Revealing Carbon Nanodots As Coreactants of the Anodic Electrochemiluminescence of Ru(bpy)$_3^{2+}$

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Supporting Information

**ABSTRACT:** Recently, research on carbon nanodots (C-dots), a new type of luminescent nanoparticles with superior optical properties, biocompatibility, and low cost, has been focused on exploring novel properties and structure-related mechanisms to extend their scope. Herein, electrochemiluminescence, a surface-sensitive tool, is used to probe the unrevealed property of carbon nanodots which is characterized by surface oxygen-containing groups. Together with chemiluminescence, carbon nanodots as the coreactants for the anodic electrochemiluminescence of Ru(bpy)$_3^{2+}$ are demonstrated for the first time. During the anodic scan, the benzylic alcohol units on the C-dots surface are oxidized “homogeneously” by electrogenerated-Ru(bpy)$_3^{3+}$ to form reductive radical intermediate, which further reduce Ru(bpy)$_3^{3+}$ into Ru(bpy)$_3^{2+}$ that produces a strong ECL emission. This work has provided an insight into the ECL mechanism of the C-dots-involved system, which will be beneficial for in-depth understanding of some peculiar phenomena of C-dots, such as photocatalytic activity and redox properties. Moreover, because of the features of C-dots, the ECL system of Ru(bpy)$_3^{2+}$/C-dots is more promising in the bioanalysis.

Carbon nanodots (C-dots), characterized by surface oxygen-containing units, have recently exhibited a great potential in biomedicine and photophysics for their superior optical properties, excellent biocompatibility, small size, and low cost. The recent work including our research has revealed that surface oxide-related states on the C-dots can capture the excitons under light excitation to give off photoluminescence (PL). Besides PL, besides PL, besides PL, and electrochemiluminescence (ECL) can be produced with chemical and electrochemical excitations. The sensitive and selective analysis for pollutants and biomolecules have been achieved on the basis of the luminescence. In addition to radiative recombination, the electrons and holes trapped by the surface states can transfer to the external electron acceptors and donors, resulting in redox reactions, based on which many photocatalysts and electrocatalyst with C-dots have been constructed. Overall, novel properties related with surface states of C-dots are worth intensive exploring for further applications. Moreover, most related work suggests that the properties of C-dots are predominantly attributed to the surface oxide-related states, but little research has been done on what the exact surface oxides or surface oxygen-containing units of C-dots are and how they dictate the surface, resulting in corresponding properties, which are crucial for deep understanding and development of C-dots. ECL, combining advantages of both electrochemical and CL techniques, is sensitive to the surface states of nanoparticles and the key step is the electron transfer between the emitter ions (annihilation mechanism) or between the emitter ion and the intermediate evolved from a coreactant (coreactant mechanism). ECL is an ideal tool for probing the surface structure and related mechanism of nanoparticles. In recent work, C-dots in the ECL system have been studied only as nanoemitters by similar approaches for fluorescent semiconductor nanoparticles, regardless of their unique surface structure of oxygen-containing units. Meanwhile, most of oxygen-containing compounds (e.g., alcohols) have been reported to serve as the coreactants in ECL. As discussed, it is essential to take oxygen-containing units on the surface into account and review the behaviors of C-dots in the ECL process. Herein, C-dots are introduced into the classic Ru(bpy)$_3^{3+}$-ECL system, and their part as coreactants for the anodic ECL of Ru(bpy)$_3^{3+}$ has been reported for the first time. The specific mechanism has been investigated in detail and the benzylic alcohol units on the C-dots surface are proposed to be responsible for the coreactant activity. This work has provided an insight into the ECL mechanism of C-dots-involved system, which will be beneficial for in-depth understanding of some peculiar phenomena of C-dots, such as photocatalytic activity and redox properties.

The C-dots used in this work were prepared by the electrochemical oxidation method (see the Supporting Information). High-resolution transmission electron microscopy (HRTEM) images (Figure S-1a in the Supporting Information) clearly exhibited that the C-dots were monodisperse and spherical nanoparticles.

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with a lattice spacing of 2.03 Å, which corresponded to the 101 facet of graphite (PDF no. 65-6212). And the graphite-structured C-dots had a narrow size distribution of 2.4 ± 0.3 nm (Figure S-1b in the Supporting Information). FT-IR and XPS characterization of C-dots demonstrated that rich oxygen-containing groups (e.g., -OH, C=O, and -COOH) capped the surface (Figure S-2a in the Supporting Information, curve I, and Figure S-2b in the Supporting Information), which made C-dots water dispersible. Besides, some unsaturated groups, such as C=C, were also detected on their surface. C-dots showed a continuously rising absorption with a defined peak at 230 nm, which was assigned to the π−π* transition of the conjugation system within C-dots (Figure S-3a in the Supporting Information).24 A series of shifting emissions of C-dots showed and the optimal emission wavelength was 449 nm when excited at 330 nm (Figure S-3b in the Supporting Information).

