Supporting Information

Self-powered Microfluidic Origami Electrochemiluminescence Biosensing Platform

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1 Reagents and instruments

$FeCl_3$, anhydrous $AlCl_3$, β-D-glucose, maltose, R-lactose and D-fructose were obtained from Beijing Chemical Reagent Company (Beijing, China), and the carbohydrate solutions were left at room temperature for 24 h before use. Al foil tape and conductive carbon ink were purchased commercially. $Ru(bpy)_3Cl_6 \cdot 6H_2O$, Luminol and glucose oxidase (from Aspergillus niger, GOx) were purchased from Sigma-Aldrich (Milwaukee, WI). All other chemicals used were of analytical reagent grade without any further purification. Double distilled water was used throughout.

Electrochemical measurements were conducted with an electrochemical workstation CHI 832B (Shanghai Chenhua Instrument Corporation, China). ECL signals were obtained by a model MPI-A capillary electrophoresis ECL system (Xi'an Remax Electronics Co. Ltd.). All of the experiments were carried out at room temperature.

2 Device fabrication

Devices were prepared according to previous reports with modifications (Fig. 1).[10] Briefly, filter paper was cut into suitable size and incubated in photoresist, and then it was coved with a high-resolution printed photomask and irradiated by UV light. The patterned paper was accomplished after washing with commercial washing liquor,

deionized water and drying with nitrogen. The patterned paper was cut into the designed shape, and the cover sheets of the ECL cell and the salt bridge was cut off. Then conductive carbon ink was printed onto the paper to serve as the carbon electrode by screen printing patterning, and aluminum foil tape was pasted in corresponding site to serve as the Al anode. Sodium chloride (20 μL), ferric chloride (10 μL) and aluminum chloride (10 μL) saturated solutions were added to the corresponding sites, and then dried at 80 ºC. Finally, the folded paper was compressed and heated for 20 min to assemble the one-battery μ-s-OECLD (Fig. 1H).

μ-s-OECLDs with two batteries in series were also fabricated with similar process (Fig. S1).

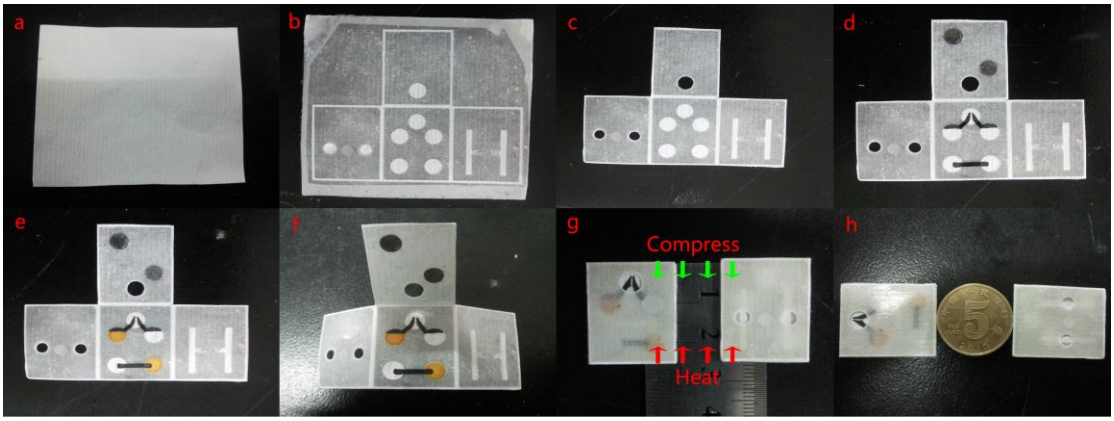

Fig. S1 Fabrication process of two-battery in series μ-s-OECLD. A: filter paper; B: paper patterning; C: size cutting; D: electrodes integrating; E: solutions adding and baking; F: paper folding; G: chip assembling; H: accomplished chips.

A simple two-battery-series system was also fabricated to drive a red LED. The differences of the fabrication process were that the electrodes were integrated in a glass slide by hands and the chip was assembled using two clips (Fig. S2).

