Electronic Supplementary Material (ESI) for Analytical Methods.

ELECTRONIC SUPPORTING INFORMATION (ESI)

Magneto-controlled microfluidic device for voltammetric immunoassay of carbohydrate antigen-125 with silver-polypyrrole nanotags

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Cyclic voltammetric characteristics of Ag-PPy nanohybrids

To investigate the cyclic voltammetric characteristics of the as-synthesized Ag-PPy nanohybrids, 50 μL of Ag-PPy suspension (25 mg mL^{-1}) was dropped on the cleaned ITO electrode, and dried at room temperature. Following that, cyclic voltammograms of Ag-PPy-modified ITO electrode was studied at different scan rates in 0.1 M $NaNO_3$ from -0.5 V to +0.4 V. As seen from Fig. S1, the peak current increased along with the rising of scan rate, while the ΔE_p expanded slowly. Moreover, the anodic and cathodic peak currents increased linearly with scan rate, v, not with $v^{1/2}$, in the range of 10 – 400 mV s^{-1}, indicating that the redox reaction is a surface process. When $n\Delta E_p < 200$ mV, the electron transfer rate constant K_s of Ag-PPy on the ITO electrode can be estimated by the following equation:[1,2]

$$\text{Log } K_s = \alpha \log (1 - \alpha) + (1 - \alpha) \log \alpha - \log (RT/nFv) - \alpha(1 - \alpha)\, nF\Delta E_p/2.3RT$$

Taking a charge transfer coefficient α of 0.5, and a scan rate of 100 mV s^{-1}, and then the electron transfer rate constant (k_s) was 4.78 ± 0.67 s^{-1}.

Characteristics of cyclic voltammetry (CV) on differently modified ITO electrodes

Cyclic voltammogram (CV) is usually used as a valuable and convenient tool to monitor the barrier of differently modified electrodes, because the electron transfer between the solution species and the electrode must occur by tunneling either through the barrier or through the defects in the barrier. Therefore, it was chosen as a marker to investigate the changes of electrode behavior after each assembly step. When electrode surface has been modified by some materials, the electron transfer kinetics is perturbed. Fig. S3 shows cyclic voltammograms of differently modified ITO electrodes in 0.1 M $NaNO_3$. No redox peaks were observed at ITO electrode (curve '*a*'), mAb_1-MB-modified ITO electrode (curve '*b*') and CA-125/mAb_1-MB/ITO (1.0 U mL^{-1} used in this case) (curve '*c*'). However, the background currents of ITO electrode decreased upon introduction of mAb_1-MB and target CA-125 in sequence, indicating that mAb_1-MB and target CA-125 had weak conductivity, and hindered electron transfer between the solution and the electrode. After CA-125/mAb_1-MB/ITO reacted with Ag-PPy-pAb_2, significantly, a couple of redox waves at -270 mV and +19 mV (*vs*. Ag/AgCl) was achieved (curve '*d*'). The redox peaks mainly derived from the silver/silver dioxide

nanocomposites, because it is easy for silver colloids to form silver/silver dioxide nanocomposites due to the instability of silver colloids under the light.[3,4] These results indicated that magneto-controlled immunoassay between mAb_1-MB and Ag-PPy-pAb_2 could be preliminarily applied for the detection of target CA-125.

