Check for updates
 Angewandte
 International Edition
 Chemie



 How to cite:
 Angew. Chem. Int. Ed. 2021, 60, 7180–7187

 International Edition:
 doi.org/10.1002/anie.202016082

 German Edition:
 doi.org/10.1002/ange.202016082

Unveiling Intrinsic Potassium Storage Behaviors of Hierarchical Nano Bi@N-Doped Carbon Nanocages Framework via In Situ Characterizations

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Abstract: Metallic bismuth has drawn attention as a promising alloying anode for advanced potassium ion batteries (PIBs). However, serious volume expansion/electrode pulverization and sluggish kinetics always lead to its inferior cycling and rate properties for practical applications. Therefore, advanced Bibased anodes via structural/compositional optimization and sur-/interface design are needed. Herein, we develop a bottomup avenue to fabricate nanoscale Bi encapsulated in a 3D Ndoped carbon nanocages (Bi@N-CNCs) framework with a void space by using a novel Bi-based metal-organic framework as the precursor. With elaborate regulation in annealing temperatures, the optimized Bi@N-CNCs electrode exhibits large reversible capacities and long-duration cyclic stability at high rates when evaluated as competitive anodes for PIBs. Insights into the intrinsic K^+ -storage processes of the Bi@N-CNCs anode are put forward from comprehensive in situ characterizations.

Introduction

Nowadays, with increasing requirements for electric vehicles, hybrid electric vehicles, and portable electronic devices, the demand for advanced energy storage devices with high electrochemical performance turns out to be more urgent. Unfortunately, the relative scarcity, increasing consumption, and uneven geographic distribution of metal lithium itself has become increasingly prominent, and induces

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 Supporting information and the ORCID identification number(s) for
 the author(s) of this article can be found under: https://doi.org/10.1002/anie.202016082. the enhanced cost of conventional lithium ion batteries (LIBs).^[1] Accordingly, it seems more significant and meaningful to explore other high-performance metal-ion batteries as competitive alternatives of common LIBs.

Considering its appealing advantages including costefficiency, earth-abundant resource of elemental potassium, as well as similar chemical/electrochemical properties between Li and K, the emerging potassium ion batteries (PIBs), as one of the most promising energy storage systems, have captured the worldwide research interests.^[2] Nevertheless, the extensive development of PIBs is still struggled by its larger atomic radius (0.138 nm), which induces more serious volume change and sluggish kinetics of electrode materials during potassiation/depotassiation processes.[3] Until now, tremendous efforts have been devoted to pursuing appropriate electrode materials for efficient storage of K ions towards PIBs. Among the retrieved anodes, the typical carbon-based materials always show more stable electrochemical behaviors, but still suffer from lower capacities and potential safety issues.^[4]

Metallic Bi, as an environment-friendly alloy anode material, is considered to be an ideal electroactive material candidate for high-performance PIBs, owing to its cost efficiency, good electronic conductivity, high theoretical capacity (ca. 385 mAh g^{-1}), large interlayer spacing for the easy accommodation of K⁺ ions, and similar standard hydrogen potential (-2.93 V) with the lithium (-3.04 V) towards high energy density.^[2] While, the inherent volume expansion (ca. 411% for PIBs) and electrode pulverization commonly lead to short cycling life and inferior rate performance of Bi anodes.^[3] One effective strategy to address these issues is to hybridize active Bi with flexible carbonaceous materials.^[5-7] For instance, Su et al. reported the ultrathin carbon film@carbon nanorods@Bi nanoparticles (NPs) composite, which delivered an improved capacity (ca. 430 mAh g^{-1} at 0.1 A g^{-1}) but poor rate behavior $(140 \text{ mAh g}^{-1} \text{ at } 1.0 \text{ A g}^{-1})$.^[6] Cheng and co-workers prepared three-dimensional (3D) porous Bi@macroporous graphene framework composite electrode that achieved a capacity of ca. 185 mA h g^{-1} at 1.0 A g^{-1} along with a modest cycling stability.^[7] Therefore, in spite of these attractive advances, it is still a huge challenge to purposefully design advanced Bi/C hybrids with exceptional electrochemical behaviors in terms of high-rate cycling stability and reversible capacities via smart optimization in microstructures and surfaces/interfaces towards PIBs. Especially note that the underlying structure-performance relationship should be further figured out for the Bi anodes as well with a series of in situ techniques.

