

Supporting Information

for

Hierarchically Porous MOF-Based Microneedles for Glucose-Responsive Infected Diabetic Wounds Treatment

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1. Supporting Tables

Table S1 Data of BET surface areas and the ratios of micropore volumes to total pore volumes of different samples. GOx@ZIF and GOx@Fe-ZIF were treated with the same concentration of TA for the same reaction time to produce GOx@ZIF@Fe-TA and GOx@Fe-ZIF-TA.

Samples	$S_{\text{BET}}/\text{m}^2\text{ g}^{-1}$	$V_{\text{micro}}/V_{\text{Total}}$
GOx@ZIF (Before TA etching)	1018.9	98.1%
GOx@Fe-ZIF (Before TA etching)	1196.6	93.8%
GOx@ZIF@Fe-TA (After TA etching)	802.4	69.1%
GOx@Fe-ZIF-TA (After TA etching)	707.7	57.4%

Table S2 Data of BET surface areas and the ratios of micropore volumes to total pore volumes of GOx@Fe-ZIF doped with different contents of Fe. When Fe content is higher than 3%, the ratio decreases dramatically, revealing the higher content Fe would be bad for the growth of ZIF.

Samples	$S_{\text{BET}}/ \text{m}^2 \text{g}^{-1}$	$V_{\text{micro}}/V_{\text{Total}}$
GOx@ZIF	1018.9	98.1%
GOx@Fe-ZIF Fe:Zn=2:98	1114.4	95.7%
GOx@Fe-ZIF Fe:Zn=3:97	1196.6	93.8%
GOx@Fe-ZIF Fe:Zn=4:96	1184.8	80.5%
GOx@Fe-ZIF Fe:Zn=6:94	1199.4	60.4%
GOx@Fe-ZIF Fe:Zn=8:92	1112.4	62.2%

2. Supporting Figures

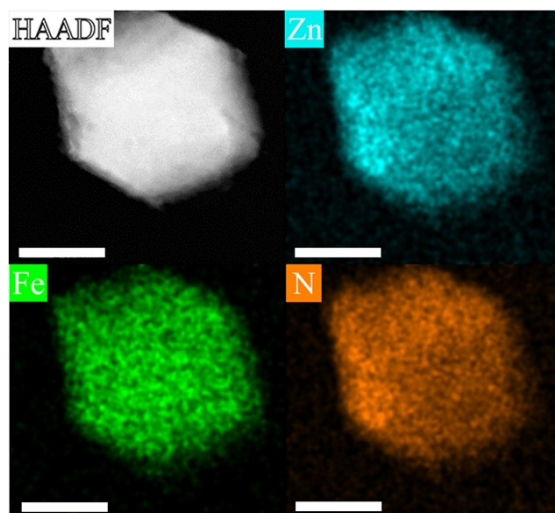


Figure S1 Elemental mapping images of GOx@Fe-ZIF (scale bar: 300 nm).

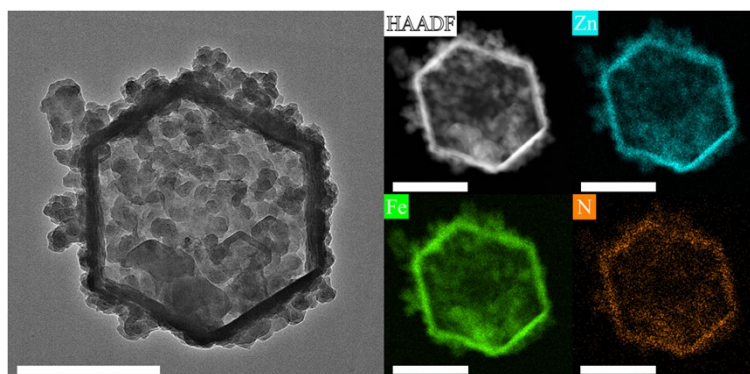


Figure S2 TEM and elemental mapping images of GOx@Fe-ZIF-TA with longer etching time. Obvious shell could be observed (scale bar: 500 nm).

