A compact Bi$_2$WO$_6$ microflowers anode for potassium-ion storage: Taming a sequential phase evolution toward stable electrochemical cycling

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**Abstract**

Potassium-ion batteries (KIBs) are considered an important alternative for lithium-ion batteries owing to the abundant potassium (K) resources and low-cost. To date, most reported anode materials for KIBs have been limited to carbonaceous materials which can well accommodate the large potassium ions (K$^+$) but show humble capacity performance. As compared, metal oxide-based anodes can potentially provide higher capacity yet cyclability is poor, which has been rarely researched. Herein, we report a sequential phase evolution mechanism for bimetallic oxide anode. Upon potassiation, the microflower-like Bi$_2$WO$_6$ undergoes a multistep evolution process, which first combines with K$^+$ then converts into a highly reversible phase of Bi, then via a solid-solution reaction eventually it forms the K$_x$Bi alloy. After repeated cycling process, such unique hierarchical and mesoporous morphology of Bi$_2$WO$_6$ can be well maintained, leading to superior cyclability with a high specific potassium storage capacity (652 mAh g$^{-1}$ at 100 mA g$^{-1}$). Even at a large current density of 1 A g$^{-1}$, a reversible specific capacity of 216 mAh g$^{-1}$ can still be delivered over 300 cycles. Such a novel working mechanism of bimetallic oxide anodes will promote the practical use of KIBs in diverse energy storage applications.

**Keywords:**
Bismuth tungstate
Bimetallic oxide anode
Microflowers architecture
Phase evolution
Potassium-ion batteries

**1. Introduction**

Lithium-ion batteries (LIBs) are currently the dominating power sources of portable electronic devices and electric vehicles, because of their high energy and power densities, as well as reliable cycling performance [1–4]. Despite the commercial success application of LIBs, the uneven distribution and limited resource of lithium in the earth’s crust (0.0065 wt%), make it difficult to meet the diversified energy demand in the future [5–7]. This prompts the development of alternative earth-abundant-element-based batteries [8,9]. Sodium-ion batteries (SIBs) has shown encouraging electrochemical performance in the last few years, such as high specific capacity, cycle life, and rate capability [10–14]. However, the high standard hydrogen potential (−2.71 V vs. SHE) limits working voltage range, hinders its industrial application [15].

Potassium, a large-ion lithophile element, is becoming increasingly favorable as an alternative choice beyond lithium for electrochemical energy storage because of its low cost, abundance and accessibility. Comparing potassium-ion batteries (KIBs) with SIBs, the former demonstrates two distinguished advantages. First, K/K$^+$ possesses a relatively low electrochemical potential (−2.93 V vs. SHE) compared with Na/Na$^+$ (−2.71 V vs. SHE), which is similar to Li/Li$^+$ (−3.04 V vs. SHE). Therefore, KIBs can provide a higher working voltage than SIBs [16–19]. Moreover, K$^+$ has a lower Lewis acidity compared with Li$^+$ and Na$^+$, demonstrating better solvation ability and charge carrying ability in organic electrolyte [20].

However, a huge challenge faced by KIBs is the dramatic volume change during electrochemical cycling, because of the large radius of K$^+$ (1.38 Å) compared with Li$^+$ (0.76 Å) and Na$^+$ (1.02 Å) [21]. Until now, carbonaceous materials (graphite, soft carbon, N-graphene, and carbon nanotubes etc.) are the most frequently studied anode material for KIBs [22–24]. Nevertheless, the low theoretical capacity of carbonaceous materials limits its future development in KIBs. As compared with carbonaceous materials, compound-based and metal-based anode materials (e.g., WS$_2$, Sn, Sb, P, Bi) that based on conversion reactions or alloying reactions for K$^+$ storage generally show a higher theoretical capacity and moderate voltage platform. But they are suffered from short cycle life and poor rate capability because of drastic volume...

