Electronic Supplementary Material (ESI) for Analyst.

Glucose Oxidase Decorated Fluorescent Metal-Organic Frameworks as Biomimetic Cascade Nanozymes for Glucose Detection Through Inner Filter Effect

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Experiments

Nitrogen sorption isotherms and Brunauer–Emmett–Teller (BET) surface areas were measured at 77 K with an ASAP 2020 physisorption analyzer (USA).

Electron spin resonance (ESR) spectra were collected using a Bruker X-band A200 with 5,5-dimethyl-1-pyridine-N-oxide (DMPO) as a trapping agent.

Fourier transform infrared (FT-IR) data were recorded on an American Nicolet AVATAR 360 FT-IR spectrometer.

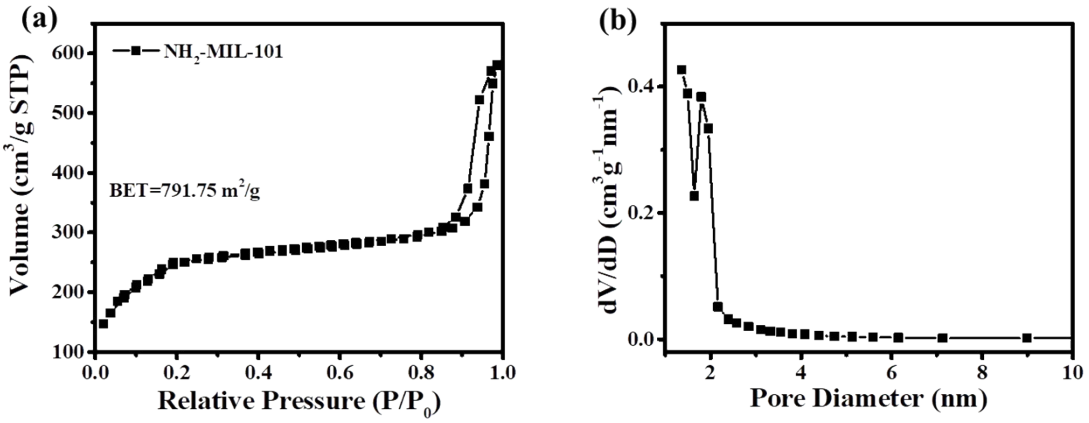

Fig. S1 (a) N_2 adsorption−desorption curves of NH_2-MIL-101, (b) pore size distribution curves of NH_2-MIL-101.

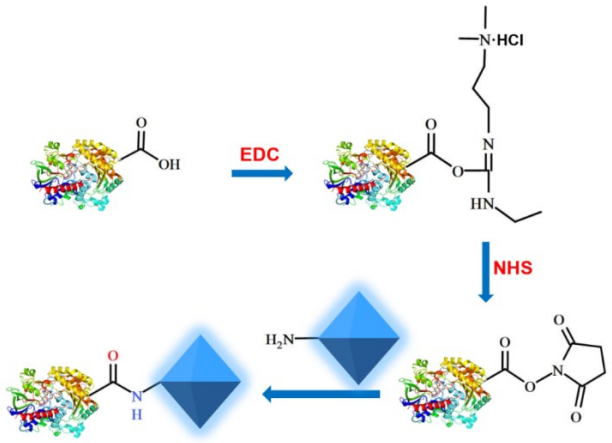

Fig. S2 EDC-/NHS-induced covalent reaction equation of NH_2-MIL-101 and GOx.

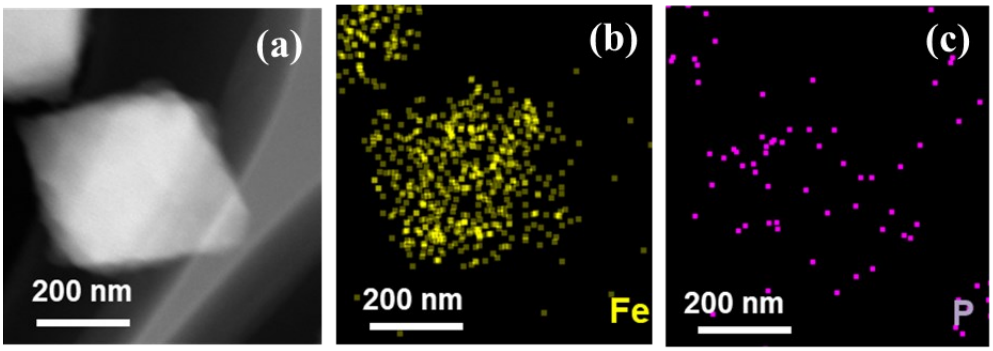

Fig. S3 HAADF-STEM image of GOx and NH_2-MIL-101 through simply mixing (a), EDS elemental mappings of Fe (b) and P (c).

