Electronic supporting information for

Core-shell ZIF-8@polydopamine nanoparticles obtained by mitigating polydopamine coating induced self-etching of MOFs: prototypical metal ion reservoirs for sticking to and killing bacteria[Ψ]

Yingxue Tu[1,++], Caifeng Lei[1, ++], Fei Deng[1], Yiang Chen[1], Ying Wang[1], Zhenkun Zhang[1,*]

1) Key Laboratory of Functional Polymer Materials of Ministry of Education, Institute of Polymer Chemistry, College of Chemistry, Nankai University, 300071 Tianjin, China

++ Equal contribution

Email: zkzhang@nankai.edu.cn

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1. Supplementary experiments

Preparation of ZIF-8 nanoparticles.

ZIF-8 NPs with a cubic shape were prepared following the previous method (Ref. 1) by using CTAB as the modulator.[1] First of all, the following solutions were prepared respectively, 0.30 g $Zn(NO_3)_2 \cdot 6H_2O$ in 30 mL ultrapure water (the solution A); 18.20 mg CTAB in 500 μL ultrapure water (the solution B); 4.52 g 2-methylimidazole (2-MeIM) in 50 mL ultrapure water (the solution C). The solution B was added dropwise into the solution A under magnetic stirring. To the resulted mixture the solution C was added dropwise under magnetic stirring. The final mixture was further stirred for 10 minutes and then was transferred to a 100 mL Teflon-lined autoclave, which was heated in an oven at 120 ^oC for 6 hours. After cooling to room temperate, the product was collected by centrifuge at 8500 rpm for 10 min and was washed by centrifuge and redispersion in fresh methanol for three times. The white solid was dried under vacuum for 48 hours. The size of the cubic ZIF-8 was ca. 70 nm as estimated from TEM.

ZIF-8 NPs with a rhombic dodecahedral shape were prepared in the absence of CTAB (Ref. 2).[2] The following solutions were first prepared: 183 mg $Zn(NO_3)_2 \cdot 6H_2O$ in 6 mL anhydrous methanol (the solution A) and 405 mg 2-methylimidazole (2-MeIM) in

10 mL methanol (the solution B) as assisted by unltrasonication. The solution B was added dropwise into the solution A and the mixture was magnetically stirred for 3 hours. Afterwards, the raw product was collected by centrifuge at 5000 rpm for 10 min and washed with methanol for three times in the same way as in the preparation the cubic ZIF-8 NPs. The final product was dried under vacuum for 48 hours. The size of the ZIF-8 was ca. 100 nm as estimated from TEM.

