

Supporting Information

HRP@ZIF-8/DNA hybrids: Functionality Integration of ZIF-8 via Biomineralization and Surface Absorption

Lei Wang^a, Wenjing Zhi^a, Dongsheng Lian^a, Yu Wang^a, Juan Han^b, Yun Wang^{a,*}

^a School of Chemistry and Chemical Engineering, Jiangsu University, 301 Xuefu Road, Zhenjiang 212013, Jiangsu Province, China

^b School of Food and Biological Engineering, Jiangsu University, 301 Xuefu Road, Zhenjiang 212013, Jiangsu Province, China

* Corresponding author: Yun Wang. E-mail: yunwang86@ujs.edu.cn

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Number of figures: 7

Number of tables: 2

Characterization methods

Laser Confocal Microscope (LSCM) was used to determine the presence of fluorescent labelled HRP within HRP@ZIF-8. Fourier transform infrared (FTIR) was performed using a Nicolet Nexus 470 Spectrometer in the region of 400- 4000 cm^{-1} . Thermal gravimetric analysis (TGA) measurements were performed on the STA449C Thermal Analyzer. Scanning electron microscope (SEM) was used to investigate the ZIF-8 and HRP@ZIF-8 morphology. Powder XRD patterns were collected using an X-ray diffractometer (XRD-6100Lab, Japan). The pore size of HRP@ZIF-8 bio-composite was determined by a BET measurement (TriStar II 3020). Fluorescence measurements were carried out using a Cary Eclipse spectrofluorometer (Varian, Australia).

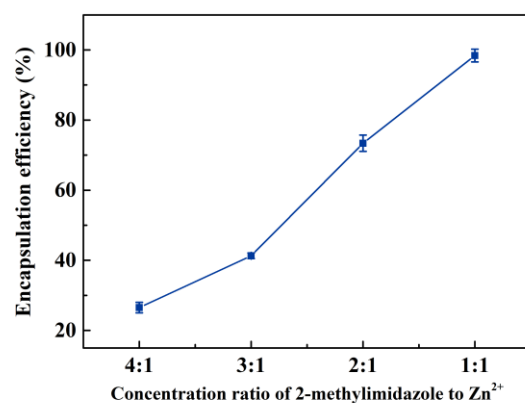


Figure S1. Effect of the concentration ratio of 2-methylimidazole to Zn^{2+} on encapsulation efficiency of HRP@ZIF-8. The error bars represent the standard deviations of triplicate experiments.

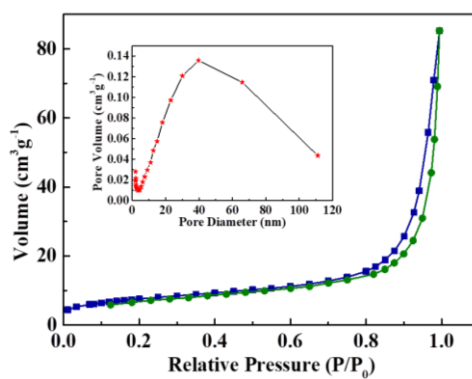


Figure S2. N_2 adsorption-desorption curves and pore diameter distributions (inset) of ZIF-8.

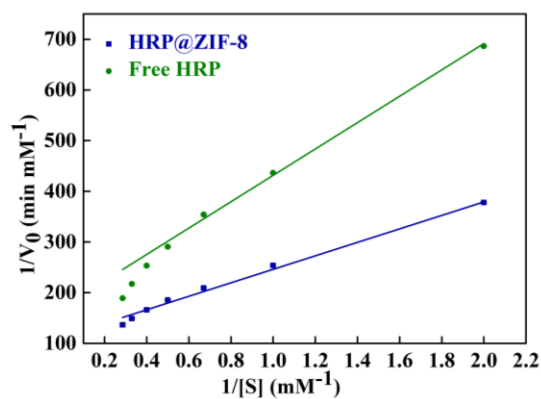


Figure S3. Lineweaver-Burk plots for determination of the kinetic parameters for free HRP and HRP@ZIF-8.

