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著者	Li Huan, Zhang Zhiguo, Huang Xiao, Lan Tongbin, Wei Mingdeng, Ma Tingli
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# Metal–organic framework derived hierarchical porous TiO<sub>2</sub> nanopills as a super stable anode for Na-ion batteries

Huan Li<sup>a</sup>, Zhiguo Zhang<sup>a</sup>, Xiao Huang<sup>a</sup>, Tongbin Lan<sup>c</sup>, Mingdeng Wei<sup>c</sup>, Tingli Ma<sup>a,b,\*</sup>

<sup>a</sup> *Graduate School of Life Science and Systems Engineering, Kyushu Institute of Technology, Wakamatsu, Kitakyushu, 808-0196, Japan*

<sup>b</sup> *School of Petroleum and Chemical Engineering, Dalian University of Technology, Liaoning, 124221, China*

<sup>c</sup> *State Key Laboratory of Photocatalysis on Energy and Environment, Fuzhou University, Fuzhou, Fujian 350002, China*

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## Abstract

Hierarchical porous TiO<sub>2</sub> nanopills were synthesized using a titanium metal-organic framework MIL-125(Ti) as precursor. The as-synthesized TiO<sub>2</sub> nanopills owned a large specific surface area of 102 m<sup>2</sup> g<sup>-1</sup> and unique porous structure. Furthermore, the obtained TiO<sub>2</sub> nanopills were applied as anode materials for Na-ion batteries for the first time. The as-synthesized TiO<sub>2</sub> nanopills achieved a high discharge capacity of 196.4 mAh g<sup>-1</sup> at a current density of 0.1 A g<sup>-1</sup>. A discharge capacity of 115.9 mAh g<sup>-1</sup> was obtained at a high current density of 0.5 A g<sup>-1</sup> and the capacity retention was remained as high as 90% even after 3000 cycles. The excellent electrochemical performance can be attributed to its unique hierarchical porous feature.

Key words: hierarchical porous structure; TiO<sub>2</sub> nanopills; metal–organic framework; Na-ion batteries

\* **Corresponding author.** Tel: 093-695-6045; Fax: 093-695-6005; E-mail: [tinglima@life.kyutech.ac.jp](mailto:tinglima@life.kyutech.ac.jp)

# 1. Introduction

In recent years, Na-ion battery is considered to be a type of highly promising energy storage device, due to the abundance of sodium, the low cost of the production methods, and higher system safety. [1-4] To date, several kinds of materials such as carbonaceous materials, [5-7] sodium alloys, [8-10] sulfides, [11, 12] titanate [13-15] and titanium dioxide have been investigated as the anodes for Na-ion batteries.

Among these materials, titanium dioxide has attracted much attention because of its exceptional stability and abundancy. [16, 17] Its excellent cyclability and rate capability reported in lithium-ion batteries lead to the further investigation about its sodium storage capability. Xiong et al prepared amorphous TiO<sub>2</sub> nanotube anode and a reversible capacity of 150 mAh g<sup>-1</sup> was reached in 15 cycles. [18] Anatase TiO<sub>2</sub> nanocrystals was first reported by Xu et al and the discharge capacity of ca. 150 mAh g<sup>-1</sup> was obtained at a current density of 50 mA g<sup>-1</sup> for 100 cycles. [19] Three different kinds of TiO<sub>2</sub> including anatase phase, amorphous and rutile phase were compared by Su group. They also demonstrated that the anatase TiO<sub>2</sub> exhibited better sodium storage capability than the other two kinds of TiO<sub>2</sub>. [20] However, although TiO<sub>2</sub> owns good cycling stability and reversibility, there is still large space to improve the discharge capacity of this material. In order to refine the electrochemical properties of TiO<sub>2</sub>, introducing doping metals and the carbon material additives is a common method reported before. [21-23] Besides, preparing nanosized material to increase the specific area can also be effective for increasing the capacity. [24, 25] It was found that nanosized TiO<sub>2</sub> can exhibit better electrochemical performance than bulk TiO<sub>2</sub>.

