POM-Based MOF-Derived Co₃O₄/CoMoO₄ Nanohybrids as Anodes for High-Performance Lithium-Ion Batteries

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ABSTRACT: Polyoxometalate (POM)-based metal–organic framework (MOF)-derived Co₃O₄/CoMoO₄ nanohybrids were successfully fabricated by a facile solvothermal method combined with a calcination process, in which a Co-based MOF, that is, ZIF-67 acts as a template while a Keggin-type POM (H₃PMo₁₂O₄₀) serves as a compositional modulator. The materials were characterized through scanning electron microscopy (SEM), X-ray diffraction (XRD), transmission electron microscopy (TEM), energy-dispersive spectroscopy (EDS) mapping, and electrochemical measurements. When the Co₃O₄/CoMoO₄ nanohybrids were applied as anode materials for lithium-ion batteries (LIBs), they display large lithium storage capacity (around 900 mAh g⁻¹ at 0.1 A g⁻¹) and high cycling stability, and they can also exhibit good rate performances. This work might shed some light on the POM-based MOF host–guest synthesis strategy for the preparation of polymetallic oxides for enhanced electrochemical energy storage and further applications.

1. INTRODUCTION

The ever-increasing energy demand and large renewable energy resource consumption lead to the booming studies on the superior performance of energy storage and conversion devices. Nowadays, lithium-ion batteries (LIBs) have gained attention globally and been applied universally in smartphones, laptops, wearable devices, and so on for the high specific energy density and long charge–discharge cycle performance. Nevertheless, requirements for the better performance of LIBs have been continuously increasing for further applications like electric vehicles and grid energy storage. It is urgent to explore new LIBs systems with high specific capacity and energy density. For commercial LIBs, graphite suffers from limited power and energy performance due to low theoretical capacity (372 mAh g⁻¹) when it is used as the anode material. So, it is highly urgent to find new alternative materials that can be used as anodes with superior specific capacity and high rate performance for LIBs. The transition-metal oxides of Co₃O₄ and CoMoO₄ have gained much interest among diverse well-researched materials because of multiple oxidations in the charge/discharge process and relatively high specific capacity (890 mAh g⁻¹ for Co₃O₄ and 980 mAh g⁻¹ for CoMoO₄). Therefore, many studies have been conducted to improve the cycling and rate performance of Co₃O₄ or CoMoO₄ by structure control and regulation like microsize particles, hollow nanospheres, porous nanowires, and composites of carbon/graphene. However, both Co₃O₄ and CoMoO₄ suffer from huge volume expansions during the charge/discharge process. Fortunately, it has been proved that the synergistic effect exists between Co₃O₄ and CoMoO₄, which can promote the performances of the anodes for LIBs. For example, Co₃O₄/CoMoO₄ were successfully prepared through a solvothermal process and combined with a thermal treatment by Yang et al., which exhibited better electrochemical performances than CoMoO₄ as the anodes for LIBs.

Recently, metal–organic frameworks (MOFs) and polyoxometalate (POM)-based MOFs have attracted extensive research interests both in LIBs and supercapacitors for the reason that they usually have controllable porous structures for the well-defined structure and high surface areas. By carefully controlling the morphology, composition, and structure of the MOFs/POM-based MOF precursors, the metal oxides can be effectively adjusted like CuO, ZnO, and MnO₂ in the composition and the structure. However, as far as we know, there are no reports about using MOFs or POM-based MOFs...
as precursors to synthesize the anodes composed of Co$_3$O$_4$/CoMoO$_4$ hybrids for LIBs. POM-based MOF-derived materials have been widely studied in the application of photo-/electrocatalysis, conducting impressive photo-/electrochemical performance.\textsuperscript{33−39}

In light of these studies talked above and based on our previous work,\textsuperscript{40−44} we propose a simple in situ self-assembly method to embed a Keggin-type POM (H$_3$PMo$_{12}$O$_{40}$) into the Co-based MOF (ZIF-67), that is, a POM-based MOF (called PMo$_{12}$O$_{40}$@ZIF-67 for short). In the following calcination of PMo$_{12}$O$_{40}$@ZIF-67, the Co$_3$O$_4$/CoMoO$_4$ nanoparticles are obtained with ZIF-67 acting as a template and POM serving as the compositional modulator, which synergistically provide the anodes of Co$_3$O$_4$/CoMoO$_4$ with remarkably better overall performance than the pristine CoMoO$_4$ or Co$_3$O$_4$ derived from ZIF-67. The abovementioned synthetic route is displayed in Scheme 1.

