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Electronic Supplementary Information (ESI)

Phase Transition of Metal–Organic Framework for the Encapsulation of Enzymes

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I. Measurements and characterizations

Tablet Machine (T69YP-15A) was produced by TIANJIN KEQI HIGN&NEW TECHNOLOGY CORPORATION. Ball-milling was produced by Grinder (GT200). Powder XRD patterns were recorded with Rigaku SmartLab using Cu Kα radiation (λ = 1.5406 Å). Morphological features were studied using scanning electron microscope (SEM, Verios G4) and field emission scanning electron microscope (FESEM, JEOL JSM-7800F). Transmission electron microscope images were taken by JEM-2100 Plus. UV-vis spectra were recorded on a Shimadzu UV-2501 spectrophotometer. The loadings of protein and activity of enzymes were detected by multi-mode reader from SYNERGY|HTX according to Bradford methods. Nitrogen sorption studies were performed in a Micromeritics ASAP 2460 adsorption apparatus at 77 K up to 1 bar. The pore textural properties including specific Langmuir and BET surface area, pore volume, and pore size were obtained by analyzing nitrogen adsorption and desorption isotherms with Micromeritics ASAP 2460 built-in software. Circular dichroism (CD) spectra of protein were analyzed by a J1500 CD Spectrometer (JASCO, Japan) in the spectrum region 190-300 nm. All fluorescent images were acquired on Zeiss LSM880 NLO (2 + 1 with BIG) Confocal Microscope System. Zeta potential of MOFs, premilled MOFs and enzymes were tested by NanoPlus-3 (OTSUKA).

Synthesis of ZIF-67(Co). 500 mL MeOH of $Co(NO_3)_2 \cdot 6H_2O$ (9.68 g, 66.6 mM) and 500 mL MeOH of 2-MIM (10.26 g, 0.25 mM) were prepared, and then 25 mL from each was picked up, mixed and stood for 24 h at room temperature. Then the samples were washed with MeOH for several times before drying at room temperature, followed by vacuuming first, and keeping at 120 °C overnight.

Synthesis of UiO-66(Zr).[1] 5 mL N, N-dimethylformamide (DMF) solution of $ZrCl_4$ (23.3 mg, 20 mM), and 5 mL DMF solution of benzene dicarboxylic acid (BDC) (16.6 mg, 20 mM) were mixed in a glass vial. 1.37 mL acetic acid was subsequently added. The mixture was sonicated for 20 min to afford a homogeneous suspension and then reacted at 120 °C for 24 h without stirring. Product was collected by centrifugation and then washed three times with DMF and three times with methanol. The product was placed in a vacuum drying oven at 120 °C overnight. UiO-66-NH_2 (500 nm) was prepared by a similar method except that BDC was replaced by 2-aminoterephthalic acid.

Synthesis of UiO-66-NH_2 (100 nm).[2] In the synthetic process, zirconium chloride (0.08 g, 0.35 mmol) and 0.42 g benzoic acid (0.42 g, 3.43 mmol) were ultrasonically dissolved in 20 mL N, N-dimethylformamide (DMF) in a 40 mL glass bottle for about 1 min, and then 2-aminoterephthalic acid (0.06 g, 0.34 mmol) was added into the above solution for about 3 min. The glass bottle was put in an oven and reacted at 120 °C for 24 h. After cooling, the precipitates were separated by centrifugation and

dispersed in DMF (6 mL). After standing for 6 h at room temperature, the suspension was centrifuged and the solvent was poured out. This washing process was repeated three times. The same operation was then carried out with ethanol (15 mL). The solids were dried at room temperature under vacuum.

Synthesis of HKUST-1. 15 mL methanol solution of $Cu(NO_3)_2 \cdot 2.5H_2O$ (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, followed by reacting at room temperature for 1 h. 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.

Synthesis of Mg-MOF-74.[3] Approximately, a 1:3.3 mixture of 2,5-dihydroxytherephalic acid to $Mg(NO_3)_2$ was sonicated in a 15:1:1(v/v) mixture of DMF, water and ethanol. The mixture was heated to 125 °C for 24 h. After cooling, the solvent was replaced with methanol and exchanged 4 times over 2 days, and finally activated at 120 °C overnight.

Variable pressing masses and pressing time studies of ZIF-8. 10 mg, 20 mg and 50 mg ZIF-8 materials purchased from Sigma-Aldrich (ACS grade) after activation were weighed and put into the chamber of the 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 1364 MPa) was applied to the above samples respectively, and withdrawn after 5 min.

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, 30 MPa (gauge pressure, actual pressure 1364 MPa) was applied to it, and withdrawn respectively after 5 min, 10 min and 20 min.

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

PISA for other MOFs. All treatment methods for other MOFs were similar to the previous operation. 20 mg ZIF-67 materials after activation were weighed and put into the chamber of T69YP-15A tablet machine. The chamber wall was shaken to make it uniformly adhere to the bottom of the pellets. After that, 30 MPa (gauge pressure, actual pressure 1364 MPa) was applied to the samples respectively, and withdrawn after 5 min. For HKUST-1 or MOF-74(Mg), the MOFs were first milled on a Grinder (GT200) under 20 Hz for 99 min, and then experienced the PISA strategy. ZIF-67 or HKUST-1 was recovered by

methanol vapor 50 °C for 24 h. MOF-74(Mg) was recovered by saturated water vapor at 25 °C for 3 days.

Enzymatic activity of free enzymes and enzymes under 1364 MPa. 25 μL of 1 mg mL^{-1} GOx was put in 0.5 mM ABTS reaction solution (phosphate buffer saline (PBS), 1 mM, pH = 7.4), and 10 μL of 1 mg mL^{-1} HRP has been added. A small amount of glucose was added to ensure the concentration of glucose being 100 mM. The activity of samples was measured by ultraviolet at 415 nm; the reaction time was 20 s.

25 μL of 1 mg mL^{-1} HRP was put in 0.5 mM ABTS reaction solution (PBS, 1 mM, pH = 7.4). A small amount of H_2O_2 was added to ensure that the concentration of H_2O_2 was 1.66 mM. The activity of samples was measured by ultraviolet at 415 nm, and the reaction time was 12 s.

50 μL of 1 mg mL^{-1} Cyt C was put in 0.5 mM ABTS reaction solution (PBS, 1 mM, pH = 7.4). A small amount of H_2O_2 was added to ensure that the concentration of H_2O_2 was 10 mM. The activity of samples was measured by ultraviolet at 415 nm, and the reaction time was 20 s.

The same amount of the enzyme under 1364 MPa was about 25 μL of 1 mg mL^{-1} pressed GOx instead of the free enzymes. The enzymatic activity is converted by the slope of time versus absorption.

CD Spectroscopy for free enzymes and enzymes under 1364 MPa. To analyze the changes in enzymes' structures in solid or solution states after mechanical pressure, the two-dimensional (2D) structures of enzymes before and after pressure were tested by circular dichroism spectra. To analyze the enzymes in solutions, 0.25 mg mL^{-1} of enzymes/water solution was prepared. Enzymes under 1364 MPa have been dissolving in water to prepare solution with the same concentration for CD test. To analyze enzymes in solid, a trace amount of pressed enzymes were ground with KBr first, and then the mixers were transferred to a small tablet machine for pressing again. The pellets have been used for CD tests in solid. From the CD spectra, the β-sheets of enzymes labeled in blue (196 nm) and α-helix of enzymes labeled in pink (222 nm) were maintained before and after loading of mechanical pressure, although some peaks slightly shifted. All of these results indicate the GOx, HRP and Cyt C have maintained their native conformation. 0.25 mg mL^{-1} of enzymes/water solution was prepared and CD measurements were performed using a J1500 CD Spectrometer (JASCO, Japan) in the spectrum region of 190–300 nm. The spectrum was collected at a rate of 60 nm per minute at a response time of 16 s.

Standard Bradford assay method. 3 mg of GOx/ZIF-8-X was dissolved in 150 μL 1% HCl/water and sonicated for 30 min. Different concentrations of bovine serum albumin (BSA) protein standard solution were prepared using Bradford solutions: 0.5 mg mL^{-1}, 0.25 mg mL^{-1}, 0.125 mg mL^{-1}, 0.0625 mg mL^{-1}, and 0 mg mL^{-1}. Then 10 μL of standard solutions has been added into 96-well plates with 300 μL of Bradford solutions for preparing standard curve by Microplate Reader at 595 nm (sample-to-Bradford

ratio 1:30). Next, 10 μL of the samples has been added into 96-well plates to demonstrate the concentrations of enzymes in ZIF-8 by Microplate Reader at 595 nm. For other enzymes/MOFs-WV, 3 mg of samples was decomposed in 150 μL of NaOH (1.875 M), neutralized with 150 of HCl (1 M). All the experiments were performed in triplicates.

Zeta potential for MOFs, premilled MOFs and enzymes. All the samples were tested in water and the concentration of samples was around 0.1 mg mL^{-1}. Data was represented as mean(n=5).

The effect of ball-milling time on the adsorption of enzyme on ZIF-8. 20 mg commercial ZIF-8 was milled in a 2 mL plastic centrifugal pipe with 3 quartz spheres on a Grinder (GT200) under 20 Hz for 5 min. Then 19 mg of prepared samples was mixed with 1 mg of GOx by grinding. The mixture was washed with water for 3 times first and added into 10 mL 0 °C water, which was stirred for 1 h. The samples were stored at 0 °C for further use. The protein loadings of GOx mixed with premilled ZIF-8 were determined to be 0.64% by the standard Bradford assay method. Control experiments without premilling have been conducted, and the protein loading of GOx mixed with ZIF-8 was determined to be 0% by the standard Bradford assay method.

20 mg commercial ZIF-8 was milled in a 2 mL plastic centrifugal pipe with 3 quartz spheres on a Grinder (GT200) under 20 Hz for 5 min. Then 19 mg of prepared samples was mixed with 1 mg of GOx by grinding and then the mixture was loaded on 91 MPa and put into 1 mL water for 24 h. The pellets were washed with water for 3 times first and then the samples were added into 10 mL 0 °C water, which were stirred for 1 h. The protein loading of GOx in GOx/ZIF-8-W was determined to be 1.24% by the standard Bradford assay method. Control experiments without premilling have been conducted, and the protein loading of GOx mixed with ZIF-8 was determined to be 0.89% by the standard Bradford assay method.

The effect of mechanical pressure on the encapsulation of enzymes in ZIF-8. 1 mg glucose oxidase (GOx), and 19 mg commercial ZIF-8 premilled for 5 min were mixed thoroughly and ground. 20 mg of GOx/ZIF-8 was amorphized via a T69YP-15A tablet machine. The dry powders were subject to an average pressure of 91 MPa, 273 MPa and 1364 MPa (9-ton, 13 mm diameter pellet die) for 5 min. GOx/ZIF-8-WV was prepared by exposing to saturated water vapor conditions at 25 °C for 72 h to fully restore their structure. After recovery, the mixture was washed with water for 3 times first and then the samples were again added into 10 mL 0 °C water, which were stirred for 1 h. The samples were stored at 0 °C for further use. The protein loadings of GOx in GOx/ZIF-8-W (91 MPa), GOx/ZIF-8-W (273 MPa) and GOx/ZIF-8-W (1364 MPa) were determined to be 0.47%, 1.05% and 0% by the standard Bradford assay method, separately.

The effect of different stimulus response repair solvents on the encapsulation of enzymes. 1 mg glucose oxidase (GOx), and 19 mg activated commercial ZIF-8 were mixed thoroughly and ground. 20 mg of GOx/ZIF-8 was amorphized via a T69YP-15A tablet machine. The dry powders were subjected to an average pressure of 273 MPa (9 ton, 13 mm diameter pellet die) for 5 min. GOx/ZIF-8-MS was prepared by exposing GOx/aZIF-8 to 1 mL of methanol solvents at room temperature for 72 h. GOx/ZIF-8-WV was prepared by exposing to saturated water vapor conditions at 25 °C for 72 h to fully restore their structure. GOx/ZIF-8-MW was prepared by 1 mL of 2-methyl imidazole/water at room temperature overnight. The mixers were washed with water for 3 times first and then the samples were again stirred with 10 mL 0 °C water for 1 h. The samples were stored at 0 °C for further use. The protein loadings of GOx in GOx/ZIF-8-MS or GOx/ZIF-8-MW were determined to be 0 or 0.1% by the standard Bradford assay method.

The effect of ZIF-8 and Mg-MOF-74 disordered degree on the encapsulation of enzymes. 20 mg commercial ZIF-8 was milled in a 2 mL plastic centrifugal pipe with 3 quartz spheres on a Grinder (GT200) under 30 Hz for 99 min. Then 19 mg of prepared samples was mixed with 1 mg of GOx by grinding. 20 mg of GOx/ZIF-8 was assembled via a T69YP-15A tablet machine. The dry powders were subjected to an average pressure of 273 MPa (9 ton, 13 mm diameter pellet die) for 5 min. GOx/ZIF-8-WV was prepared by exposing to saturated water vapor conditions at 25 °C for 72 h to fully restore their structure. The mixers were washed with water for 3 times first and then the samples were again stirred with 10 mL 0 °C water for 1 h. The samples were stored at 0 °C for further use. The protein loading of GOx in GOx/ZIF-8-WV (99 min) was determined to be 0% by the standard Bradford assay method. Control experiments for replacing ZIF-8 with ZIF-8 (premilled 10 min) have been conducted; the protein loading of GOx mixed with ZIF-8 was determined to be 0.52% by the standard Bradford assay method.
20 mg Mg-MOF-74 was milled in a 2 mL plastic centrifugal pipe with 3 quartz spheres on a Grinder (GT200) under 30 Hz for 99 min. Then 19 mg of prepared samples was mixed with 1 mg of GOx by grinding. 20 mg of GOx/aMg-MOF-74 was assembled via a T69YP-15A tablet machine. The dry powders were subjected to an average pressure of 91 MPa (9-ton, 13 mm diameter pellet die) for 5 min. GOx/aMg-MOF-74 was prepared by exposing to saturated water vapor conditions at 25 °C for 72 h to fully restore their structure. The samples were stored at 0 °C for further use. The protein loading of GOx in GOx/aMg-MOF-74-WV (99 min) was determined to be 2.05% by the standard Bradford assay method. The similar experiments for GOx/Mg-MOF-74-WV were prepared with 3.66% loading of GOx.
For the preparation of GOx/Mg-MOF-74-WV, the experimental procedures were the same as those above except that the premilled conditions for Mg-MOF-74 were 20 Hz for 5 min.
0.49 mg of GOx/aMg-MOF-74-WV was put into 100 μL of pH 7.4 PBS of 0.5 mM 2, 2'-diazo-bis-3-ethyl benzothiazoline-6-sulfonic acid (ABTS) with 10 μL of HRP (1 mg mL^{-1}). 10 μL of glucose (1 M) was

added to ensure that the concentration of glucose was 100 mM. The activity of samples was measured by Microplate Reader at 415 nm and compared with the free enzymes.
For the enzymatic activity of GOx/Mg-MOF-74-WV, the experimental procedures were the same as those above except that the amount of GOx/Mg-MOF-74-WV was 0.27 mg.

Enzymatic activity of HRP/ZIF-8-WV and Cyt C/ZIF-8-WV composites. 1 mg of HRP/ZIF-8-WV was put in 0.5 mM ABTS reaction solution (PBS, 1 mM, pH = 7.4), and 10 μL of 1 mg mL^{-1} horseradish catalase was added. 10 μL of H_2O_2 (1 mmol) was added to ensure that the concentration of H_2O_2 was 0.1 mM. The activity of samples was measured by Microplate Reader at 415 nm and compared with the free enzymes. The reaction time was 30 s. For the enzymatic activity of free enzymes, the experimental procedures were the same as those above except that the amount of free enzymes was 10 μL of 1 mg mL^{-1} HRP. The enzymatic activity was measured by the slope of time versus absorption.
0.21 mg of Cyt C/ZIF-8-WV was put in 0.5 mM ABTS reaction solution (PBS, 1 mM, pH = 7.4). 10 μL of H_2O_2 (100 mM) was added to ensure that the concentration of H_2O_2 was 10 mM. The activity of samples was measured by Microplate Reader at 415 nm and compared with the free enzymes. The reaction time was 21 s. The enzymatic activity was measured by the slope of time versus absorption. For the enzymatic activity of free enzymes, the experimental procedures were the same as those above except that the amount of free enzymes was 20 μL of 1 mg mL^{-1} Cyt C.

