Bimetal-organic-framework derived CoTiO_3 mesoporous micro-prisms anode for superior stable power sodium ion batteries

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ABSTRACT Durability, rate capability, capacity and tap density are paramount performance metrics for promising anode materials, especially for sodium ion batteries. Herein, a carbon free mesoporous CoTiO_3 micro-prism with a high tap density (1.8 g cm^{-3}) is newly developed by using a novel Co-Ti-bimetal organic framework (BMOF) as precursor. It is also interesting to find that the Co-Ti-BMOF derived carbon-free mesoporous CoTiO_3 micro-prisms deliver a superior stable and more powerful Na^+ storage than other similar reported titania, titanate and their carbon composites. Its achieved capacity retention ratio for 2,000 cycles is up to 90.1% at 5 A g^{-1} .

Keywords: sodium ion batteries, anode materials, metal-organic framework, cobalt titanate, mesoporous materials

INTRODUCTION

With the rapid expanding demand on the high rate, high energy density, long life and low cost energy storage systems for portable electronic device, electric power tools and vehicles, and storage and distribution of electric energy generated from wind, sunlight and water, massive attention have been paid to sodium ion batteries (SIBs). Compared with conventional lithium ion batteries (LIBs), SIBs are much cheaper because its earth abundance (2.74 wt%) is much larger than that of Li (0.0065 wt%) [1–7]. However, it will be a big challenge to use metallic sodium as anode, as many serious issues, including the dendrite

growth, the low Coulombic efficiency and the unstable solid electrolyte interphase caused by the intensive corrosion and active reaction of Na with electrolyte, have to been solved [8]. Before this, one of the urgent research interests for materials scientists delved into next generation SIBs is developing novel low cost anode materials with higher capacity and better cycle stability at higher power state, since the migration resistance to Na^+ is much larger than that to Li^+ .

Nowadays, various advanced carbon materials have been applied as high power anode materials for SIBs, but their relatively low capacity limit the future application [9–11]. Nanostructured transition metals (Sn, Sb, etc.) and their oxides or sulphide, as well as phosphor (P) and their compounds, have also attracted intensive interests because of their much higher theoretical sodium ion storage capacity [1–4,12]. However, the poor cyclic stability due to the larger volume change is the intrinsic drawbacks as anode materials for SIBs. Lately, titanium oxides based nanostructured materials [13–25], have been extensively studied as promising candidate anode materials due to their relatively smaller volume change than other transition metal compounds and better cyclic stability. However, their capacities and rate capability are similar or even lower than carbon anodes, which are the main challenge for their application in both high energy and high power density type batteries. Hereby, great ef-

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forts have been made to further enhance the power and cyclic stability of titanium-based compounds by the following methods, including minimizing the particle size to increase the electrochemical reactivity of TiO_2 [13], introducing conductive carbon coating/hybrid to improve the poor electric conductivity of TiO_2 [13–16], constructing porous and hierarchical nanostructure to increase the interaction surface area between active TiO_2 and electrolyte for further enhance the rate capability of TiO_2 [17–25].

Besides the aforementioned structural and additive modification, recently, doping or incorporating with other transition metal components (N, Mo, Sn and Sb) [21–25] or directly constructing transition metal titanate (*viz.*, MTiO_3 ; where M=Ni, Co, Mn) have been proposed to further promote the sodium and lithium ion storage performance of TiO_2 anodes, according to the combined intercalation and conversion reaction mechanisms [26–30]. Since the synergistic effect of TiO_2 and transition metal oxides, MTiO_3 exhibits a much higher theoretical capacity (500–1,000 mA h g^{-1} for SIBs depending on the sodium ion storage mechanism) than titanium oxides [26–28]. Some recent reports also indicate MTiO_3 presents much better cyclic stability than that of their transition metal based anodes [28–30]. However, there are only few works reported the sodium ion storage behaviors of MTiO_3 at a high charge/discharge current density at a relatively high tap density [27,28]. Particularly, our previous results indicates the feasibility to achieve high power Na^+ storage performance by introducing plenty of grain boundary and mesopores into the dense NiTiO_3 microparticles for the fast ion transportation [27]. Brown *et al.* [28] also demonstrated that the large sized CoTiO_3 prepared by high temperature solid state method could deliver capacity of 139 and 128 mA h g^{-1} during the first and second charge at 15 mA g^{-1} in a sodium ion cell, which are much higher than that of 19 mA h g^{-1} on MnTiO_3 prepared by similar solid state method. Moreover, CoTiO_3 shows much lower band gap energy (2.34 eV), larger unit cell ($a=5.49 \text{ \AA}$) and relatively lower formation temperature ($\sim 500^\circ\text{C}$) than that of NiTiO_3 (3.02 eV, $5.44 \text{ \AA}$, and $\sim 550^\circ\text{C}$, respectively) [27,31,32]. Therefore, CoTiO_3 should be more conductive and can provide larger space to accommodate the volume change during the sodiation process. Thus, it will be also very interesting and important to further understand and continuously promote the sodium ion storage performance. Hence, a carbon free mesoporous CoTiO_3 hexagonal micropism with a high tap density (1.8 g cm^{-3}) is developed by annealing a newly developed Co-Ti-

