Postprint of: Dettlaff A., Jakóbczyk P., Sobaszek M., Ficek M., Dec B., Łuczkiewicz A., Szala M., Wojas J., Ossowski T., Bogdanowicz R., Electrochemical detection of 4,4',5,5'-tetranitro-1H,1'H-2,2'-biimidazole on boron-doped diamond/graphene nanowall electrodes, IEEE SENSORS JOURNAL, Vol. 20, No 17 (2020), pp. 9637 - 9643, DOI: 10.1109/JSEN.2020.2973451

Electrochemical detection of 4,4',5,5'-tetranitro-1H,1'H-2,2'-biimidazole on boron-doped diamond/graphene nanowall electrodes

Anna Dettlaff, Paweł Jakóbczyk, Michał Sobaszek, Mateusz Ficek, Barłomiej Dec, Aneta Łuczkiewicz, Mateusz Szala, Jacek Wojtas, Tadeusz Ossowski, Robert Bogdanowicz

***Abstract*— We present a promising approach to the electroanalytical detection of a specific nitroaromatic explosive in landfill leachates (LLs) that originated from a municipal solid waste plant. The paper is focused but not limited to the sensing of 4,4',5,5'-tetranitro-1H,1'H-2,2'-biimidazole (TNBI) using differential pulse voltammetry and cyclic voltammetry. Highly electroactive nanocarbon was applied to determine low concentrations of the analyte in the complex interfering matrix as leachate samples. The mechanism of nitro- group reduction is attributed to the sensing effect, as revealed in the voltammograms of TNBI. The developed sensor model has two linear regions extending from 0.02 ppm to 1.4 ppm and from 2 ppm to 16 ppm resulting from adsorption and diffusion-controlled processes, respectively. The limit of detection was as low as 0.52 ppm (1.66 μM L^{-1}) thanks to the electrochemical performance of the joint effect of the diamond/graphene composite nanowall surface.

***Index Terms*— differential pulse voltammetry, nanocarbon electrodes, nitroaromatics, electrochemical sensor**

I. Introduction

Nowadays, the detection of explosives and their chemical traces has become increasingly important in modern society due to significant improvement in national security, and also environmental protection. Currently, sensors for nitroaromatic compounds, which offer rapid detection at the high level demanded, can be divided into two groups: physical and chemical. Physical methods are based on highly selective but very expensive techniques such as mass spectroscopy [1], energy-dispersive X-ray diffraction [2], and neutron activation [3]. Moreover, most detection methods are only applicable to vapor samples because of interference problems encountered in complex aqueous media [4]. Detecting explosives in a water-based solution, or generally in liquid solvents, is essential due to environmental pollution (e.g., soil and groundwater), as well as finding land and underwater mines.

A promising technique for detecting explosives in water is a group of electrochemical methods, e.g., differential pulse voltammetry (DPV), linear sweep voltammetry (LSV), square wave voltammetry (SWV) or cyclic voltammetry (CV). These techniques are simple, quite fast, and above all are not expensive and provide sensor miniaturization, which allows for portable and field applications. These devices provide information about the system's composition in real-time by combining a chemically selective layer with an electrochemical transducer. Thereby, the chemical energy of the selective interaction between chemical substances and the sensor is converted into an analytically useful signal. The presence of nitro groups in nitroaromatic explosives with redox properties makes electrochemical methods ideal for their electrochemical detection. They can be classed into four groups: (1) potentiometric (change of membrane potential); (2) voltammetric and amperometric (change of current for an electrochemical reaction with the applied voltage and with time, respectively); (3) conductometric (change of conductivity); (4) impedimetric (change of impedance).

This work was supported by the Polish National Science Centre [2016/22/E/ST7/00102] and the National Centre for Science and Development [347324/12/NCBR/2017]. This work was partially supported by the Science for Peace Programme of NATO (Grant no. G5147). The DS funds of the Faculty of Electronics, Telecommunications and Informatics of the Gdansk University of Technology are also acknowledged.

A. Dettlaff, was with Gdańsk University of Technology, Faculty of Electronics, Telecommunications and Informatics, Narutowicza 11/12, 80-233 Gdańsk, Poland (e-mail: anna.dettlaff@pg.edu.pl).

P. Jakóbczyk, was with Gdańsk University of Technology, Faculty of Electronics, Telecommunications and Informatics, Narutowicza 11/12, 80-233 Gdańsk, Poland (e-mail: pawel.jakobczyk@pg.edu.pl).

