Emerging 2D Materials Produced via Electrochemistry

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2D materials are important building blocks for the upcoming generation of nanostructured electronics and multifunctional devices due to their distinct chemical and physical characteristics. To this end, large-scale production of 2D materials with high purity or with specific functionalities represents a key to advancing fundamental studies as well as industrial applications. Among the state-of-the-art synthetic protocols, electrochemical exfoliation of layered materials is a very promising approach that offers high yield, great efficiency, low cost, simple instrumentation, and excellent up-scalability. Remarkably, playing with electrochemical parameters not only enables tunable material properties but also increases the material diversities from graphene to a wide spectrum of 2D semiconductors. Here, a succinct and critical survey of the recent progress in this research direction is presented, comprising the strategic design, exfoliation principles, underlying mechanisms, processing techniques, and potential applications of 2D materials. At the end of the discussion, the emerging trends, challenges, and opportunities in real practice are also highlighted.

1. Introduction

2D materials have inspired impressive passion in scientific community, as their mechanical, electrical and optical properties are superior and strikingly different from their layered bulk counterparts. Graphene, the pioneer of 2D materials, has already initiated many exciting discoveries in the fields of membranes,[1] sensors,[2] catalysts,[3] energy technologies,[4] and topological spintronic devices.[5] In spite of the remarkable progress over the last decades, the research on graphene itself is still at the cutting edge, for instance, in condensed matter physics.[6] Following this trend, a great number of atomically thin materials have been isolated or synthesized, consisting of metal chalcogenides,[7] layered double hydroxides,[8] boron nitride.[9] Recently, other novel 2D materials including phosphorene,[10] MXenes (2D metal carbides or nitrides)[11] and 2D polymers (single/few-layer 2D metal/covalent organic frameworks)[12] have been synthesized and added to the family of 2D materials. Nowadays, the family of materials features more than 150 members and ranges from intrinsic insulators, semiconductors, semimetals to metals.[13]

Although the initial investigations on 2D materials was mostly driven by fundamental research in terms of their attractive inherent properties, a clear shift was encouraged in recent years toward more application-oriented studies. For example, 2D materials are frequently involved as necessary components in functional devices and novel electronics. Therefore, they are promising candidates to revolutionize the current technologies, such as, in seawater desalination, renewable energy harnessing and quantum computing.

However, to extend their excellent physical and chemical properties to a macroscopic scale, efficient and low-cost protocols for the upscaling production are critically important. The state-of-the-art production methods comprise two opposite directions, starting from molecular precursors (bottom-up) or bulk layered materials (top-down), respectively. Bottom-up methods arrange small molecules into single- or few-layer thin films/sheets. In most occasions, the reactions take place at the gas–solid,[14] air–liquid,[15] or liquid–solid interfaces.[16] Apart from the accuracy in the structural assembly, they face complex and costly synthetic procedures and difficulties in transferring onto target substrates. On the other hand, top-down exfoliation methods rely on the extraction of individual thin sheets from their solid layered crystals, which are mainly constructed by weak out-plane van der Waals interactions. In addition, the relatively abundant bulk layered materials render the exfoliation strategies generally straightforward and economically viable. It is worth noting that, the applied driving forces in top-down methods determine not only the production rate, but also the purity and quantity of exfoliated materials.[17] For example, graphene sheets produced from scotch-tape adhesion have intact lattice structure but very limited production yield, whereas the products of wet-chemical oxidation (e.g., Hummers method) are heavily defective but readily scalable. Other approaches using liquid-phase sonication[18] or shear-force peeling[19] present severe processing drawbacks such as time-consuming agitation and low production yield. All of these limitations contribute to high costs that hurdle the production of 2D materials beyond the laboratorial scale.

Alternatively, electric current behaves as an appealing driving force to carry foreign molecules or ions into the bulk materials, thus expanding their interlayer spacing.[20] In the liquid media, the intercalation process is very efficient, accompanying with obvious structural deformation and redox reactions...
at the host electrodes. In contrast to the conventional routes, electrochemical exfoliation is simple to use at ambient conditions, as it offsets the need for multiple processing steps. This eco-friendly method also eliminates the chemical waste by recycling of electrolytes. The exfoliation reaction usually finishes in several minutes to hours, producing solution-processable 2D materials with gram-scale quantity at the laboratory level. Engineering the electrochemical cells can potentially upgrade the throughput to kilogram scale. Especially, the relevant electrochemistry (e.g., oxidation or reduction) offers a broad playground to tailor the exfoliated materials with desired thicknesses, crystal structures and chemical properties, in order to satisfy the specific requirements, such as high quality, good dispersibility, in practical applications.

Although the electrochemical exfoliation is a newly developed methodology, it has received intensive attention from both academia and industry. It represents a most powerful strategy for large-scaled production as best tradeoff in view of cost, quality and designed functionality, according to the recent studies on the exfoliated graphene and 2D semiconductors (such as transition metal sulfides/selenides, black phosphorus (BP), antimony, etc.). Many review papers have made nice summaries on the exfoliation methods and the produced materials. However, only a few of them discuss the fundamentals of electrochemistry behind this method and their impact on the properties of 2D materials. To fill this gap, in this article, we present an insightful overview on the recent advances, with a special focus on the electrochemical reactions, working mechanisms, as well as the applications of the fabricated 2D materials. We hope that this progress report will encourage the future evolution in this research field.

2. General Exfoliation Principles

As shown in Figure 1, a standard electrochemical cell consists of three electrodes (including working (WE), counter (CE) and reference electrodes (RE)), a liquid electrolyte and an external power supply. Usually, a reference electrode (e.g., Ag/AgCl and Hg/Hg2Cl2) is not mandatory for the scaled-up exfoliation. The working electrode, in the shape of rod, foil, flake, or plate, serves as either anode or cathode, corresponding to the intercalation of anions and cations, respectively. The typical anions include sulfate (SO4^{2-}), hydroxide (OH\(^{-}\)), halide (Cl\(^{-}\), Br\(^{-}\), and I\(^{-}\)), perchlorate (ClO4\(^{-}\)), trifluoroborate (BF\(_4\)^{-}), and hexafluoro-phosphate (PF\(_6\)^{-}), while the cations are alkali ions (e.g., Li\(^{+}\), Na\(^{+}\), and K\(^{+}\)), quaternary ammoniums (e.g., TBA\(^{+}\), TPA\(^{+}\), and THA\(^{+}\)) and other organic ions (e.g., BMP\(^{+}\)). The electrode materials share some common features such as good electrical conductivity and proper shapes/sizes that are compatible with the exfoliation setups. The counter electrode is made of metallic wires or pieces and the electrolytes are often composed of aqueous solution (with acids, inorganic salts, or surfactants) or nonaqueous solution (with ionic liquids, lithium-, or alkylammonium salts). The electrolytes support sufficient ionic migration and offer sufficient surface tension to prevent the exfoliated sheets from restacking. The power supply dedicates to provide either direct or alternating currents, with the feasibility to provide constant potential and/or stable current flow. Once a suitable voltage is applied between the working and counter electrodes, the insertion of ionic species into the interlayers and the subsequent electrolysis of intercalants encourage dramatic structural expansion of electrode materials, thus leading to the delamination of bulk materials into
A typical configuration of electrochemical cell and the representative reactions at the anode and cathode, respectively (abbreviations: WE: working electrode; CE: counter electrode; RE: reference electrode; TMA: tetra-methyl-ammonium; TPA: tetra-propyl-ammonium; TBA: tetra-n-butyl-ammonium; THA: tetra-n-heptyl-ammonium; BMP: 1-butyl-1-methyl-pyrrolidinium).

