Electronic Supplementary Material (ESI) for Analyst.

Pro-gastrin releasing peptide imprinted photoelectrochemical sensor based on in-situ growth of gold nanoparticles on MoS_2 nanosheet surface

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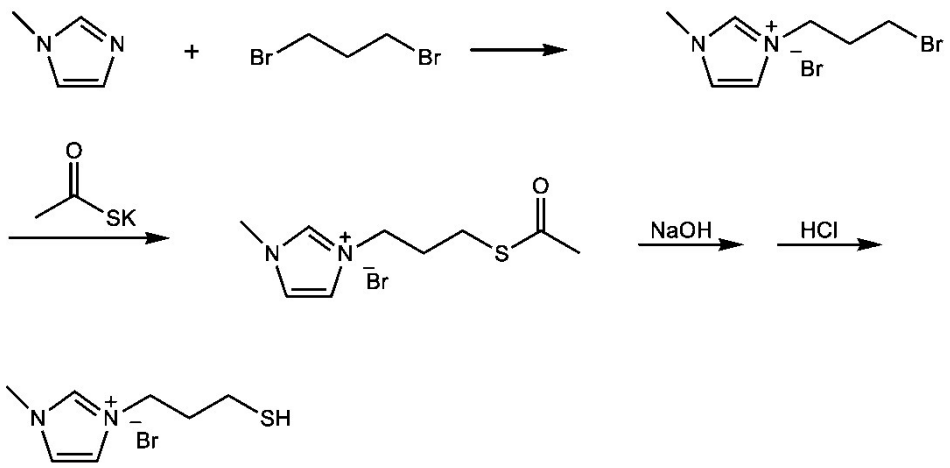
Reagents

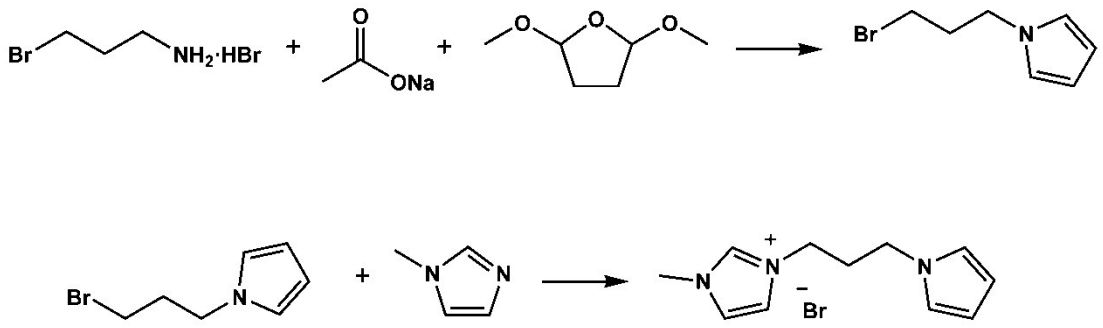
1-Methylimidazole was purchased from Xiya Reagent Co., Ltd. (Linshu, China). 1,3-Dibromopropane and potassium thioacetate were acquired from Aladdin's Reagent Company (Shanghai, China). Sodium fluoroborate was obtained from Energy Chemical's Reagent Company. (Shanghai, China). 3-Bromopropylamine hydrobromide and 2,5-Dimethoxytetrahydrofuran were supplied by the Aladdin (Shanghai, China). Chloroauric Acid was purchased from Sinopharm Chemical Reagent Co., Ltd. Human serum samples were obtained from the central hospital of Wuhan. Pro-gastrin releasing peptide (Pro-GRP) was purchased from Shanghai Linc-Bio Co., Ltd (Shanghai, China). Neuron Specific enolase (NSE) was bought from Beijing Biosynthesis Biotechnology Co., Ltd (Beijing, China). Human serum albumin (HSA) was purchased from Sinopharm Chemical Reagent Co., Ltd. Immunoglobulin (IgG) was supplied by Solarbio Company (Beijing, China). Glycine and L-Histidine were supplied by Kangda Amino Acid Company (Shanghai, China). Potassium ferricyanide, potassium ferrocyanide, sodium tetrafluoroborate and ascorbic acid (AA) were offered by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Other reagents were analytical grade and used without purifying. All the solutions were prepared with ultrapure water. Experiments were carried out at room temperature without other statements.

