



# A novel composite electrode based on tungsten oxide nanoparticles and carbon nanotubes for the electrochemical determination of paracetamol



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## ABSTRACT

An electrochemical sensor was prepared by the modification of a glassy carbon electrode (GCE) with a composite of nanoparticles of tungsten oxide ( $\text{WO}_3$ ) and carbon nanotubes (CNTs) for the quantification of paracetamol (PR). Energy dispersive X-ray analysis (EDX) and scanning electron microscopy (SEM) were performed for the characterization of the nanocomposite layer. Compared with a bare GCE and a GCE modified with CNTs, the proposed electrode ( $\text{WO}_3\text{NPs/CNTs/GCE}$ ) exhibited a well-defined redox couple for PR and a marked enhancement of the current response. The experimental results also showed that ascorbic acid (AA) did not interfere with the selective determination of PR. The proposed electrode was used for the determination of PR in 0.1 M phosphate buffer solution (PBS) at pH 7.0 using square wave voltammetry (SWV). The peak current increased linearly with the concentration of PR in the range of  $1.0 \times 10^{-9}$ – $2.0 \times 10^{-7}$  M. The detection limit (LOD) was  $5.54 \times 10^{-11}$  M (based on 3  $S_b/m$ ). The proposed voltammetric sensor provided long-time stability, improved voltammetric behavior and good reproducibility for PR. The selective, accurate and precise determination of PR makes the proposed electrode of great interest for monitoring its therapeutic use.

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## 1. Introduction

Paracetamol (PR) is an effective pain killer used for the relief of pains associated with many parts of the body [1]. The overdose of PR leads to the accumulation of toxic metabolites that may cause severe diseases [2]. Therefore, the amount of PR in pharmaceutical formulations should be controlled for the general public health. Several analytical methods have been reported for the quantification of PR such as spectrophotometry [3,4], electrophoresis [5], chromatography [6], chemiluminescence [7] and FIA [8]. However, these techniques are expensive and require time-consuming steps. They also show low sensitivity and poor selectivity.

On the other hand, electrochemical methods have received considerable attention in the analysis of biological and environmental samples due to their accuracy, sensitivity, simplicity and high selectivity [9–12].

The determination of PR has been reported using a number of modified electrodes such as carbon nanoparticles modified GCE [13], D50wx2-GNP-modified CPE [14], carbon nanotubes modified SPE [15], SWCNT-graphene/GCE [16], MWCNT modified PGE [17], SWCNT modified CE [18] and luteolin/MWCNT/GCE [19].

It was shown that the electrodes modified with both CNTs and nanoparticles presented great performances in terms of response time, increased sensitivity, resistance to surface fouling, decreased

overpotential, mass transport, catalysis, high effective surface area and detection limit [20–23].

In this paper, we report the quantification of PR in pharmaceuticals using a GCE modified with a composite of nanoparticles of  $\text{WO}_3$  and CNTs. The proposed voltammetric sensor exhibited high electrocatalytic activity, good reproducibility and excellent selectivity for PR.

## 2. Experimental

### 2.1. Chemical reagents

Paracetamol (PR), ascorbic acid (AA), uric acid (UA), dopamine (DA) and L-tyrosine (L-TRY) were obtained from Sigma Chem. Co. Nanoparticles of tungsten oxide ( $\text{WO}_3$ ) and carbon nanotubes (CNTs) were purchased from US-Nano, USA. All other chemicals were obtained from Merck or Fluka. Solutions were prepared with 0.1 M PBS at pH 7.0. Ultra-pure water was used for the preparation of solutions. Solutions were deoxygenated by purging nitrogen prior to each experiment.

### 2.2. Instrumentation

An Autolab potentiostat (Utrecht, The Netherlands) was utilized for the electrochemical measurements. A three-electrode system was used: a GCE as working electrode (3 mm in diameter), a Pt wire counter electrode and an Ag/AgCl reference electrode. Working electrodes were polished with 1  $\mu\text{m}$  and 0.3  $\mu\text{m}$  alumina slurries prior to the modification. The electrodes were then sonicated in ethanol for 10 min.

