

Polyoxometalate Cluster-Incorporated Metal-Organic Framework Hierarchical Nanotubes

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Metal-organic frameworks (MOFs) are a class of porous materials made from the co-assembly of metal ions with organic linkers,^[1] which have been widely used in gas storage,^[2] separation,^[3] and catalysis fields.^[4] In contrast to bulk crystals, MOF nanocrystals can further enhance the inherent properties and fulfill specific needs,^[5] such as for thin-film devices,^[6] or drug-delivery systems.^[7] Particularly, the construction of special nanoMOFs, for example, hollow nanostructures, has gradually drawn more attention because of their intriguing properties, such as, enlarged specific area, low density, and cost reduction.^[8] However, the synthesis of hollow MOF nanostructures, especially with high complexity, still remains a great challenge. Here for the first time we report the synthesis of hierarchical MOF nanotubes by using polyoxometalates (POMs) as structural modulators.

POMs are a class of inorganic clusters with a rich structural versatility and well-defined physical and chemical properties.^[9] POM-based MOF materials have attracted extensive interest because of their functional integrated and synergic effects.^[10] In the process of building MOF/POM composites. POMs always act as anionic templates/structure-directing

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DOI: 10.1002/smll.201503695

agents^[11] through host-guest supramolecular interactions.^[12] POMs may alter the equilibrium between metal cations and organic ligands and affect the reactants, thus manipulating the nucleation and growth processes of MOFs and therefore the resulting structure and shape. Hence, controlled synthesis of MOF nanocrystals may be achieved by using POMs to modulate the nucleation and growth processes.

Herein we utilized iron and cobalt ion as metallic nodes, 1,3,5-benzenetricarboxylic acid (H₃BTC) as the organic linker, and a N,N-dimethylformamide (DMF)/decanol mixture as the solvent. We specifically selected sodium phosphotungstate (Keggin-type POM, abbreviated as NaPW₁₂) to modulate the synthesis of MOF crystals. As a consequence, uniform hierarchical Fe/Co-BTC nanotubes could be prepared using a simple solvothermal process.

If the volume ratio of DMF/decanol was 1:1, Fe/Co-BTC nanosheet-based nanotubes (tube-1, or abbreviated T1) were synthesized. As shown in the scanning electron microscopy (SEM; Figure 1a-c), transmission electron microscopy (TEM: Figure 1d), and high-angle annular dark-field scanning TEM (HAADF-STEM; Figure 1e) images, uniform tubes with hollow cavities were clearly observed (inner diameter: ca. 72 nm). More interestingly, there were numerous flexible and interleaving nanosheets with a thickness below 10 nm on the surfaces of the inner nanotubes. Elemental mapping (Figure 1f) using energy-dispersive X-ray spectroscopy (EDX) demonstrated the even distribution of Fe, Co, O, P, and W along the tubes. X-ray photoelectron spectroscopy (XPS; Figure S1, Supporting Information) also revealed that the nanotubes were composed of Fe, Co, C, O, P, W. Moreover, the W element remained its highest valence state (VI),^[13] endowing it with a strongly oxidizing nature. The composition of the nanotubes was determined by inductively coupled plasma optical emission spectrometry (ICP-OES) and C, H, N elemental analysis, which confirmed a chemical formula of Fe₆₀Co₄PW₁₂C₇₂H₁₆₈O₂₁₀Na₇. Structural investigations were also carried out, initially by employing X-ray powder diffraction (XRD). However, the XRD pattern (Figure S2, Supporting Information) did not give any valuable information. Fortunately, FT-IR analysis (Figure 2a, Figure S3, Supporting Information) was a useful tool in this case. The carboxylate stretching frequency red shifted to 1615 cm⁻¹ from 1722 cm⁻¹ for the non-coordinated H₃BTC (Figure S3, Supporting Information), confirming the coordination of the carboxylate groups to the metal ions^[14] and thus indicating that T1 formed a coordination polymer.

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Figure 1. a–c) SEM (scale bars 500 nm, 500 nm, and 100 nm, respectively), d) TEM (scale bar 100 nm), e) HAADF-STEM of **T1** (scale bar 50 nm). f) EDX mapping images of (e). g) nitrogen adsorption (squares) and desorption (circles) isotherms of **T1** measured at 77 K. The inset shows the corresponding pore-size distribution.

