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Electrochemical oxidation of p-nitrophenol using graphene-modified electrodes, and a comparison to the performance of MWNT-based electrodes

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Abstract The electrochemical oxidation of p-nitrophenol (p-NP) has been studied comparatively on a graphene modified electrode and a multiwall carbon nanotube (MWNT) electrode by using cyclic and differential pulse voltammetry. The sensors were fabricated by modifying screen-printed electrodes with graphene and MWNT nanomaterials, respectively, both dispersed in Nafion polymer. p-NP is irreversibly oxidized at +0.9 V (vs. the Ag/AgCl) in solutions of pH 7. The height and potential of the peaks depend on pH in the range from 5 to 11. In acidic media, p-NP yields a well-defined oxidation peak at +0.96 V which gradually increases in height with the concentration of the analyte. In case of differential pulse voltammetry in sulfuric acid solution, the sensitivity is practically the same for both electrodes. The modified electrodes display an unusually wide linear response (from 10 μM to 0.62 mM of p-NP), with a detection limit of 0.6 μM in case of the graphene electrode, and of 1.3 μM in case of the MWNT electrode.

Keywords Graphene · p-nitrophenol · electrochemical oxidation · carbon nanotubes

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Introduction

The sensing of nitroaromatic compounds is of great importance to evaluate the risk of different environmental samples such as wastewater from mining, paint and pharmaceutical industries, petrochemical products or the manufacture of pesticides. Nitrophenols pollutants are harmful to environment due to their high toxic potential level for humans, animals and plants and have been included in the priority lists of monitored pollutants in many countries [1, 2].

In particular, the highly hazardous and toxic p-nitrophenol (p-NP) requires the development of simple, fast, sensitive, and accurate analytical method for its detection and quantification in different samples. A variety of methods have been used for determination of p-NP, many of them involving very complex, expensive and time consuming techniques such as spectrophotometric methods [3–5], high performance liquid chromatography technique [6–8], high performance capillary electrophoresis [9] and gas chromatography technique [10]. Electrochemical methods [11–19] have received considerable attention in the determination of nitrophenols due to their great advantages, such as simple operation, fast response, good sensitivity and in situ detection.

In this work we want to explore the applications of graphene as a novel electrode material in the electrochemical oxidation of p-NP and its quantitative analysis in aqueous solutions. Graphene, the one-atom-thick two-dimensional honeycomb lattice of sp2-bonded carbon, has attracted huge attention from scientific research groups thanks to its unique nanostructure and unusual properties such as high charge transport mobility [20, 21], high electrocatalytic activities [21–23], high transparency [24] and mechanical strength greater than steel [25].

Graphene sheets have been helpfully employed in many areas, for example, in optoelectronic devices [26, 27], in fuel cells [28, 29], electrochemical super-capacitors [30, 31] and in chemical sensors [32, 33, 36–42] and biosensors [34, 35].

Recent papers report the investigation of graphene as electrode material for detection of numerous target analytes such as dopamine [36–38], serotonin [38], ascorbic acid [39], hydrogen peroxide [40], paracetamol [41] and nitric oxide [42].

Most of the existing papers emphasize the advantages shown by graphene for electrochemical applications when compared to graphite or to carbon nanotubes. It has been reported that graphene exhibits a surface area of 2630 m^2 g^{-1}, which is much greater than that of graphite ($\sim$10 m^2 g^{-1}) and even that of carbon nanotubes (1315 m^2 g^{-1}) [43]. Alwarappan et al. [38] compared the behaviour of graphene and SWNTs for electrochemical sensing of dopamine and serotonin and they found a superior electrochemical performance of graphene sheets when comparing to that of the SWNTs. Using a four-point probe technique, they found the conductivity of graphene particles to be approximately 60 times better than that of SWNTs. In addition, Pumera's group found that the electrochemical response for biomarkers in the case of graphene is about twice that of MWNTs when used as electrode material [44]. They demonstrated that the sensitivity of graphene electrode was about 2–4 times greater than that of MWNTs for determination of free DNA bases [45].

