variety of sites for redox reactions, eliminates diffusion, and very often leads to changes in the electrochemical behavior, as has been shown, for example, for LiCoO_2 (43) (Fig. 4B). A decrease in the particle size leads to capacitor-like behavior, almost linear (supercapacitor-like) galvanostatic charge-discharge curves, and a decrease in capacity (43). Changes in electrochemical behavior induced by nanostructuring, similar to those observed for LiCoO_2 , are likely to be exhibited by other intercalation cathodes, including high-capacity materials from the lithium nickel cobalt aluminum oxide (commonly $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ or NCA) and lithium nickel cobalt manganese oxide (often $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ or $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ or NCM) families. This behavior is not necessarily exhibited by all nanomaterials, but it is necessary to consider that capacity can be both increased or decreased, with the shrinking of crystal or particle size, depending on the type of material and charge-storage mechanism. Examples are the increase in capacity in the case of silicon (3) and the decrease in capacity in the case of LiCoO_2 (43) (Fig. 4B).

Solid-state batteries, exhibiting substantially improved safety compared with the traditional ones, are considered to be one of the most promising storage technologies. In this context, there are a few considerations that make nanomaterials important for advancing this technology. First, in case of the solid-state batteries with planar geometry, nanostructuring promises to control 2D interfaces between battery components by means of the incorporation of specifically designed interface layers with nanoscale thickness and the ability to suppress parasitic reactions between electrode and electrolyte or metal dendrite growth (23–27). Additionally, nanomaterials can be used to create specific battery components. For example, nanoflakes of conductive 2D materials, such as graphene or MXene, can be assembled to form an exceptionally thin current collector layer (103). An exciting opportunity exists in the area of creating a highly conductive, uniform, and pinhole-free solid-state electrolyte layer with nanoscale thickness, which can potentially be achieved, for example, by using atomic layer deposition (104). Alternatively, Li-conducting nanofibers or nanowires could be embedded into the Li-conducting polymer matrix to produce a hybrid reinforced electrolyte layer with both high ionic conductivity and improved mechanical properties compared with the pristine one (105). Second, in case of the solid-state batteries with 3D architectures, the aforementioned nanomaterials-enabled advances are also important. However, in this case, nanomaterials can be used to construct 3D electrodes. Indeed, 3D elements in electrodes, such as pillars or cavities, often have micron-sized geometry to ensure mechanical stability. However, they can be hierarchically built out of nanoscale particles of various geometries to form pores for electrolyte penetration and to shorten diffusion distances to achieve fast transport of ions and electrons (106). Of course, building such architectures would require advanced manufacturing approaches, which we discuss below.

In addition to higher cost, compared with conventional materials, the remaining challenges related to the use of nanomaterials in energy storage devices include dealing with the sloping charge-discharge and the toxicity. For the former, the supercapacitor community knows how to handle this issue (107). Concerning the toxicity, it is important to ensure that nanomaterials have no or low toxicity and will not be harmful either during manufacturing or in the environment, once disposed. Nanomaterials, such as carbons, silicon, MXenes, or TiO_2 , are nontoxic. Moreover, nanomaterials can be degraded in the environment faster than macroscopic materials with the same composition. For example, Ti_3C_2 degradation produces TiO_2 and CO_2 , both nontoxic products, and the 2D morphology of MXene will lead to

fast biodegradation when exposed to water and air. However, it is important to study the toxicity and environmental fate of new nanomaterials to ensure that they can safely be introduced into large-volume manufacturing. Minimization of the side reactions caused by a large surface area of many nanomaterials is another major challenge. Surface chemistry passivation, electrode materials design that minimizes exposed SSA (e.g., yolk-shell particles), preconditioning of electrodes, and use of electrolytes that produce stable SEI can be used separately or together to mitigate the negative effects of side reactions.

Nanomaterials with fast ion and electron transport

Low-dimensional materials can combine high electronic and ionic conductivities by using a mechanism that is usually referred to as pseudocapacitive or surface redox energy storage (69). It was realized more than 20 years ago by Conway *et al.* that ruthenium oxide (RuO_2), having a capacitor-like behavior, has redox energy storage (faradaic process) behind its large capacitance values (108). But the cost of the rare element ruthenium coupled with the fact that this material can only operate in very thin layers has limited its practical use (109). Additionally, the amount of structural water in ruthenium oxide is a key factor for its electrochemical performance (Fig. 5A), and its control during device operation represents a major challenge (110). Transition-metal atoms on the surface of MXenes can participate in redox reactions with fully electrochemically reversible redox wave in cyclic voltammetry curves overlaid on the large rectangular area corresponding to the double-layer capacitive charge storage mechanism (57) (Fig. 5B). The example of MXenes (42, 57) has shown that both double-layer and redox capacitance can be used at very high current rates, with just ~20% electrochemical performance loss when going from 10 to 100,000 mV s^{-1} cycling (Fig. 5B). This rate would be impossible for conventional redox electrodes, which have low conductivity and a diffusion-limited charge-storage mechanism. MXenes have shown a charging time in the 1- to 10-ms range (57). At the same time, the capacitance of MXenes (up to 500 F g^{-1} and 1500 F cm^{-3} in thin films in acidic electrolyte, Fig. 5B) exceeds the capacitance of double-layer capacitor materials, such as carbons, which have 100 to 200 F g^{-1} or F cm^{-3} , while volumetrically rivaling that of ruthenium oxide thin films (1500 F cm^{-3}) (110). Thick electrodes can also work well, if restacking of the 2D sheets is prevented. In fact, vertical alignment of 2D sheets, achieved by exploiting their liquid crystalline behavior or through templating, would allow the development of MXene elec-

trodes with tens of milligrams per square centimeter. In this context, thickness-independent (up to 200 μm) capacitance of vertically aligned MXene flakes has been demonstrated (37).

In many cases, however, it is necessary to combine different materials to achieve fast transport of both electrons and ions. A good example is the design and realization of hybrid structures, which have been reported for numerous oxides (Nb_2O_5 , TiO_2 , MoO_3 , etc.) on a variety of carbon supports, such as nanotubes, graphene-based materials, and porous carbons (13). The carbon affects the electronic properties of both materials because it not only acts as a channel for electrons but also forms a heterojunction between the oxide and carbon surface. As a result, a higher capacity (~1000 $\text{mA}\cdot\text{hour g}^{-1}$) has been achieved for a graphene-iron oxide electrode compared with both only oxide (~600 $\text{mA}\cdot\text{hour g}^{-1}$), which cannot operate at high rates, and only carbon material (~400 $\text{mA}\cdot\text{hour g}^{-1}$) (111) (Fig. 5C). When combined, these materials can operate at current densities exceeding several amperes per gram. Moreover, with the correct design of the electrode architecture, a very high rate performance can also be achieved, as demonstrated for Nb_2O_5 supported on graphene or MXene (112). Building such composite architectures can also allow the use of conversion electrode materials, such as FeF_3 , CuCl_2 , or S undergoing phase transformations (21).

Another way to enable fast transport of electrons and ions is through the creation of 2D heterostructures (12), which allow the combination of highly conducting and high-energy density 2D materials. Because at least one material in the hybrid structure should have good electronic conductivity, graphene has been the primary material of choice. This approach is rather universal, with a very large number of metallically conductive and redox-active materials available (113). It has been implemented in several different systems for applications ranging from pseudocapacitors to Li-ion and Li-S batteries (113). As of now, the governing assembly principles of integrating dissimilar nanomaterials into desired architectures are poorly understood. Moreover, it is not yet known how the transport of electrons and ions occurs between dissimilar 2D sheets and through the separating electrolyte or confined fluid. What is the optimal spacing between the sheets? Is the physical contact between the particles an essential requirement for electron transport or can the hopping or tunneling serve as the dominant transport mechanism? Machine learning should allow for optimization of those systems and for understanding the guiding principles for the selection of the optimum combinations of 2D materials to achieve the best electrochemical performance (114).

