In Situ Growth of Lithiophilic MOF Layer Enabling Dendrite-free Lithium Deposition

HIGHLIGHTS

- Lithiophilic and superwetting Cu-MOF layer is in situ grown on Cu foil.
- The MOF layer provides uniform nucleation sites and promotes homogeneous Li⁺ flux.
- The MOF layer solves the Li dendrite growth from the nucleation step.
- The Cu-MOF-modified Cu foil enables prominent improved CE and lifetime.

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Yin et al., iScience 23, 101869
December 18, 2020 © 2020
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https://doi.org/10.1016/j.isci.2020.101869
In Situ Growth of Lithiophilic MOF Layer Enabling Dendrite-free Lithium Deposition

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SUMMARY

Lithium metal batteries have recently emerged as alternative energy storage systems beyond lithium-ion batteries. However, before this kind of batteries can become a viable technology, the critical issues of the Li anodes, like dendrites growth and low Coulombic efficiency (CE), need to be conquered. Herein, lithiophilic Cu-metal-organic framework thin layer (Cu-MOF TL) is in situ grown on the surface of Cu foil by a facile immersion strategy to construct a multifunctional current collector. Profiting from the high electrical conductivity and unique porous structure, the Cu-MOF TL with high affinity to electrolyte can provide uniform nucleation sites and promote homogeneous Li⁺ flux, as a result, radically restrain the Li dendrite growth, leading to stable Li plating/stripping behaviors. The modified current collector enables Li plating/stripping with a prominent CE (~97.1%) and a stable lifetime (~2500 h). Importantly, the synthesis method can be easily large-scale production in a series of organic solvents.

INTRODUCTION

Li metal with ultrahigh theoretical specific capacity (3,860 mAh g⁻¹), ultralow redox potential (~3.04 V versus RHE), and light weight (about 0.53 g cm⁻³) has been considered to be the ultimate candidate anode material for next-generation rechargeable batteries (Li et al., 2019; Shi et al., 2019; Guo et al., 2017), especially for Li-S and Li-O₂ batteries, without which the advantages of high specific capacities cannot be fully exploited. However, there are some critical issues existing for Li metal anodes that hamper their successful implementation in real batteries. As one of the most active metal elements, Li inevitably reacts with organic electrolyte to form solid electrolyte interphase (SEI) films (Liu et al., 2018; Lu et al., 2015; Wang et al., 2019a, 2019b; Wu et al., 2017a, 2017b), the infinite volume changes of Li during unremitting plating/stripping process will destruct the formed SEI films, constantly expose fresh Li to electrolyte, and continuously consume both active Li and electrolyte, leading to the underwhelming Coulombic efficiency and early cell death (Zhang et al., 2019; Zheng et al., 2017). What’s worse, the plating/stripping of Li takes place at the ion and electron conductive parts. The existence of SEI film makes Li preferentially cover the fracture sites, resulting non-uniform distribution of Li ion, giving rise to the formation of Li dendrite (Liang et al., 2016; Wu et al., 2017a, 2017b; Yan et al., 2014). Along with the growth of Li dendrites, a large overpotential and electrochemically inert dead Li will occur, further deteriorating the battery performance.

To overcome these issues, colossal efforts have been made to achieve uniform deposition of Li metal (He et al., 2019; Assegie et al., 2019; Hou et al., 2017, Hou et al., 2019; Nan et al., 2019a, Nan et al., 2019b; Kamphaus et al., 2019; Beyene et al., 2019; Wang et al., 2019a, Wang et al., 2019b). Among these, various additives have been introduced into the electrolytes to restrain the lithium dendrites by stabilizing the SEI (Zhou et al., 2019; Yang et al., 2017; Yu et al., 2019a, Yu et al., 2019b). Regrettably, the additives will experience rapid expenditure during cycling, weakening their effectiveness of inhibiting Li dendrite growth in long-term operation. For building protection layer or adopting solid-state electrolyte to stabilize the Li metal anode (Nan et al., 2019a, 2019b; Yu et al., 2019a, 2019b; Ma et al., 2014; Wang et al., 2017; Ye et al., 2017), the existence of intrinsic defects during material synthesis still has not been well solved, which will induce non-uniform Li ion distribution and finally result in dendrite growth. 3D host structures with large specific surface areas and suitable voids (Li et al., 2017; Yan et al., 2018; Chang et al., 2017; Zuo et al., 2017; Huang et al., 2019; Yang et al., 2015; Luo et al., 2020) are supposed to be an efficient strategy to mitigate the dendrite growth and facilitate the formation of uniform morphology of Li. However, this strategy simply limits the deposited metal Li into 3D matrix and does not fundamentally resolve the challenge of dendrite growth and low Coulombic efficiency (CE), need to be conquered. Herein, lithiophilic Cu-metal-organic framework thin layer (Cu-MOF TL) is in situ grown on the surface of Cu foil by a facile immersion strategy to construct a multifunctional current collector. Profiting from the high electrical conductivity and unique porous structure, the Cu-MOF TL with high affinity to electrolyte can provide uniform nucleation sites and promote homogeneous Li⁺ flux, as a result, radically restrain the Li dendrite growth, leading to stable Li plating/stripping behaviors. The modified current collector enables Li plating/stripping with a prominent CE (~97.1%) and a stable lifetime (~2500 h). Importantly, the synthesis method can be easily large-scale production in a series of organic solvents.
growth. Moreover, the high surface area of 3D hosts causes more Li surface to expose to electrolyte, enhancing side reactions and thus lowering the Coulombic efficiency. In addition, most 3D hosts require complex synthesis steps, which increase the cost and make it difficult to commercialization.

