Supporting Information for

Label-Free Polymerization Amplified Potentiometric Sensing Platform for Radical Reactions Using Polyion Sensitive Membrane Electrodes as Transducers

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Reagents and Materials. Tridodecylmethylammonium chloride ($TDMA^+Cl^-$), tetrabutyl ammonium chloride ($TBuA^+Cl^-$), tetradodecylammonium chloride ($TDDA^+Cl^-$), dinonylnaphthalene sulfonic acid ($DNNS^-H^+$), tetraphenylborate sodium (TPB^-Na^+), tetrakis(4-fluorophenyl)borate sodium ($TFPB^-Na^+$), bis(trifluoromethyl)phenyl]borate sodium ($TTFPB^-Na^+$), tetrakis(*p*-tolyl)borate sodium (TTB^-Na^+), *o*-nitrophenyl octylether (*o*-NPOE), di-*n*-octyl phthalate (DOP), bis(*o*-ethylhexyl) sebacate (DOS), 4-(2-hydroxyethyl)-1-piper-azineethanesulfonic acid (HEPES), Chelex-100 and poly(vinyl chloride) (PVC) were purchased from Sigma-Aldrich. N-(3-aminopropyl)methacrylamide (APMP), methylacrylic acid (MAA), acetylacetone, *p*-methoxyphenol, 2-methyl-2-[(dodecylsulfanylthiocarbonyl)sulfanyl]propanoic acid and horseradish peroxidase (HRP) were obtained from J&K Scientific Ltd. Hydrogen peroxide was purchased from Sinopharm Group Co. Ltd. The sequences of the oligonucleotides used in the present study 5'-TTTGGGTAGGGCGGGTTGGG-3' was purchased from Shanghai Sunny Biotech Co., Ltd. Poly-methylacrylic acid (polymer length =110), poly(diallyldimethylammonium chloride) (with different molecular weight),

polyacrylic acid (with different molecular weight),1, 4-dioxane and other reagents were obtained from Aladdin Industrial Inc.

Electrode Preparation and Electromotive Force Measurements. Polymeric liquid membranes containing PVC, different kinds of plasticizers and 1% (weight percentage) the receptor salt were prepared by the solvent-casting technique with tetrahydrofuran as the casting solvent. After transferring the cocktail into a glass ring fixed on a glass plate and letting tetrahydrofuran evaporate overnight, a uniform membrane of 200 μm thickness was obtained. Disks of 5-mm diameter were punched from the parent membrane and glued to plasticized PVC tubes (i.d. 3 mm, o.d. 5 mm) to fabricate the polymeric membrane electrodes. The inner filling medium of the electrode was 50 mM HEPES buffer (pH=7.4) contacting 10 mM NaCl. All electrodes were conditioned in 50 mM HEPES buffer (pH=7.4) containing 10 mM NaCl overnight before use. All electromotive force (EMF) values were measured using a CHI 760D electrochemical workstation (Shanghai Chenhua Apparatus Corporation, China) in the following galvanic cell in a Faraday cage: Ag, AgCl/3 M KCl/1 M LiOAc/sample solution (well-stirred, 1500 rpm)/sensing membrane/50 mM HEPES, 10 mM NaCl/AgCl, Ag.

General polymerization protocol for RAFT. 2-methyl-2-[(dodecylsulfanylthiocarbonyl)sulfanyl]propanoic acid (RAFT agent), monomer and AIBN were dissolved in methanol in the desired ratios, and the O_2 was removed by bubbling N_2 through the solution for 15 min. Polymerizations were carried out at monomer concentrations of 0.5 M and 1 M for MAA and APMA respectively. Reactions were performed at 70 °C, and conversion was monitored by ^{1}H-NMR and used to estimate the molecular weight of the polymer. The polymers were purified by precipitation from diethyl ether. Then the potential responses of the polymeric membrane electrodes to the products were recorded.

General polymerization protocol for FRP. MAA (2 M) or APMA (5 M), acac (100 mM), hydrogen peroxide (50 mM) and HRP (20 mg/ml) in buffer was degassed by bubbling N_2 for 15 min then sealed and allowed to react at 70 °C for up to 24 h. At selected time points the polymer conversion was determined. Then the potential responses of the polymeric membrane electrodes to the products were recorded.

