

Insights into the Use of Metal–Organic Framework As High-Performance Anticorrosion Coatings

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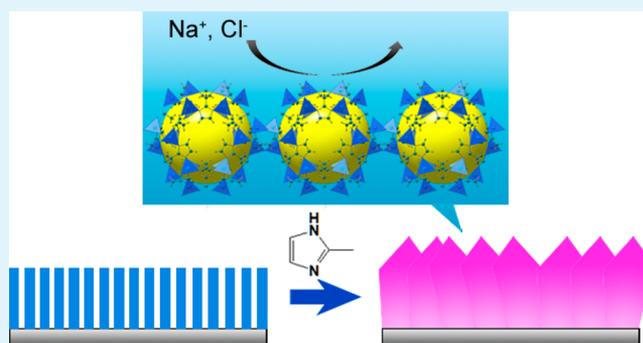
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Supporting Information

ABSTRACT: Metal–organic frameworks (MOFs) have shown great potential in gas storage and separation, energy storage and conversion, vapor sensing, and catalysis. Nevertheless, rare attention has been paid to their anticorrosion performances. At present, substantial hydrophobic and water stable MOFs (like ZIF-8), which are potentially favorable for their applications in anticorrosion industry, have been successfully designed and prepared. In this study, a facile ligand-assisted conversion strategy was employed to fully convert ZnAl-CO₃ layered double hydroxide (LDH) precursor buffer layers to well intergrown ZIF-8 coatings. DC Polarization tests indicated that prepared ZIF-8 coatings showed the corrosive current 4 orders of magnitude lower than that of bare Al substrates, demonstrating that MOF materials were superb candidates for high-performance anticorrosion coatings.

KEYWORDS: metal–organic framework, layered double hydroxide, anticorrosion, zeolitic-imidazole framework, thin film



Metal–organic frameworks (MOFs) as a new class of crystalline porous materials are composed of metal ions or metal oxide clusters coordinated by organic linkers to form highly regular porous network.^{1,2} Since pioneering works in the 1990s, MOF materials have shown unprecedented opportunities for a wide range of applications.^{3–20} Nevertheless, at present rare reports have been focused on investigating anticorrosion performances of MOFs except dopamine-grafted-MOF-5²¹ and [ZnC₁₂C₁₆].²² Since chromate and phosphate-based conversion coatings, which have historically been evaluated as an effective anticorrosion method for metallic substrates, are currently restricted because of their toxic and carcinogenic properties,^{23–26} new materials potentially competent to anticorrosion applications in industry have to be developed. At present, diverse hydrophobic and water stable MOFs (like ZIF-8,²⁷ MIL-53,²⁸ and UiO-66²⁹), which are prerequisites for potential applications in anticorrosion industry, have been designed and synthesized so that the range of candidates potentially appropriate for anticorrosion applications can be greatly expanded. Moreover, since most MOF materials have high affinity interactions with both inorganic and organic compounds, they can easily form MOF-polymer/inorganic composite anticorrosion coatings so that their anticorrosion performance may be further strengthened. Herein we take an initiative to investigate the potential application of ZIF-8,²⁷ one of the most widely studied hydrophobic and water stable MOFs, in the anticorrosion industry.

As a representative of inorganic layered compounds, layered double hydroxide (LDH) coatings have provided a cost-effective and eco-friendly way to protect metal plates (like Mg, Al, Zn and their respective alloys) against corrosion.^{30–33} Moreover, as indicated by previous studies, MOFs and LDHs have shown very strong affinity interactions. For instance, our recent research demonstrated that introduction of ZnAl LDH buffer layers could serve as not only heterogeneous nucleation center³⁴ but also single metal source of H₂ selective ZIF-8 membranes.^{35,36} Inspired by the previous research, herein we proposed to prepare ZIF-8-based anticorrosion coatings by solvothermal treatment of ZnAl-CO₃ LDH precursor buffer layers with 2-methylimidazole (2-mIm). Employment of ZnAl-CO₃ LDH precursor buffer layers had following advantages: (1) ZnAl-CO₃ LDH buffer layers enabled significant promotion of nucleation and growth of ZIF-8 coatings on Al substrates. For comparison, we also tried in situ growth of ZIF-8 coatings on bare Al substrates. Nevertheless, ZIF-8 crystals were rarely attached to substrates (SI-1); (2) prepared ZIF-8 coatings maintained higher binding strength with Al substrates; (3) with this method, metal ions present in MOF coatings and metal substrates were not necessarily identical so that the scope of MOF materials potentially appropriate for anticorrosion protection of metal substrates could be greatly expanded.

