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Multifunctional solid-state electrochemiluminescence sensing platform based on poly(ethylenimine) capped N-doped carbon dots as novel co-reactant

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ABSTRACT

A multifunctional solid-state electrochemiluminescence (ECL) sensing platform based on poly(ethylenimine) (PEI) capped N-doped carbon dots (NCDs@PEI) as novel co-reactant of $Ru(bpy)_3^{2+}$ nanosheets (RuNSs) was designed for the first time. In this route, RuNSs with large surface-to-volume ratio was used as luminophor, and NCDs@PEI, which was newly synthesized and modified in one step via a facile microwave-assisted method, was served as co-reactant. The as-prepared NCDs@PEI exhibited better catalytic effect to RuNSs than naked NCDs, due to the double enhancement contribution of NCDs and PEI to RuNSs. Simultaneously, reduced graphene oxide (rGO) was further introduced to facilitate the electron transfer and amplify the ECL signal. The developed ECL sensor (NCDs@PEI-rGO/RuNSs/GCE) exhibited desired ECL emission, with about 69-fold enhancement of the ECL intensity in comparison with RuNSs/GCE. When used as ECL probe for dopamine detection, the prepared sensor showed high sensitivity in a wide linear range of 0.01–50 μM with the detection limit of 10 nM. Moreover, the sensing platform also suggested multifunctional application for detecting other compounds including bisphenol A, catechol and hydroquinone.

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1. Introduction

Electrochemiluminescence (ECL) process involves the electron-transfer reactions between luminous agents or between luminous agent and co-reactant (Richter, 2004). And it is becoming a more valuable detection technique in analytical chemistry and bio-sensing field due to the high sensitivity, low background signal, good stability and simplified instruments (Liu et al., 2015c, 2015a; Ding et al., 2015; Xu et al., 2014). In the recent works, inorganic nanomaterials with large surface-to-volume ratio, such as nanocrystals (Hesari et al., 2015b; Jiang et al., 2015b), semiconductor quantum dots (QDs) (Xia et al., 2015), graphene QDs (Dong et al., 2015; Zhao et al., 2015), conjugated polymer dots (Dai et al., 2015), carbon QDs (Wang et al., 2015b) and other inorganic nanocomposites (Jiang et al., 2015a; Gu et al., 2015; Hesari et al., 2015a), have been widely explored as new luminophores for ECL generation. However, some inorganic nanomaterials-based ECL emitters, especially the most studied Cd-containing QDs, possess inherent shortcomings including high toxicity, poor biocompatibility and low sensitivity (Dong et al., 2013; Yang et al., 2013). Moreover, although some carbon-based QDs have been proved to exhibit exciting ECL emission properties, they only show cathodic ECL signal (Yang et al., 2013; Chen et al., 2014; Wang et al., 2015b), which are not applicable to detect biomolecules that are easily to be oxidized and not suitable to fabricate biosensors.

Metal-organic complexes, especially classic $Ru(bpy)_3^{2+}$ and its derivatives, not only can produce strong anodic ECL emission using analytes as co-reactants, but also can be covalently bonded to proper co-reactant to obtain self-enhanced ECL complexes with high luminous efficiency and stability (Zhuo et al., 2014; Wang et al., 2014; Hong et al., 2015). It is firmly believed when immobilizing $Ru(bpy)_3^{2+}$ on a solid-state substrate or preparing into nanomaterials, the Ru (II) complexes-based ECL sensor is more superior to solution-phase ECL system, such as improved ECL efficiency and stability, reduced consumption of reagent and simplified design approach (Qian et al., 2014). Therefore, many efforts have been extensively devoted to establish regenerable solid-state ECL sensors and develop effective strategies for the immobilization of $Ru(bpy)_3^{2+}$ (Li et al., 2012; Cao et al., 2013; He et al., 2013). For example, Li et al.

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(2012) prepared a novel $Ru(bpy)_3^{2+}$ nanowires via a facile solvent evaporation route, and based on which a ECL biosensor with remarkable detection performance was developed. However, most of the effective co-reactants of $Ru(bpy)_3^{2+}$, such as tripropylamine (TPA) and 2-(dibutylamino)-ethanol(DBAE) (Liu et al., 2007a, 2007b) are toxic or volatile, which limit the application of $Ru(bpy)_3^{2+}$ and affect the experimental accuracy. It has been widely accepted that compounds with abundant amine, especially tertiary amine can be served as effective co-reactant of $Ru(bpy)_3^{2+}$ to obtain significantly enhanced ECL emission. Recently, Yuan's group implemented considerable effort on using poly(ethylenimine) (PEI) or polyamidoamine (PAMAM) dendrimers, with abundant amine in their structures, as co-reactant or support to fabricate self-enhanced ECL biosensor or immunosensor (Zhuo et al., 2014; Wang et al., 2014; Hong et al., 2015; Wang et al., 2015a). This novel self-enhanced ECL system exhibits high ECL efficiency due to the shorter electron-transfer path and less energy loss.

Currently, it has been reported that carbon dots, a new member of luminescent materials with superior optical properties, low toxicity and good biocompatibility, is an eco-friendly and effective co-reactant of the anodic ECL of $Ru(bpy)_3^{2+}$ (Long et al., 2014). And we also have illustrated that N-doped carbon dots (NCDs) can further enhance the ECL signal and improve the reproducibility and stability of $Ru(bpy)_3^{2+}$ ECL system (Li et al., 2015b).

