Supporting Information

Preparation of Ag@ zeolitic imidazolate framework-67 at room temperature for electrochemical sensing of hydrogen peroxide

Yuhua Dong[a], Chengqian Duan[a,b], Qinglin Sheng[c], Jianbin Zheng[a]*

a. College of Chemistry and Materials Science, Shaanxi Provincial Key Laboratory of Electroanalytical Chemistry, Northwest University, Xi'an, Shaanxi 710069, China

b. School of Basic Medical Sciences, Ningxia Medical University, Yinchuan, Ningxia 750001, China

c. College of Food Science and Technology, Northwest University, Xi'an, Shaanxi 710069, China

* *Corresponding author. Tel.: +86-29-88302077; Fax: +86-29-88303448; E-mail address: zhengjb@nwu.edu.cn (J. B. Zheng).*

Table of Contents

1. Preparation of ZIF-8 and Ag@ZIF-8

ZIF-8 had been synthesized by reference to the synthesis method of ZIF-67. 0.75 g PVP K30, 0.2726 g $ZnCl_2$, 1.32 g 2-Methylimidazole were dissolved in 100 mL of methanolic solutions successively under stirring. Then the mixture was kept stirring at room temperature for 12 h. After washed five times with methanol and dried at room temperature, the white ZIF-8 powder was obtained.

Ag@ZIF-8 was synthesized by the similar synthesis method as Ag@ZIF-67: 50 ml of methanol solution containing 16 mmol 2-methylimidazole was added to 17 ml of the as-prepared Ag/PVP methanol solution under stirring. Then, 50 mL of the methanol solution containing 2 mmol $ZnCl_2$ was poured into the mixture quickly. After stirring vigorously for 5 minutes, the mixture was placed at room temperature for 12 hours. The Ag@ZIF-8 powder with light pink color was collected by centrifugation, washed five times with methanol, and dried by N_2.

2. Morphological and structural characterization of ZIF-8 and Ag@ZIF-8

Fig. S1 was the TEM images of ZIF-8(A, B) and Ag@ZIF-8 (C, D). From Fig. S1, it could be seen that both ZIF-8 and Ag@ZIF-8 exhibited a rhombic dodecahedron shape with an average diameter of about 700 nm. Compared to ZIF-8, some dark dots showed in the TEM image of Ag@ZIF-8 implied the existence of Ag NPs and Ag@ZIF-8 was successfully synthesized. However, unlike the TEM image of Ag@ZIF-67, there were very few parts of Ag that had not been successfully packaged in ZIF-8. This might be due to the ZIF-8 was smaller than ZIF-67, and caused the pore could hold Ag was less than ZIF-67. In addition, the atomic absorption spectrophotometer of Ag@ZIF-8 was measured, which demonstrated that the Ag@ZIF-8 composites had a low Ag content of 4.4 wt %. the Ag content in Ag@ZIF-8 was 0.1 wt % lower than that in Ag@ZIF-67.

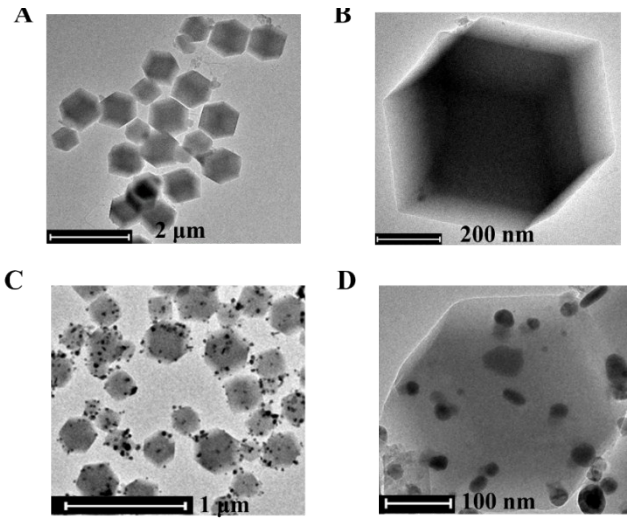

Fig. S1. TEM images of ZIF-8(A, B) and Ag@ZIF-8 (C, D)

Fig. S2 was the PXRD patterns of ZIF-8 and Ag@ZIF-8. It could be seen that the diffraction peaks of as-synthesized ZIF-8 were consistent with the simulated and reported diffraction peaks of ZIF-8 [1,2]. There were two diffraction peaks which could be indexed to the (111) and (200) crystal faces of Ag in the PXRD pattern of Ag@ZIF-8. The PXRD result demonstrated that the ZIF-8 and Ag@ZIF-8 were successfully synthesized. Compared Fig. S2 with Fig.2. (A), the diffraction peak positions were almost the same. This phenomenon might be due to the fact that ZIF-8 and ZIF-67 was the same crystal type, and their internal atoms were arranged in the same way. The inorganic elements Co and Zn had the same position in the organic skeleton.