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change during cycling [25,26]. Among them, bismuth (Bi) has recently attracted more attention for both KIBs and SIBs because of its high theoretical capacity (385 mAh g\(^{-1}\)) and volumetric capacity (3800 mAh L\(^{-1}\)) [27]. Besides, it is featured with relatively high electric conductivity, low cost ($13200/ton), and large interlayer spacing benefiting the accommodation of bigger ions, and is considered as human-metabolizable and environmentally-friendly [28,29]. However, volume change of Bi anode is quite significant (250% for SIBs and 411% for KIBs) during the charge and discharge processes [30,31]. As a result, Bi undergoes severe pulverization and loss of electrical connection between the active materials and current collector, leading to fast capacity fading [31,32]. Considering the diverse and controllable morphologies of bimetallic oxide structures, obtaining nanostructured bismuth through self-evolution reaction from bismuth-based metal oxides can be a feasible way. However, as far as we know, no relevant research has been reported. This self-evolution mechanism, if successfully realized, may effectively preserve the morphological characteristic of bismuth-based metal oxides for the desirable Bi anode, which could compensate the volume change of Bi upon cycling and boost its electrochemical performance.

Herein, we demonstrate such mechanism by reporting the one-pot synthesis of a self-assembled interlaced microflower-like Bi\(_2\)WO\(_6\) material (hereafter denoted as BWO-MF) as a convertible KIBs anode. Bi\(_2\)WO\(_6\) is a bimetalllic oxide and for the first time applied as an anode material for KIBs [33–36]. We propose such material as it possesses a relatively high theoretical capacity due to the multivalent bismuth and tungsten (~1051 mAh g\(^{-1}\)) based on the reaction: \(14\text{K}^+ + 14\text{e}^- + 2\text{K}_3\text{Bi} + 6\text{WO}_3 + 4\text{K}_2\text{O}\). Specifically, upon initial cycling, Bi\(_2\)WO\(_6\) can be converted into highly active Bi nanostructures. To be noted, the unique microflower-like structure of Bi\(_2\)WO\(_6\), which is composed of ordered and interlaced nano flakes, can effectively tolerate the strain derived from volume change of nanostructured Bi in the subsequent cycling, and thus the structural integrity can be well maintained. Our experimental observations confirm that, the BWO-MF shows a remarkable cycling performance with a capacity retention of 216 mAh g\(^{-1}\) after 300 cycles at 1000 mA g\(^{-1}\). Particularly, after the initial cycling, the decreasing rate of specific capacity of BWO-MF was only 13% after 300 cycles. These performances can be attributed to the appropriate bimetallic oxide morphology and the self-transformed highly reactive nanostructured Bi. Specifically, the microscale BWO-MF can benefit alloying reactions and sustain the reversible capacity of the nanostructured Bi by its compact micro/nano structure [37]. Secondly, the converted Bi nanostructure after first cycling can reduce the ion transfer distance and ensure fast ion intercalation/deintercalation [38]. Therefore, the as-prepared BWO-MF with such a novel working mechanism demonstrates a long-term cycle life and an excellent rate capability, providing a new avenue for the development of the next-generation high performance anode materials for KIBs.

2. Experimental section

2.1. Materials synthesis

The metal composite oxide Bi\(_2\)WO\(_6\) microflowers (denoted as BWO-MF) were fabricated by a facile hydrothermal method. 0.012 mmol of (NH\(_4\))\(_6\)H\(_2\)W\(_6\)O\(_{24}\)O\(_7\) and 0.352 mmol Bi(NO\(_3\))\(_3\) were dispersed in 40 mL of deionized H\(_2\)O to form a precursor solution. To suppress the hydrolysis reaction, 1 mL of concentrated HNO\(_3\) was added drop by drop to adjust the solution pH. After magnetic stirring for 20 min, the resulting solution was poured into a 50 mL Teflon-lined stainless steel autoclave and heated at 160 °C for 24 h. The obtained white precipitate from the autoclave was washed by deionized water and absolute ethanol three times, and then vacuum dried at 70 °C for 20 h.

