MnFe₂O₄@CNT-N as novel electrochemical nanosensor for determination of caffeine, acetaminophen and ascorbic acid

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Keywords: MnFe_2O_4 nanoparticles, N-doped carbon nanotubes, electrochemical nanosensor, caffeine, acetaminophen, ascorbic acid

Abstract

For the first time, a glassy carbon electrode (GCE) modified with novel N-doped carbon nanotubes (CNT-N) functionalized with MnFe_2O_4 nanoparticles ($\text{MnFe}_2\text{O}_4@\text{CNT-N}$) has been prepared and applied for the electrochemical determination of caffeine (CF), acetaminophen (AC) and ascorbic acid (AA). The electrochemical behaviour of CF, AC and AA on the bare GCE, CNT-N/GCE and $\text{MnFe}_2\text{O}_4@\text{CNT-N}/\text{GCE}$ were carefully investigated using cyclic voltammetry (CV) and square-wave voltammetry (SWV). Compared to bare GCE and CNT-N modified electrode, the $\text{MnFe}_2\text{O}_4@\text{CNT-N}$ modified electrode can remarkably improve the electrocatalytic activity towards the oxidation of CF, AC and AA with an increase in the anodic peak currents of 52%, 50% and 55%, respectively.

Also, the SWV anodic peaks of these molecules could be distinguished from each other at the $\text{MnFe}_2\text{O}_4@\text{CNT-N}$ modified electrode with enhanced oxidation currents. The linear response ranges for the square wave voltammetric determination of CF, AC and AA were 1.0×10^{-6} to $1.1 \times 10^{-3} \text{ mol dm}^{-3}$, 1.0×10^{-6} to $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ and 2.0×10^{-6} to $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ with detection limit ($S/N=3$) of 0.83×10^{-6} , 0.83×10^{-6} and $1.8 \times 10^{-6} \text{ mol dm}^{-3}$, respectively. The sensitivity values at the $\text{MnFe}_2\text{O}_4@\text{CNT-N}/\text{GCE}$ for the individual determination of AC, AA and CF and in the presence of the other molecules showed that the quantification of AA and CF show no interferences from the other molecules; however, AA and CF interfered in the determination of AC, with the latter molecule showing the strongest interference. Nevertheless, the obtained results show that $\text{MnFe}_2\text{O}_4@\text{CNT-N}$ composite material acted as an efficient electrochemical sensor towards the selected biomolecules.

1. Introduction

Carbon nanomaterials have been attracting increasing interest over the years due to their unique structures and properties which make them attractive for a great number of applications in several research fields[1-7]. An excellent example are carbon nanotubes (CNTs)[1, 2]. Since their discovery, CNTs have obtained remarkable attention in chemical, physical and materials fields due to their unique structure and extraordinary properties. CNTs are provided with excellent electronic properties, such as huge surface area and efficient catalytic activity, which indicates that they promote charge transfer reactions when they are used as electrode materials[8, 9]. CNTs are also extensively used in electrochemistry due to their wide potential window, low cost and electrocatalytic activity for a variety of redox reactions. Nowadays, they are widely used in electroanalytical chemistry[1, 7, 8].

CNTs structure can also be improved by chemical doping with heteroatoms such as nitrogen [10, 11]. This type of doping has been successfully employed to modify their properties, giving rise to metallic behaviour[10], affecting the lattice alignment[11], regulating the growth mechanism and enhancing biocompatibility and sensitivity when compared to pristine CNTs[12, 13]. Additionally, CNTs can be further modified by decorating them with magnetic nanoparticles (MNPs). These nano-sized materials offer additional advantages due to their size and unique physical properties[14]. Several examples of this type of nanocomposites can be found in the literature[15-18]. Considering the family of magnetic nanomaterials, magnetite (Fe_3O_4) is usually the most commonly used in sensing applications[19-22]. On the other hand, manganese(II) ferrite (MnFe_2O_4) nanoparticles are mainly used for the production of supercapacitors[23-25] and as anode material for Li-ion batteries[26].

Caffeine (CF) is the most commonly used psychoactive substance in daily human life due to the high popularity of coffee and other caffeine containing products (Coca-Cola, tea, energy drinks and cocoa)[27]. It promotes many physiological functions such as gastric acid secretion, diuresis, and stimulation of the central nervous system[28]. However, at high concentration it is toxic and causes cardiovascular disease, kidney malfunction, depression, nausea and hyperactivity[27, 28]. Acetaminophen (AC), also known as paracetamol is an analgesic and antipyretic drug, widely used for the relief of mild to moderate pain associated with headache, backache, arthritis and postoperative pain[18]. However, overdoses can lead to the accumulation of toxic metabolites, causing severe and sometimes fatal hepatotoxicity and nephrotoxicity[28]. Ascorbic acid (AA) is a vital component in the diet of human, and it is known to take part in several biological reactions. It is also very popular for its antioxidant and pH regulator properties[29]. AA exists in mammalian brain and is also often added to various food products and pharmaceuticals. AA has been used for the prevention and treatment of common cold, mental illness, infertility, cancer and AIDS. In addition to several important applications of CF, AC and AA separately, their combinations are widely used for analgesic and antipyretic effects[27, 28]. As a result of their widespread use they are present in many environmental samples.

