1. Introduction

1.1 Global energy scenario and current state-of-the-art

The current global focus is concentrated on mitigating the harmful effects of effluents released from fossil fuel usage. The primary goal is to increase utilization of renewable energy production systems such as solar, wind, and geothermal. To successfully harness the potential of these sources, many of which are intermittent and generally located far from urban centers, not only must a robust and reliable energy storage system (ESS) be developed, but lightweight and high-energy density storage devices must also be created to power consumer electronics and electrical transportation needs.

Although a diverse array of large-scale ESSs, such as pumped hydro, compressed air, and electrochemical energy storage systems (EESSs), are available, their stability, economic viability, and seamless integration with intermittent renewable energy sources.

Essential factors that determine EESS performance and end-use include the choice of electrode materials (theoretical energy density, toxicity, ease of availability, economics) and strategies for their large-scale manufacturing (e.g., abundance and scale-up costs). High volumetric and gravimetric capacity with lightweight EESS are necessary to power future electronics and devices. Increasingly, conventional electrodes have been shown to not withstand the rigors of the changing energy scenario and have posed several serious bottlenecks. Among anodes, for example, graphite is the established material of choice in commercial Li-ion batteries (LIBs) or LIB systems. However, graphite experiences non-homogenous stress during cell cycling, resulting in cracking and structural and morphological degradation. Also, graphite’s theoretical capacity is limited to a modest 372 mAh g\(^{-1}\) in LIB systems, and graphite remains electrochemically inactive towards sodium intercalation, rendering it unusable in Na-ion batteries (SIBs) or SIB systems. Hence, thorough research is needed for anode materials besides graphite.

Although various anode materials (based on intercalation, conversion, and alloying reactions) for various metal-ion batteries have been reported in the literature, an anode material that meets all desired characteristics (high capacity, cyclability, low cost, earth abundance to name a few) has not been identified. For example, metal oxides such as Fe\(_2\)O\(_3\), CuO, MnO\(_2\), and SnO\(_2\)-based anodes typically demonstrate weak electronic conductivities and must be coupled with a conductive material, thereby increasing the bulkiness of the device. These oxides also undergo significant structural distortions with progressive cell cycling, which greatly reduces their effectiveness.

In spite of their high theoretical capacities, metal-based alloy anodes, especially Sn-Sb-based systems, are
hindered by the same issue.\textsuperscript{11,12} In addition, electrode materials are often incompatible across different alkali-metal ion systems: graphite, a standard anode in LIBs demonstrates almost negligible electrochemical activity due to low thermodynamic stability of graphite intercalation compounds in SIB systems.\textsuperscript{13} Although, theoretically, Li-metal and Na-metal in their purest forms are ideal anode materials for LIBs and SIBs, dendrite formation and subsequent cell failure has restricted use of these materials as electrodes in EESS.\textsuperscript{14}

Cathode materials also face several challenges. LiCoO\textsubscript{2}, the well-established cathode material of choice for LIB systems, is a layered metal oxide; however, it demonstrates structural instability, and its practical capacity is limited to \(\approx 140\) mAh g\(^{-1}\).\textsuperscript{15} Among cathodes researched for LIB, spinel-structured cathodes such as LiMn\textsubscript{2}O\textsubscript{4} (LMO) exhibit large structural distortion due to the Jahn-Teller effect, which results in significant capacity fading.\textsuperscript{16} Padhi et al. studied phosphates as anodes in LIB systems, and although they identified a successful LiFePO\textsubscript{4} system with good cyclability, the electrode could only operate at approximately 3.3 V.\textsuperscript{17} To improve the working voltage, Co was substituted for Fe, and the LiCoPO\textsubscript{4} system provided a discharge voltage as high as 4.5 V. However, this high voltage led to electrolyte decomposition.\textsuperscript{17} Similarly, in SIB systems, metal oxides such as Na\textsubscript{2}MO\textsubscript{2} (\(M = \) transition metal) experience analogous irreversible structural distortions due to the Jahn-Teller effect, similar to the LMO systems.\textsuperscript{18} Organic materials have also been studied as cathode materials for LIB, but they have demonstrated low energy densities and low voltages.\textsuperscript{19} Similar challenges exist for electrodes for metal-ion batteries such as sodium-ion batteries (NIB), and potassium-ion batteries (KIB).

Considering these drawbacks, novel electrode materials must be designed and engineered to increase EESS efficacy. Although cathode materials for alkali-metal-ion batteries are flawed, the problem of low cyclability is more pronounced in anode materials, especially SIB and KIB. The electrolyte system is a fundamentally vital part of the battery setup, and their flammability and performance in the chosen voltage window remains an area of concern; considerable research is being conducted in this area to improve their stability and performance.\textsuperscript{20}

### 1.2 The importance of elemental layered/2D materials

The need for better anode materials in metal-ion batteries has attracted a significant amount of research interest in 2D materials.\textsuperscript{21, 22, 23, 24} These materials can be either purely elemental, such as graphene, which is mono-layered or few-layered sheets derived from graphite, or a compound, such as transition metal dichalcogenides (TMDs) (e.g., MoS\textsubscript{2} and MoSe\textsubscript{2}).\textsuperscript{25, 26} These layered materials provide distinct advantages compared to their bulk counterparts. For example, the layered structure provides exceedingly large surface areas, which increases the number of electrochemically active sites necessary to improve reaction kinetics.\textsuperscript{27} Due their sheet-like structures, 2D materials present low effective mass, which enhances the portability and decreases the bulkiness of any device designed with these materials.\textsuperscript{28} A very important aspect of these 2D materials is the ability of alternating layers of different materials to stack together to achieve stable heterostructures which have shown exciting promise for electrochemical applications.\textsuperscript{29} This ability of the 2D materials to be able to act as “building blocks” of a diverse materials complex is what sets them apart from normal materials. Also, the ability to modulate the electronic properties of these materials provides important advantages, especially for electrochemical and semiconducting applications, where this is a necessary property.\textsuperscript{10} Layered materials also are able to allow in-plane sites for the Li atoms to intercalate in, thereby greatly inhibiting volumetric expansion of the anode and improving battery cycle life.\textsuperscript{31} Electronic mobility improvements are also dramatic, for example, mobility of Li ions increase by a factor of \(10^4\) in MoS\textsubscript{2} monolayers.

Despite these improved properties, however, layered materials have certain disadvantages. For example, TMDs, specifically sulfides such as MoS\textsubscript{2}, tend to reaggregate during cell cycling, thereby losing their layered structures, resulting in capacity loss and irreversibility.\textsuperscript{32, 33} Also, compound layered materials cannot provide superior electronic conductivity and mobility properties compared to graphene, the preferred elemental 2D material,\textsuperscript{34} because these compounds, or non-elemental 2D materials, are quasi-2D, meaning, differences in the constituent elements at the atomic level do not allow them to be truly layered, which consequently influences their electronic density of states.\textsuperscript{34} Therefore, graphene is an excellent conductor, whereas MoS\textsubscript{2} is typically semiconducting. Elemental 2D materials have been hypothesized to have density of states and fermionic distribution such that they can be tuned comparatively easily to modulate their band gap.\textsuperscript{34} From a synthesis perspective, elemental 2D materials provide simpler processing and purification routes than non-elemental materials.\textsuperscript{35} Similarly, when epitaxial growth techniques are used (i.e., bottom-up synthesis techniques), heterogenous, or non-elemental 2D materials, suffer from lattice mismatch, which sometimes adversely affects their target applications.\textsuperscript{36} The high degree of variability in their structure and electronic properties makes elemental 2D materials suitable in important applications such as catalysis, gas sensing, and hydrogen/oxygen evolution reactions (HER).\textsuperscript{37-39} Therefore, this article exhaustively reviews synthesis techniques and structure and application areas of elemental 2D materials such as graphene, silicene, Germanene, phosphorene, arsenene, antimonene, and borophene primarily for electrochemical ESS (batteries and supercapacitors). Some content is also devoted to other applications such as catalysis, gas sensing, and HER.

Readers are reminded that detailed and exhaustive reviews of non-elemental 2D materials are available here.\textsuperscript{6, 31, 40-43} Although graphene was theoretically predicted in 1947, few-layered graphene has been one of the most heavily studied elemental 2D materials since it was isolated by Novoselov and Geim.\textsuperscript{44, 46} They were able to obtain few-layers of graphene by a simplified mechanical exfoliation process (“scotch-tape” technique), after which more refined exfoliation processes
were developed. Many graphene studies have investigated its performance for energy storage, sensing, and an array of applications. Graphene has also been utilized in several catalysis applications and gas sensing.

Figure 1. Typical material electrodes. a cathode alkali-ion batteries, i.e., LiCoO$_2$, NaCoO$_2$, and K$_2$CoO$_2$ b 2D elemental anodes. c Layered morphology of 2D elemental layered materials and their common forms.

2. Predicted structure and properties of elemental 2D materials

Unique physical and chemical phenomena not typically observed in their bulk forms make 2D layered materials, especially mono-elemental versions, key in forthcoming technical developments. However, new physics, properties, synthesis, and characterization techniques of these materials still pose substantial challenges. To overcome these challenges and master the processing-structure-properties correlations and applications of 2D materials, the European Commission launched a $1.1 billion project, called Graphene Flagship, in 2013. Such multinational efforts are essential for utilizing 2D materials in emerging technologies. The following sections present a concise collection of the critical properties of monoelement 2D materials, including a correlation with the most widely studied molecule (graphene).

2.1 Graphene

As the first material ever isolated down to a single atom layer, graphene’s planar structure has sp$^2$ hybridized carbon atoms in a honeycomb formation. Three in-plane σ-bonds in each lattice bond the atoms together, whereas out-of-plane π-bonds provide unpaired electrons with high mobility (Dirac/Weyl electron with very small or no mass). Weak van der Waals bonds between the graphene layers are assigned to the fourth valence electron. The in-plane bonds give defect-free graphene enormous strength (130 GPa), stiffness, and elastic modulus (1 TPa), and because it is classified as a semi-metal, graphene is a zero-gap material in regards to its electronic properties. With a band structure sensitive to its crystal structure, the valence and conduction bands touch each other at the hexagonal Brillouin zone at the Fermi energy level. The π-bond hybridization forms π- and π$^*$-bonds, making graphene the best electronic conductor at room temperature.
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Research interest in graphene, especially from an electrochemistry perspective, stems from the material’s high electrical conductivity (more than ~ 100 S cm⁻¹) and enhanced surface areas (~ 2600 m² g⁻¹) [6]. Another remarkable property of the monolayer form is the absorption of 2.3% of visible light with negligible reflectance, thus presenting 97.7% transparency [84].

2.2 Silicene

Silicon-based semiconductors are vital to the integrated circuit industry, valued at $430.8 billion as of 2018 [85]. The discovery of graphene in 2004 prompted researchers to search for a stable monolayer of silicon (silicene) to use already installed infrastructure for processing silicon for silicene, an utmost miniaturization [86]. Carbon and silicon share some properties, such as bulk silicon, which typically exhibits diamond-like tetrahedral sp³-hybridization structure [87]. Similar to graphene, the monolayer form of silicene is comprised of a honeycomb crystal structure, Dirac band structure, and low bandgap (~ 2 meV) calculated at the Dirac point [86, 88]. Nevertheless, silicene is generally unstable in air, exhibits preferential configuration with sp³ hybridization, and yields a buckled structure with reduced D₃h symmetry [89]. Although challenges must be addressed before silicene can be commercially available, this elemental 2D material is promising for future technological applications due to its non-trivial electron states and tunable bandgap [90].

2.3 Germanene

Germanium, another element from the IVA group, is also a 2D material [91]. This layered allotrope, known as germanene, is often reported as the “binder” material to silicene because both materials are in Group IV family and present buckled honeycomb structure [92, 93]. However, mechanical properties of this layered material are inferior to graphene, with fracture strength ranging from 4.1 to 4.7 GPa [94]. Likewise, germanene possesses lower (2.4 W m⁻¹ K⁻¹) and high anisotropic thermal conductivity due to its high atomic mass and buckled structure [95]. The atoms in germanene exhibit sp²-sp³ hybridization, while the buckling produces a degree of electronic anisotropy [94, 96, 97]. In fact, this buckled structure may provide properties of interest, such as topological superconductivity. Although free-standing germanene is expected to be a zero-bandgap material, its lattice distortions prevent germanene from being stable [95].

2.4 Phosphorene

Phosphorene, which is typically prepared by exfoliating black phosphorus, has a puckered structure with no sp³ P-P bonds (Figure 1c), with an in-plane P-P bond length of 2.224 Å, out-of-plane distance of 2.244 Å, and interlayer spacing of 2.1 Å [96, 97]. Unlike graphene, phosphorene exhibits a degree of anisotropy along in-plane directions [98]. Because the structure has three different chemical bonds with adjacent phosphorous atoms, monolayer phosphorene has a direct band gap of 1.75 eV with a high carrier mobility [96, 98]. Interestingly, by stacking phosphorene layers on top of each other, the band gap can be reduced to approximately 0.3 eV (bulk form) [99]. Similar to most 2D elemental species, phosphorene exhibits anisotropy, as evidenced by electron mobility along the armchair direction, which is over 10 times higher than along the zigzag direction [100]. Phosphorene also shows increased electron transport when mechanical stress is applied in the zigzag direction, although application of biaxial strain may considerably change phosphorene’s electronic band gap [101].

