



# Electrochemiluminescence sensor for hexavalent chromium based on the graphene quantum dots/peroxodisulfate system



Yingmei Chen<sup>1</sup>, Yongqiang Dong<sup>1</sup>, Huan Wu, Congqiang Chen, Yuwu Chi<sup>\*</sup>, Guonan Chen

MOE Key Laboratory of Analysis and Detection Technology for Food Safety, Fujian Provincial Key Laboratory of Analysis and Detection Technology for Food Safety, and Department of Chemistry, Fuzhou University, Fujian 350108, China

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## ABSTRACT

A electrochemiluminescent (ECL) sensor has been designed to detect hexavalent chromium (Cr(VI)) in environmental water samples based on the fact that Cr(VI) can collisionally quench the ECL signal of graphene quantum dots/peroxodisulfate (GQD/S<sub>2</sub>O<sub>8</sub><sup>2-</sup>) system. After optimizing some important experimental conditions including the concentrations of GQDs and S<sub>2</sub>O<sub>8</sub><sup>2-</sup>, response time, and pH value of solution, the ECL sensor has been finally developed. The ECL sensor exhibits a wide linear response range (50 nM–60 μM), excellent selectivity, and high sensitivity (detection limit of 20 nM, S/N=3). Furthermore, the developed sensor has been applied in the detection of Cr(VI) in a spiked river water. The result suggests that the sensor can offer a simple, green, low cost, high selectivity and sensitivity detection of Cr(VI).

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## 1. Introduction

Graphene quantum dots (GQDs), graphene nanosheets of less than 100 nm in lateral size [1], are emerging luminescent carbon nanomaterials. Due to the quantum confinement and edge effects, GQDs exhibit many unique optical properties such as photoluminescence (PL), chemiluminescence (CL), and electrochemiluminescence (ECL) [2,3]. The PL of GQDs has attracted tremendous attention, and has been applied in many fields such as bio-imaging, cell-imaging and sensing [4,5]. Contrarily, much less attention has been paid to the ECL of GQDs [6,7]. ECL is a CL that triggered by electrochemical methods. The analytical methods based on the ECL signal combine the advantages of CL and electrochemical analysis [8], and accordingly show many distinct advantages including no optical background, easy reaction control, high sensitivity and selectivity, and wide response range [9,10]. Therefore, the ECL properties of GQDs are apparently very important in terms of analytical applications. Actually, GQDs have been applied in the detection of some cations based on their ECL activities [11,12].

Chromium, an important alloying element, is predominantly used in metallurgy, e.g., electroplating, leather tanning, metal

smelt stabling and metal finishing industries [13]. In aqueous systems, chromium mainly exists in two oxidation states: trivalent chromium (Cr(III)) and hexavalent chromium (Cr(VI)) [14]. Cr(VI) is essential and beneficial for humans [15,16], while Cr(VI) is a highly toxic species and a suspected carcinogenic agent [17]. After entered blood circulation through digestive tract, Cr(VI) can damage the structure and function of hepatocytes due to its strong oxidation property, resulting in Cr(VI) hepatotoxicity [18]. Accordingly, it is vitally important to develop an effective method to precisely detect trace concentration Cr(VI). Various analysis techniques have been used to determine Cr(VI), including inductively coupled plasma mass spectrometry [19], inductively coupled plasma-optical emission spectrometry [20], inductively coupled plasma atomic emission spectrometry [21], electrothermal atomic absorption spectrometry [22], graphite furnace atomic absorption spectrometry [23], reversed-phase ion-pair chromatography [24], X-ray fluorescence spectrometry [25], ECL spectrometry [26], and stripping voltammetric methods [27,28]. However, most of these methods suffer from some disadvantages, such as complex process, long response time, low sensitivity, and high cost of the instruments. Furthermore, many methods can only detect the total quantity of chromium, but are not able to distinguish Cr(VI) from Cr(III). Therefore, developing a simple and fast method to detect Cr(VI) sensitively and selectively is of interesting.

Herein, Cr(VI) was found to be able to quench sensitively the strong cathodic ECL signal of GQD/S<sub>2</sub>O<sub>8</sub><sup>2-</sup> system. After optimizing

<sup>\*</sup> Corresponding author. Tel./fax: +86 591 22866137.  
E-mail address: [y.w.chi@fzu.edu.cn](mailto:y.w.chi@fzu.edu.cn) (Y. Chi).

<sup>1</sup> These authors contributed equally to this work.

some important experimental conditions, a sensitive and selective sensing system would be developed to detect Cr(VI) in domestic water.

## 2. Experimental

### 2.1. Chemicals

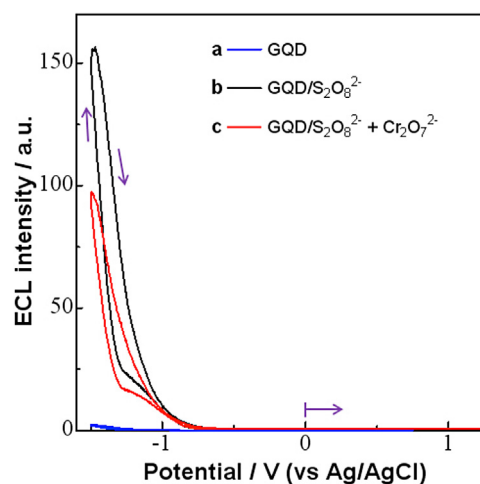
Vulcan CX-72 carbon black (Cabot Corporation) were used to prepare the single layer GQDs.  $K_2S_2O_8$  (>99.99%) was obtained from Sigma-Aldrich. All other reagents were of analytical grade and used as received. Doubly distilled water was used throughout the experiment. Phosphate-buffered saline (PBS) solutions of different pH values were prepared by titrating 0.1 M phosphoric acid solution with a concentrated sodium hydroxide solution (1 M) to the required pH values. 1 M  $KNO_3$  was added into PBS solutions through the ECL experiments to improve the conductivity.

