Supporting Information for

A Nanoscale Multi-channel Closed Bipolar Electrode Array for Electrochemiluminescence Sensing Platform

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Experimental Section

Synthetizing Au nanofibers in the channel of the PET membrane.

***Electrochemical deposition*[1-3]**

Wet etched multichannel PET membrane (10^8 per cm^2) with the diameter of 420 nm was used to deposit Au nanofibers in the channel. The first step was the sputter deposition of a gold film on one side of the sample with ion sputtering equipment and this gold film was used as a cathode during electrode deposition. Then, the membrane was inserted into an electrolytic cell consisting of two chambers (Figure S1) in such a way that a conductive metal tape contacted the gold membrane. The right chamber was washed carefully with distilled water and filled with 1% $HAuCl_4$ solution and the Pt wire electrode was placed as anode. A two-electrode arrangement was used for electrodeposition and the Au nanofibers were grown at a 500 mV potential difference between the two electrodes for 1 h. After the grown process was completed, the multi-channel membrane was removed from the cell and washed with water and ethanol. After dried with N_2, the membrane was used for SEM and the images were shown in Figure S2. From the surface of the PET membrane (Figure S2A), the ends of the Au nanofibers can be seen protruding from some of the pores, however, the nanowire ends are clearly recessed in some cases. The cross section graph (Figure S2B) can be clearly found that the Au nanofibers were filled the channels of the PET membrane with the diameter of 420 nm.

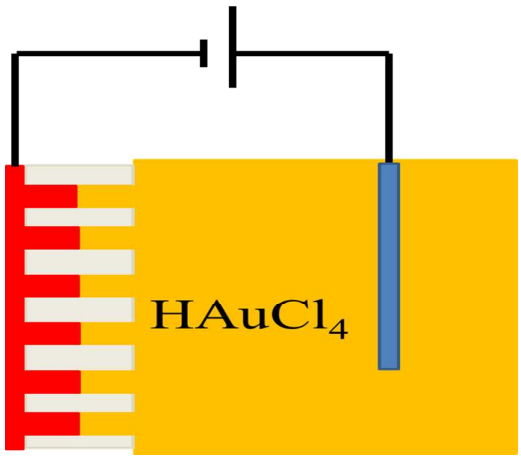

Figure S1. A schematic electrode arrangement for the synthesis of Au nanofibers though electrodeposition.

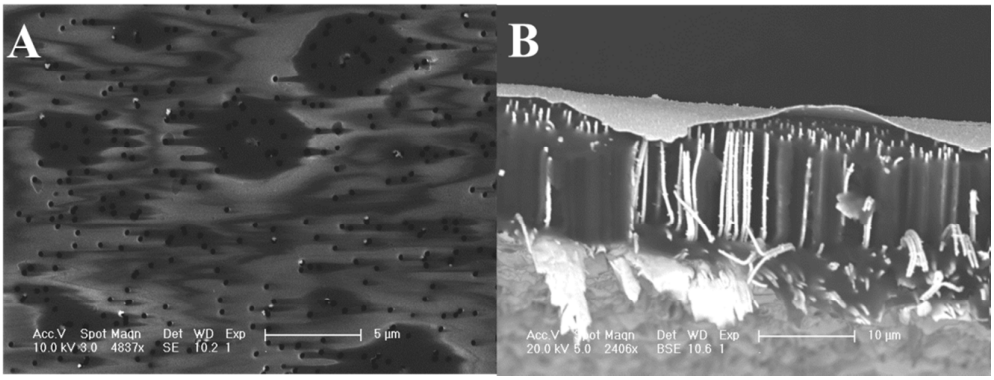

Figure S2. The SEM images of the multi-channel PET membrane after electrodepositing Au nanofibers. (A) was the surface of the membrane and (B) was cross section graph.

Chemical deposition[4-6]

The chemical deposition used for the synthesis of Au nanofibers was accomplished by a previously reported template-based method. Briefly, the wet-etched multi-channel PET membrane was placed between the two polytetrafluoroethylene half-cells consisting of two chambers (Figure S3). 1% $HAuCl_4$ was dissolved in water in order to create a saturated precursor solution. 25 mM $NaBH_4$ was prepared by dissolving

the solid powder into 2 mL of ethanol with a brief period of sonication in order to create a reducing agent solution. The reaction was initiated by simultaneously adding the precursor and reducing agent solutions into the two respective half-cells. The reduction of Au could be visually confirmed by formation of metallic material in the channel of the PET membrane, exposed to the reducing agent half-cell. The reaction was completed after 60 min, which was confirmed through the formation of metallic material on the exterior surfaces of the membrane. Finally, the membrane was removed, gently rinsed with water and ethanol, dried with N_2 for use. From the surface of the PET membrane (Figure S4A), the caps of the Au nanofibers can be seen protruding from some of the pores, that is because the wire grew inside the pore and filled, after the wire was reached the top of the pore, the caps were started to grow. From the cross section graph (Figure S4B), we can clearly find that the Au nanofibers were filled the channels of the PET membrane.