2.2. Material characterization

Powder X-ray diffraction (XRD) and in-situ XRD measurements were performed to determine the crystal structure using a Rigaku D/max-2550 PC diffractometer with Cu K\(_\alpha\) radiation source. Scanning electron microscopy (SEM) images were collected with a Hitachi SU-70 microscope at an operating voltage of 5 kV. Transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) images were recorded by using a JEOL JEM-2010 microscope. Brunauer–Emmett–Teller (BET) specific surface areas were measured using an ASAP 2020 instrument by adsorption of nitrogen at 77 K. X-ray photoelectron spectroscopy (XPS) was conducted by a Thermo PHI 5000 VersaProbe II spectrometer.

2.3. Electrochemical measurements

The electrochemical measurements were implemented by assembling CR-2032 coin cells in an argon-filled glove box, which used potassium block as the counter electrode. The working electrode was obtained with 70% nanoflake-assembled BWO-MF, 20% acetylene black and 10% polyvinylidene fluoride. The electrolyte consisted of 1 M KPF\(_6\) dissolved in EC/DME with a volume ratio of 1:1. Galvanostatic discharge and charge were performed using a LAND CT2001A battery tester in the potential window of 0–3.0 V versus K\(^+\)/K. Electrochemical impedance spectroscopy (EIS) and cyclic voltammograms (CV) were conducted on an electrochemical workstation (Bio-Logic VMP3).

3. Results and discussion

The schematic of a possible fabrication process for the BWO-MF is shown in Fig. 1. The nanostructured bimetallic oxide material can be self-assembled into compact microscale structures through an oriented aggregation mechanism [39–43]. First, the bismuth-metal cations and tungstate anions are combined by dissolving Bi(NO\(_3\))\(_3\) and (NH\(_4\))\(_6\)H\(_2\)W\(_6\)O\(_{24}\)O\(_7\) in deionized water. During the hydrothermal process, numerous amorphous precursors underwent a gradual nucleation process and then formed small crystals. With the increase of temperature and pressure, the aggregated nuclei continuously collide with others and tend to grow into hexagonal nanoflakes [44]. These freshly formed single-crystal nanoflakes are thermodynamically unstable, and thus they are prone to take a self-assembling process and grow into flower-like microstructures due to crystal-face attraction and hydrogen bonds [45, 46]. With the extension of the reaction time, the primary crystals continuously dissolve and recrystallize to fully utilize the limited space. Finally, the BWO-MF can be conveniently produced after centrifugation and desiccation. Meanwhile, Bi\(_2\)WO\(_6\) is a russellite constructed on alternating (Bi\(_2\)O\(_3\))\(_2\)\(_n\) layers and perovskite-like (WO\(_4\))\(_3\) layers. These oppositely charged layers may result in the formation of groups with polar charges on their top and bottom surfaces, which is beneficial for accommodating K\(^+\) [47].

The thin nanoflakes can grow into spherical particles with an interesting flower-like morphology. This unique radial structure enables a large surface area and numerous pores for the accommodation of K\(^+\). Figs. 2a and S1 illustrate the morphological characteristics of BWO-MF by SEM. The BWO-MF is uniform in size, with an average diameter of ~2 μm. Magnified SEM images show that each microflower is formed with several interlaced nanoflakes (Fig. 2b, c). The TEM and HRTEM images of BWO-MF (Fig. 2d, e) display the completely stacked and dense interior structure, which contains numerous pores. From the HRTEM image (Fig. 2d), a large number of nanoflakes featured with hexagonal crystalline structure are observed in the BWO-MF. The XRd pattern of the BWO-MF in Fig. 2g depicts a standard reflection pattern of Bi\(_2\)WO\(_6\) (JCPDS No. 73-2020), without any other impurities. The XRd refinement results of the BWO-MF are further performed using materials studio software (Fig. S2). After refinement, the lattice parameters of the BWO-MF (a = 5.4373 Å, b = 16.4302 Å, c = 5.4584 Å) are close to the
reported standard values. The detailed rietveld refinement data obtained for BWO-MF is listed in Table S1. Moreover, the $R_p$ and $R_{wp}$ values of BWO-MF ($R_p = 7.46\%$, $R_{wp} = 10.37\%$) suggest that the refinement result is reasonable. The selected-area electron diffraction (SAED) depicts the polycrystalline of BWO-MF (see Fig. 2h). The indexed (200), (220), (333), (226) and (113) planes in the SAED pattern are in accordance with the XRD pattern of BWO-MF. Fig. 2i and j exhibit two monocristalline regions of configured nanoflakes with lattice fringes (d-spacings 0.273 and 0.165 nm, corresponding to the (200) and (313) crystal planes). In addition, the EDS mapping images confirm that the Bi, W, and O elements are well-dispersed in the flower-like particles.