Preparation of HRP/ZIF-8-WV and Cyt C/ZIF-8-WV. 5 mg HRP or 10 mg Cyt C and 95 mg or 90 mg premilled ZIF-8 were mixed thoroughly and ground. 20 mg of enzymes/ZIF-8 was pressed via a T69YP-15A tablet machine. The dry powders were subjected to an average pressure of 91 MPa (9-ton, 13 mm diameter pellet die) for 5 min. Enzymes/ZIF-8-WV was prepared by exposing to saturated water vapor conditions at 25 °C for 72 h to fully restore their structure. The mixers were washed with water for 3 times first and then the samples were again stirred with 10 mL 0°C water for 1 h. The samples were stored at 0 °C for further use. The protein loadings of enzymes in HRP/ZIF-8-WV or Cyt C/ZIF-8-WV were determined to be 0.99 or 4.78% by the standard Bradford assay method.

Preparation of GOx/MOFs composites. 5 mg GOx and 95 mg of 5 min premilled MOFs (ZIF-8, UiO-66 or MIL-53(Fe) or MIL-53(Al)) were mixed thoroughly and ground. 20 mg of GOx/MOFs were pressed via a T69YP-15A tablet machine. The dry powders were subject to an average pressure of 91 MPa (9-ton, 13 mm diameter pellet die, the pressure used to prepare GOx/ZIF-8-WV was 273 MPa) for 5 min. GOx/MOFs-WV was prepared by exposing pellets to water vapor at room temperature for 72 h.

Enzymatic activity of GOx/MOFs composites. 1 mg of GOx/ZIF-8-WV or 0.2 mg of GOx/UiO-66-WV or 0.2 mg MIL-53 (Al) or 0.2 mg MIL-53 (Fe) were put into pH 7.4 PBS of 0.5 mM 2,2'-diazo-bis-3-ethyl benzothiazoline-6-sulfonic acid (ABTS) with 10 μL of HRP (1 mg mL^{-1}). 10 μL of glucose (1 M) was added to ensure that the concentration of glucose was 100 mM. The activity of samples was measured by Microplate Reader at 415 nm and compared with the free enzymes.
For the enzymatic activity of free enzymes, the experimental procedures were the same as those above except that the amount of free enzymes was 10 μg.

Michaelis-Menten constants of GOx, GOx/UiO-66-WV and GOx/MIL-53(Fe).0.2 mg of GOx/UiO-66-WV or 0.2 mg GOx/MIL-53 (Fe)-WV or 10 μg of GOx were put into pH 7.4 PBS of 0.5 mM 2,2'-diazo-bis-3-ethyl benzothiazoline-6-sulfonic acid (ABTS) with 10 μL of HRP (1 mg mL^{-1}). 10 μL of glucose with different concentrations was added to ensure that the concentration of glucose was 1, 2, 5, 10, 50, 100 mM. The activity of samples was measured by Microplate Reader at 415 nm. The Michaelis-Menten constants was calculated by none-linear fitting of initial reaction rate with substrate concentration according to the Michaelis-Menten equation.

Preparation of BGL/UiO-66 composites. 3 mg BGL and 20 mg of UiO-66 premilled for 5 min were mixed thoroughly and ground. The mixers were pressed via a T69YP-15A tablet machine. The dry powders were subject to an average pressure of 91 MPa (9-ton, 13 mm diameter pellet die) for 5 min. BGL/UiO-66-WV was prepared by exposing pellets to water vapor at room temperature for 72 h.

Enzymatic activity of BGL/UiO-66 composites. 0.2 mg of BGL/UiO-66-WV was put into 100 μL pH 6.0 citric buffer (20 mM). Then, 100 μL of 4-nitrophenyl β-D-glucopyranoside (pNPG, ≥98%) (4 mM) was added to ensure that the concentration of pNPG was 2 mM. The activity of samples was measured by Microplate Reader at 405 nm and compared with the free enzymes. For the enzymatic activity of free enzymes, the experimental procedures were the same as those above except that the amount of free enzymes was 10 μg.

Preparation of GOx/UiO-66-NH_2 (100 nm) composites, GOx/UiO-66-NH_2 (500 nm) composites and their activity testing. 1 mg GOx and 19 mg premilled UiO-66-NH_2 (100 nm) were mixed thoroughly and ground. GOx/UiO-66-NH_2 were pressed via a T69YP-15A tablet machine. The dry powders were subjected to an average pressure of 91 MPa (9-ton, 13 mm diameter pellet die) for 5 min. GOx/UiO-66-NH_2-WV was prepared by exposing to saturated water vapor conditions at 25 °C for 72 h to fully restore their structure. The mixers were washed with water for 3 times first and then the samples were again stirred with 10 mL 0 °C water for 1 h. The samples were stored with 1 mL water at 0 °C for further use.

The protein loading of GOx in GOx/UiO-66-NH_2-WV was determined to be 1.88% by the standard Bradford assay method.

For the preparation of GOx/UiO-66-NH_2 (500 nm)-WV, the experimental procedures were the same as those above except that the MOFs were replaced to UiO-66-NH_2 (500 nm), and the loading of GOx in GOx/UiO-66-NH_2-WV was determined to be 1.56% by the standard Bradford assay method.

0.53 mg of GOx/UiO-66-NH_2 (100 nm)-WV was put into 2.5 mL of pH 7.4 PBS of 0.5 mM 2, 2'-diazo-bis-3-ethyl benzothiazoline-6-sulfonic acid (ABTS) with 10 μL of HRP (1 mg mL^{-1}). 250 μL of glucose (1 M) was added to ensure that the concentration of glucose was 100 mM. The activity of samples was measured by Microplate Reader at 415 nm and compared with the free enzymes.

For the enzymatic activity of GOx/UiO-66-NH_2 (500 nm)-WV, the experimental procedures were the same as those above except that the amount of GOx/UiO-66-NH_2 (500 nm)-WV was 0.64 mg.

Enzymatic activity of GOx/MOFs-WV after 24 h treatment by protease. 1 mg of GOx/ZIF-8-WV or 0.2 mg of GOx/UiO-66-WV or 0.2 mg of MIL-53 (Al) or 0.2 mg of MIL-53 (Fe) was treated with 1 mg mL^{-1} protease at 40 °C for 24 h, with the rotation speed of the shaker being 120 rpm. After reaction, the solution was then poured out and 10 μL of glucose (1 M), ABTS and 10 μL of HRP (1 mg mL^{-1}) was added to ensure that the concentration of glucose was 100 mM. The activity of samples was measured by Microplate Reader at 415 nm and compared with the free enzymes. For the enzymatic activity of free enzymes, the experimental procedures were the same as those above except that the amount of free enzymes was 10 μg.

Preparation of GOx/UiO-66-WV under different mechanical pressure, aging time and their activity testing. 1 mg GOx and 19 mg premilled UiO-66 were mixed thoroughly and ground. GOx/UiO-66 were pressed via a T69YP-15A tablet machine. The dry powders were subjected to average pressures of 91 MPa or 273 MPa (9-ton, 13 mm diameter pellet die) for 5 min. GOx/UiO-66-WV was prepared by exposing to saturated water vapor conditions at 25 °C for 72 h to fully restore their structure. The mixers were washed with water for 3 times first and then the samples were again stirred with 10 mL 0 °C water for 1 h. The samples were stored with 1 mL water at 0 °C for further use. The protein loadings of GOx in GOx/UiO-66-WV (91 MPa) and GOx in GOx/UiO-66-WV (273 MPa) were determined to be 4.86% and 4.17% by the standard Bradford assay method, respectively.

0.2 mg of GOx/UiO-66-WV (91 MPa) was put into 100 μL of pH 7.4 PBS of 0.5 mM 2, 2'-diazo-bis-3-ethyl benzothiazoline-6-sulfonic acid (ABTS) with 10 μL of HRP (1 mg mL^{-1}). 10 μL of glucose (0.5 mM) was added to ensure that the concentration of glucose was 100 mM. The activity of samples was measured by Microplate Reader at 415 nm and compared with the free enzymes.

For the enzymatic activity of GOx/UiO-66-WV (273 MPa), the experimental procedures were the same

as those above except that the amount of GOx/UiO-66-WV (273 MPa) was 0.24 mg.

Preparation of HRP/UiO-66-NH_2 (500 nm)-WV composites and activity testing. 1 mg HRP and 19 mg premilled UiO-66-NH_2 were mixed thoroughly and ground. HRP/UiO-66-NH_2 was pressed via a T69YP-15A tablet machine. The dry powders were subjected to an average pressure of 91 MPa (9-ton, 13 mm diameter pellet die) for 5 min. HRP/UiO-66-NH_2-WV was prepared by exposing to saturated water vapor conditions at 25 °C for 72 h to fully restore their structure. The mixers were washed with water for 3 times first and then the samples were again stirred with 10 mL 0 °C water for 1 h. The samples were stored with 1 mL water at 0 °C for further use. The protein loading of HRP in HRP/UiO-66-NH_2-WV was determined to be 0.19 mg/mL by the standard Bradford assay method.

5.26 μL of HRP/UiO-66-NH_2-WV solution was put in 100 μL of 0.5 mM ABTS reaction solution (PBS, 1 mM, pH = 7.4). 10 μL of H_2O_2 (1 mmol) was added to ensure that the concentration of H_2O_2 was 0.1 mM. The activity of samples was measured by Microplate Reader at 415 nm and compared with the free enzymes. The reaction time was 27 s. For the enzymatic activity of free enzymes, the experimental procedures were the same as those above except that the amount of free enzymes was 10 μL of 1 mg mL^{-1} HRP. The enzymatic activity was measured by the slope of time versus absorption.

Condition optimization for the preparation of GOx/MOFs composites and activity testing.

1 mg GOx and 19 mg UiO-66 were mixed thoroughly and ground. GOx/UiO-66-W was prepared by adding 50 μL water to accelerate the aging of pressed enzymes/MOFs composites and kept at 4 °C for 24 h. GOx/MIL-53(Fe)-W was prepared by similar method. The best condition for preparing GOx/UiO-66-WV is to put the pressed samples on the mould with a cover (such as umbrella) to avoid water contacting. The loadings of GOx in GOx/UiO-66-W, GOx/MIL-53(Fe) and GOx/UiO-66-WV (best conditions) was 4.1%, 3.5% and 4%, respectively.

0.25 mg of GOx/UiO-66-WV (best conditions) or 0.25 mg of GOx/UiO-66-W or 0.29 mg of GOx/MIL-53(Fe)-W was put into 100 μL of pH 7.4 PBS of 0.5 mM 2, 2'-diazo-bis-3-ethyl benzothiazoline-6-sulfonic acid (ABTS) with 10 μL of HRP (1 mg mL^{-1}). 10 μL of glucose (0.5 mM) was added to ensure that the concentration of glucose was 100 mM. The activity of samples was measured by Microplate Reader at 415 nm and compared with the free enzymes. The enzymatic activity was measured by the slope of time versus absorption.

Recycle experiments for GOx/UiO-66-WV.

0.25 mg of GOx/UiO-66-WV (best conditions) was put into 100 μL of pH 7.4 PBS of 0.5 mM 2, 2'-diazo-bis-3-ethyl benzothiazoline-6-sulfonic acid (ABTS) with 10 μL of HRP (1 mg mL^{-1}). 10 μL of glucose (0.5 mM) was added to ensure that the concentration of glucose was 100 mM. The activity of samples

was measured by Microplate Reader at 415 nm and compared with the free enzymes. The enzymatic activity was measured by the slope of time versus absorption. After finishing the reaction, the catalysts were centrifugated rapidly and washed with water for several times. Then the samples were used to continue another cycle.

Preparation of GOx/UiO-66 (mixing and aging for 3 days), GOx/UiO-66 $_{\text{premilled 5 min}}$ (premilled for 5 min, mixing and aging for 3 days), GOx/UiO-66 $_{\text{premilled 10 min}}$ (premilled for 10 min, mixing and aging for 3 days) and their activity testing.

1 mg GOx and 19 mg UiO-66 were mixed thoroughly and ground. GOx/UiO-66 was prepared by exposing to saturated water vapor conditions at 25 °C for 72 h. GOx/UiO-66 $_{\text{premilled 5 min}}$ was prepared by mixing UiO-66 premilled for 5 min with GOx and aging for 3 days under saturated water vapor conditions at 25 °C for 72 h. GOx/UiO-66 $_{\text{premilled 10 min}}$ was prepared by mixing UiO-66 premilled for 10 min with GOx and aging for 3 days under saturated water vapor conditions at 25 °C for 72 h. All the samples were washed with water for 3 times first and then again stirred with 10 mL 0 °C water for 1 h. The samples were stored with 1 mL water at 0 °C for further use. The protein loadings of GOx in GOx/UiO-66, GOx/UiO-66 $_{\text{premilled 5 min}}$, and GOx/UiO-66 $_{\text{premilled 10 min}}$ were determined to be 4.57%, 3.2% and 4.23% respectively by the standard Bradford assay method.

Protease treatment of GOx/UiO-66, GOx/UiO-66$_{\text{premilled 5 min}}$, GOx/UiO-66$_{\text{premilled 10 min}}$.

Around 0.2 mg of GOx/UiO-66 or 0.3125 mg of GOx/UiO-66 $_{\text{premilled 5 min}}$ or 0.2 mg of GOx/UiO-66 $_{\text{premilled 10 min}}$ were treated with 1 mg mL^{-1} protease at 40 °C for 24 h, with the rotation speed of the shaker being 120 rpm. After reaction, the solution was then poured out and 10 μL of glucose (1 M), ABTS and 10 μL of HRP (1 mg mL^{-1}) were added to ensure that the concentration of glucose was 100 mM. The activity of samples was measured by Microplate Reader at 415 nm and compared with the samples without protease treatment.

The synthesis of Au/ZIF-8-WV and Pt/UiO-66-NH_2-WV.

1 mg ~13 nm-Au and 19 mg premilled ZIF-8 were mixed thoroughly and ground. MNPs/UiO-66 was pressed via a T69YP-15A tablet machine. The dry powders were subjected to an average pressure of 273 MPa (9-ton, 13 mm diameter pellet die) for 5 min. MNPs/ZIF-8-WV was prepared by exposing to saturated water vapor conditions at 25 °C for 72 h to fully restore their structure. The mixers were washed with water for 3 times first and then the samples were again stirred with 10 mL 0 °C water for 1 h. The samples were dried for TEM testing.

For the synthesis of MNPs/UiO-66-NH_2-WV, the experimental procedures were the same as those above except that both the amounts of MNPs and UiO-66-NH_2 were 10 mg, and pressure was 91 MPa.