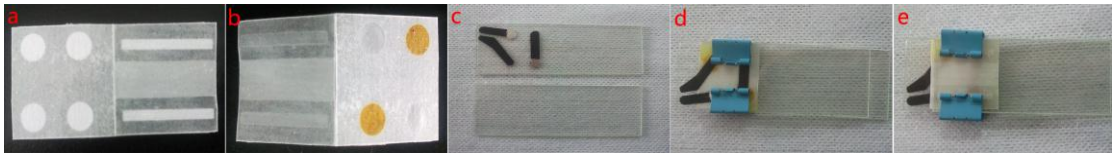

Figure S2. A simple two-battery-series system made by hands for driving a LED

3 ECL performance of ruthenium complex with two-battery-series μ-s-OECLDs

To demonstrate that our paper-based battery was also suitable for driving the ECL of ruthenium complex, the ECL experiment of $Ru(bpy)_3^{2+}$/TPrA system was conducted in a paper cell with two carbon electrodes (one for working electrode, and

another for the reference and counter electrode) first of all. 20 μL ECL solution (1 mM $Ru(bpy)_3^{2+}$ and 10 μM TPrA in 0.1 M PBS pH 7.4) was added to the cell, and the voltage (0-4 V) was imposed by a CHI 832B. It was found that the ECL intensity was highest when the voltage reached 2.61 V (**Fig. S3a**). On the other side, the closed circuit voltage (V_{cc}) of the two batteries in series integrated in our chip was also studied. Similar to the single battery design, the amount of the ECL solution added was also associated with the value of V_{cc} (**Fig. S3b**). When 20 μL ECL solution was added, the V_{cc} reached 2.65 V which was in agreement with the best driving voltage of $Ru(bpy)_3^{2+}$ ECL system (2.61V). Furthermore, the ECL behavior was studied by changing the TPrA concentration of the ECL solutions. As shown in **Fig. S3c and d**, the increased ECL signals were directly related to the concentration of TPrA. The linear relationship between ECL intensity and H_2O_2 concentration was from 1 μM to 1 mM (R = 0.996) with the detection limit down to 0.11 μM by using the signal (S) to noise ratio (N) S/N = 3. The results indicated that our design exhibited good applicability for the ruthenium complex ECL system.

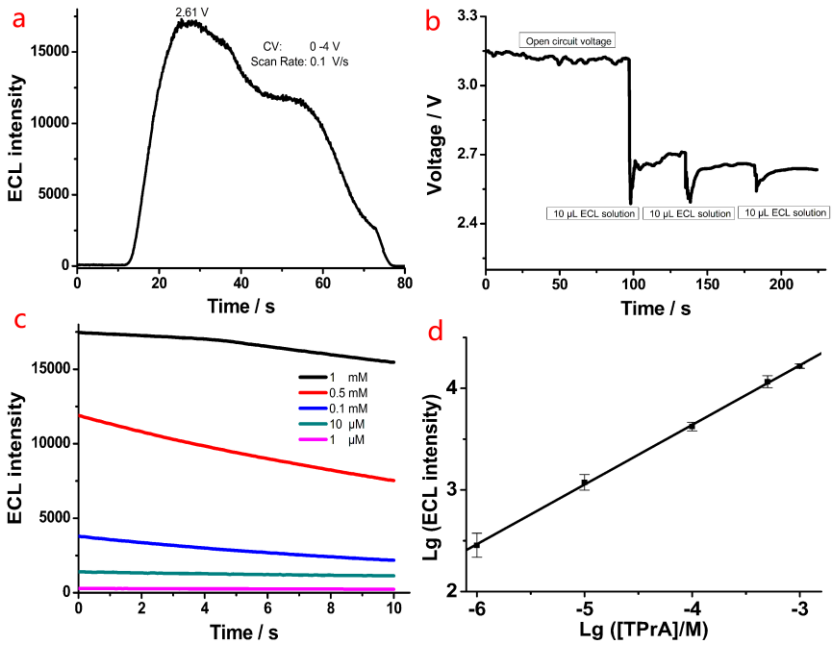

Fig. S3 Performance of our design for the $Ru(bpy)_3^{2+}$ ECL system; a: the ECL curve of $Ru(bpy)_3^{2+}$ ECL system; b: relationship between the V_{cc} and the amount of ECL solution added; c: ECL signals with different TPrA concentrations: 1 μM, 10 μM, 0.1 mM, 0.5 mM and 1 mM; d: linear relationship between ECL intensity and TPrA concentration.

