Recent Advances in 2D Heterostructures as Advanced Electrode Materials for Potassium-Ion Batteries

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Owing to the cost-effectiveness, Earth abundance, and suitable redox potential, potassium-ion batteries (PIBs) stand out as one of the best candidates for large-scale energy storage systems. However, the large radius of K⁺ and the unsatisfied specific capacity are the main challenges for their commercial applications. To address these challenges, constructing heterostructures by selecting and integrating 2D materials as host and other materials as guest are proposed as an emerging strategy to obtain electrode materials with high capacity and long life-span, thus improving the energy storage capability of PIBs. Recently, numerous studies are devoted to developing 2D-based heterostructures as electrode materials for PIBs, and significant progress is achieved. However, there is a lack of a review article for systematically summarizing the recent advances and profoundly understanding the relationship between heterostructure electrodes and their performance. In this sense, it is essential to outline the promising advanced features, to summarize the electrochemical properties and performances, and to discuss future research focuses about 2D-based heterostructures in PIBs.

1. Introduction

Renewable and sustainable energy sources, like solar, wind, geothermal, hydropower, wave, and tidal power, are essential to address the ever-increasing challenges in energy consumption and environmental deterioration. At the same time, the optimal use of electricity generated from these intermittent energy resources requires the development of large-scale and low-cost stationary energy storage systems. Currently, considerable efforts are devoted to developing stationary energy storage systems based on potassium-ion batteries (PIBs), owing to the specific advantages of PIBs compared with lithium-ion batteries (LIBs) (Figure 1a). First of all, the high abundance and low cost of potassium resources make PIBs more cost-effective than LIBs. Second, a suitable reduction potential of potassium (−2.93 V vs. standard hydrogen electrode [SHE] for K⁺/K is close to −3.04 V vs. SHE for Li⁺/Li) enables a similar operating voltage to LIBs, thus assuring a high energy density. Third, attributed to the small Stokes radius of solvated K⁺, it will facilitate the rapid shuttle of K⁺ in electrolytes. Among candidates of host materials for K⁺ insertion/extraction processes, Ti3C2Tx MXenes exhibit a poor ion diffusivity in solid-state electrodes, resulting in slow K⁺ reaction kinetics and unsatisfactory rate performance of PIBs. Meanwhile, the insertion/extraction of large K⁺ causes large volume variations and thereafter pulverization of electrode materials, leading to the low cycling stability of PIBs.

To this end, it is critical to use host materials that have the superior capability to reversibly store amounts of K⁺ and sufficient structural stability to withstand the repeated potassiation/depotassiation processes.

Among candidates of host materials for K⁺ insertion, 2D materials have drawn remarkable interests, and they mainly include elemental 2D materials (such as graphene and phosphorene) transition metal carbides/nitrides (MXenes, such as Ti3C2 and Ti3C2N), transition metal dichalcogenides (TMDs, such as MoS2, MoSe2, and WS2), and transition metal oxides (TMOs) with layered structures (such as V2O5 and MoO3) (Figure 1b,c). Their unique layered structure provides short ion-diffusion channels for rapid K⁺ transportation and their large surface areas offer abundant active sites for K⁺ adsorption. Moreover, the interlayer weak van der Waals (vdW) forces endow 2D materials with good mechanical flexibility, which can accommodate large K⁺ without deteriorating the structural integrity of the electrode during the K⁺ insertion/extraction processes. However, till now, none of these 2D materials yet have exhibited fully satisfactory capabilities for K⁺ storage. For example, the surface-dependent charge storage mechanism restricts the limited capacity of graphene-based materials. For TMDs, a changeable charge storage mechanism from intercalation to conversion reaction undergoing the first discharge cycle leads to poor capacity retention of TMDs. With respect to TMOs, the rate performance is mainly limited by the poor electronic conductivity of TMOs. For MXenes, the reversible capacity varies with the alternation of surface functional groups inherently incorporated during the MXenes synthesis process. So far, various strategies have been proposed to solve these aforementioned
issues, and the representative ones include expanding layer spacing, creating structural defects, fabricating porous structures, constructing heterostructures, and surface/interface engineering. In particular, constructing heterostructures based on different 2D materials as host and other materials as guest (depicted as 2D-based heterostructures) is a highly effective strategy because 2D-based heterostructures can offer the opportunity to combine the advantages of 2D materials and meanwhile eliminate the disadvantages of individual counterparts. Up to now, many 2D-based heterostructures with different compositions and morphologies have been designed, fabricated, and investigated as electrode materials for improving the energy storage performance of PIBs.

Given the rapid progress in the past few years, a timely summary in the field of 2D-based heterostructures for PIB applications has to be conducted. Herein, we provide a comprehensive review of recent advances in developing 2D-based heterostructures as electrode materials for PIBs. We first summarize the advanced properties of 2D-based heterostructures for PIB applications. By highlighting some typical examples (mainly including graphene-based, MXenes-based, TMD/TMOs-based heterostructures), we then introduce the main characteristics of 2D-based heterostructures for K⁺ storage and emphasize their synergic effects on optimizing electrochemical performance. Finally, we also provide an outlook on challenges and perspectives associated with 2D-based heterostructures for future PIB applications.

2. Advanced Features of 2D-Based Heterostructures for PIBs

Owing to the unique physicochemical properties, 2D-based heterostructures have been widely investigated as building blocks for future (opto-)electronics and as advanced catalysts for (photo-)electrocatalysis. Likewise, constructing 2D-based heterostructures is also revealed to provide unprecedented potentials for boosting the electrochemical performance (i.e., capacity, rate capability, and stability) of 2D materials as electrode materials for PIBs. As shown in Figure 2, many 2D materials have been assembled with other materials (e.g., 0D, 1D, 2D, or 3D) via either weak interstratification (vdW force or electrostatic attraction) or covalent bond to form 2D-based heterostructures. When integrating host 2D materials with guest functional materials, the as-obtained 2D-based heterostructures will possess enlarged interface contact and increased interlayer distance. The enlarged interface contact offers more electrochemical active sites for K⁺ storage, while the increased interlayer distance in heterostructures ensures rapid diffusion of K⁺ and compensates structural changes during the K⁺ insertion/extraction process. Moreover, due to the lattice constant differences between host 2D materials and guest functional materials, vacancies and/or distortions will be generated at the heterointerfaces in 2D-based heterostructures, which will provide additional active sites for K⁺ storage. Besides the difference
in the lattice constant, host 2D materials and guest functional materials generally have different energy bandgaps. Both theoretical and experimental studies suggest that the difference in their energy bandgaps will generate a built-in electric field in heterostructures. This additional electric field can facilitate the rapid transportation of electrons in the electrodes during the K⁺ insertion/extraction process, which enhances the charge transfer kinetics. Moreover, the existence of a built-in electric field in the heterostructures will also result in the redistribution of charges at the heterointerfaces, which further improves the conductivity of the heterostructures. In addition, constructing heterostructures is also an effective way to avoid restacking and agglomeration of 2D materials during the charging and discharging process. Attributed to these advanced features mentioned earlier, various 2D-based heterostructures consisting of different compositions and with different morphologies have been designed, synthesized, and studied as electrode materials for PIBs (Figure 2). By optimizing the compositions and morphologies of 2D-based heterostructures, it will offer the opportunity to further maximize the K⁺ storage of 2D-based heterostructures.

