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Electrochemiluminescence of Water-Soluble Carbon Nanocrystals Released Electrochemically from Graphite

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Luminescent nanocrystals have generated much excitement for a wide variety of promising applications in optoelectronic devices, biological labeling, and biomedicine.[1−4] Moreover, some semiconductor nanocrystals, such as CdSe,[5] CdTe,[6] and CdSe/ZnSe,[7] can be used as electrochemiluminescence (ECL) reagents in bioanalytical applications such as immunoassay analysis.[8,9] At the same time, however, heavy metals as the essential elements in available high-performance semiconductor quantum dots have raised serious health and environmental concerns.[10] To maintain a benign environment, low-toxicity silicon and carbon nanostructures are preferred in many fields.[11−14] Recently, fluorescent carbon nanocrystals (CNCs) of low toxicity have been prepared by laser ablation of graphite,[14,15] electrochemical oxidation of graphite,[16] electrochemical treatment of multiwalled carbon nanotubes (MWCNTs),[17] chemical oxidation of arc-discharge single-walled carbon nanotubes (SWCNTs)[18,19] and candle soot,[20] proton-beam irradiation of nanodiamonds,[21,22] and thermal oxidation of suitable molecular precursors.[23,24] However, no article to date has reported that CNCs can generate an ECL signal. Herein, we report a simple and effective method for preparing water-soluble CNCs with ECL activity by applying a scanning potential to graphite rods and present our observations on the ECL behavior during and after the preparation of CNCs.

The electrochemical preparation of CNCs was performed in an electrochemical cell consisting of a graphite rod (GR) working electrode, a Pt mesh counter electrode, a Ag/AgCl reference electrode, and pH 7.0 phosphate buffer solution (PBS). The applied potential at the GR electrode was cycled between −3.0 and 3.0 V at 0.1 V/s, and ECL and electrochemical signals were measured during CNC preparation.

A quite stable cyclic voltammogram (CV) was obtained for the GR working electrode in PBS during the continuous potential scanning, in contrast to the previous report on CNC preparation that the charging current increased during application of a scanning potential to MWCNTs in acetonitrile.[17] This indicates that the effective area of the GR electrode did not change significantly during CNC preparation in aqueous solution, suggesting a different CNC formation mechanism. Herein, we assumed that the CNCs were initially immobilized in porous graphite, after which those CNCs at the surfaces of the porous graphite were exposed to PBS, electrochemically oxidized to water-soluble particles, and released into the water phase. The assumption that the CNCs initially existed in the graphite was verified by the experiment result that water-insoluble CNCs could be extracted from the GRs by DMF. During the potential scan, weak and much stronger ECL signals were observed in the anodic (+1.5 to +3.0 V) and cathodic (−1.0 to −3.0 V) potential ranges, respectively (see Figure 1). The cathodic ECL intensity increased with the number of potential cycles before reaching a constant value after 30 cycles. ECL spectrum measurements showed that the light-emission maxima of the cathodic and anodic ECL were both at 535 nm.

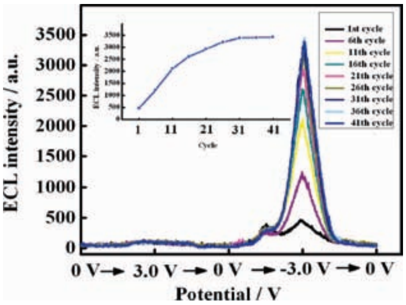

Figure 1. ECL responses obtained on a GR electrode in 0.1 M PBS (pH 7.0). The applied potential was cycled between −3.0 and 3.0 V at a scan rate of 0.1 V/s. Inset: plot of ECL intensity vs number of potential scan cycles.

As the number of scan cycles increased, the color of electrolyte solution changed from colorless to yellow and finally to dark-brown. The resulting dark-brown solution obtained by cycling the potential between −3.0 and +3.0 V in present work was very clear, i.e., almost no deposit was found. High-resolution transmission electron microscopy (HRTEM) images showed that the dark-brown solution contained two kinds of nanoparticles: well-defined spherical carbon nanoparticles with an average size of ∼20 nm and smaller nanosized CNCs (∼2 nm). A colorless CNC solution was obtained by directly ultrafiltering the dark-brown solution with a 10 kDa molecular weight cutoff (MWCO) membrane. HRTEM images indicated that the obtained CNCs were monodispersed, spherically shaped particles with an average diameter of 2.0 nm. The prepared 2.0 nm CNCs in solution were further characterized by UV−vis absorption and photoluminescence (PL). The absorption band centered at 300 nm, the maximum excitation wavelength of 330 nm, and the maximum PL emission wavelength of 455 nm (blue fluorescence) were similar to those previously reported for CNCs.[16] Additionally, the FT-IR spectrum for the dried 2.0 nm CNC sample showed the CNCs had an abundance of −COOH groups at their surfaces, which benefits CNC labeling.

