Supporting Information

Sensitive electrochemical immunosensor array for the simultaneous detection of multiple tumor markers

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Preparation of base electrode array.

Schematic diagram of the base electrode array designed in this study is shown in Fig. 1A. The electrode strips were deposited onto an epoxy film by thick-film technology. [1] A manual stainless steel pattern was utilized to produce thick-film electrodes. Eight carbon strips (18 mm × 16 mm × 0.5mm), each of them corresponding to the pattern shown in Fig. 1A, were printed on an epoxy substrate by forcing the commercial conductive carbon ink to penetrate through the mask of screen stencil using a rubber squeegee. Then the silver paste was imprinted to the area of the reference electrode designed. After each printing, the printed films were allowed to dry at 50 – 60 ℃ for 1 h. The Ag/AgCl reference electrode was obtained by electrochemical chloridization of printed silver layer in a 0.10 M hydrochloride acid solution, [2] followed to wash with water.

After that, a second layer, composed of insulating dielectric oil (Electrodag 452SS) was then printed onto the microarrays to define a window (easily covered with a 50 μL drop of solution) and the conductive bands were insulated by overlaying an insulating dielectric oil except on the electrical contact area and the working electrode area.

1. C.X. Zhang, Q. Gao, M. Aizawa, Flow injection analytical system for glucose with screen-printed enzyme biosensor incorporating Os-complex mediator, 2001, Anal. Chim. Acta , 426, 33–41.

2. J. Shen, C.C. Liu, Development of a screen-printed cholesterol biosensor: Comparing the performance of gold and platinum as theworking electrode material and fabrication using a self-assembly approach, 2007, Sens. Actuators, B 120, 417–425

