2D Heterostructures for Energy Storage

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Two-dimensional (2D) materials provide slit-shaped ion diffusion channels that enable fast movement of lithium and other ions. However, electronic conductivity, the number of intercalation sites and stability during extended cycling are also crucial for building high-performance energy storage devices. While individual 2D materials, such as graphene, show some of the required properties, none of them can offer all properties needed to maximize energy density, power density, and cycle life. Here we argue that stacking different 2D materials into heterostructured architectures opens an opportunity to construct electrodes that would combine the advantages while eliminating the shortcomings of the individual building blocks. We discuss characteristics of common 2D materials and provide examples of 2D heterostructured electrodes that showed new phenomena leading to superior electrochemical performance. We also consider electrode fabrication approaches and finally outline future steps to create 2D heterostructured electrodes that could greatly expand current energy storage technologies.

Batteries are becoming an essential component in many energy-efficient applications. They are being integrated into smart electronics, textiles, Internet of Things and electric vehicles, transforming our lifestyle. Large-scale battery-based energy storage is helping to improve the intermittency problems with renewable energy sources such as solar, wind and waves. However, current Li-ion batteries by and large cannot be charged rapidly and efficiently; they degrade quickly and have to be replaced after only hundreds of cycles [1-3]; their energy density needs to be improved.

Many electrode materials have been proposed for high-performing Li-ion batteries and beyond. However, some intrinsic problems still exist. High power density can only be achieved in systems with rapid ion and electron transport [4], but the movement of ions in bulk electrodes are often restricted due to the limited lattice space, leading to slow charge/discharge processes and fast electrode failure. Poor electronic conductivity of common battery cathode materials (oxides) limits the rate performance further [5]. High energy density requires maximization of the charge storage capability, but conventional materials offer a finite number of sites for ions intercalation and their surface cannot be used to substantially increase charge storage capacity. In many cases, electrode materials are subject to the phase transformations resulting in the formation of redox inactive phases and capacity drop. Another problem is electrode expansion and contraction that accompanies reversible intercalation of ions. Volume changes may result in cracking of the grains and delamination from the current collector, leading to capacity decrease (**Figure 1**). As a result, phase transformations and mechanical degradation of electrode materials severely limit the lifetime of batteries [6].

In the search for an energy storage technology with higher energy and power densities and longer cycle life than current Li-ion batteries, one promising solution may be 2D van der Waals heterostructures, assembled by stacking different conventional 2D materials (e.g., graphene, transition metal oxides, carbides, nitrides or chalcogenides) arranged in hetero-layered architectures. This Perspective highlights the promise of 2D van der Waals heterostructures for applications as battery electrodes by considering performance parameters such as energy, power and cyclability of the constituent 2D material blocks. We review the initial reports on the electrochemical properties of 2D heterostructures, focusing on new phenomena and enhanced electrochemistry. We then discuss the scalable fabrication strategies that enable face-to-face heterointerfaces. This Perspective also sheds light on specific challenges that need to be addressed to introduce 2D heterostructured electrodes into the next-generation energy storage devices.

Advantages and limitations of conventional 2D materials.

There is currently no solution available, but with dozens of 2D transition metal dichalcogenides (TMDCs, such as MoS_2) [7, 8], transition metal carbides and nitrides (MXenes, such as Ti_2C and Ti_3CN) [9], transition metal oxides (TMOs) with layered structures (e.g., V_2O_5) [10-12], and all kinds of graphene-based materials [13], an ultimate solution can be found. These material families consist of dozens of compounds demonstrating extraordinary chemical and structural diversity, which opens ways to tune electrode operation and maximize battery performance. *Many 2D materials* (**Box 1**) *show a high redox activity in intercalation processes* *and/or promising performance when employed as electrodes in energy storage devices, but all of them have certain limitations.*

All conventional 2D materials suffer to a certain degree from their open structure and nanoscale morphology. While a large specific surface area of 2D materials increases the contact area with electrolyte and improves kinetics of ion transfer, it may also result in consumption of large amounts of electrolyte to form a solid-electrolyte interface (SEI) layer causing irreversible capacity in the first cycle. Moreover, 2D materials usually possess a large number of active sites for ions intercalation, which trigger parasitic reactions related to electrolyte decomposition [14, 15].

To overcome these limitations, individual 2D materials [14-16], can be combined in heterostructured electrodes by alternating layers of different 2D materials (**Figure 3**). Taking into account that 2D materials can be exfoliated, producing high surface area nanosheets with controlled size [17], and atomically engineered (functionalized) to enable various surface terminations, combining metallic electrical conductivity of graphene or MXene and high redox activity of TMO, a synergistic property enhancement can be achieved when the individual layers are assembled into stacked 2D heterostructures. This research direction opens unprecedented opportunities for nanoscale design of battery electrode.

