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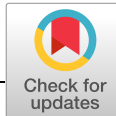
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## REVIEW

# Anode materials for potassium-ion batteries: Current status and prospects

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**Abstract**

Potassium-ion batteries (KIBs) as one of the most promising alternatives to lithium-ion batteries have been highly valued in recent years. However, progress in KIBs is largely restricted by the sluggish development in anode materials. Therefore, it is imperative to systematically outline and evaluate the recent research advances in the field of anode materials for KIBs toward promoting the development of high-performance anode materials for KIBs. In this review, the recent achievements in anode materials for KIBs are summarized. The electrochemical properties (ie. charge storage mechanism, capacity, rate performance, and cycling stability) of these reported anode materials, as well as their advantages/disadvantages, are discerned and analyzed, enabling high-performance KIBs to meet the requirements for practical applications. Finally, technological developments, scientific challenges, and future research opportunities of anode materials for KIBs are briefly reviewed.

**KEYWORDS**

anode materials, capacity and stability, electrochemical properties, energy density, potassium-ion batteries

## 1 | INTRODUCTION

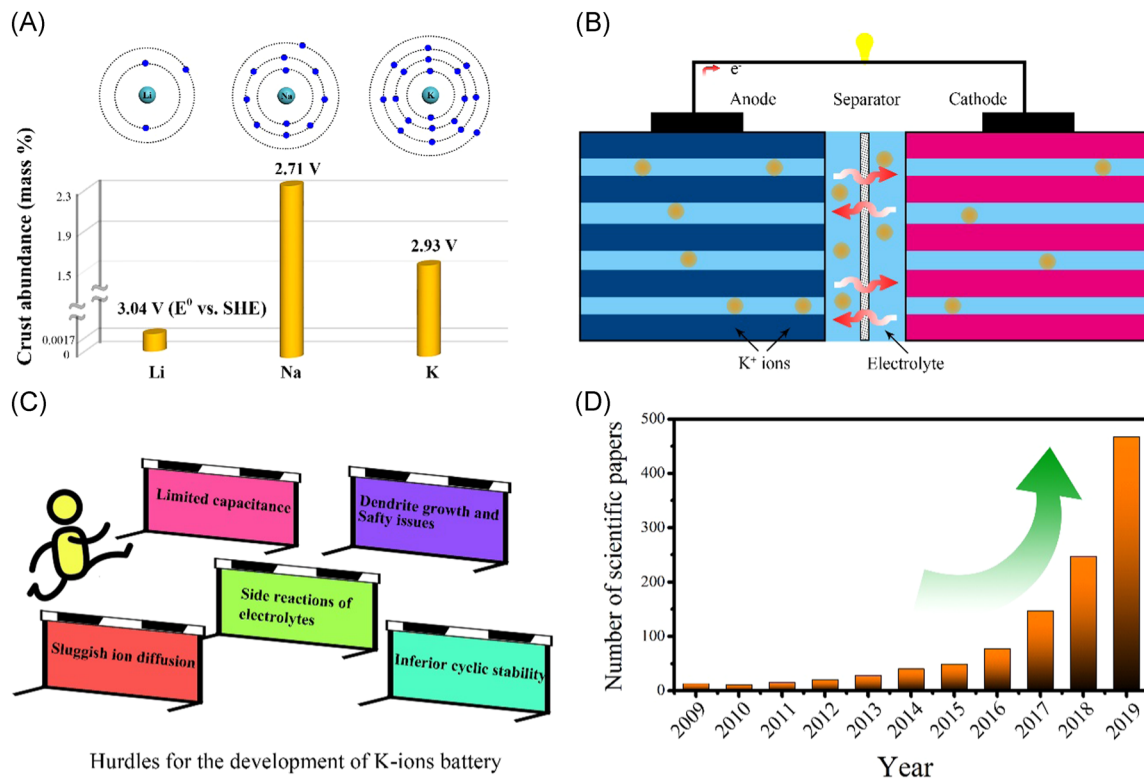
Due to the depletion of fossil fuels and the environmental pollution, clean and renewable energies such as solar, wind, tide, and geothermal play an important role in realizing the sustainable development of human society, and thus have become the fastest-growing renewable energy resources.<sup>1-16</sup> However, these clean energies are always inherently intermittent, resulting in a conflict between energy harvesting and consumption from the aspects of time and space.<sup>15,17-22</sup> To this end, the energy storage system (ESS) is considered to be an effective solution to store and deliver these intermittent energies.<sup>23</sup> So far, lithium-ion batteries (LIBs) are the dominant ESS

technology and have become indispensable in our daily life attributed to their convenience, high energy densities and lack-of-memory property.<sup>24-27</sup> With the rapid expansion of LIB applications, LIBs can hardly satisfy the growing demand for the future ESS, because of the relative scarcity (0.0017 wt% in the Earth's crust) and uneven distribution of lithium source.<sup>28</sup>

As a potential alternative to LIBs, sodium-ion batteries (SIBs) have attracted much attention owing to their high abundance of sodium in the Earth's crust and the low cost (Figure 1A).<sup>29-31</sup> Nevertheless, the relatively high-standard redox potential of Na/Na<sup>+</sup> (−2.71 V vs the standard hydrogen electrode [SHE], as shown in Table 1) leads to the smaller energy density of SIBs than that of

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**FIGURE 1** A, Abundance of Li, Na, and K metals in the Earth's crust (wt%). B, Schematic illustration of potassium-ion batteries (KIBs). C, Summary of challenges and their relationships to the KIBs. D, Number of publications on KIBs according to Web of Science

LIBs, and thus render their applications in portable electronics and electric vehicles.<sup>32–34</sup> Like lithium and sodium, potassium has similar chemical properties, which means that potassium can be utilized as the potential charge carrier and correspondingly the potassium-ion batteries (KIBs) could operate with similar principles as LIBs and SIBs. In KIBs,  $K^+$  ions shuttle between the cathode and the anode via a  $K^+$ -rich electrolyte during the charge/discharge process, which is also termed as “rocking-chair” batteries like LIBs (Figure 1B). In comparison to LIBs and SIBs, KIBs exert three significant advantages of potassium.<sup>34–39</sup> First, the lower standard redox potential of  $K/K^+$  ( $-2.93$  V vs SHE) which is much closer to that of  $Li/Li^+$  ( $-3.04$  V vs SHE) enables KIBs to have a potentially higher energy density than SIBs.<sup>40</sup> Second, the abundance of potassium in the Earth's crust would result in a lower cost of KIBs.<sup>41</sup> Third, the weaker Lewis acidity and the corresponding smaller Stokes' radius of  $K^+$  than those of both  $Li^+$  and  $Na^+$  could lead to the highest conductivity and ion mobility of  $K^+$  in the electrolyte.<sup>42,43</sup>

However, it should be admitted that the current development of KIBs is still facing four significant challenges (Figure 1C). First, KIB electrodes with high capacity to guarantee high energy density are still lacking. Second, the rate performance of KIBs is restricted by

the relatively low diffusivity of large  $K^+$  ions in solid electrodes.<sup>43</sup> Third, the low electrochemical potential of  $K^+/K$  leads to more side reactions because the solvent in the electrolyte is more easily reduced on the surface of the electrode.<sup>44</sup> Finally, also plagued by the large  $K^+$  ions, the electrode materials of KIBs usually suffer from pulverization-induced capacity fading arising from a large volume expansion during the potassiation/depotassiation process.<sup>45</sup> To address these challenges, much research efforts are devoted to understanding the electrochemical mechanism to effectively solve these problems and significantly improve the energy-storage performance of KIBs (Table 2).

So far, an astounding, increasing number of publications have reported on KIBs (Figure 1D),<sup>36,85</sup> and most research is focused on the development of high-performance electrode materials, both cathodes and anodes. Particularly for anode materials that are carriers of  $K^+$  and electrons in the charging process, volume expansion and structural damage along with the de/intercalation of  $K^+$  ions are unavoidable issues due to the large radius of  $K^+$  ion, and thus, anode materials play a significant role in the energy density and long stable cyclability of KIBs. In this review, recent research progress on anode materials for KIBs is outlined, with respect to the design and development of novel anode materials,

**TABLE 1** Physical/electrochemical properties and economic parameters of lithium, sodium, and potassium

Physical/electrochemical properties/economic parameters	Li	Na	K
Atomic number	3	11	9
Atomic mass, u	6.941	22.989	39.098
Density, g cm <sup>-3</sup>	0.535	0.968	0.856
Melting point, °C	180.45	97.72	63.38
Atomic radius, pm	145	180	220
Ionic radius, Å	0.76	1.02	1.38
Covalent radius, pm	128	166	203
Electronic shell structure	(1, 2)	(1, 2, 8)	(1, 2, 8)
Electronic configuration	(He) 2s <sup>1</sup>	(Ne) 3s <sup>1</sup>	(Ar) 4s <sup>1</sup>
Voltage vs SHE, V	-3.04	-2.71	-2.93
Theoretical capacity of the metal electrode, mAh g <sup>-1</sup>	3861	1166	685
Crust abundance, mass %	0.0017	2.3	1.5
Crust abundance, molar %	0.005	2.1	0.78
Cost of carbonate, US\$ ton <sup>-1</sup>	6500	200	1000
Cost of industrial-grade metal, US\$ ton <sup>-1</sup>	100 000	3000	13 000

particularly for the studies which show an obvious effect on the capacity and stability improvement of KIBs. A unique insight into the existing challenges and future directions of anode materials for KIBs is given in Section 3.

## 2 | CARBON-BASED MATERIALS

Owing to the remarkable K<sup>+</sup> de/intercalation ability, graphite has been first studied as an anode for KIBs. As the research developed, many novel carbon-based anode materials, besides graphite, have been explored in the last few years, such as soft carbon, hard carbon (HC), and nongraphite nanostructured carbon.

### 2.1 | Graphite materials

Since the 1940s, K-graphite intercalated compounds (K-GICs) have been reported.<sup>86-88</sup> These compounds were synthesized by using a two-zone vapor transport route, in which K vapor is introduced in a custom-made double furnace with graphite. In this method, several kinds of K-GIC are found to be formed at different stages during

the synthesis process, including KC<sub>8</sub> in Stage I, KC<sub>24</sub> in Stage II, KC<sub>36</sub> in Stage III, and KC<sub>48</sub> in Stage IV.<sup>89</sup> Nishitani et al<sup>90,91</sup> found K atoms distributed irregularly on the hexagonal carbon centers of adjacent graphite layers. Similar to the case of Li-GICs, the different stages of K-GICs were proved, according to the number of graphene layers being separated into the K-intercalated layer. For instance, K-GICs (KC<sub>8</sub>) in stage featured one graphene layer for every K-intercalated layer, which means all the graphene layers were intercalated.

