



Electrochemical reduction and in-situ electrochemiluminescence detection of nitroaromatic compounds



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ABSTRACT

An integrative method based on the combination of electrochemical reduction (ECR) and in-situ electrochemiluminescence (ECL) detection was developed for the sensitive detection of the nitroaromatic compounds (NACs), including 4-nitrotoluene (4-NT), 2,4-dinitrotoluene (2,4-DNT), 2,4,6-trinitrotoluene (TNT). An electrochemical flow cell including two working electrodes was fabricated with poly(dimethylsiloxane) (PDMS) to achieve the dual functions. The first one is a copper mesh electrode, acting as the reductor to convert the NACs to aminoaromatic compounds (AACs). Electrochemical deposition of copper nanoparticles on the surface of the copper mesh was conducted to further increase the reduction efficiency. The second one is an ECL electrode, which was used for in-situ detection of the reduced products. The ECL electrode was fabricated by the immobilization of Ru(bpy)₃²⁺ on a glassy carbon electrode (GCE) with the Nafion/the multi-wall carbon nanotubes (MWCNTs) composite film. The copper mesh electrode was arranged directly underneath the ECL electrode to ensure the reduced products could be immediately detected in-situ. An electrolytic solution consists of 33.3 mmol/L Na₂SO₄ and 16.7 mmol/L phosphate buffer solution (PBS, pH7.0) was found to be optimum for both the electrochemical reduction of the NACs and the ECL detection. The ECL intensities were proportional to the concentrations of 4-NT, 2,4-DNT and TNT in the range from 1.0 × 10⁻⁹ to 1.0 × 10⁻⁵, 3.5 × 10⁻⁹ to 1.0 × 10⁻⁵ and 7.5 × 10⁻⁹ to 1.0 × 10⁻⁵ mol/L respectively. The limit of detections (LOD) were 4.0 × 10⁻¹⁰, 1.7 × 10⁻⁹ and 3.1 × 10⁻⁹ mol/L respectively for 4-NT, 2,4-DNT and TNT. The reduction mechanism was preliminarily investigated and it was found that the presence of oxygen was critical for the reduction process, suggesting that the reductive oxygen species O₂^{•-}, OH[•] could be involved in the NACs reduction process.

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1. Introduction

Nitroaromatic compounds (NACs) refer to the organic compounds that contain aromatic rings and one or more nitro functional groups. They are often highly explosive, especially when the compound contains more than one nitro group and is impure. The one produced on the largest scale, by far, is nitrobenzene. Many explosives are produced by nitration including trinitrophenol (picric acid), 2,4,6-trinitrotoluene (TNT), and trinitroresorcinol. Particularly, the TNT as the representative explosive, exhibits detrimental effects on environment and human health [1,2]. The sensitive detection of trace amounts of NACs is important for security scrutiny in modern society and is often required in airports, train stations, customs, harbors and other

events [3]. Thus it is highly demanding to develop rapid, sensitive and simple analytical method for the detection and monitoring of these NACs at trace levels. A number of analytical techniques are available for the determination of NACs, including colorimetry [4], gas chromatography [5], fluorescence [3,6–8], surface plasmon resonance [9], chemiluminescence (CL) [10], and electrochemistry [11–15]. However, the stratographic and spectroscopic methods require expensive and bulky instrument and the electrochemical methods often lack of high sensitivity, hence these methods are usually not suitable for situ detection of NACs. As an alternative to these techniques, the electrochemiluminescence (ECL) represents a perfect combination of electrochemistry and spectroscopy. It eliminates the background disturbance of electrochemical methods and takes advantages of the high sensitivity of spectroscopic detection and the simplicity of electrochemical instrumentation [16–19]. The ECL method was extensively explored for detection of large number of amino containing compounds, so-called coreactants [16,20,21]. To the best of our knowledge, however, this

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method is rarely used for the NACs detection. This is because that the NACs are not coreactants of ECL reactions, hence they are not detectable in a normal way, although ECL analysis of NACs was reported based on their quenching effect on an ECL reaction [1,22] or with the help of biomolecules such as antibodies and aptamers [23,24]. If the NACs can be transformed to aminoaromatic compounds (AACs) by a reductive reaction, then it would be possible to detect the NACs in a normal coreactant way [25].

Therefore, an electrochemical reduction and in-situ ECL detection method was proposed for the first time for the sensitive detection of NACs. The feasibility of electrochemical reduction of NACs to AACs has been demonstrated by many previous works with the use of zero valent iron or copper electrode [26–28]. Direct electrochemical reduction of NACs can result in various products such as nitroso, hydroxylamine, azoxy, azo and hydrazo compounds. However, high yields of amines could be obtained for a few compounds such as 4-nitrotoluene (4-NT) in the presence of copper electrode [29]. The pretreatment of metal copper mesh and the associated removal of surface coatings further enhanced its reactivity.

Herein we fabricated a flow cell with poly(dimethylsiloxane) (PDMS), in which an electrodeposited copper nanoparticles on copper mesh electrode was used as the reductor and the immobilized Ru(bpy)₃²⁺ on a glassy carbon electrode (GCE) with the Nafion/the multi-wall carbon nanotubes (MWCNTs) composite film was used as the ECL electrode to achieve the in-situ ECL detection of the reduced products. Using this device, the in-situ ECL detection was implemented for the sensitive detection of NACs with the limit of detection (LOD) of 4.0×10^{-10} , 1.7×10^{-9} and 3.1×10^{-9} mol/L respectively for 4-NT, 2,4-dinitrotoluene (2,4-DNT) and TNT.