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### 2.3. Preparation of modified electrodes

Functionalized CNTs and nanoparticles of  $\text{WO}_3$  were first dispersed in chloroform. The mixture was then sonicated in an ultrasonic bath for 45 min. Afterwards, 5  $\mu\text{L}$  of the composite of  $\text{WO}_3\text{NPs}/\text{CNTs}$  was cast onto the electrode surface and chloroform allowed to evaporate in air.

### 2.4. Optimization of the surface layer

The experimental results showed an optimal ratio of 10:1 for the mixture of CNTs and  $\text{WO}_3\text{NPs}$ . The mixture should be sonicated for at least 45 min. Furthermore, the amount of composite layer on the electrode surface should be 5  $\mu\text{L}$  in order to obtain an improvement in the voltammetric response for PR. The results have shown that greater amounts of the composite resulted in remarkable decreases in the sensitivity and reproducibility.

## 3. Results and discussion

### 3.1. Characterization of modified electrode

The electrode material was characterized by SEM. An image for a layer of CNTs is shown in Fig. 1A. No aggregation was observed for CNTs indicating that they were dispersed homogeneously on the electrode surface. As shown in Fig. 1B,  $\text{WO}_3$  nanoparticles are distributed on the surface of CNTs. The EDX results also exhibited that W, O, C, Au and Pd were the major elements (Fig. 2). Meanwhile, Pd and Au were also observed due to the palladium–gold coatings of the electrode during SEM analysis.

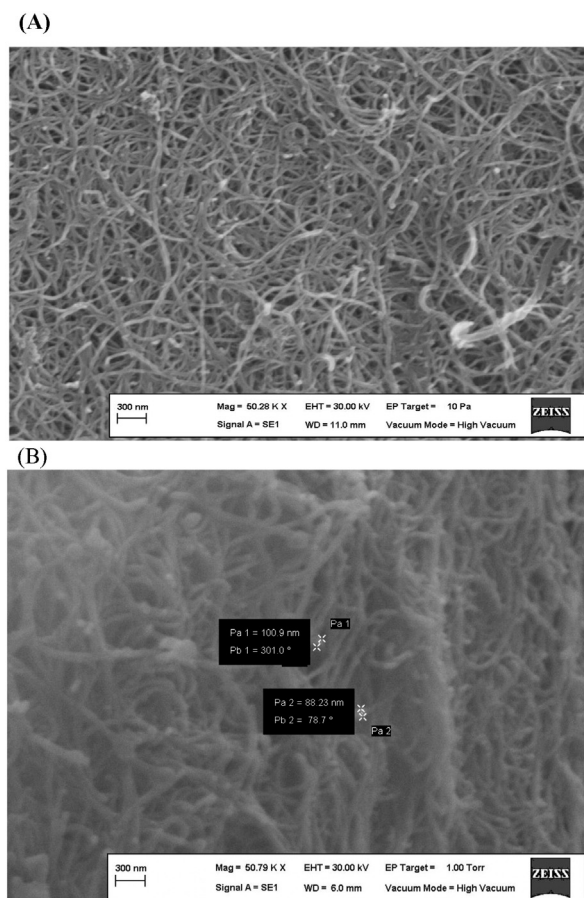


Fig. 1. SEM images of (A) CNTs/GCE, (B)  $\text{WO}_3\text{NPs}/\text{CNTs}/\text{GCE}$ .

