Ultrathin Two-Dimensional Nanomaterials

Hua Zhang*

School of Materials Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore

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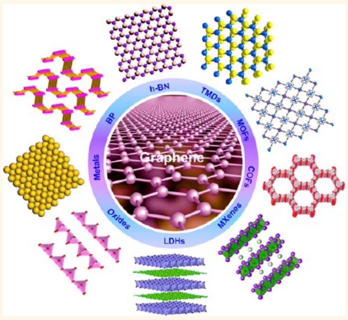
ABSTRACT The past decade has witnessed an extraordinary increase in research progress on ultrathin two-dimensional (2D) nanomaterials in the fields of condensed matter physics, materials science, and chemistry after the exfoliation of graphene from graphite in 2004. This unique class of nanomaterials has shown many unprecedented properties and thus is being explored for numerous promising applications. In this Perspective, I briefly review the state of the art in the development of ultrathin 2D nanomaterials and highlight their unique advantages. Then, I discuss the typical synthetic methods and some promising applications of ultrathin 2D nanomaterials together with some personal insights on the challenges in this research area. Finally, on the basis of the current achievement on ultrathin 2D nanomaterials, I give some personal perspectives on potential future research directions.



Ultrathin two-dimensional (2D) nanomaterials are attracting dramatically increasing interest after Novoselov, Geim, and co-workers exfoliated graphene from graphite using the mechanical cleavage method in 2004.[1] Graphene is a single-atom-thick, crystalline carbon film that exhibits various unprecedented properties, such as ultrahigh carrier mobility at room temperature ($\sim$10 000 cm^2 V^{-1} s^{-1}),[1] quantum hall effect,[2] large theoretical specific surface area (2630 m^2 g^{-1}),[3] excellent optical transparency ($\sim$97.7%),[4] high Young's modulus ($\sim$1 TPa),[5] and excellent thermal conductivity (3000−5000 W m^{-1} K^{-1}).[6]

The unexpected physical, optical, and electronic properties of graphene have inspired us to explore other ultrathin 2D nanomaterials that possess similar layered structure features but versatile properties, such as hexagonal boron nitride (h-BN),[7] transition metal dichalcogenides (TMDs; *e.g.*, MoS_2, TiS_2, TaS_2, WS_2, $MoSe_2$, WSe_2, *etc.*),[8−11] graphitic carbon nitride (g-C_3N_4),[12] layered metal oxides,[13] and layered double hydroxides (LDHs).[14] Intriguingly, many new types of ultrathin 2D crystals, such as metal−organic frameworks (MOFs),[15,16] covalent-organic frameworks (COFs),[17] polymers,[18−20] metals,[21−24] black phosphorus (BP),[25] silicene,[26] and MXenes,[27] have also been explored in recent years (Scheme 1), greatly enriching the family of ultrathin 2D nanomaterials. Because of their unique structural features and outstanding properties, ultrathin 2D nanomaterials have become a key class of materials in condensed matter physics, materials science, and chemistry. Driven by their extraordinary properties, a large number of synthetic methods, such as mechanical cleavage,[1,28−35] liquid exfoliation,[36−43] ion-intercalation and exfoliation,[44−51] anion-exchange and exfoliation,[52−55] chemical vapor deposition (CVD),[56−62] wet-chemical syntheses,[63−70] *etc.*, have been developed for the preparation of these ultrathin 2D nanomaterials. More importantly, these 2D nanomaterials are promising for a variety of applications, such as electronics/optoelectronics,[71−78] catalysis,[79−87] energy storage and conversion,[88−99] biomedicine,[100−108] sensors,[109−121] and more.[122−125]

In this Perspective, I give a brief overview of progress on the development of ultrathin 2D nanomaterials rather than offering a comprehensive review. First, I highlight the unique advantages of ultrathin 2D materials

* Address correspondence to hzhang@ntu.edu.sg.

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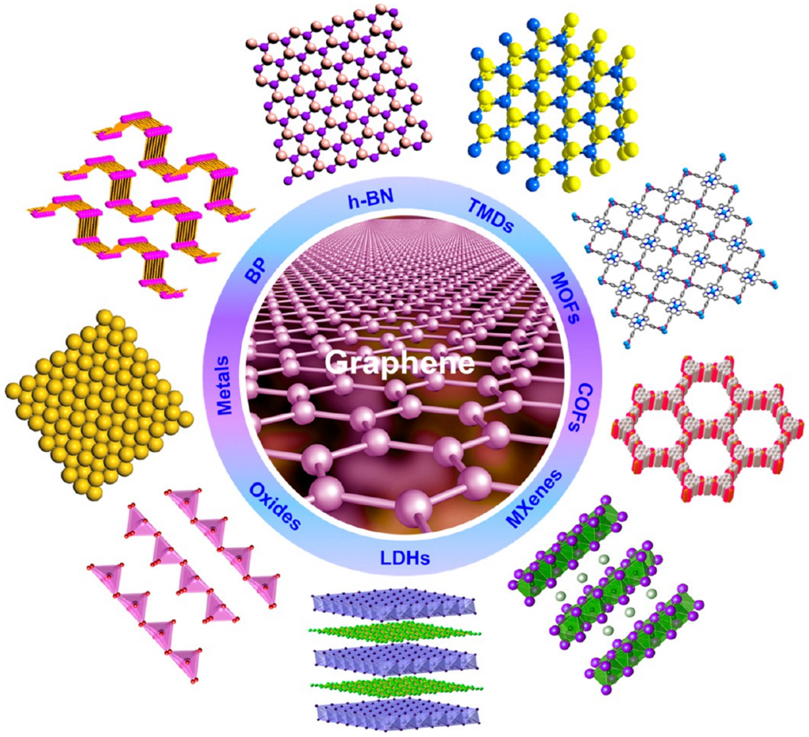


Scheme 1. Schematic illustration of different kinds of typical ultrathin 2D nanomaterials, such as graphene, h-BN, TMDs, MOFs, COFs, MXenes, LDHs, oxides, metals, and BP.

arising from their ultrathin structures. After that, I summarize and discuss the typical synthetic methods for preparation of ultrathin 2D nanomaterials and present the unique advantages of ultrathin 2D nanomaterials in some promising applications, such as electronics, catalysis and energy storage. Further, I discuss the challenges in the current synthetic methods and potential applications. Finally, I provide some personal opinions on future research directions for ultrathin 2D nanomaterials, aiming to inspire more exciting studies in the near future.

Why Ultrathin 2D Nanomaterials? Why are ultrathin 2D nanomaterials important? Do they have any unique properties that make them different from other types of nanomaterials, such as zero-dimensional (0D) nanoparticles, one-dimensional (1D) nanowires, and three-dimensional (3D) networks or their bulk counterparts? In this section, I give some examples to discuss the unique properties of ultrathin 2D nanomaterials from different aspects. Generally, there are several unique characteristics of ultrathin 2D nanomaterials compared to counterparts with different dimensionality. First, the electron confinement in two dimensions of ultrathin 2D nanomaterials without interlayer interactions, especially single-layer nanosheets, enables greatly compelling electronic properties compared to other nanomaterials, rendering them appealing candidates for fundamental condensed matter study and electronic device applications.[71] Second, the atomic thickness offers them maximum mechanical flexibility and optical transparency, making them promising for the fabrication of highly flexible and transparent electronic/optoelectronic devices.[71] Last, the large lateral size and ultrathin thickness endow them with ultrahigh specific surface area, making them highly favorable for surface-active applications.[71]

Early studies on graphene focused largely on its unique electronic properties. One of the most outstanding features benefiting from its morphology and electronic band structure is so-called massless Dirac Fermions.[71,126] Its extraordinary electronic behavior makes graphene an ideal candidate in the field of condensed matter physics for studying the quantum Hall effect, the Klein paradox, and the phenomenon of Zitterbewegung or jittery motion of the wave function in the presence of confining potentials.[2,127,128] Moreover, electrons in graphene can travel as long as a few micrometers without scattering, owing to its perfect crystal structure in the absence of defects, resulting in ultrahigh charge carrier mobility at room temperature and excellent electrical conductivity.[129] The combination of excellent conductivity and huge charge carrier mobility makes graphene ideal for electronic devices.

Another typical example is MoS_2, the most studied ultrathin 2D TMD nanosheet. Note that the indirect bandgap of ~1.3 eV can be converted to a direct bandgap of ~1.8 eV when the thickness of MoS_2 is thinned from bulk to monolayer.[130,131] One of the other attractive features of ultrathin 2D nanomaterials is that their electronic structures are highly sensitive to external stimuli, such as chemical modification, external electric fields, mechanical deformation, doping, and adsorption of other molecules or materials,[71] allowing one to tune their electronic properties in a desired manner at a highly controllable level.