In the present work, in order to further improve the sensitivity, a novel co-reactant, PEI capped NCDs (NCDs@PEI) composite was firstly prepared via a facile microwave-assisted method, which smartly combined the double enhancement contribution of PEI and NCDs to the anodic ECL of RuNSs. The as-prepared NCDs@PEI exhibited low toxicity and high catalytic effect to RuNSs. Meanwhile, reduced graphene oxide (rGO) was introduced to accelerate the electron transfer rate and amplify the ECL signal. The fabricated ECL sensing platform (NCDs@PEI-rGO/RuNSs/GCE) exhibited desired ECL intensity in comparison with RuNSs/GCE and good detection performance for analyzing some diphenol compounds.

2. Experimental

2.1. Reagents and materials

Tris(2,2-bipyridyl) dichlororuthenium(II) hexahydrate ($Ru(bpy)_3Cl_2 \cdot 6H_2O$), branched poly(ethylenimine) (PEI, Mw= 25 kDa), catechol and Nafion solution (5 wt%) were purchased from Sigma-Aldrich. Citric acid and urea were provided by Beijing Chemical Reagents Factory and GEN-VIEW SCIENTIFIC INC., respectively. Dopamine and hydroquinone were offered by Alfa Aesar. Bisphenol A was provided by Aladdin. Dopamine hydrochloride injection was purchased from local hospital. Reduced graphene oxide (rGO) synthesized according to Hummer's method was purchased from Nanjing Xianfeng Nano Co. and used directly without any treatment. Na_2HPO_4, NaH_2PO_4, KCl, $K_3Fe(CN)_6$, $K_4Fe(CN)_6$, ethanol, acetone, acetonitrile and n-propanol were of analytical grade, which were used as received without further purification.

2.2. Apparatus and characterization

Structure and morphology of the as-prepared carbon dots were characterized using a transmission electron microscopy (TEM) and selected area electron diffraction (SAED), which was operated on a TECNAI F20 field-emission TEM at an acceleration voltage of 200 kV. A D8 ADVANCE (Bruker AXS, Germany) X-ray diffractometer with Cu Kα radiation (λ=1.5406 Å) was used to record the X-ray diffraction (XRD) spectra. Fourier transformed infrared spectra (FT-IR) results were obtained from a VERTEX 70 FTIR. X-ray photoelectron spectroscopy (XPS) was measured by A Thermo ESCALAB 250 instrument, coupled with Al Kα radiation (VG Scientific, UK). A Renishaw Raman microscope (model RM2000) with a laser excitation wavelength of 514.5 nm was used to record Raman spectrum. UV–visible adsorption spectra (UV–vis) and fluorescence spectra (FL) were tested on a UV mini 1240 and a LS 55 fluorescence spectrometer, respectively. Electrochemical impedance spectroscopy (EIS) was taken on an AUTOLAB PGSTAT302N workstation.

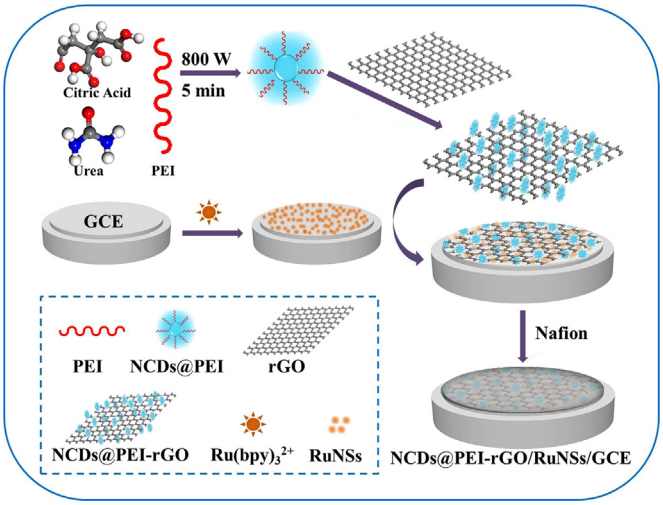
Electrochemical (EC) experiments were performed on a CHI832 electrochemical workstation (Shanghai Chenhua Apparatus Inc., China), and ECL signals were recorded simultaneously using a model MPI-E ECL analyzer (Xi'An Remax Electronic Science and Technology Co. Ltd., China) with a voltage of 800 V supplied to the photomultiplier tubes (PMT). All experiments were carried out with a standard three-electrode system. Glass carbon electrode (GCE, 3 mm) modified with different materials were used as working electrode, an Ag/AgCl (saturated KCL) as reference electrode and a Pt wire as counter electrode.

2.3. Synthesis of NCDs@PEI

The photoluminescent N-doped carbon dots modified with branched PEI (NCDs@PEI) was synthesized by a one-step facile route of microwave assisted method. Briefly, 3 g citric acid, 3 g urea and 6 g PEI was thoroughly dissolved in 10 mL ultrapure water by vigorous stirring for 0.5 h to forming a homogeneous solution in a common beaker. Next, the solution was heated for different time intervals in a domestic microwave oven (800 W). When cooled down to room temperature, the solid products were re-dissolved in deionized water, and isolated from the large carbon residual via centrifugation with 12,000 rpm for 20 min. Then the opaque supernatant solution was dialyzed against pure water using a dialysis bag with a molecular weight cutoff (MWCO) of 50 kDa for three days to remove the excessive precursors. Finally, the solution was concentrated to dry at 60 °C under vacuum to obtained powdered product. As a control, NCDs was also prepared via the same route in the absence of PEI.

2.4. Fabrication of the solid-state ECL sensing platform

Fabrication process of the solid-state ECL sensing platform is shown in Scheme 1: first, bare GCE was polished using alumina powders with average particle diameters of 0.3 and 0.05 μm, respectively, and then ultrasonically washed with distill water, ethanol, acetone and distill water successively. After dried in air,



Scheme 1. Fabrication process of the solid-state ECL biosensor .

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