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Resonance light scattering sensor of the metal complex nanoparticles using diethyl dithiocarbamate doped graphene quantum dots for highly Pb(II)-sensitive detection in water sample

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ABSTRACT

This study was aimed to detect Pb^{2+} using diethyl dithiocarbamate-doped graphene quantum dots (DDTC-GQDs) based pyrolysis of citric acid. The excitation maximum wavelength ($\lambda_{max,}$ ex = 337 nm) of the DDTC-GQDs solution was blue shift from bare GQDs ($\lambda_{max,}$ ex = 365 nm), with the same emission maximum wavelength ($\lambda_{max,}$ em = 459 nm) indicating differences in the desired N, S matrices decorating in the nanoparticles. Their resonance light scattering intensities were peaked at the same λ_{max}, ex/em = 551/553 nm without any background effect of both ionic strength and masking agent. Under optimal conditions, the linear range was 1.0–10.0 μg L^{-1} (R^2 = 0.9899), limit of detection was 0.8 μg L^{-1} and limit of quantification was 1.5 μg L^{-1}. The precision, expressed as the relative standard deviations, for intra-day and inter-day analyses was 0.87% and 4.47%, respectively. The recovery study of Pb^{2+} for real water samples was ranged between 80.8% and 109.5%. The proposed method was also proved with certified water sample containing 60 μg L^{-1} Pb^{2+} giving an excellent accuracy and was then implied satisfactorily for ultra-trace determination of Pb^{2+} in drinking water and tap water samples.

1. Introduction

Among different environment from various industrial activities including metal plating, oil refining and battery manufacturing, lead ion (Pb^{2+}) can be taken into the body via inhalation, ingestion or skin adsorption. When the body is exposed to lead, it can be accumulated in the human body throughout the lifetime attributing its cumulative serious poison effects [1–5]. Water quality has become an issue of vital importance which is an essential resource that has been threatened by pollution. In drinking water, maximum allowable limit of total Pb of 50 μg L^{-1} is considered safe by World Health Organization, whereas <15 μg L^{-1} is adopted by the United States Environmental Protection Agency [6]. Therefore, it is important to develop a simple, fast and convenient method for lead detection, especially at ultra-trace level.

Several methods have been applied for lead determination including flame atomic absorption, inductively coupled plasma - atomic emission spectrometry, spectrophotometric methods and electrothermal atomic absorption spectrometry [7–12]. However, these methods have a greater cost, higher sample volume requirements and instrumentation complexity limiting. Therefore, this study focuses on the determination of lead in water sample detected by resonance light scattering technique. Resonance light scattering (RLS) is a special light scattering occurring when the wavelength of the scattered light is located at or close to the molecular absorption band. The spectral characteristics and scattering intensity are strongly influenced by the molecular size, shape, conformation and interfacial properties, which further provide favorable new information for the study of the interaction of biological macromolecules and the molecular recognition [13,14]. In recent years, RLS technique has been widely applied in the quantitative analysis of drugs [15,16], surfactants [17], proteins [18,19], heavy metal ions [20–22] and nanoparticles [23] because of high sensitivity, rapidness, simplicity and convenience.

Regarding this method, Pb^{2+} forms complex with DDTC which is a chelating agent with strong tendency to form stable heavy metal complexes [24]. Furthermore, use of graphene quantum dots (GQDs) as an auxiliary ligand and substrate has attracted much attention in lead-diethyl dithiocarbamate (Pb-DDTC) interactions. GQDs possess large surface area, large diameter, fine surface grafting using the π-π conjugated network or surface groups and other special physical properties [25–27]. It has the carboxyl and hydroxyl groups at their edge enable them to display excellent water solubility and suitability for successive functionalization with various organic, inorganic, polymeric or biological species [28,29]. For these reasons, GQDs have attracted significant attention worldwide. Nowadays, it has been applied as sensor for

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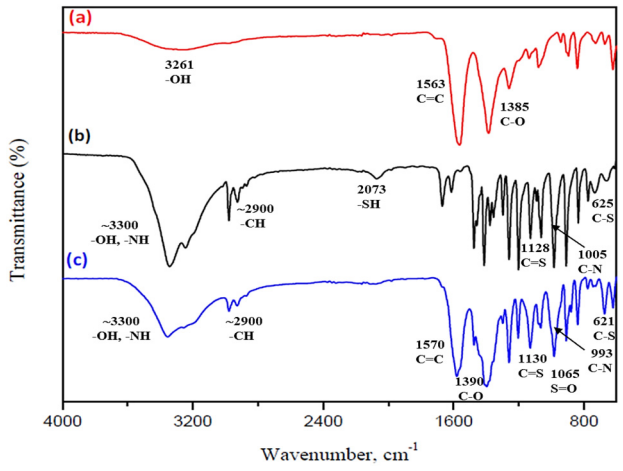

Fig. 1. FTIR of GQDs (a), DDTC (b) and DDTC-GQDs (c).

detection of various target analytes in numerous kinds of sample such as ferric ion in water sample [30], free chlorine in drinking water [31], aminothiols in blood serum [32], glucose in human serum [33] and lead in tap water and drinking water samples [34], indicating that GQDs can be used as a promising sensor for the detection of not only metal ions but also non-metal ions in various real samples.

