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Mesoporous g-C₃N₄/ β -CD nanocomposites modified glassy carbon electrode for electrochemical determination of 2,4,6-trinitrotoluene



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ABSTRACT

A novel method using mesoporous g-C₃N₄ and β -cyclodextrin nanocomposite (mpg-C₃N₄/ β -CD) for the electrochemical detection of 2,4,6-trinitrotoluene (TNT) is presented. The unique structure of the mesoporous g-C₃N₄/ β -CD nanocomposite facilitates both mpg-C₃N₄ electrocatalysis and β -CD inclusion-complexation of the analytes. When compared to GCE or mpg-C₃N₄ modified GCE, the mpg-C₃N₄/ β -CD modified glassy carbon electrode exhibits superior performance in the detection of TNT. Hence, we used mpg-C₃N₄/ β -CD modified GCE for the development of TNT detection method using linear sweep voltammetry at -0.45 V reduction potential with 100 s accumulation time. The TNT calibration curve is linear within the 1–100 μ M concentration range and the corresponding sensitivity and LOD values are 0.2μ A/ μ A-CD modified GCE sensor showed high selectivity and sensitivity to the nitroaromatic compounds. Optimized mpg-C₃N₄/ β -CD modified GCE sensor was used for the detection of TNT in a natural lake water sample with an 96.8% peak recovery. The results shown in work illustrate the potential of using g-C₃N₄/ β -CD modified GCE sensors in monitoring TNT and other nitroaromatic compounds.

1. Introduction

Globally, 2,4,6-trinitrotoluene, commonly known as TNT, is extensively used as an explosive and in military applications, which resulted in environmental contamination [1,2]. Redox sensitive TNT reacts readily through biotic and abiotic pathways which impose several health threats to humans; however, its carcinogenetic nature is debated to date. In the meantime, the International Agency for Research on Cancer classified TNT as a category 3 carcinogen [3–6]. The EPA established a lifetime health advisory guidance level of 0.002 mg per liter (mg/L) for TNT in drinking water. Therefore, continuous monitoring of TNT in different environmental compartments is essential, and development of a sensitive sensor for rapid and selective detection of TNT and other nitroaromatic compounds is a research priority.

Presently, there are a wide range TNT detection methods such as gas and liquid chromatography [7], immunoassay [8], Raman spectrometry [9], electrogenerated chemiluminescence [10,11], spectrophotometry [12] and electrochemical techniques [13–16]. When compared to these methods, electrochemical methods offer several advantages due to their low cost, portability, simple operation, species detection, sensitivity, and selectivity [17–20]. Electrochemical methods are particularly suited for the detection of nitroaromatic compounds due to excellent electron-accepting properties of NO₂ groups [17–20]. A wide range of new materials is developed to modify electrochemical sensors for selective detection of TNT with accuracy. For example, TiO₂/nano-Pt particulate modified electrodes show high electrochemical activity with

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40 μ Appm⁻¹ sensitivity in TNT detection [21]. The Ag/CS-G/GCE sensing electrode extends the linear range, e.g., 1–70 ppm in TNT detection [22]. The high sensitivity of 0.2 μ A/ μ M for the determination of TNT is achieved using AgNPs/thiol-GQD GCE [19].

We modified the glassy carbon working electrode with mesoporous graphitic-carbon nitride (mpg-C₃N₄) and β -cyclodextrins (β -CD) nanocomposite for detection of TNT. The mpg-C₃N₄/ β -CD nanocomposite used to capture nitroaromatic in the vicinity of electrode-solution interface facilitating electrochemical reduction. The selection of mesoporous $g-C_3N_4$ and β -CD was made due to the following reasons. 2-D layered graphitic-carbon nitride $(g-C_3N_4)$ is π -conjugated that has a wide range of applications [23-33]. The g-C₃N₄ is environmentally benign, stable, easy preparation, low cost, tunable electronic structure meta free semiconductor. However, g-C₃N₄ limits its applications in electrochemical analyses due to low conductivity [34]. Previously, this limitation was circumvented by designing a heterojunction structure with metal oxide nano particulates. The conical-cylindrical cavity structured β-CD with hydrophobic and hydrophilic sites enable forming unique guest-host inclusion structures [35,36]. Wei et al. developed a novel electrochemical sensor using β-CD functionalized graphene for simultaneous determination of 2-chlorophenol and 3-chlorophenol at high sensitivity, i.e., detection limits 0.2-0.09 µM, [37]. Velmurugan et al. fabricated from β -CD_{1.2mg}/GO modified sensors to detect nitroaromatic isomers with a wide concentration range 0.5-1000 µM at a low detection limit of 0.184 µM [38].

In this research, we used a different approach. We enhanced electron transfer ability of mesoporous $g-C_3N_4$ by capturing the redoxsensitive analytes viz. Nitroaromatic compounds, in the vicinity of the electrode-solution interface for subsequent reduction. For capturing, we specifically selected non - reducing β -CD (cyclic oligosaccharide with seven α -D-glucose units) for selective complexation-the inclusion of nitroaromatic compounds, presently TNT, *p*-nitrophenol, and *o*-nitrophenol. Our results demonstrated that the mesoporous $g-C_3N_4/\beta$ -CD nanocomposite (mpg- C_3N_4/β -CD) modified glassy carbon electrode (GCE) significantly promote nitroaromatic compounds detection performance. Finally, we developed a method for routine monitoring of TNT in natural water with enhanced accuracy [39–42].