M. Sobaszek, was with Gdańsk University of Technology, Faculty of Electronics, Telecommunications and Informatics, Narutowicza 11/12, 80-233 Gdańsk, Poland (e-mail: michal.sobaszek@pg.edu.pl).

M. Ficek, was with Gdańsk University of Technology, Faculty of Electronics, Telecommunications and Informatics, Narutowicza 11/12, 80-233 Gdańsk, Poland (e-mail: mateusz.ficek@pg.edu.pl).

B. Dec, was with Gdańsk University of Technology, Faculty of Electronics, Telecommunications and Informatics, Narutowicza 11/12, 80-233 Gdańsk, Poland (e-mail: bardec@pg.edu.pl).

A. Łuczkiewicz, was with Gdańsk University of Technology, Faculty of Civil and Environmental Engineering, Narutowicza 11/12, 80-233 Gdańsk, Poland (e-mail: aneta.luczkiewicz@wilis.pg.edu.pl).

M. Szala, was with Military University of Technology, S. Kaliskiego 2, 00-908 Warsaw, Poland (e-mail: mateusz.szala@wat.edu.pl).

J. Wojtas, was with Military University of Technology, S. Kaliskiego 2, 00-908 Warsaw, Poland (e-mail: jacek.wojtas@wat.edu.pl).

T. Ossowski, was with University of Gdańsk, Faculty of Chemistry, Bażyńskiego 8, 80-309 Gdańsk, Poland (e-mail: tadeusz.ossowski@ug.edu.pl).

R. Bogdanowicz, was with Gdańsk University of Technology, Faculty of Electronics, Telecommunications and Informatics, Narutowicza 11/12, 80-233 Gdańsk, Poland (e-mail: rbogdan@eti.pg.edu.pl).

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The most common explosives are TNT, HMX, RDX, which have well know detection methods [5]–[8]. Beyond these, there are other explosive materials that also require detection. One of them is 4,4',5,5'-tetranitro-1H,1'H-2,2'-biimidazole (TNBI), which is nitroaromatic based material (see Figure 1). TNBI is synthesized in two steps, the first being the reaction of glyoxal with ammonia gas in the presence of ammonium acetate. In the second step 2,2'-biimidazole is nitrated to tetranitro derivative [9], [10].

In this study, we propose electrochemical detection of TNBI using novel boron-doped diamond/graphene nanowall electrodes (B:DGNW), and to the best of our knowledge, electrochemical detection of TNBI has not previously been reported. We propose here the quantitative analysis using electrochemical sensor utilizing the DPV readout at a nanocarbon electrode.

Carbon nanowalls (CNWs), typically, can be described as planar graphene sheets grown vertically to the substrate [11]. In our previous reports, we showed that B:CNW is a promising material for the electrochemical detection of organic compounds [11], [12]. B:CNW is characterized by good electrical conductivity and a wide potential window. Moreover, CVD synthesis allows a hybrid electrode of B:DGNW to be produced [13], which combines the remarkable properties of B:CNW and BDD into a single electrode.

We show TNBI detection in an extremely complex system, which is landfill leachates (LLs). LLs are highly contaminated liquid by-products released during solid waste deposition as a result of combined physical, chemical, and biological processes as well as precipitation. LLs because of the content of ammonia nitrogen, high salinity and the presence of organochlorine compounds and polycyclic organics exhibit toxic properties relative to aquatic and terrestrial organisms, including plants. The typical features of mature and old LLs are: a strong color, high concentrations of ammonia (1000 - 5000 mg $N\text{-}NH_4$ L^{-1}), and high contents of micropollutants [14]. The detection of explosives in such conditions requires a very sensitive detection method.

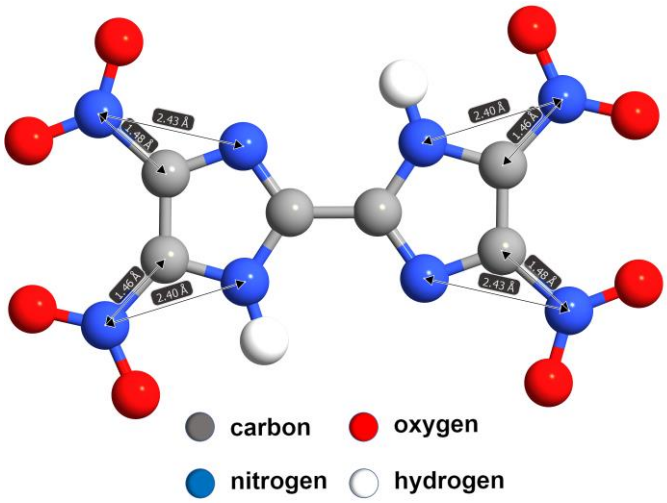

Fig. 1. Structure of 4,4',5,5'-tetranitro-1H,1'H-2,2'-biimidazole.

