

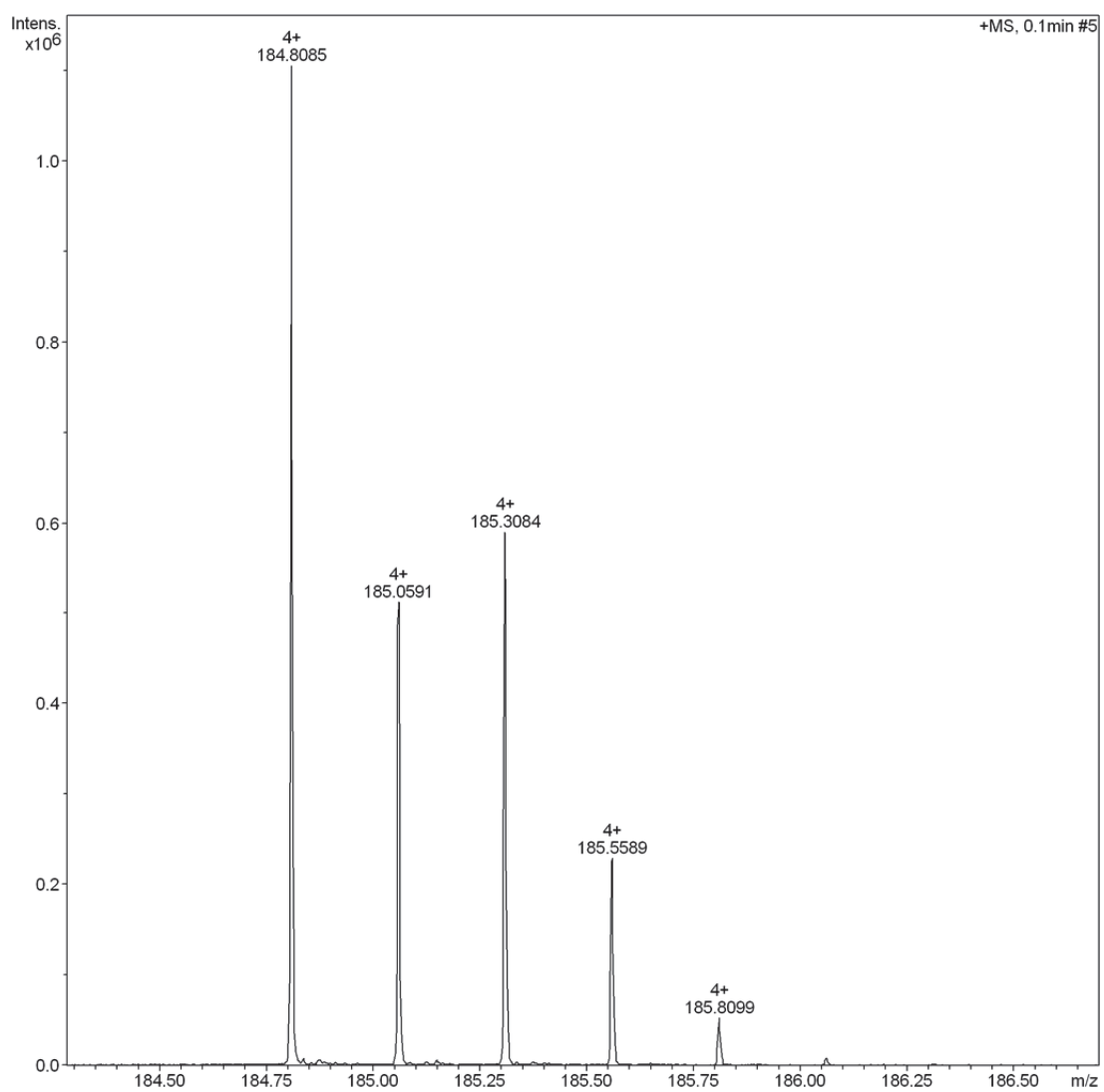
## Electronic Supplementary Information

### **Blocking the bimolecular pathway of water oxidation electrocatalyzed by a copper porphyrin with a surfactant**

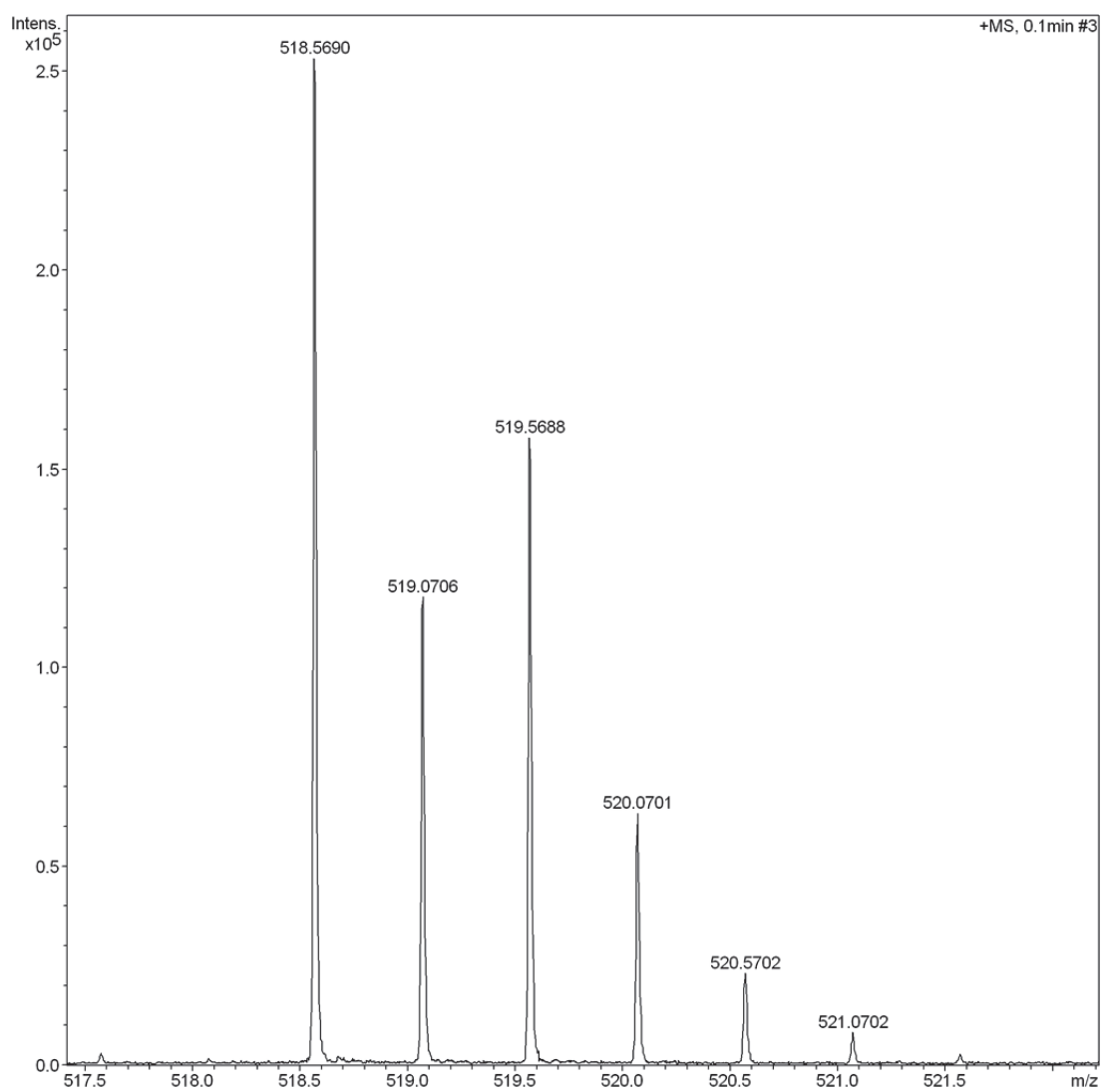
Luna Yang,<sup>a</sup> Shujiao Yang,<sup>a</sup> Jiafan Kong,<sup>a</sup> Wenjie Yuan,<sup>a</sup> Sisi Li,<sup>a</sup> Xiaohan Liu,<sup>a</sup> Rui Cao<sup>a</sup> and Wei Zhang<sup>\*a</sup>

