Talanta 132 (2015) 252–257

Contents lists available at ScienceDirect

Talanta

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

Fluorescent carbon nanodots for sensitive and selective detection of tannic acid in wines

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ARTICLE INFO

Article history:
Received 22 July 2014
Received in revised form
11 September 2014
Accepted 13 September 2014
Available online 30 September 2014

Keywords:
Carbon nanodots
Tannic acid
Wines

ABSTRACT

Herein we describe an easy one step synthesis of carbon nanodots (C-dots) by thermal carbonization of 6-bromohexylboronic acid using two different amine compounds, polyethyleneglycol bis(3-aminopropyl (PEGA) and 1,2-aminopropane (DPA), at 180 °C in atmospheric oxygen. The as-synthesized C-dots were characterized by FTIR, HRTEM, NMR and fluorescence. The C-dots prepared using PEGA showed a strong emission at 440 nm with excitation at 362 nm. These C-dots exhibited analytical potential as sensing probes for tannic acid (TA) determination. pH effect, interferences, and analytical performance of the method were investigated. The method was found effective in the linear concentration range from 0.1 to 10 mg L^{-1} TA achieving a limit of detection equal 0.018 mg L^{-1} TA. The applicability of the method was demonstrated by direct measurements of TA in red and white wine samples. Validation of the method was achieved by spiking the wine samples with different standard TA concentrations obtaining recoveries in the range (90–112.5%). A probable mechanism by which TA quenched the C-dots fluorescence was proposed.

1. Introduction

Tannic acid (TA) is a natural hydrolysable polyphenol compound present in fruits and different kinds of vegetables and, along with other condensed polyphenols, can be found in several beverages including wine, beer, coffee, black tea and white tea. TA is composed of a polyol residue derived from D-glucose, which hydroxyl groups may be partially or fully substituted with galloyl units (gallotannins) [1]. It is used as a food additive (code number E-181) as clarifying agent, flavor adjunct and flavoring agent [2] as well as additive in medicinal products due to its astringent, diuretics and anti-inflammatory activities [3,4]. Moreover, TA has also applications in the tannery industry to transform animal skins to leather and for re-tanning with Cr(III) to prevent leather putrefaction [5]. As an organic pollutant associated with the tanning industry, TA has been found to be toxic to aquatic microorganisms and may form metal complexes that alter the aquatic ecosystem [6,7]. Due to its wide range of applications, analysis of tannic acid is of importance not only in food but also in the medical and environmental fields. Many analytical methods are based on the overall oxidation properties of polyphenols and, consequently, devoted to the determination of total phenolic content rather than specific determination of each component [8–12]. However, many efforts were attempted to measure TA in several kinds of food and beverage samples, as well as in industrial waters. So, a number of methods are available to quantitatively determine tannic acid content in waters, pharmaceuticals and foods, including spectrophotometry [13], electrochemical methods [14–16], luminescence [17–19] and chromatography [20,21]. Each method has its advantages and drawbacks. For example, the determination of tannic acid in wines by the traditional spectrophotometric Folin–Ciocalteu method, based on the formation of a blue phosphotungstic phosphomolybdenum complex, is simple but lacks selectivity as many other compounds in wine interfere. Chromatographic methods allow the determination of tannic acid along other polyphenols but are time consuming and expensive. Electroanalytical methods with different types of electrodes were used for TA determination, but the presence of ascorbic acid limits the use of some of these methods, or laborious sample pretreatments are needed to remove ascorbic acid before analysis [15,16]. These examples demonstrate that sensitive, selective and rapid TA detection is still a challenge.

Recent developments in analytical nanotechnology open the opportunity to develop new sensitive and selective methods for tannic acid determination. Carbon nano dots (C-dots) were found recently to be promising materials in analytical and bioanalytical

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http://dx.doi.org/10.1016/j.talanta.2014.09.028
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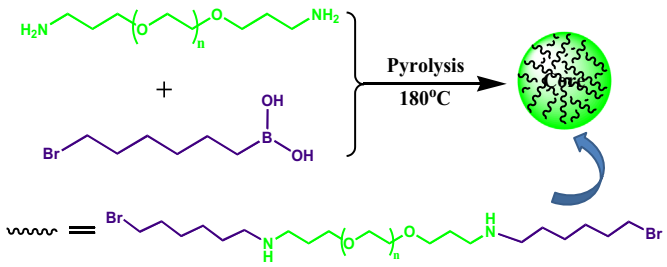

Scheme 1. Schematic representation of PEGA-C-dots synthesis .

applications, due to their unique optical properties, such as broad excitation spectra, tunable emission wavelength and stable photoluminescence [22]. Exploiting C-dots in analytical chemistry is relatively recent and most methods depend on the C-dots surface functional groups and/or their surface passivation effects. The number of analytical assays using C-dots has been increasing, but in the best of our knowledge, no work has been described for TA determination in real samples using carbon nanodots.

Herein we report a straightforward synthesis of passivated C-dots in one step via thermal carbonization method (Scheme 1), using two different amino precursors, polyethyleneglycol bis(3-aminopropyl) (PEGA) and 1,2-aminopropane (DPA). Those C-dots prepared with PEGA were found sensitive and selective fluorescent nanosensors for TA and were successfully applied to direct TA detection in real red and white wine without sample pretreatment. The synthesis reaction process as well as the mechanism for the selective sensing are also proposed.