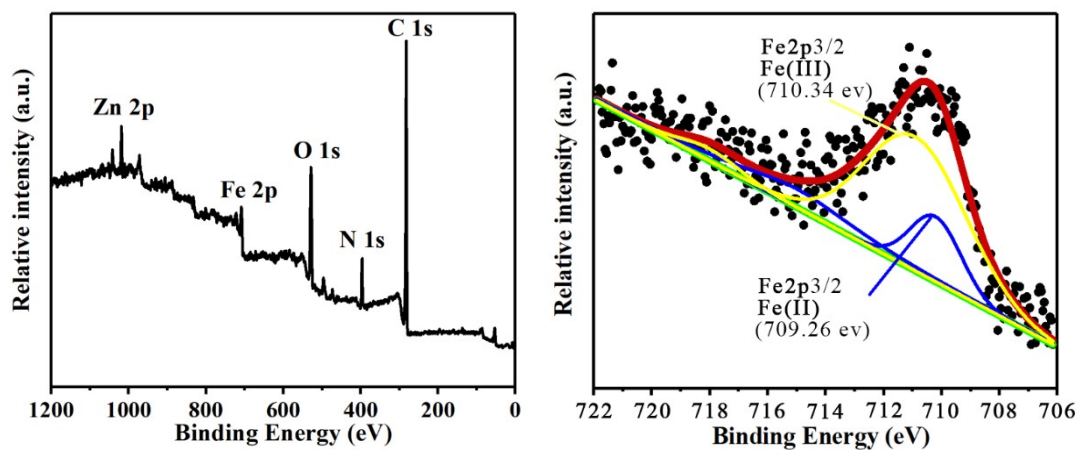


Figure S3 XPS pattern of GOx@Fe-ZIF-TA and high-resolution XPS spectrum of Fe in GOx@Fe-ZIF-TA, revealing that most of Fe in the system exist as Fe(III) before consuming glucose.¹ However, TA could convert Fe(III) to highly active Fe(II) in our system.

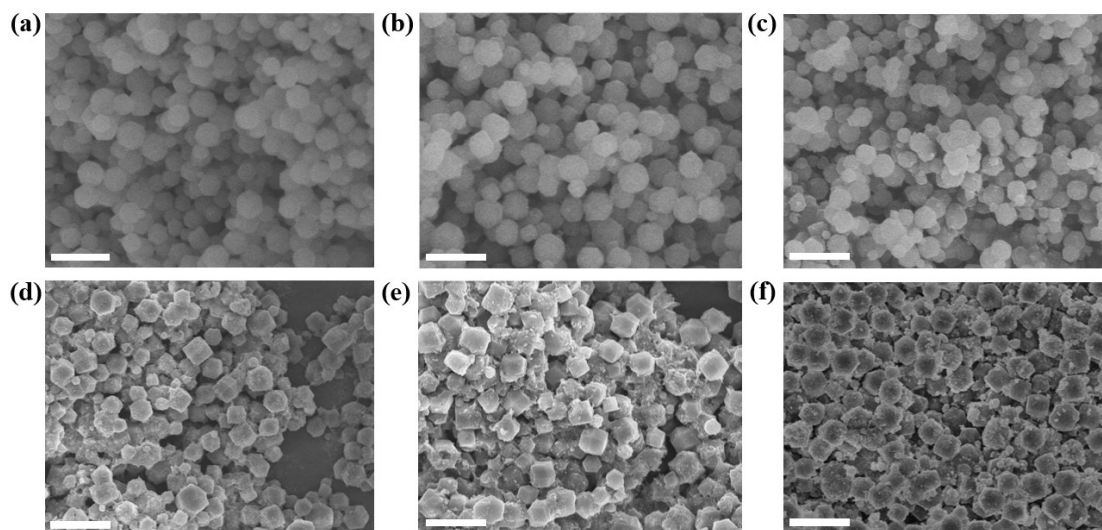


Figure S4 SEM images of GOx@Fe-ZIF doped with different contents of Fe. The molar ratio of Fe:Zn equals to 0:100 for (a), 2:98 for (b), 4:96 for (c), 6:94 for (d), 8:92 for (e), and 10:90 for (f), respectively. When Fe content is higher than 4%, more and more impurities emerged and the dodecahedral structure of MOF became less and less obvious, indicating that the excess Fe would have a bad influence on the growth of ZIF crystals. (scale bar: 1000 nm)

