# Supporting Information

## Stimuli-enabled Switch-like Paracetamol Electrochemical Sensor Based on Thermosensitive Polymer and MWCNTs-GQDs Composite Nanomaterial

**Pengcheng Zhao[a], Meijun Ni[a], Chao Chen[b,c], Zhidu Zhou[b], Xiping Li[b], Chunyan Li[a], Yixi Xie[b]*, Junjie Fei[a,c]***

[a] *Key Laboratory of Environmentally Friendly Chemistry and Applications of Ministry of Education, College of Chemistry, Xiangtan University, Xiangtan 411105, People's Republic of China*

[b] *Key Laboratory for Green Organic Synthesis and Application of Hunan Province, Xiangtan 411105, People's Republic of China*

[c] *Hunan Institute of Advanced Sensing and Information Technology, Xiangtan University, Xiangtan 411105, People's Republic of China*

** Junjie Fei, Ph.D., College of Chemistry, Xiangtan University, Xiangtan, China*

*E-mail: fei_junjie@xtu.edu.cn*

*Tel.: 86-731-58292060*

** Yixi Xie, Ph.D., College of Chemistry, Xiangtan University, Xiangtan, China*

*E-mail: xieyixige@126.com*

**Preparation of the MWCNTs-COOH**

The 90 mL of concentrated sulfuric acid was added to 30 mL of concentrated nitric acid under constant stirring to obtain the mixed acid ($H_2SO_4/HNO_3$ (3:1)). 200 mg of multi-walled carbon nanotubes were added to 120 mL of mixed acid and ultrasonically dispersed for 1 hour. Next, the dispersion was refluxed at 60 ° C for 6 hours and cooled to room temperature. The dispersion was diluted with deionized water and filtered using polytetrafluoroethylene (PTFE) microfiltration membrane (220 nm) and repeated three times. Finally, MWCNTs-COOH was vacuum dried at 60 ° C and collected.

**Preparation of the PS-PNIPAm-PS**

**Materials:** N-isopropyl-acrylamide (NIPAm) from Aladdin was recrystallized three times in the n-hexane. S, S'-Bis (α, α'-dimethyl-α''-acetic acid)-trithiocarbonate (DMATC) was synthesized according to the literature procedure. Azodiisobutyronitrile (AIBN) was obtained from Aladdin. The styrene was purified by passing through a basic alumina column. Other chemical reagents were of analytical grade.

**Preparation of PS macro-CTA:** Five milliliter of styrene (4.53 g, 43.5 mmol), DMATC (0.202 g, 0.69 mmol) and AIBN (0.012 g, 0.073 mmol) were dissolved in 5 mL 1,4-dioxane and charged into 25 mL flask with two necks. This flask was capped with rubber septa and deoxygenated by purging with nitrogen gas for 30 min. Then it immersed in an oil bath at 75 °C. After 12 h, the polymerization was quenched by rapid cooling in ice water. The solution was poured into a large quantity of cold methanol. The precipitated PS macro-CTA was collected, dried, dissolved in dichloromethane, precipitated again in cold methanol and dried in a vacuum

oven at 30 °C.

**Preparation of PS-PNIPAm-PS:** PS macro-CTA (0.366 g), NIPAm (1.606 g, 14.2 mmol) and AIBN (0.0024 g, 0.014 mmol) were dissolved in 12 ml 1,4-dioxane and charged into 50 ml flask with two necks. This flask was capped with rubber septa and deoxygenated by purging with nitrogen gas for 30 min. Then it immersed in an oil bath at 75 °C. After 12 h, the polymerization was quenched by rapid cooling in ice water. The solution was poured into a large quantity of cold ether. The precipitated PS-PNIPAm-PS was collected, dried, dissolved in dichloromethane, precipitated again in cold diethylether and dried in a vacuum oven at 30 °C.