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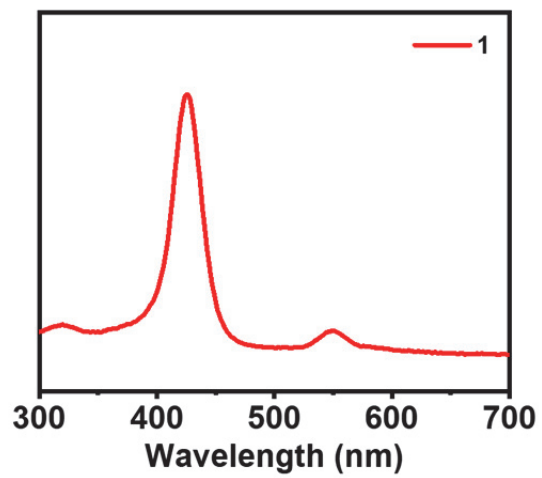
\*Corresponding author. Email: zw@snnu.edu.cn (W.Z.).



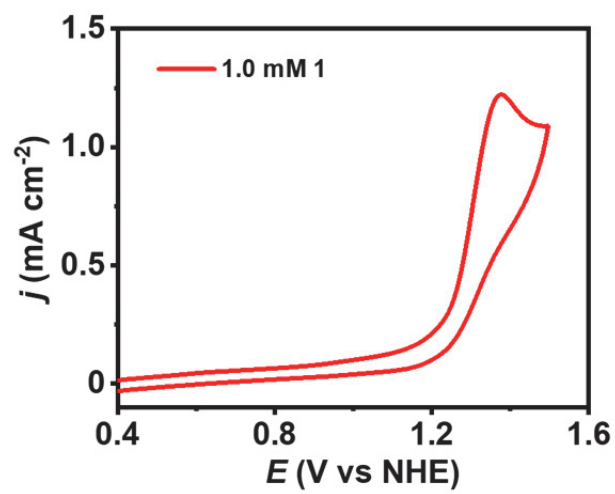
**Fig. S1** HRMS of complex **1** showing ions at a mass-to-charge ratio of 184.8085 for  $[\text{Cu-TMPyP}]^{4+}$ .



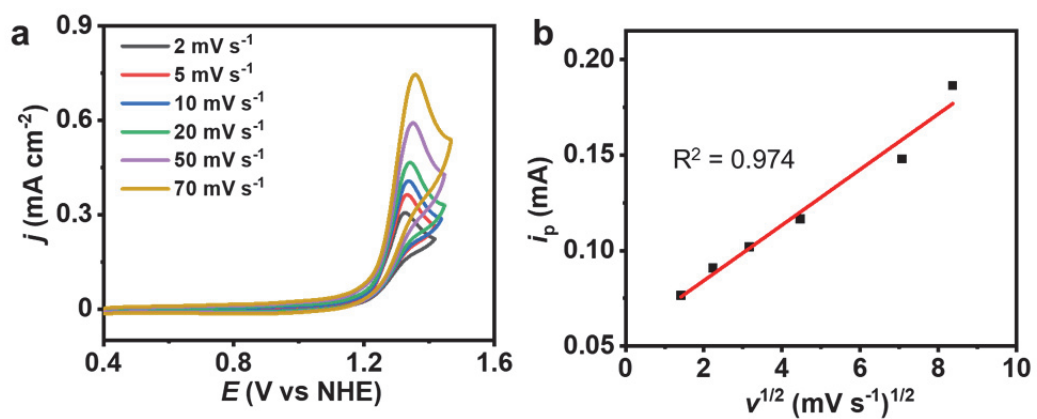
**Fig. S2** HRMS of complex **1** showing ions at a mass-to-charge ratio of 518.5690 for  $[\text{Cu-TMPyP}-(\text{OTf})_2]^{2+}$ .