On the other hand, MOFs (Metal Organic Framework) as a kind of controllable porous functional materials with a large specific surface area, has been explored in various areas in the last few years, including gas storage, [26] adsorptive separation, [27] catalysis, [28] luminescent material, [29] etc. In

addition, MOFs had also been introduced as electrode materials benefiting from their unique porous structure, functional organic linkers and uncoordinated sites. [30-32] However, it was improved that this kind of materials might not be suitable to be directly used as electrode materials for metal ion batteries since partial decomposition would occur during the cycling process. [33, 34] In fact, it had already been reported that MOFs versatile templates and precursors were used to prepare various porous nanomaterials, and further applied in the energy storage field as high-performance electrode materials. A spindle-like porous  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> was synthesized by Xu et al. using an iron-based MOF template with a bulk structure composed of clustered Fe<sub>2</sub>O<sub>3</sub> nanoparticles, and a discharge capacity as high as 911 mAh g<sup>-1</sup> was achieved after cycling for 50 times at a rate of 0.2 C. [35] Porous core/shell structured ZnO/ZnCo<sub>2</sub>O<sub>4</sub>/C hybrid was synthesized by Ge group using core/shell ZnCo-MOF precursors as reactant templates and was capable of delivering a specific capacity of 669 mAh g<sup>-1</sup> after 250 cycles under a current density of 0.5 mA g<sup>-1</sup> in lithium ion battery. [36]

Therefore, it is significant to combine the advantages of both TiO<sub>2</sub> and MOF materials and synthesize a new kind of electrode material which can not only utilize the large specific surface area and porous structure but also possess excellent stability. In fact, some researchers have already investigated the application of TiO<sub>2</sub> derived from Ti MOF as anode for lithium-ion battery. [37, 38] However, few study about the sodium storage capability of this kind of materials have been reported.

In the present work, the unique structure hierarchical porous TiO<sub>2</sub> nanopills derived from MIL-125(Ti) had been synthesized successfully and used as anode for Na-ion batteries for the first time. This hierarchical porous TiO<sub>2</sub> nanopills exhibits excellent cycling stability and capacity retention as anode for Na-ion batteries. Furthermore, the relationship between the unique 3D structure and the electrochemical properties were also investigated in detail.

## 2. Experimental

### 2.1. *The synthesis of MIL-125(Ti) and TiO<sub>2</sub>*

The MIL-125(Ti) was synthesized according to the previous reported method by Wang et al. [39] In a typical process, 0.78 ml of titanium isopropoxide (Ti(OiPr)<sub>4</sub>, Aldrich, 95%) and 1.3 g of 1,4-benzenedicarboxylic acid (Aldrich, 99%) was dissolved into a mixed solution of 15 ml N,N-dimethylmethanamide (DMF, Sinopharm, 99%) and 1.7 ml methanol (Sinopharm, 99%) under magnetic stirring. After stirring for 1h, the mixed solution was transferred into a 50 ml Teflon-lined stainless autoclave and kept at 150°C for 24 h. After cooling down to room temperature, the precursor was obtained by centrifugation and then washed by menthol and DMF for 3 times. Finally, the sample obtained was dried at 60°C overnight.

To obtain porous TiO<sub>2</sub>, the MIL-125(Ti) precursor was calcined at 380 °C for 4 h with a temperature ramp speed of 5°C/min. The obtained white powder was hierarchical porous anatase TiO<sub>2</sub>.

### 2.2. *Characterization of the samples*

The samples were characterized by scanning electron microscope (SEM, S5200 instrument), transmission electron microscope (TEM, FEI F20 S-TWIN instrument), X-ray diffraction (XRD, Axis Petro, PANalytical, CoK $\alpha$ ,  $\lambda=1.79021\text{\AA}$ ) and automatic specific surface pore distribution measuring apparatus (BET, BELSORP-MR6).