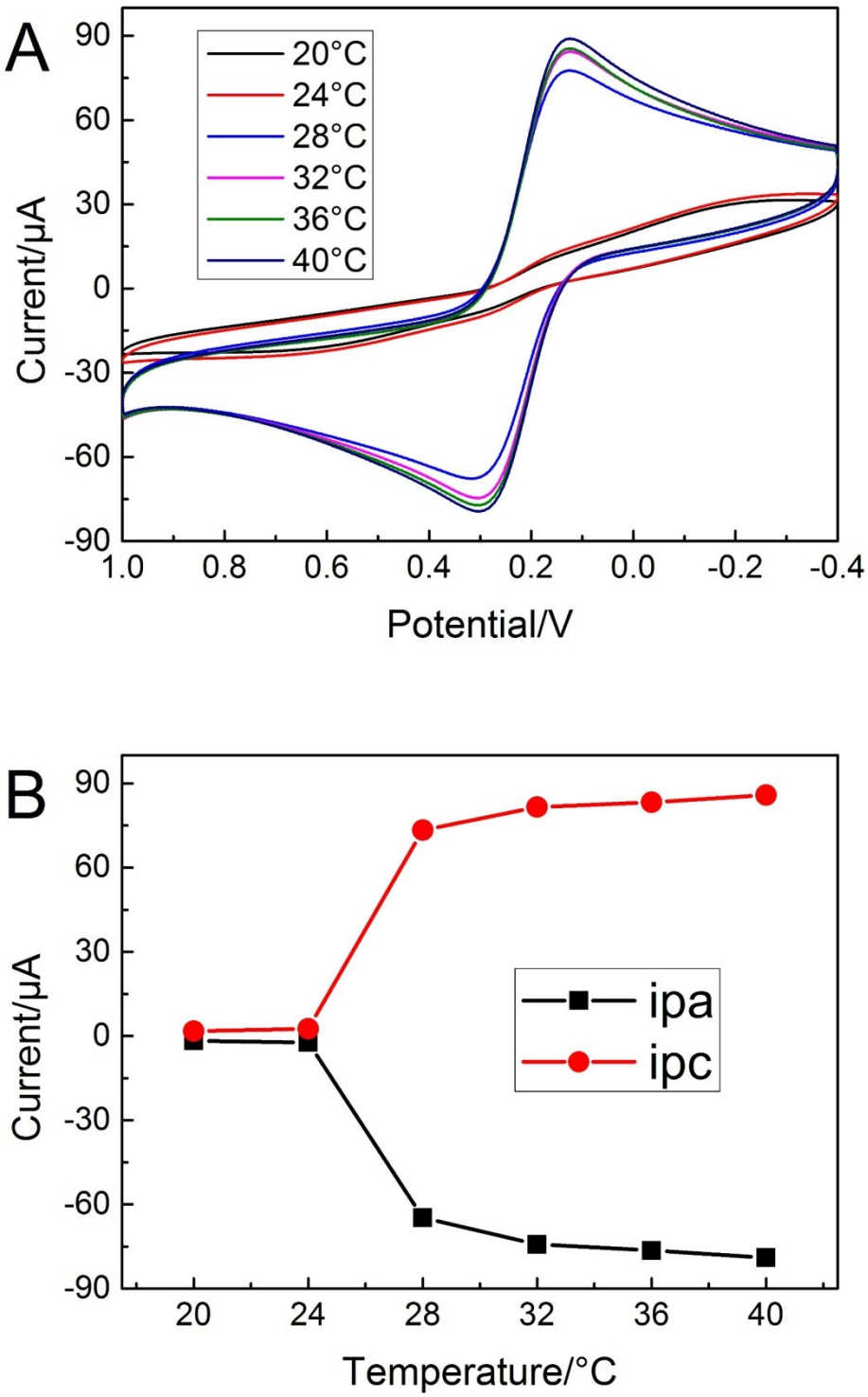


**Fig. S1.** (A) The CVs of $[Fe(CN)_6]^{3-/4-}$ probe on the PS-PNIPAm-PS/MWCNTs-GQDs/GCE from 20 °C to 40 °C. (B) The redox peaks current on the PS-PNIPAm-PS/MWCNTs-GQDs/GCE at different temperatures. Scan rate: 0.1 V/s; Supporting electrolyte: 0.1 M KCl containing 5 mM $K_3[Fe(CN)_6]$ / $K_4[Fe(CN)_6]$ (1:1).

