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Phase Transition of Metal–Organic Frameworks for Constructing Nanocomposite Materials

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Abstract

Through encapsulating functional materials, metal–organic framework (MOF) composites show extraordinary potential in various fields due to the excellent synergistic effects between the host and guests. However, many attracting functional species, such as enzymes, could be easily damaged during the synthesis of MOF composites. Herein we report a new strategy, namely pressure-amorphization-stimulation-recovery (PASR), in which crystalline MOFs were transferred to the amorphous MOFs at certain mechanical pressure, followed by recrystallization process to encapsulate functional species into MOF crystals. The reversible phase transition avoids high temperature, high ionic strength, strong acid/base conditions, etc., which is suitable for many types of functional species. To prove the feasibility of this method, enzymes, anti-cancer drugs, noble metal nanoparticles and other functional materials, have been trapped into MOFs using this strategy. The synthesized MOF composites can maintain 95.6% of the enzyme activity under the treatment of protease, or reach 40% drug loading, or achieve 98% size selectivity for olefins. This strategy has been extended to several types of MOF structures and it will pave a new way for designing MOF composites and developing further applications.

Metal–organic frameworks (MOFs) have shown potential applications in gas separation and storage due to their regular microporous structures^{1, 2}. The rich and adjustable pore environment of MOFs has expanded their applications in catalysis³, biomedicines^{4, 5} and sensors⁶⁻⁸, etc. Additionally, through combination of functional guest materials, MOF composites can obtain new properties that MOFs or guest materials do not have⁹⁻¹³. In recent years, encapsulation of functional materials into MOFs has become a sophisticated approach to obtain multifunctional MOF composites¹⁴⁻¹⁷. For example, owing to the synergy between the catalytic capability of platinum nanoparticles (Pt NPs) and size-selectivity of the ZIF-8 shell, the hybrid Pt/ZIF-8 catalysts, exhibited excellent size-selectivity for hydrogenation of olefins¹⁸. The prepared MIL-101(Fe³⁺, Cr³⁺)@Pt@MIL-101(Fe³⁺, Cr³⁺) with “sandwich” structures encapsulated Pt NPs in MOFs’ interlayers and showed increased selectivity of the hydroconversion of citronellal to citronellol mainly due to combination of the catalytic sites on Pt NPs and high selective adsorption of C=O double bonds on metal sites from MOFs¹⁹. A series of antitumoural and retroviral drugs enclosed into Fe (III) based MOFs have shown potential applications in bio-imaging²⁰. These works mentioned above showed improvement in MOFs properties after combination of functional materials.

Recently, enzyme@MOFs has gained extensive attention due to the attractive combination of stereoselectivity catalytic sites of enzyme and accessible porosity of MOFs²¹⁻²⁴. However, traditional methods for preparing MOF composites usually involve high ionic strength, high temperature and are prone to lose part or most of the enzyme activity during the synthesis of MOF composites^{18, 25-27}. Ma’s group used infiltration encapsulation strategy to restrict enzymes in MOF structures²⁸. They focused on the loading of enzymes into mesoporous MOFs to boost the recyclability of enzymes. However, this strategy required the cage of MOFs to perfectly match with the size of enzymes²¹. To

overcome this challenge, biomimetic mineralization method^{29, 30} and coprecipitation method^{31, 32} have been explored to coat enzymes with MOFs' shells during MOF composites synthesis, which could encapsulate enzymes with different sizes. However, this strategy is only suitable for ZIF-based MOFs and usually involves a specific concentration of metal ions and organic ligands, which may negatively impact the biological activity of enzymes³³. Very recently, a fast ball-milling strategy³⁴ of encapsulating β -glucosidase, invertase, β -galactosidase and catalase into MOFs has been developed by Tsung's group, and synthesized composites maintained the enzyme activity under treatment of protease in an acidic environment. However, this method involves ball milling, which slightly affects the activity of enzymes³⁴. In summary, the fabrication of enzyme@MOFs has encountered problems such as complicated preparation methods, possible deactivation of active species during the packaging process and bottlenecks in the amount of packaging, which are detrimental to the further application of enzyme@MOFs. Hence, it is critical to develop a general strategy for constructing MOF composites with well-preserved activity of the encapsulated functional species.

Previous researches have shown that mechanical force can cause phase transformations of MOFs³⁵⁻³⁹. If functional materials are not pressure sensitive, they might be trapped into MOFs matrices during the phase transformation of MOFs without any damage⁴⁰. Herein, we proposed a strategy to encapsulate functional species into the MOF structures through pressure-induced MOF amorphization and post-stimulated crystalline recovery (as shown in Scheme 1), named as pressure-amorphization-stimulation-recovery (PASR). The functional species were premixed with MOFs followed by applying certain mechanical pressure to transform MOFs into amorphous MOFs (aMOFs). Then, by exposing them in vapor/solvents, the functional species/aMOFs could be recovered to the functional species/MOF composites. Notably, the encapsulation process occurs

during the reversible phase transition of MOFs without involving any harsh conditions, and therefore is applicable to many types of functional materials. By using this strategy, a series of functionalized ZIF-8 composites have been synthesized, which achieved synergistic effects including the protection of enzyme, high drug loading, size selective catalysis, etc. In addition, PASR strategy has been demonstrated to be versatile and extendable to other types of MOFs (such as Co-ZIF-67, Cu-HKUST-1, Al-MIL-53 and Mg-MOF-74) and functional guests (such as enzymes, multi-wall carbon nanotubes (MWCNTs), Au NPs, TiO₂ NPs and SiO₂ NPs).

Results

PASR for MOFs

As a proof of concept, the procedure of the PASR for pristine MOFs was demonstrated by ZIF-8 nanocrystals. First, 10 mg of activated ZIF-8 was ground and transferred into a 13 mm pellet die, and then certain mechanical pressure (0 MPa-1,364 MPa) was applied. The effect of compression stress on the crystal structure has been systematically studied. The crystal structure, morphology and porosity of ZIF-8 were characterized by powder X-ray diffraction (PXRD), scanning electron microscopy (SEM) and Brunner-Emmet-Teller (BET), respectively (Supplementary Fig. 1, Supplementary Fig. 2 and Supplementary Fig. 5). The characteristic diffraction peaks of ZIF-8 merged into broad peaks at 1,364 MPa (Fig. 1a). Low compression loading only induced partial assembly of ZIF-8 NPs (Fig. 1c), while high compression loading resulted in the global formation of tightly packed aZIF-8 NPs (Fig. 1d). These results are in agreement with previous works on pressure-induced aZIF-8 in diamond anvil cell pressure apparatus³⁶ and confirm the successful synthesis of aZIF-8 pellets with compression loading of 1,364 MPa.

