Supporting Information

Film permeability triggered afterglow electrochemiluminescence for lipase detection

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Preparation of CN_xNS

Heptazine-based carbon nitride (CN) was prepared by heating dicyanamide at 550 °C for 4 h with a heating rate of 2.2 °C min^{-1}, and KSCN was dried in a vacuum at 140 °C overnight. Then the well-ground mixture of 0.8 g CN and 1.6 g KSCN was loaded in a crucible and put in a furnace. The mixture was heated to 400 °C in air with a heating rate of 10 °C min^{-1} for 1 h and then to 500 °C at 10 °C min^{-1} for 0.5 h. The resulting yellow bulk CN_x was thoroughly ground, dialyzed against ultrapure water using a dialysis bag with a molecular weight cutoff of 5 kDa purchased from Viskase, dried at 60 °C in a vacuum. CN_x nanosheets (CN_xNS) were then prepared by ultrasonication-mediated liquid exfoliation of bulk CN_x. Briefly, 100 mg of bulk CN_x was dispersed in 30 mL of water and then ultrasonicated for 2 h. The CN_xNS suspension was collected by centrifugation at 5000 rpm to remove the exfoliated residue, and the concentration was adjusted to 1.0 mg mL^{-1}, which was measured by weighing the powder dried from a certain volume of the suspension.

Calculation of afterglow ECL integral area

The integral area of the afterglow ECL, as illustrated in Fig.S1, was calculated using the Origin software peak integration module.

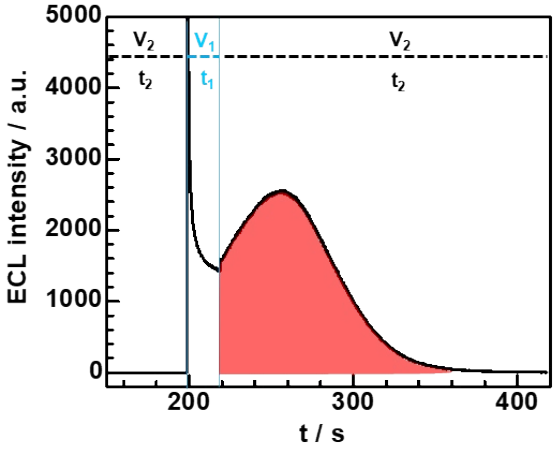

Figure S1. Diagrammatic representation of afterglow ECL integral area.

The afterglow ECL mechanism of CN_xNS-$S_2O_8^{2-}$ coreactant system

Graphitic carbon nitride nanosheets (CNNS) feature the typical structure of polymerized heptazine (PH). The KSCN-assisted post-thermal treatment incorporates CNNS with the cyanamide group (−C≡N), −OH group, nitrogen vacancy (N_v), and K^+, the obtained nanomaterials were named CN_xNS. CN_xNS consists of both PH motifs and the PH with nitrogen deficiency (PH_x) motifs. The afterglow ECL of CN_xNS mainly originated from the PH_x motifs involved ECL reaction.[1]

(1) Trapping electrons injected from electrode into the midgap state of PH_x at V_1

$$PH_x + e^- \rightarrow PH_x^{\bullet -} \qquad (R1)$$

(2) Consumption of the trapped electrons for $SO_4^{\bullet -}$ generation

$$PH_x^{\bullet -} + S_2O_8^{2-} \rightarrow PH_x + SO_4^{\bullet -} \qquad (R2)$$