With comprehensive considerations in mind, in the contribution, we, to the best of our knowledge, first successfully fabricated Bi NPs encapsulated in a 3D foam-like Ndoped carbon nanocages (denoted as Bi@N-CNCs) framework with a void space by precisely annealing a novel twodimensional (2D) Bi-based metal-organic framework (Bi-MOF) precursor towards PIBs as an attractive anode. Thanks to its unique architecture and composition, the optimized Bi@N-CNCs anode was endowed with remarkable reversible capacities and long-duration cyclic stability, especially at large current densities. More significantly, the in-depth understanding of the intrinsic potassium storage behaviors of the Bi@N-CNCs was reasonably proposed with various in situ characterizations, which will guide the future design of highperformance electrodes for next-generation PIBs.

Results and Discussion

In the work, the Bi@N-CNCs products were smartly designed and fabricated via a two-step strategy including solvothermal process and carbothermic reduction, as described in Figure 1 a. To the best of our knowledge, a novel flower-shaped Bi-MOF assembled with 2D porous nanosheets (NSs) with an average thickness of ca. 14 nm and a length of up to tens of micrometers (Supporting Information, Figures S1, S2) is first synthesized by using the glycol as the solvent, along with the Bi(NO₃)₃·5H₂O and 1,3,5-Benzenetricarboxylic acid (H₃BTC) ligand. Then, the Bi@N-CNCs is obtained by calcinating the resultant Bi-MOF at a certain temperature under Ar with the assistance of melamine as the nitrogen source. The purposefully doped nitrogen into the CNCs will



Figure 1. a) Illustration for the synthesis processes of Bi@N-CNCs products. b) FESEM image; c),d) TEM images; e) reconstructed 3D tomograms; f),g) high-magnification TEM images; h) HRTEM image; i) crystallographic model of Bi (012); j) STEM and corresponding elemental mapping images of the 850-Bi@N-CNCs. The insets in (f, h) correspond to the intensity profiles indicating the measured interlayer spacing and atomic-resolution HAADF-STEM image of the red rectangular region, respectively.

Angew. Chem. Int. Ed. 2021, 60, 7180-7187

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favor anchoring the formed bismuth atoms and prevent their agglomeration over high-temperature calcination.^[8]

Figure 1b demonstrates typical field-emission scanning electron microscopy (FESEM) image of the 850-Bi@N-CNCs, which is obtained by annealing the Bi-MOF at 850 °C. It well inherits the architecture of the Bi-MOF precursor without noticeable calcination-induced structure collapse, which is further evidenced by the low-magnification FESEM observation (Supporting Information, Figure S3a). It is worth noting that the involved 2D NS subunits, like its precursor, are evident with smooth surface (Supporting Information, Figure S3b). Further transmission electron microscopy (TEM) examinations visualize that the bismuth NPs of ca. 12 nm in size (Supporting Information, Figure S3c) are uniformly and partially filled in the pore structure of the 2D carbon skeleton constructed with the interconnected hollow N-CNCs (Figure 1c,d; Supporting Information, Figure S3d). Such characteristic hierarchical architecture can be vividly supported by the reconstructed 3D tomograms (Figure 1e) and corresponding rotation video of 3D reconstruction (Supporting Information, Movie S1), obviously revealing the even distribution of these bismuth NPs in the pores of the carbon framework, rather than simply attached on its surface. Further high-magnification TEM inspection (Figure 1 f) also visually confirms the location of ca. 13 nm Bi NPs in the hollow N-CNCs with clear internal void space, that is, a typical yolk-shell structure. Meanwhile, high-resolution TEM (HRTEM) observation (Figure 1g), corresponding to the magnified blue rectangular region in Figure 1 f, manifests the well-defined lattice fringes with a spacing of about 0.39 nm, larger than the (002) of classic graphite (0.335 nm), proving that the elemental N is successfully doped in the CNCs.^[9] Besides, the distinct lattice fringes with the spacing of ca. 0.33 nm are assigned to the interplanar distance of (012)

> crystalline plane of the hexagonal Bi (JCPDS No.44-1246, space group $R\bar{3}m$ (166)). The atomic resolution high-angle annular dark-field scanning TEM (HAADF-STEM) image (the inset in Figure 1 h) of crystal face (012) demonstrates the arrangement of bismuth atoms in a unique rhombus as labeled with the red circles, which is in agreement with the crystallographic model of Bi (012) (Figure 1 i). The STEM and corresponding elemental mapping images (Figure 1 j) confirm even distributions of elemental N, Bi, and C over the whole N-CNCs network.

