Sub-5 nm Ultrasmall Metal–Organic Framework Nanocrystals for Highly Efficient Electrochemical Energy Storage

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ABSTRACT: Synthesis of ultrasmall metal–organic framework (MOF) nanoparticles has been widely recognized as a promising route to greatly enhance their properties but remains a considerable challenge. Herein, we report one facile and effective spatially confined thermal pulverization strategy to successfully transform bulk Co-MOF particles into sub-5 nm nanocrystals encapsulated within N-doped carbon/graphene (NC/G) by using conducting polymer coated Co-MOFs/graphene oxide as precursors. This strategy involves a feasible mechanism: calcination of Co-MOFs at proper temperature in air induces the partial thermal collapse/distortion of the framework, while the uniform coating of a conducting polymer can significantly improve the decomposition temperature and maintain the component stability of Co-MOFs, thus leading to the pulverization of bulk Co-MOF particles into ultrasmall nanocrystals without oxidation. The pulverization of Co-MOFs significantly increases the contact area between Co-MOFs with electrolyte and shortens the electron and ion transport pathway. Therefore, the sub-5 nm ultrasmall MOF nanocrystals-based composites deliver an ultrahigh reversible capacity (1301 mAh g⁻¹ at 0.1 A g⁻¹), extraordinary rate performance (494 mAh g⁻¹ at 40 A g⁻¹), and outstanding cycling stability (98.6% capacity retention at 10 A g⁻¹ after 2000 cycles), which is the best performance achieved in all reported MOF-based anodes for lithium-ion batteries.

KEYWORDS: metal–organic frameworks, pulverization, ultrasmall nanocrystals, electrochemical energy storage, lithium-ion battery

Metal–organic frameworks (MOFs), also known as porous coordination polymers, have been extensively investigated as a new class of inorganic–organic hybrid materials. Because of their tunable pore sizes and structures, high specific surface, and pore volume, MOFs have recently shown their unique advantages and great potentials in energy storage and conversation, such as supercapacitors,1 lithium-ion batteries (LIBs),2,2 lithium–sulfur batteries,3–6 lithium–oxygen batteries,7 CO₂ reduction,8 oxygen evolution and reduction reactions,9–12 etc.13,14 However, when the size of materials is reduced to nanoscale dimension, physicochemical properties can change dramatically.15–19 Owning to the exceptional size-dependent properties, nanomaterials have been widely explored in various areas,15–19 including energy-related applications.10,21 Recent studies have demonstrated that compared with bulk particles, a higher specific surface and more active sites can be obtained by decreasing the size of MOFs to the nanoscale (usually with dimensional scales larger than 50 nm), which can highly enhance the electrochemical process, leading to excellent electrochemical performance.22–25 However, the investigation of ultrasmall MOF nanoparticles with sizes down to sub-5 nm in energy storage and conversion has not yet been explored so far due to lack of an efficient synthesis method. Although extensive studies have been conducted to fabricate some other ultrasmall nanomaterials, among which laser synthesis and processing,26 electrochemical processes,27 fast Joule heating,28 and atomic and molecular layer deposition29 were investigated, these methods are not applicable for MOFs because of the instabilities of MOFs under extreme conditions or different intrinsic molecular structures of MOFs. Therefore, a facile, low-cost, and scalable approach to fabricate ultrasmall MOF nanoparticles is a great challenge yet urgently desired.