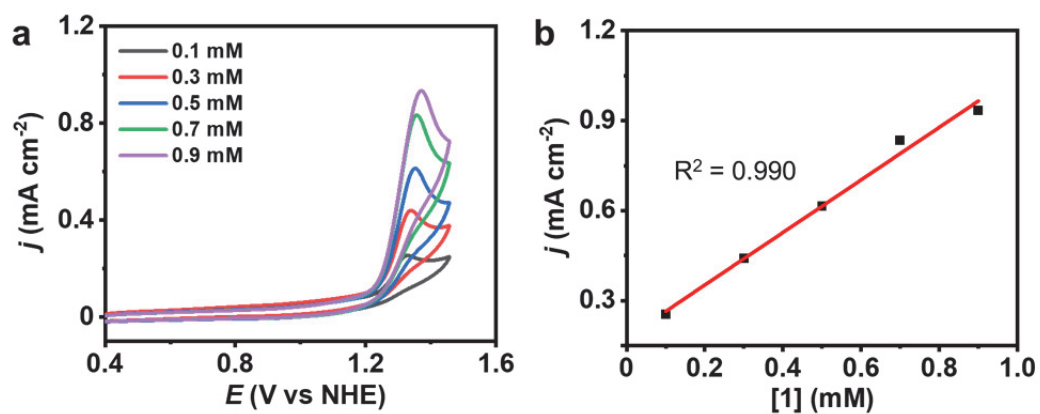
**Fig. S3** UV-vis spectrum of complex **1**. Conditions: dry acetonitrile solution, 20 °C.



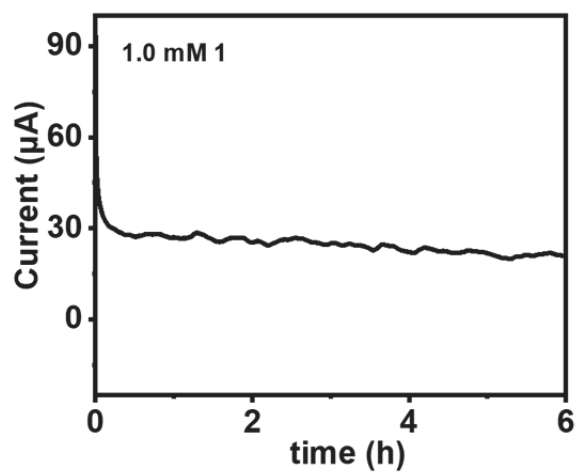
**Fig. S4** CV of 1.0 mM **1** at 100 mV s<sup>-1</sup> scan rate. Conditions: FTO working electrode ( $S = 0.25$  cm<sup>2</sup>), 0.1 M pH = 7.0 PBS, 20 °C.



**Fig. S5** (a) CVs of 1.0 mM **1** at different scan rates. Conditions: FTO working electrode ( $S = 0.25 \text{ cm}^2$ ), 0.1 M pH = 7.0 PBS, 20 °C. (b) Plot of catalytic peak currents versus the square root of scan rates ( $v^{1/2}$ ),  $R^2 = 0.974$ .

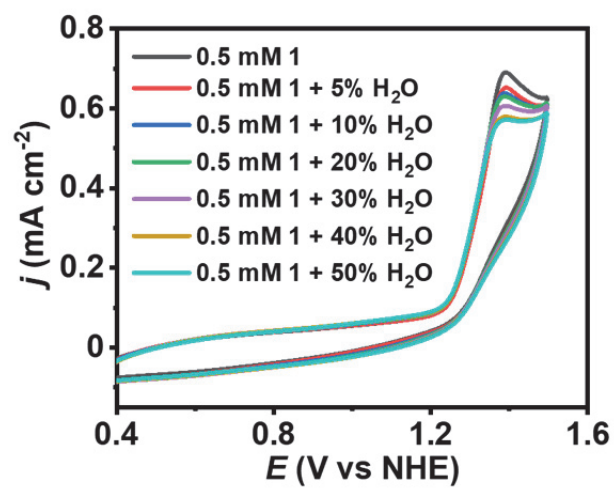


**Fig. S6** (a) CVs of **1** at different concentrations. Conditions: FTO working electrode ( $S = 0.25 \text{ cm}^2$ ), 0.1 M pH = 7.0 PBS,  $100 \text{ mV s}^{-1}$  scan rate,  $20 \text{ }^\circ\text{C}$ . (b) Plot of catalytic peak currents versus the concentrations of **1**,  $R^2 = 0.990$ .