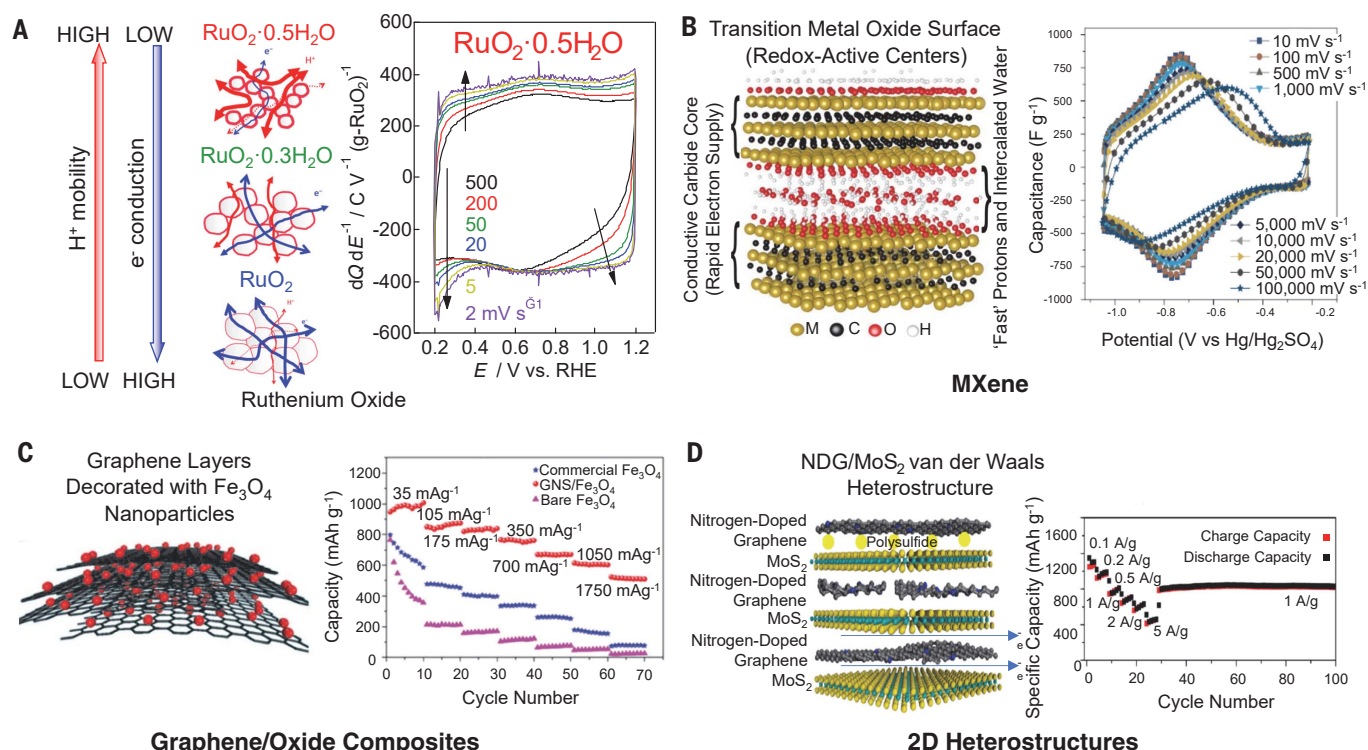


Fig. 5. Achieving fast transport of both electrons and ions in nanomaterials. (A) Schematic illustration of $\text{RuO}_2 \cdot n\text{H}_2\text{O}$ demonstrating the ability to control electronic conductivity and proton transport by tuning the material hydration and cyclic voltammetry (CV) data obtained at scan rates from 2 to 500 mV s^{-1} (145). dQ dE⁻¹, capacitance; RHE, reversible hydrogen electrode. (B) Schematic illustration of a typical M_3C_2 MXene structure and cyclic voltammetry data collected at scan rates from 10 to 100,000 mV s^{-1} for a 90-nm-thick $\text{Ti}_3\text{C}_2\text{T}_x$ film. $\text{Ti}_3\text{C}_2\text{T}_x$ possesses excellent electronic conductivity owing to an electronically conductive transition metal carbide layer. Intercalated water molecules enable accessibility of protons to the redox-active TiO_2 -like surface (57). (C) Schematic illustration of a composite material synthesized via decoration of graphene sheets with Fe_3O_4 nanoparticles and rate performance of the obtained material at current densities ranging from 35 to 1750 mA g^{-1} as compared with that of commercial Fe_3O_4 particles and nanoparticles of Fe_3O_4 synthesized using a similar approach but without the addition of graphene sheets (146). GNS, graphene nanosheets. (D) Schematic illustration of a 2D heterostructure consisting of the alternate MoS_2 and nitrogen-doped graphene (NDG) layers and its rate performance in a Li-S battery at current densities ranging from 0.1 to 5 A g^{-1} (147). [Images adapted with permission from (57, 145–147)]

Manufacturing of the nanomaterial-enabled energy storage devices

For large-scale applications, we need to build batteries and supercapacitors in a conventional format, but exploiting nanomaterials will allow faster operation, higher power, and longer lifetime compared with the current technology. For example, replacing graphite with nanostructured silicon (115) can lead to a substantial increase in the energy density over conventional batteries. One of the key advantages of nanoscale materials is that they can be used to manufacture electrodes of any size, shape, or form factor. For example, we are used to seeing conventional batteries as separate units. But there is no reason why they cannot be combined with structural elements and distributed, when electrodes can conform to any shape and be made strong, robust, and flexible. As a result, instead of occupying space under the car body or in a trunk, they can become part of the automobile structure per se, for example, forming the car body or filling the empty space in doors and under the hood. All

these properties can be achieved by using 1D and 2D materials with high mechanical properties and electronic conductivity. Beyond conventional energy storage devices for portable electronics and vehicles, there is increasing demand for flexible energy storage devices needed to power flexible electronics, including bendable, compressible, foldable, and stretchable devices. Wearable electronics (116) will require the incorporation of energy storage devices. This means that we need energy storage fibers, fabrics, and textiles and the ability to incorporate energy-storing materials into clothes. This involves the manufacture of non-toxic, strong, stretchable, and even washable conductive fibers, capable of both ionic and electronic transport. For the implantable devices, instead of traditionally used coin cells or patches, stretchable and biodegradable or biocompatible batteries could be incorporated inside the human body or battery-powered devices.

The design and realization of these devices require the incorporation of nanomaterials into functional architectures. Several strategies have

been established by (i) using flexible substrates (117) and separators (118); (ii) designing new device patterns (119) and configurations—for example, fiber-like and spring-like devices (120); (iii) compositing electrode materials into flexible matrices (32, 121), and so on. Flexible energy storage devices, including Li-ion battery (122), Na-ion battery (7), and Zn-air battery (123); flexible supercapacitors, including all-solid-state devices (124); and in-plane and fiber-like micro-supercapacitors (125) have been reported. However, the packaged microdevice performance is usually inferior in terms of total volumetric or gravimetric energy density compared with conventional batteries of supercapacitors. Nanomaterials will use different manufacturing methods (Fig. 6). Spray coating and other high-throughput manufacturing techniques (e.g., doctor blade, dip coating, electrodeposition, layer-by-layer deposition, vacuum filtration, and ink-jet printing) (10) may make these devices sufficiently inexpensive for commodity applications. For example, electrochemically exfoliated graphene has been used to formulate

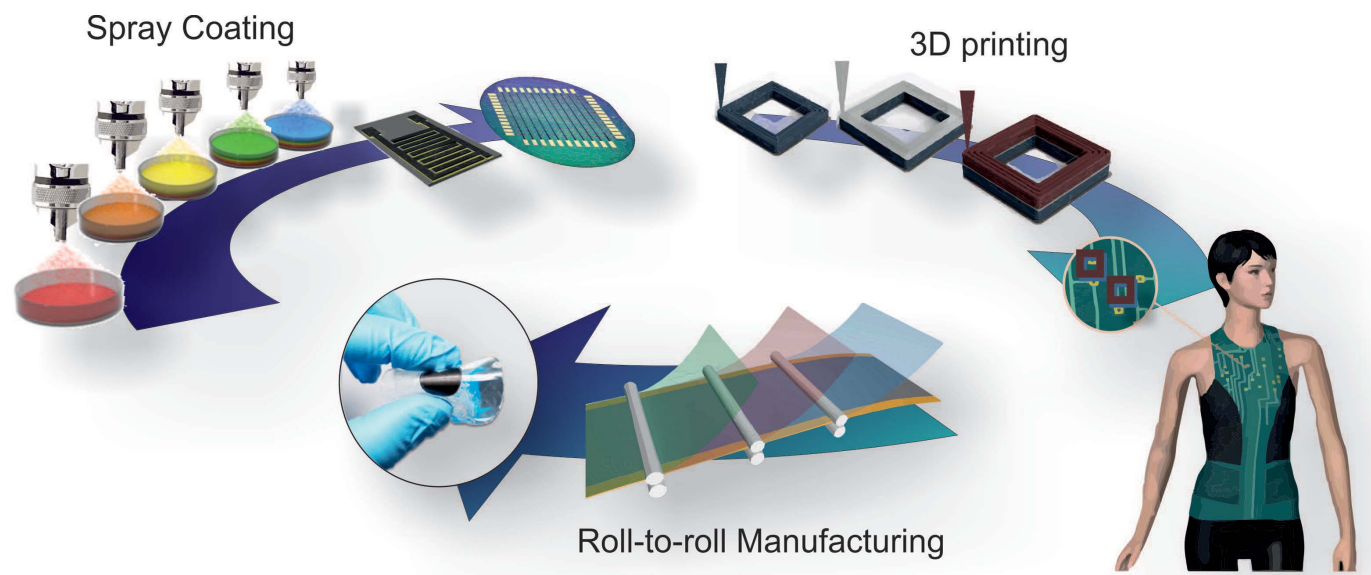


Fig. 6. Nanomaterials enable the production of next-generation energy storage systems by different manufacturing methods. [Supercapacitor array image by Husam N. Alshareef/King Abdullah University of Science and Technology (KAUST); figure wearing smart textiles image by Kristi Jost/Drexel University]

inks and manufacture in-plane micro-supercapacitors on flexible substrates and wafers by spray coating (126). Ink-jet printing has shown promise in the fabrication of flexible thin-film energy devices with large area and readily controllable thickness (127). Centrifugal casting can produce large-area sheets of 2D materials much faster than vacuum-assisted filtration. Roll-to-roll manufacturing can transform the assembly of battery-powered devices into a process similar to printing a newspaper. It is important to mention that conducting current collectors and insulating separators (in the case of sandwich-device architecture) need to be printed by the same method. Also, interdigitated and other non-sandwich energy storage device architectures become possible with printing technologies and polymer gel electrolytes, which both conduct ions and separate the electrodes.