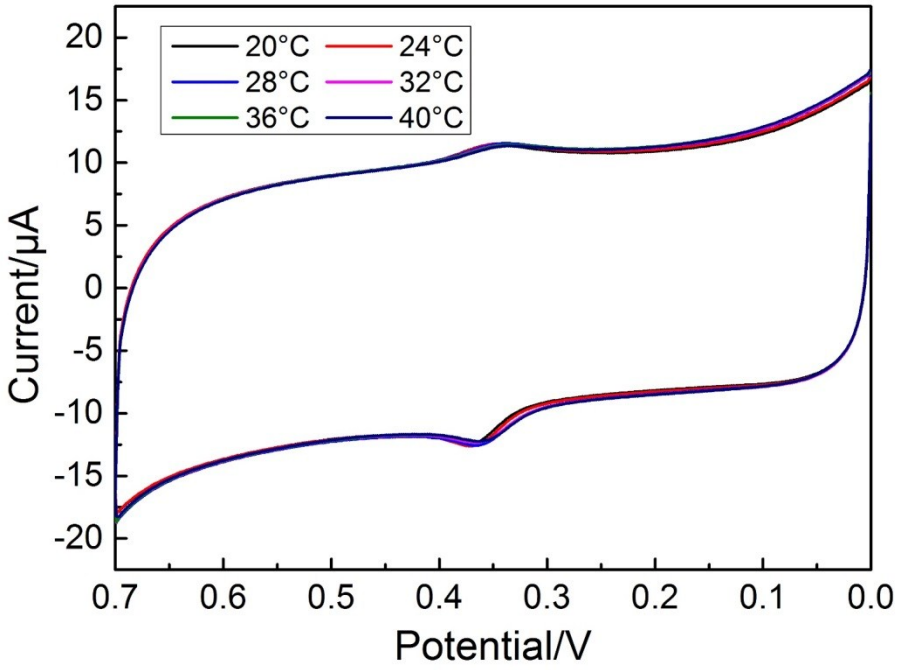


**Fig. S2.** The CVs of APAP on the MWCNTs-GQDs/GCE in 0.1 M PBS solution (pH 7.0) from 20 to 40 °C. Concentration of APAP: 20 μM.

