Carbon 121 (2017) 72–78

Contents lists available at ScienceDirect

Carbon

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

A facile method to sensitively monitor chlorinated phenols based on $Ru(bpy)_3^{2+}$ electrochemiluminescent system using graphene quantum dots as coreactants

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ARTICLE INFO

Article history:
Received 12 February 2017
Received in revised form
20 April 2017
Accepted 11 May 2017
Available online 12 May 2017

Keywords:
Graphene quantum dot
$Ru(bpy)_3^{2+}$
Electrochemiluminescence
Detection
Phenol

ABSTRACT

Except the tunable photoluminescent property, graphene quantum dots (GQDs) with special structures have also exhibited other novel properties. Herein, GQDs played a novel coreactant role in $Ru(bpy)_3^{2+}$/GQDs system to increase the anodic ECL signal of $Ru(bpy)_3^{2+}$, which has been testified by ultraviolet, fluorescence, and electrochemiluminescence (ECL) experiments. Based on the coreactant mechanism of $Ru(bpy)_3^{2+}$/GQDs system, a chlorinated phenol-related quenching ECL sensor was designed and the sensor showed a good linear relationship in the range from 0.60 to 55 μM with the detection limit of 1.4×10^{-8} M (S/N = 3). These results were not only beneficial to resolve the structure of GQDs, but also expanded the application field of GQDs.

1. Introduction

Graphene quantum dots (GQDs), characterized by surface oxygenous functional groups, have recently exhibited a great potential in biosensing and bioimaging for its small size, low cost, superior photoluminescence (PL), electrochemiluminescence (ECL), excellent biocompatibility, etc. [1–7] The synthesis methods, properties, biological applications, and comparisons with other QDs (such as carbon QDs) of GQDs have been well summarized in these comprehensive reviews [6–8]. In recent years, the ECL of GQDs has been extensively studied and shown an increasing trend [9]. GQDs could be used as ECL labeling signals for immunoassays [9–13]. Especially, GQDs could also catalyze or amplify other ECL luminophor such as CdS [14], $Ru(bpy)_3^{2+}$ [15,16], and luminol [17]. This property was generally attributed to the surface oxygen on GQDs [18], since most of oxygen-containing compounds (e.g., alcohols) have been reported to serve as the coreactants in ECL [19–21]. However, little research has been done regarding what the exact surface functional groups on GQDs were and how they resulted in the corresponding properties.

Chlorinated phenols were a typical group of persistent organic pollutants in the environment, and several of them have been listed as priority pollutants by the US Environmental Protection Agency and classified as a group 2B environmental carcinogen by International Agency for Research on Cancer. Extensive work has been carried out on the trace detection of chlorinated phenols in the past decade [22–24]. However, those methods required bulky equipment and tedious sample preparation. ECL technique represented the marriage of electrochemistry with spectroscopy and became a powerful analytical technique with the merits of rapidity, high sensitivity, and selectivity [20,21,25,26]. GQDs-based ECL sensing was a powerful detection method and has been widely reported for the detection of chemical and biological species. However, reports on the environmental detection by adopting GQDs-based ECL sensing were relatively scarce [27], though it had the merits of miniaturization, inexpensive instrumentation, excellent detection sensitivity, and high selectivity.

Herein, GQDs were introduced into the well-studied $Ru(bpy)_3^{2+}$-

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http://dx.doi.org/10.1016/j.carbon.2017.05.045

ECL system. The purpose of the present study was to reveal the role that GQDs played in the anodic ECL of $Ru(bpy)_3^{2+}$, and develop more efficient and environmentally friendly coreactants for $Ru(bpy)_3^{2+}$ ECL assays. This work has provided an insight into the knowledge of GQDs, which would be beneficial for its further application.

2. Materials and methods

2.1. Materials

Graphene sheets and $Ru(bpy)_3Cl_2{\cdot}6H_2O$ were purchased from Nanjing XFNANO Materials Tech Co., Ltd and Sigma-Aldrich Chemical Corporation, respectively. All other reagents were analytical grade and obtained from Sinopharm Chemical Reagent Co., Ltd. The ultrapure water used in the experiment was from a Synergy ultrapure water system (Millipore).

2.2. Preparation of GQDs

Graphene sheets (10 mg) were oxidized in piranha solution (10 mL, V_{H2SO4}: V_{H2O2} = 7: 3) at 80 °C for 1 h (*Caution*: piranha solution is highly corrosive). Then the obtained green mixture was diluted with deionized water (250 mL) and adjusted to neutrality with sodium hydroxide in the ice-water bath. After that, the resulting solution was dialyzed in a dialysis bag (1 kDa molar mass cutoff) for 5 days to remove the salt. After concentration, the strongly fluorescent part with nominal molecular weight of <3 kDa was obtained via ultrafilter and denoted as GQDs.

2.3. Preparation of R-GQDs

For the reduction of GQDs, excess sodium borohydride (0.1 g) was added into an aqueous GQDs (~1.0×10^{-6} g/mL 100 mL) and stirred gently overnight at room temperature. Then, dialysis was adopted to remove the excess reductant as mentioned above.

2.4. Characterization

Fluorescence spectra were recorded on a Horiba Jobin Yvon Fluorolog-3 fluorescence spectrometer. High resolution transmission electron microscopy (HR-TEM) images were performed on a JEOL JEM-2100F high-resolution field-emission transmission electron microscope. Atomic force microscope (AFM) images were taken using a SPM-9500J3 AFM by the tapping mode on the mica substrate. FT-IR spectra were obtained on a Thermo Nicolet 360 FT-IR spectrophotometer. X-ray photoelectron spectrometer (XPS) spectra were collected using a VG Multilab 2000 XPS. Raman spectra were obtained from 1200 to 3000 cm^{-1} using a confocal Raman microspectroscopy (Renishaw RM-1000, excitation at 514 nm).

