Electronic Supplementary Information (ESI)

Bipolar electrochemiluminescence sensing platform based on pencil core and paper reservoirs

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Reagents and Chemicals

Pencil core (brand: Uni, model: HB) was obtained from Shanghai Japan Mitsubishi pencil Co. Ltd. Whatman grade 1 chromatographic paper (pure cellulose paper) was obtained from Beijing Nikon Biological Technology Co. Ltd and with adjustment before using. Indium tin oxide (ITO) glass substrate (thickness: ~100 nm, resistance: <7 ohm/sq) was purchased from Kaivo Electronic Componets Co., Ltd, Zhuhai, China. The DBL sided carbon tape (8 mm×20 m) was obtained from Supplies Division of STRUCTURE PROBE, Inc. Chloroplatinic acid ($H_2PtCl_6 \cdot 6H_2O$) and hydrogen peroxide (H_2O_2) were obtained from Nanjing Chemical Co. Ltd. Ammonium oxalate $(NH_4)_2C_2O_4$ and potassium ferricyanide ($K_3[Fe(CN)_6]$) were of analytical grade and obtained from Shanghai Chemical Plant. $Ru(bpy)_3Cl_2 \cdot 6H_2O$ were purchased from Sigma-Aldrich (USA). The ECL stock solution, which was comprised of $Ru(bpy)_3^{2+}$ and $(NH_4)_2C_2O_4$, were prepared in 0.1M phosphate buffer solution (PBS, pH 7.0) with deionized water.

Instruments

The BPE and BPE-ECL was performed on a CHI 821C electrochemical workstation (Shanghai Chenhua) and MPI-M ECL Analyzer (Xi'an Remax Electronic High-Tech Ltd) The ECL images were taken by iphone 6S. The scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDAX) images were taken with a scanning electron microscope (S-3000 N, Tokyo, Japan).

The comparative bipolar performance on ITO, pencil core and carbon tape

Briefly, Pt NPs were also deposited on the ITO and carbon tape (3 cm×0.7 mm) by bipolar electrochemistry to detect H_2O_2. As shown in Fig. S1, the ITO and pencil core works very well, but the performance of carbon tape is not satisfactory. It is worth noting that the photolithographic technique followed with wet chemical etching ITO glass substrate was very difficult to operate, and that the cost of ITO is quite high comparing with the low cost of pencil core. The experimental results validate that our ECL sensing platform based on commercial pencil cores and paper reservoirs exhibits the simple operation with low cost but acceptable performance for H_2O_2 assay.

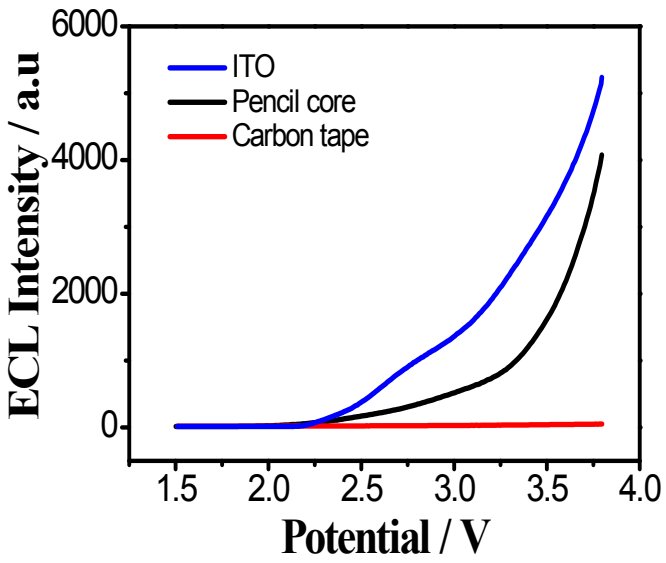


Fig. S1. The ECL-potential curves of $Ru(bpy)_3^{2+}/(NH_4)_2C_2O_4$ obtained at Pt NPs/ITO BPE and Pt NPs/pencil core BPE, and Pt NPs/carbon tape BPE towards 1.0 $\times 10^{-4}$ M H_2O_2 with PMT biased at 600 V.