Moreover, the characteristic peaks of the Keggin-structure were clearly illustrated (Figure 2a), indicating that the POM ions were retained in the final product and their structural integrity was maintained. This result was perfectly consistent with the elemental analysis by ICP-OES as the measured atomic ratio of P/W (i.e., 1:12) was equal to the calculated value in the Keggin structure. Nonetheless, the connectivities in the structure were still not totally clear.

Therefore, in order to further gain insight into the local structure and atomic environment, X-ray absorption

spectroscopy (XAS) was recorded at the XAFS beamline of the Shanghai synchrotron radiation facility (see Experimental Section). From the W L₃-edge X-ray absorption near-edge structure (XANES) spectrum (Figure 2b), it was found that the energy positions, the shape, and intensity of the absorption edges in **T1** were almost the same as those of the reference compound (NaPW₁₂). Moreover, the refined parameters of the extended X-ray absorption fine structure (EXAFS) spectra of the first coordination shell around the W atoms in **T1** and NaPW₁₂ (**Table 1**) also showed little difference. All of



Figure 2. a) Magnified FT-IR spectrum of **T1**. b) Normalized W L₃-edge XANES spectra of **T1**, **T2**, and the reference compound $(NaPW_{12})$. c) Normalized Fe K-edge XANES spectra of **T1**, **T2**. d) The k^3 -weighted Fourier transform Fe K-edge EXAFS spectra of **T1**. The experimental data (dots) are presented along with best fits of the FT magnitude (solid line).

these results confirmed the integrity of the Keggin anions. On the other hand, in the Fe K-edge XANES spectrum (Figure 2 c), the energy positions of the absorption edges revealed that the oxidation state of iron was 3+,^[15] which was in accordance with the XPS results. Furthermore, the shape and intensity of the pre-edge feature indicated that the Fe ions were in an octahedral coordination.^[15] The EXAFS analysis of the Fe atom (Figure 2d, Table 1) revealed that the Fe ions were coordinated by six oxygen atoms and also verified the presence of C atoms at distances of approximately 3.0 Å. This result suggested that the BTC linkers were connected to the Fe ions. In addition, the best fit of the Fe-K edge indicated two iron atoms in the second coordination shell, which meant that the Fe atoms were bonded to each other to form larger structure. However, there was no evidence of any W atoms



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in the second coordination sphere of the Fe atom, indicating that the Fe atoms were not coordinated to the POM ions. Based on the above results, many structural assumptions could be unambiguously confirmed, such as that **T1** is a kind of coordination polymer formed by Fe ions and the organic trimesic acid (H₃BTC), whereby the POM ions were encapsulated in the framework and there were no interactions between the iron ions and the POM anions.

The porosity is another important aspect of MOF crystals. We therefore analyzed the surface area and pore-size distribution of **T1** by Brunauer–Emmett– Teller (BET) measurements. As shown in Figure 1g, **T1** exhibited a typical type-IV isotherm, characteristic of mesoporous materials. The pore-size distribution calculated from the Barrett–Joyner–Halenda (BJH) method showed that it contained mesopores with diameters of approximately 3.83 nm. The total BET and Langmuir surface area of **T1** were 131.4 and 94.5 m² g⁻¹, respectively.

To further explore facile approaches

to fabricate hollow nanoMOFs with complex configuration, the synthetic conditions were carefully altered and optimized. Significantly, by changing the volume ratio of DMF/decanol to 7:1, another kind of well-defined nanotubes, namely, uneven-surfaced hierarchical ones (marked as sample tube-2, abbreviated **T2**), were achieved.

The morphology, composition, and structure of **T2** were similar to those of **T1**. As shown in the SEM (**Figure 3**a,c) and TEM (Figure 3b,d) images, the product consisted of uniform hierarchical tubes (total diameter: ca. 108 nm, wall thickness: ca. 48 nm) with hollow cavities and an uneven surface. Both EDX mapping (Figure 3e) and XPS analysis (Figure S4, Supporting Information) revealed that the samples were composed of Fe, Co, P, W, C, and O, however, the amount of POM in **T2** was much lower than that in **T1**. Elemental analyses

Table 1. Refined EXAFS structural parameters of Fe and W atoms; type of neighboring atom, bond distance *R*, coordination number *N*, and Debye–Waller factor, σ^2 . Error bounds (accuracies) were estimated as $R \pm 1\%$; $N \pm 5\%$; $\sigma^2 \pm 1\%$.