In order to investigate the morphological characteristics of BWO-MF after potassiation and depotassiation, ex-situ TEM study is carried out (Fig. 3g–i). When BWO-MF is discharged to 0 V (vs. K/K$^+$), the lattice fringes are clearly shown in its HRTEM images (Fig. 3h and i). The measured spacings of these lattice fringes correspond to the (102) and (103) planes of K$_2$Bi, the (220) and (222) planes of K$_2$O, and the (–111) plane of WO$_3$, respectively, based on the corresponding Fast Fourier Transformation (FFT) patterns (insets in Fig. 3h) and the XPS results. Additionally, small K$_2$O crystallites are found in the fully discharged BWO-MF. After BWO-MF is charged to 3.0 V (vs. K/K$^+$), the HRTEM image also exhibits clear lattice fringes, assigned to the (024), (310) and (400) planes of Bi$_2$O$_3$, (040) and (020) planes of WO$_2$, and (311) plane of K$_2$O, respectively, and the size of these crystallites is measured to be approximately 5 nm (Fig. 3k). The selected area electron diffraction (SAED) further confirms the polycrystalline structure of BWO-MF after potassiation and depotassiation (Fig. 3i and I), which indicates a typical polycrystalline ring pattern.

The in-situ XRD measurements can display the structural evolution during K$^+$ exchange using a Swagelok cell with an X-ray transparent...
The in-situ X-ray diffraction data for the Bi$_2$WO$_6$/K cell in the two cycles as well as the charge-discharge profile are given in Fig. 4a–c. When discharged to 0.87 V, the break down of crystalline Bi$_2$WO$_6$ is first observed followed by a gradual evolution into the intermediate phases WO$_2$, K$_2$O and Bi. Subsequently, a new diffraction peak corresponding to the Bi-K alloy structure appears due to K$^+$ reinsertion, which can be well indexed to K$_3$Bi (110). During the first discharge (potassiation) process, three reflections located at 20.78$^\circ$, 21.04$^\circ$ and 21.43$^\circ$, correspond to WO$_2$ (101), WO$_2$ (020) and WO$_2$ (011), respectively. Meanwhile, the K$_2$O (111), Bi (–101) and Bi (012) as new reflections are observed in Fig. 4a, which are consistent with other reported in-situ studies [48–50]. During the charging (depotassiation) process at around 0.67 V, K$_3$Bi peak shifts to the peak of Bi (Fig. 4a), which is formed through the depotassiation of K$_3$Bi. Following this, the peak intensities of Bi (–101) at 2$\theta$ = 25.16$^\circ$ and Bi (012) at 2$\theta$ = 27.17$^\circ$ decrease with the increasing voltage until about 3.0 V. By contrast, the Bi$_2$O$_3$ (111) and Bi$_2$O$_3$ (200) reflections emerge and rapidly grow with the increasing voltage, which indicates reversible potassiation reactions between Bi phase and Bi$_2$O$_3$ phase.