Potential for Promising Performance

Energy Density

Energy density is directly proportional to the capacity, which in turn depends on the amount of charge stored in the electrode material. 2D electrodes provide multiple sites for charge carrying ions and enable their dense packing between the layers utilizing all interlayer volume. One of the greatest advantages of 2D structures is a possibility to increase interlayer distance, opening a way to not only accommodate larger ions (such as Na^+ and K^+) and decrease energy barriers to ions movement, thus accelerating diffusion, but also incorporate larger amounts of ions leading to higher specific capacity and energy density. Intercalation of two layers of Li^+ and Na^+ ions between MXene layers has been demonstrated by both modeling and experiment [18, 19]. Presence of a transition metal in a high oxidation state, such as molybdenum or vanadium in the host structure of MoO_3, Mo_2C, V_2O_5, or V_2C, further favors accommodation of a large number of ions due to large redox capability of those multivalent metals. The increased charge storage capacity in α-MoO_3 with the layered crystal structure was achieved due to intercalation pseudocapacitance, which occurred together with redox surface pseudocapacitance in the Li-ion system [20]. The mechanism of charge storage in 2D heterostructured electrodes will most probably include elements of the following three processes: bulk ion intercalation, intercalation pseudocapacitance and surface storage. However, the mechanism may differ from system to system depending on the chemistry (constituent individual 2D materials) and geometry (thickness of the layers, orientation of 2D sheets, etc.) of 2D heterostructures. Since such electrodes have not been widely investigated yet, the mechanism of charge storage should be a subject of future studies.

Power density

In 2D systems, the entire material is the “surface” and fast surface or interlayer diffusion replaces slow bulk diffusion, resulting in a significantly higher power density [21]. However unlike highly porous structures, such as aerogels, that also offer a large interface area and nanoscale diffusion length, 2D materials allow high packing density and show excellent volumetric characteristics [22]. Similarly, to individual 2D materials, restacking may be a challenge for 2D heterostructured electrodes. High packing density and redox active surfaces, necessary for achieving high volumetric power/energy density, can be produced by carefully controlling electrode architecture, including particles orientation and morphology, as well as by introducing defects (e.g., through-holes in 2D sheets) that would assist electrolyte transport. Intercalation of ions can be facilitated by controlling strength of interaction and distance between the layers of host material, which can be achieved through chemical modifications, pillaring and control of the 2D heterostructure assembly parameters. For example, interactions between graphene and MXene layers are weak, which may lead to easier intercalation and faster diffusion of ions at the MXene-graphene interface, compared to interfaces of the same kind. Fast movement of ions can be enabled by increasing interlayer distances in 2D materials. This can be achieved by chemical pre-intercalation of large, redox non-active ions or organic molecules. The pre-intercalated species hold the layers apart as pillars; therefore this approach is often called pillaring. As a result, the use of 2D materials eliminates limitations of size and charge of electrochemically cycled ions and fast ion dynamics in narrow slit pores have been predicted in several studies (e.g., [23]). At the same time, electrons should be quickly supplied to the surfaces to keep the charge balance. This requires materials with a high electronic conductivity and high density of states at the Fermi level. 2D materials can be metallic [7, 9] or zero-band gap [13, 24] semiconductors, demonstrating excellent performance at high current densities (charge-discharge rates). For example, MXene phases exhibit metallic conductivity and show exceptional characteristics as electrodes in pseudocapacitors with a variety of charge carrying ions, including Mg^{2+} and Al^{3+} [22]. Stacking dissimilar materials with different electronic conductivities (e.g., graphene and metal oxides with different work functions) together can be a viable strategy to increase the conductivity of both and utilize high redox capacity of oxides without losing fast reaction kinetics. If a monolayer of an oxide material is placed between metal (MXene) monolayers, the conductivity issue is resolved. More interestingly, MXenes built of different transition metals (e.g., Ti and Nb) offer different potentials of ions insertion, and some of them can be used as cathodes while others can serve as anodes with the same charge carrying ions (e.g., Na^+ or Mg^{2+}) [25].