2.5 Arsenene

Arsenene comprises a monolayer of arsenic and a buckled hexagonal structure akin to elemental 2D materials from group IVA [68, 102]. If the bulk material is orthorhombic As, then the corresponding monolayer (α-As) is similar to phosphorene and exhibits a hexagonal structure [63]. On the other hand, if the gray As is the initial material, then the monolayer exhibits a buckled structure and is termed β-As [63, 64]. With a predicted Young’s modulus of 12.7 GPa, arsenene presents mechanical flexibility and high anisotropic mechanical properties [103]. In addition, arsenene has a semiconducting band structure with an indirect bandgap value of 2.49 eV and high carrier mobility [102, 104]. Mechanical strain, such as strain-induced band transition, modulates the electronic properties in this elemental monolayer species. According to Kong et al., 12% biaxial tensile strain on doped arsenene (at a temperature of 30.8 K) makes arsenene superconducting [105]. Although most arsenene research has relied on theoretical calculations or first-principle calculations, fabrication of arsenene monolayers and experimental confirmation of theoretical predictions are emerging [106].

2.6 Antimonene

Antimonene, a monolayer of antimony (Sb) metal, exists in several allotropic forms. The most stable form is the rhombohedral Beta-phase antimonene, which has a buckled hexagonal structure with promising thermal and electronic properties. The indirect band gap of the β-antimonene form is predicted to be 1.2 eV [107, 108], whereas the band gap is direct and predicted to be smaller in the α-antimonene [108]. From the visible region to ultraviolet, antimonene shows exceptional light absorbance for optical properties [108].

2.7 Borophene

Borophene is a single layer of synthesized boron atoms that exists in different phases, e.g., rectangular and rhombohedral phases [109]. Typically, four phases have been observed: 2-Pmmn,
3. Synthesis and characterization of elemental 2D nanomaterials

Synthesis of elemental 2D nanomaterials significantly impacts their physiochemical and electronic properties. The synthesis of elemental nanosheets was inspired by the fabrication of 2D graphene from bulk graphite via mechanical exfoliation in 2004.\textsuperscript{111} Because of its attractive properties and diverse implementations, numerous fabrication methods, such as bottom-up growth to top-down exfoliation processes, have been used to produce graphene.\textsuperscript{78, 84, 111-117} Based on the fabrication process of graphene, other elemental 2D nanomaterials have been synthesized, including silicene,\textsuperscript{118} germanene,\textsuperscript{119} stanene,\textsuperscript{12} phosphorene,\textsuperscript{97} arsenene,\textsuperscript{120} antimonene,\textsuperscript{121} bismuthine,\textsuperscript{122} borophene,\textsuperscript{110} and gallenene.\textsuperscript{123} This section introduces fabrication and characterization methods commonly used to produce single-elemental 2D nanomaterials for electrochemical applications. The synthesis techniques, as shown in Figure 2, can generally be classified as (a) top-down (e.g., mechanical exfoliation [cleavage], liquid exfoliation [ultrasonication], and etching) and (b) bottom-up (e.g., chemical and physical vapor deposition and wet chemical solvothermal reaction).

3.1 Graphene

3.1.1 Mechanical exfoliation In 2004, Novoselov et al. was the first research team to mechanically cleavage graphite to synthesize monocrystalline graphene by the ‘repeated peeling’ of small mesas of highly oriented pyrolytic graphite (HOPG). However, this method was not suitable for the production of a large-area graphene nanosheet. Huc et al. successfully utilized epoxy bonding and controlled reverse exfoliation of HOPG to fabricate large (~10 µm), uniform graphene flakes.\textsuperscript{124} Similarly, Shukla et al. prepared mm-sized few-layer graphene (FLG) using borosilicate glass bonded with bulk graphite and exfoliation.\textsuperscript{110} Shmavonyan et al. also showed that additional cleaving of FLG could enlarge the surface area of monolayer graphene near the monolayer region.\textsuperscript{126} Atomic force microscopy (AFM) showed a significant enlargement of the surface area of the monolayer graphene due to the additional cleaving. Raman spectra analysis of the monolayer graphene showed a sharp and symmetric 2D peak (Figure 3a.4). These methods of micromechanical cleavage paved the way for advancements in the large-scale production of graphene.

3.1.2 Liquid-phase exfoliation The production of graphene through exfoliation in the liquid phase is commonly used for large-scale synthesis. The most popular fabrication method has been the oxidation of graphite followed by the exfoliation of graphene oxide (GO). For example, Stankovich et al. exfoliated GO into individual GO and then chemically reduced them with a reducing agent (hydrazine hydrate) to produce very thin graphene-like sheets.\textsuperscript{127} Raman spectra of the reduced GO showed a higher D/G intensity ratio compared to the ratio in GO, suggesting the presence of new and smaller graphitic domains than the GO before reduction. Hernandez et al. synthesized unoxidized graphene flakes from powdered graphite by exfoliating bulk graphite in an organic solvent, N-methylpyrrolidone (NMP).\textsuperscript{128} They showed that NMP solvents allow the dispersion of graphene concentrations up to 0.01 mg ml\textsuperscript{-1}; the monolayer graphene was 7–12 wt. %.
Figure 2. Schematic illustration of the general synthesis techniques of elemental 2D elements. a Top-down approaches. b Bottom-up approaches.
Similarly, Lotya et al. utilized ultrasound to disperse graphite in a surfactant-water solution, resulting in a large number of multilayer graphene (<5 layers) and smaller amount of monolayer graphene. Transmission electron microscopy (TEM), Raman spectra, infrared (IR) spectroscopic analysis, and X-ray photoelectron spectroscopy (XPS) of these films showed defect- and oxidation-free dispersed graphene flakes. TEM images of graphene flakes revealed a monolayer graphene (Figure 3a.1), and the Raman spectra showed that the small graphene flakes exhibited a low intensity in the D-band, while the big flakes showed no D-band, which suggests that the graphene flakes had low defect content. XPS confirmed low levels of oxidation of the graphene film.

Liu et al. used expandable graphite (EG) to produce FLG in supercritical N, N-dimethylformamide (DMF) in less than 15 minutes, followed by exfoliation of FLG in supercritical DMF to produce monolayer graphene. AFM and Raman results indicated the presence of FLG (thickness ~3 nm) and monolayer graphene (thickness ~1.2 nm), but a small proportion of defects were present in the synthesized graphene sheets. Other researchers have also recently attempted to produce large-scale graphene sheets using liquid-phase exfoliation. Although liquid-phase exfoliation shows promise for synthesizing large-scale graphene, it suffers from impurity and presence of oxygen, resulting in poor electrical properties of graphene.

3.1.3 Chemical vapor deposition
Synthesis of graphene via chemical vapor deposition (CVD) is another promising technique to fabricate large-area, high-quality graphene nanosheets. Somani et al. first demonstrated synthesis of graphene sheets via CVD using camphor pyrolysis on Ni substrates. Camphor was pyrolyzed in a CVD furnace at 700–850 °C with Ar as the carrier gas. The TEM image showed interplanar spacing of approximately 0.34 nm, but the number of graphitic layers in this film was estimated to be 35. In another approach, Yu et al. produced high-quality graphene on polycrystalline Ni foils using surface segregation and substrate transfer. For synthesis, a precursor gas mixture of CH4:Ar (0.15:1.2 ratio) was utilized at 1000 °C for 20 minutes. High-resolution TEM (HRTEM) showed 3–4 layers of graphene, which was confirmed by Raman spectroscopy. According to the authors, the cooling rate significantly affects the amount and quality of the carbon segregated at the surface of the Ni, and the quality of graphene films can be administered by varying surface roughness of the substrates and the growth atmosphere of H2.

Wang et al. synthesized large-scale, substrate-free graphene sheets. These FLG sheets were synthesized from CH4:Ar (1:4 v/v) over magnesium oxide-supported cobalt catalysts at 1000 °C. The FLG was first cleaned with concentrated HCl to wash off MgO and Co and then rinsed with distilled water to obtain a neutral pH. HRTEM showed randomly aggregated, thin, crumpled graphene sheets, and Raman spectra confirmed at least five layers in the graphene sample. Sun et al. obtained monolayer pristine graphene film from a thin film (~100 nm) of spin-coated poly(methyl methacrylate) (PMMA). Cu metal was used as the catalyst substrate, and graphene was grown at a low temperature of 800 °C with a reductive gas flow (H2/Ar), resulting in monolayer graphene with a thickness of 0.7 nm as measured by AFM. The I_D/I_G intensity ratio in the Raman spectra of this PMMA-derived graphene was approximately 4, with the full-width at half-maximum (FWHM) of 30 cm−1 for the 2D peak, proving that the produced graphene was monolayer.

Park et al. used CVD to synthesize high-quality, defect-free, micrometer-scale graphene at a low temperature of 150 °C (Figure 3a.1). First, they coated a glass substrate with a 10-nm Ti layer annealed under hydrogen; TEM and Raman spectroscopy confirmed defect-free graphene synthesis on the Ti-coated substrates. In a slightly different approach, Li et al. demonstrated a CVD technique using a solid and a liquid precursor to grow graphene at low temperatures. From solid PMMA and polystyrene precursors, monolayer graphene films were grown on Cu foils at a low temperature of 400 °C. High-quality monolayer graphene films were synthesized at a growth temperature as low as 300 °C when liquid benzene was utilized as the hydrocarbon source. Macroscopic uniformity was achieved in the PMMA-derived graphene grown at 1000 °C, as shown in Figure 3a.3. SEM of graphene grown at 700 °C and 400 °C confirmed the continuity of graphene films grown at lower temperatures. Raman spectroscopy at 550 nm showed a noise-level D band, which confirmed the presence of monolayer graphene films on the SiO2/Si substrate.

Researchers in another study used CVD to synthesize large-scale, high-quality graphene from methanol, ethanol, and propanol precursors on copper foil. The Cu film was exposed to alcohol vapor for approximately 5 minutes, and the average growth temperature was 850 °C. The alcohol precursors yielded continuous monolayer sheets of graphene, and Raman spectra and XPS showed that the synthesized graphene sheets were of high quality and had no measurable doping or oxidation effect. Field-effect mobility was measured as 1800–2100 cm2/V·s at the carrier densities between 1011 cm−2 and 1012 cm−2 for large-area graphene transistors. Other studies have shown that dechlorination of hexachlorobenzene on Cu foils; food, insect, and waste; solid corone as carbon precursor; two-step CVD; plasma-assisted CVD; FG on NaCl crystal; and graphene foams are promising techniques for producing high-quality graphene using CVD.

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3.2 Silicene
Figure 3. Synthesis and characterization of graphene, silicene and germanene. **a** Graphene. **a.1** A schematic of a defect free graphene synthesis via CVD at approximately 150 °C using Ti (∼10 nm)-coated substrates. Reproduced with permission \(^\text{139}\). Copyright 2018, American Chemical Society. **a.2** TEM image of a monolayer graphene flake synthesized by liquid exfoliation. Reproduced with permission \(^\text{129}\). Copyright 2009, American Chemical Society. **a.3** Photograph of PMMA derived graphene on SiO\(_2\)/Si substrate grown at 1000 °C. Reproduced with permission \(^\text{140}\). Copyright 2011, American Chemical Society. **a.4** Raman spectra of graphite and monolayer graphene show a sharp 2D peak for graphene with FWHM of 30 cm\(^{-1}\). Reproduced with permission \(^\text{126}\). Copyright 2013, National Academy of Sciences of Armenia. **b** Silicene. **b.1** Schematic representations of a buckled silicene grown on the MoS\(_2\) substrate. Reproduced with permission \(^\text{150}\). Copyright 2014, American Chemical Society. **b.2** STM image of the 2D Si layer reveals the honeycomb-like structure. The dark centers are separated by 1.14 nm, which corresponds to (4x4) symmetry. Reprinted figure with permission from \(^\text{118}\). Copyright 2012 by the American Physical Society. **b.3** AFM image of a monolayer silicene deposited on highly oriented pyrolytic graphite (HOPG) at room temperature. The silicene thin films are indicated by a light blue arrow appears where the HOPG substrate are the darkest regions, with the small 3D Si clusters (1 nm height) indicated by white arrows. **b.4** XPS of monolayer (ML) of monolayer silicene shows the distinct peaks of Si 2p and Si 2s obtained after deposition. Reproduced with permission \(^\text{151}\). Copyright 2016, American Chemical Society. **c** Germanene. **c.1** Schematic representations of a germanene monolayer on the Al substrate. **c.2** Large scale STM image of germanene on Al (111). The line indicates the direction of Al [-1 2 -1]. Hexagonal periodicity of germanene lattice is shown in the inset using Fast Fourier transform (FFT). Reproduced with permission \(^\text{152}\). Copyright 2015, American Chemical Society. **c.3** AFM micrograph of few-layer germanene deposited on SiO\(_2\)/Si. **c.4** Raman spectrum of hydrogen-terminated germanene GeH and Ge powder shows the variation in the E\(_{2}\) peak. Copyright 2015, American Chemical Society. Reproduced with permission \(^\text{119}\). Copyright 2013, American Chemical Society.