The quality of printed films depends on the stability of active nanomaterial-based inks (10). In this context, functionalized nanoparticles are typically used for ink formulation because of their good dispersibility in solvents (both aqueous and organic). To increase the areal energy density of devices and their capacitance or capacity, it is necessary to build 3D devices with increased thickness and hierarchy of the electrodes. Therefore, it is necessary to develop 3D printing techniques and adjust them to specific conditions; for example, 0D particles and 2D sheets are easier to print compared with CNTs, but the latter can be more readily incorporated into fibers, providing mechanical strength and electrical conductivity required in this application. A 3D printed, interdigitated Li-ion microbattery was demonstrated using $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) and LiFePO_4 (LFP) as

the anode and cathode materials, respectively (128). This approach can produce distributed energy storage devices integrated with other electronic components.

The use of structural or printable energy storage (Fig. 6) adds additional requirements to the environmental and temperature stability of all components of the device. If a battery is located close to the hot part of an engine or incorporated into a part of the car body that will be subjected to sunshine over a prolonged period of time, the use of thermally stable electrolytes (e.g., ionic liquids) and other components (e.g., ceramic separators, such as ceramic nanofibers, boron nitride, or clay) may be required. In printable devices for Internet of Things and future miniaturized electronics, the use of nanomaterials should be considered not only as active components but also as binders, current collectors, sealants, and encapsulating elements. For example, the latter can be constructed using micrometer-thick polymer films with insulating 2D nanoparticles, decreasing water and oxygen permeability.

In-plane micro-supercapacitors made of carbide-derived carbons and 2D materials—including graphene, MXene, metal oxides, and conductive MOFs—are among the most popular flexible and integrated energy storage devices. Carbide-derived carbon films that possess a high SSA and narrow pore size can also be fabricated on a silicon wafer without cracking by two key steps: sputtering of metal carbides and chlorine-gas etching (129). 2D heterostructures can provide improved electron- and ion-transport pathways (12). However, most 2D materials-based in-plane micro-supercapacitors are fabricated by photolithography. 2D metal-organic coordination

framework graphene- and MXene-based in-plane micro-supercapacitors with ac line-filtering performance were fabricated by in situ layer-by-layer growth of active material on prefabricated current collectors (34). Such an approach, coupled with the exploitation of 2D materials, offers a pathway for the scalable fabrication of in-plane micro-supercapacitors.

Smart energy storage devices, which can deliver extra functions under external stimuli beyond energy storage, enable a wide range of applications. In particular, electrochromic (130), photoresponsive (131), self-healing (132), thermally responsive supercapacitors and batteries have been demonstrated. However, the fade of the performance under stimuli still hinders their practical applications. Another pathway to achieve stimuli is manipulating electrolyte—for example, by using thermally responsive polymer gels—to control the ion transport between the electrodes, which can eventually cause the on and off switching of the device. Although several prototypes have already been demonstrated, considerable challenges—for example, balance of high performance and extra functions and the integration of such smart devices into fully functioning systems—still need to be resolved (133).

Parasitic reactions between electrode nanomaterials and electrolytes (3) can cause the decomposition of electrolyte and metal consumption for metal-ion batteries and consequently result in poor energy storage performance, including low Coulombic efficiency, cycle life, and energy density, compromised safety, and so on. Many efforts—such as the development of coated electrode materials (134), electrolytes and additives (135), membranes (136), and

metal-electrolyte interfaces (137)—have been made to suppress parasitic reactions. For example, fluoroethylene carbonate additive has been used to improve the cycle life of Li-ion batteries with Si nanoparticles (60 nm) by suppression of parasitic reactions, avoiding the formation of metastable $c\text{-Li}_{15}\text{Si}_4$ phase (138). The use of nanomaterials and new materials, in general, may require the development of new electrolytes compatible with those materials, especially in confinement (139).

Conclusions

Despite certain skepticism within the battery community related to the use of nanomaterials in commercial devices, several examples in which nanostructuring led to breakthroughs in performance, such as in the case of silicon-carbon composite anodes, indicate that nanostructured materials can provide solutions to create high-energy, high-power, and long-lasting energy storage devices. Research carried out over the past decade has shown that a device's lifetime increases as a result of nanostructuring. Indeed, overcoming the strain induced by cyclic expansion and contraction of macroscale particles can compensate for lifetime limitations resulting from electrolyte breakdown on a large surface of nanomaterials. Design of encapsulated nanoparticle assemblies can further minimize the contact area with electrolyte, decreasing the irreversible processes of the first charge-discharge cycle. Large-scale implementation of Si nanoparticles in Li-ion battery anodes by Sila Nanotechnologies and other companies is a convincing demonstration of the scalability of nanomaterials for large-volume battery production. The use of hundreds of tons of multiwall CNTs as conducting and reinforcing additives in battery electrodes is an excellent example of nanoscale additive use. There are other nanomaterials—such as single-wall CNTs, graphene, and so on—used in small-volume or small-size batteries and supercapacitors. Decreased prices and increased confidence in safety (health, environmental, and operational) will open doors for a wider implementation of nanomaterials in energy storage technology. To reach full potential, nanomaterials need to be combined in sophisticated architectures that enable multiple functionalities related to the transport of electrons and ions as well as interactions between various device components or suppression of such interactions. However, enabling complex architectures requires the use of advanced processing and manufacturing techniques compatible with nanomaterials, such as 3D printing, knitting, spray and/or spin coating, roll-to-roll assembly, and others.