Several methods have been used for the determination of these molecules individually such as chromatography, spectroscopy and capillary electrophoresis[30-33]. Since CF, AC and AA are electroactive they can be detected by electrochemical methods and compared to the above methods, have the advantages of high sensitivity, low cost and simple instrumentation. However, in general their reactions are irreversible at bare electrodes and therefore require high over-potentials. Also, bare electrodes usually suffer from surface fouling. Additionally, their direct redox reactions take place

at very similar potentials at bare electrodes, which results in rather poor selectivity and difficulty on the determination of concentration of each biomolecule. This is a huge problem since some therapeutic formulations use these three molecules together. So, modification of electrodes surface with suitable electrocatalysts should improve their sensitivity and selectivity. Therefore, the design of new nanocomposites which can be successfully immobilized on electrode surfaces to provide increased sensitivity and selectivity is of great importance.

This work reports the preparation of a novel $\text{MnFe}_2\text{O}_4@\text{CNT-N}$ modified electrode for the electrochemical determination of CF, AC and AA. This composite material combines the beneficial characteristics of N-doped CNTs (*c.a.* high electrical conductivity) and MnFe_2O_4 MNPs sensing properties.

2. Experimental

2.1. Materials, reagents and methods

Sodium sulphate (99.5% Prolabo), sulphuric acid (95-97% Merck), hydrochloric acid (37%, Fisher Scientific), monobasic potassium phosphate ($\geq 99\%$, Sigma), dibasic sodium phosphate ($\geq 99\%$, Sigma Aldrich), sodium chloride ($\geq 99.5\%$, Sigma Aldrich), potassium hexacyanoferrate (III) ($\geq 99\%$, Merck), potassium chloride ($\geq 99.5\%$, Merck), manganese(II) chloride tetrahydrate (analytical grade, Sigma Aldrich), anhydrous iron(III) chloride (analytical grade, Merck), 1-amino-2-propanol (MIPA, 93%, Aldrich) and absolute ethanol (analytical grade, Fisher Scientific) were used as received. Ultrapure water (Millipore, specific resistivity $18 \text{ M}\Omega \text{ cm}$) was used throughout the experiments.

Transmission electron microscopy (TEM and high-resolution TEM) characterization was performed on a JEOL 2100F microscope operating at an

accelerating voltage of 200 kV. The samples were dispersed in acetone under sonication, followed by the immersion of a carbon-coated 200 mesh copper grid with subsequent air-drying.

X-ray photoelectron spectra were collected on an Omicron spectrometer equipped with an EA-125 hemispherical electron multichannel analyzer and an unmonochromatized Mg K α X-ray source (1253.6 eV) operated at 150 W and with a pass energy of 50 eV. The spectra were deconvoluted with the CasaXPS software and RSF database, using non-linear least squares fitting routine after a Shirley-type background correction.

The powder X-ray diffractogram (XRD) of MnFe₂O₄@CNT-N nanomaterial was recorded on a Polycrystal XPert Pro PANalytical apparatus using Ni-filtered Cu K α radiation ($\lambda = 0.15406$ nm) and a graphite monochromator, at a scan rate of 0.04° s⁻¹.

2.2 Preparation of MnFe₂O₄@CNT-N magnetic nanomaterial

The pristine CNT-N with a multiwall bamboo-like structure (external diameter = 105 nm; inner diameter = 83 nm) was synthesized by acetonitrile vapor decomposition following the procedure reported in reference[34]. The MnFe₂O₄ MNPs were immobilized on the as-prepared CNT-N by *in situ* coprecipitation, following procedures adapted from literature[35, 36]. Briefly, 0.35 mmol of MnCl₂·4H₂O were dissolved in 5 cm³ of an aqueous solution of HCl (1:4 v/v) and 1.3 mmol of FeCl₃·6H₂O were dissolved in 15 cm³ of water. Both solutions were mixed and 0.100 g of CNT-N was dispersed in the resulting medium. The mixture was heated to 100 °C under vigorous mechanical stirring, and 20 cm³ of 3.0 M MIPA solution previously heated at 100 °C was quickly added. The reaction mixture was stirred at that temperature for 2 h with vigorous mechanical stirring and, after that time, was cooled to room temperature. The

resulting nanomaterial ($\text{MnFe}_2\text{O}_4@\text{CNT-N}$) was magnetically separated, thoroughly washed with Millipore water and ethanol, and finally dried under vacuum at room temperature overnight.

