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Research Paper

# Porphyrin nanosphere–graphene oxide composite for ehanced electrochemiluminescence and sensitive detection of $Fe^{3+}$ in human serum

Linfang Li [a], Xinming Ning [b], Yaxuan Qian [a], Guiqiang Pu [a], Yanfeng Wang [a], Xiaohui Zhang [a], Huan Wang [a], Jing Chen [a], Duoliang Shan [a], Xiaoquan Lu [a,b,*]

[a] Key Laboratory of Bioelectrochemistry & Environmental Analysis of Gansu Province, College of Chemistry & Chemical Engineering, Northwest Normal University, Lanzhou 730070, PR China

[b] Tianjin Key Laboratory of Molecular Optoelectronic Science, Department of Chemistry, Tianjin University, Tianjin 300072, PR China

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ABSTRACT

An original electrochemiluminescent (ECL) luminophore porphyrin nanosphere–graphene oxide composite (TCPP NS-GO) was prepared. The TCPP NS-GO could produce greatly enhanced ECL in buffer with potassium peroxydisulfate ($K_2S_2O_8$) as the co-reactant. The enhancement ECL mechanism of TCPP NS-GO/$K_2S_2O_8$ system was investigated in detail. Moreover, The TCPP NS-GO composite had an abundant surface functional group to expand its application, which exhibited high sensitivity and selectivity to $Fe^{3+}$. The wide linear relationship between ECL intensity and $Fe^{3+}$ concentration from 0.002 to 5.128 μmol $L^{-1}$ ($R^2$ = 0.998) was found with the detection limit as low as 1 nmol $L^{-1}$. The ECL quenching mechanism of $Fe^{3+}$ was proved by UV-vis absorption spectroscopy, Fluorescence emission spectroscopy (FL) and Fourier transform infrared spectroscopy (FT-IR) analysis technology.



## 1. Introduction

Iron(III) has experienced increasing interest in biological and environmental systems owing to its significance in oxygen uptake and metabolic processes [1–4]. Iron(III) was an important component of haemoglobin, myosin and cytochrome, studies have shown that its deficiency can cause iron deficiency anaemia and aplastic anaemia, resulting in limb weakness and asthma symptoms [5–8]. Therefore, how to detect Iron(III) effectively was an important issue for life system [9,10]. In spite of various analytical techniques for $Fe^{3+}$ detection such as spectrophotometry [11], atomic absorption spectrometry [12], inductively coupled plasma mass spectrometry [13], and voltammetry [14], required complex instrumentation and tedious sample preparation procedures, limiting their application [15,16]. Thus, it was very critical to develop novel methods that could be easily applied to exclusively detect $Fe^{3+}$.

The study found that the ECL technique for more potential advantages than other analytical techniques, and many commercial ECL systems have already been used in many fields such as food-safety analysis, clinical detection, and environmental analysis [17–24]. Luminol and Ru complexes were the most famous ECL luminophores that have been studied [25–28]. In addition to these luminophores, *meso*-tetra(4-carboxyphenyl) porphyrin (TCPP) and its derivatives have aroused more and more interest [29–32]. The development of the so-called co-reactant approach in ECL has been employed in many commercially available ECL instruments, which could be used in environmentally benign and user-friendly aqueous solutions. Moreover, a novel approach with improved the ECL signal, synergistic effect of double co-reactants, was reported by Chen's group in 2015 [33]. Compared with ECL realized through annihilation, dual co-reactants not only could be harnessed but brought under control, to help the anions, cations and the limited potential window of a solvent more stability [34]. Therefore, the synergistic effect of double co-reactants of ECL was necessary.

Recently, graphene oxide (GO), as a new type of material, various of GO-based luminophores have been used in the ECL field, biology and the environmental field [35–37], due to its excellent catalytic capacity, high water solubility, and easy modification

* Corresponding author at: Key Laboratory of Bioelectrochemistry & Environmental Analysis of Gansu Province, College of Chemistry & Chemical Engineering, Northwest Normal University, Lanzhou 730070, PR China. Tel.: +86 931 797 1276; fax: +86 931 797 1276.

*E-mail address:* luxq@nwnu.edu.cn (X. Lu).