Ultrathin 2D nanomaterials also present excellent mechanical properties due to the atomic thickness and in-plane covalent bonding. Experimental results revealed that the breaking strength and Young's modulus of graphene are 42 N m^{-1} and 1.0 TPa, respectively.[5] This strength suggests that graphene is the thinnest but strongest material measured to date. More importantly, graphene can sustain elastic deformations of more than 20%. It has been demonstrated that single-layer MoS_2 nanosheets have a higher Young's modulus (∼270 GPa) than bulk MoS_2 (∼240 GPa) and steel (∼205 GPa).[132] The calculations show that covalently bound ultrathin 2D nanomaterials have excellent mechanical properties.[133] In addition, the atomic thickness of ultrathin 2D nanomaterials also guarantees their high optical transparency. Note that white light absorbance measured for graphene is ∼2.3% with negligible reflectance (∼0.1%),[4] indicating its excellent light transmittance. The combination of excellent mechanical properties, light transmittance, and electronic properties makes ultrathin 2D nanomaterials highly attractive in the fabrication of next-generation wearable, highly flexible, and transparent electronic/optoelectronic devices.

Moreover, the large lateral size and atomic thickness endow ultrathin 2D nanomaterials with ultrahigh specific surface areas and high ratios of exposed surface atoms. This feature is highly favorable for many surface-active applications, such as electrocatalysis, photocatalysis, organic catalysis, and supercapacitors, in which the high specific surface area is a critical prerequisite parameter. For example, the theoretical specific surface area of graphene is as high as 2630 m^2 g^{-1}.[3] It is reasonable to anticipate that all of the other ultrathin 2D nanomaterials also have high specific surface areas since they also have 2D nanosheet structure. Moreover, the high specific surface area makes ultrathin 2D nanomaterials promising building blocks to construct functional composites.[134−141] They not only can act as the templates for directly synthesizing other kinds of nanostructures on their surfaces, but also can be used as reinforced fillers to strengthen the resultant composites.

> The development of facile, feasible, and reliable methods for preparation of ultrathin 2D nanomaterials is of great importance for the exploration of their properties, function, and applications.

Preparation Methods. The development of facile, feasible, and reliable methods for preparation of ultrathin 2D nanomaterials is of great importance for the exploration of their properties, function, and applications. Driven by the fascinating properties and promising applications, great efforts have been devoted to the exploration of various kinds of synthetic strategies to produce ultrathin 2D nanomaterials. Many reliable synthetic methods have been developed, such as mechanical cleavage, liquid exfoliation, ion-intercalation and exfoliation, selective etching and exfoliation, chemical vapor deposition (CVD), and wet-chemical synthesis. Generally, all these methods can be classified into two categories: top-down approaches and bottom-up approaches.

Currently, most of the studied ultrathin 2D nanomaterials are derived from layered compounds.[43] The layered compound represents a class of materials that have strong intraplane covalent bonding but weak interplane van der Waals interactions. Graphite, consisting of weakly stacked graphene monolayers, is a typical example of a layered compound. In contrast to layered compounds, many other crystals are formed by covalent or ionic bonding in three dimensions. The top-down method relies on the exfoliation of layered bulk crystals into single- or few-layer nanosheets, in which various driving forces are used to break the weak van der Waals interaction between the stacked layers. The bottom-up method relies on the direct synthesis of ultrathin 2D nanomaterials from different precursors *via* chemical reactions at certain experimental conditions. Two typical bottom-up methods are CVD and wet-chemical synthesis methods. In this section, I briefly summarize the different methods used for synthesis of ultrathin 2D nanomaterials with emphasis on their advantages and disadvantages. Note that this Perspective does not cover all the synthetic methods for ultrathin 2D nanomaterials, but only focuses on those methods that are currently widely used.

Mechanical Cleavage. The mechanical cleavage method is a traditional approach for exfoliation of layered bulk crystals to obtain 2D flakes.[1,28−35] In a typical process, the bulk crystal (*e.g.*, graphite) is first attached onto a piece of Scotch tape, and another piece of Scotch tape is adhered onto the other crystal surface. After that, one of the Scotch tape pieces is detached from the crystal. This process can be repeated several times in order to obtain flakes that are thin enough and can be transferred onto a target substrate (*e.g.*, SiO_2/Si). Then, the Scotch tape with the thin flake is attached onto a target substrate under gentle pressure. Finally, the Scotch tape is peeled off from the substrate and single- or few-layer nanosheets (*e.g.*, graphene) can be easily found on the substrate using

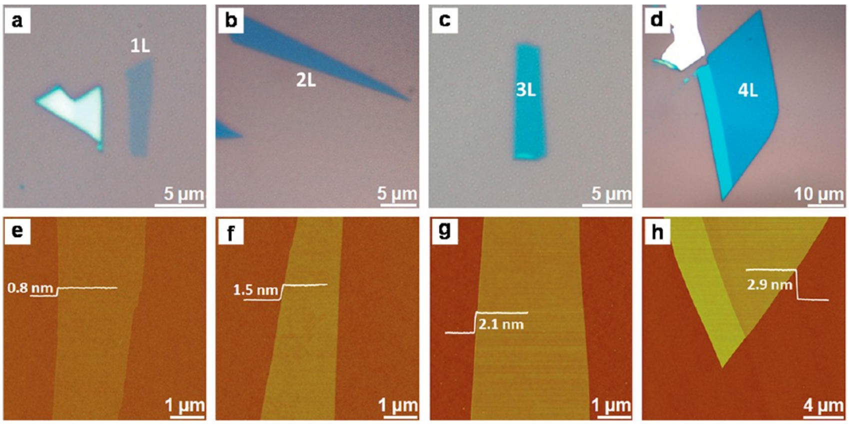


Figure 1. (a−d) Optical microscopy images of single-layer, bilayer, trilayer, and quadrilayer MoS_2 nanosheets and (e−h) the corresponding AFM images. Reproduced with permission from ref 34. Copyright 2012 John Wiley & Sons, Inc.

an optical microscope. In 2004, Novoselov, Geim, and co-workers successfully used this method to produce single-layer graphene from graphite.[1] Later on, other 2D crystals, including h-BN, MoS_2, $NbSe_2$, and $Bi_2Sr_2CaCu_2O_x$, have also been produced from layered bulk crystals.[28] Inspired by their work, many other types of single- or few-layer nanosheets have been prepared, such as other 2D TMDs (TiS_2, TaS_2, WS_2, WSe_2, $TaSe_2$, *etc.*), metal oxides, black phosphorus (BP), metal−organic frameworks (MOFs), and so on.[29−35] Figure 1 shows typical optical microscopy (OM) and atomic force microscopy (AFM) images of the mechanically exfoliated single- and few-layer MoS_2 nanosheets.[34] It is worth pointing out that it is possible to use this mechanical cleavage method to produce all of the ultrathin 2D nanosheets if their bulk crystals are layered compounds. Since these ultrathin 2D crystals are mechanically exfoliated from their layered bulk crystals and no chemical reactions occur during this process, the 2D materials obtained remain in the same crystal structures as their bulk crystals. As a result, the obtained pristine ultrathin 2D nanomaterials have excellent crystal quality with few defects and sizes of up to several tens of micrometers, which are ideal for the fundamental study of their intrinsic properties and the demonstration of electronic devices. However, several limitations of this method in its current form restrict their practical application. First, the production yield is quite low, and it cannot meet the requirements of real applications for which large amounts of materials are required. Second, a substrate is always necessary to support the produced nanosheets. Third, it is hard to control the thickness, size, and shape of the obtained 2D nanomaterials. Last, this method is only applicable to materials for which large, layered crystals are available. Therefore, to fully utilize this method, the production rate and yield must be improved to meet the large quantities required for practical applications.