Electrodeposition and the characterization of Pt nanoparticles

The electrodeposition of Pt nanoparticles on the cathodic pole of pencil core was achieved by bipolar electrochemistry. Briefly, the hydrophilic sensing cell was filled with 1% H_2PtCl_6 as electroplate liquid and hydrophilic reporting cell was full of 0.1 M PBS

buffer solution, a cyclic scanning voltage from 3.0 V to 6.0 V with a scan rate of 100 mVs^{-1} was applied to driving electrodes at two reservoirs using CHI 821C electrochemical workstation. Then the prepared Pt NPs modified pencil core was washed cleanly with double-distilled water for the following experiments. The elemental composition was measured by EDAX (Fig. S2) and SEM image (Fig. S3).

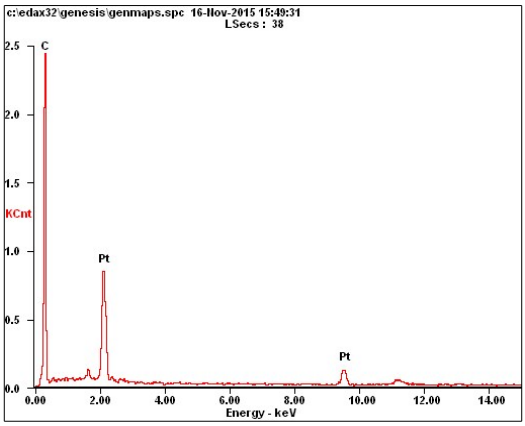


Fig. S2. EDAX of Pt NPs deposited on the electrode and the typical SEM image of Pt NPs on the pencil core

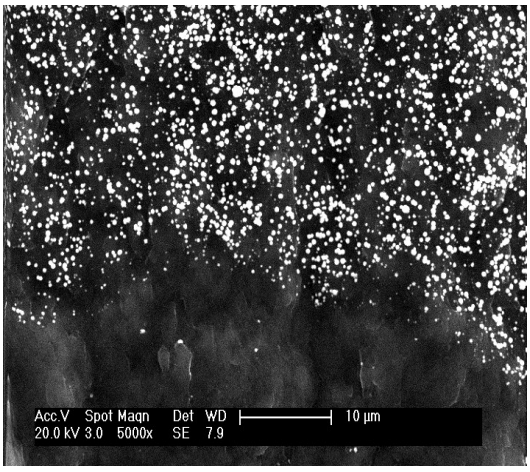


Fig. S3. The SEM image of Pt NPs on the surface of pencil core

The influence of electrodeposition time of Pt nanoparticles on electrode

The bipolar electrodeposited time of Pt NPs was optimized. As shown in Fig. S4, the ECL intensity increased with increasing electrodeposition time till about 80 s. To further prolong electrodeposition time, the ECL intensity declined.

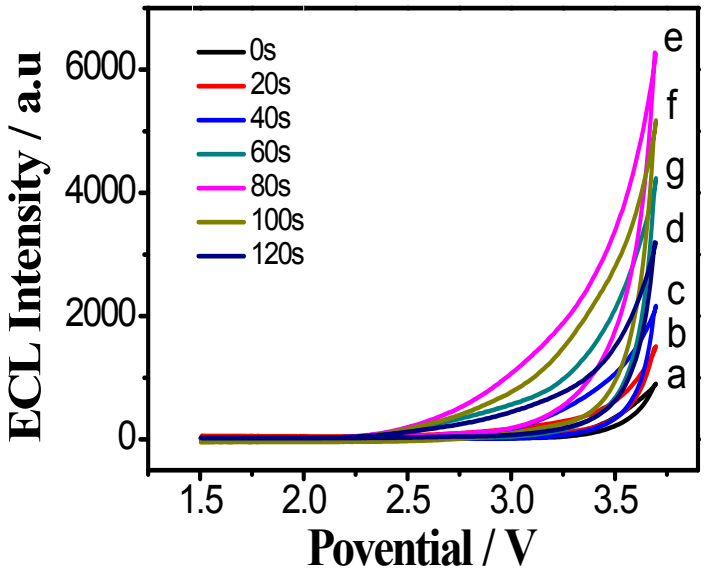


Fig. S4. The ECL curves obtained by different electrodeposition times with the scan rate of 100mV·s^{-1}