(3) Hole injection from $SO_4^{\bullet -}$ into the valence band of PH_x

$$SO_4^{\bullet -} + PH_x \rightarrow PH_x^{\bullet +} + SO_4^{2-} \qquad (R3)$$

(4) ECL emission from the annihilation reaction

$$PH_x^{\bullet -} + PH_x^{\bullet +} \rightarrow PH_x^* \qquad (R4)$$

$$PH_x^* \rightarrow PH_x + hv \qquad (R5)$$

The dependence of CN_xNS afterglow ECL area on $S_2O_8^{2-}$ concentration

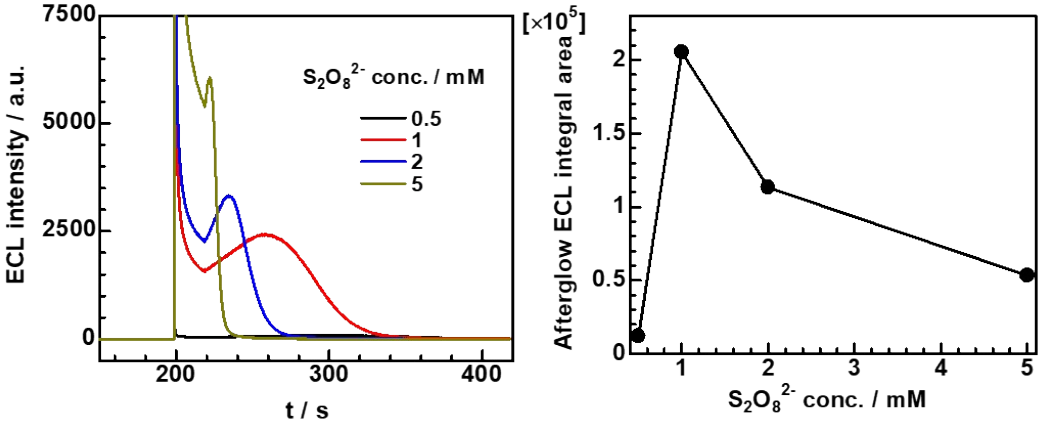

Figure S2. The dependence of CN_xNS afterglow ECL area on $S_2O_8^{2-}$ concentration. The ECL was tested in 1.0 M pH 7.0 PBS containing different concentrations of $S_2O_8^{2-}$.

The stability of the afterglow ECL emission of CN_xNS film

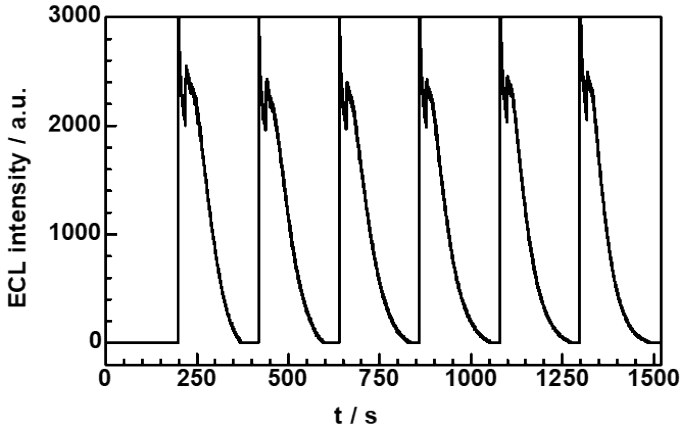

Figure S3. The afterglow ECL emission of CN_xNS film under continuous SPs for 6 cycles in 1.0 M pH 7.0 PBS containing 1 mM $S_2O_8^{2-}$.

The stability of the afterglow ECL of the CN_xNS-PCL-PEG modified electrode

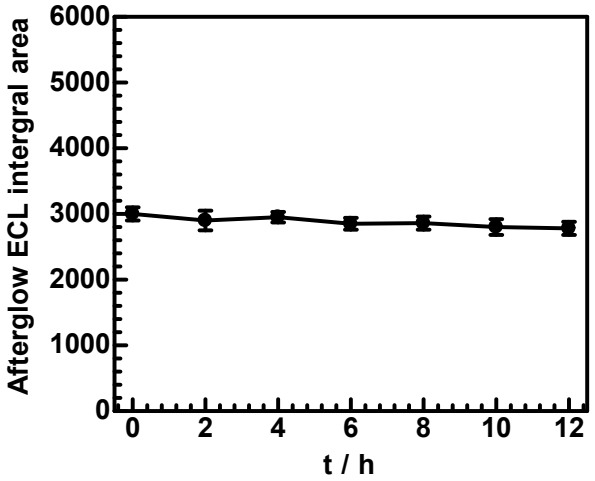

Figure S4. The afterglow ECL integral area of the CN_xNS-PCL-PEG modified electrode by immersing in 10 mM PBS at 37 ℃ for different times.