Detection of HRP, Fe^{2+} and Cu^{2+}. In a typical experiment, Chelex-100 was used to cheat the metals in the solutions used for polymerization. Then the polymerization reactions were performed in 96-well plates containing 330 μL of GOx (200 nM), glucose (10 mM), APMA (0.5 M), acac (0.5 mM) and varying concentrations of HRP, Fe^{2+} and Cu^{2+} in HEPES buffer (50 mM, pH 7.4) at room temperature for 0.5 h. Then the potential responses of the DNNS-doped polymeric membrane electrodes to the diluted products were recorded. The detection limit was calculated using the 3σ method.

Detection of Catalase. In a typical experiment, polymerization reactions (APMP) were performed in 96-well plates containing GOx (200 nM), glucose (10 mM), acac (2 mM), APMP (0.5M) and catalase at different concentrations in HEPES buffer (50 mM, pH 7.4) at room temperature for 0.5 h. Then similar method as previous described was used for catalase detection.

Detection of G-quadruplex. In a typical experiment, the G-rich nucleic acid at different concentrations were incubated for a time-interval of 30 min at 25 °C in a HEPES buffer solution, 5 mM, pH = 7.4, containing $NaNO_3$, 200 mM, and KNO_3, 20 mM, in the presence of hemin, 5×10^{-9} M. The incubation time-interval was selected as the minimum time period required to stabilize the G-quadruplex/hemin. Then polymerization reactions were performed in 96-well plates containing GOx (200 nM), glucose (10 mM), acac (0.5 mM), MAA (0.5M) in HEPES buffer (50 mM, pH 7.4) at room temperature for 0.5 h. Then similar method as previous described was used for catalase detection.

Tab. S1 Reaction conditions and characterization data for polymers prepared by RAFT polymerization

Entry	Monomer	[RAFT]:[M]:[AIBN]	Time (h)	Conversion	Polymer Length	MW (Da)
1	APMP	1:30:0.4	24	54%	30	5340
2	APMP	1:60:0.4	24	43%	50	8900
3	APMP	1:90:0.4	24	32%	59	10502
4	APMP	1:120:0.4	24	30%	93	16554
5	MAA	1:30:0.4	20	79%	48	4128
6	MAA	1:60:0.4	20	68%	60	5160
7	MAA	1:90:0.4	20	41%	87	7482
8	MAA	1:120:0.4	20	11%	100	8600

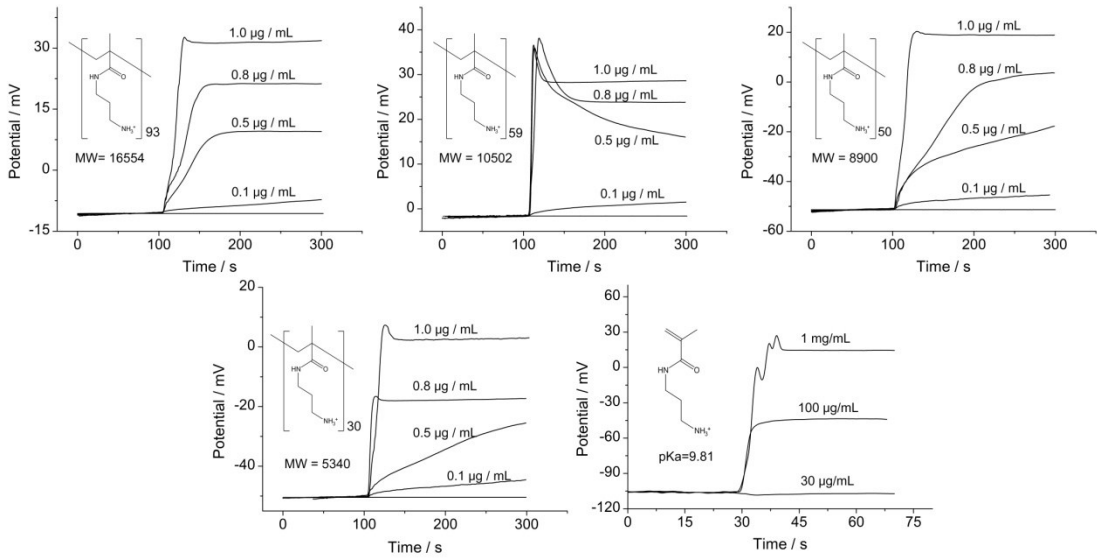

Fig. S1 Potentiometric responses of DNNS-doped polymeric membrane electrodes to varying concentrations of monomer and PAPMP with different polymer lengths generated by RAFT reactions. The sample medium was 50 mM HEPES buffer (pH=7.4).