A density functional theory (DFT) study about the intercalation behavior of alkali metals (Li, Na, and K) in graphite reveals that the formation enthalpy of KC<sub>8</sub> (-27.5 kJ mol<sup>-1</sup>) is much lower than that of LiC<sub>6</sub> (-16.5 kJ mol<sup>-1</sup>), which suggests that K<sup>+</sup> ions can more easily intercalate in graphite.<sup>89</sup> Moreover, DFT calculations also indicate that KC<sub>8</sub> has the largest diffusion coefficient, which again highlights the advantage of K<sup>+</sup> ion intercalation in graphite.<sup>92</sup> Furthermore, the kinetics during the formation of K-GICs were investigated through DFT calculation with the dispersion correction method, and the results demonstrate that the migration of K<sup>+</sup> ions via the vacancy mechanism rather than the Frenkel mechanism.<sup>93</sup> The K-storage mechanism in graphite was further experimentally verified by assembling and characterizing K/graphite cells.

Jian et al<sup>46</sup> first took the lead in finding the experimental K-storage properties of graphite. Here, graphite is the working electrode, K metal is the counter electrode, and 0.8 M KPF<sub>6</sub> in 50:50 ethylene carbonate (EC):diethyl carbonate (DEC) is the electrolyte. The resultant K/graphite cell exhibited a high specific discharge capacity of 273 mAh g<sup>-1</sup> at C/40 rate, which is close to the theoretical capacity of 279 mAh g<sup>-1</sup> for the formation of KC<sub>8</sub> (Figure 2A). Also, because of the solid electrolyte interphase (SEI) film formation, the Coulombic efficiency (CE) can stabilize well at ~99%, (Figure 2B). Ex-situ X-ray diffraction (XRD) measurements of electrochemically discharged anode materials reveal that stage-1 KC<sub>8</sub> forms via stage-3 KC<sub>36</sub> and stage-2 KC<sub>24</sub> as intermediate phases where the phase transformations are reversible in converting the KC<sub>8</sub> back to the less-crystalline graphite (Figures 2C,D). However, stage-4 and -5 compounds were hard to observe during the electrochemical process. Meanwhile, a large volume expansion ~61% is observed upon potassiation, which leads to the fast capacity fading and mediocre rate capability of the graphite anode.

Optimizing binders and electrolytes are an efficient solution to tackle the inferior cycling and rate capabilities of graphite anode.<sup>47,49</sup> For example, replacing polyvinylidene difluoride with sodium polyacrylate (PANa) can drastically improve the first-cycle CE, cyclic stability, and rate capability due to the preformed-SEI effect of the

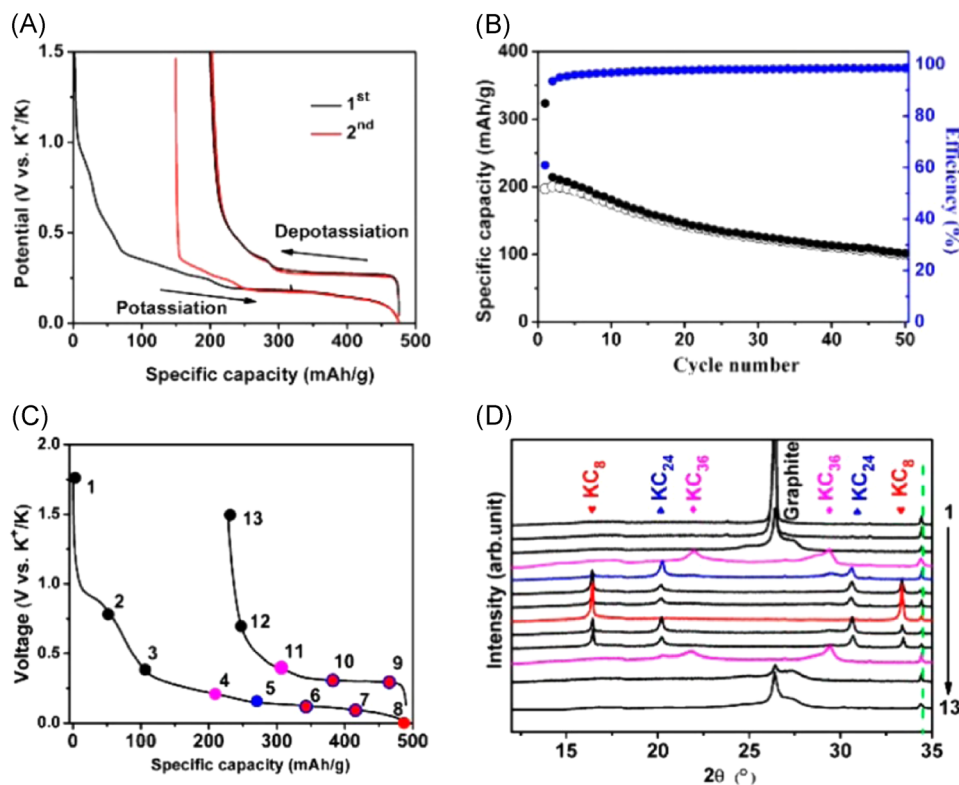
TABLE 2 Summary of recent anode materials for potassium-ion batteries

Material	Reaction	Voltage (V)	Initial capacity (mAh g <sup>-1</sup> )	Initial Coulombic efficiency	Best capacity retention	Best rate performance	Reference
Graphite	Insertion	0.01-1.5	273	57.4%	81.4% at 2 C	30.4% at 5 C	46
Graphite	Insertion	0.01-1.5	279	87%	98% at 25 mA g <sup>-1</sup>	≈95% at 15 C	47
Graphite	Insertion	0.01-1.5	246	66.5%	~89% at 20 mA g <sup>-1</sup>	~20% at 200 mA g <sup>-1</sup>	48
Graphite	Insertion	0.01-2.0	~100	~78.9%	91% at 10 mA g <sup>-1</sup>	~77% at 3 C	49
Polynanocrystalline graphite	Insertion	0.01-2.0	224	54.10%	50% at 240 mA g <sup>-1</sup>	44.8% at 200 mA g <sup>-1</sup>	50
Expanded graphite	Insertion	0.01-3.0	267	81.56%	105.07%	66.5% at 500 mA g <sup>-1</sup>	51
Hard carbon/carbon black	Insertion	0.1-1.0	200	~50%	97% at 0.1 C	~27% at 10 C	52
Hard-soft composite carbon	Insertion	0.01-2.0	261	67%	93% at 1 C	35% at 10 C	53
Hard carbon microspheres	Insertion	0.01-1.5	~270	~62%	83% at 0.1 C	52% at 5 C	54
Activated carbon	Insertion	0.01-2.0	~260	~62%	62% at 0.2 A g <sup>-1</sup>	54% at 1.0 A g <sup>-1</sup>	55
Few-layer F-doped graphene	Insertion	0.01-2.4	330	41.2%	~50% at 500 mA g <sup>-1</sup>	65% at 500 mA g <sup>-1</sup>	56
Nitrogen-doped graphene	Insertion	0.01-1.5	330	80%	96.5% at 100 mA g <sup>-1</sup>	~14% at 200 mA g <sup>-1</sup>	57
N-doped carbon microspheres	Insertion	0.01-3.0	240	75%	75% at 1.8 C	62% at 72 C	58
N-doped hierarchically porous carbon	Insertion	0.001-3.0	303	95%	44.4% at 500 mA g <sup>-1</sup>	67% at 500 mA g <sup>-1</sup>	59
Phosphorus and oxygen dual-doped graphene	Insertion	0.01-3.0	566.6	22.6%	~95% at 2 A g <sup>-1</sup>	41% at 2 A g <sup>-1</sup>	60
Nitrogen- and oxygen-doped carbon nanofiber	Insertion	0.005-3	280	31%	99.5% at 1 C	31% at 10 C	61
Hard carbon-derived from tire rubber	Insertion	0-1.8	181	33%	78% at 0.5 C	~24% at 2 C	62
Porous carbon nanofiber paper	Insertion	0-3.0	272	24.1%	77% at 0.02 A g <sup>-1</sup>	~25% at 7.7 A g <sup>-1</sup>	63
Polycrystalline soft carbon	Insertion	0.01-1.5	599	80%			64
Natural nitrogen-doped carbon nanofibers	Insertion	0.01-2.0	215.2	37.80%	90%	35.2% at 1395 mA g <sup>-1</sup>	65
Nitrogen/oxygen dual-doped hard carbon	Insertion	0.001-3.0	315	25%	76.10%	33% at 3000 mA g <sup>-1</sup>	66
K <sub>2</sub> Ti <sub>4</sub> O <sub>9</sub>	Insertion	0.01-2.5	97	20%	82% at 0.2 C	20% at 15 C	67
K <sub>2</sub> Ti <sub>4</sub> O <sub>9</sub>	Insertion	0.01-3.0	151	26%	61% at 50 mA g <sup>-1</sup>	54% at 300 mA g <sup>-1</sup>	68

(Continues)

TABLE 2 (Continued)

Material	Reaction	Voltage (V)	Initial capacity (mAh g <sup>-1</sup> )	Initial Coulombic efficiency	Best capacity retention	Best rate performance	Reference
K <sub>2</sub> Ti <sub>8</sub> O <sub>17</sub>	Insertion	0.01-3.0	118.7	65.4%	93% at 20 mA g <sup>-1</sup>	37% at 500 mA g <sup>-1</sup>	69
KTi <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub> /C	Insertion	1.2-2.8	75.6	75%	110% at 0.5 C	80% at 5 C	70
Ti <sub>3</sub> C <sub>2</sub>	Insertion	0.01-3.0	136	27%	44% at 200 mA g <sup>-1</sup>	42% at 300 mA g <sup>-1</sup>	71
Ti <sub>3</sub> CNTz	Insertion	0.01-3.0	710	28.40%	10.50%		72
TiSe <sub>2</sub>	Insertion	1.0-3.0	92.7	~67.1%	69.80%	50% at 1000 mA g <sup>-1</sup>	73
MoS <sub>2</sub>	Insertion	0.5-2.0	98	74.4%	97.50%	77% at 2.86 C	74
MoS <sub>2</sub> @RGO	Insertion/ conversion	0.01-3.0	679	~30%	~100% at 100 mA g <sup>-1</sup>	26.2% at 0.5 A g <sup>-1</sup>	75
Co <sub>3</sub> O <sub>4</sub> -Fe <sub>2</sub> O <sub>3</sub> /C	Conversion	0.01-3.0	~420	54%	~52% at 50 mA g <sup>-1</sup>		76
CoS@graphene	Insertion	0.01-2.9	434.5	64.4%	70.2% at 0.5 C	56.2% at 4 C	77
SnS <sub>2</sub> -coated RGO	Conversion/ alloying	0.01-2.0	355	56%	~71.4% at 25 mA g <sup>-1</sup>	~33.8% at 2 A g <sup>-1</sup>	78
Sb <sub>2</sub> S <sub>3</sub> -S, N-co-doped graphene composite	Conversion	0.1-3.0	548	69.7%	89.4% at 50 mA g <sup>-1</sup>	~62% at 1 A g <sup>-1</sup>	79
VSe <sub>2</sub>		0.01-2.6	366	69.10%	95.10%	45.9% at 2 A g <sup>-1</sup>	80
Black phosphorus/C	Alloying	0.01-2.0	433.2	58.50%	61%	~63% at 2 A g <sup>-1</sup>	81
Sn <sub>4</sub> P <sub>3</sub> /C	Alloying	0.01-2.0	350	60%	80%	55.6% at 1 A g <sup>-1</sup>	45
3D carbon network confined Sb nanoparticles	Alloying	0.01-2.0	478	68.20%	96.40%	~60.2% at 1 A g <sup>-1</sup>	82
K <sub>2</sub> TiP		0.1-2	270	46%	71.8% at 0.2 C	20.3% at 2 C	83
K <sub>2</sub> PC		0.1-2.0	245	44%	~88% at 0.2 C	32.2% at 2 C	83
K <sub>2</sub> TP		0.1-2.0	305.8	76.1%		~71% at 1 A g <sup>-1</sup>	84



