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Coordination-Driven Assembly of Metal-Organic Framework Coating for Catalytically Active Superhydrophobic Surface

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Here, a superhydrophobic and catalytically active Metal-Organic Framework (MOF) coating is reported by coordination-driven assembly of MOF nanoparticles and a catechol-functionalized polysiloxane polymer. This MOF coating can be fabricated by casting MOF-polymer precursor onto diverse substrates with varied coating techniques, e.g. spray coating, bar coating, and dip coating. The catechol-functionalized polymer can not only coordinate to the open metal sites on MOF surface which enables the surface functionalization and assembly of MOF nanoparticles, but also allow non-covalent interactions with casting substrates--thus improving the substrate adhesion of the MOF coating. With the well-preserved porosity and surface hydrophobicity, the MOF coating demonstrates superhydrophobicity as well as improved catalytic activity toward the Knoevenagel condensation at room temperature. Such coordination-driven assembly approach could be extended to a range of MOF systems for preparing highly functional composite materials toward various applications.

1. Introduction

Metal-organic frameworks (MOFs) as a promising class of nanoporous crystalline materials show great potential in separation,^[1] catalysis,^[2] gas storage,^[3] pollutant removal,^[4] and sensing,^[5] because of their high porosity, tunable pore sizes, structural diversity, and designable functionalities.^[6] However, the intrinsic crystallinity of MOFs makes them naturally brittle and difficult to process (e.g., they often exist as loose powders), which could cause inevitable material loss during operations with the flux of fluids and thus drastically impede the practical application of MOF materials.^[7] Coating MOFs onto diverse tailorable substrates, such as fabrics, meshes, and membranes, presents a feasible method to support powdered MOFs for a number of applications. To date, various techniques including in-situ deposition,^[8] ink-jet printing,^[9] hot pressing,^[7, 10] and spray coating^[11] have been developed to coat MOFs on a wide range of substrates.

To guarantee the robustness and longevity of MOF coatings, the adhesion between MOF nanoparticle and substrate as well as the cohesive force among MOF nanoparticles are critical. The general route to improve the adhesion of MOF coatings involves addition of polymer binders or additives.^[12] However, the poor interaction between MOF nanoparticles and simply blended polymer chains could lead to the aggregation of MOF nanoparticles and thus the lacking homogeneity of MOF coatings. Alternatively, polymers could be covalently attached to the surface of MOFs via postsynthetic modification/polymerization methods, which, however, often involve time/energy-consuming synthesis processes.^[13] On the other hand, the inherent structural features, i.e. composed of metal ions and coordination bonds, make most MOF samples hydrophilic and moisture-sensitive, limiting their application in water remediation and some moisture-containing catalytic reactions.^[14] Therefore, fabrication of hydrophobic MOF coatings with high substrate adhesion and homogeneity is of great importance for promoting the applications of MOF materials.

Herein, a highly hydrophobic and catalytically active MOF coating with high mechanical stability and homogeneity has been developed through a coordination-driven assembly strategy. The coating is fabricated by various industrial-scale coating techniques, e.g. bar coating, dip coating, and spray coating, with a MOF-polymer precursor consisting of the widely studied MOF material (zeolitic imidazolate framework-8, ZIF-8), and a previously reported catechol-terminated polysiloxane-urea copolymer (PDMS-Cat).^[15] This catechol-functionalized polymer not only acts as the linker between MOF particles to induce the assembly of the MOF particles and thus improve the mechanical stability of the MOF coating, but also enables the surface hydrophobization of MOFs as well as the immobilization of the MOF coating onto various substrates. Particularly, the catechol moieties of the polymer show strong coordination with the surface open metal sites of MOF nanoparticles, and offers ample non-covalent interactions with various solid substrates.^[16] Moreover, with the intrinsically catalytic nature of ZIF-8 and highly improved hydrophobicity, the MOF coating can be employed as an efficient heterogeneous catalyst and exhibit good catalytic activity toward Knoevenagel condensation. It is envisioned that this simple coordination-driven assembly strategy can be applied to various hydrophobic MOF coatings and facilitate their applications in separation and catalysis fields.