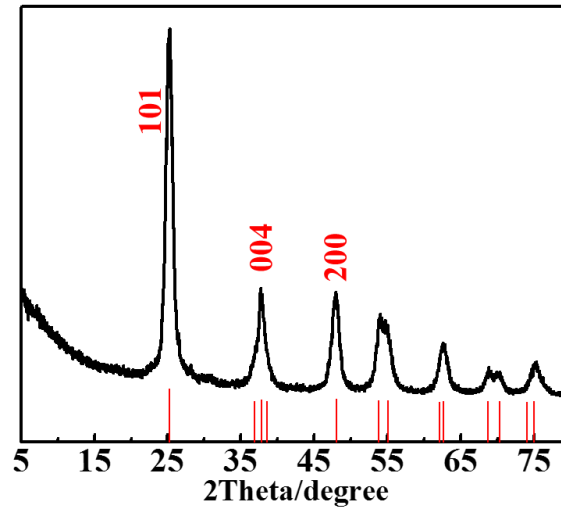
### 2.3. *Measurement of electrochemical properties*

The charge and discharge capacities were measured using CR-2025 coin cells, using sodium metal as a counter electrode. The electrode of TiO<sub>2</sub>/CB composite were fabricated with the active material TiO<sub>2</sub>, conductive material (acetylene black) and binder (PVDF) at a weight ratio of 7:2:1. The

MIL-125(Ti)/CB electrode was also prepared with the same methods for comparison. The electrolyte was 1M NaClO<sub>4</sub> in a mixed propylene carbonate (PC) and (EC) solvent (1:1) with 5% fluoroethylene carbonate (FEC) additive. A Land CT2001A battery tester machine was used to measure the electrode activities at room temperature. Charge-discharge measurements were carried out in a potential range of 0.01-3 V versus Na/Na<sup>+</sup> under different current rates. Cyclic voltammetry (CV) measurements were performed on a CHI660C electrochemical workstation at a scan rate of 0.5 mV s<sup>-1</sup> in the range of 3–0.01 V vs Na/Na<sup>+</sup>. The electrochemical impedance measurements were carried out by Zahner IM6 using a 5 mV acoscillation amplitude which was applied over the frequency of 5 MHz to 0.1 Hz frequency ranges. The equivalent circuit was fitted by the Zman 2.0 software of the Zahner IM6 electrochemical workstation.