2. RESULTS AND DISCUSSION

2.1. Structure Characterization. Figure 1a exhibits the X-ray diffraction (XRD) curves of the prepared MOF (ZIF-67) and POM-based MOF (PMo$_{12}$O$_{40}$@ZIF-67). All the diffraction peaks for both the samples are matched with simulated ZIF-67, and the results are consistent with Zhang’s results,\textsuperscript{21} which confirms that the target products are successfully obtained. After the calcination of PMo$_{12}$O$_{40}$@ZIF-67, as shown in Figure 1b, the peaks of ZIF-67 are disappeared, and the XRD patterns indicate the presence of both Co$_3$O$_4$ and CoMoO$_4$. The diffraction peaks at 2θ of 19, 31.2, 36.8, and 44.8\textdegree{} are related to the crystal planes of (111), (220), (331), and (400) for cubic Co$_3$O$_4$ (JCPDS NO. 42-1467), and the peaks located at 2θ of 19.1, 23.3, 25.5, 26.5, and 28.4\textdegree{} can also be indexed well to the formation of monoclinic CoMoO$_4$ (JCPDS NO. 21-0868). Therefore, the XRD results suggest that the Co$_3$O$_4$/CoMoO$_4$ hybrid was successfully obtained by one-step calcination of PMo$_{12}$O$_{40}$@ZIF-67. As a comparison, the pristine Co$_3$O$_4$ and CoMoO$_4$ were also successfully prepared by the aforementioned methods (as seen in the Experimental Section), which are demonstrated by XRD in Figure 1c,d.

The morphologies of the as-prepared ZIF-67 and PMo$_{12}$O$_{40}$@ZIF-67 were inspected by scanning electron microscopy (SEM). From Figure 2a,b, the particle sizes of the ZIF-67 and PMo$_{12}$O$_{40}$@ZIF-67 samples are about 0.3−0.5 μm, and ZIF-67 exhibits a legible dodecahedral morphology with a smooth surface, while PMo$_{12}$O$_{40}$@ZIF-67 maintains the framework of ZIF-67 with a relatively rough surface after the encapsulation of POMs. Furthermore, the success of embedding of POM (H$_3$PMo$_{12}$O$_{40}$) into the ZIF-67 host can be confirmed by the elemental mapping of PMo$_{12}$O$_{40}$@ZIF-67 (Figure 2c); carbon, cobalt, molybdenum, oxygen, and phosphorus elements are homogeneously distributed in the whole structure, strongly indicating that PMo$_{12}$O$_{40}$@ZIF-67 is
well synthesized and POMs are homogeneously distributed in the pores of ZIF-67 without obvious agglomeration.\textsuperscript{21}

The calcination was processed to obtain Co–Mo oxides after the complete decomposition of PMo\textsubscript{12}O\textsubscript{40}@ZIF-67 (500 °C for 2 h at a heating rate of 1 °C min\textsuperscript{-1}). The PMo\textsubscript{12}O\textsubscript{40}@ZIF-67-derived Co\textsubscript{3}O\textsubscript{4}/CoMoO\textsubscript{4} particles show irregular shapes with sizes shrunk to about ca. 100–200 nm after calcination (Figure 3a). Transmission electron microscopy (TEM) was also employed to demonstrate the morphologies and structures of Co\textsubscript{3}O\textsubscript{4}/CoMoO\textsubscript{4} (Figure 3b), from which the well-defined nanoparticles can be seen. Moreover, the energy-dispersive spectroscopy (EDS) of Co\textsubscript{3}O\textsubscript{4}/CoMoO\textsubscript{4} nanohybrids (Figure 3c) was characterized. In the hybrids, the Co-to-Mo molar ratio is 10.7:1 (as seen in Table 1), confirming that the molar ratio of Co\textsubscript{3}O\textsubscript{4} to CoMoO\textsubscript{4} in the as-prepared nanohybrids is about 3:1, which indicates that POMs do not fully occupy the pores of ZIF-67, that is, about 76.7% of POMs are embedded in PMo\textsubscript{12}O\textsubscript{40}@ZIF-67.

The pristine ZIF-67 was also annealed in the same way as in the preparation of Co\textsubscript{3}O\textsubscript{4}/CoMoO\textsubscript{4} nanohybrids to obtain Co\textsubscript{3}O\textsubscript{4} for comparison. The ZIF-67-derived Co\textsubscript{3}O\textsubscript{4} is ca. 100 nm in diameter with the irregular structure, which can be seen by SEM in Figure 3d. Figure 3e,f reveals that the diameters of the pristine CoMoO\textsubscript{4} nanorods are in the range of ca. 200–300 nm with lengths in the range of 3–5 μm on average.