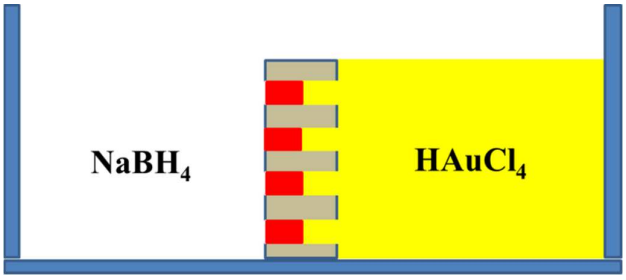

Figure S3. A schematic cell for the synthesis of Au nanofibers though chemical deposition.

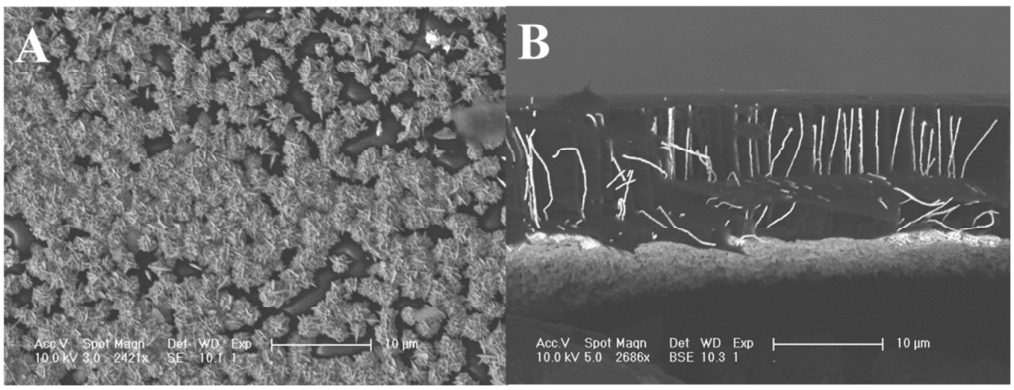

Figure S4. The SEM images of the multi-channel PET membrane after chemical deposition Au nanofibers. (A) was the surface of the membrane (the surface exposed to $HAuCl_4$) and (B) was cross section graph.

In this work, we control the diameter of the nanopore through the etching time by NaOH, and the SEM images of the nanopores under different etching time are shown in Figure S5. Statistical results show a very good linear relationship between the pore diameter and the etching time. So we can etch the nanopore with our desire diameter by controlling the etching time.

In order to verify the feasibility of the experiment on other diameter nanopore, we etched the PET membrane for 25 min and 40 min, and the diameters of the nanopore are about 320 nm and 550 nm, respectively. We used the same method to deposit Au nanofibers in the etched different diameters PET membrane, and performed ECL experiment. The results are shown in Figure S6, we found the different diameter PET membrane that deposited Au nanofibers have a strong ECL signal in 1 mM $Ru(bpy)_3^{2+}$ and 10 mM TPA solution. And the results are similar with the results in Figure 1D.

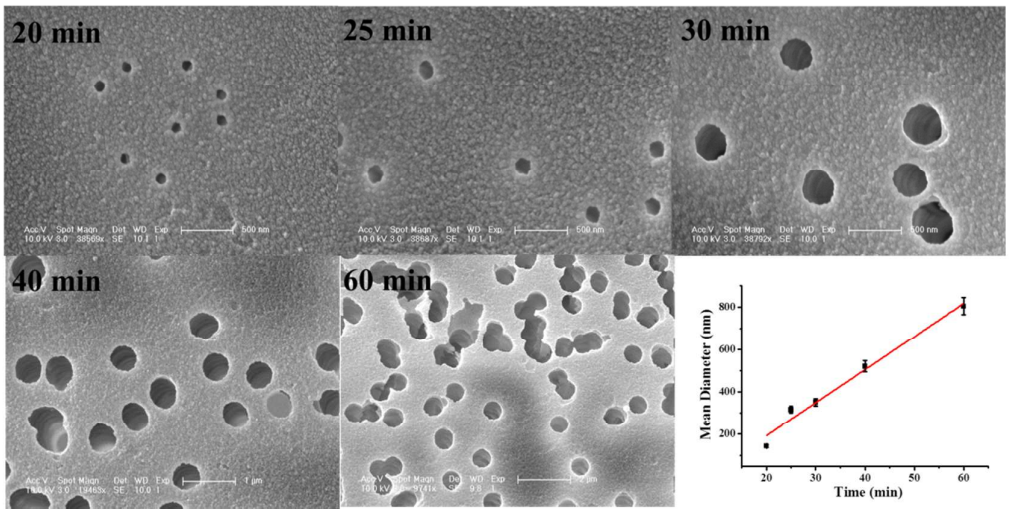

Figure S5. SEM images of the nanopores under different etching time and the statistical result of the pore diameter. A very good linear relationship between etching time and pore diameter is found.