Cycle life

By using 2D heterostructures, it is possible to minimize or eliminate expansion/contraction of the electrode materials leading to the increased lifetime of the battery and minimized mechanical and thermal losses. To improve the cyclability, electrodes with zero-volume change can be created by constructing multilayer electrode architectures, where some of the alternating building blocks (layers) would contract upon intercalation of charge carrying ions, while others would expand [26]. The long cycle life can only be achieved if no displacive phase transformations occur in the electrodes, which is usually a case with 2D materials. Hybrid 2D structures have intrinsically a better ability to accommodate and survive large stresses and strains during ion intercalation/deintercalation, because of weak bonding between their layers and large anisotropy of properties: high in-plane strength and low strength in the out-of-plane directions, where dimensional change occurs. Almost all electrode materials in lithium-ion batteries show expansion upon ion intercalation, but Ti_3C_2 paper electrodes undergo large volumetric contraction upon Li^+, Na^+, and Mg^{2+} ions intercalation [26]. Contraction of interlayer spacing was also observed during the first Mg enrichment in bilayered V_2O_5, which showed efficient reversible cycling of Mg^{2+} ions [27]. Therefore, the chemical diversity of 2D materials opens new vistas in rational design of intercalation electrodes with close to zero volumetric expansion by stacking building blocks of materials undergoing positive and negative volume changes in the multilayer architecture. Although challenging, realization of layered heterostructures would lead to the fabrication of electrodes with high mechanical and electrochemical stability (**Figure 2e**).

Pillaring and chemical pre-intercalation strategies, discussed before with respect to improving ionic diffusion in 2D materials, can also be used to create zero-expansion electrodes with improved cyclability (**Figure 4**). Pillaring of graphite is a prime example of this approach [24]. Chemical pre-intercalation of inorganic ions prior to electrochemical testing is another method that can improve stability in cycle life tests [28].

Applications of 2D Heterostructures for Energy Storage

The initial reports on building 2D van der Waals heterostructured electrodes were focused on combining TMDC compounds with various forms of carbon [29-31]. Here, we want to emphasize that the unique feature that distinguishes 2D heterostructures from other hybrid and composite materials is a face-to-face contact between two individual chemically different 2D building blocks. This interface contact maximizes charge storage capability of the constituent components and leads to synergistic effects. An intimate (direct) contact between layers of two individual 2D materials will most drastically affect electronic properties, but at the same time, inclusion of stabilizing species, such as ions and molecules, at the heterointerface will provide an ability to enhance electrochemical stability and ion diffusion. 2D heterostructures with both intimate and through-interlayer-species (quasi-intimate) interfaces should be investigated to identify the most efficiently stacked electrode architectures. At the same time, vertically stacked 2D structures are characterized by the heterointerface strain, rising from the mismatch of the in-plane lattice parameters of the constituent 2D phases, which is not possible in weakly adhered mechanically mixed materials. Integration of TMDCs with carbon is usually motivated by their limited electronic conductivity, especially along the *c* direction, but the produced 2D heterostructures demonstrated new phenomena, not observed in the case of TMDCs simply mixed with carbon. First, reducing the number of layers improved electron and ion transport leading to an enhanced electrochemical performance [32]. Second, the interlayer spacing was tuned by creating 2D heterostructures [30, 33, 34]. More specifically, one of the strategies that is believed to improve the performance of layered materials, especially in “beyond Li-ion” systems, is expansion of the interlayer spacing. For example, the interlayer distance between MoS_2 layers expanded from 0.62 nm in pure MoS_2 to 0.99 nm in a nitrogen-doped graphene NDG/MoS_2 heterostructure, with the carbon layers in-between [30]. This expanded interlayer spacing facilitates diffusion of ions and helps to accommodate the volume changes during cycling. At the same time, introduction of the NDG layer improves the electronic conductivity of MoS_2.

In the case of 2D heterostructures with an intimate contact between the layers, a mismatch in lateral dimensions of the constituent materials can complicate fabrication of stable structures. Moreover, it was shown that the average strain of ~0.1% due to the lattice mismatch between the carbon and MoS_2 sheets in the heterostructure changed the pathway of lithium storage [35]. Electrochemical testing revealed the presence of a chemical charge storage process in a MoS_2/C heterostructured electrode that does not occur in pristine MoS_2. More specifically, the interface-induced strain triggered chemical conversion reaction at higher voltages compared to pristine MoS_2. The compressive stress caused by carbon layer propagates into MoS_2 lattice and changes energetic pathway for the chemical conversion of MoS_2 into Mo and lithium polysulfides [35]. Therefore, 2D heterostructures represent a unique platform for investigating the role of the interface-induced strain in electrochemical processes.