2. Supplementary Figures

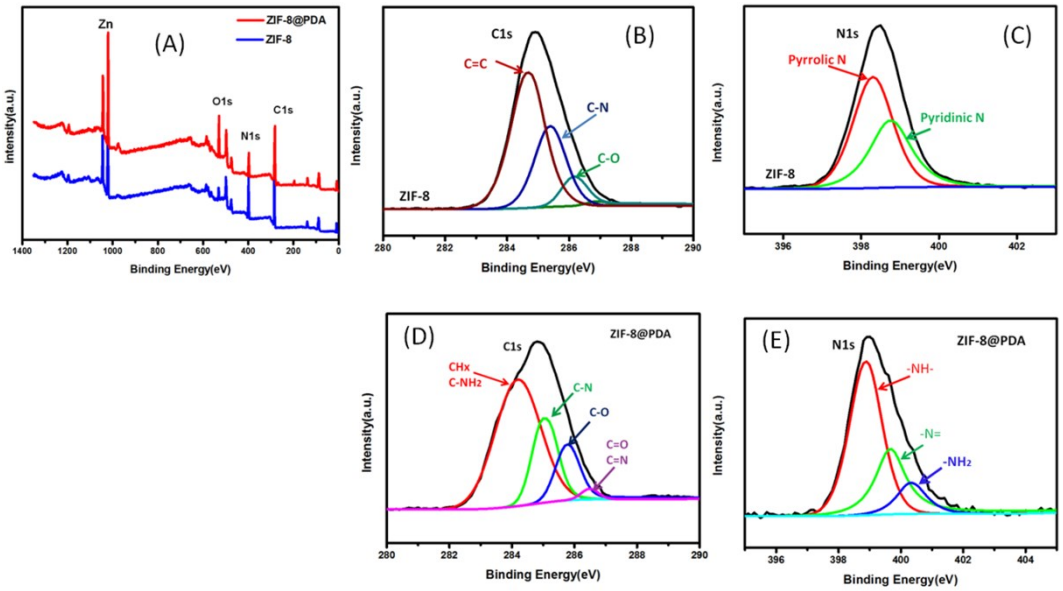

Figure S1. XPS analysis of the ZIF-8 (B and C) and ZIF-8@PDA (D and E), the scanning survey spectra were presented in (A). The ZIF-8@PDA particles were those obtained at the coating time of 1.5 hour. In the decovoluted subpeaks of the C 1s and N 1s, besides the classic peaks that can be ascribed to the carbon and nitrogen of the ZIF-8, some new subpeaks appeared in the spectra of ZIF-8@PDA: the subpeaks at 284.3 eV (CH_x/C−NH_2) and 286.5 eV (C=N/C=O) in the C1s and 403 ev (-NH2) in the N1s should be due to the oxidized intermediate compounds, such as 5,6-indolequinone that exists in the PDA layer.

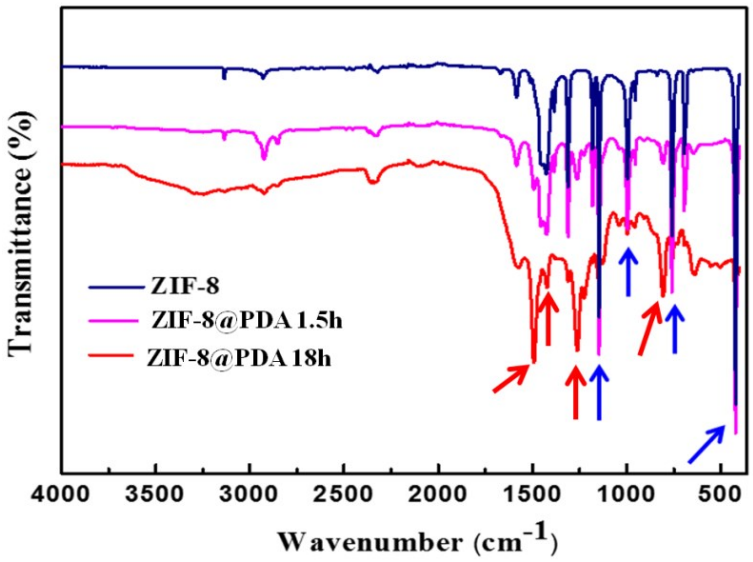

Figure S2. FT-IR spectra of ZIF-8 and the polydopamine coated one at two representative coating times. Compared to the pristine ZIF-8, there are some new adsorption peaks in the spectra of ZIF-8@PDA1.5h and ZIF-8@PDA18h as highlighted by the arrows: the one at 1723 cm^{-1} is due to C=O of the quinonyl group, the peak at around 1510 cm^{-1} is the stretching vibration of C=N, the 1353 cm^{-1} is the stretching vibration the C-N-C in the indole ring. All of these peaks are due to oxidized intermediates derived from dopamine and become stronger with the longer coating times, clearly indicating the existence of the PDA coating shell. In addition, the sharp peak at 420 cm^{-1} can be ascribed to the stretching vibration of the Zn-N bond in the ZIF-8, the adsorption due to C-N of the ZIF-8 localized at 995 and 1146 cm^{-1}. These characteristic peaks of ZIF-8 became very weak or almost disappeared in the case of ZIF-8@PDA18h, suggesting that most of the ZIF-8 was etched away.

