

Copper fumarate with high-bifunctional nanozyme activities at different pH for glucose and epinephrine colorimetric detection in human serum

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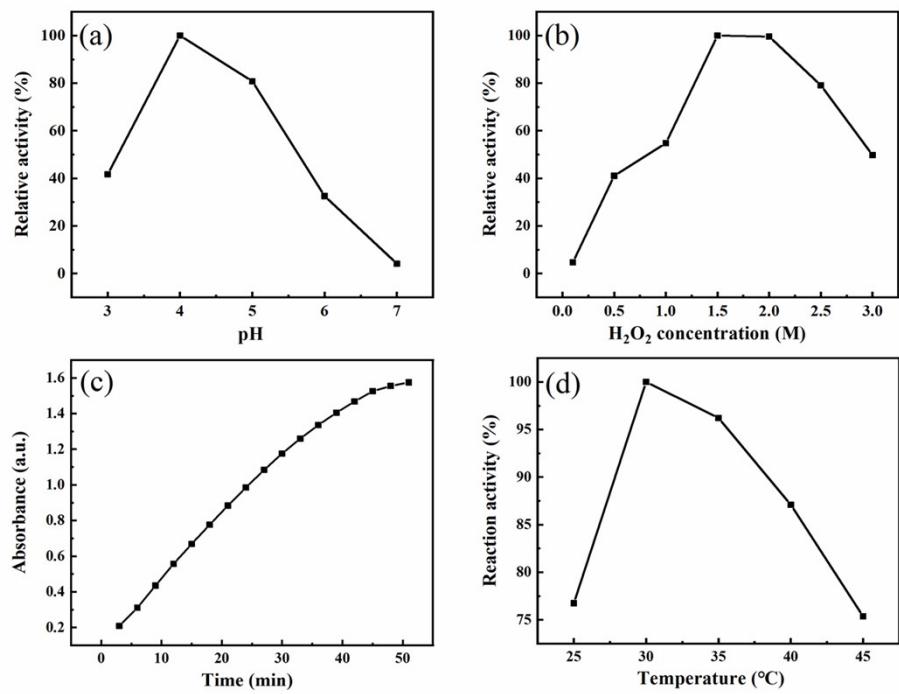
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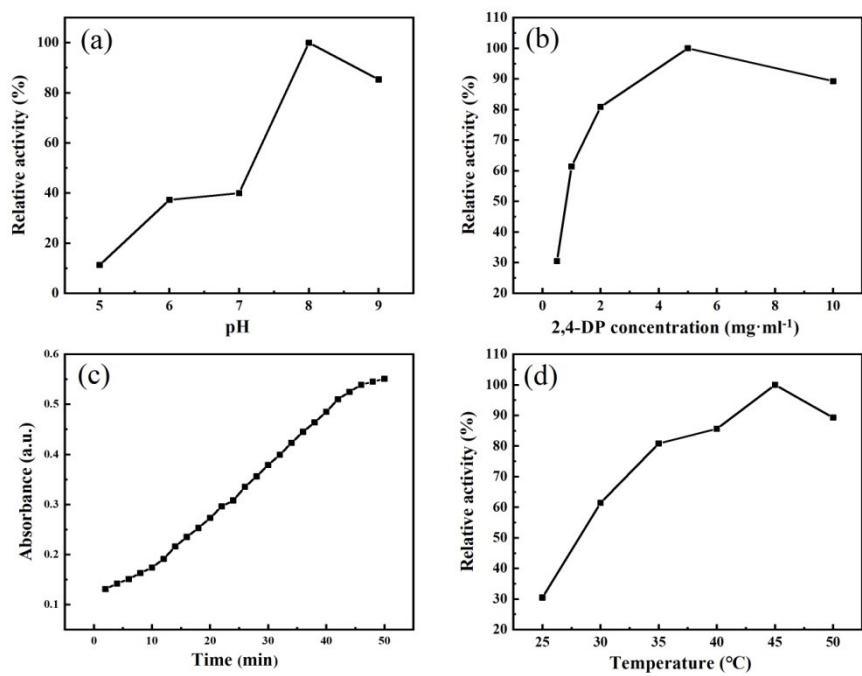
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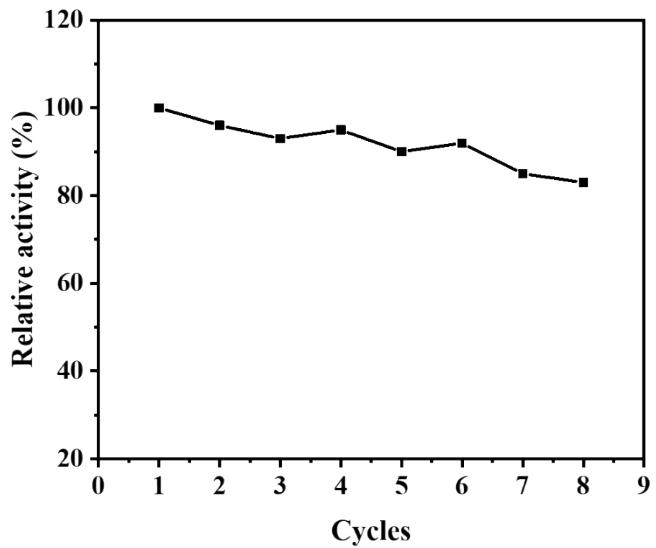
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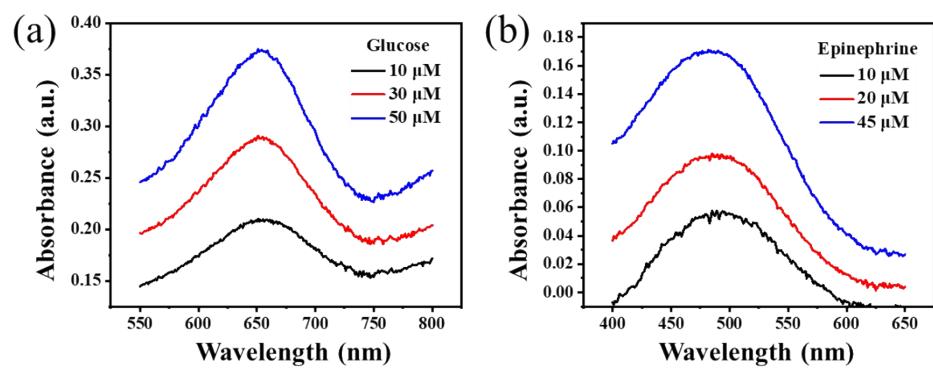
**Figure S1** Effect of (a) pH, (b) H<sub>2</sub>O<sub>2</sub> concentration, (c) time-dependent absorbance behavior at 652 nm of TMB+H<sub>2</sub>O<sub>2</sub> system, and (d) effect of temperature on the peroxidase-like property of Cu FMA. All maximum points in each curve (a, b and d) are set as 100% in H<sub>2</sub>O.



