

INFLUENCE OF IONIC LIQUID IN MODIFIED PASTE CARBON ELECTRODE TO VOLTAMETRIC SIGNALS OF 2,4,6-TRINITROTOLUENE (TNT) IN PHOSPHATE BUFFER SOLUTION

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Abstract

Fabrication of ionic liquid modified paste-carbon-electrodes (ILPCEs) and its application in measuring electrochemical properties of 2,4,6-trinitrotoluene (TNT) were investigated in this study. The modified electrodes were prepared by carbon powder (Cp) with ionic liquid 1-Butyl-3-methylimidazolium tetrafluoroborate [C_4mim][BF_4] (IL) and paraffin oil (PO) with different percentage of Cp/IL/PO in weight mixing ratios (%w). Voltametric signals of 2,4,6-trinitrotoluene in phosphate buffer solution 0.05 M with pH = 8 on these modified electrodes was recorded. The modified electrode with ratio Cp/IL/PO equal to 80:10:10 is confirmed to be the best in current signal measurement. In term of TNT electrochemical detection with 0.03-22 ppm concentration range, ILPCEs pointed out advantages over conventional glassy carbon electrode by lower detection limit, better performance in signal collecting, more stable and higher reproducible response.

Keywords: Trinitrotoluene, carbon paste, ionic liquid, modified electrodes, electrochemical sensors.

1. INTRODUCTION

Detecting of explosive compounds has been receiving considerable attention for environmental issue and national security as well. Among them, 2,4,6-trinitrotoluene (TNT) is of great environmental concern due to its toxicity and the toxicity of its derivatives. Therefore, the growing needs of rapid and sensitive detection of TNT for various (military and anti-terrorism) surveillance activities are well understood. For environmental and security applications, it has generated major demands for effective field-deployable tools for detecting TNT in marine (and other natural water) environments in a fast, simple, sensitive, reliable and cost-effective manner [1]. Up to now, TNT in the environment can be detected by different methods, for example: gas chromatography [6], liquid chromatography [7], and mass spectrometry, optical and electrochemical methods [8], in which electrochemical methods appears to be powerful method because of its high selectivity, sensitivity, wide linear range and rapid measurement. Moreover, the instrument is less

expensive, simple, compacted leading to possibility use in the environmental scale.

In the other field, Ionic Liquid (IL) is a salt in liquid state which entirely composed of anions and cations with short lived ion-pairs and melting point of their majority is below room temperature. ILs are widely known as powerful solvent and electrical conducting fluids (electrolyte). Because of this strong point, ILs has been applied for electrode modification in electrochemical measurement in some studies since 2000 [2]. Because of its hydrophobicity, high viscosity, ionic structure, ionic conductivity, very low volatility and biocompatibility are among the properties of ionic liquids making them attractive for electrode modification. Initially, research on ionic liquid modified electrodes was oriented towards fundamental studies of ion transfer across ionic liquid/aqueous solution interface. Now, almost entire research effort in this area is oriented towards their application for electrochemical sensing with multi-component films and carbon paste electrodes being more popular [2]. Until the middle of 2010, almost

300 papers about ionic liquid modified electrodes were published; it indicates a promising field for electrochemistry.

In our study, the use of electrochemical measurement to determine TNT using self-fabricated ionic liquid modified paste-carbon-electrodes (iLPCEs) was reported for the first time. In presence of iLPCEs, the successful application in TNT detection in phosphate buffer environment has been demonstrated with high sensitivity, selectivity and reproducibility.

2. EXPERIMENTAL

2.1. Preparation of the paste carbon electrodes (CPE)

Carbon paste was prepared by grinding the 80 %, 70 % graphite powder and 20 %, 30 % paraffin oil in an agate mortar by hand mixing for about 20 minute to get homogenous bare CPE. In case of iLPCEs, 1-butyl-3-methyl-imidazolium tetrafluoroborate [C₄mim][BF₄] with given weight ratio was added (table 1).

Table 1: Mixing ratio (% weight) of Carbon paste (Cp), paraffin oil (PO) and ionic liquid (IL) in modified electrodes

Number (No.)	Weight ratio (%w)		
	Cp	PO	IL
1	70	30	0
2	70	23	7
3	80	20	0
4	80	15	5
5	80	10	10
6	80	5	15
7	80	0	20

At lower %w of Cp, Cp-PO-IL mixture was too wet to make electrodes and electrode surface was damaged as dipping in the electrolyte solution during the measurement.

In this report, modified electrodes Number 1 to Number 7 correspond to No.1 to No.7 notation in figures.