However, although there are many positive reports concerning the analytical efficacy of graphene, some reports demonstrate that graphene might not provide a significant advantage over existing electrode materials [46].

In this paper, direct determination of p-NP was accomplished by applying electrochemical technique to a screen-printed electrode modified with graphene-Nafion. We investigated here whether graphene nanomaterials exhibit any advantage for p-NP detection by comparison of MWNT in terms of the sensitivity and selectivity of the response. Therefore, the graphene based electrode without any modification was utilized for the first time to study the direct voltammetric determination of p-NP by differential pulse voltammetry (DPV) technique, which is a usual electroanalytical technique with low nonfaradic current and high sensitivity.

Experimental

Reagents

Graphene nanopowder (8 mm flakes) were purchased from Grapheen Laboratories Inc. USA (https://graphene-super market.com). Multiwall carbon nanotubes (MWNT,

6–13 nm diameters and 2.5–20 μm length, 99.8% purity) were purchased from Sigma-Aldrich (www.sigmaaldrich.com) and use as received, without any further purification. The Nafion 5% solution was provided by Fluka (www.sigmaaldrich.com) and p-nitrophenol, sulphuric acid, sodium phosphates and potassium chloride were purchased from Sigma-Aldrich.

Apparatus and methods

Cyclic voltammetry and differential pulse voltammetry (DPV) were employed to study the electrochemical behaviour of p-NP at graphene and carbon nanotubes modified electrode. All experiments were carried out using a potentiostat PalmSens Instrumentation (Palm Instrument BV, The Netherlands) connected to a PC. The electrochemical measurements of p-NP were carried out in phosphate buffer solutions 0.1 M containing 0.1 M KCl, in a conventional electrochemical cell of 3 mL volume, using a three-electrode system with a planar configuration of a screen printed electrode (SPE), fabricated and purchased from Biosensor laboratory, University of Florence, Italy. The working carbon based electrode is of 3 mm diameter.

DPV measurements were performed on the following conditions: modulation time: 80 ms; pulse amplitude: 25 mV; step potential: 5 mV; scan rate: 20 mV s^{-1}; initial potential: 0.0 V; end potential: 1.1 V for p-NP determinations.

All solutions used in this work were prepared with double distilled water. All electrochemical experiments were carried out at room temperature and the potentials were referred to Ag/AgCl.

Preparation of modified electrodes

In the presence of aqueous solution of Nafion 2%, a perfluorosulfonated polymer, graphene, respectively MWNT, were homogeneously dispersed with the aid of ultrasonication, resulting solutions of 2 mg mL^{-1} concentration. 2 μL of each solution were dropped onto the SPE working surface. The graphene-Nafion and MWNT-Nafion films were obtained on the SPE surface via solvent evaporation.