II. PISA for MOFs

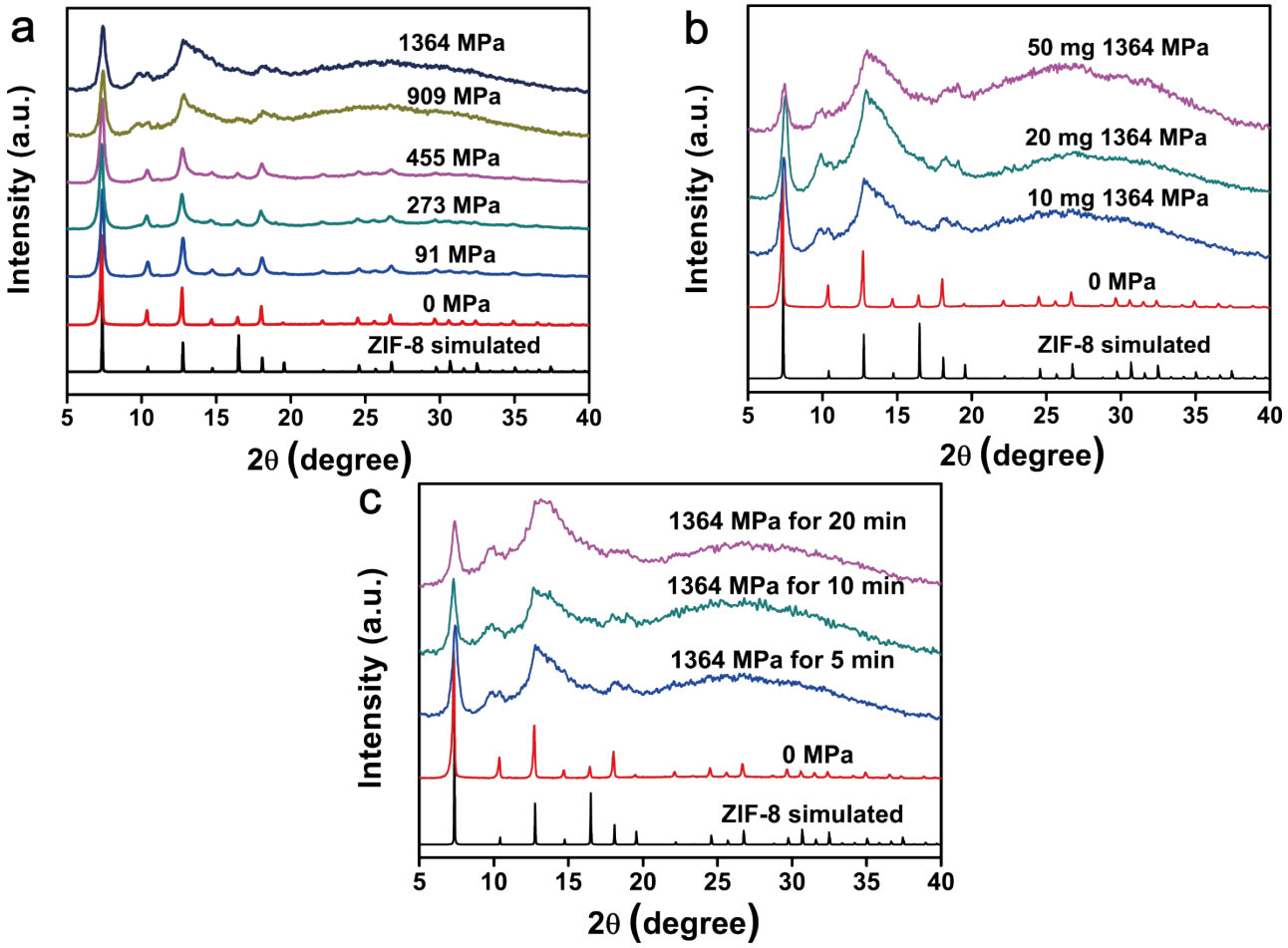

Fig. S1 PXRD analysis of pressed ZIF-8 under different pressures (a), different masses (b), and different pressing times (c).

Under low pressure, no obvious structure change was found. As the compression loading was increased to 909 MPa and 1364 MPa, the characteristic diffraction peaks of ZIF-8 above 10° merged into broad peaks (12.7° [110], 14.7° [220], 16.5° [310], 24.5° [332] and 26.7° [510]), suggesting that the pressed ZIF-8 lost partial crystallinity.

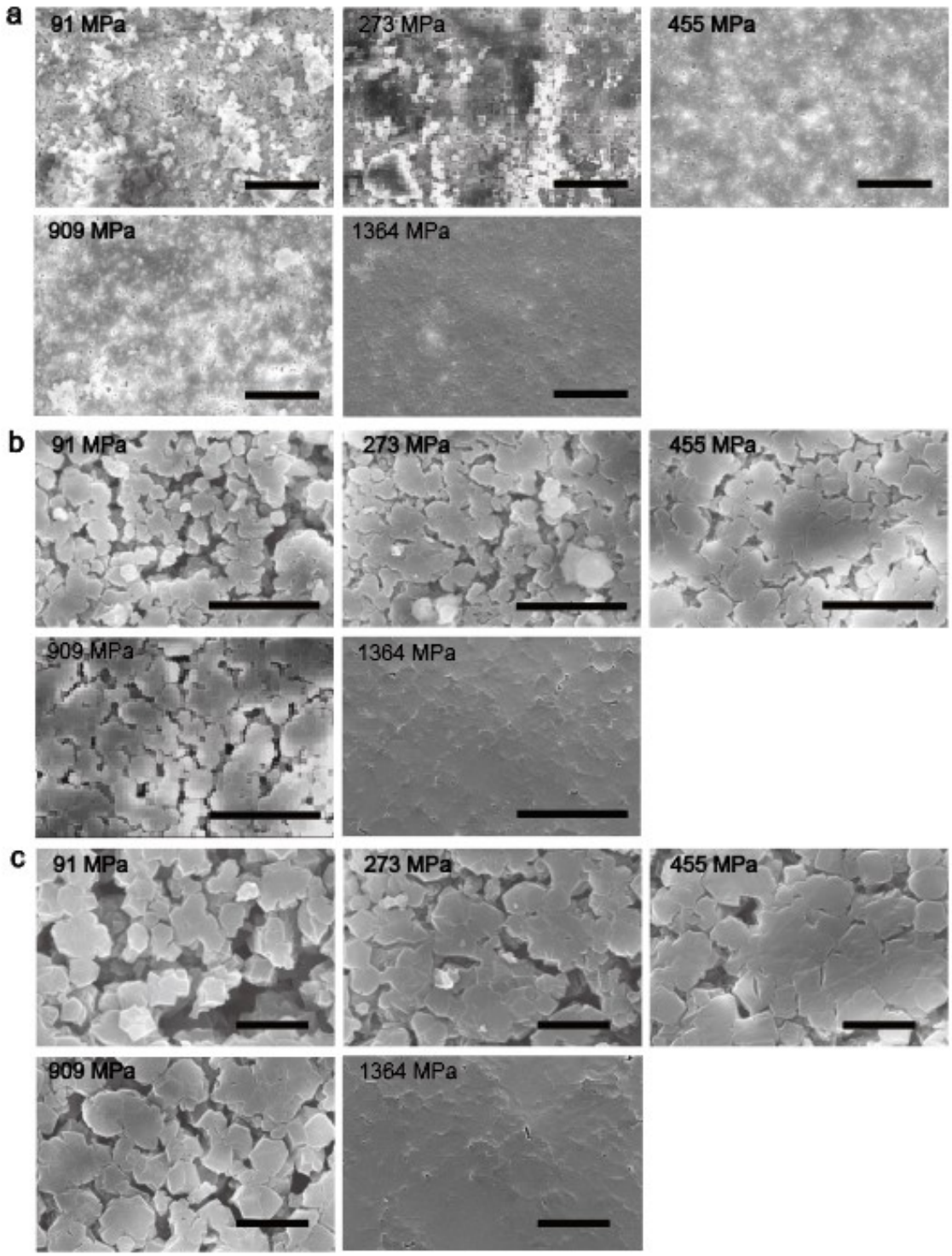

Fig. S2 SEM analysis of the pressed ZIF-8 under different pressures. (a) SEM analysis of the pressed ZIF-8 surface morphology under different pressures (magnification 10,000 times, scale bar 10 μm). (b) SEM analysis of the pressed ZIF-8 surface morphology under different pressures (magnification 50,000 times, scale bar 3 μm). (c) SEM analysis of the pressed ZIF-8 surface morphology under different pressures (magnification 100,000 times, scale bar 1 μm).

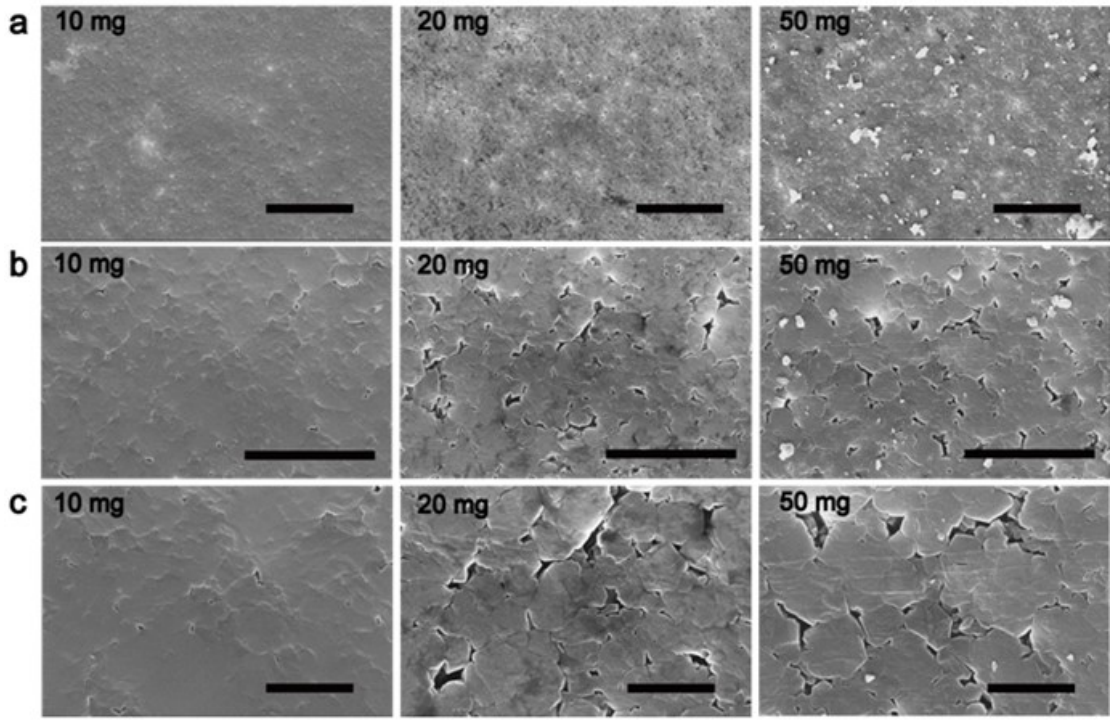

Fig. S3 SEM analysis of the pressed ZIF-8 under different masses. (**a)** SEM analysis of the pressed ZIF-8 surface morphology under different masses (magnification 10,000 times, scale bar 10 μm). (**b)** SEM analysis of the pressed ZIF-8 surface morphology under different masses (magnification 50,000 times, scale bar 3 μm). (c) SEM analysis of the pressed ZIF-8 surface morphology under different masses (magnification 100,000 times, scale bar 1 μm).

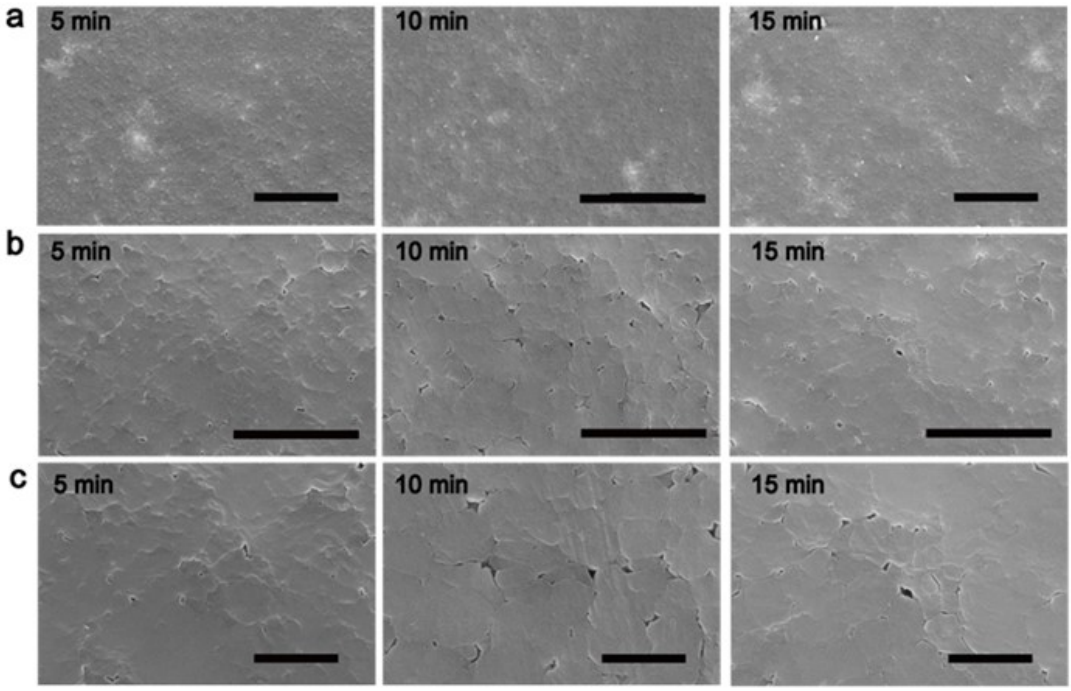

Fig. S4 SEM analysis of the pressed ZIF-8 under different pressing times. (**a)** SEM of the pressed ZIF-8 surface morphology under different pressing times (magnification 10,000 times, scale bar 10 μm). (**b)** SEM analysis of the pressed ZIF-8 surface morphology under different times (magnification 50,000 times, scale bar 3 μm). **(c)** SEM analysis of the pressed ZIF-8 surface morphology under different times (magnification 100,000 times, scale bar 1 μm).

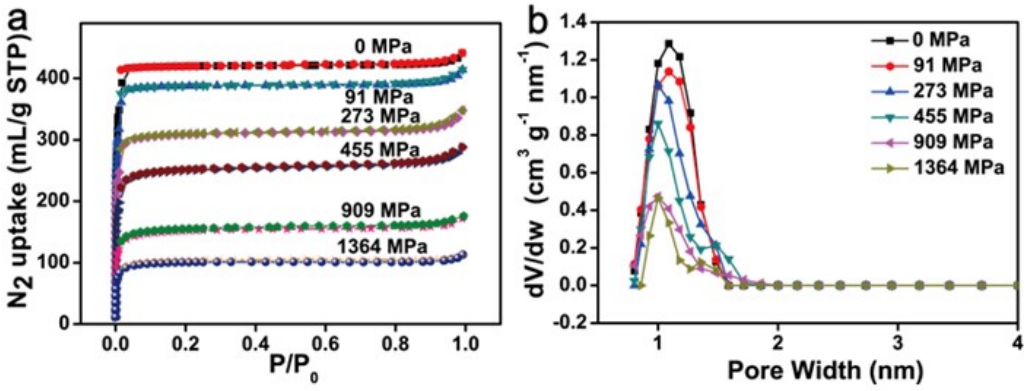

Fig. S5 N_2 sorption isotherms analysis of the pressed ZIF-8 under different pressures, and pore size distribution of the pressed ZIF-8 under different pressures. (**a)** N_2 sorption isotherms of ZIF-8 under different pressure loadings. P, pressure. P_0, saturation pressure. P/P_0, relative pressure. (**b)** Density functional theory pore size distribution indicates that the disordered ZIF-8 material has a reduced pore volume with the increasing of pressure.

Compared with the pristine ZIF-8 nanocrystals, ZIF-8 under 1364 MPa showed severely decreased Brunauer–Emmett–Teller (BET) surface areas and lost 70% porosity from 1347 $m^2\ g^{-1}$ to 404 $m^2\ g^{-1}$ as indicated by the total N_2 uptake, owing to the pore collapse upon mechanical compression. Pore volumes were also decreased from 1.3 $cm^3\ g^{-1}\ nm^{-1}$ to 0.45 $cm^3\ g^{-1}\ nm^{-1}$ with the increasing of pressure[4-5].