Conventionally, ZIF-8 is synthesized by dissolving metal ions and organic ligands in methanol solvent. Accordingly, methanol was chosen as the recovery solvent to gradually repair aMOFs. The prepared aZIF-8 pellets (compressed by 1,364 MPa) were individually exposed to saturated methanol vapor for 24 hours or immersed in methanol for 5 hours at 50 °C to recover the crystal structure. As expected, the crystallinity of ZIF-8 was reproduced as indicated by PXRD and SEM measurements. The characteristic and sharp Bragg peaks of the two samples centering at 12.7° and 18.07° appeared again after recovery, which could be ascribed to (211) and (222) facets of ZIF-8 (Fig. 1a). Another four weak Bragg peaks centering at 14.7° (220), 16.5° (310), 24.5° (332) and 26.7° (510) also emerged. The Bragg peaks of both recovered ZIF-8 pellets were broader than but identical to those of the pristine ZIF-8 nanocrystals, indicating that aZIF-8 were recrystallized under both treatments. Significant surface morphology change was observed between the amorphized and recrystallized ZIF-8 (Figs. 1e and 1f and Supplementary Figs. 6 and 7). As compared to the amorphized sample, polyhedral nanocrystals with varied sizes were found in both recovered samples. The original ZIF-8 NPs had a specific area of 1,347 m²/g and pore volume of 1.28 cm³/g·nm. After exposing aZIF-8 (surface area: 406.7 m²/g, pore volume: 0.465 cm³/g·nm) with methanol vapor and soaking in methanol solution, the specific areas of ZIF-8 pellets increased to 881.6 m²/g and 1,027.9 m²/g (Fig. 1b), respectively, and the pore volumes were slightly increased to 0.62 cm³/g·nm and 0.77 cm³/g·nm, respectively (Supplementary Fig. 8). The above experimental results jointly prove that the pressure-induced aZIF-8 can be mostly restored to the crystalline ZIF-8 under the stimulation of either methanol vapor or methanol solvents.

Accordingly, water has also been used to recover aZIF-8⁴¹, but we found that it may induce the aZIF-8 to transform into non-porous diamondoid (dia)-ZIF and ZIF-CO₃-1 structures⁴², as reflected

by PXRD (Supplementary Fig. 9) and SEM images (Supplementary Fig. 10). It is clear that two new morphologies different from ZIF-8 crystals have appeared after soaking aZIF-8 in water for 72 hours. To further accelerate the recovery of aZIF-8 into the crystalline one, 2-methyl imidazole/aqueous solvents were utilized because the 2-methyl imidazole could stabilize the structures of ZIF-8 and avoid further phase transition of ZIF-8 into other ZIF structures (Supplementary Fig. 9 and 10).

The PASR strategy is not limited to ZIF-8, but can be further extended to other MOFs (Co-ZIF-67, Cu-HKUST-1 Mg-MOF-74 and Al-MIL-53) (Supplementary Fig. 11), bringing MOFs broader application prospects. PXRD results demonstrated that all these MOFs could be amorphized by compression and subsequently reconstructed by methanol (or water) vapor/solvents exposure (Supplementary Fig. 12), indicating the proposed PASR strategy is suitable for certain MOFs.

PASR for the encapsulation of enzymes in ZIF-8

In order to verify the feasibility of PASR strategy in encapsulation, we tried to incorporate glucose oxidase (GOx) and horseradish peroxidase (HRP) into ZIF-8. After applying an axial pressure loading of 1,364 MPa to 10 mg GOx&HRP for 5 min, the enzymes' activity remained almost the same as free enzymes (Fig. 2i). This implied that such pressure will not affect the activity of GOx and HRP. Based on cascade reactions for GOx and HRP³², 90 mg ZIF-8, 5 mg GOx and 5 mg HRP were fully ground and mixed in a mortar, and then 20 mg of the mixture were pressed and recovered in methanol vapor (MV), water vapor (WV) or a trace amount of dimethylimidazole/water (MW) to obtain restored products, GOx&HRP/ZIF-8-X (X = MV, WV or MW). GOx&HRP/ZIF-8-X all showed the characteristic Bragg diffraction peaks consistent with commercial ZIF-8 NPs (Fig. 2a), but few new crystal structures such as dia-ZIF and ZIF-CO₃-1 inevitably appeared during the recovery process of GOx&HRP/ZIF-8-WV and

GOx&HRP/ZIF-8-MW. From the N₂ adsorption results (Supplementary Fig. 13), we found GOx&HRP/ZIF-8-MV had a relatively high specific surface area, indicating that the conversion degree from aZIF-8 to crystalline ZIF-8 was the highest in these samples. Through the pore size distribution, it was observed that the porosity of all the prepared GOx&HRP/ZIF-8-X was recovered (Fig. 2b). Notably, a small amount of mesopores appeared in GOx&HRP/ZIF-8-WV, suggesting some defects of ZIF-8 were induced during phase transformation (Fig. 2b). The surface morphologies of the GOx&HRP/aZIF-8 before and after water vapor recovery (Supplementary Fig. 14, Fig. 2c) were different. ZIF-8 nanocrystals and pinholes were discovered on the surface of GOx&HRP/ZIF-8-WV. Analyzing together with the data of pore size distribution, GOx&HRP/ZIF-8-WV obtained by PASR method is indeed a crystalline ZIF-8 composite with mesopores.

In order to prove the successful encapsulation of GOx and HRP, fluorescein isothiocyanate (FITC)-labeled GOx and coumarin-labeled HRP/ZIF-8-WV were prepared. From the confocal microscope graph (Fig. 2g), it can be seen that FITC-labeled GOx and coumarin-labeled HRP were evenly distributed in the ZIF-8 matrix and aZIF-8 matrix (Supplementary Fig. 16) while the mixture of ZIF-8 NPs with FITC-labeled GOx only adsorbed on the surface of ZIF-8 (Supplementary Fig. 17). The Fe element from HRP evenly distributing in the bulk structure of ZIF-8 was observed through cross-sectional SEM mapping and Transmission Electron Microscope (TEM) mapping (Figs. 3d-3f, Fig. 3h and Supplementary Figs. 14 and 15). According to the above experimental results, GOx and HRP have been completely encapsulated inside the crystalline ZIF-8 matrix through PASR strategy.

The most important purpose of preparing enzyme/MOF composites is to use MOF matrix to

protect the biological activity of enzymes. To prove that the enzymes encapsulated in MOFs have similar activity as free enzymes, the biological activity of GOx&HRP/ZIF-8-X were studied in tandem reactions. During the reactions, GOx converted glucose into gluconic acid and generated H₂O₂, which is the substrate for HRP to oxidize 2,2'-diazobis(3-ethyl benzothiazoline-6-sulfonic acid) (ABTS²⁻) to ABTS^{•+}. The absorbance at 415 nm of ABTS^{•+} is monitored as a standard for reaction progress.

The activities of GOx&HRP/ZIF-8-MV and GOx&HRP/ZIF-8-MW were preserved (55.1%, 89.1%), but lower than the activity of free enzymes (Fig. 2i), implying that organic solvents and organic salts had negative effects on the activity of enzymes^{33, 43-45}. In addition, the small windows of ZIF-8 (3.4 Å) would restrict the transportation of substrate, which might be accountable for the lower activities as well. Interestingly, due to the presence of mesopores, GOx&HRP/ZIF-8-WV exhibited the highest activity (99.8%), which favored the acceleration of reaction rates and the contact between the substrate and enzyme^{46, 47}. The contents of the two labeled enzymes in ZIF-8 were determined by using a fluorescence standard curve. GOx&HRP/aZIF-8 had 3.96% of GOx and 1.09% of HRP, probably due to the leakage of the free enzyme from aZIF-8 NPs, resulting in its lower loading amount. The GOx&HRP/ZIF-8-WV contained 4.98% of GOx and 1.78% of HRP, indicating that the recovery process is beneficial to the encapsulation of the enzyme (Supplementary Fig. 18). The experiment of encapsulating one single enzyme was also carried out and proved that the enzyme activity (94.7% for GOx and 82.4% for HRP) was maintained under the condition of water vapor recovery (Supplementary Fig. 19). These results prove that PASR strategy can maintain the activity of enzyme after encapsulation.