2. Experimental

2.1. Chemical reagents

Tris (2,2'-bipyridyl) ruthenium (II) dichloride hexahydrate (Ru(bpy)₃Cl₂·6H₂O) and Nafion (perfluorinated ion exchange powder, 5 wt% solution in a mixture of lower aliphatic alcohols and water) were purchased from Sigma Aldrich (Milwaukee, WI, USA). The multi-wall carbon nanotubes (MWCNTs, purity ≥ 95%) were obtained from Shenzhen Nanotech. Port. Co. Ltd China and they were purified and functionalized with a previously described procedure [30]. The PDMS (SYLGARD 184; Dow-Corning, Midland, MI, U.S.A.) was used to fabricate the ECR-ECL flow-detection cell. The 4-NT, 2,4-DNT, 2-methyl-5-nitroaniline (2-M-5-NA) and 2,4-diaminotoluene (2,4-DAT) were obtained from Sinopharm Chemical Reagent Co., Ltd. 4-aminotoluene (4-AT) was obtained from Aladdin Chemistry Co., Ltd. 4-methyl-3-nitroaniline (4-M-3-NA), 2,4,6-Triaminotoluene trihydrochloride (TAT) and the standard solution of TNT (1 mg/mL in acetonitrile) was obtained from J&K Scientific Ltd. All the other reagents were commercially available chemicals and were of analytical grade, except for acetonitrile which was supplied as mobile phase for reverse phase HPLC. Phosphate buffer solution (PBS) containing appropriate concentration of Na₂SO₄ solution was used as the background electrolytes. The CuSO₄ solution (0.05 mol/L) prepared in diluted sulfuric acid was used for electrochemical deposition of copper nanoparticles. Ultra-pure water (18 MΩ cm⁻¹) was used throughout the experiment.

2.2. Instruments

Electrochemical measurements and electrochemical reductive (ECR) reactions were performed on a CHI660D computer-controlled potentiostat (Chen Hua Instruments Co., Shanghai,

China). The ECL experiments were carried out on a CL analyzer (Xi'an Remax Electronic Science Tech. Co. Ltd China). The photomultiplier tube was biased at -600 V. The ECR-ECL flow-detection cell was placed directly on top of the PMT window and was enclosed in a light-tight box. A UV-vis spectroscopy was performed using a double beam UV spectrophotometer with a 1 cm quartz cuvette (Model TU-1901). A Waters 515HPLC was employed for the evaluation of the reduced products, which was equipped with an Atlantis[®] 5 μm 4.6 × 250 mm C-18 column and Waters 2487 Dual λ Absorbance Detector. The surface deposits of copper mesh were visually checked with a Keyence VHX-1000 Digital Microscope (Lens: VH-Z250R) (Keyence, Japan).

2.3. Methods

The sample solution containing electrolyte was delivered to the flow cell with a syringe pump, where the cyclic voltammetry (CV) was sequentially performed for the ECR and ECL processes. The scanning range for the ECR process was selected to be 0 to -1.3 V at a scan rate of 0.1 V/s, while a potential range from 0.5 to 1.3 V was set for ECL process. The ECL intensity was recorded for the construction of the calibration curve and quantitative analysis.

3. Results and discussion

3.1. Fabrication of the flow cell and the electrode modifications

The design and fabrication of the flow cell was critical for the achievement of the reduction and in-situ ECL detection of NACs. The highly efficient and rapid reduction of NACs to AACs have to be fulfilled in the close vicinity of the ECL electrode, otherwise the reduced products could easily diffuse away. To achieve this goal, the flow cell was fabricated with the PDMS on a pre-designed mould (Fig. 1). Both ECR and ECL electrodes were included in a way of standard three-electrode configuration. A piece of copper mesh (15 × 17 mm), positioned at the bottom side of the flow channel, served as a working electrode for ECR process [29], while the Ru(bpy)₃²⁺ modified GCE (4 mm diameter), positioned at the upper side, served for ECL detection of the reduced products. By means of the face-to-face arrangement, the ECL electrode could immediately detect the productions that were produced on the surface of copper mesh electrode. At same time, the mesh electrode could allow the emitted light to pass through the reductor and to reach the detector. Two channels (i.d. 1.0 mm) at the two ends of the flow cell were connected with an inlet and an outlet, respectively. A platinum wire and a Ag/AgCl (saturated KCl) electrode, mounted in the outlet channel, were served counter and the reference electrode for the two working electrodes. In this manner, the whole flow cell configuration was greatly simplified.

The modification of GCE is to coat the light emitting layer on the GCE. The preparation of MWCNTs/Nafion/Ru(bpy)₃²⁺ modified GCE (abbreviated as the "ECL electrode") used in this work was largely followed a previous report by Guo and Dong [31].

The ECR process was carried out with a piece of copper mesh electrode, because copper is proved to be a good electrode material for the electrochemical reduction of various organic compounds [28,29]. The mesh structure was used in order to allow electrochemically generated light at the ECL electrode can pass through the ECR electrode. In the experiment, when a mesh size of 120 was chosen, the light intensity detected for a given coreactant concentration is almost identical to that measured in its absence, suggesting that the copper mesh electrode could allow the passage of substantial amount of the electrogenerated light. To further increase the reduction efficiency, an electrochemical deposition of copper nanoparticles on the surface of the copper mesh was conducted by performing the CVs in the potential range -0.1 ~ -0.7

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