4 Optimization of pH

The optimum pH was selected using the ECL solutions with different pH values. As depicted in **Fig. S4**, when pH reached 9, the device exhibited a very low background chemiluminescence (CL) and the highest ECL response. Then pH 9 was selected for H_2O_2 detection.

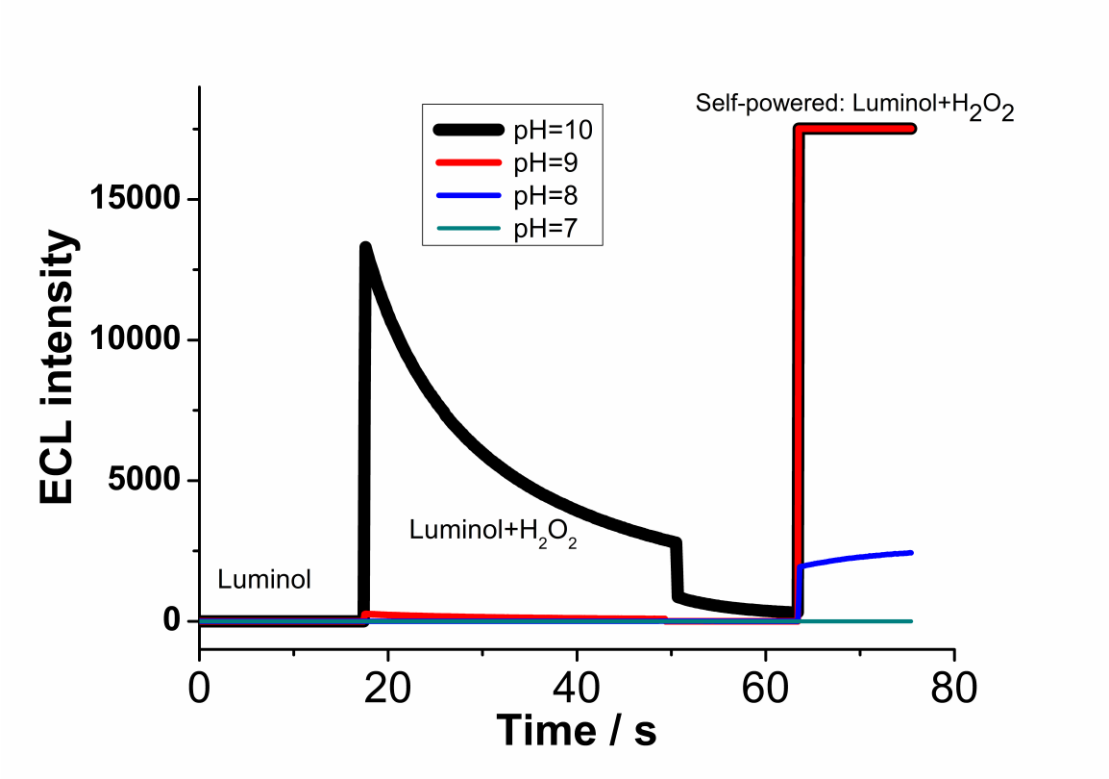

Fig. S4 The influence of pH on the response of luminol ECL system.

5 Detection of the human blood sample

For the real sample detection, two human blood samples (one of normal people and another of people with diabetes) were obtained from local hospital and centrifuged to separate erythrocytes and the serum. The supernatant solution was collected and diluted to 5 times with PBS (pH 7.0) to detect blood glucose without any purification. In this experiment, 1mg/mL GOD was used for the catalytic oxidation of glucose to achieve higher detection sensitivity. Standard samples (glucose concentration: 0.1 mM, 0.5mM, 1mM and 3 mM) and real sample solutions with catalyst system were incubated in 37 °C water bath for 25 min before using. The incubated solution (pH=7.0) and luminol solution (pH=13.0) were mixed to form the ECL solution

(pH≈9). Control experiment was conducted with serum sample from normal people without adding GOD.