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Post metalation of solvothermally grown electroactive porphyrin metal-organic framework thin films[†]

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Uniform thin films of a metal-organic framework, which is constructed from free-base porphyrin linkers and hexa-zirconium nodes (MOF-525), are solvothermally grown on conducting substrates. Subsequently, solvothermal post metalations are employed to prepare the Zn-MOF-525 and Co-MOF-525 thin films. All the thin films are electroactive in aqueous media.

Metal–organic frameworks (MOFs) are a class of three-dimensional (3D) porous materials constructed of organic linkers and metalbased nodes.^{1,2} Due to their ultrahigh surface area,³ regular nanostructured pores, tunable pore size, and high permanent porosity,⁴ MOFs have been widely applied for several applications, including gas storage,⁵ separation,⁶ chemical sensing,⁷ and catalysis.^{8,9} Owing to the high surface area feature of MOFs, electrocatalysis can be an attractive potential application for MOFs. However, compared to the other applications mentioned above, utilizing MOFs for electrochemical applications is a relatively new research field¹⁰ with only a few studies having reported the use of MOFs for electrocatalysis.^{11–15}

Due to their structural flexibility and unique electronic and optical properties, porphyrins and metalloporphyrins have been applied for various applications such as solar cells, organic electronics, and catalytic systems.^{16,17} Both the free-base porphyrins and metalloporphyrins are redox active.^{18–20} Thus, electrodes modified with the molecules of free-base porphyrins or metalloporphyrins have been utilized for various electrocatalytic applications, including oxygen reduction,²¹ CO₂ reduction,²² and L-tyrosine oxidation.²³ Various kinds of MOFs constructed from porphyrin-based linkers have been synthesized previously.^{24–26} In order to apply such porphyrin MOFs for electrocatalysis, a porphyrin MOF thin film

must be grown on a conducting substrate. Recently MOF thin films have been prepared by several methods, such as microwave-induced thermal deposition,²⁷ dip coating,²⁸ electrochemical deposition,²⁹⁻³² electrophoretic deposition,³³ layer-by-layer deposition,³⁴ and solvo-thermal method.^{35,36} Specifically, porphyrin MOF thin films have been prepared by layer-by-layer³⁷ and Langmuir–Blodgett methods,³⁸ but are still rare.

Recently and for the first time, Morris *et al.* utilized a solvothermal approach to grow porphyrin MOF thin films on conducting glass substrates.³⁹ *meso*-Tetra(4-carboxyphenyl)porphine (H₄TCPP) was used as the linker, and the cobalt-based cluster was served as the node. Since the porphyrin center of TCPP could also be metalated with cobalt simultaneously during the MOF growth, thin films of a MOF constructed by Co(m)TCPP and Co(n)-based nodes were obtained. The electrochemistry of the obtained MOF thin film in organic media was investigated. Due to the self-metalation of TCPP linkers during the MOF synthesis, the porphyrinic linkers and the MOF metal nodes have the same redox active metal in such MOF thin films.

In this study, a solvothermal method was utilized to grow MOF thin films on conducting glass substrates; the MOF is constructed from TCPP linkers and hexa-zirconium nodes (MOF-525, see Scheme 1). Since the porphyrin center cannot be metalated with Zr during the synthesis of the MOF, the obtained MOF-525 thin film is expected to act as a platform for the post metalation of its linkers with any desired metal. The characterization and post metalation of the MOF-525 microcrystalline powder have been reported previously,40 however, to date there are no studies reporting either MOF-525 thin films or the post metalations of any Zr-based porphyrin MOF film. In this study, Zn(II) and Co(III) were selected for post metalation. The obtained thin films before and after post metalation were found to be electrochemically addressable in aqueous media, which opens up several opportunities for utilizing the solvothermally grown MOF thin films for the electrocatalysis involving porphyrinic or various metalloporphyrinic units.