2. Experimental

2.1. Materials

Analytical grade dicyandiamide, molecular sieve SBA-15, acetonitrile, disodium hydrogen phosphate dodecahydrate (Na₂HPO₄·12H₂O, A.R., \geq 99.0%), sodium dihydrogen phosphate dehydrate (NaH₂PO₄·2H₂O, A.R., \geq 99.0%), 2,4,6- trinitrotoluene (TNT), *p*-nitrophenol and 2- nitrophenol were purchased from Shanghai Chemical Reagent Co. Ltd, P. R. China. All chemicals and reagents were used without further purification.

2.2. Methods

The morphology and structure of the fabricated materials were investigated by scanning electron microscopy (SEM, Quanta 200 FEG, FEI Company, USA) and transmission electron microscopy (TEM, H800, Japan). X-ray diffraction (XRD) with Cu Ka radiation ($\lambda = 0.154178$ nm) was carried out using an X-ray diffractometer (XRD, D/MAX2500V, Rigaku, Japan). The Fourier transform infrared (FTIR) spectrum of the solid substrates KBr pellets (Nicolet 67FTIR, USA).

2.3. Synthesis of mpg- C_3N_4/β -CD nanocomposite

mpg-C₃N₄ was prepared by a hard template method [43]. The methodology of g-C₃N₄ preparation was given below. Powdered \sim 1 g dicyandiamide (C₂H₄N₄) was dissolved in 30 mL ethanol/water

solution (v/v ratio 2:1). An appropriate amount of molecular sieve SBA-15 (~0.5 g) was added to the solution. After thorough mixing, the solution was ultrasonicated for 2 h and then dried at 90 °C in a shakerwater bath. The resulted white solids were placed in a tubular furnace heated at 550 °C with ramping at 2.3 C/min in N₂ atmosphere for 4 h. The pale-yellow powder thus obtained was immersed in 40 ml HF (10% w/w ratio) solution for 48 h to remove the template. Mesoporous g- C_3N_4 (designated as mpg- C_3N_4) was obtained by repeated washing and drying with water and ethanol. The mpg- C_3N_4 (1 mg) was added to 1 mL of deionized water and ultrasonicated for 30 min. Next, 2 mg of β -CD was mixed into the above solution and ultrasonicated for 1 h. The well-dispersed, homogeneous mpg- C_3N_4/β -CD suspension was preserved for further use.

2.4. Electrochemical measurements

A conventional three-electrode system consists of Ag/AgCl reference electrode, Pt counter electrode, and a mpg-C₃N₄/ β -CD modified GCE working electrode were used for our experiments. Adsorptive stripping voltammetric measurements were carried out using a computer-controlled electrochemical analyzer (model: CHI760e, China). All electrochemical experiments were carried out in a 10 ml of 0.5 M phosphate buffer solution (PBS, pH = 7). The glassy carbon electrode was first polished with 1.0 µm, 0.3 µm, and 0.05 µm aluminum trioxide powder in order. The GCE electrode was first washed using an ultrasound apparatus with 1:1 (v/v) HNO₃ solution, ethanol, and deionized water. A mpg-C₃N₄/ β -CD or g-C₃N₄ solution was added dropwise onto cleaned GCE surface with a pipette gun and dried under N₂ purging. Scheme 1 shows the steps used in the fabrication of chemically modified electrochemical sensor for TNT detection.

Adsorptive stripping voltammetric measurements were carried out in 0.5 M phosphate buffer solution (PBS, pH = 7). After the accumulation from solution to electrode surface under 0.2 V (vs. Ag/AgCl) for 120 s, linear sweep voltammetry was used to measure the electrochemical reduction of the 2,4,6-trinitrotoluene (TNT) from 0 to -1 v at 100 mV/s.

Electrochemical impedance measurements at TNT different concentrations were carried out at 0.21 V in 5 mM K₄[Fe(CN)₆]/K₃[Fe (CN)₆] containing 0.1 M KCl, and before the measurement, the adsorption from solution to electrode surface under stirring conditions for 120s was conducted.

3. Results and discussion

3.1. Morphologic characterization of mpg- C_3N_4/β -CD nanocomposite

Fig. 1(a–b) display the TEM micrographs of the mpg- C_3N_4 and mpg- C_3N_4/β -CD nanocomposites prepared at 1:2 mass ratio. As shown in Fig. 1(a), stacked lamellar structures, and tiny mesoporous are readily discerned for mpg- C_3N_4 . Fig. 1(b) indicates well-assembled mpg- C_3N_4/β -CD nanocomposites, showing that β -CD might be well dispersive on the surface of mpg- C_3N_4 . Similar conclusions as high surface area mpg- C_3N_4 and β -CD adhered on the surface can be made with the SEM micrographs shown in support documentation (Fig. S1 (a-b)). The x-ray diffractogram of mpg- C_3N_4 nanocomposites is shown in Fig. S2. Two distinct diffraction peaks correspond to (100) and (002) planes at $2\theta = ~13.2^\circ$, and $~27.4^\circ$ is ascribed to the characteristic interlayer structural packing, and inter-planar stacking of aromatic mpg- C_3N_4 systems conforms successful mpg- C_3N_4 synthesis [25,44,45].