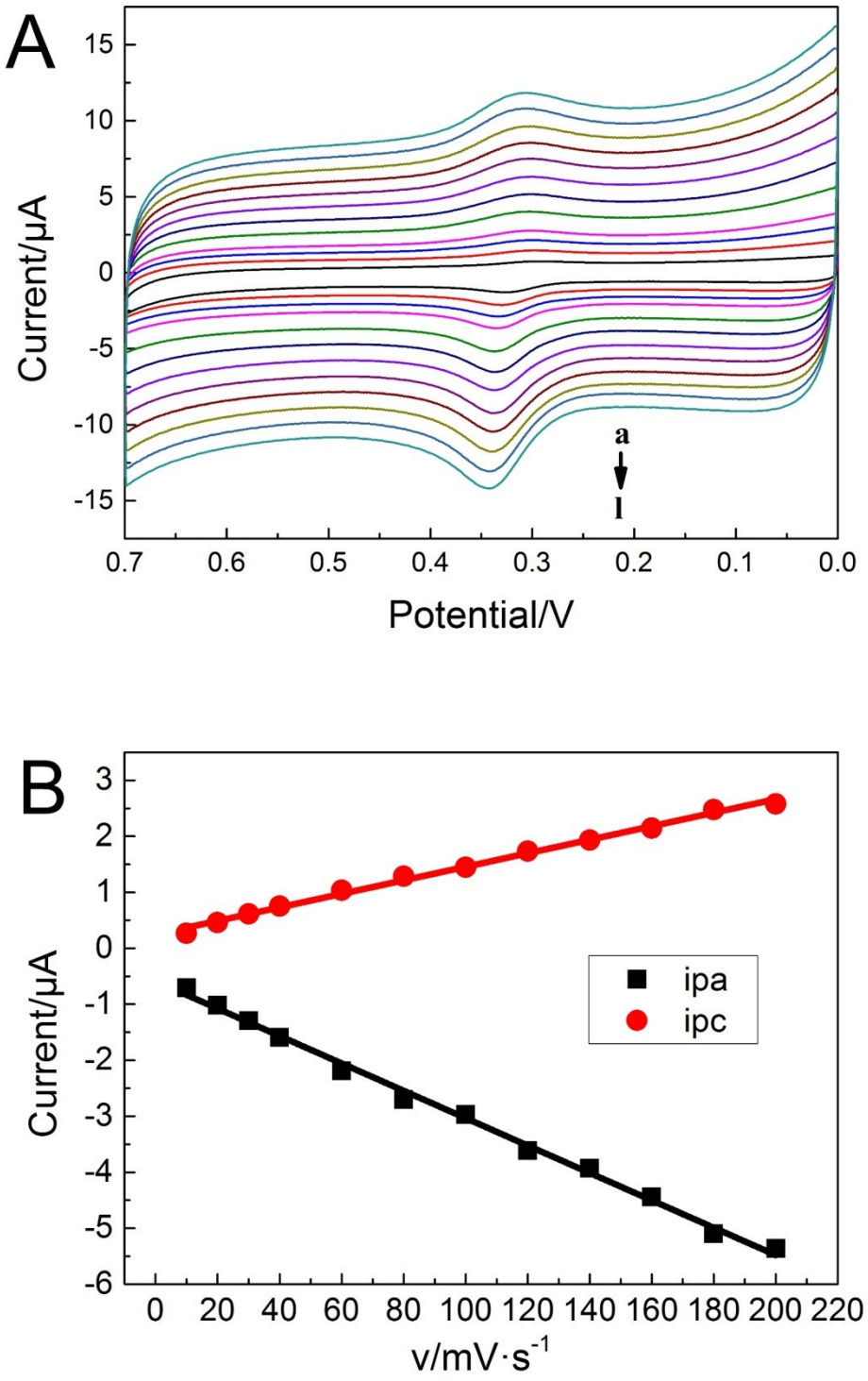


**Fig. S3.** (A) Cyclic voltammograms of 20 μM APAP on the PS-PNIPAm-PS/MWCNTs-GQDs/GCE at different scan rates (from a to m: 10, 20, 30, 40, 60, 80, 100, 120, 140, 160, 180, 200 mV/s in 0.1 M PBS (pH 7.0). (B) The dependence of redox peak currents on the scan rates (v). Testing temperature: 36 °C.

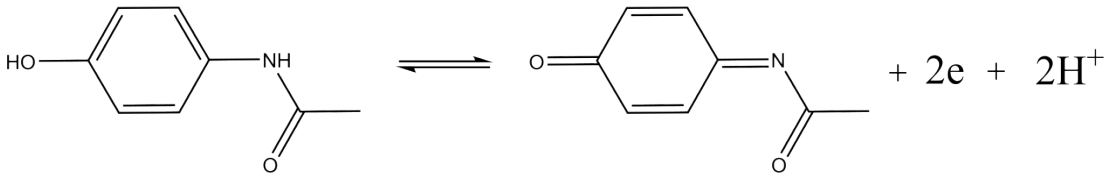


**Fig. S4.** Redox mechanism of paracetamol on the PS-PNIPAm-PS/MWCNTs-GQDs/GCE

**Optimal experimental conditions**

In order to obtain the best detection results, we conducted a conditional optimization experiment. The accumulation potential and time, which are two important factors for accumulation, were investigated by differential pulse voltammetry (DPV). When the accumulation potential changed positively from -0.10 to 0.25 V, the adsorption of APAP at the electrode surface become more efficient, and consequently the DPV peak currents increase. When the accumulation potentials are more positive than 0.25 V, the DPV peak currents decrease gradually (shown in **Fig. S5A**). Therefore, 0.25 V was fixed as the optimal accumulation potential.