Apparatus

Electrochemical measurements were performed with CHI 660 E electrochemical workstation (Chenhua Corp., Shanghai, China). A conventional three-electrode system was employed with a glassy carbon electrode in diameter of 3 mm (GCE, Wuhan Gaossunion Technology Co., Ltd., China), a Pt wire auxiliary electrode and a saturated calomel reference electrode (SCE). A white-light LED lamp (5W) is used as the excitation light source. All the photocurrent measurements were performed at a constant potential of 0 V (vs. SCE). Photocurrents were measured in a 0.1 mol L^{-1} phosphate buffer solution (pH 7.0) containing 0.15 mol L^{-1} AA. Scanning electron microscope (SEM) was carried out with SU 8010 scanning electron microscope (Hitachi, Japan). FTIR spectra were conducted on Nicolet NEXUS-470 FTIR spectrometer (Thermo Nicolet, USA). Transmission electron microscopic (TEM) images were obtained on FEI Tecnai G2 20S-TWIN instrument (FEI Company, Netherlands). The mass spectrum was obtained on Q-TOF-MS 6520A HPLC-MS spectrograph (Agilent, American). ^{1}H-NMR spectra were supplied by AVANCE Ⅲ 400 nuclear magnetic resonance spectrometer (Bruker, France).



Scheme S 1 Scheme for the synthesis of 1-(3-mercaptopropyl)-3-methyl-imidazolium bromine (MIMBr) ionic liquid.



Scheme S 2 Scheme for the synthesis of 1-(N-pyrrolpropyl)-3-methyl-imidazole bromine (PMIMBr) ionic liquid

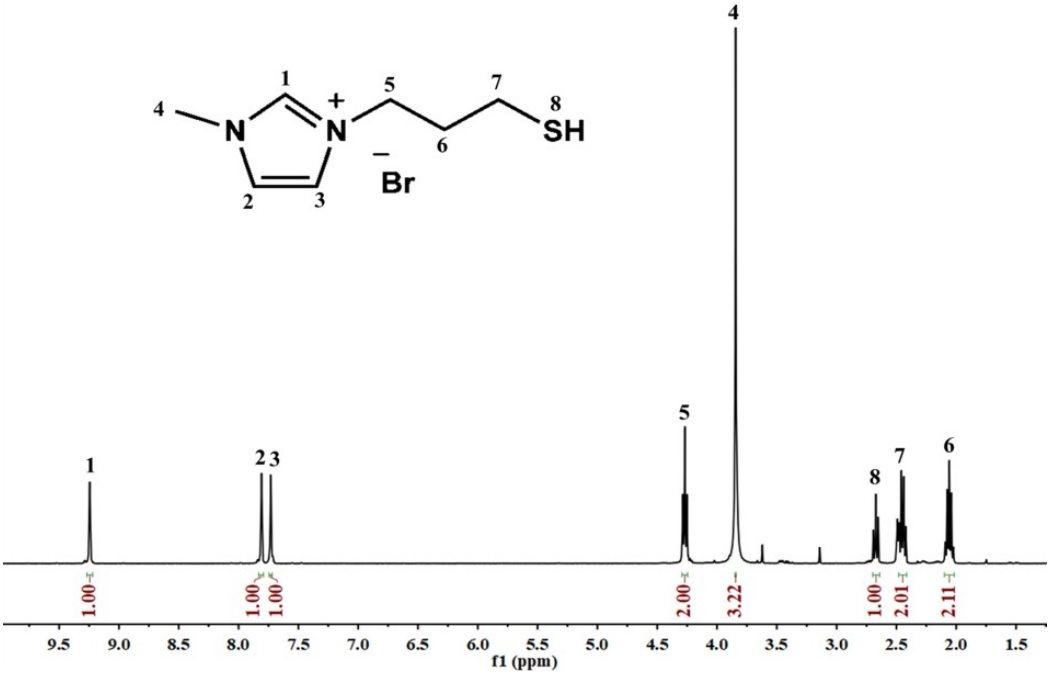


Figure S1. ^{1}H-NMR spectrum of MIMBr ionic liquid (solvent: DMSO-d_6)