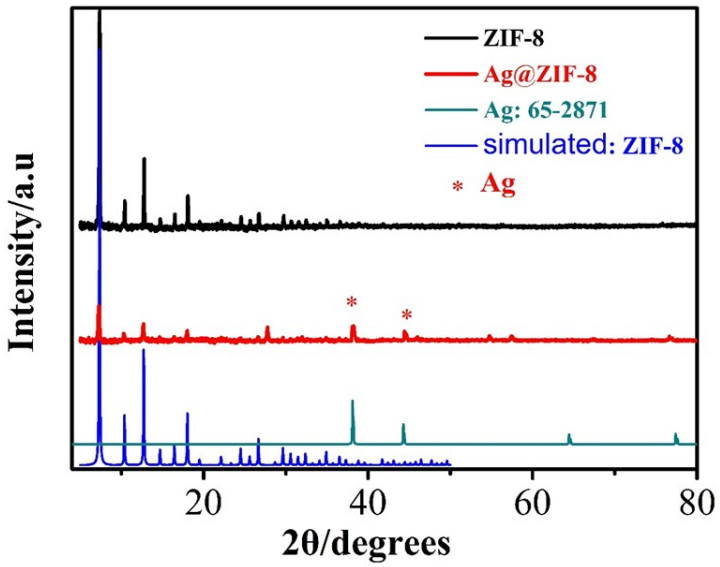

Fig. S2. PXRD patterns of ZIF-8 and Ag@ZIF-8

3. Electrochemical studies

Fig. S3 was the cyclic voltammetric responses of different modified electrodes to H_2O_2 reduction. It could be seen that bare GCE and ZIF-8/GCE showed no obvious current change before and after adding 3 mM H_2O_2 (curve a, a' and b, b') indicated that GCE and ZIF-8 had almost no catalytic effect on the reduction of H_2O_2. However, the ZIF-67/GCE, Ag/GCE, Ag@ZIF-8/GCE and Ag@ZIF-67/GCE showed obvious reduction peak increased after adding 3 mM H_2O_2 (curve c, c'; d, d'; e, e' and f, f'). The increased current response indicated that ZIF-67, Ag, Ag@ZIF-8 and Ag@ZIF-67 had catalytic effect on the reduction of H_2O_2. The current response of Ag@ZIF-67/GCE to H_2O_2 was 1.5 times higher than that of Ag@ZIF-8/GCE which might be due to ZIF-8 had almost no catalytic ability for the reduction of H_2O_2. Although Ag had a catalytic ability to H_2O_2, it was easily oxidized. The Ag was encapsulated in ZIF-67 avoided the oxidation to some extent, which might be the reason why the current response of Ag@ZIF-67/GCE to H_2O_2 reduction was 5 times higher than that of Ag/GCE. Moreover, the reduction peak potential of Ag@ZIF-67/GCE was closer to zero than ZIF-67/GCE, Ag/GCE and Ag@ZIF-8/GCE which ensured a lower noise, less interference and excellent response. Due to the synergistic effect of Ag and ZIF-67, the Ag@ZIF-67/GCE exhibited a good electrochemical response to H_2O_2 reduction with larger peak current and more well-defined peak.

