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Tunnel-structured K_xTiO_2 nanorods by in-situ carbothermal reduction as a long cycle and high rate anode for sodium-ion batteries

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ABSTRACT:

The low electronic conductivity and the sluggish sodium-ion diffusion in the compact crystal structure of Ti-based anodes seriously restrict their development in sodium ion batteries. In this study, a new hollandite K_xTiO_2 with large (2×2) tunnels is synthesized by a facile carbothermal reduction method and its sodium storage performance is investigated. XRD and TEM analysis illustrate the formation mechanism of the hollandite K_xTiO_2 upon carbothermal reduction process. Compared to the traditional layered or small (1×1) tunnel-type Ti-based materials, the hollandite K_xTiO_2 with large (2×2) tunnels may accommodate more sodium ions and facilitate the Na^+ diffusion in the structure, thus is expected to get a large capacity and realize high rate capability. The synthesized K_xTiO_2 with large (2×2) tunnels shows a stable reversible capacity of 131 mAh g^{-1} (nearly 3 times of (1×1) tunnels structured $Na_2Ti_6O_{13}$), and superior cycling stability with no obviously capacity decay even after 1000 cycles, which is significantly better than the traditional layered $Na_2Ti_3O_7$ (only 40% of capacity retention in 20 cycles). Moreover, the carbothermal process can naturally introduce oxygen vacancy and low-valent titanium as well as surface carbon coating layer to the structure, which would greatly enhance the electronic conductivity of K_xTiO_2 , thus endow this material high rate capability. With a good rate capability and long cyclability, this hollandite K_xTiO_2 can serve as a new promising anode material for room-temperature long-life sodium-ion batteries for large-scale energy storage systems. And the carbothermal reduction method is believed an effective and facile way to develop novel Ti-based anodes with simultaneously carbon coating and Ti(III) self-doping.

INTRODUCTION

Sodium ion batteries (SIBs) have been expected to be the most promising alternative to the traditional lithium ion batteries (LIBs) in electronic devices and large scale energy storage for the abundant sodium sources and similarities with LIBs.¹⁻⁴ Unfortunately, for the larger diameter of sodium ion than that of lithium ion, it is very difficult to seek for an appropriate negative materials with excellent comprehensive performances like the role acted by graphite anode in commercial LIBs.⁵⁻⁷ Considering the wide abundance, low cost, low toxicity and high safety free from Na dendrite, Ti-based anodes have been widely researched and regarded as a very promising choice for sodium-ion anode.⁸⁻¹⁴ Currently, most of the reported titanate-based anodes possess two-dimensional layered structure or small tunnel-type structure composed by edge-shared TiO_6 octahedra chains.⁵ Such compact crystal structure with small interlayer space and tight tunnels accounts for quite sluggish sodium-ion diffusion, which in turn leads to a poor rate performance. As well, the small interlayer spacing determines insufficient insertion sites for Na^+ which especially has a much larger size than Li^+ . And the insertion of Na^+ may cause structural rearrangement during the electrode redox process, resulting in the capacity fading upon cycling.¹⁵

To promote the ion diffusion and increase the reactivity of sodium storage, fabricating nanostructure is the most-frequently used way.^{16, 17} For example, nanostructures as $\text{Na}_2\text{Ti}_3\text{O}_7$ nanotubes,^{18, 19} $\text{Na}_2\text{Ti}_3\text{O}_7$ nanoarrays,²⁰ $\text{H}_2\text{Ti}_3\text{O}_7$ nanobelts,²¹ $\text{K}_2\text{Ti}_6\text{O}_{13}$ ultrafine nanowires²² have been developed to boost the electrochemical performances of Ti-based anodes for their large reaction surface area to Na^+ flux and high ion accessibility. The developed nanostructure can tremendously shorten the Na^+ diffusion length in the structure and provide high contact area with the electrolyte, thus deliver a much enhanced capacity and high rate capability for sodium

storage. However, the morphology optimization from bulk phase to nanostructure can largely increase the surface/interface Na^+ storage, it change little the amount of inherent Na^+ intercalation sites in the structure. Besides, most nanostructures cannot afford high temperature calcination. These wet-chemistry synthesized nanomaterials are usually in a limited crystalline nature with many lattice defects. Although a considerable capacity may be contributed by the large reaction surface and rich crystal defects, this additional capacity tends to decay upon the long cycle process due to the gradually lost activity and structure collapse of the nanostructure. Therefore, designing a more open structure with large diffusion tunnels and more accessible insertion sites is a more preferred way to develop high performance materials for SIBs.

