Electronic Supplementary Information

Ultrasensitive Self-enhanced Electrochemiluminescence Sensor Based on Novel PAN@Ru@PEI@Nafion Nanofibers Mat

Libo Li,[a] Limin Zhou,[b] Xiaohong Liu[a] and Tianyan You*[a]

[a] Key Laboratory of Modern Agricultural Equipment and Technology, Ministry of Education, School of Agricultural Equipment Engineering, Institute of Agricultural Engineering, Jiangsu University, Zhenjiang, Jiangsu 212013, China

[b] Anyang Institute of Technology, Anyang, Henan 455000, China

* Corresponding author. Fax/Tel: +86-511-88982992. E-mail: youty@ujs.edu.cn

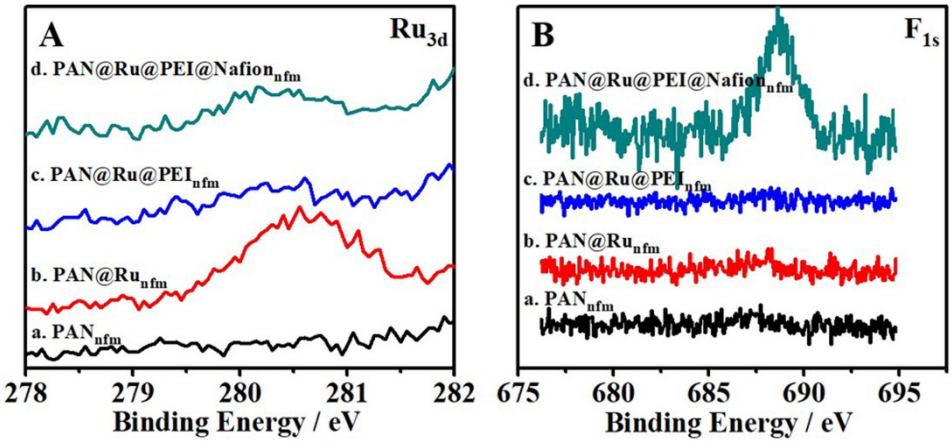

Fig S1. Core-level XPS spectra of (A) Ru_{3d} and (B) F_{1s}. Curve a, PAN_{nfm}; curve b, $PAN@Ru_{nfm}$; curve c, $PAN@Ru@PEI_{nfm}$; curve d, $PAN@Ru@PEI@Nafion_{nfm}$.

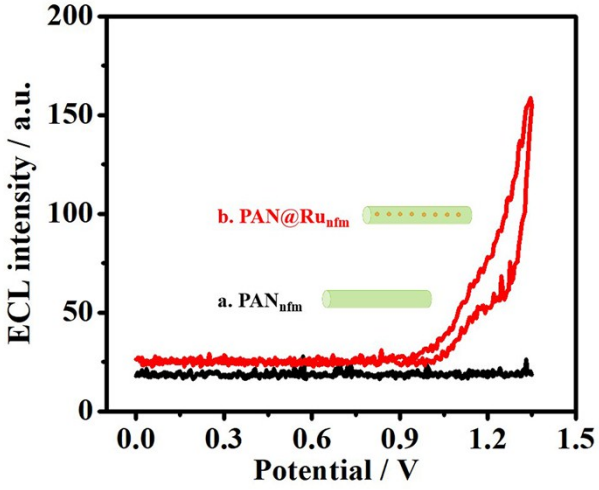

Fig S2. ECL-potential curves of (a) PAN_{nfm}/ITO and (b) $PAN@Ru_{nfm}$/ITO in 0.1 mol L^{-1} pH 7.5 PBS.