Figure 1. A typical configuration of electrochemical cell and the representative reactions at the anode and cathode, respectively.

suspended thin layers. It is worth noting that, the interaction between electrons, ions, electrolytes and electrodes has strong influence on the exfoliation efficiency and the properties of exfoliated materials.[26] For example, the anodic intercalation is generally fast because the surface oxidation can open the interlayer gallery at edge sites. However, the intercalated anions are electron donors that induce the formation of structural defects or covalent functional groups in the exfoliated 2D sheets. At the cathode, although the intercalation of cations is less efficient, the reduction reactions mainly contribute to the expansion of interlayer spacing, which facilitates the isolation of large-size, high-purity crystalline 2D materials.

3. Synthesis of 2D Materials toward Their Pristine Quality

2D materials with high structural integrity are keys to the fabrication of electronic devices. To avoid possible structural destruction during the exfoliation process, essential control over the cell parameters (such as working bias, chemistry of the electrolytes, etc.) is crucial for the efficient ionic intercalation and exclusion of unfavorable side reactions.

3.1. High-Quality Graphene

The exfoliation of graphite can be dated back to the 19th century, when intercalated or expanded graphite was discovered by annealing graphite powders with strong mineral acids, metal chlorides or other inorganic salts.[26] In the early 1980s, concentrated sulfuric acid (H₂SO₄) was reported for the incorporation into graphite by using an electrochemical method, resulting in the first-stage compound of “graphite bisulfate,” in which every adjacent graphite layers was filled with acid molecules.[27] However, after the isolation of pristine graphene from natural graphite in 2004, lots of interests and attentions came back to this “old trick,” in order to achieve comparable graphene quality but with a higher production yield.

Following its previous success in anodic intercalation, sulfuric acid has become a rational reagent in the electrolytes for electrochemical exfoliation because it weakens the interaction between adjacent layers that favors the exfoliation process. However, the direct use of concentrated sulfuric acid is problematic, as it induces severe structural disorder to the exfoliated materials. In 2011, Su et al. exfoliated highly oriented pyrolytic graphite (HOPG) and natural graphite into suspended thin graphene flakes using dilute sulfuric acid (0.5 M, pH = 0.3).[28] To suppress the oxidation from H₂SO₄, KOH solution (30 wt% in water) was added to turn the pH value to 1.2. In this respect, more than 60% of the exfoliated graphene were bilayer sheets with large dimensions up to 30 µm and with relatively high defect density (I_D/I_G = 0.5–1.0, the intensity ratio of D band to G band from Raman spectrum). The anodic intercalation was so fast that randomly detached the expanded graphite particles before the completion of exfoliation, resulting in low production yield of only 5–8 wt%. It should mention that, the yield was calculated based on the weight ratio of exfoliated sheets to the starting materials. In 2013, our group achieved a much higher exfoliation yield (60 wt%) by using more diluted sulfuric acid (0.1 M, pH = 0.7) as electrolyte and graphite foil as starting material.[29] Compared with tightly packed HOPG, graphite foils comprise disordered stacking of graphitic platelets with many flaws such as ripples, wrinkles and voids, making the intercalation process easier to occur. This strategy enabled a high fraction (80%) of 1–3 layer graphene and a moderate high carbon to oxygen (C/O) ratio of 12. Field effect transistor (FET) based on the resulting bilayer sheet revealed a hole mobility of 233 cm² V⁻¹ s⁻¹. Nonetheless, anodic intercalation in acidic electrolytes typically produce graphene sheets with a substantial level of oxidation at low pH. The interaction between sulfate ions (SO₄²⁻) and hydrogen ions (H⁺) is responsible for the successful exfoliation but is destructive to the exfoliated materials. In 2014, we employed neutral electrolytes (pH = 6.5–7.0) containing inorganic sulfate salts (such as Na₂SO₄, K₂SO₄, and (NH₄)₂SO₄) to suppress the oxidation.[30] Notably, ammonium sulfate (0.1 M) facilitated a high production rate of 16.3 g h⁻¹. Over 85% of the obtained flakes were no more than 3 layers.
and they were generally larger than 5 \( \mu m \). The quality of the exfoliated graphene sheets was further proved by a high hole mobility exceeding 300 cm\(^2\) V\(^{-1}\) s\(^{-1}\). Later in 2017, Munuera et al. proposed an alternative neutral system including sodium halides (such as NaCl, NaBr, and NaI) to delaminate graphite foils.\(^{[30]}\) Especially, sodium chloride (0.05 m) led to single/few-layer graphene sheets with an average thickness of 2–3 nm, an \( I_D/I_G \) ratio of 0.8, and high C/O ratio of 16.7. Very recently, Liu et al. found that alkaline electrolyte (pH = 13) composed of 0.1 m NaOH/Na\(_2\)SO\(_4\) mixture was very efficient to produce bilayer-rich water-dispersible graphene.\(^{[31]}\) The exfoliated sheets exhibit excellent charge transport properties, evidenced by a high mobility up to 1000 cm\(^2\) V\(^{-1}\) s\(^{-1}\) based on the tetrahertz (THz) spectroscopy characterization.

Generally, the anodic exfoliation of graphite in aqueous electrolyte undergoes the following steps: 1) electrolysis of water gives rise to massive amount of oxygen (O\(_2\)) and hydroxyl (HO\(\cdot\)) radicals, which corrode the defective sites or boundaries of the graphite anode, causing initial expansion at the outer edges. 2) Continuous oxidation further expands the interlayer gap of graphite edges to large extent, facilitating the intercalation of sulfate anions and water molecules. 3) The intercalated species decompose to abundant gases (e.g., O\(_2\), SO\(_4^{2-}\), and CO\(_x\)) that split the graphite layers and force them apart. The bubbles also flush the exfoliated sheets away from the parent electrodes. In aqueous solution, the intercalation and expansion of graphite surface caused by the intercalation and early-stage gas formation.\(^{[33]}\) Obviously, opening the graphite edges is a key step for the subsequent exfoliation. However, in reality, the radical attack is nonselective. It occurs randomly at all of the exposed graphite surfaces, inevitably leading to excess oxidation of the graphene sheets. Partial elimination of the radicals presents a sound solution to prevent this side reaction. Based on a standard ammonium sulfate electrolyte, in 2015, we examined a group of antioxidants and radical scavengers including sodium borohydride, ascorbic acid and (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) as additives in the exfoliation process.\(^{[34]}\) Especially, the addition of TEMPO could greatly suppress the oxidation but did not compromise the exfoliation efficiency, producing over 15 g h\(^{-1}\) of high-quality graphene with large dimensions (5–10 \( \mu m \) in average) and very few defects (C/O ratio = 25.3). As shown in Figure 2, TEMPO primarily reacted with the HO\(\cdot\) radicals at the anode to generate metastable TEMPO-OH and oxoammonium cations. At the cathode, these intermediate compounds were reduced to TEMPO radicals again. In this system, single graphene sheets revealed an ultrahigh hole mobility up to 405 cm\(^2\) V\(^{-1}\) s\(^{-1}\) and they still had excellent processability in N,N-dimethylformamide (DMF) (6.0 mg mL\(^{-1}\)) for the preparation of graphene ink. In 2018, Ejigu et al. explored the antioxidative properties of transition metal ions (e.g., Co\(^{2+}\), Ni\(^{2+}\), Fe\(^{3+}\), Mn\(^{2+}\), Ru\(^{3+}\), Ir\(^{3+}\), V\(^{5+}\), Ti\(^{3+}\), Pt\(^{3+}\), and Au\(^{3+}\)) in the aqueous electrolyte of 0.5 m Na\(_2\)SO\(_4\).\(^{[35]}\) In particular, cobalt(II) sulfate (0.05 m) acted as efficient HO\(\cdot\) radical scavenger that would not functionalize the exfoliated graphene sheets but solely improved their quality, leading to a very high C/O ratio of 36.
At the anode, Co^{2+} was oxidized to Co^{4+}, a well-known active agent for water oxidation, which facilitated the O_2 evolution and avoided the generation of significant amount of hydroxyl intermediate. In this way, the surface of graphite was protected from radical attack while the intercalation of anions was allowed. Likewise, the incorporation of organic molecules in the electrolytes can form an encapsulating layer on the graphene sheets to prevent excess oxidation. For example, melamine additive contributed to an increased C/O ratio from 16 to 26, in the electrolyte of sulfuric acid.[36] In another work, sulfonated aromatic hydrocarbons (SAHs) provided multiple functions such as intercalating agents, surface coating and radical cleaner.[37] Among the tested SAHs, the optimal graphene quality was achieved by using disodium naphthalene-1,5-disulfonate (SNDS), giving a C/O ratio of 50 and \( I_D/I_G \) ratio of 0.2.