The K_xTiO_2 ($0 < x < 1$) hollandite structure possesses an adequate (2×2) tunnel structure formed by double chains of edge-sharing TiO_6 octahedra that share corners with neighboring chains, and low content K ions is in the tunnel space.^{23, 24} Compared to the traditional layered or small (1×1) tunnel-type Ti-based materials,^{10, 12} the larger (2×2) tunnels in the hollandite K_xTiO_2 may accommodate more sodium ions and facilitate the Na^+ diffusion in the structure, thus is expected to get a large capacity and realize high rate capability. And the three-dimensional tunnel structure also possesses stronger skeleton stability than the two-dimensional structure upon ion insertion/extraction, which would favor a better cycle stability. Unfortunately, the reported synthesis of K_xTiO_2 seems harsh and high demands of safety ensurance since it involves the high temperature annealing in Ar- H_2 flow.²⁵⁻²⁷ To our knowledge, little research has been done on the electrochemical properties of such a hollandite structure with (2×2) tunnels for SIB up to now.

Herein, we successfully synthesize hollandite K_xTiO_2 by a mild cost-saving carbothermal reduction route and investigate its sodium storage performance. The obtained K_xTiO_2 holds a

nanorod morphology with simultaneously a high crystalline degree. More important, the in-situ carbothermal reduction process can not only coat a thin carbon layer on the material surface, but also introduce Ti^{3+} -doping and oxygen vacancy in the crystal lattice, which both solidly promote the electronic conductivity of the material.²⁹⁻³² When served as an anode material for SIB, the hollandite K_xTiO_2 shows a reversible capacity of 131 mAh g^{-1} , (nearly 3 times of (1×1) tunnels structured $\text{Na}_2\text{Ti}_6\text{O}_{13}$),¹² and good rate capability up to 1000 mA g^{-1} . Upon 1000 cycles, its capacity can keep very well with neither capacity decay nor voltage shift, which is significantly better than the traditional layered $\text{Na}_2\text{Ti}_3\text{O}_7$ (only 40% of capacity retention in 20 cycles) and also exceeds most reported Ti-based anodes.¹⁰

EXPERIMENTAL SECTION

Synthetic procedures. Firstly, the precursor nanowires were synthesized via a traditional hydrothermal method using potassium hydroxide and tetrabutyl titanate as the potassium and titanium sources, respectively.²² Then, the as-prepared white powders were mixed with glucose in ethanol. The weight ratio of glucose/precursor nanowires in the mixture is 5/8, and the concentration of glucose in ethanol is 1.875 mg/mL . After stirred for 5h, the suspension was then dried at 60°C for 12h under ambient conditions. Finally, the mixture was heated at 800°C for 6h under N_2 atmosphere.

Materials characterization. Powder X-ray diffraction (PXRD) patterns were recorded at room temperature with a PANalytical B.V. Empyrean diffractometer. The crystal structures were refined using the Rietveld method using the GSAS software package. The morphology of the product was examined by scanning electron microscopy (SEM, FEI Sirion 200) and high-resolution transmission electron microscopy (TEM, JEM 2100, JEOL). The surface state of these samples was investigated using X-ray photoelectron spectroscopy (XPS, Kratos AXIS-ULTRA

DLD-600 W). The thermogravimetric analysis (TG) was performed under air at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ with a PerkinElmer Instruments Pyris1 TGA. The elements ratio of sample was obtained by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) on Optima 4300DV (Perkin-Elmer).