> More interestingly, with the annealing temperature dropping to 550 °C, although the NSs-constructed flower-like superstructure, similar to the 850-Bi@N-CNCs, is retained well for the



resultant 550-Bi@N-CNCs, several insular bismuth particles of hundreds nanometer in size are attached to the surface of these 2D NS building blocks (Supporting Information, Figure S4a,b). Evidently, numerous Bi NPs with an average size of ca. 18.2 nm are inlaid in the carbon NSs (Supporting Information, Figure S4ce), and especially, some isolated Bi NPs are uniformly coated with an amorphous N-doped carbon (or carbon nitride) shell (Supporting Information, Figure S4d).^[10] As for the case of 700°C, no any obvious even larger dissociated Bi can be found, and just lots of Bi NPs are anchored upon the surface of and/or in the obtained 700-Bi@N-CNCs NSs (Supporting



Figure 2. a) XRD patterns and b) TG curves of 550-Bi@N-CNCs, 700-Bi@N-CNCs and 850-Bi@N-CNCs; c) Raman spectrum of 850-Bi@N-CNCs; d) Pore size distribution plots of the three samples as indicated. High-resolution XPS spectra of e) Bi 4f and f) N 1s of the 850-Bi@N-CNCs.

Information, Figure S5a-c), which is wholly distinguished from the 550-Bi@N-CNCs and 850-Bi@N-CNCs. Additionally, the size of these well-distributed Bi NPs located in the carbon skeleton increases up to ca. 35.3 nm (Supporting Information, Figure S6) when compare to that of 550-Bi@N-CNCs. In sharp contrast, the as-fabricated 1000-Bi@N-CNCs (Supporting Information, Figure S7) shows typical 2D porous NSs structure (ca. 5 nm in thickness) with smooth surface and interior nanocages, but contains a small amount of Bi species maybe in the form of single atoms, which can be well authenticated by its X-ray diffraction pattern (Supporting Information, Figure S8). Accordingly, the evolution from the Bi-MOF to Bi@N-CNCs samples coupled with the size variation of metallic Bi in the temperature range from 550 to 1000 °C, as discussed above, rationally derives the formation mechanism of the Bi@N-CNCs. It probably comprises the initial pyrolysis, Ostwald ripening, evaporation and further atomization, similar to the report by Li et al.^[8] Furthermore, it is the unique formation process that makes the Bi NPs in the marginal location of the 850-Bi@N-CNCs vanish more quickly than those in the central region (Figure 1c; Supporting Information, Figure S3b). With the synergistic contributions from Bi evaporation/sublimation, spontaneous adsorption and N-involved anchoring effect, the unique architecture, that is, Bi NPs encapsulated in the hollow N-CNCs with a void space, is obtained for the case of 850-Bi@N-CNCs.

To further investigate the phase structure, compositions, porosity and surface valence of the products, various characterizations including XRD, thermal gravimetric (TG) analysis, N₂ sorption, Raman, and X-ray photoelectron spectroscopy (XPS) were conducted in detail. As illustrated in Figure 2a, all the reflections in the XRD patterns can be successfully indexed as the hexagonal Bi with a space group of $R\bar{3}m$ (166) for the three samples without any other discernable Bi-based impurities. Especially, the broadened and low-intensity (012) peak ($2\theta = 27.2^{\circ}$) of the 850-Bi@N-CNCs