2.3. Electrochemical studies

Cyclic voltammetry measurements were carried out using an Autolab PGSTAT 30 potentiostat/galvanostat (EcoChimie B.V.) controlled by GPES software. Voltammetric measurements were performed at room temperature. A conventional three-electrode compartment cell was used. The working electrode was a glassy carbon electrode, GCE (3 mm diameter, BAS, MF-2012), the auxiliary and reference electrodes were platinum wire (7.5 cm, BAS, MW-1032) and Ag/AgCl (sat. KCl) (BAS, MF-2052), respectively. The cell was enclosed in a grounded Faraday cage and kept under Argon. A combined glass electrode (Crison) connected to a pH meter Basic 20⁺ (Crison) was used for the pH measurements.

Electrolyte solutions for cyclic voltammetry were prepared using ultra-pure water. $\text{H}_2\text{SO}_4/\text{Na}_2\text{SO}_4$ buffer solutions with pH between 2.5 and 5.0 were prepared by mixing appropriate amounts of a 0.5 mol dm^{-3} H_2SO_4 solution with a 0.5 mol dm^{-3} Na_2SO_4 solution. The phosphate buffer saline solutions (1×) were prepared using 1.44 g dibasic sodium phosphate (Na_2HPO_4), 0.24 g monobasic potassium phosphate (KH_2PO_4), 8 g sodium chloride (NaCl) and 0.2 g potassium chloride (KCl) and the pH of solutions was adjusted to 6.0 and 7.0 using $\text{HCl } 1 \text{ mol dm}^{-3}$.

The dispersion used to produce the modified electrodes was prepared as follows: 1 mg of $\text{MnFe}_2\text{O}_4@\text{CNT-N}$ in 3 mL of N,N-dimethylformamide (DMF) was sonicated for 10 min. Prior to modification, the GCE electrode was conditioned by a polishing/cleaning procedure using aluminium oxide of particle size $0.3 \text{ }\mu\text{m}$ (Buehler)

on a microcloth polishing pad (BAS Bioanalytical Systems Inc.), and then the electrode was rinsed with ultra-pure water and finally sonicated for 5 min in ultra-pure water. Electrode modification consisted in depositing a 3 μL drop of the dispersion of CNT-N or $\text{MnFe}_2\text{O}_4@\text{CNT-N}$ in DMF onto the surface of the glassy carbon electrode and the solvent was allowed to evaporate for about 20 min at room temperature.

For square-wave voltammetric determination of caffeine in the presence of AC ($2.5 \times 10^{-6} \text{ mol dm}^{-3}$) and AA ($5.0 \times 10^{-6} \text{ mol dm}^{-3}$) the concentrations of CF used were from 1.0×10^{-6} to $1.1 \times 10^{-3} \text{ mol dm}^{-3}$; for acetaminophen were from 1.0×10^{-6} to $6.5 \times 10^{-4} \text{ mol dm}^{-3}$ in the presence of $5.0 \times 10^{-6} \text{ mol dm}^{-3}$ of CF and $5.0 \times 10^{-6} \text{ mol dm}^{-3}$ of AA and for ascorbic acid determination from 1.0×10^{-6} to $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ in the presence of $5.0 \times 10^{-6} \text{ mol dm}^{-3}$ of CF and $2.5 \times 10^{-6} \text{ mol dm}^{-3}$ of AC.

3. Results and discussions

3.1 Characterization of $\text{MnFe}_2\text{O}_4@\text{CNT-N}$ magnetic nanomaterial

The $\text{MnFe}_2\text{O}_4@\text{CNT-N}$ was characterized by TEM in order to obtain information about the nanomaterial morphology. The TEM images (Figures 1A and 1B) clearly show the presence of quasi-spherical nanoparticles with 2.0–4.5 nm size throughout the CNTs surface, confirming the successful immobilization of the ferrite nanoparticles on the CNT-N nanomaterial. The TEM micrographs also reveal that the immobilization procedure did not induce any changes on the structure of the parent CNT-N (multiwall bamboo-like structure). In the high-resolution TEM image (Figure 1C) can be clearly observed the lattice fringes of both CNT and grafted nanoparticles, confirming the crystalline nature of the $\text{MnFe}_2\text{O}_4@\text{CNT-N}$ nanocomposite.

Figure 1

The surface chemical composition of the $\text{MnFe}_2\text{O}_4@\text{CNT-N}$ nanomaterial was determined by XPS (Table 1). For comparison, the surface chemical composition of CNT-N is also presented[35]. The $\text{MnFe}_2\text{O}_4@\text{CNT-N}$ sample is composed by carbon and nitrogen from the parent CNT-N as well as by manganese and iron from the anchored MnFe_2O_4 MNPs, confirming their successful incorporation on the CNT-N surface, in accordance with TEM. Furthermore, when compared with the parent CNT-N, an increase of the surface oxygen content is observed arising from the manganese(II) nanoferrite. A trace amount of chlorine could also be detected probably due to residual chloride anions from the metal salt precursors.