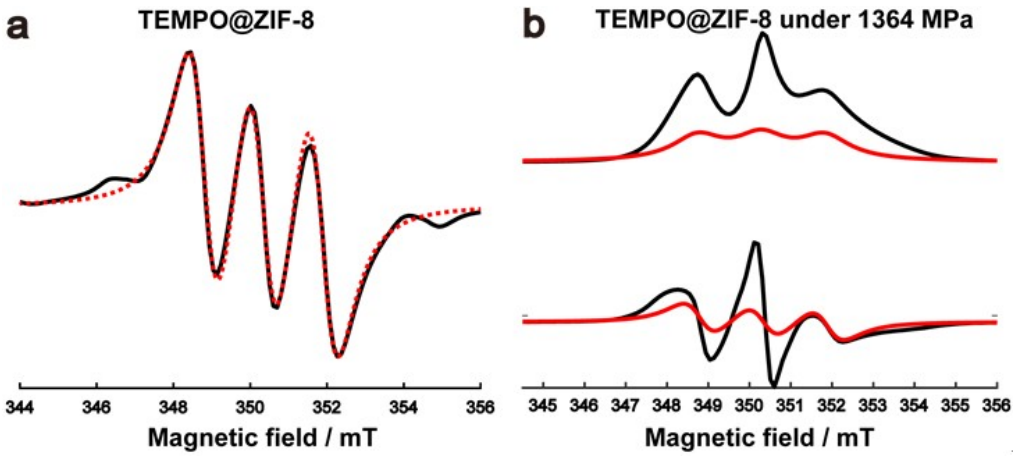

Fig. S6 EPR data simulation for ZIF-8 before and after pressure. (a) EPR data simulation for TEMPO@ZIF-8 before pressure. (b) EPR data simulation for TEMPO@ZIF-8 after pressure. Simulation was shown in red, and experimental data in black. Following parameters were used for the simulation: [2.0115, 2.0086, 2.0035], [0.52, 0.52, 3.60], [0.00 1.45] ~ 0.02 ns.

The reduction in crystallinity can also be determined by electron paramagnetic resonance (EPR)[4]. By encapsulating TEMPO into ZIF-8, room-temperature EPR spectra of TEMPO@ZIF-8 exposed under different pressure showed the degree of disorderd ZIF-8. The EPR spectrum of unperturbed fraction featured three EPR lines, which were greatly broadened due to the presence of oxygen in the cavity. In general, the damage to the pores can either result in reduction of free volume available for the radical rotation, or lead to the opening of the cage, release of the radicals, and adsorption on the surface of the particles. Both scenarios led to the slowing of the mobility of radicals and observation of powder like EPR spectra.

The spectra for TEMPO@ZIF-8 before and after 1364 MPa were characterized. A significant number of damaged cavities were found. Thus, percentage of unperturbed cavities was around 25%, suggesting 75% of porosity and crystallinity was lost for ZIF-8 under 1364 MPa[4-5]. Red ones were simulated contribution of unperturbed cavities in our sample.

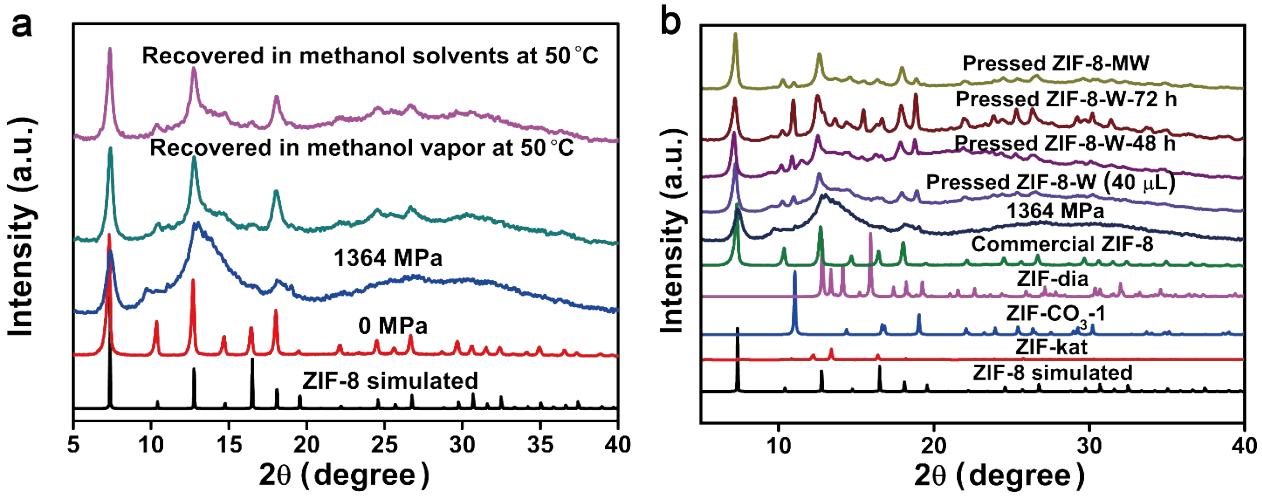

Fig. S7 PXRD analysis of ZIF-8 under 1364 MPa recovered by methanol or water or 2-methyl imidazole/water. (a) PXRD patterns of simulated ZIF-8, commercial ZIF-8, and ZIF-8 under high pressure (1364 MPa), before and after recovery (methanol vapor and solvents at 50 °C). (b) PXRD analysis of ZIF-8 under 1364 MPa, pressed ZIF-8 recovered under the treatment of 40 μL water, water for 48 h, water for 72 h, or 40 μL 2-methyl imidazole/water.

Accordingly, water has also been used to recover disordered ZIF-8, but we found that it may induce pressed ZIF-8 to transform into non-porous diamondoid (dia)-ZIF and ZIF-CO_3-1 structures as reflected by PXRD patterns and SEM images. Apparently, two new morphologies different from ZIF-8 crystals appeared after soaking pressed ZIF-8 in water for 72 h. To further accelerate the recovery of pressed ZIF-8 into the crystalline one, 2-methyl imidazole/aqueous solvent was utilized because it could stabilize the structure of ZIF-8 and avoid further phase transition of ZIF-8 into other ZIF structures.

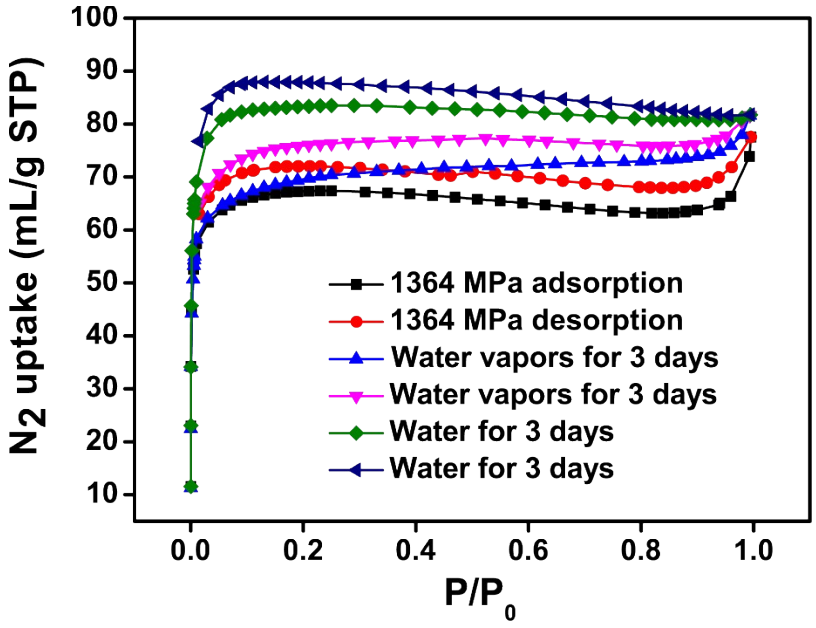

Fig. S8 N_2 gas adsorption isotherm of ZIF-8 under high pressure (1364 MPa), and after recovery (water vapor or water at 25 ^{o}C for 3 days).

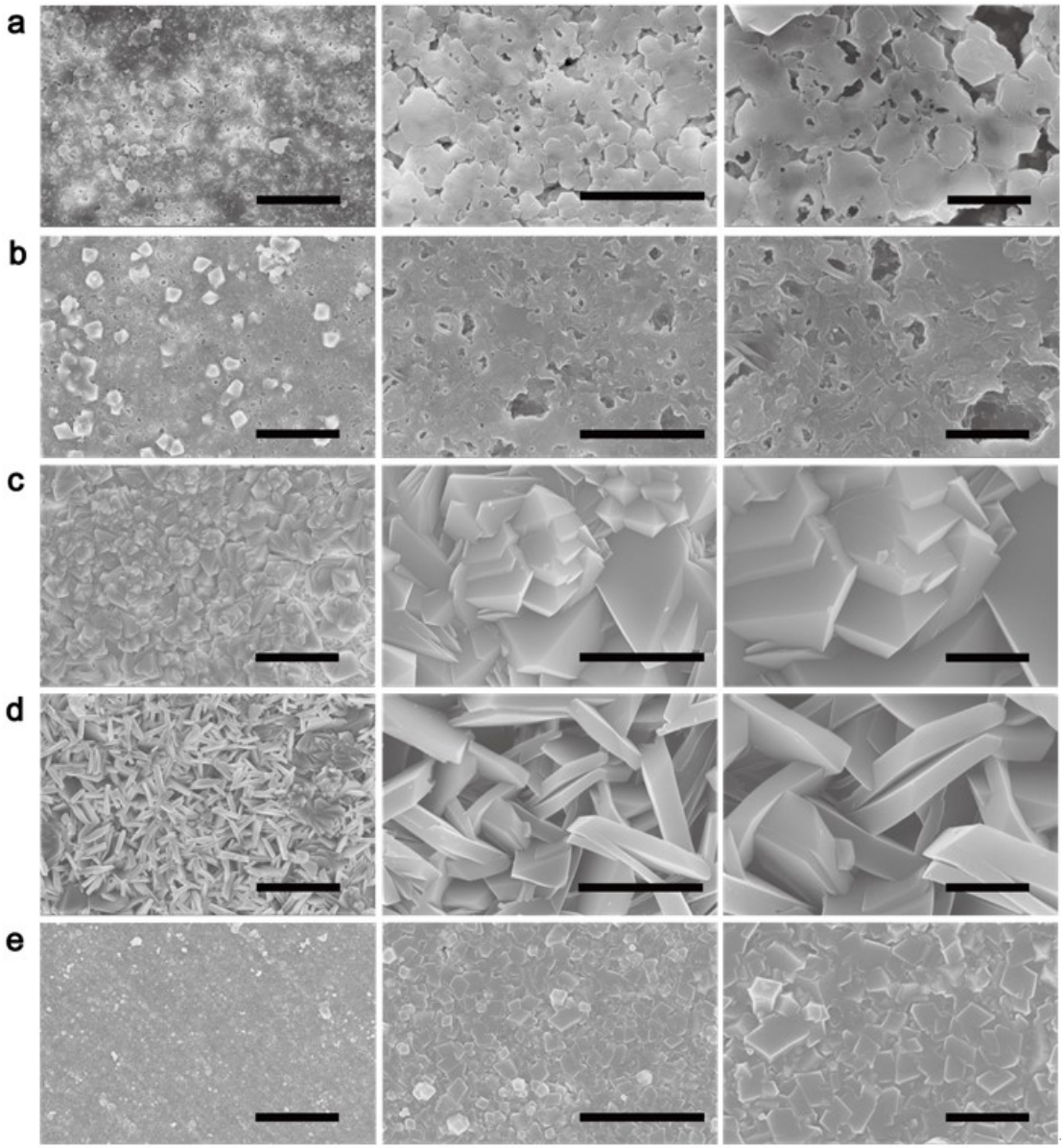

Fig. S9 SEM images of ZIF-8 under 1364 MPa recovered by water under different times or recovered by 2-methyl imidazole/water. (a) Under the treatment of 40 μL water treatment. (b) Under the treatment of water for 48 h. (c), (d) Under the treatment of water for 72 h. (e) Under the treatment of 40 μL 2-MIM/water. (magnification from left to right is 10,000, 50,000, and 100,000 times respectively. scale bar from left to right is 10, 3 and 1 μm, respectively).

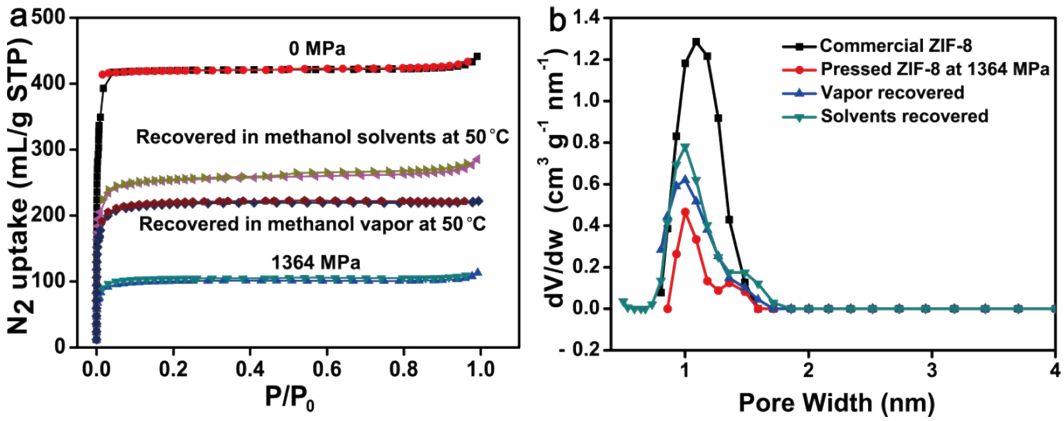

Fig. S10 Pore size distribution of optimum, the pressed ZIF-8 and the samples under methanol solvents/vapors treatment. (a) N_2 gas adsorption isotherm of commercial ZIF-8, and ZIF-8 under high pressure (1364 MPa), and after recovery (methanol vapor and solvents at 50 °C). (b) Pore size distribution of optimum, the pressed ZIF-8 and the samples under methanol solvents/vapor treatment. Density functional theory pore size distribution indicates that the recovered ZIF-8 material has a increased pore volume under the treatment of methanol solvents/vapor.

The original ZIF-8 NPs had a specific area of 1,347 $m^2\ g^{-1}$ and pore volume of 1.28 $cm^3\ g^{-1}\ nm^{-1}$. After exposing pressed ZIF-8 (surface area: 406.7 $m^2\ g^{-1}$, pore volume: 0.465 $cm^3\ g^{-1}\ nm^{-1}$) with methanol vapor and soaking in methanol solution, the specific areas of ZIF-8 pellets increased to 881.6 $m^2\ g^{-1}$ and 1027.9 $m^2\ g^{-1}$, respectively, and the pore volumes were slightly increased to 0.62 $cm^3\ g^{-1}\ nm^{-1}$ and 0.77 $cm^3\ g^{-1}\ nm^{-1}$, respectively. The above experimental results jointly prove that the pressure-induced partially disordered ZIF-8 can be generally restored to the crystalline ZIF-8 under the stimulation of either methanol vapor or methanol solvents.

