

**Electrochemical Ratiometric Immunosensor for the Detection of NMP22 Based on
ZIF-8@MWCNTs@Chit@Fc@AuNPs and AuPt-MB**

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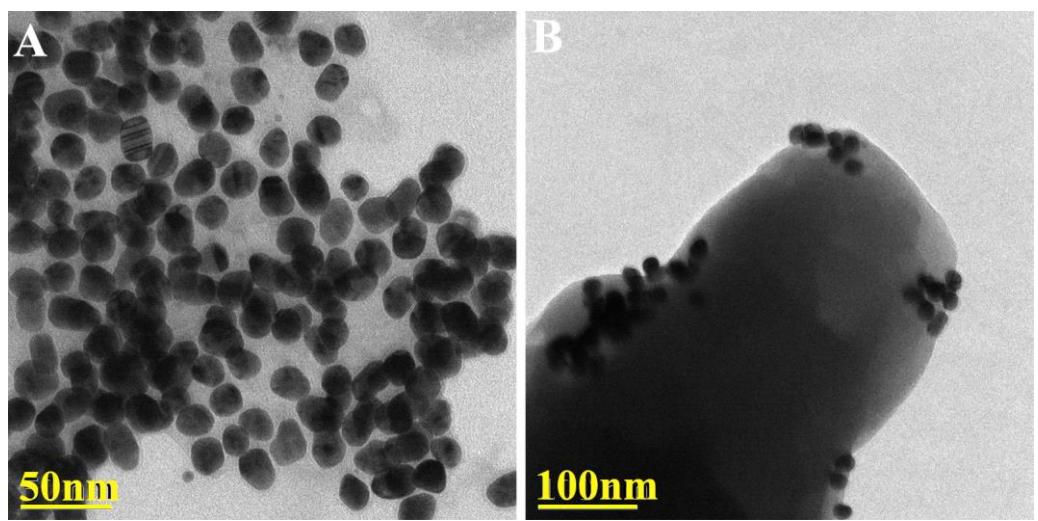


Fig. S1. TEM of AuNPs (A) and Fc@AuNPs (B).

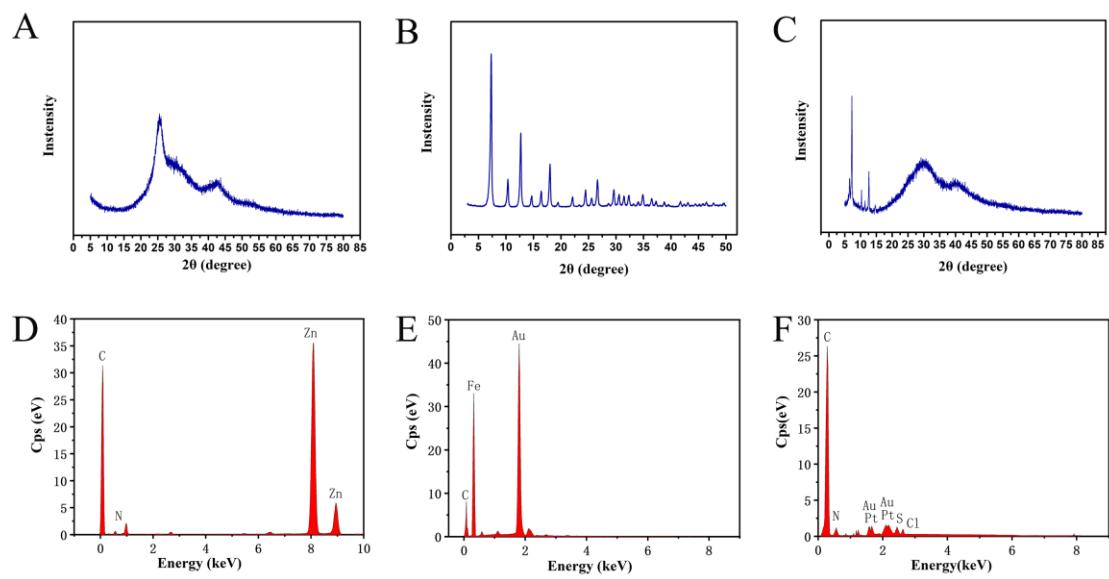


Fig. S2. XRD of MWCNTs (A), ZIF-8 (B) and ZIF-8@MWCNTs@Chits (C); EDS of the ZIF-8@MWCNTs@Chits (D), Fc@AuNPs (E) and AuPt-MB (F).