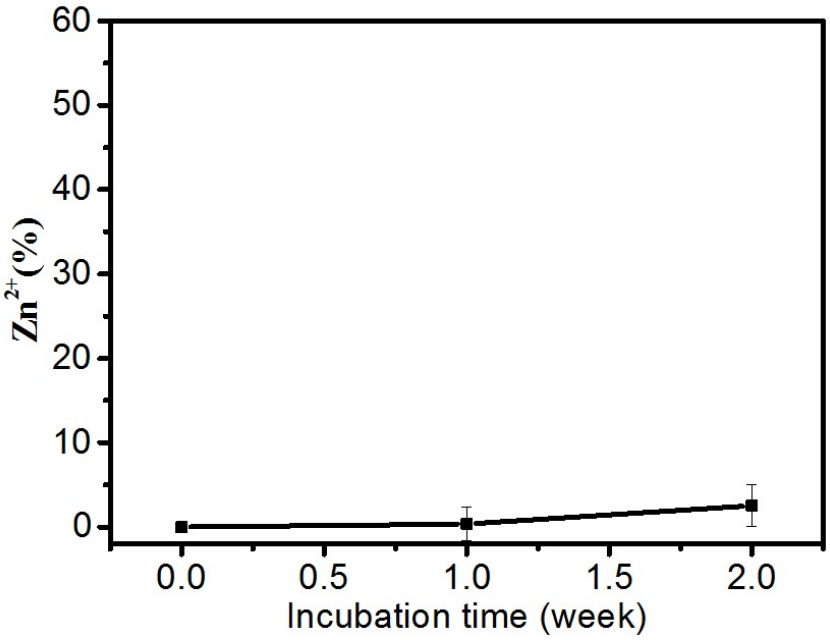

Figure S3. Etching and Zn^{2+} releasing behaviors of ZIF@PDA when stored in anhydrous ethanol. The suspension of ZIF@PDA in anhydrous ethanol (1 mg mL^{-1}) was prepared and kept shaking at room temperature. Aliquots (500 μL) were taken at one and two week, which were subjected to ICP-OES analysis after ten time dilution with ultrapure water. The relative content of free Zn^{2+} ions in the media is 0.37% and 2.53% at one and two weeks, respectively.

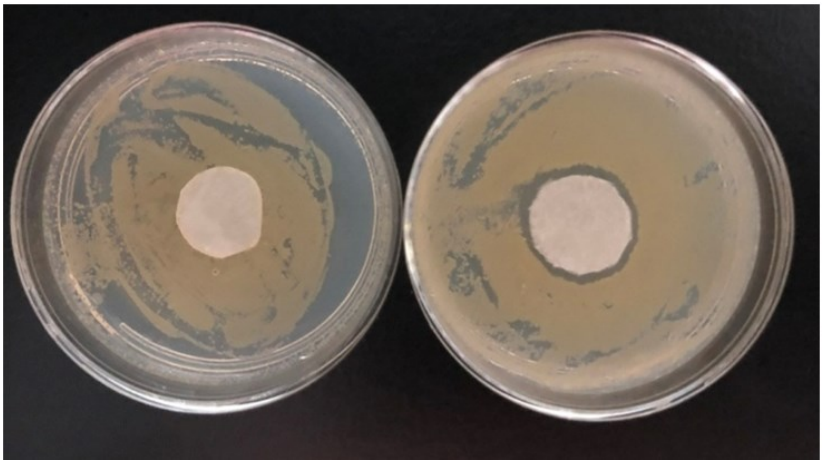

Figure S4. Determination of the zone of inhibition (ZOI). Left dish: filter paper loaded with sterilized PBS buffer; Right dish: filter paper loaded with ZIF-8@PDA. The ZIF-8@PDA was that obtained at coating time of ca. 2 hours.

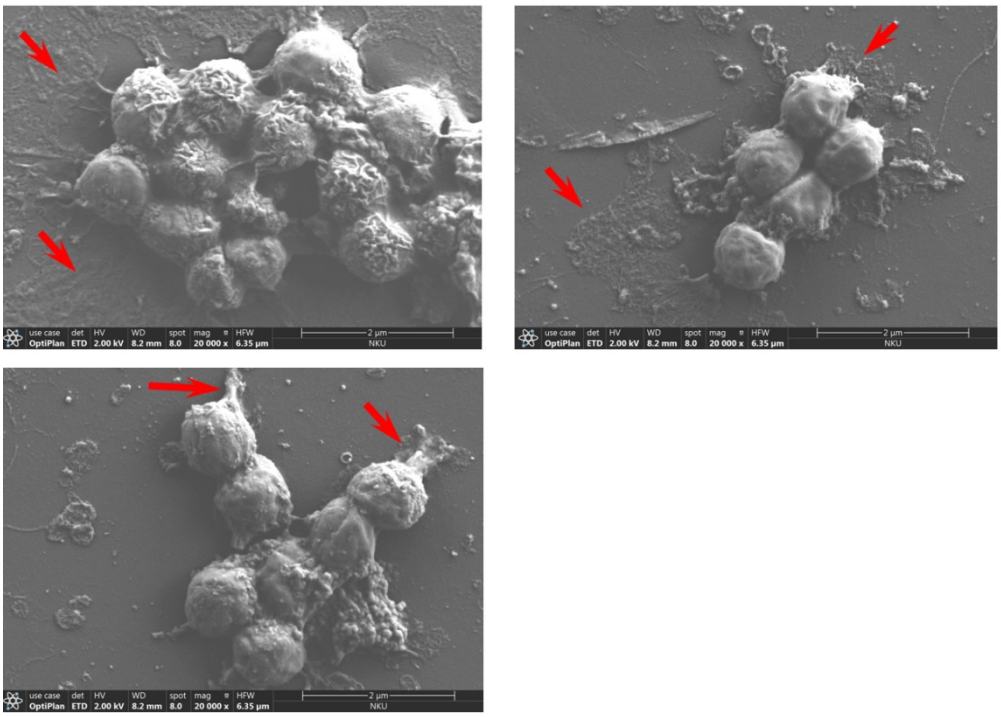

Figure S5. Morphologies of bacteria treated with ZIF-8@PDA as investigated by SEM. The bacteria were treated with ZIF-8@PDA2h for 15 h. The species highlighted by the red arrows might be the bacterial contents released from the ruptured bacteria. It is noted that all of the bacteria have a crumpled surface.