As a unique porous material, metal-organic frameworks (MOFs) have attracted considerable attention in energy storage systems (Qiao et al., 2018; Huang et al., 2017; Yin et al., 2016; Xia et al., 2015). When using MOFs to construct composite Li electrode, their large specific surface area and rich porosity can reduce local current density and alleviate volume changes during Li plating/stripping, inhibiting the dendrite growth to some extent (Bai et al., 2018; He et al., 2018; Huo et al., 2019). Moreover, the MOFs’ surface is rich in functional groups, providing uniform nucleation sites for dendrite-free lithium deposition. Despite these advantages, most MOFs materials are in powder form and poorly conductive and cannot be used directly as electrode materials. Importantly, as a host structure for Li metal, MOFs should have favorable chemical compatibility and stable electrochemical properties with Li metal.

In this study, a multifunctional current collector has been designed by in situ growth of conductive and lithiophilic Cu-MOF thin layer (Cu-MOF TL) on Cu foil through a handy and general immersion strategy to fundamentally solve the problem of Li dendrite formation. This original attempt of MOFs directly as a regulator for Li deposition can avoid the step of integrating powder state MOFs to the current collector. The coordination of Cu metal center with 7,7,8,8-Tetracyanoquinodimethane (TCNQ) organic ligand still leaves rich polar functional groups, making the Cu-MOF layer exhibit super high affinity to the organic electrolyte and strong ability to adsorb Li ion from the electrolyte. During the process of Li plating/stripping, the porous framework, super wettability with electrolyte, and homogeneous distribution of polar functional groups of the Cu-MOF TL provide uniform Li ion flux and nucleation sites, thereby solving the problem of uncontrolled Li dendrites growth from the starting point, as a result, giving rise to inspiring cycling performance and rate capability in both symmetric and full cells. It is gratifying to note that the Coulombic efficiencies have also promoted significantly compared with that of copper foil. This neoteric strategy verifies the concept of MOF-enabled dendrite-free Li metal anode, providing a new avenue to design high-performance metal-based anodes.

RESULTS AND DISCUSSION

Synthesis and Characterization of Cu-MOF-Modified Cu Foil before and after Li Deposition

Homogeneous Cu-MOF TL can in situ grow on the surface of Cu foil by just immersing the treated Cu foil into TCNQ (7,7,8,8-Tetracyanoquinodimethane) methanol solution for 30 min (Figure 1), which is easy to be largescale production. With the extension of reaction time, the Cu-MOF will grow continuously forming a bulge structure (Figure S1A and Supplemental Information), which may cause lithium dendrite growth during long-term Li plating/stripping processes. The digital photos of Cu foil and Cu-MOF-modified Cu foils with different reaction times are shown in Figures 2A–2C (inset images). With 30 min of immersion, the color of Cu foil experiences no obvious change except the appearance of a shallow green layer, indicating the ultrathin thickness of the formed Cu-MOF layer (denoted as Cu-MOF-30 min, Figure 2A). As the immersion time extended to 24 h, the color of Cu foil changes to dark green, totally different from the luminous orange color of Cu foil (Figures 2B and 2C), revealing the formation of thick Cu-MOF layer (denoted as Cu-MOF-24 h). The structural variation from crystal Cu to Cu-MOF has been confirmed by X-ray diffraction (XRD) analysis. As shown in Figure S1B, the XRD pattern of Cu-MOF-24 h are basically consistent with the Cu-TCNQ MOF reported in literature (Heintz et al., 1999), confirming the successful formation of Cu-MOF on the surface of Cu foil. The SEM images of Cu-MOF-30 min, Cu-MOF-24 h, and Cu foil are recorded in Figures 2A–2C. Different from the smooth surface of Cu foil (Figure 2C), the surface of Cu-MOF-30 min is somewhat rough because a thin layer of nanosized Cu-MOF particles homogeneously covers the Cu foil (Figure 2A). Whereas for Cu-MOF-24 h, the Cu-MOF particles continue to form and finally accumulate at some sites, resulting in an uneven surface (Figure 2B). According to the N2 adsorption-desorption analysis (Figures S1C and S1D), the Brunauer-Emmer-Teller (BET) surface area and the total pore volume of Cu-MOF-30 min and Cu-MOF-24 h together with Cu foils are 0.49 and 7.93 m² g⁻¹ and 0.008 and 0.013 cc g⁻¹, respectively, whereas the surface area and the total pore volume of Cu foil are almost zero. Since the surface area and pore volume are calculated based on the total mass of Cu foil and Cu-MOF layer, the actual specific surface area and pore volume of the Cu-MOF layer are much higher than the obtained value.

