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Copper-modified titanium phosphate nanoparticles as electrocatalyst for glucose detection

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ABSTRACT

The non-enzymatic determination of glucose is a current trend in analytical chemistry. Copper-based nanomaterials are being widely employed for the fabrication of electrochemical analytical devices for glucose monitoring. In this work, copper-modified titanium phoshate nanoparticles (CuTiPNPs) were synthesized for the first time. Interestingly, CuTiPNPs show an electrocatalytic effect towards the oxidation of glucose. These nanoparticles were characterized by different techniques such as transmission electron microscopy, X-ray photoelectron spectroscopy, X-ray diffraction, infrared spectroscopy, voltammetry and electrochemical impedance spectroscopy. Important information on the structural, morphological, surface and electrochemical properties was obtained. A mechanism involving a Cu(III) species stabilized by phosphate groups of the nanoparticles is proposed for the oxidation of glucose. The analytical performance of 8-channel screen-printed electrodes modified with CuTiPNPs for glucose determination was evaluated. A wide linear range from 25 μM to 2 mM and a limit of detection of 7 μM was obtained. The good analytical figures of merit and the good selectivity towards glucose led to the versatile and accurate non-enzymatic glucose determination in real samples such as honey and plasma.

1. INTRODUCTION

Enzymatic electrochemical biosensors have been extensively studied and used in numerous applications due to their high selectivity and sensitivity. For instance, enzymatic sensors for the determination of alcohol [1], fructose [2], or hydrogen peroxide [3] have been developed. Glucose determination is the most widespread application of these sensors for their good performance and usefulness to monitor patients with diabetes [4,5]. However, enzymatic sensors suffer from some problems such as high price or low stability. In order to minimize these issues, a current trend is the development of non-enzymatic analytical devices for the determination of several substances of interest [6,7], and especially, glucose [8–10]. For non-enzymatic glucose detection, metallic and nonmetallic-based electrodes have been previously employed. For instance, Pissinis et al. have recently reported the use of a nickel-chromium alloy electrode for carbohydrates detection [11] or Tian et al. have reported a nickel ion implanted-modified indium tin oxide electrode for glucose determination [12]. Non-enzymatic analytical devices also present different problems such as a lower selectivity than enzymatic ones and the high price of some noble metals employed. For these reasons, solving these issues is a constant concern in order to get an ideal device for non-enzymatic glucose determination.

In recent years, nanomaterials have been widely used for different electroanalytical applications [13] such as non-enzymatic glucose detection [14]. Some nanomaterials such as metallic nanostructures, carbon nanotubes or graphene have shown great catalytic effects to electrochemical reactions. Metal nanostructures (spheres, rods, cones or cubes) can be prepared from different materials, specifically gold, platinum or palladium, as they have interesting properties in catalysis and low chemical reactivity. However, the synthesis of these nanomaterials is usually high-priced for the expensive starting materials (gold, platinum or

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palladium salts). The development of novel nanomaterials with similar catalytic properties to those of the noble metals but with a lower manufacturing cost is being extensively researched. Copper nanomaterials are one example. This kind of nanomaterials have applications in fields like catalysis or analytical detectors [15,16]. For instance, glucose non-enzymatic electrochemical detection has been reported using different kinds of copper or copper oxide-modified electrodes [17–19]. The most accepted mechanism for the catalytic oxidation of sugars is the oxidation of the copper-based electrode by applying a positive potential, which, in an alkaline medium, generates Cu(III) species that react rapidly with carbohydrates [20,21]. Cu(III) species are generated only under certain conditions where they are strongly stabilized [22,23]. As stated by Baldwin et al. [21], although the different copper-based electrochemical devices reported are different in nature, the carbohydrate oxidation occurs only in a highly alkaline medium, and the electrode surface is basically in form of oxide or hydroxide, and the oxidation of glucose follows the same mechanism at the different electrodes. The mechanism proposed in several studies published in the literature is as follows:

$$CuO + OH^- \rightleftharpoons CuO(OH) + e^- \quad (1)$$

$$CuO(OH) + Glucose \rightarrow CuO + Gluconolactone \quad (2)$$

This mechanism involves the presence of CuO, which is oxidized to CuO(OH) after the application of a positive potential in an environment with high concentration of OH^- [20]. The Cu(III) species, which cause the carbohydrate oxidation, are electrogenerated in a stabilized atmosphere by the oxide and hydroxide groups. In all these cases, the presence of CuO seems critical to achieve the catalytic reaction.