II. Material and Methods

A. Chemicals

TNBI was synthsized in the Military University of Technology according to the original procedure developed by Szala and Lewczuk [9], [15]. 2,2'-Biimidazole (BI) was synthesized from glyoxal and ammonia. Next, BI was nitrated directly in the $HNO_3/H_3PO_4/P_2O_5$ system. Crude TNBI was purified by crystallization from distilled water. TNBI, in normal conditions, forms a stable dihydrate. All reagents were analytical grade and used without further purification.

B. Electrode growth

Electrode growth: B:DGNW was deposited on a <100> oriented silicon substrate using an MWPECVD system (SEKI Technotron AX5400S, Japan). A more detailed deposition procedure has been reported in the literature [11], [14], [16], [17]. The substrate temperature was kept at 700°C during the deposition process. The base pressure was about 10^{-6} Torr, while the process pressure was kept at 50 Torr. The source gas, a mixture of $H_2/CH_4/N_2$ at gas volume 300 sccm of total flow rate, was applied. Moreover, the boron doping level in the gas phase, expressed as the [B]/[C] ratio, was kept at 2000 ppm using diborane (B_2H_6) as a dopant precursor. The growth time was 6 h. The molecular composition (X-ray photoelectron spectroscopy, secondary ion mass spectrometry, Raman spectroscopy) and morphology (electron scanning microscopy) of boron-doped diamond/graphene nanowall electrodes were presented elsewhere [18].

C. Landfill leachate

The LLs used in the study were collected from the 'Eko Dolina Lezyce' municipal solid waste plant, located in northern Poland (Pomeranian region), which receives ca. 200,000 Mg of waste per year. In December 2018 three samples of LLs were taken from a storage reservoir of LLs generated by a mature cell. This cell was in operation from January 2003 to November 2011, when solid wastes were managed in accordance with an old policy that did not limit the deposition of biodegradable waste (currently a new law is in force - Directive 2018/850/EU amending Directive 1999/31/EC; for details see [14]). The LL samples were collected in high-density polyethylene (HDPE) bottles and transported (in a portable refrigerator) to the laboratory. Next, they were homogenized, then characterized in terms of their physical and chemical parameters and kept frozen (-20°C) until the analyses.

The assessed quality parameters of the LLs were as follows: pH, conductivity and oxidation-reduction potential (using a portable multi-parameter meter, a HL-HQ40d multi, HACH, Germany), total organic carbon (TOC), total phosphorus (TP), orthophosphate ($P\text{-}PO_4$), ammonia-N ($N\text{-}NH_4$), nitrate-N ($N\text{-}NO_3$), nitrite-N ($N\text{-}NO_2$), chemical oxygen demand (COD), chloride (Cl^-), sulfate (SO_4^{2-}) and sulfides (S_2^-) using a XION 500 spectrophotometer (Dr. Lange, GmbH, Germany), 5-day biochemical oxygen demand (BOD_5) using the manometric respirometric BOD OxiTop® method, total suspended solids (TSS), volatile suspended solids (VSS) and mineral suspended solid (MSS) using the gravimetric method. All measurements were based on APHA [19].

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According to the obtained results, the LL samples collected in this study were characterized as: dark brown color, pH in the alkaline range (7.8 ± 0.1), high concentrations of ammonium nitrogen (96% ± 3% of the TN) and chemical oxygen demand (3,893 ± 22 mg O_2/L, phosphorus occurred mainly as P-PO_4 (69% ± 6% of the TP), low BOD_5/COD ratio (0.07 ± 0.01) and high concentrations of chloride and sulfate (with mean values 2,610 ± 90 mg Cl^-/L and 1,650 ± 120 mg SO_4^{2-}/L, respectively). The detailed characteristics of the LLs are listed in Table S1.

