

## Supporting Information

### **Electrochemiluminescence immunosensor based on multipath signal catalytic amplification integrated in Cu<sup>2+</sup>-PEI-Pt/AuNCs nanocomposite**

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**Reagents and apparatus.**  $\beta$ 2-Microglobulin ( $\beta$ 2-MG), Carcinoembryonic antigen (CEA),  $\alpha$ -1-fetoprotein (AFP) and its antibody were purchased from Biocell Company (Zhengzhou, China). Trisodium citrate ( $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ ) was got from J&K Scientific Ltd. (Beijing, China). Chloroplatinic acid ( $\text{H}_2\text{PtCl}_6$ ), Chlorauric acid ( $\text{HAuCl}_4$ ), bovine serum albumin (BSA) and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) were bought from Sigma-Aldrich (St. Louis, MO, USA). Phosphate-buffered solution (PBS) prepared by  $\text{KH}_2\text{PO}_4$  (0.1 M),  $\text{Na}_2\text{HPO}_4$  (0.1 M) and KCl (0.1 M) (pH 7.4, 0.1 M) was used in the this work. The human serum samples were obtained from Southwest Hospital in chongqing.

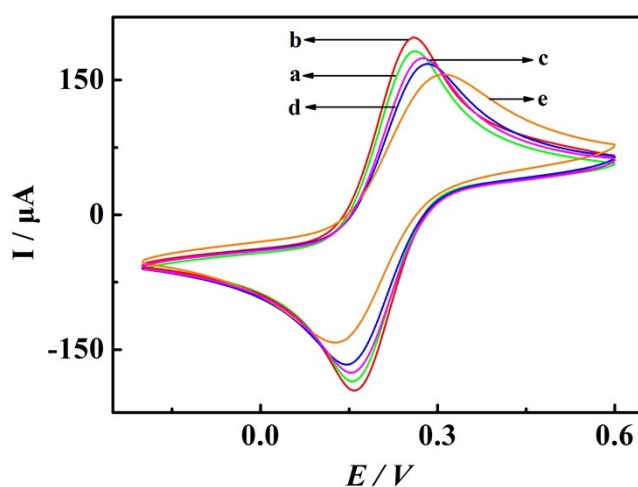
MPI-E ECL analyzer used for the ECL measurement in this work was obtained from Xi'an Remax Electronic science & Technology Co.Ltd. (potential scanning range: -2~0 V, photomultiplier tube: 800 V). The three-electrode system consist of the modified glassy carbon electrode (GCE, working electrode), Ag/AgCl (sat. KCl, reference electrode) and

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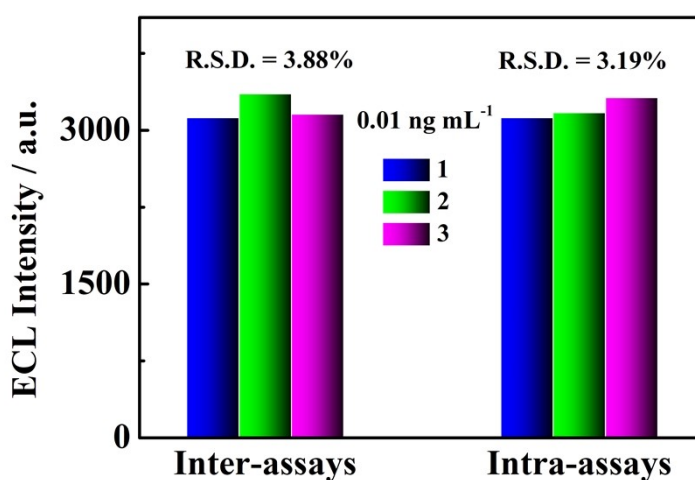
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platinum wire (counter electrode) and was used in ECL detection. The scanning electron microscopy (SEM, S-4800, Hitachi, Japan) and X-ray photoelectron spectroscopy (XPS) and were used for characterization of nanomaterials.



**Fig. S1.** CVs curves of bare (a) GCE, (b) GCE/AuNPs, (c) GCE/AuNPs/Ab, (d) GCE/AuNPs/Ab/BSA, (e) GCE/AuNPs/Ab/BSA/AFP in 5 mM  $[\text{Fe}(\text{CN})_6]^{3-/4-}$ .



**Fig. S2.** The reproducibility of intra- and inter-assays