Fabrication of 2D Heterostructured Electrodes

The electrode fabrication methods should allow for control of thickness of the layers, flake orientation and assembly of dissimilar 2D building blocks. Vacuum deposition techniques, while highly efficient for electronic applications, are not practical for creating battery electrodes. Conventional mixing of 2D components cannot prevent agglomeration of the flakes of the same material, leading to their restacking. The electrode architecture does not require formation of continuous large-area layers of the individual 2D materials. The heterointerface should be formed on the scale of the individual flakes, which can be achieved either through solution based methods, such as self-assembly in solution, or layer-by-layer (LbL) assembly. Research efforts in this area have already demonstrated stacked heterostructures based on graphene and TMDC monolayers for control of electronic properties [36-38]. LbL assembly has proven to be a versatile method that can be used to combine materials with different chemistries (metals, oxides, polymers, etc.) and morphologies (nanoparticles, nanosheets and nanowires) into a multilayer structure [39, 40]. In addition to its simplicity and low-cost, LbL assembly allows precise film thickness control. LbL assembly can be achieved on both planar and highly curved substrates. Solution based electrode film fabrication approaches allow for maintaining efficient ion transport channels. Moreover, the electrolyte or pillaring molecules/ions can be integrated within the electrode film during the assembly process, which can help addressing wettability issue of some 2D materials [41] and improve rate performance.

At the same time, the LbL process has some intrinsic challenges. First, there should be a mechanism of combining the constituent 2D materials into a stacked heterostructure. Different layers can be hold together by electrostatic forces, ionic charge transfer, hydrogen bonding, covalent attachment or hydrophobic interactions. Requirement for the efficient assembly imposes limitations because not all materials will stick to each other. It means that surface modifications are needed to introduce specific functional groups or surfactant molecules that will create a certain charge inducing interaction between the sheets of different materials. Second, flakes of the materials need to be in the face-to-face contact, without forming large gaps in-between, but at the same time enabling electrolyte accessibility. Such design is a challenge for conventional 2D materials and there are numerous papers dedicated to this subject [14, 15, 42]. Proposed solutions for the individual 2D materials are based on creating crumbled structures and porous 3D networks [43], but no studies addressed the design of 2D heterostructured electrodes to make them scalable in thickness, requiring a separate effort. Third, the conventional dipped solution adsorption (dip-LbL) approach is a relatively slow process, especially when atomically thin layers are assembled fast. Fabrication of electrodes of large sizes will require either self-assembly in solution or modified LbL assembly techniques, discussed below.

The high-speed processing of the multilayer films can be achieved through spin- or spray-assisted LbL fabrication (**Figure 3b, 3c)**. An ability to make electrodes at high throughput and low cost rapidly is attractive for industrial battery manufacturing. In addition, these assembly approaches provide flexibility in creating electrodes with different architectures. Curved or corrugated films or even films with the vertical orientation of the 2D nanosheets can be fabricated [39, 40] (**Figure 3e)**. Due to the accelerated diffusion of ions between 2D sheets [44], thicker electrodes can be made, without losing fast charge transport, if the sheets are aligned normally to the current collector surface. For example, heterostructured free-standing paper composed of acid-exfoliated few-layer thick MoS_2 sheets and reduced graphene oxide (rGO) flakes was prepared through vacuum-assisted filtration of a homogeneous aqueous dispersions followed by thermal reduction at elevated temperatures. The rGO flakes were stacked with MoS_2 sheets forming a conductive layer and a support structure for the free-standing paper [29]. Fabrication of 2D heterostructures was also achieved through LbL assembly combined with drop-casting or inkjet printing using inks of graphene, MoS_2 or WS_2, and hexagonal-boron nitride [45], showing that it is possible to overcome the manufacturing challenges.

2D heterostructures can also be manufactured by integrating 2D materials with polymers or organic molecules followed by pyrolysis. For example, a single-layer MoS_2/NDG heterostructure was prepared by electrostatic self-assembly of dopamine molecules on exfoliated MoS_2 nanoflakes, followed by annealing at 600^{o}C in Ar. Dopamine molecules carbonized to NDG, while MoS_2 preserved its monolayer morphology due to carbon layers formed in-between [30]. Another approach is based on hydrothermal treatment of soluble precursors and solid sheets of the heterostructure components. For example, a 2D MoS_2/rGO heterostructure was prepared by hydrothermal treatment of phosphomolybdic acid, L-cysteine and GO [31]. Furthermore, 2D materials can be used to design heterostructured electrodes with controlled porosity and shape them into thick 3D architectures to accommodate structural/volumetric changes and increase areal energy density [43].

