



# Nitrogen and sulfur co-doped graphene nanoribbons: A novel metal-free catalyst for high performance electrochemical detection of 2, 4, 6-trinitrotoluene (TNT)

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## ABSTRACT

In this work, through a heteroatom-doping process and the subsequent base washing strategy, a new type of metal-free nitrogen- and sulfur-codoped graphene nanoribbons (BW-NS-rGONRs) were synthesized. It was found that a considerable amount of carbonaceous oxidative debris resided in graphene oxide nanoribbons (GONRs) produced from unzipping multiwalled carbon nanotubes has a great effect on the electrocatalytic activity of rGONRs. After removing the adsorbed oxidative debris by base washing, the obtained BW-NS-rGONRs exhibited high electrical conductivity and rich defect active sites, endowing the BW-NS-rGONRs enhanced electrocatalytic activity for TNT reduction. The electrochemical sensing platform established from the BW-NS-rGONRs showed a highly sensitive and selective response to TNT with a wide linear range from 0.0008 to 5.1 ppm and a detection limit of 0.1 ppb. Moreover, the BW-NS-rGONRs-based TNT detection platform demonstrated good cyclic stability and reproducibility. Most importantly, the BW-NS-rGONRs-based sensing platform can be successfully used for TNT determination in tap water and lake water samples. The superb sensing performance is attributed to the abundant active sites from dual doping of N and S atoms, the enhanced electrical conductivity and full exposure of the active sites of BW-NS-rGONRs after base washing treatment.

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## 1. Introduction

2, 4, 6-trinitrotoluene (TNT) is a well-known explosive compound that is widely used in both military and aviation industries, forensic investigations, and the manufacturing industries of matches and fireworks, and TNT can easily accumulate in soil and groundwater during their long-term usage, storage and dumping. In addition to its security issues, TNT is also a toxic and mutagenic compound that is harmful to environment, human and wildlife health, increasing the need of sensing methods for sensitive, rapid and practical detection of TNT [1,2]. Up to now, many techniques and methods have been applied to the detection of TNT, such as

infrared and Raman spectroscopy [3], mass spectrometry [4,5], chromatography [6], solid-state microextraction [7,8], immunoassay [9,10], thermal neutron analysis [11], surface enhanced Raman spectroscopy [12], electrogenerated chemiluminescence [13]. However, most of these methods suffer limitations including cumbersome and expensive instruments, complicated synthesis processes or labeling procedures etc., all of which impede their widespread applications. In recent years, various electrochemical methods have been developed for the determination of ultratrace amounts of TNT because of their intrinsically high sensitivity and selectivity, low detection limit and their potential applications for fabricating inexpensive and portable sensors [14–16].

The electrochemical reductive stripping of TNT has been demonstrated to occur in three separate, six-electron steps, corresponding to the successive reduction of the three nitro groups in

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TNT molecule to a hydroxylamine followed by further reduction to an amine group [17]. Typically, the electrochemical techniques of cyclic voltammetry (CV) [18], linear sweep voltammetry (LSV) [19], square wave voltammetry (SWV) [20] or differential pulse voltammetry (DPV) [21] methods are applied for TNT detection in aqueous solution, which show three reductive peaks in the range of  $-0.3$  to  $-0.9$  V (Ag/AgCl), each corresponding to the complete reduction of one nitro group. However, the direct reduction of TNT at bare electrodes exhibit low sensitivity, poor selectivity and reproducibility. In recent years, the sensitivity and selectivity of electrochemical detection of TNT have been tremendously improved by taking full advantage of different nanomaterial-based electrocatalysts, for example PtPd concave nanocubes [22], VO<sub>2</sub> film [23], Pt nanoparticle ensemble-on-graphene hybrid nanosheet [19], carbon nanotubes [24], TiO<sub>2</sub>/metal nanoparticles [25], ionic liquid-graphene hybrid nanosheets [26] and N-rich carbon dots [27], etc. All these studies indicated that the TNT electrochemical sensing platforms constructed from nanomaterials can effectively enhance the detection performances. Among these reported nanomaterials, the metal-free materials are ideal candidates because of their high stability, low cost and the environmental friendliness. Thus, it is highly desirable to design novel metal-free nanomaterials and develop practicable analytical platforms to monitor ultratrace levels of TNT.