With the successful introduction of Cu-MOF layer on Cu foils, we then use them as current collectors to deposit Li to check whether they can guide dendrite-free Li deposition or not. To realize this, the
morphologies of Cu-MOF-30 min, Cu-MOF-24 h, and Cu foil after deposition of 2 mAh cm\(^{-2}\) of Li at 0.5 mA cm\(^{-2}\) have been examined. As indicated in Figures 2D and 2G, Li uniformly deposits on the Cu-MOF-30 min without dendrite formation, which is probably due to the homogeneous distribution of Cu-MOF and its porous structure and rich polar functional groups. Moreover, the deposited Li firmly connects to the Cu-MOF-30 min without any detected gaps (Figure 2G), confirming that the Cu-MOF-30 min can provide uniform nucleation sites to allow Li deposit on its surface. With regard to Cu-MOF-24 h, its bulge structure make non-uniform Li deposition and there is even some exposed Cu-MOF-24 h surfaces without Li plating (Figures 2E and 2H), which can be further identified by the black regions in the optical photograph of Li@Cu-MOF-24 h (inset of Figure 2E), demonstrating the significance of the smooth layer of Cu-MOF. Importantly, even in the non-uniform distribution of deposited Li, still no dendrite can be observed. Whereas for pure Cu foil, the deposited lithium is uneven with the clear emergence of dendrite (Figures 2F and 2I), illustrating the crucial role of Cu-MOF in regulating Li plating.

Because the electrolyte-wetting property of current collector prominently influences the Li deposition behavior, the contact angles between the electrolyte and Cu foil with and without Cu-MOF modification have been checked. As shown in Figure S1E, after an ether electrolyte droplet drops onto the surface of Cu foil, the contact angle of the electrolyte to Cu foil is 47.7\(^\circ\). By contrast, the electrolyte droplet can be entirely assimilated and diffused over the substrate once it contacts with Cu-MOF-30 min/24 h, making the contact angle of the ether electrolyte to Cu-MOF-30 min/24 h to be 0\(^\circ\) (Figures S1F and S1G). The above observations testify that the Cu-MOF modification layer is superwetting to electrolyte on account of its polar surfaces and porous structure. This strong electrolyte affinity makes the ether electrolyte flood the Cu-MOF layer, which is beneficial for reducing the cell impedance and facilitating ion diffusion process. In order to clarify the tailor effect of the polar groups of Cu-MOF on Li ion distribution, Raman measurement has been conducted. As indicated in Figure S2A, there is an obvious shift of the peak around 1,600 cm\(^{-1}\) after immersing the Cu-MOF-30 min electrode into the electrolyte, which can be attributed to the adsorption of the electrolyte by the Cu-MOF layer and its polar groups’ interaction with the Li ion. The physiochemical interactions between the polar groups of the Cu-MOF and Li ion can be further confirmed by the FT-IR spectroscopic (Figure S2B). The decreased intensity and upshift of the TCNQ\(^-\) peak indicate the TCNQ\(^-\) ion can bind Li ion, thus homogenizing the Li ion distribution.
To further illustrate the advantages of the Cu-MOF modification layer, the voltage curves of the Li plating process for the Cu foil with and without Cu-MOF modification have been given for characterizing the Li nucleation overpotential. As expected, the Cu-MOF-30 min displays the lowest voltage difference with a value of 22 mV between the voltage dip and the subsequent plateau as compared with those of Cu-MOF-24 h (29 mV) and Cu foil (31 mV, Figure 3A). Considering that the Li nucleation happens at the voltage valley bottom and the plating process initiates at the voltage plateau, the small Li nucleation overpotential induced by Cu-MOF-30 min indicates its superior lithium plating kinetic, which is in close connection with the suitable specific surface area, high electrolyte affinity, homogeneous distribution, and high electrical conductivity (0.25 S cm$^{-1}$) of the introduced Cu-MOF-30 min layer (Onodera et al., 2012).

The Li plating/stripping profiles of the Cu-MOF-30 min, Cu-MOF-24 h, and Cu foil electrodes at a fixed plating capacity of 1 mAh cm$^{-2}$ and a current density of 0.5 mA cm$^{-2}$ are shown in Figures 3B and S2E–S2H. Promisingly, the Cu-MOF-30 min electrode displays basically identical plating/stripping curves during the whole 300 cycles with ignorable capacity loss and voltage hysteresis increase (Figure 3B). As a comparison, the Cu-MOF-24 h and Cu foil electrodes exhibit obvious turbulence Li stripping curves during the repeated cycles, and the Cu foil electrode can only realize a lifetime of 150 cycles, half of that of Cu-MOF-30 min electrode, highlighting the effectiveness of the Cu-MOF modification layer and the indispensability of layer uniformity. To better evaluate and understand the reversibility of the Li metal during repeated plating/stripping on the three electrodes, the Coulombic efficiencies (CEs) are measured in half cells as the ratio of the stripping capacity versus plating capacity. As revealed in Figure 3C, the Cu-MOF-30 min electrode shows stabilized and ultrahigh CEs above 97.1% during 300 cycles at a current density of 0.5 mA cm$^{-2}$. Whereas the CEs of Cu foil display tremendous fluctuation after just 53 cycles, probably due to the fast growth of Li dendrites. Although the CEs of the Cu-MOF-24 h are stable in the initial 120
cycles, they exhibit biggish scattering and declines in the following cycles, indicating that the Cu-MOF layer can indeed inhibit Li dendrite growth to some extent, but, to further prolonging the cycling life, the homo-
geneity of the Cu-MOF layer plays a leading role.