2. Results and Discussion

ZIF-8 as a typical MOF is made of Zn(II) ions and 2-methylimidazolate linkers that exhibits a sodalite-type structure, large surface area, good chemical and thermal stability, and is low-cost and promising for many porosity-related applications.^[17] While the PDMS-Cat polymer (Figure S1) was reported featuring polydimethylsiloxane (PDMS) backbones and terminal catechol moieties, demonstrating great flexibility, hydrophobicity, ability to coordinate with different metal ions, and adhesion toward diverse substrates.^[15, 18] Therefore, ZIF-8 was selected as the model material to fabricate MOF coating, using PDMS-Cat as a multifunctional polymer binder.

The coordination-driven assembly process of ZIF-8 nanoparticles and PDMS-Cat polymer is illustrated in **Figure 1a**. ZIF-8 nanoparticles (size distribution ~200 nm-300 nm, Figure 1b) and PDMS-Cat were first dispersed/dissolved in ethanol, respectively, to form a beige coating precursor (Figure 1c), during which the surface functionalization of ZIF-8 would happen due to the coordination between catechol groups of PDMS-Cat and the open metal sites on ZIF-8 surface.^[19] In the presence of excess polymers in the precursor, such coordination and linkage would further induce the assembly of the surface functionalized ZIF-8 (denoted **PDMS@ZIF-8**). With the curing and solvent evaporation, the co-assembly of PDMS@ZIF-8 and excess polymers will form a homogenous MOF coating (denoted **ZIF-8/PDMS** coating) on the casted substrates. Figure 1d shows a photo image of the fabricated ZIF-8/PDMS coating on aluminum foil with a MOF loading of 50 wt%. The thickness of the coating could be finely adjusted and down to ~13 μm via a bar coating technique (Figure S2). The scanning electron microscope (SEM) and atomic force microscope (AFM) images indicate that the ZIF-8 nanoparticles are homogeneously dispersed in the polymer matrix (Figure S3).

To verify the surface functionalization process during the coordination-driven assembly, the MOF-polymer precursor was centrifuged and rinsed with excess ethanol several times to remove uncoordinated polymers. The dried PDMS@ZIF-8 powders were found showing fair hydrophobicity with a water contact angle (WCA) of ~126°, while the water droplet would spread on pristine ZIF-8 powders (**Figure 2a**). Meantime, the pristine ZIF-8 powders preferred to disperse in the aqueous phase and PDMS@ZIF-8 powders were found well-dispersed in the oil phase, when placing the two powders into a toluene/water solvent system (Figure S4a). These results preliminarily signify the decoration of PDMS-Cat polymer onto the ZIF-8 particle surface. Dynamic light scattering (DLS) has been utilized to identify the size and zeta potential changes of ZIF-8 nanoparticles after surface hydrophobization (Figure S4b and Table S1). A minor size increase was observed and this could be ascribed to the non-covalent attachment of polymer chains on ZIF-8 particle surface. Moreover, the X-ray

photoelectron spectroscopy (XPS) of PDMS@ZIF-8 powders also confirmed the coordination between Zn(II) and catechol groups due to the change of Zn oxidative states (Figure 2b and S4c). All the experimental results demonstrate the successful surface functionalization of ZIF-8.

ZIF-8/PDMS coating with different MOF loadings has been prepared to explore the effect of polymer content on the performance of MOF coatings. Specifically, ZIF-8/PDMS coatings with the MOF loading of 20 wt%~50 wt% were fabricated, and higher MOF loading at 60 wt% would make the coating fragile and difficult to attain the mechanical integrity (Figure S5). All of the coatings exhibit homogenous distribution of ZIF-8 nanoparticles in polymer matrix, as observed in SEM and AFM images (Figure S3), and confirmed by the energy dispersive X-ray (EDX) analysis (Figure S6). The MOF loading in the ZIF-8/PDMS coatings was manifested by thermogravimetric analysis (TGA, Figure S6c), which also demonstrates the thermal stability of these coatings. Fourier transform infrared (FT-IR) spectra show that these ZIF-8/PDMS coatings integrate the absorption characteristic peaks of both ZIF-8 and PDMS-Cat polymer (Figure 2c). The appearance of a new absorption peak at 520 cm^{-1} ascribed to Zn-O stretching vibration also corroborates the coordination of catechol groups to Zn atoms on ZIF-8.^[20] Powder X-ray diffraction (PXRD) confirms that the MOF coatings keep the same crystallinity as the parent ZIF-8 and show enhanced intensity with higher MOF loadings (Figure 2d). Overall, the co-assembly procedure and the coating fabrication do not affect the crystalline properties of ZIF-8, and the tunability of MOF loading in ZIF-8/PDMS coatings is favorable for the MOF-dependent applications.