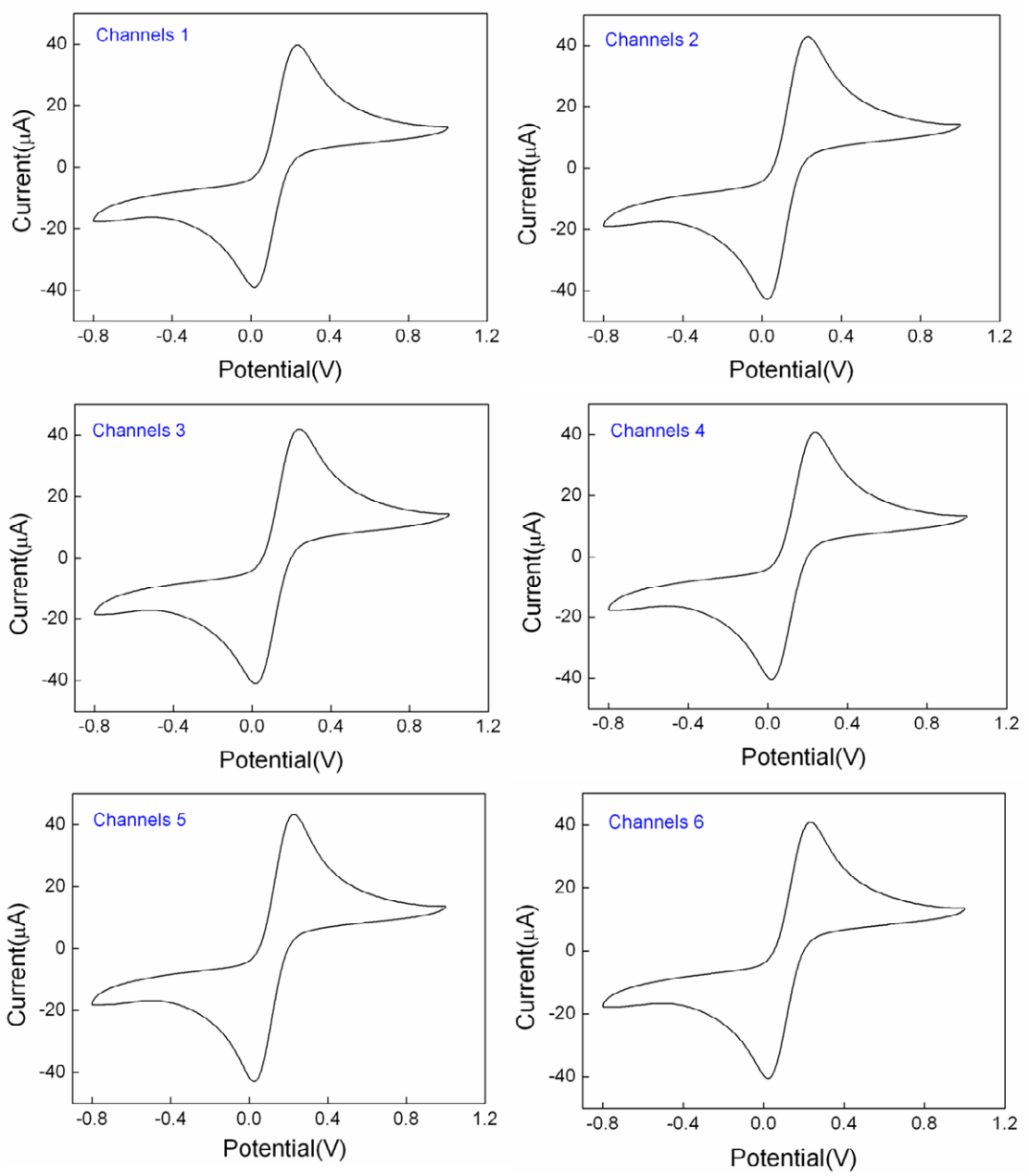

Figure S-1 Cyclic voltammograms of base electrode array fabricated in 0.1 M KCl – 5.0 mM $K_3(FeCN)_6$. Scan rate: 100 mV/s. Different channels represent different working electrodes.

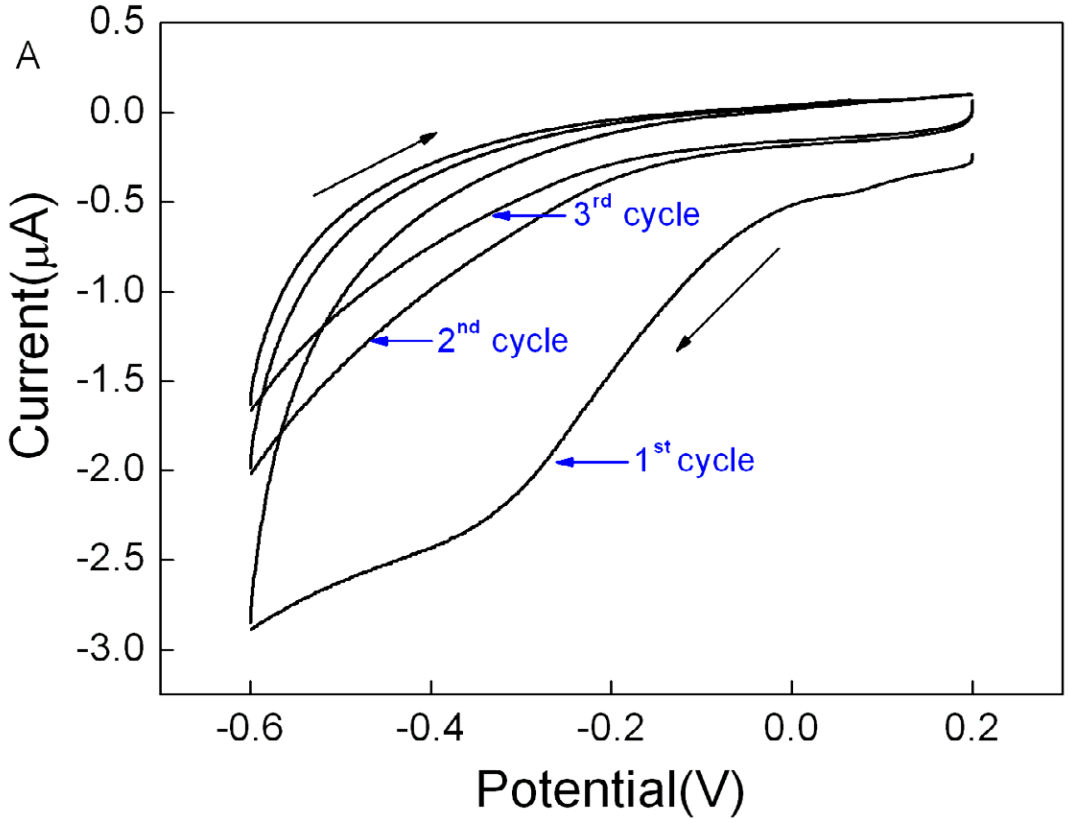

Figure S-2 A. Cyclic voltammograms for the electrochemical grafting of the aryl diazonium cation generated *in situ* from p-phenylenediamine to screen-printed carbon electrode in acid solution containing 5 mM $NaNO_2$, 5 mM p-phenylenediamine and 0.50 M HCl. Scan rate of 50 mV/s.

