Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information for

Improved stability and activity of laccase through de novo and post-synthesis immobilization on a hierarchically porous metal-organic framework (ZIF-8)

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Synthesis of copper (Cu) nanoparticles

A 0.19 g of sodium borohydride was dissolved in deionized water followed by adding sodium hydroxide solution (1 mol/L) and assigned as solution A with pH 12. Then, copper sulfate pentahydrate (2.50 g) was dissolved into 100 mL of anhydrous ethanol and water mixture solution (v/v, 2: 3) and the appropriate amount of polyethylene pyrrolid1 (PVP) was added (solution B). Then, solution A was added drop by drop into solution B under stirring for 1 h. The product was then washed by water three times and dried overnight in a vacuum drying oven at 80°C.

Synthesis of MZIF-8 and LAC@MZIF-8

To synthesize MZIF-8, $Zn(NO_3)_2 \cdot 6H_2O$ (1 mmol) was dissolved in deionized water (25 mL). Subsequently, 2-methylimidazole (8 mmol) was dissolved in deionized water (25 mL), and triethylamine (8 mmol) was added to the solution. The $Zn(NO_3)_2 \cdot 6H_2O$ and 2-methylimidazole solutions were then mixed and placed on a magnetic stirrer for 1 h at room temperature. After centrifugation and freeze-drying overnight, the white MZIF-8 powder was obtained.

The de novo synthesis of the LAC@MZIF-8 MOF was performed as follows: First, a certain quantity of laccase was dissolved in a pH 5 citric acid - disodium phosphate (CPBS) buffer solution (1 mL). This was then added to a $Zn(NO_3)_2 \cdot 6H_2O$ solution under ultrasonication, with the procedure then following that of the MZIF-8 preparation process described above.

Catalytic curve fitting method

The first-order reaction kinetics equation (Equation S1) was used to perform the nonlinear fitting for the removal rate of 2, 4-DCP catalyzed by laccase, LAC@MZIF-8, and LAC@HZIF-8 samples. According to the fitting parameter R^2, the time kinetics of the catalytic removal of 2, 4-DCP by laccase and ZIF-8 immobilized laccase material was in line with the first-order reaction kinetics equation. The catalytic removal rate had an exp1ntial correlation with time(t). The catalytic rate constant per hour of LAC@HZIF-8 was the highest, indicating that the catalytic efficiency of 2, 4-DCP immobilized by HZIF-8 was the best.

$$q_t = q_e(1 - e^{-k_1 t}) \quad (1)$$

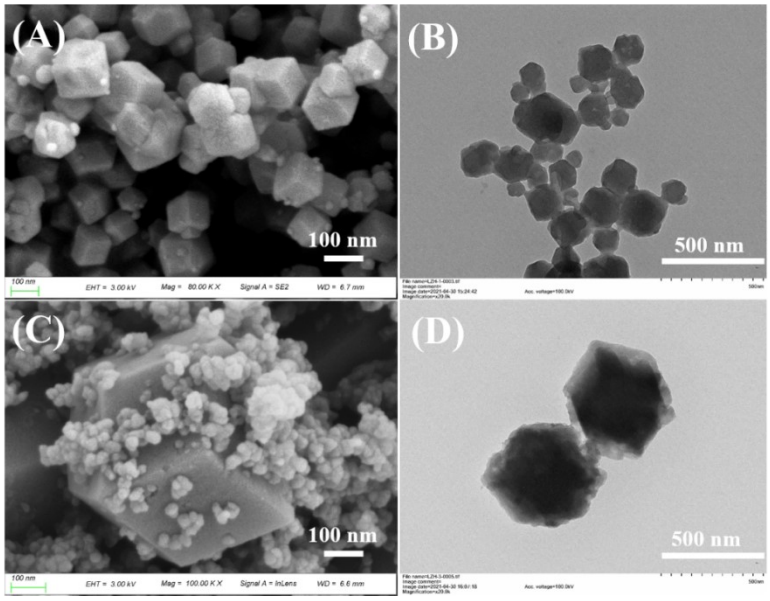


Fig S1. SEM&TEM patterns of MZIF-8, and LAC@MZIF-8. (a) SEM image of MZIF-8; (b) TEM image of MZIF-8; (c) SEM image of LAC@MZIF-8; (d) TEM image of LAC@MZIF-8