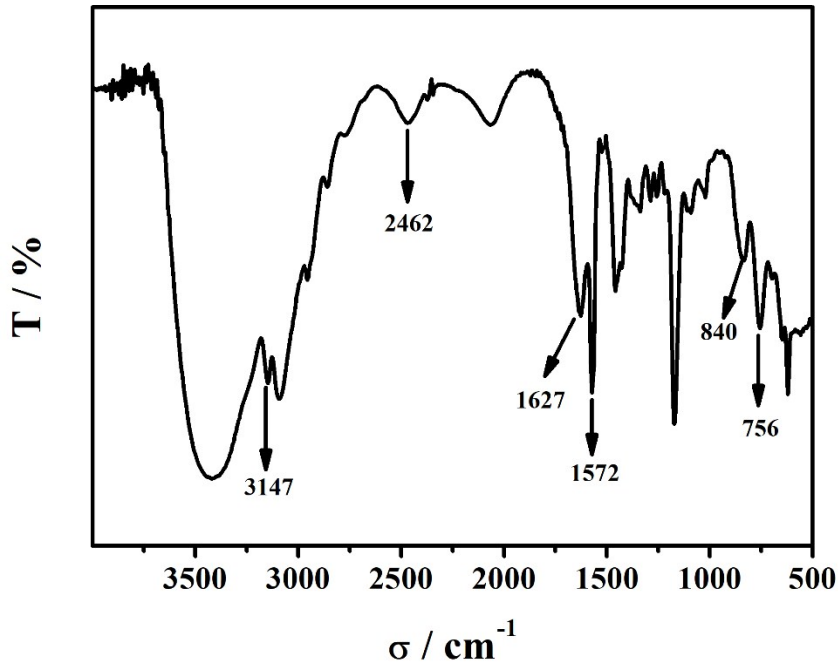


Figure S2. FTIR spectrum of MIMBr ionic liquid

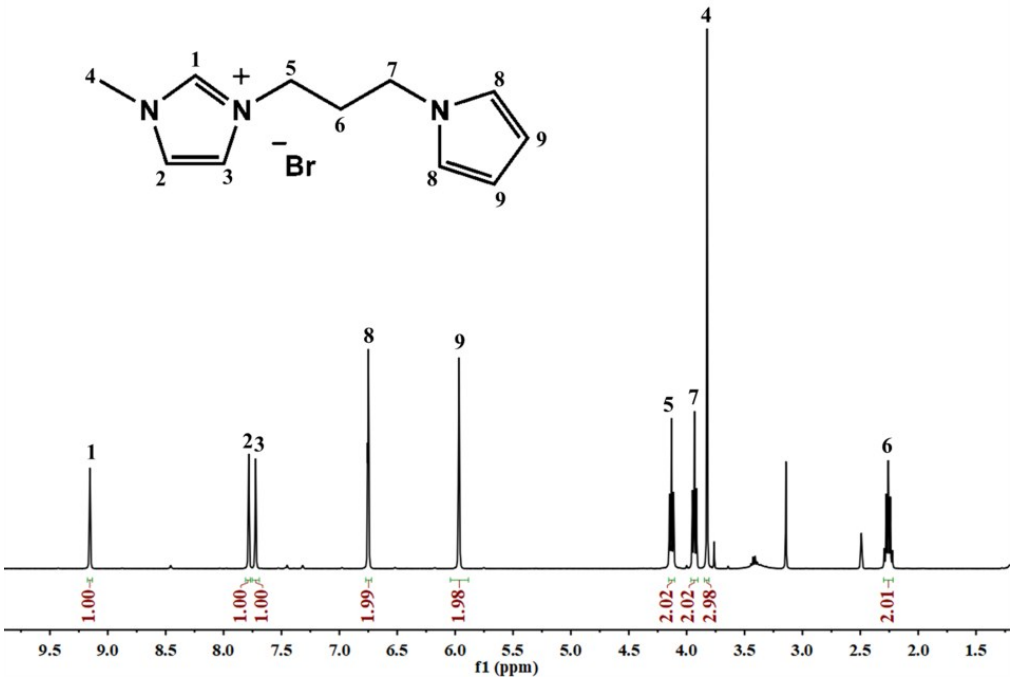


Figure S3. ^{1}H-NMR spectrum of PMIMBr ionic liquid (solvent: DMSO-d_6)