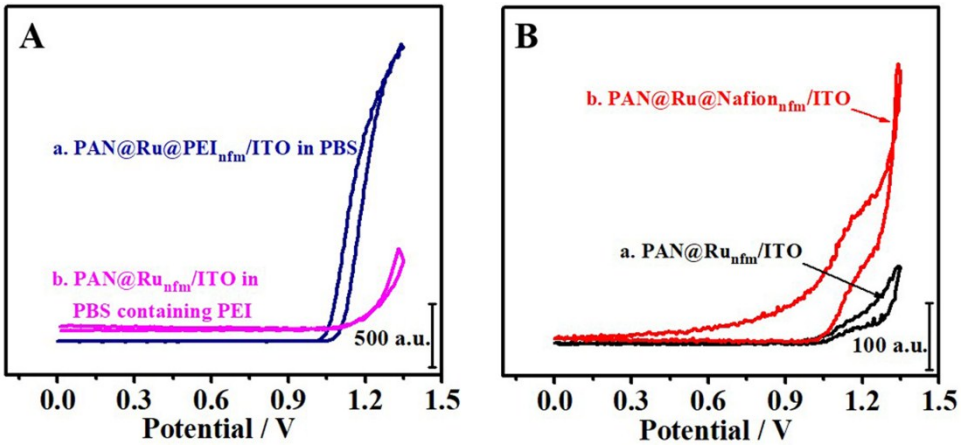

Fig S3. (A) The ECL-potential curves of PAN@Ru@PEI$_{nfm}$/ITO in 0.1 mol L^{-1} pH 7.5 PBS (a) and PAN@Ru$_{nfm}$/ITO in 0.1 mol L^{-1} pH 7.5 PBS containing 1 mg mL^{-1} PEI (b). (B) The ECL-potential curves of PAN@Ru$_{nfm}$/ITO (a) and PAN@Ru@Nafion$_{nfm}$/ITO (b) in 0.1 mol L^{-1} pH 7.5 PBS .

Fig S3A shows that the ECL intensity of PAN@Ru$_{nfm}$/ITO electrode in PBS containing 1 mg mL^{-1} PEI is only one third of that PAN@Ru@PEI$_{nfm}$/ITO in PBS, confirming coexistence of $Ru(bpy)_3^{2+}$ and PEI in electrospun PAN nanofibers mat indeed shortens the electron transfer distance and improves the luminous efficiency.

Similarly, ECL intensity of PAN@Ru@Nafion$_{nfm}$/ITO (~500 a.u.) increases about three fold in comparison with PAN@Ru$_{nfm}$/ITO (~160 a.u.), indicating that the introduction of Nation can avoid fall off of $Ru(bpy)_3^{2+}$ from the obtained nanofibers (Fig S3B).