Herein, we report a simple and environmentally friendly spatially confined pulverization method to fabricate sub-5 nm ultrasmall MOF nanocrystals through calcination in air. We first...
grow Co-MOF particles (average size of ~100 nm) uniformly on graphene oxide (GO) sheets to obtain GO/Co-MOF (GC) composites (see detailed information in the Experimental Section and Figure S1a and c) through the coordination and electrostatic interaction. Then, compact coating of conducting polypyrrole (PPy) on a GC surface by in situ polymerization was conducted to obtain GO/Co-MOFs/PPy (GCP) composites (Figure S1b). Because of the protective PPy layers, after thermal treatment of GCP at 350 °C in air, bulk MOF particles were pulverized into ultrasmall nanocrystals (average diameter of ~4.2 nm) with the surrounding PPy and GO layers converted into N-doped carbon/graphene (NC/G) simultaneously. However, without the coating of PPy, Co-MOF particles transform into metal oxide instead, as schematically shown in Figure 1. To investigate the effect of ultrasmall MOF particles on electrochemical energy storage, the ultrasmall Co-MOF nanocrystals encapsulated in NC/G (denoted as GCP350) by simple calcination of GCP at 350 °C in air were explored as binder-free anodes for lithium-ion batteries. The entire GCP350 anodes achieved ultrahigh reversible capacity (1301 mAh g⁻¹ at 0.1 A g⁻¹), extraordinary rate performance (494 mAh g⁻¹ at 40 A g⁻¹), and excellent long-term cycling stability (98.6% retention at 10 A g⁻¹ over 2000 cycles), much better than the nonpulverized MOF/G composite and representing the best performance achieved in all MOF-based anodes ever reported.

RESULTS AND DISCUSSION

Morphological evolutions of ultrasmall Co-MOF nanocrystals were first investigated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). As shown in Figure 2a, PPy was homogeneously coated on GC, and bulk Co-MOF particles with average diameters of 80–110 nm (Figure S2) were encapsulated by the GO and PPy layers. The elemental mapping images in Figure S1d–j also show the homogeneous coating of PPy on Co-MOFs. After thermal treatment of GCP at 350 °C for 2 h in air, the Co-MOF particles were homogeneously distributed and well encapsulated by NC/G, as shown in Figure 2b and Figure S3. In addition, HRTEM images (Figure 2c and d) show that the Co-MOF particles were surrounded by ultrathin layers of NC/G. Interestingly, the individual bulk Co-MOF particle in GCP was pulverized into plenty of ultrasmall nanocrystals (average diameter of ~4.2 nm, the inset in Figure 2c) with little void space between them. The lattice fringes with a spacing of about 0.25 nm are assigned to the (400) plane of Co-MOFs (JCPDS #77-1161, Figure 2e). The rings in the selected area electron diffraction (SAED) pattern (Figure 2f) also indicate the intactness of ultrasmall Co-MOF nanocrystals. The homogeneous element mapping images of C, Co, and N in Figure 2g–i also imply these spatially confined pulverized ultrasmall Co-

Figure 1. Schematic illustration of the spatially confined pulverization process: (a) GC, (b) GCP, (c) GCP350, (d) GC350.

Figure 2. TEM images of GCP (a) and GCP350 (b); (c, d) HRTEM images of GCP350 (the inset is a histogram of the size distribution of nanocrystals) and the corresponding lattice structure (e), SAED pattern (f), and element mapping images (g–i).
MOF particles are uniformly distributed and tightly wrapped by NC/G.

In order to fully understand the formation of pulverized ultrasmall Co-MOF nanocrystals, detailed structural characterizations were carefully carried out by X-ray diffraction (XRD) and Fourier transform infrared spectra (FTIR). As shown in Figure 3a, in all Co-MOFs, GC, GCP, and GCP350, the four dominant peaks at 17.2°, 24.5°, 34.9°, and 39.4° are well indexed to neat Co-MOFs (JCPDS #77-1161), demonstrating that Co-MOFs in GCP350 still existed even after calcination at 350 °C in air. For GCP350, the peak intensity decreased and the full width at half-maximum (fwhm) increased, which may result from the pulverization of bulk Co-MOFs into ultrasmall nanoparticles without oxidation during this spatially confined pulverization process. It is noteworthy that the significant increase of decomposition temperature is induced by the tight coating of PPy, which may benefit from the good affinity to other materials and high flexibility of this conductive polymer.

