

Electronic Supplemental Information

Anchoring AgBr nanoparticles on nitrogen-doped graphene for enhancement of electrochemiluminescence and radical stability

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Experimental section

Preparation of the AgBr-NG Nanocomposites: Nitrogen-doped graphene (NG) was synthesized according to our previous method.^{S1} 5 mg NG was added into 8 mL of ethylene glycol, and the suspension was sonicated for 20 min. Then, 92.8 mg of 1-hexadecyl-3-methylimidazolium bromide ([C₁₆mim]Br) was added into the suspension, and the mixture was stirred magnetically for 30 min. Next, AgNO₃, employed as the source of silver, was dissolved in the ammonia aqueous (25-28%) to obtain the [Ag(NH₃)₂]⁺ solution. The [Ag(NH₃)₂]⁺ and [C₁₆mim]Br solution was quickly added to the NG mixture, and the resulting suspensions were stirred at 90 °C in water bath for 6 h. Finally, the suspension was treated by centrifugation (10000 rpm, 10 min), and the produced solids were collected, washed thoroughly with

deionized water and dried in 50 °C. Besides, the AgBr-graphene oxide (GO) and AgBr- graphene sheets (GNs) have been synthesized by the same procedure of AgBr-NG.

Fabrication of the Modified Electrodes: Prior to modification, the glassy carbon electrode (GCE) was firstly polished with sand paper followed by 1.0, 0.3, and 0.05 mm alumina slurry, respectively. After successive sonication in ethanol and double distilled water, the electrode was rinsed with double distilled water and allowed to dry at room temperature. The procedure for the preparation of the modified electrodes was described as follows: 1.0 mg AgBr-NG was dispersed in 0.5 mL DMF to make an AgBr-NG homogeneous suspension, then 6 μL of this suspension was cast onto the pretreated GCE surface and dried in air at room temperature to form the AgBr-NG modified GCE (denoted as AgBr-NG/GCE). As a comparison, in order to keep the constant amount of AgBr, 6 μL of 0.02 mg mL⁻¹ NG, 1.81 mg mL⁻¹ AgBr suspension, 2 mg mL⁻¹ AgBr-GO suspension and 2 mg mL⁻¹ AgBr-GNs suspension were prepared to fabricate the NG/GCE, AgBr/GCE, AgBr-GO/GCE and AgBr-GNs/GCE, respectively.

Characterization: The transmission electron microscopy (TEM) images were obtained from a H800 microscope (Japan). X-ray diffraction spectra (XRD) was recorded on a Bruker D8 ADVANCE diffractometer with Cu K α ($\lambda = 1.54 \text{ \AA}$) radiation (Germany). Other characteristics were performed via Raman spectra (RM

2000 microscopic confocal Raman spectrometer, England), X-ray photoelectron spectroscopy (XPS, PHI 5000 VersaProbe, Japan). Fluorescence (FL) spectra were acquired by Hitachi F-4500 FL spectrophotometer (Tokyo, Japan).

Electrochemical Measurements: The ECL signals were carried out with a model MPI-A ECL analyzer (Xi'an Remax Electronic Science & Technology Co. Ltd., Xi'an, China) with the voltage of the photomultiplier tube (PMT) set at 800 V in the process of detection. All experiments were performed with a conventional three-electrode system where glassy carbon electrode (GCE, $\Phi = 4$ mm) was used as working electrode, Ag/AgCl (saturated KCl solution) as reference electrode and platinum wire as counter electrode, respectively. The electrochemical measurements were performed in the potential range of 0 to -1.8 V with a scan rate of 100 mV s^{-1} . The ECL spectrum was obtained by collecting the ECL peak intensity during the cyclic potential sweep with a series of optical filters at 400, 420, 440, 460, 480, 500, 520, 540, 560, 580, 600, 620, 640, 660, 680 and 700 nm.