ethylene glycol (EG) bimetal-organic-framework (BMOF) in this work for achieving superior stable and powerful sodium ion storage capability. Compared with conventional sol-gel method, co-precipitation method and other solution based method, the BMOF derivative method is easy to get pure phase mesoporous product with a uniform composition and well-defined morphology [33,34]. Especially, a small molecule, namely EG, is used as organic component to build the micropism Co-Ti-EG BMOF, instead of the commonly used large or long chain molecule, for example, 2-methylimidazole for zeolitic imidazolate frameworks [33]. Therefore, it is good for obtaining denser derivatives. Especially, Co-Ti-EG BMOF is a well-defined hexagonal micropism. Moreover, the reaction process and the quality of the final products can be precisely monitored and checked *via* visual detection of the color and state evolution during the preparation process.

EXPERIMENTAL SECTION

Raw materials

In this work, Urea (purity $\geq 99\%$, Xilong Chemical Co., Ltd.), $\text{Co}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4\text{H}_2\text{O}$ (purity $\geq 99\%$, Aladdin), titanium butoxide (TBO) (purity $\geq 98\%$, Aladdin), ethylene glycol (AR grade, Shanghai No.4 Reagent & H.V. Chemical Limited Company) and ethanol (purity $\geq 99.5\%$, Aladdin) were used as raw materials to prepare the Co-Ti-EG BMOF precursor and the final product cobalt titanate.

Synthesis of CoTiO_3 mesoporous micropism

The preparation process and the colour evolution during the preparation process of CoTiO_3 micro-prism are shown in Fig. 1. In a typical synthesis process, the Co-Ti-EG BMOF was firstly prepared as a precursor using the rationally designed solvothermal reaction. First, stoichiometric amounts of urea, cobalt acetate tetrahydrate and titanium butoxide (TBO) were successively dissolved in a molar ratio of 3:1:1 into 60 mL ethylene glycol (EG) to form a clear red solution under magnetic stirring at room temperature. Here, EG acts as both solvent and complexing agent. As shown in Fig. 1, during the magnetic stirring process, the clear red solution gradually turns to a light pink suspension. This observation indicates that EG has reacted with Ti^{4+} and Co^{2+} to form Co-Ti-EG polymer chain precursor. To further enhance the crystallinity of Co-Ti-EG BMOF, the light pink suspension of Co-Ti-EG was sealed into a 100 mL Teflon-lined stainless steel autoclave. Subsequently, the autoclave

Figure 1 The preparation and color evolution process for the preparation of mesoporous CoTiO_3 hexagonal micro-prisms.

was put into a blowing dry box preheated to 120°C . After a six-hour solvothermal reaction, Co-Ti-EG BMOF was obtained by collecting and washing the solvothermal product with ethanol for 3 times. The obtained BMOF was put in a muffle furnace and calcined at a temperature ranging from 600°C for 5 h at a heating rate of $10^\circ\text{C min}^{-1}$ under air to fully remove the organic component in BMOF. Finally, a highly crystalline CoTiO_3 green powder was obtained.

Characterization

The morphology of as-prepared precursor and the final products were characterized by using field emission scanning electron microscopy (FE-SEM, Hitachi S-4800) at an acceleration voltage of 3 kV. The optical photos were taken by digital camera. Nitrogen adsorption/desorption isotherms were obtained at 77 K using an automated adsorption apparatus (Micromeritics ASAP 2020). The surface area was calculated based on the Brunauer–Emmett–Teller (BET) equation. X-ray diffraction (XRD) patterns of the as-prepared precursor and final products were measured on an X-ray diffractometer (RIGAKU, RINT-ULTIMA III) using $\text{Cu K}\alpha$ radiation ($\lambda = 1.54051\text{\AA}$). The diffraction patterns were recorded in a 2θ range of $10\text{--}70^\circ$ with a step size of 0.01° . Fourier transform infrared spectroscopy (FTIR) was recorded on a Perkin-Elmer Spectrum One spectrometer using KBr pellets. Raman spectrum was recorded by Renishaw (England) inVia reflex spectrometer with silicon slice at room temperature, using the 532 nm laser. The data were collected by keeping the power at 50 mW, 100 scans and 1 cm^{-1} resolution. The tap density of CoTiO_3 was measured by calculating the pellet density of as-prepared

CoTiO_3 powder pressed under 20 MPa using pressing machine.