### 2.2. Electrochemical Performance

The cyclic voltamogram (CV) curves of Co\textsubscript{3}O\textsubscript{4}/CoMoO\textsubscript{4} from the initial three cycles (between 3 and 0.01 V at a rate of 0.1 mV s\textsuperscript{-1}) are depicted in Figure 4a. The cathodic peak of the first cycle centered at about 1.1 V (or a slope line) is considered as the lithiation process with the reduction of Co\textsuperscript{3+}/Mo\textsuperscript{6+} to Co\textsuperscript{0}/Mo\textsuperscript{0}. The cathodic peak observed at about 0.6 V is attributed to the solid electrolyte interphase (SEI) formation, while the initial anodic peaks observed at 1.5/2.0 V can, respectively, be attributed to the oxidation of Co\textsuperscript{0}/Mo\textsuperscript{0}. In the subsequent two cycles, the emergence of a new cathodic peak at around 1.25 V results from the sequential Li\textsuperscript{+} ions insertion into CoO and MoO\textsubscript{2}. According to the CV investigations of Co\textsubscript{3}O\textsubscript{4}/CoMoO\textsubscript{4} electrodes, possible electrochemical mechanisms and reactions are proposed as follows:\textsuperscript{21,22} eqs 1 and 2 correspond to the lithiation processes and eqs 3 and 4 correspond to the delithiation processes.

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\begin{align*}
\text{CoMoO}_8 + 8\text{Li}^+ + 8\text{e}^- &\leftrightarrow 4\text{Li}_2\text{O} + \text{Co} + \text{Mo} \quad (1) \\
\text{CoO}_2 + 8\text{Li}^+ + 8\text{e}^- &\leftrightarrow 3\text{Co} + 4\text{Li}_2\text{O} \quad (2) \\
\text{Co} + \text{Li}_2\text{O} + \text{CoO} &\leftrightarrow 2\text{Li}^+ + 2\text{e}^- \quad (3) \\
\text{Mo} + 3\text{Li}_2\text{O} &\leftrightarrow \text{MoO}_3 + 6\text{Li}^+ + 6\text{e}^- \quad (4)
\end{align*}
\]

CV measurements indicate that Co\textsubscript{3}O\textsubscript{4} and CoMoO\textsubscript{4} synergistically make contributions to the capacity when used as the anodes of LIBs. The curves matched well from the second cycle imply fine reversibility of the electrode of Co\textsubscript{3}O\textsubscript{4}/CoMoO\textsubscript{4} nanohybrids.

Figure 4b shows the curves of the first three and the 10th cycles for charge and discharge; except for the first lithiation curve, the curves of the following cycles are almost overlapped, which indicates a good cycling performance of Co\textsubscript{3}O\textsubscript{4}/CoMoO\textsubscript{4} and this is in agreement with the CV results. Notably, an obvious plateau at about 1.1 V was observed in the
initial discharge cycle, implying the reduction of Co$_3$O$_4$/CoMoO$_4$, which is also in agreement with the CV investigations (Figure 4a). From the second discharge curve, a short plateau shifting from the initial 1.1 to 1.25 V indicates the reaction between Li$^+$ and Co$_3$O$_4$/CoMoO$_4$. The specific discharge/charge capacity of the initial cycle is 1252.3/814.1 mAh g$^{-1}$, and the large capacity variance is attributed to the SEI formation. The discharge/charge capacities of the subsequent two and 10th circles for Co$_3$O$_4$/CoMoO$_4$ hybrids are 896.5/816.0, 872.1/819.2, and 834.2/814.1 mAh g$^{-1}$, respectively, indicating a good electrochemical performance with a relatively high specific capacity and low capacity attenuation.