Because silicon is in the same Group IV as graphite, advances in graphene have increased interest in silicene, a 2D hexagonal lattice derived from silicon. Silicene has a hexagonal surface pattern with a periodicity of 3.2 Å (Figure 3b.1). In 2006, Nakano et al. used chemical exfoliation of CaSi\(_2\) to prepare silicon sheets. CaSi\(_2\) was first doped with Mg, followed by absorption of CaSi\(_2\)\(·\)Mg(Si\(_2\))\(_{1.5}\) in a propylene hydrochloride solution.\(^\text{153}\) The Ca\(^{2+}\) ions were deintercalated with the evolution of hydrogen, and a light-brown
precipitates were bound covalently to the Si(111) planes. covered with n-decylamine residues. Results showed that amine nitrogen atmosphere to form a silicon sheet that was densely organic solvent. The solvents were slowly evaporated under a size (1–2 µm) and oxygen-free surfaces.

Okamoto et al. reported the synthesis of silicene with large lateral were highly symmetrical and did not oxidize during synthesis (Figure 3b.3), and XPS of the silicene confirmed that Si peaks in inertness. AFM images of the silicene showed a clean, uniform structure of a monolayer Si. The authors used scanning tunnelling microscopy (STM) and angular-resolved photoemission spectroscopy (ARPES) to confirm that the (4 × 4) 2D Si adlayer on Ag(111) was, in fact, 2D silicon sheet with a honeycomb structure (Figure 3b.2).

Tao et al. performed epitaxial silicene synthesis on Ag(111) thin film on a mica substrate without using expensive single-crystal bulk Ag. Raman spectroscopy confirmed the formation of silicene on the Ag substrate with strong peaks in the range of 515–522 cm⁻¹, which corresponded to E₂g modes and symmetric stretching of silicon atoms.

Crescenzi et al. deposited silicon directly onto graphite at room temperature substrate to demonstrate that using a highly oriented pyrolytic graphite (HOPG) substrate prevented the interaction between silicene and substrate. The sp² electronic configuration and fully honeycombed structure of the HOPG resulted in chemical inertness. AFM images of the silicene showed a clean, uniform surface (Figure 3b.3), and XPS of the silicene confirmed that Si peaks were highly symmetrical and did not oxidize during synthesis (Figure 3b.4).

Okamoto et al. reported the synthesis of silicene with large lateral size (1–2 µm) and oxygen-free surfaces. They chemically exfoliated polysilane (S₅Hₓ) with n-decylamine and dissolved the mixture in an organic solvent. The solvents were slowly evaporated under a nitrogen atmosphere to form a silicon sheet that was densely covered with n-decylamine residues. Results showed that amine precipitates were bound covalently to the Si(111) planes.

Several research groups also developed surface segregation of silicene on ZrB₂, buckled silicon on Ir(111), stabilization of silicene, freestanding silicon nanosheets (SiNSs) via hydrolysilation reactions, and magnesiothermically induced phase transition of exfoliated silicene nanosheets to successfully synthesize silicene.

3.3 Germanene

Because of its location in the periodic table of elements in the same group of carbon and silicon, germanene has also become a topic of interest in atomically thin 2D materials research. In 2013, Bianco et al. performed the first synthetization of a graphene analogue of germanium, millimeter-scale hydrogen-terminated germanium (germanane, GeH). This hydrogenated germanene was produced from CaGe2 using topochemical deintercalation. The GeH was shown to be thermally stable up to 75 °C, and XPS and FTIR confirmed that the surface layer of GeH slowly oxidized in the air over 5 months. An AFM micrograph showed mechanically exfoliated GeH sheets as single and few-layered on SiO₂/Si surfaces with lateral sizes greater than 2 µm (Figure 3c.3). Raman spectroscopy showed a shift in the E₃ modes between hydrogen-terminated germanene and germanium, as shown in Figure 3c.4.

Li et al. produced a buckled germanene sheet on a Pt(111) surface. After depositing germanium on Pt from a germanium rod mounted in an electron beam evaporator, the sample was annealed at a temperature of 600–750 K for 30 minutes. According to the authors, annealing the samples at temperatures below 800 K prevented the formation of Ge–Pt surface alloy. LEED was used to macroscopically specify the structure as a (v19 × v19) superstructure, and STM showed the lattice constant of the structure to be 12 Å. Similarly, Derivaz et al. fabricated a continuous germanene layer on an Al(111) surface. The germanene layer was characterized by a (3 × 3) superstructure with respect to the substrate (Figure 3c.1), and a large-scale STM image of Al(111) showed the long-range structure of germanene (Figure 3c.2). The thickness of the synthesized germanene was approximately 0.27 ± 0.01 nm.

Davila et al. produced atomically thin, ordered 2D germanene sheets using molecular beam epitaxy (MBE) on an Au(111) substrate. Zhang et al. showed the growth of buckled germanene on a non-metallic MoS₂ surface. Germanene’s lattice constant was 20% larger than the lattice constant of MoS₂ with an angle of 0° between them.
Figure 4. Synthesis and characterization of phosphorene, arsenene, and antimonene. **a** Phosphorene. **a.1** Schematic illustration of a phosphorene monolayer showing the conventional zigzag (a) and the armchair direction (c). **a.2** SEM image of liquid-exfoliated thin phosphorene flakes. **a.3** TEM images of few-layer phosphorene. **a.4** XPS analysis of unoxidized few-layer phosphorene sheets (black). When the sheets are exposed to light (λ = 460 nm) and oxygen, they become oxidized (blue). Reproduced with permission 162. Copyright 2015, American Chemical Society. **b** Arsenene. **b.1** Schematic illustration of monolayer arsenene with orthorhombic structure. **b.2** STEM image of the electrochemically exfoliated ultrathin flakes of few-layer arsenene. **b.3** High-resolution TEM image of the arsenene nanosheets. **b.4** XPS spectra of arsenene with peaks corresponding to elemental arsenic. Reproduced with permission 163. Copyright 2020, American Chemical Society. **c** Antimonene. **c.1** Schematic of the fabrication process high-quality monolayer antimonene. Antimony atoms are deposited onto the Ag (111) substrate which is kept at 353 K. **c.2** LEED pattern of antimonene on Ag substrate. Hexagonal diffraction patterns present a √3x√3 superstructure with respect to Ag(111) substrate. **c.3** Large scale STM image demonstrates a homogenous thin film of single-layer antimonene with a height of 2.2 Å. **c.4** XPS spectra of SB 4d with two sharp peaks assigned to Sb in antimonene, which confirms the monolayer antimonene formation. Reproduced with permission 164. Copyright 2018, American Chemical Society.

**3.4 Phosphorene**

Phosphorene, which is primarily derived from black phosphorous, is an allotrope of phosphorus, a Group V element. Phosphorus has white, red, black, blue, and violet phosphorus allotropes. Black phosphorus has a 2D morphology, making it a promising material for synthesizing phosphorene. In 2014, Liu et al. introduced phosphorene using mechanical exfoliation of layered bulk black phosphorous.97 Exfoliated phosphorene was transferred onto a SiO₂/Si substrate and then cleaned with alcohol and heated at 180 °C to remove the residue. AFM showed the thickness of the monolayer phosphorene to be 0.85 nm. During the same period, Buscema et al. and Li et al. used Scotch tape-based mechanical exfoliation to fabricate a few layers of phosphorene from the bulk crystal of black phosphorous.99, 165 Lu et al. demonstrated Ar⁺ plasma thinning and mechanical cleavage to synthesize monolayer phosphorene.166 AFM and contrast spectra determined the sample thickness, and the measured heights were 0.85 nm and 2.8 nm, respectively, which were consistent with the monolayer and pentalayer phosphorene. Raman frequency showed an increase in the intensity ratio of A²g to A¹g modes, which...
corresponded to the decrease in thickness of bulk crystal to monolayer phosphorhene. Zhang et al. reported an MBE growth of monolayer blue phosphorous on Au(111) from black phosphorus. Black phosphorus was deposited by evaporation at 260 °C and annealed at 250 °C for 60 minutes. STM showed a well-defined monolayer phosphorus with a hexagonal appearance, and the simulated STM image created by DFT with a (4 x 4) supercell of black phosphorus was in good agreement with the experimental STM image.

Castellanos-Gomez et al. proposed a modified version of the mechanical exfoliation technique to optimize the deposition of phosphorhene on substrate. Blue Nitto tape was used to cleave bulk black phosphorus, and the tape containing the thin flakes was pressed against a poly-dimethylsiloxane (PDMS) substrate. The PDMS substrate was then pressed gently onto a Si substrate to transfer the thin flakes to the Si. Use of an intermediate substrate increased the yield of the phosphorhene and decreased the contamination. A TEM image confirmed the formation of a few layers of phosphorhene after exfoliation, and TEM and Raman spectra of the flakes indicated that few-layer phosphorhene flakes were highly crystalline and stable, even in freestanding form.

Kang et al. used liquid exfoliation to fabricate phosphorhene. Black phosphorus was dispersed in NMP in a sealed-tip ultrasonication system to exfoliate in an anhydrous, oxygen-free environment. AFM height image showed that the thicknesses of the single- to few-layer nanosheets were between 16 and 128 nm. XPS spectra confirmed the high chemical quality of the exfoliated black phosphorus nanosheets with partially oxidized PO2 peaks.

Similarly, Woomer et al. synthesized crystalline monolayer and few-layer phosphorhene via liquid exfoliation from black phosphorus crystals. An SEM image confirmed the presence of phosphorhene flakes with lateral sizes between 50 μm and 50 nm (Figure 4a.2), and a TEM image revealed the thin, uniform morphology of the phosphorhene flakes (Figure 4a.3). XPS analysis also confirmed the defect-free phosphorhene layers without oxidation (Figure 4a.4). This study demonstrated a simple, scalable technique to synthesize high-quality phosphorhene. Several liquid exfoliations and mechanical exfoliations have been reported over the last decade to successfully fabricate phosphorhene nanosheets.

3.5 Arsenene
Arsenene is the layered 2D structure of another Group V element, Arsenic. In 2016, Tsai et al. studied a plasma-assisted route to prepare multilayer arsenene on an InAs substrate. The thickness of multilayer arsenene was controlled by adjusting the annealing time, power, and exposure time of plasma. According to the authors, the optimized synthesis condition was N2 plasma immersion with 100 W of power for 30 minutes and annealing at 450 °C for another 30 minutes. The heterogeneous structure of arsenene, InN, and InAs substrate were visible by TEM, and the TEM-measured interlayer distance of 0.286 nm and 0.181 nm corresponded to the (110) and (01-1) interplanar distances, respectively, of the multilayer arsenene. In 3d and As 3d, XPS spectra revealed that the InN formed during annealing pushed the arsenic atoms to the outer surface to form the layers of arsenene, which was identified at ~42.4 eV.

Gusmao et al. showed that aqueous shear exfoliation could produce arsenene nanosheets. Kitchen blenders were used to disperse and exfoliate bulk As crystals in aqueous surfactant sodium cholate (1 g L−1, SC 5 g L−1) for 2 hours. SEM images of exfoliated arsenene showed heterogeneous sub-micron nanosheets, and a TEM image revealed anisotropic arsenene sheets with a visible wrinkled structure consisting of a few layers.

Recently, Kovalska et al. exfoliated arsenic electrochemically to synthesize arsenene. Orthorhombic arsenic (Figure 4b.1) was exfoliated in a 0.01 M NH4PF6/DMF solution. STEM (Figure 4b.2) and low-magnification, bright-field TEM (Figure 4b.3) images of sonicated arsenene showed netlike, agglomerated arsenene flakes, and XPS spectra (Figure 4b.4) of the electrochemically exfoliated arsenene showed peaks that corresponded to elemental arsenic. This nonaqueous oxygen-free medium facilitates the synthesis of high-quality, few-layer arsenene.

Vishnoi et al. exfoliated grey arsenic in NMP to produce few-layer arsenene under a nitrogen atmosphere. A low-magnification TEM image and the corresponding selected area electron diffraction (SAED) pattern of few-layer arsenene showed the hexagonal lattice of rhombohedral As. Raman spectra of few-layer arsenene showed peaks at 197.2 and 256.5 cm−1, which corresponded to the Eg and A1g vibrational modes of the β-arsenene.

3.6 Antimonene
Antimonene is an exfoliated monolayer structure of Group V material antimony. Antimony has several allotropes, of which the grey antimony is the most stable and is primarily used to fabricate antimonene. Jii et al. showed Van der Waals growth of few-layer antimonene on fluorophlogopite mica substrate. Antimony powder was evaporated at 660 °C, deposited on mica substrate kept at 380 °C, and then cooled to room temperature. An AFM image of the antimonene sheet showed thicknesses of 4 nm, and Raman spectroscopy revealed buckled hexagonal structure consistent with the monolayer β-phase antimonene.