To investigate whether the ZIF-8 structure could keep the enzyme from being attacked by

other inhibitors, the free enzyme, GOx&HRP/aZIF-8 and GOx&HRP/ZIF-8-WV were immersed in 1 mg/mL protease and 1 wt% ethylene diamine tetraacetic acid (EDTA) solution for 1 hour, respectively. The GOx&HRP/ZIF-8-WV maintained 95.6% and 92.4% of enzyme activity under the treatment of protease and EDTA, respectively, whereas the activity of GOx&HRP/aZIF-8 decreased to 66.3% and 54.9% of the original value (Fig. 2j). The low loadings of enzymes and poor mass transfer caused the low activity of GOx&HRP/aZIF-8 while the mesopores and micropores from GOx&HRP/ZIF-8-WV accelerated the reaction rate and protected enzymes from being attacked by inhibitors. For free enzymes, the activities they remained were only 28.7% and 38.7%. The results show that PASR strategy can not only encapsulate but also protect enzymes desirably.

PASR for encapsulation of DOX molecules in ZIF-8

After successfully using the PASR encapsulation strategy to prepare GOx&HRP/ZIF-8-WV with high activity and stability, we tried to apply this strategy to prepare more guest/MOF composites, such as drugs/MOF composites. Doxorubicin (DOX) was used as guest molecules to be encapsulated into ZIF-8 by the PASR strategy. DOX/ZIF-8-MV was prepared by recovering in methanol vapor for 48 hours at room temperature (see Methods for details). The PXRD patterns (Fig. 3a) and N₂ adsorption curve (Supplementary Fig. 20) both showed the crystallinity and porosity of the ZIF-8 in the DOX/ZIF-8-MV. The appearance of ZIF-8 nanocrystals in the SEM (Supplementary Fig. 21 and Fig. 3b) also proved that aZIF-8 was successfully recovered. Laser confocal microscopy images in Fig. 3g and Supplementary Fig. 23 confirmed the existence of DOX guests in DOX/ZIF-8-MV. Through UV-Vis absorption spectrum, the loading of DOX was 40.4 wt% (Supplementary Fig. 24), which was superior to that reported in most literatures (Supplementary Table 1). From the

cross-sectional SEM mapping of DOX/ZIF-8-MV (Fig. 3c-3e, Supplementary Fig. 21) and high-resolution TEM element mapping (Fig. 3f, Supplementary Fig. 22), Cl element from DOX is observed to be evenly distributed in ZIF-8 carriers, further verifying the uniform encapsulation of DOX in ZIF-8.

Since the structure of ZIF-8 is unstable under acidic conditions, it can be used for sustainable pH-responsive drug releasing⁴⁸. The DOX/ZIF-8-MV exhibited a similar drug releasing behavior to the reported DOX/ZIF-8 prepared by in-situ encapsulation method^{49, 50}. The drug releasing of DOX/ZIF-8-MV has been monitored under neutral and low pH conditions (Fig. 3h). Under physiological conditions (pH = 7.4), DOX/ZIF-8-MV had a lower releasing rate, while DOX was completely released after 30 hours when the pH value was 5.0. These results confirm that through our PASR method, high drug loading and pH-responsive drug releasing can be achieved.

Generalization of PASR encapsulation strategy

The PASR strategy can also be extended to other MOFs which possess the property of crystal transformation to prepare enzyme/MOF composites. Mg-MOF-74 has large hexagon pores with the size of 1.35 nm, which is a desirable host for substrates' transportation. GOx has been encapsulated into Mg-MOF-74 by PASR (see Methods for details). It was interestingly that GOx/aMg-MOF-74 recovered in water vapor remained 96.5% activity after 2 h and then gradually lost the activity until 72 h of complete loss (Supplementary Figs. 25-26). It means the recovery time influences the activity of enzymes to a certain degree.

It is known that some NPs are difficult to be encapsulated into MOFs without the assistance of surfactants such as PVP¹⁸ or using double-solvents approach⁵¹. NPs and functional species such as Pt NPs, SiO₂, TiO₂, Au NPs and MWCNTs have been packaged into ZIF-8, HKUST-1, Mg-MOF-74

and Al-MIL-53 (Supplementary Figs. 27-30 and 32). All of the NPs have been uniformly dispersed in MOF structures as observed by SEM mapping and TEM images (Fig. 4, Supplementary Fig. 33). The catalytic selectivity of Pt/ZIF-8-MS for 1-hexene molecules was increased to 98%, indicating the encapsulation of Pt NPs in Pt/ZIF-8-MS (Supplementary Fig.31). In general, the PASR method can encapsulate different types of guest species into MOFs with different structures, which illustrates the feasibility and versatility of the PASR strategy for preparing guest/MOF composites.

Discussion

The PASR shows its specialty on three key factors. One is the synthesis of MOF composites. Different from the existing methods for the preparation of MOF composites, our method can encapsulate functional species that are not sensitive to mechanical pressure into MOF structures with no limit on the species' sorts or shapes or sizes. Secondly, the encapsulation strategy utilized the dynamic transformations of MOF structures. Compared to zeolites, MOFs are more flexible and tunable. The PASR takes advantages of MOFs' dynamic coordination bonds and endows MOFs with more flexibility and designability in nanomaterials synthesis. Thirdly, the PASR can encapsulate not only stable functional species, but also unstable functional species. Our synthetic strategy is thus general and versatile, and can seek a broad range of applications in the field of biosynthesis, drug delivery and catalysis. Hence, PASR will bring more possibility for the combination of the merits on both MOFs and functional species.

In summary, we have developed a PASR strategy, which induced functional species into MOF structures during the phase transition of MOFs by mechanical pressure and solvents/vapor recovery process. The successful synthesis of enzymes/ZIF-8-WV with mesopores has showed similar activity as free enzymes and retained high activity under the treatment of enzyme

inhibitors. Besides, anti-cancer drugs and Pt NPs have also been encapsulated into ZIF-8, which achieved synergistic effects including high drug loading and size selective catalysis. This method has been extended to other MOFs (Mg-MOF-74, HKUST-1, Al-MIL-53) and other functional species (GOx, SiO₂, TiO₂, Au NPs and MWCNTs) to prove general application. This strategy may be a good choice to design new MOF composites with new guest molecules. Functional species are not only limited to nanocomposites, luminescent molecules⁷⁻⁸ could be accommodated into MOFs for preparing photonic MOF composites. The hosts can also be changed to other structures such as coordination networks⁵² and coordination compounds⁵³. We believe the PASR strategy would be a toolbox for the synthesis of MOF composites without damaging the functionality of guest molecules and endowing MOFs with new properties for a wide range of applications, such as biosynthesis, drug delivery, catalysis and so on.

