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Indirect detection of 5-hydroxytryptamine and tyramine by using *tris*(2,2'-bipyridyl)ruthenium-graphene modified electrode coupled with capillary electrophoresis

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RESEARCH ARTICLE

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ABSTRACT

A highly sensitive and stable solid-state electrochemiluminescence (ECL) sensor was developed based on *tris*(2,2'-bipyridyl)ruthenium(II) ($Ru(bpy)_3^{2+}$) integrating with 2,2-azino-*bis*(3-ethylbenzothiazoline-6-sulfonic acid) (ABTS) functionalized graphene. $Ru(bpy)_3^{2+}$ is incorporated with the ABTS functionalized graphene based on not only the π-π stacking but also electrostatic interactions. Coupled with capillary electrophoresis (CE), this ECL sensor was used to detect tyramine and 5-hydroxytryptamine (5-HT) based on their quenching effects for the $Ru(bpy)_3^{2+}$/tripropylamine (TPA) system. The quenching mechanism was illustrated and the conditions for CE separation and ECL detection were optimized. Based on an S/N = 3, the limit of detection (LOD) for tyramine and 5-HT were 0.1 μM and 0.02 μM, respectively. The applicability of the proposed method was further illustrated in the determination of tyramine and 5-HT in human plasma samples from small intestine carcinoid patients.

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SUPPLEMENTARY MATERIALS

1. FTIR spectra data

The IR spectrum of the graphene oxide (Figure S1b) showed a C-O stretch peak at 1055 cm^{-1}, a C=O stretch at 1720 cm^{-1}, as well as strong O-H stretch at 1382 and 3423 cm^{-1}. These peaks indicated the presence of oxygen functional groups on the surface of GO [1]. The peak at 1629 cm^{-1} could be attributed to the stretching deformation vibration of intercalated water and the skeletal vibrations of unoxidized graphitic domains [2]. After reduction with hydrazine, the residual oxygen functionalities are still present on the graphene surface; however, the IR intensities of those oxygen containing groups decrease significantly (Figure S1a), indicating that graphene oxide has been well deoxygened and the graphene is successfully prepared. The assembly of ABTS on graphene results in the characteristic vibration of $-CH_2-$ groups at 2927 cm^{-1} in the IR spectrum (Figure S1c). The peaks at 1180 and 1020 cm^{-1} are assigned to the $-SO_3$ group antisymmetric and symmetric vibration adsorption, respectively [3]. Peaks at 770 and 730 cm^{-1} can be assigned to the in-plane skeleton vibration and in-plane bending vibration of the benzene ring, respectively.

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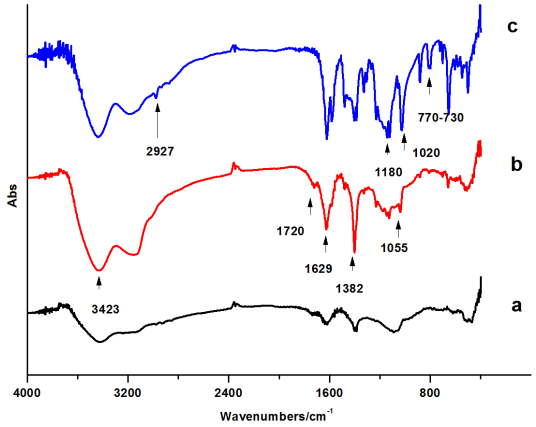

Figure S1. FT-IR spectra of the graphene (a), graphite oxide (b) and ABTS-graphene (c).

2. Optimization of the concentrations of TPA

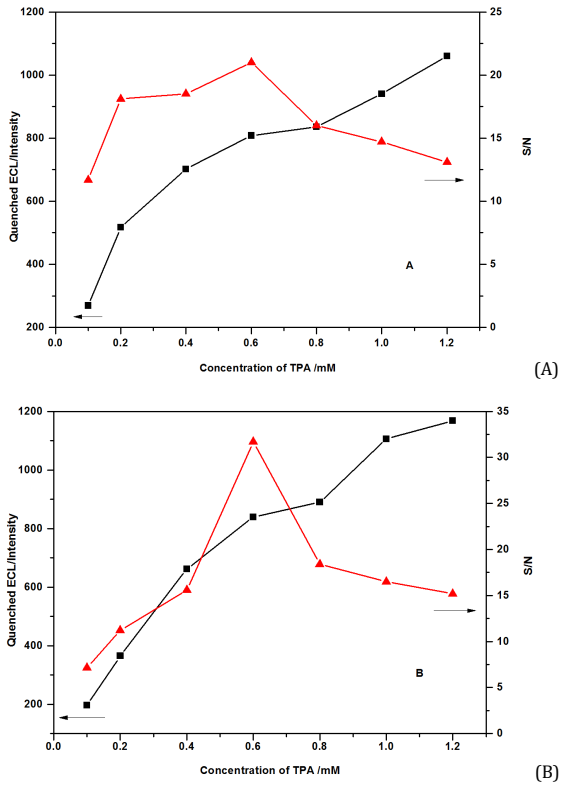

Figure S2. Effect of the TPA concentration on quenched ECL intensity for 10 μM tyramine (A), 10 μM 5-HT (B) and the ratio of S/N. Running buffer: 15 mM PBS at pH = 8.5 containing different concentration of TPA, ECL buffer: 50 mM PBS at pH = 8.0. electrokinetic injection: 10 s at 10 kV, separation voltage, 15 kV; detection potential, 1.20 V.