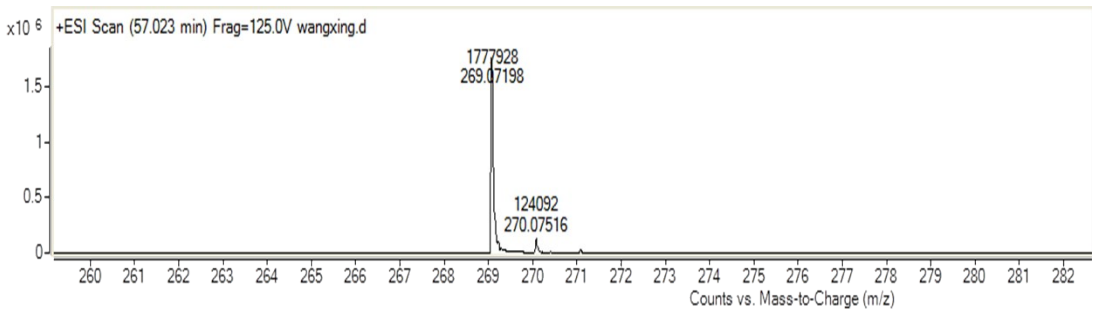


Figure S4. HPLC-MS spectrum of PMIMBr ionic liquid

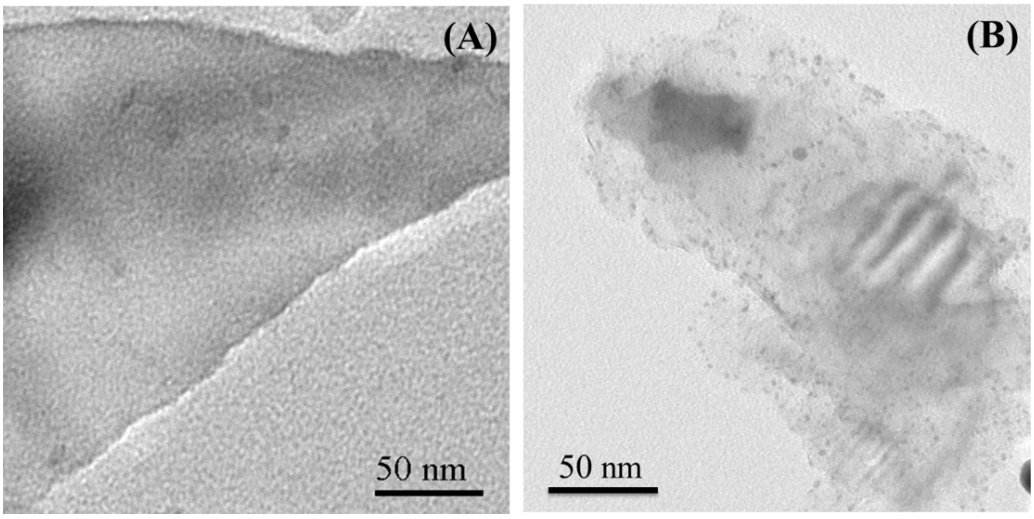


Figure S5. TEM images of 2D-MoS_2(A) and AuNPs/2D-MoS_2 nanocomposites (B)

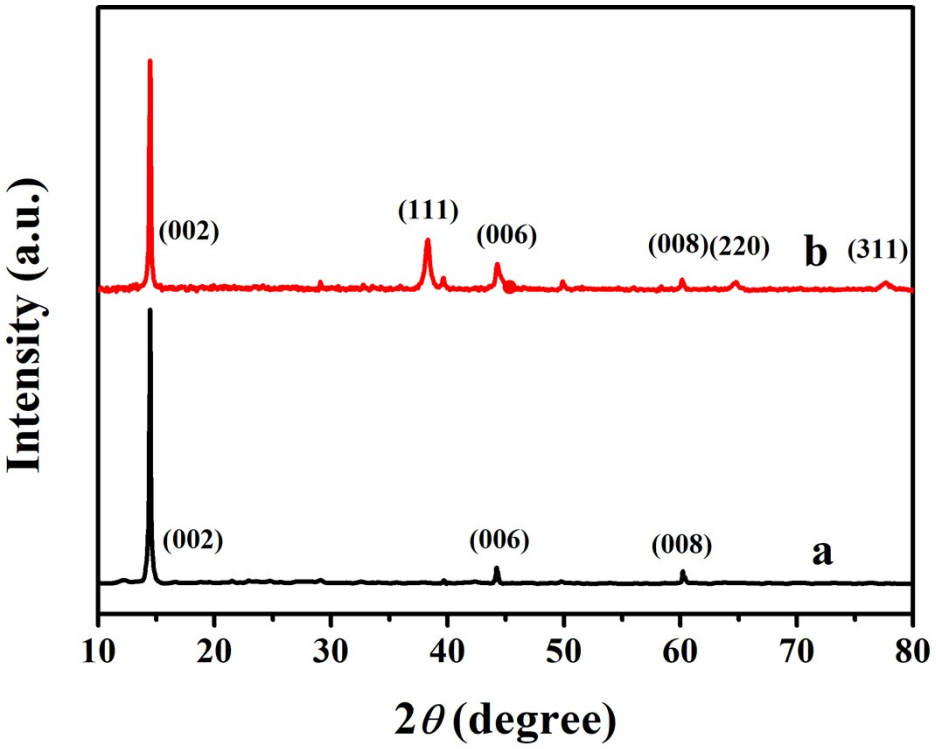


Figure S6. XRD of 2D-MoS_2 (a) andAuNPs/2D-MoS_2 nanocomposites (b)