Fig. S3 shows the XPS spectrum of mpg- C_3N_4 , showing peaks correspond to different structural C and N elements that require high-resolution spectral analysis. C 1s XPS spectrum shows four major signals (Fig. S3(b)). The deconvoluted peaks centered at 284.8, 286.5, 288.3 and 293.6 eV, respectively, were assigned to the adventitious carbon (C–C), the sp³-hybridized carbon (C-(N)₃), the sp²-hybridized carbon (N–C=N) and π - π * [46]. Fig. S3 (c) shows the deconvoluted peaks of



Scheme 1. Schematic illustration of the electrochemical sensor for nitrobenzene compounds (e.g. TNT) detection.

the N 1s spectra at 398.8 eV, 400.1 eV, 401.3 eV, and 404.6 eV, respectively, corresponding to sp²-hybridized nitrogen (C–N=C), tertiary nitrogen (N-(C)₃), free amino groups (C–N–H) and charging effects [47]. The XPS data confirmed the successful fabrication of mpg-C₃N₄ with a variety of chemical groups, including amide, hydroxyl, and carboxyl groups abutting from the surface.

Fig. 1(c) depicts the FTIR spectra of the mpg- $C_3N_4\beta$ -CD and mpg- C_3N_4/β -CD nanocomposite with a mass ratio of 1 : 2. The characteristic peaks at 1233, 1320, 1408, 1551, and $1622\,\mathrm{cm}^{-1}$, is attributed to the typical stretching vibration of CN heterocycles of mpg-C₃N₄. The peak near 3166 cm⁻¹ corresponds to the stretching modes of terminal NH groups at the defect sites of the aromatic ring. The peak at 808 cm^{-1} can be attributed to the breathing mode of triazine units [28,29,48]. β -CD has the typical absorption features of the ring vibrations at 540, 706, 746 and 903 cm^{-1} [49]. The coupled C–O/C–C stretching and O-H bending vibrations at 1033 and 1081 cm^{-1} , and the coupled C–O–C stretching/O–H bending vibrations at 1156 cm⁻¹ have been observed. The peak at 2927 cm⁻¹ is related to the typical vibrations of -CH₂. The peak at 3317 cm⁻¹ can be assigned to -OH stretching vibration [45]. The FTIR spectrum of mpg-C₃N₄/β-CD shows most of characteristic bands of mpg- C_3N_4 and β -CD, distinctly certificating that mpg-C₃N₄ were successfully functionalized by β -CD.

The N₂ adsorption-desorption isotherms and the corresponding pore size distribution curves (inset) of mpg-C₃N₄ and mpg-C₃N₄/ β -CD are shown in Fig. 1(d). According to IUPAC classification, the pristine mpg-C₃N₄ has a BET surface area of about 168 m²g⁻¹ and shows a typical type IV with an H₁ hysteresis loop at 0.5–0.9 P/P₀ which confirms the

presence of mesoporous structure [50]. As shown in Fig. 1(d) (inset), the pore sizes of mpg-C₃N₄ and mpg-C₃N₄/ β -CD are widely distributed, which indicate the existence of mesoporous structures with different sizes. After modification with β -CD, the surface area and pore structure of the mpg-C₃N₄ is slightly affected. The specific surface area of the mpg-C₃N₄/ β -CD sample is about 143 m²g⁻¹. In agreement with TEM data, the decrease of specific surface area upon β-CD addition is ascribed due to the partial covering of pores on mpg-C₃N₄. Generally, the decrease of BET leads to a decrease of electrocatalytic performance of the substrate. However, the electrocatalytic activity of mpg-C₃N₄/ β -CD composites did not decrease as expected, which indicates that the specific surface area is not the most critical factor controlling the electrocatalytic activity of mpg-C₃N₄/β-CD composites. Fig. 2(b) displays the CVs obtained at bare glassy carbon electrode, g-C₃N₄/GCE, and g-C₃N₄/ β -CD/GCE using 0.5 mM K₃[Fe (CN)₆] in 0.1 M KCl. The CV curves verify the past results obtained by the EIS date; the rate of electron transfer is higher at mpg-C₃N₄/β-CD/GCE in contrast to mpg-C₃N₄/GCE [39].