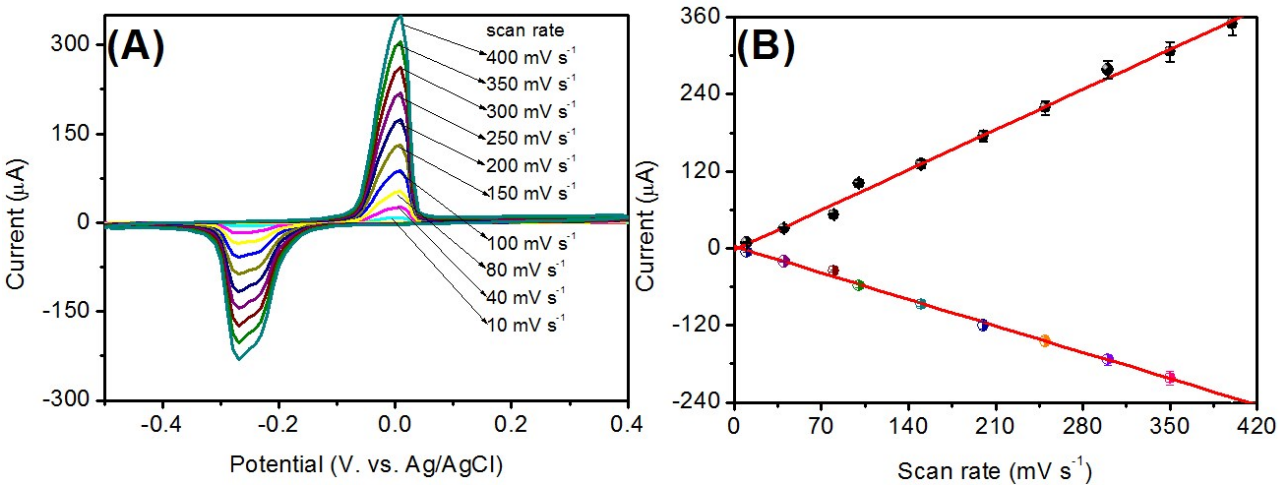

Fig. S1 (A) Cyclic voltammograms of Ag-PPy-modified ITO working electrode at different scan rates in 0.1 M $NaNO_3$, and (B) the relationship between redox peak currents and scan rate. Scan range: -0.5 – +0.4 V (*vs*. Ag/AgCl), Starting potential: -0.5 V.

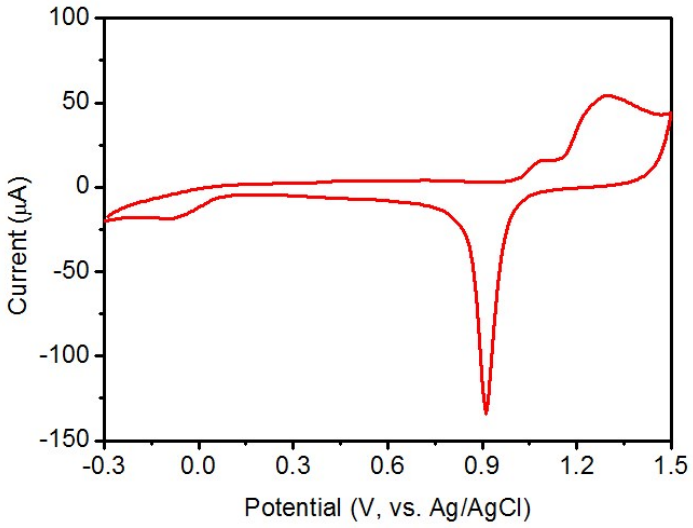

Fig. S2 Cyclic voltammogram of bare ITO working electrode in 0.1 M H_2SO_4 solution. Scan rate: 50 mV s^{-1}; Scan range: -0.3 – 1.5 V (*vs*. Ag/AgCl), Starting potential: -0.3 V.

