Talanta 153 (2016) 23–30

Contents lists available at ScienceDirect

Talanta

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

Enhancement of periodate-hydrogen peroxide chemiluminescence by nitrogen doped carbon dots and its application for the determination of pyrogallol and gallic acid

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ARTICLE INFO

Article history:
Received 16 December 2015
Received in revised form
18 February 2016
Accepted 23 February 2016
Available online 24 February 2016

Keywords:
Chemiluminescence
Nitrogen doped carbon dots
Enhancement
Mechanism
Pyrogallol
Gallic acid

ABSTRACT

A new sensitized chemiluminescence (CL) was developed to broaden the analytical application of KIO_4–H_2O_2 system. The nitrogen doped carbon dots (N-CDs) dramatically boosted the CL intensity of KIO_4–H_2O_2 system which was further enriched by basic medium. In light of EPR analysis, free radical scavenging studies and CL spectra the detail mechanism for the enhancement was conferred in the presence of N-CDs and NaOH. The results suggested that CL of KIO_4–H_2O_2 system in the presence and absence of N-CDs and NaOH proceeds via radical pathway. The enhanced CL was used for the determination of pyrogallol and gallic acid in range of 1.0×10^{-4}–1.0×10^{-7} M with 4.6×10^{-8} and 6.1×10^{-8} M limit of detection respectively. The relative standard deviation (RSD) at a concentration of 10^{-5} for gallic acid and pyrogallol was 1.4% and 2.3% respectively ($n=11$). The attained results unveil that the present method is sensitive, faster, simpler and less costly compared to other methods and could be applied to determine polyphenols in real samples.

1. Introduction

The enhancement, mechanism and potential applications of ultra-weak CL being new arising systems have gradually established research interest recently. Among them peroxide induced ultra-weak CL systems are the most important, extensively used and widely investigated one. Additionally, the periodate (IO_4^-) being colorless, avoids emission absorption problems [1], produces soft oxidation products and are of paramount importance in micro-analysis of great number of inorganic and organic compounds [2]. The IO_4^- react with H_2O_2 in acidic, neutral and basic mediums to give IO_3^- and $^1O_2$ [3], produces weak CL which were enhanced by some researcher [4], and used for the determination of certain compounds [5,6]. Similarly, the CL engendered by luminol–KIO_4 system in basic medium was enhanced [7–9] or inhibited [10] by some compounds and analytical methods have been developed founded on such vicissitudes [8–10]. Furthermore, the inhibition or enhancement of different organic compounds were linked to pH, number and position of –OH and $-NH_2$ functional groups as well as to the stability of free radicals generated in luminol–KIO_4–H_2O_2 CL reaction [11]. In addition, KIO_4 oxidizes organic compounds with vicinal –OH, –CHO, =CO, or –COOH groups, to aldehydes or ketones according to their structures [12]. Similarly, the oxidation of some polyhydric phenols like pyrogallol and gallic acid with H_2O_2 or IO_4^- was testified to give weak CL, with excited $^1O_2$ as emitter [5].

Generally, most weak CL enhancement by QDs (heavy-metal quantum dots) was brought about by an energy transfer process and is of great significance to explore the behavior of QDs for developing novel CL sensors. As, Zhou et al. demonstrated the enhancement of NaClO–H_2O_2 CL, to the catalysis of QDs, to decompose H_2O_2, producing $^1O_2$ and $(^1O_2)_2$, which by giving its energy to QDs resulted in enhanced CL [13]. These QDs, however, have raised environmental concerns, over potential toxicity and cost-effectiveness. Therefore, it is of great importance to develop simple, environmentally friendly and low-cost methods to synthesize carbon dots (CDs). CDs allocation the features of QDs, like good photo-stability and solubility in water. In tallying, CDs possess chemical stability, good biocompatibility and low toxicity, permit them to be best substitute for QDs [14,15]. However, surface-passivation is necessary to produce CDs with adequate quantum yields (QYs). Otherwise, highly photoluminescent (PL)

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http://dx.doi.org/10.1016/j.talanta.2016.02.056
0039-9140/

CDs could be produced using nitrogen containing precursors without surface-passivation [14]. As, Amino acids are inexpensive, abundant, biocompatible and environmental friendly, having both carboxyl and amino groups and may serve as an ideal molecular precursor for CDs. Cui et al. have prepared CDs using amino acid as a precursor under basic or acidic conditions through a microwave process [16], while Huang et al. recently reported microwave synthesis of N-CDs from histidine [14]. Generally, the electron-donating property of CDs was verified only under photo- and electronic induction. In contrast, Dou et al. found the electron transfer process from CDs to dissolved oxygen in concentrated NaOH without any external force by CL process [15], thus CDs take part in redox reactions to enhance CL process. Herein, one-pot easily attainable hydrothermal synthesis of fluorescent N-CDs from histidine, in environmental friendly way, without the use of any toxic reagent is reported. Up to the best of our knowledge, there is no report published to date on the CL enhancement and mechanism of KIO_4–H_2O_2–N-CDs system.