A portion of the prepared paste was then packed tightly into the cavity (5 mm in diameter, 5 mm in length) of a Teflon electrode holder, a bare gold wire (1mm in diameter) has been used for electrical contact. The composite surface was smoothed on a weighing paper and rinsed carefully with double-distilled water prior to each experiment. The

electrodes can be re-used several times with renewing working composite surface by pushing up the packed past and smoothing on the weighing paper, then washed with double-distilled water before each measurement.

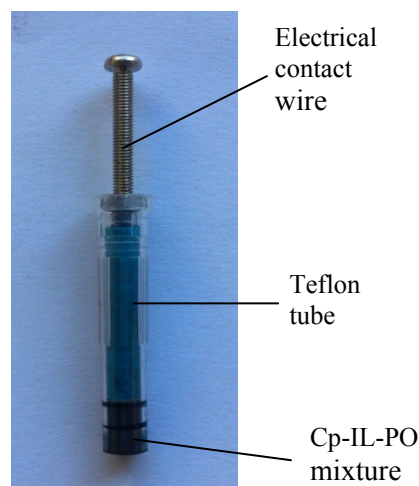


Figure 1: The ionic liquid modified carbon paste electrodes (iLPCEs)

2.2. Reagents

- 2,4,6-trinitrotoluene (TNT), PA
 - Carbon powder (Cica Reagent, Japan)
 - Parafin oil (Wako, Japan)
 - 1-Butyl-3-methyl-imidazolium tetrafluoroborate [C₄mim][BF₄]
 - Stock solution was prepared by dissolving TNT in 99.7 % ethanol at a concentration of 6 ppm and 60ppm. Stock solution was stored in a refrigerator at 4 °C in dark.
 - Electrolyte solution is K₂HPO₄ + KH₂PO₄ 0.05M (PBS) at pH 8.
- All used chemicals were of analytical reagent grade purchased from Merck (Darmstadt, Germany). Doubly distilled water was used throughout.

Samples were prepared daily for each measurement by adding gradually TNT stock solution into an available measuring flask containing the electrolyte solution.

2.3. Apparatus and procedure

All electrochemical experiments were performed on a CPA ioc HH5 electrochemical workstation. A standard three-electrode system was used comprising an iLPCE as a working electrode, a platinum electrode as an auxiliary electrode, and an Ag/AgCl electrode as a reference electrode. Measurements were carried out in a phosphate

buffer solution (0.05 M, pH 8.0) as a supporting electrolyte medium. All experiments were performed at room temperature.

Before each measurement, along with the voltammogram of the base solution was recorded, TNT stock solution was added gradually to receive the expected concentrations. Differential Pulse Polarography (DPP) voltammogram was then recorded repeatedly three times to obtain average values.

3. RESULTS AND DISCUSSION

3.1. Influence of the composition of the carbon paste electrodes

From previous studies [5] we investigated the electrochemical properties of TNT on the electrodes in conditions around the potential from 0 V to -1 V, the potential rate 150 mV/s, the pulse height 70 mV and the pulse time 40 ms.

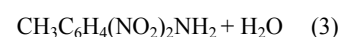
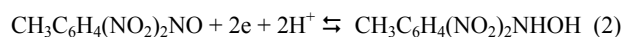
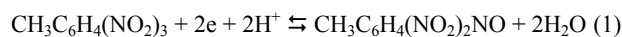
To select the components of the carbon paste and paraffin, we manufactured electrodes No.1 and No.3 with determined ratio of Carbon paste (Cp)/paraffin oil (PO) in Table 1 and manufactured the electrodes No.2 in order to compare.

The initial studies [5] showed that these electrodes provide the best current signal in the phosphate buffer solution pH equal to 8.

To investigate the electrochemical properties of TNT in PBS electrolyte environment, DPP spectrum was scanned by dimensional reduction from 0 to -1 V. As shown in figure 2, it indicates three reduction

peaks of TNT; each peak corresponds to a response reduction of a nitro group of TNT. It gives a good agreement with previous study reported by Xiaojuan Fu *et al.* [3]

The reductions of aromatic polynitro-compound are very complex. In details, the reductions of TNT are the processes of sequential reduction of the nitro groups. As mentioned, each peak corresponds to the reduction of a nitro group and subsequent reduction in whole or in part to create the final product is amino groups, corresponding to the reaction 1-3 by Brooksby shown below [4]:



The first peak (1) is a specification of TNT detection, which separates TNT from other aromatic nitro compounds. Moreover, the relative height of peak (1) reflects quantitative concentration of TNT in analyzed sample. By these reasons, the peak (1) is aimed to clarify the influence of electrode fabricated components to the electrochemical analysis of TNT in this study.

Figure 2 shows the DPP spectrum of 9 ppm TNT in PBS (pH = 8) of the electrodes. The electrode No.3 provides higher current intensity than No.1 and 2 at the same concentration by calculating relative peak height. DPP spectrum which obtained by electrode No.1 and 3 appeared to be more specific than that by No.2.