Outlook

Conventional 2D materials demonstrate many unique properties, such as high electronic conductivity, high capacity, flexibility, strength and electrochemical stability. However the challenge is to fabricate electrodes that would combine all these excellent characteristics in one structure, for example by stacking monolayers of different 2D materials together using scalable assembly or self-assembly [46, 47]. Zero-expansion electrodes would also provide structural energy storage by transforming structural components and packaging elements into energy storage devices. Luckily, 2D heterostructures can be easily manufactured into practically any shape, typically without adding binders or other additives. They can be rolled, sprayed, filtered or printed to create flexible films or 3D electrodes [48] and integrated into the vehicle/aircraft bodies or cell phone cases. Pore engineering is a potentially useful strategy to effectively mitigate restacking of 2D materials in densely packed heterostructured architectures and maximize access of ions from electrolyte to the electrode surface [49, 50]. Moreover, metallic 2D materials (Ti_3C_2) can be used as current collectors and insulating ones (BN) as separators, producing the entire storage device of 2D materials and making it all printable, as no metal foil or porous polymer separators are required. Although the cost of 2D heterostructures may be an issue at present, with continuously improving synthesis and manufacturing processes, 2D heterostructures could soon become affordable enough for storage applications. While we expect that batteries will be mainly using lithium ions, at least in the next few years, less expensive beyond-lithium ions, such as Na^+, K^+, Mg^{2+} and Al^{3+}, will be used in the future devices [14], with graphene as one of the electrode components [51, 52].

The family of 2D materials is expanding very quickly with dozens added in the past few years (borophene, silicene, phosphorene, MXenes, etc.) [53]. With well over 100 potential candidate materials – and over 10,000, if hybrids are included – the challenge now is to find which of them are the most promising for specific energy storage applications. Computational material pre-selection [18] is essential to this search, followed by experimental verification [19, 54]. Computational studies can also be used to predict the dynamics of ions confined between layers of dissimilar materials. The questions of interest are similar to the ones that are being investigated in simpler systems, such as desolvation of ions intercalating into the slit pores or location and orientation of the co-intercalating solvent molecules. Such studies have been done, for example, for organic solvent molecules intercalating between graphene sheets [55], but no information exists for dissimilar interfaces. In the electronic materials community, there have been numerous publications on electronic properties of van der Waals heterostructures. However, in the energy storage systems, there will be layers of ions and electrolyte solvent molecules between those sheets. This means that the direct transfer of knowledge from the electronic material field may not be possible, and computational analysis is critically needed. We need to build a genome for 2D material heterostructures for energy storage. As a result of these research efforts, 2D heterostructures can greatly expand the limits of current energy storage technology and open a door to next-generation batteries with improved storage capabilities, faster charging and much longer lifetimes.