should be ascribed to its nanometer-scale size,^[11] which is consistent well with the aforementioned TEM analysis. The specific contents of Bi in the 550-Bi@N-CNCs, 700-Bi@N-CNCs and 850-Bi@N-CNCs are estimated as ca. 93.6, ca. 89.5, and ca. 73.6 wt%, respectively, as calculated from TG plots (Figure 2b; Supporting Information, Equation S1), considering the combustion of carbon materials and oxidation of pure bismuth into Bi₂O₃ at 350-600 °C.^[7] The decrease in Bi contents in Bi@N-CNCs with temperature increasing is mainly attributed to the gradual evaporation of low-melting Bi, similar to that of the antimony.^[12] It is for this reason that the 850-Bi@N-CNCs is endowed with a specific surface area of ca. 18.5 m^2g^{-1} , higher than those of 550-Bi@N-CNCs (ca. 7.8 m^2g^{-1}) and 700-Bi@N-CNCs (ca. 9.7 m^2g^{-1}) (Supporting Information, Figure S9), originating from its hierarchical porosity with high-proportion tri-model micro-/meso-/macro-pores (Figure 2c), in good agreement with the TEM observations (Figure 1c; Supporting Information, Figure S3d). Such unique pore feature effectively guarantees convenient diffusion/transport of electrolyte ions to abundant active sites of the 850-Bi@N-CNCs for K⁺ storage. The existence of carbon material in the composites can be well supported by the Raman spectra (Figure 2d; Supporting Information, Figure S10), where the characteristic peaks centering at ca. 1235, ca. 1342, ca. 1490, and ca. 1592 cm⁻¹ belong to the I, D, D", and G bands, respectively.^[9] Particularly, besides the low-content D'' band, the I_D/I_G value (ca. 0.89) of the 850-Bi@N-CNCs, calculated with the integrated areas of the D and G bands, is smaller than those of the 550-Bi@N-CNCs (ca. 1.9), 700-Bi@N-CNCs (ca. 0.93), and 1000-Bi@N-CNCs (ca. 1.2), which further highlights the higher graphitization of the N-CNCs in the 850-Bi@N-CNCs, favoring for the rapid transport of electrons in the conductive carbon framework. Further XPS survey spectrum confirms the co-existence of the C, Bi, and N species in the 850-Bi@N-CNCs, along with a N/C atomic content of ca. 4.7% (Supporting Information, Figure S11). The high-resolution spectrum of Bi 4f (Figure 2e) shows two characteristic peaks, that is, $4f_{7/2}$ (ca. 159.1 eV) and $4f_{5/2}$ (ca. 164.5 eV) orbitals of metal-phase Bi.^[13] The N 1s spectrum (Figure 2 f) can be spilt into three peaks at ca. 398.8, ca. 400.7, and ca. 401.7 eV, which are related to the pyridinic-N, pyrrolic-N, and graphitic nitrogen, respectively.^[14] The former two, with a total content of ca. 2.9 at.%, favors for the enhancement of surface-controlled capacitance, and rapid diffusion of K⁺ ions,^[15] and the latter (graphitic nitrogen) is beneficial to electronic transport in the hybrid anode.^[16]

Thanks to the remarkable structural/compositional advantages mentioned above, the as-fabricated 850-Bi@N-CNCs can be highly anticipated with competitive electrochemical potassium storage properties for PIBs. Figure 3a shows the initial cyclic voltammetry (CV) curves of the 850-Bi@N-CNCs at a scanning rate of 0.1 mV s⁻¹. During the first cathodic (potassiation) process, the strong peak located at 0.33 V (vs. K^+/K) is assigned to the formation of the solid electrolyte interface (SEI) layer, and the small shoulder peak located at 0.28 V is related to the alloy reaction between K⁺ and metallic bismuth.^[5] Upon the first depotassiation process, three anodic peaks appearing at approximately 0.47, 0.52, and 1.13 V should be attributed to typical three-step dealloying reactions (namely, $K_{3}Bi{\rightarrow}K_{3}Bi_{2}{\rightarrow}KBi_{2}{\rightarrow}Bi).^{[17]}$ In the subsequent 3rd and 5th discharge processes, three stable cathodic peaks centering at 0.93, 0.44, and 0.34 V are related to the alloying process of Bi to KBi₂, K₃Bi₂, and K₃Bi, respective-



Figure 3. a) Initial three CV profiles (0.1 mV s^{-1}) and b) selected galvanostatic charge-discharge voltage plots (1.0 Ag^{-1}) of the 850-Bi@N-CNCs. c) Rate behaviors of the three Bi@N-CNCs anodes. d) Comparison in rate capabilities of 850-Bi@N-CNCs with other reported alloy anodes for KIBs in the literature. e) Cycling behaviors (1.0 Ag^{-1}) of the three Bi@N-CNCs anodes as indicated. f) Long-term cycling performance and CE values of the 850-Bi@N-CNCs at 5.0 Ag^{-1} after activation at 1.0 Ag^{-1} for 20 cycles.

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electroactive phase for the hybrid anode.

ly.^[18] The similar CV curves are clearly observed as well for

the 550-Bi@N-CNCs (Supporting Information, Figure S12a)

and 700-Bi@N-CNCs (Supporting Information, Figure S12b),

indicating the identical potassium-storage mechanism of the

three. Notably, the cathodic/anodic peaks of the 850-Bi@N-

CNCs after the first CV cycle well keep their shapes and

almost overlap, implying its high reversibility of the involved

reactions. Figure 3b profiles the selected discharge-charge voltage plots of the 850-Bi@N-CNCs anodes. These discerned

discharge/charge platforms are in good agreement with the CV observations (Figure 3a), and particularly show no

obvious difference in the voltage curves and capacity loss

with cycling from the 2nd to 300th cycles, which authenticates

the superior electrochemical reversibility of the 850-Bi@N-

CNCs electrode for efficient potassium storage. Furthermore, a large initial charge capacity of ca. 321.7 mAh g^{-1} can be

delivered by the anode along with an initial Coulombic

efficiency (CE) of ca. 78.0%, corresponding to a low irrever-

sible capacity of ca. 90.8 mAh g⁻¹ due to the formation of SEI

film. Noticeably, the first CE value of the 850-Bi@N-CNCs is

somewhat higher than other reported Bi-based anodes (Supporting Information, Table S1).^[3,5-7,17,19-24] Upon the

second discharge-charge cycle, the CE is increased rapidly

up to ca. 95.9%, coupled with a large charge capacity of ca.