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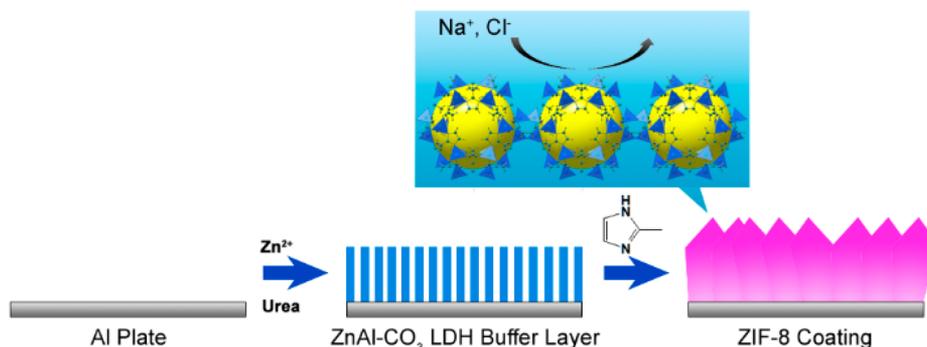


Figure 1. Schematic illustration of synthesis of ZIF-8 coatings on Al plates by partial conversion of ZnAl-CO₃ LDH precursor buffer layers under solvothermal conditions.

Experimental details could be found in the experimental section (SI-2). Briefly, ZnAl-CO₃ LDH buffer layers were prepared by vertically immersing Al plates in an aqueous precursor solution containing Zn(NO₃)₂·6H₂O and urea. Consequently, the precursor solution was sealed and put into the convective oven. Under controlled hydrothermal conditions, surface of the Al plate was partially reduced and Al³⁺ was released to the precursor solution; while urea was spontaneously hydrolyzed to NH₃ and CO₂. Owing to the excessive release of NH₃, an alkaline medium favorable for in situ nucleation and growth of ZnAl-CO₃ LDH buffer layers was formed. Simultaneously CO₂ was converted to CO₃²⁻ and preferentially intercalated into the interlayer gallery of LDH buffer layers.³⁷ In the next step, prepared ZnAl-CO₃ LDH buffer layers were subject to solvothermal treatment in a methanol solution containing 2-mIm, which not only served as organic linkers of ZIF-8 but also promoted dissolution of the ZnAl-CO₃ LDH buffer layers so that Zn²⁺ ions were evenly released to the bulk solution. Finally, Zn²⁺ ions were coordinated with 2-mIm at the solution–plate interface, thereby leading to the formation of well intergrown ZIF-8 coatings (schematically shown in Figure 1). Finally, prepared ZIF-8 coatings were subjected to the DC polarization test for quantitative evaluation of their anticorrosion properties.

First influence of synthetic temperature and chemical composition of the precursor solution on final microstructure of ZnAl-CO₃ LDH buffer layers was investigated. Experimental results indicated that prepared ZnAl-CO₃ LDH buffer layers showed considerable uniformity, compactness as well as aspect ratio under optimized reaction conditions; otherwise, some side effects, like generation large intercrystal voids and undesired impure phase, would appear (SI-3).

Prepared ZnAl-CO₃ LDH buffer layers were then subjected to SEM and XRD characterization. As shown in Figure 2a, after facile in situ hydrothermal growth, the surface of Al plates had been uniformly covered with close-packed platelike LDH crystals with grain size around 2 μm. Moreover, most LDH crystals were vertically aligned on substrates, which could be interpreted by “selective evolution” mechanism, as had been discussed in our previous results.³⁸ XRD pattern further demonstrated that prepared buffer layers indeed belonged to LDH phase with the 2θ degree around 11.6°, indicating a gallery height of 0.76 nm characteristic of carbonate intercalated LDHs (Figure 3b).^{39,40} Cross-sectional image further demonstrated that prepared ZnAl-CO₃ LDH buffer layers were highly uniform with the thickness around 5 μm (Figure 2b).