Liquid Exfoliation. Liquid exfoliation is another typical strategy that has been extensively used to exfoliate layered bulk crystals to obtain ultrathin 2D nanosheets.[36−43] The liquid exfoliation method is used to exfoliate layered bulk crystals directly in solvents, such as *N*-methylpyrrolidone (NMP) and dimethylformamide (DMF), *via* sonication.[36] In this process, the sonication can break the weak van der Waals interaction between layers, but cannot destroy the covalent bonding in each layer. It was found that good matching of the surface tension between the layer crystal and the solvent is the key factor in minimizing the energy and increasing the efficiency of exfoliation. Moreover, the solvent is also important in stabilizing the exfoliated nanosheets and prohibiting their restacking and aggregating. However, the solvents used for the efficient exfoliation are organics. The most commonly used solvent, *i.e.*, water, is not suitable for the exfoliation. Alternatively, it was found that the sonication of layered bulk crystals in aqueous polymer or surfactant solution is also effective for their exfoliation, in which the polymer or surfactant can stabilize the exfoliated nanosheets.[36] Many ultrathin 2D nanomaterials, including graphene, h-BN, TMDs (MoS_2, WS_2, $MoSe_2$, $NbSe_2$, $TaSe_2$, $NiTe_2$, and $MoTe_2$), metal oxides (*e.g.*, WO_3), metal hydroxides, MOFs, BP, have been prepared by this method from their layered bulk crystals.[36−43] It is noteworthy that this method enables the high-yield and massive production of ultrathin 2D nanomaterials in solution at low cost, since the process is quite simple. By using the optimized method, the obtained volume of exfoliated graphene can be from hundreds of milliliters to hundreds of liters (Figure 2),[43] making it promising for commercial applications. However, the yield of single-layer sheets obtained by this method is still quite low and the lateral sizes of the sheets obtained are relatively small. In addition, the toxic organic solvents are harmful and the polymers/surfactants used in the exfoliation process are undesirable for some further applications. Therefore, the experimental conditions should be

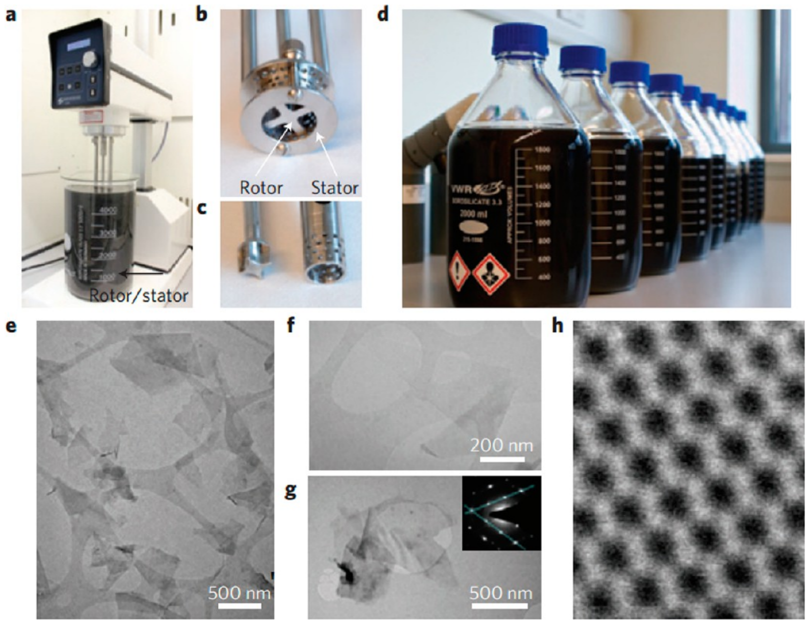


Figure 2. (a) A Silverson model L5M high-shear mixer with mixing head in a 5 L beaker of graphene dispersion. (b) Close-up view of a DD32 mm mixing head and (c) a DD16 mm mixing head with rotor (left) separated from stator. (d) Photograph of graphene-NMP dispersions. (e) Low-magnification TEM image of graphene nanosheets. (f and g) TEM and (h) high-resolution TEM images of graphene sheets. Reproduced with permission from ref 43. Copyright 2014 Nature Publishing Group.

further optimized in order to achieve high-yield exfoliation of single-layer nanosheets with large lateral sizes.

Ion-Intercalation and Exfoliation. The ion-intercalation and exfoliation method relies on the intercalation of ions into the interlayer spacing of layered bulk crystals to weaken the van de Waals interaction between layers. The intercalated compounds obtained are then exfoliated into single- or few-layer nanosheets under sonication.[44−51] The mostly common used intercalators are organometal compounds, such as butyllithium and metal naphthalenide (metal = Li, Na, K).[44,45,50] In a typical process, when TMD crystals are simply immersed or refluxed in the intercalator solution (*e.g.*, butyllithium), the cations can intercalate into the interlayer spacing of TMDs to form ion-intercalated compounds. Then, the well-dispersed single- or few-layer nanosheets can be easily obtained by sonication of the ion-intercalated compounds in water or ethanol. As a promising alternative, we developed an electrochemical method to intercalate Li^+ ions into layered compounds (Figure 3a), which allows us to monitor and control the amount of intercalated Li^+ ions precisely and thus to achieve more efficient exfoliation.[47−49] The layered bulk crystals coated on Cu foil and the Li foil are incorporated in a Li-ion battery cell as the cathode and anode, respectively (Figure 3a). Li^+ ions are intercalated into the layered bulk crystals during the discharge process (Figure 3a). This ion-intercalation and exfoliation method has successfully been used to prepare many ultrathin 2D nanosheets from their layered bulk crystals, such as graphene, h-BN, and many TMDs (*e.g.*, MoS_2, WS_2, TiS_2, TaS_2, ZrS_2, $NbSe_2$, WSe_2, Sb_2Se_3, and Bi_2Te_3) (Figure 3b).[47−49] Significantly, the production yields of this method are high. Among them, the yields of single-layer MoS_2 and TaS_2 sheets are over 90%. This method has a unique advantage as well: the Li-intercalation in TMD crystals can induce the phase transformation of TMD from the semiconducting 2H phase to the metallic 1T phase during the exfoliation process.[44,45] Phase engineering of ultrathin 2D TMDs gives rise to great opportunities for realizing superior performance for some promising applications, such as the electrocatalytic hydrogen evolution reaction, low contact resistance field-emission transistors, and electrochemical supercapacitors.[142] However, some challenges still remain. In the case of intercalation by organometal compounds, the experimental process requires high temperatures (*e.g.*, 100 °C) and long reaction times (*e.g.*, 3 days).[44,45] It is noteworthy that both the organometal compounds and Li foils are sensitive to oxygen and water, and become highly explosive when exposed to them.[47−49] For the electrochemical intercalation process, the preparation process is relatively complicated compared to other methods.

Chemical Vapor Deposition Growth. The CVD method is another typical bottom-up process used to prepare ultrathin 2D nanomaterials on substrates.[56−62] In a typical process, the given substrate is exposed to reactive precursors at high temperature and high vacuum, in which the precursors react and/or decompose on the surface of the substrate to form ultrathin 2D flakes or large-area ultrathin films. It is worth