Our GCP350 nanocomposites showed a hierarchical structure with ultrasmall Co-MOF nanocrystals encapsulated by interconnected ultrathin conductive layers of NC/G, which prompted us to further explore them as binder-free anodes for lithium-ion batteries. For comparison, the GC350 and GCP250 were also tested (Figure S13) to understand the structure–property relationship. The electrochemical performance of GCP350 was first investigated by galvanostatic discharge–charge tests between 0.01 and 3 V at 0.2 A g⁻¹. As shown in Figure 4a, GCP350 anodes delivered an initial discharge capacity of 1978 mAh g⁻¹ (calculated on the whole electrode) and a reversible charge capacity of 1192 mAh g⁻¹ with a relatively low initial Coulombic efficiency (CE) of 60.6%, caused by electrolyte decomposition and formation of a solid-electrolyte interphase (SEI). Meanwhile, the discharge–charge curves almost overlapped for the second, fifth, and 10th cycles, demonstrating the excellent cycling stability of GCP350. Cycling performance was further tested at 0.2 A g⁻¹ (Figure 4b). The capacity of GCP350 was 1201 mAh g⁻¹ with a CE above 95% in the second cycle. After 100 cycles, the capacity of GCP350 anodes still retained 1192 mAh g⁻¹ with a CE of ~99%, which is much better than that of GCP250 and GC350. The rate performance of GCP350 anodes was evaluated at current densities from 0.1 to 40 A g⁻¹. Figure 4c shows the typical galvanostatic discharge–charge curves of GCP350 under different current densities, and the reversible capacities of GCP350 are 1301, 1188, 1060, 987, 906, 801, 701, and 596 mAh g⁻¹ at current densities of 0.1, 0.2, 0.5, 1, 2, 5, 10, and 20 A g⁻¹, respectively, far surpassing those of GCP250 and GC350 (Figure 4d). Even at a superhigh current density of 40 A g⁻¹, which has never been reported for MOF-based anodes, the GCP350 can still achieve an impressive capacity of 494 mAh g⁻¹, demonstrating the superior rate performance of GCP350. Moreover, the reversible capacity of GCP350 anodes recovered to 1255 mAh g⁻¹ when the current density returned...
to 0.1 A g\(^{-1}\), indicating excellent structural stability of GCP350. To the best of our knowledge, the capacity and the rate performance of GCP350 are significantly higher than all MOF-based anodes for LIBs reported recently (Figure 4e and Table S1).\(^{41-45}\) In addition, we have also tested the control sample without Co-MOFs (Figure S14) and confirmed the extraordinary electrochemical performance of GCP350 was mainly due to the ultrasmall Co-MOF nanocrystals. The electrochemical processes of these electrodes were further investigated and compared by electrochemical impedance spectroscopy (EIS). As shown in Figure 4f, both the charge-transfer resistance in the high- to medium-frequency region and Warburg impedance in the low-frequency region of GCP350 are smaller than those of GCP250 and GC350, indicating that ultrasmall Co-MOF nanocrystals provide abundant contact area for the electrolyte to access active material, speeding up charge transfer and enhancing Li-ion diffusion, leading to the dramatic enhancement of electrochemical performance of GCP350.

The long-term cycling performance at high current densities was further investigated, as shown in Figure 4g. The GCP350 anodes delivered a capacity of 795 mAh g\(^{-1}\) at the second cycle (the initial discharge capacity is neglected because of the formation of an SEI during the first discharge process) and remained 92.9% (739 mAh g\(^{-1}\)) after 2000 cycles at 5 A g\(^{-1}\). More importantly, the capacity retention of GCP350 anodes at 10 A g\(^{-1}\) is 98.6%, with a decay rate of only 0.0007% per cycle. At such high current density, GCP350 could be fully charged in less than 5 min, which makes them of great importance in practical applications.

To better understand the excellent electrochemical performance, the reaction kinetics were analyzed by cyclic voltammetry (CV) tests at different sweeping rates from 0.2 to 10 mV/s (Figure 5a) based on the following equations:

\[ i = \alpha \nu^b, \]