Herein, C-dots were introduced into Ru(bpy)$_3$**ECL** system and their electrochemical and ECL signals were recorded at a glass carbon (GC) electrode while the potential was cycled between +0.20 and +1.40 V (Figure 1a). As shown in the voltammographs, Ru(bpy)$_3$$^{2+}$ gave a reversible redox at a formal potential of +0.07 V (Figure 1a, inset). While, upon addition of C-dots, the oxidation peak of Ru(bpy)$_3$$^{2+}$ was enhanced and the reduction peak weakened, which was more obvious with increasing the concentration of C-dots from 0.2 mg mL$^{-1}$ to 1.0 mg mL$^{-1}$. This indicated a catalytic oxidation of C-dots by Ru(bpy)$_3$$^{2+}$. The similar catalytic oxidations were also observed in the coreactant ECL systems of Ru(bpy)$_3$$^{2+}$/C-dots.25 And Ru(bpy)$_3$$^{2+}$/tripropylamine (TPrA)$_2$ was first catalytically oxidized to C$_4$O$_4$$^{2-}$ or TPrA$^{*}$ by electrogenerated Ru(bpy)$_3$$^{2+}$. The ECL curves showed that Ru(bpy)$_3$$^{2+}$/C-dots mixture gave a strong ECL signal rising at +1.00 V and peaking at +1.15 V, which was consistent with the electrochemistry of Ru(bpy)$_3$$^{2+}$, whereas Ru(bpy)$_3$$^{3+}$ or C-dots alone exhibited weak ECL signals (Figure 1a, inset). Furthermore, the normalized ECL spectrum of the mixture at 615 nm agreed with the PL spectrum of Ru(bpy)$_3$$^{2+}$ at 605 nm but distinguished from the ECL spectrum of C-dots alone at 535 nm (Figure 1b). These results demonstrated that the anodic ECL of Ru(bpy)$_3$$^{2+}$/C-dots mixture originated from Ru(bpy)$_3$$^{2+}$ assisted by C-dots. This conclusion was further confirmed by the severely suppressed ECL signal of Ru(bpy)$_3$$^{2+}$/C-dots by O$_2$ (Figure S-4 in the Supporting Information) via an energy-transfer quench of the excited state Ru(bpy)$_3$$^{2+}$.27,28

UV–vis absorption and PL emission were determined to explore the reason for C-dots assisting the anodic ECL of Ru(bpy)$_3$$^{2+}$. In the range of 300–750 nm, the mixture of Ru(bpy)$_3$$^{2+}$/C-dots exhibited a rising absorption with a broad peak at 453 nm (Figure 1c, solid line), which was a merging of absorptions from separated C-dots (dashed line) and Ru(bpy)$_3$$^{2+}$ (dotted line). Likewise, Ru(bpy)$_3$$^{3+}$ and C-dots in the mixture also keep their PL properties (Figure 1d). Since the solution of C-dots became dark brown at a high concentration, the ECL intensity of Ru(bpy)$_3$$^{2+}$/C-dots leveled off at the concentration above 0.5 mg mL$^{-1}$ from the inner filter effect of C-dots.