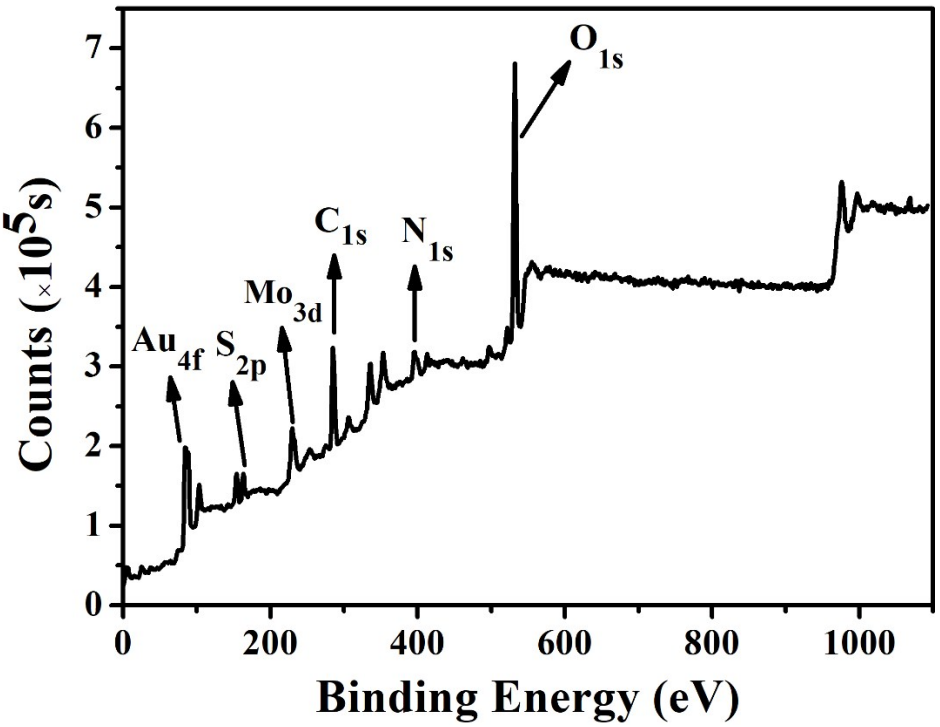


Figure S7. XPS of AuNPs/2D-MoS_2 nanocomposites

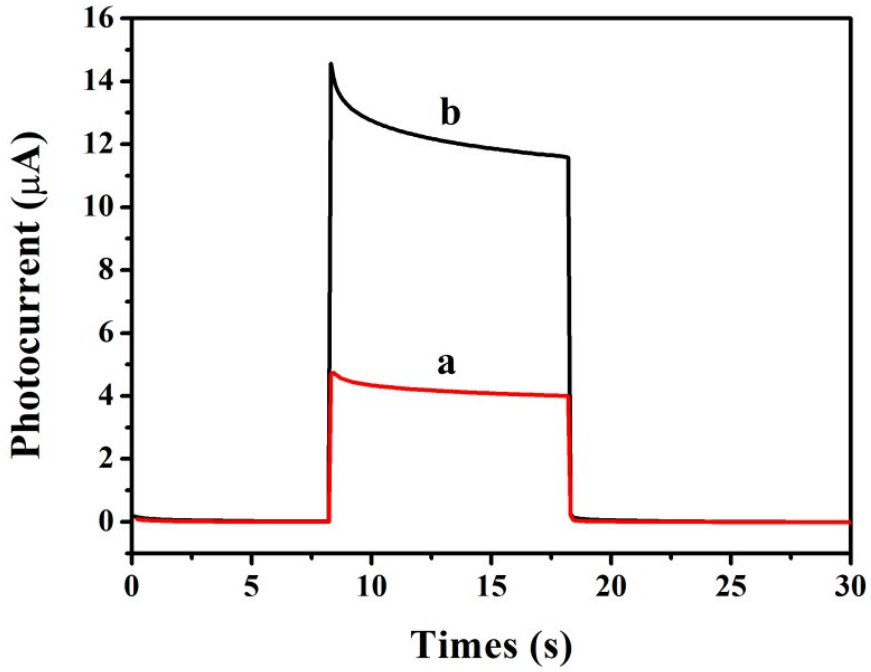


Figure S8. Photocurrent response of 2D-MoS_2(a) and AuNPs/2D-MoS_2(b)