REFERENCES AND NOTES

1. A. S. Aricò, P. Bruce, B. Scrosati, J. M. Tarascon, W. van Schalkwijk, Nanostructured materials for advanced energy conversion and storage devices. *Nat. Mater.* **4**, 366–377 (2005). doi: [10.1038/nmat1368](https://doi.org/10.1038/nmat1368); pmid: [15867920](https://pubmed.ncbi.nlm.nih.gov/15867920/)
2. P. G. Bruce, B. Scrosati, J. M. Tarascon, Nanomaterials for rechargeable lithium batteries. *Angew. Chem. Int. Ed.* **47**, 2930–2946 (2008). doi: [10.1002/anie.200702505](https://doi.org/10.1002/anie.200702505); pmid: [18338357](https://pubmed.ncbi.nlm.nih.gov/18338357/)
3. Y. Sun, N. Liu, Y. Cui, Promises and challenges of nanomaterials for lithium-based rechargeable batteries. *Nat. Energy* **1**, 16071 (2016). doi: [10.1038/nenergy.2016.71](https://doi.org/10.1038/nenergy.2016.71)
4. W. Luo et al., A thermally conductive separator for stable Li metal anodes. *Nano Lett.* **15**, 6149–6154 (2015). doi: [10.1021/acs.nanolett.5b02432](https://doi.org/10.1021/acs.nanolett.5b02432); pmid: [26237519](https://pubmed.ncbi.nlm.nih.gov/26237519/)
5. C. H. Wang et al., Titanium carbide (MXene) as a current collector for lithium-ion batteries. *ACS Omega* **3**, 12489–12494 (2018). doi: [10.1021/acsomega.8b02032](https://doi.org/10.1021/acsomega.8b02032); pmid: [31457980](https://pubmed.ncbi.nlm.nih.gov/31457980/)
6. Z. S. Wu et al., Graphene anchored with Co_3O_4 nanoparticles as anode of lithium ion batteries with enhanced reversible capacity and cyclic performance. *ACS Nano* **4**, 3187–3194 (2010). doi: [10.1021/nn100740x](https://doi.org/10.1021/nn100740x); pmid: [20455594](https://pubmed.ncbi.nlm.nih.gov/20455594/)
7. H. J. Song, D. S. Kim, J. C. Kim, S. H. Hong, D. W. Kim, An approach to flexible Na-ion batteries with exceptional rate capability and long lifespan using $\text{Na}_2\text{FeP}_2\text{O}_7$ nanoparticles on porous carbon cloth. *J. Mater. Chem. A* **5**, 5502–5510 (2017). doi: [10.1039/C7TA00727B](https://doi.org/10.1039/C7TA00727B)
8. D. Lei, J. Benson, A. Magasinski, G. Berdichevsky, G. Yushin, Transformation of bulk alloys to oxide nanowires. *Science* **355**, 267–271 (2017). doi: [10.1126/science.aal2239](https://doi.org/10.1126/science.aal2239); pmid: [28104885](https://pubmed.ncbi.nlm.nih.gov/28104885/)
9. F. Xu et al., Visualization of lithium-ion transport and phase evolution within and between manganese oxide nanorods. *Nat. Commun.* **8**, 15400 (2017). doi: [10.1038/ncomms15400](https://doi.org/10.1038/ncomms15400); pmid: [28537250](https://pubmed.ncbi.nlm.nih.gov/28537250/)
10. F. Bonaccorso, A. Bartolotta, J. N. Coleman, C. Backes, 2D-crystal-based functional inks. *Adv. Mater.* **28**, 6136–6166 (2016). doi: [10.1002/adma.201506410](https://doi.org/10.1002/adma.201506410); pmid: [27273554](https://pubmed.ncbi.nlm.nih.gov/27273554/)
11. F. Bonaccorso et al., Graphene, related two-dimensional crystals, and hybrid systems for energy conversion and storage. *Science* **347**, 1246501 (2015). doi: [10.1126/science.1246501](https://doi.org/10.1126/science.1246501); pmid: [25554791](https://pubmed.ncbi.nlm.nih.gov/25554791/)
12. E. Pomerantseva, Y. Gogotsi, Two-dimensional heterostructures for energy storage. *Nat. Energy* **2**, 17089 (2017). doi: [10.1038/nenergy.2017.89](https://doi.org/10.1038/nenergy.2017.89)
13. Q. Qu, S. Yang, X. Feng, 2D sandwich-like sheets of iron oxide grown on graphene as high energy anode material for supercapacitors. *Adv. Mater.* **23**, 5574–5580 (2011). doi: [10.1002/adma.201103042](https://doi.org/10.1002/adma.201103042); pmid: [22052661](https://pubmed.ncbi.nlm.nih.gov/22052661/)
14. Z. S. Wu et al., Three-dimensional graphene-based macro- and mesoporous frameworks for high-performance electrochemical capacitive energy storage. *J. Am. Chem. Soc.* **134**, 19532–19535 (2012). doi: [10.1021/ja308676h](https://doi.org/10.1021/ja308676h); pmid: [23148416](https://pubmed.ncbi.nlm.nih.gov/23148416/)
15. Z. S. Wu et al., Three-dimensional nitrogen and boron co-doped graphene for high-performance all-solid-state supercapacitors. *Adv. Mater.* **24**, 5130–5135 (2012). doi: [10.1002/adma.201201948](https://doi.org/10.1002/adma.201201948); pmid: [22807002](https://pubmed.ncbi.nlm.nih.gov/22807002/)
16. D. Wu, F. Zhang, H. Liang, X. Feng, Nanocomposites and macroscopic materials: Assembly of chemically modified graphene sheets. *Chem. Soc. Rev.* **41**, 6160–6177 (2012). doi: [10.1039/c2cs35179j](https://doi.org/10.1039/c2cs35179j); pmid: [22875044](https://pubmed.ncbi.nlm.nih.gov/22875044/)
17. S. Han, D. Wu, S. Li, F. Zhang, X. Feng, Porous graphene materials for advanced electrochemical energy storage and conversion devices. *Adv. Mater.* **26**, 849–864 (2014). doi: [10.1002/adma.201303115](https://doi.org/10.1002/adma.201303115); pmid: [24347321](https://pubmed.ncbi.nlm.nih.gov/24347321/)
18. K. Turcheniuk, D. Bondarev, V. Singhal, G. Yushin, Ten years left to redesign lithium-ion batteries. *Nature* **559**, 467–470 (2018). doi: [10.1038/d41586-018-05752-3](https://doi.org/10.1038/d41586-018-05752-3); pmid: [30046087](https://pubmed.ncbi.nlm.nih.gov/30046087/)
19. E. Greco et al., Few-layer graphene improves silicon performance in Li-ion battery anodes. *J. Mater. Chem. A* **5**, 19306–19315 (2017). doi: [10.1039/C7TA05395A](https://doi.org/10.1039/C7TA05395A)
20. H. Y. Sun et al., Carbon nanotubes-bridged molybdenum trioxide nanosheets as high performance anode for lithium ion batteries. *2D Materials* **5**, 015024 (2018). doi: [10.1088/2053-1583/aa9963](https://doi.org/10.1088/2053-1583/aa9963)
21. S.-H. Yu, X. Feng, N. Zhang, J. Seok, H. D. Abruña, Understanding conversion-type electrodes for lithium rechargeable batteries. *Acc. Chem. Res.* **51**, 273–281 (2018). doi: [10.1021/acs.accounts.7b00487](https://doi.org/10.1021/acs.accounts.7b00487); pmid: [29373023](https://pubmed.ncbi.nlm.nih.gov/29373023/)
22. R. Koerver et al., Chemo-mechanical expansion of lithium electrode materials—on the route to mechanically optimized all-solid-state batteries. *Energy Environ. Sci.* **11**, 2142–2158 (2018). doi: [10.1039/C8EE00907D](https://doi.org/10.1039/C8EE00907D)
