

Supporting Information

Modulation of afterglow electrochemiluminescence from nitrogen-deficient graphitic carbon nitride by pH

Lichan Chen,* Xuetao Jia, Weiye Zhao, Sixuan Cheng and Shu-Feng Zhou

College of Chemical Engineering, Huaqiao University, Xiamen 361021, China

Email: lchen@hqu.edu.cn

Experimental section

Chemicals. Dicyanamide, potassium thiocyanate (KSCN), sodium hydroxide, phosphoric acid and potassium persulfate ($K_2S_2O_8$) were from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All of the other chemicals were of reagent grade and used as received. 2.0 M PBS with different pH was prepared by mixing 2.0 M phosphoric acid and 2.0 M sodium hydroxide aqueous solution, and diluted with water to desired concentration. PBS with different pH containing $K_2S_2O_8$ was used as the electrolyte in ECL analysis. Ultrapure water, with a resistivity of 18.2 M Ω (Millipore), was used throughout this work. Dialysis bag with a molecular weight cutoff of 5 kDa was obtained from Viskase.

Preparation of g-C₃N_{4-x}NS and g-C₃N₄NS. g-C₃N_{4-x}NS and g-C₃N₄NS were prepared according to our previous report.¹ Briefly, bulk g-C₃N₄ was firstly synthesized by heating dicyanamide at 550 °C for 4 h with a heating rate of 2.2 °C/min. Subsequently, bulk g-C₃N_{4-x} was prepared by heating the well-ground mixture of 0.8 g CN and 1.6 g pre-dried KSCN in air first to 400 °C with a heating rate of 10 °C/min for 1 h then to

500 °C with a heating rate of 10 °C/min for 0.5 h. The resulting yellow powder was well ground, dialyzed against water using a dialysis bag and dried at 60 °C in a vacuum. g-C₃N_{4-x} nanosheets (g-C₃N_{4-x}NS) were then fabricated by ultrasonication-mediated exfoliation of bulk g-C₃N_{4-x} in water. 100 mg g-C₃N_{4-x} was dispersed in 30 mL water and ultrasonicated for 2 h. The g-C₃N_{4-x}NS suspension was collected by centrifugation at 5000 rpm, and the concentration of the suspension was then adjusted to 0.5 mg/mL, which was measured by weighting the powder dried from a certain volume of the suspension. g-C₃N₄NS was prepared in parallel in the absence of KSCN.

Apparatus. Fluorescence spectra were measured on a Japan Hitachi F-4600 spectrometer. UV-vis spectra were collected with a UV-vis spectrophotometer (UV2450). ECL and electrochemical responses of g-C₃N₄NS and g-C₃N_{4-x}NS were recorded on an ECL detection system (MPI-E, Remex Electronic Instrument Ltd. Co., Xi'an, China) with a three-electrode system composed of a g-C₃N₄NS or g-C₃N_{4-x}NS-modified glassy carbon electrode (GCE, 3 mm in diameter), a Pt wire counter electrode, and an Ag/AgCl (3.0 M) reference electrode. The integral area of the afterglow ECL was calculated using the Origin software peak integration module.

ECL test. Prior to electrode modification, GCEs were sequentially polished with 300 and 50 nm alumina powder and then washed ultrasonically in water. The as-polished GCE was coated with 6 μL of g-C₃N₄NS or g-C₃N_{4-x}NS with a concentration of 0.5 mg/mL and dried naturally at room temperature to form a semi-transparent film. Electrochemical methods including cyclic voltammetry (CV) and step pulse (SP) were employed for ECL activity investigation. In the case of the CV method, 0.1 M PBS

with different pH containing 1 mM $K_2S_2O_8$ were used as the electrolyte. In the case of the SP method, 1 M PBS with different pH containing 1 mM $K_2S_2O_8$ were used as the electrolyte; the potential (V_1) and duration (t_1) for electron injection from the electrode into $g-C_3N_{4-x}NS$ were set as -1.0 V and 20 s, respectively, while the potential (V_2) and time (t_2) for afterglow ECL generation were set as 0 V and 100 s, respectively. The voltage of the photomultiplier tube was set as 800 V.

Results and discussion

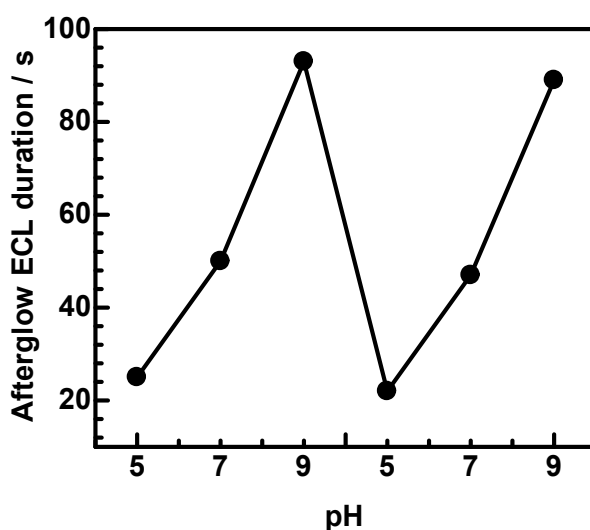


Figure S1. The afterglow ECL duration recorded by successive scanning of the $g-C_3N_{4-x}NS$ modified GCE in 1.0 M PBS with different pH containing 1 mM $K_2S_2O_8$. SP parameters: $V_1 = -1.0$ V, $t_1 = 20$ s, $V_2 = 0$ V, and $t_2 = 100$ s.