To investigate the electrochemical performance of as-prepared CoTiO_3 micro-prisms, the composite electrodes of the final product CoTiO_3 were prepared by coating their uniform slurry mixed with acetylene black (AB) and polyvinylidene fluoride (PVDF) (active materials: AB: PVDF = 75:15:10) on copper foil. After drying under 70°C for 3 h in air followed by 8 h under vacuum condition in drying boxes, the electrodes were then pressed and punched out into 13 mm (in diameter) disks. The average mass loading is about 1 mg cm^{-2} . Two-electrode sodium ion batteries were assembled in an ultrapure Ar-gas filled glove box to investigate the sodium ion storage performance of the final product CoTiO_3 . The electrolyte used was a 1 mol L^{-1} NaPF_6 in ethylene carbonate (EC) and dimethyl carbonate (DMC) in a volume ratio of 1:1 with the addition of trace FEC. Sodium discs were used as counter electrodes. Cyclic voltammetry (CV) and galvanostatic charge and discharge measurements were carried out in a voltage range of 0.01 to 3 V vs Na/Na^+ at a current density ranged from 0.25 to 5 A g^{-1} , respectively. The electrochemical impedance spectroscopy (EIS) was carried out in a frequency range of 0.01 Hz to 100 kHz, and the perturbation amplitude was controlled at 5 mV. The galvanostatic charge/discharge test was performed on a battery testing system (CT2001A, Wuhan Land). The aged cells were discharged/charged within the voltage window of 0.01 to 3.0 V at current densities corresponding to 0.5, 1, 2, 5 and 10 C rate ($1\text{ C} = 500\text{ mA h g}^{-1}$) under constant current mode.

RESULTS AND DISCUSSION

The typical preparation process and the colour evolution phenomenon of the scalable BMOF derived strategy for the desired mesoporous CoTiO_3 micro-prisms are clearly shown Fig. 1. At the beginning, one-dimensional (1D) Co-Ti BMOF were self-assembled by a rational modified solvothermal method. In a typical synthesis process, stoichiometric amounts of urea, cobalt acetate tetrahydrate and titanium butoxide (TBO) were firstly dissolved in a molar ratio of 3:1:1 into 60 mL EG to form a clear red solution under magnetic stirring at room temperature. During the continuously magnetic stirring, EG gradually reacts with Ti^{4+} and Co^{2+} to form Co-Ti-EG polymer chain precursor, meanwhile the clear red solution gradually turns to a light pink suspension. After a further crystallizing treatment under solvo-thermal condition at 120°C for 6 h in a sealed teflon-lined stainless steel, highly crystallized and well-cut hexagonal dense

Figure 2 (a) and (b) the SEM images of Co-Ti-EG DMOC, (c) and (d) the SEM images of CoTiO₃ mesoporous microprisms.

micro-prisms of pink Co-Ti-EG BMOF were finally obtained. As shown in Fig. 2a, b, the length and diameter of single Co-Ti-EG hexagonal micro-prisms are 2–4 μm and 0.5–1 μm, respectively. The well-defined XRD pattern, given in Fig. 3a, is similar with the reported pattern of Ni-Ti-EG BMOF, which indicates the self-assembling mechanism of the highly crystalline pink Co-Ti-EG BMOF are similar [27], due to the close nature of Co²⁺ with Ni²⁺.

The FTIR spectroscopy provided in Fig. 3b further confirm the metal-organic complex nature of Co-Ti-EG BMOF. The peaks centered at 2,831 and 2,931 cm⁻¹ is indexed to the symmetry and anti-symmetry stretching vibration (ν_s and ν_{as}), respectively, of C–H bonding in the group of –CH₂–, instead of –CH₃. Peaks centered in 3,403, 1,458, 1,070 and 887 cm⁻¹ can be assigned to the ν_{OH} , δ_{OH} , ν_{CO} and γ_{OH} of C–O and O–H bonding in the group of –CH₂–OH, respectively. Moreover, the peaks centered in 2,484, 1,866, 1,323 and 1,212 cm⁻¹ can be indexed to the ν_{OH} , $\nu_{C=O}$, δ_{OH} and ν_{CO} of C=O, C–O and O–H bonding in the group of –COOH, respectively. Being annealed, all organic components mentioned above have been removed and decomposed into H₂O, CO₂ and CO. As shown in Fig. 3b, no peak can be observed from the FTIR spectroscopy of the obtained CoTiO₃ micro-prisms when the wave number is larger than 800 cm⁻¹.

After being annealed at 600°C for 5 h in air, the obtained green CoTiO₃ powder featured obviously mesoporous structure that constructed with closely packed primary CoTiO₃ nanoparticles into a hexagonal micropriam, as shown in Figs 2c, d and 4a. The particle sizes of primary and secondary particles as-prepared CoTiO₃ micropisams are 50–150 nm and 500–2,000 nm, respectively, which are larger than 50–150 nm and 500–800 nm of the reported NiTiO₃ micropisams, respectively [27].

Figure 3 (a) The XRD patterns of Co-Ti-EG and CoTiO₃ prisms, (b) the FTIR spectra of the as-prepared Co-Ti-EG BMOF and its derivative CoTiO₃ micropisams, (c) N₂ adsorption–desorption isotherm profile and (d) the pore size distribution curve of the as-prepared porous CoTiO₃ prism.