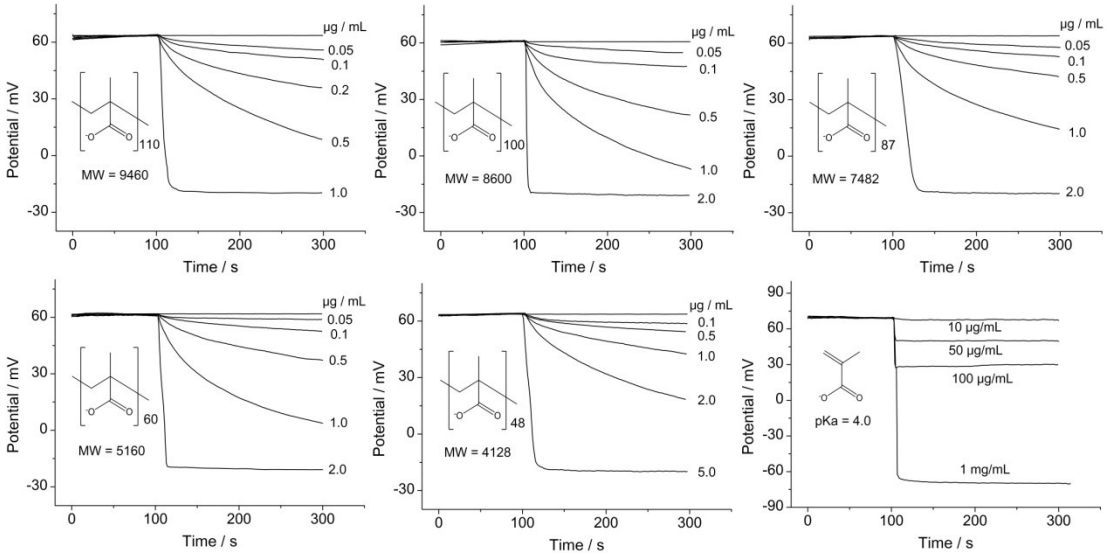

Fig. S2 Potentiometric responses of TDMACl-doped polymeric membrane electrodes to varying concentrations of monomer and PMAA with different polymer lengths generated by RAFT reactions. The sample medium was 50 mM HEPES buffer (pH=7.4).

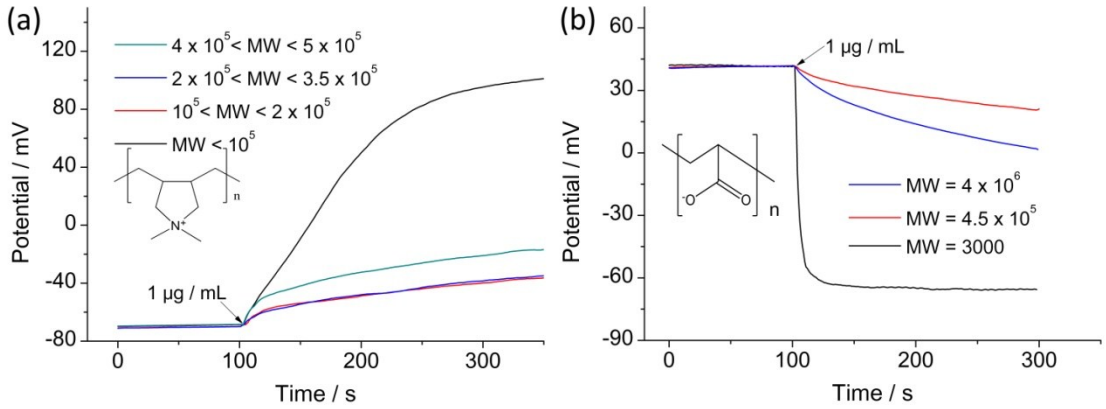

Fig. S3 Potentiometric responses of the polymeric membrane electrodes to (a) poly(diallyldimethylammonium chloride) and (b) polyacrylic acid with different molecular weights. The sample medium was 50 mM HEPES buffer (pH=7.4).