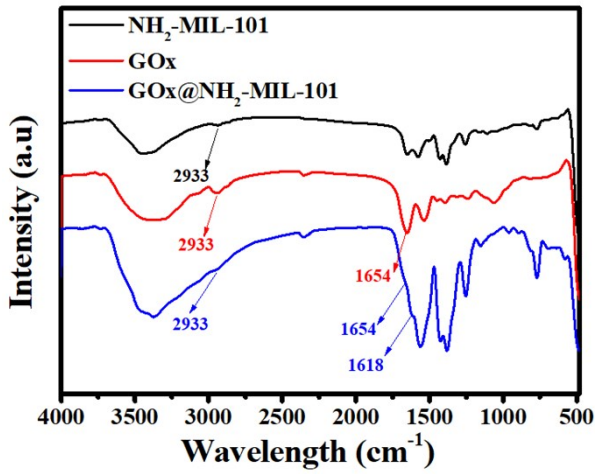

Fig. S4. FT-IR spectra of NH_2-MIL-101, GOx and GOx@NH_2-MIL-101.

To further verify the covalent reaction between NH_2-MIL-101 and GOx, the FT-IR spectra was shown in Fig. S4. For NH_2-MIL-101, the characteristic peak at 2933 cm^{-1} was attributed to N–H stretching vibration of the amine moieties. For GOx, the characteristic peak at 1654 cm^{-1} was corresponding to the stretching vibration of -C=O in carboxyl groups. For GOx@NH_2-MIL-101, the characteristic peak at 2933 cm^{-1} and 1654 cm^{-1} were significantly reduced, and a new characteristic peak appeared at 1618 cm^{-1}, which could be attributed to the vibrational stretching of -C=O in the amide groups. The results showed that GOx was loaded on NH_2-MIL-101 through amidation coupling reaction.

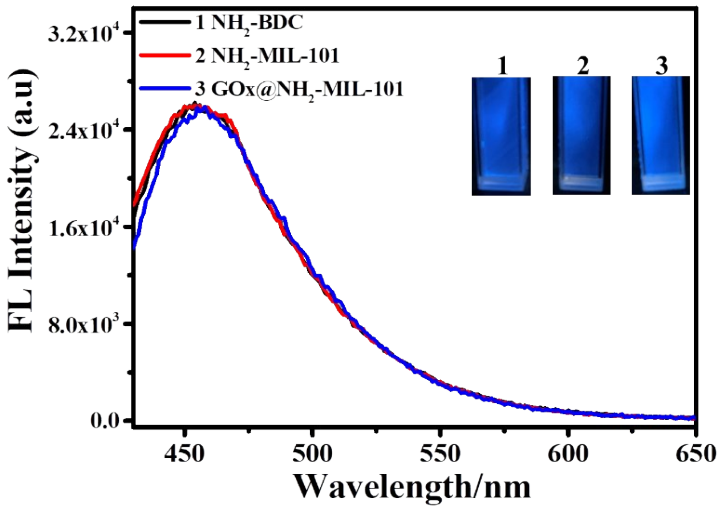

Fig. S5 Fluorescence spectra of NH_2-BDC, NH_2-MIL-101 and GOx@NH_2-MIL-101. The inset of NH_2-BDC, NH_2-MIL-101 and GOx@NH_2-MIL-101 under UV excitation.