Tsai et al. used a plasma-assisted approach to produce multilayer antimonene on InSb substrate. The InSb substrates were first immersed in the N2 to form antimonene layers at 100 W for 30 minutes and then annealed at 450 °C for 30 minutes. Raman spectra of synthesized antimonene indicated the formation of thin film. Shao et al. reported an epitaxial growth of monolayer antimonene with honeycomb structure on an Ag (111) surface (Figure 4c.1). The LEED pattern of antimonene (Figure 4c.2) showed a defect- and wrinkle-free pristine hexagonal structure. A large-scale STM image showed synthesis of the high-quality monolayer antimonene (Figure 4c.3), and the XPS spectra (Figure 4c.4) showed two distinct Sb peaks, confirming the formation of an antimonene monolayer. This high-quality flat antimonene monolayer is an excellent candidate for applications in future electronics.

Ares et al. demonstrated micromechanical exfoliation of antimonene to produce single and few-layer antimonene flakes. They used an intermediate viscoelastic surface to increase the yield and reduce the defects, and then they transferred the antimonene flakes onto a SiO2/Si substrate. A single-layer antimonene with a thickness of 0.9 nm was observed using AFM, and high-resolution TEM was used to
distinguish thick flakes from bulk and antimonene flakes confirmed
the hexagonal lattice of β-antimonene.

Gibaja et al. utilized rapid liquid-phase exfoliation to produce highly
stable, few-layer antimonene.69 Bulk antimony was dispersed in
isopropanol: a water (4:1 ratio) mixture without any surfactant to
produce micrometer-large antimonene. The exfoliated few-layer
antimonene sheets were stable under ambient conditions for long
periods of time (e.g., weeks). AFM confirmed the fabrication of few-
layer antimonene, and Raman spectra showed that the layer
thickness of ~4 nm corresponded to a monolayer or bilayer of
antimonene.

Figure 5. Synthesis and characterization of borophene. a STM images of boron deposition on clean Au(111) at 550 °C. The conventional herringbone reconstruction changes to a trigonal network, where nanoscale borophene islands emerge at the nodes resulting in templated growth across the surface (highlighted by a white dashed line). b A schematic illustration of borophene growth shows that the boron forms a cluster on the surface at low substrate temperatures. At a higher temperature of 550 °C, the born dissolves into the bulk and then separates to the surface to build up 2D borophene sheets upon cooling. c STM image of a larger borophene island shows the herringbone reconstruction (black arrows) from the Au (111) substrate (V = 1 V, I = 100 pA). d Atomic-scale periodicity in larger borophene sheets (V = -0.4 V, I = 80 pA). e FFT of the STM image in d shows a strong periodicity of ~0.66 nm in the extended borophene sheets. Reproduced with permission 174, Copyright 2019, American Chemical Society.

3.7 Borophene

Borophene, which consists of the 2D forms of elemental boron, is an
element in Group III of the periodic table of elements and has been
successfully synthesized in experiments. Depending on the bonding
between boron atoms, 16 unique allotropes of bulk boron can be
formed.175 Although these allotropes show various structures,
borophene refers to the general class of 2D boron sheets.

In 2015, Mannix et al. used an electron beam evaporator to grow
borophene sheets under UHV on Ag(111) substrate while
maintaining a temperature of 450–750 °C.112 In situ Auger electron
spectroscopy (AES) revealed a boron KLL peak on the clean Ag(111)
spectrum, confirming the formation of boron nanosheets. STM and
XPS results confirmed the metallic characteristics of borophene and
proved that bulk boron allotropes are semi-conductors at standard
conditions. Annular bright-field (ABF) images showed sheet
thicknesses of 0.27–0.31 nm, which corresponded to the monolayer
structure of boron nanosheets.

Feng et al. presented a similar experimental work using MBE to
synthesize borophene nanosheets on an Ag(111) surface under
UHV.176 They showed that the deposited borophene on the Ag
substrate had monolayer structures. STM images revealed that two
types of boron sheets were formed, a β12 sheet and a γ3 sheet, at
substrate temperatures of 570 K and 680 K, respectively. Both
showed buckled triangular lattices but different hexagonal holes in
the structure. XPS study confirmed that the sheets were inert to
oxidation and interacted only with the Ag substrate. Recently, Kiraly
et al. reported the growth of borophene on Au(111) substrates using
the MBE method.174 UHV STM showed the herringbone
reconstruction to a trigonal network of nanoscale borophene islands
(Figure 5a). Boron was diffused into Au at a high temperature of 550
°C, followed by segregation to the surface when the substrate was
cooled (Figure 5b). The magnified image of the borophene islands
revealed the atomically thin borophene with string periodicity of
~0.66 nm, as shown in Figure 5c–d.

Tai et al. used the CVD method to synthesize atomically thin γ-boron
films on a Cu substrate.177 A mixture of boron and B2O3 powder was
heated to 1100 °C and carried by H₂ gas onto a 25 µm Cu foil. An AFM image showed that the thickness of the deposited film was 0.80 nm, indicating the formation of a monolayer. HRTEM images confirmed that the monolayer lattice structure corresponded to the orthorhombic γ-B₂₃ crystal structure.

Ji et al. used a unique top-down process to synthesize high-quality ultra-thin boron nanosheets by combining liquid-exfoliation and thermal oxidation etching techniques. Highly dispersed boron sheets were prepared by exfoliating bulk boron in NMP (ethanol:water) solution and then oxidizing it at 650 °C in the air to form B₂O₃. This oxidized B₂O₃ was then dissolved into water to form BO₃⁻ with a second liquid exfoliation. Consequently, bulk boron decreased to ultra-thin boron nanosheets with an average size of 110 nm and an average thickness of 3 nm. HRTEM and high-resolution XPS confirmed the formation and crystalline nature of boron nanosheets.

4. Electrochemical properties

The outstanding physical, chemical, electronic and optical properties of the elemental 2D nanomaterials have led to numerous applications. These ultrathin nanomaterials have been explored in the areas of novel electronics and optoelectronics, energy storage and conversion, catalysts, and water treatments, etc. This section will specifically summarize the recent progress on the utilization of elemental 2D nanomaterials as electrodes in electrochemical energy storage devices (e.g. supercapacitors and rechargeable batteries).

4.1 Supercapacitors (SCs)

Supercapacitors have emerged as promising energy storage devices because of their high power density, high rate capability, excellent cycleability, low cost, and stable operating conditions. Supercapacitor materials store charges through electrostatic ion adsorption on the surface and these types of supercapacitors are known as electrical double-layer capacitors (EDLCs). Aside from EDLCs, some supercapacitor materials known as pseudocapacitors (PCs) can store charges created on the faradaic reactions on the surface of the electrode. Elemental 2D nanomaterials with only a few-layer thickness have readily available high surface areas and short diffusion path for electrolyte ions. Thus, they have received increasing attention as promising electrodes to achieve high-performance supercapacitors.

Graphene has been widely explored as a supercapacitor electrode owing to its highly tunable surface area (up to 2675 m² g⁻¹), high electrical conductivity, and theoretical capacitance (550 F g⁻¹). However, graphene layers tend to agglomerate during preparation and application, which leads to low surface area and thus resulting in poor capacitance. As a result, several routes have been developed by researchers to avoid the cluster of the graphene layers and achieve high capacitance. For example, Stoller et al. pioneered a chemically modified graphene (CMG) which had a surface area of 705 m² g⁻¹ and electrical conductivity of ~2x10⁶ S m⁻¹. These CMG materials delivered 135 and 99 F g⁻¹ in aqueous (5.5 M KOH) and organic (1M TEA BF₄ in acetonitrile) electrolytes, respectively. This study showed that the graphene material worked well with commercial electrolytes and its good electrical conductivity contributed to low equivalent series resistance (ESR). Yu et al. incorporated 1D carbon nanotubes (CNTs) to physically separate 2D graphene nanosheets. Polymer-modified graphene sheets were homogenously dispersed, and the resultant sheets were assembled sequentially with CNTs. The obtained hybrid films demonstrated gravimetric capacitance of 120 F g⁻¹ even at a high scan rate of 1 V s⁻¹, resulting from its well-defined nanoporous structure. In another approach, a three-dimensional (3D) mesoporous carbon spheres inserted between the layers of graphene sheets were used as supercapacitors by Lei et al. The mesoporous structure reduced the ion diffusion resistance and improved the electronic conductivity, which resulted in a high-rate capability of the supercapacitor. This electrode also showed capacity retention of ~94% after 1000 galvanostatic charge-discharge cycles. Xu et al. reported a hierarchical porous structure of a 3D holey graphene framework (HGF) as a high-performance free standing electrode for supercapacitor. This holey framework allowed high surface area (830 m² g⁻¹), high electron and ion transport, and high packing density. The as-prepared HGF delivered a high specific capacitance of 298 F g⁻¹ and volumetric capacitance of 212 F cm⁻³ at 1 A g⁻¹ in 1-ethyl-3-methylimidazolium tetrafluoroborate/acetoniitrile (EMIMBF₄/AN) electrolyte. Besides, some other methods have been proposed in the recent years to separate graphene sheets with nanomaterials and fabricate porous graphene frameworks to develop graphene-based high-performance supercapacitors. Among other Group IV elemental 2D materials, silicon has been investigated using density functional theory (DFT) and was shown that the quantum capacitance of silicon was larger than that of graphene due to the lower Fermi velocity near the Dirac point. Furthermore, the introduction of defects with doping could be utilized to increase the quantum
Figure 6. Structural and electrochemical characterization of phosphorene-graphene nanosheets (PG-MSCs) as a supercapacitor. a) TEM and b, c) HRTEM images of phosphorene exhibit uniform morphology and crystal lattice. The interlayer distance of 0.33 and 0.44 nm confirm the high-quality of exfoliated phosphorene. d) Cross-section SEM image shows small phosphorene nanosheets are uniformly distributed into large graphene sheets. e) Raman spectra of PG film reveals the crystalline nature of phosphorene and graphene. f) CV curves of PG-MSCs at different scan rates of 100-1000 mV s\(^{-1}\). g) Areal capacitance and h) volumetric capacitance of PG-MSCs and G-MSCs at different scan rates show the superiority of the layer-structured PG film for MSCs over planar MSCs (G-MSCs). Reproduced with permission \(^199\), Copyright 2017, American Chemical Society.

Phosphorene is the most experimentally studied supercapacitor material from Group V. One of the first studies on phosphorene as a supercapacitor electrode was reported by Hao et al.\(^200\) Authors liquid-exfoliated black-phosphorus (BP) nanoflakes and used as an electrode in polyvinyl alcohol/H\(_3\)PO\(_4\) (PVA/ H\(_3\)PO\(_4\)) electrolyte. The as-prepared electrode delivered a volumetric capacity of 17.78 F cm\(^{-3}\) at a scan rate of 0.005 V s\(^{-1}\). The charge/discharge curves showed superior EDLC behaviour of BP nanoflakes and 15.5% capacitance loss after 10000 cycles. Xiao et al. reported high-energy micro-supercapacitors (MSCs) where the electrode was fabricated by depositing phosphorene and graphene nanosheets (PG-MSCs) layer-by-layer \(^199\). The TEM exhibited uniform morphology of phosphorene
Figure 7. Structural characterization and electrochemical performance analysis of a graphene eggshell-filled graphene foam (GE@GF) as an anode in LIBs. a Schematic illustration of the graphene eggshell-filled graphene foam. b TEM images of graphene eggshell structure (scale bar = 500 nm). c HRTEM image of the red square in part b, showing crystalline shell with interlayer spacing of 0.34 nm (scale bar = 2 nm). d Raman spectroscopy shows two distinct peaks at $\sim 1580$ cm$^{-1}$ (G-band) and $2705$ cm$^{-1}$ (2D band). e Schematic illustration of the Li$^+$ intercalation into GE@GF. f GNSs shows the improved capacity GNSs electrodes. The GNSs electrodes show a broad electrochemical window (0–3.5 V). g Cycling performances of GE@GF and GF electrodes at the current density of 37 mA g$^{-1}$. g In-situ Raman spectra of GE@GF electrode discharged from 3.0 to 0.005 V vs Li/Li$^+$ (left) with details ranging from 0.25 to 0.005 V vs Li/Li$^+$ (right). Reproduced with permission 201, Copyright 2014, American Chemical Society.

nanosheets with interlayer spacings of 0.33 and 0.44 nm (Figure 6a-c). Cross-section SEM (Figure 6d) confirmed the uniform incorporation of phosphorene into the graphene nanosheets. The resultant electrode showed outstanding conductivity (319 S cm$^{-1}$) and energy density (11.6 mWh cm$^{-3}$). PG-MSCs delivered a high areal capacitance and volumetric capacitance of of $\sim 9.8$ mF cm$^{-2}$ and 37.5 F cm$^{-3}$, respectively at the scan rate of 5 mV s$^{-1}$ as shown in Figure 6(f-h). Recently, Zu et al. used phosphorene as a cathode in supercapacitors and showed a discharge capacitance of 3181.5 F g$^{-1}$ at a current density of 0.25 A g$^{-1}$ in 1 M H$_2$SO$_4$ and 0.5 M KI electrolyte 202. The capacitance retention was nearly 100% after 1000 charge/discharge cycles.