A further analysis of the phase-transition behavior since the initial
stage to the appearance of multiple phases is displayed in Fig. 4d–f. The peak patterns of the in-situ data corresponding to each main reflections are investigated. The main characteristic peaks of Bi$_2$WO$_6$ become weaker and finally achieve a steady state (Fig. 4a–c). Nevertheless, the peak intensities of WO$_2$(020) at $2\theta = 21.04^\circ$ and K$_2$O (111) at $2\theta = 25.31^\circ$ become greater in the first conversion reaction, which in-dicates that K$^+$ reacts with Bi$_2$WO$_6$ to transform into intermediate phases in this process. It also leads to low initial coulombic efficiency because of the limited reversibility of conversion reaction. With further charging, the intermediate alloy phase of K$_3$Bi is gradually converted into reversible phase Bi, as with the case in sodium-ion batteries [51–53]. Additionally, the peak intensities of the Bi$_2$O$_3$ (111) and Bi$_2$O$_3$ (200) reflections appear to be the highest when the peak intensities of Bi (−101) and Bi (012) are significantly reduced. All the above mentioned phase evolution could also be observed in Fig. S4.

The above results demonstrate that an irreversible potassi-ation reaction takes place in the first discharge process of Bi$_2$WO$_6 \rightarrow$ WO$_2$, followed by a reversible depotassiation/potassiation reaction of K$_3$Bi $\leftrightarrow$ Bi in the subsequent cycles. The whole process could involve the following equations:
The K-storage behavior of BWO-MF is first examined using cyclic voltammetry (CV) in a voltage range of 0–3.0 V (vs. K/K+). During the first cathodic scanning process, there is a reduction peak at 0.71 V, and its corresponding oxidation peak is detected around 1.26 V (Fig. 5a). The pair of redox peaks may be attributed to the conversion reaction of Bi2WO6. Moreover, two sharp peaks are found at 0.57 V and 0.06 V in further potassiation process, which can be assigned to the alloying reaction of K+ with Bi. Both peaks retain their intensities in the following cycles. According to the relationship of \( i = av^b \) between the current (i) and scan rate (v), the b-value can be obtained by fitting the log(i)-log(v) curves. Particularly, the b-value of 1 suggests that a capacitive process dominates the charge storage, while 0.5 represents a solid-state diffusion is dominating. Herein, BWO-MF/K cell demonstrates a b-value close to 0.5 (Fig. 5b), suggesting that the charge storage behavior is dominated by the solid-state diffusion. By separating the specific contribution from the diffusion-controlled and capacitive charge at a certain voltage, a calculation of the total capacitive charge contribution at a fixed rate can be conducted. As shown in Fig. 5f, the capacitive charge (shaded area) at a scan rate of 1 mV s\(^{-1}\) is separated from the total charge, which is quantified to be 47% for the BWO-MF/K cell.

Fig. 5e shows the typical charge-discharge galvanostatic cycling profile at a current density of 100 mA g\(^{-1}\). The discharge-charge capacities are 1115.9/652 mAh g\(^{-1}\), corresponding to an initial coulombic efficiency of 58.4%, due to the solid-electrolyte interphase (SEI) film formed on the electrode surface, electrolyte decomposition and irreversible K+ insertion during conversion reaction. Pre-potassiation and a special design of nanoarchitecture could be utilized to improve the low ICE. The following electrochemical cycling profiles almost overlap with a small capacity decay and voltage hysteresis. Two plateaus are displayed in the galvanostatic charge/discharge profiles of BWO-MF in the stepwise potassiation and depotassiation reactions. Fig. 5d depicts galvanostatic electrochemical cycling curves of BWO-MF at a current density of 100 mA g\(^{-1}\), which deliver a steady discharge capacity of 300 mAh g\(^{-1}\) over 50 cycles. The capacity loss during the initial several cycles may be attributed to the side reactions between the electrode and electrolyte, that is, the formation of SEI. Fig. 5e exhibits an ultrafast kinetics of BWO-MF, where the rate testing results prove a remarkable reversible capacities of 700, 472, 346, 284 and 253 mAh g\(^{-1}\) at current densities of 0.1, 0.2, 0.3, 0.5 and 1 A g\(^{-1}\), respectively. Even at a relatively large current density of 1 A g\(^{-1}\), a reversible capacity of 216 mAh g\(^{-1}\) over 300 cycles is still retained (Fig. 5g). Subsequently, to examine the structural stability of the BWO-MF, we carry out the post-mortem studies by HRTEM examinations after a cycle and 100 cycles, respectively (Fig. S6). The size and shape of the BWO-MF are still well...
improvement in rate performance and cyclic capabilities for K
ordered 2D nano-structure has gained increasing attention for its
nanotubes [75] ) have large layer spacing and a stable structure. This
[72] ) and carbon materials (soft carbon [73] , N-graphene [74] , carbon
sons of Bi
structure of BWO-MF.
believe that such a steady specific capacity and rate performance are
retained. Based on the above experimental evidence, it is reasonable to

