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Fabrication of carbon quantum dots and their application for efficient detecting $Ru(bpy)_3^{2+}$ in the solution

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ABSTRACT

Carbon quantum dots (CDs) with an average size of less than 10 nm were prepared by ionic liquid-assisted electrochemical exfoliation of graphite electrode, and developed as photoluminescence (PL) and electrochemiluminescence (ECL) probes for efficient detecting $Ru(bpy)_3^{2+}$ in the solution based on the quenching of the PL emission of CDs and enhanced ECL of $Ru(bpy)_3^{2+}$, respectively. The PL and ECL probes exhibited a detection limit of 0.72 and 0.43 μM, respectively. The PL and ECL properties of CDs and $Ru(bpy)_3^{2+}$ will provide a new route to study the novel materials and broaden the use of them in analyte detection.

1. Introduction

Ru(II) polypyridyl complexes have been extensively investigated as luminophore reagents for highly sensitive detection of many analytes, such as oxalate, peroxydisulfate, amine-related and NADH, due to their strong luminescence emission, highly electrochemical reversibility, chemical stability and excellent solubility in a variety of solvents [1–6]. These analytes can be easily either oxidized or reduced with luminophore species at or near the electrode. A subsequent rapid chemical reaction occurs to generate an intermediate that has sufficient reducing or oxidizing power to react with luminophore species to form an excited state and ECL emission. The co-reactant ECL can be used to determine either the co-reactants or $Ru(bpy)_3^{2+}$ in that the ECL intensity is proportional to the concentration of co-reactants or $Ru(bpy)_3^{2+}$ in a certain range [7].

Carbon quantum dots (CDs), namely fluorescent carbon nanoparticles with a size less than 10 nm, possess excellent biocompatibility, water solubility and unique optoelectrical properties [8]. They have successfully been used for bioimaging [9–12], biochemical and chemical analysis [13–15], photocatalysis [16] and white light-emitting devices [17]. Recently, the ECL behavior of water-soluble CDs was reported and the relevant mechanism was proposed by Zheng et al. [18]. This work potentially opens up a promising avenue for CDs used as an ECL reagent. Herein, for the first time, we study the PL and ECL behaviors of $Ru(bpy)_3^{2+}$ and CDs in solution, and develop CDs as nanoprobes for the determination of $Ru(bpy)_3^{2+}$ species.

2. Experimental

2.1. Preparation of carbon quantum dots (CDs)

The electrochemical preparation of CDs was carried out in a two-electrode configuration [19]. A high-purity graphite rod (99.9%) with a diameter of 0.6 cm^2 served as working electrode, parallel to another graphite rod as counter electrode with a distance of 2 cm. The electrolyte was the mixture of 5 mL water, 4 mL 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIm][BF_4]) and 4 mL 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIm][PF_6]). Static potentials of 15 V were applied to the two electrodes using a DC power supply for 6 h at room temperature [20]. After electrolysis, the yellowish-brown oil solution was decanted completely, then the precipitates was washed with 30 mL distilled water. After centrifugation, the yellowish-brown supernate was decanted carefully and known as original CDs solution, exhibiting a bright blue fluorescence upon irradiation with 254 and 365 nm UV light. It is notable that the CDs solution used in our experiment is 1/16 concentration of the original CDs solution and labeled as CDs solution in our study.

2.2. Characterization

The transmission electron microscopy (TEM) analysis was conducted using a JEM-2100F electron microscope (JEOL, Japan).

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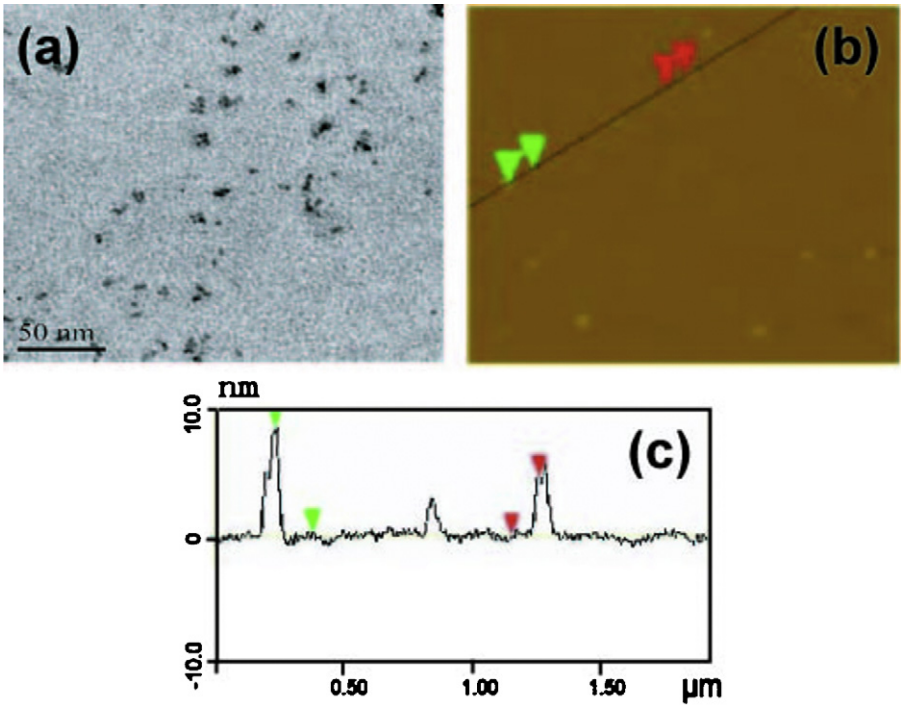

