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Full Length Article

Chemiluminescence of graphene quantum dots induced by acidic potassium permanganate and its application to quenchometric flow-injection assays of hydroquinone in water

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ABSTRACT

Graphene quantum dots (GQDs) with particle size of 4.5 ± 1.0 nm were prepared and characterized by transmission electron microscopy, UV–vis absorption spectroscopy and fluorescence spectroscopy. It was found that $KMnO_4$ could oxidize GQDs to produce a relatively intense chemiluminescence (CL) emission. The mechanism of CL generation was investigated based on absorption spectra and CL emission spectra. CL emission was attributed to the radiative recombination of oxidant-injected holes and thermally excited electrons in the GQDs. On the other hand, both $KMnO_4$ and $\bullet O_2{}^-$ could react with GQDs to produce $GQDs\bullet^+$ and $GQDs\bullet^-$. The electron-transfer annihilation of $GQDs\bullet^+$ and $GQDs\bullet^-$ could form excited-state GQDs*, which acted as the final emitter in the system. In order to show the analytic potential of GQDs–$KMnO_4$ CL system, it was applied for the determination of hydroquinone based on its diminishing effect. Under the optimized conditions, the proposed CL system exhibits excellent analytic performance for determination of hydroquinone. Calibration curve in the range of 2.49×10^{-4}–9.96×10^{-7} g mL^{-1} was linear with the correlation coefficient (r) of 0.9924. The limit of detection was 8.46×10^{-8} g mL^{-1}, and the relative standard deviation (RSD) was found to be 1.7% for 11 determinations of 4.98×10^{-6} g mL^{-1} hydroquinone. The applicability of the method was verified by applying to real tap water, lake water, and waste water samples. The recoveries were in the range of 89.7–97.1% with RSD of 0.9–2.1%. The proposed method has a good linearity, high sensitivity and good repeatability and can be applied for routine determination of hydroquinone in water.

1. Introduction

Chemiluminescence (CL) can be produced by direct oxidation of target compound to produce emitting species or by indirect enhancing or inhibitory effects of certain luminescence compounds. Metal-based quantum dots were used for enhanced CL analysis [1–3]. The carbon quantum dots (CQDs) and graphene quantum dots (GQDs) are new fluorescent carbon nanomaterial. The CQDs are always spherical with obvious crystal lattice. The GQDs possess single or few layers graphene and connected chemical groups on the edge. They are anisotropic with lateral dimension larger than the height. GQDs have gained tremendous attention owing to their unique and tunable photoluminescence (PL) properties, exceptional physicochemical properties, high photostability, biocompatibility, and small size [4]. These properties make them much more desirable for many applications compared with inorganic semiconductor QDs [5,6]. However, there were only two reports on application of GQDs in CL analysis. Ce(IV) can directly oxidize GQDs to give rise to CL emission at 470 nm and the CL was applied for the determination of uric acid [7]. Hypochlorite can directly oxidize GQDs to give rise to CL emission at 510 nm which was applied for the determination of chlorine [8]. To the best of our knowledge, the research on the CL properties of GQDs-oxidant is still in an early stage and the full potential of this material has not yet been fathomed.

Hydroquinone is widely used in tanning, cosmetics, the pharmaceutical industry, and in developing photographs, it is important environmental pollutants. It is harmful to humans and animals even in very low concentration. Therefore, it is very important to develop a highly sensitive method for the determination of hydroquinone in environmental waters. Wang et al. reviewed in 2015 the research progress of the major methods for detecting hydroquinone, including chromatography, spectrometry, chemiluminescence and electrochemistry [9]. Recently, Elghobashy et al. described successive ratio subtraction coupled with constant multiplication spectrophotometric method for determination of

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hydroquinone in complex mixture with its degradation products [10]. Although some fluorometric and colorimetric chemosensors have been developed for detection of cyanide ions and anionic species [11,12], there was only two papers for the determination of hydroquinone by the luminol–$K_3Fe(CN)_6$–ZnSe quantum dots CL system [13] and luminol–Co(II)–H_2O_2–CdTe quantum dots CL system [14]. To our knowledge there was no report for the application of GQDs-CL in hydroquinone analysis.

This work is to investigate the UV absorption, fluorescence and direct CL properties of the GQDs induced by $KMnO_4$. A mechanism of GQDs–$KMnO_4$ CL reaction was suggested based on the CL emission spectra and the effects of radical $\bullet O_2^-$ on the CL intensity. Finally, the application potential of this CL system was investigated. A sensitive flow-injection GQDs–$KMnO_4$ CL method without any luminescence reagent for the selective determination of hydroquinone in water samples was developed.

2. Experimental

2.1. Instrument

WP800T Microwave oven working at 2450 MHz with an output power of 800 W (Galanz Electrical Appliances Enterprise Co., Ltd., Shongde, China) and 84 – 1 magnetic stirring temperature control electric heating sleeve (Shandong Juancheng Hualu Electric Instrument Co., Ltd.) was used to synthesize GQDs. A Double Light Spectrophotometer (Beijing TAYASAF Science & Technology Co., Ltd, China), GL-9406 portable UV reflectance meter (Haimen kylin medical instrument factory, China) and F-7000 Fluorescence spectrophotometer (Hitachi, Japan) were used to investigate the characteristics of GQDs and mechanism of CL emission. An IFFM-E flow-injection CL analysis system (Remex Electronic Sci-Tech. Co. Ltd, Xi'an, China) was used for CL analysis.