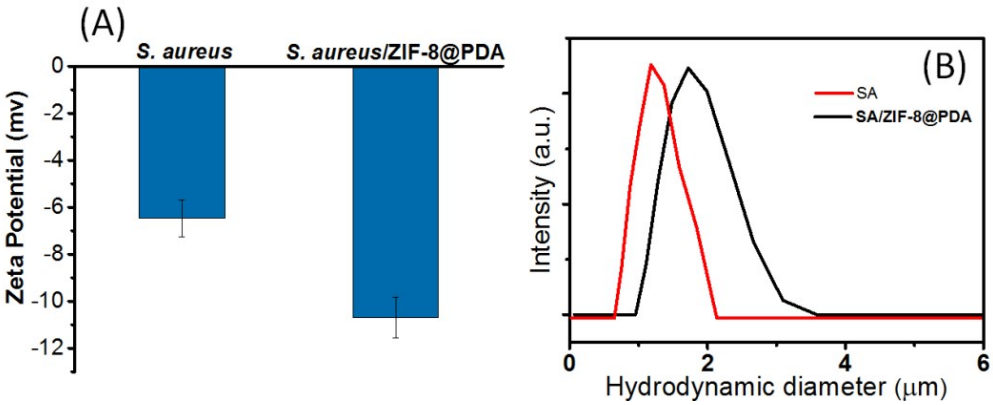

Figure S6. Zeta potentials (A) and distribution of the hydrodynamic diameter (B) by dynamic light scattering (DLS) of pristine bacteria (SA) and that treated with ZIF-8@PDA. The bacteria treated with 500 μg mL^{-1} ZIF-8@PDA2h were diluted four times with PBS. The measurements were performed on a Brookhaven zetaPALS device.

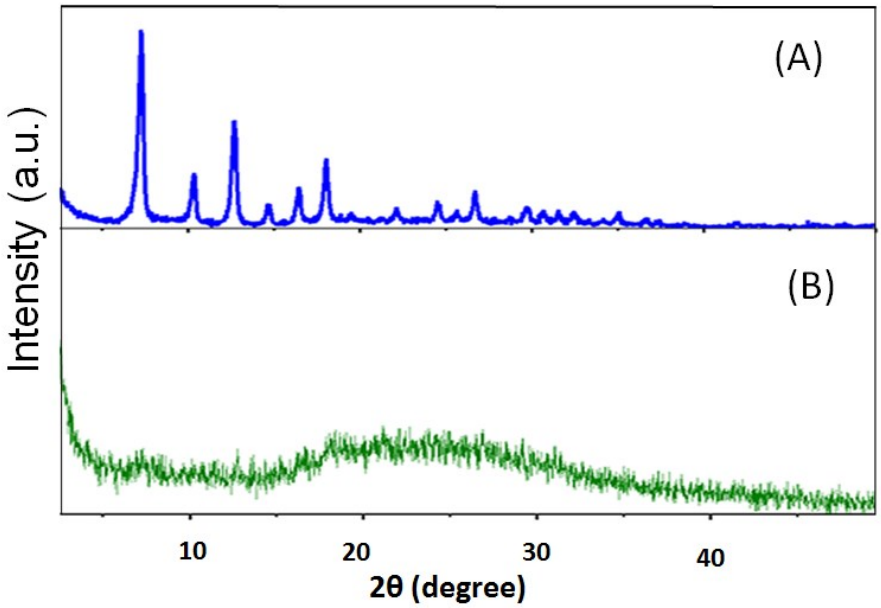

Figure S7. XRD analysis of ZIF-8@PDA before (A) and after incubating with bacteria for 15 h (B).

References

1.Y. Pan, D. Heryadi, F. Zhou, L. Zhao, G. Lestari, H. Su and Z. Lai, *CrystEngComm*, 2011, **13**, 6937-6940.

2.L.-Y. Chou, P. Hu, J. Zhuang, J. V. Morabito, K. C. Ng, Y.-C. Kao, S.-C. Wang, F.-K. Shieh, C.-H. Kuo and C.-K. Tsung, *Nanoscale*, 2015, **7**, 19408-19412.