The ECL response and images for H_2O_2 detection

Quantitative determination of H_2O_2 was performed by adding various concentrations of H_2O_2 in the sensing cell and the above-mentioned ECL reagents were added to the reporting cell. After that, the sensing cell and reporting cell induced couple reactions and a series of concentrations of H_2O_2 was reported by ECL intensity. The ECL calibration curves and images for different concentration of H_2O_2 were shown as Fig. S5 and Fig.3B.

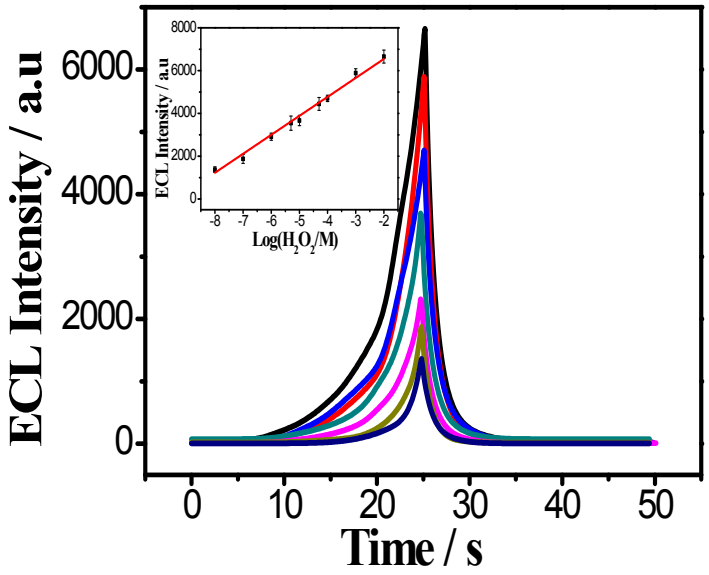
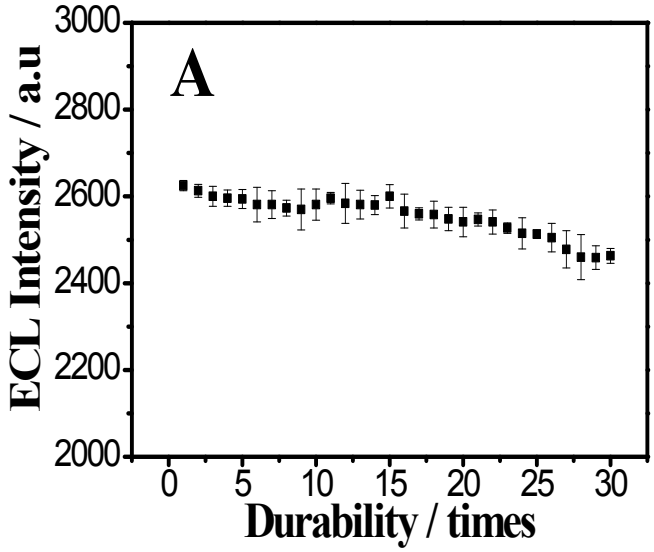
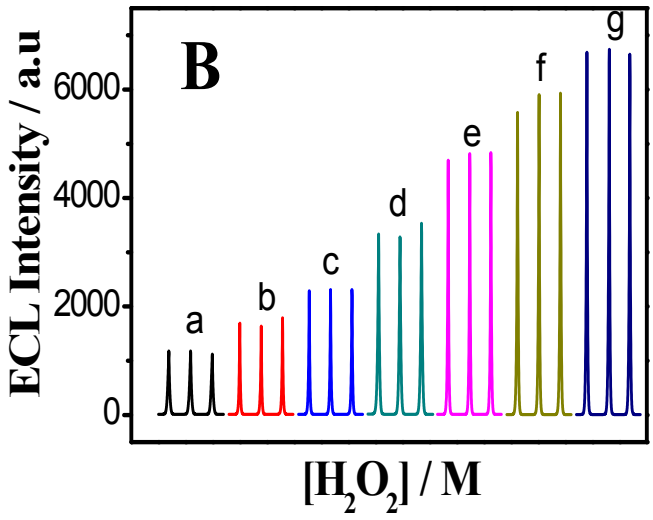