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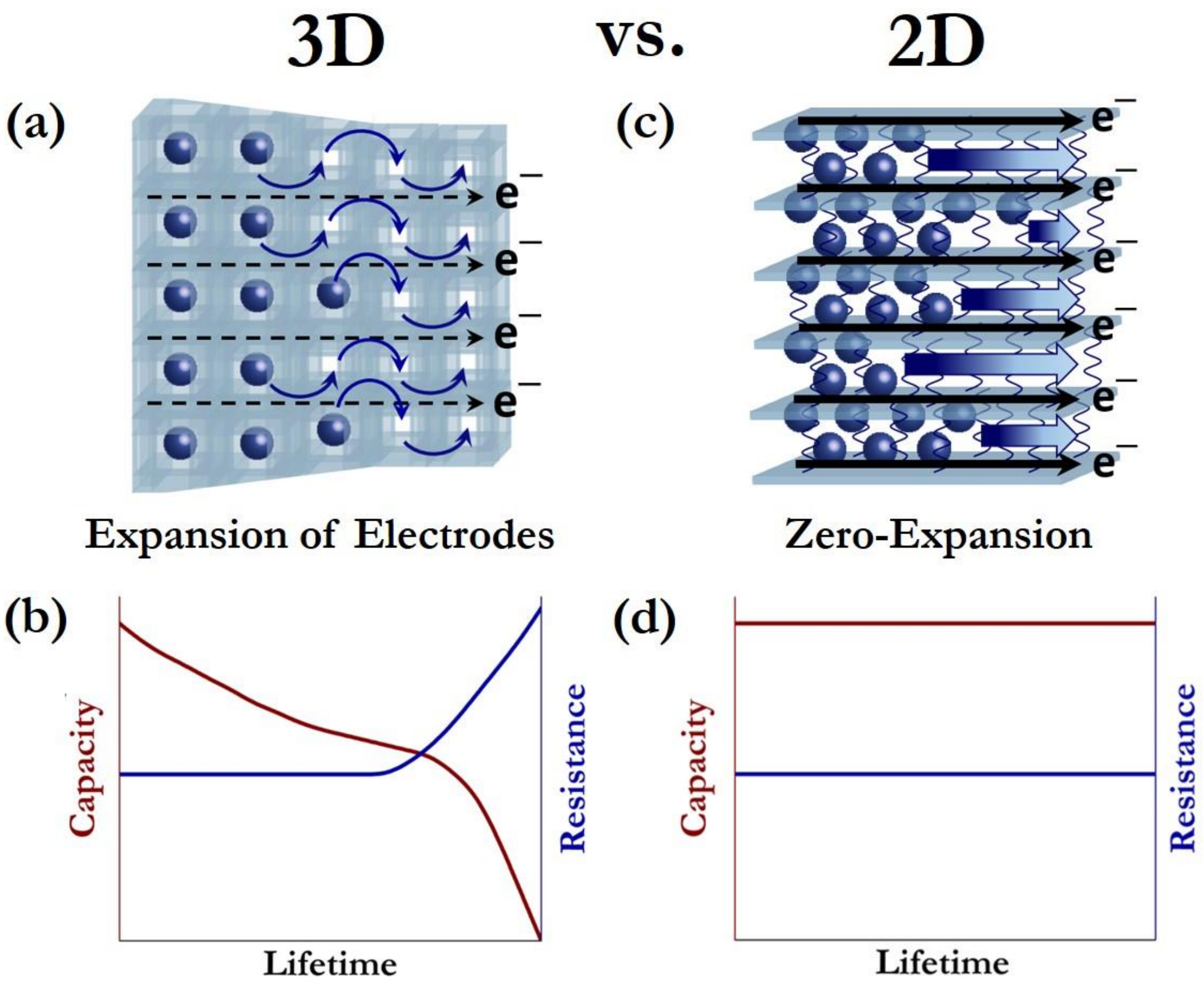
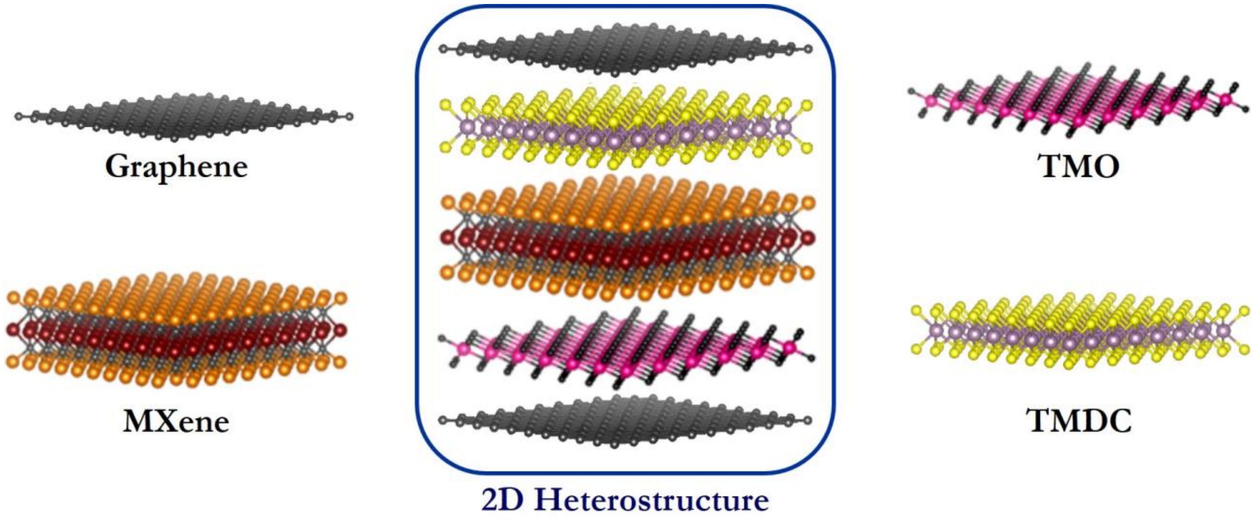


Figure 1. Overcoming limitations of current batteries by using 2D materials. (a) Schematic of a 3D intercalation electrode and (b) increase in resistance and decrease in capacity as a result of mechanical and/or chemical degradation of electrode materials. (c) A zero-expansion 2D electrode with improved kinetics of electrochemical processes and power density due to easy transport of electrons and ions and (d) stable electrochemical performance and extended lifetime due to the close-to-zero volume change of 2D electrodes.

Box 1. Advantages and limitations of different families of 2D materials.