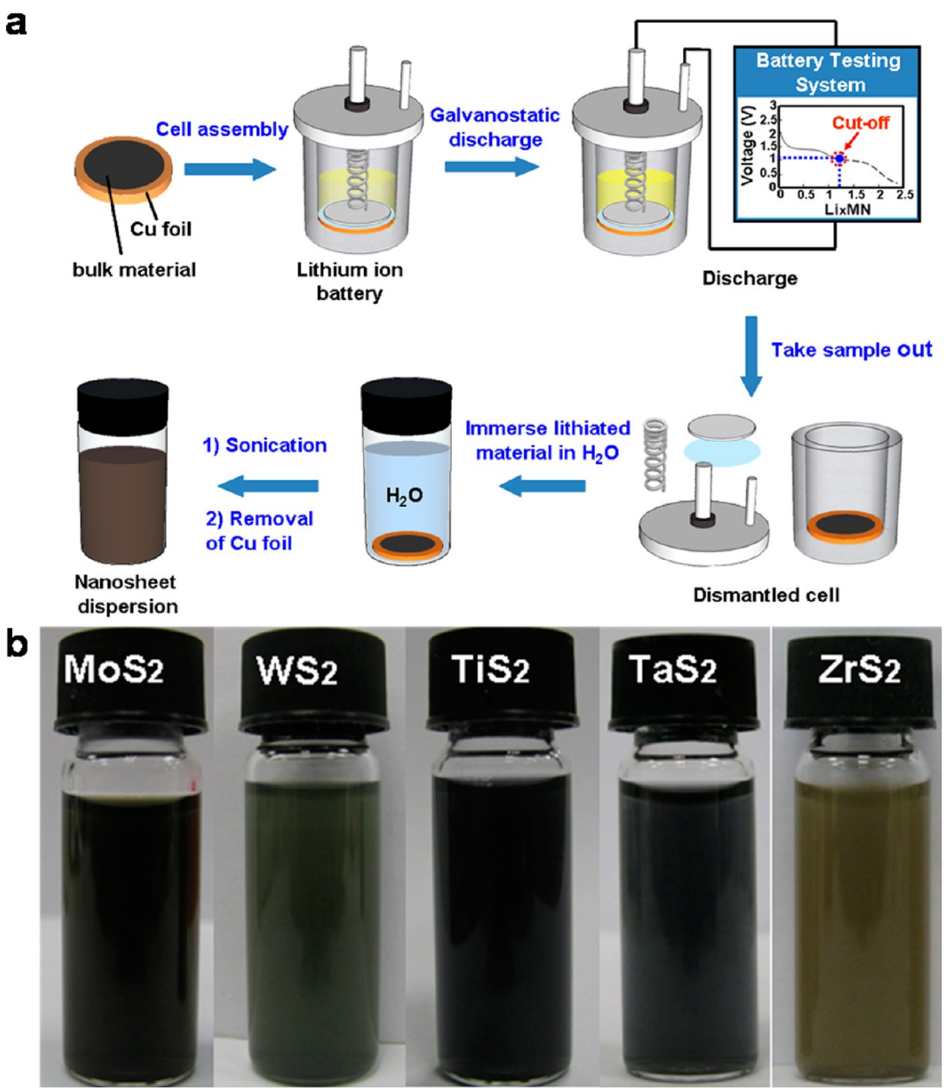


Figure 3. (a) Schematic illustration of the electrochemical Li-intercalation and exfoliation process for exfoliation of single- or few-layer TMD nanosheets. Reproduced with permission from ref 48. Copyright 2012 John Wiley & Sons, Inc. (b) Photographs of 2D nanosheet dispersions. Reproduced with permission from ref 47. Copyright 2011 John Wiley & Sons, Inc.

emphasizing that this method allows us to produce ultrathin 2D nanomaterials with high crystal quality, scalable size, tunable thickness, and excellent electronic properties. To date, this method has been successfully utilized to prepare many ultrathin 2D nanomaterials including graphene, TMDs (MoS_2, WS_2, $MoSe_2$, WSe_2, ReS_2, GaS_2, *etc.*), h-BN, topological insulators (*e.g.*, In_2Se_3 and Bi_2Se_3), and metal oxides.[56−62] Promisingly, the growth of large-area uniform graphene in wafer scale or even square meters has been achieved,[62] holding great promise for many practical applications. However, high temperature and high vacuum are normally used in the CVD growth process. In addition, a specific substrate is necessary to support the grown ultrathin 2D nanomaterials, resulting in the requirement of a transfer process to move the obtained 2D nanomaterials onto desired substrates for further studies and applications. Remaining challenges for this method include: (1) how to achieve the growth of ultrathin 2D nanomaterials on arbitrary substrates in order to avoid the complicated transfer process that is currently used and (2) how to grow high-quality ultrathin 2D nanomaterials at low temperature, which would make the CVD method simple and more efficient.

> The unprecedented physical, electronic, chemical, and optical properties of ultrathin 2D nanomaterials arising from their unique structural features offer great potential for numerous applications.

Wet-Chemical Synthesis. Wet-chemical synthesis is another typical

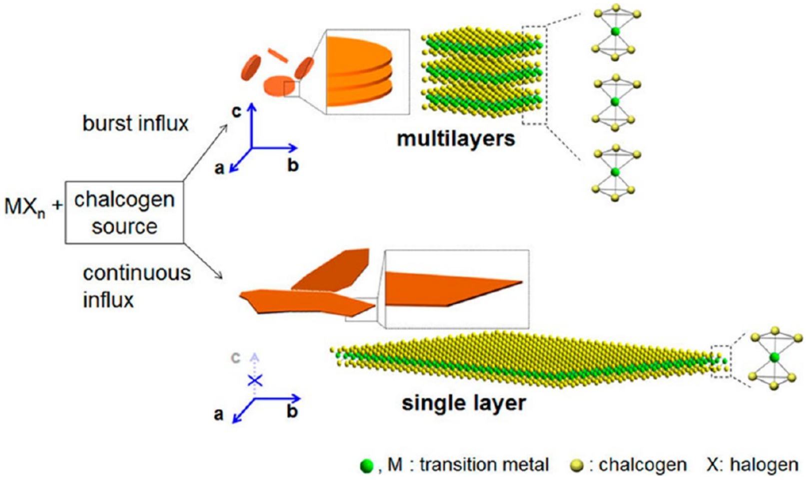


Figure 4. Schematic illustration of the wet-chemical synthesis of single- and multilayer TMD nanosheets. Reproduced from ref 65. Copyright 2014 American Chemical Society.

bottom-up method that has been widely used to produce ultrathin 2D nanomaterials.[63−70] Wet-chemical methods are used to synthesize target materials from certain precursors *via* chemical reactions in solution, in which surfactants are normally used to control the size, shape, and morphology as well as to stabilize the synthesized materials. Some widely used wet-chemical methods for nanomaterials include templated synthesis, hydro/solvothermal synthesis, self-assembly of nanocrystals, and soft colloidal synthesis. Wet-chemical methods have been demonstrated to be effective for synthesis of numerous ultrathin 2D nanomaterials, such as graphene, h-BN, g-C_3N_4, TMDs (*e.g.*, MoS_2, TiS_2, TaS_2, WS_2, and ZrS_2; Figure 4), metals, metal oxides, metal chalcogenides, LDHs, MOFs, COFs, and polymers.[63−70] It is worth pointing out that almost all the nonlayer structured ultrathin 2D nanomaterials, such as metals (*e.g.*, Au, Pd, and Rh), metal oxides (*e.g.*, TiO_2, CeO_2, In_2O_3, SnO_2, and Fe_2O_3), and metal chalcogenides (*e.g.*, PbS, CuS, SnSe, ZnSe, ZnS, and CdSe), can be synthesized by wet-chemical synthesis methods.[143] Importantly, the wet-chemical synthesis enables the realization of high-yield and massive production of ultrathin 2D nanomaterials in liquid at relatively low cost, which is potentially applicable for industrial production. In addition, size and shape control of ultrathin 2D nanomaterials is easier to achieve in wet-chemical syntheses in comparison with other methods. However, it is hard to obtain single-layer nanosheets for most of the nanomaterials synthesized by wet-chemical methods, because the synthesis is easily affected by reaction parameters, including reaction temperature, reaction time, concentration of precursors, and solvents.

Other Methods. For the synthesis of graphene sheets, another commonly used method is the modified Hummers method.[144−146] In a typical experiment, the bulk graphite crystal is first oxidized by strong oxidizing agents, for example, a mixture of potassium permanganate and concentrated sulfuric acid, to form graphite oxide. The interlayer spacing of graphite crystal is significantly expanded due to the oxidation. The expanded graphite oxide is then exfoliated into single-layer graphene oxide (GO) sheets under sonication. It is worth emphasizing that there are abundant oxygen-containing functional groups, such as carboxyl, epoxy, and hydroxyl groups, on the surface of GO sheets.[147,148] The obtained GO sheets can easily be reduced by removal of most of the functional groups on their surface to obtain reduced graphene oxide (rGO) sheets.[147] The reduction of GO sheets can be achieved by many strategies, such as chemical reduction, thermal annealing, photochemical reduction, electrochemical reduction, and so on.[147] Both the GO and the rGO sheets are normally classified as graphene derivatives,[147] although rGO is also described as graphene in some literatures. Note that the electronic properties of GO are significantly different from pristine or CVD-grown graphene. For example, in contrast to highly conductive graphene, GO is an insulating material.[147] Even after the reduction of GO, the electrical conductivity of rGO is not as good as that of the pristine graphene. Another major difference is that GO is amphiphilic, while graphene is highly hydrophobic. The different electronic, chemical, and surface properties of GO and rGO sheets make them a unique class of materials that are different from pristine graphene, especially chemically. The abundant functional groups on their surface make them ideal candidates for further covalent chemical functionalization or construction of functional composites.[134−141]

The selective etching and exfoliation method was developed for the synthesis of ultrathin 2D MXenes (*i.e.*, the group of early transition metal carbides and/or carbonitrides) from bulk MAX phases.[149−152] The MAX phases are layered materials, where M is an early transition metal, A is an A-group (mostly IIIA and IVA, or