Methods

Commercial ZIF-8 was purchased from Sigma-Aldrich (ACS grade). MIL-53(Al) and MOF-74(Mg) were supplied by the company of HWRK CHEM.

Synthesis of ZIF-67(Co). 500 mL MeOH of Co(NO₃)₂·6H₂O (9.68 g, 66.6 mM) and 500 mL water of 2-MIM (10.26 g, 0.25 mM) were mixed and stirring for a while in a glass vial, then 25 mL from each was picked up, mixed and stood for 24 hours at room temperature. Then the samples were washed with MeOH for several times before drying at room temperature vacuum first, followed by keeping them at 120 °C overnight.

Synthesis of HKUST-1. 15 mL methanol solution of Cu(NO₃)₂·2.5H₂O (0.657 g, 0.1 mM) and 15

mL BTC (0.315 g, 0.05 mM) were mixed and sonicated uniformly in a glass vial, follow by reacting at room temperature for 1 hour. Product was collected by centrifugation and then washed three times with methanol. The product was placed in a vacuum drying oven at 120 °C overnight.

Variable pressure studies of ZIF-8. 10 mg ZIF-8 material purchased from Sigma-Aldrich (ACS grade) after activation was weighed and put into the chamber of the T69YP-15A tablet machine. The chamber wall was shaken to make it uniformly adhere to the bottom of the pellets. After that, 2 MPa (gauge pressure, actual pressure 91 MPa), 6 MPa (gauge pressure, actual pressure 273 MPa), 10 MPa (gauge pressure, actual pressure 455 MPa), 20 MPa (gauge pressure, actual pressure 909 MPa), and 30 MPa (gauge pressure, actual pressure 1,364 MPa) were applied to it respectively, and withdrawn after 5 minutes.

Recovery of ZIF-8 under different conditions. 10 mg of each aZIF-8 pellets were kept in MeOH solvents at 50 °C for 5 hours or MeOH vapors at 50 °C for 24 hours. 10 mg of each aZIF-8 pellets recovered by water was conducted under the treatment of 40 µL water, or kept in a trace of water for different times (48 hours, 72 hours), or 40 µL 2-methyl imidazole/water, respectively.

PASR for other MOFs. All treatment methods for other MOFs were obeyed to previous operation. 20 mg ZIF-67/HKUST-1/MOF-74 (except MIL-53 without activation) materials after activation were weighed and put into the chamber of T69YP-15A tablet machine, respectively. The chamber wall was shaken to make it uniformly adhere to the bottom of the pellets. After that, 30 MPa (gauge pressure, actual pressure 1,364 MPa) was applied to the samples respectively, and withdrawn after 5 minutes. ZIF-67/HKUST-1/MIL-53 have been recovered by methanol vapor for 24 hours at room temperature. MOF-74 has been recovered by water solvents for 6 hours at 120 °C or water vapor at room temperature for 3 days.

Preparation of GOx&HRP/aZIF-8 composites and recovered GOx&HRP/ZIF-8 composites.

5 mg glucose oxidase (GOx), 5 mg horseradish peroxidase (HRP) and 90 mg activated commercial ZIF-8 were mixed thoroughly and ground. 20 mg of GOx&HRP/ZIF-8 were amorphized via a T69YP-15A tablet machine. The dry powders were subjected to average pressures of 1,364 MPa (9 ton, 13 mm diameter pellet die) for 5 min. GOx&HRP/ZIF-8-MV was prepared by exposing GOx&HRP/aZIF-8 to methanol vapor at room temperature for 24 hours. GOx&HRP/ZIF-8-WV was prepared by exposing to saturated water vapor conditions at 25 °C for 72 hours to fully restore their structure in a vacuum drier at Aseptic carto. GOx&HRP/ZIF-8-MW was prepared by a drop of 2-methyl imidazole/water at room temperature overnight. After recovery, the samples were soaked in 1 mL of deionized water to remove free enzymes and aggregates from the surface.

Preparation of pressed GOx/aZIF-8, HRP/aZIF-8 composite and recovered GOx/ZIF-8, HRP/ZIF-8 composites. 5 mg GOx and 95 mg activated commercial ZIF-8 were mixed thoroughly and ground. 20 mg of GOx/ZIF-8 were amorphized via a T69YP-15A tablet machine. The dry powders were subjected to average pressures of 1,364 MPa (9-ton, 13 mm diameter pellet die) for 5 min. GOx/ZIF-8-MV was prepared by exposing GOx/aZIF-8 to methanol vapor at room temperature for 24 hours. GOx/ZIF-8-WV was prepared by exposing to saturated water vapor conditions at 25 °C for 72 hours to fully restore their structure in a vacuum drier. GOx/ZIF-8-MW was prepared by a drop of 2-methyl imidazole/water at room temperature overnight. After recovery, the samples were soaked in 1 mL of deionized water to remove free enzymes and aggregates from the surface.

The experiments for encapsulating HRP were the same as those for encapsulating GOx except that

5 mg GOx was replaced with 5 mg HRP.

Enzymatic activity of free enzymes, GOx&HRP/ZIF-8 composites³². 20 mg of GOx&HRP/ZIF-8-MV or GOx&HRP/ZIF-8-WV or GOx&HRP/ZIF-8-MW were put into pH 7.4 phosphate buffer solution (PBS) of 1 mM 2,2'-diazobis(3-ethyl benzothiazoline-6-sulfonic acid) (ABTS). A small amount of glucose was added to ensure that the concentration of glucose was 1 mM. 10 min later, by diluting the solution with water, the activity of samples was measured by ultraviolet at 415 nm and compared with the free enzymes.

For the enzymatic activity of free enzymes, the experiments were the same as those above except that the amounts of free enzymes were 1 mg glucose oxidase and 0.2 mg horseradish peroxidase.

Enzymatic activity of recovered GOx/ZIF-8 and HRP/ZIF-8 composites. Around 0.5 mg of GOx/ZIF-8-MV or GOx/ZIF-8-WV or GOx/ZIF-8-MW was put in 0.5 mM ABTS reaction solution (PBS, 1mM, pH = 7.4), and 10 μ L of 1 mg/ml horseradish catalase has been added. A small amount of glucose was added to ensure that the concentration of glucose was 100 mM. The activity of samples was measured by ultraviolet at 415 nm; the reaction time was 2 min.

For the enzymatic activity of free enzymes, the experiments were the same as those above except that the amounts of free enzymes were 25 μ L of 1 mg/mL glucose oxidase.

The enzyme activity was measured by the slope of time versus absorption.

0.5 mg of HRP/ZIF-8-MV or HRP/ZIF-8-WV or HRP/ZIF-8-MW was put in 0.5 mM ABTS reaction solution (PBS, 1mM, pH = 7.4). A small amount of H₂O₂ was added to ensure that the concentration of H₂O₂ was 1.66 mM. The activity of samples was measured by ultraviolet at 415 nm, the reaction time is 2 min.

The enzyme activity was measured by the slope of time versus absorption.

For the enzymatic activity of free enzymes, the experiments were the same as those above except that the amounts of free enzymes were 25 μ L of 1 mg/ml horseradish catalase.