The N 1s high-resolution spectrum of $\text{MnFe}_2\text{O}_4@\text{CNT-N}$ (Figure S1 in the Supporting Information) presents a main band at 400.3 eV assigned to pyrrolic nitrogen with two shoulders around 398.6 and 403.0 eV corresponding to pyridinic and quaternary nitrogen, respectively, from the nitrogen-doped CNT-N support [34]. These results thus suggest that the magnetic nanoparticles are mainly attached to the CNT-N surface through pyrrolic nitrogen functionalities (dominant nitrogen-containing groups). Furthermore, the Fe 2p and Mn 2p high-resolution spectra (Figure S1 in the Supporting Information) present the characteristic 2p doublets and corresponding satellite peaks of iron and manganese cations in the +3 and +2 oxidation states[37], respectively, confirming the expected metals oxidation states in the incorporated MnFe_2O_4 nanoparticles.

The X-ray diffractogram of the $\text{MnFe}_2\text{O}_4@\text{CNT-N}$ nanomaterial (Figure 2) exhibits the characteristic Bragg reflections of manganese(II) ferrites with a spinel-type structure (space group $Fd3m$, JCPDS card 88-1965 for bulk MnFe_2O_4)[36], confirming the successful incorporation of the MnFe_2O_4 nanoparticles and their crystalline nature, in accordance with TEM and XPS. An additional peak can be detected at $2\theta = 26.8^\circ$

which corresponds to the (002) reflection of carbon nanotubes,[38] confirming that the structure of the CNT-N support was preserved upon the immobilization procedure. The (100) reflection of CNT-N is overlapped with the (400) diffraction peak of the nanoferrite.

Table 1

Figure 2

3.2. Individual electrochemical behaviour

The electroactive surface area of bare GCE, CNT-N/GCE and MnFe₂O₄@CNT-N/GCE were determined from cyclic voltammograms of $1 \times 10^{-3} \text{ mol dm}^{-3}$ K₃[Fe(CN)₆] in KCl 1 mol dm⁻³ (Figure S2) using the Randles-Sevcik equation and assuming that electrode processes are diffusion-controlled:

$$i_{pa} = 2.69 \times 10^5 n^{3/2} A D_r^{1/2} R_{\infty} v^{1/2}$$

where n is the number of electrons involved in the process (1 in this case), A is the electrode surface area (cm²), D_r the diffusion coefficient ($7.6 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$)[39], R the concentration of specie (mol cm⁻³), v is scan rate (V s⁻¹) and i_{pa} the intensity of anodic peak current (A)[40]. The obtained A values were: 0.0443, 0.0484 and 0.0673 cm² for bare GCE, CNT-N/GCE and MnFe₂O₄@CNT-N/GCE, respectively, and indicate that the modification of GCE with CNT-N leads to a minor increase in the electroactive area ($\approx 9\%$) while modification with MnFe₂O₄@CNT-N increases the electroactive area close to 50%, indicating that the immobilization of MnFe₂O₄ onto N-doped CNT provides an increase of electrode surface area due to the its nanometric size and introduces a more conductive pathway for the electron-transfer of [Fe(CN)₆]^{3-/4-}.

The voltammetric behaviour of CF, AC and AA at bare GCE was first examined by CV (Figure 3). At bare GCE electrode and under the experimental conditions used,

CF is oxidized at ≈ 1.486 V vs. Ag/AgCl, AC at ≈ 0.710 V and AA at ≈ 0.565 V. The absence of cathodic peaks on the reverse scan of the three molecules studied indicates that their oxidations are irreversible processes.

The influence of scan rate on the oxidation peak currents of CF, AC and AA was also evaluated by recording the cyclic voltammograms at different scan rates from 0.020 to 0.500 Vs^{-1} in pH 2.5 $\text{H}_2\text{SO}_4/\text{Na}_2\text{SO}_4$ buffer solutions, containing 5.0×10^{-4} mol dm^{-3} of each molecule (data not shown). For the three molecules studied, the anodic peak currents were proportional to the square root of the scan rate ($0.994 \geq r^2 \geq 0.987$), indicating that the electrochemical oxidation processes of these molecules are diffusion-controlled processes.