D. Preparation of solutions

The standard stock solutions of TNBI at 1000, 100, 10, 1 ppm concentrations were prepared in dimethyl sulfoxide (DMSO) due to the low solubility of TNBI in water. For electrochemical measurements in aqueous solutions, the aliquot volume of the standard stock solutions was added into 10 mL of electrolyte. All tests were performed in 1 ml of the sample solution.

E. Characterization techniques

The electrochemical measurements were conducted using a potentiostat–galvanostat (VMP-300, Bio-Logic, France) under EC-Lab software in a three-electrode assembly. Before the electrochemical studies, all electrolytes were purged with Ar (anaerobic conditions were also maintained during the tests). The boron-doped carbon nanowalls were used as the working electrodes (the geometric area around 0.2 cm^2), the platinum wire served as the counter electrode, and the Ag/AgCl/3.0 M KCl electrode and Ag/AgCl wires were the reference electrodes.

Firstly, cyclic voltammetry (CV) was recorded in 5 mM $[Ru(NH_3)_6]Cl_3$ in 0.5 M Na_2SO_4 on B:DGNW in the range of -0.8 V to 0.1 V at growing scan rates. Secondly, CV was performed in 0.5 M KCl in 0.1 M PBS (phosphate-buffered saline) solution at pH = 6.5 and measured for chosen scan rates at 10, 25, 100 and 300 mV s^{-1} from -1.0 V to 0.5 V. Moreover, the CV was carried out in nonaqueous solution: 0.1 M tetraethylammonium tetrafluoroborate ($TEABF_4$) in DMSO. Likewise, the cyclic voltammetry was used for the electrochemical detection of 20 ppm TNBI in 1 mL of landfill leachate and landfill leachate with 0.5 M KCl addition. The CV was also performed at pH = 7.8 (0.5 M KCl in 0.1 M PBS).

The DPV was conducted for a solution consisting of 0, 0.02, 0.14, 0.4, 0.7, 1.4, 2.0, 4.0, 8.0 11.0 and 16 ppm of TNBI 0.5 M KCl/0.1 M PBS at pH of 6.5 at the potential range 0.05 to -0.75 V (vs. Ag/AgCl/3M KCl). DPV results were obtained at the following conditions: 200 ms pulse width, 25 mV pulse height, step time 500 ms, and a scan rate of 10 mV s^{-1}.

Density Functional Theory (DFT) was utilized to estimate molecular interaction at atomic level. The QuantumATK software (version 2019.03) [20] was used to calculate the electronic and transport properties of 4,4',5,5'-tetranitro-1H,1'H-2,2'-biimidazole. In simulations, we utilized the generalized gradient approximation (GGA) with Optimized Norm-Conserving Vanderbilt (SG15) pseudopotentials [21], a linear combination of atomic orbitals, a Perdew-Burke-Ernzerhof (PBE) exchange-correlation correction with an energy cut-off of 185 Hartree. The convergence criteria were set to less than $1.0 \cdot 10^{-5}$ eV/atom of total energy change. For geometry optimization the Limited Memory Broyden–Fletcher–Goldfarb–Shanno (LBFGS) optimization algorithm. The convergence of atomic forces was less than 0.01 eV $Å^{-1}$.

III. Results and Discussion

The kinetic characteristic of $[Ru(NH_3)_6]^{2+/3+}$ redox system studied at the pristine (as-grown) boron-doped diamond/graphene nanowall electrode is presented in Fig. 1S. In Table 2S we gathered the values of potential difference between oxidation (E_{ox}) and reduction (E_{red}) peaks, called peak-to-peak separation (ΔE). The ΔE value for the low scan rate (10 mV s^{-1}) is close to the theoretical value for a reversible reaction and is equal to 61 mV. Thus, the process is mainly controlled by diffusion mechanism. The slight peak-to-peak separation indicates that B:DGNW electrode supports fast electron transfer and demonstrates desirable electronic features. Hence, aforementioned electrodes are expected to have attractive prospective for electroanalytical applications.

The Fig. 2 presents cyclic voltammograms of pristine boron-doped diamond/graphene nanowall electrode in a reference (background) solution of 0.5 M KCl with 0.1 M phosphate-buffered saline and in solutions containing 20 ppm of TNBI, as a function of scan rate. As it is shown in Figure 2, the electrode shows low background current without faradaic peaks without TNBI in the solution. This fact makes it suitable for sensing applications. In the solution of 20 ppm TNBI in 0.5 M KCl + 0.1 PBS, the two separated reduction peaks localized at -0.26 V and -0.54 V at 10 mV s^{-1} (vs. Ag/AgCl/3M KCl) were recorded. The peak maxima shifted slightly to the more negative potential with a growing scan rate: for a scan rate of 100 mV s^{-1}, the signal was localized at -0.30 V and -0.65 V. Moreover, the current density value increases linearly with the square root of the scan rate (inset Fig. 2). The peaks shift and absence of mirror oxidation signals testify the irreversibility of the reduction reaction.