Fig. 1. (a) TEM and (b) AFM images of CDs. (c) The cross-sectional view of the height profile corresponding to the line drawn in (b).

Atomic force microscopy (AFM) images were obtained by a Dimension 3100 AFM, operating in tapping mode with a scan rate of 1.20 Hz. An n-doped silicon tip with 1–10 Ω cm phosphorus (Veeco, MPP-11100-140) was used as the probe. Fourier transform infrared (FTIR) spectra were collected using a Shimadzu IRAffinity-1 FTIR spectrometer in a range of 4000–400 cm^{-1}. Light absorption properties were obtained using ultraviolet–visible (UV–vis) spectrophotometer (UV-2550, Shimadzu, Japan). The photoluminescence (PL) spectra were conducted on a fluorescence spectrophotometer (F-7000, Hitachi, Japan) at room temperature at bias potential of 400 V. The ζ potential of CDs was measured by a Zeta Potential Analyzer (ZetaPALS, Brookhaven Instruments Corporate, USA).

2.3. ECL experiments

The electrochemical measurements coupled with ECL experiments were performed by a MPI-E multifunctional electrochemiluminescent analytical system (Remex Analyse Instrument Co. Ltd, Xi'an, China) with the voltage of the photomultiplier tube (PMT) set at 800 V in aqueous solution using 0.05 M phosphate buffer solution (PBS) as supporting electrolyte. The pH value of PBS was adjusted to 7.6 by 0.1 M NaOH and H_3PO_4 solution. The working electrode was a disk platinum electrode with a diameter of 0.3 mm and the reference electrode was an Ag/AgCl electrode. A platinum wire was used as the auxiliary electrode.

2.4. Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) was carried out on a CHI electrochemical analyzer (CHI660 C Instruments). The frequency of EIS ranges from 10 Hz to 10 MHz and the alternating current (AC) signal amplitude is 5 mV. The EIS data were analysed using Zview software.

3. Results and discussion

TEM image (Fig. 1a) shows that the as-synthesized CDs are less than 10 nm in size, similar to the previous reports [12,21]. The corresponding AFM topographical image (Fig. 1b) shows that an apparent thickness of CDs is in the range 5–8 nm, in agreement with the results of TEM as shown in Fig. 1a.

Fig. 2 shows the FTIR spectrum of the as-prepared CDs. The typical peaks around 3447 and 1466 cm^{-1} are ascribed to the stretching vibrations and in-plane bending vibration of —OH, respectively [15,18]. The bands at 2943 and 2887 cm^{-1} are related to the stretching vibration of C—H in the group of $—CH_3$ or $—CH_2$, due to some ionic liquid residue in the CDs. The dull and intense band of 3447 cm^{-1} indicate the presence of hydrogen bonds, and that at

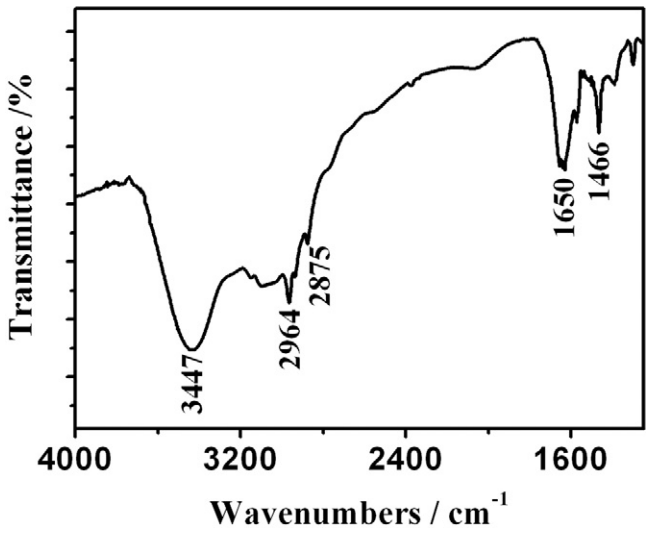

Fig. 2. FTIR spectrum of the as-prepared CDs.