In this research study, a novel RLS probe for the determination of lead based on diethyl dithiocarbamate doped graphene quantum dots was presented. In the presence of Pb^{2+} the resonance light scattering intensity of the DDTC-GQDs increases linearly by an enhancement mechanism. The interaction between Pb^{2+} and the nanoparticle ligand leads to the aggregation of the particles to form bigger volumes of the complexes. This is aimed of using the RLS probe for determination of lead. In addition, the optimum conditions including each of DDTC and GQDs concentration, pH of the solution, ionic strength, masking agent, interfering ions were investigated in details. The developed method was applied for lead determination in water samples.

2. Experimental

2.1. Materials and Reagents

All chemicals used are of analytical grade including lead(II) nitrate (Fluka Chemika, Switzerland), citric acid (Carlo Erba, Italy), sodium diethyl dithiocarbamate (Sigma Aldrich, Switzerland), sodium hydroxide (Carlo Erba, Italy), sodium chloride (Ajex Finechem Australia), acetic acid (Merck, Germany) and sodium acetate (QRec, New Zealand. Potassium dihydrogen phosphate and dipotassium hydrogen phosphate was from LOBA (India). Paraffin oil was purchased from (Ajex Finechem Australia). Deionized water (Simplicity Water Purification System, Model Simplicity 185, Millipore, U.S.A.) was used throughout the experiment.

2.2. Apparatus

Spectrofluorophotometer (Shimadzu RF-5301PC, Japan) with excitation and emission slit widths of 3 nm was mainly used. pH meter (Model Proline B21, Becthai Equipment & Chemical, Thailand), analytical balance (Model BSA224S-CW, Scientific Promotion, Thailand), quartz cell with 1-cm path length (Fisher Scientific, U.S.A.) were also used. Round bottom flask (Pyrex®, England) and hot plate with a magnetic stirrer in association with paraffin oil bath were set for citric acid pyrolysis method.

2.3. Synthesis and Characterization of GQDs and DDTC-GQDs

Graphene quantum dots were prepared by citric acid pyrolysis [35]. Briefly, 2.0 g citric acid was transferred into a 100 mL round bottom flask which was heated to 250 °C in an oil bath for about 5 min. Citric acid was liquated and its color was changed to yellow. This liquid was then dissolved by dropwise addition of a sodium hydroxide solution (0.25 M, 100 mL NaOH) with continuous stirring for 30 min. The obtained GQDs solution was stored at 4 °C before use. For DDTC doped GQDs synthesis, the GQDs as prepared via citric acid pyrolysis were simultaneously treated with 1% (w/w) DDTC, 2.0 g of citric acid and 1.0 g of DDTC was transferred into a 100 mL round bottom flask, which was heated to 250 °C in an oil bath for about 5 min and then dissolved in NaOH solution as mentioned above. The DDTC-GQDs solution was also stored at 4 °C before use.

2.4. Resonance Light Scattering (RLS) Measurement

For RLS measurement, 0.5 mL solution of 1000 mg L^{-1} 1% DDTC-GQDs was mixed with 0.25 mL of 20 mg L^{-1} of DDTC and 0.1 M NaCl in 1.0 M acetate buffer solution at pH 6.0. Various concentrations of Pb^{2+} were added into the solution mixture and adjusted to 5 mL with the buffer solution. The RLS intensities of the mixture solutions were recorded at 553 nm with fixed excitation and emission slit widths of the spectrofluorophotometer used.

2.5. Optimization of the RLS Probe for Lead Ion

For optimum conditions of the proposed method, the experimental parameters affecting the RLS intensity were investigated in detail including effects of the amount of DDTC doped in GQDs, the concentration of DDTC doped GQDs, solution pH, incubation time, ionic strength and masking agent.

2.5.1. Effect of Solution pH

Effect of the solution pH toward the RLS enhancement of Pb-DDTC-(DDTC-GQDs) was investigated by varying pH of the solution from 2 to 10 using acetate buffer and phosphate buffer solutions. The experiment was carried out by adjusting the two 1.0 M buffer solutions containing 100 mg L^{-1} 1% DDTC-GQDs, 1 mg L^{-1} DDTC and 4 μg L^{-1} Pb^{2+} to the desired pH solution.

2.5.2. Effects of Ionic Strength and Masking Agent

The effects of ionic strength and masking agent on the RLS intensity of the system were investigated using NaCl and EDTA, respectively. The concentrations of NaCl and EDTA used were varied from 0.001 to 1.0 M NaCl and 0.001 to 0.5 M EDTA, respectively. The experiment was carried out by adjusting 4 μg L^{-1} Pb^{2+} containing 1 mg L^{-1} DDTC to the desired concentrations of both ionic strength and masking agent.

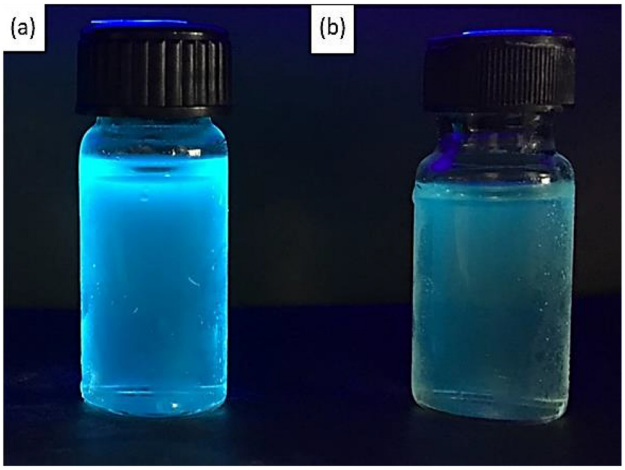

Fig. 2. The blue emission of GQDs (a) and DDTC-GQDs (b) under UV illumination. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)