For a deeper understanding of the essence of the reduction mechanism of TNBI, a CV was also conducted in a nonaqueous solution in 0.1 M $TEABF_4$ in DMSO (see Fig. 3). The results show no reduction peaks from the TNBI compound. There is only a cathodic signal at about -0.65 V and an anodic signal at about -0.44 V from the background.

The voltammograms recorded in the aqueous solution at 300 mV s^{-1} show two reduction peaks localized at about -0.25 V and -0.65 V. There is no research of electrochemical behavior of 4,4',5,5'-tetranitro-1H,1'H-2,2'-biimidazole, however the papers of the electroanalytical determination of other nitro explosives show that the peaks localized in the range of 0 to -1.2 V usually corresponds to the nitro moiety reduction [22]–[24]. The reduction of trinitro compound 2,4,6-trinitrotoluene (TNT), which is the most commonly used explosive compounds, results in three reduction peaks [22], [23], [25], whereas reduction of dinitro compound 2,4-dinitrotoluene (DNT) gives two peaks [24]. Thus we assume that the amount of reduction signals is attributed to the number of -NO_2 moieties in the nitroexplosives. The TNBI compound contains four nitro groups; thus we expected to observe four cathodic peaks. However, TNBI shows a diagonal chemical symmetry of nitro groups. Referring to the structure of TNBI (see Fig. 1), there are

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two pairs of $-NO_2$ of equivalent significance: nitro moiety localized at the 4 - 4' position and 5 - 5' position. There is a distance difference of nitrogen atoms (in the ring and in $-NO_2$ moiety) between 4 - 4' position and 5 - 5' position equal to 0.04 Å resulting from hydrogen interaction of hydrogen from N-H and oxygen from adjacent $-NO_2$ group. Calculated by DFT electron localization in TNBI compound is presented in Fig. 2S. Thus, we assumed that the two observed peaks corresponds to the reduction of the two pairs of nitro groups.

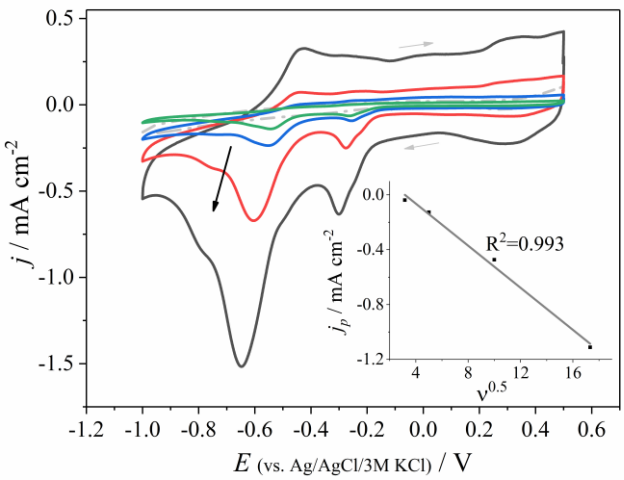

Fig. 2. CV curves recorded as a function of scan rate (from 10 to 300 mV s^{-1}) of 20 ppm TNBI in 0.5 M KCl + 0.1 PBS on B:DGNW electrode (pH = 6.5). Background current is presented as the dash-dot curve. Inset: the plot of j_p versus $\nu^{0.5}$ for the peak localized at ca. -0.6 V.

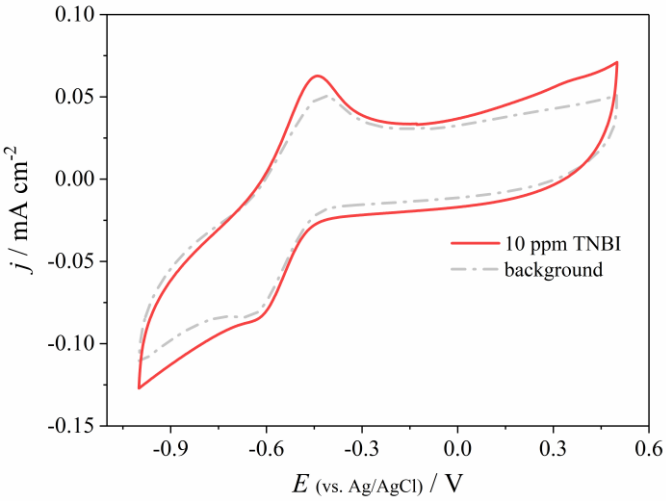

Fig. 3. Current densities of 10 ppm TNBI on B:DGNW recorded in 0.1 M $TEABF_4$ in DMSO at scan rate 100 mV s^{-1}.