The ECL measurements were conducted on a MPI-E II ECL analytical system (Xi'an Remex Analytical Instrument Co., Ltd.) with a three-electrode configuration including a glass carbon working electrode, a Pt-wire counter electrode, and a Ag/AgCl reference electrode. By using cyclic voltammetry within the potential region of −1.5–0 V at a scan rate of 0.1 V s^{-1}, ECL signals of GQDs and 0.2 μM $Ru(bpy)_3^{2+}$ in the electrolyte containing phosphate buffer solution (PBS, 0.2 M, pH 7.2) were obtained and collected simultaneously by the photomultiplier tube (PMT) biased at 900 V. The ECL spectrum was obtained by collecting the ECL peak data at + 1.13 V with 10 pieces of long-pass filters from 700 to 455 nm between the cell and photomultiplier.

3. Results and discussion

GQDs were prepared according to the previous report with a little modification [28]. TEM image suggested that uniform and monodisperse GQDs with an average diameter of (2.8 ± 0.2) nm (statistical analysis of at least 200 GQDs) were obtained (Fig. 1a and c). HR-TEM images (Fig. S1a) indicated that the lattice spacing of GQDs was about 2.13 Å and 1.80 Å, corresponding to the 100 and 102 facet of graphite (PDF#65-6212), respectively. AFM measurements showed that the topographic heights of GQDs were both about 1 nm (Fig. S1b), indicating that most of GQDs were present in a single layer. GQDs exhibited excitation-dependent properties with the maximum emission peak at 497 nm (Fig. 1d). Under irradiation with a 365 nm UV lamp, GQDs showed bright blue-green PL (Fig. 1b) with a quantum yield of 7.4% (Quinine sulfate as reference). XPS showed that the oxygen-to-carbon ratio of graphene and GQDs was 0.14 and 0.61, respectively. As shown in Fourier transform infrared spectroscopy (FT-IR) (Fig. 2a), GQDs displayed the stretching vibrations of O–H (3435 cm^{-1}), C–H (2925 and 2850 cm^{-1}), COOH (1723 cm^{-1}), C=O (1618 cm^{-1}), and C–O (1096 cm^{-1}), along with the rocking vibrations of C–H (1433 and 1338 cm^{-1}). Both FT-IR and XPS spectra showed that the density of oxygenous groups on GQDs was obviously increased in comparison with the starting material graphene. Besides, some unsaturated groups, such as C=C, were also detected on GQDs surface from the Uv–vis absorption (Fig. 1d). GQDs showed a continuously rising absorption with a defined peak at 290 nm, which was assigned to the π-π^* transition of the conjugation system within GQDs. The Raman spectrum (Fig. S2) also provided convincing evidence of the conjugation system within GQDs. The relative intensity of the “disorder” D-band and the crystalline G-band (I_D/I_G) for as-produced GQDs in this work was only around 0.840, similar to that of GQDs fabricated from graphite intercalation compounds (0.873) [29]. It indicated the high quality of as-prepared GQDs, which was attributed to the proper oxidation system.

We have recently reported a solvothermal transformation of graphene to GQDs in piranha solution. More specifically, a pair of reversible redox peaks with the formal potential located at 0.29 V and an irreversible oxidation peak located at 0.85 V were detected by electrochemical method (Fig. 3c). The reversible redox peaks have already been attributed to *ortho*-quinone derivatives at the edge of GQDs in our previous work [28]. Based on the specific reaction between *ortho*-quinones and 1,2-diamines, an efficient edge-functionalization strategy has been successfully employed to tune the PL properties of GQDs. In this work, we are not only interested in the origin of the irreversible oxidation peak from GQDs, but also its related application.

Herein, GQDs were introduced into the typical $Ru(bpy)_3^{2+}$-ECL system. Their electrochemical behaviors and ECL signals were recorded at the glass carbon electrode (GCE). As shown in Fig. 3a, GQDs alone exhibited an irreversible redox located at 0.85 V (black curve). $Ru(bpy)_3^{2+}$ alone showed a reversible redox with a formal potential of +1.07 V (blue curve). After the addition of GQDs, the oxidation peak of $Ru(bpy)_3^{2+}$ was increased while the reduction peak was almost disappeared (green curve). This indicated a catalytic oxidation of GQDs by electrogenerated $Ru(bpy)_3^{3+}$. The similar catalytic oxidations were also observed in the coreactant ECL systems $Ru(bpy)_3^{2+}$/tripropylamine (TPrA) [30], where TPrA was first catalytically oxidized to $TPrA^{+\bullet}$ by electrogenerated $Ru(bpy)_3^{3+}$. The ECL curves showed that the mixture $Ru(bpy)_3^{2+}$/GQDs exhibited a strong ECL signal rising at + 1.00 V and peaking at + 1.13 V (Fig. 3b, green curve), which was consistent with the electrochemistry of $Ru(bpy)_3^{3+}$. However, $Ru(bpy)_3^{2+}$ (blue curve) or GQDs (black curve) alone showed weak anodic ECL signals. Furthermore, the ECL spectrum of the mixture at 600 nm agreed with the PL spectrum of