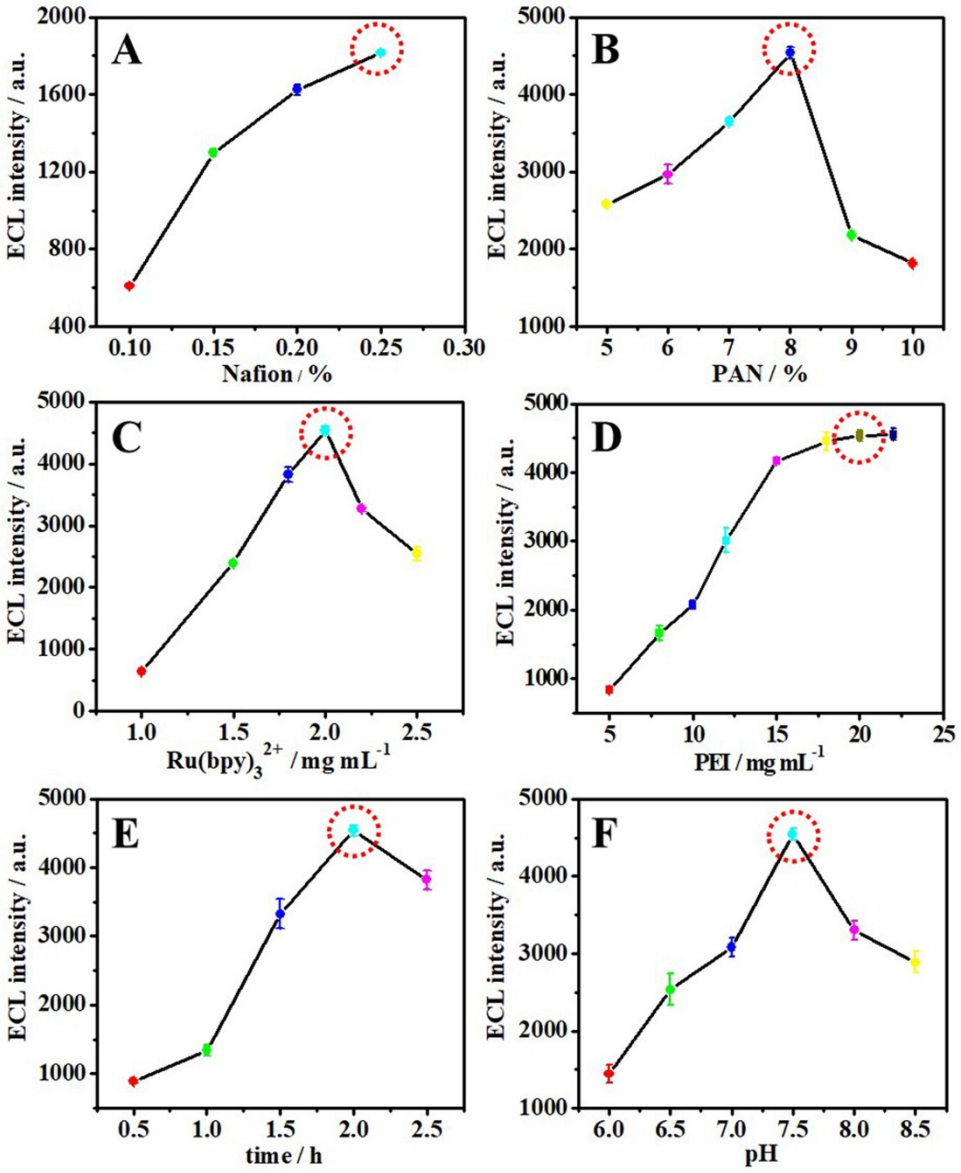

Fig S4. Effect of (A) Nafion, (B) PAN, (C) $Ru(bpy)_3^{2+}$, (D) PEI, (E) collection time and (F) pH value of buffer solution on the ECL intensity of the prepared self-enhanced ECL sensor. Buffer, 0.1 mol L^{-1} PBS; Scan rate, 0.1 V s^{-1}.

Table S1. Comparison of analytical performance of the proposed sensor with other methods to detect α-Naphthol.

Method	Linear range (mol L^{-1})	LOD (mol L^{-1})	Refs
The meso-$NiCo_2O_4$-modified carbon paste electrode	2.0×10^{-8} - 2.0×10^{-5}	7.0×10^{-9}	[1]
Electrochemically reduced graphene oxide-based DPV method	5.0×10^{-9} - 2.0×10^{-5}	1.0×10^{-9}	[2]
Poly(3-methylthiophene)-nano-Au-based electrochemical method	7.0×10^{-7} - 1.5×10^{-4}	1.0×10^{-7}	[3]
G-DNA modified gold electrode by electrochemical impedance spectroscopy	1.0×10^{-9} - 1.0×10^{-4}	1.0×10^{-10}	[4]
Capillary electrophoresis-diode array detection	1.7×10^{-5} - 3.5×10^{-3}	4.4×10^{-6}	[5]
Field-amplified sample injection-capillary electrophoresis-ultraviolet detection	1.4×10^{-6} - 2.8×10^{-4}	2.6×10^{-7}	[6]
Magnetic graphitized carbon black-based HPLC-ultraviolet detection	6.9×10^{-8} - 3.5×10^{-5}	6.2×10^{-9}	[7]
Magnetic solid phase extraction with MgAl-LDHs as adsorbents prior to HPLC	3.5×10^{-9} - 1.4×10^{-6}	1.5×10^{-9}	[8]
Fluorescence dye-incorporated SH-β-cyclodextrin functionalized AuNPs	1.0×10^{-8} - 8.0×10^{-6}	8.0×10^{-9}	[9]
PAN@Ru@PEI@$Nafion_{nfm}$-based ECL sensor	1.0×10^{-12} - 1.0×10^{-7}	1.0×10^{-12}	Our work

Table S2. Assay of α-Naphthol in tap water using the developed method.

Sample	Added (10^{-9} mol L^{-1})	Found (10^{-9} mol L^{-1})	Recovery (%)	RSD (%)
Tap water	0	-	-	-
	1.00	0.94	94.0	3.53
	5.00	4.79	95.8	4.62

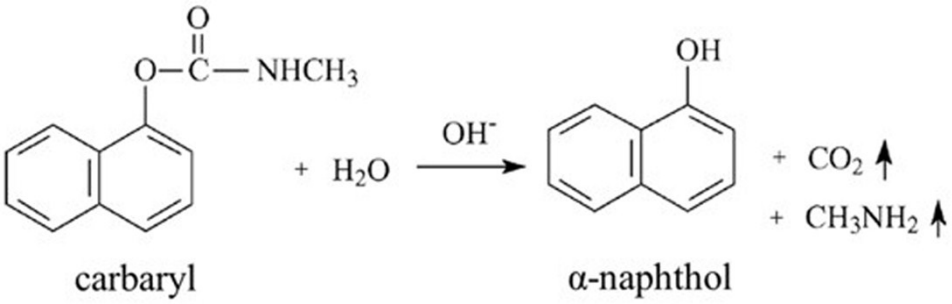

Fig S5. Hydrolysis of carbaryl under basic conditions.

Table S3. Assay of α-Naphthol from carbaryl hydrolysis using the developed ECL sensor and HPLC method.

Sample	This work (10^{-9} mol L^{-1})	HPLC (10^{-9} mol L^{-1})	RSD (%)
1	6.07	6.14	-1.11
2	5.76	6.14	-6.05
3	6.22	6.14	1.32
4	62.54	61.36	1.93
5	67.47	61.36	9.95
6	57.58	61.36	-6.16

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