The process of reduction was presented only in protic solutions. Hence, we think that the reduction mechanism takes place in a similar way as among other nitroaromatic compounds, such as 2,4,6-trinitrotoluene, in which proton is necessary to start the reduction process [7], [22], [24]–[27].

Subsequently, differential pulse voltammetry was performed. Fig. 4 presents the background and baseline subtracted voltammograms for various concentrations of TNBI in de-aerated 0.5 M KCl/0.1 PBS. The DPV diagrams were obtained for the reduction of four nitro groups in nitroaromatic compounds on B:DGNW. Similarly to the CV results, two reduction peaks were observed: at -0.25 V and -0.53 V. The shape of the reduction pick of the nitro groups in TNBI seems to be a complex process. It may be due to the susceptibility to proton reactions and high reactivity of the radical molecules generated during the cathodic process. We assumed, similar to TNT mechanism, that during the reduction process not only reduced and protonated forms of TNBI are created but also nitro-hydroxylamine and amine forms.

The reduction peak observed at about -0.53 V exhibited the most favorable characteristics for TNBI, and was chosen for the subsequent quantitative analysis.

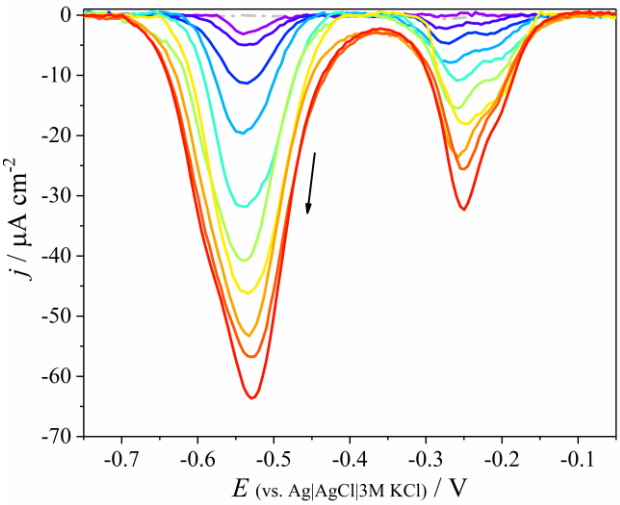

Fig. 4. Differential pulse voltammetry of TNBI recorded on B:DGNW electrode (concentrations: 0.02; 0.14; 0.4; 0.7; 1.4; 2.0; 4.0; 8.0; 11.0; 16.0 ppm; background is presented as dash-dot curve).

As shown in Fig. 5, the peak current is proportional to the TNBI concentration in two regions: from 0.02 ppm to 1.4 ppm and from 2 ppm to 16 ppm. The calibration curves exhibit two different linear responses depending on the explosive concentration. This phenomenon may be related to the different detection mechanisms: adsorption-controlled process (for concentrations lower than 1.4 ppm TNBI), and diffusion-controlled process (for concentrations higher than 1.4 ppm), which agrees with the literature [12].

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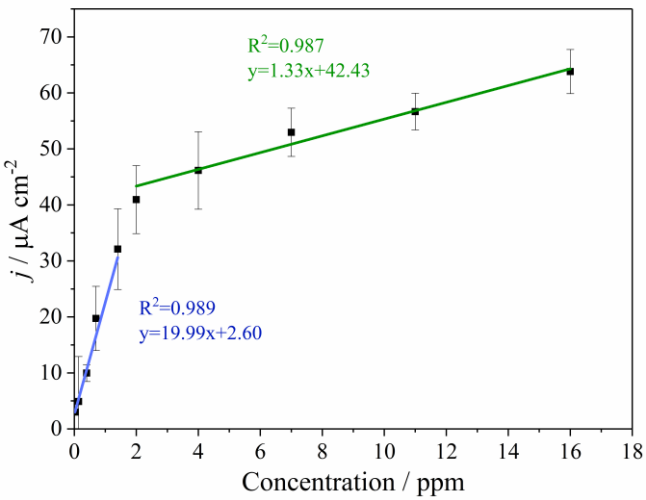

Fig. 5. Calibration curves of TNBI on B:DGNW based on the reduction peak observed at -0.53 V (the error bars represent the standard deviation).