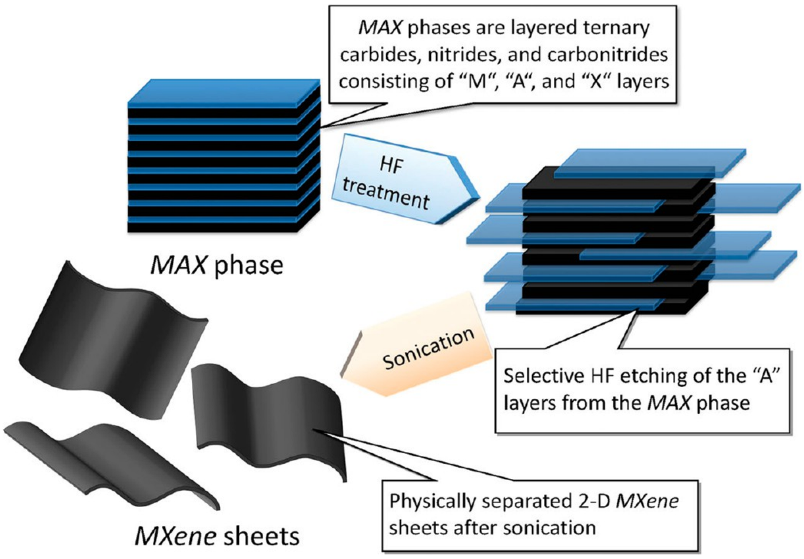


Figure 5. Schematic illustration of the synthesis process of MXenes from MAX phases. Reproduced from ref 150. Copyright 2012 American Chemical Society.

groups 13 and 14) element, and X is either C and/or N.[153] They have strong in-plane M−X covalent/metallic/ionic bonding. However, in contrast to van der Waals stacked layered compounds, such as graphite and TMDs, the interactions between layers in MAX phases also includes metallic bonding when A is Al.[153] This metallic bonding is stronger than van der Waals interactions, making it impossible to exfoliate MAX phases into ultrathin 2D nanomaterials by those exfoliation strategies used for graphene or TMDs.[153] To this end, a selective etching and exfoliation method has been developed (Figure 5).[149−152] In a typical process, a powder of a MAX phase is immersed and stirred in aqueous HF solution for a period of time. During this process, the HF can selectively etch the A layers in the MAX phase without disrupting the M−X bonds due to the relatively weak strength of the M−A bonding compared to the M−X bonding (Figure 5). After selective etching, an intermediate product with a loosely packed structure like expanded graphite can be obtained. Then, the ultrathin 2D MXenes can be prepared by sonication of the intermediate product in solution (Figure 5). The chemical reaction occurs during the etching process, which is different from the other exfoliation methods. This is the reason the prepared ultrathin 2D nanosheets have been labeled as MXenes, and the removal of A represents the etching of A layers from the MAX phases. Until now, many MXenes, such as Ti_3C_2, Ti_2C, Nb_2C, V_2C, $(Ti_{0.5},Nb_{0.5})_2C$, $(V_{0.5},Cr_{0.5})_3C_2$, Ti_3CN, and Ta_4C_3, have been prepared in high yield and large scales.[149−152] However, not all of the MAX phases can be exfoliated into MXenes using this method. Moreover, the etching agent used in the process, *i.e.*, HF, is a strong corrosive chemical. Bearing this in mind, safer etching agents are expected to be explored to replace HF during the preparation of MXenes.

Applications. The unprecedented physical, electronic, chemical, and optical properties of ultrathin 2D nanomaterials arising from their unique structural features offer great potential for numerous applications. The abundant numbers in the family of ultrathin 2D nanomaterials with versatile properties enable us to select materials that are specific to the desired application. Ultrathin 2D nanomaterials have been explored for various applications in electronics, optoelectronics, sensors, catalysis, gas separation, energy storage and conversion, water remediation, and biomedicine. In this section, I highlight some promising applications of ultrathin 2D nanomaterials, particularly focusing on electronics, catalysis, and energy storage.

Electronics. The enthusiasm for ultrathin 2D nanomaterials for electronics applications is motivated by the observation of ultrahigh carrier mobility in graphene when it is used as the channel material in field-emission transistors (FETs).[1] However, the lack of bandgap makes graphene unsuitable for being integrated into high-performance and low-power FET devices due to the resultant small on/off ratios and high turn-off currents.[71] Fortunately, some ultrathin 2D TMDs are semiconductors and most of their bandgaps are within 1−2 eV, making them ideal as channel materials in FETs (Figure 6).[154] It has been demonstrated that 2D TMD-based FETs can exhibit high on/off ratios, low subthreshold swings, and high carrier mobilities (from few to several hundred $cm^2\ V^{-1}\ s^{-1}$).[154] Promisingly, a recent report demonstrated that the mobility of FETs while using few-layer BP as the channel material can reach up to 1000 $cm^2\ V^{-1}\ s^{-1}$ at room temperature.[77] Note that a recent review paper provides a detailed discussion on 2D materials for electronics, in which the advantages

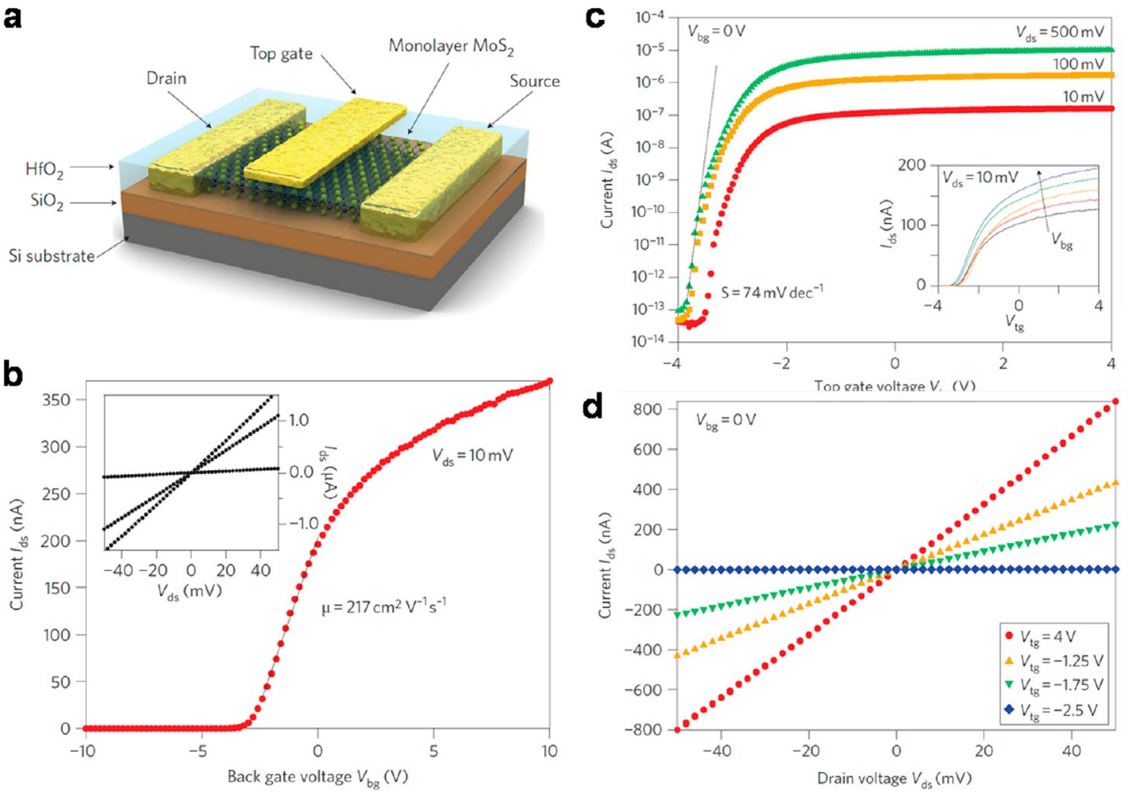


Figure 6. (a) Three-dimensional schematic illustration of the single-layer MoS_2-based FET device. (b) Room-temperature transfer characteristic for the FET device. (c) $I_{ds}-V_{tg}$ curve recorded at bias voltage ranging from 10 to 500 mV. (d) $I_{ds}-V_{ds}$ curves recorded at different V_{tg}. Reproduced with permission from ref 73b. Copyright 2011 Nature Publishing Group.

