Short Communication

Electrochemiluminescence of CdSe Quantum Dots Composited with Nitrogen-Doped Carbon Nanotubes

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Abstract
A nanocomposite of CdSe quantum dots with nitrogen-doped carbon nanotubes was prepared for enhancing the electrochemiluminescent (ECL) emission of quantum dots. With hydrogen peroxide as co-reactant, the nanocomposite modified electrode showed a cathodic ECL emission with a starting potential of −0.97 V (vs. Ag/AgCl) in phosphate buffer solution, which was five-times stronger than that from pure CdSe quantum dots and three-times stronger than that from CdSe quantum dots composited with carbon nanotubes. The latter showed a starting potential of −1.19 V. This result led to a sensitive ECL sensing of hydrogen peroxide with good stability, acceptable reproducibility and a detection limit down to 2.1×10^{-7} mol L^{-1}. Nitrogen-doped carbon nanotubes could be used as a good material for the construction of sensitive ECL biosensors for chemical and biochemical analysis.

Keywords: Electrochemiluminescence, Quantum dots, Sensors, Nitrogen-doped carbon nanotubes, Hydrogen peroxide

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Nanomaterials have been widely applied in microelectronics, nonlinear optics, catalysis and sensor science due to the amplification or catalytic effect of the nanostructures [1]. Among the multifarious functional nanomaterials, water soluble quantum dots (QDs) are of considerable interest in bioassay and bioimaging [2]. Their application in electrochemiluminescent (ECL) sensing has gained particular concern since the first ECL sensor based on CdSe QDs was reported in 2004 [3]. Owing to the low ECL intensity and high excited potential of QDs, new methods to decrease the excited potential and enhance ECL emission are urgently needed for the development of novel ECL sensors [4]. In view of the excellent electrocatalytic ability of carbon nanotubes (CNTs) [5], they have been used to reduce the injection barrier of electrons to the QDs for improving the ECL response [4] and constructing ECL immunosensors [6]. This work examined the sensitizing effect of nitrogen-doped carbon nanotubes (NCNTs) to the ECL emission of CdSe QDs.

NCNTs possess the nanostructure and some characteristics similar with the CNTs [7]. However, they exhibit better conductivity and lower toxicity than CNTs [8]. In this communication, upon the composition of CdSe QDs with NCNTs, the cathodic ECL emission from the QDs in presence of hydrogen peroxide as co-reactant was greatly enhanced and the starting potential to produce the ECL response also shifted positively. Furthermore, the ECL intensity was 3-fold that from multiwalled carbon nanotubes (MWCNTs) composited CdSe QDs, and the starting potential was also 0.22 V more positive than that of MWCNTs composited CdSe QDs, indicating NCNTs were better candidates for improving the ECL response. The CdSe QDs-NCNTs nanocomposite modified electrode showed stable ECL response to hydrogen peroxide, led to a novel ECL biosensor for hydrogen peroxide.

The photoluminescence (PL) spectrum (excited at 428 nm) of CdSe QDs solution that was prepared by 100-times dilution of the as-synthesized CdSe QDs solution showed a relatively narrow emission with a maximum intensity at 551 nm (not shown). The narrow PL emission indicated a narrow size distribution. The first UV-vis absorption peak occurred at 425 nm (not shown), from which the size of the resulting CdSe QDs and the concentration of QD solution could be estimated to be 1.77 nm and 24.5 μmol L^{-1} from the adsorption peak and Peng's empirical equations [9]. The similar excited and absorption wavelength indicated the emitter was the excited state of QDs (QDs*).

X-Ray photoelectron spectroscopic (XPS) characterization was performed to analyze the composition of NCNTs (Fig. 1c). The N 1s XPS spectrum showed three peaks around 399, 401 and 404.5 eV, respectively. The first peak came from the pyridine-like N atoms, i.e., the nitrogen in a ring structure folding only two carbon atoms, called pyridinic nitrogen, and the second peak was from the graphite-like structure called graphitic nitrogen. The third peak was attributed to the molecular nitrogen encapsulating in nitrogen-doped carbon nanotubes [10].