**FIGURE 2** A, GPD profiles of graphite for the initial two cycles between 0.01 and 1.5 V at C/40. B, Cycling performance of graphite at C/2. C, First-cycle GPD potential profiles at C/10. D, X-ray diffraction patterns of electrodes corresponding to the marked selected states of charges in (C). Reprinted with permission.<sup>46</sup> Copyright 2015, American Chemical Society

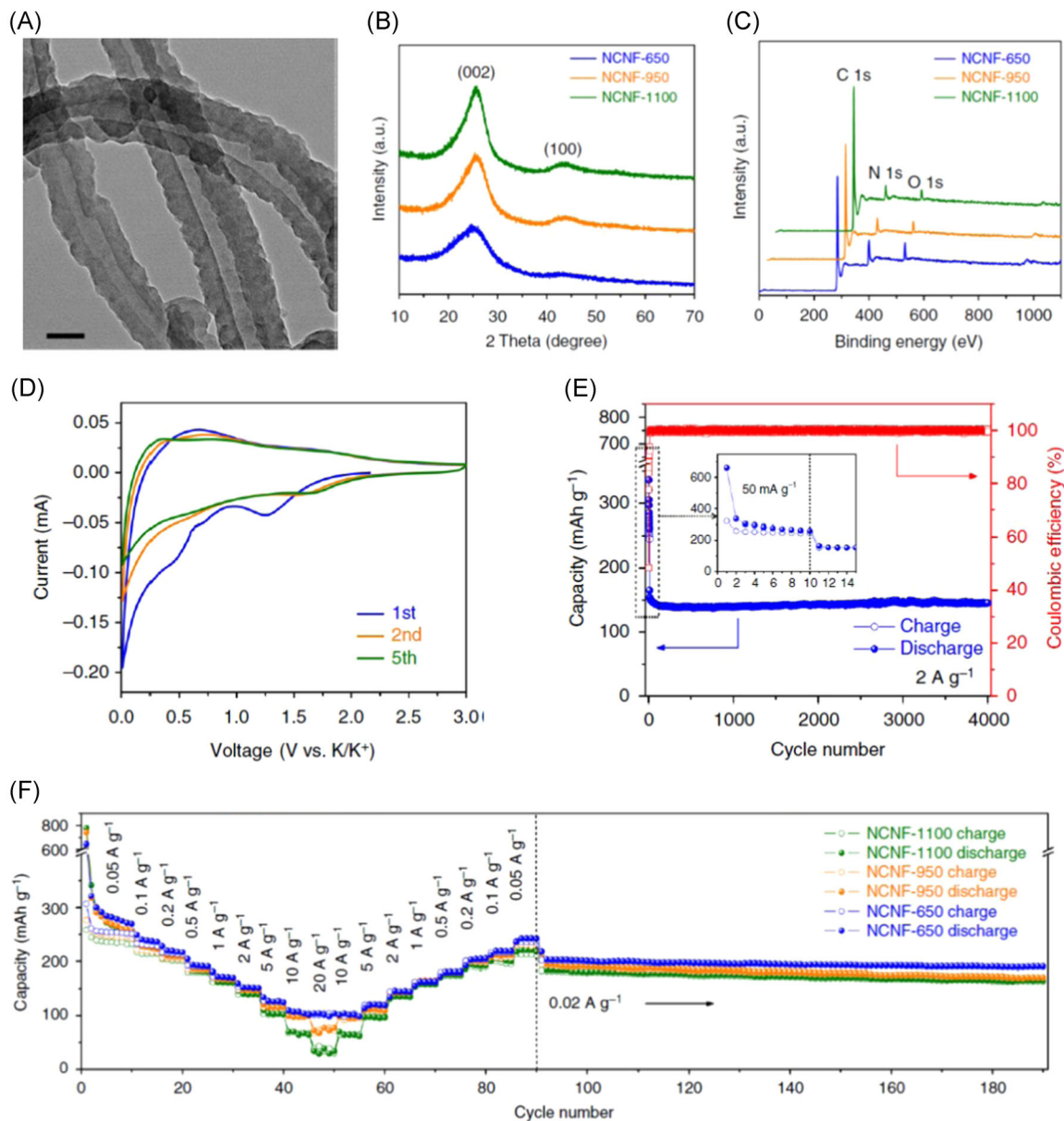
binder PANa. With PANa as the binders, less K is consumed for the formation of SEI-layer in the first discharge cycle of the cell. As the electrolytes also have a strong impact on the formation of stable SEI layers, further tuning the compositions of electrolytes, especially solvents, can also help to improve the performance of the graphite anode. Compared to EC:dimethyl carbonate (EC:DMC) and EC:DEC, EC:propylene carbonate (EC:PC) as the solvent of the electrolytes, enables the graphite anode to have the best capacity retention and the highest first-cycle CE. The reason might be the high solubilizing ability and high ionic conductivity of KPF<sub>6</sub> in EC:PC than those in both EC:DMC and EC:DEC. Apart from graphite, several forms of nongraphite carbon have also been reported to successfully intercalate K, including soft-carbon and hard-carbon microspheres.

### 2.1.1 | Soft carbon and hard carbon

A kind of soft carbon was synthesized via pyrolysis of 3,4,9,10-perylene-tetracarboxylicacid-dianhydride at 900°C and it delivers a capacity of 273 mAh g<sup>-1</sup>, which is similar to that of graphite.<sup>53</sup> The problem of soft carbon is that the potential profile of soft carbon-based KIBs exhibits only slopes instead of the plateaus at 0.3 V being observed in

graphite in a graphite/K cell, indicating an unstable discharge voltage. Recently, three kinds of N-doping soft carbon nanofibers (NCNFs) were fabricated by carbonizing polypyrrole nanofibers at 650°C, 950°C, and 1100°C, respectively.<sup>94</sup> These NCNFs have a unique hollow interior structure and rough surface with high structural defects and are beneficial for K-storage (Figure 3A). Besides this, the N-doping content of NCNFs decreases along with the increase of the carbonization temperature (Figures 3B,C). Due to the high N-doping content and unique structure, NCNF-650 shows the best cycling and rate performance among its counterparts. The NCNF-650 exhibits a capacity of 146 mAh g<sup>-1</sup> at 2 A g<sup>-1</sup> after 4000 cycles (Figures 3D,E) and a rate capability of 101 mAh g<sup>-1</sup> at a 20 A g<sup>-1</sup> (Figure 3F).

Apart from soft carbon, HC can also be used as a KIBs anode with good capacity and long cycle life. More importantly, the discharging plateau of HC is usually above 0.1 V, enabling reducing the risk of K-metal plating and ensure safety. Vaalma et al<sup>95</sup> proved experimentally the electrochemical K<sup>+</sup> intercalation behavior of the HC anode based on its initial voltage profile at 0.1 C. This anode outputs capacities of 200 mAh g<sup>-1</sup> at 0.1 C in the potential window of 0.2 to 2.0 V (Figure 4A). The sloping potential between 1.2 and 0.3 V vs K<sup>+</sup>/K is mostly associated with the intercalation of K<sup>+</sup> ions (100 mAh g<sup>-1</sup>)



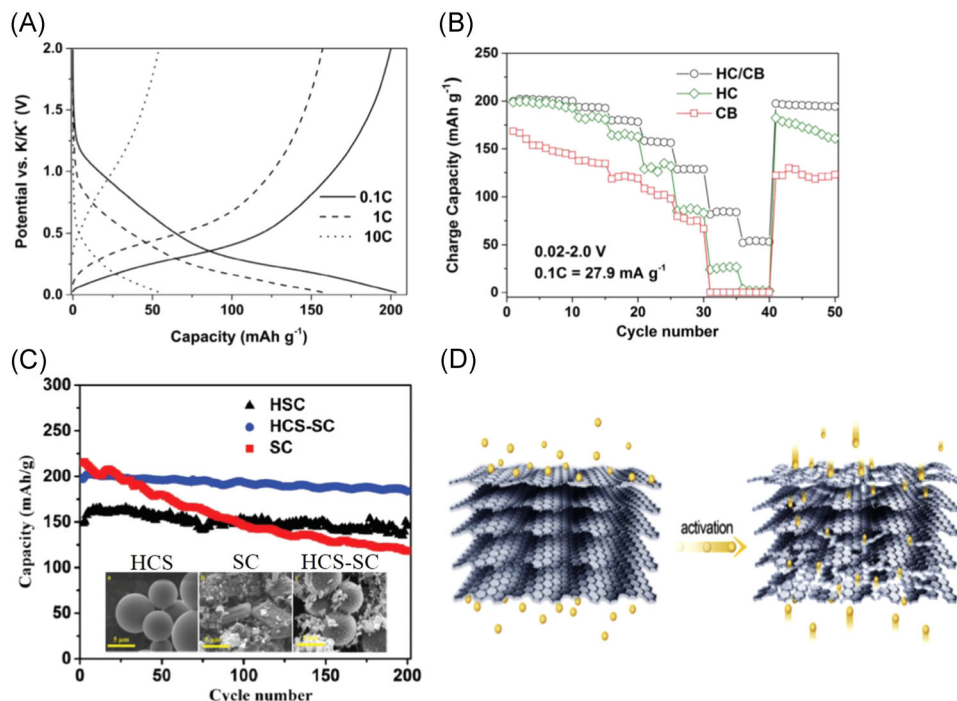
**FIGURE 3** A, Transmission electron microscopy image of NCNF-650. (B) XRD patterns and (C) XPS survey spectra of NCNFs. D, CV curves of NCNF-650. E, Long-term cycling performance of NCNF-650 at a high rate of  $2 \text{ A g}^{-1}$ . F, Rate performance of NCNFs with rates ranging from  $0.05$  to  $20 \text{ A g}^{-1}$ . Reprinted with permission.<sup>94</sup> Copyright 2018, Springer Nature. NCNF, N-doping soft carbon nanofibers; XPS, X-ray photoelectron spectroscopy; XRD, X-ray diffraction

into the distorted graphitic sheets, while the low-potential plateau between  $0.3$  and  $0.02 \text{ V}$  vs  $\text{K}^+/\text{K}$  is correlated with micropore filling ( $100 \text{ mAh g}^{-1}$ ). Furthermore, the role of high-conductive additives of carbon black (CB) is highlighted, and the rate capacity of the HC/CB electrode is greatly improved by adding CB (Figure 4B).