3.2. Electrochemical characterization

Electrochemical impedance spectroscopy (EIS) is based on probing impedance variations in reactions at the electrode-solution interfaces. Relative efficiency of electron transfer rates upon the modification of glassy carbon electrode (GCE) with g-C₃N₄ derived nanocomposites was determined by EIS measurements using 5 mM K₄ [Fe (CN)₆]/K₃[Fe (CN)₆] in 0.1 M KCl. The relative magnitude of the diameter of the



Fig. 1. (a) and (b) TEM image of mpg- C_3N_4 and mpg- C_3N_4/β -CD. (c) FTIR spectra of mpg- C_3N_4 and mpg- C_3N_4/β -CD. (d) The N_2 adsorption-desorption isotherms and the corresponding pore size distribution curves (inset) of mpg- C_3N_4 and mpg- C_3N_4/β -CD.

semi-circle in the EIS measures electron transfer efficiency at an electrolyte/electrode interface. As in Fig. 2 (a), when compared to mpg- C_3N_4 or mpg- C_3N_4/β -CD modified GCE, the bare GCE show a semi-circle with the largest diameter. The electron transfer resistance (R_{et}) for bare GCE, mpg- C_3N_4/GCE , and mpg- C_3N_4/β -CD/GCE are 250.9, 76.7, and 53.9 Ω , respectively. Out of three electrodes considered, i.e., bare GCE, mpg- C_3N_4/GCE , and mpg- C_3N_4/β -CD/GCE, the most efficient electron transfer occurs at the mpg- C_3N_4/β -CD/modified GCE electrode interface. The incorporation of β -CD into the mpg- C_3N_4 nanocomposite significantly improves electron transfer efficiency because β -CD can act as a host to guest compounds forming host-guest inclusion complexes [30]. Further with the introduction of CD, the specific surface area, and the pore structure of the mpg- C_3N_4/β -CD composite increased significantly favoring electron transfer. Fig. 2(b) shows the

cyclic voltammograms (CVs) obtained for bare GCE, mpg-C₃N₄/GCE, and mpg-C₃N₄/ β -CD/GCE sensors in 0.5 mM K₃[Fe (CN)₆] in 0.1 M KCl. The CV data further confirm our EIS data showing the highest electron transfer rates at the mpg-C₃N₄/ β -CD/GCE interface [39].

3.3. Electrochemical detection of 2,4,6-trinitrotoluene

The response current of TNT in pH 7.00 buffer measured in LSV mode was optimized with the following parameters; accumulation time, deposition potential, and pH. Fig. S4(a) shows the current - accumulation time plot for TNT measured within 0–240 s. The TNT response current steadily increases with the accumulation time reaching a plateau at about 80s. Herein, in consideration of achieving perfect results, 100 s optimal time was chosen for subsequent studies. Figure S (4)b



Fig. 2. (a) EIS of bare GCE, mpg-C₃N₄ modified GCE, and mpg-C₃N₄/ β -CD GCE in 5 mM K₄[Fe(CN)₆]/K₃[Fe(CN)₆] containing 0.1 M KCl. (b)CV responses of bare GCE, mpg-C₃N₄ modified GCE, and mpg-C₃N₄/ β -CD modified GCE of 5 mM K₄[Fe(CN)₆]/K₃[Fe(CN)₆] in 0.1 M KCl.

shows the variation of TNT response current vs. depositional potential at 100 s accumulation time. The depositional potential was varied between 0 and 1.2 V. The plot shows two linear segments having a break at 0.2 V. The linear segment with the highest slope, i.e., 0-0.2 V segment, is most sensitive for TNT response current. Additionally, small bubbles could be observed on the modified electrode surface when the deposition potential was higher than 0.4 V. This might be due to the generation of oxygen. The end of this linear segment, viz. 0.2 V is taken as the optimal TNT depositional potential. The variation of TNT response current in LSV mode with the solution pH was also examined at 100 s accumulation time and 0.2 V depositional potential. As shown in Fig. S4(c) the variation of response current reaches a maximum at pH 7. which was chosen as the optimal value. TNT is a reactive molecule which may transform both at extremely acid and alkaline conditions. For example, in alkaline solutions (pH > 11) TNT converts into hexahydro-1,3,5-trinitro-1,3,5-triazine [51]. The depositional potential is specific for TNT. Therefore, degradation products may not accumulate at the deposition potential set for TNT. As expected, the TNT response current vs. pH shows a maximum at pH 7.00.

Under the above-optimized detection conditions, we studied electro-reduction of TNT on the bare GCE, mpg-C₃N₄ GCE, and mpg- C_3N_4/β -CD GCE, respectively. Fig. 3 (a) shows the linear sweep voltammetry responses of TNT with different concentrations ranging from 0 to 100 μ M using bare GCE, mpg-C₃N₄ GCE, and mpg-C₃N₄/ β -CD GCE sensors under LSV mode. The three peaks noted with GCE sensors correspond to the transformation of three -NO2 groups in TNT as detailed in the later section. The -NO2 group is a suitable electron acceptor, and in TNT the redox potentials are dependent on the nature and position of other functional groups. As shown earlier [52], the TNT reduction is multi-facet electrons transfer process, which converts -NO2 \rightarrow -NHOH \rightarrow - NH₂. The process is believed to repeat sequentially for three -NO₂ groups in TNT, which results in three peaks. In principle, any -NO₂ voltage peak can be used for the detection of TNT. Due to comparably high sensitivity and signal to noise ratio, the voltage peak at -0.45 V is selected for TNT detection [8]. Accordingly, the calibration curves constructed in the TNT range 0-100 µM using bare GCE, mpg-C₃N₄ GCE, and mpg-C₃N₄/β-CD GCE sensors are shown in Fig. 3 (c). With all sensors, the TNT calibration curves are linear for the