Results and discussions

Voltammetric oxidation of p-nitrophenol

The electrochemical behavior of p-NP on graphene-Nafion electrode was studied first by cyclic voltammetry. As presented in Fig. 1, when 0.15 mM p-NP was added into phosphate buffer pH 7, a well-defined oxidation peak was
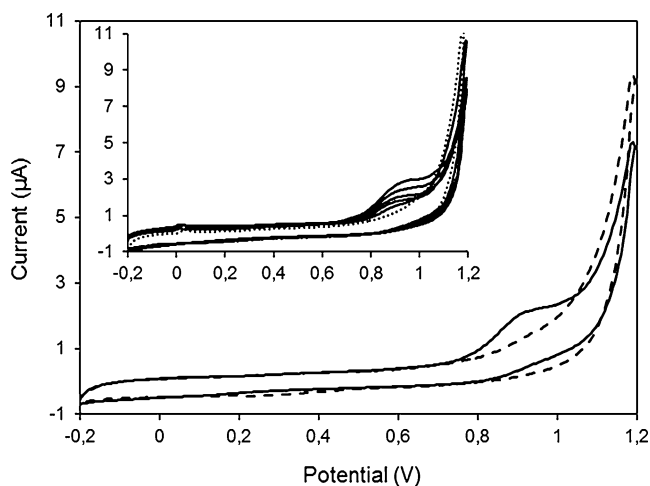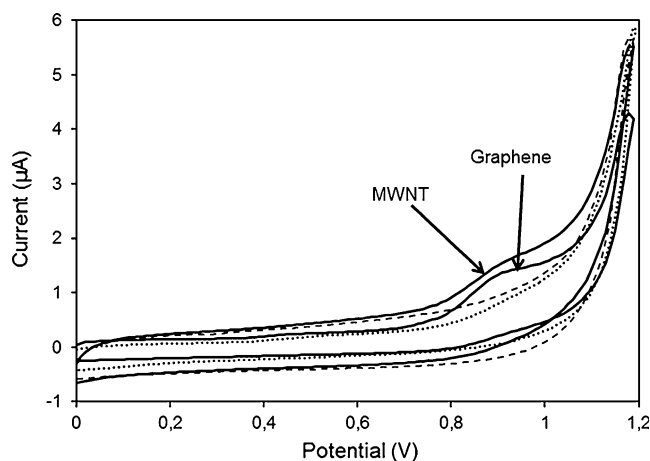
Fig. 1 Voltammetric behaviour of graphene-Nafion electrode in phosphate buffer solution 0.1 M, pH 7 before (*dotted line*) and after (*solid line*) addition of 0.15 mM p-NP. Inset: Voltammetric responses of graphene-Nafion electrode for oxidation of increasing concentrations of p-NP: 0.05; 0.1; 0.15; 0.25 and 0.35 mM. Scan rate: 50 mV s^{-1}

Fig. 2 Comparative responses of MWNT-Nafion electrode and graphene-Nafion electrode towards oxidation of 0.1 mM p-NP in phosphate buffer pH 7. Capacitive current of MWNT-Nafion electrode (dashed) and graphene-Nafion electrode (dotted) in phosphate buffer, pH 7. Scan rate: 50 mV s^{-1}

observed at +0.9 V during the anodic sweep from −0.2 to 1.20 V. On the following reverse scan from 1.20 to −0.2 V, no corresponding reduction peak was observed, concluding therefore that the oxidation of p-NP at graphene modified electrode is totally irreversible under these experimental conditions. The oxidation peak appears at lower potential value than the typical potential region reported for the oxidation of p-NP (1.1–1.4 V vs Ag/AgCl or SCE) [14, 16, 47, 48].

The inset of Fig. 1 shows a significant increase of the anodic peaks current observed at the graphene modified electrode when increasing the concentration of p-NP. These results demonstrate that the modifier material acts as promoter to enhance the electrochemical oxidation.

Electrocatalytic oxidation of 0.1 mM p-NP was investigated comparatively with graphene-Nafion and MWNT-Nafion electrodes and presented in Fig. 2. Compared with the voltammetric response of MWNT-Nafion electrode towards p-NP, graphene-Nafion electrode exhibited rather similar current response for p-NP oxidation after subtracting the background current recorded in absence of p-NP (dotted line for graphene and dashed line for MWNT electrodes). The background/capacitive current is larger for MWNT electrode than for graphene electrode, which can indicate a larger surface area of the carbon nanotube composite, but the oxidation peak at graphene electrode is sharper than that one appeared at MWNT electrode, which can be explained by a slightly higher heterogeneous electron transfer rate between p-NP and electrode surface.