Electrochemical impedance spectroscopy (EIS) analysis is then conducted to investigate the interface sta-
bility of the three electrodes at different cycles. The impedances are calculated by fitting the EIS data to an
equivalent electrical circuit including electrolyte resistance (Rs), charge transfer resistance at the electro-
lyte-electrode interface (Rct), Warburg element (W0), and constant phase elements (CPE) (inset in Fig-
ure S2D). From Figure S2Da n dTable S1, we can see that the semicircles at the high-intermediate fre-
quencies of the Cu-MOF-30 min electrode gradually decrease and stabilize within 100 cycles, revealing
the outstanding electrode interface stability derived from the homogeneous nucleation and stable depo-
sition/dissolution of Li metal endowed by Cu-MOF-30 min. For Cu-MOF-24 h electrode, the semicircles
continuously increase in the 100 cycles, associating with unstable interface structure from incessant growth
of Li dendrites. In comparison, the semicircle of the Cu foil decreases to almost zero at the 100th cycle, indi-
cating the short circuit of the cell induced by serious uncontrolled growth of Li dendrites. Because the
modified Cu-MOF-30 min layer has good conductivity and is in-situ grown on the copper foil, there is no
obvious interface resistance between them. Furthermore, the high conductivity of the Cu-MOF-30 min
layer can enable Li directly deposit on its surface without the requirement of passing thought the Cu-
MOF-30 min layer, decreasing the interface impedance between MOF layer and deposited Li layer. Be-
sides, the Cu-MOF-30 min layer can behave as an effective regulator to allow dendrite-free Li deposition.

Figure 3. Li Plating/Stripping Behavior on Cu, Cu-MOF-30 min, and Cu-MOF-24 h Electrodes

(A) Nucleation overpotentials of Li on the Cu, Cu-MOF-30 min, and Cu-MOF-24 h electrodes at a current density of 0.5 mA cm
^-2.

(B) The typical Li plating/stripping profiles of the Cu-MOF-30 min electrode at a fixed plating capacity of 1 mAh cm
^-2 and a current density of 0.5 mA cm
^-2.

(C) The comparison of Coulombic efficiencies of Li plating/striping on the Cu, Cu-MOF-30 min, and Cu-MOF-24 h
electrodes with an areal capacity of 1.0 mAh cm
^-2 at a current density of 0.5 mA cm
^-2.
with dense morphology, facilitating the formation of stable SEI film and guaranteeing a stable electrode/electrolyte interface. The impedance decreases upon cycling when using Cu-MOF-30 min can be ascribed to the stabilization of the SEI in the early stage and its enabled dendrite-free and dense Li plating/stripping. The excellent interface stability of Cu-MOF-30 min is profiting for plating/stripping Li at a lower and stabilized voltage. The exchange current density can be calculated according to the below equation:

\[ j_0 = \frac{RT}{nF \Delta R_{ct}} \]  

(Equation 1)

where \( \Delta R_{ct} \) is the charge-transfer resistance at the electrode-electrolyte interface.

According to the \( \Delta R_{ct} \) values from Table S1, the \( j_0 \) for Cu, Cu-MOF-30 min, and Cu-MOF-24 h after 10 cycles is calculated to be 0.586, 0.635, and 0.165 mA cm\(^{-2}\). The higher \( j_0 \) for Cu-MOF-30 min means that the introduced homogeneous Cu-MOF layer can accelerate the charge transfer and ion diffusion processes, thus an enhanced Li plating/stripping kinetic.

**Electrochemical Testing of Li@Cu-MOF Electrode in Symmetric Cells**

To further verify the suppress ability of Li dendrite growth endowed by Cu-MOF modification layer, symmetric cells based on these three electrodes have been assembled. All the electrodes were preloaded with 2 mAh cm\(^{-2}\) of Li at a current density of 0.5 mA cm\(^{-2}\). Figure 4A displays the voltage versus time profiles of the Li@Cu-, Li@Cu-MOF-30 min-, and Li@Cu-MOF-24 h-based symmetric cells during repeated Li plating/stripping cycling. It can be observed that the Li@Cu-MOF-30 min-based symmetric cell exhibits a very stable overpotential around 13.1 mV and achieves an ultra-long lifespan over 2,500 h with no voltage fluctuation, manifesting that the Cu-MOF-30 min modification layer can effectively inhibit the growth of Li dendrites. In contrast, the Li@Cu-MOF-24 h-based symmetric cell can only realize 1,070 h of stable cycling, after which, the voltage hysteresis experiences a serious increase due to that the bulge structure of Cu-MOF-24 h leads to inhomogeneous distribution of Li ion, thus resulting in Li dendrite growth. For Cu-foil-based symmetric cell, the overpotential continuously increases with the progress of Li plating/stripping in the initial 623 h, and then there is sudden voltage drop and significant voltage fluctuation in the following cycles. The untimely failure of Li@Cu||Li@Cu symmetric cell is mainly due to the serious issues such as the
uncontrolled Li dendrite growth, aggravated adverse reactions, and formation of dead Li. To further verify the effectuality of Cu-MOF-30 min, the current density and cycling capacity are increased to 2 mA cm$^{-2}$ and 5 mAh cm$^{-2}$ (Figure S3A). It can be observed that the symmetric cell can realize 350 h stable cycling with low overpotential (~0.35 mV) and no obvious voltage fluctuation, demonstrating the effectiveness of the Cu-MOF-30 min in restraining the Li dendrite growth.

