

# Sensitive voltammetric determination of xanthinol nicotinate at a carbon nanotubes–ionic liquid gel modified electrode

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## Abstract

The electrochemistry of xanthinol nicotinate (Xan) was studied by cyclic voltammetry at a glassy carbon electrode modified by a gel containing multi-walled carbon nanotubes (MWNTs) and room-temperature ionic liquid of 1-butyl-3-methylimidazolium hexafluorophosphate (BMIMPF<sub>6</sub>). The modified electrode exhibited good promotion to the electrochemical oxidation of Xan and an ultrasensitive electrochemical method was proposed for the determination of Xan. This method was successfully applied to the determination of Xan in Xan tablets.

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Since the discovery of carbon nanotubes (CNTs) [1], there has been enormous interest in exploring and exploiting their unique properties [2]. CNTs displayed excellent electrocatalytic properties towards redox reaction of different biomolecules [3]. Room-temperature ionic liquid (RTIL), comprising of organic cations and various anions, represents a new kind of nonaqueous but polar solvent. Recently, increasing attention has been paid on the modified electrodes with ionic liquids and nanomaterial composite in hope for combining their unique advantages. For example, Xiao et al. developed the sensitive voltammetric determination of chloramphenicol by using single-wall carbon nanotube–gold nanoparticle–ionic liquid composite film modified glassy carbon (GC) electrodes [4].

Xanthinol nicotinate (Xan) is a vasodilator drug used in the management of peripheral and cerebral vascular disorders and in hyperlipidaemias for over 40 years [5]. Only a few methods such as spectrophotometric [6] and capillary isotachopheresis method [7] were reported for the determination of Xan. In this work, the electrochemical behavior of Xan at a carbon nanotubes–ionic liquids gel film coated glassy carbon electrode was investigated by voltammetric method, and a new method for the determination of Xan was developed.

## 1. Experimental

Electrochemical measurements were performed on a CHI 660A electrochemical workstation (CH Instruments Company). A three-electrode system was used, including a bare glassy carbon electrode ( $\Phi = 3.0$  mm) or a modified

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GC electrode as working electrode, an saturated calomel electrode (SCE) as reference electrode and a platinum wire as counter electrode.

The multi-walled carbon nanotubes (MWNTs) were from Shenzhen Nanotech Port Co. Ltd. (Shenzhen, China). The ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate (BMIMPF<sub>6</sub>, purity 98%) was from Acros Organics and used as received. Xanthinol nicotinate was from Henan Provincial Institute of Food and Drug Control (Henan, China), and its stock solution ( $1.0 \times 10^{-2}$  mol/L) was prepared with anhydrous ethanol. All other chemicals used were of analytical reagent grade. Ultra-pure water from a Gen Pure UV-TOC/UF ultra-pure water system (TKA Wasseraufbereitungssysteme GmbH) was used through all the experimental procedures.

12 mg purified MWNTs mixed with 0.2 mL BMIMPF<sub>6</sub> were ground with an agate mortar for about 20 min, and a black gel was formed. The GC electrode was polished with alumina and washed ultrasonically in ultra-pure water and anhydrous ethanol, respectively. Then the GC electrode was rubbed over the carbon nanotubes gel placed on a smooth glass slide, and the gel was mechanically attached to the electrode surface. Finally, after the gel on the electrode surface was smoothed with a spatula to leave a thin gel film on the GCE surface, the gel modified glassy carbon electrode (denominated as MWNTs-IL-Gel/GC electrode in this paper) was fabricated.

## 2. Results and discussion

The electrochemical behaviors of the K<sub>3</sub>Fe(CN)<sub>6</sub>/K<sub>4</sub>Fe(CN)<sub>6</sub> were used as an electrochemical probe to characterize different electrodes including bare GCE and MWNTs-IL-Gel/GC electrode. The active areas of bare GCE and modified electrode are estimated according to the Randles–Sevcik equation [8]:

$$I_p = 269n^{3/2}AD^{1/2}v^{1/2}c \quad (1)$$

It is 0.052 cm<sup>2</sup> (average of three measurements) for the bare GC electrodes, and 0.075 cm<sup>2</sup> for the MWNTs-IL-Gel/GC electrode. Evidently, the modified electrode increased by nearly 50% in area.

Fig. 1 shows the cyclic voltammograms of xanthinol nicotinate at different modified electrodes and unmodified GCE in Britton–Robinson buffer solution (pH 5.5) at a scan rate of 0.1 V/s. As a result, Xan does not produce discernible peaks on bare GCE under this condition. On MWNTs/GCE, Xan produces a small oxidation peak at 0.84 V. On the MWNTs-IL-Gel/GC electrode, the peak increase markedly at the first anodic scan, and no corresponding reduction peak is observed on the reverse scan, suggesting that the electrode reaction of Xan at the MWNTs-IL-Gel/GC electrode is totally irreversible.