These results are in agreement to some previously reported remarks pointing out no difference in the electrochemical behavior of SWNTs (rolled up single graphene sheet) and graphene (stacked graphene sheet) [49, 50]. Similarly, the results are consistent with those reported by Alwarappan et al. [38] who compared the electrochemistry of SWNTs and graphene using cyclic voltammetry and differential pulse voltammetry and they found out that the heterogeneous electronic transfer is faster on graphene, providing thus well-resolved oxidative peaks for a mixture of analytes, while SWNTs provided one broad signal, due to slower heterogeneous electronic transfer.
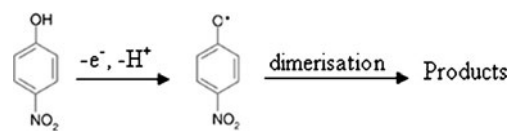
$$\tag{1}$$

As the oxidation reaction of p-NP involves the formation of a radical (Eq. 1), it is interesting to investigate if the oxidation products undergo any adsorption process on the electrode surface, influencing the sensitivity of the detection method. Thus, 10 successive voltammetric measurements in the presence of 0.1 mM p-NP in phosphate buffer solution pH 7 have been performed for graphene electrode.

As shown in Fig. 3, the oxidation peak current gradually decreased with increasing the number of cyclic potential scans. This result may be attributed to a progressively deposition of the oxidative product of p-NP (dimer or polymer) on the electrode surface, impeding further electro-oxidation of p-NP. Thus, in the following studies, the oxidation peak current for p-NP measurements was recorded in the first anodic scan in order to acquire higher sensitivity and better reproducibility.
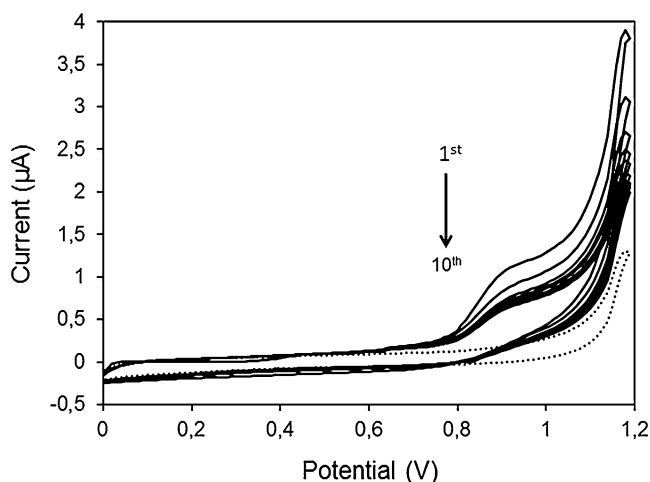
Fig. 3 Stability of the voltammetric response of graphene electrodes for oxidation of 0.1 mM p-NP in phosphate buffer pH 7. Scan rate: 50 mV s^{-1}

Fig. 4 Influence of buffer pH on the electrochemical oxidation of p-NP 0.3 mM at graphene modified electrode

The dependence of the peak current response with the scan rate has been studied for 0.3 mM p-NP at graphene-Nafion electrode in the 10–200 mV s^{-1} range. The peak current intensity increase is linear with the scan rate, suggesting that the oxidation of p-NP is an irreversible process in the studied range controlled by adsorption of the species, which correspond with above experiment concerning the stability and is consistent with other reports referring to the oxidation/reduction of p-NP on carbon based electrodes [13–15].

The pH value of the supporting electrolyte has a significant influence in the determination of p-NP, by varying both the peak current and peak potential. As shown in Fig. 4, the oxidation peak potential of p-NP is shifted to less positive potential with increasing pH value from 5 to 11. The Ip decreases with increasing pH from 5 to 9, then at pH 11 the oxidation peak is very weakly defined. The peak current of p-NP reaches its maximum value in acidic media. Therefore, for a better sensitivity, 0.1 M phosphate buffer solution pH 5 is used as supporting electrolyte for further electrochemical experiments.