Antimonene was reported as an electrode material of a supercapacitor by Martínez-Periñán et al. 203 Antimonene demonstrated a high capacitance of 1578 F g$^{-1}$ at high current density of 14 A g$^{-1}$ in 0.5 M H$_2$SO$_4$. According to the authors, the high value of the capacitance was the result of both EDLC and Faradaic reactions.

Among other elemental 2D materials, borophene was reported to be used as an electrode in supercapacitors. Li et al. demonstrated that few-layer boron sheets produced via liquid-phase exfoliation showed promising performance as supercapacitor electrode materials 73. The DMF-exfoliated boron sheets showed a specific capacitance of 147.6 F g$^{-1}$ at a current density of 0.3 A g$^{-1}$ in 1-butyl-3-methylimidazolium hexafluorophosphate as the electrolyte and 88.7% capacitance retention after 6000 cycles. The high specific capacitance and good rate capability of the as-prepared supercapacitor were attributed to the excellent electronic conductivity and layer structure of the B sheets, which offered abundant active sites and fast access of electrolyte ions.

In general, only a limited number of elemental materials were reported as supercapacitor electrodes. The agglomeration of layers after exfoliation and instability in the atmosphere lower the number of active sites and electronic conductivity of the elemental materials, leading to the poor performance of the supercapacitors. Thus, future
studies are required to improve the architectures of the materials to enable efficient charge intercalation and deintercalation.

4.2 Rechargeable Batteries

In order to improve the performance of the future electronics and devices, rechargeable batteries must improve storage capacities. Besides, to adopt the advances in small, wearable, flexible electronics, the future energy storage devices must be light-weight and have high energy density. In this regard, elemental 2D materials are being considered as electrode materials in energy storage systems due to their large surface areas and form factor.

4.2.1 Graphene

4.2.1.1 Lithium-ion batteries (LIBs) Graphite is widely used in LIBs as anode material owing to its low voltage range and reasonable specific capacity (372 mAh g\(^{-1}\)) corresponding to the formation of graphite intercalation compounds (LiC\(_n\)) \(^{204}\). However, to improve the reversible capacity and stability of the LIBs, new electrode materials need to be developed. Graphene-based anode is considered a potential alternative as an anode in LIBs, because of its high specific surface area and superior electronic conductivity. \(^{111, 205}\) Li\(^+\) ions can intercalate on each side of the graphene sheet forming Li\(_x\)C\(_6\) and hence can provide a maximum theoretical capacity of 740 mAh g\(^{-1}\). \(^{206}\)

Large quantities of graphene nanosheets synthesized using chemical exfoliation were reported as anodes in LIBs by Wang et al. in 2009 \(^{207}\). The graphene nanosheets were evaluated in the potential range of 0.02 to 3.0 V at 1C rate and delivered a reversible capacity of 650 mAh g\(^{-1}\) in the initial cycle. The larger part of the specific capacity (>70 %) was below 0.5 V, which was attributed to the lithium binding on the basal plane of graphene nanosheets. The graphene anode showed a specific capacity of 460 mAh g\(^{-1}\) after 100 cycles exhibiting enhanced lithium storage than that of graphite anode. Similarly, graphene nanosheets (GNSs) were synthesized from artificial graphite (AG) by a fast heating process and ultrasonic treatment by Guo et al. \(^{208}\). The SEM showed the entangled GNSs with a curled and corrugated morphology of graphene. From XRD, it was found that the (002) peak of GNSs became weakened resulting in reduced crystallite size, which corresponded to formation of defects in GNSs. This was further confirmed by FTIR, which supported the presence of oxygen-functional group in GNSs. The as-prepared GNSs exhibited a reversible capacity of 672 mAh g\(^{-1}\) at 0.2 mA cm\(^{-2}\) which was almost twice the capacity of the AG. The enhanced performance of the GNSs was attributed to the storage of Li\(^+\) ion on both sides of the nanosheets along with the presence of functional groups and nanopores.

Goh et al. introduced graphene “eggshell” in LIBs \(^{207}\). They filled the void of graphene foam with curved graphene sheets, which after etching produced a graphene eggshell in graphene foam structure (GE@GF) as shown in Figure 7a. TEM images (Figure 7b-c) revealed thin graphene layers with crystalline shell structure. Raman spectrum (Figure 7d) analysis confirmed the presence of few-layer graphene in the hybrid GE@GF. The Li\(^+\) intercalation into GE@GF was presented by a schematic in Figure 7e. The electrochemical performance of the both electrodes exhibited that the initial coulombic efficiency increased from 66.3% for GF to 77.5% for GE@GF electrode. For GE@GF electrode, the first cycle reversible capacity after 45 cycles changed from 328 mAh g\(^{-1}\) to 368 mAh g\(^{-1}\), which was contributed to the interfacial storage of Li\(^+\) onto hollow graphene shell. In situ Raman spectroscopy (Figure 7f) showed the intercalation mechanism of Li\(^+\) into the Ge@GF electrode. The Raman showed that G-band gradually moved to higher wave number from 3.0 to 0.005 V vs Li/Li\(^+\), which indicated the doping of graphene by Li. The Li doping level reached its maximum level and disappeared at 0.14 V, which was the indication of formation of intercalation compound LiC\(_6\). According to this study, morphology control of the graphene foam by filling it with graphene sheets could improve the initial Coulombic efficiency of the unfilled graphene foam by 17%.

Functionalizing or doping of GNSs with nanomaterials is another approach to increase the storage capacity and stability of LIBs. Functional groups prevent the restacking of the of GNSs and thus presenting a large surface area for the electrolyte adsorption and immersion on the electrode materials. For example, Wang et al. grew Mn\(_3\)O\(_4\) on reduced graphene oxide (rGO) sheets for application in LIBs. The Mn\(_3\)O\(_4/rGO\) hybrid anode showed high capacity of 900 mAh g\(^{-1}\) at 40 mA g\(^{-1}\) \(^{209}\). This performance was achieved due to the intimate interaction of the Mn\(_3\)O\(_4\) nanoparticles with rGO sheets that made insulating Mn\(_3\)O\(_4\) particles electrochemically active. A similar strategy was adopted by Zhou et al. where graphene was produced by in situ reductions of iron hydroxide between graphene nanosheets \(^{210}\). The composite showed a high specific capacity of 1026 mAh g\(^{-1}\) at 35 mA g\(^{-1}\) after 30 cycles. The interleaved network of GNSs enhanced the electrical conductivity of the electrode as well as reduced the pulverization of the Fe\(_x\)O\(_y\) particles. As a result, the GNS/Fe\(_x\)O\(_y\) composite exhibited improved cycle stability and rate capability. The composite electrode exhibited 500 mAh g\(^{-1}\) at the current density of 700 mA g\(^{-1}\) after 100 cycles.

Besides, TiO\(_2\), Fe\(_x\)O\(_y\), CoO\(_x\), Li\(_x\)Ti\(_2\)O\(_4\), NiO, NiCo\(_2\)O\(_4\) have also been reported to make hybrid nanocomposites with graphene as advanced LIB anodes \(^{211-216}\). Jiang et al. introduced monolayer Mo\(_2\)S\(_3\) nanosheets with graphene aerogel to improve the electrochemical performance of LIBs \(^{217}\). The structural and morphological compatibility of Mo\(_2\)S\(_3\) graphene composite aerogels prevented the restacking and aggregation of Mo\(_2\)S\(_3\) and graphene nanosheets and exhibited a high reversible capacity of 1200 mAh g\(^{-1}\) at 100 mA g\(^{-1}\). Layered-by-layered Sn\(_x\)S\(_y\)/graphene hybrid nanosheets were fabricated by Xia et al. to improve the conductivity of Sn\(_x\)S\(_y\) \(^{218}\). Graphene acted as a buffer to suppress the volume change during lithiation/de-lithiation of Sn\(_x\)S\(_y\) leading to a high rate capability of 567.8 mAh g\(^{-1}\) at 2000 mA g\(^{-1}\).

4.2.1.2 Lithium-Sulfur (Li-S) batteries Because of high theoretical capacity (1675 mAh g\(^{-1}\)) and high energy density (2600 mAh g\(^{-1}\)), Li-S battery are regarded as high energy rechargeable battery. Li-S batteries utilize lithium as anode and sulfur as the cathode. However, due to the large volume expansion and dissolution of lithium polysulfides, Li-S battery shows poor kinetics. Introducing graphene into sulfur can accommodate the volume expansion and also provide high surface area and capacity \(^{219}\). Li et al. coated the sulfur with rGO to confine the polysulfides \(^{220}\). When the polysulfide anions diffused into the electrolyte, the rGO...
coating restricted the sulfur and polysulfide anions in the carbon framework, thus decreased the shuttling loss. As a result, a reversible capacity of 667 mAh g\(^{-1}\) at a high current density of 1.6 A g\(^{-1}\) after 200 cycles was achieved.

A graphene-coated mesoporous carbon/sulfur composite was introduced by Zhou et al.\(^{221}\). Mesoporous carbon acted as a buffer against the volume change of sulfur and provided an efficient diffusion path for Li\(^+\) ions during the charge/discharge process. The conductive rGO coating physically and chemically prevented the dissolution of polysulfides from the cathode as well as provided fast electron transport in the composite structure. The composite with 53 wt.% sulfur exhibited a reversible discharge capacity of 734 mAh g\(^{-1}\) after 100 cycles at 0.5 C. Another approach is to introduce polymer into sulfur in addition to graphene. The polymer acts as a buffer against the volume expansion and graphene provides the electrical conducting path. Sulfur composites with curved graphene (CG) and coated with polyaniline (PANI) was reported as a composite cathode for Li-S batteries by Li et al.\(^{222}\). The composite (CG-S@PANI) electrode delivered a specific capacity of 1300 mAh g\(^{-1}\) at 33.44 mA g\(^{-1}\). The combination of graphene and PANI coating provided an electronically conductive network that led to improved cyclic stability of the electrode.

In a different approach, Qiu et al. utilized nitrogen-doped graphene (NG) sheets as a matrix to wrap around sulfur particles.\(^{223}\) The highly conductive NG sheets with a large surface area significantly improved electronic conductivity. Besides, the self-generated curvature and wrinkles of the NG sheets facilitated electrolyte access throughout the structure and accommodated the volume change of S during charge/discharge. The Li/S@NG delivered a high specific discharge capacity of ~1167 mAh g\(^{-1}\) at 335 mA g\(^{-1}\) and showed excellent coulombic efficiency of 97% after 2000 cycles.

Ding et al. tailored the structure of GNSs with KOH to create dense nanorods on the surface of the sheets.\(^{224}\) Sulfur was uniformly distributed and confined within the nanorods and maintained intimate contact with the tailored GNSs. The nanorods served as ‘micro-reactors’ for the electrochemical reactions, which suppressed the diffusion of polysulfides, leading to improved cyclic stability. The resultant nanocomposites exhibited an initial reversible capacity of 1379 mAh g\(^{-1}\) at 0.2 C and after 100 cycles the capacity retention was 74% at 1C.

4.2.1.3 Na-ion batteries (SIBs) Similar to LIBs, graphene-based nanomaterials are promising electrode materials for energy storage in SIBs.\(^{225}\) A Na\(^+\) ion (1.02 Å) has a larger ionic radius than that of Li\(^+\) ion (0.76 Å), the electrode must possess large intercalation sites to diffuse large Na\(^+\) ions. Whereas graphite cannot accommodate Na\(^+\) ions, graphene can provide larger interlayer distances to store a larger number of Na\(^+\) ions.\(^{226, 227}\)

Wang et al. reported rGO as an anode in SIBs for the first time in 2013.\(^{226}\) The as synthesized rGO allowed significant Na\(^+\) ion insertion because of its large interlayer distances (~0.371 nm) and disordered structures. High magnification SEM images showed the layered, thin, and wrinkled structure of rGO as shown in Figure 8a. HRTEM images (Figure 8b-c) confirmed the thin layers with larger interlayers spacing than graphite. Raman spectrum further confirmed the presence of graphene sheets in Figure 8d. rGO anode showed a reversible capacity of 174.3 mAh g\(^{-1}\) at 40 mA g\(^{-1}\) after 250 cycles (Figure 8e). Besides, rGO yielded a specific capacity of 141 mAh g\(^{-1}\) at 100 mA g\(^{-1}\) over 1000 cycles (Figure 8f).