23. J. W. Jung et al., Rational design of protective In_2O_3 layer-coated carbon nanopaper membrane: Toward stable cathode for long-cycle Li- O_2 batteries. *Nano Energy* **46**, 193–202 (2018). doi: [10.1016/j.nanoen.2018.01.045](https://doi.org/10.1016/j.nanoen.2018.01.045)
24. Y. S. Jung et al., Unexpected improved performance of ALD coated LiCoO_2 /graphite Li-ion batteries. *Adv. Energy Mater.* **3**, 213–219 (2013). doi: [10.1002/aenm.201200370](https://doi.org/10.1002/aenm.201200370)
25. S. Neudeck et al., Effect of low-temperature Al_2O_3 ALD coating on Ni-rich layered oxide composite cathode on the long-term cycling performance of lithium-ion batteries. *Sci. Rep.* **9**, 5328 (2019). doi: [10.1038/s41598-019-41767-0](https://doi.org/10.1038/s41598-019-41767-0); pmid: [30926918](https://pubmed.ncbi.nlm.nih.gov/30926918/)
26. A. P. Wang, S. Kadam, H. Li, S. Q. Shi, Y. Qi, Review on modeling of the anode solid electrolyte interphase (SEI) for lithium-ion batteries. *npj Comput. Mater.* **4**, 15 (2018). doi: [10.1038/s41524-018-0064-0](https://doi.org/10.1038/s41524-018-0064-0)
27. L. Fan, H. L. L. Zhuang, L. N. Gao, Y. Y. Lu, L. A. Archer, Regulating Li deposition at artificial solid electrolyte interphases. *J. Mater. Chem. A Mater. Energy Sustain.* **5**, 3483–3492 (2017). doi: [10.1039/C6TA10204B](https://doi.org/10.1039/C6TA10204B)
28. P. Simon, Y. Gogotsi, Materials for electrochemical capacitors. *Nat. Mater.* **7**, 845–854 (2008). doi: [10.1038/nmat2297](https://doi.org/10.1038/nmat2297); pmid: [18956000](https://pubmed.ncbi.nlm.nih.gov/18956000/)
29. G. Zhang, L. Zhang, J. Zhang, A review of electrode materials for electrochemical supercapacitors. *Chem. Soc. Rev.* **41**, 797–828 (2012). doi: [10.1039/C1CS15060J](https://doi.org/10.1039/C1CS15060J); pmid: [21779609](https://pubmed.ncbi.nlm.nih.gov/21779609/)
30. B. Scrosati, J. Garche, Lithium batteries: Status, prospects and future. *J. Power Sources* **195**, 2419–2430 (2010). doi: [10.1016/j.jpowsour.2009.11.048](https://doi.org/10.1016/j.jpowsour.2009.11.048)
31. H. Wu et al., Stable cycling of double-walled silicon nanotube battery anodes through solid-electrolyte interphase control. *Nat. Nanotechnol.* **7**, 310–315 (2012). doi: [10.1038/nnano.2012.35](https://doi.org/10.1038/nnano.2012.35); pmid: [22447161](https://pubmed.ncbi.nlm.nih.gov/22447161/)
32. R. Mo, D. Rooney, K. Sun, H. Y. Yang, 3D nitrogen-doped graphene foam with encapsulated germanium/nitrogen-doped graphene yolk-shell nanoarchitecture for high-performance flexible Li-ion battery. *Nat. Commun.* **8**, 13949 (2017). doi: [10.1038/ncomms13949](https://doi.org/10.1038/ncomms13949); pmid: [28051065](https://pubmed.ncbi.nlm.nih.gov/28051065/)
33. D. Sheberla et al., Conductive MOF electrodes for stable supercapacitors with high areal capacitance. *Nat. Mater.* **16**, 220–224 (2017). doi: [10.1038/nmat4766](https://doi.org/10.1038/nmat4766); pmid: [27723738](https://pubmed.ncbi.nlm.nih.gov/27723738/)
34. C. Yang et al., Coordination polymer framework based on-chip micro-supercapacitors with AC line-filtering performance. *Angew. Chem. Int. Ed.* **56**, 3920–3924 (2017). doi: [10.1002/anie.201700679](https://doi.org/10.1002/anie.201700679); pmid: [28267257](https://pubmed.ncbi.nlm.nih.gov/28267257/)
35. Y. Mao et al., Foldable interpenetrated metal-organic frameworks/carbon nanotubes thin film for lithium-sulfur batteries. *Nat. Commun.* **8**, 14628 (2017). doi: [10.1038/ncomms14628](https://doi.org/10.1038/ncomms14628); pmid: [28262801](https://pubmed.ncbi.nlm.nih.gov/28262801/)
36. C. R. DeBlase, K. E. Silberstein, T. T. Truong, H. D. Abruña, W. R. Dichtel, β -Ketoneamine-linked covalent organic frameworks capable of pseudocapacitive energy storage. *J. Am. Chem. Soc.* **135**, 16821–16824 (2013). doi: [10.1021/ja409421d](https://doi.org/10.1021/ja409421d); pmid: [24147596](https://pubmed.ncbi.nlm.nih.gov/24147596/)
37. Y. Xia et al., Thickness-independent capacitance of vertically aligned liquid-crystalline MXenes. *Nature* **557**, 409–412 (2018). doi: [10.1038/s41586-018-0109-z](https://doi.org/10.1038/s41586-018-0109-z); pmid: [29769673](https://pubmed.ncbi.nlm.nih.gov/29769673/)
38. L. Borchardt et al., Toward a molecular design of porous carbon materials. *Mater. Today* **20**, 592–610 (2017). doi: [10.1016/j.mattod.2017.06.002](https://doi.org/10.1016/j.mattod.2017.06.002)
39. Z. J. Fan et al., Asymmetric supercapacitors based on graphene/MnO₂ and activated carbon nanofiber electrodes with high power and energy density. *Adv. Funct. Mater.* **21**, 2366–2375 (2011). doi: [10.1002/adfm.201100058](https://doi.org/10.1002/adfm.201100058)
40. D. Wang et al., Self-assembled TiO_2 -graphene hybrid nanostructures for enhanced Li-ion insertion. *ACS Nano* **3**, 907–914 (2009). doi: [10.1021/nn900150y](https://doi.org/10.1021/nn900150y); pmid: [19323486](https://pubmed.ncbi.nlm.nih.gov/19323486/)
41. A. K. Geim, K. S. Novoselov, The rise of graphene. *Nat. Mater.* **6**, 183–191 (2007). doi: [10.1038/nmat1849](https://doi.org/10.1038/nmat1849); pmid: [17330084](https://pubmed.ncbi.nlm.nih.gov/17330084/)
42. B. Anasori, M. R. Lukatskaya, Y. Gogotsi, 2D metal carbides and nitrides (MXenes) for energy storage. *Nat. Rev. Mater.* **2**, 16098 (2017). doi: [10.1038/natrevmats.2016.98](https://doi.org/10.1038/natrevmats.2016.98)
43. M. Okubo et al., Nanosize effect on high-rate Li-ion intercalation in LiCoO_2 electrode. *J. Am. Chem. Soc.* **129**, 7444–7452 (2007). doi: [10.1021/ja0681927](https://doi.org/10.1021/ja0681927); pmid: [17511453](https://pubmed.ncbi.nlm.nih.gov/17511453/)
44. E. V. Shevchenko, D. V. Talapin, N. A. Kotov, S. O'Brien, C. B. Murray, Structural diversity in binary nanoparticle superlattices. *Nature* **439**, 55–59 (2006). doi: [10.1038/nature04414](https://doi.org/10.1038/nature04414); pmid: [16397494](https://pubmed.ncbi.nlm.nih.gov/16397494/)
45. Y. Song et al., Role of interfacial oxide in high-efficiency graphene-silicon Schottky barrier solar cells. *Nano Lett.* **15**, 2104–2110 (2015). doi: [10.1021/nl505011f](https://doi.org/10.1021/nl505011f); pmid: [25685934](https://pubmed.ncbi.nlm.nih.gov/25685934/)