variation of TNT in the range 0–100 μM TNT. When mpg-C₃N₄/ β -CD GCE sensor has used the separation of voltammograms and response current are high. The data shown below show that the mpg-C₃N₄/ β -CD modified GCE shows best electroanalytical performance in the detection of TNT to sensitivity and LOD values achieved due to unique mpg-C₃N₄ modifications by β -CD. Therefore, we chose mpg-C₃N₄/ β -CD modified GCE electrode in the development of TNT detection method.

We used EIS to examine interfacial charge transferring at the bare & modified GCE electrodes and as a sensor to probe nitroaromatic compounds. TNT was used as index molecule with the K_4 [Fe (CN)₆]/ K_3 [Fe $(CN)_6$] redox probe for the study. Fig. 4 shows the EIS spectra of bare glassy carbon electrode (GCE), mpg-C₃N₄/GCE, and mpg-C₃N₄/β-CD/ GCE as working electrodes in cells containing 0-20 uM TNT and 5 mM K_4 [Fe (CN)₆]/ K_3 [Fe (CN)₆] in 0.1 M KCl solution. The diameter of the semicircles, which corresponds to the measure of electron transfer resistance, increases with the TNT concentration (in the range $0-20\,\mu\text{M}$ TNT). The R_{ct} values were determined by the Randle equivalent circuit model. The highest R_{ct} value is~1000 Ω shown at mpg-C₃N₄/ β -CD/GCE electrode interface with the 20 μ M TNT. The R_{ct} values of bare GCE is markedly lower, i.e., \sim 450 Ω at 20 μ M TNT. When the GCE electrode is modified only with mpg-C₃N₄, the estimated maximal R_{ct} ~690 Ω at 20 μM TNT. The enhanced R_{ct} values of mpg-C_3N_4/\beta-CD/GCE confirms decoration of the electrode surface with β -CD. When compared to bare GCE, the incorporation of mpg-C₃N₄ on GCE shows enhanced specific surface area, i.e., mpg-C₃N₄ 168 m²/g, mpg-C₃N₄/ β -CD 143 m²/g. The surface sites of β -CD exhibit dual characteristics, i.e., hydrophobic and hydrophilic sites. This property can facilitate capturing TNT by β -CD host efficiently. The formation of stable guest-host complexes inhibits charge transfer, thereby hindering access the Fe $(CN)_6^{3-/4}$ redox probe to the electrode surface. Therefore, the electrode-solution monolayer region of the mpg-C₃N₄ - β -CD GCE is considered under charge transfer control for migration of electrons. The bare glassy carbon electrode (GCE), mpg-C₃N₄ modified GCE, and mpg-C₃N₄/β-CD modified GCE were used for the impedimetric detection of TNT. The TNT calibrations carried out in the range 0-20 µM are shown in Figure e-f. In all cases, a linear relationship was observed. The sensitivities are given as 11.771/ bare GCE, 14.380/mpg-C₃N₄/GCE, and 28.024/mpg-C₃N₄/β-CD/GCE. The limits of TNT detection with the three working electrodes are 1.040



Fig. 3. LSV responses of TNT on bare GCE (a), mpg- C_3N_4 modified GCE (b), and mpg- C_3N_4/β -CD modified GCE(c) at different concentrations with the response to the blank solution (dotted line) in 0.5 M PBS (pH 7.0). (d–f) Calibration plot of the peak currents vs. the TNT concentrations corresponding to (a–c).



Fig. 4. EIS spectra of bare GCE (a), mpg-C₃N₄/GCE (b), and mpg-C₃N₄/ β -CD/GCE (c) in 5 mM K₄[Fe(CN)₆]/K₃[Fe(CN)₆] containing 0.1 M KCl at TNT different concentrations. (d–f) Calibration plot of ΔR_{ct} vs. the TNT concentrations corresponding to (a–c).

 $\mu M/bare$ GCE, $0.610\,\mu M/mpg\text{-}C_3N_4/\text{GCE}$, and $0.299\,\mu M/mpg\text{-}C_3N_4/\beta\text{-}CD/GCE$. The excellent sensitivity and detection limits incorporated with linearity (as judged by R^2 values) recorded for mpg- $C_3N_4/\beta\text{-}CD/$ GCE sensor prompted to use it for further investigations into the detection of TNT and other nitroaromatic compounds in real environmental conditions as shown below.

It's apparent that the mpg-C₃N₄/ β -CD GCE exhibits greater cathodic current density from TNT reduction compared to mpg-C₃N₄/GCE and bare GCE. And also, the sensitivity and detection limit of the mpg-C₃N₄/ β -CD and some previously reported electrode materials for electrochemical determination of TNT are summarized in Table 1. In light of comprehensive electrochemical performance and economic practicability, the mpg-C₃N₄/ β -CD has potential for practical application for detecting TNT.