The SEM images of both CdSe QDs-MWCNTs and CdSe QDs-NCNTs nanocomposite films displayed well-dispersed interdigitated structures, and the outer diameters of the nanocomposites were in the range from 40 to 60 nm (Fig. 1a and b). The CdSe QDs-NCNTs nanocomposite showed denser coverage of CdSe QDs than the CdSe QDs-MWCNTs nanocomposite, which was beneficial to obtaining stronger response. This uniform nanostructure and the better conductivity of NCNTs would accelerate the electron transfer between the CdSe QDs and electrode.

When a bare glass slide was coated with NCNTs, the contact angle decreased from 38° to 8°, while the contact angle decreased to 15° when it was coated with MWCNTs (Fig. 1d, e and f), indicating a better hydrophilicity of NCNTs. It was coincidental with the previous report [11], in which the nitrogen doped carbon nanotubes contained more hydrophilic groups after acid treatment. The good hydrophilicity resulted in more loading of the CdSe QDs on NCNTs due to the hydrophilic surface of the TGA-coated CdSe QDs.

The CdSe QDs modified GCE showed a cathodic ECL emission starting at -1.30 V in 0.1 mol L^{-1} pH 9.0 PBS containing 10 mmol L^{-1} H_2O_2 (Fig. 2a). The ECL mechanism was similar to that reported in [3]. Briefly, the CdSe QDs were reduced to form the anion radical in cathodic process (curve a in inset), which was then oxidized by H_2O_2 to produce exited species followed with emission to lead to ECL signal. Obviously the reduction of CdSe QDs was a key step. At CdSe QDs-MWCNTs modified GCE the ECL emission was greatly improved and the starting potential shifted to -1.19 V (Fig. 2b). This was contributed to the electrocatalysis of MWCNTs to the reduction of CdSe QDs, resulting in a stronger ECL response and a more positive reduction potential (curve b in inset). The sensitizing effect could be further enhanced by compositing NCNTs with CdSe QDs (Fig. 2c) due to the better conductivity and hydrophilicity of NCNTs. At CdSe QDs-NCNTs nanocomposite modified GCE the ECL intensity was ca. 3-fold and 5-fold higher than those observed at CdSe QDs-MWCNTs and CdSe QDs film modified electrodes, respectively. Furthermore, the starting potential to produce the ECL emission was at -0.97 V, 0.22 V more positive than that from CdSe QDs-MWCNTs film modified electrode, at which the reduction of CdSe QDs could be observed (not shown). Compared with NCNTs modified electrode, the CdSe QDs-NCNTs modified electrode showed lower background and reduction current of hydrogen peroxide due to the presence of semiconductor. The better electrocatalysis of NCNTs than MWCNTs came from the more edge-plane-like defects [12] and the bamboo-like morphology of NCNTs [13]. Moreover, N atom which was embedded in the hexagonal carbon network contained an additional electron when compared to C atom, so NCNTs could exhibit metallic properties [8]. These advantages not only facili-