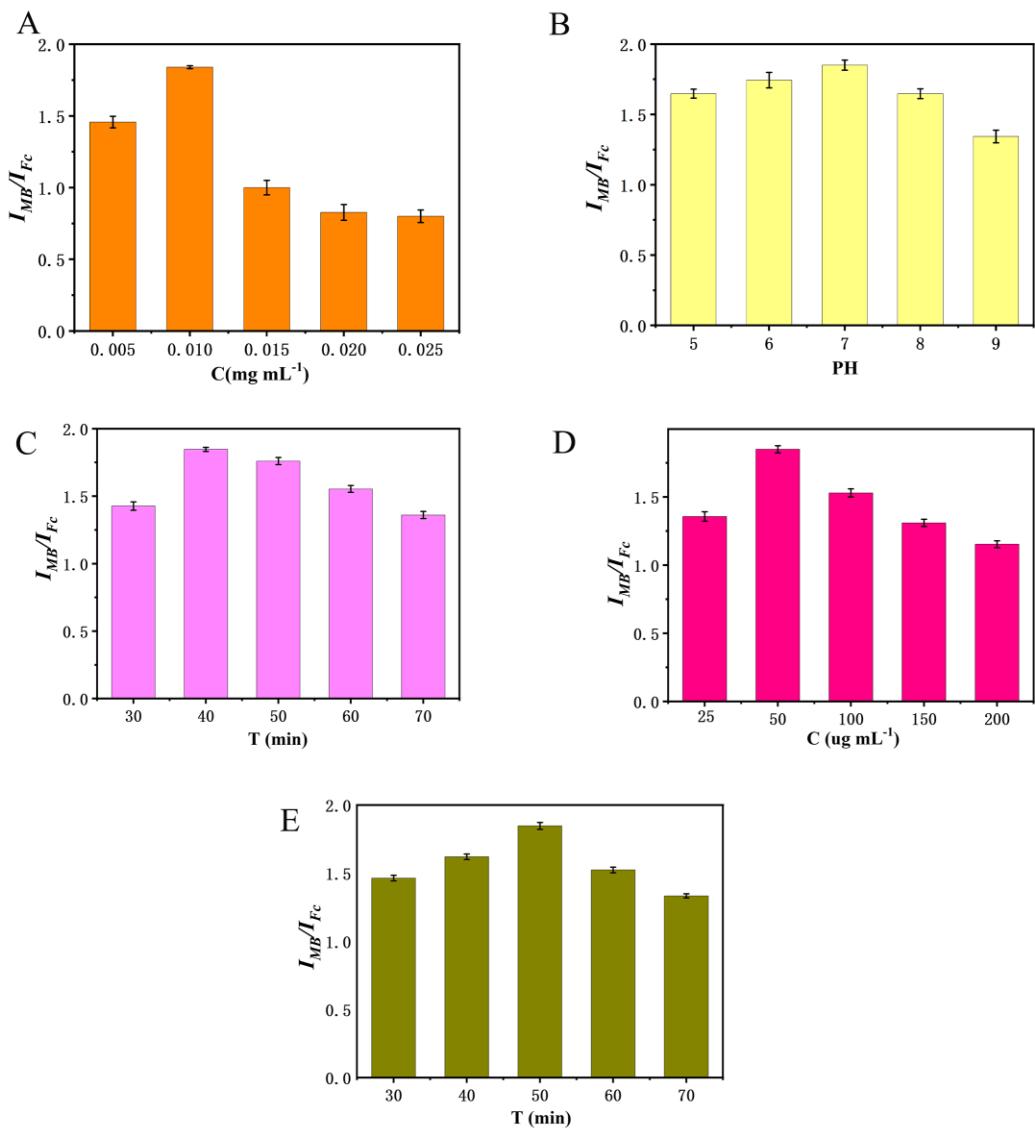


Fig. S3. Optimization of the experimental conditions (A) for concentration of the substrate material, (B) for the pH value of PBS, (C) for the incubation time of NMP22, (D) for the concentration of NMP22-Ab₁ and (E) for the incubation time of AuPt-MB-Ab₂.