3. Electrochemical Performance of 2D-Based Heterostructures for PIBs

3.1. Graphene-Based Heterostructures

As known, there are many forms of carbon materials, such as graphite, graphene, hard carbon, and soft carbon materials. Among them, graphite with a theoretical specific capacity of 279 mAh g⁻¹ (corresponding to the formation of KC₈) and a low working voltage (<0.4 V vs. K/K⁺) has attracted considerable interest as PIB anode materials. So far, some strategies have been developed to further improve the capacity of graphite for PIBs. For example, bulk graphite has been exfoliated into monolayer or a few layers of graphene to provide more active sites on the sides of the graphene layer or functionalized graphene layer and finally delivers a high specific capacity over 350 mAh g⁻¹. However, the aggregation of graphene with monolayer or a few layers will lead to the reduction of active sites for K⁺ absorption. To this end, constructing graphene-based heterostructures is proposed to enhance K⁺ storage performance. This strategy could effectively prevent the stacking of graphene and enable to enhance the capacity by

Figure 2. Scheme of different kinds of 2D-based heterostructures constructed by assembling host 2D materials with guest 0D, 1D, 2D, or 3D materials for the enhanced PIB performance.
combining with high theoretical specific capacity materials, such as Sn (660 mAh g\(^{-1}\)) and SnS\(_2\) (733 mAh g\(^{-1}\)).\(^{[61,76-78]}\)

As is known, the small size of nanodots and nanoparticles can reduce the ion diffusion length; thus, Wu and co-workers proposed the fabrication of 2D–0D heterostructures to shorten the ion diffusion length and improve the electrochemical performance.\(^{[62]}\) They constructed heterostructures consisting of SnSb\(_2\)Te\(_4\) nanodots and few-layer graphene (SnSb\(_2\)Te\(_4\)/G) via a ball-milling method (Figure 3a). The SnSb\(_2\)Te\(_4\) with good conductivity and large interlayer spacing can guarantee high specific capacity and provide open ion-diffusion channels (Figure 3b).\(^{[62]}\) It was worth noting that SnSb\(_2\)Te\(_4\) is a new quantum material with unique structure, where electrons can only move freely along the 2D surface of the material. Therefore, increasing the surface area of SnSb\(_2\)Te\(_4\) can improve its conductivity by expanding lateral space. As an anode in PIBs, the SnSb\(_2\)Te\(_4\)/G heterostructures not only exhibited an excellent discharge specific capacity of 450, 362, 325, 289, 255, 215, and 153 mAh g\(^{-1}\) at different current densities of 0.05, 0.1, 0.2, 0.5, 1, 2, 5 A g\(^{-1}\), respectively (Figure 3c).\(^{[62]}\) but also improved the surface pseudocapacitance as high as 66.3% in the whole capacity charge storage at a scan rate of 0.8 mV s\(^{-1}\). The good electrochemical performance was attributed to accelerating the transportation of ions/electrons by the p–n heterojunction (Figure 3d,e). In addition, forming heterostructures also resulted in strong electronic coupling between SnSb\(_2\)Te\(_4\) and Te-doped graphene to ensure structural and cyclic stability. In another example, phosphorus nanoparticles were uniformly embedded in reduced graphene oxide (P@RGO heterostructures) via vaporization heating treatment in a stainless-steel autoclave (Figure 3f).\(^{[79]}\) The presence of strong P–C covalent bonds could adhere P nanoparticles in the RGO host and obtain the active materials with enlarged interlayer spacing (Figure 3g), which is beneficial for the structural durability of the electrode materials during the cycling process. As a result, the P@RGO heterostructures presented a high charge/discharge capacity of 628.7 and 521.4 mAh g\(^{-1}\) in the second cycle, at 100 mA g\(^{-1}\). Even at 500 mA g\(^{-1}\), it also could keep a capacity of 253 mAh g\(^{-1}\) after 500 cycles (Figure 3h). Vishnuprakash et al. fabricated V\(_2\)O\(_5\) nanorod@rGO heterostructures, in which V\(_2\)O\(_5\) nanorods were supported by rGO nanosheets to offer more active sites.\(^{[80]}\) The V\(_2\)O\(_5\) nanorod@rGO heterostructures showed a good specific capacity and a long cycle life as a cathode electrode for PIBs. After 500 cycles, the capacity was retained as high as 271 mAh g\(^{-1}\) (about 80% of its initial discharge capacity). It still delivered the capacity of 50 mAh g\(^{-1}\) at the high current density of 2940 mA g\(^{-1}\).

Compared with individual 2D materials, the 2D–2D heterostructures offer a novel platform to improve the K\(^{+}\) storage performance. The 2D–2D vdW heterostructures of BiSbOCl/rGO were synthesized as electrode materials for PIBs.\(^{[61]}\) As shown in Figure 4a,b, bimetallic oxchloride nanosheets with Bi and Sb dispersed on rGO nanosheets via vdW force. The 2D vdW heterostructures in the form of nanosheets/nanosheets (NS/NS) displayed the strongest vdW force than that of nanoparticles/nanoparticles (NP/NP) and nanoparticles/nanosheets (NP/NS), which enlarged the contact area between the nanosheets (Figure 4c). Thus, the Bi\(_{0.51}\)Sb\(_{0.49}\)OCl/rGO heterostructures showed ultralong stability (running 9 months) with a Coulombic efficiency (CE) close to 100% even after 1000 cycles, at 100 mA g\(^{-1}\) (Figure 4d), and delivered a high discharge capacity of 407 mAh g\(^{-1}\) at 100 mA g\(^{-1}\). To explore the practicability, full-cell PIBs were assembled with Bi\(_{0.51}\)Sb\(_{0.49}\)OCl/rGO heterostructures as anode and perylenetetracarboxylic dianhydride (PTCDA) as cathode. The full cell presented a high discharge capacity of 225 mAh g\(^{-1}\) after 50 cycles (Figure 4e). They also investigated the K\(^{+}\) storage mechanism by operando X-ray diffraction (XRD). During discharging in the first cycle, the lattice of Bi\(_{0.51}\)Sb\(_{0.49}\)OCl underwent irreversible changes because Bi\(^{3+}\) and Sb\(^{4+}\) were reduced to Bi and Sb, respectively. Then, the further alloying reaction between Bi–Sb alloy and K\(^{+}\) was carried out to deliver the additional specific capacity. In addition, the experiments demonstrated that the ratio of Bi, Cl, and Sb in the precursors was vital to synthesizing the uniform 2D vdW heterostructures of Bi\(_{0.51}\)Sb\(_{0.49}\)OCl nanosheets on the rGO nanosheets.\(^{[61]}\) In another case, the 2D–2D multilayered heterostructures of VOPO\(_4\)–graphene was fabricated as a zero-strain cathode material for PIBs (Figure 4f).\(^{[81]}\) By adjusting the mass ratio between VOPO\(_4\) nanosheets and cationic-surfactant-modified graphene, self-assembled VOPO\(_4\)–graphene multilayered heterostructures were obtained. The lattice strain of VOPO\(_4\)–graphene heterostructures was confirmed to be 3.2% through Raman spectroscopy mapping and density functional theory (DFT) calculations. The lower strain of the crystalline lattices in VOPO\(_4\)–graphene heterostructures benefited from the intercalation/deintercalation of larger K\(^{+}\) compared with simply restacked VOPO\(_4\) nanoflakes. The in situ XRD characterizations revealed that there was only a 2.0% volume change for VOPO\(_4\)–graphene multilayered heterostructures during cycling. These results demonstrated the superiority of heterostructures. After 100 cycles, the stable reversible capacity was as high as 160 mAh g\(^{-1}\) at 16 mA g\(^{-1}\) without obvious capacity decay. Even under a high current density of 3200 mAh g\(^{-1}\), it still maintained 80 mAh g\(^{-1}\). The good electrochemical performance is attributed to the robust 2D multilayered heterostructures.\(^{[81]}\)