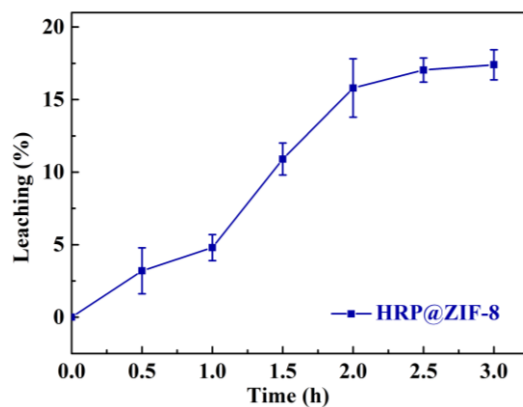


Figure S4. Enzyme leaching test of HRP@ZIF-8 after different incubation time at 60 °C.

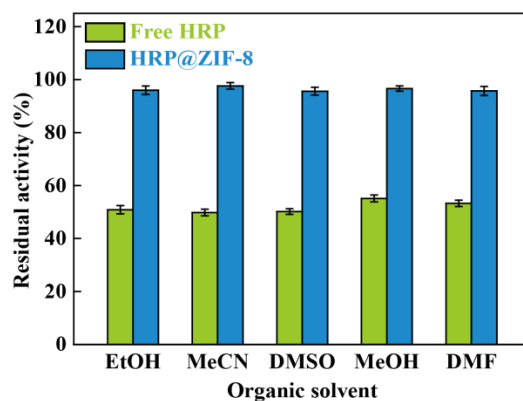


Figure S5. Effect of organic solvents on the relative activity of free HRP and HRP@ZIF-8. The error bars represent the standard deviations of triplicate experiments.

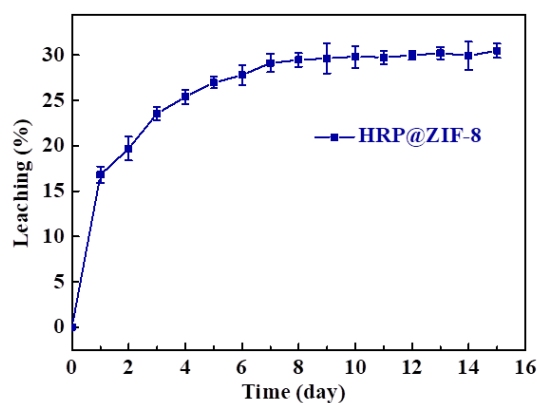


Figure S6. Enzyme leaching test of HRP@ZIF-8 after different incubation time at 4 °C.



Scheme S1. Sequential reactions of the enzyme.

Table S1. The kinetic parameters of free HRP and HRP@ZIF-8.

| Kinetic parameters | Free HRP | HRP@ZIF-8 |
|--|----------|-----------|
| K_m (mM) | 1.5207 | 1.1773 |
| V_{\max} ($\mu\text{M} \cdot \text{min}^{-1}$) | 5.8 | 8.9 |

Table S2. Comparison of immobilized enzyme for the detection of phenol.

| Immobilized enzyme | Detection limit | Solution | Reference |
|--|-------------------|---------------------------|--------------------------------------|
| HRP@ $\text{Cu}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ | 1.0 μM | 0.1 M PBS buffer (pH 7.4) | ACS Appl. Mater. Interfaces 2014 [1] |
| ZIF-8@BHb | 1.0 μM | 0.1 M PBS buffer (pH 7.4) | ACS Appl. Mater. Interfaces 2016 [2] |

References

- (1) Lin, Z.; Xiao, Y.; Yin, Y. Q.; Hu, W. L.; Liu, W.; Yang, H. H. Facile synthesis of enzyme-inorganic hybrid nanoflowers and its application as a colorimetric platform for visual detection of hydrogen peroxide and phenol. ACS Appl. Mater. Interfaces 2014, 6, 10775-10782, DOI: 10.1021/am502757e.
- (2) Yin, Y. Q.; Gao, C. L.; Xiao, Q.; Lin, G.; Lin, Z.; Cai, Z. W.; Yang, H. H. Protein-metal organic framework hybrid composites with intrinsic peroxidase-like activity as a colorimetric biosensing platform. ACS Appl. Mater. Interfaces 2016, 8, 29052-29061, DOI: 10.1021/acsami.6b09893.