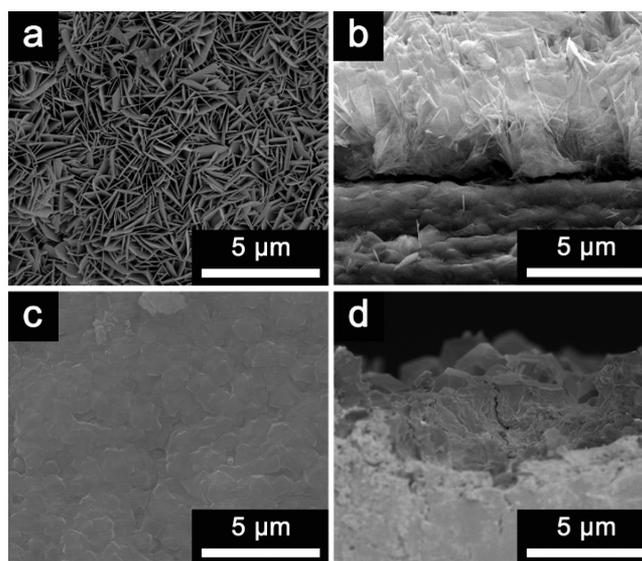


Figure 2. (a) Top and (b) cross-sectional views of ZnAl-CO₃ LDH buffer layers prepared by in situ hydrothermal growth; (c) top and (d) cross-sectional views of ZIF-8 coatings prepared by ligand-assisted solvothermal conversion of ZnAl-CO₃ LDH precursor buffer layers at 140 °C for 24 h (experimental details are shown in SI-2, and photographs of prepared samples are shown in SI-4).

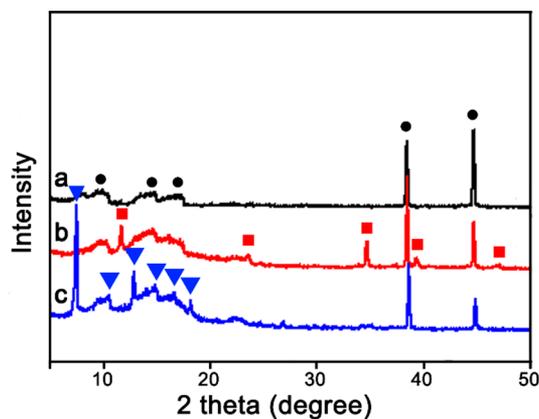


Figure 3. X-ray diffraction peaks from (a) bare Al substrates (denoted by black circles), (b) ZnAl LDH buffer layers prepared by in situ hydrothermal growth (denoted by red cubes) and (c) ZIF-8 coatings prepared by ligand-assisted conversion of ZnAl-CO₃ LDH precursor buffer layers under controlled solvothermal conditions (denoted by blue triangles).