The electrochemical oxidation of CF, AC and AA was then investigated by CV at the CNT-N and $\text{MnFe}_2\text{O}_4@\text{CNT-N}$ modified electrodes. Figure 3 shows the cyclic voltammograms of 5.0×10^{-4} mol dm^{-3} solutions of CF, AC and AA at bare GCE, CNT-N/GCE and $\text{MnFe}_2\text{O}_4@\text{CNT-N/GCE}$. At CNT-N modified electrode the oxidation of CF occurs at the same potential as bare GCE (1.482 V), but it shows an increase in peak current of $\approx 5\%$ for the former modified electrode, whereas for the $\text{MnFe}_2\text{O}_4@\text{CNT-N}$ modified electrode the peak current increases $\approx 52\%$ when compared with the bare GCE (Figure 3(a)). For AC, the modification of GCE with CNT-N also leads to small differences in peak potentials ($E_{\text{pa}} = 0.700$ V) and in peak currents ($\approx 5\%$ increase). For $\text{MnFe}_2\text{O}_4@\text{CNT-N/GCE}$ the AC oxidation peak is observed at less positive potentials, *c.a.* 0.636 V vs. Ag/AgCl (peak potential decrease of ≈ 0.064 V when compared to bare GCE) and similarly to CF, the peak current increases $\approx 50\%$; additionally, a new small cathodic peak is observed at ≈ 0.589 V which is attributed to the partial reduction of AC[41]. For AA, electrode modifications lead to more significant changes: its oxidation peak is observed at ≈ 0.522 V vs. Ag/AgCl at CNT-N/GCE and the peak current

increased close to 23%, while at $\text{MnFe}_2\text{O}_4@\text{CNT-N}/\text{GCE}$ the peak is observed at 0.483 V (potential decrease of ≈ 0.173 V) and peak current increases close to 55%, in both cases when compared to the bare GCE electrode. These results show that the modification of GCE with $\text{MnFe}_2\text{O}_4@\text{CNT-N}/\text{GCE}$ leads to an improvement in the overall electrochemical performance towards biomolecules oxidation, which is due to the fact that manganese ferrite nanoparticles accelerate the electrochemical reactions. MnFe_2O_4 nanoparticles act as catalysts where the transition metals having partially filled d orbitals (Mn^{2+} or Fe^{3+}) are expected to be the active sites for the oxidation of the three molecules studied here. However, the simultaneous determination of CF, AC and AA by cyclic voltammetry is somewhat difficult due to AC and AA oxidation potentials proximity.

For all the biomolecules, the modification of GCE with CNT-N leads to small changes in the oxidation potentials but to an increase in peak currents, more significantly to AA. These changes are due to the high electrical conductivity of CNT-N. Still, much more significant results were obtained for GCE modification with the $\text{MnFe}_2\text{O}_4@\text{CNT-N}$ nanocomposite: increase of peak currents of 50% and higher decrease of over-potentials. These effects are crucial for the application of modified electrodes in electrocatalysis. In $\text{MnFe}_2\text{O}_4@\text{CNT-N}$ modified GCE we associate the high electrical conductivity of CNT-N with the unique properties of MnFe_2O_4 nanoparticles: high electron transfer and large surface area to volume ratio. Consequently, both components contribute to the overall improvement of electrocatalytic performance.

Also, as for the bare glassy GCE the influence of scan rate on the oxidation peak currents of CF, AC and AA at $\text{MnFe}_2\text{O}_4@\text{CNT-N}/\text{GCE}$ was evaluated by recording the cyclic voltammograms at different scan rates from 0.020 to 0.500 Vs^{-1} in pH 2.5

H₂SO₄/Na₂SO₄ buffer solutions, containing 5.0×10^{-4} mol dm⁻³ of each molecule (data not shown). For all species, a diffusion-controlled process was maintained with i_{pa} proportional to $\nu^{1/2}$ ($0.992 \geq r^2 \geq 0.985$).

Figure 3

As a consequence of oxidation potentials proximity, square-wave voltammetry (SWV) was used to further investigate CF, AC and AA electrocatalytic behaviour. Figure 4 shows the SWV curves of 5.0×10^{-4} mol dm⁻³ CF, 5.0×10^{-4} mol dm⁻³ AC and 5.0×10^{-4} mol dm⁻³ AA pH 2.5 H₂SO₄/Na₂SO₄ buffer solutions at bare GCE, CNT-N/GCE and MnFe₂O₄@CNT-N/GCE. As observed for cyclic voltammetric results the immobilization of CNT-N and MnFe₂O₄@CNT-N at the GCE surface lead to some changes in the square-wave curves of each species when compared to the GCE. At the bare electrode peaks of CF, AC and AA are observed at 1.453, 0.660 and 0.507 V, for CNT-N modified electrode the peak potentials of CF (1.443 V) and AC (0.639 V) are very similar to bare electrode, but the peak corresponding to AA oxidation shifted $\approx$ 0.200 V to less positive potentials (0.297 V). At MnFe₂O₄@CNT-N/GCE the peaks still slightly shift to less positive potentials when compared to CNT-N and are observed at 1.423 (CF), 0.614 (AC) and 0.294 V (AA), respectively. These potentials are similar to those obtained for CV except for AA oxidation peak that in SWV appears at less positive potentials which may be a consequence of some interactions between the biomolecule and the modified surface electrode and to the fact that this is a more sensitive technique. The larger peak separation obtained by SWV for anodic peaks of AC and AA constitutes an advantage for subsequent simultaneous electrochemical determination of these molecules in solution.