Enzyme activity of the GOx&HRP/aZIF-8 or GOx&HRP/ZIF-8-WV after 1 hour treatment with inhibitors³². 20 mg of GOx&HRP/aZIF-8 or GOx&HRP/ZIF-8-WV was treated with 1 mg/ml protease and 1 wt% ethylene diamine tetraacetic acid (EDTA) for 1 hour respectively. The solution was then poured out and placed in a phosphate buffer solution (PBS) of pH 7.4 of 1 mM 2, 2'-diazobis(3-ethyl benzothiazoline-6-sulfonic acid) (ABTS). A small amount of glucose was added to ensure that the concentration of glucose was 1 mM. 10 min later, by diluting the solution with water, the activity of samples was measured by ultraviolet at 415 nm and compared with the free enzymes.

For the enzymatic activity of free enzymes, the experiments were the same as those above except that the amounts of free enzymes were 1 mg glucose oxidase and 0.2 mg horseradish peroxidase.

Procedures for labeling enzymes with dyes³². According to previous report, 8 mg of FITC or N-Succinimidyl 7-hydroxycoumarin-3-carboxylate dissolved in DMSO (2 mg/mL) was slowly added in to 1 mL of GOx or HRP solution (5 mg/mL of enzyme in 0.5 M, pH 9.5 carbonate buffer). The solution was shaken for 6 h at 150 rpm at 37 °C in dark. Free FITC or coumarin was removed via dialysis against de-ionized water. The fluorescent molecule-labeled enzymes were freeze-dried and then dissolved in water for the subsequent synthesis of fluorescently labeled GOx&HRP/ZIF-8 composite. Laser scanning confocal microscope images were taken on a Zeiss LSM880 NLO (2 + 1 with BIG) confocal microscope. The detection wavelengths were 488 nm

and 405 nm for FITC and coumarin, respectively.

Characterization of the contents of enzymes in ZIF-8. According to previous methods, FITC labelled GOx and coumarin labelled HRP have been dissolved into 1% HCl/water solution for fluorescence tests at different concentrations, respectively. Emission data at 525 nm for FITC labelled GOx ($\lambda_{\text{ex}} = 440$ nm) have been analyzed for standard curve. Emission data at 445 nm for coumarin labelled HRP ($\lambda_{\text{ex}} = 355$ nm) have been analyzed for standard curve. Then the pressed and water vapor' recovered FITC labelled GOx&coumarin labelled HRP after washing have been digested by 1% HCl/water for detecting the amounts of enzymes.

Preparation of DOX/aZIF-8 and DOX/ZIF-8-MV. Ground DOX/ZIF-8 with a mass ratio of 1:1 was amorphized via a T69YP-15A tablet machine. 20 mg of the dry powders were subjected to average pressures of 1,364 MPa (9-ton, 13 mm diameter pellet die) for 5 min. The DOX/aZIF-8 was directly exposed to MeOH methanol at room temperature for 48 hours. After that, our samples have been dialyzed with water for one week.

Drug releasing experiments of DOX/ZIF-8-MV. Two of 1.5 mg DOX/ZIF-8-MV composites were weighed and dissolved in the buffer solution of 3 mL PBS (pH = 7.4) by ultrasound, respectively. Then they were transferred to the dialysis bag through a pipette gun. One of the buffer solutions outside the dialysis bag was 30 mL PBS (pH = 7.4) and the other one was 30 mL PBS (pH = 5.0) at 37 °C, respectively. The whole system was carried out in a shaker. The fluorescence of the solution outside the dialysis bag was monitored each hour, and then the release of DOX was measured by standard curve.

Characterization of the contents of drugs in ZIF-8. 2 mg DOX/ZIF-8 composite was dissolved

in the 1wt% HCl (H₂O) solution. Ultrasound made DOX/ZIF-8 completely dissolve into homogeneous solution and dilute continuously. The drug molecular content was determined by ultraviolet and standard curve method.

Preparation of GOx/aMg-MOF-74, and recovered GOx/aMg-MOF-74 composites. 5 mg GOx and 95 mg activated commercial Mg-MOF-74 were mixed thoroughly and ground. 20 mg of GOx/Mg-MOF-74 were amorphized via a T69YP-15A tablet machine. The dry powders were subjected to average pressures of 1,364 MPa (9-ton, 13 mm diameter pellet die) for 5 min. Mg-MOF-74-WV was prepared by exposing GOx/aMg-MOF-74 to water vapor at room temperature for 2 hours, 5 hours or 72 hours.

Enzymatic activity of GOx/aMg-MOF-74, and GOx/Mg-MOF-74-W composites. Around 0.5 mg of GOx/aMg-MOF-74 or GOx/Mg-MOF-74-W composites were put in 0.5 mM ABTS reaction solution (PBS, 1mM, pH = 7.4), and 10 μ L of 1 mg/mL horseradish catalase was added. A small amount of glucose was added to ensure that the concentration of glucose was 100 mM. The activity of samples was measured by ultraviolet at 415 nm, and the reaction time was 2 min.

For the enzymatic activity of free enzymes, the experiments were the same as those above except that the amounts of free enzymes were 25 μ L of 1 mg/mL glucose oxidase.

The enzyme activity was measured by the slope of time versus absorption.

Preparation of Pt/aZIF-8 and Pt/ZIF-8-MS. Ground Pt/ZIF-8 was amorphized via a T69YP-15A tablet machine. The dry powders were subjected to average pressures of 1,364 MPa (9-ton, 13 mm diameter pellet die) for 5 min. The Pt/aZIF-8 was directly exposed to MeOH solvents at 50 °C. The contents of Pt for the pressed Pt/ZIF-8 and recovered Pt/ZIF-8 were

determined by inductively coupled plasma (ICP) spectroscopy to be 2.28 wt% and 1.80 wt% (mass fraction ratio), respectively.

Pt/ZIF-8, Pt/aZIF-8 and Pt/ZIF-8-MS composites for catalytic hydrogenation. Hydrogenation of olefins catalyzed by Pt/ZIF-8: all samples were pre-dried for 12 hours at 120 °C to activate ZIF-8. Pt/ZIF-8 or Pt/aZIF-8 or Pt/ZIF-8-MS composites catalyst was added to 5 mL glass bottle to seal the glass bottle with silica gel plug. Pull the gas out of the bottle with a syringe and repeat it three times. 3 mL ethyl acetate solution was added into the syringe, and then n-hexene (40 µL) and cis-cyclooctene (40 µL) were injected into the syringe. The catalysis was taken under static reaction for 48 hours at room temperature. The conversion of 1-hexene and cyclooctene was determined by gas chromatography.

Preparation of other functional species/MOF composites. 5 mg functional species and 95 mg activated MOFs (except Al-MIL-53) were mixed thoroughly and ground. 20 mg of functional/species were amorphized via a T69YP-15A tablet machine. The dry powders were subjected to average pressures of 1,364 MPa (9-ton, 13 mm diameter pellet die) for 5 min. TiO₂/HKUST-1-MS or SiO₂/HKUST-1-MS was prepared by exposing to methanol solvents at room temperature for 24 hours. Au NPs/MIL-53 or MWCNTs/MIL-53 was prepared by exposing to methanol vapor at room temperature for 24 hours. Au NPs/Mg-MOF-74-W or MWCNTs/Mg-MOF-74-W was prepared by exposing to water solvents or vapor at 120 °C for 5 min or 6 hours.