Doping with heteroatoms, such as nitrogen, sulfur, and phosphorus can effectively increase the capacity of HC materials through generating defect sites and functional groups.<sup>96</sup> A sulfur/nitrogen dual-doped hard-carbon material (SNHC) was prepared via a facile pyrolysis method. The SNHC exhibits abundant defect sites, functional groups, and

a hierarchical micro/mesopore structure, which is beneficial to improving the specific capacity. As a result, this SNHC delivers a high capacity of  $293.8 \text{ mAh g}^{-1}$  at  $0.1 \text{ A g}^{-1}$ . Furthermore, the cycle performance is highly stable at both low and high rates, with a capacity of  $213.7 \text{ mAh g}^{-1}$  over 500 cycles at  $0.1 \text{ A g}^{-1}$ , and  $143.6 \text{ mAh g}^{-1}$  over 1200 cycles at  $3 \text{ A g}^{-1}$ , respectively.<sup>97</sup> In addition, a kind of S/O co-doped porous HC microsphere (PCMs) was prepared. The PCMs possess an enlarged interlayer spacing, high surface area, enormous structural defects and functional groups, resulting from the porous framework and the S/O co-doping. Consequently, PCMs exhibit a high capacity of  $226.6 \text{ mAh g}^{-1}$  at





**FIGURE 4** A, Potential profiles recorded at 0.1 C (cycle 10), 1 C (cycle 28), and 10 C (cycle 38) for the HC/CB composite. B, Rate Performance of HC, CB, and HC/CB within 0.02 and 2.0 V range. Reprinted with permission.<sup>95</sup> Copyright 2016, ECS. D Long cycling performance at 1 C rate of hard carbon spheres (HCS), SC, and HCS-SC. Reprinted with permission.<sup>53</sup> Copyright 2017, John Wiley and Sons; D, Schematic illustration of the activation process. Reprinted with permission.<sup>55</sup> Copyright 2017, Elsevier. CB, carbon black; HC, hard carbon; SC, soft carbon

50 mA g<sup>-1</sup> after 100 cycles and superior rate capability of 158.1 mAh g<sup>-1</sup> at 1000 mA g<sup>-1</sup>. Furthermore, it can also maintain a highly reversible capacity of above 108.4 mAh g<sup>-1</sup> for over 2000 cycles at 1000 mA g<sup>-1</sup>.<sup>98</sup>

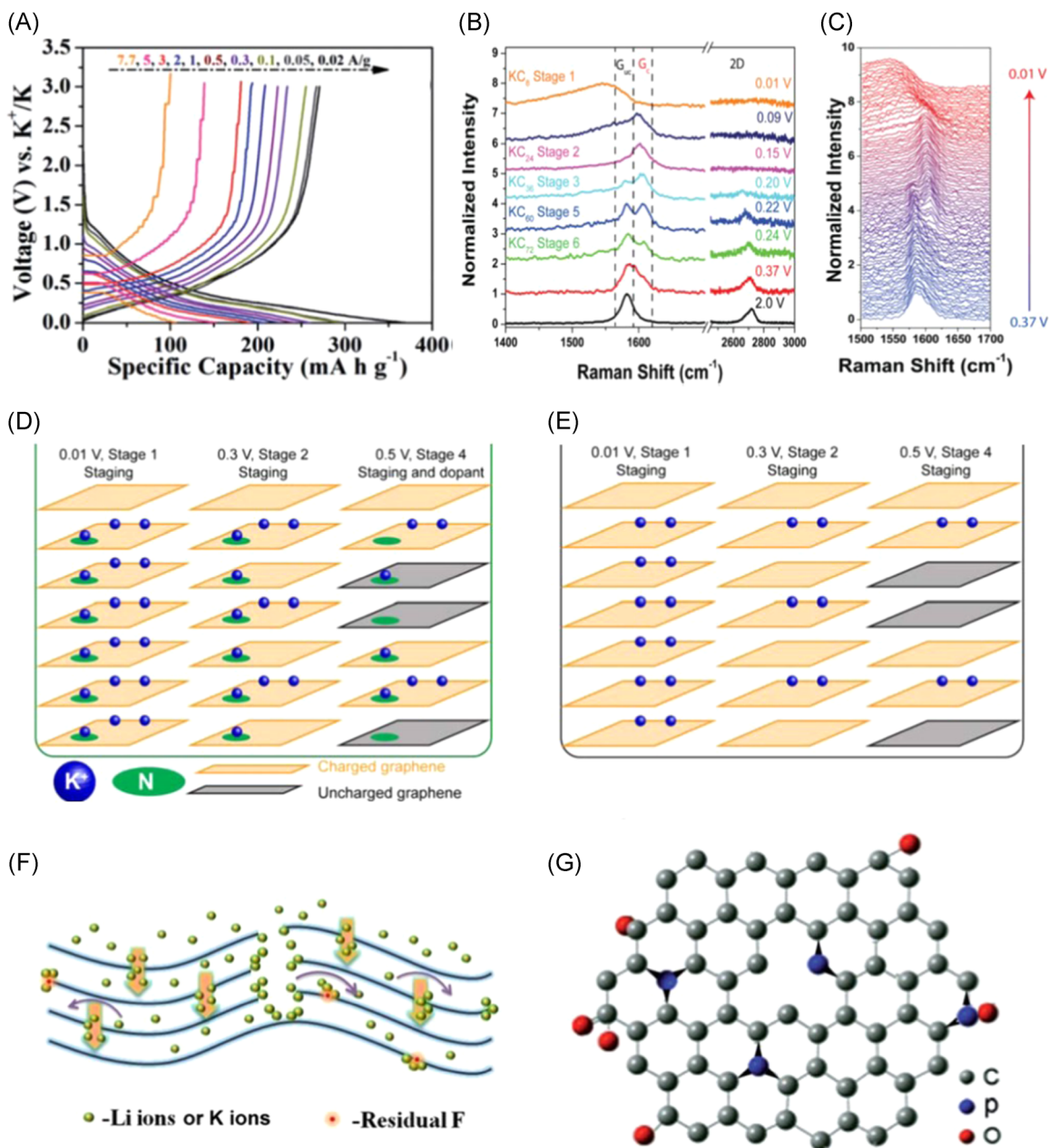
A hard-soft carbon composite was recently designed to improve the limited rate capability of HC and the capacity fading of SC.<sup>54</sup> Compared with the pure SC and HC, the hard-soft carbon composite, with 20 wt% SC distributed in a matrix-phase of HC microspheres, exhibits a high specific capacity and rate performance. It displays a superior initial capacity of 261 mAh g<sup>-1</sup> at 0.1 C and outstanding cycle performance of 93% capacity retention after 200 cycles at 1 C (Figure 4C). As another nongraphite carbon, activated carbon shows a similar intercalation behavior as graphite. This activated carbon exhibits relatively large d-spacings in the (100) crystal planes (graphite: 0.334 nm vs activated carbon: 0.358 nm), being beneficial to facilitating rapid intercalation/deintercalation of K<sup>+</sup> ions (Figure 4D).

### 2.1.2 | Nanostructured nongraphite carbon

Nanostructured carbon materials, such as carbon nanofibers (CNFs) and graphene, can also be utilized as

anodes for KIBs. Self-supported free-standing CNFs arrays can directly serve as electrodes without binders.<sup>31</sup> The CNFs display a high initial discharge capacity of 680 mAh g<sup>-1</sup> at 50 mA g<sup>-1</sup> in the first cycle and gradually stabilizes at 80 mAh g<sup>-1</sup> after 20th cycles.<sup>99</sup> Similarly, porous CNFs with a high rate capacity of 100 mAh g<sup>-1</sup> at 7.7 A g<sup>-1</sup> were reported (Figure 5A).<sup>63</sup> Moreover, a negligible capacity decay per cycle was observed with the capacity changing from 270 to 211 mAh g<sup>-1</sup> after 1200 cycles at 20 mA g<sup>-1</sup>, ascribed to the fact that the porous structure can effectively relieve the volume expansion during the intercalation of K<sup>+</sup> ions.

Graphene has also been investigated as a potential anode for KIBs.<sup>101</sup> Reduced graphene oxide fabricated from a modified Hummer's method delivers a capacity of about 50 mAh g<sup>-1</sup> at 100 mA g<sup>-1</sup> which is much smaller than that of graphite.<sup>102</sup> Share et al<sup>100</sup> used few-layer graphene (FLG) as anode and investigated its electrochemical performance. The FLG produced reversible capacities of ~150 mAh g<sup>-1</sup> at 100 mA g<sup>-1</sup> for 100 cycles, with CEs over 90%. The intercalation mechanism of K<sup>+</sup> ions into FLG was revealed via in situ Raman spectroscopy, which enables comparing the ratio of the graphene uncharged peak and charged peak in the Raman spectra and assigned them to the different stages of K-GICs (Figures 5B,C). A one-/two-dimensional



**FIGURE 5** A, Voltage profiles of the carbon nanofiber anodes in potassium-ion batteries. Reprinted with permission.<sup>63</sup> Copyright 2017, The Royal Society of Chemistry. B, Selective Raman spectra taken at different states of charge as indicated in the LSV. C, Waterfall plot of all Raman spectra taken between 0.37 and 0.01 V. Reprinted with permission.<sup>100</sup> Copyright 2016, The Royal Society of Chemistry. D, Schematic of the staging and defect storage mechanism in N-FLG and FLG (E). Reprinted with permission.<sup>57</sup> Copyright 2016, American Chemical Society. F, Li, or K-ion diffusion mechanism. Reprinted with permission.<sup>56</sup> Copyright 2016, American Chemical Society. G, Schematic of phosphorus and oxygen dual-doped graphene. Reprinted with permission.<sup>60</sup> Copyright 2017, The Royal Society of Chemistry. FLG, few-layer graphene

(1D/2D)  $C_3N_4$ /rGO composite was synthesized and the unique 1D/2D morphology prevents the restacking of graphene layers and aggregation of  $C_3N_4$  nanoparticles. Owing to this unique structure, the composite delivers a specific capacity of  $464.9 \text{ mAh g}^{-1}$  after 200 cycles at  $1 \text{ A g}^{-1}$ . Furthermore, it showed minimal capacity fading with  $228.6 \text{ mAh g}^{-1}$  after 1000 cycles at  $10 \text{ A g}^{-1}$ .<sup>103</sup>

Noteworthy, heteroatom (F, N, P, B, and O) doping into the carbon matrix tends to create defect sites that can attract alkali ions, and meanwhile, improve the electrical conductivity properties of a carbonaceous matrix by enhancing the ion/electron diffusion velocity.<sup>104-109</sup> The nitrogen doping of FLG can increase the  $K^+$  ion storage capability to over  $350 \text{ mAh g}^{-1}$ , demonstrating N-doping activates the

distributed storage sites in the carbon lattice and, therefore, offers extra charge capacity (Figures 5D,E).<sup>57</sup> Recently, a few-layer F-doped graphene foam was prepared, exhibiting a high capacity of  $165.9 \text{ mAh g}^{-1}$  at  $500 \text{ mA g}^{-1}$  after 200 cycles.<sup>56</sup> The high electrochemical performance is largely ascribed to the improvement of the electrochemical reactivity and numerous defect sites, as well as electrical conductivity, attributed to F-doping and the unique framework (Figure 5F). Dual-doped graphene (PODG) material with P and O doping is another example.<sup>60</sup> The large interlayer spacing induced by P and O dual doping enables the PODG to deliver a high capacity of  $474 \text{ mAh g}^{-1}$  at  $50 \text{ mA g}^{-1}$  after 50 cycles and it retained a capacity of  $160 \text{ mAh g}^{-1}$  at  $2000 \text{ mA g}^{-1}$  after 600 cycles. (Figure 5G).