The mechanical properties of ZIF-8/PDMS coatings have been tested by rheological tests and micro-hardness indentation.^[21] As observed from the rheological frequency sweep curves (Figure S7), all of the MOF coatings display a solid nature and their storage moduli (G') would escalate from 23.0 MPa to 36.5 MPa with increased ZIF-8 content. Meantime, the temperature sweep curves shown in **Figure 3a** specify that the coatings could undergo a

structure change and are softened with ascending temperatures, when the loss moduli (G'') gradually increased and exceeded G' . This feature is derived from the intrinsic properties of the PDMS-Cat polymer,^[15] which could not only benefit for realizing the thermal healing ability and thus damage tolerance of the coatings (Figure 3d), but also endow the coatings with good reprocessability. Moreover, micro-hardness indentation demonstrates the relatively high modulus and hardness of these MOF coatings, with the 50 wt% ZIF-8 loaded MOF coating showing the highest modulus of ~654 MPa and the hardness of 36.8 MPa (Figure 3b and Table S2).

Besides the bulk mechanical stability, interfacial adhesion to diverse substrates is highly desired for the MOF coatings. The substrate adhesion of ZIF-8/PDMS coatings has been characterized by the shear strength tests of the coatings sandwiched between two identical substrates.^[22] As shown in Figure 3c, the ZIF-8/PDMS coatings demonstrate satisfactory adhesion to various substrates, including glass, metal of aluminum plate, and a plastic of polymethylmethacrylate (PMMA). Particularly, the MOF coating containing 30 wt% of ZIF-8 presents the highest shear strength up to 3.9 MPa on glass and 1.5 MPa on aluminum plate. The excellent adhesive feature of the abundant catechol moieties should be responsible for the good substrate adhesion of these coatings. This is because catechol moieties could adhere to diverse surfaces by various non-covalent interactions such as hydrogen bonding and metal-coordination, or forming covalent bonds with surface amines through Michael-type addition.^[16a] However, further increase of MOF loadings would weaken the coating adhesion to substrates, probably because of the decreased contact area between polymers and substrates.

Conferring hydrophobicity or even superhydrophobicity to the MOF coating is highly appreciated for MOF catalyzed reactions which take place in gas-involved or oil-water mixed phases.^[23] Due to the synergy of low surface energy of PDMS backbones of the polymer and surface roughness provided by assembled ZIF-8 nanoparticles, the ZIF-8/PDMS coating demonstrates enhanced hydrophobicity.^[24] To enable a sufficient surface roughness and thus

superhydrophobicity of the MOF coating, ZIF-8/PDMS with 50 wt% MOF loading has been selected as the optimal sample and spray coated onto different substrates. **Figure 4a** shows the ZIF-8/PDMS coating on carbon cloth with a WCA of $\sim 156^\circ$, implying the superhydrophobicity of the coating. The surface morphology of the coating can be observed by the SEM image (Figure 4b). This superhydrophobic MOF coating has also been demonstrated on a stainless-steel mesh (Figure S8). For reality applications, long-term damage and corrosion resistance are highly important for superhydrophobic coatings.^[25] The mechanical durability of the ZIF-8/PDMS coating was evaluated by tape-peeling test and sandpaper abrasion, where the coating maintained superhydrophobicity even after 30 times of tape peeling and 70 times of abrasion (Figure S9), indicating the mechanical robustness of the coating. In addition, the chemical stability of the coating was also tested by immersing in high concentration acidic and alkaline solutions as well as different organic solvents. After immersion for 24 h, all WCAs of the coating were still about 150° , demonstrating impressive resistance to both acidic and basic solutions (Figure S10a). However, the ZIF-8/PDMS coating was not resistant to organic solvents due to the poor anti-swelling property of the PDMS-Cat polymer (Figure S10b).^[15]

