



# Sulfur and nitrogen co-doped carbon dots sensors for nitric oxide fluorescence quantification



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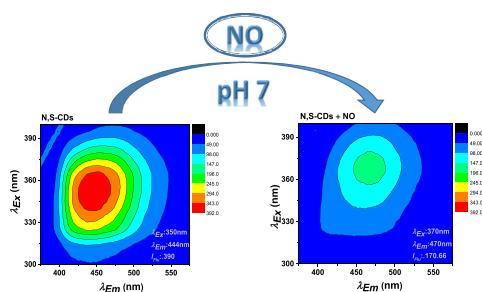
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## HIGHLIGHTS

- S,N co-doped CDs were microwave synthesized from citric acid, urea and sodium thiosulfate.
- The NO fluorescence sensing was evaluated at pH 7.
- The selective and sensitive detection of NO at pH 7 was achieved.
- Good NO quantification results in serum samples were obtained.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 17 October 2016

Received in revised form

11 November 2016

Accepted 5 January 2017

Available online 25 January 2017

### Keywords:

Carbon dots

Citric acid

Urea

Sodium thiosulfate

Nitric oxide

Fluorescence quenching

pH 7

## ABSTRACT

Microwave synthesized sulfur and nitrogen co-doped carbon dots responded selectively to nitric oxide (NO) at pH 7. Citric acid, urea and sodium thiosulfate in the proportion of 1:1:3 were used respectively as carbon, nitrogen and sulfur sources in the carbon dots microwave synthesis. For this synthesis, the three compounds were diluted in 15 mL of water and exposed for 5 min to a microwave radiation of 700 W. It is observed that the main factor contributing to the increased sensitivity and selectivity response to NO at pH 7 is the sodium thiosulfate used as sulfur source. A linear response range from 1 to 25  $\mu\text{M}$  with a sensitivity of 16  $\mu\text{M}^{-1}$  and a detection limit of 0.3  $\mu\text{M}$  were obtained. The NO quantification capability was assessed in standard and in fortified serum solutions.

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## 1. Introduction

Reactive Oxygen (ROS) and Nitrogen Species (RNS) are typically

involved in numerous physiological and pathological processes acting as signaling molecules [1]. The nitric oxide (NO), one of most studied ROS/RNS, it is a free radical that plays as a physiological messenger and as effector in mammalian cells. It has a vital role in vascular and neuronal signal transduction, bioenergetics, immunity and cell death regulation. However at high concentrations it can be injurious to cells and can be associated with some diseases [2–5].

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Sensors based in nanoparticles (NPs) have attracted much attention due their own specific characteristics [6]. Recently some sensors based in NPs have been developed for the NO detection [7–24]. NO optical nanosensors based in NPs as gold NPs (AuNPs), carbon nanotubes (CNT) and quantum dots (QDs) were developed. Two AuNPs optical sensors to NO detection based on immobilization of AuNPs onto a fiber optic were reported [7,8]. CNT were used in optical sensors with potential for NO sensing [9,10]. The NO detection using QDs is usually based on fluorescence quenching of QDs by NO. TEA modified CdSe-QDs were quenched with NO [11]. QDs with chitosan (CS) were used as NO sensors [12,13]. A CdSe-QDs sensor stabilized by CS and mercaptosuccinic acid was showed by Simões et al. [14]. A sensor synthesized by adsorption of CdSe/ZnS-QDs on polymethacrylate was presented [15]. An optical fiber sensor based on CdSe-QDs using cellulose as NO sensitive membrane was developed [16]. CdSe functionalized with trivalent porphyrin were used in NO sensing [17]. Modified hyperbranched polyether nanospheres and QDs were reported in NO detection [18]. The detection based on the degradation of the polymethyl methacrylate molecule (PMMA) by NO in CdS-PMMA nanocomposites was presented [19]. Ferric dithiocarbamate compounds were used in the QDs functionalization for NO sensors [20,21]. Organogel–CdSe/ZnS QDs hybrid materials showed fluorescence sensitivity towards NO [22]. CdSe/ZnS-QDs coordinated with dirhodium complex were presented [23]. A QDs system capable of releasing NO and meanwhile detecting the NO release under conditions similar to physiological environment based on the fluorescence quenching by NO was presented [24].

The carbon Dots (CDs), the nanoparticles focus of the present work, had become to be a priority for the scientific research due to their non-toxicity and biocompatible properties [25]. Furthermore CDs also can be functionalized and conjugated with various compounds and therefore could be used in several analytical and bio-analytical applications [26]. A great number of methods for the CDs synthesis have proposed in last years. One of the most used method of synthesis is the microwave synthesis due to the fact that it is a rapid and simple method of CDs synthesis [27]. Different kind of precursors like carbohydrates, chitosan, citric acid (CA), amines and others can be used in CDs production [28,29]. Many CDs were microwave synthesized having as precursors CA combined with different amines [30–32]. Also the CDs can be doped to increase their quantum yield ( $\Phi$ ), to provide sensibility and selectivity as sensor to adjust their compositions and structures. Some works presented the CDs microwave synthesis from CA as carbon source and urea (UR) as nitrogen source [33–35].