3.4. Interference study

The selectivity of the mpg-C₃N₄/ β -CD-modified electrode was examined in the presence of para or ortho nitrophenols. As shown in Fig. 5 (a) the TNT calibration curves were constructed (range 10–100 μ M) in the presence of 200 μ M para or ortho nitrophenols. Cathode peak of TNT at -0.45 V is very consistent irrespective of the existence of para

or ortho nitrophenols. Nitro functional groups in the para or ortho positions in aromatic ring structure yield cathodic peaks at -0.63 V or -0.77 V, respectively. However, the cathodic peak at -0.45 V shows no variation in the presence of o- or p-nitrophenols. Additionally, LSV responses toward 30 μ M TNT with the successive addition of 50 μ M-250 μ M p-NP and o-NP are shown in Fig. 6. It can be found that the values of the cathodic peaks at -0.45 V change slightly. The values decrease only 6.01% and 8.09% respectively with addition of 250 μ M p-NP, and o-NP into the solution containing 30 μ M TNT. Our data confirm that the cathodic peak at -0.45 V is highly selective for TNT detection that can be used in the presence of o- or p-nitrophenols.

3.5. Evaluation of reproducibility and stability

Fig. 7(a) displays LSV responses of $30 \,\mu$ M TNT on five mpg-C₃N₄/ β -CD modified GCE. The relative standard deviation (RSD) of the experiments for the five electrodes was 1.59%, indicating excellent signal reproducibility. Fig. 7(b) shows LSV responses of the mpg-C₃N₄/ β -CD modified GCE towards 30 μ M TNT in successive seven days. The mpg-C₃N₄/ β -CD modified GCE was stored at room temperature. The relative standard deviation (RSD) was 1.19%. It can be found that the responses were stable.

Table 1

 $Comparison \ of \ electrochemical \ sensing \ performances \ toward \ TNT \ of \ C_3N_4/\beta-CD \ nanocomposite \ with \ previously \ reported \ sensing \ systems.$

Sensors	Linear range (µM)	LOD (ppb)	Sensitivity ($\mu A/\mu M$)	ref
Ag nanoparticles/carboxylic sodium groups functionalized graphene/GCE	4.4-308.4	450		[22]
Ionic liquid gel-polymer electrolyte/disposable gold thin film electrode	4.4–44	370	6.45×10^{-6}	[14]
Disposable carbon screen-printed electrode	1-200	90.8		[20]
Boron doped diamond electrode	11-110	10		[53]
Nitrogen-doped graphene/GCE	0.5-8.8	29.5	0.99	[54]
1-Butyl-3-methylimidazolium Tetrafluoroborate/carbon paste electrode	6.6-132.2	88.8	0.039	[1]
TiO ₂ /nano-Pt particles/Carbon Electrode	8.8-22	200		[21]
Carbon fibre microelectrode	0.4-44	30	0.32	[55]
Mpg-C ₃ N ₄ /β-CD/GCE	1–100	68	0.2	This work



Fig. 5. LSV response obtained with mpg-C₃N₄/ β -CD GCE for the successive addition of TNT (10 μ M–100 μ M) in the presence of 200 μ M p-NP (a), and o-NP (b). (c) and (d) are the calibration plots of the peak currents vs. the TNT concentrations corresponding to (a) and (b).

3.6. Natural lake water analysis

In Fig. S5 (a & b) TNT calibration curves were constructed using lake water. Apart from the lake water matrix, other experimental conditions were kept at optimized values. As shown in Fig. S5 (b), the calibration curve is linear (I = 0.19542[TNT] (μ M)+0.88667 R² = 0.99964). The response to the blank solution (dotted line in Figure S-5 (a)) indicate the high selectivity of mpg-C₃N₄/ β -CD GCE for TNT, and the baseline data show the presence of low interfering electroactive compounds in lake water. When compared to the data shown in Fig. 3, there is a small reduction in sensitivity.

Given the current demand for on-site detection of pollutants in the environment, we measured TNT concentration in the water sample taken from the Hubing Lake and Feicui Lake in Hefei University of Technology, China. Initial screening shows no TNT detection in the lake water. A TNT spike recovery was carried out to determine method precision in the lake water matrix using our method (shown in Table 2). When $30 \,\mu\text{M}$, $50 \,\mu\text{M}$ and $70 \,\mu\text{M}$ TNT are spiked, it can be found that all the recovery values are larger than 96%. The result indicates that the mpg-C₃N₄/ β -CD nanocomposites modified GCE holds the possible applications for detection of TNT contamination in aqueous environment.

4. Conclusions

The mpg-C₃N₄/ β -CD nanocomposites are fabricated for selective detection of TNT with 0.2 μ A/ μ M sensitivity and 68 ppb limit of



Fig. 6. LSV responses of TNT obtained with mpg- C_3N_4/β -CD GCE for the successive addition of *P*-nitrophenol(a) and O-nitrophenol (b) (50 μ M–250 μ M) in the presence of 30 μ M TNT.