Electrochemical measurement. Electrochemical measurements were performed using 2032 coin-type cells with thin sodium metal used as both the reference and counter electrodes. 1 M sodium hexafluorophosphate (NaPF_6) in EC (Ethylene Carbonate): DEC (Dimethyl Carbonate) with FEC (Fluoro Ethylene Carbonate) was used as electrolyte. The K_xTiO_2 electrodes were fabricated by mixing 70 wt.% of the active material, 20 wt.% of C45, and 10 wt.% poly (vinylidene fluoride) (PVDF) in N-methyl-2-Pyrrolidone (NMP). The obtained slurries were coated uniformly onto copper foils and then dried in a vacuum oven at $80\text{ }^{\circ}\text{C}$ for 12 h to remove the solvent before pressing. Finally the electrode film was punched into disks of 10 mm in diameter for half-cell tests. Cyclic voltammetry (CV) studies were carried out at room temperature using CHI660e electrochemical workstation at a scan rate of 0.1 mV s^{-1} in the voltage window 0.01-3 V vs. Na^+/Na . Galvanostatic charge/discharge measurements were performed in a voltage range of 0.01-3 V vs. Na^+/Na at different current densities on the automatic battery testing system LAND CT2001A model. The dQ/dV tests were carried out on an automatic battery testing system of Hokuto Denko (HJ1001SD8).

RESULTS AND DISCUSSION

Figure 1a shows the XRD patterns of the precursor and its heating products obtained at different annealing conditions. The as-prepared precursor by hydrothermal method shows broad XRD peaks, indicating its low crystallinity and tiny particle size. When heated without the presence of carbon source, the diffraction peaks grow rapidly in intensity and more peaks can be

detected. All the detected peaks can be well indexed to the $K_2Ti_6O_{13}$ phase, which suggests that the as-prepared precursor is a low crystalline $K_2Ti_6O_{13}$. Interestingly, when carbon source is introduced to the heat treatment process at 800 °C for 4h, the XRD patterns show obviously different characteristic peaks. It can be seen that a new phase (K_xTiO_2) in addition to $K_2Ti_6O_{13}$ appears. The observed co-existence of two phases in the intermediate product clearly demonstrates the reduction strength of carbon at high temperature. With prolonged heat treatment (800 °C for 6h), the $K_2Ti_6O_{13}$ phase completely disappears and all the detected diffraction peaks in the XRD pattern can be indexed to the hollandite K_xTiO_2 on the basis of tetragonal symmetry space group of I4/m. The above results suggest the completely phase transformation from $K_2Ti_6O_{13}$ to K_xTiO_2 after 6h carbothermal reduction treatment.

Figure 1b shows the schematic crystal structures of the as-prepared precursor and its carbothermal reduction product. By carbothermal reduction process, the $K_2Ti_6O_{13}$ precursor with (1×1) tunnels transforms to the hollandite K_xTiO_2 with (2×2) tunnels. The hollandite-type structure comprises double chains of TiO_6 octahedra forming (2×2) tunnels, which has been proved to be suitable for the reversible insertion/extraction of lithium ions.²³ In order to determine the positions and content of K ions in the tunnels, the Rietveld refinement of the structure has been carried out as shown in Figure S1 and Table S1. The refinement results show that K is on the 2b sites (0, 0, 1/2) and Ti, O1, and O2 on the 8h sites (x, y, 0) and K atom is located in the center of the tunnel space of K_xTiO_2 , which is well consistent with the previous reports. The resulting R factors reaches $wRp = 0.0468$, $Rp = 0.0303$, and the refined lattice parameters are listed in Table S1. The results, in general, give a nominal chemical composition of $K_{0.25}TiO_2$, which is closely matching the EDS result ($K_{0.26}TiO_2$) Figure S2. Compared to the (1×1) tunnels of $K_2Ti_6O_{13}$ precursor, the larger (2×2) tunnels of the hollandite K_xTiO_2 would

provide a privileged pathway for Na ions diffusion. In view of this, it is expected that K_xTiO_2 would be more favorable for the incorporation and diffusion of Na ions when used in sodium ion batteries. Furthermore, the unique large (2×2) tunnel structure may also help to tolerate the structural strains upon Na^+ insertion/extraction, which can favor a superior cycling stability.