Compared with bare sulfate ions, these bulky anions led to low intercalation efficiency and limited production yield.

In contrast to the extensive studies on the manipulation of anions, the control of cations attracts less focus. In 2011, Wang et al. reported that the intercalation of lithium ions resulted in the exfoliation of graphite at cathode.[38] Compared with aqueous solutions, in this system, nonaqueous electrolyte made of LiClO_4 and propylene carbonate (PC) could offer a much larger electrochemical window. At a high potential of −15 ± 5 V, cointercalation of solvated species (like Li^+:2 PC and Li^+:3 PC) promoted a high yield (70%) of few-layer graphene sheets. Thin conductive film assembled with the exfoliated sheets exhibited a low sheet resistance of 15 \( \Omega \) sq\(^{-1}\). Given that lithium ions are not big enough to expand the graphite, an additional sonication step was required to complete the delamination of intercalated compounds.[39]

By contrast, large cations present low success for the exfoliation,[40] because they are difficult to migrate into graphite cathodes in organic solvents, especially when the graphite edges are not preliminarily expanded. In 2017, we developed an elegant exfoliation strategy to overcome this limitation. The electrolyte was made of 0.1 M tetra-\( n \)-butyl-ammonium bisulfate (TBA HSO_4) in water and an alternating potential (±10 V, 0.1 Hz, rectangular shape) was applied between graphite anode and cathode (Figure 3a).[41] The regular variation of applied potential, at every 5 s, enabled an ultrafast graphite exfoliation simultaneously at the anode and cathode, achieving an outstanding production rate of 20 g h\(^{-1}\). At the beginning, the anode (+10 V) was largely expanded due to the intercalation of sulfate anions. When the anodic bias switched from positive to negative (−10 V), the reduction of sulfate anions and cointercalated water gave rise to abundant gases that further enlarged the interlayer distance and allowed the subsequent intercalation of TBA\(^+\) cations (Figure 3c). By comparison, the initial intercalation of TBA\(^+\) cations at the cathode (−10 V) are less efficient because of their large sizes. However, when changing to a positive potential (+10 V), sulfate anions boosted the interlayer expansion of graphite that permitted more TBA\(^+\) cations to move in. Importantly, in situ cathodic reduction during exfoliation process could kick out the oxide groups, thereby improving the graphene quality. 75% of the exfoliated sheets were 1–3 layers and a bilayer sheet demonstrated a high hole mobility of 430 cm^2 V\(^{-1}\) s\(^{-1}\).

In 2018, Li et al. applied similar alternating currents (±10 V, 0.1 Hz) to exfoliate dual graphite electrodes in 0.1 M ammonium sulfate. A small amount of thiourea (CH_3NCS, 1%) was added into the electrolyte to regulate the hydroxyl radicals at low temperature (e.g., 10 °C), to produce graphene sheets with a remarkable C/O ratio up to 37.1.[42]
Table 1. A summary of the electrochemical exfoliation and anodic oxidation of graphite.

| Starting materials | Electrolytes | Working potentials | Yield/ throughput | Thickness/layers | C/O ratio | Hole mobility (cm² V⁻¹ s⁻¹) | Ref. |
|--------------------|--------------|--------------------|-------------------|-----------------|-----------|----------------------------|------|
| HOPG/natural graphite | 0.5 M H₂SO₄ + KOH (pH = 1.2) | 1) +2.5 V, 1 min; 2) Switching +10 V, 2 s; −10 V, 5 s | 5–8 wt% | ≤2 nm | – | 0.5–1.0 | 5.5–17 | [28] |
| Graphite foil | 0.1 M H₂SO₄ | +10 V, 10 min | 60 wt%; 4.2 g h⁻¹ | 1–3 layers | 12.3 | 0.4 | 233 | [29] |
| Graphite foil | 0.1 M (NH₄)₂SO₄ | +10 V, 10 min | 75 wt%; 16.3 g h⁻¹ | 1–3 layers | 17.2 | 0.25 | 310 | [23] |
| Graphite foil | 0.05 M NaCl | +10 V, 60 min | – | 2–3 nm | 16.7 | 0.8 | – | [30] |
| Expanded graphite foil | 0.1 M NaOH + Na₂SO₄ | 1) +3 V, 3 min; 2) +10 V, 30 min | – | 2–3 nm | 9.7–26.4 | 1.3 | 1000 (from THz spectroscopy) | [31] |
| Expanded graphite foils | (NH₄)₂SO₄ + 1 mg mL⁻¹ TEMPO | +10 V, 10 min | 75 wt%; 15.1 g h⁻¹ | 1–3 layers | 25.3 | 0.1 | 405 | [34] |
| Expanded graphite foil | Na₂SO₄ + 0.05 M CoSO₄ | +20 V, 120 min | – | Monolayer and few layers | 36 | 0.05 | – | [35] |
| Bulk graphite/graphite powder | 0.1 M H₂SO₄ + 1 mg mL⁻¹ melamine | ⩽20 V, 10 min | 1.5 g h⁻¹ | 1–3 layers | 26.2 | <0.45 | – | [36] |
| Graphite foil | 0.2 M SDS in water | +10 V, 60 min | – | 2.5 nm | 50 | 0.2 | – | [37] |
| Graphite foil | 30 mg mL⁻¹ LiClO₄ in PC | −15 ± 5 V | >70 wt%; 0.12 g h⁻¹ | <5 layers | – | <0.1 | – | [38] |
| Graphite foils | 0.1 M TBA HSQ + NaOH | ±10 V, 0.1 Hz | 75 wt%; 20 g h⁻¹ | 1–3 layers | 21.2 | 0.15 | 430 | [41] |
| Graphite foils | 0.1 M (NH₄)₂SO₄ + 1% thiourea | ±10 V, 0.1 Hz, 60 min | – | – | 18.1–37.1 | 0.06–0.14 | – | [42] |
| HOPG/graphite rod | 0.1 M (NH₄)₂SO₄ | switching +7 V or +10 V, 1 s; −0.5 V, 3 s | 77 wt% | <5 layers | 21.2 | 0.29 | – | [43] |
| Graphite foil | 0.5 M LiClO₄ in water | 1) +2.0 V, 2 min; 2) +10 V (graphene oxide) | – | 6–8 layers | 4.0 | 1.0 | – | [45] |
| Graphite flakes | 1.0 M H₂SO₄ in saturated (NH₄)₂SO₄ | anodic, 0.6 A, 24 h | 40 wt% (graphene oxide) | 1.5 nm | 3.64 | 1.0 | – | [46] |
| Graphite foil | 1) 95% H₂SO₄ 2) 0.1 M (NH₄)₂SO₄ | 1) +2.2 V, 10 min; 2) +10 V (graphene oxide) | 71 wt% monolayers | 4.6 | 1.48 ± 0.01 | – | [47] |
| Graphite foil | 1) 98% H₂SO₄ 2) 50% H₂SO₄ | 1) +1.6 V, 20 min; 2) +5 V (graphene oxide) | 96 wt%; 12 g h⁻¹ | 1–3 layers | 1.5–1.8 | >1.0 | – | [48] |

Moreover, alternating currents with different potential curves (e.g., linear or sinusoidal shapes) were proposed to control the intercalation/stripping of sulfate anions into the graphite layers. This protocol could produce graphene sheets with low defect density \(I_D/I_G = 0.38\) and a high C/O of 21.2. [43]

In general, the exfoliation of graphite is dominated by many factors such as types of graphite, [44] species of the electrolytes, power sources, etc. In Table 1, we summarize the influence of experimental arrangement on the properties of the exfoliated graphene sheets. Sulfate anions are apparently the most popular intercalants for the production of graphene-based materials, either with high quality or with high specific functional groups.