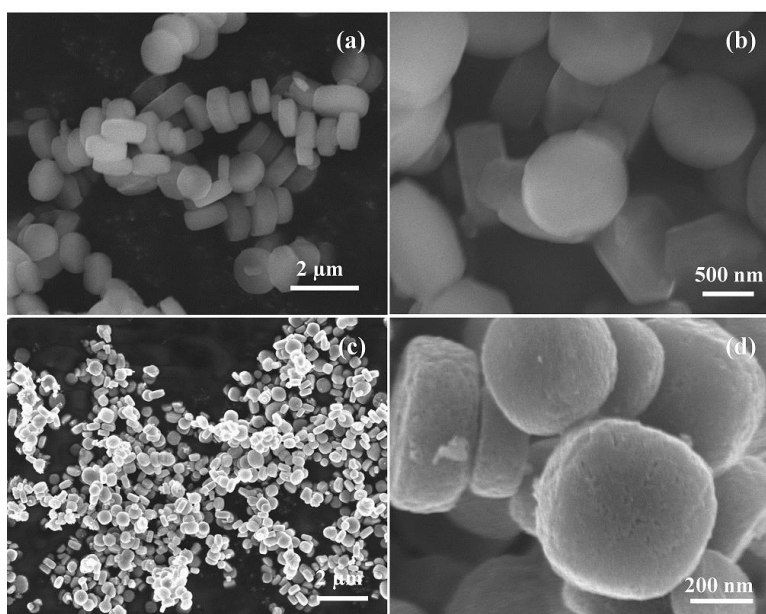
### 3. Results and discussion

To study the crystalline phase of the MIL-125(Ti) precursor and hierarchical porous TiO<sub>2</sub>, XRD patterns of the two samples are displayed in Fig. 1 and Fig. S1, respectively. Fig. S1 showed that the XRD pattern of MIL-125(Ti) was in good agreement with the previous report. [39] The sharp and strong peaks indicated the large size of MIL-125(Ti). After calcined at 380°C, all the peaks in Fig. 1 could be indexed to anatase TiO<sub>2</sub> (JCPDs-01-078-2486) with no any peaks coming from MIL-125(Ti). The major diffraction peaks appeared at 2θ values of 25°, 37° and 47° could be indexed to (101), (004) and (200) face of anatase TiO<sub>2</sub>, respectively.



**Figure 1** XRD pattern of hierarchically porous TiO<sub>2</sub>.

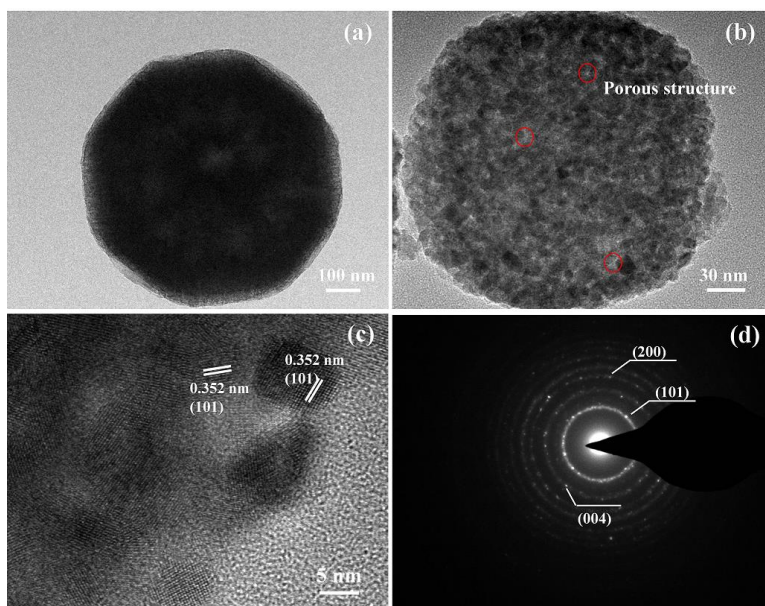
Fig. 2 showed the SEM images of MIL-125(Ti) and hierarchical porous TiO<sub>2</sub>. It can be seen from Fig. 2a-b that a large number of circles in microsize scale for the MIL-125(Ti) precursor with a uniform diameter of ca. 1 μm. After calcined at 380°C, the anatase TiO<sub>2</sub> derived from MIL-125(Ti) could remain the integrated morphology of circles and exhibited a hierarchical porous structure composed of nanoparticles, which was depicted in Fig. 2c-d. However, the particle size of the as-synthesized TiO<sub>2</sub> crystal had been reduced to ca. 500-700 nm due to the loss of C and H atoms during the calcinations process.



**Figure 2** SEM images of MIL-125(Ti) precursor (a-b) and the hierarchically porous TiO<sub>2</sub> (c-d) derived from MIL-125(Ti).