Graphene-based electrodes exhibit high electrical conductivity and mechanical strength, but demonstrate moderate capacity due to the charge storage on the surface only and show little control over composition, suffering from decrease in conductivity due to surface terminations [13, 14, 51, 52]. TMDCs show high initial capacities, but undergo a conversion reaction on the first discharge cycle leading to poor capacity retention. When cycling is limited to the range of the reversible intercalation reaction, TMDC-based electrodes exhibit better cycling stability, but the capacity value drops significantly [8, 14]. Moreover, while some TMDCs demonstrate relatively high electronic conductivity, many of the phases are semiconducting [7]. TMOs show high redox activity in intercalation reactions and relatively high working potentials making them especially attractive for use as cathodes. However, low electronic conductivity of oxides imposes a requirement to mix them with a conductive additive to improve their performance [5, 14]. MXene phases have high electronic conductivity and mechanical strength, and can store a large amount of charge due to the pseudocapacitive mechanism [9]. However electrochemical properties of MXenes strongly depend on the synthesis conditions and surface chemistry, and methods for control of their surface terminations need to be developed to minimize irreversible capacity. **By building heterostructures made of stacked different 2D sheets, it is possible to combine the advantages and eliminate the disadvantages of the individual materials.** Except for graphene, multiple elements can form structures, schematically shown in this Box; and a large variety of individual 2D materials can be used to form heterostructures. The 2D heterostructure, shown in the center, is purely a schematic illustrating a concept of creating face-to-face heterointerfaces between layers of different 2D materials.



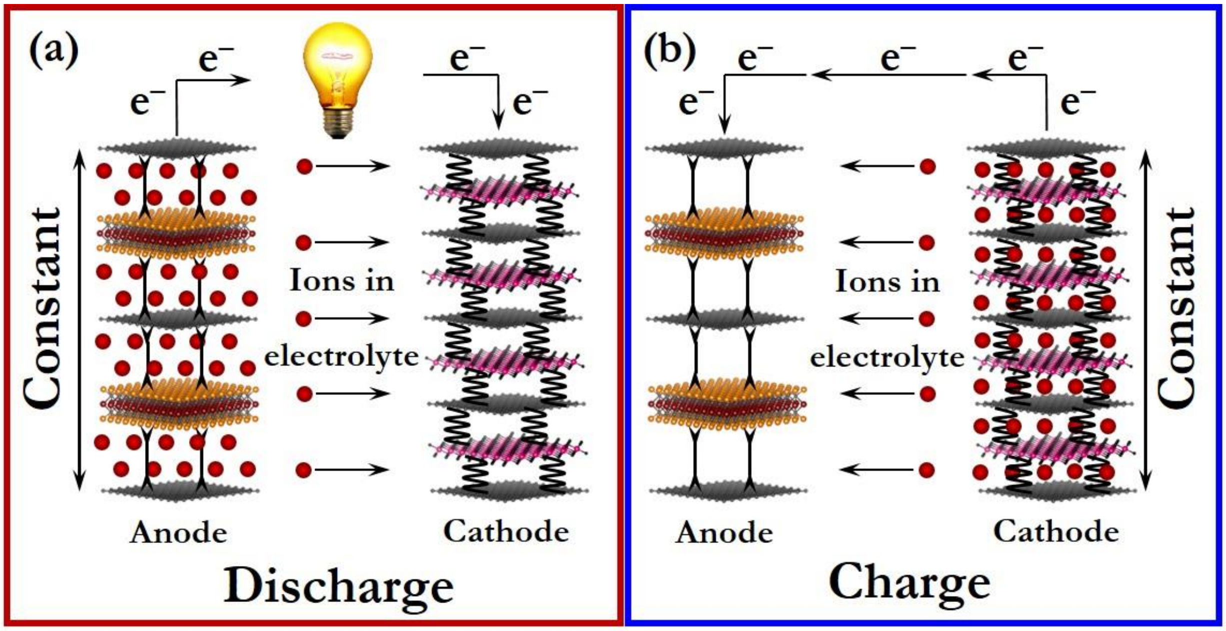


Figure 2. Schematic illustration of (a) discharge and (b) charge processes in a battery with 2D heterostructured pillared electrodes. Pillaring can be used as an effective strategy to conserve the interlayer distance in 2D heterostructures enabling zero-volume change in both electrodes during battery cycling thus improving mechanical and electrochemical stability of the system leading to extended cycle life. Different combinations of layered materials can be used to construct 2D heterostructured electrodes, as shown in Box 1.