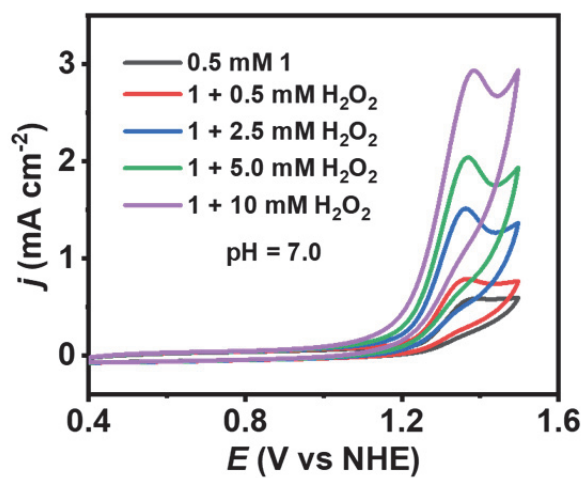


**Fig. S7** CPE of 1.0 mM **1** at an applied potential of 1.30 V. Conditions: FTO working electrode ( $S = 0.25 \text{ cm}^2$ ), 0.1 M pH = 7.0 PBS, 20 °C.

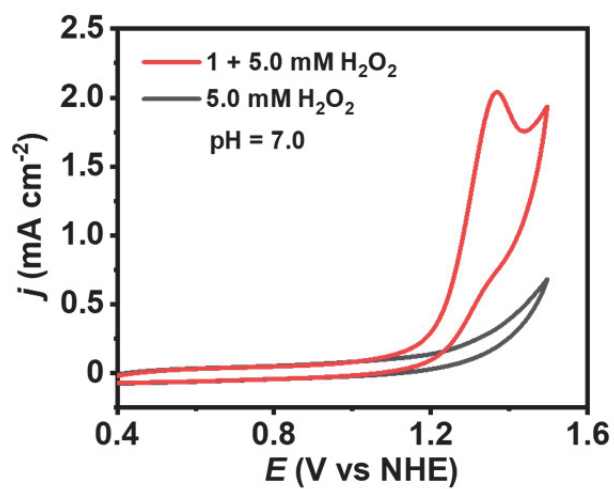




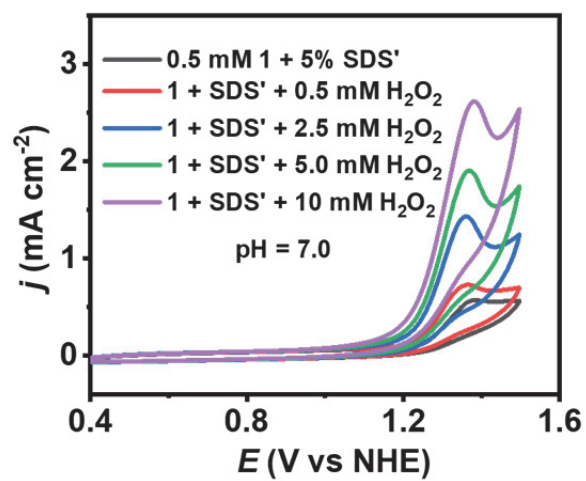
**Fig. S8** CVs of 0.5 mM **1** +  $x\%$  H<sub>2</sub>O at 100 mV s<sup>-1</sup> scan rate. Conditions: GC working electrode ( $S = 0.07$  cm<sup>2</sup>), 0.1 M pH = 7.0 PBS, 20 °C.



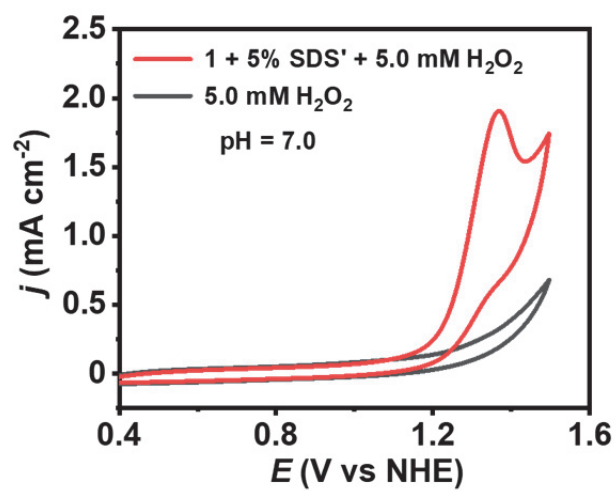
**Fig. S9** CVs of 0.5 mM **1** with the addition of different concentrations of H<sub>2</sub>O<sub>2</sub>. Conditions: GC working electrode, 0.1 M pH = 7.0 PBS, scan rate 100 mV s<sup>-1</sup>, 20 °C.