 328.7 mAh g^{-1} , which is even higher than that of the 1000-

Bi@N-CNCs anode (ca. 104.6 mAhg⁻¹) (Supporting Infor-

mation, Figure S13a), revealing that metallic Bi is the real

Figure 3c collects the rate behaviors of the three anodes as indicated within the wide current density range from 0.5 to 10 Ag^{-1} . Competitively, the 850-Bi@N-CNCs electrode exhibits reversible capacities of ca. 334.3, ca. 321.8, ca. 312.7, ca. 259.7, and ca. 235.5 mAh g^{-1} at current densities of 0.5, 1.0, 2.0, 5.0, and 10.0 $A\,g^{-1},$ corresponding to a capacity retention of ca. 70.4%. While, with a 20-time increase in current rate from 0.5 to 10 Ag^{-1} , the 550-Bi@N-CNCs, 700-Bi@N-CNCs, and 1000-Bi@N-CNCs (Supporting Information, Figure S13b) just obtain ca. 284.5/ca. 170.1, ca. 318.4/ca. 201.1, and ca. 104.2/ca. 92.8 mAh g^{-1} at 0.5/10 A g^{-1} , respectively. The serious capacity degradations are evident for the 550-Bi@N-CNCs (ca. 40.2%) 700-Bi@N-CNCs and (ca. 36.9%). Particularly, the largest capacities of the 850-Bi@N-CNCs with the lowest Bi content at the same rates reveal the highest electrochemical utilization of active Bi for high-efficiency K⁺ storage. Additionally, with the current rate switched back to 1.0 A g⁻¹, a reversible capacity of ca. 332.2 mAh g⁻¹ still can be achieved by the 850-Bi@N-CNCs, and further remains stable for a long cycle period, which is apparently superior to those of the 550-Bi@N-CNCs (ca. 241.5 mAh g⁻¹), 700-Bi@N-CNCs (ca. 303.6 mAh g⁻¹), and 1000-Bi@N-CNCs (ca. 96.4 mAh g⁻¹) (Supporting Information, Figure S13b). It is particularly worth mentioning that the rate behaviors of the 850-Bi@N-CNCs are comparable to, and even better than other reported alloy-type anodes,^[5,17,21,25-30] as compared in Figure 3 d, for which its exceptional K⁺ ion diffusion coefficients (D_{K^+}) of ca. 10^{-7} cm⁻²s⁻¹ (Supporting Information, Figure 2 d) should account.

