



## Mesoporous chitosan/silica hybrid material applied for development of electrochemical sensor for paracetamol in presence of dopamine



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### ARTICLE INFO

#### Article history:

Received 22 January 2015

Received in revised form

28 May 2015

Accepted 9 June 2015

Available online 17 June 2015

#### Keywords:

Mesoporous material

Carbon-paste electrode

Acetaminophen

### ABSTRACT

A mesoporous and thermally stable chitosan/silica bioinorganic hybrid material prepared with 0.5, 1.0, 2.0 and 4.0% w/w chitosan/silica was obtained by sol–gel method. The use of HF as catalyst resulted in samples with specific surface area between 400 and 472 m<sup>2</sup> g<sup>-1</sup> and mesopore diameters between 5 and 9 nm. These pore size distributions allowed the immobilization of the electroactive species, copper (II) tetrasulfonic phthalocyanine, on the surface of the hybrid material samples. The material was applied in the preparation of carbon paste electrodes that showed a satisfactory electrocatalytic activity for the redox reactions of paracetamol (p-acetylaminophenol). The electrode prepared with 1% w/w chitosan/silica showed a higher response current and cyclic voltammetry (CV) studies indicated that the paracetamol oxidation-reduction process on the electrode surface is controlled by diffusion. CV and differential pulse voltammetry (DPV) studies using this electrode, at different concentrations of paracetamol, presented a linear response in a wide range (39.8–458 μmol L<sup>-1</sup> for CV and 19.9–385 μmol L<sup>-1</sup> for DPV). It showed a low detection limit and high sensitivity. This electrode was also tested for paracetamol oxidation in the presence of dopamine (3,4-dihydroxyphenethylamine) presenting excellent selectivity, sensitivity (146 μA L mmol<sup>-1</sup>), reproducibility and low detection limit (0.513 μmol L<sup>-1</sup>). These results indicated the new material presents textural characteristics to make electrodes that can be applied as sensor for paracetamol determination, alone or in the simultaneous determination of both, paracetamol and dopamine.

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### 1. Introduction

Nowadays the research for the development of hybrid materials with adequate textural properties like high surface area and specific pore diameter in the mesopore range is in evidence [1–5]. In this context silica based hybrid materials containing chitosan have been developed mainly due to their potential applications for enzymes immobilization and for the development of electrochemical sensors [6–8]. The chitosan is considered an ideal support for immobilization of various electroactive species like proteins and enzymes for the preparation of electrochemical sensors and biosensors [9,10]. These hybrid materials should present suitable textural properties like high surface area and mesoporosity [11–13], which allow the immobilization of large molecules, other nanostructured and

electroactive species, like copper phthalocyanine-3,4',4''-tetrasulfonate (CuPc), giving more versatility in the applications. The metallophthalocyanines are electroactive species, well known for their excellent catalytic properties for several reactions [14] which can be applied also to improve electrochemical characteristics of the material used to make the electrodes. They have been used in the preparation of electrochemical sensors to detect several analytes and also for the dopamine [15–18]. The CuPc electroactive species was not immobilized in mesoporous hybrid chitosan/silica yet.

The sol–gel method is an excellent strategy to obtain chitosan/silica hybrid materials because the synthesis can be performed at room temperature, allowing the incorporation of organic compounds. It is possible the preparation of homogeneous bioinorganic hybrid materials with the organic and inorganic moieties dispersed at molecular or nanometric level. Another advantage is the planning of physicochemical characteristics, mainly the surface area and pore diameter of the materials, through the control of experimental synthesis parameters [19,20]. Some precursors applied in the synthesis of

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chitosan/silica hybrid materials have been 3-glycidoxypropyltrimethoxysilane [21,22], 3-aminopropyltriethoxysilane, tetramethylorthosilicate [23,24] sodium silicate [25] and tetraethylorthosilicate (TEOS) [26,27]. The morphological and textural properties are very influenced by these precursors that can produce scaffold [21,22] spherical [21,25,28], and also compact structures [23]. These materials can present varied porosities with pores of different sizes and shapes [23,25]. The catalyst used in the sol–gel process, for synthesis of these hybrids, is also very important to define the pores structure. The catalysts commonly used are HCl [24,25] and NaOH [21,25]. The HF is a nucleophilic catalyst and when it is used in small quantities, near 1% in volume, it affords a mesoporous structure to hybrid materials with pores between 5 and 10 nm [29,30]. However it was not applied yet in the preparation of chitosan/silica hybrids.

The paracetamol (acetaminophenol, N-acetyl-p-aminophenol) is one of the most used drugs, applied as analgesic and antipyretic. Therefore, it is present in various biological systems or water disposals. Considering that it is metabolized in the liver, high level of this compound can cause accumulation of toxic metabolites producing hepatotoxicity, urinary and digestive problems, thus its determination in aqueous medium is very important [31,32]. The paracetamol determination has been performed through electrochemical sensors and it was found that dopamine (3,4-dihydroxyphenethylamine) is a frequent interfering in this process because it is also present in many biological systems. Additionally, it was observed that the oxidation potential of both, paracetamol and dopamine, is very similar for most electrodes [33–35]. Due to these facts the simultaneous electrochemical determination of these species deserves to be more studied.