The rate performances of the three electrodes-based symmetric cells are estimated at diversified current densities from 0.2 to 5 mA cm$^{-2}$ with a constant areal capacity of 1 mAh cm$^{-2}$ (Figure 4B). The overpotential of Li@Cu-MOF-30 min-based cell increases steadily in spite of the continuous and rapid increase of current density. The average overpotentials are 7.1, 12.2, 17.3, 28.1, and 55.3 mV at current densities of 0.2, 0.5, 1, 2, and 5 mA cm$^{-2}$, separately. After suffering from the rapid change of current densities, the overpotential of 7.3 mV can still be regained by reducing the rate back to 0.2 mA cm$^{-2}$ and keeping this value without significant alteration after another 100 h of Li plating/stripping. By comparison, the Li@Cu-MOF-24 h-based cell can only be steadily cycled at current densities below 1 mA cm$^{-2}$ and displays larger overpotential and random voltage fluctuations at 2 mA cm$^{-2}$. This high current density makes the cell fall down and cannot return to its original state when reducing the current density to 0.2 mA cm$^{-2}$ again. The situation is even worse for Cu-foil-based cell. Just at a current density of 1 mA cm$^{-2}$, the overpotential of the cell increases rapidly and the voltage suffers serious rising and falling until the battery is short-circuited.

**Morphology Evolution of Li@Cu-MOF Electrode**

The morphology evolution of the Li@Cu, Li@Cu-MOF-30 min, and Li@Cu-MOF-24 electrodes after multiple cycles are explored by SEM images. As shown in Figure 5A, the Li metal on Cu foil cannot be completely stripped with the remnant of some branch type Li after the 10th stripping process. Although the Li metal on Cu-MOF-30 min and Cu-MOF-24 h electrodes is almost completely removed and no residual Li can be observed (Figures 5B and 5C), indicating that the Cu-MOF can facilitate the Li plating/stripping to be proceeded in a highly reversible manner. Moreover, the surface structures of Cu-MOF-30 min and Cu-MOF-24 h electrodes resemble well to their original states without any Li deposition/dissolution-induced morphology change, confirming the steadiness structure of the Cu-MOF, which can be further supported by the almost negligible change of the TCNQ$^-$ peak in the Fourier transform infrared (FT-IR) spectra before and after cycling (Figure S2C) (Ma et al., 2018). After 100 cycles at Li plating state, the surface of Li@Cu becomes porous with numerous fibrous Li dendrites (Figure 5D). This high surface area will excessively consume Li and electrolyte, resulting in low CEs. Even worse, the dendritic Li can be detached from the electrode, further deteriorating the battery performance or pierce the diaphragm, short-circuiting the cell. In contrast, the Li@Cu-MOF-30 min exhibits a compact surface composed of large-sized Li particles without forming any dendritic Li (Figure 5E). Although the surface structure of Li@Cu-MOF-24 h is much better than that of Li@Cu (Figure S4F), we can still observe Li dendrite growth in some areas, which can be ascribed to the non-uniformity of the Cu-MOF-24 h layer.

In order to further investigate the effect of the Cu-MOF modification layer on lithium deposition, the morphologies of the Cu foil, Cu-MOF-30 min, and Cu-MOF-24 h electrodes with different plating amounts of lithium have been studied. The SEM images of the Cu foil, Cu-MOF-30 min, and Cu-MOF-24 h deposited with 0.1, 0.2, and 0.5 mAh cm$^{-2}$ of Li are displayed in Figures S4G–S4O. Clearly, as the plating capacity increases, more and more Li particles with narrow size distribution are deposited on the surface of Cu-MOF-30 min (Figures S13J–S13L), indicating that the Cu-MOF-30 min can provide uniform Li nucleation sites and regulate dendrite-free Li deposition. The Li dendrite formation on Cu foil and non-uniform deposition on Cu-MOF-24 h demonstrate that both the Cu-MOF modification layer and its uniformity are indispensable for restraining the Li dendrite growth (Figures S4G–S4I and S4M–S4O).

**Assessment of Electrochemical Performance in Full Cells**

To probe the practical applications of the designed Cu-MOF-30 min current collector, full cells are assembled by pairing Li-loaded Cu-MOF-30 min anode with LiFePO$_4$ (LFP) cathode. Benefiting from the long-term cycling stability of the Li@Cu-MOF-30 min anode, the full cell can achieve a high capacity of 119.8 mAh g$^{-1}$ with a CE of 99.7% at 0.5 C after 100 cycles (a capacity retention of 85.1%, Figure 5A), which are much better than the corresponding values of the counterparts (109.5 and 100.8 mAh g$^{-1}$ with capacity reservations of 77.7% and 70.1% for Li@Cu-MOF-24 h- and Li@Cu-based full cells after 100 cycles). To further qualify the impact of the Li@Cu-MOF-30 min anode on the full cell performance, we have checked the cycling stability of the full cell at 1 C. It can be seen from Figure S3B that the full cell with Li@Cu-MOF-30 min
anode can maintain a high reversible capacity of 68.9 mAh g\(^{-1}\) even after 200 cycles (a capacity retention of 69.4%), higher than those of the values of the Li@Cu-based full cell (53.3 mAh g\(^{-1}\) with a capacity retention of 53.8% after 200 cycles). Because these cells use the same cathode and electrolyte, the performance discrepancy is mainly induced by the disparate properties of the anodes. The superior Li utilization of the Li@Cu-MOF-30 min-based full cell can be further supported by the typical charge-discharge profiles. As can be seen from Figure 5B, the Li@Cu-MOF-30 min-based full cell displays elevated electrochemical kinetics and reduced polarization, verified by the increased initial capacity and decreased voltage difference between the charge and discharge platforms (64, 77, and 150 mV for Li@Cu-MOF-30 min-, Li@Cu-MOF-24 h-, and Li@Cu-based cells). As the cycle progresses, the overpotentials of these three cells decrease but the one with Li@Cu-MOF-30 min anode still exhibits much better performance than the others (Figure 5C). The rate performance of the Li@Cu-MOF-30 min||LFP cell is shown in Figure 5D, which can deliver average specific discharge capacities of 148.2, 129.9, 110.1, and 74.2 mAh g\(^{-1}\) at rates of 0.1, 0.2, 0.5, and 1 C, separately. When the current densities return to 0.5, 0.2, and 0.1 C, discharge capacities of 107.7, 118.6, and 129.8 mAh g\(^{-1}\) can be achieved, which almost recover to the original values, verifying the excellent rate capability of the Li@Cu-MOF-30 min||LFP cell. The corresponding charge-discharge curves at different rates further confirm this (Figure 5E). The superior cycling and rate capability of the Li@Cu-MOF-30 min-based full cell proves that the outstanding cycling and rate performance of the Li@Cu-MOF-30 min anode can be finely maintained in the full cells.

