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bifunctionalized by luminol analogue–metal complexes
in neutral and alkaline media

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bifunctionalized by luminol analogue/metal complexes was
observed in neutral and alkaline medium without coreactant. The
excellent ECL activity in neutral medium is very promising for the
detection of biological compounds occurring in physiological
environments.
Direct electrochemiluminescence of gold nanoparticles bifunctionalized by luminol analogue–metal complexes in neutral and alkaline media†

Jiangnan Shu, Wei Wang and Hua Cui*

Electrochemiluminescence of gold nanoparticles bifunctionalized by luminol analogue–metal complexes was studied for the first time. Strong direct electrochemiluminescence was observed in neutral and alkaline media without an additional coreactant.

Functionalized gold nanoparticles (GNPs) are particularly attractive due to their unique optical properties, excellent catalytic activity, good biocompatibility and stability. In recent years, attention has been paid to chemiluminescence (CL) functionalized gold nanoparticles (CL-GNPs). CL reagents, such as Ru(II) complexes, luminol and N-(aminobutyl)-N-(ethylisoluminol) (ABEI), have been successfully used for the preparation of CL functionalized gold nanoparticles with broad applications from public health and food safety to environmental science. More recently, a new concept of grafting catalyst metal ions on the surface of CL-GNPs has been reported by our group. 2-[Bis[2-carboxymethyl-2-oxo-2-(2-sulfanylethyl)amino]ethyl]amino]ethyl][amino]acetic acid (DTDTPA) first interacted with various metal ions to form DTDTPA–metal complexes, and then DTDTPA–metal complexes were grafted to the surface of ABEI-GNPs by the Au–S bond. These as-synthesized gold nanoparticles bifunctionalized by CL reagents and catalyst metal complexes (BF-GNPs) exhibited excellent CL activity. However, electrochemiluminescence (ECL) of BF-GNPs has not been explored, to the best of our knowledge.

ECL is light emission from the reactions between electro-generated oxidation species and electrogenerated reduction species or between electrognerated species and coreactants. ECL has superior advantages over conventional CL, such as better reproducibility, lower background signals, and easier temporal and spatial control of ECL reactions. Increasing investigations resulted in highly sensitive and selective detection methods, which have been proved to be useful for analytical applications. Luminol and its analogues, as typical CL reagents, have also been widely used for ECL studies. However, most of the ECL studies on luminol and its analogues have been limited to strong alkaline solution. Their ECL behaviors in neutral and weak alkaline media have been rarely reported, which is essential for their applications under physiological conditions. Besides, hydrogen peroxide is needed as a coreactant in order to achieve high ECL intensity in most studies. Furthermore, although luminol and its analogue functionalized nanomaterials exhibited unique CL activity, their ECL properties were not ideal even in the presence of hydrogen peroxide under strong alkaline conditions and almost no ECL emission was observed in neutral and weak alkaline media. Herein, we report the ECL behaviors of gold nanoparticles bifunctionalized by luminol analogue–metal complexes on a bare ITO electrode for the first time. It was found that BF-GNPs could directly generate outstanding ECL emission in neutral and alkaline aqueous solutions without an additional coreactant.

The gold nanoparticles bifunctionalized by luminol analogue–metal complexes were prepared as described previously with some modifications (see ESI†). The characterization results demonstrated that the gold nanoparticles bifunctionalized by luminol analogue–metal complexes with the diameter of about 20 nm were successfully synthesized (ESI†, Fig. S1–S4). The ECL behaviors of gold nanoparticles bifunctionalized by luminol analogue–metal complexes in neutral and alkaline aqueous solutions at a bare ITO electrode were studied by cyclic voltammetry using Co2+/DTDTPA/ABEI-GNPs as a model of gold nanoparticles bifunctionalized by luminol analogue–metal complexes as shown in Fig. 1. When the pH was 8.0 (Fig. 1A), Co2+/DTDTPA/ABEI-GNPs exhibited a well-defined ECL peak in 0.02 M phosphate buffer solution (PB) on the positive scan, while almost no ECL emission was observed for ABEI-GNPs. When the pH was 11.1 (Fig. 1B), a strong ECL peak was observed for Co2+/DTDTPA/ABEI-GNPs and weak ECL for ABEI-GNPs. The ECL intensity of Co2+/DTDTPA/ABEI-GNPs was over 2 orders of magnitude higher than that of ABEI-GNPs under both neutral and alkaline conditions.
The effects of pH on the \(I_{\text{ECL}}-E\) curves of Co\(^{2+}/\text{DTDTPA/ABEI-GNPs}\) were examined in the pH range of 7.74–11.78 as shown in Fig. S5 (ESI†). The ECL intensity increased with increasing pH from 7.74 to 11.11. When the pH was around 11.11, a maximal ECL intensity was obtained. Although the maximal emission occurring at pH 11.11 was much stronger than that occurring at pH 7.74, the emission intensity of Co\(^{2+}/\text{DTDTPA/ABEI-GNPs}\) in neutral solution on an ITO electrode was still good enough because only a high voltage of \(\sim 500\) V was applied to the photomultiplier tube (PMT). The result indicated that outstanding ECL property of Co\(^{2+}/\text{DTDTPA/ABEI-GNPs}\) could be obtained on a bare ITO electrode under both neutral and alkaline conditions. Compared with ECL emission of the hemin/G-quadruplex catalyzed luminol-H\(_2\)O\(_2\) system, BF-GNPs do not need an additional coreactant H\(_2\)O\(_2\) and is less sensitive to the environment.\(^{21}\)