Fig. S5. The ECL profiles as a function of H_2O_2 concentration in 0.1 M PBS (pH 7.0) and calibration curve with 0.7 mm pencil core as bipolar electrode. PMT was biased at 600 V.

Durability, stability and reproducibility of the BPE-ECL sensing platform

The durability of BPE sensor for H_2O_2 detection was tested via a single pencil core experiment. The assay was carried out under the same experimental procedures as above. The durability of a single pencil core was evaluated over 30 times by monitoring the ECL response towards 5×10^{-8} M H_2O_2. The result was shown in Fig. S6A. When the single pencil core was used for thirty times, the ECL intensity decreased only 10%. The stability of the sensing platform is a main factor for assessing the sensor. As shown in Fig. S6B, the relatively stable ECL curves could be obtained at each concentration of H_2O_2. Furthermore, the reproducibility of this chip was assayed, five different pencil core BPEs chips were fabricated independently. As shown in Fig. S6C, the relative standard deviation was 3.78%, indicating the acceptable reproducibility of sensing platform.


A
ECL Intensity / a.u
3000
2800
2600
2400
2200
2000
0
5
10
15
20
25
30
Durability / times


B
ECL Intensity / a.u
6000
4000
2000
0
a
b
c
d
e
f
g
[H2O2] / M

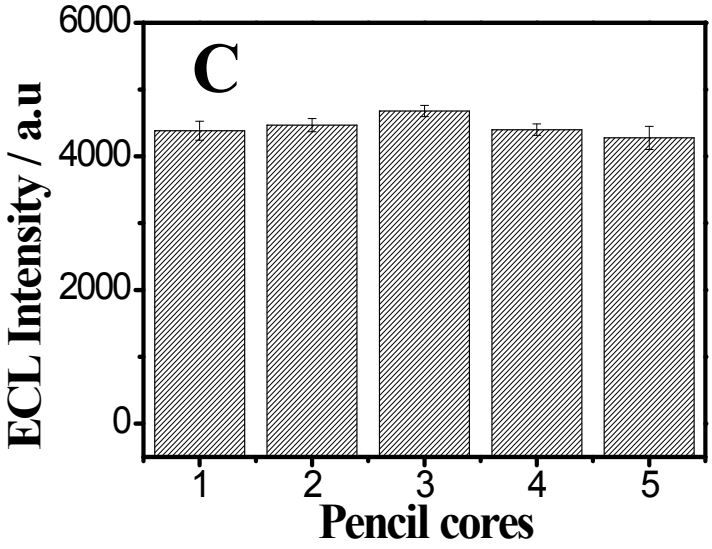


Fig. S6. (A) The durability of a single pencil core bipolar electrode towards 5×10^{-8} M H_2O_2; (B) The stability of proposed bipolar electrode for the detection of various H_2O_2 concentrations: 1.0×10^{-8}, 1.0×10^{-7}, 1.0×10^{-6}, 1.0×10^{-5}, 1.0×10^{-4}, 1.0×10^{-3}, 1.0×10^{-2} M (from a to g); (C) The reproducibility of the pencil core bipolar electrodes (RSD =3.78%).