## 2.2 | Noncarbon-based materials

Noncarbon-based anodes are another important anode candidate for KIBs. According to the  $\text{K}^+$  ions storage mechanism, the noncarbon anodes are generally divided into three main categories, that is, intercalation compounds, alloying compounds, and conversion-type compounds.

### 2.2.1 | Noncarbon-based intercalation anodes

For secondary batteries, titanium-based materials are one of the important intercalation anodes. Among them,  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  and  $\text{Na}_2\text{Ti}_3\text{O}_7$  have been widely studied as intercalation anodes for LIBs and SIBs. Analogs of these compounds like potassium tetratitanate ( $\text{K}_2\text{Ti}_4\text{O}_9$ ) are believed to be promising intercalation anodes for KIBs.

$\text{K}_2\text{Ti}_4\text{O}_9$  has a layered structure with an interlayer gap suitable for accommodating K ions (Figure 6A).<sup>67</sup> It exhibits an initial discharge capacity of  $80 \text{ mAh g}^{-1}$  at  $100 \text{ mA g}^{-1}$  and  $97 \text{ mAh g}^{-1}$  at  $30 \text{ mA g}^{-1}$ , respectively. To improve the cyclic stability of  $\text{K}_2\text{Ti}_4\text{O}_9$ , further modifications such as control of particle size and porosity is carried out. For instance, ultrathin nanoribbons of potassium titanate (M-KTO,  $\text{K}_2\text{Ti}_4\text{O}_9$ ) were fabricated by simultaneous oxidation and alkalization process of  $\text{Ti}_3\text{C}_2$  MXene nanosheets (Figure 6B).<sup>68</sup> M-KTO has suitable interlayer spacing, ultrathin thickness, and narrow width as well as an open microporous network. As a result, it exhibits an outstanding reversible capacity of  $151 \text{ mAh g}^{-1}$  at  $50 \text{ mA g}^{-1}$  and long-term stable cyclability over 900 cycles.

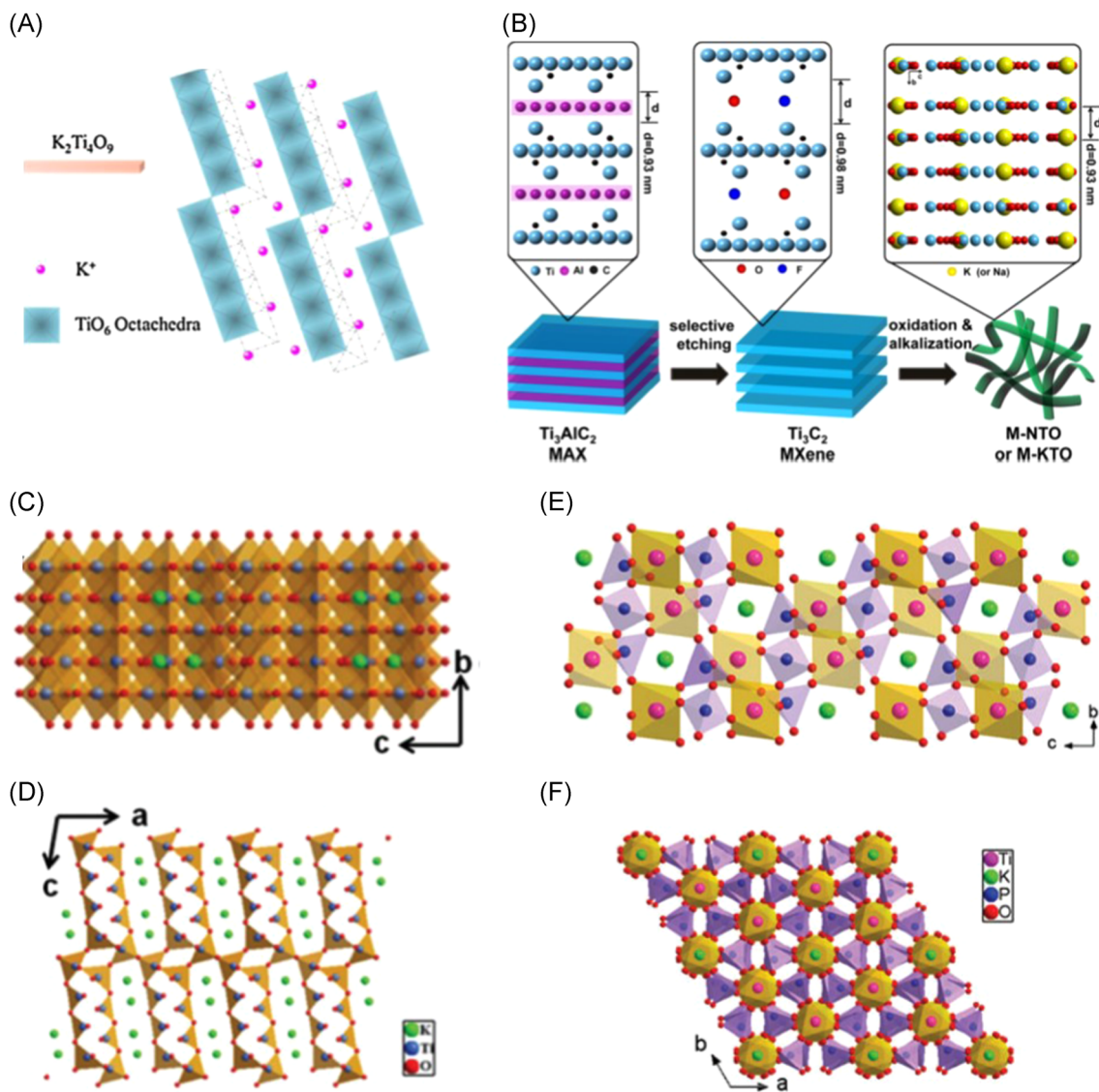
As another titanium-based compound, unique  $\text{K}_2\text{Ti}_8\text{O}_{17}$  nanorods were prepared and studied as anodes for KIBs.<sup>69</sup> The special nanorod morphology of  $\text{K}_2\text{Ti}_8\text{O}_{17}$  provides both a large contact area with the electrolyte and numerous surface-active sites, beneficial for  $\text{K}^+$  ions storage (Figures 6C,D).

Furthermore, the stepped layered structure of  $\text{TiO}_6$  octahedrons has large interstitial spaces and open channels for  $\text{K}^+$  ions fast transport. Benefiting from the unique structure,  $\text{K}_2\text{Ti}_8\text{O}_{17}$  nanorods have a high initial discharge capacity of  $181.5 \text{ mAh g}^{-1}$  at  $20 \text{ mA g}^{-1}$  and retain  $110.7 \text{ mAh g}^{-1}$  after 50 cycles, as well as a high rate capacity of  $44.2 \text{ mAh g}^{-1}$  at  $500 \text{ mA g}^{-1}$ .

$\text{KTi}_2(\text{PO}_4)_3$  is a kind of NASICON-type polyanionic compound, its structure has enough space to accommodate  $\text{K}^+$  ions transport into the crystal, which benefits the cycling stability of KIBs, as shown in Figures 6E,F.<sup>111</sup> Although the three-dimensional (3D) framework of the  $\text{KTi}_2(\text{PO}_4)_3$  crystal provides large interstitial spaces and offers open channels for K-ion transport, their conductivity is relatively low. In response to this issue, a nanocubic  $\text{KTi}_2(\text{PO}_4)_3$  was prepared and coated with a thin layer of carbon to improve its electronic conductivity. The carbon-coated  $\text{KTi}_2(\text{PO}_4)_3$  delivers a discharge capacity of  $75.6 \text{ mAh g}^{-1}$  at 0.5 C in the first cycle and retains cycling stability up to 100 cycles.

Recently, 2D transition metal carbides and carbonitride (MXene) materials have attracted much attention because of their intriguing geometry and electronic and electrochemical properties. Usually, MXenes are synthesized by etching thin metal layers from MAX phases, where M stands for the transition metal (eg. Ti, V, Cr, Mo, and Nb), A represents the elements from groups 13 and 14 (eg. Al, Si, Sn, and Ga), X signifies carbon and/or nitrogen.<sup>112-115</sup> A  $\text{Ti}_3\text{CNT}_z$  anode was developed by etching aluminum from their corresponding MAX phases.<sup>116</sup> It shows an ultrahigh initial discharge capacity of  $710 \text{ mAh g}^{-1}$  at  $20 \text{ mA g}^{-1}$  but poor cycling stability, only  $75 \text{ mAh g}^{-1}$  capacity was maintained after 100 consecutive cycles. The XRD study indicates that there is an irreversible expansion in the c-lattice of this  $\text{Ti}_3\text{CNT}_z$  at the first potassiation cycle because  $\text{K}^+$  ions were trapped and blocked between the layers and hardly extracted at the following cycles and, thus, lead to significant capacity fading (Figure 7A). To improve the electrochemical performance, alkaliized  $\text{Ti}_3\text{C}_2$  MXene nanoribbons were fabricated with a unique structure.<sup>72</sup> Benefiting from the expanded interlayer spacing, 3D porous framework, and narrow widths,  $\text{Ti}_3\text{C}_2$  delivers a high reversible capacity of  $136 \text{ mAh g}^{-1}$  at  $20 \text{ mA g}^{-1}$  and an outstanding long-term cyclability of about  $42 \text{ mAh g}^{-1}$  after 500 cycles at  $200 \text{ mA g}^{-1}$ .