2. Experimental

2.1. Materials

All the reagents used were highly pure analytical grade chemicals and used without further purification. The following reagents were used in this study: polyethylene glycol bis(3-aminopropyl) (PEGA), 6-bromohexylboronic acid (BrHBA), glucose, fructose, sucrose, gallic acid, citric acid, calcium chloride, and disodium hydrogen phosphate, all purchased from Sigma-Aldrich. Ascorbic acid, sodium fluoride, potassium chloride, and sodium sulfite were purchased from Merck. 1,2-diaminopropane, tartaric acid and caffeine were purchased from Fluka. NaOH, and HCl were purchased from Prolabo. TA was purchased from Hopkin & Williams chemicals (England).

2.2. Synthesis of C-dots

PEGA-C-dots and DAP-C-dots were synthesized by a thermal carbonization method, using PEGA and DAP, respectively. Typically, 1 mmol of PEGA was dissolved in about 25 mL of milli-Q water. To this solution, 0.25 mmol of BrHBA was added. The solution was then stirred and heated at 150 °C. The heating was continued until near dryness, after which 1 mL of milli-Q water was added. The process was repeated 5 times. Finally the temperature was raised to 180 °C. A yellow solution was formed and heating continued until obtaining a reddish-brown color solution to ensure the formation of the C-dots. The obtained PEGA-C-dots solution was then completed to 25 mL of milli-Q water filtered by nylon filters (0.45 μm) and purified through dialyzer tube (MWCO, 3.5 kDa) for 3 days. The purified solution was divided into two aliquots, the first one was dried completely for characterization analysis while the second was used for the analysis experiments of tannic acid. The pH of the aqueous PEGA-C-dots solution resulted to be 6.43. The same procedure was carried out to prepare DAP-C-dots using DAP instead of PEGA.

2.3. Spectrofluorimetric measurements

In a typical pH effect determination procedure, 100 μL of TA (so that the final concentration is 5 mg L^{-1}) were diluted by about 4 mL of universal buffer (in the range 3–11.5) and then 100 μL of C-dots solution was added. Finally, the solution was completed by the same buffer until a final volume of 5 mL. The fluorescence was measured immediately after the preparation in a 1-cm quartz cuvette 3 times at 440 nm with excitation at 362 nm and slit widths of excitation and emission as 20 and 10 nm, respectively. The average fluorescence data were calculated and presented as a graph. Similarly, for interference measurements, 100 μL of TA (final concentration is 5 mg L^{-1}) was mixed with the interference material (final concentration is 10 mg L^{-1}) and diluted by about 4 mL of universal buffer solution pH=9. Then, 100 μL of C-dots solution was added and finally the solution was completed to 5 mL using the same buffer solution. The subsequent fluorescence was measured as mentioned above with the same instrumental conditions.

2.4. Fluorescence quantum yield measurement

The fluorescence quantum yield was calculated through the well-established comparative method using quinine sulfate as a reference. The following equations were used in the quantum yield measurement:

$$\Phi_C = \Phi_{st}\frac{F_C}{F_{st}}\frac{A_{st}}{A_C}\frac{{n_C}^2}{{n_{st}}^2} \quad (1)$$

$$\Phi_C = \Phi_{st}\frac{G_C}{G_{st}}\frac{{n_C}^2}{{n_{st}}^2} \quad (2)$$

where ϕ is the quantum yield, F is the calculated integrated fluorescence intensity, n is the refractive index, A is the optical density (measured with a UV–Vis spectrophotometer, Perkin Elmer, Lambda 900), and G is the gradient of F vs A linear plot. The subscripts C and st refer to C-dots and the reference fluorophore, respectively. Quinine sulfate dissolved in 0.1 M H_2SO_4 (n=1.33) of quantum yield equal 0.54 at λ_{ex}=350 nm was used as a reference. C-dots were dissolved in milli-Q water (n=1.33).

2.5. Analysis of wine samples

The white wine sample (Soldepeñas, www.felixsolis.com) and red wine samples (Don Mendo, www.sanvelro.com) were used in the application experiment. The pHs of the wines were found 3.31 and 3.43, respectively. TA standards were prepared in 10% ethanol solution to avoid the effect of alcohol and sample pretreatment. Wine samples were diluted so that the alcoholic content was reduced to 10%. In a typical procedure, 100 μL of sample were spiked by 100 μL standard TA (0, 1, and 3 mg L^{-1}) followed by 4 mL buffer solution pH=9 (Na_2HPO_4 and NaOH and/or HCl) and 100 μL of the PEGA-C-dots solution. Finally, the solution was diluted to 5 mL by the same buffer. Fluorescence was measured at 440 nm with excitation at 362 nm. TA was quantified by running a calibration curve using standard solutions. All determinations were carried out in triplicate.

2.6. Instrumentation

HRTEM (JEOL JEM-2100F, 200 kV) was used to determine the size and morphology of the synthesized C-dots. A Varian 620-IR instrument was used to analyze FTIR spectra in the range 600 to 4000 cm^{-1}. ^{1}HNMR and ^{13}CNMR (NAV400 with 9.0 T magnet shielded, 600 MHz) were used for structural analysis of the synthesized C-dots in D_2O