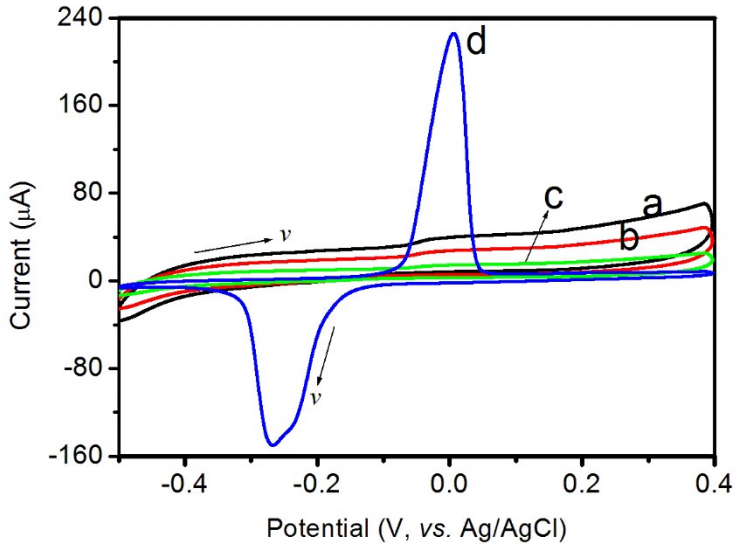

Fig. S3 Cyclic voltammograms of (a) bare ITO electrode, (b) electrode '*a*' after modification with mAb_1-MB (50 μL, 25 mg mL^{-1}), (c) electrode '*b*' after incubation with 1.0 U mL^{-1} CA-125, and (d) electrode '*c*' after reaction with Ag-PPy-pAb_2 (50 μL, 25 mg mL^{-1}) in 0.1 M $NaNO_3$ (scan range: -0.5 – 0.4 V; scan rate: 50 mV s^{-1}).

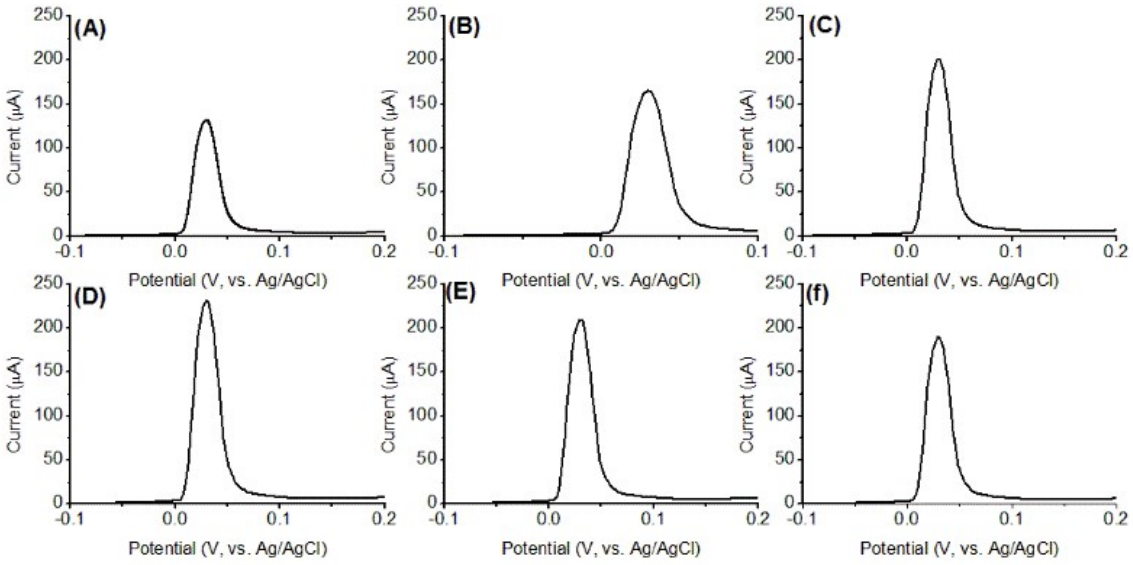

Fig. S4 LSV responses of electrochemical immunosensing platform based on the as-prepared Ag-PPy nanohybrids with different volume ratios between pyrrole and $AgNO_3$: (A) 5 : 3, (B) 2 : 1, (C) 5 : 2, (D) 5 : 1, (E) 10 : 1, and (F) 20 : 1, in 0.1 M $NaNO_3$ solution (1.0 U mL^{-1} CA-125 used in this case) from -100 mV to +200 mV (*vs*. Ag/AgCl) at 50 mV s^{-1}.