Sample	Central atom	Neighbor type	<i>R</i> [Å]	Ν	$\sigma^2 [10^{-3} { m \AA}^2]$
Reference compound	W	0	1.70	1.5	2.2
		0	1.89	3.0	1.3
		0	2.25	1.5	1.1
T1	W	0	1.71	1.1	1.3
		0	1.86	2.8	5.6
		0	2.24	1.9	7.1
T1	Fe	0	1.98	6	10.4
		С	3.05	5	2.8
		0	3.30	5	3.4
		Fe	3.41	2	6.3

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Figure 3. a,c) SEM; b,d) TEM, e) HAADF-STEM (scale bar 50 nm) and EDX elemental mapping of **T2**. f) The k³-weighted Fourier transform Fe K-edge EXAFS spectra of **T2**. The experimental data (dots) are presented along with a best fit of the FT magnitude (solid line). g) SEM, and h) TEM images of FeBTC nanotubes.

confirmed a formula of $Fe_{60}Co_6C_{100}H_{169}O_{154.5}P_{0.31}W_{3.84}Na_{8.6}$. Similarly, the structural information was obtained from FT-IR and XAS. Both the characteristic peaks of the Keggin structure and a red shift of the carboxylate stretching frequency were identified by FT-IR (Figure S6, Supporting Information).^[14] From the XANES spectrum (Figure 2b) and EXAFS analysis (Table S1, Supporting Information) of the W atoms, it was found that the POM was intact. Moreover, C atoms were observed in the second coordination shell of the Fe atoms without any evidence of W atoms in the same coordination shell (Figure 3f, Table S1). Thus it was confirmed that the structure of **T2** was similar to **T1**: it was also a kind of coordination polymer and POM ions were located in the pores of the framework. From the nitrogen

adsorption–desorption isotherms and pore-size distribution measurements (Figure S7, Supporting Information), a total BET surface area of **T2** of 373.2 m² g⁻¹ and mesopores with diameters of approximately 3.82 nm were found.

We then tried to investigate the formation mechanisms of **T1** and **T2**. Because of its simpler structure, compared to that of **T1**, we first studied the **T2** system. Interestingly, in the absence of the cobalt precursor, while keeping the other synthetic conditions the same, the resultant morphology of the **T2** compound showed little difference. Well-defined nanotubes could still be prepared (Figure 3g,h). However, in the absence of POMs the reaction yielded irregular solid aggregates (marked as **MOF1**, abbreviated **M1**, Figure S8, Supporting Information). Therefore, it was speculated that the determining factor in the formation process of the nanotubes was the presence of POMs instead of the cobalt precursor.

Considering that POMs tend to act as an anionic template/structure-directing agent through host-guest supramolecular interactions in the process of building MOF/ POM composites,^[16] it seems possible that the POMs altered the equilibrium between the metal cations and the organic ligands and thus regulated the synthesis of the MOFs. Hence, we tried to study the mechanism from the perspective of the supramolecular interactions between the metal and the POM ions. In order to simplify the problem, we investigated the homometallic (Fe) system based on the fact that the final results of homo- (Fe) and hetero-(Fe/Co) metallic systems showed little difference (Figure 3). Direct evidence of the interaction was obtained from ³¹P NMR spectra of solutions prepared from Fe(NO₃)₃·9H₂O and NaPW₁₂. Upon adding Fe^{III} cations, the ³¹P resonance of the POM anions showed a significant shift from -10.159 ppm to 40.736 ppm (Figure 4a), indicating a change in the local environment of the central P atom in the POM anion. Such impact was the result of the interaction with the Fe^{III} cations. The peak broadening might be attributed to the intricate or random orientation of the Fe^{III} cations around the surface of the POM anions.^[17] Substantial evidence was further obtained from UV-vis spectroscopy measurements in DMF/decanol (v/v = 1:1) solution. [UV-vis measurements in DMF/decanol (v/v = 7:1) solution are shown in Figure S9, Supporting Information]. As shown in Figure 4b (line A), iron(iii) acetylacetonate [Fe(acac)₃] possessed strong electronic absorptions in the 300-600 nm spectral region. The individual bands near 350 and 440 nm could be assigned to metal-to-ligand charge transfer (MLCT) and ligand-to-metal charge transfer (LMCT) transitions, respectively.^[18] After addition of the POM solution, the absorption intensities of the peaks around 350 and 440 nm significantly weakened, accompanied by a slight blue shift in the peaks (Figure 4b, line B-D). This would indicate the occurrence of a ligand-exchange reaction (acac⁻ in Fe(acac)₃ was replaced by POM anions), which could further be verified by an increase in the pH after addition of the POM aqueous solution. The possible reactions were as follows:

 $Fe(acac)_3 + xPOM^{n-} =$

$$\left[\operatorname{Fe}(\operatorname{acac})_{y}(\operatorname{POM})_{x}\right]^{(xn-3+y)-} + (3-y)(\operatorname{acac})^{-}$$
(1)

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 $acac^{-}+H_2O = Hacac + OH^{-}$

(2)

The acac⁻ was subject to hydrolysis in water, forming acetylacetone (Hacac) and the hydroxyl ion (OH⁻). The released OH⁻ greatly increased the rate of deprotonation of the organic ligand (H₃BTC). After this, complexation between the metal ions and the organic ligands occurred, leading to the formation of the coordination polymers.

To gain further insight into the evolution process, we carried out time-dependent experiments and monitored the solvothermal process using various characterization techniques, for example, TEM and EDX analysis to verify its morphology and compositional change respectively. For the T2 system (Figure 4c), at a reaction time of 10 min, the products were uniform solid nanorods with a diameter of around 52 nm (Figure 4c1). The EDX mapping of a single nanorod (Figure S10, Supporting Information) showed that the P, W, Fe, and Co elements were distributed evenly. Prolonging the reaction time to 20 min did not alter the morphology, however, the diameter of the nanorods increased to around 102 nm (Figure 4c2). Interestingly, after careful observation an image contrast could be found across the individual nanorods. Moreover, the EDX line-scanning profile of the Fe element (Figure 4c3) showed a valley-like structure: the intensity at the edge was much higher than at the center. Therefore, the nanorod proved to have a core-shell structure. That is, the initial nanorod (the core, dark area) was surrounded by a uniform coating (light area). As time increased, the core dissolved gradually, leading to the formation of cavities (Figure 4c4). When the core dissolved completely, only the outer layer was left, and, as such, nanotubes were obtained (Figure 4c5).

Based on the above results, it could be concluded that the formation of nanotubes was caused by a dissolution of the core. In the initial stage, due to complexation of the metal ions and POM anions, H₃BTC was quickly deprotonated by the released OH⁻. Driven by the reaction kinetics, the deprotonated BTC rapidly coordinated to the metal ions, leading to the formation of coordination polymers with encapsulated POM anions. Then a shell started to form on the surface of the core. Interestingly, the POM content in the shell was lower than that in the core, which was verified by a decrease in the tungsten/iron molar ratio as the shell grew (Figure S11, Supporting Information, and Figure 4c6). After that, the core started to dissolve, maybe because the core is thermodynamically unstable in this synthetic system. In accordance with the above analysis, the relative amount of W to Fe decreased further during this process. Through formation and coalescence of vacancies, hollow voids were formed and the content of W reached its minimal value.

The evolution processes for the **T1** structure were similar to that of **T2**: the pre-formed nanorods were coated with a uniform layer, which then dissolved gradually, leading to hollow nanorods. At the same time, nanosheets grew on the surface of these hollow nanorods. Finally, perfect nanosheetbased hierarchical nanotubes were obtained. (See Supporting Information for a detailed description.)

Considering that MOFs show promoting effect on catalytic reactions involving gases,^[19] we chose the removal of sulfurbased harmful industrial chemicals under mild conditions with

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Figure 4. a) ³¹P NMR spectra of a solution of A) NaPW₁₂; B) $Fe(NO_3)_3$ ·9H₂O and NaPW₁₂. b) UV–vis spectra of A) DMF/decanol solution of $Fe(acac)_3$; B–D) solution (A) plus added 0.1 mL NaPW₁₂ aqueous solution collected at different times. c) TEM (scale bars 200 nm) images of **T2** collected at different reaction times: c1) 10 min, c2) 20 min, c4) 1 h, c5) 2 h. c3) EDX line-scanning profiles for Fe and W along a single nanorod collected at 20 min. (Other elements are omitted for clarity.) c6) Change in percentage of W during 3 h of reaction time based on EDX results.