$\text{MoS}_2$  has an S-Mo-S layered structure and is able to maintain a wider interlayer spacing and an open 2D diffusion pathway for  $\text{K}^+$  ion intercalation and transportation.<sup>117</sup> Owing to the stable layered structure,  $\text{MoS}_2$  shows good cycle stability with 97.5% of the 10th capacity retained after 200 cycles at  $20 \text{ mA g}^{-1}$ .<sup>74</sup> Furthermore, the  $\text{K}^+$  ion intercalation process and the corresponding phase

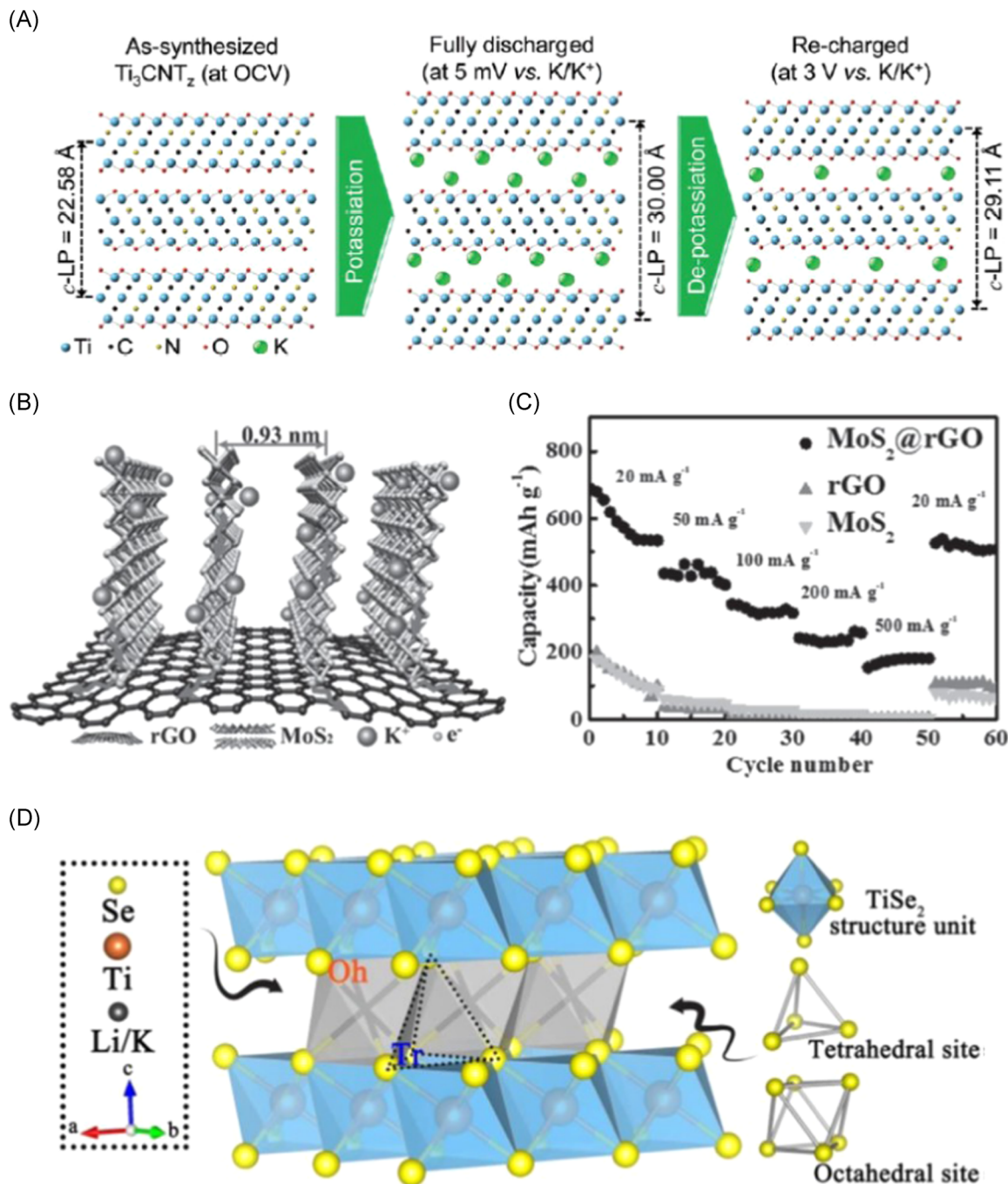


**FIGURE 6** A, Crystal structure of  $K_2Ti_4O_9$ . Reprinted with permission from Yang Cao et al.<sup>110</sup> Copyright 2014, Elsevier. B, Schematic illustration of the fabrication of M-NTO (nanoribbons of sodium titanate,  $NaTi_{1.5}O_{8.3}$ ) or M-KTO nanoribbons. Reprinted with permission.<sup>68</sup> Copyright 2017, American Chemical Society; C, D, Projections of the  $K_2Ti_8O_{17}$  structure along the<sup>79</sup>  $[100]$  and  $[010]$  directions. Reprinted with permission.<sup>69</sup> Copyright 2016, The Royal Society of Chemistry; E, F, Projections of the  $KTi_2(PO_4)_3$  structure along the<sup>79</sup>  $[100]$  and  $[001]$  directions respectively. Reprinted with permission.<sup>111</sup> Copyright 2016, the Royal Society of Chemistry. KTO, potassium titanate

evolutions in  $MoS_2$  were also revealed. In detail, a hexagonal  $K_xMoS_2$  ( $x > 0.4$ ) was formed in the process of intercalation and the phase is unstable when reaching a higher  $K^+$  ion intercalation ratio, leading to the degradation of  $MoS_2$  and reduction to Mo and  $K_xS$  species. To further improve the electrochemical performance, petal-like  $MoS_2$  nanosheets vertically grown on graphene sheets ( $MoS_2@rGO$ ) were fabricated via a two-step solvothermal method (Figure 7B).<sup>75</sup> Owing to the synergistic effect of  $MoS_2$  nanosheets and the flexible graphene backbone, the composites deliver a high initial charge capacity of  $679 \text{ mAh g}^{-1}$  at  $20 \text{ mA g}^{-1}$  and retain a charge capacity of  $380 \text{ mAh g}^{-1}$  at a  $100 \text{ mA g}^{-1}$  after 100 cycles. Compared to the  $MoS_2$  and rGO counterparts,

$MoS_2@rGO$  shows the best rate performance with capacities of 427, 313, 232, and  $178 \text{ mAh g}^{-1}$  at 50, 100, 200, and  $500 \text{ mA g}^{-1}$ , respectively (Figure 7C).

The large interlayer space and high electrical conductivity also make metal selenide materials (such as  $MoSe_2$  and  $TiSe_2$ ) attractive for KIBs. A carbon-coating and N-doping  $MoSe_2$  composite shows a good rate performance and long cycling stability with a discharge capacity of  $258 \text{ mAh g}^{-1}$  at  $100 \text{ mA g}^{-1}$  after 300 cycles and a capacity of  $197 \text{ mAh g}^{-1}$  at  $1000 \text{ mA g}^{-1}$ .<sup>118</sup>  $TiSe_2$  was synthesized via a powder-sintering approach and the crystal structure is shown in Figure 7D.<sup>73</sup> Owing to the large interlayer space,  $TiSe_2$  delivers an initial charge capacity of  $92.7 \text{ mAh g}^{-1}$  and maintains a reversible



**FIGURE 7** A, Schematic for the structure of  $\text{Ti}_3\text{CNO}_2$  before and after electrochemical potassiation and depotassiation.  $\text{O}_2$  was used instead of  $\text{T}_2$  for simplicity (c-LP stands for the c-lattice parameter). Reprinted with permission.<sup>72</sup> Copyright 2017, The Royal Society of Chemistry. B, Schematic illustration showing the paths for K-ion diffusion and electron conduction in the  $\text{MoS}_2@\text{rGO}$  composites. C, Rate performances of the  $\text{MoS}_2@\text{rGO}$ ,  $\text{MoS}_2$  particle, and pure rGO anodes at different current densities. Reprinted with permission.<sup>75</sup> Copyright 2017, John Wiley and Sons. D, Crystal structure of  $\text{TiSe}_2$  with octahedral sites (Oh) as well as the adjacent tetrahedral sites (Tr). Reprinted with permission.<sup>73</sup> Copyright 2018, Elsevier

capacity of 64.7 mAh g<sup>-1</sup> after the 100th cycle at 65 mA g<sup>-1</sup>. Furthermore, the potassiation/depotassiation reaction mechanism was unraveled by the analysis of in situ XRD, during the intercalation/extraction process of K<sup>+</sup> ions,  $\text{TiSe}_2$  goes through three-phase stages of  $\text{K}_{0.25}\text{TiSe}_2$ ,  $\text{K}_{0.58}\text{TiSe}_2$ , and  $\text{K}_x\text{TiSe}_2$  ( $x \approx 0.7$ ) by a series of tests.

## 2.2.2 | Conversion-type anodes

Several transition metal oxides and transition metal sulfides have been reported as conversion anodes, owing to their high theoretical capacities and redox reversibility. A composite of  $\text{Co}_3\text{O}_4\text{-Fe}_2\text{O}_3$  nanoparticles in a super

P carbon matrix ( $\text{Co}_3\text{O}_4\text{-Fe}_2\text{O}_3/\text{C}$ ) was fabricated via the molten salt method, and here, the carbon matrix is able to enhance the conductivity as well as reduce the impact of volume change.<sup>76</sup> The electrochemical reaction process in the hybrid  $\text{Co}_3\text{O}_4\text{-Fe}_2\text{O}_3/\text{C}$  was proposed as follows: (a)  $\text{Fe}_2\text{O}_3 + 6\text{K}^+ + 6\text{e}^- \rightleftharpoons 2\text{Fe} + 3\text{K}_2\text{O}$  and (b)  $\text{Co}_3\text{O}_4 + 8\text{K}^+ + 8\text{e}^- \rightleftharpoons 3\text{Co} + 4\text{K}_2\text{O}$ . This composite delivers a high reversible capacity of  $220\text{ mAh g}^{-1}$  at  $50\text{ mA g}^{-1}$  for 50 cycles. A  $\text{Co}_3\text{O}_4@\text{N-doped}$  composite with a N-doped amorphous carbon layer coating over  $\text{Co}_3\text{O}_4$  nanoparticles was studied as another example. Due to the conductive carbon layer, the conductivity and  $\text{K}^+$  diffusion rate of the composite were increased, and the layer also inhibited the formation of aggregated intermediates, improving the cycling performance. Due to these advantages, the  $\text{Co}_3\text{O}_4@\text{N-C}$  was able to retain about  $213\text{ mAh g}^{-1}$  after 740 cycles.<sup>119</sup> Likewise, a composite of  $\text{SnS}_2\text{-rGO}$  was designed by treating the peroxostannate-graphene oxide composite with  $\text{H}_2\text{S}$ .<sup>120</sup> The composite exhibits a high initial capacity of about  $350\text{ mAh g}^{-1}$  and retains over  $250\text{ mAh g}^{-1}$  after 30 cycles. Later on, CoS quantum dot (QDs) nanoclusters anchored on graphene nanosheets ( $\text{CoS}@G\text{-25}$ ) were reported (Figure 8A).<sup>77</sup> CoS QDs display a capacity of  $310.8\text{ mAh g}^{-1}$  at  $500\text{ mA g}^{-1}$  for 100 cycles. Subsequently, an architecture of  $\text{Sb}_2\text{S}_3$  nanoparticles dispersed in porous S, N co-doped graphene framework ( $\text{Sb}_2\text{S}_3\text{-SNG}$ ) was designed and shows good electrochemical performance, attributed to the porous co-doping graphene framework, which can buffer volume expansion and promote fast electron and ion transfer.<sup>79</sup> In detail, it exhibits a high reversible capacity of  $548\text{ mAh g}^{-1}$  at  $20\text{ mA g}^{-1}$ , outstanding cycling stability with a CE of 89.4% at  $50\text{ mA g}^{-1}$  for 100 cycles, and an excellent rate capability of  $340\text{ mAh g}^{-1}$  at  $1000\text{ mA g}^{-1}$ .

