Supporting Information

Ingenious microenvironment regulation of metal-organic framework (MOF) nanoreactor for electrochemical detection of chlorogenic acid

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Content

Symbol

The electroactive effective surface area (Ae) was calculated according to the Randle Sevicik equation (1):

$$I_p = (2.69 \times 10^5) n^{3/2} D^{1/2} v^{1/2} AC \quad (1)$$

where I_p, n, D, υ and C represent the peak current, the number of transferred electrons, the diffusion coefficient (ferricyanide), scan rate and the concentration of the redox probe.[S1] Thus, the electroactive effective surface area of GCE, ZIF-8/GCE, PcFe@ZIF-8/GCE and Au/PcFe@HZIF-8/GCE were 0.043, 0.101, 0.124, and 0.169 cm^2, respectively.

The diffusion coefficient of CGA was calculated to be 8.43 × 10^{-6} cm^2 s^{-1} based on the simplified Randles-Sevcik equation (2) and (3).

$$I_p = kn^{3/2} A\sqrt{DvC} \quad (2)$$

$$D = \frac{\left(\frac{I_p}{\sqrt{v}}\right)^2}{k^2 \times n^3 \times A^2 \times C^2} = \frac{Slope^2}{k^2 \times n^3 \times A^2 \times C^2} \quad (3)$$

k is a constant of 2.69 × 10^5 (C mol^{-1} $V^{-½}$), n is the number of electrons transferred during the redox event, A is effective surface area of electrode (cm^2), D is the diffusion coefficient of the analyte (cm^2 s^{-1}), C is the analyte concentration and υ is the scan rate.[S2]

The standard heterogeneous electron transfer rate constant (K_s) was calculated to be 7.81 x 10^{-3} cm s^{-1} based on the equation (4).[S3]

$$logK_s = -0.48\alpha + 0.52 + log[nF\alpha V_c D/2.303RT]^{1/2} \quad (4)$$

The Gileadi method (equation 2) was used to calculate the heterogeneous electron transfer rate constant (K_s) (cm s^{-1}), α is 0.5, n is 2, F is the Faraday constant (C mol^{-1}), V_c is the scan rate (V s^{-1}), D is the diffusion coefficient (cm^2 s^{-1}), R is the gas constant of 8.314 (J K^{-1} mol^{-1}), T is the room temperature (298 K).

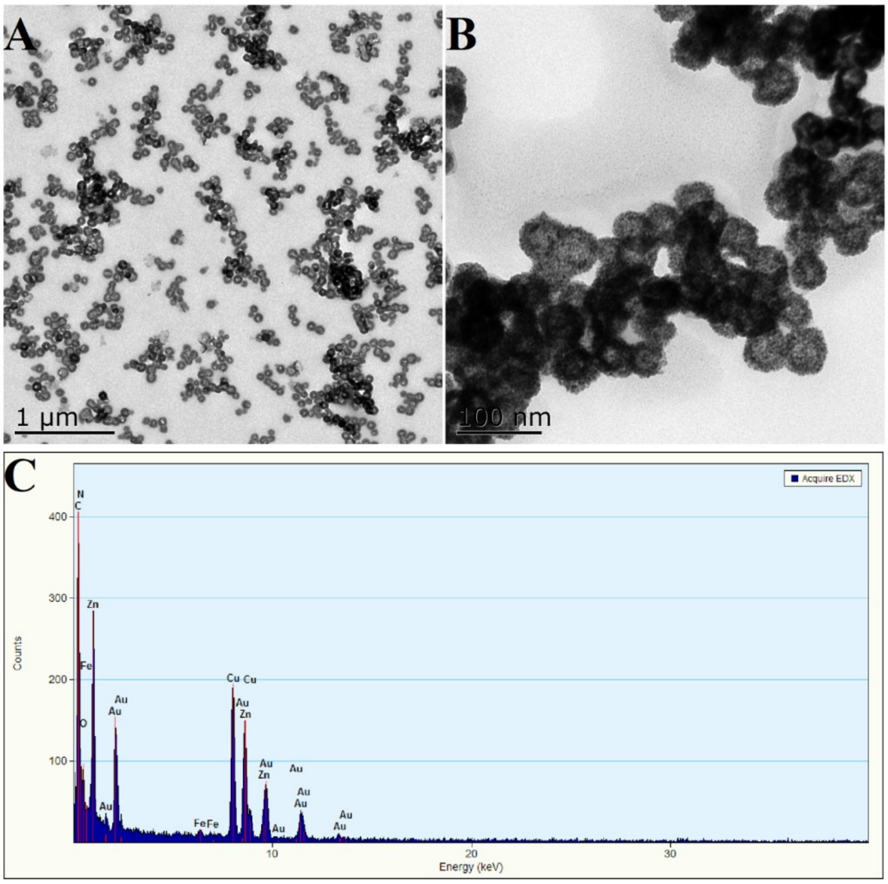

Fig. S1 TEM images of unreduced Au/PcFe@HZIF-8 (A), Au/PcFe@HZIF-8 (B) and EDX of Au/PcFe@HZIF-8 (C).