Doping CDs with heteroatoms (e.g., oxygen, nitrogen, phosphor, boron or sulfur) allows adjusting their compositions and structures and is one way of tuning their electronic and optical properties [36]. Generally the quantum yield of the doped CDs is higher than the  $\Phi$  of the non-doped CDs. Nitrogen doping CDs is a well established procedure [37,38]. More recently sulfur and nitrogen co-doped CDs prepared from various precursors have been reported [39–45]. The synergistic effect of the various dopants allows the synthesis of CDs with different characteristics and can have diverse applications [46]. The sulfur and nitrogen co-doped CDs commonly exhibit higher catalytic activity to the oxygen reduction reaction compared with the nitrogen doped CDs through a cooperative effect [36,47]. The co-doped sulfur atoms can help to enhance the effect of nitrogen doping through this cooperative effect. For the sulfur and nitrogen co-doped CDs, the sulfur atoms seems to be able to eliminate the O states and enhance the N states [48].

Two applications of CDs as NO nanoprobe were discussed [49,50]. In one of the works the ratiometric sensing of NO based in CDs through the fluorescence resonance energy transfer (FRET) process was assessed [49]. More recently, a NO sensor based in CDs

microwave synthesized from CA and EDA showed selective fluorescence sensing of NO and ONOO<sup>-</sup> in the presence of the main ROS/RNS. A greater sensitivity was obtained for the determination of ONOO<sup>-</sup> at pH 7 and 10 and a lower sensitivity for the determination of NO at pH 4 [50].

In this work a selective and sensitive sensor to NO detection and quantification at pH 7 based on microwave synthesized CDs prepared from CA, UR and sodium thiosulfate (ST) was developed. The fluorescence response of the synthesized CDs relatively to NO in the presence of other ROS/RNS and the NO quantification capability in standard and in fortified serum solutions were evaluated.

## 2. Experimental

### 2.1. Reagents

Citric Acid (CA), urea (UR), sodium thiosulfate (ST), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), hydrogen chloride (HCl), potassium superoxide (KO<sub>2</sub>), sodium hypochlorite 3.5% (NaClO), sodium nitrite (NaNO<sub>2</sub>), sodium nitrate (NaNO<sub>3</sub>), sodium chloride (NaCl), potassium chloride (KCl), ethylenediamine tetraacetic acid (EDTA), iron(II) sulfate (FeSO<sub>4</sub>·7H<sub>2</sub>O), iron(III) nitrate [Fe<sub>3</sub>(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O], magnesium chloride (MgCl<sub>2</sub>·6H<sub>2</sub>O), copper(II) sulfate (CuSO<sub>4</sub>·5H<sub>2</sub>O), sodium phosphate dibasic (Na<sub>2</sub>HPO<sub>4</sub>), monosodium phosphate (NaH<sub>2</sub>PO<sub>4</sub>), sodium hydroxide (NaOH) analytical grade reagents and Milli-Q water with a resistivity 18 MΩ cm at 25 °C were used in all the work.

### 2.2. Solutions

Saturated NO solutions (1.9 mM) were prepared by bubbling argon for 15 min in water and follow bubbling NO another 15 min. ONOO<sup>-</sup> solutions were prepared in a refrigerated beaker under constant stirring by mixing 100 mL of NaNO<sub>2</sub> 600 mM, 100 mL of H<sub>2</sub>O<sub>2</sub> 600 mM in HCl 0.6 M and 100 mL of NaOH 3.6 M. The solution will turn yellow indicating the formation of ONOO<sup>-</sup>. The agitation is maintained until no O<sub>2</sub> is formed. The hydroxyl (HO·) was generated in situ by the Fenton reaction by addition of a 5 fold excess of H<sub>2</sub>O<sub>2</sub> to the EDTA-Fe(II) complex formed with different concentrations of FeSO<sub>4</sub>. Serum fortified sample solutions were done respectively in water by rigorous dilution to the desired concentrations. The solutions of H<sub>2</sub>O<sub>2</sub>, KO<sub>2</sub>, NaClO, NaNO<sub>3</sub>, NaNO<sub>2</sub> were prepared in water.

All the experiences were made at pH 7. The phosphate buffer 0.01 M (pH 7) used was prepared through weighting the required mass of NaH<sub>2</sub>PO<sub>4</sub> and Na<sub>2</sub>HPO<sub>4</sub>. Solutions of HCl and NaOH 0.1 M were also prepared in order to adjust the pH of the phosphate buffer solution and in order to evaluate the influence of pH in the CDs fluorescence.

### 2.3. Instrumentation

The fluorescence sensing evaluations were made using a QE65000 charge-coupled detector, a 380 nm light emitting diode (LED), a sampling compartment (CUV-ALL-UV 4-way) and two 1.0 mm core diameter fiber optics (P1000-2-UV-VIS) from Ocean Optics. One of the fibers guides the light from the source to the sampling compartment and the other guide the emitted light to the detector. The reaction time profiles were obtained collecting the signal at the maximum emission wavelength, every 10 s with an integration time of 300 ms. A difference between the initial and the final fluorescence intensity measured after 10 min the addition of the ROS/RNS (intensity variation) were used in all the work.

The absorbance and fluorescence spectra were obtained in a standard 1 cm fluorescence quartz cell and collected respectively in a Jasco V-530 UV-Visible spectrophotometer and in a Jasco FP-

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