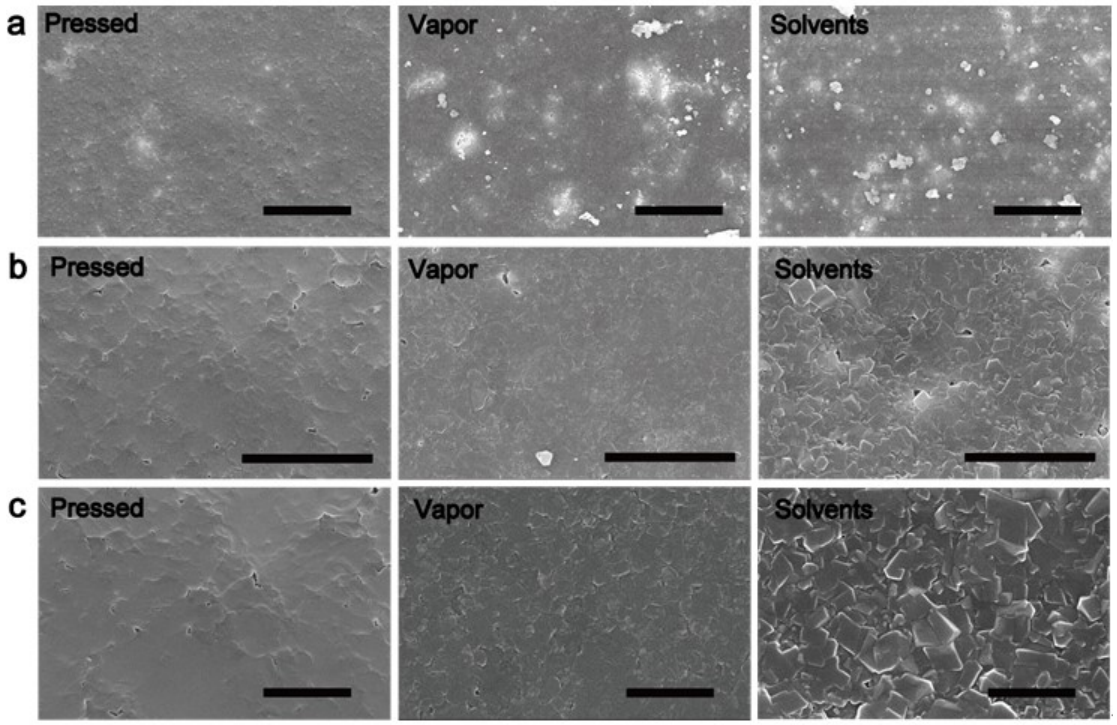

Fig. S11 SEM analysis of the pressed ZIF-8 and the samples under methanol solvents/vapor treatment. a SEM analysis of the pressed ZIF-8 and the samples under methanol vapor/solvents treatment (magnification 10,000 times, scale bar 10 μm). b SEM analysis of the pressed ZIF-8 and the samples under methanol vapor/solvents treatment (magnification 50,000 times, scale bar 3 μm). c SEM analysis of the pressed ZIF-8 and the samples under methanol vapor/solvents treatment (magnification 100,000 times, scale bar 1 μm).

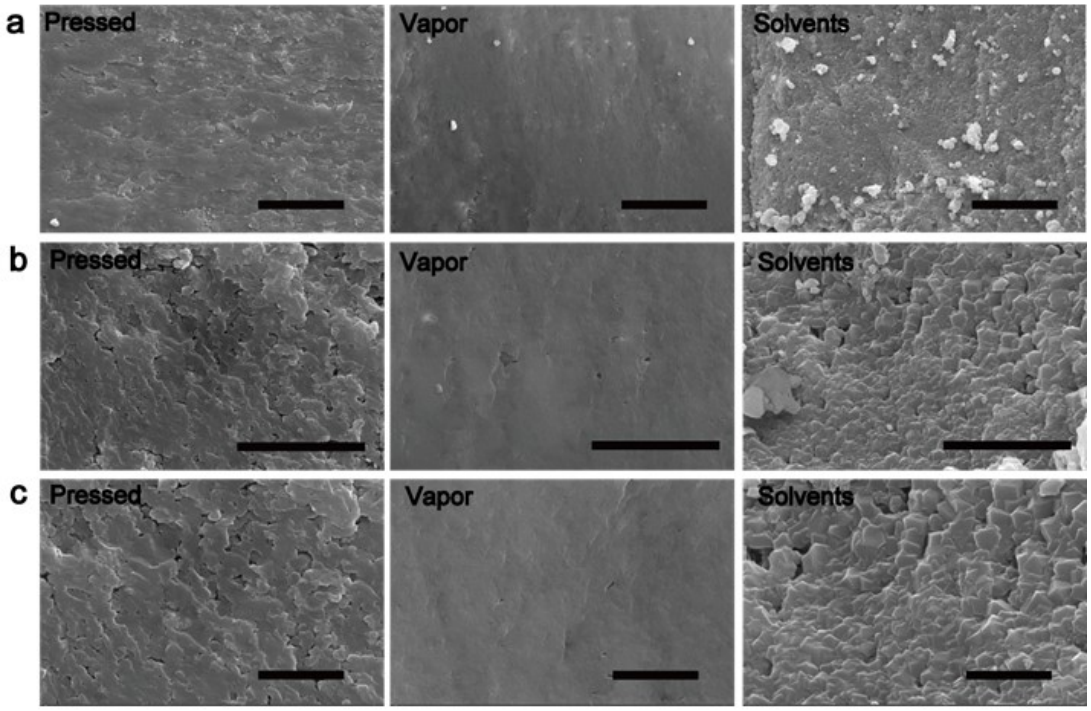

Fig. S12 Cross section SEM analysis of the pressed ZIF-8 and the samples under methanol solvents/vapor treatment. **(a)** Cross section SEM analysis of the pressed ZIF-8 and the samples under methanol vapor/solvents treatment (magnification 10,000 times, scale bar 10 μm). (**b)** Cross section SEM analysis of the pressed ZIF-8 and the samples under methanol vapor/solvents treatment (magnification 50,000 times, scale bar 3 μm). (**c)** Cross section SEM analysis of the pressed ZIF-8 and the samples under methanol vapor/solvents treatment (magnification 100,000 times, scale bar 1 μm).

In the case of methanol soaking, large polyhedral nanocrystals with a high degree of crystallinity and unambiguous grain boundaries were observed in both surface and cross-section SEM images, indicating a complete recrystallization of ZIF-8 due to the effective infiltration of methanol solvents into the pressed ZIF-8 pellet. On the contrary, in the case of methanol vapor exposed samples, small ZIF-8 nanocrystals were only found on the surface and few ZIF-8 nanocrystals were observed from the cross-section SEM images. These results indicate that the recrystallization by methanol vapor exposure predominantly occurs at and near the surface of the compressed pellet.

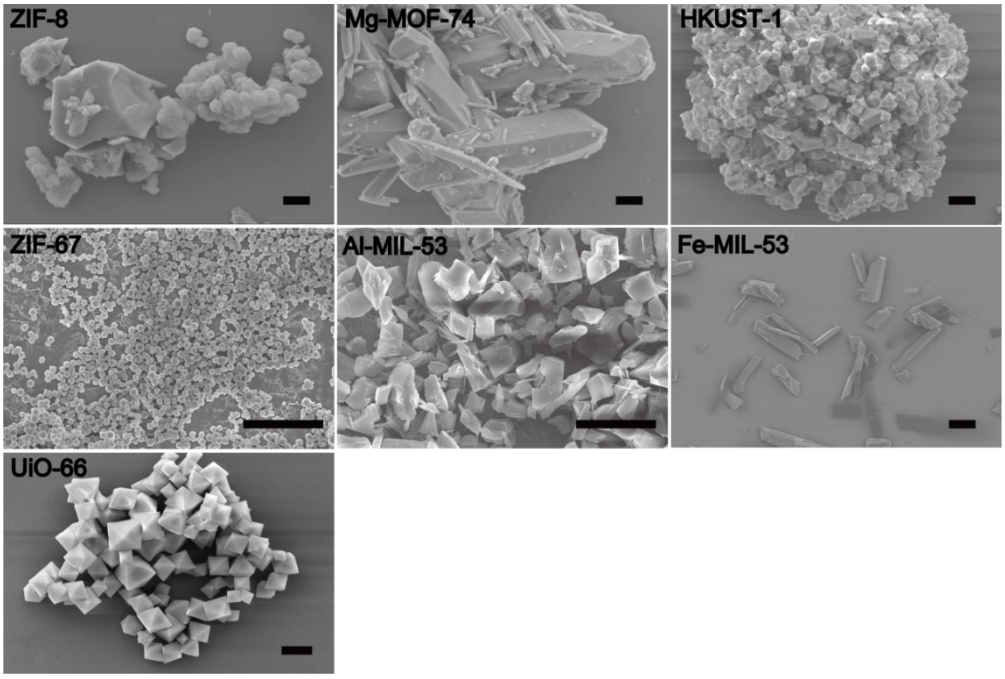

Fig. S13 SEM images of ZIF-8, Mg-MOF-74, HKUST-1, ZIF-67, UiO-66, MIL-53(Al) and MIL-53(Fe). SEM images of ZIF-8 (scale bar 1 μm), Mg-MOF-74 (scale bar 1 μm), HKUST-1 (scale bar 1 μm), ZIF-67 (scale bar 10 μm), Al-MIL-53 (scale bar 10 μm), Fe-MIL-53 (scale bar 10 μm), UiO-66 (scale bar 1 μm).

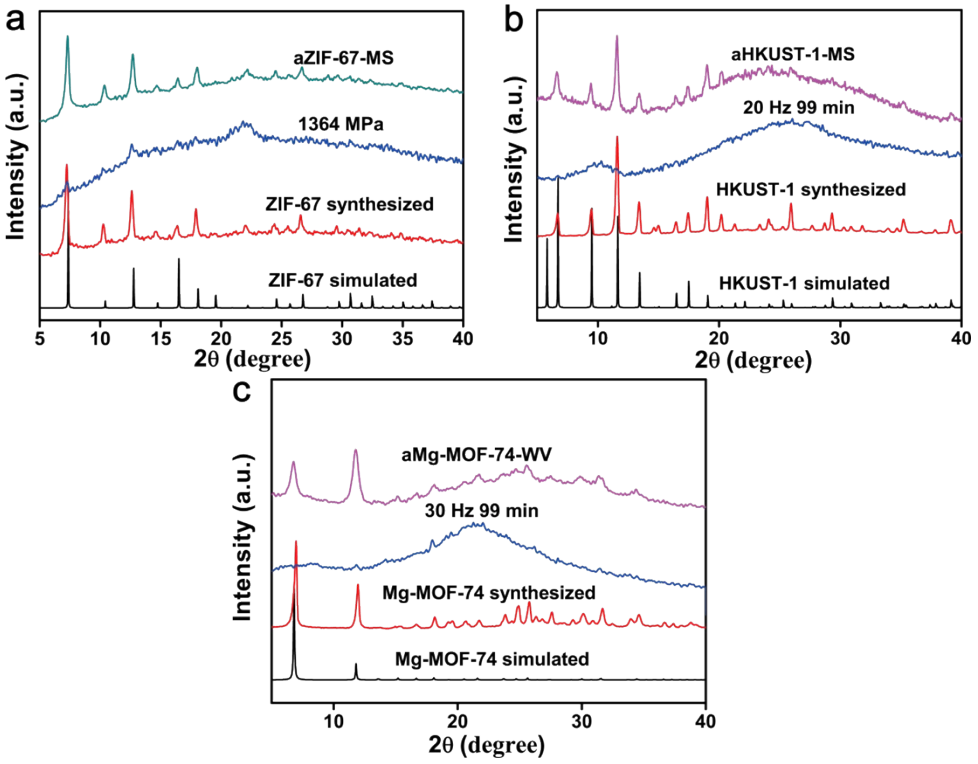

Fig. S14 XRD patterns of pressed and recovered process of ZIF-67, HKUST-1 and Mg-MOF-74. (a) PXRD patterns of pressed and recovered process of ZIF-67. (b) PXRD patterns of pressed (ball-milling) and recovered process of HKUST-1. (c) PXRD patterns of pressed (ball-milling) and recovered process of Mg-MOF-74.

The process of PISA is applicable not only to ZIF-8, but also to other MOFs (Co-ZIF-67, Cu-HKUST-1 and Mg-MOF-74), bringing MOFs broader application prospects. PXRD results demonstrated that all these partially disordered MOFs could be reconstructed by methanol (or water) vapor/solvents exposure, indicating the proposed partially disordered–recovery strategy is suitable for a variety of MOFs.

III. PISA for the encapsulation of GOx in ZIF-8

The compression time and ZIF-8 loading amount were also investigated to optimize the pressure-induced disordered conditions. Different from the significant pressure-dependent reduction in crystallinity, both PXRD and SEM measurements revealed that the extrusion time and ZIF-8 loading amount had little influence on PISA. For convenience, our samples were compressed for 5 min with the loading of 20 mg for encapsulation experiments.

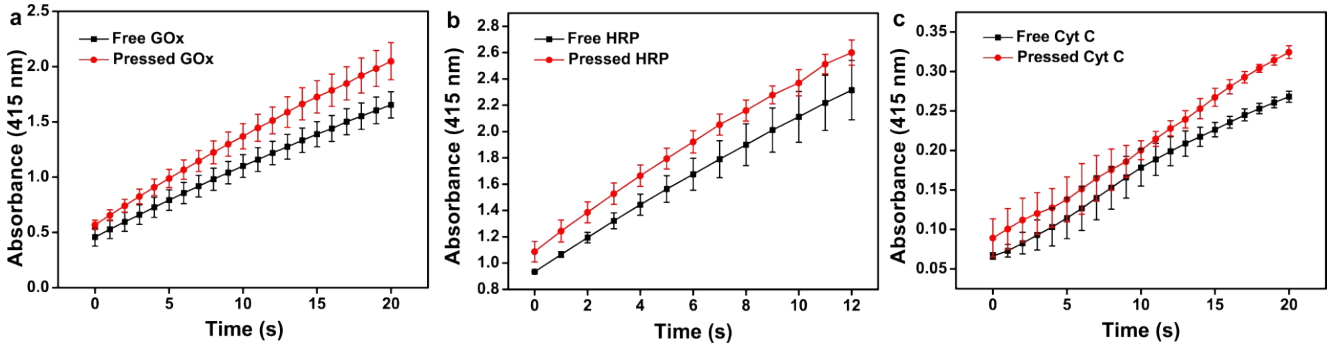

Fig. S15 Biological activity of GOx or HRP or Cyt C under 1364 MPa for 5 min. (a) Comparison of activity for GOx before and after mechanical pressure ($k_{free\ GOx}$=0.0603 s^{-1}, $k_{pressed\ GOx}$=0.0762 s^{-1}). (b) Comparison of activity for HRP before and after mechanical pressure ($k_{free\ HRP}$=0.123 s^{-1}, $k_{pressed\ HRP}$=0.126 s^{-1}). (c) Comparison of activity for Cyt C before and after mechanical pressure ($k_{free\ Cyt\ C}$=0.0104 s^{-1}, $k_{pressed\ Cyt\ C}$=0.0123 s^{-1}).

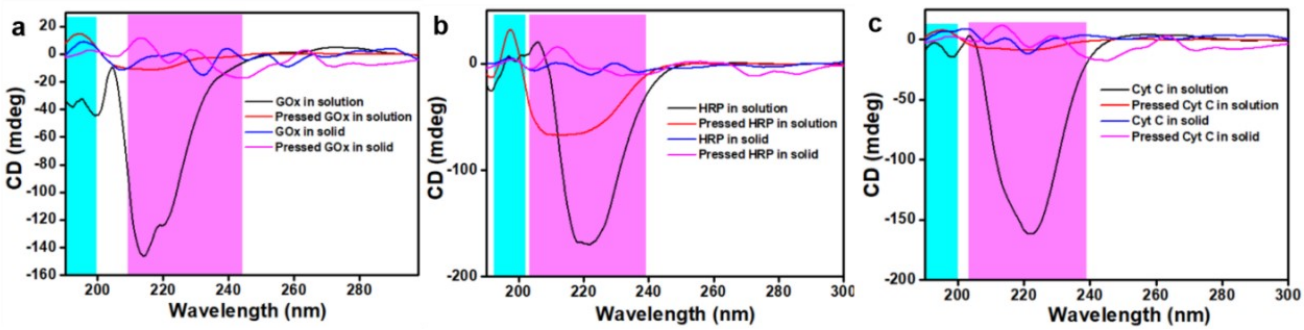

Fig. S16 Circular dichroism spectra of enzymes in solution, pressed enzymes dissolving in solution, enzymes in solid and pressed enzymes in solid. (a) Circular dichroism spectrum of GOx in solution, pressed GOx dissolving in solution, GOx in solid and pressed GOx in solid. The β-sheets of enzymes labeled in blue (196 nm) and α-helix of enzymes labeled in pink (222 nm) were maintained before and after loading mechanical pressure. (b) Circular dichroism spectra of HRP in solution, pressed HRP dissolving in solution, HRP in solid and pressed HRP in solid. The β-sheets of enzymes labeled in blue

(196 nm) and α-helix of enzymes labeled in pink (222 nm) were maintained before and after loading mechanical pressure. (c) Circular dichroism spectra of Cyt C in solution, pressed Cyt C dissolving in solution, Cyt C in solid and pressed Cyt C in solid. The β-sheets of enzymes labeled in blue (196 nm) and α-helix of enzymes labeled in pink (222 nm) were maintained before and after loading mechanical pressure.