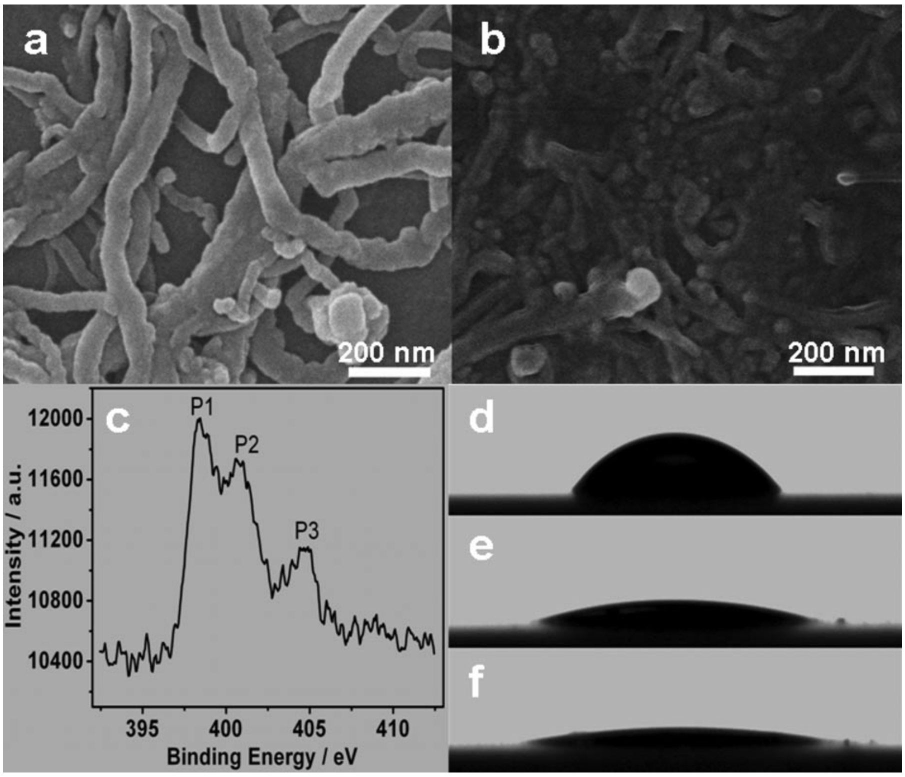

Fig. 1. Scanning electron micrographs of CdSe QDs-MWCNTs (a) and CdSe QDs-NCNTs (b) coated films. N 1s XPS spectrum of NCNTs (c), and contact angle graphs of bare (d), MWCNTs (e) and NCNTs (f) modified substrates.

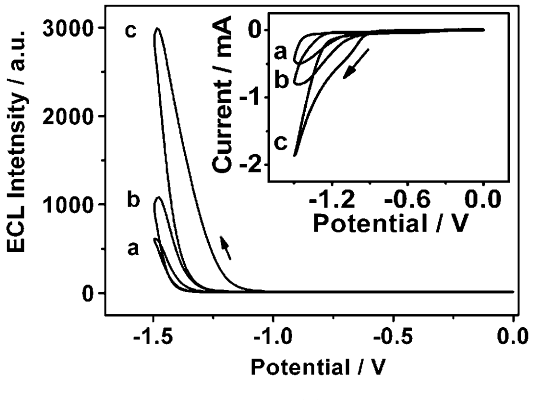

Fig. 2. ECL curves of CdSe QDs (a), CdSe QDs-MWCNTs (b) and CdSe QDs-NCNTs (c) modified electrodes in air-saturated 0.1 mol L^{-1} PBS (pH 9.0) containing 10 mmol L^{-1} H_2O_2 at 100 mV s^{-1} (vs. Ag/AgCl). Inset: corresponding cyclic voltammograms.

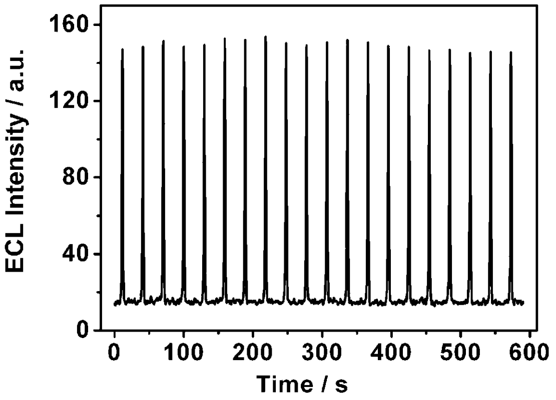

Fig. 4. ECL emission from the CdSe QDs-NCNTs nanocomposite film in N_2-saturated 0.1 mol L^{-1} pH 9.0 PBS containing 5.0 μmol L^{-1} H_2O_2 under continuous cyclic scans between 0 and -1.5 V for 20 cycles at 100 mV s^{-1}.

tated the electron transfer between the CdSe QDs and the electrode, but also improved the immobilization of CdSe QDs, thus enhanced the ECL emission of QDs.