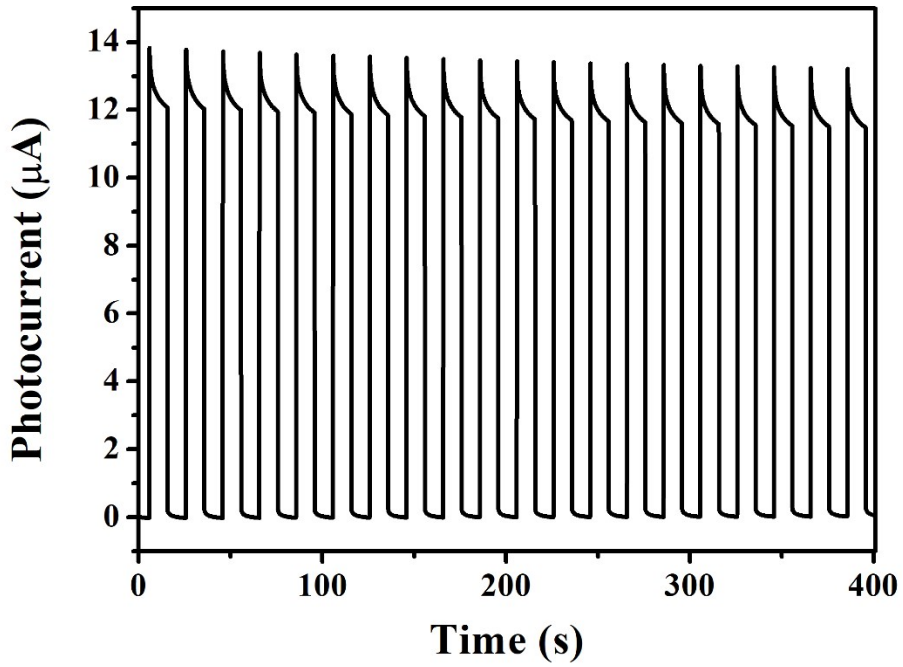


Figure S9. Stability of photocurrent response of AuNPs/2D-MoS_2/GCE

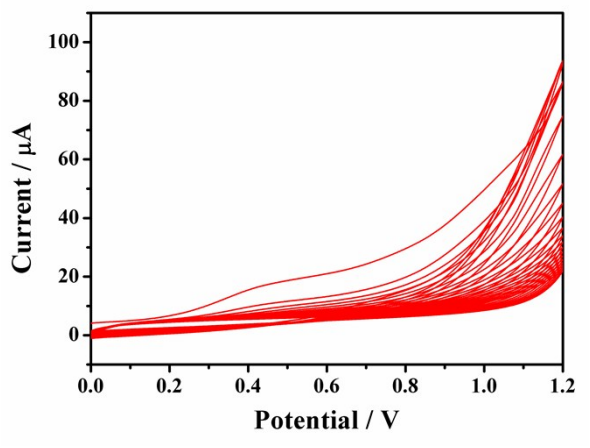


Figure S 10 Cyclic voltammograms for the electrochemical polymerization of PMIMBr ionic liquid in the presence of Pro-GRP.

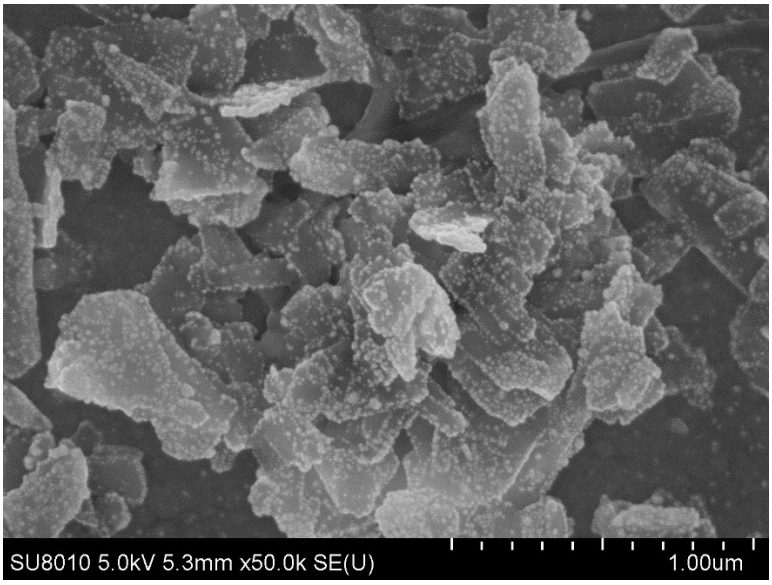


Figure S11. Morphological image of a non-imprinted film modified electrode surface characterized with scanning electron microscope.