Square wave voltammograms also present significant changes in peaks currents upon electrode modification. The GCE modification with CNT-N leads to small changes in CF and AC peak currents as they increase less than 15%, but for AA the peak current is greatly increased ($\approx 150\%$). These results show that CNT-N probably has a higher interaction with AA species leading to better detection. At $\text{MnFe}_2\text{O}_4@\text{CNT-N}/\text{GCE}$ more distinctive changes are observed for AA and AC where the i_p increase is of ≈ 540 and 240% , respectively, when compared to bare GCE; for CF the i_p increase is only of $\approx 30\%$. These results show that electrode modification with $\text{MnFe}_2\text{O}_4@\text{CNT-N}$ leads to better results when compared to CNT-N modification, so this hybrid was used for further investigations. The sensitivity of the $\text{MnFe}_2\text{O}_4@\text{CNT-N}$ modified electrode towards the oxidation of caffeine, acetaminophen and ascorbic acid was found to be 0.034 , 0.123 and $0.021 \mu\text{A}/\mu\text{mol dm}^{-3}$, respectively.

Figure 4

3.3. Determination of CF, AC and AA in a mixture at $\text{MnFe}_2\text{O}_4@\text{CTN-N}/\text{GCE}$

Square-wave voltammetry was used to investigate the electrocatalytic behaviour of $\text{MnFe}_2\text{O}_4@\text{CTN-N}$ modified electrode towards oxidation of CF, AC and AA in a mixture. Figure 5 shows the SWV curves at bare and $\text{MnFe}_2\text{O}_4@\text{CNT-N}$ modified electrode in a $\text{H}_2\text{SO}_4/\text{Na}_2\text{SO}_4$ buffer solution containing $5.0 \times 10^{-4} \text{ mol dm}^{-3}$ of CF, $5.0 \times 10^{-4} \text{ mol dm}^{-3}$ of AC and $2.5 \times 10^{-4} \text{ mol dm}^{-3}$ of AA. At bare GCE two peaks are observed, one at $\approx 1.543 \text{ V}$ attributed to CF and another broad one at $\approx 0.750 \text{ V}$ that corresponds to both AA and AC, making it impossible their simultaneous determination. On the other hand, at the $\text{MnFe}_2\text{O}_4@\text{CNT-N}$ modified electrode three

well defined oxidation peaks are observed at 1.460, 0.615 and 0.398 V corresponding to the oxidation of CF, AC and AA, respectively.

Since all the peaks could be resolved at MnFe₂O₄@CNT-N modified electrode, the determination of each molecule in the presence of the others was performed. Figure 6 shows selected square wave voltammograms recorded for the addition of increasing concentrations of CF, AC and AA (Figures 6(a), 6(b) and 6(c), respectively). The oxidation peak current of CF increases linearly ($i = 0.038 c_{CF} - 0.28$, $r^2 = 0.999$,) with the increasing concentration of CF from 1.0×10^{-6} to 1.1×10^{-3} mol dm⁻³ in the presence of AC and AA, with sensitivity 0.038 A/ mol dm⁻³ and a detection limit of 0.83×10^{-6} mol dm⁻³. Similar behaviour was observed for the determination of AC ($i = 0.038 c_{AC} + 0.58$, $r^2 = 0.998$) in the range of 1.0×10^{-6} to 1.0×10^{-3} mol dm⁻³ and for the determination of AA ($i = 0.033 c_{AA} + 0.006$, $r^2 = 0.997$) in the range of 2.0×10^{-6} to 1.0×10^{-4} mol dm⁻³, both in the presence of the other two molecules. The sensitivity and detection limit obtained for AC were 0.038 A/ mol dm⁻³ and 0.83×10^{-6} mol dm⁻³, and for AA were 0.033 A/ mol dm⁻³ and 1.8×10^{-6} mol dm⁻³, respectively. The sensitivity of the MnFe₂O₄@CNT-N modified electrode towards the oxidation of CF and AA in the presence of the other molecules is close to the values obtained for each in the absence of the other molecules. For AC in the presence of the other molecules, the sensitivity of the modified electrode is 3 times lower than the value obtained in the absence of the other molecules. The similarity in the sensitivity values for AA and CF in the mixture and individually, indicates that no significant interferences in oxidation processes of these compounds occurs at MnFe₂O₄@CNT-N modified electrode; for AC, the results suggest some interference in the presence of AA and CF. In order to evaluate if the interference was due to AA or CF, the quantification of AC was performed in the presence of AA and CF individually (Figure S4a and b, SI). The sensitivity of AC in the

presence of CF and AA were 0.042 ($r^2=0.989$) and 0.070 ($r^2=0.990$) $\mu\text{A}/\mu\text{mol dm}^{-3}$, respectively. These results suggest that CF has a stronger interference than AA in AC quantification.