The morphology changes before and after carbothermal reduction are revealed in Figure 2. Before heat treatment, the as-prepared low crystalline $K_2Ti_6O_{13}$ precursor is composed of micro-sized spherical particles which are radially assembled by uniform ultrafine nanowires of 5-10 nm in diameter, as shown in Figure 2a. After carbothermal reduction, the spherical particle morphology mainly keeps the same, while, the nanowires grow to nanorods. TEM images in Figure 2c and d further reveal that the nanorods possess an average diameter of 50-100 nm, much larger than its precursor due to the size growth during high temperature. Detailed analysis by HRTEM in Figure 2e and f demonstrates that the surface of the nanorods is coated by a carbon layer about 3 nm. The energy dispersive X-ray elemental mappings of an individual nanorod in Figure S3 further exhibit that K, Ti, O elements are homogeneously distributed and the carbon is mainly distributed on the surface of nanorod. The carbon content of the sample is about 14.4% according to the TG test of the final products under air atmosphere. (Figure S4) The highly ordered lattice fringes with their spacing about 0.51 nm and 0.32 nm respectively coincide with the (200) and (130) facet of K_xTiO_2 , suggesting a high crystallization of the product obtained by the carbothermal reduction process.

To investigate the formation mechanism of the hollandite K_xTiO_2 , we did the TEM observation on the products obtained at different stage of carbothermal reduction process, as shown in Figure 3. At the initial stage of heat treatment (800 °C for 2h), (Figure 3a), the ultrafine nanowires of $K_2Ti_6O_{13}$ precursor grow to nanorods with increased crystalline at the same time.

The clear lattice fringes with interplanar spacing of 0.64 nm corresponds to (20-1) plane, well indicating the high crystalline of $K_2Ti_6O_{13}$. Besides, it is noted that the surface of the nanorods has been coated by a thin carbon layer attributed to the pyrolysis of organic carbon source (as presented in scheme I). With prolonged heat treatment, as shown in Figure 3b, the size of nanorods increase gradually and the interplanar angle of (110) and (20-1) is 69° , corresponding to the $K_2Ti_6O_{13}$ phase. However, a new lattice fringes different from the main phase on the surface of nanorods are observed, implying the surface reduction caused by the carbon. With further heat treatment for 4h at $800^\circ C$, the nanorod are found to contain two obviously different phases as demonstrated in Figure 3c, showing a partially structural rearrangement inside the nanorod in the case of insufficient carbothermal reduction time. The phase in one side of the nanorod with the lattice spacing of 0.32 nm matches well with the K_xTiO_2 structure with its surface clearly coated by a carbon layer. While, the residue part of the nanorod corresponds to a different phase lattice, as illustrating in scheme III. Furthermore, the formed K_xTiO_2 demonstrates a highly crystalline. Based on the discussion above, it can be concluded that the reduction strength of carbon at high temperature is enough to initiate the phase transformation from (1×1) tunnels $K_2Ti_6O_{13}$ to (2×2) tunnels K_xTiO_2 from surface to bulk. These observations are in well accordance with the results of XRD analysis.

Based on the above XRD and TEM analysis, we speculate that the formation of the hollandite K_xTiO_2 undergoes the schematic process as shown in Figure 4. The carbothermal reduction process can be divided into three steps. Firstly, the low crystalline ultrafine precursor nanowires grow to nanorods with increased crystalline upon annealing process, at the same time, their surface is coated by a carbon layer derived from the pyrolysis of carbon source as shown in step I. Then, $K_2Ti_6O_{13}$ nanorods are transforming to K_xTiO_2 through surface reduction process

with prolonged heat treatment as illustrated in Step II. At last, step III schemes that $\text{K}_2\text{Ti}_6\text{O}_{13}$ nanorods have transformed to K_xTiO_2 completely at the final stage of heat treatment. During the whole heat treatment process, carbon source functions with two important roles on the formation of K_xTiO_2 : (i) the reducing power of carbon when heated with $\text{K}_2\text{Ti}_6\text{O}_{13}$ may lead to the generation of oxygen vacancy on the surface, which promotes the bulk phase transformation from $\text{K}_2\text{Ti}_6\text{O}_{13}$ to hollandite K_xTiO_2 with mixed-valence (Ti(IV)/Ti(III)); and (ii) during the heat treatment process, the carbonization not only reduced the surface Ti(IV) to Ti(III), but also formed a carbon layer on the surface of K_xTiO_2 . The resulted mixed-valent titanium can enhance the intrinsic electronic conductivity, and the in-situ coated surface carbon layer improves the electronic conductivity between particles. The presence of Ti(III) and surface coating layer, together with the large tunnel structure, endow the hollandite K_xTiO_2 both good conductivity and large reactivity towards sodium ion storage.