 O_2 , which is a significant reaction in the chemical and petroleum industries, as a laboratory test reaction to assess the catalytic capabilities of these hierachical nanotubes. In detail,

the oxidation of thiols to less toxic and less odorous disulfides was examined (**Figure 5**a). Reports have shown that the Fe,^[20] $Co^{[21]}$ centers, and POM unit^[10b] can all act as active sites for

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Figure 5. a) Aerobic oxidation of thiophenol to diphenyldisulfide. Reaction conditions: thiophenol (1 mmol), catalyst (12.5 mg, preactivated at 140 °C for 3 h), acetonitrile (5 mL), 60 °C. b) Conversion (%) as a function of time in the oxidation of *p*-toluenethiol over **T1** (A), **T2** (B), **M1** (C), and **P1** (D). c) Recyclability of **T1** for the oxidation of *p*-toluenethiol using O_2 . d) Products and yields of isolated products from the oxidation of *p*-toluenethiol to disulfides catalyzed by **T1** for 12 h. e) Charge–discharge voltage profiles of **T3** for the 1st, 2nd, 3rd, 5th, and 10th cycles in the voltage range 0.01–3 V at a current rate of 200 mA g⁻¹. f) Capacity and Coulombic efficiency versus cycle number of **T3** at a current rate of 200 mA g⁻¹.

thiol oxidation. Figure 5b shows the oxygen-based oxidation of p-toluenethiol in acetonitrile solution catalyzed by **T1**, **T2**, **M1**, or NaPW₁₂ (marked as POM1, abbreviated **P1**) under identical conditions. It was found that **T1** exhibited higher catalytic properties than either **M1** or **P1**. In other words, the properties of the composite were better than those of the individual components, thus confirming the synergistic effect of the composite. Interestingly, the activity of **T2** was almost the same as that of **T1**, which may be attributed to its high specific surface area (related to the adsorption and storage captivity of oxygen). The morphologies

of both **T1** and **T2** were retained after the catalytic reaction, as revealed by TEM (Figure S14, Supporting Information). After catalysis, the **T1** component was separated by centrifugation, washed with acetonitrile, and then reused. The corresponding product yields are shown in Figure 5c. It could be seen that the catalyst showed an excellent reusability: the yield (87.5%) in the fifth cycle was only slightly lower than that in the first cycle (92.5%). Furthermore, substrates with different kinds [including electron-donating (**1a-e**) and -withdrawing ((1)**f**) groups] and position [including ortho- ((1)**a**), meta- ((1)**b**), and para- (**1c-f**)



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position] of their substituent groups could all be oxidized to give the corresponding oxidation products (Figure 5d).

MOFs and their derivatives may serve as a platform for clean and renewable energy, such as in hydrogen production and storage, and in lithium-ion batteries (LIBs).^[19] The hierarchical tubular architecture has a high specific surface area, which is beneficial for mass transport, increases the active sites, and provides shorter Li⁺-ion diffusion channels, thus making this architecture a promising candidate for LIBs anode.^[22] Hence, we carried out electrochemical measurements to evaluate the performance of the thermally annealed product of T1 (marked as T3). As the TEM image (Figure S15, Supporting Information) shows, after thermal annealing in N_2 , the tubular structure was mostly preserved. Combined with EDX, Raman, and XRD results, T3 was shown to be a mixture of carbon, iron/cobalt oxide, and tungstates (Figure S16-S18). Figure 5e displays the voltage capacity profiles for the first, second, third, fifth, and tenth cycles at a current density of a 200 mA g^{-1} over a potential range between 0.01 V and 3 V (vs. Li⁺/Li). The first discharge and charge capacities were 859.1 and 568.5 mA h g⁻¹, delivering an initial Coulombic efficiency of 66.2%. From the third cycle onward, the T3 exhibited a high Coulombic efficiency of around 95% (Figure 5f), indicating the excellent reversible Li⁺ insertion/extraction of the composite electrode. The cycling stability tested at a current of 200 mA g⁻¹ is shown in Figure 5f. The irreversible capacity loss during the initial discharge/charge process might be related to lithium loss due to the formation of a solid electrolyte interface (SEI) layer^[23] and incomplete conversion reaction.^[24] From the third cycle onwards, the reversible capacity started to increase gradually, which is common for metal-oxide anode materials.^[24] This phenomenon probably is related to the gradual electrochemical activation process of the anode electrodes, such as the wetting of the electrolyte into the electrode,^[23b] as well as interfacial Li storage.^[23a,c] Afterwards, the capacity was well retained. Even after 50 cycles, the electrode could still deliver a capacity of $639.3 \text{ mA h g}^{-1}$.