Clearly, it is of very considerable interest to study the ECL behavior of CNCs, since no ECL research, to the best of our knowledge, has been carried out on CNCs with low cytotoxicity, excellent water-solubility, and easy surface modification. Herein, ECL of the obtained CNC solution was studied in detail at a Pt disk working electrode. The ECL emission of the CNCs was observed when the potential was cycled between +1.8 and −1.5 V (see Figure 2). ECL spectrum measurements showed that the ECL emission maximum was at 535 nm, which is consistent with the result obtained during CNC preparation. The accordance between the ECL spectra of the CNC preparation solution and the purified CNC solution implies that ECL provides a potential

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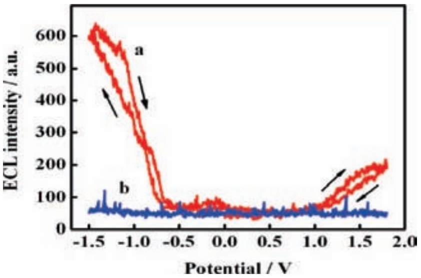

Figure 2. ECL responses (a) with and (b) without CNCs at a Pt electrode in 0.1 M PBS (pH 7.0). ν= 0.1V/s.

monitoring technique for the preparation and screening of quantum dots. Evidently, the ECL behavior of CNCs is very similar to that of other semiconductor nanocrystals, such as CdSe,[5] CdTe,[6] CdSe/ZnSe,[7] and Si NCs;[12] consequently, the ECL mechanism of the CNCs was suggested to involve the formation of excited-state CNCs (R*) via electron-transfer (ET) annihilation of negatively charged ($R^{\bullet-}$) and positively charged ($R^{\bullet+}$) CNCs (i.e., the ET1 route, $R^{\bullet+}-R^{\bullet-}$ annihilation, as shown in Figure 3).[12] The intensity of cathodic ECL was larger than that of anodic ECL, indicating that $R^{\bullet+}$ is more stable than $R^{\bullet-}$. The maximum ECL emission wavelength (535 nm) was substantially red-shifted from PL maximum (455 nm), which can be explained by the fact that the energy separations of the CNC surface states (for ECL emission) are smaller than the band gaps of the CNC core (for PL emission).[5,12]

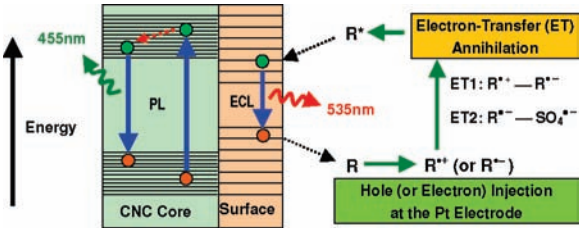

Figure 3. Schematic illustration of the ECL and PL mechanisms in CNCs. $R^{\bullet+}$, $R^{\bullet-}$, and R* represent negatively charged, positively charged, and excited-state CNCs, respectively.

Additionally, the ECL behavior of CNCs in the presence of peroxydisulfate ($S_2O_8^{2-}$), a coreactant commonly used in ECL systems, was also investigated. Figure 4 shows that the ECL intensity of CNCs in the presence of $S_2O_8^{2-}$ was greatly enhanced, suggesting that ET annihilation of $R^{\bullet-}$ and the strongly oxidizing $SO_4^{\bullet-}$ radicals produced by electroreduction of $S_2O_8^{2-}$ (i.e., the ET2 route, $R^{\bullet+}-SO_4^{\bullet-}$ annihilation, as shown in Figure 3) might be involved in CNC$-S_2O_8^{2-}$ ECL processes. Moreover, Figure 4 also shows that a stable and sensitive ECL response of CNCs could be obtained by using $S_2O_8^{2-}$ as a coreactant (see the inset in Figure 3), suggesting attractive applications of CNCs in ECL sensing.

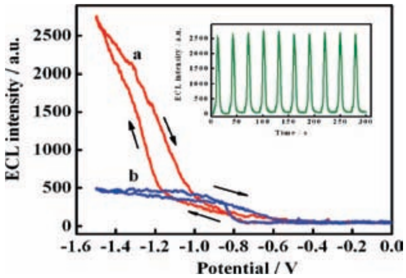

Figure 4. ECL of CNCs in aqueous 0.1 M PBS solution (pH 7.0) in the (a) presence and (b) absence of 1 mM $K_2S_2O_8$. Inset: ECL responses of CNCs/$S_2O_8^{2-}$ obtained during a continuous potential scan at 0.1 V/s.

In conclusion, CNCs with ECL activity have been prepared by a simple and effective electrochemical method. The CNCs were probably obtained by electrochemical release of CNCs initially immobilized in a graphite rod into the supporting electrolyte. The ECL behavior and mechanism in CNCs have been studied in detail. This kind of CNC is envisioned to have promising applications in the development of new types of biosensors and display devices in the future [for example, replacing $Ru(bpy)_3^{2+}$ as a fine ECL reagent in the detection of DNAs and proteins[25]] on the basis of its strong ECL emission, low cytotoxicity, excellent water solubility, good stability, ease of labeling, low cost, and environmental friendliness.

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Supporting Information Available: Experimental procedures and instrumentation; cyclic voltammograms, HRTEM images, and UV−vis absorption, photoluminescence, and FT-IR spectra of CNCs; discussion of the CNC formation mechanism; and complete ref 14. This material is available free of charge via the Internet at http://pubs.acs.org.

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