Fig. 7. (a) LSV responses of five mpg- C_3N_4/β -CD modified GCE toward 30 μ M TNT. (b) LSV responses of mpg- C_3N_4/β -CD modified GCE toward 30 μ M TNT in the successive seven days.

Table 2Determination of TNT in water in real samples.

Samples	TNT Added (µM)	TNT Found (µM)	RSD(%)	Recovery (%)
Lake water 1	30	30.05	1.14	100.17
	50	48.07	0.61	96.14
	70	69.35	0.24	99.07
Lake water 2	30	28.84	0.98	96.13
	50	48.36	0.78	96.72
	70	67.86	0.23	96.94

detection. The unique structure of the newly fabricated mpg- C_3N_4/β -CD nanocomposite shows electrocatalytic properties with inclusion capabilities of β -CD. The mpg- C_3N_4/β -CD-modified electrode sensor shows high selectivity for TNT showing a distinct voltammetric peak even in the presence of *p*-nitrophenol and *o*-nitrophenol. Our results show the applicability of mpg- C_3N_4/β -CD modified GCE as an electrochemical detector for the determination of nitroaromatic compounds in natural water due to its high selectivity, rapid response, high sensitivity, and extended linear detection range.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.talanta.2019.120410.

References

- H.T.T. Vu, H.T.V. Le, Y.T.H. Pham, H.Q. Le, P.H. Pham, Bull. Korean Chem. Soc. 37 (2016) 378–385.
- [2] M.S. Goh, M. Pumera, Anal. Bioanal. Chem. 399 (2011) 127-131.
- [3] T.W. Chen, Z.H. Sheng, K. Wang, F.B. Wang, X.H. Xia, Chem. Asian J. 6 (2011) 1210–1216.
- [4] S. Singh, V.K. Meena, B. Mizaikoff, S.P. Singh, C.R. Suri, Anal. Methods 8 (2016) 7158–7169.
- [5] J. Zang, C.X. Guo, F. Hu, L. Yu, C.M. Li, Anal. Chim. Acta 683 (2011) 187-191.

- [6] G. Shi, Y. Qu, Y. Zhai, Y. Liu, Z. Sun, J. Yang, L. Jin, Electrochem. Commun. 9 (2007) 1719–1724.
- [7] P. Ryan, D. Zabetakis, D.A. Stenger, S.A. Trammell, Sensors 15 (2015) 17048–17056.
- [8] A. Bromberg, R.A. Mathies, Electrophoresis 25 (2004) 1895–1900.
- [9] M. Liu, W. Chen, Biosens. Bioelectron. 46 (2013) 68–73.
- [10] S. Parajuli, X. Jing, W. Miao, Electrochim. Acta 180 (2015) 196–201.
- [11] T.L. Pittman, B. Thomson, W. Miao, Anal. Chim. Acta 632 (2009) 197-202.
- [12] A. Üzer, E. Erçağ, R. Apak, Anal. Chim. Acta 534 (2005) 307–317.
- [13] C.X. Yuan, Y.R. Fan, Z. Tao, H.X. Guo, J.X. Zhang, Y.L. Wang, D.L. Shan, X.Q. Lu, Biosens. Bioelectron. 58 (2014) 85–91.
- [14] H.A. Yu, J. Lee, S.W. Lewis, D.S. Silvester, Anal. Chem. 89 (2017) 4729-4736.
- [15] J. Wang, S.B. Hocevar, B. Ogorevc, Electrochem. Commun. 6 (2004) 176-179.
- [16] B.K. Ong, H.L. Poh, C.K. Chua, M. Pumera, Electroanalysis 24 (2012) 2085–2093.
- [17] R. Zhang, C.L. Sun, Y.J. Lu, W. Chen, Anal. Chem. 87 (2015) 12262–12269.
- [18] M.C. Casey, D.E. Cliffel, Anal. Chem. 87 (2015) 334–337.
- [19] F. Shahdost-Fard, M. Roushani, Biosens. Bioelectron. 87 (2017) 724–731.
 [20] J.S. Caygill, S.D. Collyer, J.L. Holmes, F. Davis, S.P. Higson, Analyst 138 (2013)
- 346–352.[21] B. Filanovsky, B. Markovsky, T. Bourenko, N. Perkas, R. Persky, A. Gedanken,
- D. Aurbach, Adv. Funct. Mater. 17 (2007) 1487–1492.
 [22] X. Lu, H. Qi, X. Zhang, Z. Xue, J. Jin, X. Zhou, X. Liu, Chem. Commun. 47 (2011) 12494.
- [23] J. Feng, Y. Li, M. Li, F. Li, J. Han, Y. Dong, Z. Chen, P. Wang, H. Liu, Q. Wei, Biosens. Bioelectron. 91 (2017) 441–448.
- [24] X. Li, Y. Feng, M. Li, W. Li, H. Wei, D. Song, Adv. Funct. Mater. 25 (2015) 6858–6866.
- [25] M. Sun, Y. Fang, Y. Kong, S. Sun, Z. Yu, A. Umar, Dalton Trans. 45 (2016) 12702–12709.
- [26] Y. Li, X. Feng, Z. Lu, H. Yin, F. Liu, Q. Xiang, J. Colloid Interface Sci. 513 (2018) 866–876.
- [27] Y. Shiraishi, S. Kanazawa, Y. Sugano, D. Tsukamoto, H. Sakamoto, S. Ichikawa, T. Hirai, ACS Catal. 4 (2014) 774–780.
- [28] B. Chai, T. Peng, J. Mao, K. Li, L. Zan, Phys. Chem. Chem. Phys. : Phys. Chem. Chem. Phys. 14 (2012) 16745–16752.
- [29] M. Xu, L. Han, S. Dong, ACS Appl. Mater. Interfaces 5 (2013) 12533-12540.
- [30] K. Srinivasan, T. Stalin, K. Sivakumar, Spectrochim. Acta A Mol. Biomol. Spectrosc. 94 (2012) 89–100.
- [31] K. Srinivasan, T. Stalin, A. Shanmugapriya, K. Sivakumar, J. Mol. Struct. 1036 (2013) 494–504.
- [32] K. Srinivasan, T. Stalin, J. Incl. Phenom. Macrocycl. Chem. 78 (2013) 337-350.
- [33] R. Periasamy, S. Kothainayaki, R. Rajamohan, K. Sivakumar, Carbohydr. Polym.
- 114 (2014) 558–566.
- [35] S. Palanisamy, K. Thangavelu, S.-M. Chen, V. Velusamy, M.-H. Chang, T.-W. Chen, F.M.A. Al-Hemaid, M.A. Ali, S.K. Ramaraj, Sens. Actuators B Chem. 243 (2017) 888–894.
- [36] X. Ma, Y. Xie, Y. Yu, L. Lu, G. Liu, Y. Yu, C. Hu, J. Electroanal. Chem. 823 (2018) 437–444.
- [37] M. Wei, D. Tian, S. Liu, X. Zheng, S. Duan, C. Zhou, Sens. Actuators B Chem. 195 (2014) 452–458.
- [38] M. Velmurugan, N. Karikalan, S.M. Chen, Z.C. Dai, J. Colloid Interface Sci. 490 (2017) 365–371.
- [39] J.A. Rather, P. Debnath, K. De Wael, Electroanalysis 25 (2013) 2145–2150.
- [40] C. Martínez-Sánchez, L.M. Torres-Rodríguez, R.F. García-de la Cruz, Electroanalysis 28 (2016) 3055–3065.
- [41] C. Xu, J. Wang, L. Wan, J. Lin, X. Wang, J. Mater. Chem. 21 (2011) 10463.
- [42] X. Zhang, L. Wu, J. Zhou, X. Zhang, J. Chen, J. Electroanal. Chem. 742 (2015)