In addition to the aforementioned 2D heterostructures via layer-by-layer assembly, the 2D materials also can be vertically grown on another type of 2D material to form a novel kind of 2D heterostructure. For example, Xie et al. reported the heterostructures of ultrathin MoS\(_2\) vertically grown on rGO through a two-step solvothermal method (Figure 5a).\(^{[63]}\) These MoS\(_2\)/rGO heterostructures were tightly coupled by C—O—Mo bonds between MoS\(_2\) and rGO. The unique heterostructures not only expanded the MoS\(_2\) layer spacing from 0.63 to 0.93 nm but also restrained the self-stacking of 2D and increased the active area (Figure 5b). It provided the pathway for rapid ionic and electronic transportation, which enabled to deliver a high rate capacity (Figure 5c). This vertical heterostructures could increase the contact area between the active material and the electrolyte, resulting in a charming pseudocapacitance. On the contrary, some research suggests that such kinds of heterostructures are easily destroyed and agglomerated after certain cycles due to the shuttle effect of polysulfides. For example, layer-by-layer 2D vdW heterostructures (C/MoS\(_2\)/G) and self-assembled vertical covalent bond heterostructures (MoS\(_2\)/G) were designed and fabricated.\(^{[82]}\) The C/MoS\(_2\)/G vdW heterostructures were prepared by combining oxidative polymerization and post sulfidation. In brief, the heterostructure precursors were first anchored on...
GO by introducing the induced reagent and then thermal sulfidation in a reduction environment was conducted. In comparison with MoS$_2$/G that MoS$_2$ nanosheets were vertically grown on graphene (Figure 5d), MoS$_2$ nanosheets in the C/MoS$_2$/G vdW heterostructures were confined by graphene and amorphous carbon, which could effectively prevent the agglomeration of the MoS$_2$ nanosheets and offer space to buffer huge volume changes of MoS$_2$ and release the mechanical stress during cycling. In addition, the C/MoS$_2$/G heterostructures also inhibited the dissolution of intermediate polysulfide products into the electrolyte to realize an ultralong lifespan of 4000 cycles at a high current density of 5 A g$^{-1}$ (Figure 5e).
The 3D–2D Bi₃S₄@rGO heterostructures under the assistance of the visible light irradiation were constructed. Owing to the different Fermi levels between rGO and Bi₃S₄ microspheres, a built-in electric field was introduced at the Bi₃S₄@rGO heterointerface with the electric field direction from rGO to Bi₃S₄. This built-in electric field in 3D–2D Bi₃S₄@rGO heterostructures was proved to facilitate the K⁺ transport. As a result, Bi₂S₃@rGO exhibited a remarkable rate capability (237 mAh g⁻¹ at 2 A g⁻¹ after 300 cycles) and delivered a high specific capacity of 538 mAh g⁻¹ at 0.2 A g⁻¹. In another example, bimetallic selenides (MoSe₂/CoSe₂) were wrapped in N-, S-co-doped porous hollow carbon nanospheres with rGO (rGO@MCSe). When rGO@MCSe was served as an anode for PIBs, it displayed a high reversible capacity of 417.8 mAh g⁻¹ at 0.1 A g⁻¹ after 100 cycles and a high rate capability performance of 310.4 mAh g⁻¹ at 5 A g⁻¹.

In summary, graphene and/or functional graphene can support the mixed-dimensional materials by either vdW forces or covalent bonds. Generally, graphene layers not only work as the highly conductive matrix but also alleviate the volume expansion. Meanwhile, the construction of graphene-based heterostructures can impede the self-stacking of graphene nanosheets and increase the absorbing active sites. Therefore, both the potassium storage capacity and the lifespan of graphene-based heterostructures can be promoted.

3.2. MXenes-Based Heterostructures

MXenes (Ti₃C₂Tx, in which Tx represents surficial termination groups such as −OH, −F, etc.) are novel kinds of 2D materials. Due to their outstanding electrical conductivity, ionic conductivity, scalable layer spacing, and open 2D channel, MXenes have been widely applied in the fields of energy storage, catalysis, supercapacitors and so on. In 2013, the electrochemical behavior of MXenes in PIBs was first investigated. The DFT results demonstrate that K atoms can be adsorbed on the surface of Ti₃C₂ and the capacity of Ti₃C₂ can reach 191.8 mAh g⁻¹. Further researches have identified that the composition, surface chemistry, and structural construction of MXenes have significant effect on their electrochemical properties. A series of cations (like Li⁺, K⁺, and Al⁺³) can be intercalated into Ti₃C₂Tx nanosheets, which reveals the great potentials of MXenes as electrode materials for batteries. For example, K₅Ti₃O₉ nanoribbons showed a reversible capacity of 151 mAh g⁻¹ at 50 mA g⁻¹ when being applied as electrode materials for PIBs. Although MXenes provide a rich chemically active interface and short ion-diffusion length, their specific capacity is still not satisfied. Therefore, advanced MXenes need to be further developed to achieve better electrochemical performance.

As known, quantum dots with ultrasmall size would shorten the K⁺ diffusion path, but the high surface energy of quantum dots easily leads to the agglomeration of quantum dots. To this end, Cao et al. designed and synthesized 0D–2D heterostructures composed of Cu₁₀Sb₃S₁₃ quantum dots and few-layer Ti₃C₂ (named CAS–Ti₃C₂) via a multistep process and investigated as an anode for PIBs. Cu₁₀Sb₃S₁₃ quantum dots were easily anchored onto the host Ti₃C₂ nanosheets under...
sonication. Due to the presence of the strong Ti—S bonds between Cu$_{12}$Sb$_{13}$ quantum dots and Ti$_3$C$_2$ nanosheets, the CAS—Ti$_3$C$_2$ heterostructures can not only restrain the agglomeration of active materials but also ensure the good structural stability of heterostructures. In addition, CAS—Ti$_3$C$_2$ heterostructures exhibited an insertion—conversion— alloying mechanism for K$^+$ storage. The CAS—Ti$_3$C$_2$ heterostructures delivered an ultrahigh initial specific capacity of 1582.7/905.6 mAh g$^{-1}$ (discharge/charge) at 50 mA g$^{-1}$, corresponding CE of 57.2% (Figure 6b). The CAS—Ti$_3$C$_2$ exhibited a high CE of ≈100% in the following cycles, which implied the high reversible capacity. It also displayed an ultralong cycling life up to 1800 cycles at 1.0 A g$^{-1}$ with a capacity of 175.6 mAh g$^{-1}$ (Figure 6c).

Furthermore, 2D—1D heterostructures of MXene@N-doped carbonaceous nanofibers were fabricated as PIB anode, which presented a reversible capacity (349.2 mAh g$^{-1}$ at 0.1 A g$^{-1}$) and an ultralong lifespan (201.5 mAh g$^{-1}$ at 1 A g$^{-1}$ after 1800 cycles). The ultrastable electrochemical performance was attributed to the high-density distribution of 2D MXenes on N-doped carbon nanofiber and the formation of self-supported...
porous heterostructures. The unique structure can take full advantages of the high surface-controlled capacitive storage of 2D MXenes and the rapid electron transfer of 1D N-doped carbon nanofiber. It is also found that strongly coupled 2D transition metal chalcogenide–MXene–carbonaceous nanoribbons (MSe–MXene–CNRib) have excellent Na\(^+\)/K\(^+\)-ion storage performance.\(^{[99]}\) Transition metal selenides (including Cu\(_{1.75}\)Se, NiSe\(_2\), and CoSe\(_2\)) were anchored on one surface of the MXene nanosheets by coupling with terminated groups, while the carbonaceous nanoribbons (CNRib) were attached on another surface of MXene nanosheets via amino bridging groups and hydrogen bonds to obtain unique heterostructures (Figure 6d). These unique MXenes-based heterostructures could present a “Janus” interfacial effect with different bonds’ interaction, which was joined via strong chemical bonds rather than vdW forces. Serving as anode electrode for PIBs, the Cu\(_{1.75}\)Se–MXene–CNRib electrode maintained a high reversible capacity of 305.6 mAh g\(^{-1}\) at a high current density of 1.0 A g\(^{-1}\) after 400 cycles (Figure 6e). In addition, the pseudocapacitive storage contributed a high ratio of 78.5% on the whole

