Surpporting Information

A solid-state electrochemiluminescent sensor based on C_{60} /graphite-like carbon nitride nanosheet for detecting melamine

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Fig. S1 (A) UV-vis absorption spectra and (B) FT-IR spectra of (a) C_{60} , (b) $g-C_3N_4$ NS, and (c) $C_{60}/g-C_3N_4$ NS.

Fig. S2 Comparison of ECL intensity of (a) $g-C_3N_4$ NS/GCE and (b) $C_{60}/g-C_3N_4$ NS/GCE in 0.10 M PBS (pH 8.0) containing 0.010 M $K_2S_2O_8$.

Fig. S3 Effects of (A) the pH of PBS, (B) the concentration of $K_2S_2O_8$ and (C) the scan rate on the ECL intensity of the sensor with 2.0×10^{-12} M melamine.

 Table S1 Comparison of the analytical performance of different melamine ECL sensors.



Fig. S1



Fig. S2

Optimization of detection conditions

In order to achieve a high sensitivity of this ECL system, the pH of PBS, the concentration of $K_2S_2O_8$ and the scan rate were optimized. The effect of pH on ECL intensity was investigated in the range of pH 6.0~9.0 with 2.0×10^{-12} M melamine. As seen in Fig. S3A, the change of ECL intensity (ΔI) enhanced when pH varied from 6.0 to 8.0, then fell down as pH ranged from 8.0 to 9.0. At low pH, the proton could be readily reduced at the negative potential, which suppressed the electro-reduction of g-C₃N₄ NS, leading to a decrease in ECL intensity. At too high pH, the formation of excited state of C₃N₄ (g-C₃N₄^{*}) was inhibited due to the fact that the strong oxidant SO₄⁻⁻ (negatively charged radical of S₂O₈²⁻) would react with OH⁻,¹ resulting in a decrease of ECL emission. Thus, pH 8.0 was chosen as the optimal pH in the further experiments.



Fig. S3

The effect of $K_2S_2O_8$ concentration on the analytical performance of the ECL sensor was also investigated. As shown in Fig. S3B, with the increase of $K_2S_2O_8$ concentration from 0.0020 to 0.010 M, ΔI gradually increased, and reached the maximum at 0.010 M. Further increase in the $K_2S_2O_8$ concentration from 0.012 to 0.016 M resulted in a decrease of the ECL intensity. According to the ECL emission mechanisms, the g-C₃N₄^{*} was generated from the interaction between negatively charged radical of g-C₃N₄ (g-C₃N₄^{*-}) and SO₄^{*-}. Excess S₂O₈²⁻ would react easily with g-C₃N₄^{*-}, thus suppressed the generation of g-C₃N₄^{*.2} So, 0.010 M was adopted as the optimal concentration of $K_2S_2O_8$ for subsequent study.

The effect of the scan rate on ECL intensity depended on the chemical kinetics of the ECL system as well as the rate of $K_2S_2O_8$ diffusion toward the solid modified electrode. Fig. S3C depicts the effect of scan rate on ECL intensity. The ECL intensity increased with the increase of scan rate from 25 mV s⁻¹ to100 mV s⁻¹, and decreased beyond 100 mV s⁻¹. At high scan rates, the diffusion of the $S_2O_8^{2-}$ from the solution to the electrode surface would be much slower than the consumption of $S_2O_8^{2-}$ on the electrode interface, resulting in a low transient concentration of $S_2O_8^{2-}$ near the electrode surface accompanying with a decrease of ECL signal.³ Thus, 100 m V s⁻¹ was chosen as the scanning rate in subsequent experiments.

Electrode	Method	Linear range (M)	Limit of detection (M)	Reference
mSiO ₂ nanospheres /	ECL	7.81×10 ⁻⁹ -5×10 ⁻⁶	2.6×10-9	16
Ru(bpy)32+ /Nafon/GCE				
Р-	ECL	1×10 ⁻¹³ -1×10 ⁻⁸	1×10 ⁻¹³	17
RGO/Ru(bpy)3 ²⁺ /@SiO ₂ /N				
afion/GCE				
MPA ^a -capped CdTe QDs /	ECL	10 ⁻⁹ -5×10 ⁻⁵	6.74 ×10 ⁻¹⁰	35
GCE				
chemically converted	ECL	1×10 ⁻¹⁵ -1×10 ⁻¹¹	1×10 ⁻¹⁵	34
graphene/GCE				
PFO/GCE	ECL	9.0×10 ⁻¹¹ -1.1×10 ⁻⁸	1×10 ⁻¹¹	36
C_{60}/g - C_3N_4 NS	ECL	5.0×10 ⁻¹³ -1.9×10 ⁻⁸	1.3×10 ⁻¹³	This work

Table S1

1. C. M. Cheng, Y. Huang, X. Q. Tian, B. Z. Zheng, H. Y. Yuan, D. Xiao, S. P. Xie and M. M. F. Choi, *Anal. Chem.*, 2012, **84**, 4754–4759.

2. X. J. Li, Z. K. Guo, J. X. Li, Y. Zhang, H.M. Ma, X.H. Pang, B. Du and Q. Wei, *Anal. Chim. Acta.*, 2015, **854**, 40–46.

3. X. M. Fu, J. H. Feng, X. R. Tan, Q. Y. Lu, R. Yuan and S. H. Chen, *RSC Adv.*, 2015, **5**, 42698–42704.