Furthermore, the 850-Bi@N-CNCs anode displays remarkable cycling performance. As illustrated in Figure 5e, ca. 99.6% of the second capacity, that is, ca. 327.5 mAg^{-1} , still can be retained after 300 consecutive cycles at a current density of 1.0 A g⁻¹. In contrast, the faster capacity decay can be observed for both the 550-Bi@N-CNCs and 700-Bi@N-CNCs, along with capacity degradation of ca. 67.8% and ca. 90.2%, respectively. Although relatively stable capacities can be obtained by the 1000-Bi@N-CNCs, a low capacity of ca. 90.4 mAhg⁻¹ is just maintained (Supporting Information, Figure S15). The rigid structure integrity of the 850-Bi@N-CNCs over the uninterrupted cycle is reasonably responsible for its superior cyclic behaviors, benefiting from the collaborative contributions from nano-dimensional Bi and inherent void space in the rigid N-CNCs skeleton with exceptional electronic conductivity (Supporting Information, Figure S16a). Obviously, after repeated alloying/dealloying processes, the ultra-small Bi NPs are still perfectly wrapped with the N-CNCs (Supporting Information, Figure S16b-d), and the intact 3D hybrid architecture with accordant elemental distributions can be well retained (Supporting Information, Figure S17). The expanded lattice space of ca. 0.40 nm for the N-CNCs is conducive to the convenient transport of potassium ions (Supporting Information, Figure S16d). While, as for the 550-Bi@N-CNCs (Supporting Information, Figure S18a-c) and 700-Bi@N-CNCs (Supporting Information, Figure S18d-f) electrodes, owing to the serious volume change of electrodes in each cycle, the contact form of the Bi NPs will inevitably change, resulting in the ongoing formation of an unstable SEI layer on its surface. As a result, the significant capacity decay is observed for the two during 300 cycles. The 1000-Bi@N-CNCs anode well maintains its unique 3D porous architecture (Supporting Information, Figure S18g-i) owing to the absence of alloying/dealloying reactions, which is reasonably responsible for its appealing electrochemical stability. More impressively, the 850-Bi@N-CNCs hybrid anode shows long-duration cycle stability especially at high rates, as illustrated in Figure 3 f. Remarkably, after 20-cycle activation at 1.0 Ag^{-1} , the capacity of the 850-Bi@N-CNCs electrode remains as ca. 224 mAhg⁻¹ over further 1200 consecutive cycles at a high current density of 5.0 Ag^{-1} , indicating a superb capacity retention of ca. 95.3%, along with an average reversible capacity loss of 0.004 % per cycle. The specific capacities of the 550-Bi@N-CNCs (Supporting Information, Figure S19) and 700-Bi@N-CNCs (Supporting Information, Figure S20) are both only ca. 183 mAh g^{-1} over 500 cycles at 5.0 A g⁻¹, corresponding to capacity degradations of ca. 0.044 % and ca. 0.041 % per cycle for the two, respectively. Furthermore, the 1000-Bi@N-CNCs electrode only has a low reversible capacity of ca. 79.1 mAh g⁻¹ after 1000 cycles at 5.0 A g⁻¹ (Supporting Information, Figure S21). One especially notes that the high-rate cycling properties of the 850-Bi@N-CNCs anode evidently surpass other reported Bi-based anodes (Supporting Information, Table S1).^[3,5–7,17,19–24]

To further figure out the superior structural stability enabled by sufficient void design in the case of 850-Bi@N-CNCs, in situ TEM investigations into the microstructure/ morphology evolution over the electrochemical potassiation/ depotassiation processes were performed. Figure 4a shows the in situ TEM nano battery set-up, which is composed of the electroactive Bi@N-CNCs and potassium metal counter electrode, coupled with the K₂O layer grown on the surface of metallic potassium as solid electrolyte in the cell.^[29] Once the contact between two electrodes was built, an appropriate bias of 2.0 V was applied to initiate the involved electrochemical reactions. Figure 4b-d present the time-resolved TEM images of the 850-Bi@N-CNCs during consecutive potassiation process, which can be further visualized clearly from the video (Supporting Information, Movie S2). Clearly, the K⁺ is first driven to penetrate the N-CNCs framework, and then, the alloying process of Bi with K occurs along with the noticeable volume expansion. With the continuous insertion of K⁺, the Bi NPs are gradually potassiated accompanied with size expansion from ca. 26 to ca. 39 nm after potassiation for 240 s, as indicated by red circles. The interior void of hollow N-CNCs was fully filled by the expanded Bi NPs. If the NPs were assumed as the regular spheres with isotropic volume expansion, the 3D volume expansion is estimated to be ca. 338% for the case, while the 2D projection width of the hierarchical carbon framework expands from ca. 195 to ca. 201 nm, confirming the rigid structure stability of the conductive carbon skeleton. During the following depotassiation process driven by employing a reversed bias of -2.0 V, the whole Bi-K allov is gradually de-alloyed and finally recovers to Bi NPs, as presented in Figure 4e-g. Apparently, the elastic shrinkage of the N-CNCs on the 2D projection to its original width of ca. 191 nm is observed, along with the discerned Bi NPs of ca. 22 nm in size (Figure 4g). After the first charge-discharge cycle, the 850-Bi@N-CNCs almost restores their original state (Supporting Information, Movie S2). Moreover, after 20 potassiation/ depotassiation cycles, the well-defined 850-Bi@N-CNCs still can maintains its structural integrity without noticeable structure rupture (Supporting Information, Movie S3), which authenticates that the internal void space and elastic shell of N-CNCs can effectively relieve the volume expansion of Bi NPs. By contrast, the bismuth NPs in the 550-Bi@N-CNCs (Supporting Information, Figure S22; Movie S4) and 700-Bi@N-CNCs (Supporting Information, Figure S23; Movie S5) are both broken and seriously agglomerated after the depotassiation process. The comparative real-time observations here visualize the superior structural reversibility of the 850-Bi@N-CNCs, which ensures the formation of a stable vet thin





Figure 4. a) Illustration of the in situ TEM nanobattery device. b)–g) Time-resolved TEM images of the 850-Bi@N-CNCs during (b–d) potassiation and (e–g) depotassiation. h) Description of the potassiation/depotassiation processes of the Bi@N-CNCs electrodes with Bi particles of different size confined in the carbon nanocages. The size changes of the N-CNCs and Bi particles were measured and indicated by red arrows.

