Electronic Supplementary Material (ESI) for RSC Advances.

Electronic Supplementary Information

A 'signal on-off' electrochemical peptide biosensor for matrix metalloproteinase 2 based on target induced cleavage of peptide

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S1. Size distribution of prepared pPtNPs.

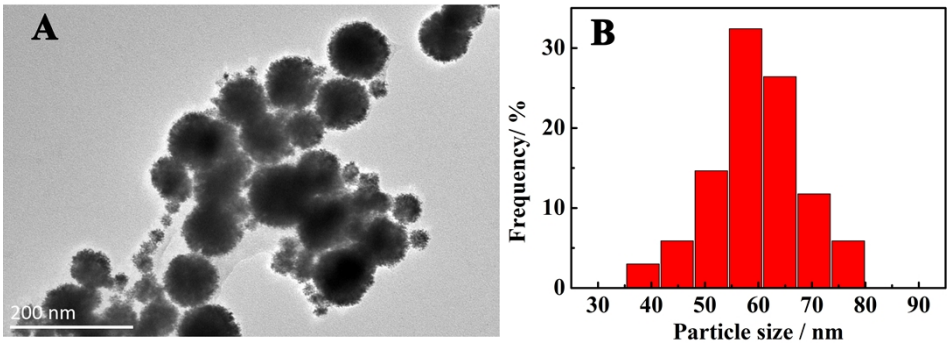

Fig. S1 TEM image of pPtNPs (A) and the size distributing histogram of pPtNPs (B).

S2. XPS spectra of individual element

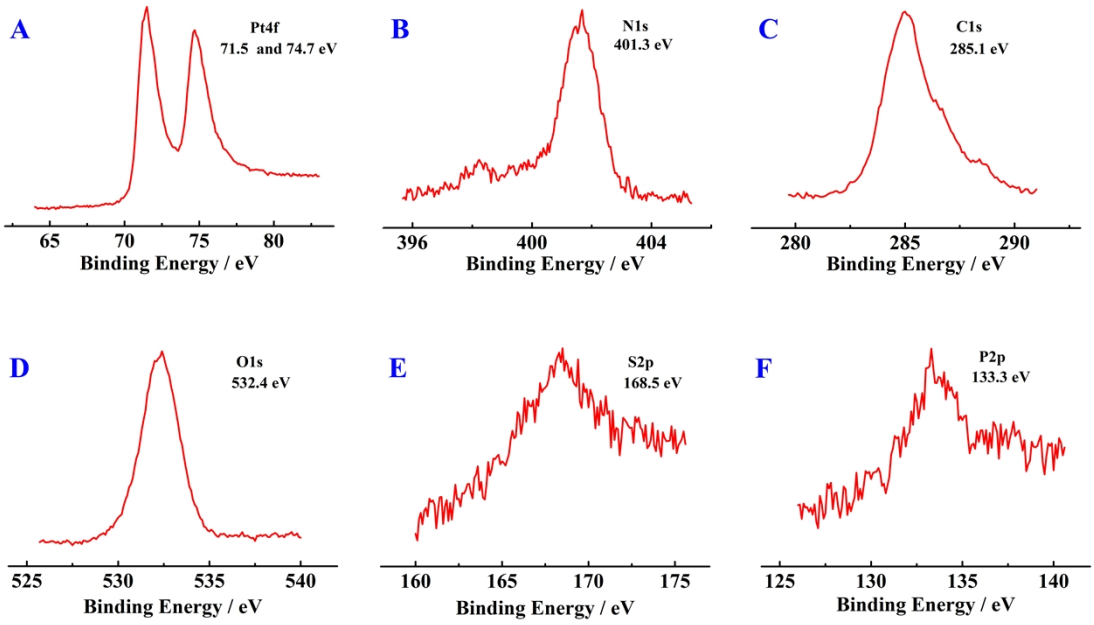

Fig. S2 XPS spectra of pPtNPs immobilized with S1 and P1: Pt4f region (A), N1s region (B), C1s region (C), O1s region (D), S2p region (E), P2p region (F).

S3. Polyacrylamide gel electrophoresis analysis of HCR

The gel electrophoresis analysis of S1, S2 and HCR between S1 and S2 was shown in Fig. S3. Clearly, one mission band was observed only in the presence of S1 or S2 (lane 1 and lane 2). Once S1 and S2 were present at the same time, dsDNA

polymer was formed through HCR of S1 and S2. As expected, the emission bands of high-molecular weight structure can be obviously observed (lane 3), indicating the successful formation of dsDNA polymer from S1 and S2.