The DPV response of Graphene/Nafion to p-NP oxidation

The DPV response of the graphene modified electrode to successive additions of p-NP into 0.1 M phosphate buffer solutions pH 5 was shown in Fig. 5. With each addition of p-NP, the height of oxidation peak appeared at about +0.96 V increased gradually. The inset in Fig. 5 illustrate the calibration plot, showing a linear relationship between the oxidation peak current and the concentration of p-NP within the investigated range from 25 μM to 0.62 mM. The linear dependence of the peak current on the analyte concentration is described by the following equation: Ip
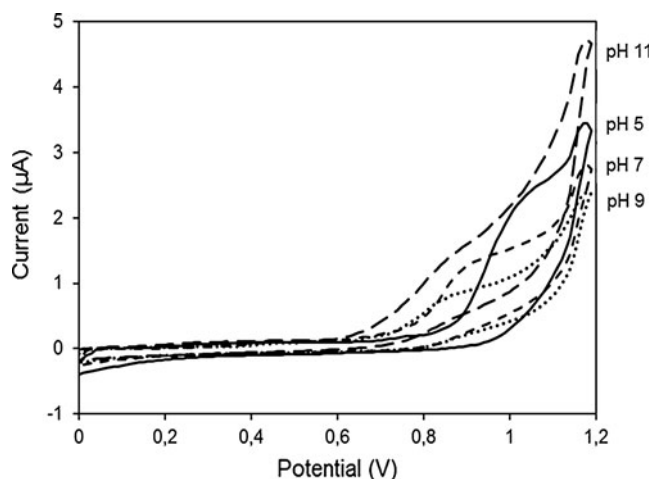
(μA)$=3.01 \times C_{p-NP}$ (mM)$+0.645$ with a correlation coefficient $R^2=0.987$. The detection limit, calculated for three times standard deviation for ten voltammograms of the blank signal, was 3.5 μM. Similar value for sensitivity extracted from the slope of the calibration graph was obtained for MWNT modified electrode (data not shown).

In all the previous experiments, the electrochemical behaviour of p-NP was investigated in aqueous phosphate buffer solution at graphene, respectively MWNT electrodes. The oxidation of p-NP has been investigated further in acidic media, using comparatively both types of electrodes.

Figure 6 shows the variation of the peak current with increasing concentrations of p-NP at graphene electrode (A) and MWNT electrode (B). It should be noted that the oxidation peak for p-NP is sharper and better defined in H_2SO_4 than in aqueous phosphate solution with a peak
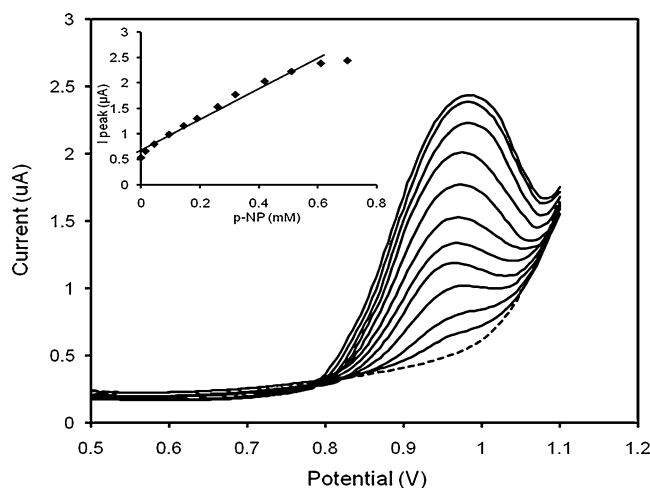
Fig. 5 DPV responses obtained on graphene-Nafion electrode using different p-NP concentrations: 0; 0.025; 0.05; 0.1; 0.15; 0.2; 0.27; 0.35, 0.44; 0.53; 0.62 and 0.72 mM in phosphate buffer pH 5. Inset: calibration curve for the oxidation procces of p-NP