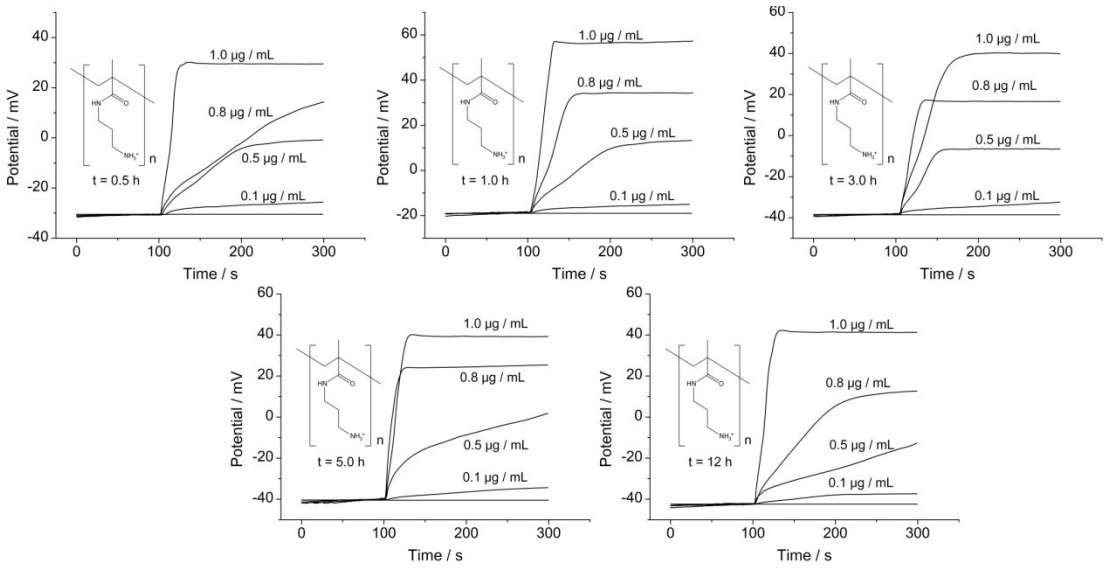

Fig. S4 Potentiometric responses of DNNS-doped polymeric membrane electrodes to varying concentrations of monomer and PAPMP generated by FRP reactions at different time intervals. The sample medium was 50 mM HEPES buffer (pH=7.4).

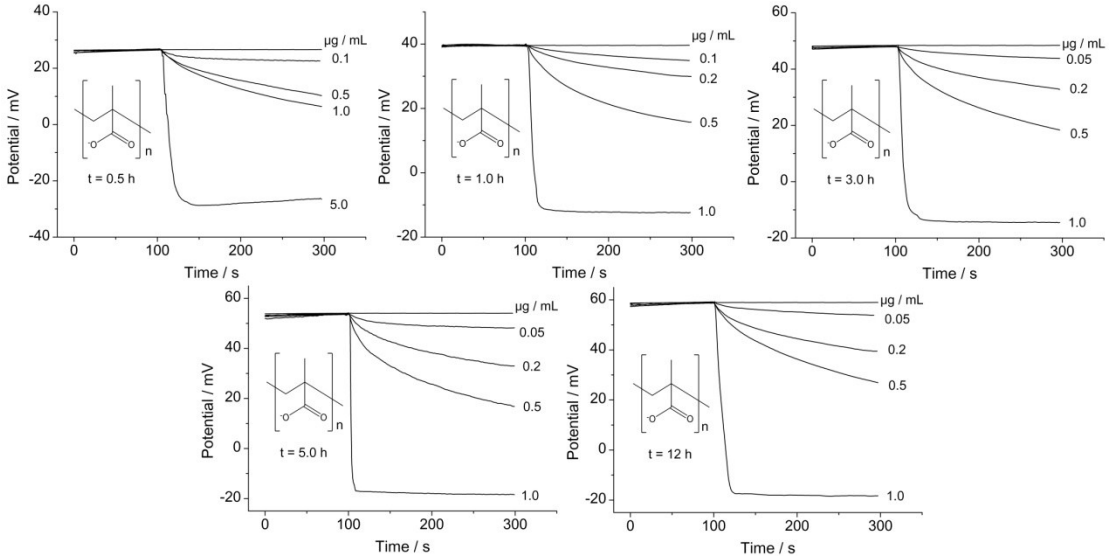

Fig. S5 Potentiometric responses of TDMACl-doped polymeric membrane electrodes to varying concentrations of monomer and PMAA generated by FRP reactions at different time intervals. The sample medium was 50 mM HEPES buffer (pH=7.4).