Figure 6. a) Scheme for the fabrication of CAS–Ti\(_3\)C\(_2\) heterostructures. b) Charge–discharge profiles of CAS–Ti\(_3\)C\(_2\) heterostructures between 0.01 and 2.6 V. c) Cycling performance comparison of CAS–Ti\(_3\)C\(_2\) heterostructures, Cu\(_{1.75}\)Sb\(_2\)S\(_{13}\) quantum dots, and Ti\(_3\)C\(_2\) nanosheets. a–c) Reproduced with permission.\(^{[97]}\) Copyright 2021, Wiley-VCH. d) Schematic illustration of MSe on MXene-coated fungal-derived CNRib heterostructures. e) Cycling performance at 0.1 and 1.0 A g\(^{-1}\) and f) the pseudocapacitive-dominated proportions at the sweep rates of 1.0 mV s\(^{-1}\) of Cu\(_{1.75}\)Se–MXene–CNRib heterostructures. d–f) Reproduced with permission.\(^{[99]}\) Copyright 2021, Springer Nature.
capacity storage (Figure 6f). The results indicated that Cu0.75Se–MXene–CNRib electrode was favorable for surface-dominated K+ storage, particularly at high rates. Furthermore, the DFT calculations were conducted to verify the possibility of the diffusion behaviors of K+ at the interface of the heterostructures. It confirmed that the MoSe2–MXene–CNRib electrode showed improved electronic conductivities and reduced diffusion barriers, which were supposed to boost the K+ adsorption and diffusion kinetics. Obviously, the unique ternary heterostructures offered plenty of active sites and additional storage interfaces, ensuring the heterostructures for excellent cycling stability and fast transport for big alkali metal ions.

To further enhance the electrochemical performance of MXenes-based materials, various 2D–2D heterostructures based on MXenes have been designed and fabricated. For example, Li et al. synthesized layered Ti3C2Te MXene/MoS2 heterostructures and they displayed a reversible capacity of 290.7 mAh g\(^{-1}\) at 0.05 A g\(^{-1}\) as PIB electrode materials.\(^{[100]}\) Recently, novel carbon-coated MoSe2/MXene heterostructures were fabricated by a multistep reaction.\(^{[101]}\) As shown in Figure 7a, MoSe2 nanosheets were vertically anchored on the MXene substrate with Ti–O–Mo bonds to form robust heterostructures. These kinds of heterostructures with strong covalent bonds benefited to boost the charge transfer kinetics of K+ and maintained the stability of the structure. In addition, the MXenes-based heterostructures could provide more active sites on the surface for adsorption of K+ and offer a 2D diffusion pathway to facilitate the transport of K+. The potassium storage capacity was 355 mAh g\(^{-1}\) after 100 cycles (Figure 7b).\(^{[102]}\) Moreover, the pseudocapacitive contribution of MoSe2/MXene heterostructures was as high as 90.2% at the scan rate of 1.2 mV s\(^{-1}\). Cao et al. constructed MXenes and SnS2 nanosheet heterostructures via a simple hydrothermal reaction.\(^{[102]}\) The vertical SnS2 nanosheets were uniformly grown on N,S codoped MXene sheets (SnS2–NSs/MXene). As shown in Figure 7c,d, the morphology and lattice fringes of the SnS2–NSs/MXene were characterized by scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HRTEM), which indicated enlarged SnS2 layer spacing and ensured resulting heterostructure materials with the merits of outstanding electrical conductivity and mechanical stability. Severe as an anode of PIBs, it exhibited excellent cycling performance and rate behavior. The reversible capacity was as high as 206.1 mAh g\(^{-1}\) at a current density of 0.5 A g\(^{-1}\) even after 800 cycles (Figure 7e).\(^{[103]}\) Likewise, the ultrathin SnS2/Ti3C2Tex heterostructures with a thickness of about 5 nm were synthesized by assembling the few-layer SnS2 and Ti3C2Te\(_{x}\).\(^{[103]}\) When used as anode for PIBs, the ultrathin SnS2/Ti3C2Te\(_{x}\) heterostructures demonstrated the remarkable capacity of 462.1 mAh g\(^{-1}\) at 0.1 A g\(^{-1}\) and maintained the reversible capacity of 85.5 mAh g\(^{-1}\) at the high current density of 2.0 A g\(^{-1}\) after 460 cycles. In addition, Zhao et al. designed and synthesized the layer-by-layer heterostructures of PDDA–NPNCTi3C2 (N-rich porous carbon nanosheets/Ti3C2) under the PDDA [poly (diacetyldimethylammonium chloride)], which generated more active sites and enlarged the layer spacing.\(^{[104]}\) As a result, the heterostructures presented outstanding specific capacities (358.4 mAh g\(^{-1}\) after 300 cycles at 100 mAh g\(^{-1}\)) and great structural stability (252.2 mAh g\(^{-1}\) after 2000 cycles at 1.0 A g\(^{-1}\)). Recently, Wu and coworkers obtained the 2D–2D heterostructure electrode materials of black phosphorene@V\(_{2}\)CT\(_{x}\) (donated as BPE@V\(_{2}\)CT\(_{x}\), (T = OH or F), by an electrostatic attraction assembly without surfactant (Figure 7f).\(^{[105]}\) With 2D interlayer heterostructures, it could make full use of the merits of the expanded interlayer spacing and charge redistribution between adjacent interfaces, which facilitated the K+ insertion/extraction and accelerated the K+ transport kinetics. They also applied DFT calculations and galvanostatic intermittent titration technique (GITT) to verify the enhanced adsorption of K+ and fast diffusion of K+ in BPE@V\(_{2}\)CT\(_{x}\) heterostructures. As an anode for PIBs, BPE@V\(_{2}\)CT\(_{x}\) exhibited as high reversible capacity of 593.6 mAh g\(^{-1}\) at 0.1 A g\(^{-1}\) and exceptional cycling stability of 485 mAh g\(^{-1}\) after 3000 cycles at 200 mA g\(^{-1}\), corresponding to 91% capacity retention.\(^{[106]}\) Compared with BPE and V\(_{2}\)CT\(_{x}\), the BPE@V\(_{2}\)CT\(_{x}\) heterostructures delivered the highest reversible capacity of 570 mAh g\(^{-1}\) under a current density of 0.1 A g\(^{-1}\) after 500 cycles (Figure 7g).

Furthermore, a two-step chemical vapor deposition route was exploited to obtain N-doped graphene/ReSe\(_2/Ti3C2\) MXene (3D-2D) heterostructures.\(^{[105]}\) The capacity of N-doped graphene/ReSe\(_2/Ti3C2\) MXene reached 395.3 mAh g\(^{-1}\) at 0.1 A g\(^{-1}\). Even at high current densities of 5 and 10 A g\(^{-1}\), it still achieved capacities of 154.7 and 137.5 mAh g\(^{-1}\), respectively. Moreover, DFT calculations revealed the origin of the favored K+ adsorption/diffusion and the improved electron conductivity. Compared with bare ReSe\(_2\), G/ReSe\(_2\) possessed a very low bandgap, indicating that G/ReSe\(_2\) brought higher electronic conductivity. These results verified the superiority of the N-doped graphene/ReSe\(_2/MXene heterostructures.

As emerging 2D nanomaterials, MXenes are usually used as good conductive substrates to support other materials for forming new types of MXenes-based heterostructures. These heterostructures have robust structures achieved by the covalent bonds or vdW interactions, which improve the mechanical properties of the heterostructures and accommodate the huge change of volume. In short, MXenes-based heterostructures show a promising application potential for K storage.