As the various uses of MOFs are derived from their high porosity, the N_2 adsorption isotherm has been conducted to evidence the preserved porosity of the ZIF-8/PDMS coating. Brunauer-Emmett-Teller (BET) surface area of the MOF coating is calculated to be $625 \text{ m}^2 \text{ g}^{-1}$ (Figure S11), more than one third of the pristine ZIF-8, indicating the possibility for applying the MOF coating in diverse separation and catalysis fields. For demonstration, this ZIF-8/PDMS coating was utilized in heterogeneous catalysis with the Knoevenagel condensation of benzaldehyde and malononitrile as an example (Figure 4c), where water is one of the reaction products.^[26] In this catalytic study, ZIF-8/PDMS coating on stainless-steel mesh was cut and dropped into a dimethyl sulfoxide (DMSO) solution containing benzaldehyde and malononitrile. The reaction was carried out at room temperature and the

resulting products were analyzed by ^1H NMR analysis. Note that the ZIF-8/PDMS coating shows superior catalytic reactivity that is comparable to pristine ZIF-8 (Figure 4d, Table S3 and S4), on account of the synergistic effect of preserved porosity and surface hydrophobicity that favors the enrichment of the oily reactants. To analyze the contribution of each component to the catalytic activity, Knoevenagel condensation experiments were also conducted using pristine PDMS-Cat polymer (Table S5). Importantly, it showed no catalytic activity, indicating that catalytic activity of ZIF-8/PDMS coating originates solely from ZIF-8 nanoparticles. Besides, the strong attachment of ZIF-8/PDMS coating to substrates by the assistance of catechol chemistry endows the MOF coating with convenient recovery and good recyclability after a catalytic reaction. As shown in Figure 4e, even after five catalytic cycles, the ZIF-8/PDMS catalyst still achieves a yield of more than 90%, indicating its excellent catalytic recyclability in this Knoevenagel reaction.

3. Conclusion

In summary, a coordination-driven assembly approach has been developed for accessing highly hydrophobic and catalytically active MOF coatings that integrate ZIF-8 nano-crystals and a catechol-functionalized polysiloxane polymer. The coating was applied by various coating techniques on diverse substrates. During the curing process of the coating, the strong coordination between ZIF-8 nanoparticles and the polymer not only enabled the fast surface functionalization of ZIF-8 and thus the hydrophobicity of the coating, but also endowed the coating with good mechanical stability. Meanwhile the abundant non-covalent interactions between the polymer matrix and substrates ensured the high substrate adhesion of the coating. Moreover, the coating showed superior catalytic activity toward Knoevenagel condensation with the synergistic effect of retained porosity of ZIF-8 and hydrophobicity. We believe that this approach could be extended to many other MOFs and is promising for preparing functional MOF composites with various applications including gas storage, separation and catalysis.

4. Experimental Section

Materials: Without further descriptions, all the chemicals were purchased from Sigma-Aldrich and used as received. ZIF-8 was prepared by the coordination between $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ and 2-methylimidazole in an aqueous medium according to the literature.^[17b] Before use, the as-prepared ZIF-8 was soaked in excess methanol for two days and then activated in a vacuum oven at 120°C for one day. PDMS-Cat polymer was synthesized by previously reported one-pot copolymerization of bis-aminopropyl-terminated poly(dimethylsiloxane) (PDMS, $M_n = 870$, Gelest Inc.), isophorone diisocyanate, and dopamine hydrochloride with the molar ratio of 5 : 5.5 : 1.^[15] Notably, the as-prepared polymer was stored in a vial with N_2 protection at -20°C to prevent the oxidation of catechol groups before use.