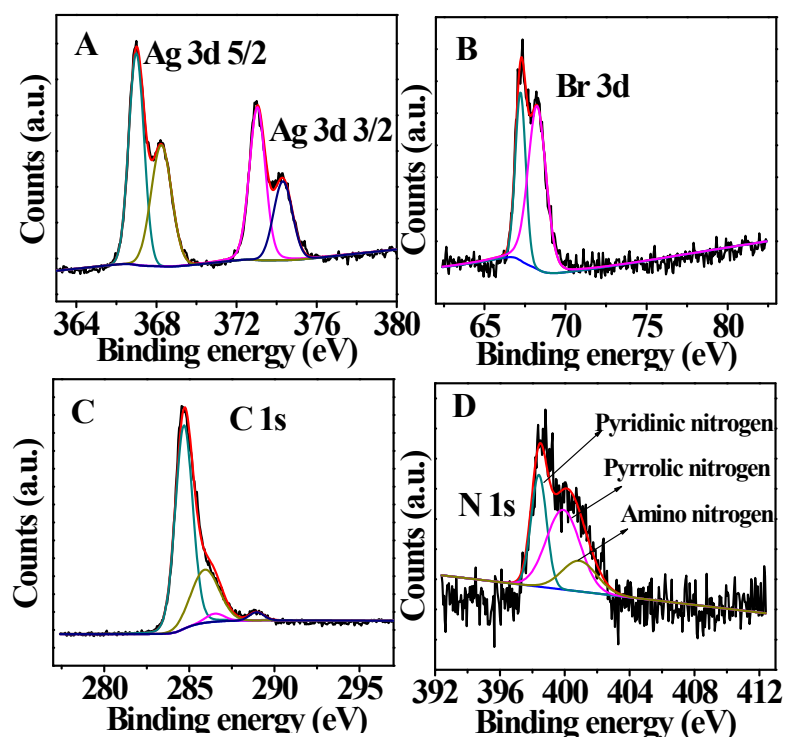


Fig. S1 The high-resolution XPS spectra of Ag 3d (A), Br 3d (B), C 1s (C), and N 1s in the synthesized AgBr-NG nanocomposites.

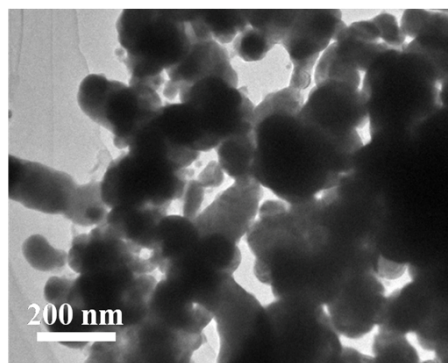


Fig. S2 TEM images of the as-prepared AgBr nanoparticles without the presence of NG.

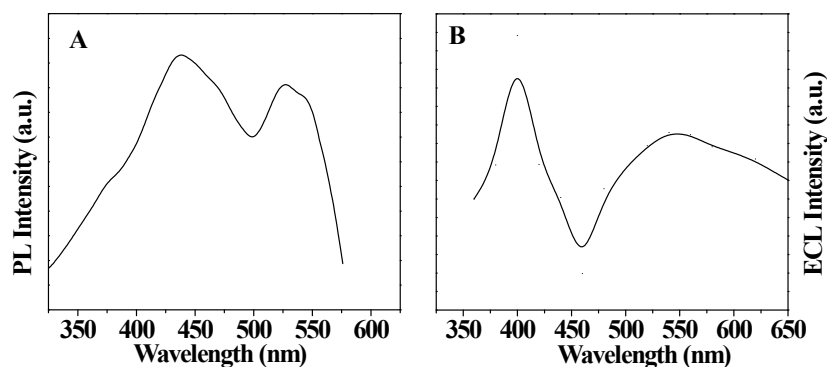


Fig. S3 (A) Photoluminescence ($E_x = 200$ nm) and (B) ECL spectra AgBr-NG modified electrode in 0.10 M PBS containing 0.07 mM $K_2S_2O_8$ by cycling the potential between 0.00 and -1.80 V (vs Ag/AgCl) at 0.14 V/s.