and current limitations of 2D materials for electronics are discussed.[154] In addition, ultrathin 2D nanomaterials possess another important characteristic, *i.e.*, excellent mechanical flexibility. The coexistence of high carrier mobility, large bandgap, and excellent mechanical flexibility in some ultrathin 2D nanomaterials, such as MoS_2, WS_2, MoS_2, WSe_2, ZrS_2, BP, *etc.*, makes them highly favorable for the construction of high-performance, low-power, and highly flexible electronics.[155] A recent review paper has given a detailed discussion on 2D flexible electronics.[155]

Besides FETs and flexible electronics, ultrathin 2D nanomaterials are also promising for other electronics applications. For example, graphene has been demonstrated to be a promising electrode material for future electronics, and is expected to possess merits including wearability, high flexibility, and transparency, due to its excellent conductivity, mechanical flexibility, and optical transparency.[156] Graphene electrodes have been integrated into many devices, such as solar cells, organic light-emitting diodes (OLEDs), and nonvolatile memory devices.[156] Moreover, the excellent conductivity and optical transparency of graphene also make it an ideal candidate for some electronic products, such as touch screen displays and e-paper (electronic paper).[154]

Catalysis. Due to their ultrahigh specific surface areas, some ultrathin 2D nanomaterials have shown excellent performance in catalysis, especially in electrocatalysis. For example, ultrathin 2D TMDs (*e.g.*, MoS_2 and WS_2) have been found to be highly active for the electrocatalytic hydrogen evolution reaction.[157−159] Doped graphene (*e.g.*, N-doped graphene) sheets have been demonstrated to be promising as highly efficient metal-free electrocatalysts for the oxygen reduction reaction.[160] In addition, LDH nanosheets have been used as highly active catalysts for the electrocatalytic oxygen evolution reaction.[85,86] Generally, the electrical conductivity and effectively active sites are two key parameters for achieving excellent activities in electrocatalytic reactions. Engineering defects, strains, and/or crystal boundaries, and doping heteroatoms in ultrathin 2D nanomaterials are two of the most effective ways to increase the number of active sites and thus to realize superior performance for electrocatalysis. For example, engineering rich defects or incorporating oxygen atoms in the MoS_2 sheet can significantly enhance its activity for the electrocatalytic hydrogen evolution reaction (Figure 7a).[157,158] Another typical example is that doping N, S, P, and/or B atoms in graphene is highly favorable for improving its electrocatalytic activity toward the oxygen reduction reaction.[160] Although graphene itself is nearly inert for electrocatalysis, the heteroatom-doped graphene exhibits excellent activity toward the electrocatalytic oxygen evolution reaction.

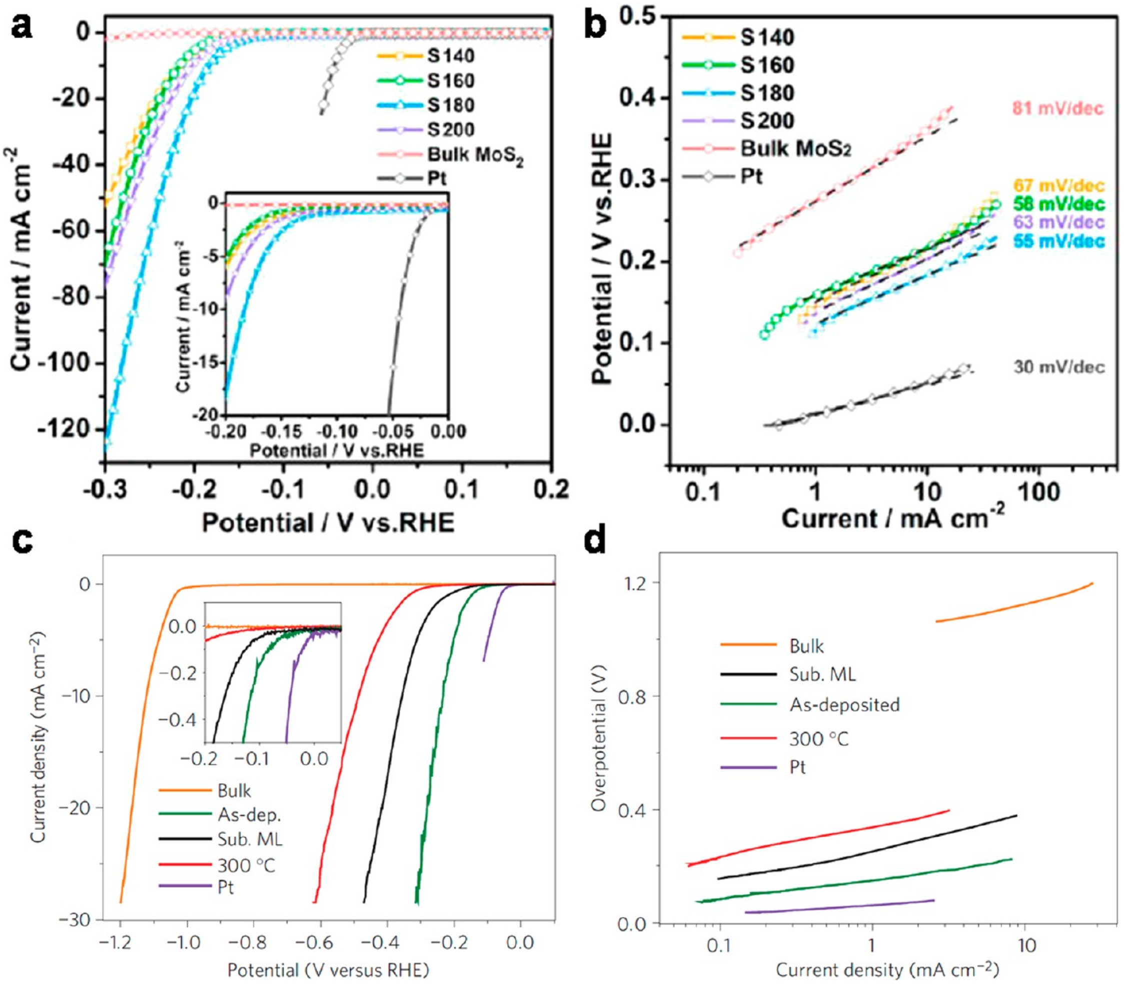


Figure 7. (a) Polarization curves and (b) corresponding Tafel plots of the oxygen-incorporated MoS_2 ultrathin nanosheets. Reproduced from ref 158. Copyright 2013 American Chemical Society. (c) Polarization curves of WS_2-based electrocatalysts and (d) their corresponding Tafel plots obtained from the polarization curves. Reproduced with permission from ref 159. Copyright 2013 Nature Publishing Group.

Phase engineering or hybridization with a highly conductive matrix has also been proven to be a promising strategy to enhance the conductivity of ultrathin 2D nanomaterials and thus to achieve superior electrocatalytic activities. For example, metallic 1T-phase MoS_2 nanosheets exhibit enhanced catalytic performance compared to the 2H-phase MoS_2 after the phase transformation from 2H to 1T, which is due to the excellent conductivity of 1T MoS_2 nanosheets (Figure 7b).[159] The electrocatalytic activity of 2D TMDs (*e.g.*, MoS_2 and WS_2) toward the hydrogen evolution reaction can be significantly enhanced by their hybridization with highly conductivity materials, such as graphene, carbon nanotubes, or noble metals.[140] The doped graphene-based catalysts and 2D TMD-based catalysts have great potential to replace the current used precious Pt-based catalysts for oxygen reduction reactions and hydrogen evolution reactions, respectively, due to their excellent catalytic activities, which are comparable to those of the Pt-based catalysts, but much less expensive.