2.2. Chemicals and reagents

Poly(ethylene glycol) with average molecular weight of 200 (PEG 200) were purchased from Merck (Darmstadt, Germany). Citric acid (99.5%), sodium hydroxide (96.0%), sulfuric acid(98.0%), potassium permanganate (99.5%), glutathione (98%), and hydroquinone (99.0%), were purchased form Kermel Chemical Reagent Co., Ltd. (Tianjin, China). Diperiodato-nicklate(IV), diperiodato-cuprate(III), and diperiodato-argenate(III) were prepared by oxidizing Ni(II), Cu(II), and Ag(I) in alkaline solutions according to the literature [15]. Hydroquinone stock solutions, 2.59×10^{-3} g mL^{-1} was prepared and stored in a refrigerator at 4 °C to keep dark. More dilute solutions were prepared freshly by diluting the stock solution with deionized water.

2.3. Synthesis of GQDs

GQDs were synthesized according to the literature [16]. Briefly, 2 g citric acid was put into a 5 mL beaker and heated to 200 °C using a heating mantle. About 5 min later, the citric acid was melted. Subsequently, the color of the liquid was changed from colorless to pale yellow, and then orange in 30 min, implying the formation of GQDs. Concentration and dialysis were used to purify the obtained products. 100 mL of 10 mg mL^{-1} NaOH solution was added into the orange liquid drop wise with continuous and vigorous stirring. The obtained solutions (adjusted to pH 7) were stable for at least one month in the refrigerator at 4 °C.

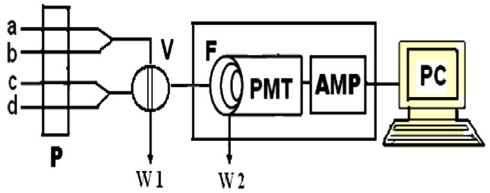

Fig. 1. Schematic diagram of flow injection chemiluminescence analysis system, P—peristaltic pump; V—sampling inlet valve; F—flowing cell: a flat spiral-coiled colorless glass tube (i.d. 1.0 mm, total diameter of the flow cell 3 cm, without gas between loops); PMT—photomultiplier tube; AMP—amplifier; PC—recorder; W—waste; a—mixture solution of GQDs; b—H_2SO_4 solution; c—$KMnO_4$ solution; d—sample solution.

2.4. CL monitoring

A flow-injection CL analysis system is shown in Fig. 1. Sampling volume 120 μL and flow rate 3.0 mL/min. Calibration curve for the quenching value of CL intensity (peak height) versus logarithm of analyte concentration was constructed for the analysis of real samples.

3. Results and discussion

3.1. Characterization of GQDs

The size and the edge-shape effects of GQDs are significant for the visible light absorption properties of GQDs. The sizes of GQDs were controlled via varying the reaction temperatures. The edge-shape effect is enhanced with an increase in size of square GQDs [17]. In this work, a simple carbonization method was used for synthesis of GQDs. The TEM image of the GQDs is shown in Fig. 2. GQDs present nearly monodisperse nanoparticles with particle size of 4.5 ± 1.0 nm for 100 GQDs.

The photographs inserted in Fig. 3 shows the prepared GQDs exhibit a bright blue emission under ultraviolet radiation (365 nm). The UV–vis absorption spectrum of the prepared GQDs exhibits typical absorption of graphene derivatives in the UV region (200–300 nm) which was assigned to the π–π^* transition of aromatic sp^2 domains [18]. Another broad band at ~345 nm was also observed, which is associated with the n–π^* transition of C=O bond of surface carboxylic groups [19].

In the present work, the optical properties of the photoluminescence (PL) spectrum of the GQD$_S$ were explored (Fig. 3). When excited at 300–425 nm with increments of 25 nm, the GQD$_S$ exhibit an excitation-dependent PL emission, this implies the uniformity of both the size and the surface state of those sp^2 clusters contained in GQDs, which is responsible for the fluorescence of GQD$_S$. A corresponding PL emission peak is broad due to the wide size distribution of GQD$_S$. Moreover, the emission wavelength red-shifted with increasing excitation wavelength. The PL emission peak should be attributed to the $n \rightarrow \pi^*$ transition of C=O bond of surface carboxylic groups [20]. The maximum PL emission at ~470 nm for the prepared GQDs was found with an excitation wavelength of 400 nm [7]. The spectroscopic properties of GQDs may vary depending on the method of preparation and the functional groups at the edges of the particles. As compared with the metal-based quantum dots, GQDs showed low-cost, low toxicity, highly soluble in various solvents and can be equipped with functional groups at their edges.

3.2. Choice of oxidant and optimization of CL reaction conditions

A relatively strong CL emission of GQDs was induced by direct chemical oxidation with Ce(IV) [7] and hypochlorite [8]. In this