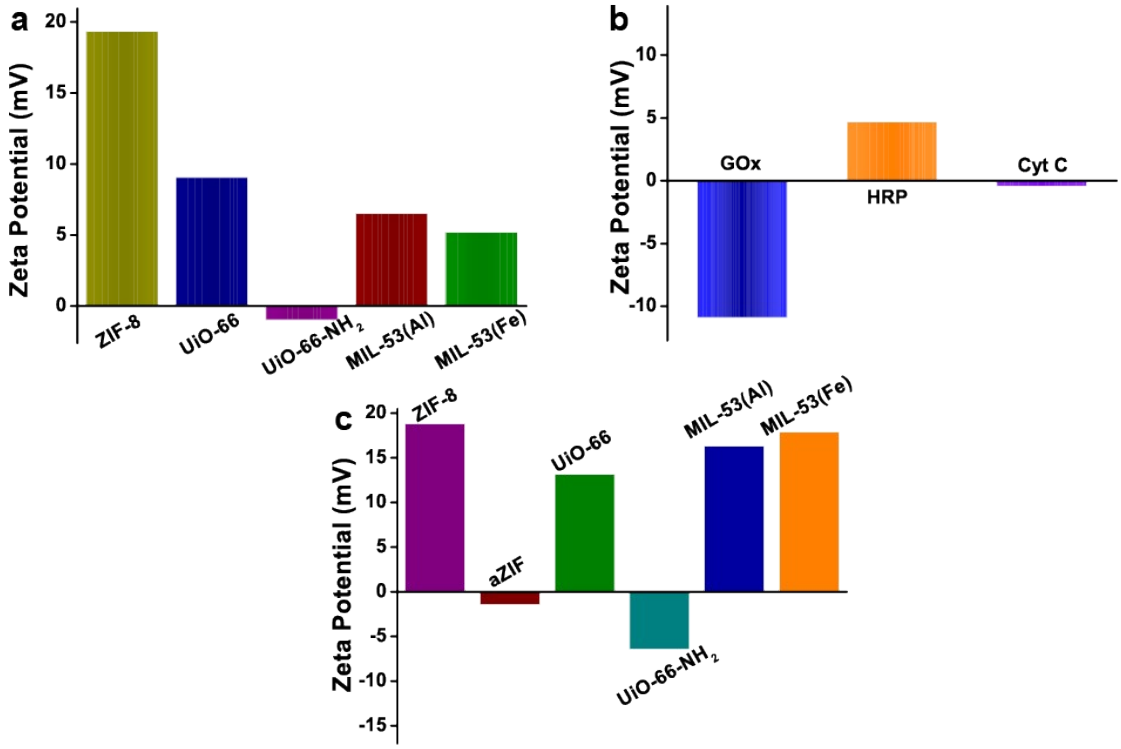

Fig. S17 Zeta potentials of MOFs, enzymes and premilled MOFs. (a) Zeta potential of ZIF-8, UiO-66, UiO-66-NH_2, MIL-53(Al) and MIL-53(Fe). (b) Zeta potentials of GOx, HRP and Cyt C. (c) Zeta potentials of premilled ZIF-8, UiO-66, UiO-66-NH_2, MIL-53(Al) and MIL-53(Fe).

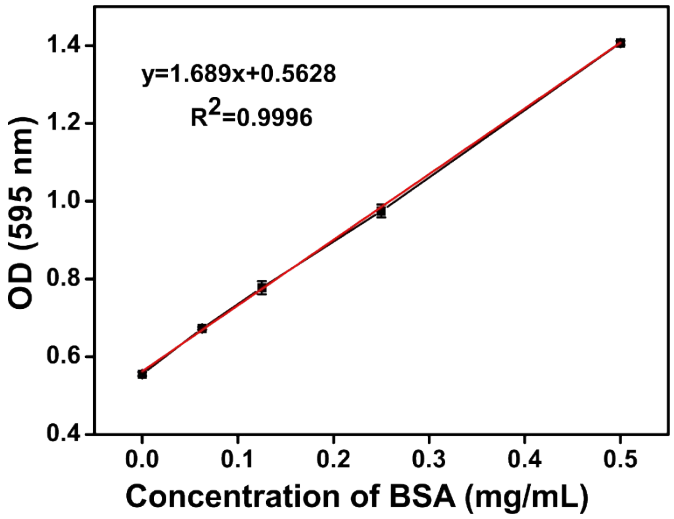

Fig. S18 Bradford assay of the BSA concentration for determination of enzymes in different MOFs.The corresponding standard calibration line of the Bradford assay is shown above.

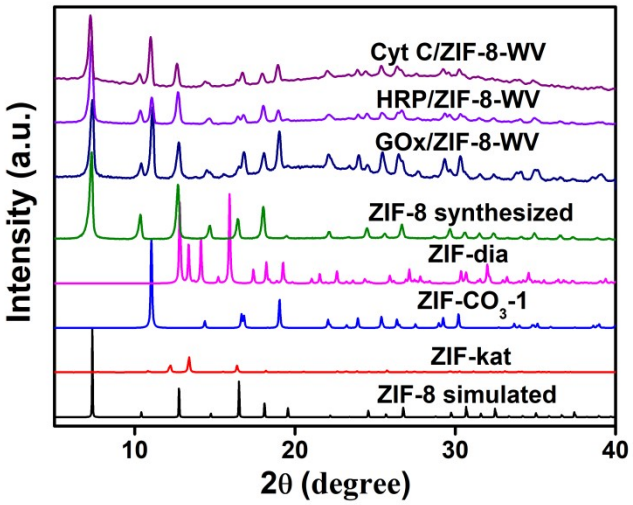

Fig. S19 PXRD patterns of enzymes/ZIF-8-WV. By using the "ZIF phase-analysis"-application-Version 1.0.0 from the paper,[6] the ratio of ZIF-CO_3-1 in GOx/ZIF-WV was 94% and that of ZIF-8 was 6%. The application is hosted at the Technical University of Graz and deployed on-premises using Shiny-Server.

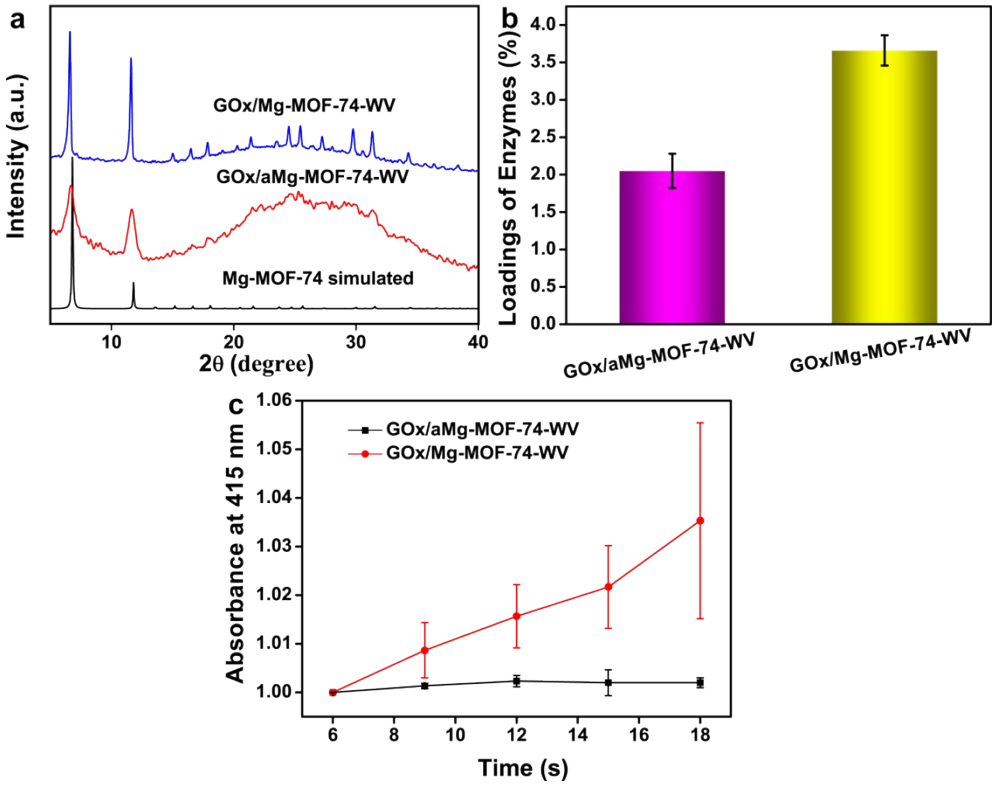

Fig. S20 PXRD patterns, loadings of GOx, activity of GOx/aMg-MOF-74-WV and GOx/Mg-MOF-74-WV. (a) PXRD patterns of stimulated Mg-MOF-74, GOx/aMg-MOF-74-WV and GOx/Mg-MOF-74-WV. (b) Loadings of GOx in GOx/aMg-MOF-74-WV, and GOx in GOx/Mg-MOF-74-WV. (c) Activity of GOx/aMg-MOF-74-WV and GOx/Mg-MOF-74-WV.

IV. Universality of PISA encapsulation strategy

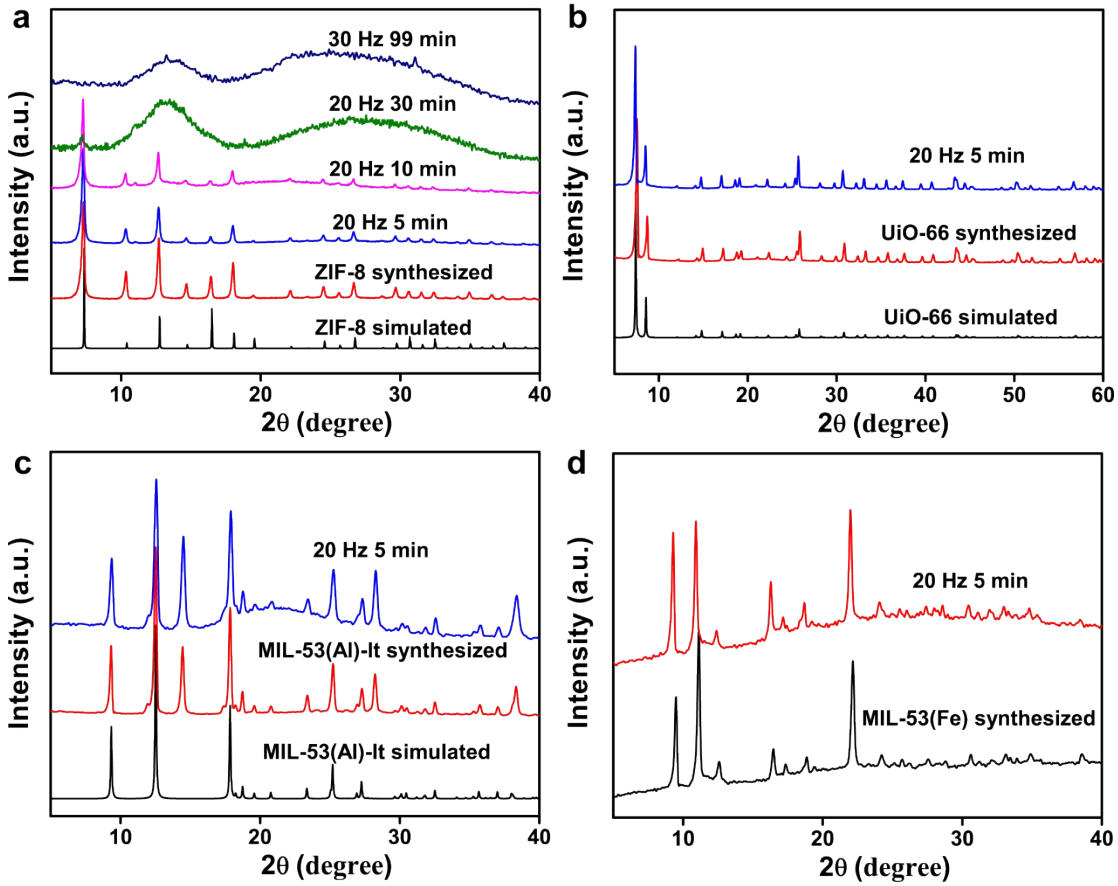

Fig. S21 PXRD patterns of MOFs after milling. (a) PXRD patterns of ZIF-8 under milling for 5 min (20 Hz), 10 min (20 Hz), 30 min (20 Hz), and 99 min (30 Hz). (b) PXRD patterns of UiO-66 under milling for 5 min (20 Hz). (c) PXRD patterns of MIL-53(Al) under milling for 5 min (20 Hz). (d) PXRD patterns of MIL-53(Fe) under milling for 5 min (20 Hz) ('It' means low temperature phase of MIL-53(Al)).

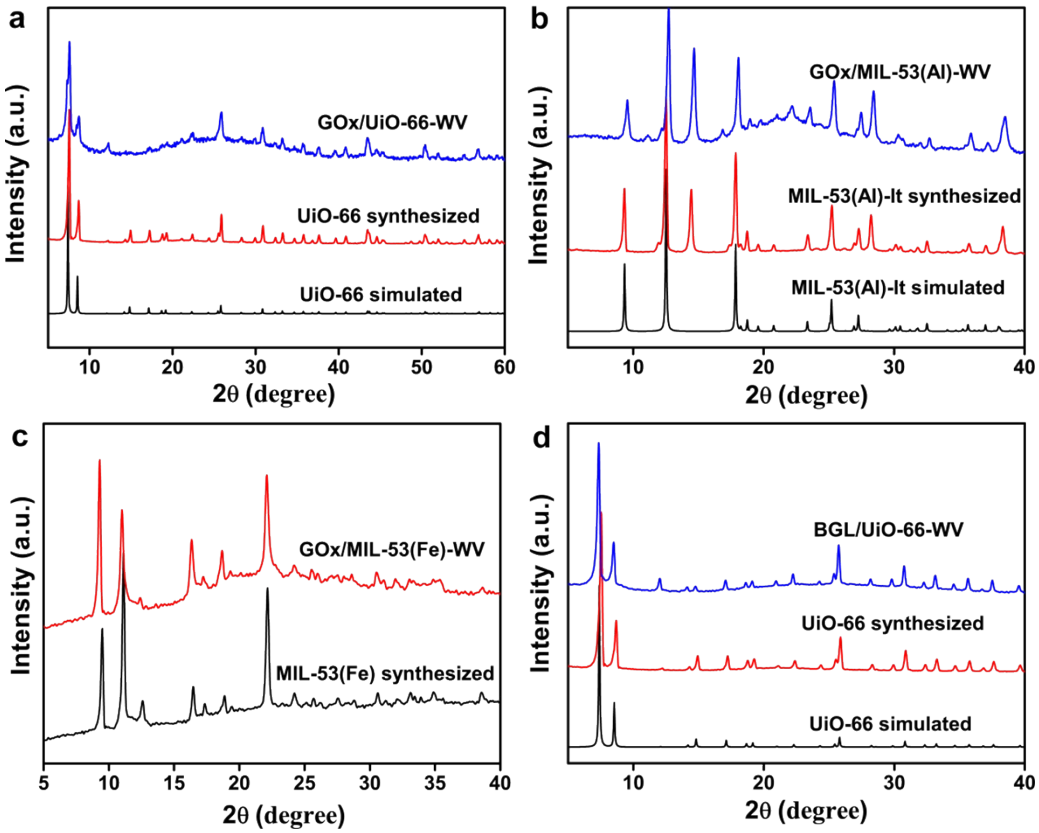

Fig. S22 PXRD patterns of GOx/MOFs-WV. (a) PXRD patterns of GOx/UiO-66-WV. (b) PXRD patterns of GOx/MIL-53(Al)-low temperature(It)-WV. (c) PXRD patterns of GOx/MIL-53(Fe)-WV. (d) PXRD patterns of β-gal/UiO-66-WV ('It' means low temperature phase of MIL-53(Al)).