3.2. Phosphorene

Given that graphene is a gapless semimetal, its application in electronic devices requires size confinement or surface functionalization in order to generate a bandgap. [49] Therefore, other 2D materials with direct band gaps are especially appealing. For example, phosphorene is a typical 2D semiconductor, of which the direct bandgap varies according to its thickness, from a large gap (2.0 eV in monolayers) to a narrow gap (0.3 eV in bulk crystal). [50] The adjacent phosphorene sheets are assembled into layered BP by weak van der Waals interaction. However, unlike the sp²-hybridized graphite, BP has a 3S²P³ valence shell configuration, leading to a puckered honeycomb lattice. In
2014, Li et al. reported the isolation of few-layer phosphorene sheets by scotch-tape exfoliation method. FET devices based on a 6.5 nm thick sheet exhibited hole-dominated ambipolar transport characteristics with an on/off ratio exceeding $10^5$. An outstanding charge-carrier mobility of $1000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ was measured in vacuum ($\approx 1 \times 10^{-5} \text{ mbar}$) on a 10 nm thick single sheet. Besides, many other intriguing properties, such as in-plane anisotropy, strong infrared responsivity and spontaneous electric polarization were explored, highlighting the potential use of phosphorene in high-performance photonic and electronic devices.

Although BP is the most thermodynamically stable phosphorus allotrope, the phosphorus atoms with unpaired electrons are prone to oxidation. The ambient degradation of phosphorene occurs rapidly within a few hours, once exposed to oxygen, water moisture and visible light. This process modifies the surfaces of phosphorene with oxide groups and therefore largely deteriorates the charge-transport properties. In 2015, Erande et al. carried out the electrochemical exfoliation of bulk BP in an aqueous solution of 0.5 m Na$_2$SO$_4$. The intercalation of sulfate ions led to few-layer BP sheets with dimensions of 5–10 $\mu$m. Similarly, in 2017, Ambrosi et al. presented an anodic intercalation method to delaminate bulk BP crystals to few-layer-thick BP nanosheets in 0.5 m sulfuric acid. However, the exfoliated sheets by these methods have a high density of functional groups, according to the strong oxidation peak in X-ray photoelectron spectroscopy (XPS) spectra. Because BP is sensitive to anodic oxidation, thereafter, the cathodic intercalation has been widely used to preserve the intact quality of phosphorene (Figure 4a). TBA$^+$ cations and many organic solvents, such as DMF, PC, dimethyl sulfoxide (DMSO) have been studied in this system. For example, Huang et al. produced few-layer crystalline phosphorene sheets in anhydrous DMF dissolved with 0.5 m tetrabutylammonium hexafluorophosphate (TBA PF$_6$). The modulation of working potential (from $-2.5$ to $-15$ V) could control the intercalation process of TBA$^+$ cations. Interestingly, the exfoliated sheets revealed a tunable thickness distribution from 2.5 to 3.7 nm and 2.9 to 3.3 nm, by applying a bias of $-10$ and $-15$ V, respectively. The XPS spectra showed the characteristic P 2p$^{"{a}_{1/2}}$ and P 2p$^{"{b}_{1/2}}$ doublets of high-quality phosphorene. Even though a small peak of P–O bond (PO$_x$) was noticeable, the intensity was much weaker than the previous reports. In another work, Xiao et al. applied a high voltage of $-30$ V to drive the intercalation of TBA$^+$ cations in...
PC, resulting in thin BP sheets in the range of 2–7 nm.\(^{[59]}\) In 2018, Li et al. investigated an alternative electrolyte containing DMSO and 0.001 m tetrabutylammonium tetrafluoroborate (TBA BF\(_4\)) to expand the BP cathode at a voltage of −5 V.\(^{[60]}\) The intercalation and expansion process were explored under an optical microscope in a microelectrochemical cell (Figure 4b) and the fully expanded BP was dispersed in DMSO through manual shaking (Figure 4c). Raman spectra (532 nm laser; Figure 4d) revealed high crystallinity of the resulting BP sheets. Most of them were 1–5 layers and had an average dimension of 10 \(\mu\)m\(^2\). Thanks to the well-preserved crystal structure, a hole mobility up to 100 cm\(^2\) V\(^{-1}\) s\(^{-1}\) was recorded on the single-sheet FET devices.

Nonetheless, the electronic properties of the phosphorene sheets from scalable exfoliation methods are still inferior to those from mechanical approaches. To address this challenge, we carried out a systematic study to find out the optimal exfoliation conditions.\(^{[61]}\) The exfoliation process was performed in deoxygenated anhydrous electrolyte and dark glove box to exclude any possible degradation. PC was selected as the solvent because it provides similar surface tension to that of the exfoliated BP sheets, thereby stabilizing them against restacking (Figure 4e,f). In this system, quaternary ammonium cations (i.e., tetra-alkyl-ammonium, alkyl = methyl, ethyl, or n-butyl) displayed superior efficiency to alkali ions (e.g., Li\(^+\), Na\(^+\), and K\(^+\)) in terms of the speed of intercalation and expansion. Besides the sole TBA intercalation, the reduction of bisulfate anions gave rise to the in situ growth of bubbles inside the BP interlayer space (HSO\(_4\)\(^−\) \(\rightarrow\) SO\(_4\)\(^2−\) + H\(^+\), 2H\(^+\) + 2e \(\rightarrow\) H\(_2\)) and further boosted the exfoliation efficiency. This strategy resulted in a high exfoliation yield up to 78% and thin BP flakes with average dimension around 4 \(\mu\)m\(^2\) (Figure 4g). The exfoliated sheets presented intact lattice with orthogonally symmetric structure, as evidenced by high-resolution transmission electron microscopy (HR-TEM) (Figure 4h) and the XPS spectrum did not show any oxidation peaks. FET devices based on single sheets illustrated remarkable hole mobility of 252 \(\pm\) 18 cm\(^2\) V\(^{-1}\) s\(^{-1}\) and excellent on/off ratio of (1.2 \(\pm\) 0.15) \(\times\) 10\(^5\) at 143 K under vacuum. These properties are well comparable with the phosphorene and did not alter the intrinsic lattice structure of MoS\(_2\). A backgate FET device based on a monolayer exfoliated MoS\(_2\) sheet exhibited n-type semiconductor properties with an on/off ratio over 10\(^6\) but a relatively low mobility of 1.2 cm\(^2\) V\(^{-1}\) s\(^{-1}\), mostly due to the anodic oxidation (Figure 5c,d). Later on, quaternary ammonium salts with diverse alkyl chains (from C\(_4\) to C\(_7\)) were used to expand bulk MoS\(_2\) crystals at the cathode and to preserve their original material quality. For example, TBA cations with C\(_7\) alkyl groups enabled the production of high-quality semiconducting MoS\(_2\) sheets with total yield of about 70%, much larger than those from liquid sonication (<40%).\(^{[74]}\)