Surface functionalization of ZIF-8: ZIF-8 powders were first redispersed in ethanol with a weight concentration of 100 mg/mL, and then PDMS-Cat polymer (10 wt% to ZIF-8) was added into the ZIF-8 suspension and dissolved in ethanol. Following sonicating the suspension for 4 h, a homogeneously dispersed precursor was obtained. The MOF-polymer precursor was subsequently centrifuged and rinsed with ethanol for three times to remove excess polymers. The surface-functionalized ZIF-8 can be obtained by drying the precipitate in a vacuum oven at 60°C.

Coating ZIF-8/PDMS on diverse substrates: The ZIF/PDMS precursors with different concentrations (100 mg/mL and 250 mg/mL) and mass fractions of ZIF-8 (20 wt%-60 wt%) were prepared as abovementioned. The as-prepared precursors were then coated on various substrates, including glass, aluminum foil, stainless-steel mesh, and carbon cloth, through diverse coating techniques, i.e. bar coating, dip coating, and spray coating. For bar coating, the ZIF-8/PDMS precursor (250 mg/mL) was coated on substrates by a baker film applicator (Elcometer 3520). For dip coating, the substrate was immersed in the ZIF-8/PDMS precursor

(100 mg/mL) and then lifted slowly in a constant speed (~2 mm/s). Spray coating was conducted by a 0.3 mm nozzle with 3 bar airflow and 100 mg/mL of the precursor was used.

Characterization: SEM images and EDX mapping data were obtained by using FEI Quanta 450 FEG. For the measurements, the samples were placed on carbon tapes and coated with platinum. AFM images were obtained on Bruker Dimension Icon with a RTESPA-150 tip in the PeakForce tapping mode. Dynamic light scattering (DLS) was measured by Malvern Zetasizer Nano-ZS ZEN3600 using ethanol as the medium. XPS was performed with a Scanning Auger XPS (PHI5802). FT-IR spectra were tested by an IR spectrometer (PerkinElmer Spectrum 100) with 2 cm^{-1} of resolution. PXRD results were recorded by a Bruker D2 Phaser diffractometer. TGA was performed on a TA Q600 differential thermal analyzer. Optical images were taken by a Nikon D5500 camera. Contact angles were measured on an OCA 20 system (Data Physics). Micro-hardness indentation was conducted in a micro-hardness tester (Fischer HM2000 XYp) and the data were obtained in the average of 5 points. The rheological measurements were performed on a rotational rheometer (Malvern Kinexus Lab+). Shear strength tests were performed on Instron 5566 with the strain rate of 10 mm/min to acquire the break stress, where the two substrates were adhered by the ZIF-8/PDMS composites and placed in a vertical direction. The porosity and surface area analysis was performed using a Quantachrome Autosorb iQ gas sorption analyzer.

Catalytic Reaction: A glass vial charged with ZIF-8/PDMS-50% (~20 mg) coated stainless-steel mesh and a magnetic stir bar was transferred into a N_2 filled glovebox. Benzaldehyde (1 mmol, stored in N_2 -filled glovebox) was added. After taking out the glass vial, malononitrile (1.2 mmol) and $\text{DMSO-}d_6$ (3.0 mL) were added. The mixture was immediately screw-capped and stirred at room temperature (23°C). During the reaction, the mixture was withdrawn and filtered at intervals through a $0.22\ \mu\text{m}$ membrane filter for all samples (each sample of 0.1 mL), then each of the filtrates was diluted using $\text{DMSO-}d_6$ (0.5 mL) and quantified by solution ^1H NMR spectroscopy (Bruker Ultrashield 400). For control experiments, the