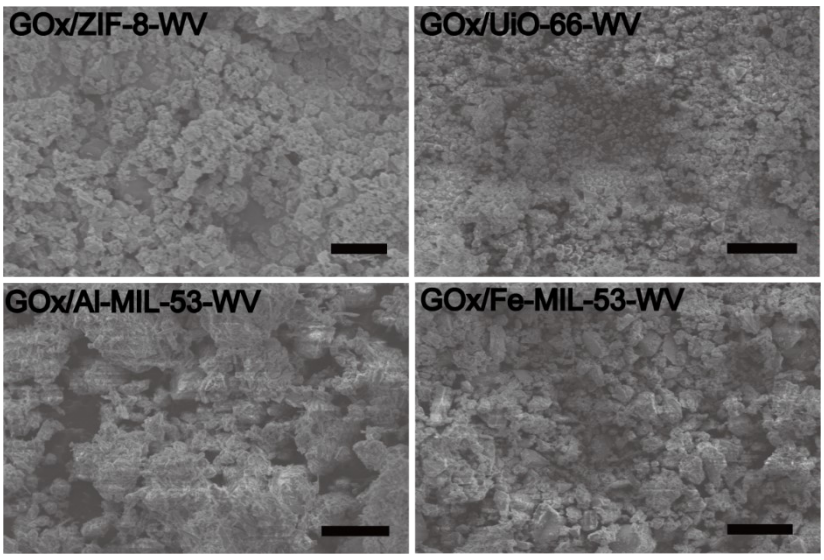

Fig. S23 SEM images of GOx/MOFs-WV. GOx/ZIF-8-WV (scale bar: 3 μm), GOx/UiO-66-WV (scale bar: 10 μm), GOx/MIL-53-Al-WV (scale bar: 10 μm), GOx/MIL-53-Fe-WV (scale bar: 10 μm).

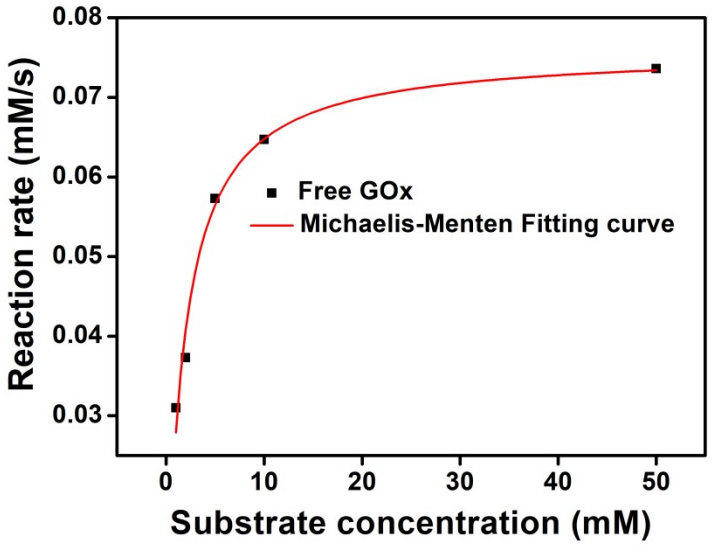

Fig. S24 Michaelis-Menten fitting of free GOx. Source data are provided as a Source Data file.

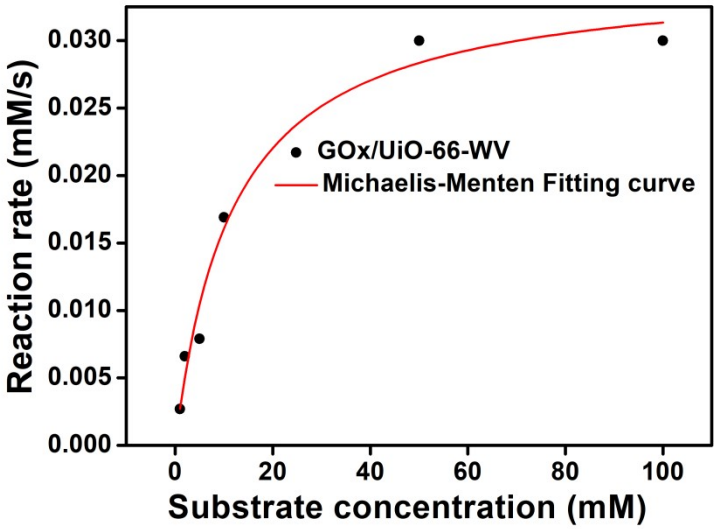

Fig. S25 Michaelis-Menten fitting of GOx/UiO-66-WV. Source data are provided as a Source Data file.

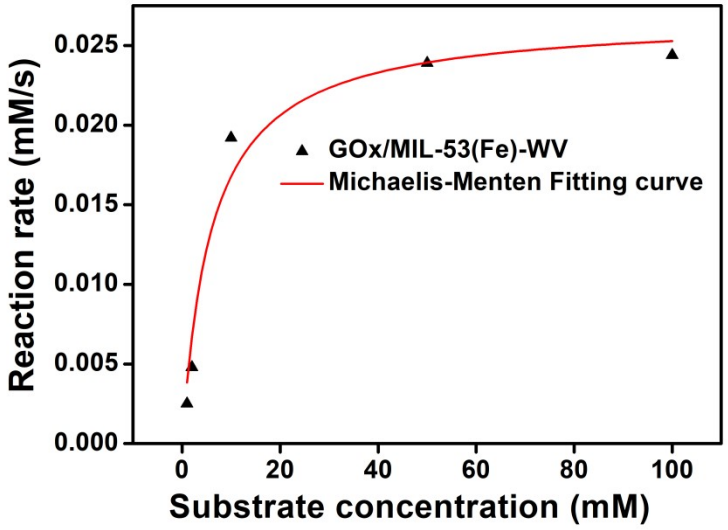

Fig. S26 Michaelis-Menten fitting of GOx/MIL-53(Fe)-WV. Source data are provided as a Source Data file.

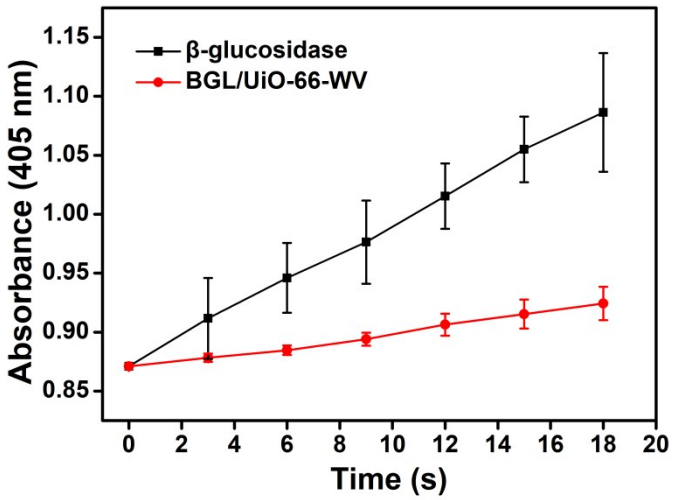

Fig. S27 Comparison of enzymatic activity between free enzymes and BGL/UiO-66-WV.

Enhancing the reproducibility of experiments

In this section, the general protocol has been given to find the best conditions to use PISA. Several key factors that may affect the activity of enzymes have been systematically researched. Here, UiO-66-NH_2 with different sizes have been chosen to study the effect of different grain size on enzyme encapsulation. ~100 nm UiO-66-NH_2 and ~500 nm UiO-66-NH_2 were chosen to encapsulate GOx. After the

encapsulation of GOx, their crystal structures and morphology showed negligible change (Fig. S28 and S29). The encapsulation amount of the enzyme was about 1.88% for 100 nm UiO-66-NH_2 and 1.56% for around 500 nm UiO-66-NH_2. However, GOx/UiO-66-NH_2 with a diameter around 500 nm showed higher activity (Fig. S30), which may result from the position of the enzyme being encapsulated on the outer surface. It is proved that the larger grain size may be more favorable for the preservation of enzyme activity. Another factor was pressure. ~500 nm UiO-66 has been chosen to research the influence of pressure on the encapsulation of enzymes. Different pressures (91 MPa or 273 MPa) for PISA can regulate the activity of enzymes after encapsulation, which indicates that larger damage degree (273 MPa) will affect the enzyme activity and the substrate mass transfer rate (Fig. S30). The third point was aging time. We found that the loading amount and activity of enzyme were improved with the increase of recovery time (Fig. S30 and S31). It is suggested that the long-time aging was also beneficial to improve the encapsulation quantity and enzyme activity. The fourth important factor for maintaining high enzymatic activity is the surface electrical matching between enzyme and MOFs. In view of the surface charge matching between premilled UiO-66-NH_2 (−6.45 mV) and HRP (4.67 mV), we packed HRP into UiO-66-NH_2 structure, and the enzyme activity can be well maintained (Fig. S30) by washing HRP/UiO-66-NH_2 with protease solution. To make the recovery process more efficient, 50 μL was used to replace water vapor to accelerate the aging process at 4 ℃. After 24 h recovery, GOx/UiO-66-W and GOx/MIL-53(Fe)-W can maintain 66% and 19.4% of relative activity compared to free enzymes. In additon, we found that by recovering pressed enzymes/MOF composites in a surface covered mould (keep away from water contacting), GOx/UiO-66-WV can show almost 100% activity compared to free enzymes, which means partially leaching of metal ions and organic ligands may influence the activity of enzymes during the water infiltrating process. All in all, larger crystal size, lower pressure (91 MPa), longer time aging (3 days), electrostatic properties matching and avoiding water contacting are beneficial to the improvement of enzymatic activity.

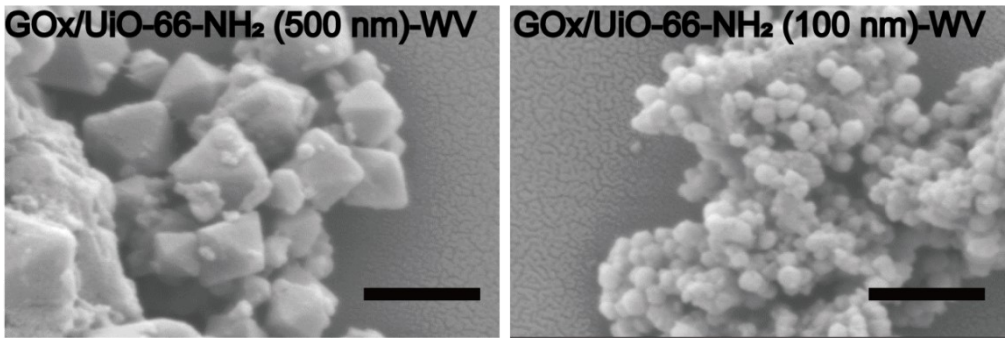

Fig. S28 SEM images of GOx/UiO-66-NH_2 (500 nm)-WV and GOx/UiO-66-NH_2 (100 nm)-WV (scale bar: 1 μm).

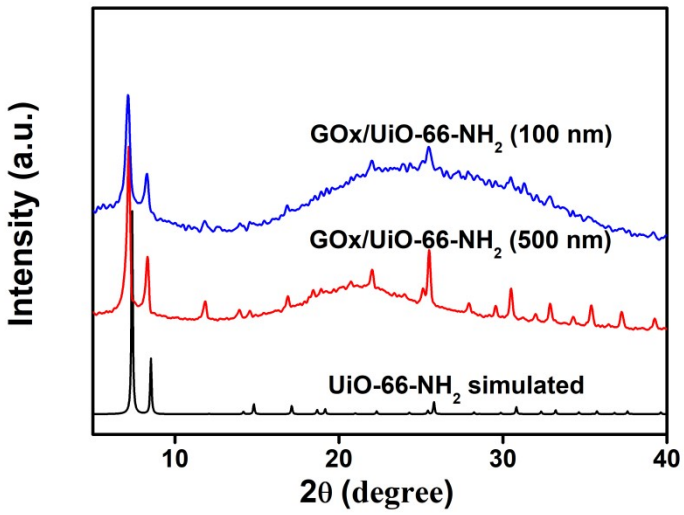

Fig. S29 PXRD patterns of GOx/UiO-66-NH_2 (500 nm)-WV and GOx/UiO-66-NH_2 (100 nm)-WV.

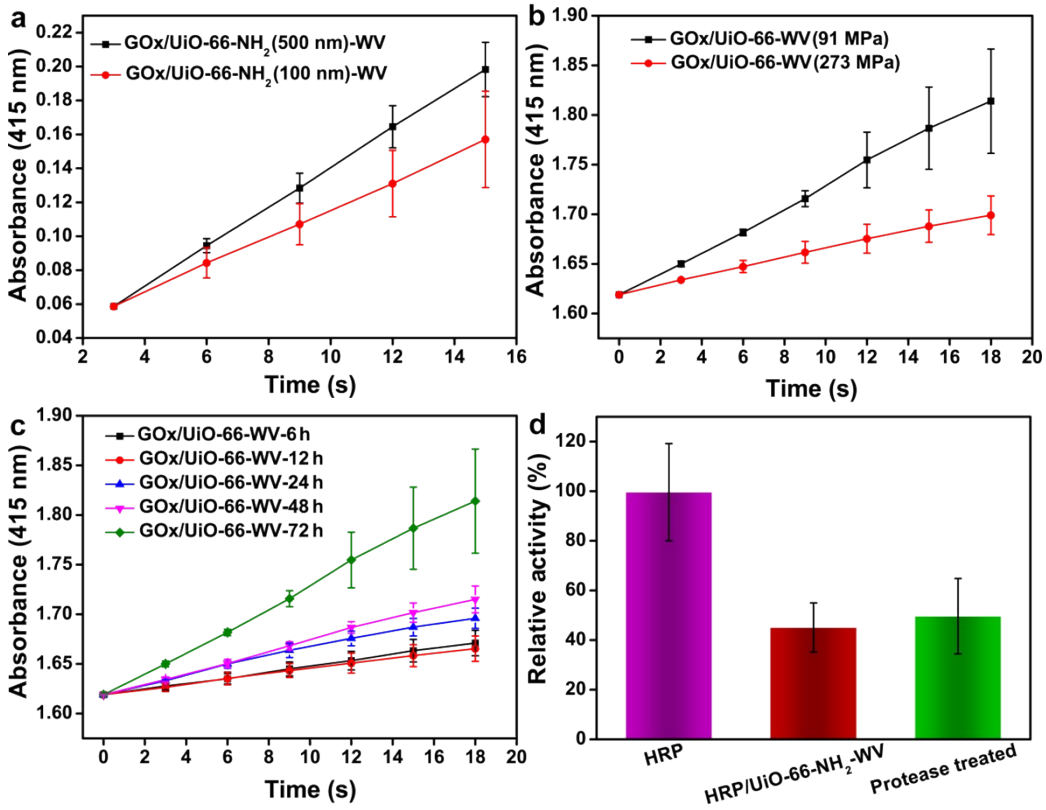

Fig. S30 Protocol for the encapsulation of enzymes in MOFs by PISA. (a) Comparison of enzymatic activity between GOx/UiO-66-NH_2 (500 nm)-WV and GOx/UiO-66-NH_2 (100 nm)-WV. (b) Comparison of enzymatic activity between GOx/UiO-66-WV prepared under 91 MPa and 273 MPa. (c) Comparison of enzymatic activity between GOx/UiO-66-WV aged under 6, 12, 24, 48, 72 h. (d) Comparison of enzymatic activity between free HRP, HRP/UiO-66-NH_2-WV and HRP/UiO-66-NH_2-WV after protease treatment.