Graphene can also act as a buffer against volume expansion in SIBs and provide electrical conductivity to electroactive nanomaterials. Cha et al. reported nitrogen-doped graphene decorated with TiO\(_2\) as anode for SIBs.\(^{228}\) The nitrogen-doped graphene improved the electron transfer because of its high electrical conductivity. Nitrogen doping increased the wettability of electrode/electrolyte and porous graphene structure increased Na\(^+\) ion storage capacity. The as-synthesized TiO\(_2\)/nitrogen-doped open-pore channelled graphene (TNCG) composite as an anode delivered a high reversible capacity of 405 mAh g\(^{-1}\) at 50 mA g\(^{-1}\).

In another approach, Li et al. incorporated rGO to Fe\(_2\)O\(_3\), Fe\(_3\)O\(_4\) single crystallites of ~300 nm particle size were uniformly distributed on rGO nanosheets.\(^{229}\) The rGO provided a conductive network for electron transport and as well as the flexible matrix of rGO buffered the volume change during cycling. The uniform presence of Fe\(_2\)O\(_3\) on the rGO was confirmed by the Raman and the TEM images. In SIBs, this Fe\(_2\)O\(_3\)/rGO composite anode exhibited a very high reversible capacity of 610 mAh g\(^{-1}\) at 50 mA g\(^{-1}\), and a strong cycle ability with 82% capacity retention after 100 cycles.

Besides, several other metal oxides such as SnO, SnO\(_2\), CuO, Sb\(_2\)O\(_3\), Fe\(_2\)O\(_3\), Co\(_3\)O\(_4\), MoO\(_3\), V\(_2\)O\(_5\) distributed on the surface of graphene nanosheets have reported as anodes in SIBs.\(^{222, 230-238}\)
Figure 8. Structural characterization and electrochemical performance analysis of a graphene sheets (rGO) as an anode in SIBs. a High magnification SEM (at 70K) shows the rGO nanosheets with thin wrinkled structure of graphene layers. b The TEM exhibits the transparent nanosheets implying the presence of few layers with dark ripples of the sheets. c High resolution TEM (HRTEM) shows the interlayer spacings of the (002) planes are 0.365-0.371 nm at different area. d The Raman spectra of rGO nanosheets exhibit distinctive peaks of D band (1334.8 cm$^{-1}$) and G band (1603.4 cm$^{-1}$) for carbon material. e rGO nanosheets electrode in SIBs exhibits 174.3 and 93.3 mAh g$^{-1}$ respectively at 0.2 C (40 mA g$^{-1}$) and 1 C (200 mA g$^{-1}$) after 250 cycles. g. f rGO shows a good cycling performance delivering the capacity of 141 mAh g$^{-1}$ over 1000 cycles.

Sulfides/graphene composites have also been studied extensively as electrode materials in SIBs owing to their unique physical and chemical properties. David et al. reported a self-standing MoS$_2$/graphene electrode as an anode in SIBs. The composite electrode showed good cycling ability and a stable specific capacity of 230 mAh g$^{-1}$ at 25 mA g$^{-1}$ with efficiency reaching ~99%. Xie et al. synthesized SnS$_2$ nanoplatelet@graphene composite using a morphology-controlled hydrothermal method from L-cysteine. The as-synthesized nanocomposite delivered a high capacity of 725 mAh g$^{-1}$ at 20 mA g$^{-1}$ as an anode in SIBs. The graphene nanosheets provided electronic conductivity and acted as buffer for the SnS$_2$ nanoplatelets during Na$^+$ ion intercalation processes.

4.2.1.4 Potassium-ion batteries (KIBs) Because of abundancy in the earth’s crust, potassium (K) is another promising alternative to lithium for batteries. However, graphite intercalation compound KC$_6$ provide low capacity compared to conventional intercalation compound LiC$_6$ in LIBs.

The introduction of defects or doping sites into the carbon structure is an effective strategy to increase the performance of graphene in KIBs. Share et al. demonstrated that few-layered graphene doped with nitrogen (N-FLG) could increase the storage capacity of potassium to over 350 mAh g$^{-1}$, where the theoretical maximum of graphite was 278 mAh g$^{-1}$. This study showed that nitrogen doped FLG achieved improved performance compared to undoped FLG (Figure 9). The Raman spectra of N-FLG had multiple peaks including D and D', which were induced from nitrogen doping. TEM confirmed the layered structure of N-FLG with 5−25 layers as shown in Figure 9b. XPS showed the relative concentration of N was ~2.2 at% in the lattice (Figure 9c). There were four bonding configurations of nitrogen, among which 42.4% was pyridinic nitrogen (N-6), 33.6% was pyrrolic nitrogen (N-5), 14% was graphitic nitrogen (N-Q), and 10% was N−O as shown in Figure 9d. The storage capacity and coulombic efficiency of N-FLG were significantly improved over FLG. N-FLG demonstrated a cycling ability of 210 mAh g$^{-1}$ after 100 cycles at 100 mA g$^{-1}$ (Figure 9f).
Functional phosphorus and oxygen dual-doped graphene (PODG) was introduced by Ma et al. as the anode for KIB. They synthesized the PODG by thermal annealing of triphenylphosphine and graphite oxide precursors. A-synthesized PODG showed long cycling stability and delivered a capacity of 474 mAh g\(^{-1}\) at 50 mA g\(^{-1}\) after 50 cycles. This electrode also exhibited high rate capability of 160 mAh g\(^{-1}\) at 2000 mA g\(^{-1}\) after 600 cycles. Large interlayer spacing in the PODG, due to the introduction of phosphorus and oxygen, facilitated the K\(^+\) intercalation and delivered the superior electrochemical performance.

These studies demonstrate that by incorporating nanomaterials into graphene it is possible to overcome the limitations of graphene anodes in KIBs.

### 4.2.2 Silicene

Similar to graphene, silicene, with a honeycomb lattice, van der Waals (vdW) interlayer interactions, and high specific area, could serve as high-capacity anode material. First-principle calculations suggest that silicene does not suffer from irreversible structural changes and so volume change is small during lithiation/delithiation. The energy barrier for Li diffusion are smaller for silicene than that of bulk silicon. The Li diffusion energy barrier on monolayer silicene with zigzag edges can allow for up to 80 times faster diffusion among the various edge morphologies of monolayer and multilayer silicene.

Using DFT calculations, Xu et al. predicted the theoretical capacity of single-layer silicene could reach up to 1196 mAh g\(^{-1}\) for Li\(^+\) ion storage. But, silicon-based electrodes show severe capacity fading due to structural degradation and interfacial instability during lithiation and delithiation. To address the structural degradation and interface instability issues, Zhang et al. developed an intrinsically dual stabilized silicon building block, namely silicene flowers (SF).

In the as-synthesized silicene flowers, thin silicene nanoplates accommodated the volume change of Si which ensured the...
Figure 10. Structural characterization and electrochemical performance analysis of a silicene flower (SF) as an anode in a rechargeable battery. a Schematic illustration of SF synthesized by magnesiothermic reduction of silica fume at > 850 °C. The synthesized SF block provides three-dimensional electron transport channels and reduces Li\(^+\) ion diffusion length. b SEM image of shows the flower-like architecture of the SF with diameters ranging from ~1-10 µm. c TEM image reveals the interconnected nanoplatelets with interpenetrating pores (<20 nm) throughout the SF. d Raman spectrum of SF and silicon nanoparticle show an intense peak at 515 cm\(^{-1}\), which corresponds the honeycomb silicene lattice. e Cycling performance of the silicene flower and Si particles over 600 cycles reveals excellent cycling stability of the SF electrode at 2000 mA g\(^{-1}\). Reproduced with permission \(^\text{246}\), Copyright 2017, American Chemical Society.

In another approach, Shi et al. introduced graphene as a substrate with a silicene layer to prevent structural degradation during cycling \(^\text{247}\). Freestanding silicene and graphene-silicene superlattice were reported as an electrode in SIBs. The calculated theoretical capacities of 954 mAh g\(^{-1}\) for freestanding silicene and 730 mAh g\(^{-1}\) for the graphene-silicene were shown, which were higher than that of graphite. Besides, freestanding silicene showed an energy barrier of 0.16 eV for Na\(^+\) diffusion which was significantly lower than that of graphene.

Silicene has also been evaluated as potential cathode material in Li-S batteries. First-principle calculations showed that adsorption of lithium polysulfides (LiPS) on silicene was thermodynamically stable \(^\text{250}\). S atoms anchored on the silicon surface could provide a theoretical capacity of 891 mAh g\(^{-1}\) without dissolution and migration of LiPS during cycling \(^\text{251}\). This sulfur anchored silicene offered a
constructive way to implement sulfur-based cathode materials for Li–S batteries with improved electrochemical performance.

4.2.3 Germanene

Germanene is anticipated to show similar behaviour to graphene and silicene due to its comparable honeycomb structure and electronic properties. To find the compatibility of germanene as anode material, several first-principles calculations based on DFT have been proposed over the last decade. Sharma et al. suggested that the adsorption of Li atom at the hollow site of germanene was energetically favourable. The Bader charge analysis indicated ionic bonding between Li and Ge atoms and showed that the charge was transferred from adsorbed Li atom to germanene sheet. The calculated theoretical capacities for monolayer and bi-layer germanene were 369 mAh g\(^{-1}\) and 276 mAh g\(^{-1}\), respectively as anodes in LIBs.

Zhu et al. proposed a hybrid structure of germanene on a semiconducting MgX\(_2\) (X = Cl, Br, and I) substrate as an anode in LIBs, based on first-principles calculations. They showed that Li will not cluster and the presence of MgX\(_2\) increased the Li\(^+\) ion storage capacity of germanene (279 mAh g\(^{-1}\) on MgCl\(_2\)). Li\(^+\) diffusion energy barrier of 0.29 eV was obtained for the hybrid structures.

In a different approach, Zhao et al. reported methyl terminated germanene (GeCH\(_3\)) as an anode material for LIBs. They synthesized few-layer (4-5 nm thickness) GeCH\(_3\) nanosheets by liquid-phase exfoliation. A sandwiched GeCH\(_3\)/rGO nanocomposites were also prepared by adding rGO as a conductive agent. GeCH\(_3\) exhibited a high initial capacity of 1202 mAh g\(^{-1}\) at 0.2 A g\(^{-1}\). GeCH\(_3\)/rGO nanocomposite exhibited a capacity of 2516 mAh g\(^{-1}\) initially and 1058 mAh g\(^{-1}\) after 100 cycles at 0.2 A g\(^{-1}\). The introduction of methyl groups increased the interlayer spacing of germanene and improved the stability, whereas rGO increased the electronic conductivity.

As an alternate to LIBs, Bhuvaneswari et al. studied the electronic properties of bare and hydrogenated germanene (BGe and HGe) nanosheets using density functional theory in SIBs. The negative magnitude of the adsorption energies on Na\(^+\) on BGe and HGe indicated the strong surface assimilation of Na/Na\(^+\) on germanene nanosheet. The density of states (DOS) spectrum and adsorption energy confirmed the stability of the germanene sheets as anodes for SIBs.

These studies suggest that germanene nanosheets can be used as anode material in next generation metal-ion batteries and provide useful insights on how to evaluate germanene experimentally in the future.

4.2.7 Phosphorene

Phosphorene is one of the most promising elemental materials utilized as anode in metal-ion batteries. Due to its puckered structure, high electrical conductivity (~300 S m\(^{-1}\)), and low band gap, phosphorene are beneficial for both high energy and power densities.

Li et al. theoretically investigated the adsorption and diffusion behaviour of Li in both phosphorous and phosphorene. This study found that the diffusion energy barrier of Li\(^+\) in phosphorene was 0.08 eV along the zigzag direction, which was 10\(^2\)~10\(^3\) times faster than that of graphene. The calculated average voltage of phosphorene in LIBs was predicted to be 2.9 V, higher than the existing anode materials. Moreover, intercalation of Li changed the semiconducting phosphorene to metallic phosphorene, which increased the electrical conductivity of the phosphorene electrode.

Sun et al. introduced a hybrid material of few layer phosphorene placed between graphene layers as anode in SIBs. Here, the graphene layers acted as a buffer to volumetric expansion during cycling and also provided electrical paths, whereas the phosphorene layers offered a short path for Na\(^+\) ion diffusion during sodiation/dissodiation processes. As a result, a high specific capacity of 2,440 mAh g\(^{-1}\) at a current.
density of 0.05 A g⁻¹ was achieved, which was the 94% of theoretical capacity of phosphorus. In situ TEM and ex situ XRD techniques revealed the formation of a Na₃P alloy because of intercalation of Na⁺ ions into the phosphorene layers. In another study, these hybrid phosphorene/graphene anode in SIB delivered a high rate capability of 1120.6 mAh g⁻¹ at 5 A g⁻¹.²⁵⁸ Black phosphorus suffers from structural instability at ambient conditions, which limits the performance of phosphorus electrode for LIBs.²⁵⁹ Chowdhury et al. introduced h-BN to cap the black-phosphorene (Pn) and used it as an anode material in LIBs and SIBs. The binding energy of h-BN/black-Pn heterostructure with lithium and sodium were greatly improved. As a result, the heterostructure electrode suffered a low volume change during charge/discharge processes. The heterostructure also underwent a phase transition from semiconductor to metal during lithiation and sodiation. As a result, high specific capacities of 607 and 445 mA h g⁻¹ was achieved from h-BN-capped black-Pn electrode respectively, for LIB and SIB.