where \(i\) is the peak current, \(\nu\) is the sweep rate, \(\alpha\) is a constant, and \(b\) is an adjustable parameter.\(^{46-48}\) As shown in Figure 5b, when the scan rate is below 1 mV/s, a \(b\) value of 0.89 for the oxidation peak in Figure 5a can be calculated, indicating the electrochemical process of GCP350 is related to both capacitive and diffusion-controlled current to the total current at 0.2 mV/s; the peak current, \(\nu\) is the sweep rate, \(\alpha\) is a constant, and \(b\) is an adjustable parameter.\(^{46-48}\) A \(b\) value of 1 indicates that the electrochemical reaction is non-Faradaic capacitive-controlled. When \(b = 0.5\), it indicates that the current is limited by semi-infinite linear diffusion.\(^{46-48}\) As shown in Figure 5b, when the scan rate is below 1 mV/s, a \(b\) value of 0.89 for the oxidation peak in Figure 5a can be calculated, indicating the electrochemical process of GCP350 is related to both capacitive and diffusion behaviors. When the scan rate is above 1 mV/s, the \(b\) value decreases from 0.89 to 0.8, implying an increased high-rate diffusion-limited process of GCP350 at high current densities, which may result from the increase of resistance at high rates.\(^{36}\)

It is well known that a surface-controlled reaction is favorable to obtain excellent high-rate performance. Hence, the contribution of surface capacitive-controlled and diffusion-controlled processes to the capacity of GCP at different sweep rates was further investigated according to the following equation:

\[ i = k_1\nu + k_2\nu^{1/2}, \]

where surface capacitive- and diffusion-controlled contribution is weighted by \(k_1\) and \(k_2\).

Figure 4. Electrochemical characterizations of GCP350, GCP250, and GC350 anodes. (a) Charge−discharge curves of GCP350 anodes at 0.2 A g\(^{-1}\); (b) cycling performance of GCP350, GCP250, and GC350 anodes at 0.2 A g\(^{-1}\); (c) charge−discharge curves of GCP350 anodes at different current densities; (d) rate performance of GCP350, GCP250, and GC350 anodes; (e) comparison of GCP350 and other representative MOF-based electrodes; (f) EIS plots of GCP350, GCP250, and GC350 anodes; (g) cycling performance of GCP350 anodes at 5 and 10 A g\(^{-1}\) for 2000 cycles.

Figure 5. (a) CV curves at different scan rates from 0.2 to 10 mV/s; (b) \(b\) value at different scan rates, calculated from peak current and scan rate from (a); (c) separation of the contribution of capacitive- and diffusion-controlled current to the total current at 0.2 mV/s; (d) contribution ratio of capacitive- and diffusion-controlled capacities at different scan rates; (e) schematic illustration of enhanced ion/electron transport in pulverized ultrasmall MOF nanocrystals.
respectively.\(^6\) As shown in Figure 5c, the normalized contribution ratio of capacitive-controlled capacity (the red zone) at 0.2 mV/s is about 49.6%, while that of diffusion-controlled capacity is about 50.4%. By gradually increasing the scan rate, the capacitive-controlled contribution ratio improves significantly from 50.4% at 0.2 mV/s to 91.9% at 10 mV/s, as shown in Figure 5d. The enhanced capacitive-controlled behavior mainly results from the ultrasmall size of Co-MOF nanocrystals and ultrathin carbonaceous layers\(^9\) since ultrasmall Co-MOF nanocrystals provide abundant contact area for the electrolyte to access the active material (the surface area increased from 138 m\(^2\) g\(^{-1}\) for GCP to 392 m\(^2\) g\(^{-1}\) for GCP350 during pulverization based on \(N_2\) adsorption–desorption analysis in Figure S15), speeding up charge transfer and enhancing Li-ion diffusion, as schematically shown in Figure 5e.

Based on the above discussion, the excellent electrochemical performance of GCP350 can be attributed to the following points. First, the spatially confined pulverization of MOFs into ultrasmall nanocrystals provides a large contact area for electrolyte with active materials, significantly shortening the Li-ion and electron diffusion distance. Meanwhile, ultrasmall Co-MOFs with high surface area, together with two-dimensional ultrathin NC/G layers, provide sufficient accessible sites for Li-ion storage. Second, the void space between ultrasmall Co-MOF nanocrystals and the robust coating layer of NC/G can effectively buffer the volume change and therefore alleviate the capacity loss during the long-term cycling. Third, the interconnected conductive NC/G layer can prompt electron transportation as a whole network. Owing to the above synergetic merits, the GCP350 anodes exhibit significantly enhanced lithium-storage performance compared to previous MOF-based anodes.