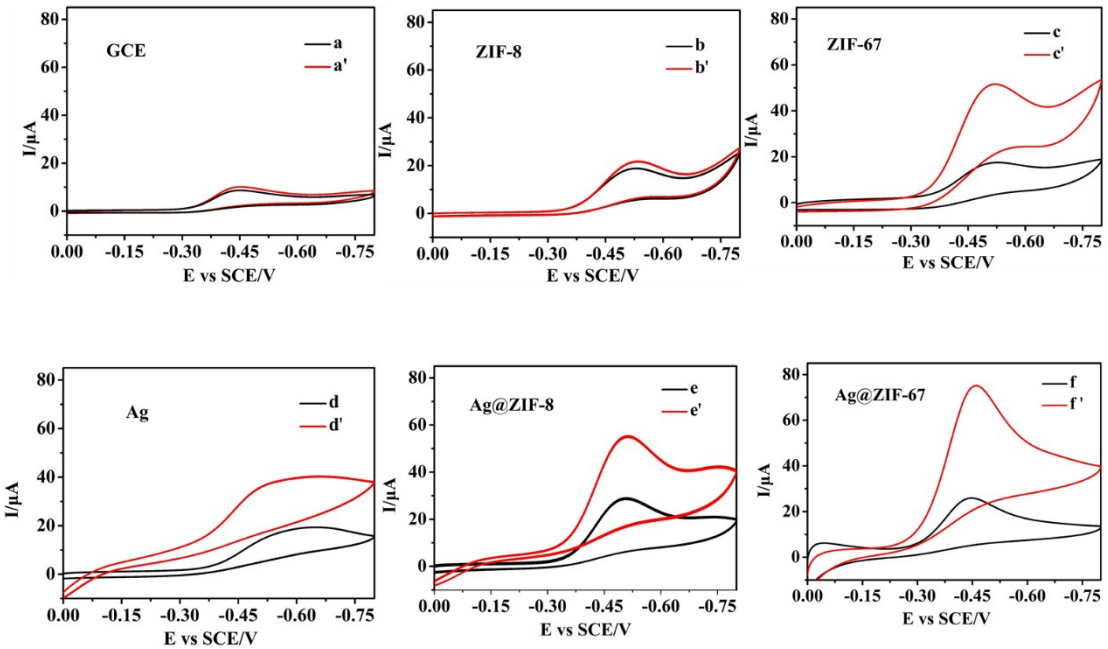

Fig. S3. CVs obtained by the bare GCE (a, a'), ZIF-8/GCE (b, b'), ZIF-67/GCE (c, c'), Ag/GCE (d, d'), Ag@ZIF-8/GCE (e, e') and Ag@ZIF-67/GCE (f, f') in 0.2 M NaOH without (a, b, c, d, e, f) and with 3 mM H_2O_2 (a', b', c', d', e', f'). Scan rate: 100 mV/s

The tendency of different modified electrodes' amperometric responses to the successive additions of H_2O_2 was consistent with that of cyclic voltammetry: The Ag@ZIF-67/GCE had the largest response current and minimum background current to H_2O_2.

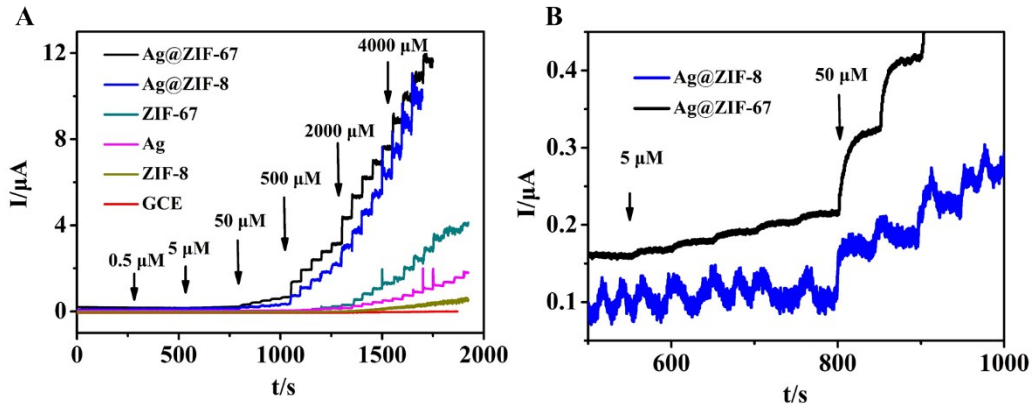

Fig. S4. (A) Amperometric responses of bare GCE, ZIF-8/GCE, ZIF-67/GCE, Ag/GCE, Ag@ZIF-8/GCE and Ag@ZIF-67/GCE after successive injection of H_2O_2 into the 0.2 M NaOH under stirring; (B) An enlarged view of the amperometric responses of Ag@ZIF-8/GCE and Ag@ZIF-67/GCE when low concentrations of H_2O_2 were added. Working potential: -0.25 V

4. References

[1] Venna, S. R., & Carreon, M. A. Highly permeable zeolite imidazolate framework-8 membranes for CO_2/CH_4 separation. Journal of the American Chemical Society, 2009,132(1), 76-78.

[2] Pan, Y. C., Liu, Y. Y., Zeng, G. F., Zhao, L., Lai, Z. P. Rapid synthesis of zeolitic imidazolate framework-8 (ZIF-8) nanocrystals in an aqueous system. Chemical Communications, 2011, 47(7), 2071-2073.