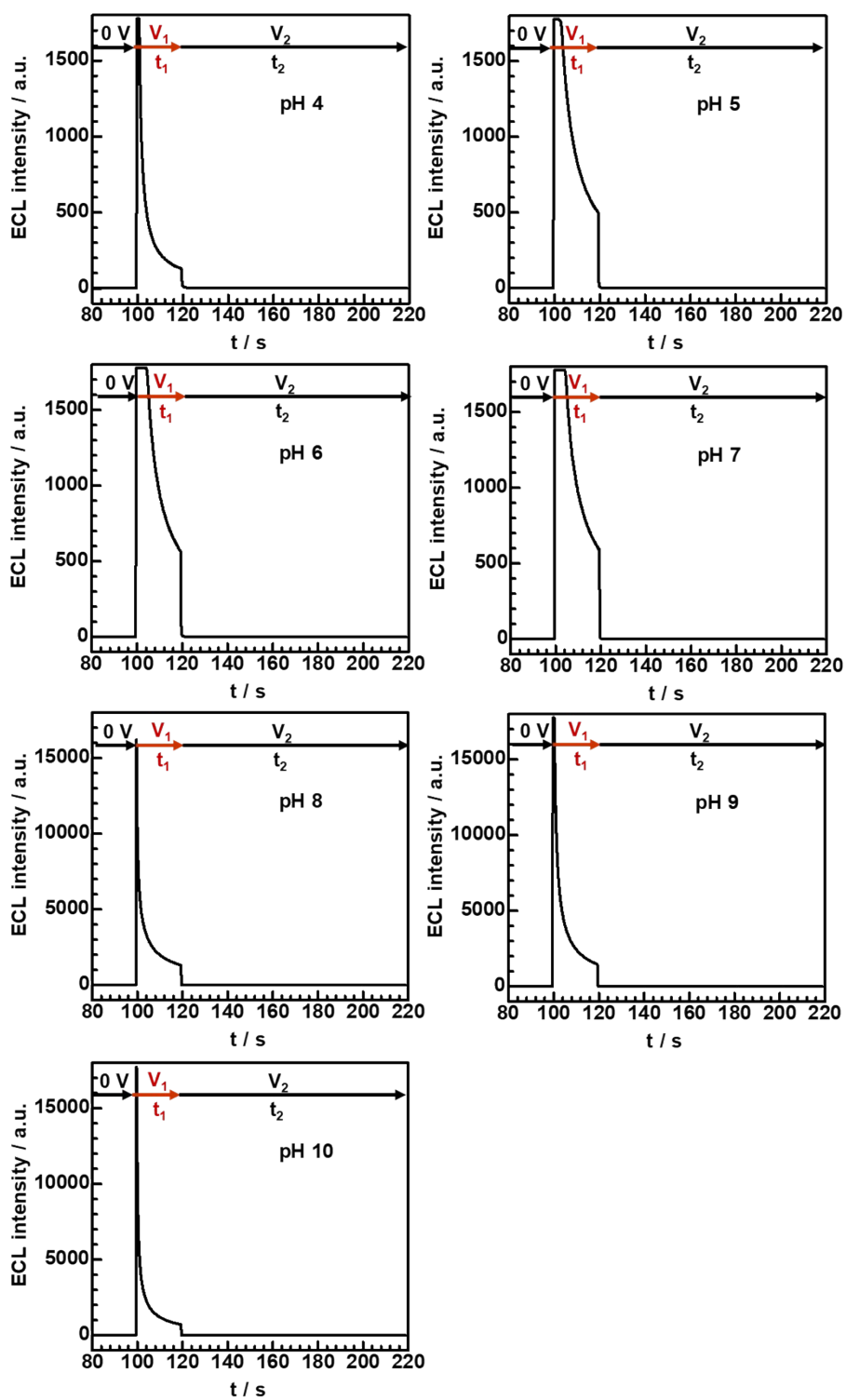


Figure S2. Cathodic afterglow ECL emission from $g\text{-C}_3\text{N}_4\text{NS}$ in 1.0 M PBS with different pH containing 1 mM $\text{K}_2\text{S}_2\text{O}_8$. SP parameters: $V_1 = -1.0$ V, $t_1 = 20$ s, $V_2 = 0$ V, and $t_2 = 100$ s.

References

1. L. Chen, X. Zhu, J. Wei, L. Tian, C. Hu, X. Xiang and S.-F. Zhou, *Anal Chem*, 2023, **95**, 2917-2924.