With an increasing solution pH from pH 7.0 to 10.0, the ECL intensity of the CdSe QDs-NCNTs nanocomposite film in the presence of 6.0 μmol L^{-1} H_2O_2 increased greatly and then trended to a constant value at pH 9.0 (not shown). Considering the analytical performance of the ECL sensor, pH 9.0 was chosen for the determination procedure. The ECL response of the CdSe QDs-NCNTs nanocomposite modified GCE to hydrogen peroxide in N_2-saturated 0.1 mol L^{-1} pH 9.0 PBS containing 0.1 mol L^{-1} KNO_3 was shown in Figure 3. A linear relation between the ECL intensity and hydrogen peroxide concentration was obtained from 3.0×10^{-7} to 2.0×10^{-5} mol L^{-1} ($R = 0.9987$, $n = 15$). The detection limit was 2.1×10^{-7} mol L^{-1} at a signal-to-noise ratio of 3, which was much lower than those of some amperometric biosensors [14] and an ECL sensor based on polycrystalline TiO_2 film [15]. The relative standard deviation for three measurements at the H_2O_2 concentration of 6.0×10^{-6} mol L^{-1} was 1.8%, indicating acceptable reproducibility.

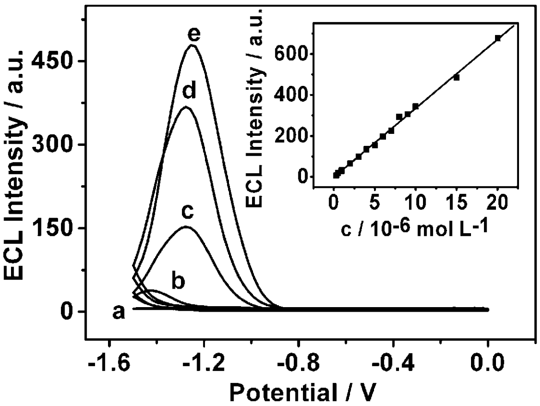

Fig. 3. ECL curves of CdSe QDs-NCNTs modified electrode in N_2-saturated 0.1 mol L^{-1} pH 9.0 PBS containing 0.0 (a), 1.0 (b), 5.0 (c), 10.0 (d) and 15.0 (e) μmol L^{-1} H_2O_2 at 100 mV s^{-1} (vs. Ag/AgCl). Inset: linear calibration curve for H_2O_2 detection.

The stability of ECL emission of the CdSe QDs-NCNTs nanocomposite modified GCE was shown in Figure 4. Upon successive scans between 0 and -1.5 V for 20 cycles in N_2-saturated 0.1 mol L^{-1} pH 9.0 PBS containing 5.0 μmol L^{-1} H_2O_2, no obvious change was observed.

In summary, this paper used for the first time the nitrogen-doped carbon nanotubes to enhance the ECL emission of quantum dots for structuring a sensitive ECL sensor. The presence of NCNTs obviously decreased the potential barriers of electron injection into CdSe QDs and dramatically enhanced the intensity of ECL. The excellent sensitizing effect of NCNTs would not only promote the development of novel ECL sensors based on CdSe QDs but also accelerate the application of quantum dots in bioanalysis.

Experimental

Thioglycolic acid (TGA), Se powder, $CdCl_2 \cdot 2.5\,H_2O$ and $NaBH_4$ were purchased from Alfa Aesar (Tianjin, China). Poly (diallyldimethylammonium chloride) solution (PDDA; 20 wt.%, MW = 200 000–350 000) was obtained from Sigma-Aldrich (USA). All other reagents were of analytical reagent grade and used as received. 0.1 mol L^{-1} phosphate buffer solutions containing 0.1 mol L^{-1} KNO_3 as supporting electrolyte (PBS) was used throughout the work. Aqueous solutions were prepared with twice-distilled water.