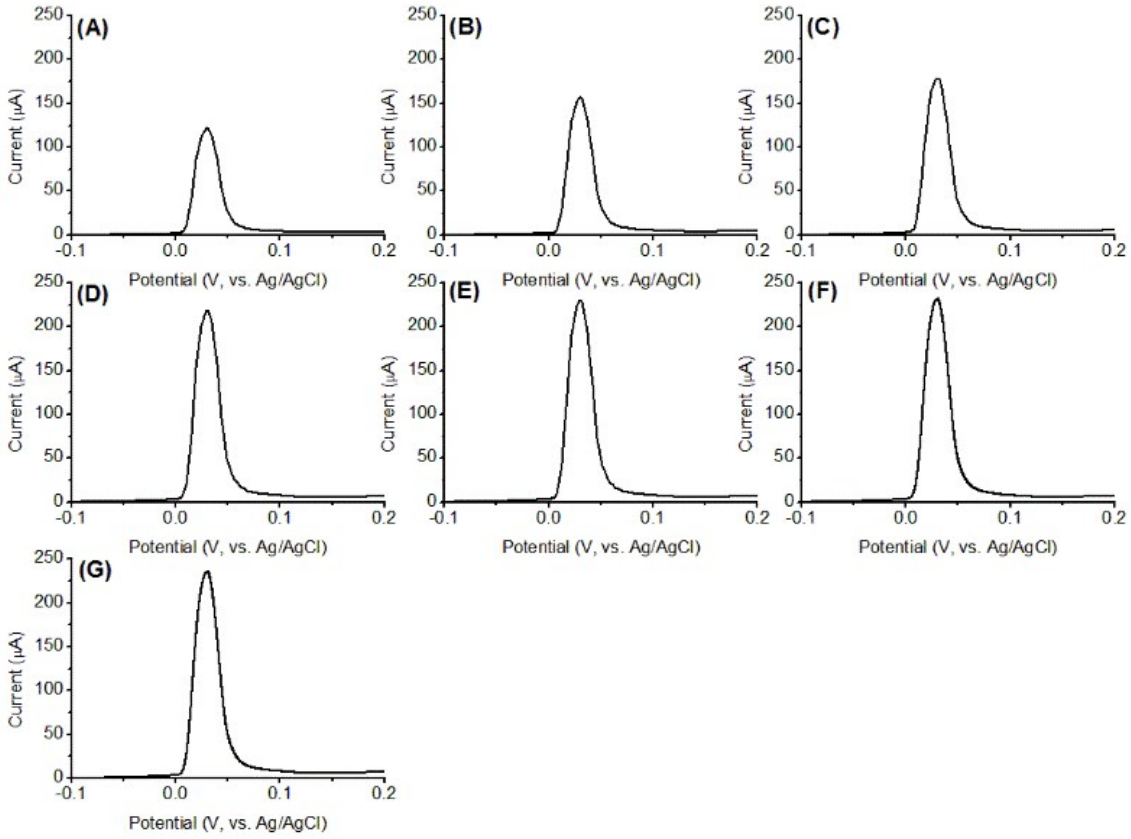

Fig. S5 LSV responses of electrochemical immunosensing platform by using various incubation/immunoreaction times between mAb_1-MB and CA-125/Ag-PPy-pAb_2: (A) 5 min, (B) 10 min, (C) 15 min, (D) 20 min, (E) 25 min, (F) 30 min and (G) 35 min in 0.1 M $NaNO_3$ solution (1.0 U mL^{-1} CA-125 used in this case) from -100 mV to +200 mV (*vs*. Ag/AgCl) at 50 mV s^{-1}.