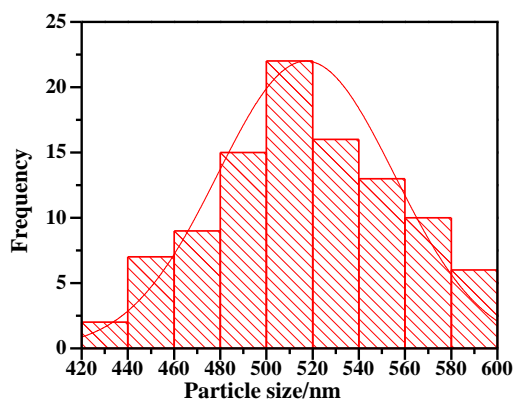
Moreover, the detailed analysis of TiO<sub>2</sub> sample and MIL-125(Ti) was investigated by TEM and SAED measurements. The HRTEM image in Fig. 3a confirmed that the MIL-125(Ti) was made of bulk with a diameter of ca. 1 μm. Fig. 3b presented the basic morphology of nanopills hadn't been changed for the TiO<sub>2</sub> sample after calcined. However, the anatase TiO<sub>2</sub> derived from MIL-125(Ti) cubic changed to a porous structure and was composed of nanoparticles smaller than 10 nm, as depicted in Fig. 3b. As shown in Fig. 3c, a lattice fringe of 0.352 nm which corresponds to (101) face of TiO<sub>2</sub> can be observed. The different direction of lattice fringe proved the existence of nanoparticles as well. Besides, the SAED pattern in Fig. 3d delivered some typical crystal planes of anatase TiO<sub>2</sub>, which was consistent with the XRD pattern of anatase TiO<sub>2</sub>.





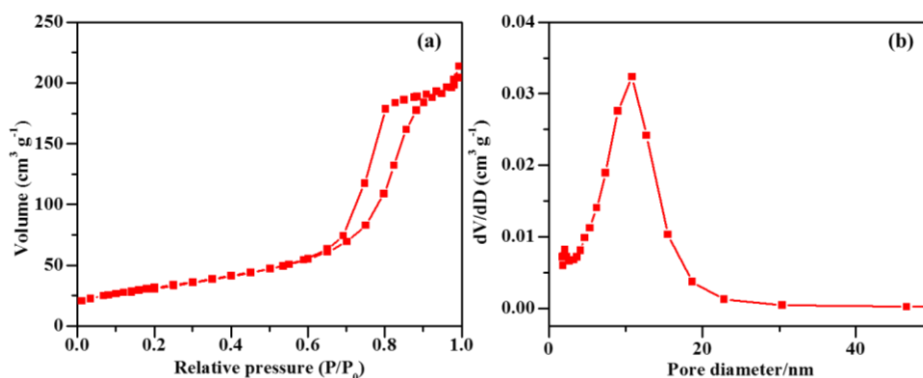
**Figure 3** (a) TEM image of MIL-125(Ti) precursor, (b) TEM image, (c) HRTEM image and (d) SAED pattern of the hierarchically porous TiO<sub>2</sub> derived from MIL-125(Ti).

In order to further investigate the homogeneity and hierarchical structure of hierarchical porous TiO<sub>2</sub> nanopills, the particle size distribution of sample was shown in Fig. 4. As depicted in Fig. 4, the particle size of hierarchical porous TiO<sub>2</sub> nanopills ranges from 400-600 nm, and an average particle size of 520 nm could be obtained, which was in good agreement with the SEM and TEM results. In addition, the particle size distribution of MIL-125(Ti) precursor was also shown in Fig.S2 as a comparison. As depicted in Fig. S2, the particle size of MIL-125(Ti) precursor ranges from 0.88-1.52 μm, and have an average size of 1.18 μm.



**Figure 4** Size distribution of hierarchically porous TiO<sub>2</sub>.

Nitrogen adsorption-desorption isotherm characterization was used to further investigate the pore size distribution and specific surface area of the hierarchical porous TiO<sub>2</sub>. As shown in Fig. 5, the hierarchical porous TiO<sub>2</sub> showed a specific surface area as high as 102 m<sup>2</sup> g<sup>-1</sup>. The pore diameter distribution result in Fig. 5b showed that the hierarchical TiO<sub>2</sub> nanopills had a mean pore size value of ca. 11 nm, in agreement with the results of TEM measurement, indicating the existence of mesopores. Such a large BET surface area and complex porous structure of hierarchical porous TiO<sub>2</sub> could be propitious to the diffusion of Na ions and electrolyte. The MIL-125(Ti) was also tested with the same method as a comparison, as depicted in Fig. S3. The MIL-125(Ti) had a large specific surface area of 1167 m<sup>2</sup> g<sup>-1</sup>.