Electrochemical Na-storage performances of the hollandite K_xTiO_2 electrode are evaluated as shown in Figure 5. The cyclic voltammetry (CV) exhibits two pairs of obvious redox peaks at the potential of 0.8/0.5 V and 1.3/1.2 V, respectively (see Figure 5a). The reversible redox peaks at lower potentials about 0.01/0.08 V can be assigned to the Na ion intercalation in conductive additive (C45).³³ And the position of redox peaks almost keep no change for the following continuous sweeps, suggesting the highly reversible insertion/extraction reaction. A broad shoulder peak at about 0.8 V is observed in the first sodiation scan and disappears in the second sodiation scan, which may be associated with the formation of a solid-electrolyte interface (SEI) film due to irreversible reduction of the electrolyte.³⁴ The rate capability of K_xTiO_2 at different rates is displayed in Figure 5b and c. As the current density increases from 20 to 1000 mA g^{-1} , the shape discharge/charge profile is well preserved at different current density, indicating the

stable host structure even over fast Na^+ insertion/extraction. And the charge/discharge curves are in well correspondence with the redox peaks in the CV curves. It exhibits a reversible capacity of 131 mAh g^{-1} at a small current of 20 mA g^{-1} , (nearly 3 times of (1×1) tunnels structured $\text{Na}_2\text{Ti}_6\text{O}_{13}$),¹² even at a high density of 1000 mA g^{-1} , 51% of the initial capacity (67 mAh g^{-1}) can be maintained. In contrast, at the same current density of 20 mA g^{-1} , the bulk $\text{K}_2\text{Ti}_6\text{O}_{13}$ with small (1×1) tunnels only delivers a capacity of 67 mAh g^{-1} .²² J. C. P´erez-Flores and co-workers also reported the electrochemical performance of hollandite $\text{TiO}_2\text{-H}$ obtained with solid state synthesis.²⁴ It only exhibits a reversible charge–discharge capacity of 85 mA h g^{-1} at C/8 (41 mA g^{-1}) rate in the 2.5–0.2 V voltage range, and the capacity decayed fast within few cycles. The higher reversible capacity of hollandite K_xTiO_2 should be attributed to its larger (2×2) tunnels and higher electronic conductivity. Figure 5d displays the long cycling performance of the hollandite K_xTiO_2 . Even after 1000 cycles, no obviously capacity decay is observed at a current density of 200 mA g^{-1} and the coulombic efficiency remains nearly 100% during cycling. As far as we know, this impressive long-term cyclic stability is better than those of most reported Ti-based anodes for sodium-ion batteries.³⁵⁻³⁷

Figure 6 exhibits the rate capability comparison of low crystalline $\text{K}_2\text{Ti}_6\text{O}_{13}$ and the hollandite K_xTiO_2 . Even at a large current density of 1000 mA g^{-1} , the K_xTiO_2 still can keep 51% of the initial capacity (67 mAh g^{-1}), higher than 33% of the $\text{K}_2\text{Ti}_6\text{O}_{13}$ nanowires. Although the $\text{K}_2\text{Ti}_6\text{O}_{13}$ nanowires possess larger specific area due to its ultrafine nanowires with a diameter of only 5-10 nm, the hollandite K_xTiO_2 nanorods with an average diameter of 50-100 nm exhibits better rate performance instead. This indicates that such good rate performance should be ascribed to the open structure and enhanced electronic conductivity of K_xTiO_2 rather than the nanosize effect.