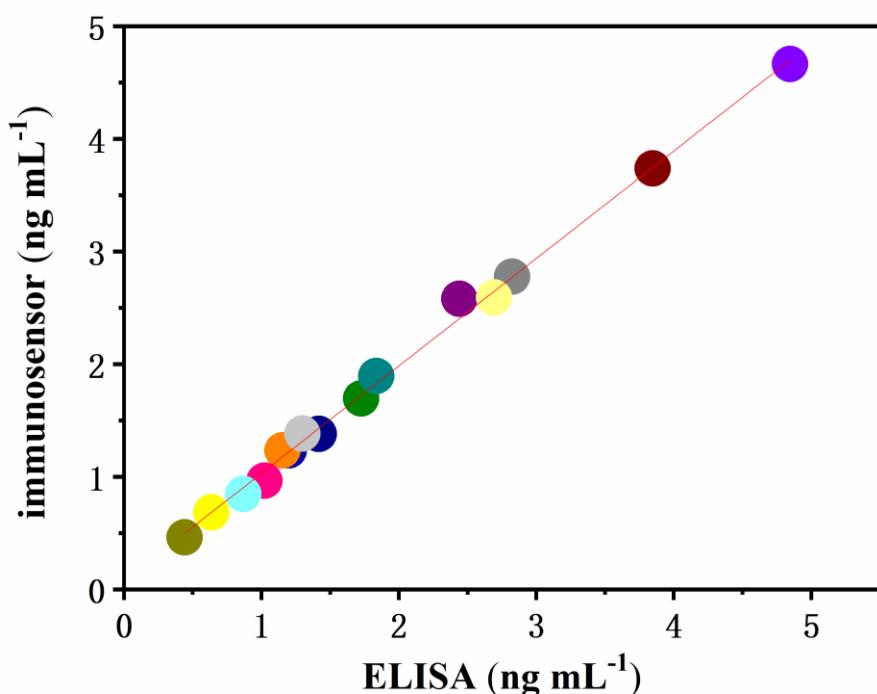


Fig. S4. Correlation analysis between ratiometric electrochemical immunosensor and human NMP22 ELISA kit for detection of human urinary NMP22 (n=16).

Table S1 The comparison of methods to detection of nmp22.

Sensor	Material	Linear range	Detection limit	Ref.
electrochemical ratiometric immunosensor	ZIF-8@MWCNTs@Chit@Fc@AuNPs	0.01 pg mL ⁻¹ -1000 ng mL ⁻¹	3.33 fg mL ⁻¹	This Work
dual-channel immunosensor	sulfur-doped graphene sheet (S-GS)	0.1 pg mL ⁻¹ -0.3 ng mL ⁻¹	25 fg mL ⁻¹	Ren. et al ⁴³
label-free electrochemical immunosensor	AuNPs-PtNPs-MOFs	0.005 -0.5 ng mL ⁻¹ 0.5 -20 ng mL ⁻¹	1.7 ng mL ⁻¹	Zhao. et al ³⁸
microfluidic immunoassay	polydimethylsiloxane (PDMS)	4 -16 ng mL ⁻¹	2.57 ng mL ⁻¹	Guan. et al ⁹
fluorescence immunoassay	nitrogen doped carbon dots (NCDs)	1.3 -16.3 ng mL ⁻¹	0.047 ng mL ⁻¹	Othman. et al ⁴⁴
label-free electrochemical immunosensor	rGO-TEPA@Cu-MOFs@SiO ₂ @AgNPs	0.1 pg mL ⁻¹ -1000 ng mL ⁻¹	33.3 fg mL ⁻¹	Rong. et al ⁴⁵

Table S2 Ratiometric electrochemical immunosensor and ELISA kit for the detection of NMP22 in urine.

Sample	ELISA	Sensor	Relative error (%)
1	0.637	0.682	-6.93
2	0.44	0.461	-4.81
3	1.418	1.381	2.61
4	2.44	2.578	-5.68
5	3.846	3.736	2.87
6	1.725	1.695	1.73
7	1.835	1.893	-3.17
8	1.198	1.234	-3.02
9	1.154	1.234	-6.94
10	4.846	4.665	3.74
11	1.022	0.964	5.67
12	4.604	4.447	3.42
13	1.297	1.384	-6.71
14	2.824	2.777	1.68
15	2.692	2.59	3.78
16	0.868	0.847	2.49

Reference

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