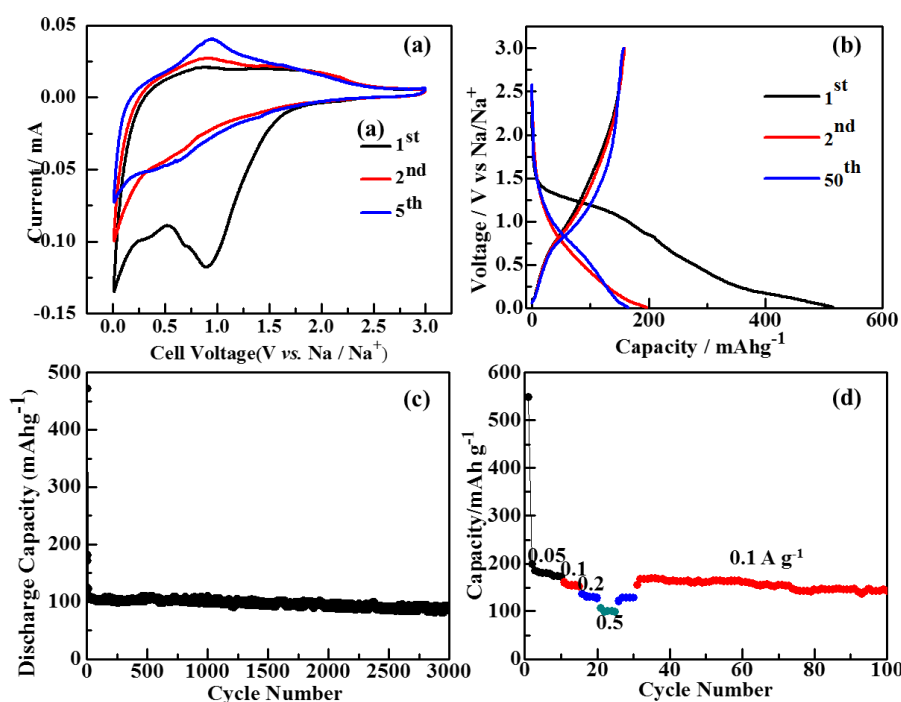


**Figure 5** (a) N<sub>2</sub> adsorption-desorption isotherms and (b) pore size distributions from the adsorption branch through the BJH method of hierarchically porous TiO<sub>2</sub> nanopills.

CV curves of the hierarchical porous TiO<sub>2</sub> anode are shown in Fig. 6a. For the initial cycle, a redox peak at 0.87 V could be observed, which disappeared in the following cycles; this might be ascribed to the decomposition of electrolyte, the formation of solid electrolyte interphase (SEI) film and some irreversible structure change of the active materials. [40-42] Upon subsequent cycling, an oxidation peak at 0.75V and a redox peak at 0.5V could be observed which could be assigned to the reversible reduction of Ti<sup>4+</sup>/Ti<sup>3+</sup>. Besides, the oxidation and redox peaks for each cycle did not change, illustrating the reversibility of sodium ions storage process in the electrode.

Fig. 6b shows the discharge-charge profiles of TiO<sub>2</sub>/CB electrode at a current density of 0.1 A g<sup>-1</sup> in a