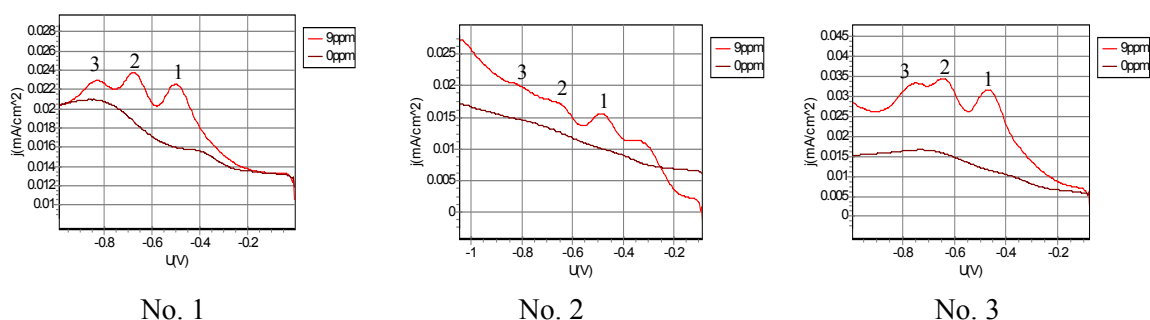


Figure 2: DPP voltammograms of the 9 ppm TNT solution in PBS pH = 8 obtained by different electrodes

From the DPP spectrum of three electrodes, the graph of the dependence of the current on the concentration of TNT solution in phosphate buffer pH 8 in figure 3 was plotted. As shown in figure 3, the calibration curves were established with high correlation with R^2 coefficient is about 99 %, the electrode No.3 is confirmed to be the best in three electrodes in term of collecting current signal. In the

case of preserving the carbon paste ratio is 70 % with addition of IL at rest (electrode No.2), the spectrum does not provide any valuable result. Overall, electrode No.3 was chosen for further analysis.

As shown in figure 4, the DPP voltammograms in TNT solution with different concentrations were obtained using the electrode No.3. The reduction peaks of TNT are clearly

observed, relative heights of peak linearly reflect total amount of TNT concentration in analyzed solution.

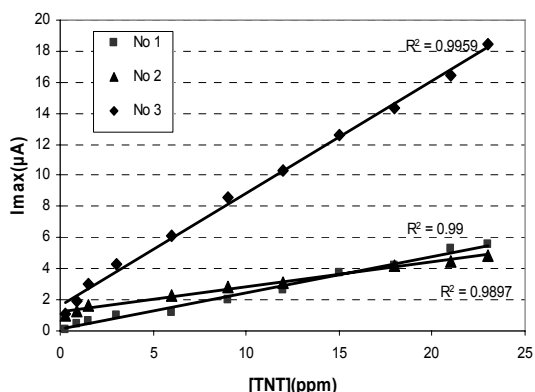


Figure 3: Dependence of the current on the concentration of TNT in PBS pH = 8

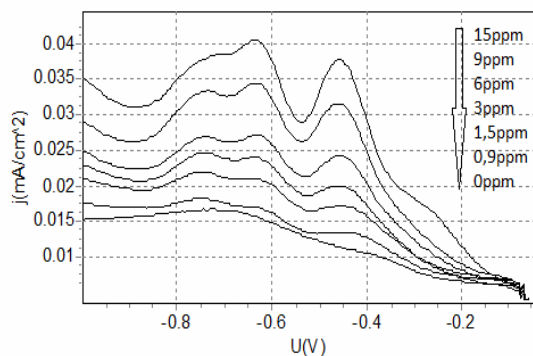


Figure 4: DPP spectrums of TNT obtained in PBS pH = 8 using electrode No.3

3.2. Effect of varying IL quantity to iLPCE electrochemical properties

To examine the effect of IL quantity to electrochemical properties of the electrodes, the electrode No.4, 5, 6, 7 were made with calculated Cp/PO/IL %w ratio as shown in table 1. Volt-amperes signal of TNT with 0.03-22 ppm concentration range was also collected using fabricated electrodes. In this experiment, by using electrodes No.3, 4, 5, we observed current signal and collected DPP spectrum of TNT. On the other hand, electrode No.6 and No.7 did not shown any current signal because the electrolyte solution (PBS) leads to electrode surface degeneracy

From volt-amperes signal acquired using electrodes No.3-5, dependence of reduction current intensity on TNT concentration was plotted (figure 5).