Gallic acid is an important polyphenol with significant applications, and has increasing interest as food preservative and antioxidant [17–19], in pharmaceutical industry [20], due to their biological properties, including antihistaminic, anti-inflammatory, antitumor activities, protecting against cardiovascular diseases and scavenging of free radicals [21]. Moreover, gallic acid has many other applications such as used for making dyes, inks, acting as anti-fungal, anti-viral, as reducing agent and anti-allergic possessing [22,23]. Additionally, it can be used as clarifying agent in wine industry, flavoring agent in foods, meat products and to treat albuminuria and diabetes [22]. However, gallic acid is often used as an indicator of adulteration of fruit juices and alcoholic beverages [24]. Indeed, the perseverance of gallic acid is of interest not only due to its importance in food, medicine and industrial products, but also due to its toxicity to animals, possibly because of its reactions with macromolecules, like DNA and proteoglycans [25]. As, many in vivo and in vitro studies in animals, human and cell culture have marked its subsequent actions [26]. Therefore, developing sensitive method for gallic acid is very essential. Similarly, pyrogallol is a vital polyphenol with stout reducing properties and has been widely used as an antioxidant, scavenger of free radicals and reactive oxygen species [27]. On the other hand, pyrogallol has been widely used in many industries, including pharmaceuticals, plastics and cosmetics, acting as an antiseptic and dying material. Ever since, an active ingredient in industry, pyrogallol is usually found in industrial wastes. It is very essential to develop a sensitive method for pyrogallol monitoring because of concern of its inherent toxicity and environmental threat [20]. Thus the fortitude of pyrogallol is very important in chemical, environmental, clinical and biological systems. In summary, due to importance of gallic acid and pyrogallol, a need is felt for a better analytical method for its determination with high sensitivity. Based on this, a rapid, simple and direct detection method was proposed for gallic acid and pyrogallol determination. Moreover, this CL system showed virtuous performances such as high sensitivity and reproducibility, wide linear range and short analysis time.

2. Experimental

2.1. Chemicals and materials

Analytical grade chemicals were used during our work.HCl were obtained from Tianjin Kaitong Chemicals Co. (Tianjin, China) and 2,2,6,6-Tetramethyl-4-piperidine (TEMP) from SigmaAldrich (St. Louis, MO, USA). Whereas, thiourea, NaN_3, H_2O_2, ascorbic acid and NaOH were purchased from Beijing Chemical Reagent Co. (Beijing, China), nitro blue tetrazolium chloride (NBT) from Nacalai Tesque Inc. (Tokyo, Japan) and DMPO (5,5-Dimethyl-1-pyrroline N-oxide) from Tokyo Kasei Kogyo Co. Ltd. (Tokyo, Japan). In addition, histidine was purchased from Beijing Dingguochangsheng Biotechnology Co. Ltd. and KIO_4 from Beijing Zhonglian Chemical Reagents (Beijing, China).The solutions were prepared in distilled water and stored at 4 °C.

2.2. Apparatus

The CL was carried out with a BPCL Luminescence analyzer (Department of Chemistry, Tsinghua University, Beijing, China). Similarly, F-7000 fluorescence spectrophotometer (Hitachi, Japan) was arrayed for the photoluminescence and UV-3900s Spectrophotometer (Hitachi, Japan) for absorption studies. In addition, N-CDs were characterized by transmission electron microscope (TEM, Tecnai G2 20S-Twin, FEI Company, USA) at 200 kV. While, Bruker spectrometer (ESP-300E, Bruker, Germany) was deployed for EPR analysis.

2.3. Preparation and characterization of N-CDs

A commercial autoclave reactor (30 mL with Teflon lining and having stainless steel sheet) was used to prepare N-CDs. For this purpose 20 mL of 0.1 M solution i.e. a total of 3.1 g of histidine was dissolved into 20 mL distilled water and transferred to 30 mL Teflon lined autoclave. The reaction vessel was maintained at 240 °C for 8 h and then cooled to room temperature. As a result, brownish black solution was obtained which was filtered from 0.22 μm membrane and used as such for CL studies without any further processes.

Indeed, a nitrogen-rich amino acid, histidine was used as a lone source to synthesize N-CDs through one-pot hydrothermal method. The syntheses was carried out, without the involvement of salt, base, acid, organic solvent or any other reagent, in an environmental friendly way. In this process, the high temperature (240 °C) and pressure supplied energy by hydrothermal route, enabling dehydration and carbonization through reaction between the amino and carboxyl groups of histidine. As a result, the prepared N-CDs possess excellent solubility in water without any surface passivation, which may instigate from –COOH, –OH and –NH^{3+} groups on its surface [14]. Furthermore, HR-TEM studies showed that the average size of the N-CDs were 5 nm (Fig. 1). Moreover, the concentration of N-CDs solution was calculated according to the concentration of precursor solution.

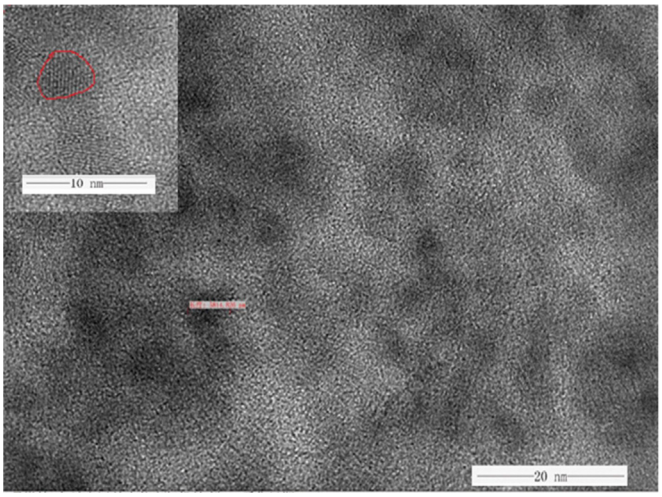

Fig. 1. HR-TEM image of the water soluble N-CDs. A single N-CD magnified in the inset. The corresponding size histograms are given aside.