The water-soluble CdSe QDs were prepared using TGA as stabilizing agent according to the previous report [16]. The Se source was obtained from the reaction between Se powder and $NaBH_4$ in air-free twice-distilled water. After refluxed at 100 °C for 4 h, the formed CdSe colloid was dialyzed exhaustively against water overnight at room temperature to obtain CdSe QDs solution. Finally, the product was condensed by ultrafiltration at 10 000 rpm for 10 min, and the upper phase was decanted and kept at 4 °C. The obtained CdSe QDs solution could be stable for

3 months, and its concentration and the size of QDs were detected with the UV-vis absorption [9].

MWCNTs with diameter of about 40–60 nm were obtained from Shenzhen Nanotech Port Company. The NCNTs were synthesized through the chemical vapor deposition method according to the method previously reported [13] and were refluxed in 6 mol L^{-1} NaOH at 110 °C for 4 h to remove the Al_2O_3 support [17] and were successively refluxing in 1 mol L^{-1} H_2SO_4 for 8 h to remove residual Fe catalysts. Both NCNTs and MWCNTs were suspended in a 3:1 (v:v) mixture of concentrated sulfuric acid and nitric acid, and ultrasonicated at 60 °C for about 2 h, respectively [11]. The suspensions were centrifuged, and the treated NCNTs and MWCNTs were ultrasonically washed with twice-distilled water till the suspensions showed a pH of 7.0, which were finally diluted to a concentration of 0.5 mg mL^{-1} for electrochemical study and preparation of nanocomposites.

The CdSe QDs-NCNTs nanocomposite was synthesized by mixing the NCNTs suspension obtained-above (0.5 mg mL^{-1}) with the CdSe QDs solution (0.12 mmol L^{-1}) in the volume ratio 1:1 under ultrasonication for 30 min [4].

The glassy carbon electrode (GCE) with 5-mm diameter was successively polished to a mirror finish with 0.3 μm and 0.05 μm alumina slurry, and then washed ultrasonically in twice-distilled water. The electrode was rinsed with twice-distilled water and then dried under a stream of nitrogen. A 10.0-μL suspension of CdSe QDs-NCNTs was dropped on the surface of the pretreated GCE and dried at room temperature to form the CdSe QDs-NCNTs modified GCE. Afterwards, a drop of 6.0 μL 0.5% PDDA solution was cast on the membrane to stabilize the CdSe QDs-NCNTs modified GCE. As control, the CdSe QDs-MWCNTs and CdSe QDs modified GCEs were also prepared with the same procedure and the same quantity of CdSe QDs. After dried in air at 4 °C, the formed architectures were washed with twice-distilled water and stored in 0.1 mol L^{-1} pH 9.0 PBS at 4 °C.

The electrochemical and ECL measurements were carried out on a MPI-A multifunctional analytical system (Xi'an Remex Analytical Instrument Ltd. Co.) at room temperature with a configuration consisting of a glassy carbon electrode (GCE) working electrode, a platinum counter electrode, and an Ag/AgCl (saturated KCl solution) reference electrode. The observation window for ECL was placed in front of the photomultiplier tube biased at − 800 V.

UV-vis absorption spectrum was recorded with UV-3600 UV-vis-NIR photospectrometer (Shimadzu Co., Japan). Photoluminescence (PL) spectrum was obtained on a Jasco FP 820 fluorometer (Jasco Co., Japan). Scanning electron microscopic (SEM) images of different films formed on indium tin oxide slides were obtained on a Hitachi S-4800 scanning electron microscope (Hitachi Co, Japan). XPS measurements were performed with an ESCA Lab MK2 spectrometer. A monochromatic Al Kα X-ray source was operated in CAE (constant analyzer energy) mode (CAE = 70 eV for survey spectrum and 20 eV for N 1 s spectrum). The static water contact angles were measured at 25 °C by an OCA30 contact angle measurement device (Dataphysics Co., Germany) employing drops of pure deionized water. The readings were stabilized and taken within 60 s after addition.

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