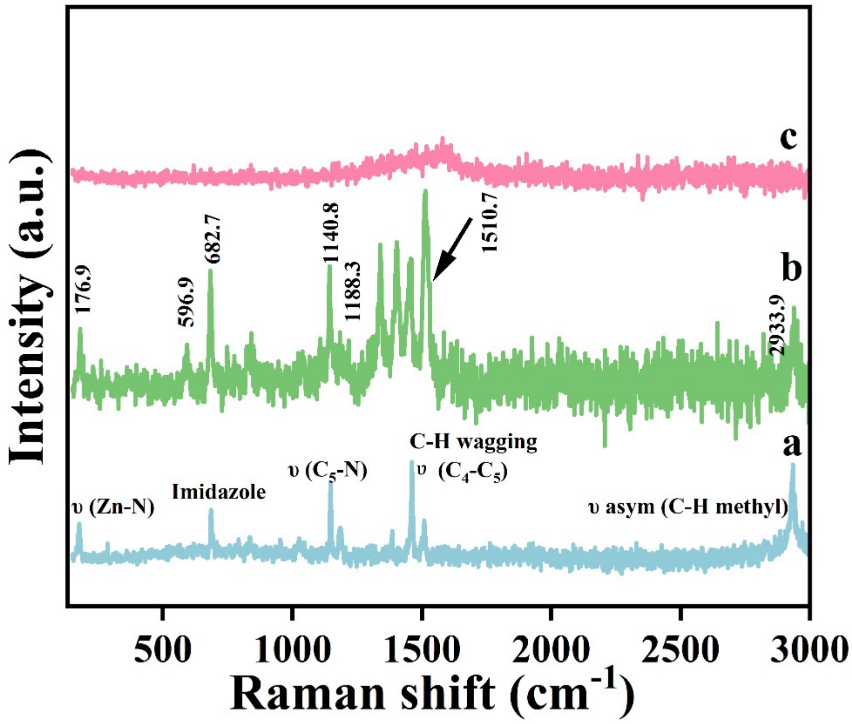

Fig. S2 Raman spectra of ZIF-8 (a), PcFe@ZIF-8 (b) and Au/PcFe@HZIF-8 (c).

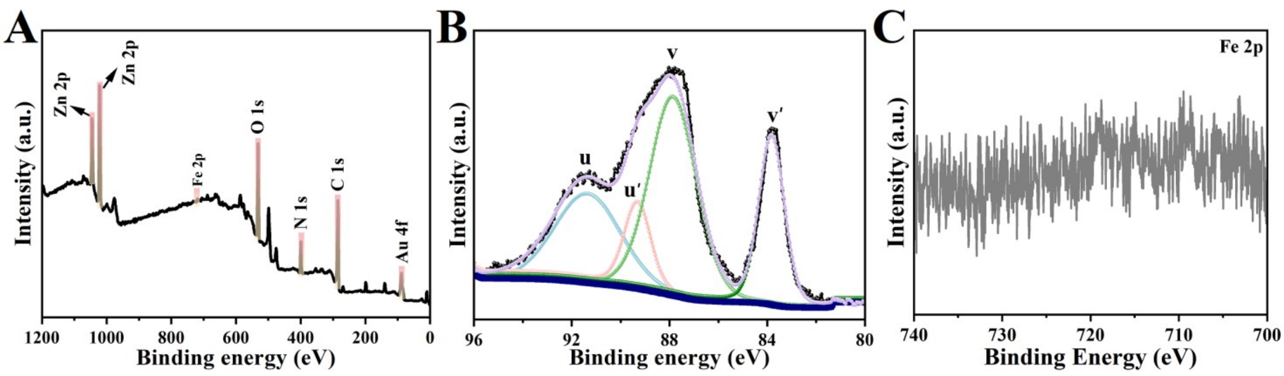

Fig. S3 XPS analysis of survey spectrum (A), Au 4f-Zn 3p (B) and Fe 2p (C) of Au/PcFe@HZIF-8.

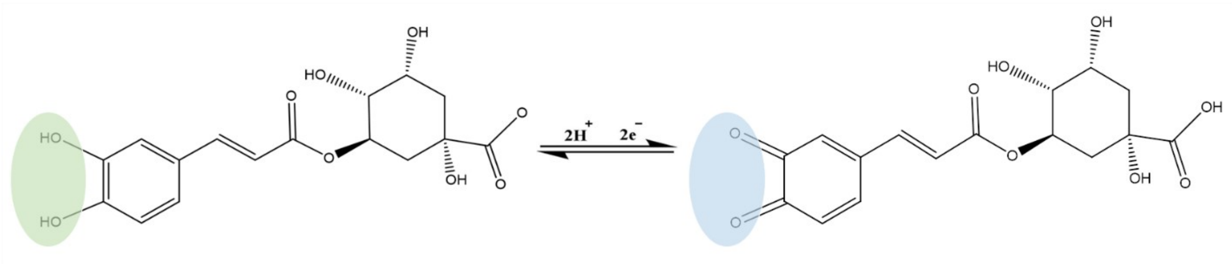

Fig. S4 Schematic diagram of chlorogenic acid reaction mechanism.

References

S1 G. K. Jayaprakash, B. E. Kumara Swamy, S. Rajendrachari and S. C. Sharma, *J. Mol. Liq.*, 2021, **334**, 116348.

S2 A. J. Bard and L. R. Faulkner, Electrochemical Methods: Fundamentals and Applications, Wiley, New York, 2001.

S3 H. Muhammad, I. A. Tahiri, M. Muhammad, Z. Masood, M. A. Versiani, O. Khaliq, M. Latif, M. Hanif, *J. Electroanal. Chem.*, 2016, **775**, 157-162.