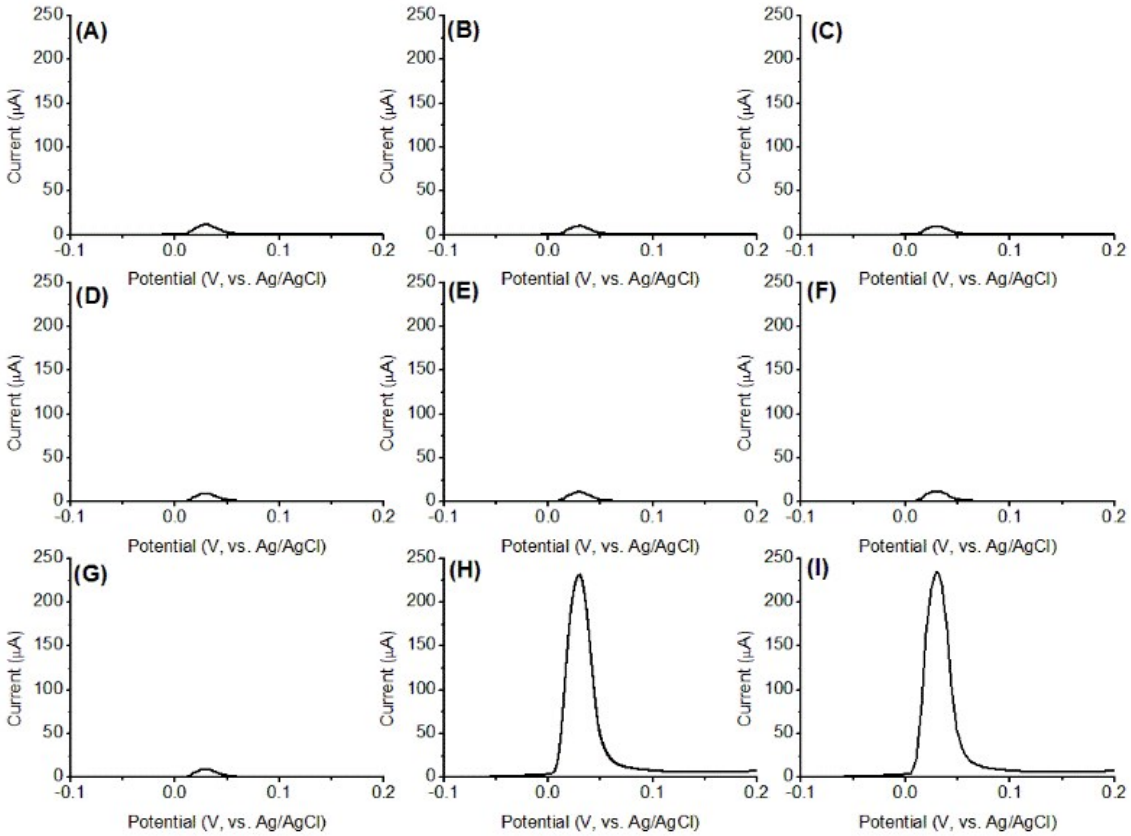

Fig. S6 LSV responses of electrochemical immunosensing platform in 0.1 M $NaNO_3$ toward different analysts: (A) 1000 ng mL^{-1} NSE, (B) 1000 ng mL^{-1} CEA, (C) 1000 ng mL^{-1} AFP, (D) 1000 ng mL^{-1} PSA, (E) 1000 U mL^{-1} CA 15-3, (F) 1000 U mL^{-1} CA 19-9, (G) 1000 ng mL^{-1} HIgG, (H) 1.0 U mL^{-1} CA-125 and (I) mixture containing the above-mentioned analytes from -100 mV to +200 mV (*vs*. Ag/AgCl) at 50 mV s^{-1}.