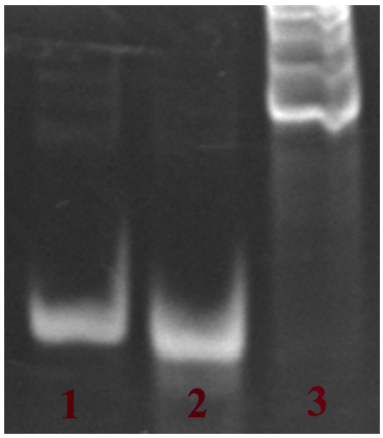

Fig. S3 Polyacrylamide gel electrophoresis characterization: 2.5 μM S1 (lane 1), 2.5 μM S2 (lane 2), their mixture (lane 3) (HCR time was 60 min).

S4. Optimization of detection conditions

In order to improve the analytical performance of the proposed biosensor, some experimental parameters, including MMP-2 incubation time, H_2O_2 concentration and pH of testing buffer, were optimized. Fig. S4A shows the DPV response of the proposed biosensor incubated with 100 pg mL^{-1} MMP-2 for 0 min to 140 min in 0.1 M PBS (pH 7.0) without 2.22 mM H_2O_2. Obviously, the electrochemical signal remarkably decreased with the increasing of incubation time and reached a plateau at about 120 min, suggesting the completion of the peptide cleavage by MMP-2. Therefore, 120 min was selected as the optimized incubation time.

Moreover, the bioelectrocatalytic efficiency and sensitivity of the biosensor are affected by the amount of H_2O_2 in testing buffer in this work. Fig. S4B displays DPV

responses of proposed biosensor in 0.1 M PBS (pH 7.0) with different volume of 30 mM H_2O_2 (20, 40, 60, 80 and 100 μL). The increase of H_2O_2 concentration resulted in the enhancement of DPV peak current, which tended to level off at 80 μL (equivalent to 2.22 mM H_2O_2 in PBS). Thus, 2.22 mM of H_2O_2 in tested cell was used in the following experiments.

The DPV response of the proposed biosensor was further investigated in 0.1 M PBS containing 2.22 mM H_2O_2 with different pH of 5.0-8.0. As shown in Fig. S4C, the best electrochemical signal was observed at pH 7.0. So, the subsequent measurements were carried out in pH 7.0 PBS (0.1 M).