Han et al. systematically investigated phosphorene as an anode material using DFT for magnesium-ion batteries (MIBs).²⁶⁰ Their studies revealed that phosphorene bonded with Mg strongly in the cationic state. The diffusion energy barrier of Mg on phosphorene only 0.09 eV along the zigzag allowing fast and anisotropic diffusion of Mg⁺ ions. Therefore, the theoretical specific capacity of 865 mAh g⁻¹ was achieved with an average voltage of 0.833 V as an anode in MIBs.

Given these advantages of high capacity, cyclic stability, high ion mobility, and good electrical conductivity, monolayer phosphorene presents abundant opportunities as an anode material for metal-ion batteries.

4.2.4 Arsenene

Arsenene, as a monolayer arsenic sheet with a honeycomb structure, has lately been considered as electrode materials due to its electronic structure and high stability.²⁶¹,²⁶² To understand the electrochemical reactions that occur at arsenene electrodes, the cycling performance of arsenene has been investigated theoretically using density functional theory (DFT). High theoretical capacity, low
diffusion barrier, and low open-circuit voltage make arsenene a promising anode material for rechargeable batteries. Benzidi et al. employed DFT to investigate the interactions of Li, Na, and Mg ions with the arsenene monolayer to use it as an anode in metal-ion batteries. This study showed that the bonding of Li, Na, and Mg atoms with the arsenene monolayer was strong, which was beneficial for battery applications. The negative adsorption energies of Li, Na, and Mg ions on the valley sites were -2.55, -1.91, and -1.10 eV, respectively. Besides, arsenene showed high theoretical capacities of 1609.77, 1073.18, and 1430 mAh g\(^{-1}\) for Li, Na, and Mg respectively, which were higher than the capacity of commercial graphite (372 mAh g\(^{-1}\)) in LIBs. Besides, the diffusion energy barrier of the Li, Na, and Mg ions were calculated to be 0.16, 0.05, and 0.016 eV, respectively. In addition, Ab Initio Molecular Dynamics (AIMD) simulation showed that Li, Na, and Mg were reasonably stable at high temperatures (600 K).

Ye et al. reported insertion materials based on arsenene as alternatives to Mg metal anodes. Mg anodes suffer from pulverization and sluggish diffusion of Mg\(^{2+}\) ion. Ye et al. employed first-principles calculations to show that Mg-adsorbed arsenene systems had good energetic stability. Mg was adsorbed on monolayer/bilayer arsenene and arsenene/graphene heterostructure with adsorption energies of 0.82–2.48 eV, suggesting. Monolayer arsenene exhibited low barriers (0.08–0.33 eV) for Mg diffusion and ~3 times higher specific capacity (1429.41 mAh g\(^{-1}\)) than the bilayer arsenene (536.60 mAh g\(^{-1}\)) and arsenene/graphene heterostructure (409.90 mAh g\(^{-1}\)). Also, volume changes were <16% during the magnesiation process, suggesting a good cycling reversibility.

4.2.5 Antimonene

Antimonene is another recently discovered promising electrode material for rechargeable batteries. Because of its successful fabrication, excellent stability under ambient conditions, good electrical properties, and low price, antimonene is being considered for metal-ion adsorption. For example, Sengupta et al. reported ab-initio studies on the Li\(^+\) and Na\(^+\) adsorption of a free-standing monolayer antimonene properties. Their study showed that antimonene as an anode material in SIBs provided a specific capacity of 320 mAh g\(^{-1}\) with a small diffusion barrier of 0.114 eV for Na atoms. For Li ions, antimonene provided a lower specific capacity of 208 mAh g\(^{-1}\) and also a higher diffusion barrier of 0.38 eV for Li atoms. The calculated high capacity and good Na\(^+\) diffusion can also be favourable for Na-air batteries and supercapacitors.

Su et al. showed that nano-scale modification is an alternative strategy to improve the cycling performance of Sb in LIBs. They systematically investigated Li adsorption of monolayer antimonene using first-principles calculations based on vdW corrected DFT. β-phase monolayer antimonene with buckled hexagonal structure was selected for their calculation because of its higher thermodynamic stability as shown in Figure 12a. The authors considered four typical adsorption sites (H, T\(_1\), T\(_2\), and B) for single Li atom, and showed that H, T\(_1\), and T\(_2\) had stable and favourable sites for Li adsorption (Figure 12b). A calculation was shown for the change in adsorption energy and Bader charge with respect to Li concentration in Li\(_2\)Sb. The adsorption energies increased form 1.70 eV to 1.91 eV revealing strong adsorption of Li on antimonene at high Li concentration. Furthermore, almost constant Bader charge of Li suggested formation of strong ion bonds at all concentration of Li atoms. A fast diffusion of Li atom on antimonene was observed with a low energy barrier of 0.20 eV, whereas for bulk Sb the energy barrier was 1.73 eV (Figure 12c). Antimonene also suffered relatively small volume change during lithiation, which could improve the cycling ability of the antimonene in LIBs. Gao et al. utilized tailored engineering to exfoliate β-phase antimonene from bulk Sb, and evaluated experimentally as anode in LIBs. Using ultrasonication with different power intensities, two types of tailored engineering, vertical direction and omnidirectional, were used to produce 2D antimonene and Sb nanoparticles (NPs). Both antimonene and antimony NPs exhibited stable electrochemical performances. Antimonene delivered 584.1 mAh g\(^{-1}\) and Sb NPs delivered 552.3 mAh g\(^{-1}\) after 100 cycles with the coulombic efficiencies close to 100% at 330 mA g\(^{-1}\), whereas the capacity of bulk Sb dropped significantly after 20 cycles. At higher current density of 3300 mA g\(^{-1}\), antimonene exhibited a capacity of 488 mAh g\(^{-1}\), which also indicated its excellent high rate capability. Theoretical simulation revealed that Li\(^+\) ion diffusion energy barrier for β-phase antimonene was 0.25 eV, which was smaller than the diffusion energy barrier (1.14 eV) of antimony. As a result, antimonene with large dimension could provide cycling stability and high rate capability for LIBs, compared to the bulk counterparts.

In another study, Wang et al. introduce graphene to antimonene to overcome volume expansion and structural degradation of alloy Sb during lithiation. They first-principle calculation results revealed that the graphene/antimonene (G/Sb) heterostructure had negligible band gap of 0.06 eV, which was smaller than that of monolayer β-antimonene (1.24 eV). Thus, introducing graphene ensured high conductivity and fast electron transport in the G/Sb electrode during charge/discharge process. Also, the volume expansion of the Li adsorbed G/Sb heterostructure was 1.2%, whereas it was 15% for monolayer β-antimonene. These results provided a good argument for the G/Sb heterostructure as an anode for LIBs.

Tian et al. evaluated Na\(^+\) storage properties of 2D few-layer antimonene (FLA) in situ synchrotron XRD and ex situ selected-area electron diffraction (SAED) showed that the FLA...
underwent a phase evolution during cycling which was completely reversible (Sb ≈ NaSb ≈ Na₃Sb). The calculated Na⁺ diffusion energy barrier for FLA was 0.14 eV, which was smaller than graphene (0.22 eV). Due to this, the FLA maintained a stable capacity of 620 mA g⁻¹ at 66 mA g⁻¹ and showed a high rate capability of 429 mAh g⁻¹ at 3300 mA g⁻¹. Comparing to the theoretical capacity of Sb (660 mAh g⁻¹), the FLA offered excellent potential as anode in SIBs.

In another study recently, the adsorption of Na atom in β-antimonene was studied by Upadhyay et al. 268. Using first-principles calculation they showed the semiconducting antimonene could obtain metallic nature after Na adsorption, leading to better conductivity and charge transfer in β-antimonene. The antimonene electrode was expected to be stable during sodiation. The study predicted that monolayer antimonene could adsorb three layers of Na providing maximum specific capacity of 421.63 mAh g⁻¹. These results suggest that elemental antimonene can be an interesting candidate as anode material for rechargeable batteries with a large specific capacity, less volume expansion, low diffusion barrier, excellent rate capability, and long cycling performance.

### 4.2.6 Borophene

After its successful synthesis, recently 2D borophene has been of interest as electrode for metal-ion batteries due to its puckered structure and metallic characteristics 269. Mainly, theoretical or first-principles calculations are utilized to investigate the potential of borophene as an anode material for metal-ion batteries. The adsorption energy of a single lithium atom on borophene was found to be −1.12 eV, which was enough to ensure stability during the intercalation/deintercalation 270. The fully lithiated Li₀.75B phase of borophene had a Li adsorption energy of −0.06 eV/atom. This study by Jiang et al. showed that Li₀.75B corresponded to a theoretical specific capacity of 1860 mAh g⁻¹. In addition, the diffusion energy barrier of 2.6 eV allowed faster diffusion of Li atoms along the path of corrugated borophene. AIMD simulations at 300 K also proved that the lithium atom could freely move along the path. More importantly, the metallic nature of borophene was unchanged during the whole lithiation process maintaining excellent electronic conductivity.

Zhang et al. reported that borophene could be ideal for both Li⁺ and Na⁺ adsorption by using first-principles calculations 74. They showed that borophene maintained metallic characteristics and thus good electric conductivity during both lithiation and sodiation. Besides, the small diffusion energy barrier of ~0.3 eV for Na⁺ corresponded to...
Table 1 - Performance of elemental 2D materials as electrodes in various EES systems.

| Materials                        | EESS, Electrolyte chemistry | Voltage range (V) | Performance[a] | Ref  |
|----------------------------------|-----------------------------|-------------------|----------------|------|
| Vacuum-assisted graphene         | SC, EMIMBF₄                 | 0.01-4.0          | 284.5 F g⁻¹/1 A g⁻¹ | 271  |
| Hydrogen-annealed graphene       | SC, EMIMBF₄                 | 0.1-4.0           | 306.03 F g⁻¹/1 A g⁻¹ | 272  |
| B-doped graphene                 | LIB, 1 M LiPF₆ in EC:DEC (1:1) | 0.01-3.0          | 1227/30/50     | 273  |
| Functionalized graphene framework| LIB, 1 M LiPF₆ in EC:DMC:EMC (1:1:1) | 1.5-4.5          | 344/200/50     | 274  |
| I-doped graphene                 | LIB, 1 M LiPF₆ in EC:DEC (1:1) | 0.01-3.0          | 1565/200/100   | 275  |
| N, F- Codoped Reduced Graphene   | LIB, 1 M LiPF₆ in EC:DEC:EMC (1:1:1) | 0.01-3.0          | 344/500/2000   | 276  |
| Binder-free graphene             | LIB, 1 M LiPF₆ in EC:DMC (1:1) | 0.01-3.0          | 500/100/100    | 277  |
| Single-layered graphene          | SIB, 1 M NaPF₆ in EC:DEC (1:1) | 0.003-2.8         | 15.9/20/5⁰     | 278  |
| Crumpled graphene paper          | SIB, 1 M NaClO₄ in PEC      | 0.005-2.5         | 125/500/1000   | 279  |
| N-doped graphene sheets          | SIB, 1 M NaPF₆ in EC:DMC (1:1) | 0.01-3.0          | 155.2/260/50   | 280  |
| N- and S-doped graphene sheets   | SIB, 1 M NaClO₄ in EC:PC:FEC (1:1:0.02) | 0.01-3.0          | 289/100/100    | 281  |
| Material Type                  | Electrolyte       | Current Density | Capacity (mAh g\(^{-1}\)) | | | |
|-------------------------------|-------------------|----------------|-----------------------------|---|---|---|
| N-Doped Graphene              | KIB, 0.8 M KPF\(_6\) in EC:DEC (1:1) | 0.01-1.5 | 210/100/100 |
| Activated-crumpled graphene   | KIB, 0.8 M KPF\(_6\) in EC:DEC (1:1) | 0.01-3.0 | 245/2800/500 |
| P, O-codoped graphene         | KIB, 0.8 M KPF\(_6\) in EC:DEC (1:1) | 0.01-3.0 | 160/600/2000 |
| Silicene sheets               | LIB, 1 M LiPF\(_6\) in EC:DMC (1:1) | 0.05-3.0 | 149/10/50 |
| Silicene flowers              | LIB, 1 M LiPF\(_6\) in EC:DEC (1:1) with 5% FEC | 0.01-2.0 | 1100/600/2000 |
| Germanene/rGO                 | LIB, 1 M LiPF\(_6\) in EC:DMC; DEC (1:1:1) with 2% FEC | 0.01-2.0 | 1058/100/200 |
| Hydrogenated germanene        | LIB, 1 M LiPF\(_6\) in EC:DMC (1:1) | 0.01-2.5 | 341/100/1 C\(^{\circ}\) |
| Phosphorene                   | Supercapacitor, 1 M H\(_2\)SO\(_4\) | 0.01-0.8 | 684.3 F g\(^{-1}\)/2.5 A g\(^{-1}\) |
| Phosphorene-graphene          | LIB, 1 M LiPF\(_6\) in EC:DMC (1:1) | 0.01-3.0 | 432/800/500 |
| Phosphorene-graphene          | SIB, 1 M NaClO\(_4\) in PC with 5% FEC | 0.02-1.5 | 1582.6/100/1000 |
| Few-layer phosphorene         | SIB, 1 M NaClO\(_4\) in PC with 5% FEC | 0.02-1.5 | 603.3/100/1500 |
| Antimonene/SPE                | SC, 0.5 M H\(_2\)SO\(_4\) | 0.01-3.0 | 1578 F g\(^{-1}\)/14 A g\(^{-1}\) |
| Antimonene/Mxene              | SC, 1 M H\(_2\)SO\(_4\) | 0.01-2.0 | 827.56 F cm\(^{-3}\)/0.2 mA cm\(^{-2}\) |