References

1. He, Y., Zhou, W., Qian, G., Chen, B. Methane storage in metal–organic frameworks. *Chem. Soc. Rev.* **43**, 5657-5678(2014).
2. Zhao, X., Wang, Y., Li, D.-S., Bu, X., Feng, P. Metal–Organic Frameworks for Separation. *Adv. Mater.* **30**, 1705189(2018).
3. Yang, Q., Xu, Q., Jiang, H.-L. Metal–organic frameworks meet metal nanoparticles: synergistic effect for enhanced catalysis. *Chem. Soc. Rev.* **46**, 4774-4808(2017).
4. McKinlay, A. C., Morris, R. E., Horcajada, P., Férey, G., Gref, R., Couvreur, P., *et al.* BioMOFs: Metal–Organic Frameworks for Biological and Medical Applications. *Angew. Chem. Int. Ed.* **49**, 6260-6266(2010).
5. Horcajada, P., Gref, R., Baati, T., Allan, P. K., Maurin, G., Couvreur, P., *et al.* Metal–Organic Frameworks in Biomedicine. *Chem. Rev.* **112**, 1232-1268(2012).
6. Wang, P.-L., Xie, L.-H., Joseph, E. A., Li, J.-R., Su, X.-O., Zhou, H.-C. Metal–Organic Frameworks for Food Safety. *Chem. Rev.* **119**, 10638-10690(2019).
7. Cui, Y., Yue, Y., Qian, G., Chen, B. Luminescent Functional Metal–Organic Frameworks. *Chem. Rev.* **112**, 1126-1162(2012).
8. Cui, Y., Zhang, J., He, H., Qian, G. Photonic functional metal–organic frameworks. *Chem. Soc. Rev.* **47**, 5740-5785(2018).
9. Chen, L., Luque, R., Li, Y. Encapsulation of metal nanostructures into metal–organic frameworks. *Dalton. T.* **47**, 3663-3668(2018).
10. Chen, L., Luque, R., Li, Y. Controllable design of tunable nanostructures inside metal–organic frameworks. *Chem. Soc. Rev.* **46**, 4614-4630(2017).
11. Juan-Alcañiz, J., Gascon, J., Kapteijn, F. Metal–organic frameworks as scaffolds for the encapsulation of active species: state of the art and future perspectives. *J. Mater. Chem.* **22**, 10102-10118(2012).
12. Furukawa, H., Cordova, K. E., O’Keeffe, M., Yaghi, O. M. The chemistry and applications of metal-organic frameworks. *Science*. **341**, 1230444(2013).
13. Wang, T., Gao, L., Hou, J., Herou, S. J., Griffiths, J. T., Li, W., *et al.* Rational approach to guest confinement inside MOF cavities for low-temperature catalysis. *Nat. Commun.* **10**, 1340(2019).
14. Falcaro, P., Furukawa, S. Doping Light Emitters into Metal–Organic Frameworks. *Angew. Chem. Int. Ed.* **51**, 8431-8433(2012).
15. Kirchon, A., Feng, L., Drake, H. F., Joseph, E. A., Zhou, H.-C. From fundamentals to applications: a toolbox for robust and multifunctional MOF materials. *Chem. Soc. Rev.* **47**, 8611-8638(2018).

16. Falcaro, P., Hill, A. J., Nairn, K. M., Jasieniak, J., Mardel, J. I., Bastow, T. J., *et al.* A new method to position and functionalize metal-organic framework crystals. *Nat. Commun.* **2**, 237(2011).
17. Mao, Y., Li, J., Cao, W., Ying, Y., Hu, P., Liu, Y., *et al.* General incorporation of diverse components inside metal-organic framework thin films at room temperature. *Nat. Commun.* **5**, 5532(2014).
18. Lu, G., Li, S., Guo, Z., Farha, O. K., Hauser, B. G., Qi, X., *et al.* Imparting functionality to a metal-organic framework material by controlled nanoparticle encapsulation. *Nat. Chem.* **4**, 310(2012).
19. Zhao, M., Yuan, K., Wang, Y., Li, G., Guo, J., Gu, L., *et al.* Metal-organic frameworks as selectivity regulators for hydrogenation reactions. *Nat.* **539**, 76(2016).
20. Horcajada, P., Chalati, T., Serre, C., Gillet, B., Sebrie, C., Baati, T., *et al.* Porous metal-organic-framework nanoscale carriers as a potential platform for drug delivery and imaging. *Nat. Mater.* **9**, 172(2010).
21. Lian, X., Fang, Y., Joseph, E., Wang, Q., Li, J., Banerjee, S., *et al.* Enzyme-MOF (metal-organic framework) composites. *Chem. Soc. Rev.* **46**, 3386-3401(2017).
22. Hu, Y., Dai, L., Liu, D., Du, W., Wang, Y. Progress & prospect of metal-organic frameworks (MOFs) for enzyme immobilization (enzyme/MOFs). *Renew. Sust. Energ. Rev.* **91**, 793-801(2018).
23. Huang, S., Kou, X., Shen, J., Chen, G., Ouyang, G. Armoring the Enzymes with Metal-Organic Frameworks. *Angew. Chem. Int. Ed.* **59**, 2-15(2020).
24. Mehta, J., Bhardwaj, N., Bhardwaj, S. K., Kim, K.-H., Deep, A. Recent advances in enzyme immobilization techniques: Metal-organic frameworks as novel substrates. *Coord. Chem. Rev.* **322**, 30-40(2016).
25. Guan, J., Hu, Y., Wang, Y., Li, H., Xu, Z., Zhang, T., *et al.* Controlled Encapsulation of Functional Organic Molecules within Metal-Organic Frameworks: In Situ Crystalline Structure Transformation. *Adv. Mater.* **29**, 1606290(2017).
26. Morabito, J. V., Chou, L.-Y., Li, Z., Manna, C. M., Petroff, C. A., Kyada, R. J., *et al.* Molecular Encapsulation beyond the Aperture Size Limit through Dissociative Linker Exchange in Metal-Organic Framework Crystals. *J. Am. Chem. Soc.* **136**, 12540-12543(2014).
27. Li, Z., Rayder, T. M., Luo, L., Byers, J. A., Tsung, C.-K. Aperture-Opening Encapsulation of a Transition Metal Catalyst in a Metal-Organic Framework for CO₂ Hydrogenation. *J. Am. Chem. Soc.* **140**, 8082-8085(2018).
28. Lykourinou, V., Chen, Y., Wang, X.-S., Meng, L., Hoang, T., Ming, L.-J., *et al.* Immobilization of MP-11 into a Mesoporous Metal-Organic Framework, MP-11@mesoMOF: A New Platform for Enzymatic Catalysis. *J. Am. Chem. Soc.* **133**, 10382-10385(2011).
29. Liang, K., Ricco, R., Doherty, C. M., Styles, M. J., Bell, S. G., Kirby, N., *et al.* Biomimetic mineralization of

metal-organic frameworks as protective coatings for biomacromolecules. *Nat. Commun.* **6**, 7240-7240(2015).