Beyond electrocatalysis, ultrathin 2D nanomaterials also have promising applications in other catalytic reactions. Ultrathin noble metal nanosheets have shown excellent catalytic activities for organic reactions. For example, single-layer Rh nanosheets exhibited excellent catalytic performance for catalytic hydrogenation and hydroformylation reactions due to the 100% exposure of surface Rh atoms in Rh nanosheets.[24] Moreover, ultrathin metal oxide nanosheets (*e.g.*, CeO_2 and SnO_2) can be used as highly active catalysts for catalytic CO oxidation.[161,162] In addition, excellent photocatalytic activities for water splitting have been achieved with some ultrathin 2D nanomaterials, such as g-C_3N_4,[87] ZnSe,[163] and CdS.[164]

Energy Storage. The exploration of reliable materials for energy storage is of great importance due to the increasing demand of energy in the world. Lithium-ion batteries (LIBs) are one of the most important energy storage devices in modern society for portable electronics, laptops, and electric vehicles.[165] The

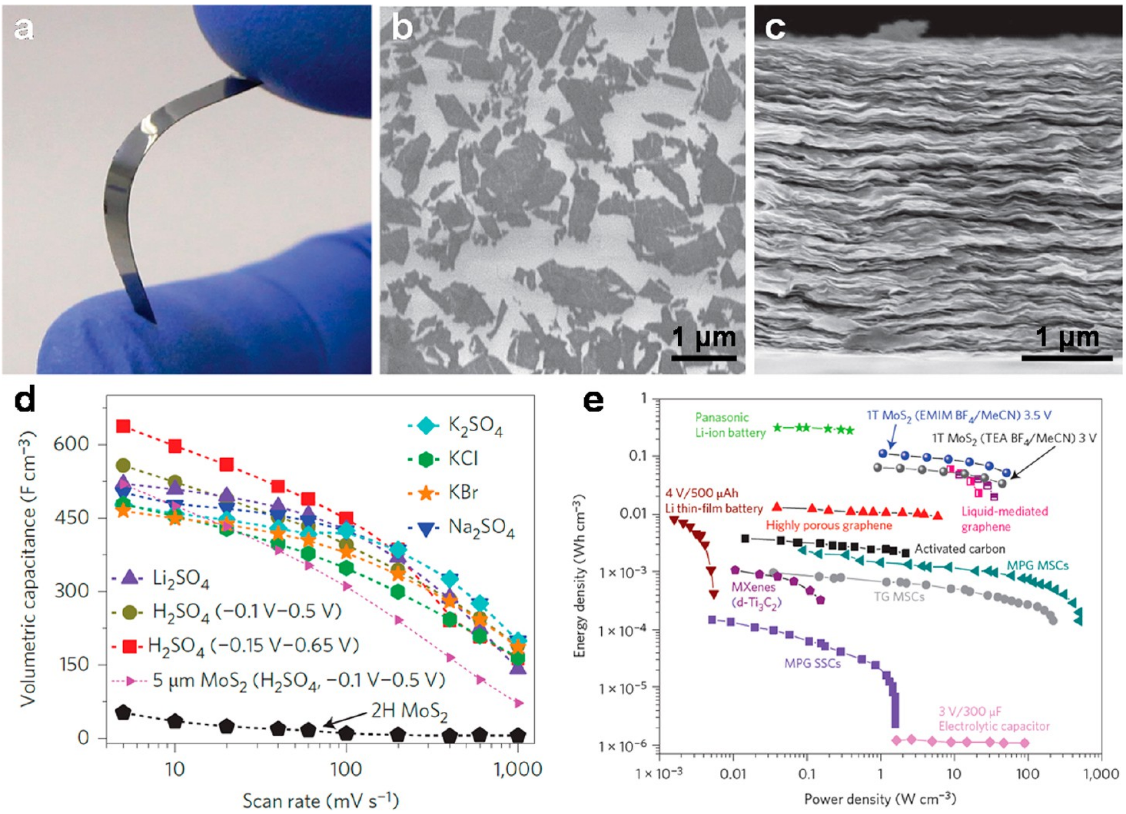


Figure 8. (a) Photograph of electrode consisting of chemically exfoliated 1T MoS_2 on a flexible polyimide substrate. (b) SEM image of as-exfoliated monolayer 1T-phase MoS_2 nanosheets. (c) SEM image of the side view of the electrode. (d) Evolution of the volumetric capacitance of the 1T-phase MoS_2 electrodes with scan rate for different electrolytes and 1 μm- and 5 μm-thick films. (e) Ragone plot of the best volumetric power and volumetric energy densities reported from various materials. Reproduced with permission from ref 95. Copyright 2015 Nature Publishing Group.

potential application of ultrathin 2D nanomaterials in LIBs has also been extensively explored over the past decade. Due to their high surface-to-volume ratios, short diffusion paths, and good conductivity, some ultrathin 2D nanomaterials have the potential to be the electrodes for LIBs.[166] Compared with 3D bulk crystals, ultrathin 2D nanomaterials normally show higher specific Li-storage capacity, because they have a higher ultrathin specific surface area and thus can accommodate more Li^+ ions during the Li^+ ion intercalation process. For example, graphene sheets present much higher specific capacities compared to graphite when used as electrodes in LIBs.[88] However, one of the disadvantages of ultrathin 2D nanomaterials is their aggregation during the electrode fabrication process, which significantly decreases their cycling stability. One effective way to solve this issue is to hybridize the ultrathin 2D nanomaterial with another type of nanomaterial to form hierarchical hybrid nanostructures.[135,140] By doing so, the structural collapse and the aggregation of ultrathin 2D nanomaterials can be avoided to a certain extent and better cycling performance of the electrode materials can be achieved. In commercial LIBs, some conductive additives (*e.g.*, graphite and carbon black) are included in the cathodes to overcome the poor conductivity of the active electrode materials (*e.g.*, metal oxides). Bearing this in mind, ultrathin 2D nanomaterials, especially graphene, can be promising conductive fillers in electrode materials to enhance their conductivity significantly due to their unique structural features and excellent conductivity.

Supercapacitors are another important type of energy storage device, which received increasing research interest in recent years due to their high power density, ultrafast charging–discharging rate, and long cycle life.[167] There are two kinds of supercapacitors: the electric double-layer capacitor and the pseudocapacitor. The former is based on the electrostatic storage of electrical energy within electrochemical double-layer capacitors. Carbon materials (*e.g.*, activated carbon) with a high surface area are commonly used as the electrodes to achieve nanoscopic charge separation at the electrode–electrolyte interface, thus realizing superior rate performance. The pseudocapacitor relies on reversible redox reactions, intercalation, or electrosorption that occur on electrode materials, which are commonly composed of metal oxides or metal hydroxides. The specific surface area, intrinsic conductivity, and chemical stability are three critical factors of a material for electric double-layer capacitor applications. The ultrahigh specific surface, excellent intrinsic conductivity, and good resistance to oxidation make some ultrathin 2D nanomaterials, such as graphene, MXenes, and TMDs, compelling candidates for supercapacitor applications. For example, graphene-based electrochemical supercapacitors have shown high capacitance, high energy, and powder densities.[3,90,91] In addition to graphene, MXenes (*e.g.*, Ti_4C_3) and metal hydroxides (*e.g.*, β-$Co(OH)_2$) have also shown promising results when assembled as electrodes in supercapacitor devices.[93,94,96,98] Moreover, it has been reported that metallic 1T-phase MoS_2 nanosheets can also be used as promising electrode materials for supercapacitor applications due to their good conductivity (Figure 8).[95]

CONCLUSIONS AND PERSONAL PERSPECTIVES FOR FUTURE PROSPECTS

Current research on ultrathin 2D nanomaterials is still at an early stage, especially for newly emerging materials such as TMDs, BP, MXenes, MOFs, and COFs. One can anticipate that many opportunities exist in this fascinating research area. In this section, I give some personal opinions on future research directions remaining to be explored in the near future.

Although a large number of ultrathin 2D nanomaterials have been prepared and studied, they represent only the tip of the iceberg of materials that we know exist in nature. The exploration of new ultrathin 2D nanomaterials is always an attractive topic. Therefore, the most straightforward idea for future research is to synthesize novel ultrathin 2D nanomaterials. For example, Pt, one of the most studied noble metals, is a robust catalyst for some electrocatalytic reactions, such as oxygen reduction reactions and hydrogen evolution reactions. It can be predicted that ultrathin Pt nanosheets with single or few atomic layers, which have not yet been prepared, should exhibit excellent catalytic activity toward the aforementioned electrocatalytic reactions due to its ultrathin-thickness-induced ultrahigh specific surface area. The synthesis of ultrathin 2D Pt nanostructures with single or few atomic layers is expected to be realized in the near future. Besides ultrathin single-component 2D noble metal nanostructures, the preparation of ultrathin 2D alloyed noble metal nanomaterials could be another interesting topic, although it would be challenging.