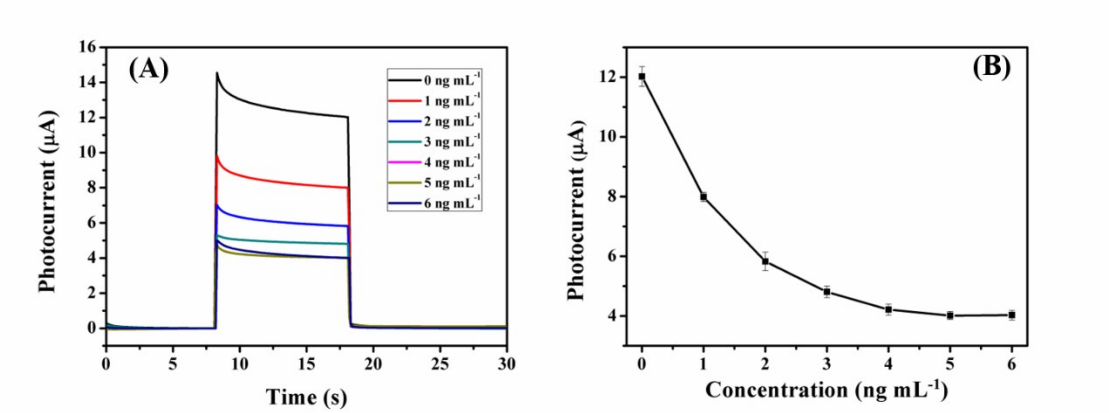


Figure S 12. Photocurrent responses of molecularly imprinted film electrode fabricated with different concentrations of Pro-GRP.

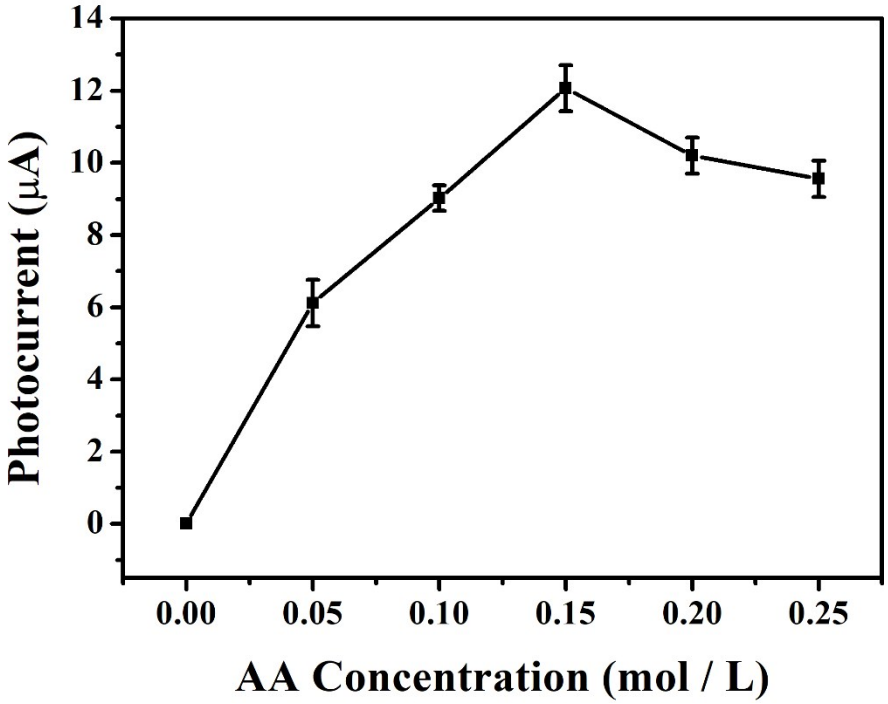


Figure S13. Influence of ascorbic acid concentration on the photocurrent response of AuNPs/2D-MoS_2/GCE