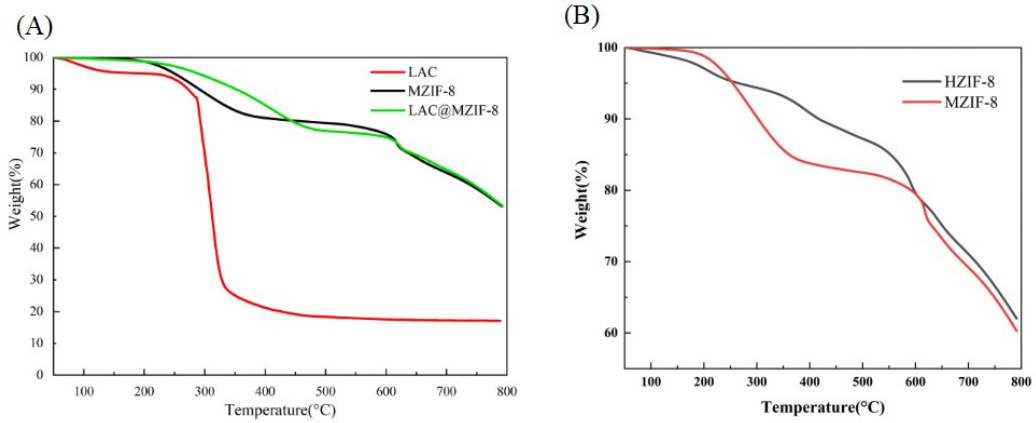
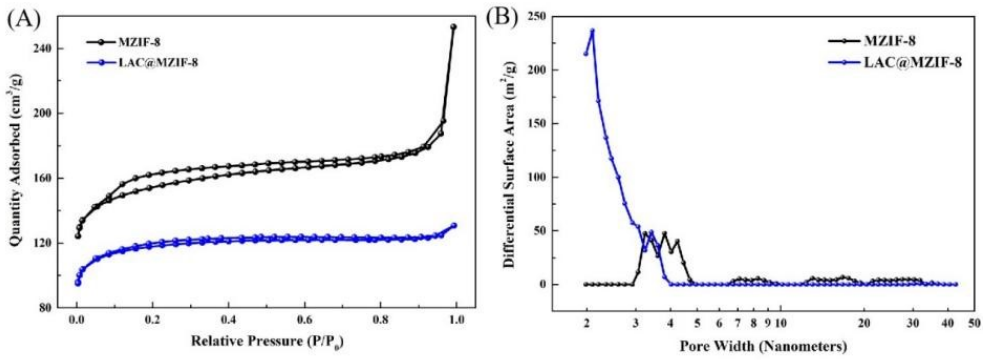
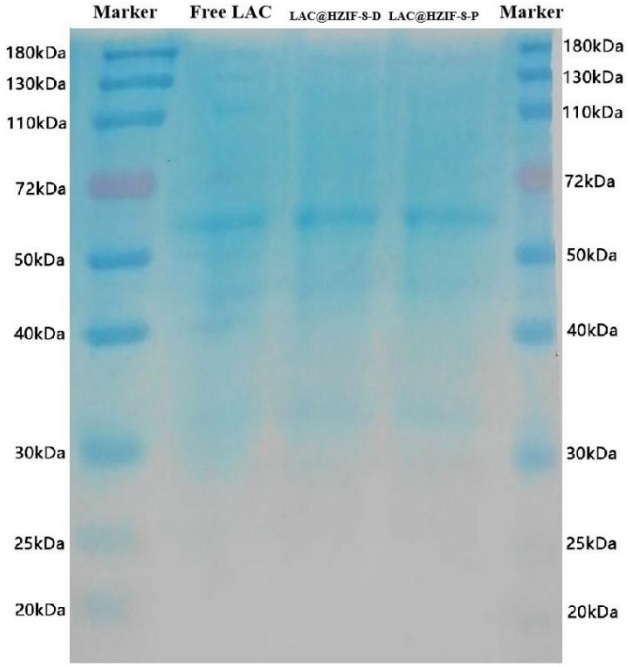


Fig S2. The TGA curve of (a) LAC, MZIF-8，LAC@MZIF-8; (b) MZIF-8, HZIF-8



FigS3. N_2 adsorption/desorption isotherms and the pore size distribution images of MZIF-8 and LAC@MZIF-8. (a) N_2 adsorption/desorption isotherms image of the MZIF-8, and LAC@MZIF-8; (b) pore size distribution image of



the MZIF-8, and LAC@MZIF-8.