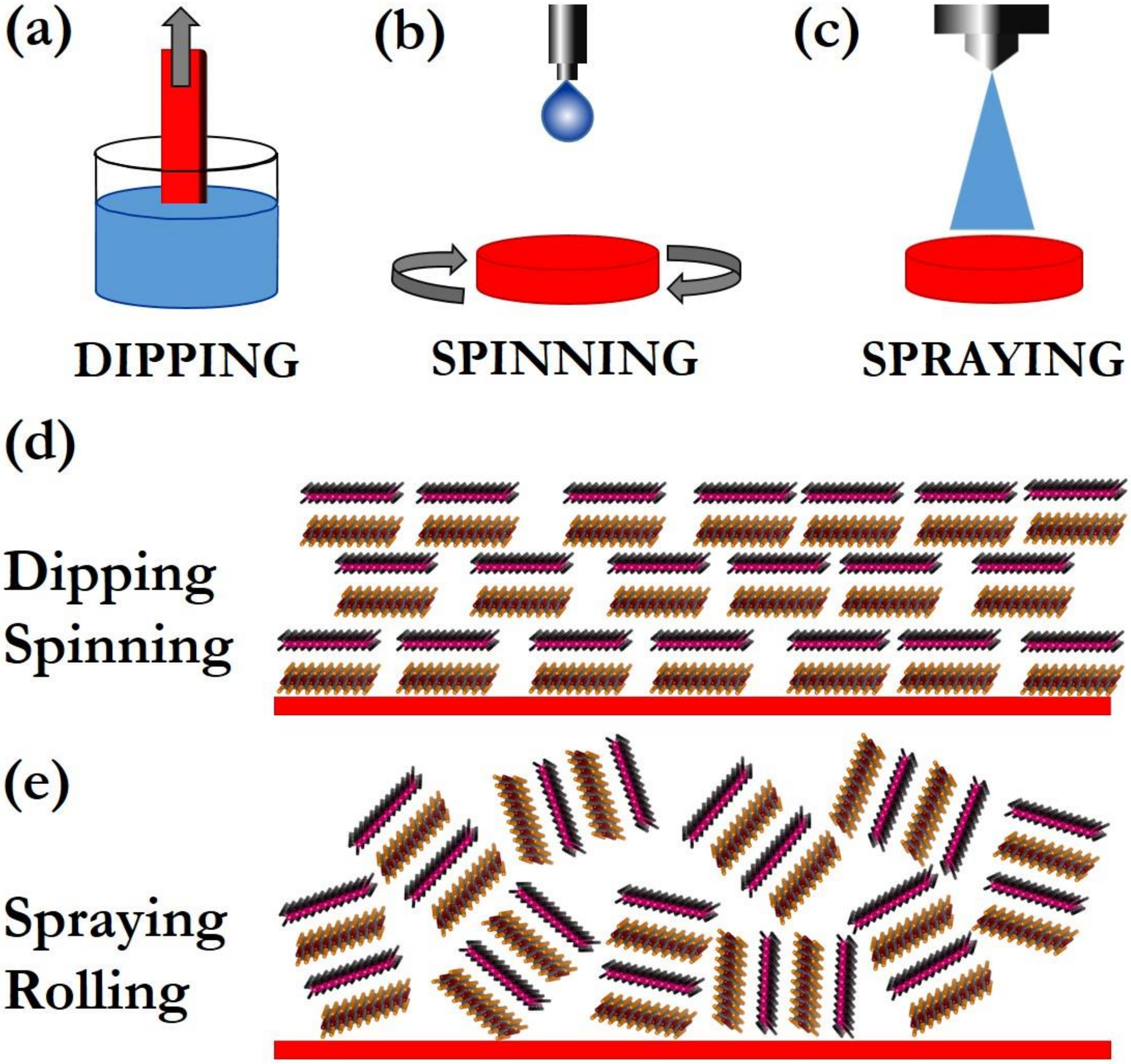


Figure 3. Fabrication of 2D heterostructured electrodes through layer-by-layer assembly. (a – c) Schematic illustration of the variations of LbL method potentially leading to the formation of the electrode films with different geometry (orientation of the constituent nanoflakes). (d) Schematic illustration of the electrode film with the majority of nanoflakes oriented parallel to the substrate impeding electrolyte penetration. Such electrode architecture can be obtained using dipping-LbL or spinning-LbL. (e) Schematic illustration of the electrode film with random orientation of nanoflakes forming 3D continuous percolation network for both electrolyte penetration and electron transport. Such electrode architecture can be obtained through spraying-LbL, rolling-LbL or combination of thereof (spray/roll-LbL).

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