Fig. 6 DPV responses obtained on graphene-Nafion electrode (**a**) and MWNT-Nafion electrode (**b**) for increasing p-NP concentrations: 0; 0.01; 0.025; 0.05; 0.1; 0.15; 0.2; 0.27; 0.35, 0.44; 0.53; 0.62 and 0.9 mM p-NP in H_2SO_4 20 mM solution
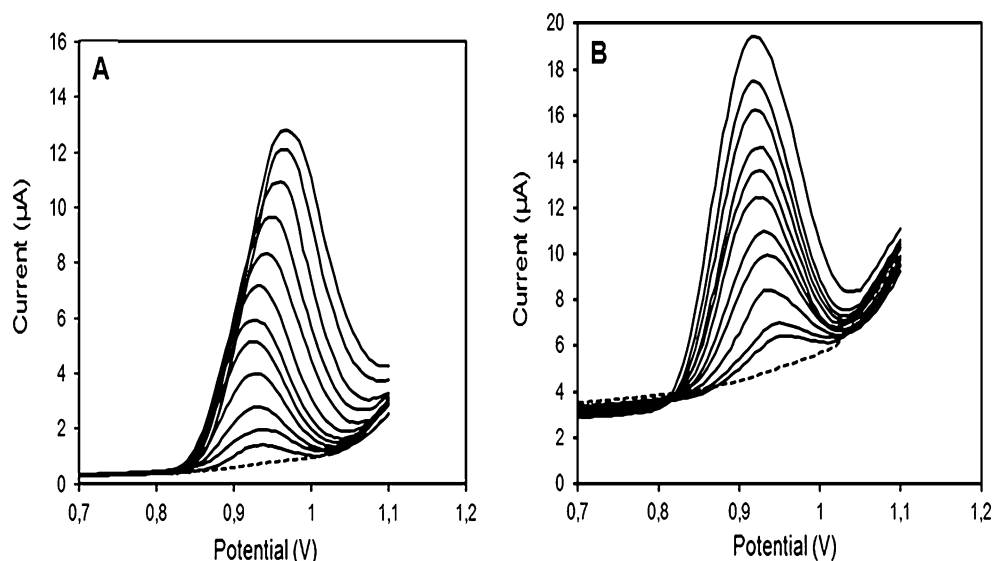
potential of +0.92 V which slightly shifts to more positive value with increasing the concentration. The calibration plots indicates a good linearity between the concentration of p-NP and the peak current with a regression equation of I (μA)$=17.154$ C_{pNP}(mM)$+2.032$ ($R^2=0.9837$) for graphene electrodes and I(μA)$=18.203$ C_{pNP}(mM)$+6.701$ ($R^2=0.9801$) for MWNT electrodes (data not shown).

The oxidation peak currents increase linearly with the concentration of p-NP in the range from 10 μM to 0.62 mM for graphene electrode. In case of MWNT electrode the linear range starts from 25 μM p-NP. There is no dramatic difference between the sensitivities of these materials toward the detection of p-NP. A higher background current for MWNT electrode indicate a higher specific surface area than graphene, but on the other hand this results in a bigger background noise for the blank measurement, leading further to a slightly higher limit of detection. As calculated for signal/noise = 3, limits of detection obtained in H_2SO_4 solution is 0.6 μM p-NP for graphene electrode and 1.3 μM for MWNT

electrode. The obtained values are lower than that reported for Nafion/glassy carbon electrode [12], but higher than that of obtained for reduction of p-NP at MWNT-Nafion/GCE [11] or at SWNT/GCE [18]. Overall, the analytical performance of graphene and MWNT electrodes for p-NP detection are greatly increased when determinations are performed in H_2SO_4 compared to buffered solutions.