Fig S4. Electrophoresis gel of (from the left to the right): (a) a protein Marker; (b) Free LAC; (c) LAC@HZIF-8-D and (d) LAC@HZIF-8-P.

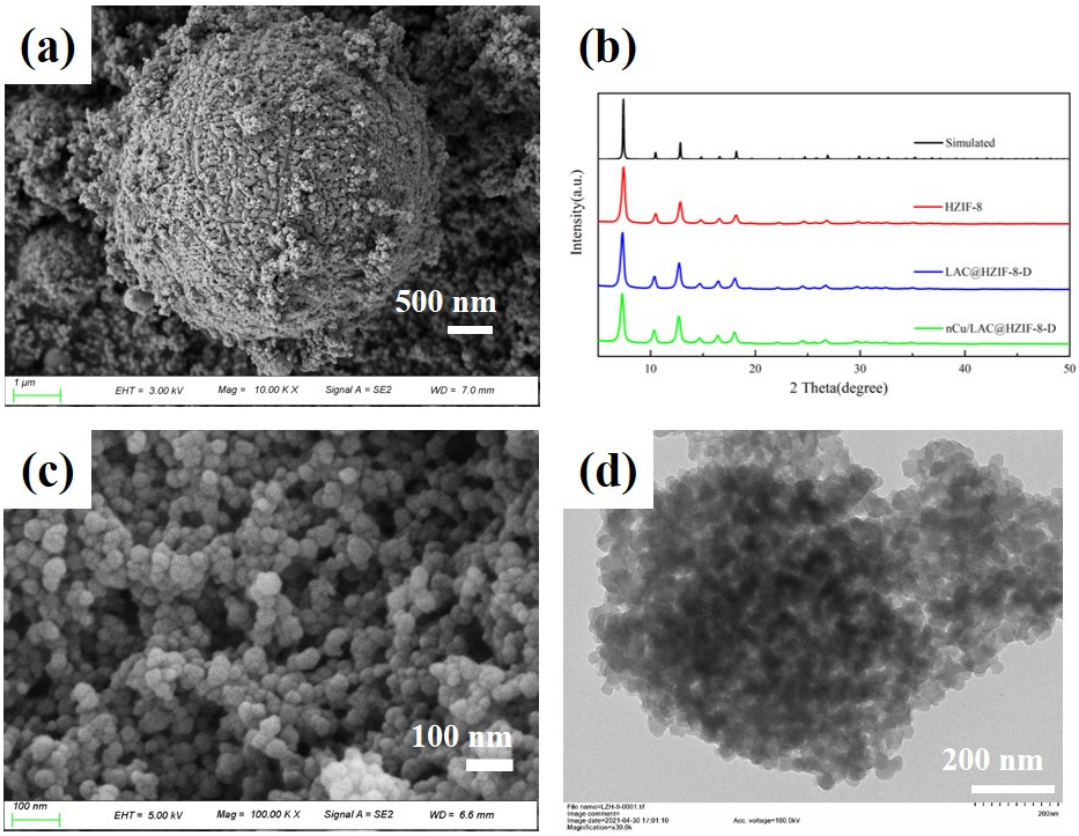


Fig S5. (a) SEM pattern of the nCu; (b) The XRD pattern of HZIF-8, LAC@HZIF-8-D, nCu/LAC@HZIF-8-D ; (c) SEM pattern of the nCu/LAC@HZIF-8; (d) TEM pattern of the nCu/LAC@HZIF-8

TableS1. The specific surface area of ZIF-8, LAC@ZIF-8-D and LAC@HZIF-8-P

Sample	S_{BET} (m^2/g)	S_{micro} (m^2/g)	S_{meso} (m^2/g)
MZIF-8	585	460	124
LAC@MZIF-8	452	387	65
HZIF-8	1153	736	417
LAC@HZIF-8-D	1118	649	468
LAC@HZIF-8-P	1021	610	410