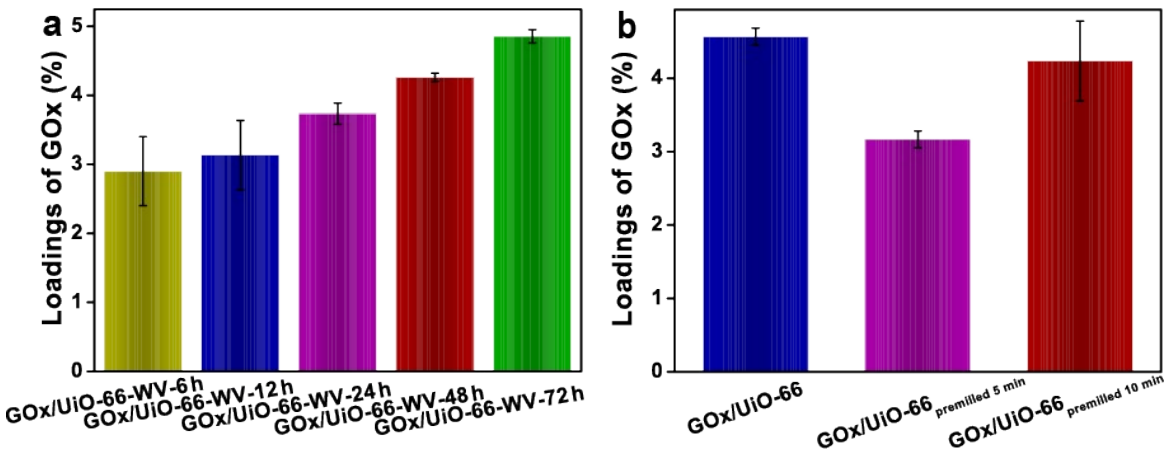

Fig. S31 Comparison of enzyme's loadings under different aging time and premilling time for preparing GOx/UiO-66.

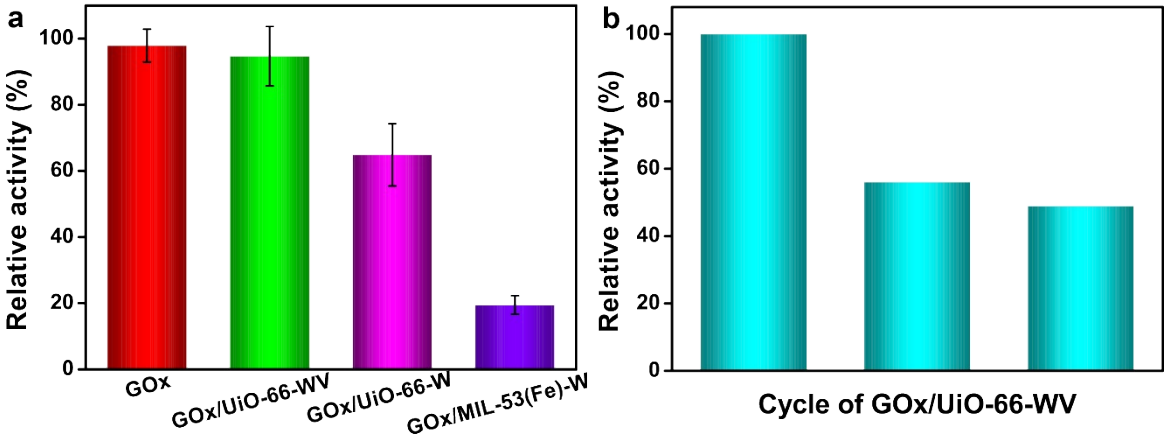

Fig. S32 Optimization of PISA strategy. (a) Comparison of enzymatic activity between free GOx, GOx/UiO-66-WV(pressed samples were put in a mould with an umbrella to avoid the falling water droplets) , GOx/UiO-66-W and GOx/MIL-53(Fe)-W(50 μL water were added on the surface of the pressed samples and keeping at 4 ℃ for 24 h). (b) Recycle performance of GOx/UiO-66-WV and relative activity.

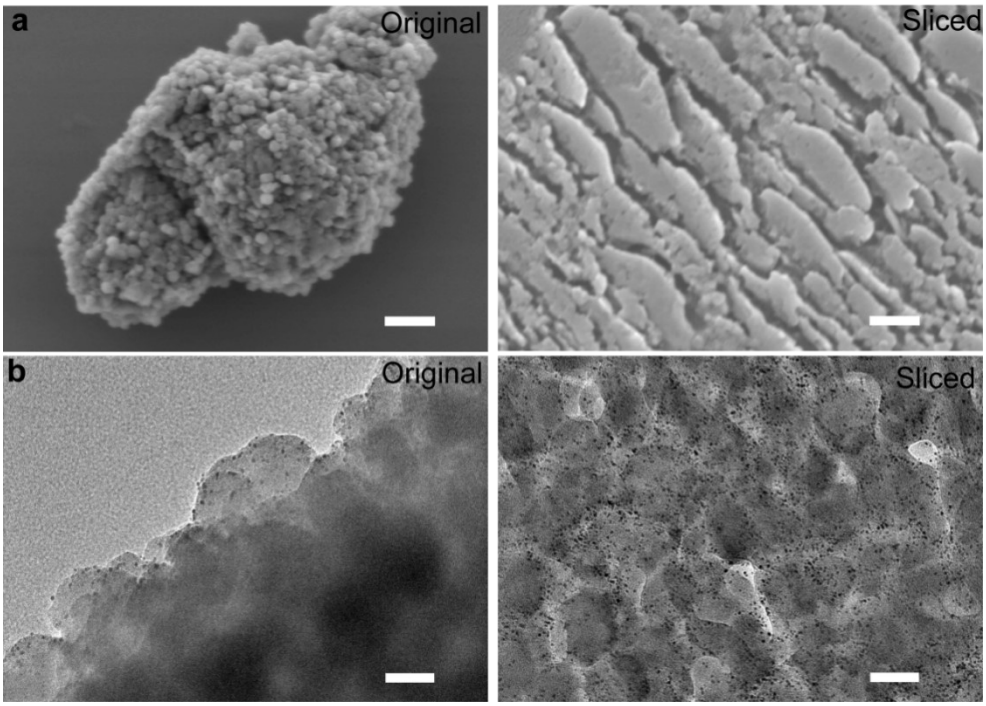

Fig. S33 Characterization of an 80-nm-thick ultramicrotomed Pt/UiO-66-NH_2 (~100 nm)-WV samples. (a) SEM image of Pt/UiO-66-NH_2-WV and sliced samples. (b) TEM image of Pt/UiO-66-NH_2-WV and sliced samples (scale bar: 400 nm for a, 50 nm for b).

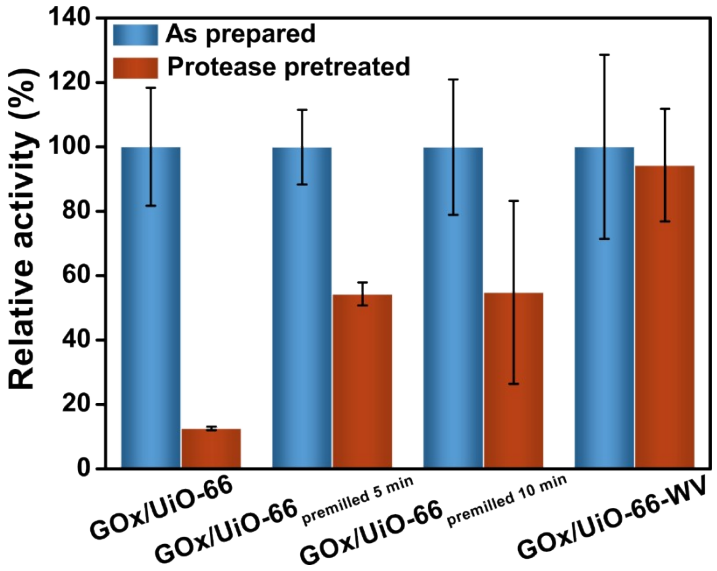

Fig. S34. Biological activity of GOx/UiO-66. Biological activity of GOx/UiO-66 (mixing and aging for 3 days), GOx/UiO-66 $_{\text{premilled 5 min}}$ (premilled for 5 min, mixing and aging for 3 days), GOx/UiO-66 $_{\text{premilled 10 min}}$ (premilled for 10 min, mixing and aging for 3 days), GOx/UiO-66-WV before and after the treatment of 1 mg mL^{-1} protease at 40 °C for 24 h.

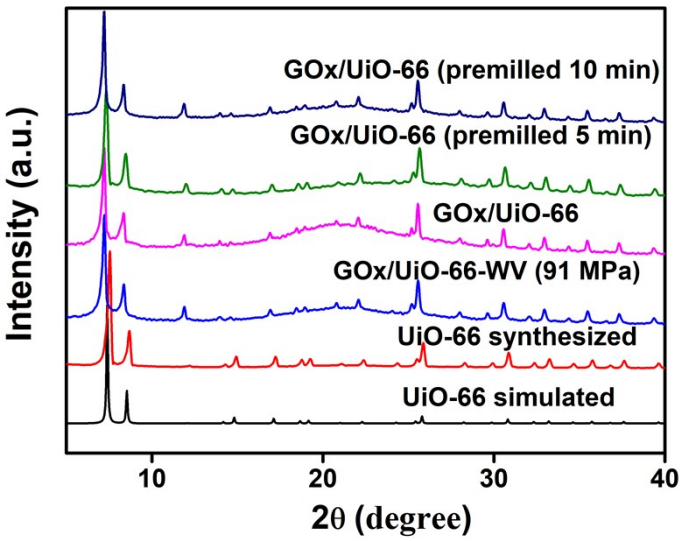

Fig. S35 PXRD of GOx/UiO-66-WV under different treatments. PXRD patterns of GOx/UiO-66-WV prepared under 91 MPa, PXRD patterns of mixed GOx/UiO-66 after aging, mixed GOx/UiO-66 (premilled 5 min) after aging and mixed GOx/UiO-66 (premilled 10 min) after aging

V. Molecular dynamics simulations

The GROMACS 4.67 package was applied to the MD simulations.[7-10] The model for MOFs can be obtained from previous work.[11, 12] For protein, the GROMOS96 force fields were used.[13] The charge of UiO-66 was decreased to 0.15 times compared to the reference, to keep the system stabilized and the protein structure.

To study the adsorption process of protein on the truncated MOFs, the truncated MOFs were placed in simulation boxed with dimensions of 23.5296 × 6.7648 × 20.7648 nm^3 for ZIF-8 and 18.2986 × 8.2986 × 34.1493 nm^3 for UIO-66, respectively. The truncated facet was [111] facet. According to the experiment, the [100] facet favors the ligand exposure, and the [111] facet favors the metal-clusters exposure. The protein was put above the MOFs on the facets junction. The system was neutralized almost to zero by counter ions. The positions of these MOFs were frozen and protein can move freely during the simulation. The cutoff distance for a short-range non-bonded interaction was chosen to be 12 Å and long-range electrostatic and V-rescale bath coupling scheme were used.[14, 15] The NVT Ensemble was applied, and the simulations were run over 4000 ps in steps of 2 fs. The Fig.s of simulation results were captured by visual molecular dynamics (VMD).[16]

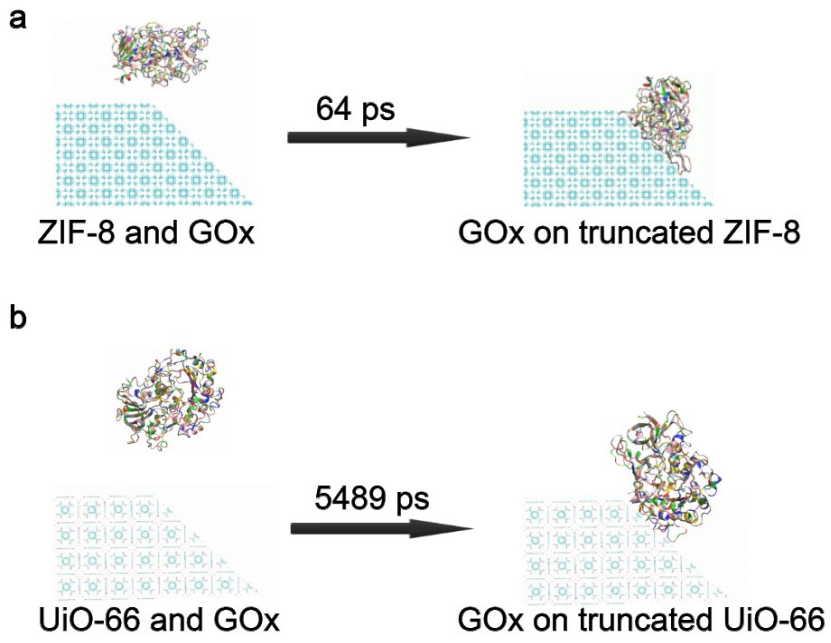

Fig. S36 Molecular dynamics simulations of the process of GOx absorbed on the truncated ZIF-8 (a) and UiO-66 (b). The truncated facet was [111] facet. According to the experiment, the [100] facet may favor the ligand exposure, and the [111] facet favors the metal-clusters exposure. The simulation results demonstrated the protein tends to absorb on the facets junction of MOFs.

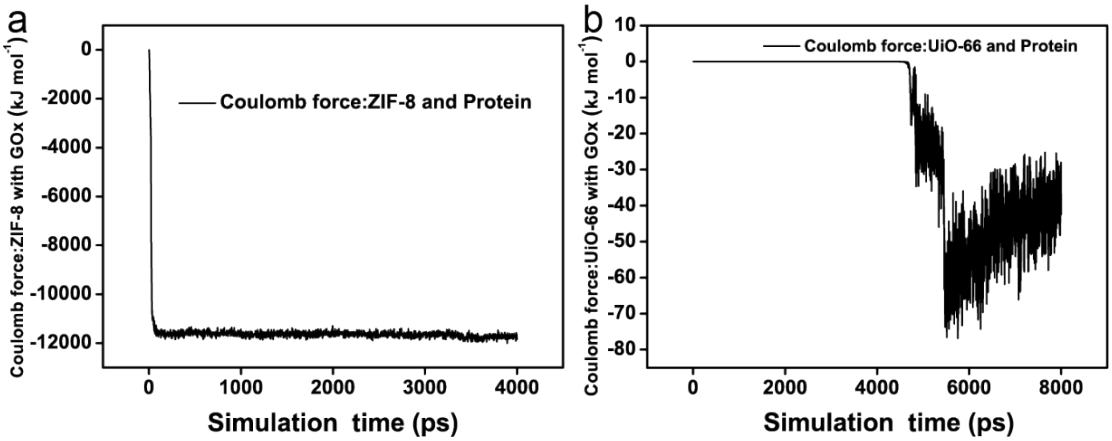

Fig. S37 (a) Coulomb force between truncated ZIF-8 and GOx, (b) Coulomb force between truncated UiO-66 and GOx. Simulations were run over 4000 ps in steps of 2 fs. The Fig.s of simulation results were captured by visual molecular dynamics (VMD).

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