The exfoliated sheets were dispersible in DMF (0.5 mg mL\(^{-1}\)), ranging from 6 to 10 layers with lateral dimension up to 50 \(\mu\)m. In 2018, Lin et al. explored tetra-n-heptyl-ammonium (THA) cations with C\(_7\) alkyl chains as intercalants to exfoliate MoS\(_2\) crystals in acetonitrile.\(^{[75]}\) This exfoliation process driven by a negative potential from −5 to −10 V resulted in solution-processable MoS\(_2\) nanosheets (10 mg mL\(^{-1}\) in isopropanol) with mean dimensions of 0.5–2 \(\mu\)m and average thickness of 3.8 \(\pm\) 0.9 nm. As-prepared MoS\(_2\) nanosheets demonstrated high

### 3.3. Transition Metal Dichalcogenides (TMDs)

Another important class of semiconductors are TMDs. They have a general formula of MX\(_2\), where M stands for transition metals (e.g., molybdenum, tungsten) and X refers to chalcogen atoms (e.g., sulfur, selenium or tellurium).\(^{[62]}\) TMD sheets present direct bandgaps at monolayers, spanning from 1.0 to 2.0 eV. The values may change according to the chemical composition and strain level.\(^{[63]}\) For example, single-layer molybdenum disulfide (MoS\(_2\)) has a bandgap of 1.9 eV, high in-plane mobility of 200–500 cm\(^2\) V\(^{-1}\) s\(^{-1}\) and high on/off ratio over 10\(^8\).\(^{[11]}\) Thanks to their excellent electronic properties and strong spin-orbit coupling, TMDs have been widely used in many fields including transistors,\(^{[64]}\) optoelectronics,\(^{[65]}\) spintronics,\(^{[66]}\) and energy harvesting.\(^{[67]}\)

The lamellar structures of TMDs are good hosts for a wide spectrum of electron-donating agents, such as Lewis bases and alkali metals.\(^{[68]}\) Organolithium compounds (e.g., n-butyl-lithium) are popularly utilized in chemical exfoliation methods, to afford expanded TMD lattice (i.e., Li\(_x\)MX\(_2\)) in hexane solution.\(^{[69]}\) The subsequent sonication-assisted hydration process separates the lithiated compounds into individual layers. However, the lithiation process usually takes several days to complete, and the sonication gives submicron-sized sheets with a low yield of monolayers. In 2011, Zeng et al. illustrated a battery-type cell to intercalate lithium ions into the TMD cathode, using 1.0 m LiPF\(_6\) in a 1:1 (volume ratio) mixture of ethyl carbonate (EC) and dimethyl carbonate (DMC) as electrolyte.\(^{[70]}\) Then, the fully intercalated TMD layers will be separated by treatment with protic solvents, due to the in situ gas formation between layers. Compared with the traditional diffusion kinetics, the electrically driven Li intercalation was more efficient, and importantly, could be well controlled through the discharge curves. A series of TMDs, such as MoS\(_2\), WS\(_2\), TiS\(_2\), TaS\(_2\), ZrS\(_2\), NbSe\(_2\), and WSe\(_2\), could be produced by this methodology and a large fraction of the exfoliated sheets were monolayers.\(^{[71]}\) To overcome the limited production from coin-shaped batteries, in 2018, Garah et al. achieved the scalable exfoliation of MoS\(_2\) in a mixed solution of lithium chloride in DMSO.\(^{[72]}\) The exfoliated materials were rich in mono-, bi- and trilayers and 60% of the sheets were semiconducting 2H-MoS\(_2\). However, lithium intercalation constantly transforms TMDs from original semiconducting phase to a distorted metallic phase.\(^{[73]}\) The mixed lattice structures resulted in significantly low mobility (e.g., 0.02 cm\(^2\) V\(^{-1}\) s\(^{-1}\)) and on/off ratio (e.g., 100), being a drawback for high-performance electronic devices.\(^{[74]}\)

On the other hand, the insertion of organic cations avoids the structural phase transition. In 2014, Liu et al. exfoliated bulk MoS\(_2\) crystal into single and few-layer sheets with large lateral sizes (up to 50 \(\mu\)m), using 0.5 m aqueous sodium sulfate electrolyte (Figure 5a,b).\(^{[74]}\) When applying a potential of +10 V, the intercalation of sulfate anions facilitated rapid delamination and did not alter the intrinsic lattice structure of MoS\(_2\). A backgate FET device based on a monolayer exfoliated MoS\(_2\) sheet exhibited n-type semiconductor properties with an on/off ratio over 10\(^6\) but a relatively low mobility of 1.2 cm\(^2\) V\(^{-1}\) s\(^{-1}\), mostly due to the anodic oxidation (Figure 5c,d). Later on, quaternary ammonium salts with diverse alkyl chains (from C\(_4\) to C\(_7\)) were used to expand bulk MoS\(_2\) crystals at the cathode and to preserve their original material quality. For example, TBA cations with C\(_7\) alkyl groups enabled the production of high-quality semiconducting MoS\(_2\) sheets with total yield of about 70%, much larger than those from liquid sonication (<40%).\(^{[74]}\)
purity of semiconducting phases that exhibited an electron mobility of 10 cm$^2$ V$^{-1}$ s$^{-1}$ and a current modulation exceeding $10^5$ from single-sheet based FET devices. This method was also versatile for the production of other 2D materials such as WSe$_2$, NbSe$_2$, and Bi$_2$Se$_3$. Recently, Yu et al. utilized TPA$^+$ cations with C$_3$ alkyl groups for the rapid synthesis of ultrathin vanadium diselenide (VSe$_2$) sheets in PC.[75] A high fraction (93.9%) of the exfoliated flakes were thinner than five layers, in which 43% were monolayers with an average lateral dimension of 40 µm (Figure 5e). Because VSe$_2$ sheets were very sensitive to oxygen, surface passivation with a layer of thiol molecules was required to prevent their structural degradation in air. Notably, monolayer VSe$_2$ exhibited robust ferromagnetic properties at room temperature, showing a magnetic moment of 0.3 µ$_B$ per vanadium atoms (Figure 5f,g).

In Table 2, we summarize the key parameters for the synthesis of 2D semiconductors. In general, bulk layered precursors with interlayer distances from 0.3 to 1.0 nm requires large cations or molecules for efficient structural expansion. Besides, the exfoliation at the cathode is favorable to protect the original lattice structures of 2D sheets.