30. Chen, W.-H., Vázquez-González, M., Zoabi, A., Abu-Reziq, R., Willner, I. Biocatalytic cascades driven by enzymes encapsulated in metal-organic framework nanoparticles. *Nat. Catal.* **1**, 689-695(2018).
31. Lyu, F., Zhang, Y., Zare, R. N., Ge, J., Liu, Z. One-Pot Synthesis of Protein-Embedded Metal-Organic Frameworks with Enhanced Biological Activities. *Nano. Lett.* **14**, 5761-5765(2014).
32. Wu, X., Ge, J., Yang, C., Hou, M., Liu, Z. Facile synthesis of multiple enzyme-containing metal-organic frameworks in a biomolecule-friendly environment. *Chem. Commun.* **51**, 13408-13411(2015).
33. Chen, G., Kou, X., Huang, S., Tong, L., Shen, Y., Zhu, W., *et al.* Modulating the Biofunctionality of Metal-Organic-Framework-Encapsulated Enzymes through Controllable Embedding Patterns. *Angew. Chem. Int. Ed.* **59**, 2867-2874(2020).
34. Wei, T.-H., Wu, S.-H., Huang, Y.-D., Lo, W.-S., Williams, B. P., Chen, S.-Y., *et al.* Rapid mechanochemical encapsulation of biocatalysts into robust metal-organic frameworks. *Nat. Commun.* **10**, 5002(2019).
35. Chapman, K. W., Halder, G. J., Chupas, P. J. Pressure-induced amorphization and porosity modification in a metal-organic framework. *J. Am. Chem. Soc.* **131**, 17546-17547(2009).
36. Chapman, K. W., Sava, D. F., Halder, G. J., Chupas, P. J., Nenoff, T. M. Trapping guests within a nanoporous metal-organic framework through pressure-induced amorphization. *J. Am. Chem. Soc.* **133**, 18583-18585(2011).
37. Ortiz, A. I. U., Boutin, A., Fuchs, A. H., Coudert, F. o.-X. Investigating the pressure-induced amorphization of zeolitic imidazolate framework ZIF-8: mechanical instability due to shear mode softening. *J. Phys. Chem. Lett.* **4**, 1861-1865(2013).
38. Zhao, P., Bennett, T. D., Casati, N. P., Lampronti, G. I., Moggach, S. A., Redfern, S. A. Pressure-induced oversaturation and phase transition in zeolitic imidazolate frameworks with remarkable mechanical stability. *Dalton. T.* **44**, 4498-4503(2015).
39. Yuan, S., Sun, X., Pang, J., Lollar, C., Qin, J.-S., Perry, Z., *et al.* PCN-250 under pressure: sequential phase transformation and the implications for MOF densification. *Joule.* **1**, 806-815(2017).
40. Monteagudo-Olivan, R., Paseta, L., Potier, G., López-Ram-de-Viu, P., Coronas, J. Solvent-Free Encapsulation at High Pressure with Carboxylate-Based MOFs. *Eur. J. Inorg. Chem.* **2019**, 29-36(2019).
41. Panda, T., Horike, S., Hagi, K., Ogiwara, N., Kadota, K., Itakura, T., *et al.* Mechanical Alloying of Metal-Organic Frameworks. *Angew. Chem. Int. Ed.* **129**, 2453-2457(2017).
42. Carraro, F., Velásquez-Hernández, M. d. J., Astria, E., Liang, W., Twight, L., Parise, C., *et al.* Phase dependent encapsulation and release profile of ZIF-based biocomposites. *Chem. Sci.* **11**, 3397-3404(2020).

43. Herskovits, T. T., Gadegbeku, B., Jaillet, H. On the structural stability and solvent denaturation of proteins. I. Denaturation by the alcohols and glycols. *J. Biol. Chem.* **245**, 2588-2598(1970).
44. Toba, S., Merz, K. M. The Concept of Solvent Compatibility and Its Impact on Protein Stability and Activity Enhancement in Nonaqueous Solvents. *J. Am. Chem. Soc.* **119**, 9939-9948(1997).
45. Vasileva, N., Godjevargova, T. Study of the effect of some organic solvents on the activity and stability of glucose oxidase. *Mat. Sci. Eng. C.* **25**, 17-21(2005).
46. Wu, X., Yue, H., Zhang, Y., Gao, X., Li, X., Wang, L., *et al.* Packaging and delivering enzymes by amorphous metal-organic frameworks. *Nat. Commun.* **10**, 5165(2019).
47. Hu, C., Bai, Y., Hou, M., Wang, Y., Wang, L., Cao, X., *et al.* Defect-induced activity enhancement of enzyme-encapsulated metal-organic frameworks revealed in microfluidic gradient mixing synthesis. *Sci. Adv.* **6**, eaax5785(2020).
48. Sun, C.-Y., Qin, C., Wang, X.-L., Yang, G.-S., Shao, K.-Z., Lan, Y.-Q., *et al.* Zeolitic imidazolate framework-8 as efficient pH-sensitive drug delivery vehicle. *Dalton. T.* **41**, 6906-6909(2012).
49. Zheng, H., Zhang, Y., Liu, L., Wan, W., Guo, P., Nyström, A. M., *et al.* One-pot synthesis of metal-organic frameworks with encapsulated target molecules and their applications for controlled drug delivery. *J. Am. Chem. Soc.* **138**, 962-968(2016).
50. Zheng, C., Wang, Y., Phua, S. Z. F., Lim, W. Q., Zhao, Y. ZnO-DOX@ ZIF-8 Core-Shell Nanoparticles for pH-Responsive Drug Delivery. *ACS. Biomater. Sci. Eng.* **3**, 2223-2229(2017).
51. Aijaz, A., Karkamkar, A. J., Choi, Y., Tsumori, N., Ronnebro, E., Autrey, T., *et al.* Immobilizing Highly Catalytically Active Pt Nanoparticles inside the Pores of Metal-Organic Framework: A Double Solvents Approach. *J. Am. Chem. Soc.* **134**, 13926-13929(2012).
52. Hosono, N., Kitagawa, S. Modular Design of Porous Soft Materials via Self-Organization of Metal-Organic Cages. *Acc. Chem. Res.* **51**, 2437-2446(2018).
53. Jin, M., Sumitani, T., Sato, H., Seki, T., Ito, H. Mechanical-Stimulation-Triggered and Solvent-Vapor-Induced Reverse Single-Crystal-to-Single-Crystal Phase Transitions with Alterations of the Luminescence Color. *J. Am. Chem. Soc.* **140**, 2875-2879(2018).

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Author contributions

Z.Ren, W.Q. Zhou and A/Prof J.N. Weng contributed equally in this paper.

Z.Ren, W.Q. Zhou and A/Prof J.N. Weng designed and performed experiments, analyzed the results and drafted the manuscript. Z.Y. Qin and L.W. Liu gave assistance on catalytic experiments and manuscript revision. W.Q. Zhou and N.Ji were responsible for the drug releasing process. Islam Khalil, A/Prof J.N. Weng, A/Prof B. Zheng and Prof J.S. Wu helped revise manuscript. Professor F.W. Huo, Professor and W.N. Zhang supervised the project, helped design the experiments, and revised the manuscript. All authors contributed to the analysis of this paper.