The effect of the initial scan direction on ECL emission was studied. Fig. 2 shows \(I_{\text{ECL}}-E\) curves and cyclic voltammograms (CVs) of Co\(^{2+}/\text{DTDTPA/ABEI-GNPs}\) under air-saturated conditions in initial negative and positive scan directions. When the initial scan direction was negative (Fig. 2A), CV demonstrated a cathodic peak at \(-0.75\) V (cvp1) on the negative scan. Upon reversal of the potential scan, an anodic peak was found at \(0.36\) V (cvp2). Among them, cvp2 disappeared in blank solution without ABEI or Co\(^{2+}/\text{DTDTPA/ABEI-GNPs}\), corresponding to the oxidation of ABEI (inset [a] in Fig. 2A). cvp1 was the reduction of the dissolved oxygen in solution to HOO\(^-\) according to previous studies.\(^{11,22}\) In \(I_{\text{ECL}}-E\) curves of Co\(^{2+}/\text{DTDTPA/ABEI-GNPs}\) dispersed in 0.02 M PB on a bare ITO electrode, ECL-1 and ECL-2 were observed at \(-0.78\) and 0.54 V, corresponding to two voltammetric peaks (cvp1 and cvp 2), respectively. Accordingly, ECL-1 and ECL-2 were related to the reduction of the dissolved oxygen to HOO\(^-\) and the oxidation of ABEI, respectively. Furthermore, when the initial scan direction was positive as shown in Fig. 2D, ECL-2 intensity was lower than that in the initial negative scan. The result revealed that ECL-2 could be enhanced by species produced on the negative potential scan.

The effect of various atmospheres, including air, oxygen and nitrogen atmospheres, on ECL emission was also examined. Fig. S6 (ESI†) shows the \(I_{\text{ECL}}-E\) curves of Co\(^{2+}/\text{DTDTPA/ABEI-GNPs}\) in 0.02 M PB under various atmospheres using the initial negative scan. Compared with the ECL peaks under an air atmosphere, the intensity of both ECL peaks increased
It was suggested that Co2+ could react with ABEI to produce ABEI radicals. Upon the reverse scan, OOH− and ABEI− were electro-oxidized to O2− and ABEI+ radicals, respectively. ECL-2, corresponding to the oxidation of ABEI (cvp2), appeared at 0.54 V, which was related to the generation of O2− and ABEI+. On the other hand, OOH− is ready to be decomposed to HO+ radicals on the surface of gold nanoparticles. The −COO− group in DTDTPA molecules may react with O2− to form −CO3−. Radicals such as HO+, O2− and −CO3− could react with ABEI+ and HO2− to facilitate the formation of ABEI+ and O2−. Finally, ABEI+ reacted with O2− to form the excited state oxidation product of ABEI, accompanied by light emission. It has been reported that gold nanoparticles as catalysts could facilitate radical generation and electron transfer in chemical reactions. The ECL reactions involved several radical generation and multi-step electron transfers. Gold nanoparticles as nanosized ECL reaction platforms could effectively facilitate radical generation and electron transfer in the ECL reactions, leading to strong ECL emission of Co2+/DTDTPA/ABEI-GNPs dispersed in a solution without an additional coreactant.

The effect of metal ions in metal/DTDTPA/ABEI-GNPs, including Co2+, Cu2+, Pb2+, Ni2+, Hg2+, Cr3+, Eu3+, La3+, Gd3+, Sm3+, Er3+, Dy3+, Ce4+ and Ce3+, on the ECL emission was explored. The ECL–E curves of fourteen kinds of metal–DTDTPA complex–ABEI-GNPs dispersed in alkaline solution are shown in Fig. 4. Most of the metal–DTDTPA complex/ABEI-GNPs exhibited good ECL properties. Among them, Co2+/DTDTPA/ABEI-GNPs demonstrated the strongest ECL intensity, which may be due to the fact that Co2+ has the strongest catalytic effect on luminol-type CL reaction.
ECL property of Co^{2+}/DTDTDPA/ABEI-GNPs with a double-step pulse potential is of analytical application potential.

In conclusion, this work has demonstrated for the first time that the Co^{2+}/DTDTDPA/ABEI-GNPs could directly generate outstanding ECL emission in neutral and alkaline media without an additional coreactant. The ECL emission of Co^{2+}/DTDTDPA/ABEI-GNPs was over 2 orders of magnitude higher than that of ABEI-GNPs in neutral and alkaline media. Two ECL peaks, including ECL-1 at −0.78 V and ECL-2 at 0.54 V, were found on a bare ITO electrode under conventional CV conditions. These ECL peaks were related to OOH^− electroreduced by the dissolved oxygen and ABEI^+ electrooxidized by ABEI, followed by the generation of various intermediates such as Co−OOH^+, HO^−, O^2− and −CO_4^{−2}. Gold nanoparticles as nanosized ECL reaction platforms could effectively facilitate radical generation and electron transfer in the ECL reactions, leading to strong ECL emission of Co^{2+}/DTDTDPA/ABEI-GNPs dispersed in a solution without an additional coreactant. Fourteen transition and rare earth metal ions used for metal−DTDTPA complex-ABEI-GNPs exhibited good ECL property. Among them, Co^{2+}/DTDTDPA/ABEI-GNPs demonstrated the strongest ECL intensity. Luminol-type CL reagents functionalized on the surface of the nanocomposites such as luminol, isoluminol and ABEI showed good ECL activity without H_2O_2 and ABEI was the best one. Besides, stable and strong ECL emission can be obtained upon continuous pulse potential. In particular, excellent ECL activity in neutral and weak alkaline media implies that BF-GNPs have a good application prospect for the sensitive detection of biologically important compounds occurring at physiological pH.

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References