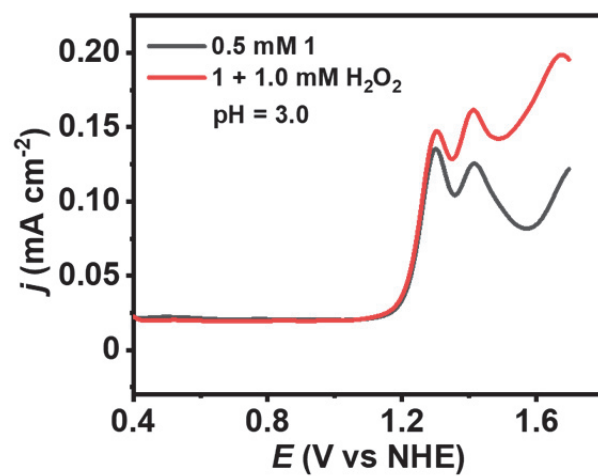
**Fig. S10** CVs of 5.0 mM H<sub>2</sub>O<sub>2</sub> with 0.5 mM **1**. Conditions: GC working electrode, 0.1 M pH = 7.0 PBS, scan rate 100 mV s<sup>-1</sup>, 20 °C.



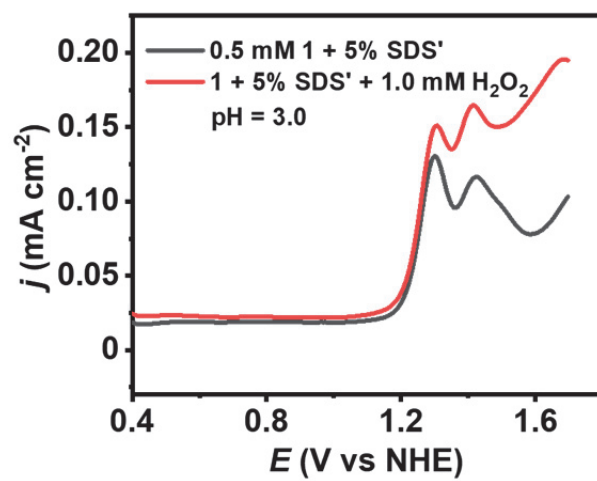
**Fig. S11** CVs of 0.5 mM **1** + 5% SDS' with the addition of different concentrations of H<sub>2</sub>O<sub>2</sub>. Conditions: GC working electrode, 0.1 M pH = 7.0 PBS, scan rate 100 mV s<sup>-1</sup>, 20 °C.



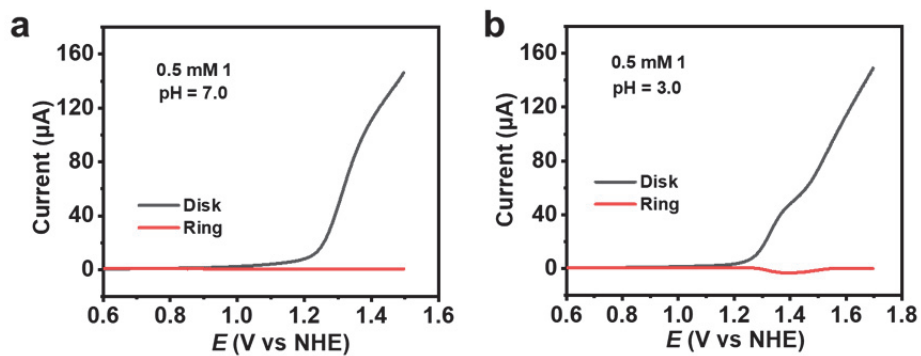
**Fig. S12** CVs of 5.0 mM H<sub>2</sub>O<sub>2</sub> with 0.5 mM **1** + 5% **SDS'**. Conditions: GC working electrode, 0.1 M pH = 7.0 PBS, scan rate 100 mV s<sup>-1</sup>, 20 °C.



**Fig. S13** DPVs of 0.5 mM **1** with the addition of 1.0 mM H<sub>2</sub>O<sub>2</sub>. Conditions: GC working electrode, 0.1 M pH = 3.0 PBS, 20 °C.