### 3.2. Voltammetric behavior of paracetamol

Voltammograms of  $1.5 \times 10^{-7}$  M PR at GCE (a), CNTs/GCE (b) and  $\text{WO}_3\text{NPs}/\text{CNTs}/\text{GCE}$  (c) are given in Fig. 3. At bare GCE (Fig. 3a), PR exhibited a broad oxidation peak 470 mV and a corresponding reduction peak at 195 mV. However, the GCE modified with CNTs exhibited a high catalytic effect towards the oxidation of PR. It was shown that CNTs/GCE exhibited an improved anodic peak at 419 mV for PR and a corresponding cathodic peak at 397 mV (Fig. 3b). The improvement in the voltammetry of PR at CNTs/GCE was mainly due to the increased sensitivity, decreased overpotential and resistance to surface fouling provided by the layer of CNTs on the surface. However, the voltammetric behavior of PR was greatly improved at a GCE modified with a composite of CNTs and nanoparticles of  $\text{WO}_3$ . The  $\text{WO}_3\text{NPs}/\text{CNTs}/\text{GCE}$  system exhibited a well-defined anodic peak at 411 mV with a corresponding reduction peak at 389 mV for PR (Fig. 3c). The peak potential separation ( $\Delta E_p$ ) was 22 mV for PR indicating a reversible two-electron process. Compared with the bare GCE and the GCE modified with CNTs, the voltammetric behavior of PR has been improved at  $\text{WO}_3\text{NPs}/\text{CNTs}/\text{GCE}$ . The results showed that the  $\text{WO}_3\text{NPs}/\text{CNTs}/\text{GCE}$  system exhibited good catalytic activity, improved peaks and enhanced current responses for PR. The composite material on the surface provided several advantageous such as increased sensitivity, decreased overpotential, high effective surface area and enhancement of mass transport.

CVs of PR were recorded at different scan rates to acquire the mechanism responsible for the oxidation and reduction of PR at  $\text{WO}_3\text{NPs}/\text{CNTs}/\text{GCE}$  (Fig. 4A). The peak currents were linear with sweep rates over the range from 10 to 100 mV/s (Fig. 4B). Also, the slope of logarithm of the current response against the logarithm of sweep rate was close to 1 indicating that the oxidation of PR at  $\text{WO}_3\text{NPs}/\text{CNTs}/\text{GCE}$  was a surface controlled process.

The effect of pH on the peak potential of PR was also examined. Fig. 5A shows the cyclic voltammograms of PR at various pH values. The peak potential of PR shifted in the negative direction with increasing pH. This indicates that the electrode reaction of PR at  $\text{WO}_3\text{NPs}/\text{CNTs}/\text{GCE}$  involves the transfer of protons. Fig. 5B shows the plots of peak currents against the solution pH. The linear equation for the anodic peak was  $E_{pa}$  (mV) =  $-59.64 \text{ pH} + 851.78$  ( $R^2 = 0.9982$ ) with a slope of 59.6 mV/pH. This indicates that the proportion of electrons and protons is  $1e^-/1H^+$ . These experimental results show that the oxidation of PR at the proposed electrode involves two protons since two electrons are transferred.

### 3.3. Calibration plot

Square wave voltammetric determination of PR at  $\text{WO}_3\text{NPs}/\text{CNTs}/\text{GCE}$  was carried out in 0.1 M PBS at pH 7.0. SWVs of various concentrations of PR at  $\text{WO}_3\text{NPs}/\text{CNTs}/\text{GCE}$  are given in Fig. 6A. As shown in Fig. 6B, the response of the peak current of PR was linear with its concentration over the range from  $1.0 \times 10^{-9}$  to  $2.0 \times 10^{-7}$  M with a detection limit of  $5.54 \times 10^{-11}$  M (the limit of detection, LOD, is based on  $3 S_b/m$  where  $S_b$  is the standard deviation of the blank signal and  $m$  is the slope of the regression equation). The linear equation obtained was  $I_{pa}$  ( $\mu\text{A}$ ) =  $0.4938 + 0.1011C$  (nM) ( $R^2 = 0.9983$ ). Table 1 shows the analytical parameters of a number of electrodes for the quantification of PR. The proposed electrode provided the lowest detection limit for PR as compared to the reported values as shown in Table 1. The parameters obtained in this study clearly indicate that the proposed electrode is more sensitive for the determination of PR as the composite of CNTs and  $\text{WO}_3$  nanoparticles provides an increased sensitivity and a lower detection limit when compared to CNTs and polymer modified electrodes [17,2840,49].

Fig. 7A shows a CV of the mixture of AA and PR at a naked GCE. As seen, only one broad peak was observed. Fig. 7B shows the CVs of increasing concentrations of PR in the presence of AA. The current

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