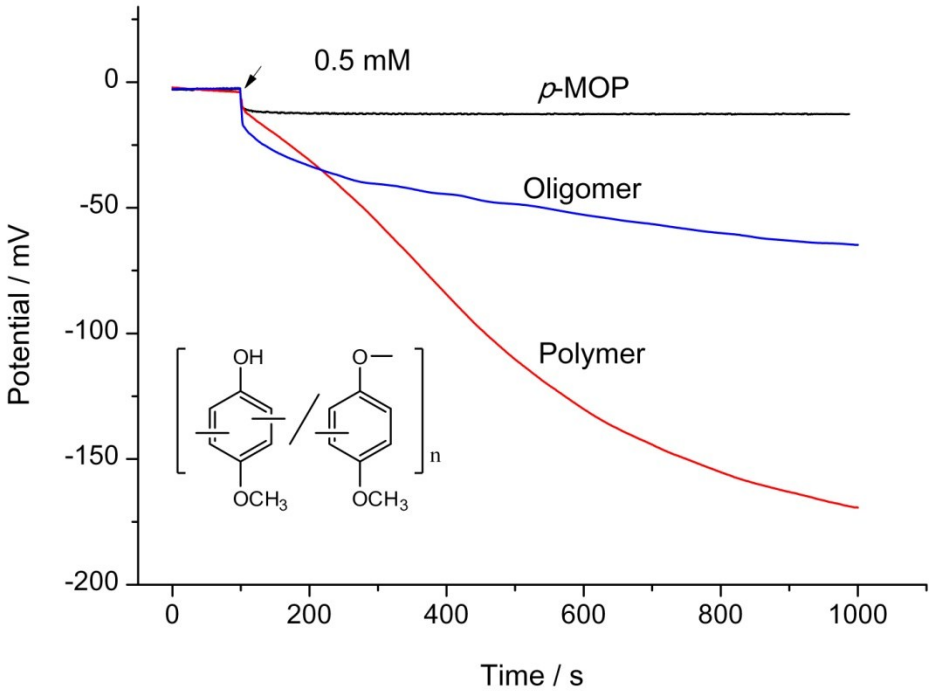

Fig. S6 Potentiometric responses of TDMACl-doped polymeric membrane electrodes to 0.5 mM p-MOP, oligomers (products from FRP reaction processed in aqueous buffer) and polymers (products from FRP reaction processed in organic/aqueous buffer mixture). The sample medium was 50 mM HEPES buffer (pH=7.4).

