MOF-derived porous ZnO-Co₃O₄ nanocages as peroxidase mimics for colorimetric detection of copper(II) ions in serum

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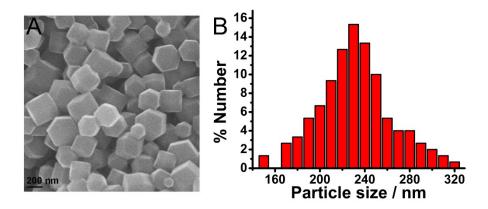


Figure S1 (A) The SEM image of ZnCo-ZIF. (B) Histogram of the size distribution of ZnCo-ZIF.

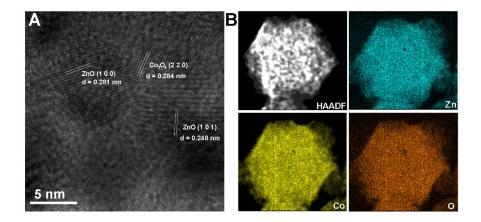


Figure S2 (A) HRTEM image of ZnO-Co $_3$ O $_4$ NCs. (B) TEM elemental mappings of ZnO-Co $_3$ O $_4$ NCs.

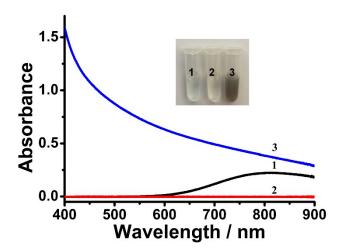


Figure S3 The UV-Vis spectra of Cu^{2+} and Cys at high concentrations. Insert were the corresponding photographs of different samples. 1: 20 mM Cu^{2+} , 2: 20 mM Cys, 3: 20 mM $Cu^{2+} + 20$ mM Cys.

As indicated in Figure S3, after mixing Cu²⁺ and Cys, the insoluble products were generated, demonstrating that Cys can react with Cu²⁺ to give mercaptide.

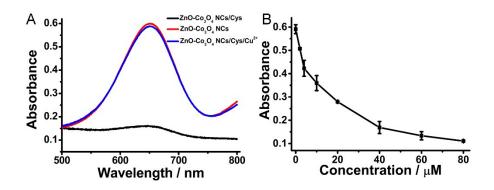


Figure S4 (A) The absorbance spectra of the different reaction systems containing ZnO-Co₃O₄ NCs, ZnO-Co₃O₄ NCs/Cys and ZnO-Co₃O₄ NCs/Cys/Cu²⁺. (B) The change of peroxidase activity of ZnO-Co₃O₄ NCs in the presence of different concentrations of Cys.

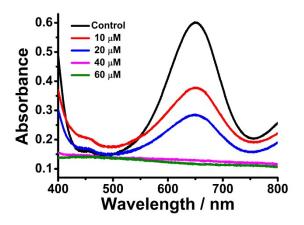


Figure S5 The reduction of oxidized TMB induced by different concentrations of Cys.

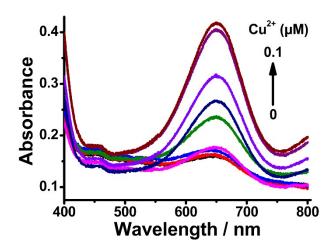


Figure S6 The absorbance spectra of TMB in the reaction systems of $ZnO-Co_3O_4$ NCs/Cys containing different concentrations of Cu^{2+} .

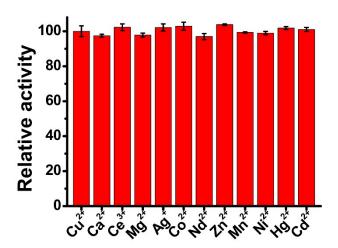


Figure S7 The responses of ZnO-Co₃O₄ NCs/Cys to Cu²⁺ in the presence of other metal ions. The concentrations of other metal ions and Cu²⁺ were 1 μ M and 0.1 μ M, respectively.

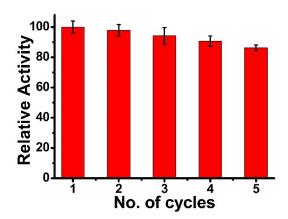


Figure S8 The responses of the ZnO-Co $_3$ O $_4$ NCs to Cu $^{2+}$ in five successive recycling catalysis.

 $\begin{table}{c} \textbf{Table S1} The comparison of the analytical performance of this method for Cu^{2+} \\ detection with previous nanomaterials based colorimetric methods. \\ \end{table}$

| Nanomaterials | LOD (µM) | linear range (μM) | References |
|--|----------|-------------------|------------|
| Urchin-like Co ₉ S ₈ | 0.09 | 0.5-10 | [45] |
| 4-MBA modified AgNPs | 0.025 | 0.1-100 | [46] |
| GSH-AuNCs | 0.011 | 0.1-1 | [47] |
| rGO@AgNPs | 0.0098 | 0.02-1.5 | [48] |
| N-CDots/AuNCs | 0.15 | 1-60 | [49] |
| DNA modified AuNPs | 20 | 20-100 | [50] |
| ZnO-Co ₃ O ₄ NCs | 0.00108 | 0.002-0.1 | This work |