Figure 4 (a) low and (b) high resolution TEM images of as-prepared CoTiO₃ mesoporous micro-prism.

The sharp XRD pattern present in Fig. 3a is consistent with the standard pattern based on PDF#15-0866, which indicates the pure ilmenite structure of CoTiO₃. The HRTEM image in Fig. 4b corresponding to the selected area also clearly confirms the lattice fringes of the (012) ($d_{012}=0.37$ nm) crystallographic planes of ilmenite CoTiO₃. Furthermore, the pore size is mainly 20–150 nm, average 50 nm, as clarified by the TEM images shown in Fig. 4a and the pore size distribution curve given in Fig. 3d. The total pore volume and the BET specific surface area calculated based on the N₂ adsorption–desorption isotherm profile in Fig. 3c is about 0.2 cm³ g^{−1} and 15.6 m² g^{−1}, respectively. The mesoporous structure can provide effective channel for the adequately infiltration of electrolyte inside the CoTiO₃ micro-prism to increase the efficiency and achieve high rate sodium ion transportations. Moreover, the interconnected nanoscale primary particle in turn can promote the rate performance of CoTiO₃ secondary micro-prisms by decreasing the solid state diffusion of sodium within the nano-size CoTiO₃ particles and creating large amount of disorder state interface for shortcut diffusion of Na⁺ during the charge/discharge process. Considering the intrinsic low volume change during Na⁺ insertion/extraction, the as-prepared mesoporous CoTiO₃ hexagonal micro-prisms would show desirable rate and cyclic performance, in terms of the abovementioned unique metrics. The energy dispersive spectrometer (EDS) analysis results given in Fig. 5a confirm that the atomic ratio of Ti and Co is close to 1:1 for ideal CoTiO₃. As shown Fig. 5b, the Raman modes (absorption at 696, 604, 451, 382, 334, 266, 236 cm^{−1}) are consistent with the observed Raman modes of the reported CoTiO₃ [35]. The strongest Raman mode at 696 cm^{−1} on CoTiO₃ should arise from the highest frequency vibrational mode of CoO₆ octahedra that is the symmetric stretching mode. No additional bands corresponding to TiO₂ and D/G bonds of carbon could be

Figure 5 (a) The EDS spectroscopy of the selected area in the inset SEM image, (b) the Raman spectrum and (c) the electrochemical impedance spectroscopy of as-prepared CoTiO₃ micropriams.

found from the observed Raman spectrum, which further confirm the as-prepared product is carbon-free pure phase CoTiO₃, instead of the mixture of carbon, TiO₂ and cobalt oxides.

To understand the Na⁺ storage properties of CoTiO₃, the electrodes made of desired CoTiO₃ mesoporous micro-prisms were used as working electrode; metallic sodium and glass fiber membrane were used as counter/reference electrode and separator, respectively. The electrochemical performance were tested in a two-electrode setup in an electrolyte of 1 mol L^{−1} NaPF₆ in ethylene carbonate (EC) + propylene carbonate (PC) in a volume ratio of 1:1 with the addition of trace amounts of fluor-ethylene carbonate (FEC). The obtained sodium ion storage properties are given in Fig. 6. During initial cycling at 0.5 C in sodium ion batteries, the discharge/charge capacity of CoTiO₃ are 551.3/161.3 mA h g^{−1} at room temperature, as can be seen in the charge/discharge voltage profiles shown in Fig. 6a. The initial coulombic efficiency is ~29.3%, comparable to mesoporous NiTiO₃ micro-prisms [27]. The observed initial discharge capacities, namely 551.3 mA h g^{−1}, are comparable to the theoretical capacity of CoTiO₃ (519.5 mA h g^{−1}) based on the following initial sodiation mechanism:

The slightly higher discharge capacity than theoretical value should be accounted for the formation of solid

Figure 6 The electrochemical performance of the desired CoTiO₃ mesoporous micro-prisms anode materials: (a) the first cycle at 0.5 C and (b) the 20th cycle charge/discharge voltage profiles and (c) cyclic and rate capability for the as-prepared CoTiO₃ at a current density of 0.5, 1, 2, 5 and 10, respectively; (d) the cyclic performance and coulombic efficiency at 10 C for 1,000 cycles, (e) the capacity retention ratio of the as-prepared CoTiO₃ micro-prisms from 20th to 200th cycles to the reported NiTiO₃ micro-prisms [27]. (1 C = 500 mA g⁻¹) (f) Cyclic voltammetry curves at 0.1 mV s⁻¹ during the initial five cycles.

electrolyte interphase on the surface of CoTiO₃ nanoparticles. The low discharge capacity than reported NiTiO₃ should be caused by the much large particle size and much lower specific surface area (Table 1). The probable reversible de-sodiation mechanism responsible for the charge capacity of 161.3 mA h g⁻¹ could be as follows:

Most of the irreversible capacity should be caused by the irreversible reaction. Only partially newly formed Co

and Na₂O react to CoO and Na⁺. In this case, x is around 0.17. This should be one of the main reasons resulted in the low initial coulombic efficiency. The relatively large particle size and low specific surface area could be another reason responsible for the relatively lower electrochemical activity, since the sodium ion storage performance is highly affected by the increase of particle size [14]. Therefore, the obtained CoTiO₃ mesoporous micro-prism deliver a much higher capacity and rate performance than that of reported CoTiO₃ (139 mA h g⁻¹) synthesized by solid state method, as given in Table 1 [28]. Additionally, the large irreversible conversion re-

Table 1 A comprehensive comparison of the sodium ion storage properties of present CoTiO₃ mesoporous micro-prism, reported NiTiO₃ and TiO₂-based nanostructured anode materials

No	Materials and morphology	PP / SP* size	Low rate capacity (mA h g ⁻¹)	High rate capacity (mA h g ⁻¹)	High rate stability (%)	Ref.
1	CoTiO ₃ mesoporous hexagonal microprism	50–150 nm/L: 2–4 μm, D: 0.5–1 μm, 15.6 m ² g ⁻¹	161 (250 mA g ⁻¹)	72.3 (5 A g ⁻¹)	90.1 (2,000 cycle, 5 A g ⁻¹)	Present work
2	CoTiO ₃ prepared by solid state method	/	139 (250 mA g ⁻¹)	/	/	[28]
3	NiTiO ₃ nanoparticles	3–5 nm /	~400 (250 mA g ⁻¹)	192 (4 A g ⁻¹)	88.4 (200 cycle, 0.5 A g ⁻¹)	[26]
4	NiTiO ₃ mesoporous hexagonal microprism	30–100 nm/L: 2–4 μm, D: 0.5–1 μm, 30 m ² g ⁻¹	278 (250 mA g ⁻¹)	118 (5 A g ⁻¹)	44.3 (1,000 cycle, 5 A g ⁻¹)	[27]
5	Anatase C-coated TiO ₂ nanoparticles	40 nm / 11 nm /	~135 (335 mA g ⁻¹) 195	50 (3.35 A g ⁻¹) 135	/	[14]
6	Graphene-rich wrapped petal-like rutile TiO ₂ tuned by carbon dots	~10 nm / D: ~300 nm	~185 (167 mA g ⁻¹)	59.8 (4.2 A g ⁻¹)	100 (1,000 cycles 3.35 A g ⁻¹)	[15]
7	Anatase TiO ₂ nanopores	~20 nm / 55.573 m ² g ⁻¹	~164.3 (167 mA g ⁻¹)	46.4 (3.35 A g ⁻¹)	102.6 (200 cycles 0.84 A g ⁻¹)	[18]
8	Mo-doped anatase TiO ₂	/	~162.4 (167 mA g ⁻¹)	~109.5 (1.67 A g ⁻¹)	109.2 (100 cycles 0.03 A g ⁻¹)	[24]
9	Anatase TiO ₂	/	~89.6 (167 mA g ⁻¹)	~43.9 (1.67 A g ⁻¹)	108.8 (100 cycles 0.03 A g ⁻¹)	[24]
10	Olive-like TiO ₂ coated with carbon	/ 80 nm / 150 nm	~225 (167 mA g ⁻¹) ~202	~105 (6.7 A g ⁻¹) ~75	94.6 (1,000 cycles 3.36 A g ⁻¹) 96.1	[13]
11	N ₂ -doped mesoporous TiO ₂ nanofiber	25 nm D: 500 nm	220 (336 mA g ⁻¹)	~108 (3.36 A g ⁻¹)	94.0 (500 cycles 3.36 A g ⁻¹)	[21]
12	Mesoporous TiO ₂ nanofiber	25 nm D: 500 nm	173 (336 mA g ⁻¹)	~87 (3.36 A g ⁻¹)	94.3 (500 cycles 3.36 A g ⁻¹)	[21]
13	Carbon-coated rutile titanium dioxide	10–50 nm	~130.6 (336 mA g ⁻¹)	~70.6 (3.36 A g ⁻¹)	99 (500 cycles 3.36 A g ⁻¹)	[16]
14	Rutile titanium dioxide	10–50 nm	~55 (336 mA g ⁻¹)	~22.6 (3.36 A g ⁻¹)	/	[16]

*PP: primary particle / SP: secondary particle.

action also could be confirmed by the CV analysis results, shown in Fig. 6f. During the subsequent cycles, the electrochemical performance is gradually get stabilization, as observed from the evolution of the charge/discharge profiles and the CV curves (Fig. 6b, f).

As shown in Fig. 6f, three oxidation peaks (located at 0.86, 1.21 and 2.00 V, respectively) and one broad (0.90 V), should be responsible for the re-oxidation of Co⁰ and Ti³⁺ to Co²⁺ and Ti⁴⁺ due to the extraction of Na⁺ from the host structure. The reduction peaks located at 0.90 and 0.36 V are apparent from the second cycle. The results observed from CV test is consistent with the gal-

vanostatic charge/discharge profiles shown in Fig. 6a, b, which also indicate similar sodium storage behaviour of as-developed CoTiO₃ mesoporous prisms with that of NiTiO₃ reported in [26–28].