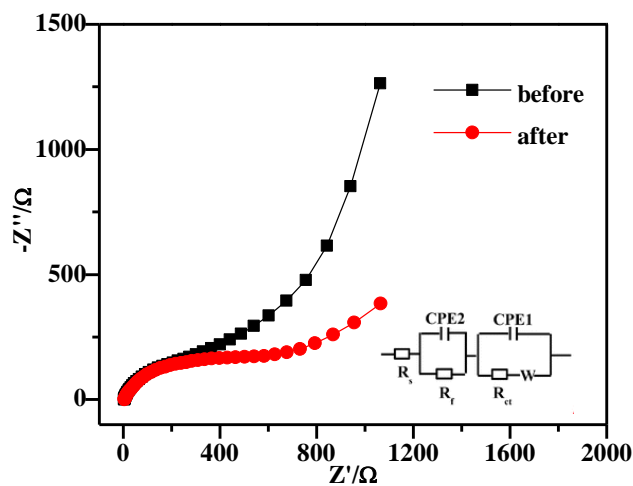
voltage range of 0.01-3V for 1<sup>st</sup>, 2<sup>nd</sup> and 50<sup>th</sup> cycles, respectively. An initial discharge capacity of 516.2 mA h g<sup>-1</sup> could be obtained due to the formation of solid electrolyte interphase (SEI) film just corresponding to the result of CV curves. Besides, it exhibited a discharge capacity of 196.4 and 164.3 mA h g<sup>-1</sup> for the 2<sup>nd</sup> and 50<sup>th</sup> cycles, respectively, which illustrated the excellent cycling stability of the hierarchical porous TiO<sub>2</sub> anode. As a comparison, the MIL-125(Ti) was tested at the same current density. As depicted in Fig. S4, a discharge capacity of 115.9 and 71.6 mA h g<sup>-1</sup> for the 2<sup>nd</sup> and 10<sup>th</sup> cycles at a current density of 0.05 A g<sup>-1</sup> were obtained, respectively. This result demonstrated that MIL-125(Ti) cannot exhibit good electrochemical performance for Na-ion batteries, because of the possibly decomposition during cycling process.



**Figure 6** (a) CV curves for the 1<sup>st</sup>, 2<sup>nd</sup> and 5<sup>th</sup> cycles at a scan rate of 0.5 mV s<sup>-1</sup>, (b) charge-discharge profiles for the 1<sup>st</sup>, 2<sup>nd</sup> and 50<sup>th</sup> cycles at a current density of 0.1 A g<sup>-1</sup>, (c) cycling performance at a current density of 0.5 A g<sup>-1</sup> and (d) rate performance of the hierarchically porous TiO<sub>2</sub> electrode.

The hierarchical porous TiO<sub>2</sub> anode was also tested at a current density of 0.5 A g<sup>-1</sup>, as shown in Fig. 6c. The cell was cycled at a relative small current density of 0.05 A g<sup>-1</sup> for the initial three cycles for the

activation of the electrode. A high discharge capacity of 100 mA h g<sup>-1</sup> could be remained even after 3000 cycles. Moreover, the capacity retention could be remained as high as 90%, indicating the excellent cycling stability of this material. In addition, the cycling stability of hierarchical porous TiO<sub>2</sub> nanopills were better than most previous reports. [18, 19, 24, 25] Fig. 6d presents the rate capability of hierarchical porous TiO<sub>2</sub> from 0.05 to 0.5 A g<sup>-1</sup>. The reversible discharge capacities of hierarchical porous TiO<sub>2</sub> could reach 170 mAh g<sup>-1</sup> at 0.05 A g<sup>-1</sup> and 110 mAh g<sup>-1</sup> at a relatively high rate of 0.5 A g<sup>-1</sup>, respectively. Besides, a specific capacity of 160 mA h g<sup>-1</sup> could be achieved when the current density was returned to an initial value of 0.1 A g<sup>-1</sup> after 30 cycles, and could continually remain for 100 cycles, which indicated this material owns a high reversibility. In addition, the SEM and TEM images of the TiO<sub>2</sub>/CB electrode after cycling were offered in Fig.S6 and S7 to further assume the structural stability, respectively.