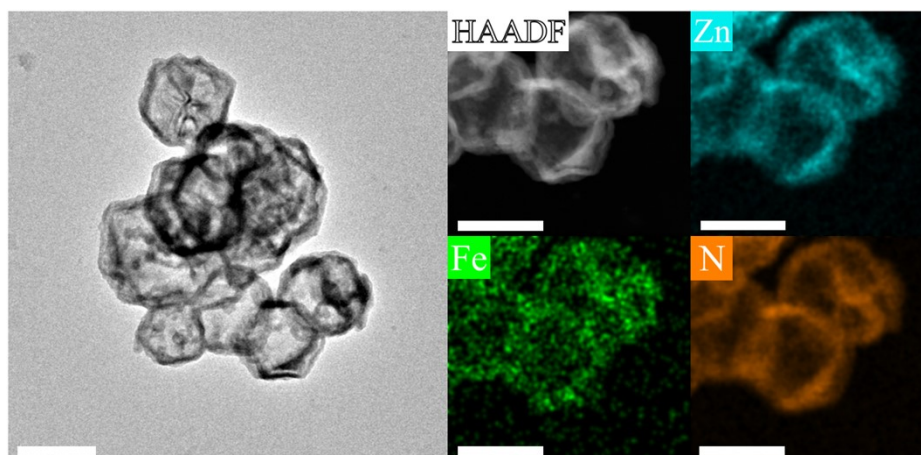


Figure S5 TEM and elemental mapping images of GOx@ZIF@Fe-TA synthesized with the previous reported strategy.²(scale bar: 500 nm)

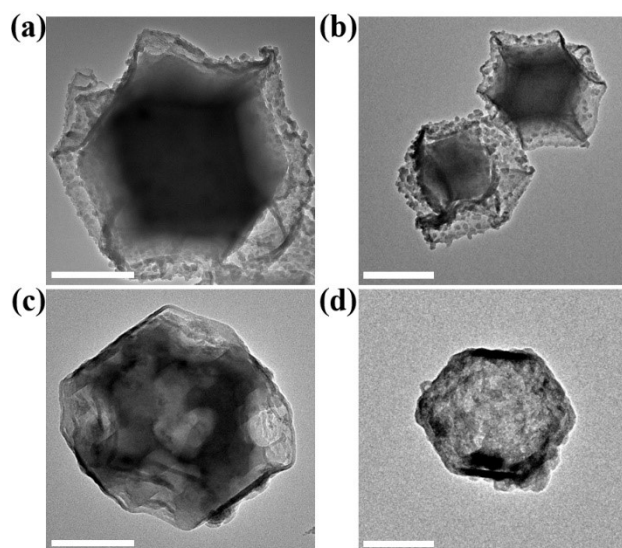


Figure S6 TEM images of GOx@ZIF@Fe-TA and GOx@Fe-ZIF-TA at different time intervals during the etching process with the same concentration of TA. (a) TEM image of GOx@ZIF@Fe-TA at 1 min. (b) TEM image of GOx@ZIF@Fe-TA at 2 min. (c) TEM image of GOx@Fe-ZIF-TA at 1 min. (d) TEM image of GOx@Fe-ZIF-TA at 2 min. (scale bar: 200 nm)

3. Supporting References

1. Q. Ouyang, F. Kou, P. E. Tsang, J. Lian, J. Xian, J. Fang and Z. Fang, Green synthesis of Fe-based material using tea polyphenols and its application as a heterogeneous Fenton-like catalyst for the degradation of lincomycin, *J. Clean. Prod.*, 2019, **232**, 1492-1498.
2. L. Zhang, S. S. Wan, C. X. Li, L. Xu, H. Cheng and X. Z. Zhang, An adenosine triphosphate-responsive autocatalytic Fenton nanoparticle for tumor ablation with self-supplied H₂O₂ and acceleration of Fe(III)/Fe(II) conversion, *Nano Lett.*, 2018, **18**, 7609-7618.