

Supporting Information for

**Strong electrochemiluminescence based on electron transfer between
Tris(2,2'-bipyridine)ruthenium(III) and SnO NPs@MWCNTs**

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Experimental section

Reagents. The multi-walled carbon nanotubes were obtained from Shenzhen Nanotech. Port. Co. Ltd. The purity was 95%. The as-received MWCNTs were first treated by refluxing in nitric acid (40%) at 110 °C for 2 h to improve their dispersibility in aqueous solution by forming oxygen containing functional groups on their side walls. Tris(2,2'-bipyridyl) dichlororuthenium(II) hexahydrate ($\text{Ru}(\text{bpy})_3\text{Cl}_2 \cdot 6\text{H}_2\text{O}$) were purchased from Alfa Aesar. Hydrochloric acid (38%), Tin(IV) chloride, Tin(II) chloride dihydrate were obtained from Sinopharm Chemical Reagent Co.,Ltd. All other reagents were of analytical reagent grade and were used without further purification. Distilled water was used in all aqueous solution preparations and washings.

Preparation of SnO coated multi-wall carbon nanotubes. The SnO@MWCNTs composites were prepared according to other report.¹ Briefly, acid-treated MWCNTs (2.5mg) were added into 10 mL distilled H_2O followed by ultrasonication for 10 min. Then 0.25g of hydrous $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ was added, and the solution was stirred for 2 h at room temperature. The suspension were filtrated and washed with completed by redistilled water and then dried under vacuum at 90 °C for 6 h. The SnO@MWCNTs composites were finally characterized using X-ray diffraction (XRD) with Cu KR radiation and high-resolution transmission electron microscopy (HRTEM, Tecnai G2 F20 S-TWIN 200KV)

Preparation of SnO NPs@MWCNTs modified electrode. Before modification, the GC electrode (4.0mm in diameter) was polished with a 0.3-and a 0.05- μm aluminum slurry, respectively, rinsed thoroughly with redistilled water, and then sonicated in

redistilled water for 2 min. The resulting GC electrode was coated by hand with 5 μ L SnO@MWCNTs suspension. The solvents were allowed to evaporate at room temperature in the air. And then, a stable film was formed on the surface of GC electrode.

ECL measurement. ECL and electrochemical measurements were carried out on an ECL detection system (MPI-E, Remex Electronic Instrument Lt. Co., Xi'an, China), equipped with a three-electrode ECL cell. The reference electrode was an Ag/AgCl (3 mol L⁻¹ KCl) electrode, and the counter electrode was a Pt wire electrode. ECL spectra were measured by placing cutoff filters of 535, 555, 575, 620, 640, 680, and 705 nm (provided by Beijing Institute of Biophysics, Academia Sinica, China) before the photomultiplier tube (PMT) window and detecting the intensities of ECL passing through these filters respectively under same experimental conditions.

Calculation on the redox reaction energy. It has been known that the formal redox potential of E⁰'(Sn(OH)₆²⁻/HSnO₂⁻) is -0.93 V vs NHE.² The redox potential can be estimated to be -0.31V in our experiment condition by employing the Nernst formula. When the Sn(II) reduces Ru(bpy)₃³⁺ into Ru(bpy)₃²⁺ (E⁰(Ru(bpy)₃³⁺/Ru(bpy)₃²⁺) =1.26V vs NHE),³ they should provide adequate energy to produce excited state Ru(bpy)₃^{2+*}. We estimate the energy (- ΔH°) available in Eq. by employing the following equation:³

$$-\Delta H = E^0(\text{Ru}(\text{bpy})_3^{3+}/\text{Ru}(\text{bpy})_3^{2+}) - E^{0'}(\text{Sn}(\text{OH})_6^{2-}/\text{HSnO}_2^-) - 0.1\text{eV}$$

Where 0.1 eV is an estimate of the entropy term ($T\Delta S^{\circ}$) at 25 °C. Then, $-\Delta H^{\circ}$ was compared with the energy (2.12 eV) of Ru(bpy)₃^{2+*}. The estimated $-\Delta H^{\circ}$ was 1.57 eV, which is lower than the energy of Ru(bpy)₃^{2+*}, therefore, Eq. is the energy-insufficient system.