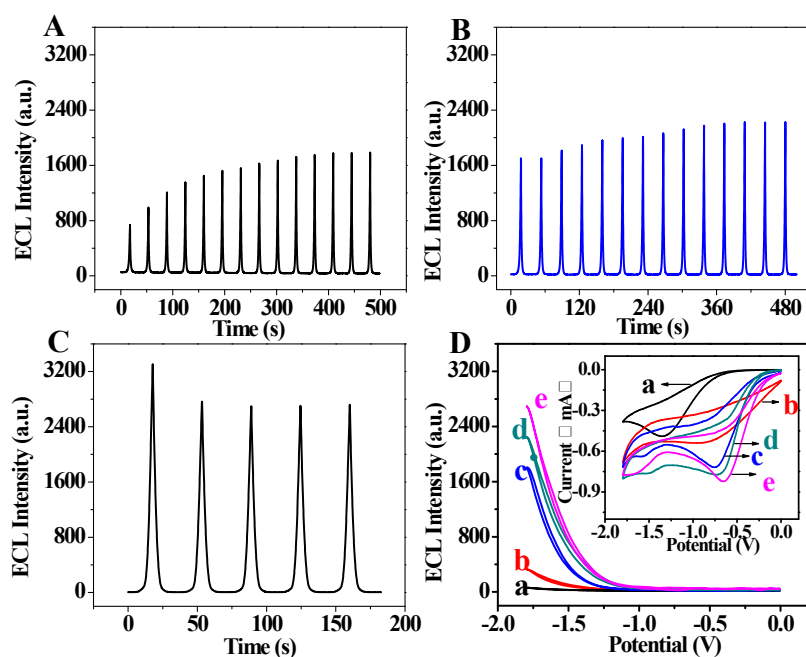


Fig. S4 The comparisons among the ECL performance of AgBr-GO (A), AgBr-GNs (B) and AgBr-NG (C) modified GCE. (D) ECL curves of the bare GCE (a), NG/GCE (b), AgBr-GO/GCE (c), AgBr-GNs/GCE (d) and AgBr-NG/GCE (e) in 0.1 M PBS (pH = 8.0) containing 0.07 M $K_2S_2O_8$ at 0.14 V/s. Inset: the corresponding cyclic voltammograms of them.

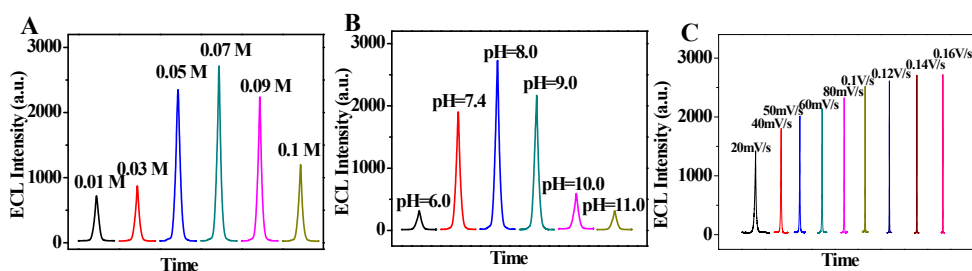


Fig. S5 Effects of (A) concentration of $K_2S_2O_8$ (B) pH and (C) scan rate on ECL intensity of AgBr-NG/GCE.

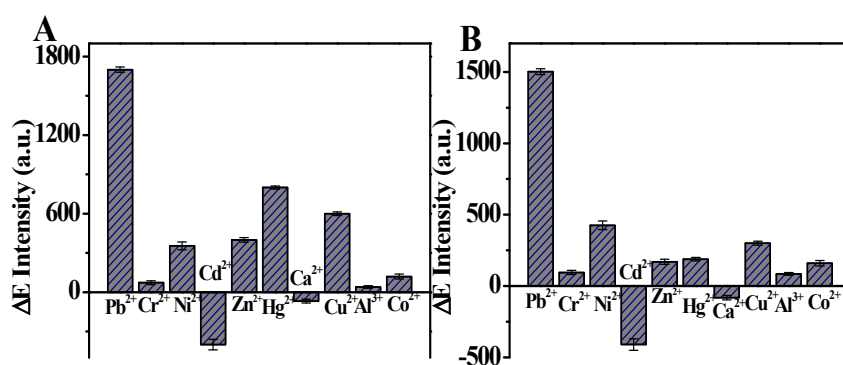


Fig. S6 The ECL intensity changes of AgBr-NG/GCE before and after the addition of $40 \mu M$ metal ions (Pb^{2+} , Cr^{2+} , Ni^{2+} , Cd^{2+} , Zn^{2+} , Hg^{2+} , Ca^{2+} , Cu^{2+} , Al^{3+} and Co^{2+}). The error bars represent the standard deviation for a series of three measurements. $K_2S_2O_8$, 0.07 M; PBS, 0.1 M; pH 8.0; Scan rate : 0.14 V/s.

Discussion on Electrochemical and ECL Behaviors of the Modified Electrode

Fig. S4 showed the ECL performances of AgBr-GO, AgBr-GNs and AgBr-NG, respectively. The results revealed that AgBr-NG was superior to that of AgBr-GO and AgBr-GNs in Fig. S4. The AgBr-NG modified electrode not only enhanced the ECL intensity but also shortened the time of obtaining the stable signals (Fig. S4A, B and

C), which may be ascribed to that NG had more outstanding electrochemical performances such as more electrocatalytic activity and more excellent conductivity compared with GO and GNs.^{S2,S3} For example, our previous work demonstrated that NG-based nanocomposites exhibited higher ECL activities compared with undoped graphene-based nanocomposites.^{S2a}