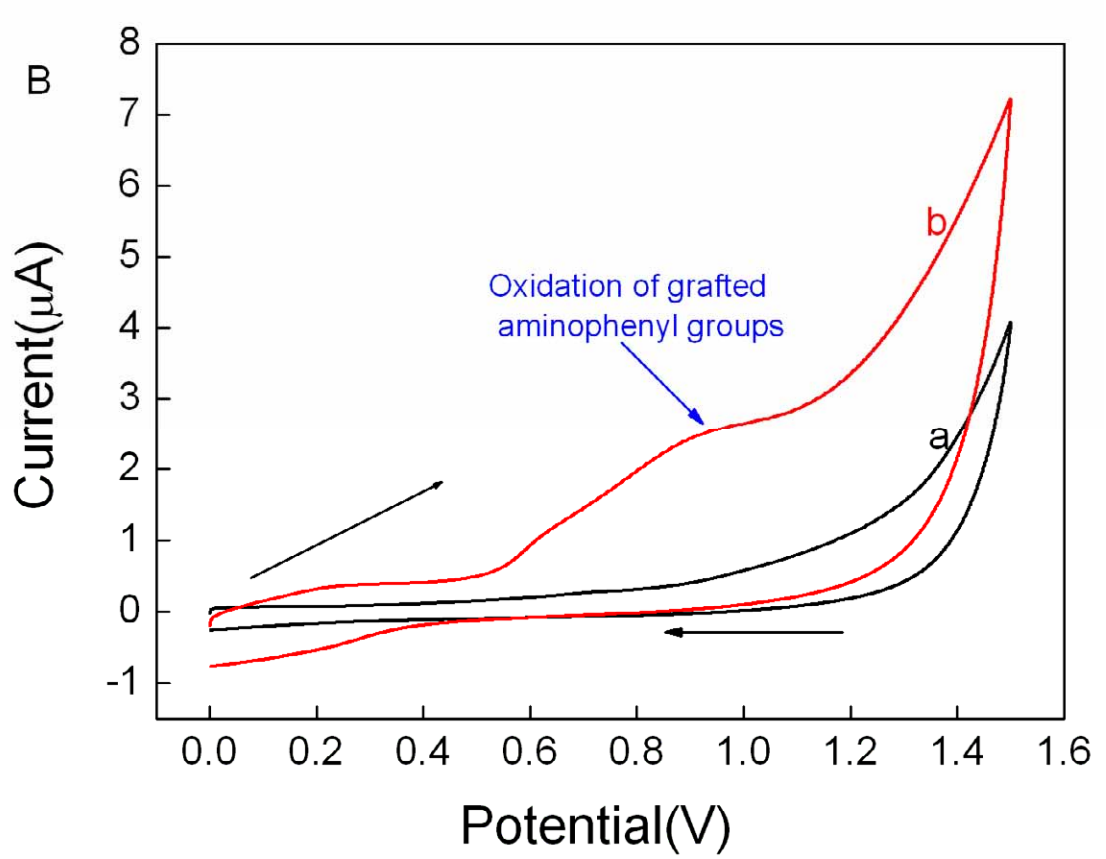

Figure S-2B. Cyclic voltammograms of a screen-printed carbon electrode modified by aminophenyl groups in 0.10 M PBS (pH＝7.0) at a scan rate of 100 mV/s. (a) at bare screen-printed carbon electrode, (b) at aminophenyl groups modified electrode.