The effect of scan rates on the peak currents at the MWNTs-IL-Gel/GC electrode in pH 5.5 Britton–Robinson buffer were investigated by cyclic voltammetry in the presence of  $1.0 \times 10^{-5}$  mol/L of Xan. The oxidation peak current increases linearly with the square root of scan rate  $v$  (V/s), following equation:  $I_p(\mu\text{A}) = -13.13 + 136.1^{1/2}(\text{V/s})$  ( $r = 0.999$ ), suggesting that the electrode process is controlled by the diffusion step, which seems to

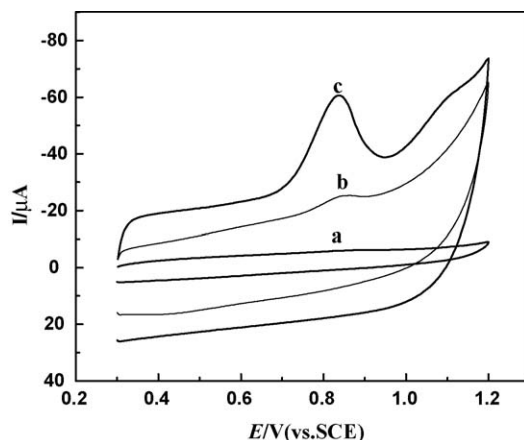


Fig. 1. Cyclic voltammograms of GCE (a), MWNTs/GCE (b) and MWNTs-IL-Gel/GCE (c) in  $1.0 \times 10^{-5}$  mol/L Xan in pH 5.5 Britton–Robinson buffer. Scan rate: 0.1 V/s.

Table 1  
Determination results of xanthinol nicotinate in Xan tablets.

Sample	Labeled (g/tablet)	Measured <sup>a</sup> (g/tablet)	R.S.D. (%)	Added (g/tablet)	Total found (g/tablet)	Recovery (%)
Xan tablets	0.1	0.098	2.9	0	0.093	
				0.085	0.171	96.1
				0.10	0.190	98.4

<sup>a</sup> Average value of 5 measurements.

be disagreed with the fact that Xan is accumulated on the electrode. It may be related to the diffusion of Xan in the BMIMPF<sub>6</sub> film.

To optimize the determination conditions of Xan, the effects of buffer systems such as, pH 2.3–9.3 Britton–Robinson buffer, pH 3.0–6.0 acetic acid–acetate buffer, and pH 5.0–9.0 phosphate buffer, were examined. The result showed that highest peak current of Xan was obtained in pH 5.5 Britton–Robinson buffer. Thus, pH 5.5 Britton–Robinson buffer was used as the supporting electrolyte for determining Xan.

In B–R buffer solution, the oxidation peak potential shifted negatively with solution pH increasing and obeyed the equation:  $E_p$  (V) = 1.26–0.077 pH ( $r = 0.994$ ) in the range of pH from 2.3 to 9.3 indicating that the electrochemical process involved proton transfer.

The relationship between the anodic peak currents and the concentration of Xan was examined by linear sweep voltammetry in pH 5.5 Britton–Robinson buffer. The linear ranges were from  $5.0 \times 10^{-8}$  to  $9.0 \times 10^{-7}$  mol/L and  $1.0 \times 10^{-6}$  to  $1.2 \times 10^{-5}$  mol/L, respectively. The regression equations were:  $I_p$  ( $\mu\text{A}$ ) =  $1.45 + 6.67 \times 10^6 c$  (mol/L) ( $r = 0.996$ ) and  $I_p$  ( $\mu\text{A}$ ) =  $4.60 + 2.45 \times 10^6 c$  (mol/L) ( $r = 0.998$ ), respectively. The detection limit was estimated to be  $2 \times 10^{-8}$  mol/L ( $S/N = 3$ ).

The MWNTs-IL-Gel/GC electrode could be easily regenerated by repetitive cycling in a blank solution for several times. For ten successive determination of a  $5.0 \times 10^{-6}$  mol/L Xan with the same electrode regenerated after every determination, the R.S.D. was calculated to be 3.6%. Additionally,  $5.0 \times 10^{-6}$  mol/L Xan solution is determined with 8 modified electrodes prepared by the same method, and the R.S.D. was 4.5%.

The influence of some metal ions and organic compounds were tested. The results showed that for  $5.0 \times 10^{-6}$  mol/L Xan, 200-fold of K<sup>+</sup>, Na<sup>+</sup>, Ca<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup>, Pb<sup>2+</sup>, 100-fold of Vitamin E, Vitamin C, glucose, galactose and fecula did not interfere the determination (signal change below 5%).

The MWNTs-IL-Gel/GC electrode was used to the determination of Xan in commercially available drug (0.1 g per tablet). The results (shown in Table 1) are in good agreement with the content marked in the label. Therefore, a new sensitive method for the determination of Xan was established.

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