conditions were kept unchanged and ZIF-8 powders (10 mg) or PDMS-Cat film (10 mg) were employed. The yield in percentage of the condensation reaction is calculated by the mathematical expression described in Supporting Information.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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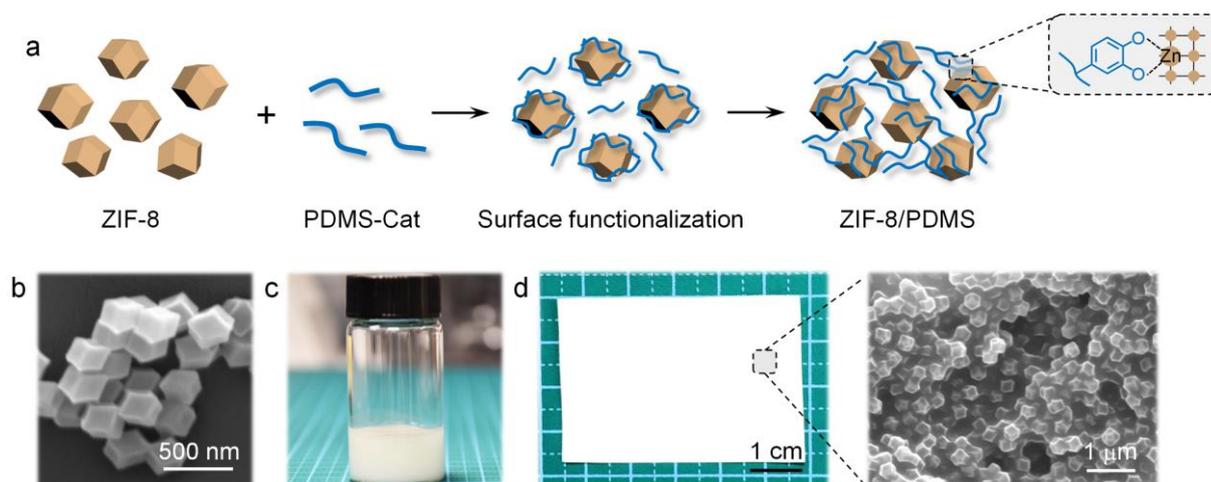


Figure 1. Fabrication of ZIF-8/PDMS coating by coordination-driven assembly. (a) Schematic illustration of the assembly process during coating: hybridization of ZIF-8 and PDMS-Cat polymer, surface functionalization of ZIF-8, and concentrating to a homogeneous coating. (b) SEM image of ZIF-8 nanoparticles. (c) Photograph showing the coating precursor with ZIF-8 nanoparticles and PDMS-Cat polymer well-dispersed in ethanol. (d) Photograph of the ZIF-8/PDMS coating on aluminum foil and SEM image showing the surface morphology of the coating.