In summary, we have rationally designed a one-pot solvothermal strategy to synthesize two kinds of bi-metallic hierarchical Fe/Co-BTC nanotubes modulated by Keggin-type POMs. Considering that both POMs and MOFs are two large classes of species with various compositions and structures, we expect our endeavor may further the study of constructing novel MOF-based nanostructures. On the other hand, these hierarchical tubes possess diverse intriguing properties, such as low density, enlarged specific area and capacious pores, which benefit the process of mass transport and the increase of active sites; thus making these architectures promising candidates for various applications. As a proof-of-concept, these nanotubes show an excellent catalytic performance for the detoxification of sulfur compounds with O_2 and a remarkable cycling stability as anode materials for lithium-ion batteries.

Experimental Section

Preparation of **T1**: Iron(iii) acetylacetonate (Fe(acac)₃, 80.4 mg) and cobalt(iii) acetylacetonate (Co(acac)₃, 10.1 mg) were dissolved in a dimethylformamide (DMF)/decanol mixture (32 mL, v/v = 1:1). Then NaPW₁₂ (110 mg), 3.0 mL of water and

0.35 mL of 1,3,5-benzenetricarboxylic acid (H_3BTC) solution were added successively into the DMF/decanol solution. After stirring for several minutes, the starting solution was transferred into a 40-mL Teflon-lined stainless-steel autoclave. The sealed vessel was then heated at 100 °C for 3 h before it was cooled down to room temperature. The products were separated via centrifugation at 8000 rpm for 6 minutes and further purified with DMF and ethanol for several times. The same procedures were also applied to the preparation of **T2**, unless otherwise noted.

Preparation of **T2**: Fe(acac)₃ (80.4 mg), Co(acac)₃ (10.1 mg), DMF/ decanol mixture (32 mL, v/v = 7:1), NaPW₁₂ (110 mg), 2.6 mL of water and 0.35 mL of H₃BTC were used in the same procedure as for **T1**.

Preparation of T3: The as-formed **T1** was thermally treated at 500 °C at a heating rate of 1 °C min⁻¹ in N₂, and the final product of **T3** was obtained.

Aerobic Oxidation of Thiophenol: Thiophenol (1 mmol), **T1**, or **T2** (12.5 mg, preactivated at 140 °C for 3 h) dispersed in acetonitrile (5 mL) were added to an oven-dried Schlenk tube, and the system was evacuated and refilled with O_2 (balloon) for three times. The reaction was assumed to start when the reactor was introduced into an oil bath at 60 °C and vigorously stirred (ca. 1600 rpm). Aliquots were taken at specific times to determine the component concentrations by gas chromatography–mass spectrometry (GCMS-QP 2010 SE, Shimadzu, Japan).

Electrochemical Measurements: The electrochemical performance of the as-prepared products were measured using a twoelectrode cell. To prepare the working electrode, a mixture of the active materials, carbon black, and polyvinylidene fluoride (PVDF) in a weight ratio of 70:20:10 was ground in a mortar with N-methy1-2-pyrrolidone (NMP) as the solvent to make a slurry. The mass loading of the electrodes was about 2 mg cm^{-2} . To assemble the Li-ion batteries a Li foil was used as the counter electrode and a solution of 1 M LiPF₆ in ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1 in volume) was used as the electrolyte. Cyclic voltammetry (CV) was performed in the voltage range of 30.01 V (vs. Li/Li⁺) at a sweep rate of 0.2 mV s⁻¹. The charge/discharge curves and cycling capacity were evaluated at the cut-off voltages of 0.01 and 3.0 V for a current density of 200 mA g^{-1} for 50 cycles. For the high rate testing, the discharge current was gradually increased from 200 mA g^{-1} to 1000, 2000, and 5000 mA g⁻¹, then decreased again to 200 mA g⁻¹ in a step-by-step manner (10 cycles for each). All the charge/discharge measurements were performed symmetrically at room temperature.