Currently, different kinds of modified electrodes have been used for paracetamol determination like glassy carbon [36], carbon-paste [37], carbon films [34], boron doped diamond [38] and carbon nanotube modified electrodes [39]. Although, there are many reports about electrochemical determination of paracetamol some aspects need improvement such as the sensibility, detection limits, selectivity and reproducibility in the presence of interfering. These improvements can be obtained through the development of electrodes modified with new materials presenting adequate textural characteristics.

In this work, it is described the synthesis of a mesoporous chitosan/silica bioinorganic hybrid material by sol–gel method, using TEOS and chitosan as precursors of inorganic and organic moieties, respectively. The HF was used as catalyst to afford mesoporous structure. Four samples with different organic/inorganic weight percentages were prepared and characterized by elemental and thermogravimetric analyses, nitrogen adsorption–desorption isotherms, infrared spectroscopy and scanning electron microscopy. The electroactive species copper phthalocyanine-3,4',4'',4'''-tetrasulfonate (CuPc) was immobilized on the surface of the hybrid chitosan/silica for the first time and the resulting material was used in the preparation of carbon paste electrodes (CPE). The CPE was applied in the electrochemical determination of paracetamol (PR) alone and in the presence of dopamine (DP) by using cyclic voltammetry and pulse differential voltammetry.

## 2. Experimental section

### 2.1. Reagents

Chitosan (CS, Mw: 100,000–300,000 g mol<sup>-1</sup>, deacetylating grade: 95%), N,N-dimethylformamide, tetraethylorthosilicate (TEOS), carbon graphite (99.9%), potassium chloride, copper phthalocyanine-3,4',4'',4'''-tetrasulfonic acid tetrasodium (CuPc), dopamine hydrochloride (DP) and paracetamol (PR) were

purchased from Sigma Aldrich, ethanol, hydrofluoric acid, phosphoric acid, acetic glacial acid and boric acid were obtained from Merck. Formamide was acquired from Vetec. All chemicals employed were of analytical grade and used as received without any further purification.

### 2.2. Preparation of the bioinorganic hybrid chitosan/silica (SiO<sub>2</sub>-CS)

Four samples of the hybrid material were prepared using different amounts 0.5, 1.0, 2.0 and 4.0 %w/w, chitosan/silica. The preparation of each sample involves the following steps: (1) dissolution of CS, (2) hydrolysis of TEOS and preparation of hybrid. In step (1) the chitosan was dissolved in 1.3 mL of water and 0.050 mL of HCl 37%. After complete dissolution, it was added 0.15 mL of HF 40% as catalyst. The mixture remained under stirring for 10 min Table 1 summarizes the amounts of CS used in the preparation of samples. In step (2) 5.0 mL of TEOS were hydrolyzed in a mixture of 2.5 mL of ethanol, 0.3 mL of water and 0.05 mL of HCl 37%. After vigorous stirring at 25 °C for 1 h it was added 3.0 mL of formamide, this mixture was maintained under stirring for 15 min more. Subsequently, to this solution it was slowly added the solution obtained in the step (1), under stirring. The system remained 10 min under stirring and was kept standing for 40 days at 45 °C, for polycondensation and solvent evaporation. After that, the xerogels obtained were thermally treated at 90 °C, in vacuum, during 2 h and they were comminuted in an agate mortar, washed with ethanol, water and ethyl ether. Finally, the xerogel was dried under vacuum (10 Pa) at 90 °C, during 2 h. The hybrid material samples were designated as 0.5SiO<sub>2</sub>-CS, 1.0SiO<sub>2</sub>-CS, 2.0SiO<sub>2</sub>-CS and 4.0SiO<sub>2</sub>-CS, indicating the percentile of CS added to each sample.

### 2.3. Copper (II) tetrasulfonic phthalocyanine immobilization on hybrid material

The SiO<sub>2</sub>-CS hybrid samples (200 mg), previously washed with 0.01 mol L<sup>-1</sup> HCl solution, were immersed in a 2.4 × 10<sup>-4</sup> mol L<sup>-1</sup> copper phthalocyanine-3,4',4'',4'''-tetrasulfonate (CuPc) solution (20 mL) and the mixtures were stirred for 24 h at 25 °C. The modified solids were filtered and washed with distilled water and ethanol, finally they were dried in an oven, at 70 °C, for 3 h. The resulting solids were assigned as 0.5SiO<sub>2</sub>-CS/CuPc, 1.0SiO<sub>2</sub>-CS/CuPc, 2.0SiO<sub>2</sub>-CS/CuPc and 4.0SiO<sub>2</sub>-CS/CuPc.

### 2.4. Elemental analysis

The elemental analysis of the samples was made using a CHN Perkin Elmer M CHNS/O Analyzer, model 2400. The analyses were made in triplicate.

### 2.5. Infrared analysis

Self-supporting disks of the hybrid material samples, with a diameter of 2.5 cm, weighing ca.100 mg were prepared. The disks were heated under vacuum (10<sup>-3</sup> Torr) in an IR cell which is described elsewhere in details [40]. The spectra were obtained

**Table 1**  
Amount of chitosan used for preparation of hybrid material.

Sample	% CS (w/w)	CS (mg)
0.5SiO <sub>2</sub> -CS	0.5	6.6
1.0SiO <sub>2</sub> -CS	1.0	13.2
2.0SiO <sub>2</sub> -CS	2.0	26.4
4.0SiO <sub>2</sub> -CS	4.0	52.8

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