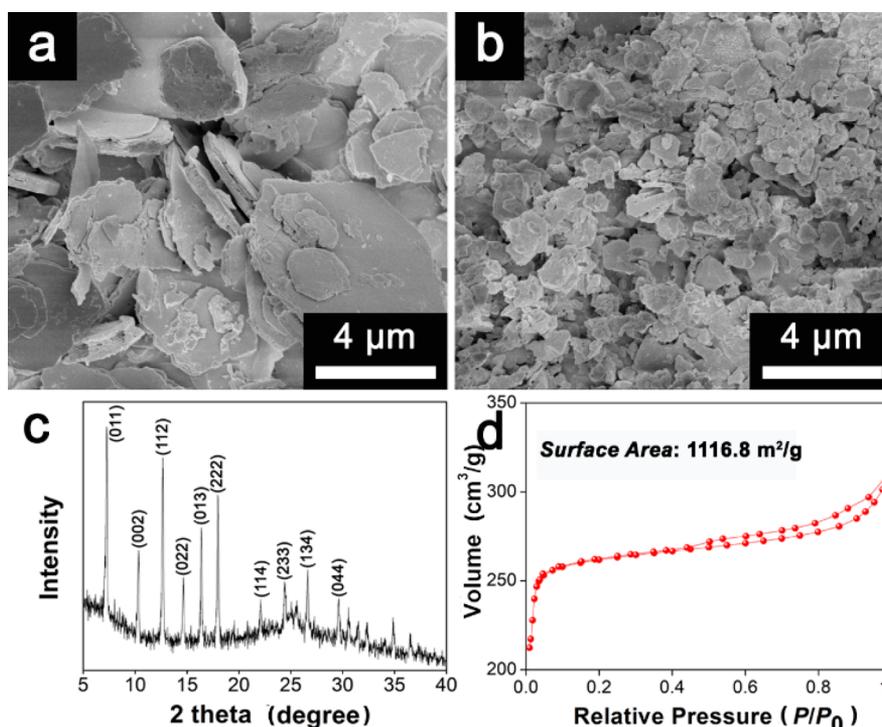


Figure 4. SEM images of (a) ZnAl-CO₃ LDH powders prepared by hydrothermal growth and (b) ZIF-8 powders prepared by solvothermal treatment of prepared ZnAl-CO₃ LDH powders; (c) XRD and (d) Ar adsorption/desorption isotherms of prepared ZIF-8 powders.

In the next step, prepared ZnAl-CO₃ LDH buffer layers were further immersed in a methanol solution containing 2-mIm. Experimental results demonstrated that increasing the reaction temperature and time was beneficial to improvement of conversion rates of LDH buffer layers and final formation of defect-free ZIF-8 coatings (SI-5). Prepared ZIF-8 coatings with optimized microstructure were then subject to SEM and XRD characterization. Results showed that after facile solvothermal treatment with 2-mIm, surface of Al plates had been evenly covered with well intergrown ZIF-8 coatings (Figure 3c). No conspicuous intercrystal defects could be discerned (Figure 2c). Cross-sectional image further indicated that thickness of prepared ZIF-8 coatings remained around 5 μm (Figure 2d).

To elucidate whether ZIF-8 solvothermally synthesized from ZnAl-CO₃ LDH precursor buffer layers showed any remarkable difference from ones prepared by conventional solvothermal growth, herein we further prepared ZIF-8 powders by solvothermal treatment of plate-like ZnAl-CO₃ LDH crystals with 2-mIm. Results showed that ZnAl-CO₃ LDHs could be fully converted to pure ZIF-8 phase under proper solvothermal conditions as confirmed by SEM (Figure 4a, b) and XRD results (Figure 4c). Additionally, Ar adsorption/desorption isotherms were further measured to determine the pore structure of prepared ZIF-8. The BET surface area reached 1116.8 m² g⁻¹ (Figure 4d), which was considerably lower than the ZIF-8 phase prepared by conventional solvothermal growth.⁴¹ In a word, ZIF-8 phase prepared from ZnAl-CO₃ LDHs was identical with those previously reported in literature so that the following DC polarization test should be a true reflection of anticorrosion performance of pure ZIF-8 phase.

DC polarization represented an effective tool for evaluation of the performance of anticorrosion coatings.^{42–46} In addition to ZIF-8-coated Al plates, herein both ZnAl-CO₃ LDH buffer layer-modified and bare Al plates were also subject to the test for reference. Results showed that I_{corr} for bare Al plates

reached $\sim 1 \times 10^{-4}$ A cm⁻² (Figure 5a). After coating Al plates with ZnAl-CO₃ LDH buffer layers, the I_{corr} was reduced by 2