3.3. 2D Transition Metal Dichalcogenides/Transition Metal Oxide-Based Heterostructures

2D TMDs (e.g., MoS\(_2\), MoSe\(_2\), WSe\(_2\), WS\(_2\)) classical examples of 2D atomic crystals, and they have been extensively explored for energy storage applications over the past years.\(^{[106–109]}\) In particular, TMDs show huge potential as electrode materials for PIBs, and the K+ storage in TMDs is usually via the combination of conversion and insertion reaction, offering higher theoretical specific capacity than carbon-based materials.\(^{[29,109–112]}\) Unfortunately, the low conductivity and brittle structures within the operating voltage restricted the applications of TMDs for K+ storage.\(^{[23,29]}\)

Recently, bamboo-like hollow tubes with MoS\(_2\)/N-doped C heterostructures were reported as anode materials for PIBs (Figure 8a,b).\(^{[111]}\) The heterostructures stacked by MoS\(_2\) nanosheets and N-doped C layers can effectively enhance the conductivity and protect the structural integrity. Meanwhile, the heterostructures exhibited an expanded interlayer distance up to 1 nm (Figure 8c). DFT results confirmed that the MoS\(_2\)/N-doped C atomic interface offered additional active sites to
absorb K\textsuperscript{+} and decreased the diffusion energy barrier of K\textsuperscript{+}. Therefore, it exhibited long cycling performance of the reversible capacity of 151 mAh g\textsuperscript{-1} at the current density of 0.5 A g\textsuperscript{-1} after 1000 cycles.\textsuperscript{113} Zhang et al. fabricated the 2D/2D heterostructures of the dual carbon-coated MoS\textsubscript{2} nanosheets (MoS\textsubscript{2}/C@NDG) through a facile hydrothermal method.\textsuperscript{109} These heterostructures not only provided enough space to buffer the volume change and prevent the agglomeration of MoS\textsubscript{2}, but also improve the electronic conductivity of MoS\textsubscript{2} and boost the rapid of K\textsuperscript{+} diffusion during cycling. Thus, it delivered a high specific capacity of 443.6 mAh g\textsuperscript{-1} at 100 mA g\textsuperscript{-1} and a remarkable rate performance of 176.6 mAh g\textsuperscript{-1} at 2.0 A g\textsuperscript{-1}.

In addition, multiphase heterostructures were also investigated as PIB electrode materials. For instance, ternary heterostructures of MoS\textsubscript{2}-based (denoted as Fe\textsubscript{9}S\textsubscript{10}@MoS\textsubscript{2}@C) were designed by introducing Fe\textsubscript{9}S\textsubscript{10} core for PIBs.\textsuperscript{114} Owing to the different energy bandgap of the Fe\textsubscript{9}S\textsubscript{10} (0 eV) and MoS\textsubscript{2} (1.17 eV), a strong built-in electric field was formed at the heterointerface, which boosted the fast K\textsuperscript{+} extraction during the charging process. The concentrations of K\textsuperscript{+} on Fe\textsubscript{9}S\textsubscript{10} and MoS\textsubscript{2} area were different due to the reaction reversibility of Fe\textsubscript{9}S\textsubscript{10}, which helped the fast K\textsuperscript{+} insertion during the discharging process (Figure 8d). The Fe\textsubscript{9}S\textsubscript{10}@MoS\textsubscript{2}@C heterostructures demonstrated a high initial capacity of 321 mAh g\textsuperscript{-1} at 0.2 A g\textsuperscript{-1} and...
good cycling performance (with 95.4% capacity retention) even at a high current density of 2.0 A g⁻¹ after 50 cycles for PIBs. By combing p-type MoS₂ with n-type Bi₂S₃, carbon-coated Bi₂S₃/MoS₂ heterostructures were synthesized. The uniform carbon layer could improve the structural stability, and at the same time the carbon-coated Bi₂S₃/MoS₂ heterostructures effectively boosted the charge transport and accelerated the reaction kinetics. Therefore, the enhanced potassium storage performance of carbon-coated Bi₂S₃/MoS₂ heterostructures could be attributed to the synergistic effects of all three components. It maintained a capacity of 382.8 mAh g⁻¹ at 0.1 A g⁻¹ after 100 cycles. At a high current density of 3 A g⁻¹, the carbon-coated Bi₂S₃/MoS₂ heterostructures still delivered a capacity of 300.2 mAh g⁻¹.

Xing et al. also investigated the electrochemical properties of three-layered heterostructure TiNb₂O₆@MoS₂/C core/shell microspheres as an anode for PIBs (Figure 8e). The core of oxygen-atom-unsaturated metallic TiNb₂O₆ was deemed to be the main reason for enhancing the electron mobility of the microspheres. The porous TiNb₂O₆ core not only could provide more active sites for the tight growth of MoS₂ and restrain the
agglomeration of the MoS$_2$ nanosheets, but also could availably increase the flexible contact between the heterostructure materials and electrolyte.\cite{116} As a result, the electrode exhibited outstanding performance with a high capacity of 424 mAh g$^{-1}$ at 100 mA g$^{-1}$ after 50 cycles. Even at a high current density of 1.0 A g$^{-1}$, the average capacity was 175 mAh g$^{-1}$ after 300 cycles (Figure 8f).\cite{116} Hierarchical chrysanthemum-like MoS$_2$/Sb heterostructures were encapsulated into the N-doped graphene.\cite{117}

Benefiting from the advantage of the synergetic effect between the heterointerface of MoS$_2$ and Sb, the electrode displayed a large specific capacity of 359.5 mAh g$^{-1}$ at 50 mA g$^{-1}$. At a current density of 2.0 A g$^{-1}$, the capacity still reached 233.2 mAh g$^{-1}$ with a low capacity loss of 0.027% per cycle during 1000 cycles.

1T-MoS$_2$ has a narrow bandgap and enriched metallic properties, but it is unstable and hard to be directly used for energy storage.\cite{118,119,120} Some researchers have prepared 1T-MoS$_2$-based heterostructures for PIBs. For instance, Wu et al. designed the few-layer 1T/2H-MoS$_2$/covalent nanosheets to be anchored on N-doped carbon nanotube hollow polyhedron (denoted as NCNHP), as shown in Figure 9a.\cite{121} The heterostructures with the hollow structure created enough voids to alleviate the volume change, resulting in an ultrastable performance of 281.2 mAh g$^{-1}$ after 500 cycles with a good capacity retention 66.7% (Figure 9b). Moreover, they also assembled full-cell PIBs with 1T/2H-MoS$_2$/CNCHP as anode and K$_2$Fe[Fe(CN)$_6$] as cathode, which presented a lifetime over 100 cycles (136.1 mAh g$^{-1}$) at 100 mA g$^{-1}$ (Figure 9c).\cite{121} Zhou et al. utilized 1T-MoS$_2$/MoO$_x$/NC (N-doped carbon) for K$^+$ storage.\cite{122} After 400 cycles, it still had the capacity of 120 mAh g$^{-1}$ at the current density of 500 mA g$^{-1}$. The stable electrochemical K$^+$ storage property of 1T-MoS$_2$ was attributed to its good electrical conductivity.