It is believed that the presence of Ti^{3+} can significantly enhance the inherent electronic conductivity and carbon thermal reduction can effectively introduce low-valent titanium to the host material.²⁹⁻³² Figure 7 shows the X-ray photoelectron spectroscopy (XPS) of K_xTiO_2 . The survey scan of XPS (Figure 7a) contains no signal of impurity elements except K, Ti, O and C. The carbon signals are ascribed to carbon coating on the surface of the sample originated from the pyrolysis of carbon source. The C 1s peak is fitted by four peaks, corresponding to C–C, C–O, C=O and O–C=O, respectively.³⁸ Two additional peaks at higher binding energy (>290 eV) in Figure 7b should be attributed to K $2p_{3/2}$ and K $2p_{1/2}$. The Ti 2p core level spectrum shows two sets of doublets that are attributed to the presence of Ti(IV) and Ti(III), and the $\text{Ti}^{3+}/\text{Ti}^{4+}$ ratio is about 0.35. As XPS is a surface-sensitive technique, we have carried out the inductively coupled plasma-atomic emission spectroscopy analyses (ICP-AES) to determine the element ratio of the bulk sample. And the ICP-AES results shows that the chemical compositions is $\text{K}_{0.23}\text{TiO}_2$. According to the law of charge conservation, we can get the $\text{Ti}^{3+}/\text{Ti}^{4+}$ ratio of the bulk sample is about 0.30. The O 1s spectrum in Figure 7d provides auxiliary evidence of the oxygen vacancy, where the peak at 530.9 eV belongs to the O^{2-} ions in the O-Ti-O lattice and a small shoulder peak at 533.2 eV is due to the oxygen vacancy sites on the surface. Hence, the introducing of Ti(III) should be related to the formation of the oxygen vacancy induced by the reduction power of carbon. This has been supported by many previous experimental and theoretical studies.³⁹⁻⁴³ The presence of Ti^{3+} and oxygen vacancy together with the surface carbon coating guarantee the material both good intrinsic and surface conductivity, thus can enable a better rate performance of K_xTiO_2 than the $\text{K}_2\text{Ti}_6\text{O}_{13}$ nanowires.

The hollandite structure not only exhibits the higher capacity and better rate capability, but also shows stable reaction potential. The cycling stability can be illustrated through dQ/dV

curves as shown in Figure 8a. The two pairs of charge/discharge peaks keep no change in position during cycling and are consistent with the redox peaks of CV curves, suggesting a highly stable insertion/extraction reaction. The ultrahigh cycling stability may be ascribed to the rigid tunnel structure. The open tunnel structure can facilitate ion transport and tolerance of the distortion during Na^+ insertion/extraction. Figure 8b shows XRD patterns of the hollandite K_xTiO_2 electrode before and after cycling. All the main peaks of hollandite K_xTiO_2 phase are still detected even after cycling, implying that the stable tunnel structure can be well maintained upon repeated sodium insertion/extraction processes. The morphology changes in the typical electrode before and after cycling are also investigated by TEM. As revealed in Figure 8c and d, the hollandite K_xTiO_2 retains its original nanorod morphology and the clear lattice fringes with unchanged spacing of 0.32 nm verify that the electrode still maintains its high crystallinity, indicating the robust structural stability of this material.

CONCLUSION

In summary, the hollandite K_xTiO_2 nanorods with open (2×2) tunnels were successfully obtained by a mild cost-saving in-situ carbothermal reduction route and its sodium storage performance was investigated. The XRD and TEM analysis illustrated the formation mechanism of the hollandite K_xTiO_2 . When carbon source is introduced to the heat treatment process, the reducing power of carbon leads to the generation of oxygen vacancy on the surface of $\text{K}_2\text{Ti}_6\text{O}_{13}$ precursor, which promoted the bulk phase transformation from (1×1) tunnel $\text{K}_2\text{Ti}_6\text{O}_{13}$ to (2×2) hollandite K_xTiO_2 . This hollandite K_xTiO_2 demonstrates a stable reversible capacity of 131 mAh g^{-1} and excellent rate capability of 67 mAh g^{-1} at 1000 mA g^{-1} due to the privileged pathway for Na^+ diffusion in the open tunnel structure. And the capacity of K_xTiO_2 can maintain very well with nearly no capacity decay upon 1000 cycles, demonstrating the good stability of this

hollandite type structure. The superior capacity and rate performance of K_xTiO_2 to $K_2Ti_6O_{13}$ precursor can be attributed to the introducing of Ti(III) and oxygen vacancy by carbothermal reduction, the larger open tunnels of hollandite structure, and the existence of in-situ surface carbon coating layer. With excellent rate capability and long cyclability, this hollandite K_xTiO_2 can serve as a new promising anode material for room-temperature long-life sodium-ion batteries for large-scale energy storage systems. And the carbothermal reduction method is believed an effective and facile way to develop novel Ti-based anodes with simultaneously carbon coating and Ti(III) self-doping.

SUPPORTING INFORMATION

Supporting Information. Rietveld XRD refinement results, SEM and EDS spectrum, elemental mapping images, and TG curve of the prepared K_xTiO_2 sample.