Calculation on the ECL efficiency. The ECL efficiency of Sn(II)-Ru(bpy)₃²⁺ was estimated according to following equation:³

$$\phi_{ECL} = \phi_{ECL}^0 (IQ^0 / I^0Q)$$

where ϕ_{ECL} , ϕ_{ECL}^0 are ECL efficiencies of Sn(II)-Ru(bpy)₃²⁺ (the target ECL system) and C₂O₄²⁻-Ru(bpy)₃²⁺ (the reference ECL system, $\phi_{ECL}^0=2.0\%$), I and I⁰ are integrated ECL intensities, Q and Q⁰ are charges passed for Sn(II)-Ru(bpy)₃²⁺ and C₂O₄²⁻-Ru(bpy)₃²⁺ systems at an oxidized Pt electrode, respectively.

XRD patterns. The well-resolved peaks (●) in the XRD patterns (curve (b) in Fig. S1) correspond to (101), (110), (002), (200), (112), (211), and (202) crystal planes of the tetragonal SnO (JCPDS No. 06-0395).

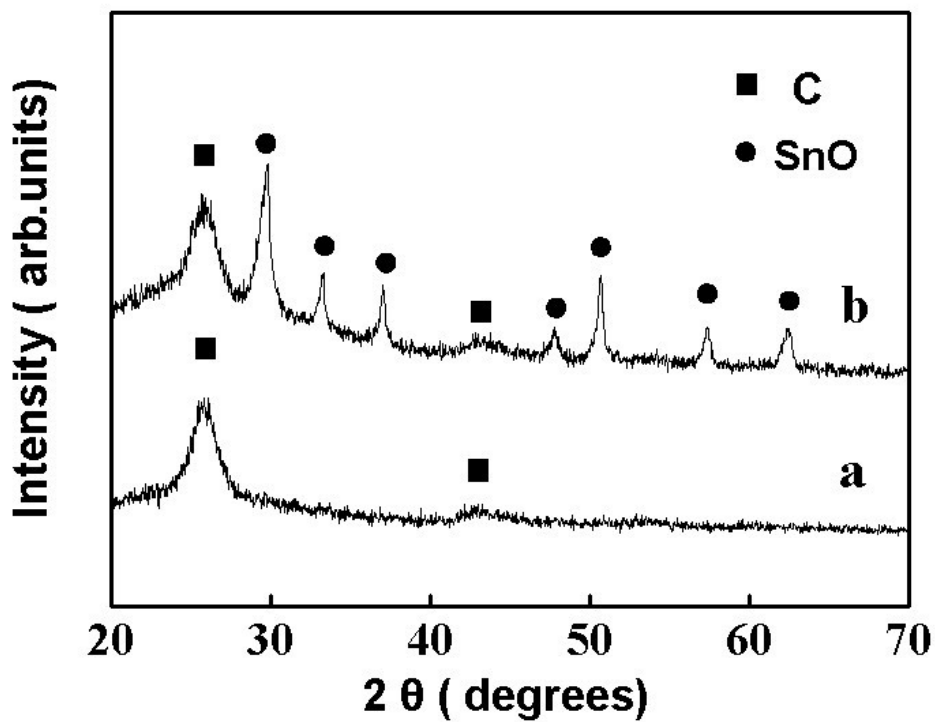


Figure S1 XRD patterns of MWCNTs (a) and SnO NPs@MWCNTs composites (b)