Interestingly, it is also glad to find from Fig. 6c that the charge capacity retention ratio of the obtained CoTiO₃ significantly increased from 72.2% at 0.5 C to 81.6% at 1 C, to 86.5% at 2 C, and further increased to 91.7% at 5 C, and finally increase to 94.5% at 10 C, from the 20th to 200th cycle. Even after cycling at 10 C for 2,000 cycles, the capacity retention ratio is maintained at 90.1%, as can be seen in Fig. 6d. At the same time, the chare/discharge

Figure 7 The SEM images of the CoTiO₃ electrode tested for 2,000 cycles: at low (a) and high (b) magnifications.

coulombic efficiency is around 100%. As shown in Fig. 6e, the observed capacity retention ratio of CoTiO₃ mesoporous micro-prisms is much higher than that of the just reported NiTiO₃ with similar morphology. Together with the long term cyclic testing results shown in Fig. 6d, the SEM images of the tested electrode of CoTiO₃ shown in Fig. 7 further confirm the electrochemical stability of as-prepared CoTiO₃. As shown in Fig. 7, the structure of mesoporous CoTiO₃ microprism is maintained after 2,000 cycles, only a thin layer of solid electrolyte interphase grow on the surface of CoTiO₃ particles.

Based on above observation, present CoTiO₃ micro-prisms can provide much superior rate and excellent cyclic performance at high current density at such high tap density (1.8 g cm⁻³). As present in Table 1, the as-prepared pure CoTiO₃ micro-prisms also deliver significantly higher capacity and better rate capability than typical carbon materials [9–11], and pure TiO₂ anode materials, meanwhile, show similar or even better electrochemical performance with N, Mo, Sn doped TiO₂ and ultra-small sized TiO₂ [13–24]. The better electrical conductivity of CoTiO₃ than NiTiO₃, TiO₂, because of the narrower band gap of CoTiO₃ (2.34 eV) than NiTiO₃ (3.02 eV) and TiO₂ (3.3 eV), should be one of the reason responsible for the much enhanced sodium ion storage performance [31,32]. Comparing to the reported counterparts, NiTiO₃ nanoparticle and micro-prisms, the initial capacity of CoTiO₃ are lower than reported NiTiO₃ [26,27]. However, the preserved charge capacity of CoTiO₃ at 10 C after 2,000 cycles still kept 62.6 mA h g⁻¹, which is much higher than 51.1 mA h g⁻¹ of reported NiTiO₃ [27]. Especially at high rate, the capacity retention ratio of the reported NiTiO₃ at 10 C is only 44.3% from the 20th to 1,000th cycle, 46% lower than 90.3% achieved by as-prepared CoTiO₃. The larger pore size of the obtained CoTiO₃ mesoporous micro-prism than NiTiO₃ is helpful to accommodate the volume change during the (de-)sodiation process, which will be good for the im-

provement of cyclic stability. The exceptional rate capability of the as-prepared CoTiO₃ could also be clarified by EIS testing results. As present in Fig. 5c, after 5 cycles the inner resistance, including the contact resistance, resistance of SEI layer and charge transfer resistance, greatly decreased after being activated. The observed inner resistance of carbon-free mesoporous CoTiO₃ microprism is even lower than the reported carbon fiber electrode for sodium ion batteries [9]. Therefore, all the above results indicate that the as-prepared CoTiO₃ mesoporous micro-prisms can be potential anode materials for superior power stable sodium ion storage, once the surface condition of CoTiO₃ with conductive carbon and the primary particle size, the quality of the electrolyte and battery assembly process are properly optimized.

CONCLUSIONS

In this paper, a bimetal organic framework (BMOF)-derived mesoporous CoTiO₃ micro-prisms was prepared as potential anode materials for superior power and cyclic stable sodium ion storage. The as-prepared CoTiO₃ shows unique characteristics, including the mesoporous structure formed by the interconnection of nano-size primary CoTiO₃ particle, the relatively high tap density (1.8 g cm⁻³) hexagonal 1D micro-prism formed by close-packing nano-size primary CoTiO₃ particle, relatively higher conductivity and the small volume change during the discharge/charge process. All characteristics endow the obtained nanostructured CoTiO₃ micro-prism with following superior rate and cyclic performance. From the 20th to the 200th cycle, the corresponding charge capacity retention ratio are 72.2%, 81.6%, 86.5%, 91.7%, and finally increase to 94.5% at 0.5, 1, 2, 5 and 10 C, respectively. Even after cycling at 10 C for 2,000 cycles, the capacity retention ratio is maintained at 90.1%. Coupled with the scalable preparation method, the superior sodium ion storage performance brings to the fore mesoporous CoTiO₃ hexagonal micro-prism as a contender anode for long durability and high power sodium ion batteries.