The DPV peak currents increase rapidly with the increase of accumulation time from 0 to 160 s. Rapid adsorption of APAP on the surface of the PS-PNIPAm-PS/MWCNTs-GQDs/GCE is responsible for this phenomenon. We can observe the accumulation time above 60 s, the DPV peak currents increase slow (shown in **Fig. S5B**). Therefore, 60 s was chosen as the accumulation time.

According to the previous research, we determined the optimal experimental conditions for temperature, pH, enrichment potential, and enrichment time were 36 °C, 7.0, 0.25 V, 60 s.

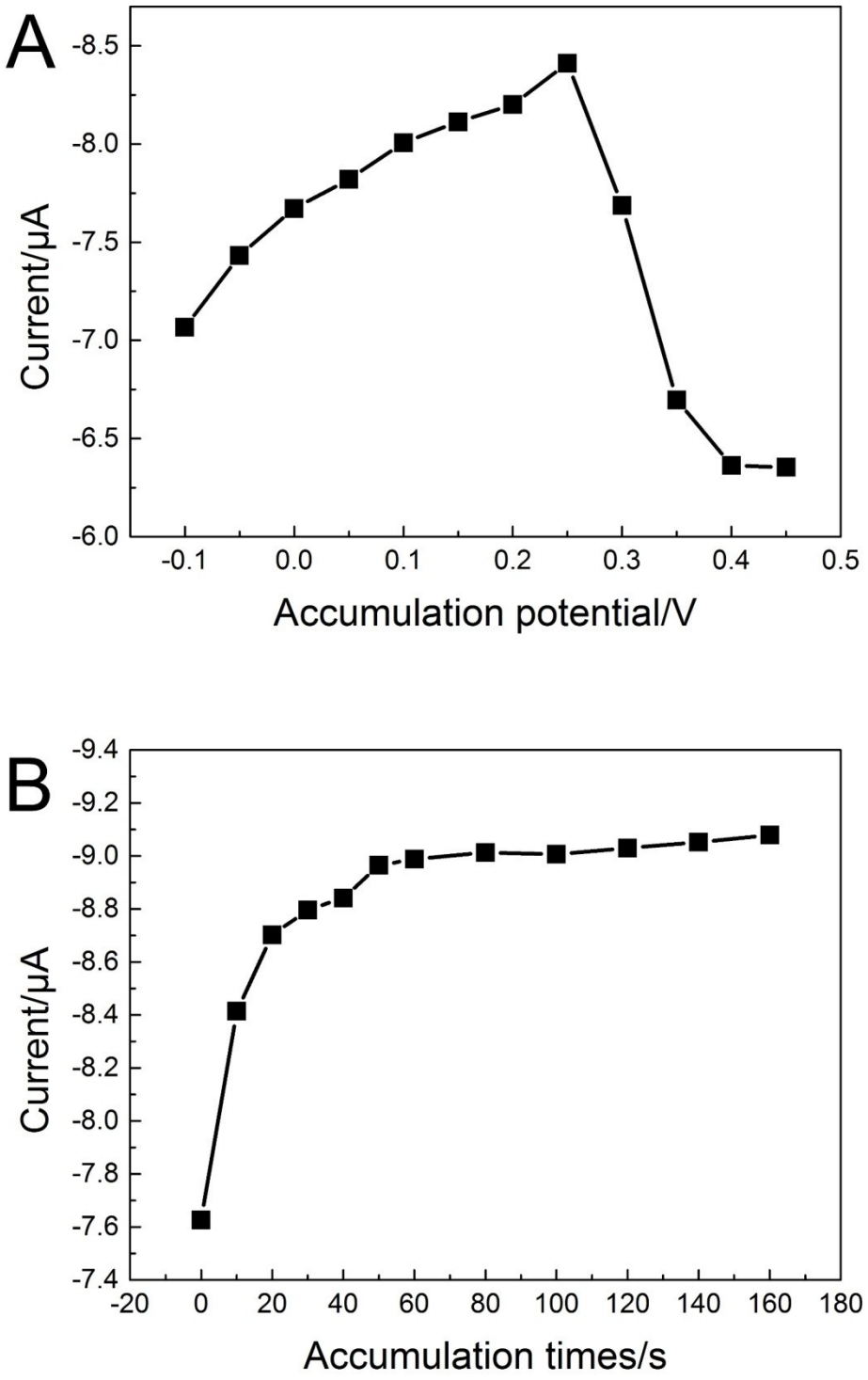


**Fig. S5.** (A) Influence of accumulation potential on the oxidation peak current of 20 μM APAP. Accumulation time: 60s. (B) Influence of accumulation time on the oxidation peak current of 20 μM APAP. Accumulation potential: 0.25V. Testing temperature: 36 °C.