Some common components found in human fluids or wastewater samples were investigated as possible interferents in the determination of 0.1 mM p-NP by adding the appropriate amount of interferent to the analyte solution. Paracetamol gives an oxidation peak at +0.3 V, very well separated from oxidation peak of p-NP, without interfering in the voltammetric response to p-NP (Fig. 7a). Ascorbic acid did not give any response even at high concentrations as 0.5 mM in the p-NP oxidation proccess (Fig. 7b). Big concentrations of uric acid give raise to small oxidation peaks at +0.25 V potential, but not affecting the oxidative response for p-NP (Fig. 7c).
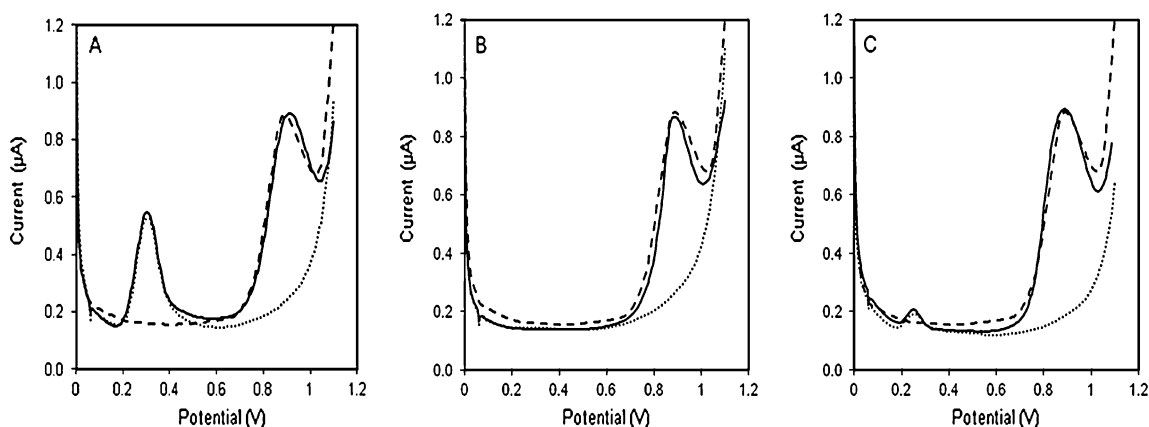
Fig. 7 Study of interferences in the DPV determination of p-NP at graphene-Nafion electrode in phosphate buffer pH 5: (*dashed line*) 0.1 mM p-NP; (*dotted line*) 0.2 mM paracetamol (**a**), 0.5 mM ascorbic acid (**b**), 0.4 mM uric acid (**c**); (*solid line*) mixture of 0.1 mM p-NP with 0.2 mM paracetamol (**a**), with 0.5 mM ascorbic acid (**b**) and with 0.4 mM uric acid (**c**)

Conclusions

This article described a novel electrode based on graphene nanopowder dispersed in Nafion polymer and used as an effective sensor for voltametric detection of p-nitrophenol. The electrochemical oxidation of p-NP at the graphene-modified electrode were examined by cyclic voltammetry and differential pulse voltammetry and compared to multiwall carbon nanotube (MWNT) modified electrode. It has been shown that the oxidation of p-NP give raise to an anodic peak at +0.9 V in phosphate buffer pH 7 with a similar behavior at both graphene and MWNT electrodes.

The dependence of the oxidation peak current and potential with the scan rate and pH of supporting electrolyte has been investigated. The peak current of p-NP reaches its maximum value in acidic media; therefore the calibrations of both sensors were performed in buffer pH 5 with good analytical parameters and comparable with each other.

It has been demonstrated that graphene electrode is a suitable sensor for the determination of micromolar concentrations of p-NP in H_2SO_4 solution. The current intensity of the oxidation peaks increase linearly with the increase of p-NP concentration, with a good sensitivity in the range of 10 μM–0.62 mM. The limits of detection of p-NP using DPV was 0.6 μM at graphene electrode and 1.3 μM at MWNT electrode. Low detection limits and linear responses over wide ranges of analyte concentration, even in the presence of some common interferents, prove a good electrochemical activity of graphene towards p-NP oxidation, similar to that exhibited by MWNT material.

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