SEI layer on the outer robust N-CNCs,^[31–34] and a close electronic contact between the continuous carbon network and Bi NPs meantime.^[35–37] While for the 550-Bi@N-CNCs or 700-Bi@N-CNCs, the repetitive rupturing and reformation of the passivating SEI film occur, and always convert the cyclable K species in electrode sur-/interfaces to dead K in the SEI, eventually leading to the death of the batteries due to the K exhaustion.

Coupled with the in situ TEM observations, in situ selected area electron diffraction (SAED) is further employed for in-depth understanding of the phase evolution over the alloying process of the 850-Bi@N-CNCs during the first discharge process (Supporting Information, Movie S6). Typical SAED pattern of the fresh 850-Bi@N-CNCs show a strong diffraction ring, corresponding to the (012) plane of the well-crystallized Bi NPs (Figure 5a). In the early stage of potassiation reaction, the diffraction rings related to the (400)/(511) planes of cubic KBi₂ with a space group of $Fd\bar{3}m$ (227) appear, which evidences that bismuth NPs are partially alloyed to form KBi₂ due to insufficient potassium supply.^[31]

as shown in Figure 5b. After full potassiation, all the diffraction signals are well indexed into the hexagonal K₃Bi with a space group of P63/mmc (194) (Figure 5c). Therefore, the phase transition of electroactive bismuth in the first potassium process of the 850-Bi@N-CNCs is as follows: Bi-KBi2-K3Bi, indicating the two-step alloying reaction for our case here. Corresponding ex situ TEM and SA-ED observations (Supporting Information, Figure S24) further corroborate that the final potassiation product of metal Bi is the K₃Bi phase indeed. Corresponding crystal lattice structure evolution of the 850-Bi@N-CNSs is schematically shown in Figure 5d for more intuitively understanding of the two-step alloying potassiation during the first discharge process.

To further authenticate the two-step alloying reactions involved K⁺-storage mechanism of our 850-Bi@N-CNCs electrode, in situ XRD was conducted as well. As manifested in Figure 5e, the initial discharge profile of 850-Bi@N-CNCs shows the a long slope. In the initial discharge stage, the intensities of typical reflections $(2\theta = 27.2,$ 37.9 and 39.6°) for the metallic Bi gradually decrease. Then, with the voltage dropping down

to ca. 0.4 V, two new peaks arise at 31.1 and 32.5°, which can be indexed to cubic KBi₂ (JCPDS No. 03-0698). When the discharge voltage further decreases to ca. 0.2 V, the peaks of Bi and KBi2 still exist. Meanwhile, two new diffraction peaks related to the hexagonal K₃Bi (JCPDS No. 04-0642) emerge at $2\theta = 28.9$ and 29.5° , accompanied by the complete disappearance of characteristic signals from Bi and KBi₂. Therefore, the two-step alloying reactions involved in the 850-Bi@N-CNCs can be well supported by both in situ SAED and XRD observations. One should particularly note that the observation here is somewhat distinguished from other previous reports about Bi-based anodes in the same electrolyte systems, where the three-step or one-step alloy reactions take place.^[5,18] Such unique difference is probably ascribed to specific microstructures, that is, nanoscale Bi NPs (<20 nm) confined in the 3D porous carbon framework, which shows enormous influence on the surfaces/interfaces and phase transition of active Bi species, and verifies that the potassiation process of Bi anodes is mainly controlled by kinetics rather than the thermodynamics system.^[5] The in situ XRD GDCh



cathode/anode is designed as around 1:1.2 to guarantee that the cathode is the capacity-limiting electrode. Corresponding differential capacity vs. voltage profiles $(dQ dV^{-1})$ of the two electrodes reveal an average operating voltage of ca. 3.01 V for the unique 850-Bi@N-CNSs//KFe-[Fe(CN)₆] device (Supporting Information, Figure S26c). The average operating voltage of the potassium ion full battery is ca. 2.2 V, with an initial discharge capacity of ca. 78.7 mAh g⁻¹ at 0.1 A g⁻¹ (Supporting Information, Figure S26d). It should be noted that the device displays large energy densities of about 170–105 $Wh kg^{-1}$ (from the 1st to 210th cycle) calculated based on the total mass of cathode and anode materials, along with high CE values from ca. 94.1 to ca. 98.7% (Supporting Information, Figure S26d). This corroborates that the 850-Bi@N-CNSs hold an enormous promise towards next-generation PIBs^[38-40] as an attractive anode.