MOF-525 thin films (Fig. S1(a), ESI[†]) were grown on fluorinedoped tin oxide (FTO) conducting glass substrates by a solvothermal



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Scheme 1 MOF-525 crystal structure and schematic representation of its solvothermally grown thin film. For simplicity hydrogen atoms are not shown.

approach (experimental details are included in the ESI[†]). The X-ray diffraction (XRD) pattern of the MOF-525 powder obtained during the growth of thin film is shown in Fig. 1(a) (pattern (ii)). Diffraction peaks at 4.5° , 6.4° , 7.8° , and 9.1° can be observed in the pattern of the MOF-525 powder; all of these peaks agree well with the simulated XRD pattern of MOF-525 reported previously (pattern (i) in Fig. 1(a)).⁴⁰ The XRD pattern of the MOF-525 thin film shown in pattern (iii) in Fig. 1(a) is consistent with that of the MOF-525 powder, indicating that the obtained thin film is composed of crystalline MOF-525. The nitrogen adsorption-desorption isotherm of the MOF-525 powder was also measured, as shown in Fig. 1(b), from which a Brunauer-Emmett-Teller (BET) surface area was calculated to be 2415 $m^2 g^{-1}$. This value is in agreement with the value previously reported by Morris et al.40 Additionally, the pore size distribution of the MOF-525 powder was estimated by using the density functional theory (DFT) method. As shown in the inset of Fig. 1(b), the material possesses a pore size of 1.8 nm, which is in excellent agreement with the cage size appearing in the MOF-525 crystal structure.



Fig. 1 (a) XRD patterns of (i) simulated MOF-525 reported by Morris et al.,⁴⁰ (ii) MOF-525 powder, (iii) MOF-525 thin film, (iv) Zn-MOF-525 thin film, and (v) Co-MOF-525 thin film. (b) The nitrogen adsorption-desorption isotherm of the MOF-525 powder; inset shows the DFT pore size distribution of the MOF-525 powder.



Fig. 2 SEM images of MOF-525 thin films at (a) high magnification, (b) medium magnification, and (c) low magnification. (d) Cross-section SEM image of the MOF-525 thin film. SEM images of (e) the Zn-MOF-525 thin film and (f) the Co-MOF-525 thin film.

Scanning electron microscopy (SEM) images were used to investigate the morphologies of the obtained MOF-525 thin films and powder. Fig. 2(a) to (c) show the SEM images of the obtained MOF-525 thin films at high, medium, and low magnifications, respectively. It can be observed that several cubic crystals, with the size ranging from 500 to 1000 nm, were directly grown on the FTO substrate (Fig. 2(a)). The observed cubic morphology is consistent with the morphology of the MOF-525 powder reported previously.40 These cubic crystals embed into each other to bring about the MOF-525 thin film on the substrate with high coverage (Fig. 2(b)). Fig. 2(c) reveals the morphology of the MOF-525 thin film in a larger region, which shows that the cubic crystals of MOF-525 were uniformly grown on the FTO substrate. The cross-sectional SEM image of the MOF-525 thin film reveals a nice adhesion between those cubic crystals and the FTO layer (Fig. 2(d)). The film thickness is approximately consistent with the size of the cubic crystals. The SEM image of the MOF-525 powder, obtained during the growth of thin film, is also shown in Fig. S2 (ESI⁺), and it also shows cubic crystals as expected. According to the XRD patterns, SEM images, and nitrogen adsorption-desorption isotherm (from powder only), one can conclude that both, powder and thin films, are composed of MOF-525.

After confirming that the solvothermally grown thin films were composed of MOF-525, post metalations of the obtained films were conducted to prepare the Zn-MOF-525 and Co-MOF-525 thin films (Fig. S1(b) and (c); see experimental details in ESI†). Both the XRD patterns (patterns (iv) and (v) in Fig. 1(a)) and SEM images (Fig. 2(e) and (f)) suggest that the crystallinity and morphology of the MOF-525 thin films are preserved after the metalations. Energy dispersive X-ray spectroscopy (EDS) suggests that the distribution of Zn or Co is uniform across the cubic crystals of the metalated MOF-525 thin film with a high degree of metalation (see Fig. S3 and S4, and detailed discussion in ESI†).

UV-visible spectra of the NaOH solutions containing the digested MOF-525, Zn-MOF-525, and Co-MOF-525 thin films are shown in Fig. 3 with the enlarged Q-band region shown in the inset. For the digested MOF-525 thin film, a typical Soret



Fig. 3 UV-visible spectra of the digested MOF-525, Zn-MOF-525, and Co-MOF-525 thin films in 1.0 M NaOH aqueous solutions. Inset: enlarged spectra in the Q-band region.