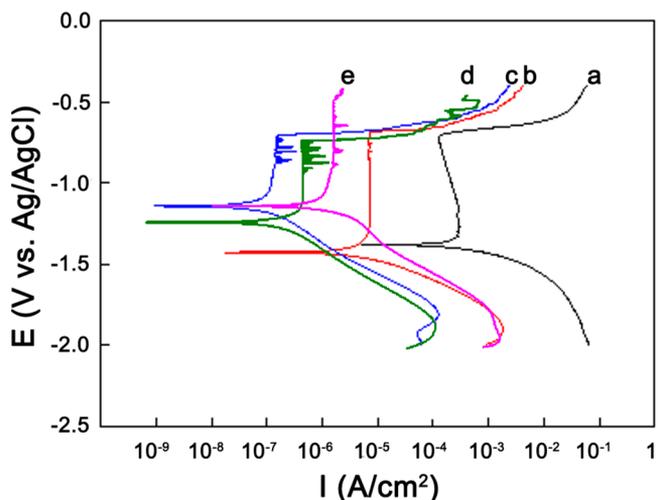


Figure 5. DC polarization curves for (a) bare Al plates, (b) ZnAl-CO₃ LDH buffer layers prepared by in situ hydrothermal growth, (c) ZIF-8 coatings prepared by ligand-assisted conversion of ZnAl-CO₃ LDH precursor buffer layers and ZIF-8 coatings after immersion in corrosive media (pH = 6 and 3.5 wt % NaCl) for (d) 1 day and (e) 5 days.

orders of magnitude ($\sim 1 \times 10^{-6}$ A cm⁻², Figure 5b). A further large decrease of I_{corr} to $\sim 1 \times 10^{-8}$ A cm⁻² could be achieved in the case of ZIF-8-coated Al plates (Figure 5c), which was comparable with the best quality inorganic anticorrosive coatings (summarized in SI-6). Even after long time immersion in the corrosive media (pH = 6 and 3.5 wt % NaCl solution) up to 5 days, the I_{corr} of ZIF-8-coated Al plates remained fairly low (Figure 5d, e). It could, therefore, be deduced that MOF

materials were potentially superb candidates for high-performance anticorrosive coatings.

Strong adhesion of anticorrosion coatings to the metal surface is of vital importance for their practical applications.⁴⁷ Herein scratch test was further employed to evaluate the adhesion strength of ZIF-8 coatings to Al plates. It was observed that no peeling off occurred after cross cutting through ZIF-8 coatings, which unambiguously demonstrated the strong adhesion of MOF coatings to the surface of Al plates (Figure 6). Considering the framework and functional diversity

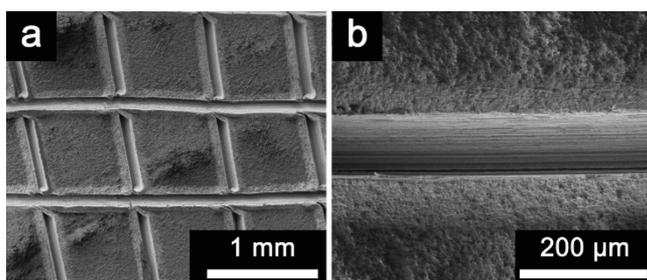


Figure 6. Evaluation of the adhesion between the ZIF-8 coatings and Al substrates by scratch test. (a) SEM image of surface morphology of the scratched ZIF-8 coating and (b) the enlarged image.

of MOF materials, there was no doubt that MOF materials could potentially play an important role in the field of corrosion protection in form of compact coatings or barrier fillers.

In summary, with the facile ligand-assisted conversion concept, for the first time we have successfully prepared anticorrosive ZIF-8 coatings on Al plates. Owing to the intrinsic hydrophobicity and water stability of ZIF-8 as well as uniform and well-intergrown microstructures of prepared ZIF-8 coatings, an excellent anticorrosion performance was finally achieved. Taking into consideration the fact that diverse hydrophobic and water stable MOF materials have been developed, it is believed that MOFs are potentially qualified candidates for anticorrosion applications in form of sparsely distributed MOF barrier fillers or compact MOF-based coatings.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.7b18713.

Experimental details and characterizations (PDF)

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS

MOF, metal–organic framework; LDH, layered double hydroxide; 2-mIm, 2-methylimidazole; ZIF-8, zeolitic imidazolate framework-8; MIL-53, materials of the Institute Lavoisier-53; UiO-66, Universitetet i Oslo-66; I_{corr} , corrosive current

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