Titanium phosphate nanoparticles (TiPNPs) have been recently developed [24]. TiPNPs, consisting in a core of crystalline $NaTi_2(PO_4)_3$ and a shell of amorphous titanium hydrogenphosphate and dihydrogenphosphate [24], have shown to be able to interchange their acid protons by metal cations, and therefore to introduce a high amount of metals in its pore structure. These properties make them particularly suitable for the removal of heavy metals in polluted environments [25]. Another application with great potential is as label for electrochemical sensors after the introduction of a metal easily measured by voltammetry. The ability to introduce different metals allows the use in multiplexing biosensing [26–28]. Recently, it was found that these metal-modified nanoparticles could show indirect electrocatalytic effects [29] after the *in situ* reduction of the metal to generate metallic nanoparticles on the electrode surface. For instance, silver-modified TiPNPs showed a catalytic effect towards the hydrogen evolution reaction, which could be used for quantification of these nanoparticles or as a detection method for biosensors, as it has been the case for other nanoparticles with electrocatalytic properties [30]. However, the direct electrocatalysis of reactions with TiPNPs has not been reported to date. So far, just a few metals have been introduced into the TiPNPs structure such as Cd, Pb or Ag, used for the mentioned applications, although, the introduction of other metals may prove useful for new applications.

Screen-printed electrodes are one of the most used platforms for the development of electrochemical sensors and biosensors. Their low cost, miniaturization, robustness and disposable character are valuable properties for sensing applications. It is worth noting the versatility of screen-printed electrodes to be modified either by adsorption or by covalent bonds with different materials. The disposable character eliminates the issues associated to cleaning the working electrode after performing a measurement, issues typically found with conventional electrodes. Glucose detection using screen-printed electrodes have been carried out following different approaches such as the direct electrochemistry of glucose oxidase [31], an Os-complex mediator in a Flow Injection Analysis system [32], or a gold-nanodendrite electrode [33]. On the other hand, the development of screen-printed devices continues to evolve with current trends, being the simultaneous analysis of several samples using multichannel devices one of its latest hits, which allows a considerable saving of time. As biosensing applications are time consuming, 8-channel screen-printed cards have been employed for the development of electrochemical biosensors [34–36] with other great advantages such as the low reagent consumption. Similar to ELISA plates but integrating electrochemical detection, 96-channel screen-printed cards is a new alternative to further decrease analysis time being able to measure several samples simultaneously [37].

In this paper, a simple method to synthesize and functionalize titanium phosphate nanoparticles with copper (CuTiPNPs) and their application for non-enzymatic glucose detection using multichannel screen-printed electrodes is described. CuTiPNPs were characterized using different microscopic, structural and electrochemical techniques, obtaining relevant information about its structure and behaviour. CuTiPNPs showed a great electrocatalytic effect towards the glucose oxidation, achieving the detection of low glucose concentrations with a miniaturized and disposable device able to measure 8 samples simultaneously. The developed analytical device performed well in real samples applications.

2. MATERIALS AND METHODS

2.1. Instrumentation

Voltammetric measurements were performed with a μStat 8000 (DropSens, Spain) potentiostat interfaced to a Pentium 4 2.4 GHz computer system and controlled by DropView 8400 2.0 software. All measurements were carried out at room temperature. 8-channel screen-printed electrochemical cards (8xSPCEs) were purchased from DropSens (Spain). Each array is formed by eight 3-electrode electrochemical cells (25 μL volume) with carbon-based working and counter electrodes, whereas quasireference electrodes and electric contacts are made of silver (Fig. S1). All the indicated potentials are related to the silver quasireference electrode. This device has dimensions of 4.0 × 7.9 × 0.06 cm (length x width x height) and the diameter of the working electrodes is 2.56 mm (geometric area of 5.14 mm^2). The 8-channel arrays were connected to the potentiostat through a specific connector, DRP-CAST1 × 8. An Elmasonic P ultrasonic bath (Elma GmbG, Germany) was also employed to disperse the nanoparticles in the solution.

The high resolution transmission electron micrographs (HRTEM) were obtained on a JEOL JEM 2100 transmission electron microscope with an accelerating voltage of 200 kV. X-ray diffraction (XRD) patterns were performed with a Bruker D8 X-ray diffractometer with a Cu Kα X-ray source, λ = 0.15418 nm. Fourier transform infrared (FTIR) spectroscopic measurements were taken on a Perkin Elmer FT Paragon 1000 using KBr pressed disks.

2.2. Reagents and solutions

Sulfuric acid (97%), dried ethanol, sodium hydroxide, potassium chloride and glucose were purchased from Merck (Spain). Phosphoric acid (H_3PO_4, crystalline), docusate sodium salt (AOT), titanium(IV) butoxide (TBOT), copper(II) acetate, xylose, fructose, sacarose, hexaammineruthenium(III) chloride, hexaammineruthenium(II) chloride, potassium ferrocyanide, potassium ferricyanide, dopamine hydrochloride, ascorbic acid and uric acid