The cyclic stability of the chosen material (Co$_3$O$_4$/CoMoO$_4$ nanohybrids) is also characterized between 3 and 0.01 V at 0.1 mA g$^{-1}$. The pristine Co$_3$O$_4$ or CoMoO$_4$ electrodes are also investigated in the same condition with the Co$_3$O$_4$/CoMoO$_4$ nanohybrids for comparison. Despite the large capacity loss after the initial cycle due to the irreversible reaction of eq 1, the curves in Figure 4c show that the specific capacities of the anodes of Co$_3$O$_4$/CoMoO$_4$ nanohybrids decrease a bit after the second cycle and increase in the next several cycles, exhibiting relatively stable cycling stability. After the 50th cycle, the reversible specific capacity of Co$_3$O$_4$/CoMoO$_4$ nanohybrids can still be maintained at 750.6 mAh g$^{-1}$ with a capacity retention of around 89.6%. The Co$_3$O$_4$ and CoMoO$_4$ electrodes are investigated under the same conditions as a reference, and the specific capacities of only 134.4 and 445.9 mAh g$^{-1}$ are observed for the pristine Co$_3$O$_4$ and CoMoO$_4$ electrodes, respectively, at the 50th cycle. This may be ascribed to the synergistic effect between Co$_3$O$_4$ and CoMoO$_4$ (eqs 1–4).21–23

Further investigations on the rate performance of the electrodes of Co$_3$O$_4$/CoMoO$_4$ nanohybrids are depicted in Figure 4d. The electrode shows relatively high reversible specific capacities of 797.2, 686.4, 465.9, 301.7, and 166.8 mAh g$^{-1}$ at different current densities from 0.1 to 2 A g$^{-1}$. After that, the capacities can still remain at 280/406.7/617.3/795.4 mAh g$^{-1}$ at a current density of 1/0.5/0.2/0.1 A g$^{-1}$. The capacity retention is around 99.8%, indicating a remarkable high rate capability and capacity recoverability of the electrodes of Co$_3$O$_4$/CoMoO$_4$ nanohybrids. Compared to the pristine Co$_3$O$_4$ and CoMoO$_4$, the Co$_3$O$_4$/CoMoO$_4$ nanohybrids in this work exhibit a better electrochemical performance. The excellent lithium storage performance of Co$_3$O$_4$/CoMoO$_4$ can be attributed to the unique hollow structure and the synergistic effect between Co$_3$O$_4$ and CoMoO$_4$.22,23 First, the hollow dodecahedron structure can...
shorten the ionic diffusion pathways and increase the contact area with the electrolyte on the one hand while accommodating the volume expansion in the cycling process on the other hand. Second, when CoMoO₄ or Mo reacts with Li⁺, Co₃O₄ or Co acts as the buffer to alleviate the stress and the volume expansion.¹¹,¹²,¹³ Third, Co and Mo can effectively enhance the electrical conductivity of the nanohybrids, resulting in an excellent electrochemical performance.

To further clarify the better performance of the Co₃O₄/CoMoO₄ electrodes than the Co₃O₄ or CoMoO₄ electrodes, the EIS of the electrodes of Co₃O₄/CoMoO₄ nanohybrids, pristine Co₃O₄ and CoMoO₄ were characterized (Figure 5a), and all the correlative Nyquist plots display quasi-semicircles in both high- and mid-frequency zones, followed by slope lines in the low-frequency zone. As is depicted in the equivalent circuit (inset of Figure 5a), R₀ stands for the general Ohmic resistance among the electrolyte, the electrodes, and the separator. The high-frequency semicircle was assigned to the resistance of the SEI film (RSEI), while the mid-frequency semicircle was attributed to charge transfer resistance (Rct). The slope line located at low frequency was due to the Li⁺ diffusion inside the electrode material, and the Warburg impedance component was chosen in the equivalent circuit. Among all the samples, it is obvious that the Co₃O₄/CoMoO₄ electrode demonstrates the smallest R₀ (4.1 Ω) and Rct (32.2 Ω), based on the equivalent circuit (Figure 5a, inset). Furthermore, the Co₃O₄/CoMoO₄ electrodes before and after cycling are characterized (Figure 5b), which depicts that, after cycling, R₀ and Rct both decrease compared to those before cycling. Thus, the material of Co₃O₄/CoMoO₄ derived from PMo₁₂O₄₀@ZIF-67 can be recognized as an ideal anode for LIBs.

3. CONCLUSIONS
To conclude, this study first proposes a facile way to synthesize the anodes composed of Co₃O₄/CoMoO₄ nanohybrids for LIBs using POM-based MOFs (PMo₁₂O₄₀@ZIF-67) as precursors. Both cycling performance and rate capability were highly improved compared to the pristine Co₃O₄ and CoMoO₄. The as-synthesized Co₃O₄/CoMoO₄ exhibits relatively high capacity, excellent rate performances, and capacity recoverability, and it is believed that the satisfactory electrochemical performances could be attributed to the facile design of the synthetic method and the synergistic effect in the Co₃O₄/CoMoO₄ nanohybrids. This study illustrates that the as-obtained material of Co₃O₄/CoMoO₄ nanohybrids is promising in the application of the anode for LIBs, and we believe that the POM-based MOF guest-synthesis strategy may spark some inspirations to construct other polyanmetallic oxides for enhanced electrochemical energy storage and further applications.