Received 7 November 2017; accepted 30 January 2018;
published online 11 February 2018

- 1 Xiao Y, Lee SH, Sun YK. The application of metal sulfides in sodium ion batteries. *Adv Energy Mater*, 2017, 7: 1601329
- 2 Kang W, Wang Y, Xu J. Recent progress in layered metal dichalcogenide nanostructures as electrodes for high-performance sodium-ion batteries. *J Mater Chem A*, 2017, 5: 7667–7690
- 3 Lao M, Zhang Y, Luo W, *et al.* Alloy-based anode materials toward advanced sodium-ion batteries. *Adv Mater*, 2017, 29: 1700622

- 4 Liu Z, Zhang Y, Zhao H, *et al.* Constructing monodispersed MoSe₂ anchored on graphene: a superior nanomaterial for sodium storage. *Sci China Mater*, 2017, 60: 167–177
- 5 Zhang Q, Huang Y, Liu Y, *et al.* F-doped O₃-NaNi_{1/3}Fe_{1/3}Mn_{1/3}O₂ as high-performance cathode materials for sodium-ion batteries. *Sci China Mater*, 2017, 60: 629–636
- 6 Tao W, Xu ML, Zhu YR, *et al.* Structure and electrochemical performance of BaLi_{2-x}Na_xTi₆O₁₄ (0 ≤ x ≤ 2) as anode materials for lithium-ion battery. *Sci China Mater*, 2017, 60: 728–738
- 7 Fang Y, Yu XY, Lou XWD. A practical high-energy cathode for sodium-ion batteries based on uniform P2-Na_{0.7}CoO₂ microspheres. *Angew Chem Int Ed*, 2017, 56: 5801–5805
- 8 Zhao Y, Goncharova LV, Zhang Q, *et al.* Inorganic–organic coating *via* molecular layer deposition enables long life sodium metal anode. *Nano Lett*, 2017, 17: 5653–5659
- 9 Chen T, Liu Y, Pan L, *et al.* Electrospun carbon nanofibers as anode materials for sodium ion batteries with excellent cycle performance. *J Mater Chem A*, 2014, 2: 4117–4121
- 10 Xiao L, Cao Y, Henderson WA, *et al.* Hard carbon nanoparticles as high-capacity, high-stability anodic materials for Na-ion batteries. *Nano Energy*, 2016, 19: 279–288
- 11 Li Z, Bommier C, Chong ZS, *et al.* Mechanism of Na-ion storage in hard carbon anodes revealed by heteroatom doping. *Adv Energy Mater*, 2017, 7: 1602894
- 12 Rahman MM, Glushenkov AM, Ramireddy T, *et al.* Electrochemical investigation of sodium reactivity with nanostructured Co₃O₄ for sodium-ion batteries. *Chem Commun*, 2014, 50: 5057–5060
- 13 Chen J, Zhang Y, Zou G, *et al.* Size-tunable olive-like anatase TiO₂ coated with carbon as superior anode for sodium-ion batteries. *Small*, 2016, 12: 5554–5563
- 14 Tahir MN, Oschmann B, Buchholz D, *et al.* Extraordinary performance of carbon-coated anatase TiO₂ as sodium-ion anode. *Adv Energy Mater*, 2016, 6: 1501489
- 15 Zhang Y, Foster CW, Banks CE, *et al.* Graphene-rich wrapped petal-like rutile TiO₂ tuned by carbon dots for high-performance sodium storage. *Adv Mater*, 2016, 28: 9391–9399
- 16 Zou G, Chen J, Zhang Y, *et al.* Carbon-coated rutile titanium dioxide derived from titanium-metal organic framework with enhanced sodium storage behavior. *J Power Sources*, 2016, 325: 25–34
- 17 Zhang W, Lan T, Ding T, *et al.* Carbon coated anatase TiO₂ mesocrystals enabling ultrastable and robust sodium storage. *J Power Sources*, 2017, 359: 64–70
- 18 Li S, Xie L, Hou H, *et al.* Alternating voltage induced ordered anatase TiO₂ nanopores: An electrochemical investigation of sodium storage. *J Power Sources*, 2016, 336: 196–202
- 19 Hong KJ, Kim SO. Atomic layer deposition assisted sacrificial template synthesis of mesoporous TiO₂ electrode for high performance lithium ion battery anodes. *Energy Storage Mater*, 2016, 2: 27–34
- 20 Cui Z, Li C, Yu P, *et al.* Reaction pathway and wiring network dependent Li/Na storage of micro-sized conversion anode with mesoporosity and metallic conductivity. *J Mater Chem A*, 2015, 3: 509–514
- 21 Wu Y, Liu X, Yang Z, *et al.* Nitrogen-doped ordered mesoporous anatase TiO₂ nanofibers as anode materials for high performance sodium-ion batteries. *Small*, 2016, 12: 3522–3529
- 22 Wang N, Bai Z, Qian Y, *et al.* Double-walled Sb@TiO_{2-x} nanotubes as a superior high-rate and ultralong-lifespan anode material for Na-ion and Li-ion batteries. *Adv Mater*, 2016, 28: 4126–4133
- 23 Yan D, Yu C, Bai Y, *et al.* Sn-doped TiO₂ nanotubes as superior anode materials for sodium ion batteries. *Chem Commun*, 2015, 51: 8261–8264
- 24 Liao H, Xie L, Zhang Y, *et al.* Mo-doped gray anatase TiO₂: lattice expansion for enhanced sodium storage. *Electrochim Acta*, 2016, 219: 227–234
- 25 He H, Wang H, Sun D, *et al.* N-doped rutile TiO₂/C with significantly enhanced Na storage capacity for Na-ion batteries. *Electrochim Acta*, 2017, 236: 43–52
- 26 Kalubarme RS, Inamdar AI, Bhange DS, *et al.* Nickel-titanium oxide as a novel anode material for rechargeable sodium-ion batteries. *J Mater Chem A*, 2016, 4: 17419–17430
- 27 Huang ZD, Zhang TT, Lu H, *et al.* Grain-boundary-rich mesoporous NiTiO₃ micro-prism as high tap-density, super rate and long life anode for sodium and lithium ion batteries. *Energy Storage Mater*, 2017, doi: 10.1016/j.ensm.2017.08.012
- 28 Brown ZL, Smith S, Obrovac MN. Mixed transition metal titanate and vanadate negative electrode materials for Na-ion batteries. *J Electrochem Soc*, 2015, 162: A15–A20
- 29 Guo S, Liu J, Qiu S, *et al.* Porous ternary TiO₂/MnTiO₃@C hybrid microspheres as anode materials with enhanced electrochemical performances. *J Mater Chem A*, 2015, 3: 23895–23904
- 30 Bai X, Li T, Zhao XY, *et al.* Al₂O₃-modified Ti–Mn–O nanocomposite coated with nitrogen-doped carbon as anode material for high power lithium-ion battery. *RSC Adv*, 2016, 6: 40953–40961
- 31 Lin YJ, Chang YH, Yang WD, *et al.* Synthesis and characterization of ilmenite NiTiO₃ and CoTiO₃ prepared by a modified Pechini method. *J Non-Crystalline Solids*, 2006, 352: 789–794
- 32 Acharya T, Choudhary RNP. Structural, dielectric and impedance characteristics of CoTiO₃. *Mater Chem Phys*, 2016, 177: 131–139
- 33 Yilmaz G, Yam KM, Zhang C, *et al.* *In situ* transformation of MOFs into layered double hydroxide embedded metal sulfides for improved electrocatalytic and supercapacitive performance. *Adv Mater*, 2017, 29: 1606814
- 34 Wu S, Zhu Y, Huo Y, *et al.* Bimetallic organic frameworks derived CuNi/carbon nanocomposites as efficient electrocatalysts for oxygen reduction reaction. *Sci China Mater*, 2017, 60: 654–663
- 35 Zhou GW, Lee DK, Kim YH, Kim CW, Kang YS. Preparation and spectroscopic characterization of ilmenite-type CoTiO₃ nanoparticles. *Bull Korean Chem Soc*, 2006, 27(3): 368–372