Besides, the ECL-potential and cyclic voltammograms (CV) of bare electrode, NG, AgBr-GO and AgBr-GNs with $K_2S_2O_8$ have been explored in our work. The ECL responses of the different modified electrodes were investigated in 0.1 M PBS (pH = 8) containing 0.07 M $K_2S_2O_8$, which were recorded simultaneously when the CV were performed. For the bare GCE (Fig. S4D inset curve a), a cathodic peak was observed at $\square -1.35$ V, which was ascribed to the reduction peak of $K_2S_2O_8$ and the overlap peak of dissolved oxygen.^{S4} Similar peaks appearing at NG/GCE (curve b), AgBr-GO/GCE (curve c), AgBr-GNs/GCE (curve d) and AgBr-NG/GCE (curve e), the onset potential of ECL at the AgBr-NG/GCE was more positive than that of other four kinds of modified electrodes (inset of Fig. S4D). Moreover, curves in the inset of Fig. S4D showed the peak current of the AgBr-NG nanocomposite film was enhanced more than that of AgBr-GO and AgBr-GNs film, which manifested that the doped NG could facilitate the electro-chemical redox process of $K_2S_2O_8$ (equal 1: $S_2O_8^{2-} + e^- \rightarrow S_2O_8^{\bullet 3-}$), resulting in the production of more AgBr* and the ECL enhancement of the AgBr-NG.^{S2a} All these results implied that the presence of the nanocomposite AgBr-NG immobilized on the electrode could not only markedly enhance the ECL signal of the modified electrode, but also decreased the potential barriers of the ECL reaction

obviously compared with AgBr-GO and AgBr-GNs film.

Optimization of ECL Working Conditions.

In order to explore the analytical application, the optimal ECL working conditions of the AgBr-NG/GCE were sought by studying the effects of concentration and pH of the electrolyte solution on the ECL of AgBr-NG. Fig. S5A showed the effect of $K_2S_2O_8$ concentration and the ECL intensity increased gradually with the increase of the $K_2S_2O_8$ concentration until it reached a maximum at 0.07 M. Further the increase in $K_2S_2O_8$ concentration caused the decrease in ECL intensity as excess $S_2O_8^{2-}$ would react readily with the negatively charged AgBr which inhibited the formation of the excited-state $AgBr^*$, which was similar to the previous report.^{S5} Consequently, 0.07 M was chosen as the optimal $K_2S_2O_8$ concentration and used throughout this work.

Recent research has stated that the ECL behavior of nano-semiconductors is very sensitive to its surface states,^{S6} and the pH of the medium may alter the surface states of the AgBr-NG nanocomposites due to the adsorption of Lewis bases. Therefore, the effect of pH from 6.0 to 11.0 on the ECL sensor performance was also investigated in our studies (Fig. S5B). As can be seen, the maximum ECL intensity could be obtained at pH 8.0. The possible reason is as follows: at too high pH, the strong oxidant $SO_4^{\bullet-}$ is consumed via the scavenging effect of OH^- and at low pH, the proton could be reduced easily at the negative potential and thus the electro-reduction of AgBr-NG is inhibited.^{S7}

The ECL emission intensity of AgBr-NG/K₂S₂O₈ system can also be influenced by the scan rate. As displayed in Fig. S5C, the ECL intensity increases with the scan rate in the range of 0.02~0.16 V/s, and tends to keep stable when the scan rate is higher than 0.14 V/s. Thus the ECL sensing system for Pb²⁺ was performed at the potential scan rate of 0.14 V/s.

Mechanism of the ECL Quenching of AgBr-NG/K₂S₂O₈ System by Pb²⁺.

The sensing platform based on the ECL system quenching of by Pb²⁺ has been reported.^{S8} According to previous reports,^{S8,S9} the carbon materials with functional groups, such as hydroxyl and carboxyl groups, as well as doped nitrogen were reported to have complexation ability with metal ions and some heavy metal ions would affect (either catalyze or quench) the oxidation of thiol group. Thus, presumably, the quenched mechanism of the lead ion was that some functional groups of AgBr-NG including hydroxyl and carboxyl groups and doped nitrogen could serve as effective coordination groups for metal ions, leading to the decrease of corresponding ECL emission and L-cysteine could prevail over AgBr-NG and result in de-complexation of metal ion-AgBr-NG complex, giving rise to the recovery of ECL. Interestingly, the addition of L-cysteine could recover the quenched ECL induced by all the metal ions (40 μM) except Pb²⁺ (Fig. S6). In other words, the proposed novel ECL sensor for Pb²⁺ was based on the competitive coordination between L-cysteine and AgBr-NG for metal ions. Therefore, the constructed ECL platform could be applied to detect Pb²⁺.

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