97–103.

- [43] X. Chen, Y.-S. Jun, K. Takanabe, K. Maeda, K. Domen, X. Fu, M. Antonietti, X. Wang, Chem. Mater. 21 (2009) 4093–4095.
- [44] H. Yan, H. Yang, J. Alloy. Comp. 509 (2011) L26-L29.
- [45] J. Liu, T. Zhang, Z. Wang, G. Dawson, W. Chen, J. Mater. Chem. 21 (2011) 14398.
 [46] J. Xiao, Y. Xie, F. Nawaz, Y. Wang, P. Du, H. Cao, Appl. Catal. B Environ. 183
- (2016) 417–425. [47] B. Long, J. Lin, X. Wang, J. Mater. Chem. 2 (2014) 2942.
- [48] S.C. Yan, Z.S. Li, Z.G. Zou, Langmuir : the ACS J Surface. Colloids 25 (2009) 10397–10401.
- [49] W. Feng, C. Liu, S. Lu, C. Zhang, X. Zhu, Y. Liang, J. Nan, Microchimica Acta 181 (2014) 501–509.
- [50] K. Kailasam, A. Fischer, G. Zhang, J. Zhang, M. Schwarze, M. Schröder, X. Wang, R. Schomäcker, A. Thomas, Chemsuschem 8 (2015) 1404–1410.
- [51] M. Emmrich, Environ. Sci. Technol. 33 (1999) 3802–3805.
 [52] Z. Hong-Xia, C. An-Min, H. Jin-Song, W. Li-Jun, L. Shuit-Tong, Anal. Chem. 78
- [20] Z. Hong Ata, C. Alevini, H. Shebong, W. Hobin, L. Shafe Long, Anal. Chem. 76 (2006) 1967–1971.
 [53] J. de Sanoit, E. Vanhove, P. Mailley, P. Bergonzo, Electrochim. Acta 54 (24) (2009)
- 5688–5693.
- [54] T.-W. Chen, J.-Y. Xu, Z.-H. Sheng, K. Wang, F.-B. Wang, T.-M. Liang, X.-H. Xia, Electrochem. Commun. 16 (1) (2012) 30–33.
- [55] L. Agui, D. Vega-Montenegro, P. Yanez-Sedeno, J.M. Pingarron, Anal. Bioanal. Chem. 382 (2) (2005) 381–387.