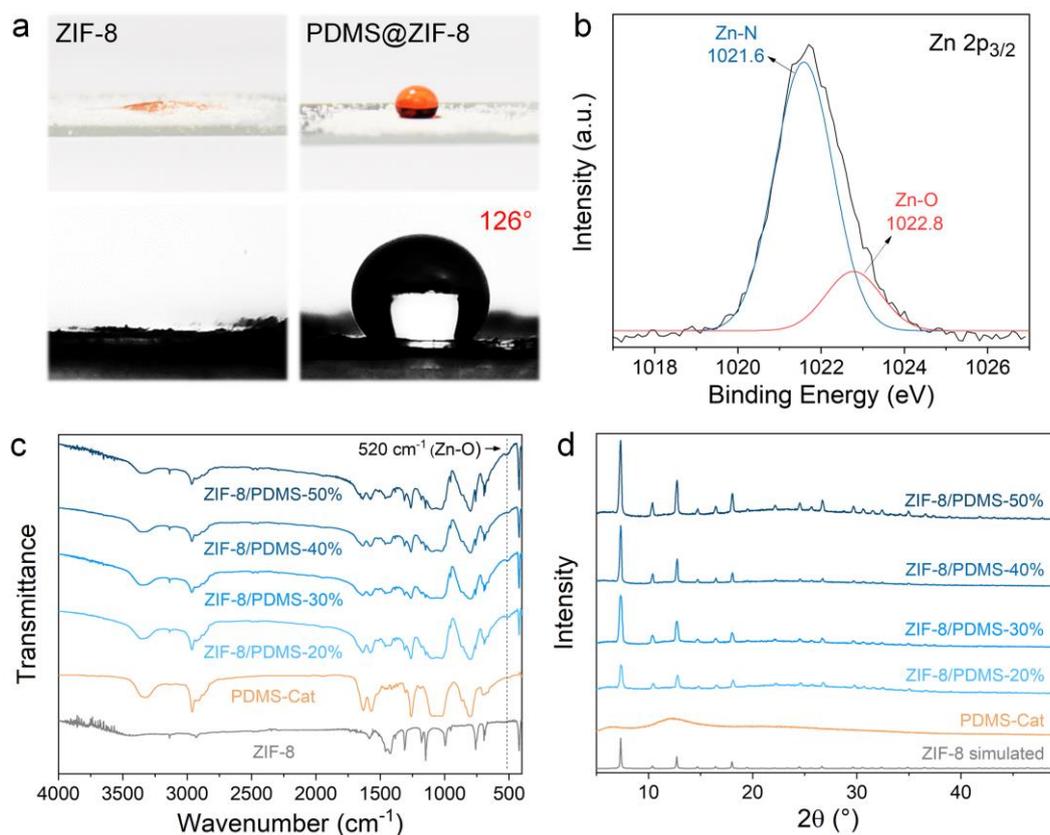


Figure 2. Surface and physicochemical properties of ZIF-8/PDMS coatings. (a) Photograph of water droplets (10 μL , dyed with carmine) spreading on ZIF-8 powder and repelled by surface functionalized PDMS@ ZIF-8 powder. (b) Zn $2p_{3/2}$ XPS spectrum of PDMS@ZIF-8 powder, which could be deconvoluted and fitted to two peaks assigned to the Zn(II) oxidation states of Zn-N and Zn-O bonds. (c) FT-IR and (d) PXRD spectra of ZIF-8, PDMS-Cat polymer, and ZIF-8/PDMS with different MOF loadings.