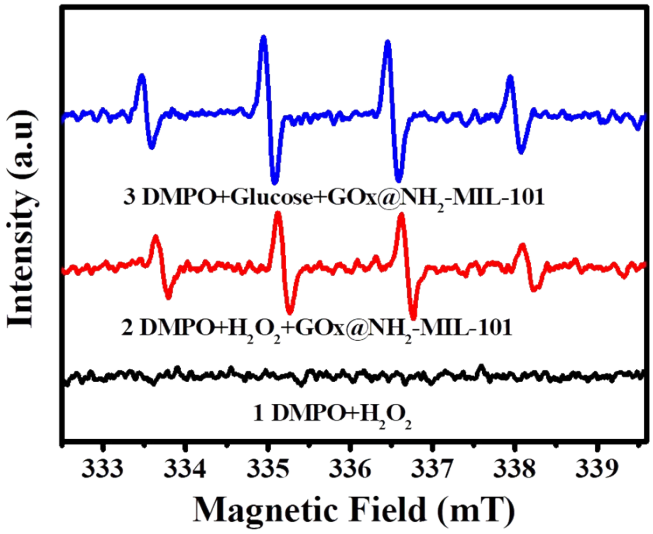

Fig. S6 ESR spectra of DMPO+H_2O_2, DMPO+H_2O_2+ GOx@NH_2-MIL-101, DMPO +Glucose+ GOx@NH_2-MIL-101.

As shown in Fig. S6, in the absence of GOx@NH_2-MIL-101 and glucose, no ESR signal was observed. In the presence of GOx@NH_2-MIL-101 and H_2O_2, remarkable characteristic peaks were detected, corresponding to the typical DMPO-•OH with an intensity ratio of 1 : 2 : 2 : 1, suggesting the generation of •OH. Alternatively, in the presence of GOx@NH_2-MIL-101 and glucose, the same characteristic peaks were also detected.

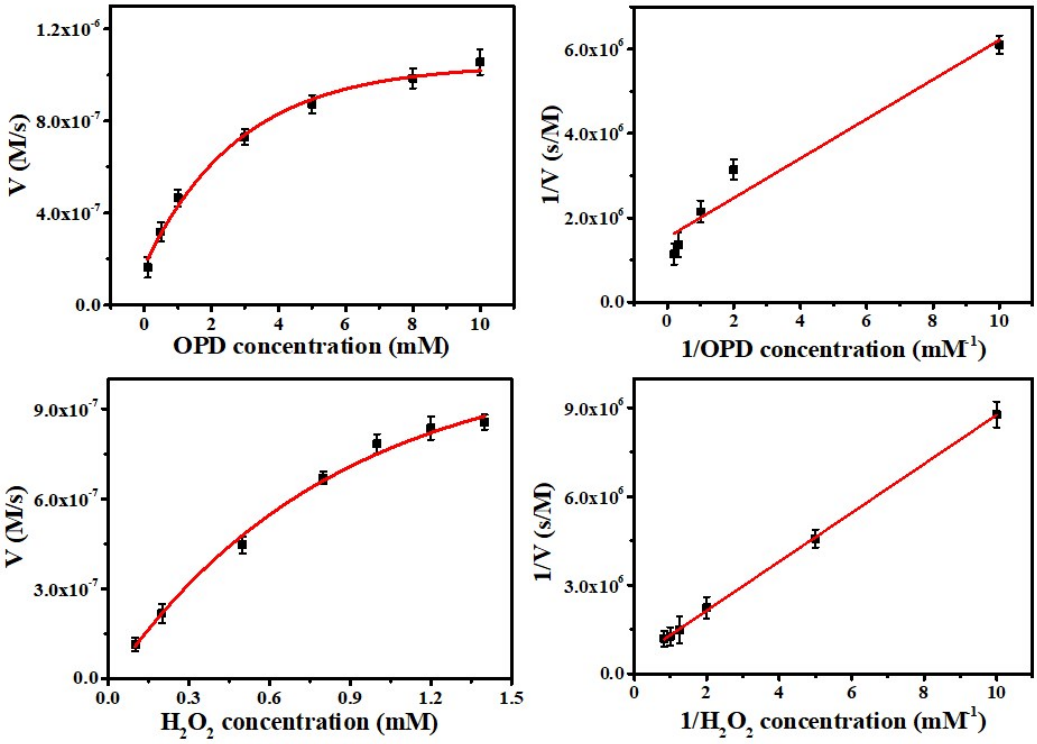

Fig. S7 Steady-state kinetic analysis of the GOx@NH_2-MIL-101.

