Sensitive electrochemiluminescence resonance energy transfer (ECL-RET) between Ru(bpy)$_3^{2+}$ and Au nanorod for hydrogen peroxide detection

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Received April 4, 2016; accepted May 18, 2016; published online October 26, 2016

Here, we developed a novel electrochemiluminescence resonance energy transfer (ECL-RET) approach between Ru(bpy)$_3^{2+}$ and Au nanorods (NRs) for sensitive determination of H$_2$O$_2$. Au NRs were synthesized through silver ion-assisted seed-mediated method which exhibited an obvious absorption peak at about 627 nm. They were modified at glassy carbon electrode (GCE) surface which showed a significant ECL quenching efficiency about 56.5% due to the ECL-RET process. This Au NRs modified electrode was then utilized to measure the concentration of H$_2$O$_2$ on the basis of the significant quenching effect of H$_2$O$_2$ on Ru(bpy)$_3^{2+}$ ECL. Results demonstrated that the decrement of ECL intensity at Au NRs modified electrode had ~ 6.6-fold enhancement as compared with that at bare electrode.

electrochemiluminescence, resonance energy transfer, Au NRs

1 Introduction

Electrochemiluminescence (ECL), which combines the outstanding advantages of electrochemical and luminescent techniques, has been widely used in sensing small molecules [1], disease markers [2], DNA [3], and cancer cells [4,5]. Resonance energy transfer (RET) based on ECL [6–10] is a type of nonradiative energy transfer that occurs between ECL species (donor) and a suitable acceptor which is similar with fluorescence resonance energy transfer (FRET). Recently, it has attracted increasing attention due to their inherent advantages, for example, it eliminates the utilization of excitation light source and there is no background noise arising from the acceptor. It has been proven to be an effective tool for providing new biological information related to the biomolecules interactions [10]. Thus, a variety of ECL-RET strategies have been designed and developed, such as using Ru(bpy)$_3^{2+}$ or quantum dots as ECL donor and size tunable nanomaterials or dye as acceptor [11–13].

Since Ru(bpy)$_3^{2+}$ can produce intense anodic ECL by reacting with tripropylamine (TPA) at a wavelength of 620 nm, it is considered as a good candidate ECL donor. However, only a few researches have been reported for using Ru(bpy)$_3^{2+}$ as ECL donor [14,15]. In our previous work, we have developed a sensitive ECL-RET strategy based on the energy transfer between GO-Au/RuSi@ Ru(bpy)$_3^{2+}$ and Au@Ag$_2$S nanoparticles (NPs) for sensitive detection of DNA [14]. The excitation spectra of acceptor can be easily adjusted by controlling the amount of Ag$_2$S at Au surface. Lu’s group has developed a novel ECL-RET pair using Ru(bpy)$_3^{2+}$ as ECL donor and malachite green/crystal violet as acceptor [15]. Therefore, it is highly required to develop novel and sensitive ECL-RET pair.
As well known, the efficiency of the ECL-RET process depends on the overlap of the emission spectra of ECL species and the excitation spectra of acceptor as well as the distance between the donor and the acceptor. In order to enhance the ECL-RET efficiency and improve the sensitivity of this approach, great efforts have been devoted to the synthesis of suitable acceptors. Among these, Au nanomaterials hold great promise as acceptors in ECL-RET because of their size-dependent excitation spectra which cover the whole visible spectrum range. However, most of the previous studies employed Au NPs to enhance the ECL signal of Ru(bpy)$_2^{2+}$ due to its superior catalysis effect and the increased electrode area [16,17]. To the best of our knowledge, there is still no report about investigating the energy transfer between Ru(bpy)$_2^{2+}$ and Au nanorods (NRs).

In the present work, we synthesized Au NRs with silver ion-assisted seed-mediated method whose absorption spectra were adjusted to ca. 620 nm through controlling the amounts of Ag$^+$. The ECL-RET was investigated at a glassy carbon electrode modified with Au NRs in the presence of Ru(bpy)$_2^{2+}$ and TPA. Results indicated that the ECL quenching efficiency was correlated with the concentration of the Au NRs and its excitation spectra. Through ECL-RET, the ECL intensity can be decreased about 56.5%. This ECL-RET strategy was then used to detect the concentration of hydrogen peroxide based on the catalysis effect of Au NRs and the quenching effect of H$_2$O$_2$ on Ru(bpy)$_2^{2+}$ signal.