Table S1. Comparison of the analytical performances of the ECL sensor in the determination of lipase activity with those of other sensors

Methods	Sensing mechanism	Linear range	Detection limit	Ref
ECL	Lipase degradation induced afterglow ECL recovery	0.001-10 U L^{-1}	1 mU L^{-1}	This work
Fluorescence	aggregation-induced emission (AIE) using tetraphenylethylene (TPE) derivative	0-80 U L^{-1}	0.13 U L^{-1}	[2]
Fluorescence	lipase-regulated carbon dots surface trap state	0-9 mg mL^{-1}	0.01 mg mL^{-1}	[3]
Naked eye	Phase separation-induced viscosity change	0.052-30 U L^{-1}	0.052 U L^{-1}	[4]
Colorimetry	Lipase hydrolysis of the carboxyl ester bond in Tween 80 controlled the rate of AuNRs reshaping	0-4.5 mg mL^{-1}	0.017 mg mL^{-1}	[5]
Electrochemistry	lipase hydrolysis of substrate layer deposited on a PCB stick electrode induced impedance changes	9.9-1680 U L^{-1}	8 U L^{-1}	[6]
Surface-enhanced resonance Raman scattering (SERS)	lipase hydrolysis at the 8-hydroxyl position of dye turned on the SERRS signal	-	0.2 ng mL^{-1}	[7]

The afterglow ECL response of the CN_xNS-PCL-PEG modified electrode and the CN_xNS-PCL modified electrode towards 1 mU mL^{-1} lipase

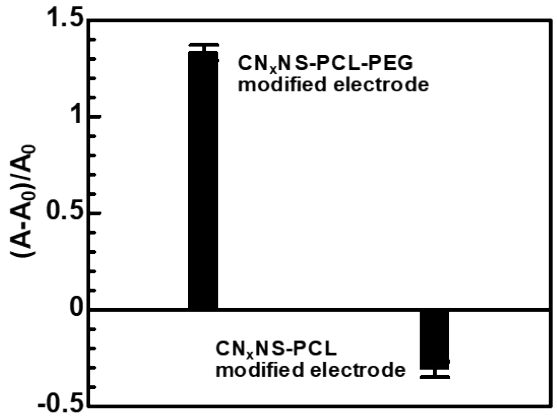

Figure S5. The afterglow ECL recovery factor measured by immersing the CN_xNS-PCL-PEG modified electrode and the CN_xNS-PCL modified electrode in 10 mM PBS containing 1 mU mL^{-1} lipase at 37 ℃ for 60 min.

The diluted skin toner detection

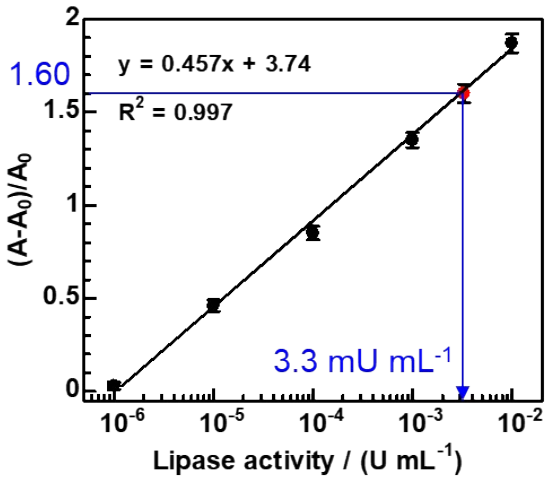

Figure S6. Detection of the lipase activity in the 100-fold diluted skin toner.

References

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