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Figure 1. (a) The X-ray diffraction patterns of hydrothermal product and the products heated under different conditions. (Magenta) Low crystalline $K_2Ti_6O_{13}$ precursor without heat treatment, (dark cyan) high crystalline $K_2Ti_6O_{13}$ obtained at 800 °C for 6h without presence of carbon source in heating, (blue) the intermediate heating product with presence of carbon source at 800 °C for 4h, (red) the final heating product with presence of carbon source at 800 °C for 6h. (b) Schematic structure illustration of $K_2Ti_6O_{13}$ precursor (left) and the hollandite K_xTiO_2 product (right).

Figure 2. (a) The SEM image of low crystalline $K_2Ti_6O_{13}$ precursor prepared via hydrothermal method, (b-f) SEM and TEM images of the hollandite K_xTiO_2 sample obtained after heating with carbon source at 800 °C for 6h.

Figure 3. The HRTEM image of intermediate products obtained at different stage of the carbothermal reduction process. (a) the $K_2Ti_6O_{13}$ nanorods obtained at the initial stage of heating the nanowire precursor with carbon source, scheme (I) represents that the nanowires has grown to nanorods with its surface coated by a carbon layer; (b) $K_2Ti_6O_{13}$ nanorods with lattice rearrangement observed at its surface edge, scheme (II) illustrates the size growing of the $K_2Ti_6O_{13}$ nanorod with simultaneously phase conversion occurred at the surface due to carbon reduction; (c) Further carbothermal reduction process leads to phase transformation propagating from surface to the bulk of the nanorod, scheme (III) illustrates the mixed phase lattices in the nanorod which attribute to the co-existence of the $K_2Ti_6O_{13}$ precursor phase and the final K_xTiO_2 product phase.

Figure 4. Schematic representation of the preparation process for the hollandite K_xTiO_2 . The $K_2Ti_6O_{13}$ nanowires were synthesized via a traditional hydrothermal method, then the as-prepared nanowires were mixed with glucose in ethanol and further heated at 800 °C under N_2 atmosphere. Step I: The $K_2Ti_6O_{13}$ nanowires grew to nanorods with increased crystalline and were coated by a carbon layer at the initial stage of heat treatment. Step II: $K_2Ti_6O_{13}$ nanorods are transforming to K_xTiO_2 through surface reduction process with prolonged heat treatment. Step III: $K_2Ti_6O_{13}$ nanorods have transformed to K_xTiO_2 completely at the final stage of heat treatment.

Figure 5. (a) CV curves of the hollandite K_xTiO_2 at a scan rate of $0.1\ mV\ s^{-1}$ from 0.01 V to 3 V vs. Na^+/Na . (b) Discharge and charge curves of the hollandite K_xTiO_2 . (c) Rate performance and (d) cycling performance of the hollandite K_xTiO_2 .

Figure 6. The rate capability comparison of low crystalline K₂Ti₆O₁₃ precursor and the hollandite K_xTiO₂.

Figure 7. (a) The survey scan of XPS of the hollandite K_xTiO_2 . (b) High-resolution C 1s and K 2p XPS spectrum, (c) Ti 2p XPS spectrum and (d) O 1s XPS spectrum of the hollandite K_xTiO_2 .

Figure 8. (a) The dQ/dV curves at $20\text{ mA } g^{-1}$ and (b) The XRD patterns of the hollandite K_xTiO_2 electrode before and after cycling. (c, d) TEM image and HRTEM of the hollandite K_xTiO_2 electrode after 50 cycles at $200\text{ mA } g^{-1}$.

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A new tunnel-structured K_xTiO_2 nanorods with open (2×2) tunnels are successfully obtained by a mild cost-saving in-situ carbothermal reduction route. When carbon source is introduced to the heat treatment process, the reducing power of carbon leads to the generation of oxygen vacancy on the surface of $K_2Ti_6O_{13}$, which promoted the bulk phase transformation from (1×1) tunnel $K_2Ti_6O_{13}$ to (2×2) hollandite K_xTiO_2 . Attributed to the larger open tunnels of hollandite structure, the introducing of Ti(III) and oxygen vacancy, and existence of surface carbon coating layer, the K_xTiO_2 exhibits large capacity, superior rate performance and long cycle stability.