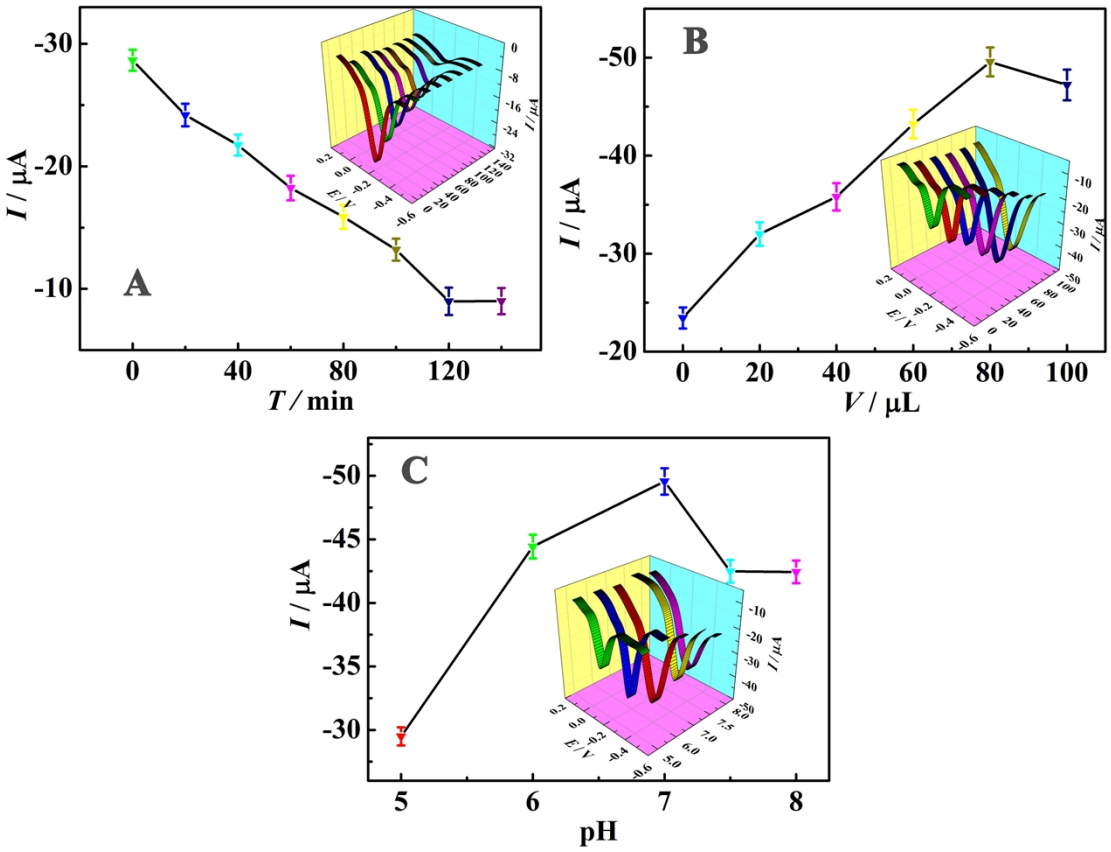

Fig. S4 Effect of different detection conditions on the electrochemical performance of proposed biosensor: MMP-2 incubation time (A), H_2O_2 concentration (B) and pH of testing buffer (C). The inserts are DPV signals obtained in different PBS.

S5.The stability measurement of the proposed biosensor for MMP-2

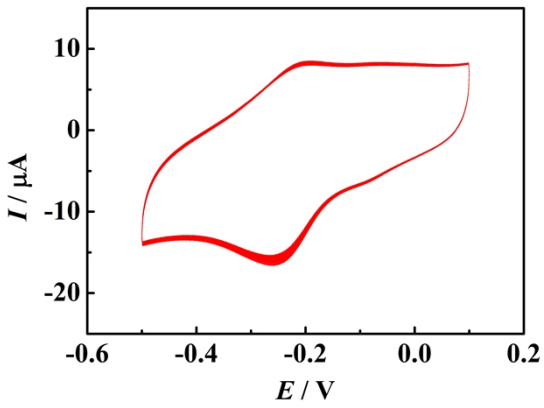

Fig. S5 CV responses of the proposed biosensor for 100 pg mL^{-1} MMP-2 in 0.1 M PBS (pH 7.0) at the scan rate of 100 mV s^{-1}.

Table S1

The performance comparison of MMP-2 biosensors based on different methodologies.

Analytical methods[a]	Linear range	Detection limit	References
Photoluminescence	-	72 ng mL^{-1}	1
Fluorescence	14.4-144 ng mL^{-1}	3.61 ng mL^{-1}	2
SPR	0-7.2 ng mL^{-1}	36 pg mL^{-1}	3
FRET	0.076-0.76 μg mL^{-1}	12.5 ng mL^{-1}	4
Bioluminescent	50-1000 ng mL^{-1}	-	5
BRET	-	2 ng mL^{-1}	6
DPV	0.1-1 μg mL^{-1}	0.1 μg mL^{-1}	7
DPV	1-10000 pg mL^{-1}	0.32 pg mL^{-1}	Our work

[a] SPR: surface plasmon resonance, FRET: fluorescence resonance energy transfer, BRET: bioluminescent resonance energy transfer, DPV: differential pulse voltammetry.

References

1. J. Li, C. H. Lu, Q. H. Yao, X. L. Zhang, J. J. Liu, H. H. Yang and G. N. Chen, *Biosens. Bioelectron.*, 2011, **26**, 3894–3899.
2. W. Cheng, Y. L. Chen, F. Yan, L. Ding, S. J. Ding, H. X. Ju and Y. B. Yin, *Chem. Commun.*, 2011, **47**, 2877–2879.
3. U. Pieper-Fürst, U. Kleuser, W. F.M. Stöcklein, A. Warsinke and F. W. Scheller, *Anal. Biochem.*, 2004, **332**, 160–167.
4. X. Wang, Y. Q. Xia, Y. Y. Liu, W. X. Qi, Q. Q. Sun, Q. Zhao and B. Tang, *Chem. Eur. J.*, 2012, **18**, 7189–7195.
5. Y. P. Kim, W. L. Daniel, Z. Y. Xia, H. X. Xie, C. A. Mirkin and J. H. Rao, *Chem. Commun.*, 2010, **46**, 76–78.
6. H. Q. Yao, Y. Zhang, F. Xiao, Z. Y. Xia and J. H. Rao, *Angew. Chem. Int. Ed*., 2007, **46**, 4346–4349.
7. L. M. Ning, P. Miao, T. Gao, H. Y. Wang and G. X. Li, *Electrochim. Acta*, 2013, **111**, 499–503.