Similarly,  $\text{VSe}_2$  also follows a combination of intercalation and conversion reactions. It consists of two steps: first,  $\text{K}^+$  ions intercalate into  $\text{VSe}_2$  to form  $\text{K}_x\text{VSe}_2$  (Figure 8B) and second,  $\text{K}_x\text{VSe}_2$  decomposes into V and  $\text{K}_2\text{Se}$  through a conversion reaction.<sup>80</sup> Benefiting from the merits of a unique 2D nanostructure and high electron/ion conductivity, the nanosheets output a high reversible capacity of  $366\text{ mAh g}^{-1}$  at  $100\text{ mA g}^{-1}$  and a high rate capability of  $169\text{ mAh g}^{-1}$  at  $2000\text{ mA g}^{-1}$ .

### 2.2.3 | Alloy anodes

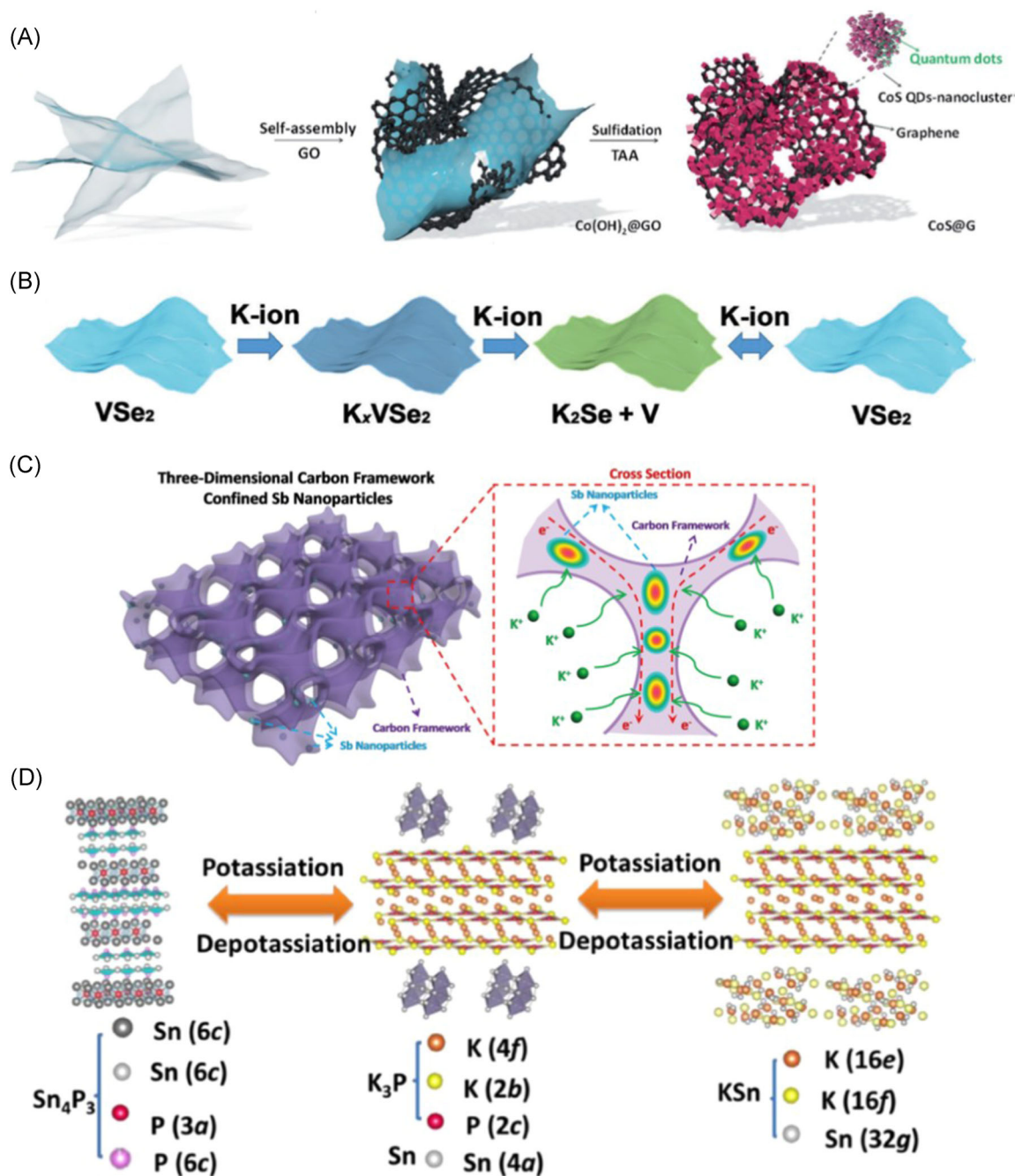
Alloy anodes take advantage of the alloying reactions between certain elements (group 14 or 15 elements) and alkali metals to achieve surprisingly higher specific capacities for KIBs.<sup>122-125</sup> With the help of DFT calculations, the energetics associated with different anode materials were computed, indicating high theoretical

capacities might be achieved by alloy anodes.<sup>126</sup> However, the volume expansion for the K alloying anodes is also large because of the intrinsically larger ionic radius of  $\text{K}^+$  ions. As a result, strategies (morphology optimization and surface engineering, etc.) should be found for the alloy anodes to prevent active material pulverization upon cycling and obtain better electrochemical performance.

McCulloch et al.<sup>127</sup> first reported the electrochemical model of the Sb-C composite as KIBs anodes and the Sb-C composite exhibits a high reversible capacity of  $650\text{ mAh g}^{-1}$ , about 98% of theoretical capacity.<sup>127</sup> Thereafter, a 3D  $\text{SbNPs}@C$  composite was developed with Sb nanoparticles being wrapped into the 3D carbon framework via a freeze-drying treatment. The unique 3D structure network improves the effective contact area between electrode and electrolyte (Figure 8C).<sup>121</sup> In addition, the carbon matrix can not only avoid the agglomeration of Sb particles but also enhances the conductivity of the overall electrode. The 3D  $\text{SbNPs}@C$  anode delivers a high reversible capacity of  $478\text{ mAh g}^{-1}$  at  $200\text{ mA g}^{-1}$  and a remarkable rate capability of  $288\text{ mAh g}^{-1}$  at  $1000\text{ mA g}^{-1}$ . Furthermore, the reaction mechanism is investigated through in situ XRD analysis, concluding a two-step alloying process where an intermediate phase  $\text{K}_x\text{Sb}$  and a  $\text{K}_3\text{Sb}$  phase are formed during the cycles. Recently, a unique  $\text{Sb}@CSN$  (Sb nanoparticles @ carbon sphere network) composite was prepared and shows a high capacity of  $551\text{ mAh g}^{-1}$  at  $100\text{ mA g}^{-1}$  after 100 cycles with only a 0.06% capacity decay per cycle and  $504\text{ mAh g}^{-1}$  after 220 cycles at a high current density of  $200\text{ mA g}^{-1}$ .<sup>128</sup>

An Sn-carbon composite was prepared and showed a reversible capacity of  $110\text{ mAh g}^{-1}$  at  $25\text{ mA g}^{-1}$  after 30 cycles.<sup>129</sup> Furthermore, in situ XRD tests demonstrated the working principle of Sn anodes with the  $\text{K}_2\text{Sn}_5$  and  $\text{K}_4\text{Sn}_{23}$  forming in the reaction process. Later, the reaction mechanism of Sn anodes in KIBs was further revealed using in situ TEM testing by Wang et al.<sup>130</sup> A two-step potassiation mechanism was proposed: (1) the formation of a  $\text{KSn}$  phase after full reaction and (2) the reversible formation of the nanopore and pulverization during the cycling of Sn nanoparticles.

A  $\text{Sn}_4\text{P}_3/\text{C}$  electrode was prepared with a good cycling capacity of  $307.2\text{ mAh g}^{-1}$  after 50 cycles and a good rate capability of  $221.9\text{ mAh g}^{-1}$  at  $1\text{ A g}^{-1}$ .<sup>45</sup> The mechanism of this composite may be described as follows: (a)  $\text{Sn}_4\text{P}_3 + (9 - 3x)\text{K} \rightleftharpoons 4\text{Sn} + 3\text{K}_{3-x}\text{P}$ , (b)  $23\text{Sn} + 4\text{K} \rightleftharpoons \text{K}_4\text{Sn}_{23}$ , and (c)  $\text{K}_4\text{Sn}_{23} + 19\text{K} \rightleftharpoons 23\text{KSn}$ . Upon potassiation, a conversion reaction first occurs where the  $\text{Sn}_4\text{P}_3$  compound breaks into small Sn particles and a  $\text{K}_{3-x}\text{P}$  matrix (Figure 8D). Subsequently, K is inserted into Sn to first form  $\text{K}_4\text{Sn}_{23}$  and finally  $\text{KSn}$  through the alloying



**FIGURE 8** A, Schematic illustration of the synthesis process for the CoS@G-25 composite. Reprinted with permission.<sup>77</sup> Copyright 2017, John Wiley and Sons. B, Schematic illustration of the reversible K<sup>+</sup> ion storage in the ultrathin VSe<sub>2</sub> nanosheets. Reprinted with permission.<sup>80</sup> Copyright 2018, John Wiley and Sons. C, Schematic illustration of the 3D SbNPs@C hybrid electrode with large electrode-electrolyte contact area, short K-ion diffusion distances and fast electron transport network. Reprinted with permission.<sup>121</sup> Copyright 2018, The Royal Society of Chemistry. D, Potassiation/depotassiation process in Sn<sub>4</sub>P<sub>3</sub>/C electrode. Reprinted with permission.<sup>45</sup> Copyright 2017, American Chemical Society

reaction. During the depotassiation, KSn de-alloys first to form Sn, and then Sn reacts with K<sub>3-x</sub>P to convert it back to Sn<sub>4</sub>P<sub>3</sub>, thus, the stepped formation of K-Sn (K<sub>4</sub>Sn<sub>23</sub>, KSn) and K-P alloy (K<sub>3-x</sub>P) phases.