4. EXPERIMENTAL SECTION
4.1. Materials. All of the chemicals for syntheses used in this study were purchased commercially and used as received. Cobaltous nitrate hexahydrate (Co(NO₃)₂·6H₂O, ≥98.5%), 2-methylimidazole (2-MeIM, ≥99%), tetrahydrofuran (THF, ≥99%), phosphomolybdic acid hydrate (H₃PMo₁₂O₄₀·nH₂O, ≥99.6%), and sodium molybdate dihydrate (NaMoO₄·2H₂O, ≥99%) were purchased from Sinopharm Chemical Reagent Co., while tetrahydrofuran (THF, ≥99%) from Aladdin.

4.2. Synthesis of PMo₁₂O₄₀@ZIF-67 and ZIF-67 Nanoparticles. In a general synthesis process, PMo₁₂O₄₀@ZIF-67 hybrids were prepared by a solvothermal reaction. H₃PMo₁₂O₄₀·nH₂O and Co(NO₃)₂·6H₂O (Co/Mo molar ratio = 8:1) were dissolved in deionized water (marked as solution A). 2-MeIM (molar ratio of Co and 2-MeIM = 1:12) was dissolved into THF (marked as solution B). Then, solutions A and B were mixed together and then moved to a hydrothermal reactor and heated up to 120 °C for 10 h. After that, the obtained crystals were centrifuged with the mixture of deionized water and ethanol (1:1 in volume) for at least 6 times after cooling down. Subsequently, the desired products were obtained by drying the solids at 70 °C for 12 h.

ZIF-67 nanoparticles were prepared using a method similar to that used for the preparation of PMo₁₂O₄₀@ZIF-67. The only difference was the absence of H₃PMo₁₂O₄₀·nH₂O in solution A.

4.3. Synthesis of Co₃O₄/CoMoO₄ and Co₃O₄ Nanoparticles. CoMoO₄ nanoparticles were prepared by a hydrothermal method. A mixture of Co(NO₃)₂·6H₂O and NaMoO₄ in deionized water (Co/Mo molar ratio = 1:1) was vigorously stirred for 30 min. Then, the mixture mentioned above was transferred to a hydrothermal reactor, heated to 90 °C, and kept for 10 h. After cooling down, the obtained powders were centrifuged with the mixture of deionized water and ethanol (1:1 in volume) for at least 6 times. Finally, the solids were dried at 70 °C overnight and calcined at 350 °C for 1 h to afford the desired product.

4.5. Physical Characterization. The X-ray diffraction test (XRD) (D8 Advance, Cu Kα radiation, λ = 1.5406 Å) was used to characterize the crystal structures of the materials. Scanning electron microscopy (SEM) (Quanta FEG 250, 20 kV) and transmission electron microscopy (TEM) (JEOL-2100F, 10 kV) were used to inspect the morphologies of the obtained materials. The compositions of the materials were inspected by energy-dispersive spectroscopy (EDS) (JEOL-2100F, 10 kV).

4.6. Electrochemical Measurements. All anodes were prepared via mixing Co₃O₄/CoMoO₄ powders (70 wt %) with carbon black (20 wt %) as a conducting agent and sodium carboxymethyl cellulose (CMC) (10 wt %) as a binder into water to produce a uniform mixture. Then, the mixture was subsequently coated on a copper foil, dried at 120 °C for 10 h, and then cut into discs (14 mm in diameter) to obtain the anodes of Co₃O₄/CoMoO₄. The active mass loaded was about 0.9 mg cm⁻². After that, the anodes were assembled into 2032-type coin cells in an Ar-filled glovebox, with lithium metal foils as the reference and counter electrodes, microporous polypropylene membrane as separators, and 1 M LiPF₆ dissolved in EC, DEC, and EMC (1:1:1, by volume) was chosen as the electrolyte. The discharge/charge curves were determined through cycling at various current densities between 3 and 0.01 V. Cyclic voltammogram (CV) measurements were characterized at 0.01–3 V (vs Li/Li⁺) at a sweep rate of 0.5 mV s⁻¹, while electrochemical impedance...
spectroscopy (EIS) measurement evaluation was conducted with an AC amplitude of 0.01 V from 10^5 to 0.01 Hz. Both CV and EIS measurements were evaluated by an electrochemical workstation (CHI660E, China).

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