4. Synthesis of 2D Materials with Designed Functionality

Surface functionalization is a powerful tool to modify the chemical and physical properties of 2D materials in terms of their reactivity, wettability, dispersibility and processability in solutions. As mentioned before, the anodic exfoliation in aqueous media comprises not only physical ionic intercalation but also oxidation reactions. Although chemical reactions are often considered as side reactions that introduce unfavorable groups on crystalline 2D materials, they provide one-pot routes to produce
The complete oxidation process requires a long period (e.g., several hours or days), involving the release of hazardous byproducts. However, the oxidation content of GO was close to that achieved at 10 V to prepare highly oxidized GO sheets with a thickness of 2.5–4.5 nm. Besides halide ions, other oxidative anions, such as perchlorate ions (ClO$_4^-$), were investigated at +10 V to prepare highly oxidized GO sheets with a thickness of 1.9, 2.8, and 3.9 nm, respectively. In 2014, Kakaei and Hasanpour studied the anodic intercalation and oxidation of chloride ions (Cl$^-$) gave rise to gaseous chlorine that separated graphite layers into mono-, bi-, and trilayer of GO sheets with the thickness of 1.9, 2.8, and 3.9 nm, respectively. In 2014, Kakaei and Hasanpour studied the anodic intercalation and oxidation of chloride ions (Cl$^-$) gave rise to gaseous chlorine that separated graphite layers into mono-, bi-, and trilayer of GO sheets with the thickness of 1.9, 2.8, and 3.9 nm, respectively. In 2014, Kakaei and Hasanpour studied the anodic intercalation and oxidation of chloride ions (Cl$^-$) gave rise to gaseous chlorine that separated graphite layers into mono-, bi-, and trilayer of GO sheets with the thickness of 1.9, 2.8, and 3.9 nm, respectively. In 2014, Kakaei and Hasanpour studied the anodic intercalation and oxidation of chloride ions (Cl$^-$) gave rise to gaseous chlorine that separated graphite layers into mono-, bi-, and trilayer of GO sheets with the thickness of 1.9, 2.8, and 3.9 nm, respectively. In 2014, Kakaei and Hasanpour studied the anodic intercalation and oxidation of chloride ions (Cl$^-$) gave rise to gaseous chlorine that separated graphite layers into mono-, bi-, and trilayer of GO sheets with the thickness of 1.9, 2.8, and 3.9 nm, respectively. In 2014, Kakaei and Hasanpour studied the anodic intercalation and oxidation of chloride ions (Cl$^-$) gave rise to gaseous chlorine that separated graphite layers into mono-, bi-, and trilayer of GO sheets with the thickness of 1.9, 2.8, and 3.9 nm, respectively. In 2014, Kakaei and Hasanpour studied the anodic intercalation and oxidation of chloride ions (Cl$^-$) gave rise to gaseous chlorine that separated graphite layers into mono-, bi-, and trilayer of GO sheets with the thickness of 1.9, 2.8, and 3.9 nm, respectively. In 2014, Kakaei and Hasanpour studied the anodic intercalation and oxidation of chloride ions (Cl$^-$) gave rise to gaseous chlorine that separated graphite layers into mono-, bi-, and trilayer of GO sheets with the thickness of 1.9, 2.8, and 3.9 nm, respectively. In 2014, Kakaei and Hasanpour studied the anodic intercalation and oxidation of chloride ions (Cl$^-$) gave rise to gaseous chlorine that separated graphite layers into mono-, bi-, and trilayer of GO sheets with the thickness of 1.9, 2.8, and 3.9 nm, respectively. In 2014, Kakaei and Hasanpour studied the anodic intercalation and oxidation of chloride ions (Cl$^-$) gave rise to gaseous chlorine that separated graphite layers into mono-, bi-, and trilayer of GO sheets with the thickness of 1.9, 2.8, and 3.9 nm, respectively. In 2014, Kakaei and Hasanpour studied the anodic intercalation and oxidation of chloride ions (Cl$^-$) gave rise to gaseous chlorine that separated graphite layers into mono-, bi-, and trilayer of GO sheets with the thickness of 1.9, 2.8, and 3.9 nm, respectively. In 2014, Kakaei and Hasanpour studied the anodic intercalation and oxidation of chloride ions (Cl$^-$) gave rise to gaseous chlorine that separated graphite layers into mono-, bi-, and trilayer of GO sheets with the thickness of 1.9, 2.8, and 3.9 nm, respectively. In 2014, Kakaei and Hasanpour studied the anodic intercalation and oxidation of chloride ions (Cl$^-$) gave rise to gaseous chlorine that separated graphite layers into mono-, bi-, and trilayer of GO sheets with the thickness of 1.9, 2.8, and 3.9 nm, respectively. In 2014, Kakaei and Hasanpour studied the anodic intercalation and oxidation of chloride ions (Cl$^-$) gave rise to gaseous chlorine that separated graphite layers into mono-, bi-, and trilayer of GO sheets with the thickness of 1.9, 2.8, and 3.9 nm, respectively. In 2014, Kakaei and Hasanpour studied the anodic intercalation and oxidation of chloride ions (Cl$^-$) gave rise to gaseous chlorine that separated graphite layers into mono-, bi-, and trilayer of GO sheets with the thickness of 1.9, 2.8, and 3.9 nm, respectively.
the anodic oxidation of graphite flakes in a confined metal mesh, using a mixture of 1.0 M H₂SO₄ and saturated (NH₄)₂SO₄ solution as electrolyte. The as-prepared GO sheets displayed long-term dispersibility in water, DMF, isopropyl alcohol and ethanol at high concentrations over 2.0 mg mL⁻¹. Nonetheless, the production yield from this method was lower than 40 wt%, even after 48 h of oxidation. Most likely, the large amount of water in dilute electrolytes hinder the formation of graphite intercalated compounds (GIC) with a low stage index (n ≤ 2), where the stage n suggests the number of graphene layers separated by two nearest layer of intercalant. In 2017, Cao et al. reported a two-step electrochemical method, which was able to produce GO sheets with a high yield of 71 wt%. The first step was performed in 95 wt% concentrated H₂SO₄ by applying a bias of 1.0–2.2 V, aiming at fully intercalated stage 1 GIC. Then, the second oxidation/exfoliation step was carried out at 10 V in 0.1 M aqueous solution of (NH₄)₂SO₄. As a result, 90% of the exfoliated GO sheets were monolayers with an average size of 3.1 µm and a C/O ratio of 4.6. Almost at the same time, a modified two-step strategy was explored by Pei et al. to prepare GO sheets with a high level of oxygen content. The first intercalation step was similar to the previous report, using 98 wt% H₂SO₄ at a low voltage of 1.6 V, resulting in the blue stage-1 GICs. The subsequent rapid oxidation required a suitable concentration of H₂SO₄, normally in the range of 40–60 wt%, to achieve highly oxidized GO with C/O ratio of 1.5–1.8. This value even surpassed those from classic chemical oxidation routes, achieving GO sheets with good dispersibility and nanoscale thickness, which was the same as Hummer's...
methods (Figure 6d,e). Based on the mechanism study, abundant radical intermediates (e.g., \(^*\)OH, \(^*\)O, and \(^*\)OOH) from electrolytic water splitting were the major reason for the extensive graphite oxidation. This scalable method resulted in very high exfoliation yield (96 wt%) and high fraction (95%) of monolayers. The production rate (12 g h\(^{-1}\)) was comparable with Cao’s method (Figure 6f), while the average size of GO sheets (\(\leq 1 \mu m\)) are much smaller (Figure 6g). Using glassy carbon asgraphic material in this method decreased the size of GO further to nanometer scale (e.g., 4 nm). The synthesis of nano-GO quantum dots did not require the first intercalation step. The water electrolytic oxidation in 50 wt% \(H_2SO_4\) contributed to high density of oxides with a C/O ratio of 1.4.[88]

Apart from the oxide groups, other heteroatoms can also incorporate into the graphene matrix during anodic exfoliation. Notably, a single-step strategy using 0.1 m \(NaBF_4\) as electrolyte enabled fluorinated graphene sheets with large lateral size up to 12 \(\mu m\) and a high yield (>70%) of 1–3 layers.[89] A considerable amount of fluorine (3 at%) and oxygen (19 at%) paved a way to fabricate flexible and robust micro-supercapacitors with high energy density.

