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Graphene quantum dots/bisulfite assisted chemiluminescence of rhodamine B-H_2O_2 system for sensitive recognition of HCHO

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ABSTRACT

A novel and powerful chemiluminescence (CL) system was developed based on the promoting effect of graphene quantum dots (GQDs)/bisulfite on rhodamine B (RB)-H_2O_2 CL reaction. GQDs were synthesized by a simple, green and affordable approach and characterized using their distinctive absorption and emission patterns. X-ray diffraction (XRD), Fourier transform infrared (FT-IR) transmission and transmission electron microscopy (TEM) analysis were implemented for complementary studies on the structural and morphological characteristics of GQDs. The simultaneous enhancing effect of the synthesized GQDs and bisulfite on the CL emission of RB-H_2O_2 reaction provided a more strong and efficient CL system. The mechanism of CL emission was described. Furthermore, HCHO as a well-known pollutant, could selectively diminish the developed CL system. This effect was linearly proportional to HCHO concentration which turned the introduced CL system to a susceptible chemosensor for HCHO. Under the optimized operational condition, the linear changing of CL response was obtained in HCHO concentration ranges of 0.02–5 $\mu g\,L^{-1}$ and 5–11 $\mu g\,L^{-1}$, with limit of detection (LOD) and quantification (LOQ) of 6 $ng\,L^{-1}$ and 20 $ng\,L^{-1}$, respectively. Ultimately, presented CL chemosensor was served as an accurate tool for determination of formaldehyde concentration in water and wastewater samples.

1. Introduction

Chemiluminescence (CL), as an electromagnetic emission through a chemical reaction, have been extensively accepted as a potent analytical device with a large diversity of advantages such as the ease of operation, simple and inexpensive instrumentation with a very low detection limit and excellent sensitivity [1]. In recent decades, nanomaterials have been effectively exploited as an active unit in various CL systems due to their unique physicochemical attributes [1–3]. Several researchers have reported the positive effect of various nanostructures on CL reactions that reveal the high potential of nano-assisted CL methods for analytical purpose [1–4]. In reported systems, the studied nanomaterials acted as the emitting luminophore, catalyst and/or energy acceptor.

Carbonaceous compounds, as an old companion of human kind, have been attracted the attention of the researchers for using them to develop modern science and technology [5]. In the last two decades, we witnessed the discovery of the carbon-based nanomaterial (CBN). Graphene, an important subclass of CBN, has two-dimensional (2D) structure which consists of a single sheet of carbon atoms arranged in a honeycomb configuration [5–9]. The impressive characteristics of low toxicity, excellent chemical and thermal stability, high flexibility and unique electrical and optical properties of graphene has captivated the scientists' consideration [5,9–11]. Graphene quantum dots (GQDs) are small fractions of graphene with the sizes of less than 100 nm. Conversion of two-dimension graphene sheets to zero-dimension GQDs results in development of quantum confinement and edge effects following presence of band gap in GQDs [12–16]. Consequently, GQDs show potent photoluminescence properties which extend their range of applicability. Moreover, the layer structure of graphene is maintained in GQDs, thus, they have higher surface area with a better surface grafting features compared to other carbon-based nanostructures. GQDs display great water solubility, low toxicity, outstanding stability, and desirable biocompatibil-

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ity [12,15,17–19]. So, it is expected that the application of GQDs in CL analytical methods provide many important benefits. From the reports, GQDs participate in CL systems as emitting species, catalysts or cause an efficient CL resonance energy transfer. For example, Al-Ogaidi et al. [20] have evaluated the participation of GQDs as energy acceptors in a CL resonance energy transfer process and have introduced an immunoassay for ovarian cancer biomarker CA-125. In another study, Amjadi et al. [18,21,22] reported some sensitive CL analytical application of GQDs based on their catalytic and emitting activities.

Formaldehyde (HCHO) belongs to the aldehyde class with a characteristic pungent odor which is a well-known toxic compound. It has serious hazardous effect on human health, since, it stimulates critical cells of human body like nervous and sight systems and also brings about insomnia, nausea, headaches, and allergic skin reactions [23–27]. The certain characteristics of HCHO such as preservation, disinfectant and bleaching have paved the way for implementation of this organic compound in several industrial sectors, such as food, coating, adhesive and cosmetics [27]. On the other hand, automobile exhaust gases and photo-oxidation of hydrocarbons are key sources of HCHO that result in its existence in the atmosphere which cause atmospheric deposition and aquatic environment contamination [28]. International Agency for Research on Cancer (IARC), the Environmental Protection Agency (EPA), the US National Toxicology Program, and the Occupational Safety and Health Association (OSHA) evaluated the cancer risk of HCHO on human and categorized this compound as a carcinogenic [25]. Contamination of aquatic environment with HCHO remains a challenge for analytical researches to construct a novel technique for simple and accurate determination of this compound. Various procedures have been introduced for this purpose, including fluorimetry [29–33], surface-enhanced Raman scattering (SERS) [26,34,35], chromatography [23,25], spectrophotometry [36–39], and chemiluminescence (CL) [28,40–43]. Among these procedures, CL technique causes great sensation, so that several valuable surveys have been triggered for implementation of CL as a promising procedure in important fields [44].