2 Experimental

2.1 Materials

HAuCl$_4$, Ru(bpy)$_2^{2+}$, tripropylamine (TPA) were obtained from Sigma-Aldrich (USA). ECL detection solution was 10 mL of 0.1 M phosphate buffer solution (PBS, pH 7.4) containing 0.05 mM Ru(bpy)$_2^{2+}$ and 0.25 mM TPA. All solutions were prepared using Millipore (model milli-Q) purified water and stored at 4 °C in a refrigerator. All the other chemicals were of analytical grade.

2.2 Apparatus

The electrochemical and ECL emission curves were obtained on a MPI-E multifunctional electrochemical and chemiluminescent analytical system (Xi’an Remax Electronic Science &Technology Co. Ltd., Xi’an, China) with a conventional three-electrode system at room temperature. It consists of glassy carbon electrode (GCE) as working electrode, a Pt wire counter electrode and a saturated calomel reference electrode (SCE). The voltage of the e photomultiplier tube (PMT) was set at 700 V in the process of detection. Transmission electron microscopy (TEM) was performed on JEM-2000CX (JEOL, Japan). Cyclic voltammetry (CV) was carried out on a CHI 660 electrochemical working station (CH Instruments, China) at GCE in the solution of 0.10 M KCl containing 2.5 mM K$_4$[Fe(CN)$_6$]/K$_4$[Fe(CN)$_6$] (1:1) mixture. The UV-Vis absorption spectra were obtained on a U-4100 UV-Vis photospectrometer (Hitachi, Japan).

2.3 Synthesis of Au NRs

Au NRs were prepared with silver ion-assisted seed-mediated method according to previous study with minor modification [18,19]. Briefly, the seed solution was prepared by adding a freshly prepared ice-cold 0.01 M NaBH$_4$ solution (0.6 mL) into a mixture of 1% HAuCl$_4$ (0.103 mL) and 0.1 M hexadecyl trimethyl ammonium bromide (CTAB, 10 mL). The mixture was then vigorously stirred for 2 min. The obtained seed solution was kept at 30 °C for 2 h. The growth solution was prepared by reduction of 1% HAuCl$_4$ (0.412 mL) in a solution containing 0.01 M AgNO$_3$ and 0.1 M CTAB (20 mL). In order to make sure the ECL-RET between Ru(bpy)$_2^{2+}$ and Au NRs, we should adjust the absorption of Au NRs to about 620 nm (Au NR-1) by controlling the amounts of Ag$^+$. Au NRs were prepared by adding 0.025 mL of AgNO$_3$. As a control, we synthesized Au NRs-2 by introducing 0.05 mL of AgNO$_3$, 0.16 mL of ascorbic acid solution (0.1 M) and CTAB-stabilized seed solution (0.048 mL) were added. The solution was then left undisturbed 20 h in a 30 °C water bath to generate Au NRs. The obtained solution was washed twice and then redispersed with 2 mL pure water.

2.4 Preparation of the Au NRs modified GCE

GCE was polished with sand papers and then polished to mirror smoothness with aqueous slurries of alumina powders (0.05 μm Al$_2$O$_3$) on a polishing silk before the surface modification. Then the GCE was thoroughly rinsed with water. Au NRs modified GCE was achieved by dropping 10 μL diluted Au NRs solution onto the pretreated surface of GCE and evaporated in air at room temperature. Then, the Au NRs modified GCE was stored in PBS (pH 7.4) for characterization and further detection.

3 Results and discussion

3.1 Characterization of Au NRs

Previous studies have demonstrated that the absorption spectra of Au NRs were closely related with its size and shape [20]. To ensure the high ECL-RET efficiency between Ru(bpy)$_2^{2+}$ and Au NRs, the size of the Au NRs should be chosen carefully. Figure 1 depicts the TEM images of two kinds of Au NRs synthesized with different amount of Ag$^+$. It can be seen that the average aspect ratio of Au NRs-1 and Au NRs-2 were 1.95 (32.3±5.7 nm in length and 16.6±3.5 nm in width, Figure 1(a)) and 2.05 (38.0±5.7 nm in length and 18.5±4.0 nm in width, Figure 1(b)). The corresponding UV-Vis spectra of these two Au NRs are shown in