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Figures:

Scheme.1 Schematic illustration of the pressure-amorphization-stimulation-recovery (PASR) process of preparing MOF composites. The MOF composites were synthesized via the two-step approach of enclosing functional species by transforming premixed functional species/MOFs into amorphous states, and then recovering the framework structure through exposing them in solvents' or vapor's environment.

Fig. 1 **a** PXRD patterns of simulated ZIF-8, commercial ZIF-8, and ZIF-8 under high pressure (1,364 MPa), before and after recovery (methanol vapor and solvents at 50 °C). **b** N₂ gas adsorption isotherms of commercial ZIF-8, and ZIF-8 under high pressure (1,364 MPa), and after recovery (methanol vapor and solvents at 50 °C). **c** Scanning electron microscopy data of ZIF-8 at low pressure (91 MPa). **d** Scanning electron microscopy data of ZIF-8 at high pressure (1,364 MPa). **e** Scanning electron microscopy data of aZIF-8 recovered in methanol vapor. **f** Scanning electron microscopy data of aZIF-8 recovered in methanol solvents. (scale bars: 2 μm).

Fig. 2 **a** PXRD patterns for the mixed GOx&HRP with ZIF-8, GOx&HRP/aZIF-8 and GOx&HRP/ZIF-8-X (X=MV, WV and MW). **b** Pore size distribution of GOx&HRP/ZIF-8, GOx&HRP/aZIF-8 and GOx&HRP/ZIF-8-X (inset is the enlarged image). **c** Surface morphology of the GOx&HRP/ZIF-8-WV (scale bar: 2 μ m). **d** The cross-section image of the recovered GOx&HRP/ZIF-8-WV (scale bar: 50 μ m). **e-f** EDS mapping of the Fe and Zn elements in GOx&HRP/ZIF-8-WV (scale bar: 25 μ m). **g** Laser confocal fluorescence microscopy imaging of the FITC-GOx&coumarin-HRP/ZIF-8-WV (scale bar: 400 μ m). **h** TEM image and elemental mappings of GOx&HRP/ZIF-8-WV (h) (scale bar: 250 nm). **i** Comparing activity of pressed enzymes, enzymes under methanol

treatment and GOx&HRP/ZIF-8-X (X=MV, WV and MW). **j** Stability performance of free enzymes, GOx&HRP/aZIF-8 and GOx&HRP/ZIF-8-WV under the treatment of 1 mg/mL EDTA and 1 mg/mL protease.

Fig. 3 **a** PXRD analysis of premixed DOX/ZIF-8, DOX/aZIF-8 and DOX/ZIF-8-MV. **b** Surface morphology of the recovered DOX/ZIF-8-MV (scale bar: 2 μ m), **c** The cross-section image of DOX/ZIF-8-MV (scale bar: 50 μ m). **d-e** EDS mapping of the recovered DOX/ZIF-8-MV (scale bar: 25 μ m). **f** TEM image and elemental mappings of DOX/ZIF-8-MV (scale bar: 500 nm). **g** Laser confocal fluorescence microscopy imaging of the DOX/ZIF-8-MV (scale bar: 200 μ m). **h** Drug releasing performance of recovered DOX/ZIF-8-MV under pH 5.0 and pH 7.4.

Fig. 4 **a** SEM analysis of the Pt/ZIF-8-MS (scale bar: 2 μm). **b** The cross-section images of the Pt/ZIF-8-MS (scale bar: 50 μm). **c-d** EDS mapping of the Pt/ZIF-8-MS (scale bar: 25 μm). **e** SEM analysis of the TiO₂/HKUST-1-MS (scale bar: 2 μm). **f** The cross-section images of the TiO₂/HKUST-1-MS (scale bar: 50 μm). **g-h** EDS mapping of the TiO₂/HKUST-1-MS (scale bar: 25 μm). **i** SEM analysis of the Au/Mg-MOF-74-W (scale bar: 2 μm). **j** The cross-section images of the Au/Mg-MOF-74-W (scale bar: 50 μm). **k-l** EDS mapping of the Au/Mg-MOF-74-W (scale bar: 25 μm). **m-n** TEM images of MWCNTs/MOF-74-W (scale bar: 400 nm, 200 nm). **o-p** TEM images of MWCNTs/MIL-53-MV (scale bar: 400 nm, 1 μm).

Functional species such as enzymes, drugs and functional NPs have been encapsulated into MOFs by a general pressure-amorphization-stimulation-recovery (PASR) strategy, which provided a potential prospect for constructing nanocomposites materials through phase transition of MOFs.

Figures

Figure 1

a PXRD patterns of simulated ZIF-8, commercial ZIF-8, and ZIF-8 under high pressure (1,364 MPa), before and after recovery (methanol vapor and solvents at 50 oC). b N₂ gas adsorption isotherms of commercial ZIF-8, and ZIF-8 under high pressure (1,364 MPa), and after recovery (methanol vapor and solvents at 50 oC). c Scanning electron microscopy data of ZIF-8 at low pressure (91 MPa). d Scanning electron

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of the FITC-GOx&coumarin-HRP/ZIF-8-WV (scale bar: 400 μm). h TEM image and elemental mappings of GOx&HRP/ZIF-8-WV (h) (scale bar: 250 nm). i Comparing activity of pressed enzymes, enzymes under methanol treatment and GOx&HRP/ZIF-8-X (X=MV, WV and MW). j Stability performance of free enzymes, GOx&HRP/aZIF-8 and GOx&HRP/ZIF-8-WV under the treatment of 1 mg/mL EDTA and 1 mg/mL protease.

Figure 3

a PXRD analysis of premixed DOX/ZIF-8, DOX/aZIF-8 and DOX/ZIF-8-MV. b Surface morphology of the recovered DOX/ZIF-8-MV (scale bar: 2 μm), c The cross-section image of DOX/ZIF-8-MV (scale bar: 50 μm). d-e EDS mapping of the recovered DOX/ZIF-8-MV (scale bar: 25 μm). f TEM image and elemental mappings of DOX/ZIF-8-MV (scale bar: 500 nm). g Laser confocal fluorescence microscopy imaging of the DOX/ZIF-8-MV (scale bar: 200 μm). h Drug releasing performance of recovered DOX/ZIF-8 composites under pH 5.0 and pH 7.4.

Figure 4

a SEM analysis of the Pt/ZIF-8-MS (scale bar: 2 μm). b The cross-section images of the Pt/ZIF-8-MS (scale bar: 50 μm). c-d EDS mapping of the Pt/ZIF-8-MS (scale bar: 25 μm). e SEM analysis of the TiO₂/HKUST-1-MS (scale bar: 2 μm). f The cross-section images of the TiO₂/HKUST-1-MS (scale bar: 50 μm). g-h EDS mapping of the TiO₂/HKUST-1-MS (scale bar: 25 μm). i SEM analysis of the Au/Mg-MOF-74-W (scale bar: 2 μm). j The cross-section images of the Au/Mg-MOF-74-W (scale bar: 50 μm). k-l EDS mapping of the Au/Mg-MOF-74-W (scale bar: 25 μm). m-n TEM images of MWCNTs/MOF-74-W (scale bar: 400 nm, 200 nm). o-p TEM images of MWCNTs/MIL-53-MV (scale bar: 400 nm, 1 μm).

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