The Universality and Effectiveness of the Synthesis Method
Apart from TCNQ methanol solution, uniform Cu-MOF modification layer can also be in situ formed in TCNQ ethanol, n-butanol, and diethyl ether solutions by controlling the reaction time (Figures S5A–S5H), demonstrating the universality of the synthesis method. Moreover, no matter in which solution Cu-MOF is formed, they all can realize dendrite-free Li deposition, thus achieving splendid CEs (>97%) and long-term cycling stability (>2000 h, Figures S5I–S5N).

Figure 5. Electrochemical Performance of Full Cells
(A) Cycling performance of the Li@Cu||LFP, Li@Cu-MOF-30 min||LFP, and Li@Cu-MOF-24 h||LFP full cells at 0.5 C and the Coulombic efficiencies of the Li@Cu-MOF-30 min||LFP cell.
(B and C) The corresponding voltage profiles of these three cells at 1th cycle (B) and 100th cycle (C).
(D) Rate capability of the Li@Cu-MOF-30 min||LFP cell.
(E) Voltage profiles of the Li@Cu-MOF-30 min||LFP cell at different rates.
The successful conquer of the critical issue of uncontrolled Li dendrite formation during repetitive Li plating/stripping by introducing uniform Cu-TCNQ MOF modification layer on Cu foil can be attributed to its unique advantages: (1) in situ grown on Cu foil, avoiding complex electrode preparation process and volume change induced peeling off from Cu foil; (2) high conductivity (Fang et al., 2017), making Li directly deposit on its surface without the requirement of passing thought the Cu-MOF layer, decreasing the interface impedance; (3) abundant surface functional groups, providing homogeneous nucleation sites for dendrite-free Li deposition; (4) large surface area, promoting the uniform distribution of Li ion flux and dissipating the high current density to small local current; (5) super high affinity to electrolyte, facilitating the diffusion process of Li ion. All these merits make the lithiophilic Cu-MOF thin layer behave as an effective current collector to realize dendrite-free Li plating/stripping (Figure 1), solving the long-lasting issue of uncontrolled Li dendrite growth for Li anode in a facile, economical, and applicable method.

Conclusions
In summary, a multifunctional lithiophilic Cu-MOF thin modification layer has been in situ introduced on the surface of Cu foil by a facile immersion strategy to overcome the long-lasting dendrite growth issue of Li metal anode. During Li plating process, the designed Cu-MOF layer can behave as an effective regulator to allow dendrite-free Li deposition with the help of its abundant polar surface functional groups, superior affinity with electrolyte, and high conductivity. Simultaneously, its unique porous structure with appropriate specific surface area can effectively reduce the high current density to small local current and alleviate the volume change induced by Li deposition/dissolution. Benefiting from these advantages, the Cu-MOF-layer-modified Cu foil permits Li plating/stripping in a highly reversible manner, thus achieving superior CEs (above 97.1%) and outstanding long-term cycling stability (over 2,500 h at 1 mA h cm$^{-2}$ and 0.5 mA cm$^{-2}$). In addition, the full cells by pairing the finite Li-loaded Cu-MOF anode with LFP cathode deliver excellent electrochemical performances, portending the practical application possibility of the newly designed current collector. It is also very appealing that the synthesis method can be easily mass-produced and extended to a series of organic solvents. This strategy manifests a promising way of using multifarious MOFs materials to design high-performance metal-based anodes.

Limitations of the Study
In this work, we demonstrated a lithiophilic Cu-metal-organic framework thin layer (Cu-MOF TL)-modified Cu foil for achieving dendrite-free Li metal anode. However, the influence of the coating thickness on inhibition of Li dendrite growth should be further explored. In situ characterization (in situ XRD/Raman/SEM, etc.) on the interface of Li/functional current collector should be explored to further explain the mechanism.

Resource Availability
Lead Contact
Further information and requests for resources and reagents should be directed to the Lead Contact, Gang Huang (ghuang@ciac.ac.cn).

Materials Availability
This study did not generate new unique reagents.

Data and Code Availability
This study did not generate any datasets.

METHODS
All methods can be found in the accompanying Transparent Methods supplemental file.

SUPPLEMENTAL INFORMATION
Supplemental Information can be found online at https://doi.org/10.1016/j.isci.2020.101869.

ACKNOWLEDGMENTS
This work is supported by the National Key R&D Program of China (Grant No. 2017YFE0198100), the National Natural Science Foundation of China (Grant No. 21975250), the Major Projects of Baotou Rare Earth
Research and Development Center, Chinese Academy of Sciences (Grant No. ZK2017H1970), and the Scientific and Technological Developing Project of Jilin Province (Grant No. 2018020109BGX).