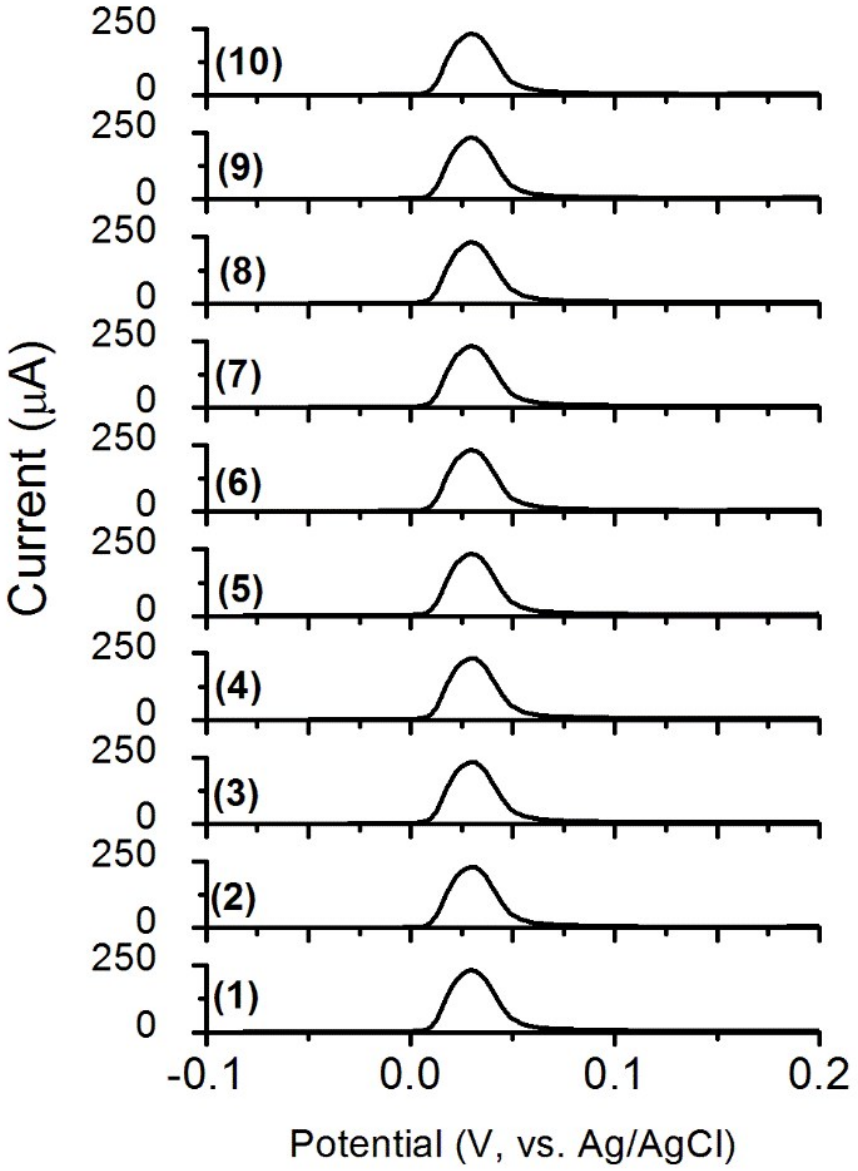

Fig. S7 LSV responses of electrochemical immunosensing platform in 0.1 M $NaNO_3$ toward 1.0 U mL^{-1} CA-125 with repeated assay times (from bottom to upper: 1st time to 10th time) on the magneto-controlled sensing interface by attaching or detaching the external magnet from -100 mV to +200 mV (*vs*. Ag/AgCl) at 50 mV s^{-1}.

