Electronic Supplementary Material (ESI) for Chemical Communications
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Supporting Information

1.Experimental

1.1 Chemicals

All the reagents were of analytical grade or better. Tyrosinase, lucigenin (N,N'-dimethyl-9',9-biacridinium dinitrate) and 5% Nafion were purchased from sigma company. Chitosan (CS, M.W. 1.68×10^5, 91.7% after deacetylation), 30% (v/v) H_2O_2 and hydrochloric acid adrenal injection were purchased from commercial sources and used as received. SiC nanoparticles with an average particle size of 15 nm, supplied by MTI Corporation, USA were used in this work.

1.2 Preparation of the Tyr/CS/SiC modified electrode

Figure 1 shows the schematic of the fabrication process for the electrochemi-luminescent composite sensor and its principle for adrenaline assay. Firstly, the SiC powder was dissolved in 0.5 wt% CS solution, and sonicated to mix homogeneously. And then the GCE was polished with 0.05 μm alumina slurry and sonicated in ethanol and deionized water for 5 min each, and immersed in the previous SiC solution, deposited on the GCE surface via potentiostatic electrochemical polymerization at -2.0 V. The CS/SiC modified electrode was successively rinsed with deionized water, ethanol for several times, and dried at room temperature. Tyrosinase was modified on the electrode surface via the electrostatic interaction. Firstly, the tyrosinase was dissolved in PBS solution (pH 7.0), and 0.1% Nafion was added into the above solution. Next, 3.0 μL of the mixture was dropped onto the surface of the CS/SiC modified electrode. After drying 1.0 h at room temperature, the Tyr/CS/SiC modified electrode was obtained.

1.3 ECL assay

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Above Tyr/CS/SiC modified electrode was immersed into the solution containing different concentrations of adrenaline for 20 min, and then rinsed using distilled water for ECL assay. A control experiment was also performed. CS/SiC modified electrode was immersed into the solution containing 1 mg/mL Tyr and 5×10^{-6} mol/L adrenaline.

1.4 ECL assay.

The ECL detection system contains a BPCL-Weak Luminescence Analyzer (Institute of Biophysics, Chinese Academy of Science, Beijing, China), a CHI 620 electrochemical system (CH Instruments, USA) and an ECL cell. 2 mL solution containing 1.0 $\times10^{-5}$ mol/L lucigenin, 1×10^{-8} mol/L H_2O_2, and 0.01 mol/L KCl was transferred to the ECL cell. A conventional three-electrode system was used as the electrolytic system, which composed a glass carbon electrode (GCE) as the working electrode, platinum wire as the counter electrode and an Ag/AgCl (sat. KCl) electrode as the reference electrode.

2. Analysis of real samples

In this study, the proposed method is applied to detect adrenaline in hydrochloric acid adrenal injection (1.0 mg/mL) and clinical serum samples. To the hydrochloric acid adrenal injection, 3 samples with different concentrations is prepared before determination. Each sample is tested for five times under the optimum condition. And the recoveries are examined by the standard addition method to verify the accuracy of the proposed method. The results are listed in Table S2 (see Supporting Information), and the recoveries are in the range of 85.8~106.2%. To clinical serum samples, it is found that there is no ECL response based on this modified electrode. The reason may be the adrenal concentration of the plasma samples is not in the range of linear response of this modified electrode. Next, adrenal standard solutions were added into

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the solution, and then the ECL signals were recorded, shown in Table S3. The recoveries are in the range of 91.0~115.9%. These results demonstrate that the proposed method can be applied to detect adrenaline in real samples successfully.