*The cycling data are in the following form: specific capacity (mAh g\(^{-1}\))/cycle number/current density (mA g\(^{-1}\)). \(^{\circ}\) Capacity is in \(\mu\)Ah cm\(^{-2}\). \(^{\circ}\) C-rate. EMIMBF\(_4\), 1-ethyl-3-methylimidazolium tetrafluoroborate; EC-ethylene carbonate; PC-polypropylene carbonate; DEC-diethyl carbonate; DMC-dimethyl carbonate; FEC-fluoroethylene carbonate.
Theoretical specific capacity of 1984 mAh g\(^{-1}\) in \(\beta_{12}\) borophene and 1240 mAh g\(^{-1}\) in \(\chi_{0}\) borophene. It was found that, the average open-circuit voltage of 0.53 V during sodiation/dissodiation could effectively inhibit dendrites formation, and thus increasing the energy density.\(^{289}\)

Introducing vacancy defects or doping can further enhance the metallic nature of the borophene. Lie et al. showed that a vacancy in the puckered structure of the borophene could introduce a dangling bond, and thus increase the Fermi level significantly.\(^{290}\) As a result, the metallic characteristics of the borophene became more prominent and excellent electrical conductivity was achieved. However, the defects in borophene weakened the Na\(^+\) adsorption on the surface. So, it is essential to control the generation of defects during synthesis of borophene material.

Given these advantages, borophene is considered to be a promising anode material for both LIBs and SIBs with high power density.

Borophene has also been studied as an anchoring material for sulfur cathodes in Li-S batteries.\(^{291, 292}\) Borophene can effectively adsorb lithium polysulphides that are formed during discharge cycles and suppress the shuttle effect, resulting in improved utilization of active material. Due to high electrical conductivity and small deformation of borophene, borophene is a helpful host to S cathode during charge/discharge processes. Particularly, defective borophene showed moderate adsorption energies of 1-3 eV. As a result, defective borophene could effectively suppress the shuttle effect, and also maintain the shape of their structures during cycling. According to these results, it is expected that borophene can also be a favourable anchoring material for Li-S batteries.

The performances of elemental 2D materials as electrodes in various ESSS are presented in Table 1.

### 5 Electrochemical applications beyond energy storage

#### 5.1 Electrochemical sensing

Pristine graphene and its derivatives have been experimentally proven to have high sensitivities to various gas molecules. The 2D structure of graphene nanosheets ensures superior chemical sensing performance, such as high sensitivity and low noise, due to high electron mobility and conductance at room temperature, high surface-to-volume ratio, and less crystal defects.\(^{115}\) The extreme sensitivity of a single electron charge (or low concentration < 1 ppb) is achievable with graphene at room temperature.\(^{115, 298}\) In 2007, Schedin et al. prepared graphene microfabricated devices via micromechanical cleavage of graphite to detect various common gases (NO\(_2\), NH\(_3\), H\(_2\)O, and CO). Their study successfully demonstrated the ultra-high sensitivity and fast response of graphene sensor functionality and highlighted linear response to the concentration of adsorbates.\(^{115}\) Other researchers have investigated several more common or organic gases (e.g., H\(_2\), Cl\(_2\), CO\(_2\), \(\text{CH}_3\text{OH}\), \(\text{CH}_2\text{OH}\), \(\text{CH}_3\text{O}\), \(\text{CHCl}_3\), \(\text{CH}_3\text{CN}\)) that are detectable via pristine graphene or rGO. Improved sensitivity or enrichment of adsorbates types can be achieved by surface functionalization (doping with nanoparticles) at the surface or by the introduction of defects to the pristine graphene sheets.\(^{298}\)

Graphene-related studies fulfill the significant demand to develop gas sensors for extremely toxic compounds. Current research focus has extended to other graphene-like 2D materials since pristine graphene is unable to detect some toxic gases and common gases. Other elemental 2D materials have recently been proposed and synthesized. Although experimental studies on novel 2D materials have been limited to fundamental investigations of physical or chemical properties, numerous computational studies, especially DFT simulations, have predicted the gas-sensing properties of graphene-like materials. The working principle of elemental 2D materials as gas sensors shares common factors with graphene and its well-known Dirac fermions. For example, silicene and germanene, which consist of Group IV elements, have similar (to graphene) Dirac cone structures and tiny band gaps at the Dirac points. Once gas molecules are chemically adsorbed, charge-transfer occurs, leading to the band gap opening at the Dirac points and the change of certain electrical properties, such as conductance.\(^{115}\) The working principle of gas sensing is presented in Figure 13. The amount of opening is related to the number of molecules adsorbed, which enables highly accurate concentration measurements. This “band-gap engineering” often converts the material to a p-type or n-type semiconductor sensor. Elements from different groups, such as \(\text{B_{12}}\) borophene with a graphene-like monolayer structure and hexagonal vacancy at the center of the structure, follows the same principle.

![Gas sensing](Image)

**Figure 13. Working principle of gas sensing (left) and catalysis (right) of elemental 2D materials.** Inspired from ref.\(^{115, 288}\)
5.2 Catalysis

Electrochemical catalysis is another potential application for elemental 2D materials. The water-splitting reaction, which has been widely studied to produce a clean, renewable energy source, is governed by two core reactions, the hydrogen evolution reaction (HER) and the oxygen reduction reaction (ORR), that both require high catalytic performance.\(^2\)\(^9\)\(^\) Because graphene has high electron conductivity and surface-to-volume ratio and is conventionally used as a carrier of other 2D or nanoparticle catalysts, Xie et al. proposed a fabrication method of pristine graphene single-layer and bi-layer electrodes on an SiO\(_2\) wafer for a catalysis application.\(^2\)\(^8\) The prepared electrodes showed stable HER catalytic performance for as long as 20 hours. The results suggest stability but less performance than highly oriented pyrolytic graphite. Due to the high chemical stability of pristine graphene, catalysts may not be able to deliver a better performance than Pt-based or other metallic catalysts without doping. However, the development of metal-free HER catalysts still provides beneficial abundance, durability and cost-effectiveness.\(^2\)\(^9\),\(^3\)\(^0\)

The catalytic activities of novel elemental 2D materials are limited to first-study stages such as gas-sensing applications. Gas adsorption investigations have provided some predictions of catalytic behavior.\(^3\)\(^0\),\(^3\)\(^2\) Catalytic behavior is primarily related to the adsorption and disassociation of certain elements (or chemical groups) on the surface of a 2D material, as shown in Figure 13. For example, in computational studies, hydrogenation of CO\(_2\) is achieved via H\(_2\) disassociation and CO\(_2\) adsorption at the surface of silicene.\(^3\)\(^3\) However, adsorbed CO\(_2\) can eventually form carboxylic (COOH) species through multistep reactions with H species. The reduction of nitrobenzene (PhNO\(_2\)) silicene to aniline (PhNH\(_2\)) depends on N-O adsorption and disassociation.\(^3\)\(^3\)

Another type of catalytic activity is predicted from the photocatalytic property of semiconductors for HER or ORR.\(^3\)\(^4\) As mentioned, the band-gap engineering of Dirac materials (silicene or germanene) can alter the redox potentials of the material to reach an optimum position between conduction band minimum and valence band maximum.

| Elemental 2D | DFT functionals + basis set | Adsorbates | Adsorption energy, Ea (eV) | Band gap, Eg (meV) | Ref |
|-------------|-----------------------------|------------|-----------------------------|-------------------|----|
| Borophene   | B3LYP + 6-31G(d)             | NO\(_2\)   | -2.32                       | -                 | 305 |
|             | B3LYP + 6-31G(d)             | NO         | -1.79                       | -                 | 305 |
|             | B3LYP + 6-31G(d)             | NH\(_3\)   | -1.75                       | -                 | 305 |
|             | B3LYP + 6-31G(d)             | CO\(_2\)   | -0.36                       | -                 | 305 |
|             | B3LYP + 6-31G(d)             | CO         | -1.38                       | -                 | 305 |
| B\(_{36}\)  | B97D + 6-31G(d)              | HCOH       | -10.5 ~ -1.2                | 360 ~ 980         | 306 |
| B\(_{36}\)  | B97D + 6-31G(d)              | HCN        | -0.55 ~ -0.50               | -                 | 307 |
| Silicene    | GGA-PBE                      | NO\(_2\)   | -1.53, -1.12                | 173, 168          | 308 |
|             | GGA-PBE                      | NO         | -0.57                       | 103               | 308 |
|             | GGA-PBE                      | NH\(_3\)   | -0.60 ~ -0.24               | 79 ~ 471          | 308 |
|             | GGA-PBE, BLYP + LANL2DZ      | CO         | -0.99, -0.63                | -                 | 309 |
|             | GGA-PBE                      | SO\(_2\)   | -1.08                       | -                 | 310 |
|             | GGA-PBE                      | H\(_2\)S   | -0.212                      | -                 | 310 |
| Germanene   | GGA-PBE                      | CO\(_2\)   | -0.42                       | -                 | 311 |
|             | GGA-PBE                      | SO\(_2\)   | -1.56                       | 140               | 311 |
|             | GGA-PBE                      | H\(_2\)S   | -0.58                       | 40                | 311 |
| Phosphorene | GGA-PBE                      | NO\(_2\)   | -0.63                       | -                 | 312 |
|             | LDA                          | NH\(_3\)   | -0.50                       | -                 | 312 |
|             | LDA                          | CO\(_2\)   | -0.41                       | -                 | 312 |
|             | LDA                          | CO         | -0.33                       | -                 | 312 |
| Arsenene    | GGA-PBE                      | NO\(_2\)   | -0.44                       | -                 | 313 |
|             | GGA-PBE                      | SO\(_2\)   | -0.34                       | -                 | 313 |
|             | GGA-PBE                      | NO         | -0.15                       | -                 | 314 |
|             | GGA-PBE                      | NH\(_3\)   | -0.16                       | -                 | 314 |
|             | GGA-PBE                      | N\(_2\)    | -0.13                       | -                 | 314 |
|             | GGA-PBE                      | CO\(_2\)   | -0.33                       | -                 | 314 |
|             | GGA-PBE                      | CO         | -0.23                       | -                 | 314 |
| Antimonene  | GGA-PBE                      | NO\(_2\)   | -0.813                      | -                 | 315 |
|             | GGA-PBE                      | NO         | -0.416                      | -                 | 315 |
Conclusions

In conclusion, as mitigation of global greenhouse gas emission becomes a primary target, the development of robust, reliable, and economically feasible EESSs achieves greater significance. Layered materials have shown promise to seamlessly overcome the drawbacks of conventional systems and advantageously impact EESSs. Because these materials have large interlayer spaces, improved electronic transport properties, and structural stability, they not only improve the performance and kinetics of existing state-of-the-art LIB systems, but they also provide reasonable and stable performances for systems that place excessive demands on electrode systems due to large ions, such as SIB and KIB systems. Due to their relatively low costs, these novel ESSs, (e.g., SIB and KIB systems) offer potential electrical energy storage at the grid scale (MWh to GWh); therefore, application of layered materials as electrodes may quickly facilitate the transition to large-scale smart grid storage.

Unlike graphene and TMDs, research on many mono-element 2D materials is still in its infancy. Many factors must be optimized, especially synthesis and successful scaling up, before mono-element 2D materials can be fully manifested in practical devices and EESSs. A significant quantity of research is being devoted, therefore, to increasing understanding of the properties of these novel 2D materials, specifically phosphorene, antimonene, and silicene. However, considerable bottlenecks exist before they can be successfully commercialized, such as the successful scaling up of the synthesis for electrochemical applications, elucidating their structure-property relationships, and the systematic study of these materials for electrochemical, catalytic, and sensing applications. First step towards the large-scale synthesis of elemental 2D materials would be to understand these materials at a fundamental level with more reliable and low-cost technologies. Secondly, strategies should be developed to mitigate the degradation of the materials and ensure long-term stability of these materials in the environment. Finally, systematic studies should be carried out to establish a reliable statistical approach to understand the relationship and benefit of elemental 2D materials relative to its 3D counterpart. Greater innovation and research will lead to widespread deployment of these materials and help improve global energy.

Conflicts of interest

There are no conflicts to declare.

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