As a coreactant in an ECL process, it should be capable of forming reductive or oxidative species during a unidirectional voltammetric scan.19,20 In the present case, C-dots as coreactants should be able to produce a reductive intermediate to reduce the electrogenerated Ru(bpy)$_3$$^{3+}$ to the excited state Ru(bpy)$_3$$^{2+}$ that can emit light. To demonstrate this, the CL technique was used herein, since Ru(bpy)$_3$$^{3+}$ could give off the CL emission when reacting with a reductive agent.30 The CL signal of Ru(bpy)$_3$$^{3+}$/C-dots were monitored on a flow injection analysis system by injecting C-dots into a continuous flow of 0.05 mol L$^{-1}$ H$_2$SO$_4$ solution containing 100 μmol L$^{-1}$ Ru(bpy)$_3$$^{3+}$ obtained by chemically oxidizing Ru(bpy)$_3$$^{2+}$ with PbO$_2$.25,31 As shown in Figure 2b,c, strong CL emissions were detected and the intensity linearly increased with increasing the concentration of C-dots from 0.002 to 0.1 mg mL$^{-1}$, suggesting C-dots actually functioned as reductive intermediates in the CL process of Ru(bpy)$_3$$^{3+}$. In a typical CL process of Ru(bpy)$_3$$^{3+}$, the other agent usually undergoes a chemical reaction (decomposition or deprotonation) after one-electron oxidation by Ru(bpy)$_3$$^{3+}$ and further form reductive intermediates that can reduce Ru(bpy)$_3$$^{3+}$ to the excited state Ru(bpy)$_3$$^{2+}$ and generate the excited state Ru(bpy)$_3$$^{2+}$ in a homogeneous oxidation by electro-generated Ru(bpy)$_3$$^{3+}$. This can be further confirmed by voltammetry of Ru(bpy)$_3$$^{3+}$/C-dots. Instead of a pair of reversible redox peaks (Figure 1a, inset), Ru(bpy)$_3$$^{3+}$ in the mixture with C-dots showed an enhanced oxidation peak at +1.12 V and a weakened reduction peak at +1.00 V, implying...
that C-dots were involved in the catalytic route during the anodic scan. Electrogenerated Ru(bpy)$_3^{3+}$ chemically oxidized C-dots to produce Ru(bpy)$_3^{2+}$ at the electrode surface, which would subsequently be electro-oxidized to Ru(bpy)$_3^{3+}$ as the oxidant for the next cycle. Ru(bpy)$_3^{2+/3+}$ acted as a redox mediator, resulting in an enhanced Ru(bpy)$_3^{2+}$ oxidation peak together with a weakened reduction peak. Also, the electro-catalytic oxidation current showed a linear dependence on the concentration of added C-dots from 0.02 to 1.0 mg mL$^{-1}$ (Figure 2d), demonstrating a “homogeneous” oxidation of C-dots by electrogenerated Ru(bpy)$_3^{3+}$. Therefore, the linearly increased signals of ECL, CL, and electrocatalytic current with increasing concentration of C-dots suggested that the ECL of Ru(bpy)$_3^{2+}$/C-dots was mainly carried out in a catalytic...
Ru(bpy)$_3$C-dots cannot be absolutely excluded. Considering that alcohols which was proposed to contain many benzylic alcohol could be converted to alkoxide radical after one-electron deprotonation and further to corresponding aldehyde. Benzyl alcohol can be converted to the reductive intermediate upon a subsequent deprotonation, and further reduce Ru(bpy)$_3$ to form the excited state Ru(bpy)$_3^*$, producing an anodic ECL emission. Meanwhile, the direct electro-oxidation of C-dots also may contribute to the anodic ECL of Ru(bpy)$_3$. To further prove the key role of benzylic alcohol units, the anodic ECL signals from Ru(bpy)$_3$ together with C-dots treated in different manners were determined. As shown in Figure 3c, when using the deoxygenated C-dots with a few alcohol units (Figure S-2a in the Supporting Information, curve II) instead of as-prepared C-dots, the anodic ECL emission of Ru(bpy)$_3$ nearly disappeared (Figure 3c, dotted). On the contrary, the anodic ECL intensity increased a lot (Figure 3c, dashed) by selectively reducing the C-dots with NaBH$_4$ to form more alcohols on the surface (Figure S-2a in the Supporting Information, curve III). Moreover, the ECL intensity increased sharply with pH increasing from 6 to 10 (Figure 3d), indicating that deprotonation of α-H in benzylic alcohol is a key step in the ECL process. Therefore, a mechanism for Ru(bpy)$_3$/C-dots ECL reactions was proposed in Scheme 1. During the anodic scan, the benzylic alcohol units on C-dots are oxidized by electrogenerated Ru(bpy)$_3^{2+}$/benzyl alcohol, turn to the related reductive intermediate upon a subsequent deprotonation, and further reduce Ru(bpy)$_3$ to Ru(bpy)$_3^{2+}$, producing an anodic ECL emission. Meanwhile, the direct electro-oxidation of C-dots also may contribute to the anodic ECL of Ru(bpy)$_3$. For C-dots are provided with many virtues, and the novel ECL system of Ru(bpy)$_3$/C-dots would have a great potential in bioanalytical applications. The anodic ECL exhibited a robust stability during the 15 continuous cycles (Figure 4a) and an excellent 1-week repeatability with a relative standard deviation of 1.1%, providing a premise for bioanalysis. To further demonstrate this potency, dopamine (DA), an essential neurotransmitter closely associated with many disorders of nervous system such as Parkinson’s disease, was used as a model molecule to be quantitatively determined. As shown in Figure 4b, with the addition of 10 μmol L$^{-1}$ DA, the ECL
The intensity of Ru(bpy)$_2^{3+}$/C-dots decreased a lot, while β-mercaptoethanol, an antioxidation reagent for DA, efficiently retrieved the ECL signal quenched by DA. This suggested a quenching mechanism involving energy-transfer between benzoquinone species (oxidation product of DA) and excited state Ru(bpy)$_2^{3+}$. On the basis of the mechanism, the DA molecules were quantitatively determined in the range of 0.5–20 μmol L$^{-1}$ (Figure 4b, inset), and the linear dependence of I$_{0}$/I on the concentration of DA followed the Stern–Volmer equation, I$_{0}$/I = 1 + K$_{sv}[Q]$, with the constant K$_{sv}$ of 1.0 × 10$^{5}$ M$^{-1}$ (R = 0.998). The limit of determination was 0.3 μmol L$^{-1}$, and the relative standard deviation for four separated measurements of 10 μmol L$^{-1}$ DA was 3.6%.

In summary, C-dots have been demonstrated to be the coreactants for the anodic ECL of Ru(bpy)$_2^{3+}$ for the first time. The related mechanism was also put forward with the aid of CL, PL, absorption, and multiple treatments. It has been found that the benzylic alcohol units on the C-dots are responsible for their capability as coreactants in the anodic ECL process of Ru(bpy)$_2^{3+}$/C-dots. C-dots possess many merits, for example, excellent water dispersibility, low toxicity, large specificity, and ease of biofunctionalization; thus, the system of molecules. This work has deepened and broadened the development of C-dots.

**REFERENCES**

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