Acknowledgements This work was supported by the National Natural Science Foundation of China (51402155 and 21373107), Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD) (YX03002), Jiangsu National Synergistic Innovation Center for Advanced Materials (SICAM), Foundation of NJUPT (NY217077), PolyU Start-up Fund for New Recruits (No. 1-ZE8R).

Author contributions Huang ZD proposed the idea of this work, gave advices on the preparation and characterization of materials, and prepared this manuscript. Zhang TT conducted most of the experiments and results analysis. Lu H, Yang J and Bai L provided assistance to Zhang TT on preparing the active materials. Chen Y and Yang XS helped to measure the high resolution TEM and discussed the crystal structure of CoTiO₃. Liu RQ and Lin XJ aided to characterize the electrochemical performances. Li Y and Li P conducted the measurement of specific surface area and pore size distribution. Feng XM, Liu X and Lin XJ gave help to the discussion on the self-assembly process and

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Conflict of interest The authors declare that they have no conflict of interest.

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双金属-有机框架材料衍生介孔微米棱柱状超高功率和稳定性钠离子电池负极

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摘要 负极材料的循环、倍率、容量和堆积密度是评价钠离子电池性能的关键指标。为此本工作开发了一种新型的钴-钛双金属-有机框架结构材料并以其作为前躯体衍生制备了具有 1.8 g cm^{-3} 高堆积密度的无碳介孔钛酸钴微米棱柱状材料。作为钠离子电池负极材料该种材料展示了超高稳定性同时拥有比其他类似的钛氧化物、钛酸盐及其碳基复合材料更优异的倍率性能, 其在 5 A g^{-1} 的电流密度下循环2000圈后容量保持率高达90.1%。