46. J. Gao *et al.*, Aging of transition metal dichalcogenide monolayers. *ACS Nano* **10**, 2628–2635 (2016). doi: [10.1021/acsnano.5b07677](#); pmid: [26808328](#)
47. C. R. Ryder, J. D. Wood, S. A. Wells, M. C. Hersam, Chemically tailoring semiconducting two-dimensional transition metal dichalcogenides and black phosphorus. *ACS Nano* **10**, 3900–3917 (2016). doi: [10.1021/acsnano.6b01091](#); pmid: [27018800](#)
48. G. H. Gao, T. Cagin, W. A. Goddard III, Energetics, structure, mechanical and vibrational properties of single-walled carbon nanotubes. *Nanotechnology* **9**, 184–191 (1998). doi: [10.1088/0957-4484/9/3/007](#)
49. F. Bonaccorso *et al.*, Density gradient ultracentrifugation of nanotubes: Interplay of bundling and surfactants encapsulation. *J. Phys. Chem. C* **114**, 17267–17285 (2010). doi: [10.1021/jp1030174](#)
50. Y. Yuan *et al.*, The influence of large cations on the electrochemical properties of tunnel-structured metal oxides. *Nat. Commun.* **7**, 13374 (2016). doi: [10.1038/ncomms13374](#); pmid: [27869120](#)
51. J. Hassoun *et al.*, An advanced lithium-ion battery based on a graphene anode and a lithium iron phosphate cathode. *Nano Lett.* **14**, 4901–4906 (2014). doi: [10.1021/nl502429m](#); pmid: [25026051](#)
52. Y. Hao *et al.*, The role of surface oxygen in the growth of large single-crystal graphene on copper. *Science* **342**, 720–723 (2013). doi: [10.1126/science.1243879](#); pmid: [24158906](#)
53. J. S. Bunch, Y. Yaish, M. Brink, K. Bolotin, P. L. McEuen, Coulomb oscillations and Hall effect in quasi-2D graphite quantum dots. *Nano Lett.* **5**, 287–290 (2005). doi: [10.1021/nl048111+](#); pmid: [15794612](#)
54. Y. Hernandez *et al.*, High-yield production of graphene by liquid-phase exfoliation of graphite. *Nat. Nanotechnol.* **3**, 563–568 (2008). doi: [10.1038/nnano.2008.215](#); pmid: [18772919](#)
55. J. N. Coleman *et al.*, Two-dimensional nanosheets produced by liquid exfoliation of layered materials. *Science* **331**, 568–571 (2011). doi: [10.1126/science.1194975](#); pmid: [21292974](#)
56. A. E. Del Rio Castillo *et al.*, High-yield production of 2D crystals by wet-jet milling. *Mater. Horiz.* **5**, 890–904 (2018). doi: [10.1039/C8MH00487K](#)
57. M. R. Lukatskaya *et al.*, Ultra-high-rate pseudocapacitive energy storage in two-dimensional transition metal carbides. *Nat. Energy* **2**, 17105 (2017). doi: [10.1038/nenergy.2017.105](#)
58. J. Qiao, X. Kong, Z.-X. Hu, F. Yang, W. Ji, High-mobility transport anisotropy and linear dichroism in few-layer black phosphorus. *Nat. Commun.* **5**, 4475 (2014). doi: [10.1038/ncomms5475](#); pmid: [25042376](#)
59. G. Centi, S. Perathoner, Catalysis by layered materials: A review. *Microporous Mesoporous Mater.* **107**, 3–15 (2008). doi: [10.1016/j.micromeso.2007.03.011](#)
60. A. Vu, Y. Q. Qian, A. Stein, Porous electrode materials for lithium-ion batteries—how to prepare them and what makes them special. *Adv. Energy Mater.* **2**, 1056–1085 (2012). doi: [10.1002/aenm.201200320](#)
61. L. M. Zhou *et al.*, Recent developments on and prospects for electrode materials with hierarchical structures for lithium-ion batteries. *Adv. Energy Mater.* **8**, 1701415 (2018). doi: [10.1002/aenm.201701415](#)
62. E. Uchaker, G. Z. Cao, Mesocrystals as electrode materials for lithium-ion batteries. *Nano Today* **9**, 499–524 (2014). doi: [10.1016/j.nantod.2014.06.004](#)
63. D.-W. Wang, F. Li, M. Liu, G. Q. Lu, H.-M. Cheng, 3D aperiodic hierarchical porous graphitic carbon material for high-rate electrochemical capacitive energy storage. *Angew. Chem. Int. Ed.* **47**, 373–376 (2008). doi: [10.1002/anie.200702721](#); pmid: [18022983](#)
64. M. Melillo, F. Zhu, M. A. Snyder, J. Mittal, Water transport through nanotubes with varying interaction strength between tube wall and water. *J. Phys. Chem. Lett.* **2**, 2978–2983 (2011). doi: [10.1021/jz2012319](#); pmid: [25606067](#)
65. T. Miyake, M. Rolandi, Grotthuss mechanisms: From proton transport in proton wires to bioprotonic devices. *J. Phys. Condens. Matter* **28**, 023001 (2016). doi: [10.1088/0953-8984/28/2/023001](#); pmid: [26657711](#)
66. N. Li, M. D. Guiver, Ion transport by nanochannels in ion-containing aromatic copolymers. *Macromolecules* **47**, 2175–2198 (2014). doi: [10.1021/ma402254h](#)
67. M.-Q. Zhao *et al.*, Magnesium-ion storage capability of MXenes. *ACS Appl. Energy Mater.* **2**, 1572–1578 (2019). doi: [10.1021/acsaem.8b02253](#)
68. A. VahidMohammadi, A. Hadjikhani, S. Shahbazmohamadi, M. Beidaghi, Two-dimensional vanadium carbide (MXene) as a high-capacity cathode material for rechargeable aluminum batteries. *ACS Nano* **11**, 11135–11144 (2017). doi: [10.1021/acsnano.7b05350](#); pmid: [29039915](#)
69. P. Simon, Y. Gogotsi, B. Dunn, Materials science. Where do batteries end and supercapacitors begin? *Science* **343**, 1210–1211 (2014). doi: [10.1126/science.1249625](#); pmid: [24626920](#)
70. D. Kundu, B. D. Adams, V. Duffort, S. H. Vajargah, L. F. Nazar, A high-capacity and long-life aqueous rechargeable zinc battery using a metal oxide intercalation cathode. *Nat. Energy* **1**, 16119 (2016). doi: [10.1038/nenergy.2016.119](#)
71. V. Augustyn, Y. Gogotsi, 2D materials with nanoconfined fluids for electrochemical energy storage. *Joule* **1**, 443–452 (2017). doi: [10.1016/j.joule.2017.09.008](#)
72. J. C. Burns *et al.*, The impact of intentionally added water to the electrolyte of Li-ion cells. *J. Electrochem. Soc.* **160**, A2281–A2287 (2013). doi: [10.1149/2.101311jes](#)
73. L. W. Wang *et al.*, Correlating lithium hydroxyl accumulation with capacity retention in V₂O₅ aerogel cathodes. *ACS Appl. Mater. Interfaces* **8**, 11532–11538 (2016). doi: [10.1021/acsami.6b02759](#); pmid: [27104947](#)
74. S. Ilani, L. A. K. Donev, M. Kindermann, P. L. McEuen, Measurement of the quantum capacitance of interacting electrons in carbon nanotubes. *Nat. Phys.* **2**, 687–691 (2006). doi: [10.1038/nphys412](#)
75. I. Demiroglu, F. M. Peeters, O. Gülsüren, D. Çakır, C. Sevik, Alkali metal intercalation in MXene/graphene heterostructures: A new platform for ion battery applications. *J. Phys. Chem. Lett.* **10**, 727–734 (2019). doi: [10.1021/acs.jpclett.8b03056](#); pmid: [30694678](#)
76. D. K. Bediako *et al.*, Heterointerface effects in the electrointercalation of van der Waals heterostructures. *Nature* **558**, 425–429 (2018). doi: [10.1038/s41586-018-0205-0](#); pmid: [29925970](#)
77. J. Yan *et al.*, Flexible MXene/graphene films for ultrafast supercapacitors with outstanding volumetric capacitance. *Adv. Funct. Mater.* **27**, 1701264 (2017). doi: [10.1002/adfm.201701264](#)
78. N. Liu *et al.*, A pomegranate-inspired nanoscale design for large-volume-change lithium battery anodes. *Nat. Nanotechnol.* **9**, 187–192 (2014). doi: [10.1038/nnano.2014.6](#); pmid: [24531496](#)