### 2.2. Preparation of GQDs

GQDs were synthesized by refluxed Vulcan CX-72 carbon black with concentrated nitric acid according a chemical oxidation method that has been described elsewhere [29]. Briefly, 2 g of dried CX-72 carbon black was dissolved in 500 mL 6 M  $HNO_3$  and then refluxing for 24 h. After cooling to room temperature, the suspension was centrifuged (2770 g) for 10 min. The obtain supernatant was heated at 200 °C to evaporate the water and nitric acid to obtain reddish-brown powder.

### 2.3. Analysis of a real sample

A water sample was collected from Min River (Fujian, China). Suitable aliquots (500  $\mu$ L) of this river water were spiked with standard potassium dichromate solutions (10  $\mu$ L, final concentration, 0–50  $\mu$ M). The spiked samples were then diluted to 1 mL with PBS (0.1 M, pH 7.0) containing GQDs (final concentration, 0.2  $mg\ mL^{-1}$ ),  $K_2S_2O_8$  (final concentration, 1 M), Ethylenediaminetetraacetic acid disodium salt (EDTA) (final concentration, 0.1 mM) and  $KNO_3$  (final concentration, 1 M) then analyzed using the developed sensing technique.



**Fig. 1.** ECL response of GQD/ $S_2O_8^{2-}$  coreactant system to  $Cr_2O_7^{2-}$  in aqueous solution (concentration of GQDs, 0.2  $mg\ mL^{-1}$ ; concentration of  $K_2S_2O_8$ , 200  $\mu$ M; concentration of  $Cr_2O_7^{2-}$ , 20  $\mu$ M; GQDs potential window,  $-1.50$  to  $+1.30$  V; scan rate, 0.2 V/s; starting potential, 0V; initial scan direction, positive; solution pH, 7).

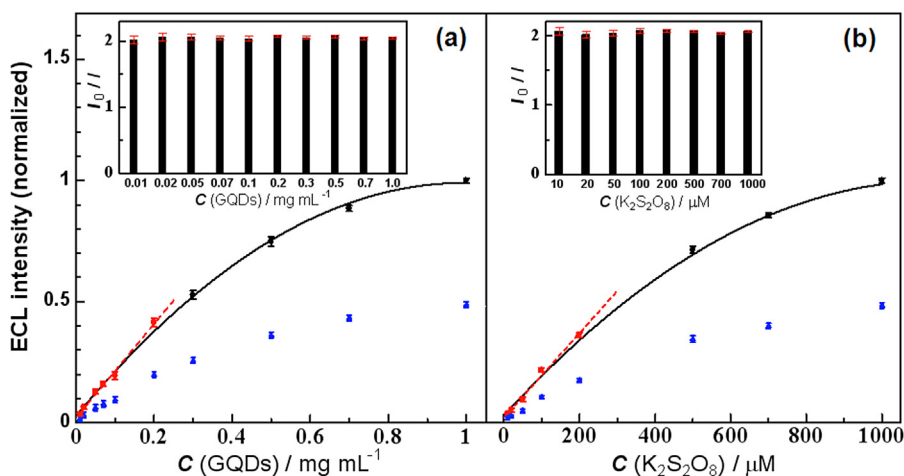
### 2.4. Instrumentation

ECL and electrochemical measurements were carried out on an ECL detection system (MPI-E, Remex Electroic Instrument Ltd. Co., Xi'an, China) equipped with a home-made ECL cell, which has been described in detail elsewhere [30]. An atomic absorption (AAS) spectrophotometer (TAS-986, Beijing Persee Corporation, China) was used to detect the Cr(VI) concentration of the Min River water sample.

## 3. Results and discussion

### 3.1. ECL response of GQD/ $S_2O_8^{2-}$ system toward Cr(VI) and the corresponding mechanism

The as-prepared GQDs have uniform lateral size of  $\sim 10$  nm without obvious lattice fringe (figures are not shown). The topographic heights range mainly from 0.3 to 0.9 nm, with an



**Fig. 2.** Effects of GQD concentration (a) and  $K_2S_2O_8$  concentration (b) on ECL responses of GQD/ $S_2O_8^{2-}$  system in the absence (red and black) and presence (blue) of 20  $\mu$ M Cr(VI). Other experimental conditions include 200  $\mu$ M  $K_2S_2O_8$  in (a); 0.2  $mg\ mL^{-1}$  GQDs in (b); potential window of  $-1.50$  to  $+1.30$  V; scan rate of 0.2 V/s; and pH 7. The insets show the ECL quenching ratio at different concentration of GQDs (left) and  $K_2S_2O_8$  (right). (For interpretation of the references to color in this figure legend as well as in the text, the reader is referred to the web version of this article.)

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