Figure

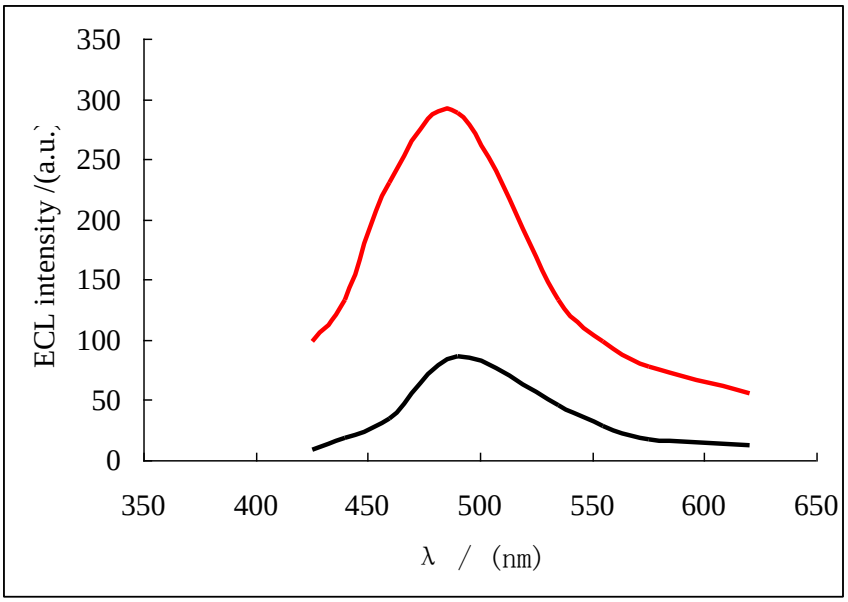

Figure S1 The ECL spectrum of lucigenin on the Tyr/CS/SiC modified electrode in the absence (black line) and presence (red line) of H_2O_2 (1×10^{-8} mol/L). Scan rate: 150mV/s.

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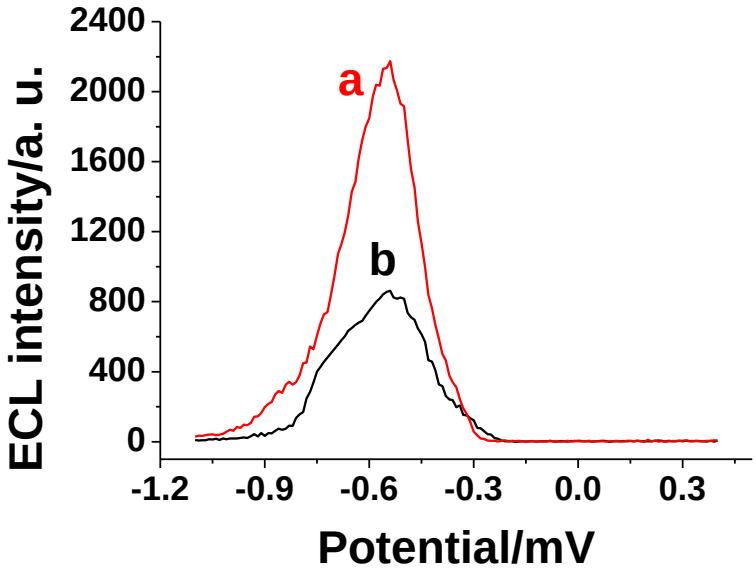

Figure S2 The ECL spectrograms of different electrodes. a. Tyr/CS/SiC modified electrode in the solution containing 5×10^{-6} mol/L adrenaline; b. Control experiment: CS/SiC modified electrode in the solution containing 5×10^{-6} mol/L adrenaline and 1 mg/mL Tyr

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Table T1 The specificity of the proposed method

Interferent	Relative concentration ratio
Na^{+}, SO_4^{2-}, NO^{3-}	1000
Ac^{-}, HPO_4^{2-}	500
EDTA, Citric Acid, Oxalic Acid, Glucose	200
Noradrenaline, Cl^{-}	100
Vitamin C, Dopamine, Uric Acid, L- lysine	50
Fe^{3+}, Ca^{2+}, Mg^{2+}	5
Pb^{2+}, Cu^{2+}, Zn^{2+}	2

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Table T2 Adrenaline assay in hydrochloric acid adrenal injection samples by the proposed method (n = 5).

Sample number	$C_{adrenaline}$(mol/L)			Recovery (%)
	Diluted (mol/L)	Added (mol/L)	Found after adding (mol/L)	
1	4.40×10^{-8}	1.00×10^{-8}	5.11×10^{-8}	94.6
2	4.40×10^{-7}	1.00×10^{-6}	1.24×10^{-6}	85.8
3	4.40×10^{-6}	1.00×10^{-7}	4.78×10^{-6}	106.2
4	1.32×10^{-5}	1.00×10^{-5}	2.03×10^{-5}	87.6

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Table T3 Adrenaline assay in clinical serum samples by the proposed method (n = 5).

Sample	Add adrenaline (mol/L)	Detection after Addition (mol/L)	Recovery (%)
1	1.00×10^{-8}	1.07×10^{-8}	104.1
	2.00×10^{-8}	1.90×10^{-8}	95.4
	5.00×10^{-8}	5.10×10^{-8}	106.9
2	1.00×10^{-8}	0.99×10^{-8}	104.0
	2.00×10^{-8}	2.23×10^{-8}	113.2
	5.00×10^{-8}	5.01×10^{-8}	100.5
3	1.00×10^{-8}	1.12×10^{-8}	115.9
	2.00×10^{-8}	1.95×10^{-8}	98.1
	5.00×10^{-8}	4.90×10^{-8}	91.0