XAS analysis: i) Data collection: W L₃-edge and Fe K-edge EXAFS measurements were carried out at beamline 14W1 of the Shanghai Synchrotron Radiation Facility (SSRF). The X-ray was monochromatized by a double-crystal Si (111) monochromator. The storage ring of SSRF was operated at 3.5 GeV with a current of 300 mA. ii) Data analysis: the acquired EXAFS data were processed according to standard procedures using the WinXAS3.1 program.^[25] Theoretical amplitudes and phase-shift functions were calculated using FEFF8.2 code^[26] by integrating the structural parameters of the Fe(C₂O₄)(H₂O)₂ and NaH₂(PW₁₂O₄₀)(H₂O)₁₂WO₃ foil.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Acknowledgements

This work was supported by NSFC (21431003, 21521091, 11375198, 11574280, U1232131, U1532112), and the State Key Project of Fundamental Research for Nanoscience and Nanotechnology (2014CB932500). The authors thank the Hefei Synchrotron Radiation Facility (NSRL), Shanghai Synchrotron Radiation Facility (BL14W1, SSRF), and Beijing Synchrotron Radiation Facility (1W1B, BSRF) for their help with the XAS tests.

- a) H. Furukawa, K. E. Cordova, M. O'Keeffe, O. M. Yaghi, *Science* **2013**, *341*, 1230444; b) Y. Cui, Y. Yue, G. Qian, B. Chen, *Chem. Rev.* **2011**, *112*, 1126; c) G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S. Surblé, I. Margiolaki, *Science* **2005**, *309*, 2040; d) C. R. Murdock, D. M. Jenkins, *J. Am. Chem. Soc.* **2014**, *136*, 10983.
- [2] a) K. Sumida, D. L. Rogow, J. A. Mason, T. M. McDonald,
 E. D. Bloch, Z. R. Herm, T.-H. Bae, J. R. Long, *Chem. Rev.* 2011, *112*, 724; b) O. K. Farha, A. Özgür Yazaydın, I. Eryazici,
 C. D. Malliakas, B. G. Hauser, M. G. Kanatzidis, S. T. Nguyen,
 R. Q. Snurr, J. T. Hupp, *Nat. Chem.* 2010, *2*, 944.
- [3] J.-R. Li, J. Sculley, H.-C. Zhou, Chem. Rev. 2011, 112, 869.
- [4] M. Yoon, R. Srirambalaji, K. Kim, Chem. Rev. 2011, 112, 1196.
- [5] a) A. Carné, C. Carbonell, I. Imaz, D. Maspoch, *Chem. Soc. Rev.* **2011**, 40, 291; b) G. Lu, S. Li, Z. Guo, O. K. Farha, B. G. Hauser, X. Qi, Y. Wang, X. Wang, S. Han, X. Liu, J. S. DuChene, H. Zhang, Q. Zhang, X. Chen, J. Ma, S. C. J. Loo, W. D. Wei, Y. Yang, J. T. Hupp, F. Huo, *Nat. Chem.* **2012**, 4, 310; c) W. Zhang, Z.-Y. Wu, H.-L. Jiang, S.-H. Yu, *J. Am. Chem. Soc.* **2014**, *136*, 14385.
- [6] A. Bétard, R. A. Fischer, Chem. Rev. 2011, 112, 1055.
- [7] K. M. L. Taylor-Pashow, J. D. Rocca, Z. Xie, S. Tran, W. Lin, J. Am. Chem. Soc. 2009, 131, 14261.
- [8] a) Z. Zhang, Y. Chen, X. Xu, J. Zhang, G. Xiang, W. He, X. Wang, *Angew. Chem. Int. Ed.* 2014, *53*, 429; b) Z. Zhang, Y. Chen, S. He, J. Zhang, X. Xu, Y. Yang, F. Nosheen, F. Saleem, W. He, X. Wang, *Angew. Chem. Int. Ed.* 2014, *53*, 12517; c) L. Zhang, H. B. Wu, S. Madhavi, H. H. Hng, X. W. Lou, *J. Am. Chem. Soc.* 2012, *134*, 17388; d) T. Fukino, H. Joo, Y. Hisada, M. Obana, H. Yamagishi, T. Hikima, M. Takata, N. Fujita, T. Aida, *Science* 2014, *344*, 499.
- [9] a) D.-L. Long, R. Tsunashima, L. Cronin, Angew. Chem. Int. Ed. 2010, 49, 1736; b) P. Yin, T. Li, R. S. Forgan, C. Lydon, X. Zuo,