As known, transition-metal sulfides (ReS
[31] , Bi@C [69] ), all of which belong to the alloy-based anode for KIBs.
(CBi@P/GA [65] , Bi@3DGFs [68] , Bi/rGo [27] , Bi
[69] ), all of which belong to the alloy-based anode for KIBs. This
fig. 5). (a) Cyclic voltammograms of the BWO-MF recorded at different scan rates (0.1, 0.2, 0.3, 0.5 and 1.0 mV s
-1); (b) Linear plot of the relationship between log (ip) and log(v) for anodic scan of the BWO-MF electrode; (c) Discharge/charge voltage profiles at 100 mA g
-1; (d) Cycling performance at 100 mA g
-1; (e) Rate performance at a current density range of 100–1000 mA g
-1; (f) Separation of the capacitive currents (k
1p,1/2) and diffusion current (k
3v) in BWO-MF at a scan rate of 1 mV s
-1; (g) Cycling performance at 1000 mA g
-1.

Besides the above electrochemical tests, fair and detailed compari-
sions of Bi
WO
6 anode with the available mainstream electrode materials are
considerably important. The five radar charts in Fig. 6 compare the prop-
erties of almost thirty recently-reported electrode materials in term of
initial coulombic efficiency (ICE.), specific capacity at low/high rates
(SCL. and SCH.), cyclability (Cyc.) and capacity retention (CR.). Herein,
the radar chart is applied to describe the relationship among the relative
molecular weight (M
w), the number of inserted K
+, and theoretical ca-
pacity. The materials that are compared include Sn-based anodes
(SnSb@NC [54] , Sn foil [55] , SnP
2 [49] ), Sb-based anodes (Sb@CSN [56] , Bi,Sb
2S
9 [57] , SB@C [58] , SB@G@C [59] , NP-Sb [60] ), P-based anodes (P@N-PHCFNs [61] , GeP
2 [62] , P@CN [63] , BP-C [64] , C@P/GA [65] ), Ge-based anodes (NP-Ge [66] ) and Bi-based anodes
(Bi
2WO
6 (this work), Bi@N-C [67] , Bi@3DGPs [68] , Bi/rGo [27] , Bi
[31] , Bi@C [69] ), all of which belong to the alloy-based anode for KIBs. As
known, transition-metal sulfides (ReS
2 [70] , 2H-MoS
2 [71] , TiS
2 [72] ) and carbon materials (soft carbon [73] , N-graphene [74] , carbon
nanotubes [75] ) have large layer spacing and a stable structure. This
ordered 2D nano-structure has gained increasing attention for its
improvement in rate performance and cyclic capabilities for K
storage. Furthermore, many sodium super ionic conductor (NASICON)
phosphates and vanadates have confirmed their capability to store ions,
including Li
+, Na
+, and K
+, as anode (KTi
5(PO
4)@C [76] , K
2Ti
4O
17 [77] , K
2Ti
6O
14 [78] , FeVO
4 [79] , KTi
2(PO
4)@C [80] , and so on) (The detailed
values are shown in Tables S2 and S3). Unfortunately, the electric
conductivity of these anode materials is relatively low (< 10
-12 S/cm),
which might cause sluggish kinetics and fail to attain the theoretical
capacity. As displayed in the radar map in Fig. 6e, the Bi-based anode
shows preferable electrochemical performance. This can be explained by
its unique structure, including large crystal lattice spacing for ion
insertion, and high theoretical gravimetric capacity (383 mAh g
-1) for
KIBs. In particular, Bi
2WO
6 anode in this work can deliver a considerable
actual specific capacity. According to the comparison between Bi
2WO
6
and transition-metal sulfides, although the initial coulombic efficiency
of Bi
2WO
6 (58.4%) is lower than the initial coulombic efficiencies of
transition-metal sulfides (ReS
2 (67.3%), 2H-MoS
2 (97.5%), and TiS
2
(96%)), the practical capacity of Bi
2WO
6 (396.2 mAh g
-1) is higher than
that of ReS
2 (350 mAh g
-1), and almost 8 times that of 2H-MoS
2
(50 mAh g
-1) and 4.5 times that of TiS
2 (85 mAh g
-1) in the same
working window. This low ICE derives from the decomposition of the
electrolyte and the formation of SEI. Moreover, the high surface area
could lead to more severe side reactions along with a thicker SEI, which
is a common challenge for anode materials with a high specific surface
area [81–84]. In Fig. 6d we can also observe that the biggest limitations
of phosphates and vanadates are their low specific capacity and poor
cyclability. To make better understanding, the correlations between
relative molecular weight ($M_w$), the number of inserted $K^+$, and theoretical capacity need more thorough comparison, and the value of the theoretical capacity for representative anode material is expressed by contour intensity (Fig. S7). It can be seen that, though the $M_w$ of bismuth is large, its theoretical capacity is still considerable. Therefore, $\text{Bi}_2\text{WO}_6$ can be a promising candidate as the anode for KIBs because of the above mentioned outstanding electrochemical performance. Nevertheless, there are very limited explorations on developing anode materials for KIBs by obtaining self-transformed products. A possible explanation for such superior electrochemical performance is that the existence of the as-produced $\text{WO}_2$ and $\text{K}_2\text{O}$ etc. around the electrochemical active sites provides space-confinement and structure stabilizing effects. This self-evolution strategy, which is well exemplified by BWO-MF, is likely to extend to other bimetallic oxide anodes with analogous potassiation reactions to improve their cyclability.