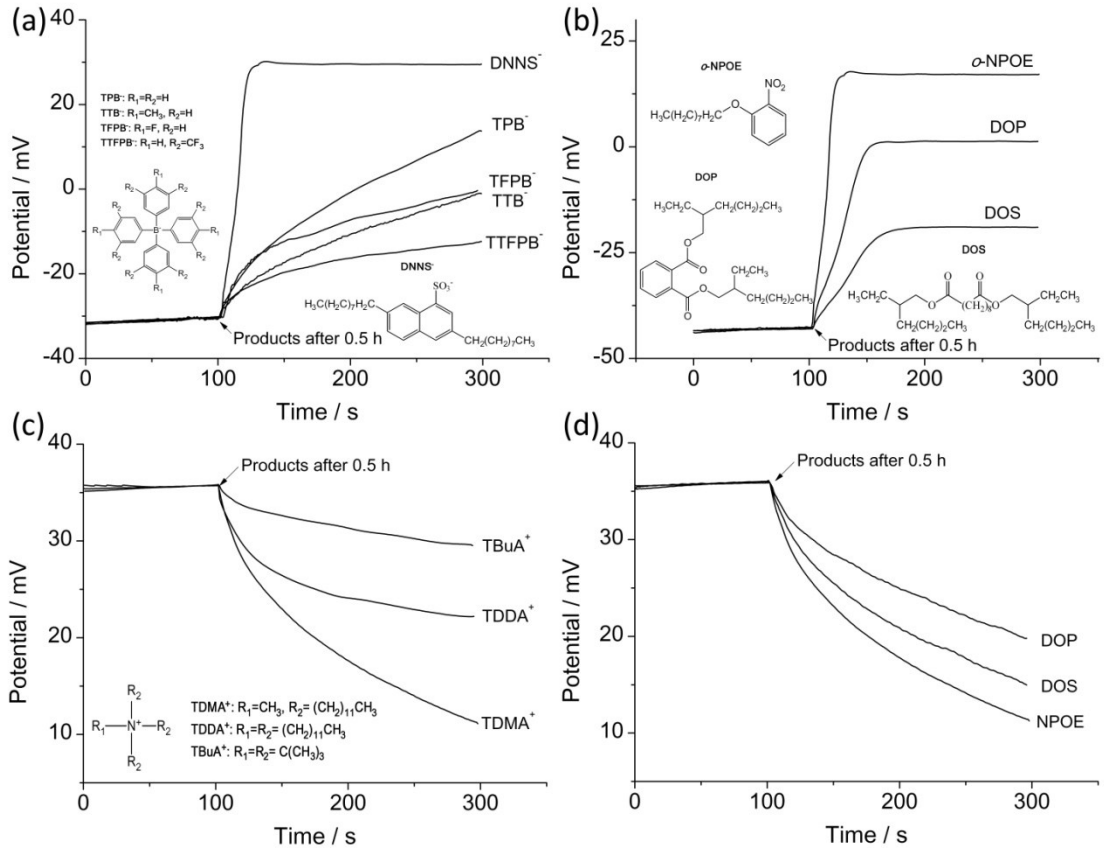

Fig. S7 Potentiometric responses of (a) NPOE plasticized polymeric membrane electrodes containing different recognition elements, (b) DNNS-doped polymeric membrane electrodes plasticized with different plasticizers to the PAPMP, (c) NPOE plasticized polymeric membrane electrodes containing different recognition elements, (d) TDMACl-doped polymeric membrane electrodes plasticized with different plasticizers to the PMAA generated from FRP after 0.5 h. The sample medium was 50 mM HEPES buffer (pH=7.4).

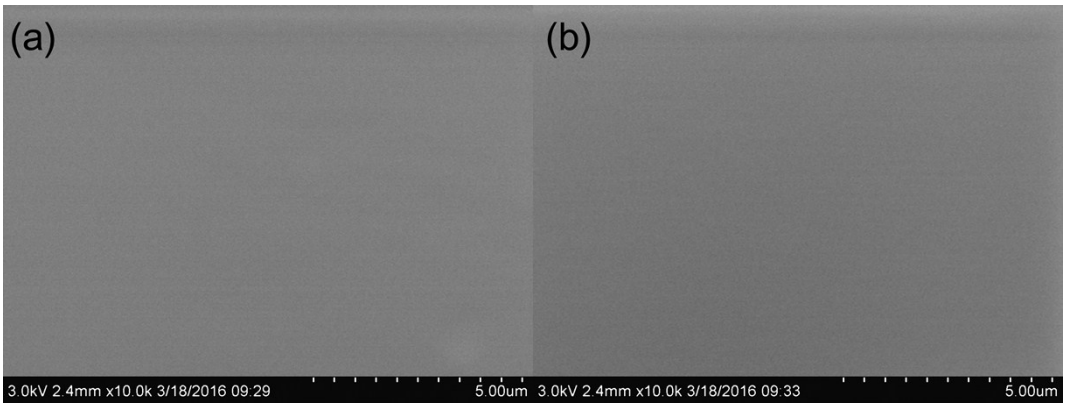

Fig. S8 SEM of the (a) polyanion and (b) polycation sensitive membranes.