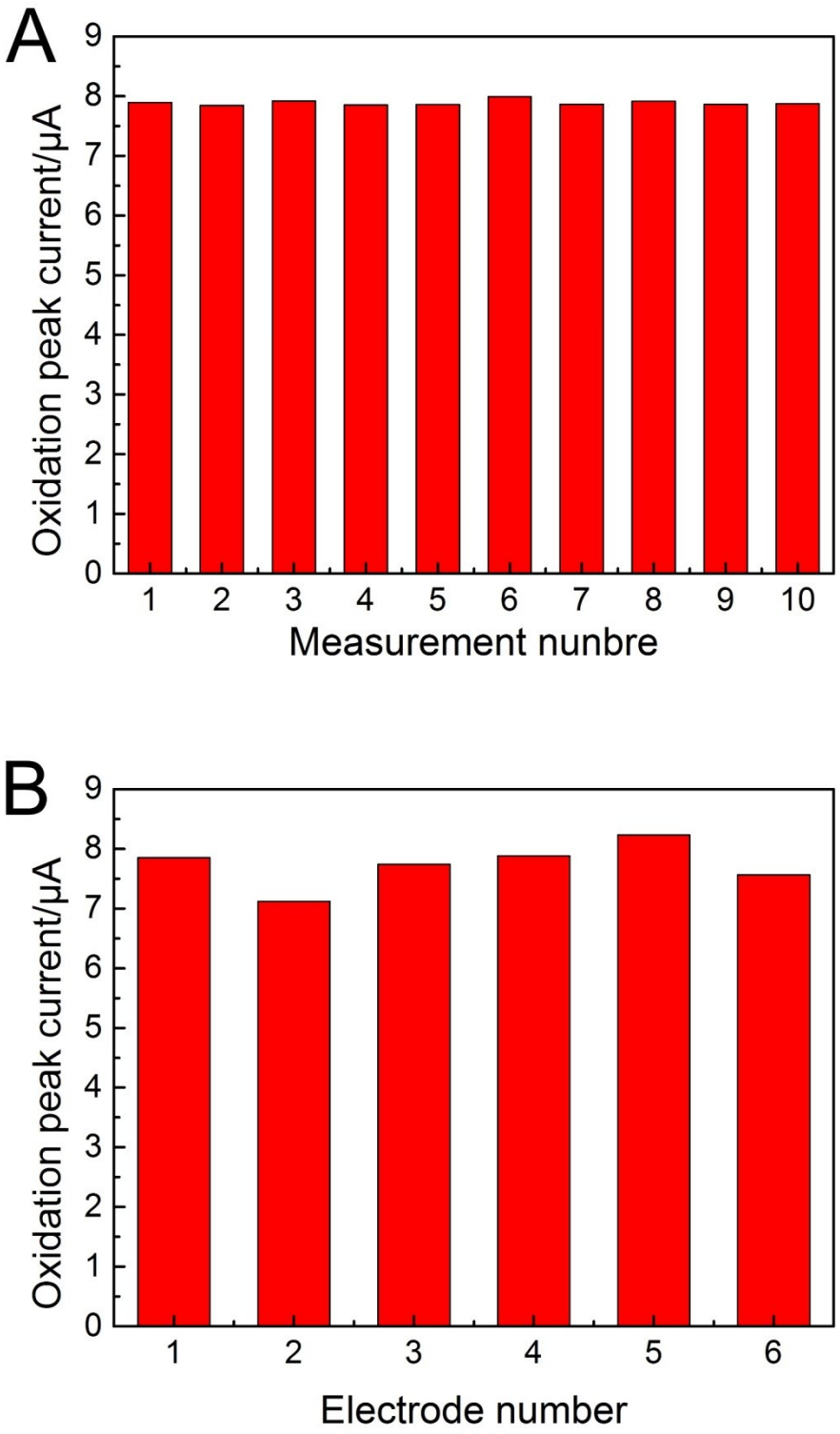


**Fig. S6.** (A) CV responses of the same modified electrode toward 10 μM paracetamol collected from 10 repeat measurements. (B) CV responses of six independent electrodes prepared under the same condition toward 10 μM paracetamol. Testing temperature: 36 °C.