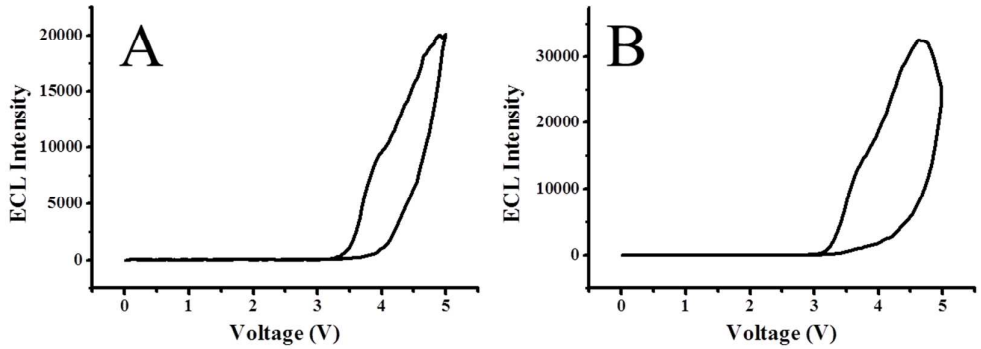

Figure S6. The linear sweep voltammetry curve of the fabricated sensor after deposited Au nanofibers in different diameters nanopore of PET membranes . (A) the diameter was about 320 nm and (B) was about 550 nm

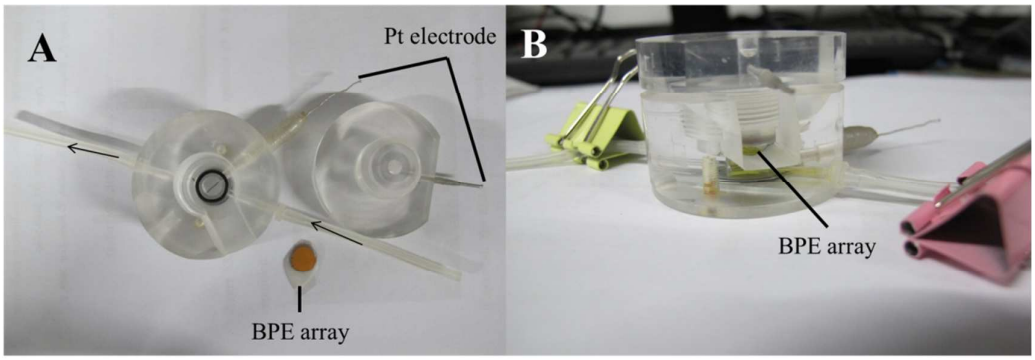

Figure S7. The home-made electrochemical reaction cell that used for ECL measurement. (A) and (B) were the photos of the cell before and after assembling, respectively.

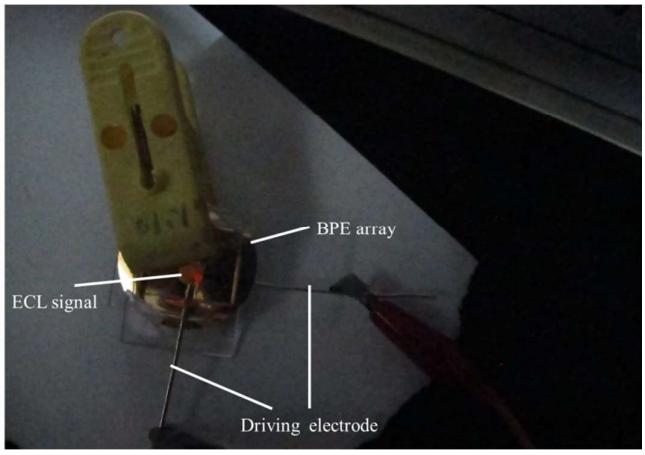

Figure S8. The visual ECL behavior of our design under the driving voltage of 5 V in the ECL solution containing 100 mM TPA and 1 mM $Ru(bpy)_3^{2+}$. The reaction cell was specially fabricated with glass slide and PDMS for visual ECL experiment.

Table S1. AFP and CEA concentration in human serum detected by our device.

Sample	AFP concentration			CEA concentration		
Human serum	Our device	Roche Immunoassay Analyzer (Elecsys2010)	Error	Our device	Roche Immunoassay Analyzer (Elecsys2010)	Error
	162	157.1	-3.12%	29.6	31.1	4.82%

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