79. Y. K. Sun *et al.*, High-energy cathode material for long-life and safe lithium batteries. *Nat. Mater.* **8**, 320–324 (2009). doi: [10.1038/nmat2418](#); pmid: [19305398](#)
80. Y. Xu *et al.*, Solution processable holey graphene oxide and its derived macrostructures for high-performance supercapacitors. *Nano Lett.* **15**, 4605–4610 (2015). doi: [10.1021/acs.nanolett.5b01212](#); pmid: [26056845](#)
81. H. Zhang, X. Yu, P. V. Braun, Three-dimensional bicontinuous ultrafast-charge and -discharge bulk battery electrodes. *Nat. Nanotechnol.* **6**, 277–281 (2011). doi: [10.1038/nnano.2011.38](#); pmid: [21423184](#)
82. J. W. Long, B. Dunn, D. R. Rolison, H. S. White, Three-dimensional battery architectures. *Chem. Rev.* **104**, 4463–4492 (2004). doi: [10.1021/cr020740i](#); pmid: [15669159](#)
83. N. S. Ergang *et al.*, Photonic crystal structures as a basis for a three-dimensionally interpenetrating electrochemical-cell system. *Adv. Mater.* **18**, 1750–1753 (2006). doi: [10.1002/adma.200600295](#)
84. H. S. Min *et al.*, Fabrication and properties of a carbon/polyppyrrrole three-dimensional microbattery. *J. Power Sources* **178**, 795–800 (2008). doi: [10.1016/j.jpowsour.2007.10.003](#)
85. K. T. Nam *et al.*, Stamped microbattery electrodes based on self-assembled M13 viruses. *Proc. Natl. Acad. Sci. U.S.A.* **105**, 17227–17231 (2008). doi: [10.1073/pnas.0711620105](#); pmid: [18753629](#)
86. J. G. Werner, G. G. Rodriguez-Calero, H. D. Abruna, U. Wiesner, Block copolymer derived 3-D interpenetrating multifunctional gyroidal nanohybrids for electrical energy storage. *Energy Environ. Sci.* **11**, 1261–1270 (2018). doi: [10.1039/c7ee03571c](#)
87. M. N. Obrovac, V. L. Chevrier, Alloy negative electrodes for Li-ion batteries. *Chem. Rev.* **114**, 11444–11502 (2014). doi: [10.1021/cr500207g](#); pmid: [25399614](#)
88. F. Luo *et al.*, Review—Nano-silicon/carbon composite anode materials towards practical application for next generation Li-ion batteries. *J. Electrochem. Soc.* **162**, A2509–A2528 (2015). doi: [10.1149/2.0131514jes](#)
89. Z. Wei Seh *et al.*, Sulphur-TiO₂ yolk-shell nanoarchitecture with internal void space for long-cycle lithium-sulphur batteries. *Nat. Commun.* **4**, 1331 (2013). doi: [10.1038/ncomms2327](#); pmid: [23299881](#)
90. N. Nitta, F. Wu, J. T. Lee, G. Yushin, Li-ion battery materials: Present and future. *Mater. Today* **18**, 252–264 (2015). doi: [10.1016/j.mattod.2014.10.040](#)
91. K. He *et al.*, Sodiation via heterogeneous disproportionation in FeF₂ electrodes for sodium-ion batteries. *ACS Nano* **8**, 7251–7259 (2014). doi: [10.1021/nn502284y](#); pmid: [24911154](#)
92. F. Wang *et al.*, Tracking lithium transport and electrochemical reactions in nanoparticles. *Nat. Commun.* **3**, 1201 (2012). doi: [10.1038/ncomms2185](#); pmid: [23149745](#)
93. E. S. Takeuchi *et al.*, Electrochemical reduction of silver vanadium phosphorous oxide, Ag₂VO₂PO₄: The formation of electrically conductive metallic silver nanoparticles. *Chem. Mater.* **21**, 4934–4939 (2009). doi: [10.1021/cm902102k](#); pmid: [20161435](#)
94. Z. W. Seh, Y. Sun, Q. Zhang, Y. Cui, Designing high-energy lithium-sulfur batteries. *Chem. Soc. Rev.* **45**, 5605–5634 (2016). doi: [10.1039/C5CS00410A](#); pmid: [27460222](#)
95. X. Ji, K. T. Lee, L. F. Nazar, A highly ordered nanostructured carbon-sulphur cathode for lithium-sulphur batteries. *Nat. Mater.* **8**, 500–506 (2009). doi: [10.1038/nmat2460](#); pmid: [19448613](#)
96. A. S. Levitt *et al.*, Electrospun MXene/carbon nanofibers as supercapacitor electrodes. *J. Mater. Chem. A Mater. Energy Sustain.* **7**, 269–277 (2019). doi: [10.1039/C8TA09810G](#)
97. X. Liang, Y. Rangom, C. Y. Kwok, Q. Pang, L. F. Nazar, Interwoven MXene nanosheet/carbon-nanotube composites as Li-S cathode hosts. *Adv. Mater.* **29**, 1603040 (2017). doi: [10.1002/adma.201603040](#); pmid: [27859697](#)
98. Y. M. Sun *et al.*, Graphite-encapsulated Li-metal hybrid anodes for high-capacity Li batteries. *Chem* **1**, 287–297 (2016). doi: [10.1016/j.chempr.2016.07.009](#)
99. W. Liu *et al.*, Core-shell nanoparticle coating as an interfacial layer for dendrite-free lithium metal anodes. *ACS Cent. Sci.* **3**, 135–140 (2017). doi: [10.1021/acscentsci.6b00389](#); pmid: [28602780](#)
100. D. Lin, Y. Liu, Y. Cui, Reviving the lithium metal anode for high-energy batteries. *Nat. Nanotechnol.* **12**, 194–206 (2017). doi: [10.1038/nnano.2017.16](#); pmid: [28265117](#)
101. X.-B. Cheng *et al.*, Nanodiamonds suppress the growth of lithium dendrites. *Nat. Commun.* **8**, 336 (2017). doi: [10.1038/s41467-017-00519-2](#); pmid: [28839134](#)
102. K. Yan *et al.*, Selective deposition and stable encapsulation of lithium through heterogeneous seeded growth. *Nat. Energy* **1**, 16010 (2016). doi: [10.1038/nenergy.2016.10](#)
103. Y. Shi *et al.*, Graphene-based integrated electrodes for flexible lithium ion batteries. *2D Materials* **2**, 024004 (2015). doi: [10.1088/2053-1583/2/2/024004](#)
104. A. J. Pearce *et al.*, Nanoscale solid state batteries enabled by thermal atomic layer deposition of a lithium polyphosphazene solid state electrolyte. *Chem. Mater.* **29**, 3740–3753 (2017). doi: [10.1021/acs.chemmater.7b00805](#)
105. K. K. Fu *et al.*, Flexible, solid-state, ion-conducting membrane with 3D garnet nanofiber networks for lithium batteries. *Proc. Natl. Acad. Sci. U.S.A.* **113**, 7094–7099 (2016). doi: [10.1073/pnas.1600422113](#); pmid: [27307440](#)
106. K. Gerasopoulos *et al.*, Hierarchical three-dimensional microbattery electrodes combining bottom-up self-assembly and top-down micromachining. *ACS Nano* **6**, 6422–6432 (2012). doi: [10.1021/nr301981p](#); pmid: [22670634](#)
107. M. R. Lukatskaya, B. Dunn, Y. Gogotsi, Multidimensional materials and device architectures for future hybrid energy storage. *Nat. Commun.* **7**, 12647 (2016). doi: [10.1038/ncomms12647](#); pmid: [27600869](#)
108. B. E. Conway, Transition from supercapacitor to battery behavior in electrochemical energy storage. *J. Electrochem. Soc.* **138**, 1539–1548 (1991). doi: [10.1149/1.2085829](#)
109. G. Calogero, A. Bartolotta, G. Di Marco, A. Di Carlo, F. Bonaccorso, Vegetable-based dye-sensitized solar cells. *Chem. Soc. Rev.* **44**, 3244–3294 (2015). doi: [10.1039/C4CS00309H](#); pmid: [25855097](#)
110. W. Sugimoto, H. Iwata, Y. Yasunaga, Y. Murakami, Y. Takasu, Preparation of ruthenic acid nanosheets and utilization of its interlayer surface for electrochemical energy storage. *Angew. Chem. Int. Ed.* **42**, 4092–4096 (2003). doi: [10.1002/anie.200351691](#); pmid: [12973779](#)
111. S. Yang *et al.*, Porous iron oxide ribbons grown on graphene for high-performance lithium storage. *Sci. Rep.* **2**, 427 (2012). doi: [10.1038/srep00427](#); pmid: [22645643](#)
112. C. Zhang *et al.*, Layered orthorhombic Nb₂O₅/Nb₄C₃T_x and TiO₂/Ti₃C₂T_x hierarchical composites for high performance Li-ion batteries. *Adv. Funct. Mater.* **26**, 4143–4151 (2016). doi: [10.1002/adfm.201600682](#)