The linear regression analysis of the calibration curves in Fig. 5 yields the correlation coefficient R^2 = 0.989, slope of 19.99 μA cm^{-2} ppm^{-1} and R^2 = 0.987, slope of 1.33 μA cm^{-2} ppm^{-1} for lower and upper concentrations, respectively. The limit of detection (LOD) and limit of quantitation (LOQ) were calculated based on the equations containing the standard deviation of the blank signal σ (without TNBI) and the slope of the calibration curve: LOD=3.3·σ/slope, LOQ=10·σ/slope [23], [28]. The limit of detection was equal to 0.52 ppm (1.66 μM L^{-1}), whereas the LOQ was 1.58 ppm (5.03 μM L^{-1}). TNBI compound was detected for the first time, so there is no data to compare the sensitivity and LOD/LOQ of this electrode. For comparison, the detection limits of the most common compound, which is TNT, is in the range of 1 ppb to 1 ppm for carbon materials [29].

Further to this, the proposed model of the electrochemical sensor was tested in a real-life sample, which was landfill leachates. First, the measurements were done in a blank electrolyte (background leachate) to check for the presence of any interferences originating from the electrolyte. Next, cyclic voltammetry was performed in LLs containing 20 ppm TNBI with the addition of KCl salt, and next, the measurements were carried out in pure leachate (Fig. 6). The results were compared to the previously used electrolyte 0.5 M KCl/0.1 M PBS (pH=6.5). Due to the different pH values of the LLs, we decided to check the response of the system in pH similar to landfill leachates (Fig. 3S).

The increase of the pH of 0.5 M KCl/0.1 M PBS solution caused the shift of the cathodic peak maxima towards a lower potential (from -0.57 V to -0.69 V and from -0.23 to -0.33 V). Moreover, the peak height decreased (from -0.34 mA cm^{-2} to -0.25 mA cm^{-2} for the signal localized at around -0.6 V). This phenomenon can be explained by the mechanism of reduction of nitro groups, which requires the presence of a proton. Access to protons in an alkaline environment is lower compared to an acidic environment.

Fig. 6 illustrates that it is possible to use the boron-doped diamond/graphene nanowall electrodes as a 4,4',5,5'-tetranitro-1H,1'H-2,2'-biimidazole sensor. Moreover, there is no need to add additional salt into the LLs to increase the conductivity of the solution. However, the quantitative analysis should be performed for the peak localized at -0.65 V, because the signal at about -0.3 V was not observed in such a complicated matrix.

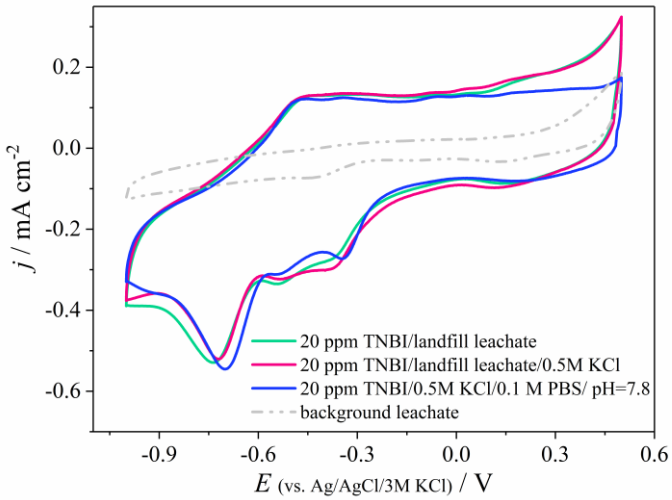

Fig. 6. Electrochemical detection of 20 ppm TNBI in landfill leachates and landfill leachates with 0.5M KCl (scan rate: 100 mV s^{-1}).

IV. Conclusion

In this article, we have presented for the first time the electrochemical behavior of 4,4',5,5'-tetranitro-1H,1'H-2,2'-biimidazol. Cyclic voltammograms of TNBI revealed two major reduction peaks, which correspond to the four nitro-group reduction.