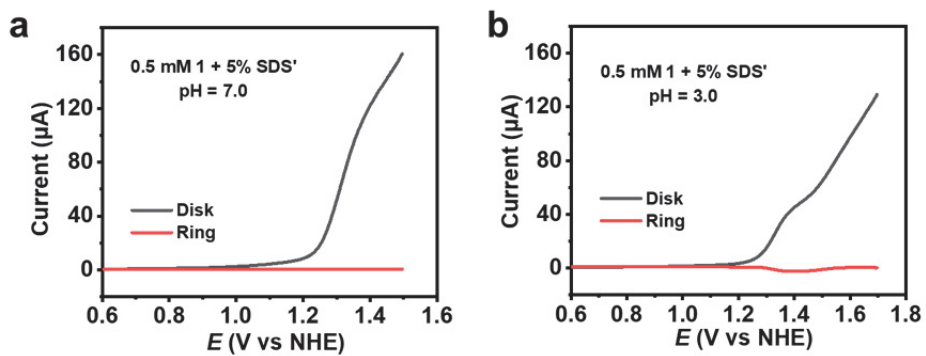


**Fig. S14** DPVs of 0.5 mM **1** + 5% **SDS'** with the addition 1.0 mM H<sub>2</sub>O<sub>2</sub>. Conditions: GC working electrode, 0.1 M pH = 3.0 PBS, 20 °C.

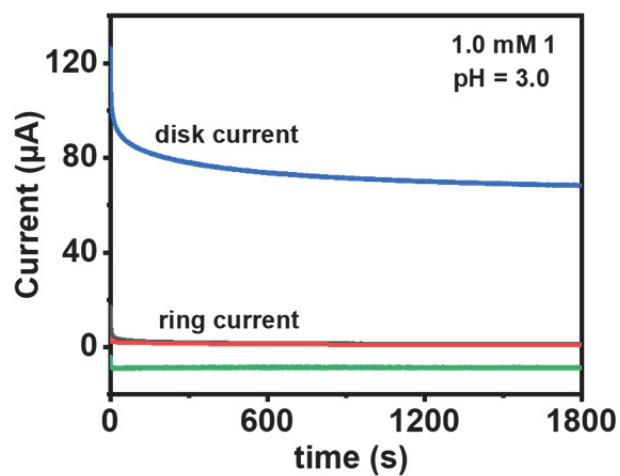


**Fig. S15** (a, b) RRDE measurements of 0.5 mM **1** at 1000 rpm in 0.1 M pH = 7.0 and pH = 3.0 PBS. Conditions: Pt ring electrode at 0.70 V, scan rate 10 mV s<sup>-1</sup>, 20 °C.

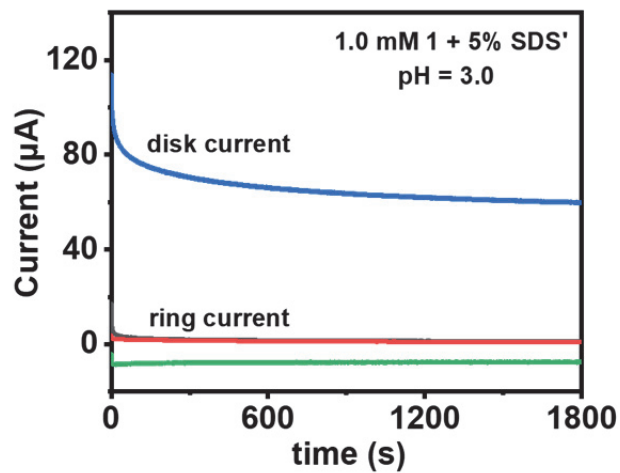




**Fig. S16** (a, b) RRDE measurements of 0.5 mM **1** + 5% **SDS'** at 1000 rpm in 0.1 M pH = 7.0 and pH = 3.0 PBS. Conditions: Pt ring electrode at 0.70 V, scan rate 10 mV s<sup>-1</sup>, 20 °C.



**Fig. S17** (a) CPE measurements with 1.0 mM **1** (blue and green) or without **1** (black and red). Conditions: GC disk electrode at an applied potential of 1.40 V and Pt ring electrode at an applied potential at 0.70 V in a 0.1 M pH = 3.0 PBS at 1600 rpm, 20 °C.



**Fig. S18** (b) CPE measurements with 1.0 mM **1** + 5% **SDS'** (blue and green) and without **1** + 5% **SDS'** (black and red). Conditions: GC disk electrode at an applied potential of 1.40 V and Pt ring electrode at an applied potential at 0.70 V in a 0.1 M pH = 3.0 PBS at 1600 rpm, 20 °C.