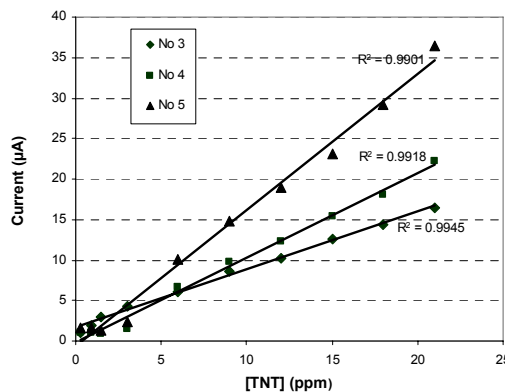


Figure 5: Dependence of reduction current intensity of iLPCEs on TNT concentration in PBS pH = 8

As shown in figure 5, calibration curves were established with high correlation, the R^2 coefficient is over 99%, which indicates high sensitivity and selectivity of fabricated iLPCEs.

Compare between three electrodes in Figure 5, it indicates that higher percent of IL provides better current intensity, the highest current signal obtained at the electrode No.5 with mixing ratio (Cp/IL/PO) equals to 80:10:10. With higher IL mixing percentage, the electrode surface showed to be unstable in phosphate buffer solution pH = 8. By these results, iLPCE No.5 was selected for further analysis in our study.

3.3. Dependence of reduction current intensity on TNT adsorption time

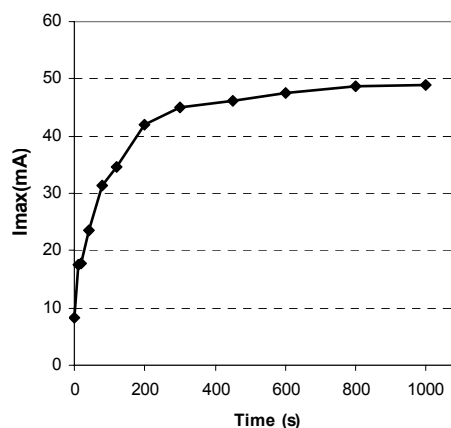


Figure 6: Dependence of TNT adsorption time on reduction current intensity using iLPCE No.5

Further experiments were performed using iLPCE No.5 for 30 ppm TNT solution. Before collecting voltammogram, we applied a potential of -1 V for 50 second in order to electrochemically reactivate the iLPCEs. TNT adsorption time was set by: 0s, 10s, 20s, 40s, 80s, 120s, 200s, 300s, 450s,

600s, 800s, 1000s then maximum reduction current intensity (I_{\max}) was evaluated. The results are shown in Figure 6, it points out that the peak signal increased from 0s to 600s, after 600, no growing of I_{\max} is observed. It can be explained by fully adsorption of TNT on iLPCEs surface was carried out after 600s immersing. So, 600s adsorption time is chosen as optimized immersion time.

3.4. Comparison between iLPCE No.5 and glassy carbon electrode in TNT detection

In order to clarify application of iLPCE in detecting TNT, iLPCE No.5 was compared with glassy carbon electrode in detection of TNT with 3-21ppm concentration range. The experiments were performed in PBS pH = 8 electrolyte solution, results are shown in figure 7.

Figure 7 indicates that iLPCE No.5 provides much higher efficiency in determining TNT concentration than conventional glassy carbon electrode in same PBS electrolyte solution. Limit of detection of TNT measured by iLPCE No.5 calculated to be 88.6 ppb; it is proved to be much smaller than that obtained by glassy carbon electrode (680 ppb).

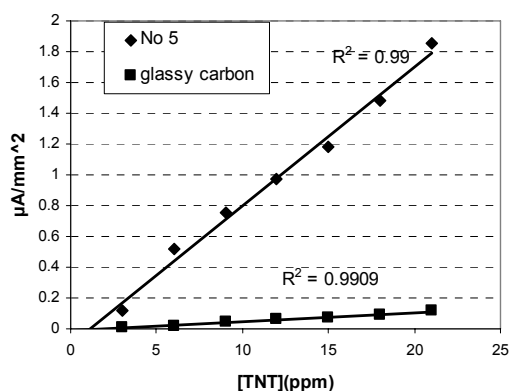


Figure 7: Dependence of the TNT peak current density on the TNT concentration in PBS pH = 8

4. CONCLUSIONS

Ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate [C₄mim][BF₄] as an agent, paraffin oil as binder in combination with the carbon paste was applied to fabricated electrodes in our study. In term of investigating electrochemical properties of explosive compound TNT in PBS pH = 8 electrolyte, ionic liquid modified paste-carbon-electrodes (iLPCEs) with %w equal to 80:10:10 shows great advantages over conventional glassy

carbon electrode. By using Differential Pulse Polarography (DPP) from 0V to -1V and TNT 600s adsorption time, our iLPCE reveals to be high sensitive and selective method which can identify TNT with ~8 times lower in concentration than glassy carbon electrode, also better in signal collecting, more stable and higher reproducible response. By this study, the results opened up possibility of higher performance Ionic liquid-sensor for TNT determination; not only in laboratory scale but also in environment.

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