4.2. Transition Metal Carbides (MXene)

MXene is an emerging class of 2D ceramics that have a general composition of \(M_{n-1}X_T\) \((n = 1, 2, or 3)\), where M stands for early transition metals (such as Ti, Mo, Nb, and V), X refers to carbon and/or nitrogen, and T is the functional terminations at the surfaces (such as \(-O, -OH, and -F\)).[90] Since 2011, the fast growth of MXene family sheds light on the development of batteries,[91] supercapacitors,[92] membranes,[93] photothermal conversion,[94] and thermoelectric devices.[95] Compared with traditional 2D materials, MXenes demonstrate great advantages in fundamental and practical applications because of the unique combination of hydrophilic surfaces and high electrical conductivity.[78]

In general, the production of MXenes relies on the selective etching of aluminum (\(A\)) layers from their corresponding layered hexagonal MAX phases, because the strength of M–A bonding is relatively weaker than that of M–X bonding.[96] However, in contrast to van der Waals intercalation, the metallic M–A bond is much stronger. Therefore, mechanical exfoliation methods, such as sonication and shear mixing, are in principle impossible to break M–A bond and to separate MXene layers apart. On the other hand, chemical etching using hydrofluoric acid (\(HF\)) can efficiently remove Al atoms and replace them with functional groups.[97] Depending on the chemical formula of MAX precursors (such as \(Ti_3AlC_2\), \(Ti_2AlC\), and \(Nb_2AlC\)), the HF concentration varies from 10% to 50%, and the required reaction time extends from 2 to 90 h.[98] In 2014, Ghidiu et al. presented a modified method to etch \(Ti_3AlC_2\) in a mixed solution of \(LiF\) (5 m) and \(HCl\) (6 m) at 40 °C, to produce conductive clay (i.e., \(Ti_3C_2T_x\)).[99] In this method, the in situ release of chloride ions enable rapid etching of Al atoms and break the Ti–Al bonds \((Ti_3AlC_2 – 3 e^- + 3 Cl^- = Ti_3C_2 + AlCl_3)\). Afterward, the spontaneous intercalation of ammonium hydroxide opens the boundaries of etched materials, revealed by an increasing d-spacing from 17 ± 0.8 Å (\(Ti_3AlC_2\)) to 21 ± 2.5 Å (\(Ti_3C_2T_x\)) (Figure 7b,c). This step is essential for the subsequent diffusion of chloride ions and the complete etching of aluminum from the surfaces. At a constant potential of 5 V, the entire etching process took no more than 5 h under ambient conditions, resulting in \(Ti_3C_2T_x\) \((T_x = O and OH)\) sheets with large sizes (up to 18.6 \(\mu m\)) and with high yield (over 90%) of single and bilayers (Figure 7d).

5. Applications of the Exfoliated 2D Materials

Because of the exceptional physicochemical and electronic properties, 2D materials have played important roles in a wide scope of applications, including FETs,[103] photodetectors,[104] sensors,[105] energy storage and conversion,[106] etc. Especially, the properties of 2D sheets are tailorable by electrochemical engineering to meet specific demands. Depending on the fabrication routes, the layout of the exfoliated 2D materials varies from single nanosheets, powders, thin films, membranes to 3D foams or aerogels. In this session, we mainly discuss the recent application progress in energy storage and conversion as well as large-area thin-film (optoelectronic) devices based on the electrochemically exfoliated 2D materials. Due to the limited space, only a few prominent examples of applications are presented in the text below.
5.1. Energy Storage and Conversion

Exfoliated graphene (EG) represents a new generation of graphene, which provides a popular choice for energy-related application.[107] However, the restacking of graphene sheets, particularly in the form of powders, severely decreases the surface area. Therefore, the functionalization and blending of EG with other active materials such as polyaniline (PANI), poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS), metal oxides, metal wires, suggests a rational option to avoid this problem. The addition of a small amount of EG sheets (e.g., 2.0 wt%) into LiFePO4 particles improved the capacity of LiFePO4-based lithium-ion batteries to 208 mAh g\(^{-1}\), which is 22% higher than the theoretical value (170 mAh g\(^{-1}\)).[108]

Likewise, EG-polyaniline hybrid sheets were excellent platforms to decorate well-dispersed inorganic nanoparticles. Especially, their combination with silicon nanoparticles delivered an outstanding reversible capacity of 1310 mAh g\(^{-1}\) after 100 cycles at a current density of 1.0 A g\(^{-1}\).[109] In another report, a novel hierarchical EG-MoS2 composite was prepared by patterning vertically aligned MoS2 on EG sheets. It exhibited great potential for the use as active material in batteries, due to the great mechanical stability, rapid charge transport kinetics and highly exposed active sites.[110] The as-produced EG-MoS2 with 95 wt% mass loading of MoS2 exhibited an ultrahigh capacity of 1250 mAh g\(^{-1}\) after 150 cycles for lithium storage. Moreover, it displayed an impressive cycling stability (509 mAh g\(^{-1}\) after 250 cycles at 1.0 A g\(^{-1}\)) for sodium ion batteries. Recently, EG sheets were employed as protective layers to stabilize few-layer phosphorene thus to increase the overall electrochemical performance (Figure 8a).[111] The P–O and P–O–C bonds were formed in the sandwich-structured phosphorene-EG composite through chemical activation. With an optimal mass ratio (1:1) of phosphorene and EG, this hybrid anode material showed a specific capacity of 2311 mAh g\(^{-1}\) at 0.1 A g\(^{-1}\) for Na-ion storage (Figure 8b,c). In addition, this composite revealed good reversible and cycling properties with a capacity retention of 83.9% after 100 cycles (Figure 8d).

In addition, EG is a well-known candidate for supercapacitors (SCs) and micro-supercapacitors (MSCs), derived from its large surface area, excellent mechanical flexibility, and high electrical conductivity.[112–115] For example, inkjet printing of concentrated EG inks (2.3 mg mL\(^{-1}\), in a mixture of cyclohexanone and terpineol) allowed for the scalable fabrication of MSCs arrays on arbitrary substrates. Especially, the efficient integration of EG with pseudocapacitive materials, in the form of layer-stacked heterostructures or hybrid films, led to a significant improvement of the device performances.[112,114] All-solid-state SCs based on an alternating stacked film of EG and 2D thiophene nanosheets delivered an areal capacitance of \(\approx 3.9 \text{ mF cm}^{-2}\) and a volumetric capacitance of \(\approx 375 \text{ F cm}^{-3}\). Moreover, the energy density and power density reached 13 mW h cm\(^{-3}\) and 776 W cm\(^{-3}\), respectively.[112] Remarkably, the compact hybrid film consisting of PANI/polypyrrole-functionalyzed graphene sheets exhibited an outstanding areal capacitance of 368 mF cm\(^{-2}\) and an ultrahigh volumetric capacitance of 736 F cm\(^{-3}\) at 10 mV s\(^{-1}\).[114]

Recently, MXene has become a “star material” in the field of SCs, because of its high capacitance resulting from abundant functional groups (e.g., –OH, –O, and –F) and good electrical conductivity. However, MXene flakes made from HF etching are usually smaller than 1 \(\mu\)m,[99] resulting in huge contact...

![Figure 7. a) Schematic of the etching and delamination process of Ti3C2Tx sheets. b,c) Cross-sectional HR-TEM images of Ti3AlC2 and Ti3C2Tx, respectively. d) SEM image of the delaminated Ti3C2Tx sheets. Reproduced with permission.[78] Copyright 2018, Wiley-VCH.](image-url)
resistance when used as electrode materials. Therefore, the addition of EG into MXene ink not only improves the processability but also reduces the thin-film resistance. Flexible MSCs based on MXene-EG hybrid electrode revealed an areal capacitance up to 3.26 mF cm\(^{-2}\) and volumetric capacitance of 33 F cm\(^{-3}\) at 2.0 mV s\(^{-1}\).[92] Besides, the elimination of fluoride termination is an efficient route to boost the device performance. For example, flexible all-solid-state SC based on fluoride-free MXene demonstrated high areal and volumetric capacitances of 220 mF cm\(^{-2}\) and 439 F cm\(^{-3}\), respectively, at a scan rate of 5 mA cm\(^{-2}\), superior to those of LiF/HCl-etched MXenes (Figure 8e–g).[78] Moreover, the device showed a long-term stability with 94.2% capacitance retention up to 10000 charge–discharge cycles at 5.0 mA cm\(^{-2}\) (Figure 8h).