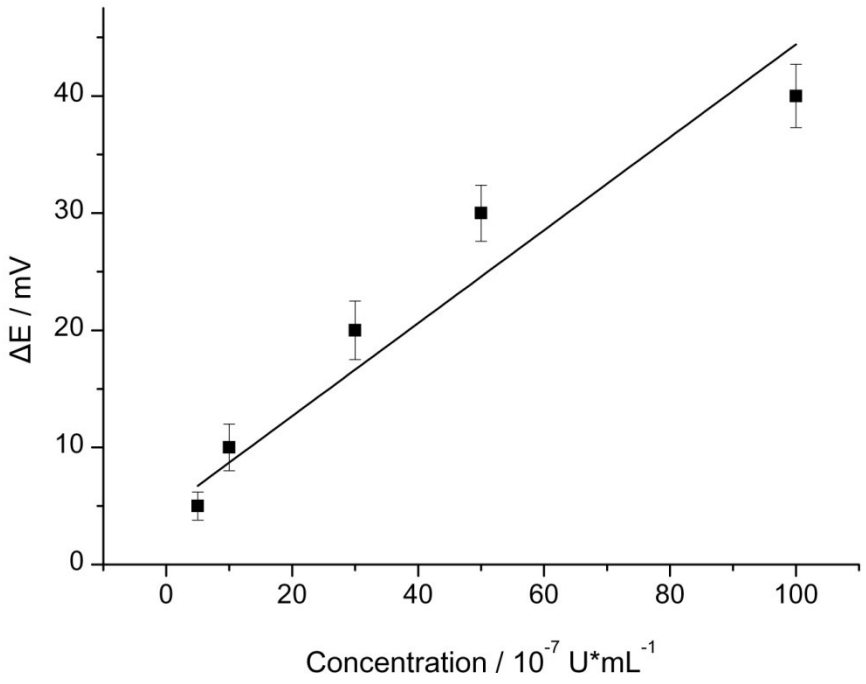

Fig. S9 Calibration curve for HRP detection. Each error bar represents one standard deviation of 3 replications.

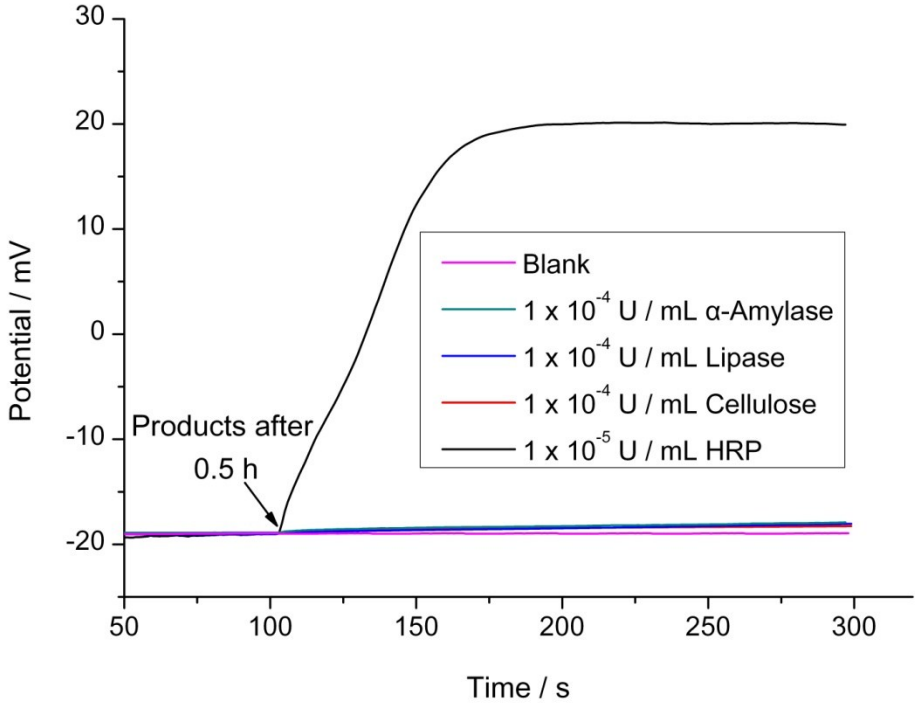

Fig. S10 Potentiometric detection of 1×10^{-5} M HRP, 1×10^{-4} M cellulose, 1×10^{-4} M lipase and 1×10^{-4} M α-amylase using the proposed sensing platform.