**Figure S2** (a) Effect of pH on the laccase-like activity of Cu FMA, (b) effect of 2,4-DP concentration on the laccase-like activity of Cu FMA, (c) time-dependent absorbance behaviour at 510 nm of 2,4-DP+4-AAP system catalyzed by Cu FMA, and (d) effect of temperature on the laccase-like property of Cu FMA. All maximum points in each curve (a, b and d) are set as 100% in H<sub>2</sub>O.



**Figure S3** Relative activity of Cu FMA in the colorimetric reaction during the recycling and reuse process. The condition for recycling experiments: 5 mg/mL Cu FMA, 5 mM TMB, 1.5 M H<sub>2</sub>O<sub>2</sub>, pH 4, 30°C, 45 min.



**Figure S4** The UV-Vis spectra of different concentrations for (a) glucose and (b) epinephrine in human serum.

**Table S1** Comparison of kinetic parameters of Cu FMA with HRP and laccase.  $K_m$  is the Michaelis-Menten constant,  $V_{max}$  is the maximal reaction velocity, and  $k_{cat}$  is the catalytic constant.

| Catalyst             | Substrate                     | $K_m$ (mM) | $V_{max}$ ( $10^{-8}$ M s <sup>-1</sup> ) | $k_{cat}$ (s <sup>-1</sup> ) |
|----------------------|-------------------------------|------------|---|------------------------------|
|                      | TMB                           | 1.10       | 1.79                                      | $9.04 \times 10^3$           |
| Cu FMA               | H <sub>2</sub> O <sub>2</sub> | 0.34       | 1.43                                      | $7.23 \times 10^3$           |
|                      | 2,4-DP                        | 0.45       | 5.72                                      | $2.89 \times 10^4$           |
| HRP <sup>1</sup>     | TMB                           | 0.43       | 10.00                                     | $4.00 \times 10^3$           |
|                      | H <sub>2</sub> O <sub>2</sub> | 3.7        | 8.71                                      | $3.48 \times 10^3$           |
| Laccase <sup>2</sup> | 2,4-DP                        | 0.41       | 10.68                                     | $6.89 \times 10^{-2}$        |

**Table S2** Comparative table of colorimetric detection for glucose and epinephrine

|             | Sensing probe | Linear range ( $\mu\text{M}$ ) | Detection limit ( $\mu\text{M}$ ) | Reference    |
|-------------|---------------|--------------------------------|-----------------------------------|--------------|
|             | Cu-Ag/rGO     | 1-30                           | 3.8                               | <sup>3</sup> |
|             | CuS           | 5-200                          | 7.2                               | <sup>4</sup> |
| Glucose     | Cu            | 500-15000                      | 450                               | <sup>5</sup> |
|             | Cu-MOF        | 8-140                          | 2.7                               | <sup>6</sup> |
|             | Cu FMA        | 10-300                         | 0.2                               | This work    |
|             | CH-Cu         | 27-270                         | 1.6                               | <sup>2</sup> |
|             | CuO NRs       | 0.6-18                         | 0.6                               | <sup>7</sup> |
| Epinephrine | CTNs          | 4.5-90                         | 3.4                               | <sup>8</sup> |
|             | Cu-Cys NLs    | 9-455                          | 2.7                               | <sup>9</sup> |
|             | Cu FMA        | 2.7-54.6                       | 1.1                               | This work    |

**Table S3** Determination of glucose and epinephrine added in diluted human blood serum with proposed Cu FMA colorimetric method.

|             | Added ( $\mu\text{M}$ ) | Absorbance<br>(a.u.) | Found ( $\mu\text{M}$ ) |
|-------------|-------------------------|----------------------|-------------------------|
| Glucose     | 10.00                   | 0.2076               | 10.24                   |
|             | 30.00                   | 0.2879               | 30.02                   |
|             | 50.00                   | 0.3726               | 50.88                   |
| Epinephrine | 10.00                   | 0.0577               | 9.19                    |
|             | 20.00                   | 0.0979               | 21.75                   |
|             | 45.00                   | 0.1694               | 44.09                   |

## References

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