4. Conclusions and outlooks

To conclude, a sequential phase evolution mechanism for potassiation is reported and exemplified by the bimetallic oxide $\text{Bi}_2\text{WO}_6$. We have confirmed that this microflower-like anode can achieve superior specific capacity and cycle stability through the initial multistep self-evolution. The in-situ XRD study indicates that the potassiation of $\text{Bi}_2\text{WO}_6$ proceeds via a conversion reaction from $\text{Bi}_2\text{WO}_6$ to a highly active $\text{Bi}$ phase and the alloying reactions of $\text{K}_3\text{Bi}$ formation. Additionally, with the microflower-like structure, the obtained BWO-MF possesses the desired structure for KIBs application. The advantages of this mechanism lie in two aspects: on the one hand, the nano-sized highly active $\text{Bi}$ from conversion reaction inherited the porous structure of the $\text{Bi}_2\text{WO}_6$, which could alleviate the volume change of $\text{Bi}$ and significantly reduce the ions/electro diffusion length; on the other hand, the flower-like mesoporous frameworks composed of interconnected nanoflakes provide the robustness which is crucial to keep the structural integrity after repeated charge/discharge. As a result, the prepared BWO-MF electrode displays a reversible potassiation capacity of 216 mAh g$^{-1}$ and remains its stability over 300 cycles at a current density of 1 A g$^{-1}$.

In the follow-up work, the low ICE is expected to be tackled via pre-potassiation and special nanoarchitecture design [85–87]. The outstanding electrochemical performance and unique multiphase transitions indicate that the $\text{Bi}$-based nanostructure has great promise as the KIB anode, which will may attract numerous attention from both academic research and large-scale application in the coming future.
Supporting information

Supplementary data associated with this article can be found in this submission, including SEM, TEM, HRTEM, BET, XPS spectra, charge/discharge curves, long-life cycling performances, rate performances, cyclic voltammograms, compared initial Coulombic efficiency, in-situ XRD evolution of microflower-like Bi$_2$WO$_6$.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.nanoen.2021.105784.

References

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