**CONCLUSIONS**

In conclusion, we report a facile thermal-assisted spatially confined pulverization method to fabricate ultrasmall Co-MOF nanocrystals with diameters down to sub-5 nm. When used as free-standing anodes for LIBs, the GCP350 exhibited ultrahigh reversible capacities (1301 mAh g\(^{-1}\) at 0.1 A g\(^{-1}\)), excellent rate performance (494 mAh g\(^{-1}\) at 40 A g\(^{-1}\)), and superior long-term cycling stability (98.6% capacity retention at 10 A g\(^{-1}\) after 2000 cycles), which is the best performance for MOFs-based LIB anodes so far. This versatile space-confined pulverization strategy can also be applied to other MOFs with suitable protective layers under proper temperatures and may provide a universal route to large-scale synthesis of ultrasmall functional MOF nanocrystals with promising applications in energy storage and conversion and beyond.

**EXPERIMENTAL SECTION**

**Synthesis of Graphene Oxide.** Natural graphite powder (325 mesh, Aladdin, 99.95% metal basis) was used to synthesize GO via a modified Hummers’ method. All the other chemicals were purchased from Sigma or Aladdin and used without purification.

**Synthesis of GO-Co-MOFs-Polypryrole.** First, 40 mg of GO and 0.2 mL of potassium hexacyanocobaldate (Co\(_6\)Co(CN)\(_{16}\)) (0.5 M) were dissolved in 80 mL of deionized water and then mixed under magnetic stirring and ultrasound for 10 and 5 min, respectively. A 2 mL amount of cobalt chloride (CoCl\(_2\)) (0.5 M) was poured into the above solution, followed by stirring for 1 h. Second, 120 mg of ammonium persulfate ((NH\(_4\))\(_2\)S\(_2\)O\(_8\)) and 120 \(\mu\)L of pyrrole were added into the above solution subsequently, followed by constantly stirring overnight for coating of polypryrole. Third, the solution was centrifuged three times and then freeze-dried overnight to get a GCP aerogel. A graphene oxide/Co-MOF aerogel and graphene oxide/PPy (GP) were obtained by the same procedures without the addition of pyrrole and potassium hexacyanocobaldate/cobalt chloride, respectively.

**Preparation of GCP350 Composites.** The GCP350 nanocomposites were obtained by one-step thermal treatment of the GCP aerogel in air. Typically, the GCP aerogel was heated gradually to 350 °C at a rate of 10 °C/min and maintained for 2 h in air. GCP350 and GP350 were obtained by calcination of the GC and GP aerogel under the same conditions. GCP250 was prepared by calcination of GCP at 250 °C for 2 h in air.

**Characterizations.** The morphology characterizations were performed on a field emission scanning electron microscope (Zeiss Ultra-55) and transmission electron microscope (FEI Tecnai G2 20TWIN, 200 kV). PANalytical X’pert PRO X-ray diffraction (Cu Ko) was used to complete the XRD analysis from 10° to 80°. A Pyris 1 thermogravimetric analyzer was used to carry out TGA tests at a heating rate of 10 °C/min in air. FTIR was measured on a ThermoFisher Nicolet 6700 Fourier transform infrared spectrometer. XPS was performed on a PHI 5000C ESCA System. An Autosorb IQ gas sorption system was used to conduct BET tests at 77 K.

**Electrochemical Characterization.** The free-standing GCP350 films obtained by compression of the GCP350 aerogel were used directly as anodes for lithium-ion batteries. The areal mass loading of GCP350 was ~1.5 mg cm\(^{-2}\). LIBs were assembled in an argon-filled glovebox with Cellard 2400 and metallic lithium as separator and counter electrode, respectively. LiPF\(_6\) (1 M) in EC/DMC (1:1 by volume ratio) was used as the electrolyte. The galvanostatic experiments were tested on a battery testing system (LAND, Wuhan China) in the voltage window from 0.01 to 3 V at different current densities. A CHI 760D electrochemical workstation was used to perform EIS in the frequency range of 100 kHz to 0.01 Hz and CV curves in the potential range of 0.01–3 V at different scanning rates.

**ASSOCIATED CONTENT**

\* Supporting Information

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**Notes**

The authors declare no competing financial interest.

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