Supporting Information

Anodic electrogenerated chemiluminescence of self-assembled peptide nanotubes in aqueous system

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Part I. Experimental details

1. Chemicals

Diphenylalanine (FF) peptide in a lyophilized form was obtained from Bachem (Bubendorf, Switzerland). 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) was purchased from Sigma-Aldrich. Na₂HPO₄ and NaH₂PO₄ were obtained from Beijing Chemicals Inc. (Beijing, China). 0.1 M phosphate-buffered solution (PBS, pH 7.4) containing 20 mM tri-*n*-propylamine (TPrA) and 0.1 M NaCl was used as the electrolyte in ECL analysis. All other reagents were of analytical grade and used as received without further purification. All solutions were prepared with deionized, doubly distilled water (DDW).

2. Synthesis of peptide nanotubes (PNTs)

A FF stock solution was freshly prepared by dissolving the lyophilized FF powder in HFIP at a concentration of 100 mg·mL⁻¹. The stock solution was then mixed with DDW to a final concentration of 2 mg·mL⁻¹. Then the self-assembled PNTs suspension was obtained.

3. Preparation of PNTs-modified electrodes

Prior to use, the glassy carbon electrode (GCE, diameter 3 mm) was polished carefully with 1.0, 0.3 and 0.05 μ m alumina slurry, respectively, followed by washing thoroughly with water. Then the electrode was sonicated in water and allowed to dry in a stream of N₂. 6 μ L of PNTs suspension was dropped on the surface of the clean GCE and dried at room temperature as the PNTs/GCE. The FF monomer-modified GCE was prepared by dropping 6 μ L of FF/HFIP stock solution (2 mg·mL⁻¹) on the surface of the clean GCE as the FF/GCE.

4. Apparatus

Scanning electron microscopy (SEM) images were recorded with a Zeiss Supra55 field emission scanning electron microscope. Transmission electron microscopy

(TEM) images were taken on a JEOL JEM-2100 electron microscope with an accelerating voltage of 100 kV. Fourier Transform Infrared (FTIR) spectra were measured on a Bruker Vertex 70 FT-IR spectrometer. Powder samples were obtained by scraping the PNTs from silicon substrates and mixing with KBr into a disk for the FTIR measurements. X-ray diffraction (XRD) measurements were performed using a Shimadzu XRD-6000 X-ray diffractometer with Cu K α radiation ($\lambda = 0.154$ nm) at a scan rate of 5° min⁻¹. UV-Vis spectra were recorded using a UV-2501PC spectrophotometer (Shimadzu, Japan). Photoluminescence (PL) spectra were obtained on a RF-5301PC spectrophotometer (Shimadzu, Japan). The concentration of Cu²⁺ in real sample was determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES, Shimadzu, Japan). The ECL spectra were recorded by collecting the ECL data during the cyclic potential sweep with a series of optical filters at 535, 555, 575, 590, 605, 625, 665, 690 and 710 nm. Cyclic voltammetric and ECL measurements were carried out with a Model MPI-E Electrochemiluminescence Analyzer (Xi'an Remex Analytic Instrument Co., Ltd, Xi'an, China). The voltage of the photomultiplier tube was set at 800 V in the process of ECL detection. A conventional three-electrode system was used in the experiment with a bare or modified GCE, a platinum wire as the counter electrode, and an Ag/AgCl electrode (saturated KCl) as the reference electrode.





Fig. S1 A typical TEM image (A), XRD pattern (B), FTIR (C) and UV–Vis (D) spectra of the self-assembled PNTs. The inset in the (D) displays the enlarged view of the part spectrum.



Fig. S2 ECL potential curves of the FF/GCE (curve a) and PNTs/GCE (curve b) in 0.1 M PBS (pH 7.4) containing 0.1 M NaCl and 20 mM TPrA. The inset displays the enlarged view of curve a.



Fig. S3 ECL potential curve of the PNTs/GCE in the absence of 20 mM TPrA in 0.1 M PBS (pH 7.4) containing 0.1 M NaCl.



Fig. S4 Cyclic voltammograms of the PNTs/GCE in the presence (a) and absence of 20 mM TPrA in 0.1 M PBS (pH 7.4) containing 0.1 M NaCl. Scanning rate: $0.1 \text{ V} \cdot \text{s}^{-1}$.

After 20 mM TPrA was added into the solution, an anodic peak at 0.9 V was clearly observed (curve a in the Fig. S4). When TPrA was absent in the solution, no apparent anodic peak was observed on the PNTs/GCE (curve b in the Fig. S4). This indicated that the anodic peak at 0.9 V was attributed to the oxidation of TPrA.



Fig. S5 ECL potential curve of the PNTs self-assembled at alkaline solution. The inset is a typical SEM image of the PNTs.



Fig. S6 Effects of (A) the volumes of PNTs dropped on the GCE, (B) TPrA concentration, (C) pH of solution, and (D) scan rate on the ECL intensity of the PNTs/GCE.



Fig. S7 ECL-time curves of the bare GCE (A) in 0.10 M PBS (pH 7.4) containing 0.10 M NaCl, 20 mM TPA and 1.0 mM $Ru(bpy)_3^{2+}$, and the PNTs/GCE (B) in 0.10 M PBS (pH 7.4) containing 0.10 M NaCl and 20 mM TPrA. Potential pulse is applied from 0.00 V to +1.40 V vs. Ag/AgCl reference electrode.

Fig. S8 ECL intensities of the PNTs/GCEs with different kinds of coreactants with the same concentration of 20 mM, measured in 0.10 M PBS (pH 7.4) containing 0.10 M NaCl.



Fig. S9 Comparison of the quenching effect of various metal ions (60 nM) on the PNTs-based ECL sensor. The quenching coefficient is determined in terms of $(I_o-I)/I_o$, where I_o and I are the ECL intensities in the absence and presence of metal ions, respectively.