113. Y. Zhu *et al.*, Structural engineering of 2D nanomaterials for energy storage and catalysis. *Adv. Mater.* **30**, e1706347 (2018). doi: [10.1002/adma.201706347](https://doi.org/10.1002/adma.201706347); pmid: [29430788](https://pubmed.ncbi.nlm.nih.gov/29430788/)
114. N. C. Frey *et al.*, Prediction of synthesis of 2D metal carbides and nitrides (MXenes) and their precursors with positive and unlabeled machine learning. *ACS Nano* **13**, 3031–3041 (2019). doi: [10.1021/acsnano.8b08014](https://doi.org/10.1021/acsnano.8b08014); pmid: [30830760](https://pubmed.ncbi.nlm.nih.gov/30830760/)
115. I. Kovalenko *et al.*, A major constituent of brown algae for use in high-capacity Li-ion batteries. *Science* **334**, 75–79 (2011). doi: [10.1126/science.1209150](https://doi.org/10.1126/science.1209150); pmid: [21903777](https://pubmed.ncbi.nlm.nih.gov/21903777/)
116. A. Nathan *et al.*, Flexible electronics: The next ubiquitous platform. *Proc. IEEE* **100**, 1486–1517 (2012). doi: [10.1109/JPROC.2012.2190168](https://doi.org/10.1109/JPROC.2012.2190168)
117. W. Gao *et al.*, Direct laser writing of micro-supercapacitors on hydrated graphite oxide films. *Nat. Nanotechnol.* **6**, 496–500 (2011). doi: [10.1038/nnano.2011.110](https://doi.org/10.1038/nnano.2011.110); pmid: [21804554](https://pubmed.ncbi.nlm.nih.gov/21804554/)
118. L. Y. Yuan *et al.*, Polypyrrole-coated paper for flexible solid-state energy storage. *Energy Environ. Sci.* **6**, 470–476 (2013). doi: [10.1039/c2ee23977a](https://doi.org/10.1039/c2ee23977a)
119. M. Park *et al.*, Postpatterned electrodes for flexible node-type lithium-ion batteries. *Adv. Mater.* **29**, 1605773 (2017). doi: [10.1002/adma.201605773](https://doi.org/10.1002/adma.201605773); pmid: [28102602](https://pubmed.ncbi.nlm.nih.gov/28102602/)
120. Y. Zhang *et al.*, Flexible and stretchable lithium-ion batteries and supercapacitors based on electrically conducting carbon nanotube fiber springs. *Angew. Chem. Int. Ed.* **53**, 14564–14568 (2014). doi: [10.1002/anie.201409366](https://doi.org/10.1002/anie.201409366); pmid: [25358468](https://pubmed.ncbi.nlm.nih.gov/25358468/)
121. H. Sun *et al.*, Three-dimensional holey-graphene/niobia composite architectures for ultrahigh-rate energy storage. *Science* **356**, 599–604 (2017). doi: [10.1126/science.aam5852](https://doi.org/10.1126/science.aam5852); pmid: [28495745](https://pubmed.ncbi.nlm.nih.gov/28495745/)
122. X. Pu *et al.*, A self-charging power unit by integration of a textile triboelectric nanogenerator and a flexible lithium-ion battery for wearable electronics. *Adv. Mater.* **27**, 2472–2478 (2015). doi: [10.1002/adma.201500311](https://doi.org/10.1002/adma.201500311); pmid: [25736078](https://pubmed.ncbi.nlm.nih.gov/25736078/)
123. P. Tan *et al.*, Flexible Zn- and Li-air batteries: Recent advances, challenges, and future perspectives. *Energy Environ. Sci.* **10**, 2056–2080 (2017). doi: [10.1039/C7EE01913K](https://doi.org/10.1039/C7EE01913K)
124. Z. S. Wu, Z. Liu, K. Parvez, X. Feng, K. Müllen, Ultrathin printable graphene supercapacitors with AC line-filtering performance. *Adv. Mater.* **27**, 3669–3675 (2015). doi: [10.1002/adma.201501208](https://doi.org/10.1002/adma.201501208); pmid: [25973974](https://pubmed.ncbi.nlm.nih.gov/25973974/)
125. N. A. Kyeremateng, T. Brousse, D. Pech, Microsupercapacitors as miniaturized energy-storage components for on-chip electronics. *Nat. Nanotechnol.* **12**, 7–15 (2017). doi: [10.1038/nnano.2016.196](https://doi.org/10.1038/nnano.2016.196); pmid: [27819693](https://pubmed.ncbi.nlm.nih.gov/27819693/)
126. Z. Liu *et al.*, Ultraflexible in-plane micro-supercapacitors by direct printing of solution-processable electrochemically exfoliated graphene. *Adv. Mater.* **28**, 2217–2222 (2016). doi: [10.1002/adma.201505304](https://doi.org/10.1002/adma.201505304); pmid: [26784382](https://pubmed.ncbi.nlm.nih.gov/26784382/)
127. J. Li *et al.*, Scalable fabrication and integration of graphene microsupercapacitors through full inkjet printing. *ACS Nano* **11**, 8249–8256 (2017). doi: [10.1021/acsnano.7b03354](https://doi.org/10.1021/acsnano.7b03354); pmid: [28682595](https://pubmed.ncbi.nlm.nih.gov/28682595/)
128. K. Sun *et al.*, 3D printing of interdigitated Li-ion microbattery architectures. *Adv. Mater.* **25**, 4539–4543 (2013). doi: [10.1002/adma.201301036](https://doi.org/10.1002/adma.201301036); pmid: [23776158](https://pubmed.ncbi.nlm.nih.gov/23776158/)
129. P. Huang *et al.*, On-chip and freestanding elastic carbon films for micro-supercapacitors. *Science* **351**, 691–695 (2016). doi: [10.1126/science.aad3345](https://doi.org/10.1126/science.aad3345); pmid: [26912855](https://pubmed.ncbi.nlm.nih.gov/26912855/)
130. P. Zhang *et al.*, Stimulus-responsive micro-supercapacitors with ultrahigh energy density and reversible electrochromic window. *Adv. Mater.* **29**, 1604491 (2017). doi: [10.1002/adma.201604491](https://doi.org/10.1002/adma.201604491); pmid: [27922733](https://pubmed.ncbi.nlm.nih.gov/27922733/)
131. Z. Liu *et al.*, Photoswitchable micro-supercapacitor based on a diarylethene-graphene composite film. *J. Am. Chem. Soc.* **139**, 9443–9446 (2017). doi: [10.1021/jacs.7b04491](https://doi.org/10.1021/jacs.7b04491); pmid: [28650642](https://pubmed.ncbi.nlm.nih.gov/28650642/)
132. Y. Huang *et al.*, A self-healable and highly stretchable supercapacitor based on a dual crosslinked polyelectrolyte. *Nat. Commun.* **6**, 10310 (2015). doi: [10.1038/ncomms10310](https://doi.org/10.1038/ncomms10310); pmid: [26691661](https://pubmed.ncbi.nlm.nih.gov/26691661/)
133. P. Zhang, F. Wang, M. Yu, X. Zhuang, X. Feng, Two-dimensional materials for miniaturized energy storage devices: From individual devices to smart integrated systems. *Chem. Soc. Rev.* **47**, 7426–7451 (2018). doi: [10.1039/C8CS00561C](https://doi.org/10.1039/C8CS00561C); pmid: [30206606](https://pubmed.ncbi.nlm.nih.gov/30206606/)
134. J. Y. Luo, W. J. Cui, P. He, Y. Y. Xia, Raising the cycling stability of aqueous lithium-ion batteries by eliminating oxygen in the electrolyte. *Nat. Chem.* **2**, 760–765 (2010). doi: [10.1038/nchem.763](https://doi.org/10.1038/nchem.763); pmid: [20729897](https://pubmed.ncbi.nlm.nih.gov/20729897/)
135. M. A. Deyab, 1-Allyl-3-methylimidazolium bis (trifluoromethylsulfonyl)imide as an effective organic additive in aluminum-air battery. *Electrochim. Acta* **244**, 178–183 (2017). doi: [10.1016/j.electacta.2017.05.116](https://doi.org/10.1016/j.electacta.2017.05.116)
136. S. Wei *et al.*, Highly stable sodium batteries enabled by functional ionic polymer membranes. *Adv. Mater.* **29**, 1605512 (2017). doi: [10.1002/adma.201605512](https://doi.org/10.1002/adma.201605512); pmid: [28112842](https://pubmed.ncbi.nlm.nih.gov/28112842/)
137. M. D. Tikekar, S. Choudhury, Z. Y. Tu, L. A. Archer, Design principles for electrolytes and interfaces for stable lithium-metal batteries. *Nat. Energy* **1**, 16114 (2016). doi: [10.1038/nenergy.2016.114](https://doi.org/10.1038/nenergy.2016.114)
138. H. Gao *et al.*, Parasitic reactions in nanosized silicon anodes for lithium-ion batteries. *Nano Lett.* **17**, 1512–1519 (2017). doi: [10.1021/acs.nanolett.6b04551](https://doi.org/10.1021/acs.nanolett.6b04551); pmid: [28177638](https://pubmed.ncbi.nlm.nih.gov/28177638/)
139. X. Wang *et al.*, Influences from solvents on charge storage in titanium carbide MXenes. *Nat. Energy* **4**, 241–248 (2019). doi: [10.1038/s41560-019-0339-9](https://doi.org/10.1038/s41560-019-0339-9)
140. A. J. Calahorra *et al.*, Luminescence and magnetic properties of three metal–organic frameworks based on the 5-(1*H*-tetrazol-5-yl)sophthalic acid ligand. *CrystEngComm* **15**, 7636–7639 (2013). doi: [10.1039/c3ce40869h](https://doi.org/10.1039/c3ce40869h)
141. G. K. Dimitrakakis, E. Tylanakis, G. E. Froudakis, Pillared graphene: A new 3-D network nanostructure for enhanced hydrogen storage. *Nano Lett.* **8**, 3166–3170 (2008). doi: [10.1021/nl801417w](https://doi.org/10.1021/nl801417w); pmid: [18800853](https://pubmed.ncbi.nlm.nih.gov/18800853/)
142. L. E. Shea-Rohwer, J. E. Martin, X. Cai, D. F. Kelley, Red-emitting quantum dots for solid-state lighting. *ECS J. Solid State Sci. Technol.* **2**, R3112–R3118 (2013). doi: [10.1149/2.015302jss](https://doi.org/10.1149/2.015302jss)
143. H. Hu, Z. Zhao, Y. Gogotsi, J. Qiu, Compressible carbon nanotube–graphene hybrid aerogels with superhydrophobicity and superoleophilicity for oil sorption. *Environ. Sci. Technol. Lett.* **1**, 214–220 (2014). doi: [10.1021/ez500021w](https://doi.org/10.1021/ez500021w)
144. X. H. Liu *et al.*, Size-dependent fracture of silicon nanoparticles during lithiation. *ACS Nano* **6**, 1522–1531 (2012). doi: [10.1021/nl204476h](https://doi.org/10.1021/nl204476h); pmid: [22217200](https://pubmed.ncbi.nlm.nih.gov/22217200/)
145. W. Sugimoto, H. Iwata, K. Yokoshima, Y. Murakami, Y. Takasu, Proton and electron conductivity in hydrous ruthenium oxides evaluated by electrochemical impedance spectroscopy: The origin of large capacitance. *J. Phys. Chem. B* **109**, 7330–7338 (2005). doi: [10.1021/jp044252o](https://doi.org/10.1021/jp044252o); pmid: [16851839](https://pubmed.ncbi.nlm.nih.gov/16851839/)
146. G. Zhou *et al.*, Graphene-wrapped Fe₃O₄ anode material with improved reversible capacity and cyclic stability for lithium ion batteries. *Chem. Mater.* **22**, 5306–5313 (2010). doi: [10.1021/cm101532x](https://doi.org/10.1021/cm101532x)
147. C. Zhao *et al.*, Self-assembly-induced alternately stacked single-layer MoS₂ and N-doped graphene: A novel van der Waals heterostructure for lithium-ion batteries. *ACS Appl. Mater. Interfaces* **8**, 2372–2379 (2016). doi: [10.1021/acsami.5b11492](https://doi.org/10.1021/acsami.5b11492); pmid: [26745784](https://pubmed.ncbi.nlm.nih.gov/26745784/)

ACKNOWLEDGMENTS

Funding: E.P. acknowledges support from National Science Foundation award no. DMR-1752623. F.B. acknowledges funding from the European Union's Horizon 2020 research and innovation program under grant agreement no. 785219–GrapheneCore2 and thanks A. E. Del Rio Castillo and H. Sun for useful discussions. X.F. thanks EU Graphene Flagship, ERC T2DCP, Coordination Networks: Building Blocks for Functional Systems (SPP 1928, COORNET), and the Center of Advancing Electronics Dresden (cfaed). Y.G.'s research on energy storage was supported through the Fluid Interface Reactions, Structures, and Transport (FIRST) Center, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, and Office of Basic Energy Sciences.

Competing interests: None declared.

10.1126/science.aan8285