Conclusion

In the work, we first devised a simple yet efficient two-step method including solvothermal process and subsequent calcination to controllably synthesize

Figure 5. Time-lapse diffraction patterns revealing the phase evolution of the 850-Bi@N-CNCs in reaction with K: a) pristine Bi NPs in the N-CNCs; b) Bi alloyed with K in the early stage to form KBi_2 ; c) formation of K_3Bi upon further alloyed with K. d) In situ XRD analysis of the 850-Bi@N-CNCs upon the first galvanostatic potassiation/depotassiation process: contour plot (the right) and line plot (the middle), and corresponding discharge/charge curves (the left). e) Illustration of crystalline structure evolution during the first potassiation process.

examination further demonstrates that the well-defined K_3Bi phase can be transformed to the pure metal bismuth over the first charge process via a typical three-step way, corresponding to the three identifiable platforms, which is slightly distinct from the initial discharge counterpart. Typically, the K⁺ extraction process of K_3Bi first happens at ca. 0.55 V, and results in the formation of K_3Bi_2 .^[19] Then, further depotassiation process of K_3Bi_2 produces the KBi_2 phase at ca. 0.7 V. Finally, pure bismuth recovers once again with the disappearance of KBi₂ at ca. 1.10 V.

To explore potential applications of the 850-Bi@N-CNSs towards commercial PIBs, a full PIB device was assembled by using the Prussian blue analogue of KFe[Fe(CN)₆]^[32] (Supporting Information, Figure S25) as cathode material and prepotassiated 850-Bi@N-CNSs as the anode (Supporting Information, Figure S26a). The obtained KFe[Fe(CN)₆] can provide a stable reversible capacity of ca. 70 mAh g⁻¹ along with a high CE value of ca. 98.8% within the potential range from 2.0 to 4.5 V (vs. K/K⁺) at 0.1 A g⁻¹ (Supporting Information, Figure S25b, S26b). The capacity ratio of

nano Bi encapsulated in 3D porous N-CNCs framework with an appropriate void space by using a novel Bi-based MOF as the precursor. With attentive regulation of calcination temperatures, the underlying formation processes of the Bi@N-CNCs products were proposed, and the optimized 850-Bi@N-CNCs exhibited exceptional electrochemical potassium-storage properties both in half-cell and full-cell systems, thanks to its unique structure/composition merits. With the synergistic contributions from 3D conductive N-CNCs network and nanoscale effect of active Bi NPs, typically, the 850-Bi@N-CNCs was optimized and endowed with large reversible capacities of ca. 334.3 and ca. 221.3 mAhg⁻¹ at current densities of 0.5 and 10.0 A g⁻¹, respectively, along with a longterm cycling stability of ca. 0.004 % capacity degradation per cycle over 1200 cycles at 5.0 Ag^{-1} . Besides, the assembled 850-Bi@N-CNCs//KFe[Fe(CN)₆] full cell displayed a large energy densities of ca. 170 Wh kg⁻¹. More importantly, a series of in situ characterizations including TEM, SAED and XRD were comprehensively conducted to shed light on in-depth understanding of the intrinsic electrochemical K⁺-storage behaviors of the 850-Bi@N-CNCs anode. More significantly, we strongly believe that our methodology here is highly universal to versatile fabrication of other Bi-based alloys towards high-performance secondary batteries, and other energy-related application.

Acknowledgements

This work is supported by the National Natural Science Foundation of China (No. 51772127, 51772131, 52072151, 61471307, 11874334), Taishan Scholars (No. ts201712050), Major Program of Shandong Province Natural Science Foundation (ZR2018ZB0317), Natural Science Doctoral Foundation of Shandong Province (ZR2019BEM038), the "Double-First Class" Foundation of Materials and Intelligent Manufacturing Discipline of Xiamen University, Youth Innovation Promotion Association of the CAS (2020458), Collaborative Innovation Program of Hefei Science Center, the CAS (2020HSC-CIP013) and Collaborative Innovation Center of Technology and Equipment for Biological Diagnosis and Therapy in Universities of Shandong.

Conflict of interest

The authors declare no conflict of interest.

Keywords: bismuth · in situ characterization · N-doped carbon nanocage frameworks · potassium ion batteries

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Manuscript received: December 2, 2020 Accepted manuscript online: December 28, 2020 Version of record online: February 17, 2021