HRTEM images

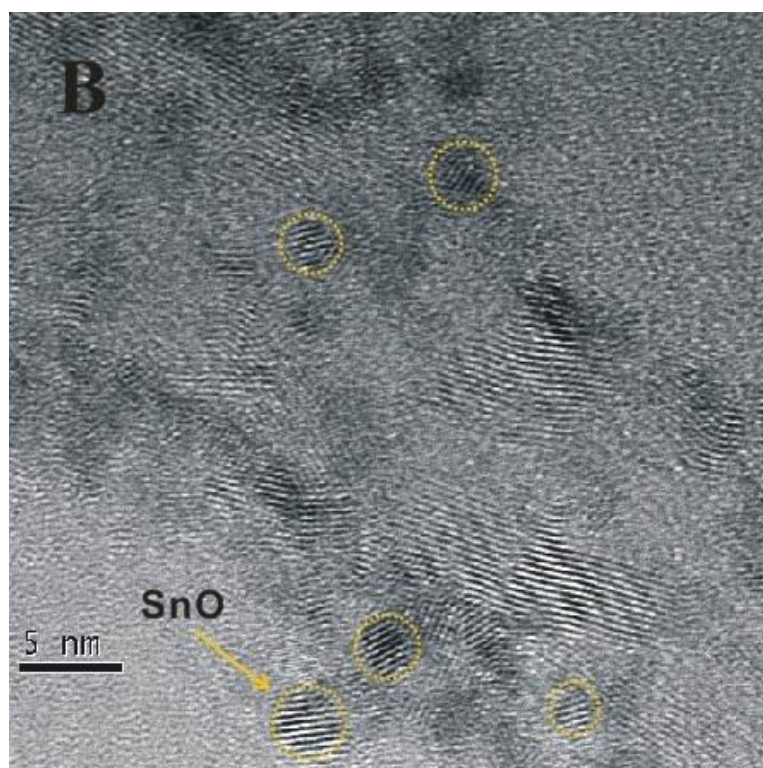
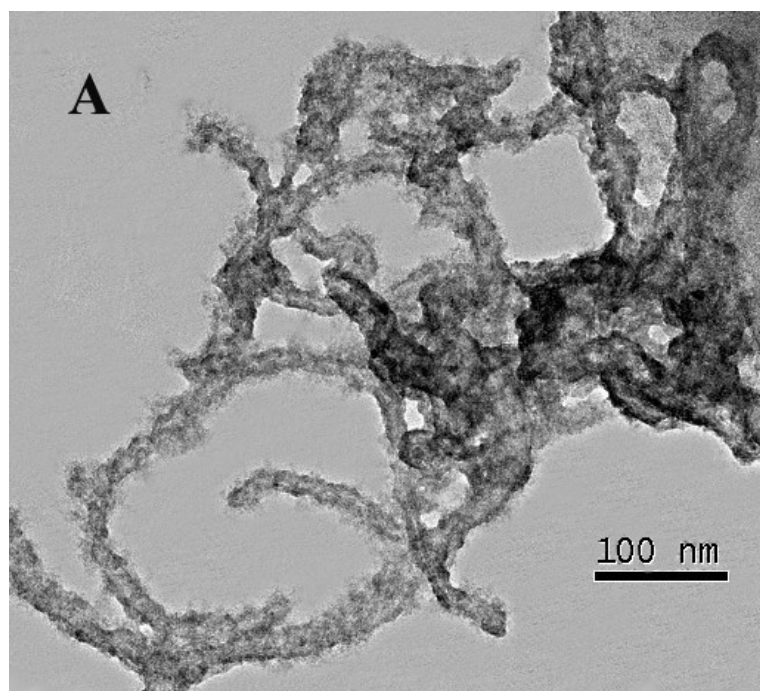


Figure S2. TEM images of SnO coated MWCNT prepared (A) low magnification; (B) high magnification

ECL data

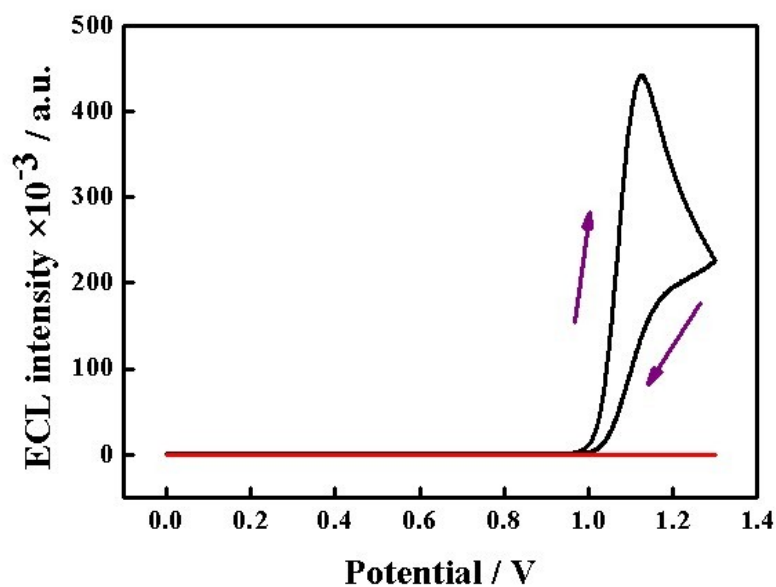


Figure S3. ECL response obtained at a Au electrode (4.0mm in diameter) in phosphate solutions (0.1M, pH=7.4) containing: (a) 0.5 mM SnCl_2 ; (b) 0.1 mM $\text{Ru}(\text{bpy})_3^{2+}$ + 0.5 mM SnCl_2 . Scan rate was 100 mV/s.