Here, a strong CL system based on rhodamine B (RB) oxidation was introduced as a high efficient and sensitive chemosensor for HCHO. GQDs were synthesized via a simple and green approach and it is indicated that prepared GQDs have a remarkable promoting effect on the chemiluminescence emission produced by RB-H_2O_2 reaction. Subsequent investigations revealed that the presence of sodium dodecyl sulfonate (SDS) and sodium bisulfite lead to a greater enhancement effect of GQDs. Furthermore, it is interestingly observed that HCHO manifested diminishing effect on the resulted RB-H_2O_2-GQDs-SDS-$NaHSO_3$ CL system. The quenching influence of HCHO on the RB-H_2O_2-GQDs-SDS-$NaHSO_3$ caused a considerable sensation for employing of the aforementioned CL technique for HCHO determination (Scheme 1).

2. Experimental

2.1. Chemicals and instruments

Most of the chemicals including glucose, rhodamine B (RB), sodium bisulfite, sodium dodecyl sulfate (SDS), etc. were of analytical grade and purchased from Merck Co. (Germany) and employed without further purifying process. Deionized water was consumed throughout the experiments. Stock standard solution of HCHO (50 mg L^{-1}) was provided by dilution of 125 μL of 37% HCHO solution using deionized water.

The CL responses of the associated reactions were received through a FB12 luminometer (Berthold detection systems, Germany) as emission detector and a connected computer for

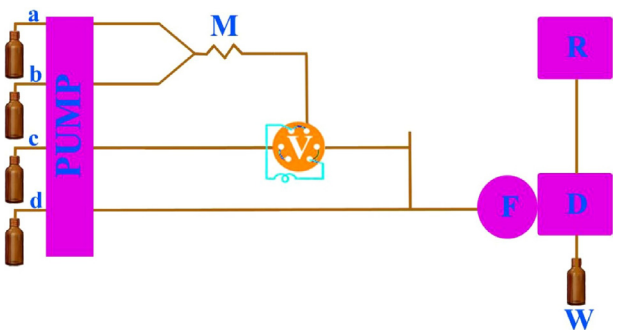

Fig. 1. Schematic diagram of flow-injection CL system; (a): NaOH solution; (b): Mixture of rhodamine B, GQDs, SDS and $NaHSO_3$ with or without HCHO sample or standard solution (c): H_2O as the carrier; (d): H_2O_2 solution; M: mixing tube; V: injection valve; F: flow cell; W: waste; D: detector (photomultiplier tube); and R: recorder (computer).

data evaluations. Ultraviolet–visible (UV–vis) spectra were collected by an UV–vis spectrophotometer (S2000, WPA Lightwave, England). The crystal phase (crystalline phase configuration) of the prepared GQDs was assessed via the X-ray diffraction (XRD) spectrum achieved from Siemens X-ray powder diffractometer (D5000, Siemens, Germany) occupying Cu Kα as the exciting source (λ = 1.54056 Å) at room temperature. The Fourier transform infrared (FT-IR) appraisal was accomplished on a IR-spectrometer (Tensor 27, Bruker, Germany). Moreover, the morphological assays of GQDs were conducted by the participation of transmission electron microscopy (TEM) image gained from Cs-corrected TEM (JEM-2200FS, JEOL, Japan) acting at 200 kV. For recording CL spectra, spectrofluorometer (Shimadzu RF-5301, Japan) without excitation source was employed.

2.2. Procedure of CL assessments

Fig. 1 illustrates the schematic arrangement of different divisions of the employed CL system in flow mode. This apparatus was composed of four channels constructed by polytetrafluoroethylene (PTFE) tubes with internal diameter (i.d.) of 1.0 mm (NaOH solution in line *a*, the mixture of RB, GQDs, SDS and $NaHSO_3$ with or without HCHO standard or sample solutions in line *b*, deionized water as carrier in line *c*, and H_2O_2 solution as oxidant in the line *d*). The carrier stream was carrying the mixed output of the streams concerning to line (a) and (b), combined by Y-pieces. This was conducted via a six-port valve possessing 150 μL loop. CL emission was triggered after the inserting of the mixed streams to the flow cell and combining with H_2O_2 solution, which was placed in front of the detector. The mentioned structure was equipped with software provided by the Berthold Company to process the CL emission. The determination of HCHO was accomplished regarding to the quenching impact of HCHO on the CL which was calculated using the formula: $\Delta I = I_0 - I_s$, where I_0 and I_s are representative of CL responses in the absence and presence of HCHO, respectively.

2.3. Synthesis of graphene quantum dots

GQDs were synthesized by glucose as a the main precursor [18]. Briefly, 6.0 g of pure glucose powder was melted. The heating was continued to complete the polymerization process of glucose molecules leading to the formation of a clear and orange color solution. This color change of the solution was an indicator for the GQDs production. 25 mL of deionized water was added to the resultant liquid with vigorous stirring. It is worthy to note that the resultant GQDs can be kept in the refrigerator at 4 °C for a long time without any changes. Moreover, the sizes of the synthesized GQDs could be