Figure 5

Figure 6

To the best of our knowledge no reports can be found in the literature considering the use of modified electrodes with this type of nanoparticles and carbon materials for the determination of caffeine, acetaminophen and ascorbic acid. Nevertheless, Table 2 shows, for comparison, some analytical parameters for the determination of these molecules obtained at different modified electrodes based on similar nanoparticles [18, 20] or carbon materials [28, 42-44]. For example, the $\text{Fe}_2\text{O}_3/\text{rGO}/\text{GCE}$ [20] (rGO, reduced graphene oxide) shows much larger linear range for AA than that obtained for this work, but the detection limit determined is 11 times higher than ours. Similar behaviour was observed for a carbon-coated nickel magnetic nanoparticles modified electrode[18] where the detection limit for AA is ≈ 23 times higher. This modified electrode also showed electrocatalytic activity for AC oxidation with much lower linear ranges and higher detection limit than those obtained for the $\text{MnFe}_2\text{O}_4@\text{CNT-N}$ modified electrode. The GCE modified with Lt/fMWCNT (luteolin functionalized multi-walled carbon nanotubes) showed similar detection limit for AC and higher (4 times) for CF, but the linear ranges are much narrower. For CF determination, the detection limits obtained are comparable to those for $\text{MnFe}_2\text{O}_4@\text{CNT-N}$ modified electrode but with narrower linear ranges.

Table 2

Finally, the stability and robustness of the modified electrode was evaluated by measuring and comparing the i_{pa} of 0.5 mM CF in a pH 2.5 H₂SO₄/Na₂SO₄ buffer solution at the modified electrode at the beginning and at the end of all the experiments (data not shown). No significant decrease in the peak current and position was observed, confirming the electrochemical stability of the MnFe₂O₄@CNT-N modified electrode.

The reproducibility was investigated by measuring the electrocatalytic current signal of 0.25 mM AA in a solution containing 0.5 mM CF and 0.5 mM AC for three identically as-prepared MnFe₂O₄@CNT-N-modified electrodes (Figure S3, Supporting Information) and a RSD less than 3.5% was obtained for all peaks. This shows not only the reproducibility of the MnFe₂O₄@CNT-N-modified electrodes, but also their sensitivity because it allows the simultaneous determination of AA, CF and AC.

4. Conclusions

This study demonstrated that combining the properties of MnFe₂O₄ magnetic nanoparticles with the unique characteristic of N-doped carbon nanotubes, an excellent electrochemical sensor based on MnFe₂O₄@CNT-N nanocomposite was fabricated for the determination of caffeine, acetaminophen and ascorbic acid. Compared with bare GCE and CNT-N/GCE, the MnFe₂O₄@CNT-N modified electrode displayed higher electrocatalytic activity toward the oxidation of caffeine, acetaminophen and ascorbic acid. Their oxidations at MnFe₂O₄@CNT-N modified electrodes showed three well defined oxidation peaks with good peak separation, enhanced oxidation currents and slightly less positive oxidation potentials. Additionally, excellent linear ranges were obtained for the SWV determination of CF and AC, with AA showing an upper limit

ten times lower; nevertheless all showed good detection limits. Furthermore, the $\text{MnFe}_2\text{O}_4@\text{CNT-N}/\text{GCE}$ allowed the determination of AA and CF in the presence of the other biomolecules, whereas AA and CF interfered in the determination of AC, with the latter molecule showing the strongest interference. These results proved that $\text{MnFe}_2\text{O}_4@\text{CNT-N}$ nanocomposite is a promising candidate for further applications in the electrocatalytic field.

Acknowledgments

The authors thank Fundação para a Ciência e a Tecnologia (FCT) for financial support through grants no. PEst-C/EQB/LA0006/2013 and FCOMP-01-0124-FEDER-037285, Operation NORTE-07-0124-FEDER-000067–Nanochemistry and MICINN of Spain (Projects CTQ-2011-29272-C04-01 and -03) for financial support. DMF also thanks FCT for her PD grant SFRH/BPD/74877/2010. The authors acknowledge Miss Marta Costa for the for the preparation of MnFe_2O_4 nanoparticles.

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Captions to Figures

Figure 1. (A, B) TEM and (C) HR-TEM micrographs of $\text{MnFe}_2\text{O}_4@\text{CNT-N}$ nanomaterial.

Figure 2. X-ray diffractogram of $\text{MnFe}_2\text{O}_4@\text{CNT-N}$ nanomaterial. The Bragg reflections of the nanoferrite and CNT-N are highlighted in black and red, respectively.