The heterostructures of MoS$_2$ or MoSe$_2$ on N-doped carbon (MoS$_2$/MoSe$_2$-on-NC) were also fabricated by a sacrificial template and subsequent sulfidation/selenization.\cite{123} As PIB anode, the MoS$_2$-on-NC presented a high capacity of 399 mAh g$^{-1}$ at the current density of 1 A g$^{-1}$ after 5000 cycles, corresponding to the capacity decay per cycle of 0.0043%. MoSe$_2$-on-NC also delivered a reversible capacity of 247 mAh g$^{-1}$ at the current density of 1 A g$^{-1}$ after 4800 cycles, corresponding to the CE of $\approx$100%. The unique heterostructures in the composite played two key roles: 1) the built-in electric field effectively accelerates the charge transfer and improves the K$^+$ reaction kinetics and 2) the strong covalent bonds (i.e., C–S, C–Se, C–Mo bonds) could maintain structural stability. In addition, Liu et al. also synthesized MoSe$_2$–MoO$_3$ quantum dot heterostructures with the help of a sacrificial template.\cite{28} When used as an anode for PIBs, it displayed the excellent capacity of 308.7 mAh g$^{-1}$ after 300 cycles at 50 mA g$^{-1}$. Compared with MoO$_3$, MoO$_2$ has a higher conductivity. Thus, Jiang et al. synthesized the heterostructures of MoSe$_2$@MoO$_2$ nanostructured materials (Figure 9d).\cite{124} In the composite, metallic MoO$_2$ nanoparticles not only improved the electrical conductivity but also prevented ultrathin MoSe$_2$ nanosheets from being stacked, which resulted in a larger active surface for K$^+$ adsorption. The difference in the bandgap between MoSe$_2$ (1.51 eV) and MoO$_2$ (0.9 eV) could generate a built-in electric field at the heterointerface, and it thus boosted K$^+$ transfer during cycling (Figure 9e). As a result, MoSe$_2$@MoO$_2$ was able to deliver a capacity of 255 mAh g$^{-1}$ at 500 mA g$^{-1}$ after 100 cycles with a CE close to 100% (Figure 9f). As for combining with alloy-type materials, the heterostructures of MoSe$_2$–graphene covalently connected with SnS (SnS@MoSe$_2$-GR) and were obtained.\cite{125} It was noted that a build-in electric field was generated at the heterointerface between MoSe$_2$ and SnS because of the unbalanced charge distribution. It was ensured that the SnS@MoSe$_2$-GR showed great electrochemical performance. Serving as PIB anode, it maintained a stable capacity of 311.6 at 50 mAh g$^{-1}$ after 100 cycles and 120 mAh g$^{-1}$ at 500 mAh g$^{-1}$ after 3500 cycles, respectively.

In addition, TMO-based heterostructures were also prepared as electrode materials for PIBs.\cite{58,126} For example, the hierarchical TiO$_2$/C tubular heterostructures were synthesized as anodes for PIBs.\cite{58} DFT calculations and density of state data indicated that the TiO$_2$/C heterostructures had a lower energy barrier for potassium storage and a higher conductivity than those of TiO$_2$–C hybrids. Hence, TiO$_2$/C heterostructures exhibited a reversible capacity of 240.8 mAh g$^{-1}$ at the current density of 100 mAh g$^{-1}$. Even at 500 mAh g$^{-1}$ after 1200 cycles, the high capacity of 132.8 mAh g$^{-1}$ could be still maintained.

Compared with the individual 2D TMDs or TMOs, integrating TMDs and/or TMOs-based heterostructures provides more potential for storing K$^+$. For example, the heterostructures with various phase components and rich valence states can possess adjustable conductivity properties and tunable bandgaps, which greatly affect the properties of heterostructures materials and thereafter enhanced chemical performance for PIBs. Thus, to enhance the K$^+$ storage performance, some factors should be considered in the rational design and regulation of TMDs and/or TMOs-based heterostructures, such as crystal structure, nanosheet size and thickness, and interlayer bonding states.

### 3.4. Other Heterostructures for PIBs

In recent years, more 2D materials have been exploited.\cite{127,128} Except for elemental 2D and TMDs/TMOs, the main group of metal chalcogenide 2D materials has also attracted attention, such as SnS and SnS$_2$.\cite{129,130} SnS and SnS$_2$ can generally provide high specific capacities owing to the multielectron reactions and the following alloying reactions.\cite{46,131,132} In addition, theoretical calculations showed that the diffusion potential of K$^+$ at the surface of SnS$_2$ is very low, so SnS$_2$ has the potential as a high-density battery material.\cite{133} However, they could be impeded by the huge volume expansion, which will lead to rapid capacity decay and the unsatisfied lifespan.\cite{133,134,135} Thus, developing heterostructure materials with SnS$_2$ or SnS has been proposed to enhance the cycling performance. Cao et al. constructed layered VS$_4$/SnS (1D–2D) heterostructures anchored on graphene (VS$_4$/SnS@C) through solvothermal and sulfidation reaction (Figure 10a).\cite{136} Owing to the advantage of the heterostructure framework, the composite showed a high specific surface area. At the same time, the different types of SnS and VS$_4$ could form a built-in electric field at the interface of the heterostructure, which could boost the charge transfer and improve the K$^+$ insertion/extraction kinetics. The most important thing is that the presence of S$_2^2-$ in the structure could weaken the shuttle effect of polysulfides; thus, the active material VS$_4$/SnS@C demonstrated better structural stability and electrochemical performance. When being evaluated as an anode for PIBs, VS$_4$/
Figure 9. a) Schematic illustration of K\textsuperscript{+} diffusion pathways in 1T/2H-MoS\textsubscript{2}/NCNHP heterostructures. b) Cycling performance of 1T/2H-MoS\textsubscript{2}/NCNHP at 1.0 A g\textsuperscript{-1} (insets: the morphology of 1T/2H-MoS\textsubscript{2}/NCNHP before and after 500 cycles). c) Cycling performance at 0.1 A g\textsuperscript{-1} and optical photograph of LED lightened up by K-ion full cell. a–c) Reproduced with permission.\textsuperscript{[121]} Copyright 2020, Wiley-VCH. d) Schematic illustration of the preparation of MoSe\textsubscript{2}@MoO\textsubscript{2} heterostructures. e) Summary of the enhanced ion transportation mechanisms of MoSe\textsubscript{2}@MoO\textsubscript{2} heterostructures in PIBs. f) Cycling performance of MoSe\textsubscript{2}@MoO\textsubscript{2} heterostructures at 500 mA g\textsuperscript{-1}. d–f) Reproduced with permission.\textsuperscript{[124]} Copyright 2020, Elsevier.

Figure 10. a) Schematic of the fabrication of VS\textsubscript{4}/SnS@C heterostructures. b) Ultralong cycling performances of VS\textsubscript{4}/SnS@C heterostructures for K\textsuperscript{+} storage. a,b) Reproduced with permission.\textsuperscript{[136]} Copyright 2021, Wiley-VCH. c) Illustration of fabricating CoSe\textsubscript{2}/FeSe\textsubscript{2}@C heterostructures. d,e) HAADF–STEM image and the corresponding schematic diagram of the heterostructures of CoSe\textsubscript{2}/FeSe\textsubscript{2}. c–e) Reproduced with permission.\textsuperscript{[141]} Copyright 2021, Wiley-VCH.
SnS@C showed a remarkable cycling stability at different current densities, in which a specific capacity of 227 and 168.4 mAh g\(^{-1}\) was retained over 3000 and 6000 cycles at 0.5 and 1 A g\(^{-1}\), respectively (Figure 10b).\(^{[136]}\) Suo et al. synthesized the heterostructures of SnS\(_2\)/SnO\(_2\) with good conductive stainless steel mesh (SSM) as a free-standing electrode for PIBs.\(^{[137]}\) Due to the merit of binder-/conductive-additive free and special heterostructures, the SnS\(_2\)/SnO\(_2\)/SSM electrode produced a reversible specific capacity of 394 mAh g\(^{-1}\) at the current density of 50 mA g\(^{-1}\) over 100 cycles.