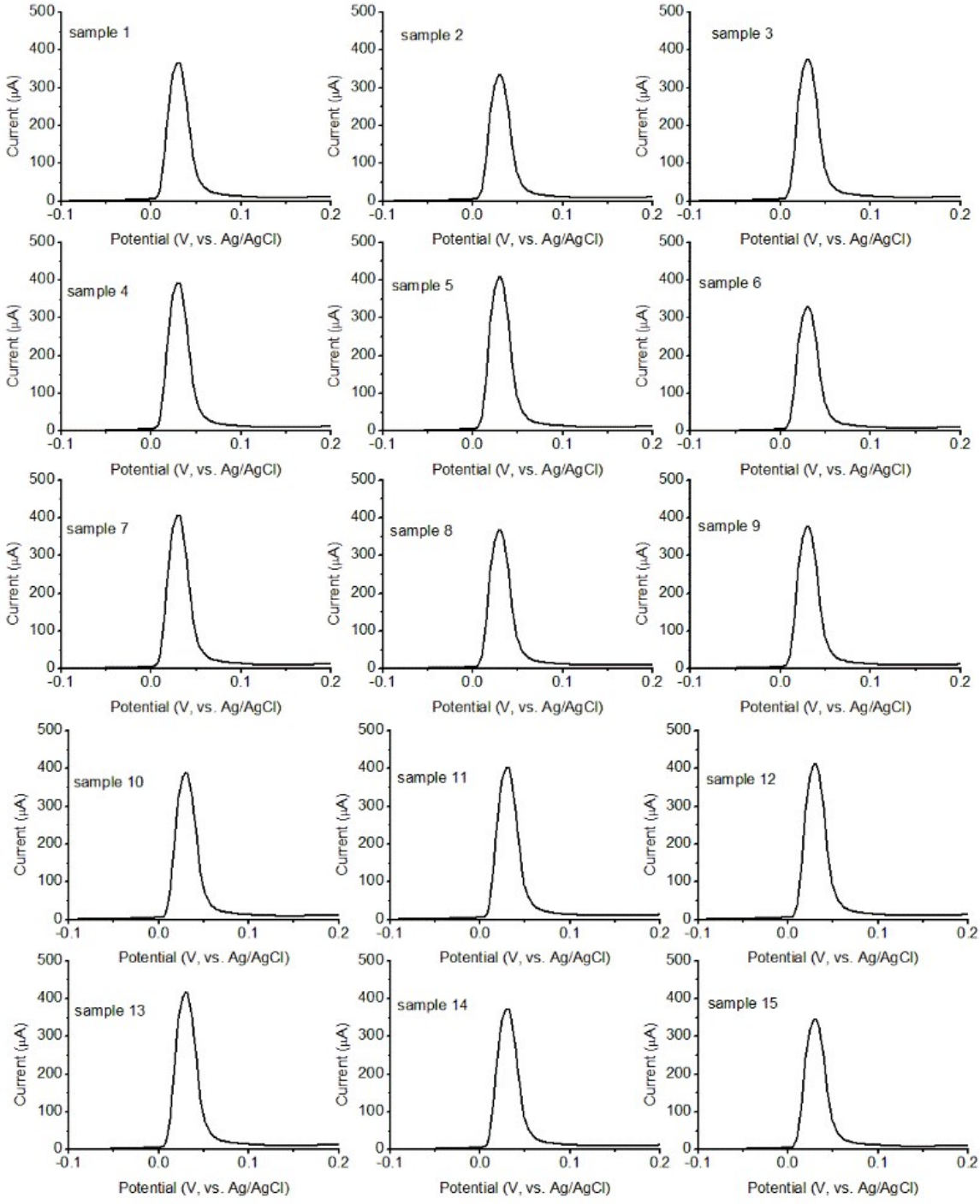

Fig. S8 LSV responses of electrochemical immunosensing platform in 0.1 M $NaNO_3$ toward 15 human serum specimens from -100 mV to +200 mV (*vs*. Ag/AgCl) at 50 mV s^{-1}.

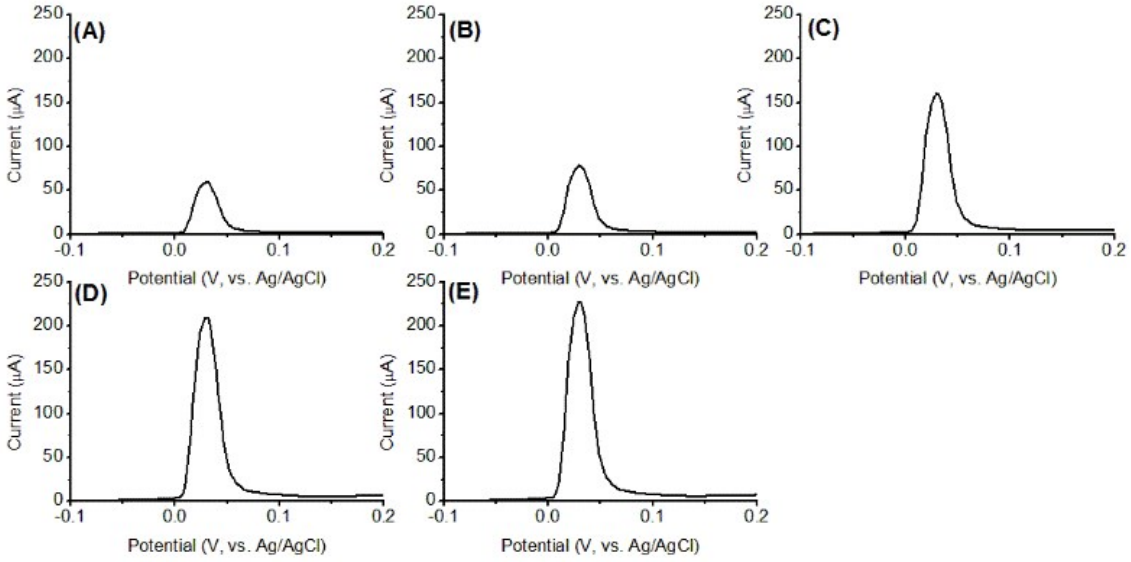

Fig. S9 LSV responses of electrochemical immunosensing platform in 0.1 M $NaNO_3$ for the analysis of 5 spiked blank calf serum samples including 5.0, 10, 100, 500 and 1000 pg mL^{-1} CA-125 from -100 mV to +200 mV (*vs*. Ag/AgCl) at 50 mV s^{-1}.

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