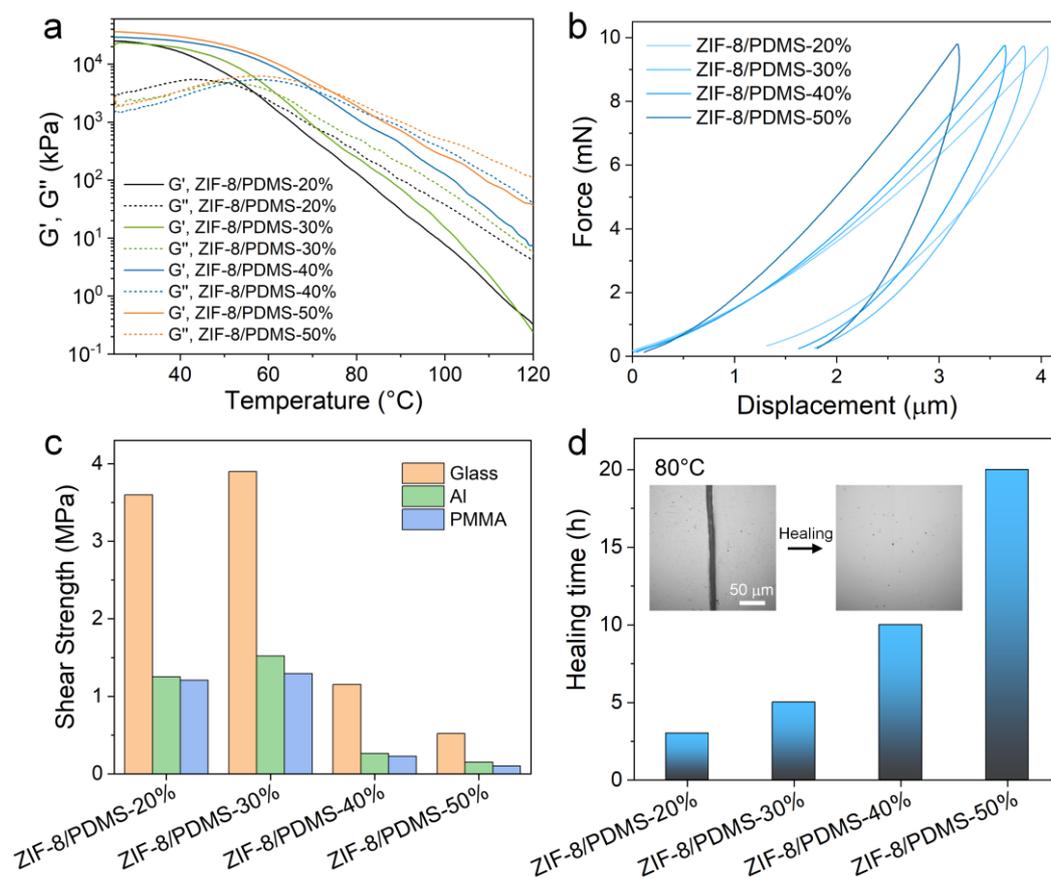


Figure 3. Mechanical properties of ZIF-8/PDMS coatings. (a) Rheological temperature sweep and (b) micro-hardness indentation tests of ZIF-8/PDMS coatings with different MOF loadings. (c) Shear strength tests of ZIF-8/PDMS coatings on various substrates. (d) Thermal healing ability of ZIF-8/PDMS coatings at 80°C. Inset is the optical images of the coating after damaged by a doctor blade and then healed.

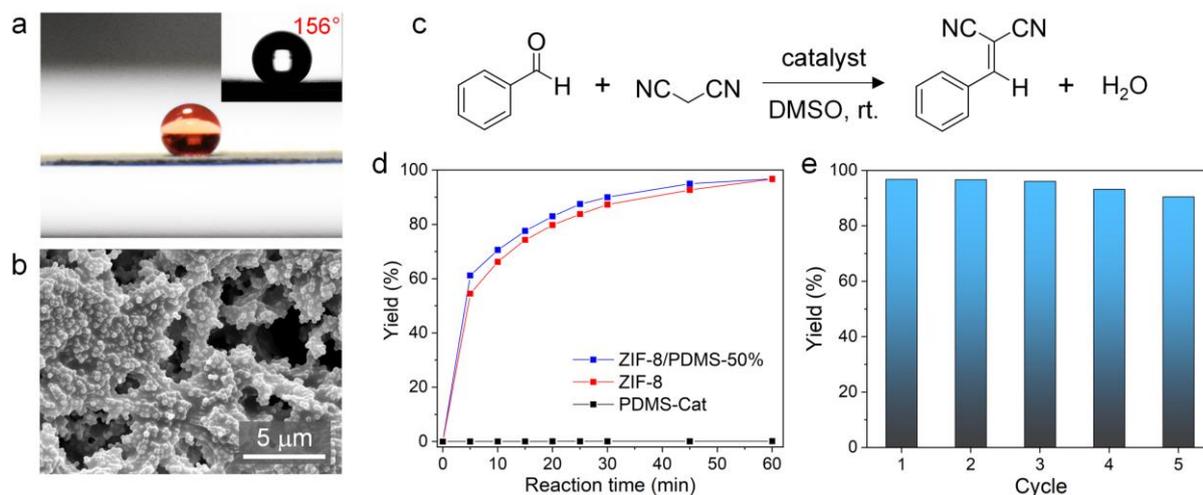


Figure 4. Superhydrophobicity and catalytic reactivity of ZIF-8/PDMS coatings. (a) Photograph of a water droplet on ZIF-8/PDMS coated carbon cloth with a WCA of 156°. (b) SEM image showing surface morphology of the ZIF-8/PDMS coating in (a). (c) Knoevenagel condensation of benzaldehyde with malononitrile using catalyst. (d) Effect of different catalysts, including ZIF-8/PDMS, pristine ZIF-8 and PDMS-Cat polymer, on reaction yield. (e) Recycle test of the ZIF-8/PDMS coating on the reaction yield.

A **coordination-driven assembly approach** is introduced to prepare metal-organic framework (MOF) coating with superhydrophobicity and catalytic activity. The assembly process happens between a catechol-terminated polysiloxane polymer and MOF nanoparticles, which not only enables the surface hydrophobization of MOF but also makes the MOF coating mechanically robust and adhesive to various substrates.

Keyword: metal-organic framework, polymer, coordination-driven assembly, superhydrophobic coating, catalysis

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Coordination-Driven Assembly of Metal-Organic Framework Coating for Catalytically Active Superhydrophobic Surface