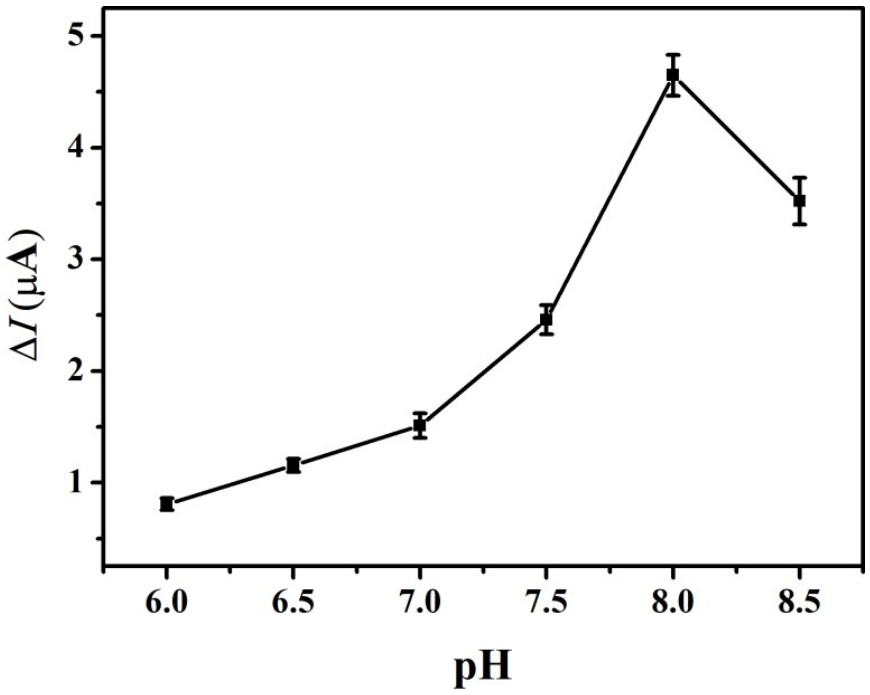


Figure S14. Effects of pH values on the photocurrent response of the imprinted sensor towards Pro-GRP.

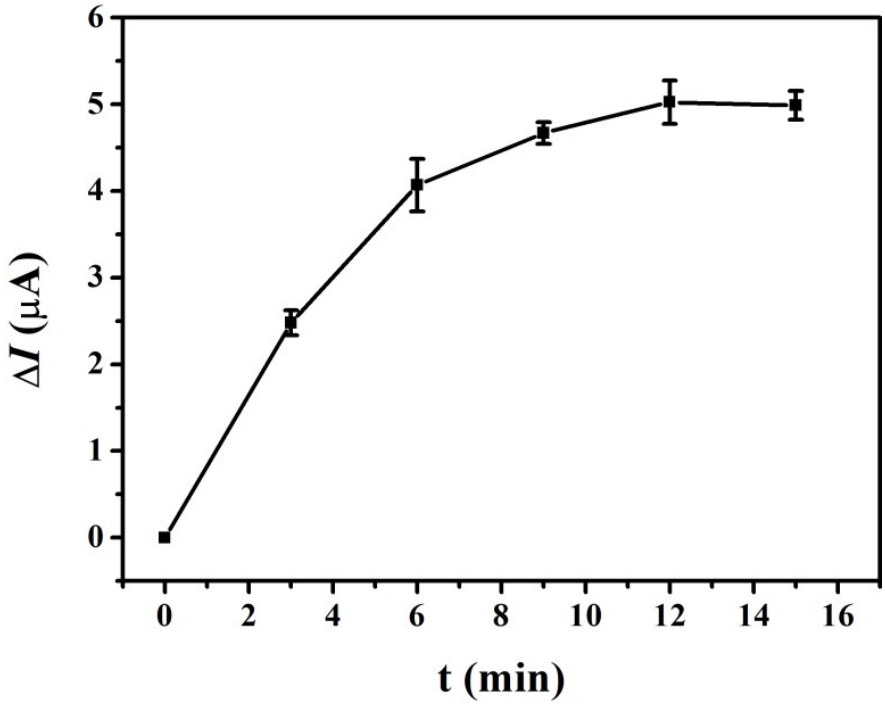


Figure S15. Influence of incubation time on the photocurrent response of the imprinted sensor toward Pro-GRP at the concentration of 1.0 ng mL^{-1}

Table S1. Comparison of analytical characteristics for Pro-GRP assay

Method	Detection time	Detection limit (ng mL^{-1})
ELISA	2 h	0.0019 [1]
Electrochemical immunosensor	25 min	0.01 [2]
LC-MS	40 min	0.0139 [3]
LC-MS/MS	30 min	0.09 [4]
Fluorescent molecularly imprinted	5 min	0.075 [5]
This method	12 min	0.0032

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[2] Zhong, Z. Y.; Peng, N.; Qing, Y.; Shan, J. L.; Li, M. X.; Guan, W.; Dai, N.; Gu, X. Q.; Wang, D. *Electrochim. Acta* **2011**, *56*, 5624 – 5629.

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Table S 2. Determination of Pro-GRP in clinical serum samples

Molecular imprinted sensor		Electrochemiluminescence	Relative
Concentration ($ng\ mL^{-1}$)	RSD (%)	Concentration ($ng\ mL^{-1}$)	Deviation (%)
0.848	1.67	0.857	-1.05
0.959	2.95	0.923	3.90
0.026	3.62	0.025	4.01

Table S 3. Recoveries for determining Pro-GRP (n=3)

Sample	Concentration ng mL^{-1}	Added ng mL^{-1}	Detected ng mL^{-1}	Recovery (%)	RSD (%)
1	0.857	1.0	1.81	95.3	4.06
2	0.923	1.0	1.94	98.7	1.83
3	0.025	1.0	1.044	101.9	3.33