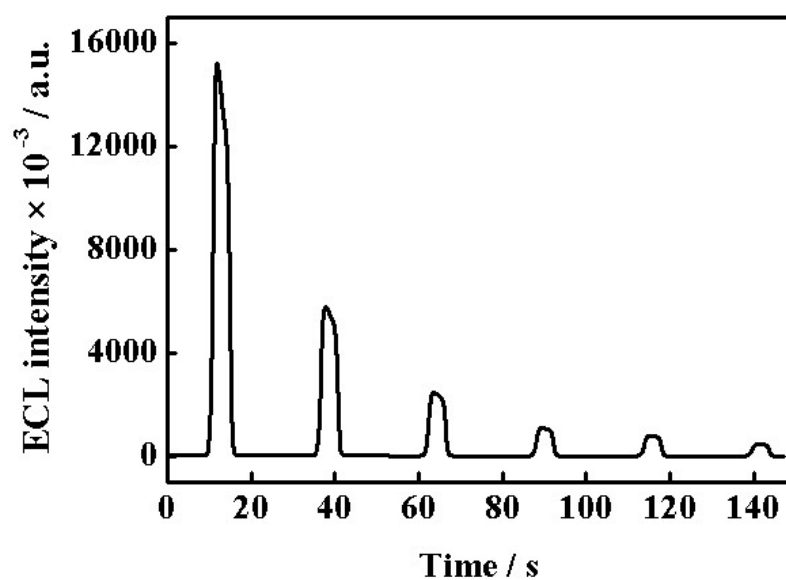


Figure S4. ECL responses of 0.1mM $\text{Ru}(\text{bpy})_3^{2+}$ / 0.5mM SnCl_2 obtained at bare gold electrode during a continuous potential from 0 to 1.3V scan at 0.1 V/s.

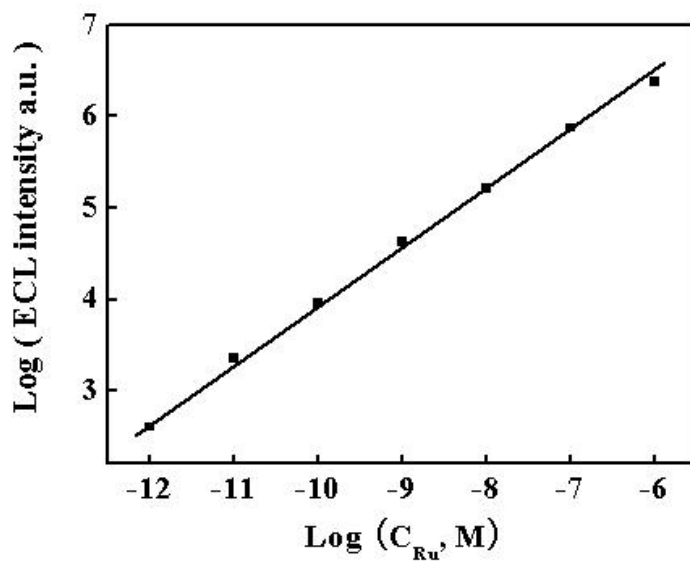


Figure S5. Calibration curves of $\text{Ru}(\text{bpy})_3^{2+}$ at a SnO NPs@MWCNTs composite-modified electrode.

Reference:

1. H. Fang, X. Sun, L. Qian, D.Wang, F. Li, Y. Chu, F. Wang, H.Cheng. *J. Phys. Chem. C*, **2008**, *112*, 5790-5794.
2. B.Jakuszewski, S. Taniewska-Osenka, Roca. *Chem.*, 1962, *36*, 329-334.
3. M. Richter, *Chem. Rev.*, 2004, *104*, 3003-3036.