Food Chemistry 260 (2018) 13–18

Contents lists available at ScienceDirect

Food Chemistry

journal homepage: www.elsevier.com/locate/foodchem

Carbon dots based dual-emission silica nanoparticles as ratiometric fluorescent probe for nitrite determination in food samples

Guoqiang Xiang[a,*], Yule Wang[b], Heng Zhang[a], Huanhuan Fan[a], Lu Fan[b], Lijun He[a], Xiuming Jiang[a], Wenjie Zhao[a]

[a] School of Chemistry and Chemical Engineering, Henan University of Technology, Zhengzhou 450001, PR China
[b] School of Food Science and Technology, Henan University of Technology, Zhengzhou 450001, PR China

ARTICLE INFO

Keywords:
Ratiometric fluorescent probe
Nitrite
Silica nanoparticles
Food samples

ABSTRACT

In this work, a simple and effective strategy for designing a ratiometric fluorescent nanosensor was described. A carbon dots (CDs) based dual-emission nanosensor for nitrite was prepared by coating the CDs on to dye-doped silica nanoparticles. Dual-emission silica nanoparticles fluorescence was quenched in sulfuric acid using potassium bromate ($KBrO_3$). The nitrite present catalyzed the $KBrO_3$ oxidation, resulting in ratiometric fluorescence response of the dual-emission silica nanoparticles. Several important parameters affecting the performance of the nanosensor were investigated. Under optimized conditions, the limit of detection was 1.0 ng mL^{-1} and the linear range 10–160 ng mL^{-1}. Furthermore, the sensor was suitable for nitrite determination in different food samples.

1. Introduction

Nitrite is a chemically active substance that exists widely in the environment including food products. Nitrate and nitrite are used in combination with sodium chloride as antimicrobial agents in processed meats to inhibit the growth of bacterial spoilage. Examples include Clostridium botulinum, which generates botulin toxin that is responsible for muscular paralysis and neuronal complications (Cammack et al., 1999). Additionally, nitrite is widely used in food industries because of its ability to react with meat myoglobin to generate mononitrosylhaemochrome, which gives the characteristic red color of cured meat (Cammack et al., 1999). However, excess nitrite in foods is harmful, especially for pregnant women and infants (Burden, 1961; Canbay, Sahin, Kiran, & Akyilmaz, 2015; Seike et al., 2004; L. Wang et al., 2015). Thus, its presence in food has been limited by authorities in many regions globally. An acceptable daily intake of 0.06 mg (kg body weight)$^{-1}$ of nitrite was established by the Joint FAO/WHO Expert Committee on Food additives in 2002 (FAO/WHO, 2003) (EU Directive). The World Health Organization (WHO) has set the maximum limit of nitrite in drinking water to 3.0 mg L^{-1} (or 65 μM) (WHO, 2004).

Overall, the quantitative determination of nitrite concentrations is of great importance, especially in food quality control (QC). Many methods for nitrite determination have been developed, including chromatographic techniques (Akyuz and Ata, 2009; Croitoru, 2012; Fang, Ohata, & Honda, 2009), electrochemical detection (Rajalakshmi et al., 2015; Turdean et al., 2015), spectrophotometry (Nagaraja, Al-Tayar, Shivakumar, Shrestha, & Gowda, 2010; Senra-Ferreiro, Pena-Pereira, Lavilla, & Bendicho, 2010; Tsikas, 2007; Zhang, Wang, Wang, Cui, & Fu, 1996), and spectrofluorimetric methods (Wang et al., 2015, 2016). Zhao, Zhao, and Li (2015) reviewed the analytical methods for nitrite based on electrochemical and spectroscopy. It was be pointed out that spectroscopic methodologies, especially spectrofluorimetry has lower limit of detection. Recently, several fluorescent probes for nitrite with good sensitivity and selectivity were reported (Biswas, Chowdhury, & Ray, 2004; Hong, Wei, Liang, Zhang, & Zhang, 2000; Kojima et al., 1999; Liu et al., 2009; Tsikas, 2007). Unfortunately, most of these probes are synthesized in the laboratory. Thus, they are either commercially unavailable or can only be purchased at high-cost. Thus, developing a highly sensitive and specific fluorescent probe for nitrite determination is still a major challenge.