3. Effect of detection potential

Figure S3 showed the ECL intensity as a function of the potential applied on the working electrode (1.10 - 1.35 V). As increase of applied potential, the quenched ECL intensity for both 5-HT and tyramine increased and reached a maximum value at 1.20 V. When the potential exceeded 1.20 V, the quenched ECL responses markedly decreased, possibly resulted from the negative effect of the oxidation of water. Furthermore, too high potentials also led to huge background noises and an unstable baseline.

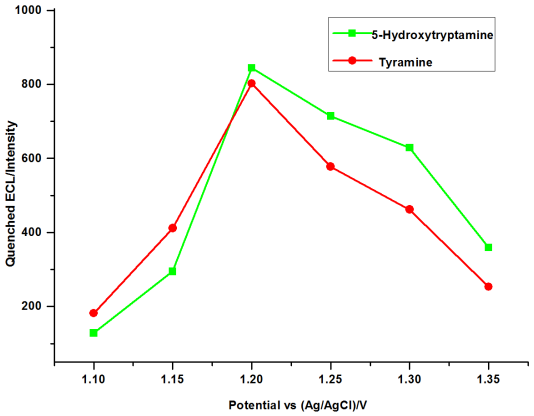

Figure S3. Effect of the detection potential on quenched ECL intensity of 10 μM 5-HT and 10 μM tyramine. Running buffer: 15 mM PBS at pH = 8.5 containing 0.6 mM TPA; ECL buffer: 50 mM PBS at pH 8.0. electrokinetic injection: 10 s at 10 kV; separation voltage, 15 kV.

4. Effect of pH of the buffer in detection cell

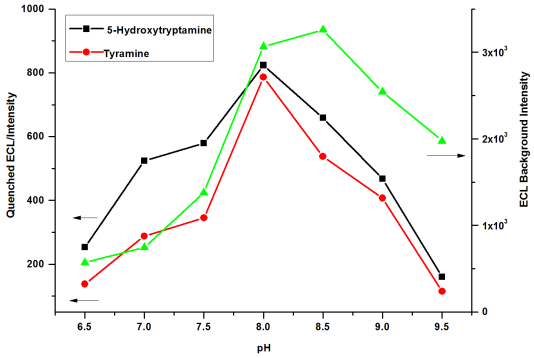

Figure S4. Effect of pH of the buffer in detection cell on quenched ECL intensity of 10 μM 5-HT, 10 μM tyramine and ECL background signal intensity. Running buffer: 15 mM PBS at pH = 8.5 containing 0.6 mM TPA, ECL buffer: 50 mM PBS. electrokinetic injection: 10 s at 10 kV, separation voltage, 15 kV, detection potential, 1.20 V.

5. Effects of pH of running buffer

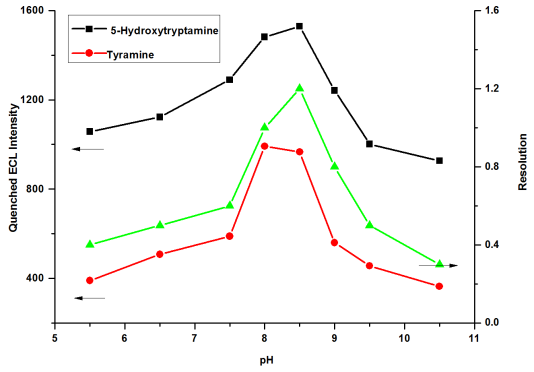

Figure S5. Effects of pH of the running buffer solution on the quenched ECL intensity for the two analytes and Rs. Running buffer: 15 mM PBS containing 0.6 mM TPA; ECL buffer: 50 mM PBS. electrokinetic injection: 10 s at 10 kV; separation voltage, 15 kV, detection potential, 1.20 V.

6. Effects of concentration of running buffer

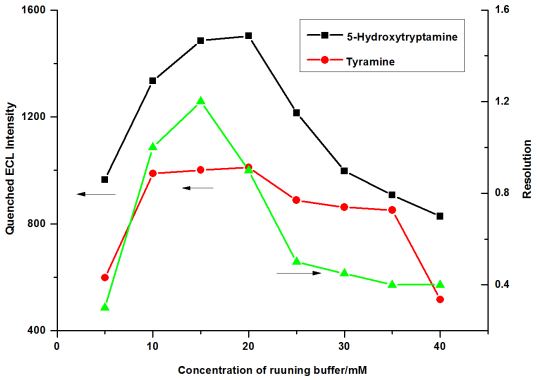

Figure S6. Effects of ionic concentration of running buffer solution on the quenched ECL intensity for the two analytes and Rs. Running buffer: PBS at pH = 8.5 containing 0.6 mM TPA; ECL buffer: 50 mM PBS. electrokinetic injection: 10 s at 10 kV; separation voltage, 15 kV, detection potential, 1.20 V.

Reference

[S-1] Titelman, G. I.; Gelman, V.; Bron, S.; Khalfin, R. L.; Cohen, Y.; Bianco-Peled, H. *Carbon*. **2005**, *43(3)*, 641-649.
[S-2] Jeong, H. K.; Lee, Y. P.; Lahaye, R. J.; Park, M. H.; An, K. H.; Kim, I. J.; Yang, C. W.; Park, C. Y.; Ruoff, R. S.; Lee, Y. H. *J. Am. Chem. Soc.* **2008**, *130(4)*, 1362-1366.
[S-3] Yang, J. C.; Jablonsky, M. J.; Mays, J. W. *Polymer* **2002**, *43(19)*, 5125-5132.