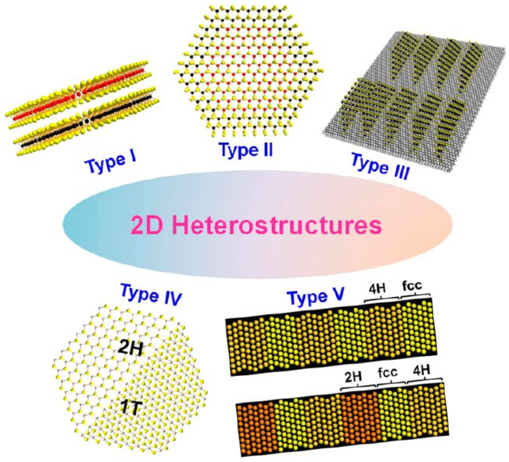
Moreover, MOFs have been explored for many promising applications, such as gas storage, separations, and catalysis, due to their tunable structure and function, large surface area, and highly ordered pores. However, MOFs are considered to be inert for the fabrication of electronic devices because of their poor electrical conductivity and difficult film-forming ability. The construction of conductive or semiconductive 2D MOFs is one of the promising possible solutions for integration of MOFs into electronic devices.

TMDs are a big family, which includes many related compounds. Some of them, such as MoS_2, WS_2, $MoSe_2$, and WSe_2, have been widely studied and have shown great promise in applications including electronics, optoelectronics, electrocatalysis, and energy storage, while some other TMDs with different chemical and electronic properties have not been prepared yet. Therefore, novel ultrathin 2D TMDs, especially the multicomponent (*e.g.* ternary, quaternary, etc.) TMDs, are also expected to be synthesized, and their properties and potential applications explored in the near future.

Phase engineering of ultrathin 2D nanomaterials is an interesting topic. The crystal phase of a material plays an essential role in determining its physical, chemical, and electronic properties. The ability to engineer the crystal phase of a material enables us to tune its intrinsic properties. Note that some TMDs (*e.g.*, MoS_2, WS_2, *etc.*) have two main crystal phases, *i.e.*, 2H and 1T phases.[142] For example, for MoS_2, the 2H phase is semiconducting, but the 1T phase is metallic.[142] The semiconducting 2H-phase of MoS_2 can be transformed into the metallic 1T phase *via* the intercalation of the layered MoS_2 with butyllithium. Therefore, phase engineering of TMDs affords great opportunities to tune materials properties for specific applications. For example, metallic 1T-phase 2D TMDs (*e.g.*, MoS_2 or WS_2) possessing superior conductivity than the 2H phase have shown enhanced performance for electrocatalytic hydrogen evolution and supercapacitors.[95,159,168]

Besides TMDs, noble metals also have different crystal phases. As a typical example, Au normally crystallizes in the face-centered cubic (fcc) phase.[21] However, we recently synthesized ultrathin Au nanostructures with unconventional hexagonal 2H and 4H phases.[22,169] Moreover, both the 2H and 4H Au nanostructures can undergo phase transformations to the fcc phase *via* simple ligand exchange or surface noble metal coatings.[22,169,170] It is expected that ultrathin Au nanostructures with different crystal phases should exhibit different optical, catalytic, and plasmonic properties. Therefore, the synthesis of nanomaterials with new crystal phases will be one of the promising directions in the field of ultrathin 2D nanomaterials. For example, noble metal nanostructures with a 6H phase have not yet been synthesized. Phase engineering between different metal nanostructure phases in ambient conditions is another interesting but challenging topic. For example, we have recently demonstrated the phase transformation from pure 2H or 4H to fcc in ultrathin 2D Au nanostructures.[169,170]

From an application point of view, one future research direction is the rational design and synthesis of ultrathin 2D nanomaterials with desired structural features, such as size, thickness, crystal phase, defects, doping, and so on, for specific applications. For example, electronic device applications require that an ultrathin 2D nanomaterial possess high crystal quality, suitable bandgap, and large lateral size, while electrocatalysis relies on its defects, large exposed active edge site, and excellent conductivity. However, most current studies on the applications of ultrathin 2D nanomaterials only focus on simple proof-of-concept demonstrations. Therefore, robust cooperation between diverse research groups with different perspectives and goals could lead to realization of the rational design and synthesis of ultrathin 2D nanomaterials with desired structural characteristics for specific applications at highly controllable levels. Another appealing research direction is to explore ultrathin 2D nanomaterials for new promising applications. For example, although research on MoS_2 has been conducted for decades, its excellent electrocatalytic activity toward hydrogen evolution reactions was identified recently.[171] It is anticipated that some other ultrathin 2D nanomaterials that still require further exploration and identification will have great potential for specific applications.



Scheme 2. Schematic illustration of five types of 2D heterostructures that can be constructed from ultrathin 2D nanomaterials. Note that types IV and V show examples of crystal-phase heterostructures, which are composed of the same component but with different crystal phases.

Due to their single-crystalline nature and extraordinary aspect ratios, ultrathin 2D nanomaterials could be compelling platforms for the creation of 2D heterostructures. More importantly, it is possible to engineer microsized 2D p−n heterojunctions at the atomic/nanometer scale based on ultrathin 2D nanomaterials. One of the most promising research directions is the construction of various kinds of 2D heterostructures based on ultrathin 2D nanomaterials with well-defined structures, compositions, crystal phases, and interfaces in order to explore their potential in applications, such as electronics, optoelectronics, photocatalysis, and solar cells. For example, five types of 2D heterostructures can be constructed from ultrathin 2D nanomaterials (Scheme 2). Type I is based on the layer-by-layer deposition/growth of two different kinds of ultrathin 2D nanomaterials to form vertical 2D heterostructures. In particular, the epitaxial growth of one 2D nanosheet onto another is interesting. Several reports have demonstrated the preparation of type I 2D vertical heterostructures by growth of TMDs, h-BN, or topological insulators on graphene sheets[172−175] or *in situ* epitaxial growth 2D TMD/semiconductor vertical heterostructures (*e.g.*, CuS/TiS_2).[176] Type II is based on the growth of one kind of ultrathin 2D nanosheet from the edge of another to form an in-plane 2D heterostructure. As an example, WSe_2-WS_2, $MoSe_2-MoS_2$, and $MoSe_2-WSe_2$ heterostructures have been achieved.[177−180] Impressively, the in-plane and vertical 2D TMD heterostructures can be recognized as p−n junctions, which are the basic building block for many modern electronic devices, such as diodes, transistors, solar cells, LEDs, and integrated circuits.[177−180] Therefore, the construction of p−n junctions with well-defined structures is fundamentally and technologically significant in modern electronics and optoelectronics. Unlike the conventional Si-based p−n junction, these in-plane and vertical 2D TMD heterostructures have atomic thickness, offering great opportunities for engineering functional devices at the atomic/nanoscale level. Recent research has shown that these 2D p−n junctions have some promising applications in FETs and photodiodes with superior performance compared to the artificially stacked heterostructures.[177,179,180] Type III is based on the vertical growth of aligned ultrathin 2D nanosheet arrays on another ultrathin 2D nanomaterial substrate to form hierarchical heterostructures. Note that all the aforementioned three types of 2D heterostructures are based on different components, and some related research has indeed recently been done.[172−180]

As mentioned above, phase engineering of ultrathin 2D nanomaterials has recently received considerable attention. Bearing this in mind, two types of 2D crystal-phase heterostructures might be prepared. Crystal-phase heterostructures represent a kind of novel heterostructure that is composed of the same chemical component but with different crystal phases (Scheme 2). Type IV is based on partially engineering the crystal phase in a TMD nanosheet. Taking MoS_2 as an example, after converting its 2H phase to the 1T phase in a part of the MoS_2 nanosheet, the 2D in-plane 2H-1T MoS_2 heterostructure was formed.[168] Type V is based on the generation of binary, ternary, or multiple phase patterns in ultrathin 2D noble metal nanostructures to form 2D heterostructure superlattices. As mentioned above, fcc, 2H, and 4H Au nanostructures have been successfully synthesized by wet-chemical methods and the phase transformation from the 2H or 4H to fcc transition has been realized.[21,22,169,170] Therefore, it is possible to prepare crystal-phase superlattices in ultrathin 2D Au nanomaterials by using wet-chemical syntheses combined with self-assembly or lithographic processes. For example, ultrathin 2D Au nanostructures with two phase patterns (*e.g.*, 4H−fcc) might be constructed by selective phase engineering of a 4H Au nanoribbon (top scheme of type V in Scheme 2). Besides binary phase heterostructures, ternary phase (*e.g.*, 2H−fcc−4H) patterns might also be obtained in ultrathin 2D Au nanostructures (bottom scheme of type V in Scheme 2). The crystal-phase heterostructures of novel metals (type V) might have promising applications in catalysis, waveguide, surface-enhanced Raman spectroscopy, *etc.* Therefore, one fascinating future direction would be to prepare novel 2D heterostructures based on ultrathin 2D nanomaterials and explore their various promising applications.

Conflict of Interest: The authors declare no competing financial interest.

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