Carbon dots (CDs) have been investigated as fluorophores for the sensitive and selective detection of heavy metal cations and anions due to their superior fluorescent properties, easy preparation, low-cost, and great potential for fluorescence-based analytical applications (Chaudhary, Kumar, Kaur, & Mehta, 2016; Du, Zeng, Ming, & Wu, 2013; Lu et al., 2017; C. Wang et al., 2016; Yang, Guo, Jia, & Zhang, 2017). Zhang's group reported a new method for the selective and sensitive fluorescence detection of nitrite ions in water using nitrogen-doped CDs as a fluorophore (Zhang, Kang, Wang, Zhang, & Zhao,

* Corresponding author.
E-mail address: xianggq@haut.edu.cn (G. Xiang).

https://doi.org/10.1016/j.foodchem.2018.03.150
Received 4 May 2017; Received in revised form 18 March 2018; Accepted 31 March 2018
Available online 02 April 2018

2016). Published reports suggested that catalytic kinetics based on fluorimetry methods could be setup according to fluorescence quenching arising from the catalytic oxidation of fluorophores (Bu et al., 2008; Chen, Liu, & Gao, 2013; Feng and Liu, 2008; Zhu et al., 2014). However, so far, no reports demonstrated the utilization of CDs as fluorophores for the selective and sensitive detection of NO_2^- in food samples based on the catalytic oxidation of fluorophores.

Herein and for the first time, we introduced the catalytic oxidation of CDs for the selective and sensitive detection of NO_2^- in food samples. The CDs and Rhodamine B (RhB) were grafted on silica nanoparticles, and the two resulting fluorescence emission peaks were monitored. The fluorescence intensity was quenched by the oxidation effect of potassium bromate in H_2SO_4 media, which was catalyzed to yield an enhanced fluorescence quenching effect in presence of NO_2^-. A sensitive ratiometric fluorescence nanosensor was accordingly developed based on the catalytic oxidation induced by the dual-emission silica nanoparticles. The selectivity and sensitivity of this ratiometric fluorescence nanosensor towards NO_2^- were carefully investigated, and the feasibility of NO_2^- determination in different food products was examined.

2. Experimental and methods

2.1. Apparatus and reagents

The fluorescence was measured using a Varian Cary Eclipse fluorescence spectrophotometer. Transmission electron microscopy (TEM) was recorded using a JEM-2011 TEM. Fourier transform infrared (FT-IR) spectra in KBr were collected on a WQF-510 FT-IR spectrometer (Beijing Rayleigh Analytical Instrument Co., Ltd., Beijing, China).

N-(β-aminoethyl)-γ-aminopropylmethyldimethoxysilane (AEAPMS), aminopropyltriethoxysilane (APTES), Rhodamine B (RhB) and anhydrous citric acid (Analytical Reagent, AR) were purchased from Aladdin reagent company (Shanghai, China). Tetraethoxysilane (TEOS, AR) and $KBrO_3$ (AR) were from Sinopharm Chemical Reagent (Shanghai, China), and sodium nitrite (AR) from J&K Scientific (Beijing, China). Ethanol, NH_4OH, H_2SO_4 and other reagents were purchased from Beijing chemicals (Beijing, China). Ultrapure water (18 MΩ cm^{-1}) was used in all experiments.

2.2. Methods

2.2.1. Preparation of organosilane functionalized CDs

The CDs-coated dual-emission silica nanoparticles were prepared according to the reported methods (Dong et al., 2012; Liu, Zhang, Bing, & Shangguan, 2014). The preparation procedure included three main steps, as shown in Fig. 1. The organosilane functionalized CDs were first prepared by the pyrolysis of anhydrous citric acid in AEAPMS at 230 °C for 1 min (Wang, Xie, Zhang, Liu, & Zhang, 2011). After purification by petroleum ether, the obtained product (0.4 mL) was added to 1.6 mL ethanol.