Moreover, we have developed a model of TNBI electrochemical sensor based on a boron-doped diamond/graphene nanowall electrode characterized by high sensitivity and selectivity for nitroaromatic-based explosives. The lower detection limit of the sensor has reached 0.52 ppm (1.66 μM L^{-1}), and its response showed two linear regions extending from 0.02 ppm to 1.4 ppm and from 2 ppm to 16 ppm.

The ability of the sensor to detect TNBI in real wastewater systems was also demonstrated. This shows the significant potential of using the proposed method to detect nitro compounds in an extremely complex, real matrix, such as landfill leachates.

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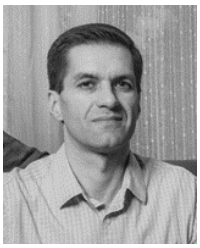
This article has been accepted for publication in a future issue of this journal, but has not been fully edited. Content may change prior to final publication. Citation information: DOI 10.1109/JSEN.2020.2973451, IEEE Sensors Journal

A. Dettlaff In 2013, she obtained a master's degree at the Faculty of Chemistry of the Gdańsk University of Technology on the specialization Monitoring and Environmental Pollution Analytical with honors. In the years 2013-2017 she was a Ph.D. student in the field of Chemical Technology, during which she was involved in the work entitled "Nanocomposites based on conducting polymer and carbon materials for supercapacitor application". In 2015 she took a three-month research internship in Oldenburg (Germany). She received the title of doctor of technical sciences in 2017. She presented the results of her scientific work at many national and international conferences (including Switzerland, France). Her research interests include carbon materials, electrochemical sensors, and materials for storage and energy conversion.

P. Jakóbczyk (born 1985) obtained his Ph.D. degree in Chemistry from the Poznan University of Technology in 2013. From 2013 to 2016, Paweł was assistant and since 2016 has been adjunct in the Institute of Chemistry and Technical Electrochemistry at the Faculty of Chemical Technology, Poznan University of Technology. His research activities are devoted to electrochemical methods of material characterization, with special attention to the material development for applications to energy conversion/storage. Currently, Paweł works as a postdoctoral researcher in the Department of Metrology and Optoelectronics at the Gdansk University of Technology.

M. Sobaszek was born in Gdansk in 1984. In the summer of 2009 he received a Master degree in Materials Engineering and in 2017 Ph.D. in Electronics at Gdansk University of Technology. Currently he is an Assistant Professor at the Faculty of Electronics at Gdansk University of Technology. For more than 7 years, he has gained experience in depositing and characterizing thin films using PA CVD and CVD methods such as diamond semiconductor, nanotube, nanoscale, etc. The main topics of interest are: diamond base optical and electronic sensors, environmental protection, storage, and energy conversion.



J. Wojtas (born 1977), received his Ph.D. degree with honors in Electronics from the Military University of Technology in 2007. Member of the Committee of Metrology and Scientific Equipment of the Polish Academy of Sciences. Member of the Metrology Council appointed by the Polish Minister of Development. Professor of MUT, an expert in optical signal detection, optoelectronic metrology and optoelectronic sensors for detecting traces of various volatile compounds. His research are focused on the use of state-of-the-art laser technology in optoelectronic gas sensors for environmental applications (gaseous pollution monitoring), medical diagnostics (detecting diseases biomarkers in human breath) and for safety systems (explosives detection). More than 230 scientific publications, an associate editor in 1 JCR journal and reviewer in over 20 journals and grant agencies.

R. Bogdanowicz (born 1976) received his Ph.D. degree with honors in Electronics from the Gdansk University of Technology in 2009. He worked as a post-doc researcher in Ernst-Moritz-Arndt-Universität Greifswald Institut für Physik in 2010 and 2011. He moved back to the Gdansk University of Technology in 2011, as an assistant professor in the Department of Metrology and Optoelectronics. His current domains of interest include selective CVD diamond growth and nanocrystalline diamond doping for environmental and biochemical nanosensors. In 2015 he held a scholarship Fulbright Senior Scholar Program at the California Institute of Technology (Caltech) in the group of prof. William Goddard (Materials and Process Simulation Center) working on hybrid 3D diamond structures. Prof. Bogdanowicz has published more than 100 scientific papers and book chapters, proceedings, and special journal issues (e.g., Diamond and Related Materials). He has served on several journal editorial boards and currently serves as an Associate Editor for 2 JCR journals, and reviewer for over 30 journals and granting agencies.