Researchers also tried to exploit other heterostructures as PIB electrode materials.\(^{[138]}\) For example, the heterostructures are made up of non-2D materials such as CoSe\(_2\), CoS\(_2\), FeS\(_2\), and FeSe\(_2\).\(^{[139–147]}\) As an example, the hierarchical CoSe\(_2\)–FeSe\(_2\)/C heterostructures were constructed by applied MOFs as sacrificial template (Figure 10c).\(^{[141]}\) The introduction of FeSe\(_2\) with a narrow bandgap could induce the formation of a built-in electric field inside the material and boost the reaction kinetics of K\(^{+}\). More importantly, rich atomic vacancies and a slightly disordered atomic arrangement of CoSe\(_2\)–FeSe\(_2\)/C heterointerface were certified by high-angle-annular dark-field scanning transmission electron microscopy (HAADF-STEM) (Figure 10d,e), which afforded more active sites during the charging-discharging process. As a result, the heterostructure electrode materials obtained a high capacity of 401.1 mAh g\(^{-1}\) at 0.1 A g\(^{-1}\) and even 275 mAh g\(^{-1}\) at a high current density of 2 A g\(^{-1}\). Suo et al. developed the CoS\(_2\)/CuCo\(_2\)S\(_4\) hollow sphere heterostructures coated with nitrogen-doped carbon (CoS\(_2\)/CuCo\(_2\)S\(_4\)/NCs).\(^{[142]}\) The CoS\(_2\)/CuCo\(_2\)S\(_4\)/NC electrode maintained a high rate capability of 309 mAh g\(^{-1}\) at 0.5 A g\(^{-1}\) after 250 cycles with ether-based electrolyte. These hollow sphere heterostructures were beneficial for boosting the K\(^{+}\) transportation and providing more space for the intercalation/deintercalation of K\(^{+}\).

Given the above, constructing heterostructures to change the electronic properties and mitigate the shuttle effect of active materials will guarantee the fast kinetics of K\(^{+}\). Moreover, some heterostructures electrode materials with mix-dimension have been successfully fabricated, which are endowed with suitable ion-diffusion channels and a good strain-release property to facilitate ion transport and buffer the severe volume variation during K\(^{+}\) insertion/extraction, thus effectively promoting the applications of PIBs.

4. Conclusions and Outlook

In this review, we have presented an overview of the recent progresses on the design, synthesis, and applications of 2D-based heterostructures in particular graphene-, MXenes-, TMDs-, and TMOS-based heterostructures as electrode materials for PIBs. Details in compositions, synthetic methods, and electrochemical properties of these 2D-based heterostructures are summarized in Table 1. As shown in Table 1, the synthesis of 2D-based heterostructures is usually a complex and multistep process that is a combination of different synthetic techniques, including chemical vapor deposition (CVD), hydrothermal, freeze drying, annealing, spray pyrolysis, etching, and so on. Through such a complex and multistep process, different 2D materials are integrated with other functional materials via either vdW forces or covalent bonds to obtain 2D-based heterostructures. In comparison with individual 2D materials, these 2D-based heterostructures as electrode materials for PIBs exhibit significant improvement in initial CE (ICCE), rate performance, and cycling stability, owing to their unique structural, physicochemical, and electronic properties including 1) the enlarged interface contact and vacancies and/or distortions at the heterointerfaces that offer abundant electrochemical active sites for K\(^{+}\) storage; 2) the built-in electric field in 2D-based heterostructures that promotes the charge transfer kinetics during the K\(^{+}\) insertion/extraction process; and 2) the hierarchical configuration of 2D-based heterostructures which alleviates the volume variation of 2D materials during the charging and discharging process. Although some encouraging advances have been achieved in the past years, much research efforts are needed for pursuing with the aims of developing 2D-based heterostructures for practical PIB applications.

As aforementioned, the K\(^{+}\) storage performance of 2D-based heterostructures is highly dependent on their components and morphologies. Even consisting of the same components, changes in morphologies (i.e., the size, shape, and spatial arrangement of each component and/or the ensemble) of 2D-based heterostructures might result in a significant difference in their electrochemical performance. Currently, the synthesis of 2D-based heterostructures is usually a complex and multistep synthesis process, and the experimental conditions in each step have to be well controlled because slight variations in experimental conditions would lead to morphology changes of the as-obtained 2D-based heterostructures and thus influence the electrochemical performance. Therefore, a facile synthetic strategy should be developed to controllably produce 2D-based heterostructures with high consistency in morphologies. Moreover, this synthetic strategy also should be cost effective and scalable, so as to satisfy the industrial-scale production of 2D-based heterostructures for PIBs. Besides the consistency in morphologies, the optimization in components and morphologies of 2D-based heterostructures are also of great significance. The attainable potassium-ion storage capacity of 2D-based heterostructures relates to the theoretical capacity of both host 2D materials and guest functional materials in 2D-based heterostructures. Integrating host 2D materials with one kind of guest functional material that has a high theoretical specific capacity has been demonstrated as an effective way to obtain 2D-based heterostructures with a high specific capacity.\(^{[63,112]}\) However, it should be noted that the overall specific capacity of 2D-based heterostructures will not be the sample sum of the theoretical specific capacity of host 2D materials and guest functional materials. The morphologies of 2D-based heterostructures have to be optimized toward enlarging the interface contact area and hence creating more active sites for K\(^{+}\) storage and strengthening the interactions to facilitate K\(^{+}\) storage kinetics. Only then will a high specific capacity, which is even higher than the sum of the theoretical specific capacity of host 2D materials and guest functional materials, be achieved and at the same time realize high rate performance. In addition, the K\(^{+}\) storage mechanism of 2D-based heterostructures might be different from both host 2D materials and guest functional materials. A better understanding of the effect of the morphologies of 2D-based heterostructures as
Table 1. Summary of the materials, synthetic methods, and electrochemical performance of reported 2D-based heterostructures for PIBs.

