## **Supporting Information**

## Electrochemically Controlled ATRP for Cleavage-Based Electrochemical Detection of Prostate-Specific Antigen at the Concentration of Femtomolar Level

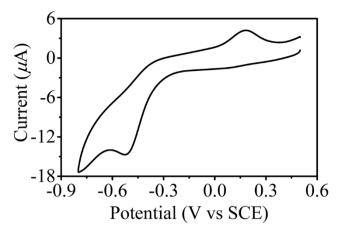
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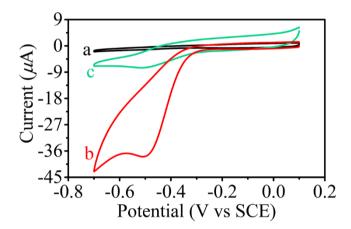
University, Guangzhou 510006, P. R. China. E-mail: <a href="mailto:ccywzhang@gzhu.edu.cn">ccywzhang@gzhu.edu.cn</a>. Tel.:
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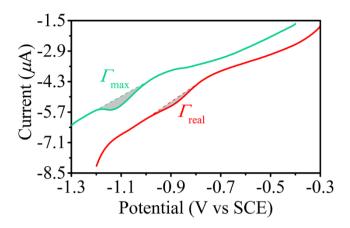
- **Figure S-1:** Cyclic voltammogram of the AuE/MCH/P-COOH/Zr(IV)/BPAA in the FcMMA-free polymerization solution.
- **Figure S-2:** Reduction wave of the dissolved oxygen.
- **Figure S-3:** Reductive desorption of PSA peptides using LSV.
- **Figure S-4:** Elemental mappings of Zr and Br.
- **Figure S-5:** Peak currents before and after a storage at 4 °C for two weeks.
- **Figure S-6:** Peak current toward the untreated NHS.



**Figure S-1:** Cyclic voltammogram of the AuE/MCH/P-COOH/Zr(IV)/BPAA in the FcMMA-free polymerization solution. PSA, 10 nM; scan rate, 0.1 V s<sup>-1</sup>.



**Figure S-2:** Cyclic voltammogram of the AuE/MCH/P-COOH/Zr(IV)/BPAA in the (a)  $N_2$ - or (b)  $O_2$ -saturated, FcMMA- and  $Cu^{II}Br/Me_6TREN$ -free polymerization solution, or in the (c)  $N_2$ -saturated, FcMMA-free polymerization solution. PSA, 10 nM; scan rate, 0.1 V s<sup>-1</sup>;  $Cu^{II}Br/Me_6TREN$ , 0.5 mM. From curves b and c, it is clear to see that the reduction wave of oxygen overlaps with that of the  $Cu^{II}Br/Me_6TREN$  deactivator. That is, the dissolved oxygen is consumed during the electrogeneration of  $Cu^{I}/Me_6TREN$  activators. That's why the eATRP of FcMMA in this work can be performed without deoxygenating.



**Figure S-3:** LSV curves of reductive desorption of PSA peptides in 0.5 M KOH (N<sub>2</sub> saturated). Scan rate, 0.02 V s<sup>-1</sup>; quiet time, 30 s. The  $\Gamma$  values can be calculated according to  $\Gamma = Q/FAv$ , where Q, F, A, and v represent the integral value of the desorption wave (~0.0236  $\mu$ A V for  $\Gamma_{real}$  and ~0.0488  $\mu$ A V for  $\Gamma_{max}$ ), the Faraday constant, the electrochemical surface area (0.071 cm<sup>2</sup>), and the scan rate (0.02 V s<sup>-1</sup>).

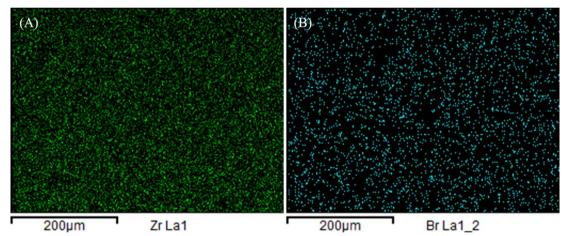
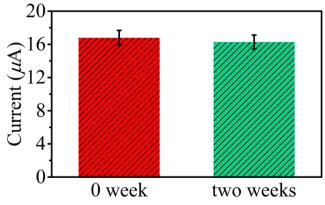
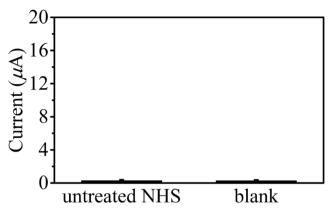


Figure S-4: Elemental mappings of (A) Zr and (B) Br. PSA, 10 nM.



**Figure S-5:** Peak currents of the AuE/MCH/P-COOH/Zr(IV)/BPAA/Fc before and after a storage for two weeks. PSA, 10 nM. Error bars show the standard deviations (n = 4).



**Figure S-6:** Peak currents derived from the untreated NHS and the blank control. Error bars show the standard deviations (n = 4).