Z. N. Zheng, B. Lee, D. Long, L. Cronin, T. Liu, J. Am. Chem. Soc.
 2013, 135, 13425; c) X.-B. Han, Z.-M. Zhang, T. Zhang, Y.-G. Li,
 W. Lin, W. You, Z.-M. Su, E.-B. Wang, J. Am. Chem. Soc. 2014, 136, 5359.

- [10] a) C.-Y. Sun, S.-X. Liu, D.-D. Liang, K.-Z. Shao, Y.-H. Ren, Z.-M. Su, J. Am. Chem. Soc. 2009, 131, 1883; b) J. Song, Z. Luo, D. K. Britt, H. Furukawa, O. M. Yaghi, K. I. Hardcastle, C. L. Hill, J. Am. Chem. Soc. 2011, 133, 16839.
- [11] N. Stock, S. Biswas, Chem. Rev. 2012, 112, 933.
- [12] R. Yu, X.-F. Kuang, X.-Y. Wu, C.-Z. Lu, J. P. Donahue, Coord. Chem. Rev. 2009, 253, 2872.
- [13] P. Niu, J. Hao, Langmuir 2011, 27, 13590.
- [14] S. Xiang, L. Li, J. Zhang, X. Tan, H. Cui, J. Shi, Y. Hu, L. Chen, C.-Y. Su, S. L. James, J. Mater. Chem. 2012, 22, 1862.
- [15] T. Birsa Čelič, M. Rangus, K. Lázár, V. Kaučič, N. Zabukovec Logar, Angew. Chem. Int. Ed. 2012, 51, 12490.
- [16] D.-Y. Du, J.-S. Qin, S.-L. Li, Z.-M. Su, Y.-Q. Lan, *Chem. Soc. Rev.* **2014**, *43*, 4615.
- [17] S. R. Bajpe, C. E. A. Kirschhock, A. Aerts, E. Breynaert, G. Absillis, T. N. Parac-Vogt, L. Giebeler, J. A. Martens, *Chem. Eur. J.* 2010, 16, 3926.
- [18] E. M. S. Maçôas, R. Kananavicius, P. Myllyperkiö, M. Pettersson, H. Kunttu, J. Phys. Chem. A 2007, 111, 2054.
- [19] X. Xu, Z. Zhang, X. Wang, Adv. Mater. 2015, 27, 5365.
- [20] A. Dhakshinamoorthy, M. Alvaro, P. Horcajada, E. Gibson, M. Vishnuvarthan, A. Vimont, J.-M. Grenèche, C. Serre, M. Daturi, H. Garcia, ACS Catal. 2012, 2, 2060.
- [21] L. Menini, M. C. Pereira, A. C. Ferreira, J. D. Fabris, E. V. Gusevskaya, *Appl. Catal. A. Gen* **2011**, *392*, 151.
- [22] P.-P. Wang, H. Sun, Y. Ji, W. Li, X. Wang, Adv. Mater. 2014, 26, 964.
- [23] a) P. Xiong, B. Liu, V. Teran, Y. Zhao, L. Peng, X. Wang, G. Yu, *ACS Nano* 2014, *8*, 8610; b) H. Wu, G. Yu, L. Pan, N. Liu, M. T. McDowell, Z. Bao, Y. Cui, *Nat. Commun.* 2013, *4*, 1943; c) Y. Sun, X. Hu, W. Luo, F. Xia, Y. Huang, *Adv. Funct. Mater.* 2013, *23*, 2436.
- [24] F. Zou, X. Hu, Z. Li, L. Qie, C. Hu, R. Zeng, Y. Jiang, Y. Huang, Adv. Mater. 2014, 26, 6622.
- [25] T. Ressler, J. Synchrotron Rad. 1998, 5, 118.
- [26] A. L. Ankudinov, B. Ravel, J. J. Rehr, S. D. Conradson, *Phys. Rev. B* 1998, 58, 7565.

Received: December 7, 2015 Revised: February 19, 2016 Published online: April 21, 2016