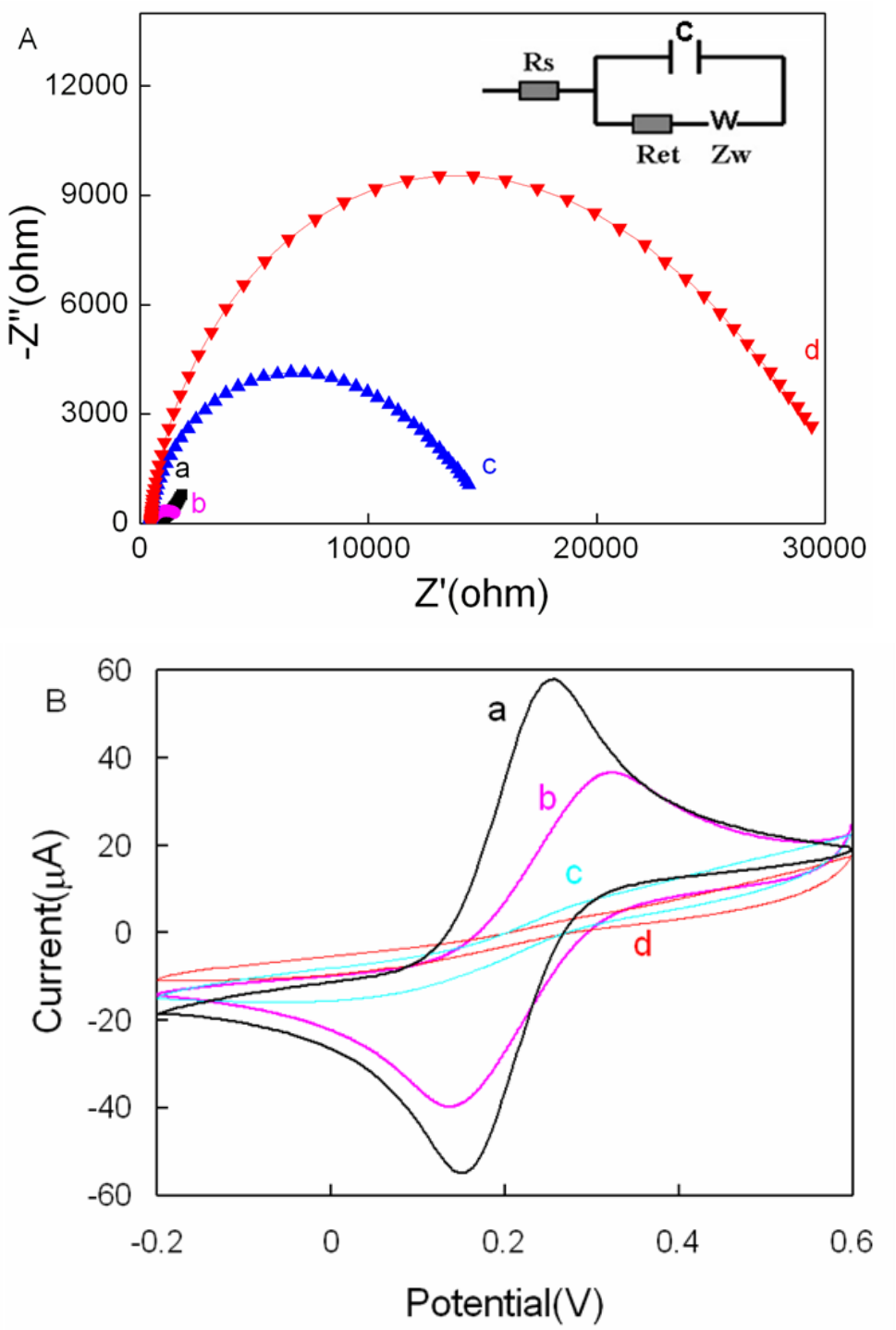

Figure S-3. Nyquist plots of impedance spectra (A) and cyclic voltammograms (B) obtained at (a) bare screen-printed carbon electrode; (b) aminophenyl groups modified electrode; (c) aldehyde groups modified electrode; (d) capture antibody modified electrode.

The measurement conditions: 0.10 M PBS containing 5 mM $K_3[Fe(CN)_6]$, 5 mM $K_4[Fe(CN)_6]$ and 0.10 M KCl (pH＝7.0)

(A) The biased potential of 0.226 V, the frequency from 100 kHz to 0.1 Hz, and the amplitude of 5.0 mV. The inset shows the equivalent circuit applied to fit the impedance spectra.

(B) Scan rate in cyclic voltammogram, 50 mV/s.