| Materials                              | Synthetic methods                             | Electrode | ICE [%] | Rate performance [mAh g\(^{-1}\)/mA g\(^{-1}\)] | Cycling stability [mAh g\(^{-1}\)/mA g\(^{-1}\) Cycles] | Ref. |
|----------------------------------------|-----------------------------------------------|-----------|---------|-----------------------------------------------|-------------------------------------------------------|-----|
| SnSb\(_2\)Te\(_4\)/G                  | Multiple ball milling                          | Anode     | 77.9    | 368/100; 153/5000                              | 200th                                                 | [62]|
| 2D VOPO\(_4\)---graphene heterostructures | Freeze drying, solution-phase self-assembly   | Cathode   | --      | 130/80; 80/3200                               | 2000th                                               | [48]|
| Bi\(_2\)S@rGO                         | A visible light-assisted method                | Anode     | 72.7    | 538/200; 50/2940                               | 100th                                               | [81]|
| rGO@MCSe                              | Hydrothermal, annealing, freeze drying         | Anode     | 65.3    | 310.4/5000; 417.8/5000                         | 100th                                               | [84]|
| V\(_2\)O\(_5\) nanorod@rGO            | Hydrothermal, annealing                        | Cathode   | 96      | 50/2940; 271/147                               | 50th                                                | [80]|
| Sb@Sb\(_2\)O\(_3\)@N-3DCHs            | Spray drying, annealing                        | Anode     | 60.5    | 239/5000; 319/2000                             | 1000th                                              | [139]|
| Bi\(_{0.33}\)Sb\(_{0.67}\)OCl/rGO       | Wet chemistry, freeze drying                  | Anode     | 55.9    | 407/100; 360/100; 319/1000                     | 1000th                                              | [61]|
| N-doped graphene /ReSe\(_2\)/Ti\(_3\)C\(_2\) MXene | Etching, hydrothermal, Freeze drying          | Anode     | --      | 138/10000; 90/5000                             | 300th                                               | [105]|
| MoSe\(_2\)/MXene@C                     | Hydrothermal, in situ polymerization, annealing| Anode     | 54.2    | 356/200; 234/2000                             | 100th                                               | [101]|
| Ti\(_3\)C\(_2\)T\(_x\)/MXene NCrib     | Etching, hydrothermal                          | Anode     | --      | 371.1/100; 60.7/5000                           | 100th                                               | [89]|
| MXene/Mo\(_2\)S-0.1                    | Etching, hydrothermal                          | Anode     | 66.5    | 290.7/50; 145.5/500                            | 50th                                                | [100]|
| PDDA-NPCN/Ti\(_3\)C\(_2\)             | Electrostatic attraction self-assembly        | Anode     | 73.2    | 499.8/100; 252.2/1000                          | 1000th                                              | [104]|
| BPE@V\(_2\)C\(_2\)                    | Ice bath ultrasonic, exfoliated,              | Anode     | 75.1    | 593.6/100; 485/200                            | 300th                                               | [60]|
| SnS\(_2\)/NS3/MXene                   | Hydrothermal                                  | Anode     | 31      | 342.4/50; 206.1/500                            | 800th                                               | [102]|
| Cu\(_{1.75}\)Se@NCrib                  | Hydrothermal, freeze drying, calcinations      | Anode     | 54.6    | 435.3/100; 305/1000                            | 800th                                               | [98]|
| Cu\(_{1.25}\)Sb\(_{0.5}\)/Ti\(_3\)C\(_2\) nanosheets | Hydrothermal, freeze drying, sonication       | anode     | 57.2    | 571.8/100; 175.6/1000                          | 1000th                                              | [97]|
| SnS\(_2\)/Ti\(_3\)C\(_2\) heterostructures | Wet chemistry                                | Anode     | 60.8    | 462.1/100; 85.5/1000                           | 1000th                                              | [93]|
| MoSe\(_2\)/MoO\(_2\) heterojunction   | Hydrothermal                                  | Anode     | 50      | 365/100; 255/1000                             | 100th                                               | [124]|
| MoSe\(_2\)/CNTs                        | Acid treatment, hydrothermal, annealing        | Anode     | 69.3    | 209.7/5000; 159/2000                           | 1000th                                              | [145]|
| QDs MoSe\(_2\)--MoO\(_3\)             | Grinding, selenization                        | Anode     | 56.3    | 320.8/50; 218.5/2000                           | 100th                                               | [28]|
| MoS\(_2\)-on-NC                        | Sacrificial template, annealing                | Anode     | --      | 399/1000; 139/1000; 247/1000                    | 5000th                                              | [123]|
| MoSe\(_2\)-on-NC                       | Hydrothermal                                  | Anode     | 73.1    | 377/100; 120/5000                             | 5000th                                              | [125]|
| SnS@MoSe\(_2\)-GR                      | Hydrothermal                                  | Anode     | 50.45   | 450/50; 424/500                               | 50th                                                | [116]|
| MoS\(_2\)/N-doped-C                    | Hydrothermal                                  | Anode     | --      | 451/50; 151/500                               | 100th                                               | [113]|
| CoS\(_2\)/NC@MoS\(_2\) (DHNCs)         | Pyrolysis, Hydrothermal, annealing             | Anode     | 89.1    | 122/1000; 100/1000                            | 100th                                               | [144]|
| TT/2H-MoS\(_2\)/NCNHP                  | Hydrothermal                                  | Anode     | 63.9    | 519.2/50; 281.2/100                            | 50th                                                | [136]|
| TiNb\(_2\)O\(_6\)/MoS\(_2\)/C         | Hydrothermal                                  | Anode     | 50.45   | 450/50; 424/500                               | 50th                                                | [116]|

In the full cell:

- SnS\(_2\)/Ti\(_3\)C\(_2\) heterostructures: 136.1/100 after 100th
- MoSe\(_2\)/MoO\(_2\) heterojunction: 131/500; 175/1000 after 300th
- CoS\(_2\)/NC@MoS\(_2\) (DHNCs): 144/100 after 100th
- TT/2H-MoS\(_2\)/NCNHP: 144/100 after 100th
- TiNb\(_2\)O\(_6\)/MoS\(_2\)/C: 175/1000 after 300th
as well as the interactions between host 2D materials and guest functional materials on the K⁺ storage mechanism of 2D-based heterostructures might lead to optimized synergetic effects for realizing high potassium-ion storage capability. Therefore, theoretical calculations and advanced in/ex situ characterizations should be systematically combined to reveal the potassium-ion storage mechanism of 2D-based heterostructures, providing a guideline for optimizing the morphologies and components of 2D-based heterostructures.

Despite these challenges, the 2D-based heterostructures open a new possibility for breaking the electrochemical property limits of individual 2D materials for K⁺ storage. With further research efforts in this field, it is highly expected that high-performance electrode materials based on stable 2D-based heterostructures will be fabricated to promote the development of PIBs.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

2D-based heterostructures, covalent bonds, electrode materials, potassium-ion batteries, van der Waals forces

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Table 1. Continued.

| Materials | Synthetic methods | Electrode | ICE [%] | Rate performance [mAh g⁻¹/ mA g⁻¹] | Cycling stability [mAh g⁻¹/ mA g⁻¹] Ref. Cycles |
|----------|--------------------|-----------|---------|-------------------------------------|-----------------------------------------------|
| MoS₂/C@NDG | Hydrothermal, annealing | Anode 59.3 | 443.6/100; 176.6/2000 | 220.7/1000 after 150th [109] |
| Bi₂S₃/MoS₂@NC | Hydrothermal | Anode 79.98 | 300.2/3000 | 201.6/1000 after 200th [115] |
| 1T-MoS₂/MoO₃@NC | Hydrothermal, annealing | Anode 78.2 | 257.9/50; 128.8/500 | 120/500 after 400th; 69.7/800 after 400th [122] |
| MoS₂/Sb N-doped graphene | Hydrothermal, freeze drying, annealing | Anode 59.3 | 345.5/50; 235.4/200 | 296.7/500 after 200th; 170.1/2000 after 1000th [117] |
| Fe₃S₉@MoS₂@C | In situ polymerization, sulfidation | Anode 71 | 288/500; 127/5000 | 389.23/2000 after 50th [114] |
| MoS₂–WS₂–C | Spray pyrolysis, annealing | Anode 65 | 377/100; 176/500 | 350/100 after 100th; 291/500 after 50th [112] |
| Sandwich-like MoS₂@SnO₂@C | Hydrothermal, annealing | Anode 73 | 597/50; 345/100 | 312/50 after 25th; 250/200 after 20th [14] |
| MoS₂@rGO | Two-step hydrothermal | Anode – | 679/20; 178/500 | 381/100 after 100th [63] |
| C/MoS₂/G | Hydrothermal, annealing | Anode 40 | 362.5/100; 195.4/10 000 | 346/500 after 200th; 126.4/5000 after 4000h [82] |
| CoSe₂–SnSe₂@NC | Hydrothermal, annealing | Anode 70 | 368/100; 249/1000 | 369/500 after 200th [147] |
| SnS₂/SnO₂/S5M | Hydrothermal | Anode 65.6 | 470/50; 150/1000 | 394/50 after 100th; 155/500 after 250th [137] |
| CoSe₂–FeSe₂@C–II | Sacrificial template, annealing | Anode 71.42 | 420/100; 325/1000 | 271.4/2000 after 300h [141] |
| H-TiO₂–C heterostructures | Wet-chemical method | anode 49.1 | 240.8/100; 114.6/1000 | 132.8/500 after 1200 h [58] |
| VS₄/SnS@C heterostructures | Hydrothermal, freeze drying, annealing | Anode 52.2 | 270.1/100; 162.1/5000 | 227/500 after 3000th; 168.4/1000 after 6000h [136] |

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