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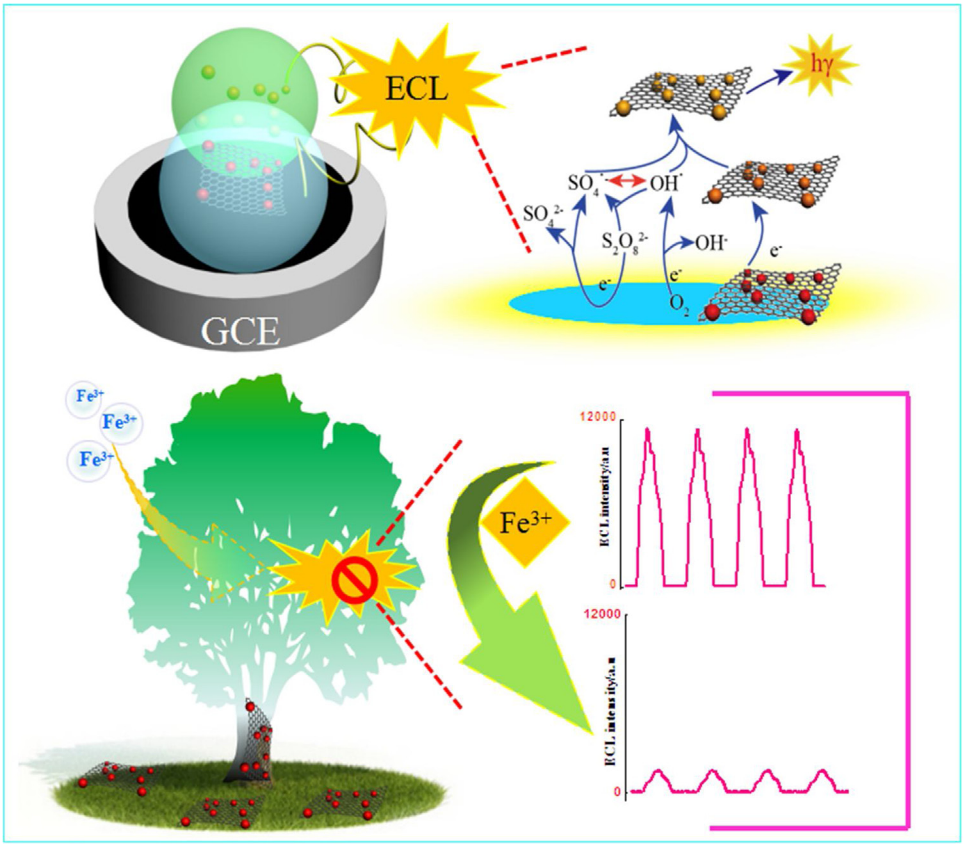


**Scheme 1.** Schematic for the ECL of TCPP NS-GO/$K_2S_2O_8$ system with sensitive detection of $Fe^{3+}$.

[38–41]. Meanwhile, the investigation of organic-based nanostructures was also recognized for potential applications because of their unprecedented optical, electronic, chemical, and mechanical properties. It has reported that luminol-capped AuNPs (lumAuNPs) and ruthenium-silica composite with ECL signal was described [42,43]. The ECL signal of TCPP NS could be effectively amplified in the presence of GO, which produced co-reactant from oxygen reduction. Therefore, the composite based on TCPP NS and GO was found to be attractive for designing promising ECL system.

In this work, we have synthesized a one-dimensional TCPP NS-GO, finding the TCPP NS-GO/$K_2S_2O_8$ system exhibited greatly enhanced ECL, thus, ca. ~10 and ~12 fold enhanced ECL intensity compared to TCPP NS/$K_2S_2O_8$ system or TCPP NS-GO composite in PBS, respectively. The mechanism of TCPP NS-GO/$K_2S_2O_8$ system in PBS was studied. Moreover, the sensor based on the TCPP NS-GO/$K_2S_2O_8$ ECL system could be used for the detection of $Fe^{3+}$sensitively and specially. The general principle of ECL was described in the Scheme 1.

## 2. Experimental

### 2.1. Reagents

GO and TCPP were prepared in our laboratory according to the earlier reports [44,45]. $K_2S_2O_8$ was purchased from Shuangshuang Chemical Co. (Yantai, China). All other reagents were of analytical reagent grade and used as received. The 0.1 mol $L^{-1}$ phosphate buffer (pH 7.0) was used as the supporting electrolytic solution. Ultrapure water was used throughout this work.

### 2.2. Apparatus

SEM images were recorded on a Phenom ProX scanning electron microscope (Netherlands). Cyclic voltammogram (CV) and ECL measurements were recorded on the MPI-A ECL detection system (Xi'an Remex Analytical Instrument Ltd. Co.). A three-electrode system configuration consisting of an Ag/AgCl (saturated KCl) electrode as the reference electrode, a platinum wire electrode as the counter electrode and the modified glassy carbon electrodes (3 mm diameter, GCE) as the working electrodes. FL spectra were measured by the RF5301 FL spectrophotometer (Shimadzu, Tokyo). The UV–vis absorption spectra were obtained on a UV-1102 spectrophotometer (Tianmei scientific instrument Co. Ltd). FT-IR spectra were taken with the NEXUS870 spectrometer (Nicolet instrument Co. USA). The pH of the solution was recorded on a PB-10 (RenHe Instrument Co.).

### 2.3. Preparation of the TCPP NS-GO composite

The synthesized TCPP was characterized by mass spectra and nuclear magnetic resonance spectra, GO was characterized by X-ray powder diffraction (Supporting Information, Fig. S1, S2, S3). They were consistent with previous reports [46–48]. Synthesis of TCPP NS, in detail, 12 mg of TCPP was dispersed into water (2 ml) by ultrasonic treatment for about 30 min. After that, the obtained purple solution was stirred for 40 min with the color changing to red. TCPP NS-GO composite was prepared as follows: firstly, 1 mg $mL^{-1}$ GO solution was treated by ultrasonic for 10 h to completely disperse GO. Then, TCPP NS (6 mg $mL^{-1}$) was added to the obtained GO suspension and stirred in a fume hood at room temperature for 30 min.