2.2.2. Preparation of RhB-doped silica nanoparticles

During this step, RhB was pre-coupled with APTES through the reaction between the carboxylic group of rhodamine and amino group of APTES in ethanol under constant stirring for 24 h at room temperature. The obtained RhB-APAES solution (100 μL), TEOS (50 μL) and ammonia (200 μL) were then added to ethanol (5 mL), and the mixture was left under constant stirring at room temperature for 8 h. Subsequently, the reaction mixture was centrifuged, and the silica nanoparticles were collected then washed three times with ethanol. Next, the obtained nanoparticles were ultrasonically dispersed in 5.0 mL ethanol for 10 min then 50 μL TEOS and 100 μL ammonia were added to the solution under constant stirring for 24 h at room temperature. The formed dye-doped silica nanoparticles were finally collected by centrifugation and washed three times with ethanol then redispersed in 5.0 mL ethanol.

2.2.3. Preparation of CDs-coated dual-emission silica nanoparticles

A 3.0 mL volume of dye-doped silica nanoparticles obtained above was mixed with 100 μL ammonia. After stirring for 30 min, a 10 μL CDs was added to the mixture and stirred for 15 h at room temperature. The reaction mixture was centrifuged, and the obtained CDs-coated dual-emission silica nanoparticles were washed three times with ethanol then redispersed in ethanol at concentration of 10 mg mL^{-1}.

2.3. Analytical procedure

First, a 1.0 mL solution of CDs-coated silica nanoparticles (10 mg mL^{-1}) was mixed with 50 μL H_2SO_4 (2.0 M) and 1.0 mL $KBrO_3$ (6.0×10^{-3} M) in a 10 mL graduated tube. A certain amount of nitrite standard solution (or the sample solution) was added to the test tube. After diluting with ultrapure water to the required volume, the mixture was shaken thoroughly, and then left to rest for 5 min in a water bath at 60 °C prior to the fluorescence measurements. Simultaneously, a reagent blank was prepared without addition of the nitrite standard solution or sample solution.

The fluorescence intensities of the dual emission peaks (460 nm and 572 nm) for the test solution (F^{460} and F^{572}) and the reagent blank (F_0^{460} and F_0^{572}) were directly measured using a Varian Cary Eclipse fluorescence spectrophotometer with an excitation wavelength of 360 nm. The spectrometric quantities were calculated according to: $\Delta F^{460} = F_0^{460} - F^{460}$, $\Delta F^{572} = F_0^{572} - F^{572}$, and the $\Delta F^{460}/\Delta F^{572}$.

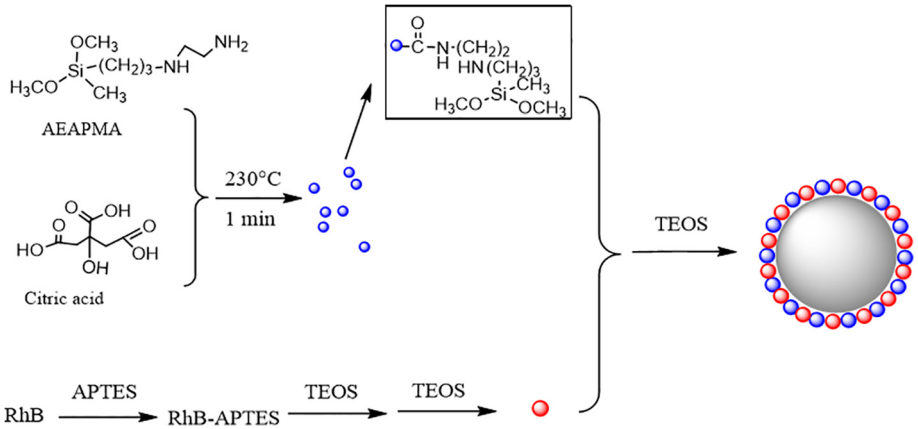

Fig. 1. A schematic diagram of the preparation process of CDs-coated dual emission silica nanoparticles (RhB-Rhodamine B, APTES-Aminopropyltriethoxysilane, TEOS-Tetraethoxysilane).