AUTHOR CONTRIBUTIONS
L.W., Y.C., and G.H. designed the research idea and experiments. D.Y., Z.W., and Q.L. together completed related experiments, and H.X. was responsible for the SEM characterization. D.Y. and G.H. wrote the paper.

DECLARATION OF INTERESTS
The authors declare no competing interests.

Received: May 25, 2020
Revised: October 26, 2020
Accepted: November 23, 2020
Published: December 18, 2020

REFERENCES


Supplemental Information

In Situ Growth of Lithiophilic MOF Layer
Enabling Dendrite-free Lithium Deposition

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This supplemental file includes:

- Transparent Methods
- Supplemental Figures S1 to S5 and Table S1

The sequence is the same as they are mentioned in the main text.
Transparent Methods

Raw Materials. 7,7,8,8-Tetracyanoquinodimethane (TCNQ) was obtained from Aladdin Chemical Co., Ltd. Methanol, ethanol, diethyl ether, n-butanol, acetone and hydrochloric acid were supplied by Beijing Chemical Works. Copper foil was purchased from Hefei Kejing Materials Technology Co., Ltd. All reagents were analytical purity and used without further purification.

In situ synthesis of Cu-MOF layer on Cu foil. The preparation of Cu-MOF thin coating layer was as follows. First, Cu foils with a size of 4 cm×4 cm were flattened by a roller press machine and followed by dipping in 1 M HCl and acetone solution for 10 min, respectively, to remove adsorbed dust and surface impurities. Then, the N₂ dried Cu foils were quickly immersed in 0.05 mg ml⁻¹ TCNQ methanol solution at room temperature for 30 min (marked as Cu-MOF-30 min) and 24 h (marked as Cu-MOF-24 h). After this, the Cu foils with Cu-MOF coating layers were taken out of the solution, rinsed with methanol for several times and dried with N₂. The Cu-MOF coating layer could also be synthesized in TCNQ ethanol, n-butanol, diethyl ether solutions following the above procedures (denoted as Cu-MOF/E, Cu-MOF/B and Cu-MOF/D, separately).

Materials Characterization. The X-ray diffraction (XRD) measurements were performed on a Bruker D8 Focus power X-ray diffractometer using Cu radiation. The scanning electron microscope (SEM) images were obtained on a Hitachi S-4800 field emission instrument. The BET surface area and pore size distribution were tested by a Micromeritics ASAP 2010 instrument. Since the Cu-MOF coating layer is not easy to be scraped off from Cu foil, the integrated current collector is directly cut into small pieces for testing. The contact angle was tested by a contact angle measuring device (DSA-100). The Fourier transform infrared (FT-IR) spectra was operated with VERTEX 70.

Electrochemical measurements. CR2025 type coin cells were assembled to appraise the lithium deposition behaviors of the as-prepared current collectors. The Cu foils with and without Cu-MOF modification were punched into disks and used as the working electrode. Metallic lithium foil was used as the counter electrode and Celgard 2400 microporous membrane was employed as the separator. The electrolyte was 100 μL with 1 M lithium bis
(trifluoromethane sulfonyl) imide (LiTFSI) in a mixed solvent of 1,3-dioxolane (DOL) and dimethoxyethane (DME) (1:1 v/v) with 0.1 M lithium nitrate (LiNO₃). The electrochemistry performance was tested with a LAND CT2001A multi-channel battery testing system at room temperature. First, the batteries were cycled at 50 μA between 0.01-1.00 V for five cycles to form stable SEI films. Afterward, a certain amount of metallic lithium was deposited on Cu-MOF and Cu current collectors. The Coulombic efficiencies of each cell were tested by first depositing 1 mAh cm⁻² of Li onto the prepared current collectors at a current density of 0.5 mA cm⁻² and then stripping the Li metal until the potential up to 0.5 V. For the cycling stability test, the Li@Cu-MOF (Li@Cu) electrodes with pre-stored Li were assembled into symmetrical cells and charged-discharged at a constant current density. The electrochemical impedance spectra (EIS) measurement was conducted on a BioLogic VMP3 electrochemical workstation.

The full cells were assembled by using Li@Cu-MOF (Li@Cu) with a Li loading amount of 2 mAh cm⁻² as anode, LiFePO₄ (LFP) as cathode, 1 M lithium bis (trifluoromethane sulfonyl) imide (LiTFSI) dissolved in a mixed solvent of 1,3-dioxolane (DOL) and dimethoxyethane (DME) (1:1 v/v) with 0.1 M lithium nitrate (LiNO₃) as electrolyte and Celgard 2400 microporous membrane as separator. The electrolyte amount was 100 μL. The LFP cathodes were prepared by mixing commercial LFP, carbon black and poly(vinylidene difluoride) in a mass ratio of 8:1:1 in N-methyl-2-pyrrolidone. The resulting slurry was then coated on an Al foil and dried at 60 °C under vacuum overnight. The cathode was punched into 12 mm disks and the mass loading of LFP was ~7 mg cm⁻², making the negative to positive electrode capacity ratio is 1.89. Galvanostatic discharge/charge tests were performed on a LAND CT2001A multi-channel battery testing system at room temperature. All the current densities and specific capacities were calculated based on the active mass of cathodes.
Figure S1. Schematic illustration and characterization of Cu-MOF. Related to Figure 1 and 2.
(A) Schematic illustration for the in situ growth of Cu-MOF thick layer on Cu foil by extending the reaction time and its effect on lithium deposition.
(B) XRD pattern of the Cu-MOF-24 h.
(C, D) \( \text{N}_2 \) adsorption-desorption isotherms of Cu-MOF-30 min (C) and Cu-MOF-24 h (D).
(E-G) Contact angle measurement of Cu (E), Cu-MOF-30 min (F) and Cu-MOF-24 h (G). The inset images in Figure S1C-D are the Pore size distribution curves of Cu-MOF-30 min and Cu-MOF-24 h.
Figure S2. The tailor effect of Cu-MOF and the electrochemical performance of electrodes. Related to Figure 3.