Metal Bi can also serve as the anode in KIBs and delivers an excellent capacity of 322 mAh g<sup>-1</sup> with high

CE of 86.9% after 300 cycles at 2 C.<sup>82</sup> It is found that Bi undergoes three two-phase reactions: Bi ⇌ KBi<sub>2</sub>, KBi<sub>2</sub> ⇌ K<sub>3</sub>Bi<sub>2</sub>, and K<sub>3</sub>Bi<sub>2</sub> ⇌ K<sub>3</sub>Bi. During this process, the bulk Bi gradually evolved to a 3D porous network, which allows fast K<sup>+</sup> ion transmission and buffers the volume change, thus resulting in the outstanding stability.

Recently, a composite of Bi and N-doped carbon (Bi@N-C) was synthesized through a solvothermal method.<sup>131</sup> The multicore-shell structure has a conductive porous N-doped carbon shell with the nanosized Bi being encapsulated inside. This unique nanostructure not only prevents the volume expansion during the potassiation /depotassiation process but also forms a stable SEI during cycling. As a result, the Bi@N-C exhibits an excellent rate performance of 152 mAh g<sup>-1</sup> at 100 A g<sup>-1</sup> and long cycle life of 203 mAh g<sup>-1</sup> at 10 A g<sup>-1</sup> after 1000 cycles.

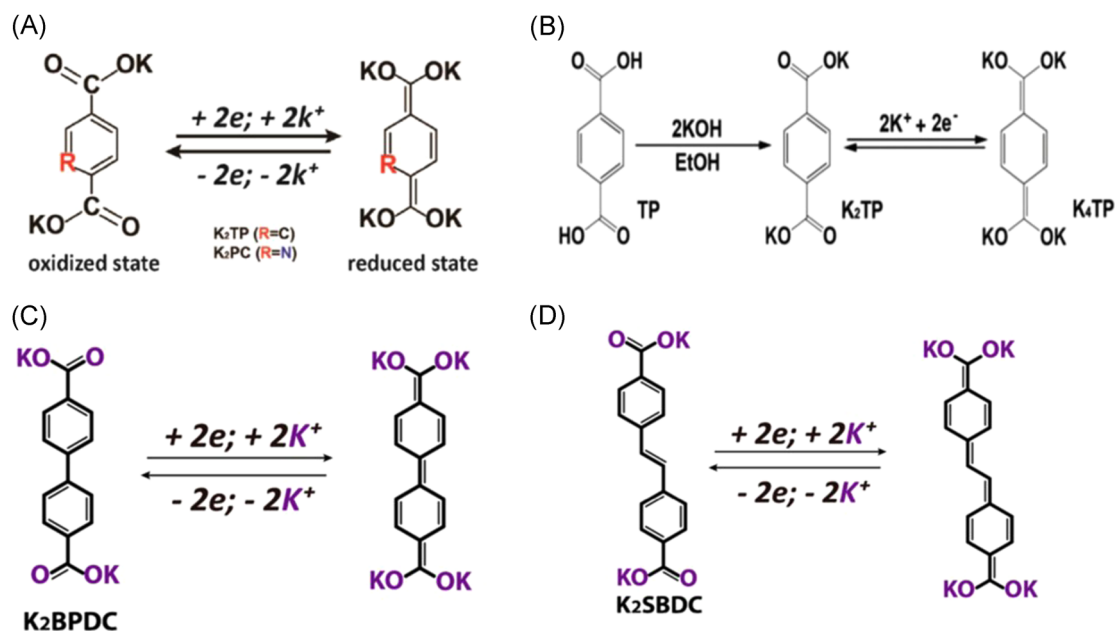
## 2.3 | Organic compounds

Compared with inorganic materials, organic compounds offer several advantages such as good structural controllability, abundant resources, and is cost-effective, which make them one of the most promising anode materials for KIBs.<sup>132-134</sup> Besides this, different from the inorganic solid/crystal constituted by the covalent/ionic bond, the solid/crystal state of organic materials is mainly interacted by van der Waals forces, indicating more void space and low energy barrier for accommodating large K<sup>+</sup> ions.<sup>135</sup>

Para-aromatic dicarboxylic acids such as dipotassium terephthalate (K<sub>2</sub>TP) and 2,5-pyridinedicarboxylate (K<sub>2</sub>PC) have been designed (Figure 9A).<sup>83,84</sup> The K<sub>2</sub>PC anode exhibits a higher discharge capacity of 181 mAh g<sup>-1</sup> at 0.2 C for 100 cycles than that of K<sub>2</sub>TP, due to K<sub>2</sub>PC possessing a better

electron affinity than K<sub>2</sub>TP for involving the electron-deficient pyridine ring, which derives from the lowest empty molecular orbital in K<sub>2</sub>PC. At the same time, another kind of K<sub>2</sub>TP was synthesized via the reaction of terephthalic acid with KOH in aqueous solution (Figure 9B). This K<sub>2</sub>TP anode shows a large discharging capacity of 249 mAh g<sup>-1</sup> with CEs of nearly 100% at 200 mA g<sup>-1</sup> after 100 cycles and high capacity retention of 94.6% after 500 cycles at 1000 mA g<sup>-1</sup>. The high performance is attributed to the active carboxylate groups, flexible layered molecular structure, and the robust SEI film.

As members of para-conjugated dicarboxylates embedded in biphenyl skeletons, potassium 1,1'-biphenyl-4,4'-dicarboxylate (K<sub>2</sub>BPDC) and potassium 4,4'-E-stilbenedicarboxylate (K<sub>2</sub>SBDC) were studied as anodes for KIBs (Figures 9C,D).<sup>136</sup> The larger  $\pi$ -conjugated biphenyl skeletons of these two organic compounds are more favorable for intermolecular electron transport than that of the K<sub>2</sub>TP. In light of this, remarkable capacities of 120 mAh g<sup>-1</sup> for K<sub>2</sub>BPDC and 80 mAh g<sup>-1</sup> for K<sub>2</sub>SBDC at 20 mA g<sup>-1</sup> for 100 cycles were achieved, respectively. However, K<sub>2</sub>BPDC displays higher rate capacities (105/93/76/52 mAh g<sup>-1</sup>) than those of K<sub>2</sub>SBDC (74/55/40/26 mAh g<sup>-1</sup>) at larger current densities of 50/100/200/500 mA g<sup>-1</sup>, as K<sub>2</sub>BPDC has a relatively high electronic conductivity compared to that of K<sub>2</sub>SBDC. Notably, the capacity of K<sub>2</sub>BPDC also achieves excellent cyclic stability of 75 mAh g<sup>-1</sup> at 1 A g<sup>-1</sup> for 3000 cycles.



**FIGURE 9** A, Illustration of the electrochemical mechanism of K<sub>2</sub>TP and K<sub>2</sub>PC in potassium-ion batteries. Reprinted with permission.<sup>83</sup> Copyright 2017, Elsevier. B, Schematic illustration of the synthesis and reversible K<sup>+</sup> insertion/extraction of K<sub>2</sub>TP. Reprinted with permission.<sup>84</sup> Copyright 2017, The Royal Society of Chemistry. C, Chemical structures of the potassium 1,1'-biphenyl-4,4'-dicarboxylate (K<sub>2</sub>BPDC) and (D) the potassium 4,4'-E-stilbenedicarboxylate (K<sub>2</sub>SBDC). Reprinted with permission.<sup>135</sup> Copyright 2017, American Chemical Society



### 3 | CONCLUSION AND PERSPECTIVES

In this review, we have comprehensively summarized recent progress in developing anode materials for KIBs. The strengths and weaknesses of the developed anode materials for KIBs have been elucidated, assessed, and analyzed in detail. Despite the rapid progress in anode material development and significant improvement in KIBs performance achieved, more in-depth research is still necessary to address the capacity and stability of anode materials for KIBs to meet the requirements of KIBs for practical applications.

Among many carbonaceous anode materials, graphite is one of the most promising candidates, owing to its low-cost and mature technology developed in LIBs. More importantly, the stable  $K^+$  ions de/intercalation voltage plateau of graphite is above 0.1 V vs  $K^+/K$  to guarantee both high working voltage and high energy density, but it is still imperative to further understand the mechanism of  $K^+$  ions insertion/extraction from graphite as well as the formation and growth of SEI film on the graphite surface. Other carbonaceous materials besides graphite such as HC, soft carbon, and nanostructured carbon materials have also been demonstrated as KIBs anodes with desirable electrochemical performance. In particular, many nongraphite carbons have exhibited high capacities at high current rates even cycling over hundreds of cycles. Nevertheless, the first CE (always less than 60%) and volumetric capacities of these nongraphite carbons still need to be further improved. Noncarbonaceous anodes, such as alloys and conversion electrodes, are also considered as alternatives for the graphite anode attributed to both high gravimetric and volumetric energy density. Apart from that, noncarbonaceous anodes also suffer from huge volume changes during the de/intercalation of large  $K^+$  ions, giving rise to structural failure and rapid capacity decay, thus buffering volume variations is the key point in developing novel noncarbonaceous anode with high capacity. Shape controlling, compositional designing, and functional group modification may be promising solutions. Finally, low-cost organic anode materials have gained much popularity, but further research is still required to solve their solubility issue and relatively low energy density.

To date, many strategies have been proposed to improve the performance of KIBs, including nanostructuring, heteroatom doping, and electrolytes/binder optimizing. Nanostructures generally produce high surface areas, increase the contact area of the electrode and electrolyte, and improve active reaction sites, which can enable fast ion transportation during charging/discharging. For carbon-based materials, heteroatom doping is an effective way to enhance electrical conductivity, enlarge surface reaction sites, and generate defect sites and functional groups,

resulting in improving the specific capacity of carbon materials. The aim of optimizing electrolytes/binders is forming stable SEI films, which can reduce the volume expansion and, thus, alleviate pulverization. Another purpose is reducing the solubility of electrode materials in electrolytes and alleviating the decomposition reaction of electrolyte, especially at high voltage.

Overall, it should be admitted that the development of anode materials is still inadequate, and most reported KIBs anodes to deliver an inferior performance compared with LIBs and SIBs. Nevertheless, with improvements in material structure design, the further understanding of the fundamentals of electrochemical behaviors in KIBs, and the exploration of compatible electrolytes and binders, KIBs will become a competitive application in future energy storage systems.

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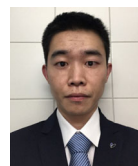
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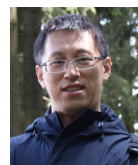


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