**Figure 7** EIS of the hierarchically porous TiO<sub>2</sub> electrode before and after 2000 cycles.

**Table 1** Impedance parameters calculated from an equivalent circuit model.

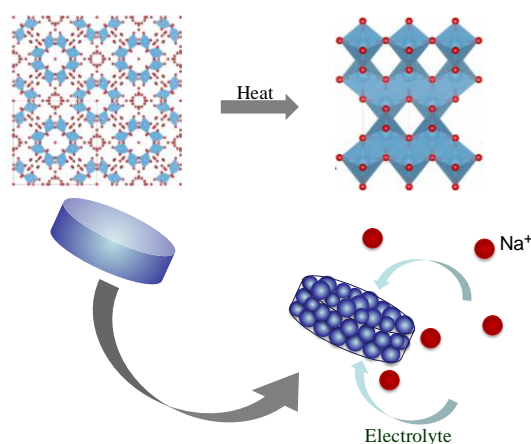
Samples	Rs(Ω)	Rct(Ω)
Before	3.22	31.27

After	3.78	16.54
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Fig. 7 shows the EIS plots of a hierarchical porous TiO<sub>2</sub>/CB composite electrode before and after cycling for 2000 cycles at 0.5 A g<sup>-1</sup>. It can be seen that the plots are all composed of a semicircle at high frequencies which were related to the Ohmic resistance and charge transfer resistance, and a short inclined line in low frequency regions which was due to the ion diffusion within the anode. [29] The semicircle for the hierarchical porous TiO<sub>2</sub> electrode before cycling was a little smaller than that of the sample after cycling, indicating that the charge transfer resistance increased after 2000 cycles. In order to further analysis this phenomenon, the impedance plots of the TiO<sub>2</sub>/CB electrode before and after cycling were both fitted by using an equivalent circuit model, as shown in the inset of Fig. 7. The equivalent circuit model included the electrolyte resistance R<sub>s</sub>, the SEI resistance R<sub>f</sub>, the charge-transfer resistance R<sub>ct</sub>, the Warburg impedance (W) related to the diffusion rate of Na ions into the bulk of the electrode and two constant phase elements (CPE1 and CPE2) which correspond to the charge-transfer resistance and interfacial resistance, respectively. From the EIS fitting values shown in Table. 1, R<sub>s</sub> values increased slightly from 3.22 Ω to 3.78 Ω after cycling for 2000 cycles. However, the charge transfer resistance R<sub>ct</sub> decreased after 2000 cycles, which could be due to the reduction of the nanocomposite into their corresponding metals during the irreversible reactions. This phenomenon also appeared in similar metal oxide electrode materials in lithium ion batteries. [43, 44]

In this study, hierarchical porous TiO<sub>2</sub> derived from MIL-125(Ti) exhibited excellent electrochemical performance which is considered to be due to its unique intrinsic characteristics including the following aspects, as illustrated in Fig. 8. Firstly, the as prepared TiO<sub>2</sub> retained the basic framework of MIL-125(Ti) which could benefit for the diffusion of electrolyte. Secondly, the porous structure could be

advantageous for promoting electrode/electrolyte wettability and increasing ion absorption sites by generating extrinsic defects. Thirdly, this material has a large specific surface area which could effectively increase the contact between electrolyte and active mass, further improving the storage capabilities for Na-ions. As mentioned above, these advantages lead to the excellent electrochemical properties of hierarchical porous TiO<sub>2</sub> nanopills.



**Figure 8** The diffusion and storage of Na<sup>+</sup> ions in the hierarchical porous TiO<sub>2</sub> nanopills.

## Conclusions

In summary, the unique hierarchical porous TiO<sub>2</sub> nanopills derived from MIL-125(Ti) had been synthesized successfully by hydrothermal method and the following calcination. For the first time, this material was used as the anode material for Na-ion batteries. The materials exhibited high reversible capacity and excellent rate capability. We obtained a high specific capacity of 196.4 and 115.9 mA h g<sup>-1</sup> at 0.1 A g<sup>-1</sup> for the 2<sup>nd</sup> cycle and 0.5 A g<sup>-1</sup>, respectively. Furthermore, it still remained a capacity of 100 mA h g<sup>-1</sup> and a capacity retention as high as 90% even after cycling for 3000 times at a high current density of 0.5 A g<sup>-1</sup>. Therefore, this kind of anode material can be a promising candidate for the high-capacity rechargeable Na-ion batteries. Our results indicate this kind of material derived from MOF can be applied as the potential electrodes for the other energy storage devices.

## Acknowledgments

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