(A) Raman spectra of Cu-MOF-30 min electrode before and after immersing into the electrolyte.

(B, C) FT-IR spectra of Cu-MOF-30 min before and after immersing into the electrolyte (B), before and after plating/stripping of Li for 10 and 100 cycles (C).

(D) Nyquist plots of Li || Li@Cu, Li || Li@Cu-MOF-30 min and Li || Li@Cu-MOF-24 h cells before and after 10 and 100 cycles of Li plating/striping processes.

(E, F) Typical Li plating/stripping profiles of Cu foil electrodes at a fixed plating capacity of 1 mAh cm\(^{-2}\) and a current density of 0.5 mA cm\(^{-2}\).

(G, H) Typical Li plating/stripping profiles of Cu-MOF-24 h electrodes at a fixed plating capacity of 1 mAh cm\(^{-2}\) and a current density of 0.5 mA cm\(^{-2}\).
Table S1. Fitting results for the Nyquist plots of Li || Li@Cu, Li || Li@Cu-MOF-30 min and Li || Li@Cu-MOF-24 h cells. Related to Figure 3.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$R_c(\Omega)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>68.33</td>
</tr>
<tr>
<td>Cu 10th</td>
<td>38.77</td>
</tr>
<tr>
<td>Cu 100th</td>
<td>4.73</td>
</tr>
<tr>
<td>Cu-MOF-30 min</td>
<td>66.31</td>
</tr>
<tr>
<td>Cu-MOF-30 min 10th</td>
<td>35.83</td>
</tr>
<tr>
<td>Cu-MOF-30 min 100th</td>
<td>37.39</td>
</tr>
<tr>
<td>Cu-MOF-24 h</td>
<td>95.42</td>
</tr>
<tr>
<td>Cu-MOF-24 h 10th</td>
<td>137.40</td>
</tr>
<tr>
<td>Cu-MOF-24 h 100th</td>
<td>137.83</td>
</tr>
</tbody>
</table>
Figure S3. Long-term cycling performance of Li@Cu-MOF-30 min. Related to Figure 4 and 5.

(A) Long-term cycling performance of Li@Cu-MOF-30 min based symmetric cell at a cycling capacity of 5 mAh cm\(^{-2}\) and a current density of 2 mA cm\(^{-2}\).

(B) Cycling performance of the Li@Cu || LFP and Li@Cu-MOF-30 min || LFP full cells at 1 C and the Coulombic efficiencies of the Li@Cu-MOF-30 min || LFP cell.
Figure S4. Morphology evolution of Cu and Cu-MOF electrodes. Related to Figure 3 and 4.

(A-C) SEM images of Cu (A), Cu-MOF-30 (B) and Cu-MOF-24 h (C) electrodes after 10 cycles at Li stripping state.

(D-F) SEM images of Cu (D), Cu-MOF-30 (E) and Cu-MOF-24 h (F) electrodes after 100 cycles at Li plating state.

(G-I) SEM images of Li plating on Cu with areal capacities of 0.1 (G), 0.2 (H) and 0.5 (I) mAh cm⁻².

(J-L) SEM images of Li plating on Cu-MOF-30 min with areal capacities of 0.1 (J), 0.2 (K) and 0.5 (L) mAh cm⁻².
(M-O) SEM images of Li plating on Cu-MOF-24 h electrodes with areal capacities of 0.1 (M), 0.2 (N) and 0.5 (O) mAh cm$^2$. 
Figure S5. The characterization of Cu-MOF formed at different solvents. Related to Figure 2-4.

(A) Digital photos of Cu-MOF coated Cu foils formed at different solvents and their corresponding digital photos after deposition of Li metal.
(B) XRD patterns of Cu-MOF formed at different solvents.
(C-E) SEM images of Cu-MOF TL formed at ethanol (C), n-butanol (D) and diethyl ether (E) solvents for 30 min.
(F-H) SEM images of Cu-MOF/E (F), Cu-MOF/B (G) and Cu-MOF/D (H) deposited with 2.0 mAh cm\(^{-2}\) of Li at a current density of 0.5 mA cm\(^{-2}\).
(I-K) Coulombic efficiencies of Li plating/stripping on Cu-MOF/E (I), Cu-MOF/B (J) and Cu-MOF/D (K) electrodes.
(L-N) Long-term cycling performances of Li@Cu-MOF/E (L), Li@Cu-MOF/B (M) and Li@Cu-MOF/D (N) symmetric cells.

The inset images in Figure S5C-H are the high magnification SEM photos of Cu-MOF/E, Li@Cu-MOF/B and Li@Cu-MOF/D and the cross-sectional images of Li@Cu-MOF/E, Li@Cu-MOF/B and Li@Cu-MOF/D electrodes.