Figure 3. Cyclic voltammograms of $5.0 \times 10^{-4} \text{ mol dm}^{-3}$ CF (a), $5.0 \times 10^{-4} \text{ mol dm}^{-3}$ AC (b) and $5.0 \times 10^{-4} \text{ mol dm}^{-3}$ AA (c) at bare GCE, CNT-N/GCE and $\text{MnFe}_2\text{O}_4@\text{CNT-N/GCE}$ in pH 2.5 $\text{H}_2\text{SO}_4/\text{Na}_2\text{SO}_4$ buffer solution; scan rate 0.05 V s^{-1} .

Figure 4. Square-wave voltammetric responses of $5.0 \times 10^{-4} \text{ mol dm}^{-3}$ CF (a), $5.0 \times 10^{-4} \text{ mol dm}^{-3}$ AC (b) and $5.0 \times 10^{-4} \text{ mol dm}^{-3}$ AA (c) at bare GCE, CNT-N/GCE and $\text{MnFe}_2\text{O}_4@\text{CNT-N/GCE}$ in pH 2.5 $\text{H}_2\text{SO}_4/\text{Na}_2\text{SO}_4$ buffer solution; scan rate 0.05 V s^{-1} .

Figure 5. Square-wave voltammetric responses of $5.0 \times 10^{-4} \text{ mol dm}^{-3}$ CF, $5.0 \times 10^{-4} \text{ mol dm}^{-3}$ AC and $2.5 \times 10^{-4} \text{ mol dm}^{-3}$ AA in pH 2.5 buffer solution at $\text{MnFe}_2\text{O}_4@\text{CNT-N/GCE}$ (green) and bare GCE (black).

Figure 6. Square-wave voltammetric responses at $\text{MnFe}_2\text{O}_4@\text{CNT-N/GCE}$ in pH 2.5 buffer solution containing: (a) $5.0 \times 10^{-6} \text{ mol dm}^{-3}$ AA, $2.5 \times 10^{-6} \text{ mol dm}^{-3}$ AC and different concentrations of CF from 1.0×10^{-6} to $1.1 \times 10^{-3} \text{ mol dm}^{-3}$, (b) $5.0 \times 10^{-6} \text{ mol dm}^{-3}$ AA, $5.0 \times 10^{-6} \text{ mol dm}^{-3}$ CF and different concentrations of AC from 1.0×10^{-6} to $1.0 \times 10^{-3} \text{ mol dm}^{-3}$, (c) $5.0 \times 10^{-6} \text{ mol dm}^{-3}$ CF, $2.5 \times 10^{-6} \text{ mol dm}^{-3}$ AC and different concentrations of AA

from 2.0×10^{-6} to 1.0×10^{-4} mol dm⁻³. Insets show the plots of the anodic peak current as a function of CF, AC and AA concentrations.

FIGURES

Figure 1.

Figure 2.

Figure 3.

Figure 4.

Figure 5.

Figure 6.

TABLES

Table 1. Surface atomic percentages for CNT-N based nanomaterials obtained by XPS^a

Material	Atomic %					
	C 1s	N 1s	O 1s	Mn 2p _{3/2}	Fe 2p _{3/2}	Cl 2p
CNT-N ^b	88.4	5.0	6.6	—	—	—
MnFe ₂ O ₄ @ CNT-N	68.0	5.1	19.5	1.2	5.1	1.1

^a Determined by the areas of the respective bands in the high-resolution XPS spectra.

^b Values from reference[34].

Table 2. The detection limits and linear ranges of different modified electrodes for the determination of AA, AC and CF.

Electrode Materials	Detection limit ($\times 10^{-6}$ mol dm $^{-3}$) ^a			Linear range ($\times 10^{-6}$ mol dm $^{-3}$)			Reference
	AA	AC	CF	AA	AC	CF	
MnFe ₂ O ₄ @CNT-N/GCE	1.8	0.83	0.83	2 – 100	1 – 1000	1 – 1100	This work
Fe ₃ O ₄ /rGO/GCE	20	-	-	160 – 7200	-	-	[20]
C-Ni/GCE ^b	41	2.3	-	140 – 1300	7.8 – 110	-	[18]
N-MWCNT/AuNPs	-	0.35	-	-	63 – 190	-	[39]
Lt/fMWCNT/GCE ^c	-	0.78	3.54	-	0.9 – 80	10 – 110	[28]
LMC/Nafion/GCE ^d	-	-	0.47	-	-	1.3 - 230	[40]
MWCNT-Nafion/GCE	-	-	0.51	-	-	2.9 – 377	[41]

^a Detection limit(DL)=3 σ /slope, where σ is the standard deviation of the blank

^b Carbon-coated nickel magnetic nanoparticles

^c Luteolin functionalized multi-walled carbon nanotubes (MWCNT)

^d Large mesoporous carbon