Table S1. The kinetic parameters of GOx@NH_2-MIL-101

Nanozyme	Substrate	K_m (mmol)	V_{max} (mol·L·s^{-1})
GOx@NH_2-MIL-101	OPD	0.6287	2.14×10^{-6}
	H_2O_2	0.4287	3.29×10^{-6}

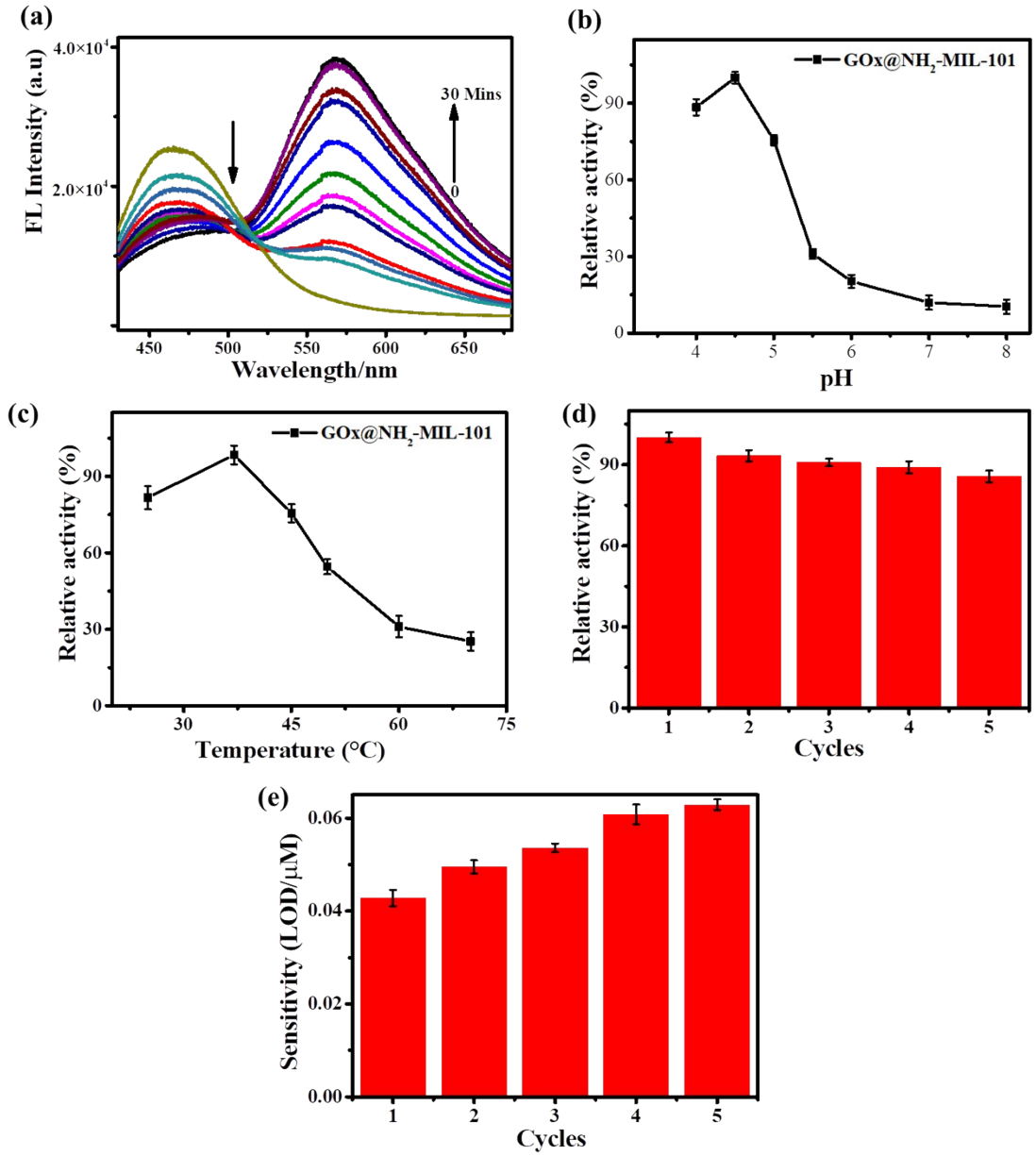

Fig. S8 (a) Fluorescence spectra of GOx@NH_2-MIL-101-OPD-glucose system varies with reaction time, (b) pH-dependent relative activity, (c) temperature-dependent relative activity, (d) reproducibility and (e) sensitivity after 5 cycles of GOx@NH_2-MIL-101 with OPD as substrates. Error bars represent the standard deviations from at least 3 measurements.