Graphene has attracted enormous attention due to its remarkable physicochemical properties since it was first reported by Novoselov and Geim in 2004 [28]. It shows great potential in various applications including dye-sensitized solar cells [29], fuel cells [30], supercapacitors [31], sensors [32], Li-ion batteries [33] and so on. In particular, graphene and its derivatives, such as graphene oxide (GO) and reduced graphene oxide nanoribbons (rGONRs)-based electrochemical sensors have recently received more and more research interests because graphene and its derivatives can not only provide large domains for target molecules binding but also effectively accelerate the electron transfer and thus realize the signal amplification. For instance, Shang et al. [34] reported that the electrode modified by graphene nanoflake films showed faster electron-transfer kinetics and much enhanced electrocatalytic activity for simultaneously determining dopamine (DA), ascorbic acid (AA) and uric acid (UA) than the bare solid-state electrode. Dong et al. [35] demonstrated that glassy carbon electrode (GCE) modified with chemically reduced graphene oxide exhibited more favorable electron transfer kinetics and greatly enhanced electrochemical reactivity than graphite-modified GCE and bare GCE for sensing H<sub>2</sub>O<sub>2</sub> and reduced nicotinamide adenine dinucleotide (NADH). Among the present carbon materials, due to the increased active sites of short graphene oxide nanoribbons (GONRs), Sun et al. [36] found that GONRs-modified GCE exhibited outperformed performance than bare GCE, graphene-modified GCE and MWCNT-modified GCE for the electrochemical detection of AA, UA and DA. In another work, Guo et al. [26] used ionic liquid-functionalized graphene as an enhancing material for rapidly electrochemical detection of TNT, and they found that the fabricated TNT sensor exhibited 6.2 and 51.4-fold higher current signals than ionic liquid-functionalized carbon nanotubes and bare GCE, respectively. Despite tremendous progresses, the activity and stability of pure graphene and its derivatives are still far from that desired for the practical applications of electrochemical sensors. A possible approach to improve the electrochemical sensing performance is to introduce abundant defects and functional groups into graphene and its derivatives to increase the number of catalytic sites. On the one hand, the oxidation of graphene provides a potential route to increase its defect level. However, harsh oxidation conditions could lead to the loss of high electrical conductivity of graphene, a desirable property for charge transport during

electrochemical applications. Recently, Rourke et al. [37] and Zhu et al. [38] have demonstrated that GO produced by the modified Hummers method is composed of functionalized graphene sheets decorated by strong bound oxidative debris which are resulted from the disruption of graphene nanosheets in harshly oxidative and strong acidic condition. It was indicated that those carbonaceous oxidative debris can dramatically influence the electrical properties and electrochemical behaviors of GO. For instance, the conductivity of purified GO after removing the oxidative debris by base washing is roughly five orders enhanced than the initial GO, and the peak potential separation from the base-treated GO (275 mV) is much smaller than that from initial GO (608 mV) for electrochemical detection of DA. This obvious difference between GO and the base-purified GO indicates that base washing is an efficient strategy to improve the conductivity and electrochemical behaviors of GO and other harshly oxidative carbon nanomaterials. Actually, similar results have also been found in oxidized carbon nanotubes and carbon fibers [39,40]. On the other hand, the heteroatom doping of carbon nanomaterials has been theoretically and experimentally revealed to be an efficient strategy for enhancing the charge delocalization and asymmetric spin density of carbon atoms, and thus creating more active sites. Moreover, the heteroatom co-doping can also trigger the synergistic effect for electrochemical reactions [41,42]. On the basis of the previous studies, it would therefore be imperative to develop a suitable strategy to produce abundant active sites on graphene nanoribbons while retaining their structure and conductivity for fabricating advanced metal-free sensing materials for TNT.

In this study, a new type of metal-free nanomaterial was developed based on base washed nitrogen- and sulfur-codoped graphene nanoribbons (BW-NS-rGONRs). Compared to graphene nanosheets, with the doping of nitrogen and sulfur atoms, the edge- and defect-rich graphene oxide nanoribbons facilitate the formation of catalytically active sites for TNT electrochemical reduction. To further enhance the electrocatalytic activity, base washing treatment was also performed and the obtained BW-NS-rGONRs showed high catalytic activity for electroreduction of TNT. The electrochemical sensing platform fabricated from BW-NS-rGONRs showed a sensitive and selective response to TNT with a wide linear range from 0.0008 to 5.1 ppm and a detection limit of 0.1 ppb. The BW-NS-rGONRs-based sensing platform can also be applied for TNT detection in real water systems with satisfactory results.

## 2. Experimental

### 2.1. Chemicals

Thiourea (CH<sub>4</sub>N<sub>2</sub>S, A.R., ≥99.0%) was purchased from Beijing Yili Fine Chemicals Co., Ltd. Urea (CH<sub>4</sub>N<sub>2</sub>O, A.R., ≥99.0%), sodium hydroxide (NaOH, A.R., ≥96.0%), hydrochloric acid (HCl, A.R., ≥36–38%), sodium dihydrogen phosphate dihydrate (NaH<sub>2</sub>PO<sub>4</sub>·2H<sub>2</sub>O, A.R., ≥99.0%), disodium hydrogen phosphate dodecahydrate (Na<sub>2</sub>HPO<sub>4</sub>·12H<sub>2</sub>O, A.R., ≥99.0%), potassium hexacyanoferrate (III) (K<sub>3</sub>[Fe(CN)<sub>6</sub>], A.R., ≥99.5%) and potassium hexacyanoferrate (II) (K<sub>4</sub>[Fe(CN)<sub>6</sub>], A.R., ≥99.5%) were all obtained from Beijing Chemical Works. 2-nitrotoluene (2-NT), 4-nitrotoluene (4-NT), 2,4-dinitrotoluene (2, 4-DNT), 2, 6-dinitrotoluene (2, 6-DNT) and nitrobenzene (NB) were all purchased from Alfa Aesar. 2, 4, 6-trinitrotoluene (TNT) was supplied by the Institute of Forensic Science, Ministry of Public Security (China), and its stock solution (3 mg mL<sup>-1</sup>) was prepared in acetonitrile. For TNT electrochemical detection, four standard stock solutions of 1 mg mL<sup>-1</sup>, 0.1 mg mL<sup>-1</sup>, 0.01 mg mL<sup>-1</sup> and 0.001 mg mL<sup>-1</sup> were prepared by diluting the initial 3 mg mL<sup>-1</sup>

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