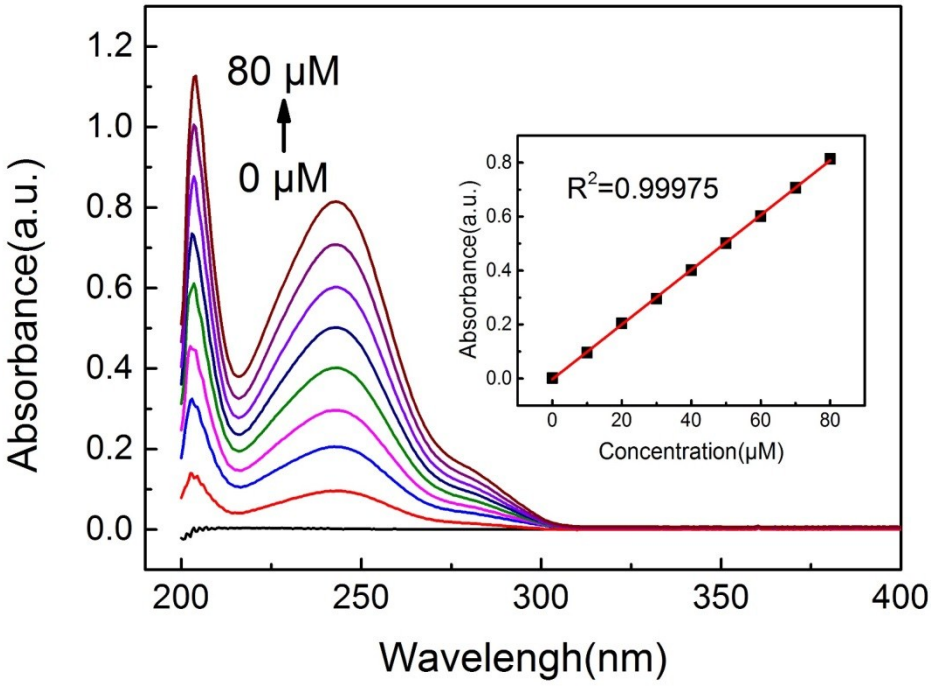


**Fig. S7.** UV-vis spectra to various concentrations of paracetamol standard solution from 0 μM to 80 μM. Inset is the linear calibration curve of absorbances and paracetamol concentrations.