Apart from energy storage devices, exfoliated 2D materials with high density of exposed active sites are suitable for energy conversion such as hydrogen evolution reaction (HER) and oxygen evolution reaction (OER). Very recently, NiPS\(_3\) flakes with high crystallinity and pure phase structure were prepared from a cathodic exfoliation approach (Figure 8i).[116] Due to the fully exposed P and S atoms, the obtained monolayer NiPS\(_3\) flakes possessed ultrahigh electrochemically active surface area and low reaction resistance, offering an ideal model for HER, OER and overall water splitting. The HER and OER overpotentials of the NiPS\(_3\) at 10 mA cm\(^{-2}\) were only 158 and 300 mV, respectively (Figure 8j). Using NiPS\(_3\) as both anode and cathode, the electrocatalytic overall water splitting in a 1.0 M KOH solution delivered a combined overpotential of 330 mV (Figure 8k), which was much better than the performance of RuO\(_2\)–Pt/C couple.

5.2. Large-Area Thin-Film (Opto)Electronic Devices

The excellent solution processability of 2D nanosheets facilitates the formation of stable and concentrated dispersions/inks, providing great feasibility to fabricate large-area thin-film devices. The continuous and homogeneous thin films could be constructed by various solution-processing techniques such as inkjet printing, spray coating, spin coating, and vacuum filtration. For instance, transparent conductive electrode (TCE) made by spray coating of EG dispersion exhibited a sheet...
resistance ($R_s$) of 0.52 kΩ sq$^{-1}$ at 70% transmittance and 0.18 kΩ sq$^{-1}$ at 55% transmittance.\cite{117} The addition of silver nanowires (AgNW) into EG ink sharply decreased the resistance down to 13.7 Ω sq$^{-1}$ at 89% transmittance.\cite{118} AgNW-EG TCE was very stable to air exposure, showing negligible variation of the $R_s$ value after 120 days. Additionally, the remarkable electrical and optical properties were comparable with those of commercial ITO glass. Similar to the incorporation of AgNW, a small amount (1.0–1.3 wt%) of conductive polymers (e.g., PEDOT:PSS) enabled hybrid EG-polymer thin films with low $R_s$ values of 1200 and 500 Ω sq$^{-1}$, corresponding to 90% and 80% transmittance, respectively.\cite{119}

Based on the spray coating of solution-processable 2D semiconductor inks, wafer-scale thin MoS$_2$ film was prepared for back-gate n-type FETs (Figure 9a–d).\cite{77} The thin film delivered an average mobility of around 7–11 cm$^2$ V$^{-1}$ s$^{-1}$ and an on/off ratio of $10^6$, which were comparable to the devices made of single MoS$_2$ nanosheets (about 10 cm$^2$ V$^{-1}$ s$^{-1}$). Furthermore, complex logic gates were created by integrating an array of MoS$_2$ thin-film transistors, leading to the desired logic function for the potential use in computational circuits. Likewise, inkjet printing of the stable and concentrated BP dispersion (2 mg mL$^{-1}$) resulted in thin BP film on flexible and transparent polyethylene terephthalate substrate, which are very attractive for broadband large-area photodetectors (Figure 9e–g).\cite{60} The photoresponsivity and external quantum efficiency were calculated to be -1.51 mA W$^{-1}$ and -0.35%, respectively. Because of the highly exposed surface area, electrochemically exfoliated 2D materials are promising sensing platforms that demonstrate high sensitivity to external stimuli, such as chemical modification, adsorption of other molecules, and chemical doping. As shown in Figure 9i–l, compact MoS$_2$ thin film was
functionalized with antibodies for detecting the target VP40 matrix protein from Ebola virus. The fabricated biosensor exhibited a remarkable analytic sensitivity with the limit of detection down to picomolar levels.

6. Conclusion and Perspective

According to the great progress achieved in recent years, electrochemical approaches have become one of the mainstream methods to prepare solution-processable 2D materials, including graphene-based flakes and semiconductors. For the fundamental studies, sustainable efforts have been devoted to pushing the limit to high phase purity, high structural integrity and precise functionalization. For the application-oriented research, the major concerns are production cost and scalability. The quality of individual flakes is still important, however, not the main focus for the large-scale production. The challenges remain in both directions, because the complete mechanisms behind are not yet explicitly understood. Therefore, the following critical points should be carefully considered for the future studies.

6.1. New Electrolytes

The selection of proper electrolytes is always important for successful exfoliation. In the ideal case, the electrolyte should have good conductivity and the sizes of solvated ions matches well with the interlayer gap of the electrode materials, which is beneficial for the efficient intercalation. Moreover, the reduction or oxidation of the intercalants need to produce gaseous species that subsequently detach the layers but are not destructive to the 2D sheets. The electrolytes also should exhibit close surface tension to the exfoliated flakes, thus to prevent them from restacking. In addition, easy removal of solvents and electrolytes is essential for many occasions, such as the fabrication of electronic devices. So far, most exfoliation methods using water or organic solvents face serious issues, for example, inevitable oxidation or insufficient intercalation. The exploration of mixed solvent systems suggests a good direction to achieve desirable material properties.

6.2. New Precursors

Many layered materials with strong in-plane bonds and weak interlayer connection are in principle good candidates for the exfoliation process. However, the starting materials in the electrochemical methods require good electrical conductivity (or at least semiconducting property) and proper dimensions that can handle within the reactors. Bulk crystals with poor conductivity often cause large drop of the applied potential because of the intrinsic high resistance. Powder crystals, even though some of them are good conductors, have the same problem due to the huge contact resistance between each particles or flakes. Therefore, technical challenges must overcome to grow large pieces of high-quality layered crystals. In addition, the exfoliation of new “star materials” with unique properties, such as magnetism and porous structure, is necessary for advancing applications.

6.3. New Strategies

The exfoliation process actually involves many factors, such as working electrodes, electrolytes, intercalants, power supplies, cell architectures and other operational conditions. So far, the development of new exfoliation strategies depended on trial and error. Therefore, systematic studies on the regulation of these parameters are essentially critical. For the small-batch production, the combination with other methods, such as ball milling, shear mixing and thermal shock, is a good option to improve the exfoliation yield and to further reduce the sheet thickness. For the scaled-up process, electrochemical engineering shall focus on the technical innovation such as continuous feed, nonstop production, automatic separation, purification and recycle of electrolytes.

6.4. New Fundamental Insights

In theory, the exfoliation process contains three distinct stages: ion intercalation, interlayer expansion, and stripping from the electrodes. However, in practice, these stages do not occur in sequence and they take place at any part of electrodes, resulting in a wide distribution of layer numbers and lateral sizes. The multiple chemical reactions at the electrode/electrolyte interfaces lead to inhomogeneous oxygen content, defect density and surface functionalities. To date, the clear pictures related to the intercalation, reaction and fragmentation are still missing. Therefore, the collaboration between in situ characterization techniques (e.g., TEM, operando spectroscopy (e.g., Raman and X-ray diffraction) and theoretical modeling will be helpful for an in-depth understanding of the fundamental mechanism. This direction would be challenging but very helpful to make breakthrough of the current research.

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Conflict of Interest

The authors declare no conflict of interest.

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2D materials, black phosphorus, graphene, MXene, transition metal dichalcogenides

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