band at 413 nm and four Q bands located between 500 and 700 nm can be clearly observed (Fig. 3); this spectrum is consistent with the reported UV-visible spectrum of free-base TCPP.42,43 The four Q bands observed in the spectrum also confirm that the porphyrinic units in the MOF-525 thin film are free-base TCPP instead of zirconium(IV) porphyrin complexes.^{44–46} The UV-visible spectrum of the digested Zn-MOF-525 thin film shows a Soret band at 427 nm along with three Q bands, which consist of the strongest one at 565 nm, a medium one at 605 nm, and a weak one at 520 nm. This spectrum agrees well with the UV-visible spectrum of ZnTCPP reported previously,43,47 confirming that all the TCPP units in the Zn-MOF-525 thin film were metalated successfully. For the digested Co-MOF-525 thin film, a Soret band located at 430 nm and two Q bands located at 550 nm and 590 nm can be observed in Fig. 3. This spectrum agrees with the characteristic spectrum of Co(m)TCPP leaving a chloride group on the Co(m) center,⁴⁸ supporting the conclusion that a high degree of metalation of the MOF-525 thin film with Co(III) was achieved.

Since it is known that Zr-based MOFs possess excellent stability in water under neutral and acidic conditions,^{49,50} the MOF-525 and metalated MOF-525 thin films grown on conducting substrates are expected to be suitable for electrochemical applications in aqueous solutions. To investigate the electrochemical properties of the MOF films in aqueous media, cyclic voltammetric (CV) curves of the MOF-525, Zn-MOF-525, and Co-MOF-525 thin films were obtained in 0.1 M KCl solution (Fig. 4). A broad redox hump can be observed at around 0.8 V vs. Ag/AgCl/KCl (sat'd) in the CV curve of the MOF-525 thin film, which may correspond to the redox reaction of the free-base TCPP linkers in the MOF thin film. For the Co-MOF-525 thin film, a much larger redox hump can be observed at 0.8 V, which corresponds to the redox reaction of Co(III)TCPP; this observation indicates that the redox activity of the MOF-525 thin film could be further improved by the post metalation of Co(m). A much higher redox signal at a lower potential of around 0.7 V can be observed in the CV curve of the Zn-MOF-525 thin film. This result suggests that the redox



Fig. 4 $\,$ CV curves of the MOF-525, Zn-MOF-525, and Co-MOF-525 thin films, measured in 0.1 M KCl aqueous solution at a scan rate of 25 mV s $^{-1}$.

reaction of ZnTCPP in the MOF-525 thin film possesses a higher redox activity than the free-base TCPP and Co(III)TCPP. Significant redox signals appear in all the three CV curves, suggesting that the porphyrinic units in all the MOF-525, Zn-MOF-525, and Co-MOF-525 thin films are electrochemically addressable in aqueous solution. Charge can be transferred by hopping through the repeating redox active units in MOF thin films, rendering the MOF thin films to become electroactive.^{39,41,51} The broad redox humps appearing in all CV curves may be attributed to the sluggish diffusion of ions through the small pores of MOF-525; this drawback may be improved by designing the thin films of porphyrin MOFs which possess larger pore sizes. The MOF-525 thin film shows promising electrochemical stability in the KCl aqueous solution (see Fig. S5 and detailed discussion in ESI[†]), which opens up the opportunities for utilizing it in various electrochemical applications in aqueous media.

In order to explore the reason for the difference in redox activity of the MOF-525 and metalated MOF-525 thin films, chronoamperometric experiments were conducted (Fig. S6, ESI†). It can be found that the apparent diffusion coefficient (D_{app}) of the Zn-MOF-525 thin film is higher than that of the Co-MOF-525 thin film, and the Co-MOF-525 thin film attains a higher D_{app} than the MOF-525 thin film; this tendency agrees well with the CV signals. This tendency indicates that the Zn-MOF-525 thin film provides either faster charge hopping or faster ion diffusion compared to the Co-MOF-525 and MOF-525 thin films, which may be the reason for its much higher redox signal compared to those of the Co-MOF-525 and MOF-525 thin films in the CV curves (see Fig. S6 and its detailed discussion in the ESI†).

In summary, a thin film of a Zr-based porphyrin MOF (MOF-525) was grown on a conducting glass electrode *via* a solvothermal approach. The obtained thin film is composed of uniformly distributed cubic crystals of MOF-525 with size ranging from 500 to 1000 nm. Both cobalt and zinc could be uniformly post-metalated on the free-base TCPP linkers of MOF-525 thin films. All the MOF-525, Zn-MOF-525, and Co-MOF-525 thin films are electrochemically addressable in

aqueous solution. The result implies that the obtained MOF-525 thin films may be further applied for several potential electrocatalytic applications involving porphyrinic or various metalloporphyrinic units. Ongoing work is underway to utilize these MOF-525 thin films for various electrocatalytic applications in aqueous media.

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