Journal of Electroanalytical Chemistry 762 (2016) 80–86

Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

journal homepage: www.elsevier.com/locate/jelechem

Improved electrogenerated chemiluminescence of luminol by cobalt nanoparticles decorated multi-walled carbon nanotubes

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ARTICLE INFO

Article history:
Received 6 October 2015
Received in revised form 9 December 2015
Accepted 22 December 2015
Available online 28 December 2015

Keywords:
Electrochemiluminescence
Multi-walled carbon nanotubes
Co nanoparticles
Luminol
Hydrogen peroxide
Glucose

ABSTRACT

Multi-walled carbon nanotubes (MWCNTs) were decorated with cobalt nanoparticles (Co-NPs) by a simple thermal decomposition method. The prepared nanohybrid material (nanoCo-MWCNTs) was then cast on the surface of a glassy carbon electrode (GCE) as a novel electrocatalyst for the construction of a sensitive electrochemiluminescence (ECL) sensor. The fabricated sensor (GCE/nanoCo-MWCNTs/Nafion) showed excellent electrocatalytic activity toward luminol and H_2O_2 oxidation reactions at neutral media. Under optimal experimental conditions, the ECL signal intensity of the sensor was linear with the concentration of luminol in the range between 80 nM and 140 μM ($r = 0.9963$) and also with the concentration of H_2O_2 in the range between 1 nM and 240 μM ($r = 0.9980$). Detection limits ($S/N = 3$) for luminol and H_2O_2 were 8.7 and 0.2 nM, respectively. The relative standard deviations (RSD) for repetitive measurements of 100 μM luminol ($n = 10$) and 10 μM H_2O_2 ($n = 11$) were 1.6% and 2.0%, respectively. Also, the prepared sensor was further modified with glucose oxidase (GOx) to fabricate a glucose ECL based biosensor (GCE/nanoCo-MWCNTs/GOx/Nafion). The fabricated ECL biosensor exhibited excellent performance toward glucose detection in the concentration range between 0.5 and 600 μM with a satisfactory detection limit (50 nM) and reproducibility (2.3%).

1. Introduction

Electrogenerated chemiluminescence or electrochemiluminescence (ECL) is an attractive analytical tool with broad applications in different research areas. ECL is a hybrid technique which provides electrochemical and spectral information, simultaneously [1]. Simple and low-cost instrumental set up, excellent sensitivity and low background signal are the most important features of ECL [2,3]. An increased interest is observed for ECL investigations and this fact has been reflected in the number of reviews [4–9] which report the effectiveness of ECL detection method and its wide analytical applications.

Luminol (3-aminophthalhydrazide) is the most popular organic luminescent species which can be oxidized at the electrode surface. The subsequent chemical reaction between the oxidized luminol and H_2O_2 (or O_2) produces ECL signal. Since the first report on the observation of ECL response for luminol at the electrode surface in alkaline solution [10], numerous attempts have been done to find effective approaches for the enhancement of ECL signal intensity of luminol in neutral medium [11–14]. It has been shown that the ECL reaction of luminol with oxygen or hydrogen peroxide is more efficient in alkaline medium through modification of the electrode surface with nano-materials [12,15].

With the development of nanotechnology, various types of nanostructured materials with outstanding properties are being synthesized and applied for the construction of novel sensors and biosensors. Nanostructured materials provide higher effective surface area and higher catalytic activity in comparison with their respective bulk materials. The catalytic effect of some nano-structured materials such as multiwalled carbon nanotubes (MWCNTs) [16,17], Au nanoparticles (NPs) [18–20]; Pt-NPs [21], Ag-NPs [22–24] and TiO_2-NPs [25] on chemiluminescence (CL) and ECL reactions have been investigated for luminol-H_2O_2 and luminol-O_2 systems in alkaline and neutral media. Discovering of carbon nanotubes (CNTs) by Iijima [26] and surface functionalization of CNTs with nanoparticles (so called "decoration process") [27] revealed a new class of nanohybrid materials with the integrated properties of two components [28]. It seems, the application of this class of nanohybrid materials for ECL measurements provides novel opportunities for developing a new generation of (bio)sensors. Our previous studies [13,29,30] obviously demonstrated that this class of nanohybrid materials noticeably improved the sensitivity of detection. The observed enhancement was attributed to the surface area and electrocatalytic activity of the nanohybrid materials which promote the rate of electron transfer reactions of luminol, oxygen and hydrogen peroxide at the electrode surface and also catalyze the generation of

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http://dx.doi.org/10.1016/j.jelechem.2015.12.035
1572-6657/

reactive oxygen species (ROSs) [15]. ROSs are strong oxidizing radicals and generally highly reactive species due to the presence of unpaired valence shell electron. Singlet oxygen ($^1O_2$), superoxide hydrogen ($HO_2^{\cdot}$), superoxide radical ($O_2^{\cdot-}$), hydroxyl radical ($OH^{\cdot}$) and inorganic or organic peroxides are the most well-known ROSs.

Glucose is an important carbohydrate which is introduced as a source of energy for living organisms. Its determination is vital because of its importance in clinical and industrial purposes. Rapid glucose monitoring is essential for treatment and control of diabetes. Among numerous methods which have been developed for the fast and accurate determination of glucose, electrochemical and optical based methods are the most common methods. In this context, ECL can be proposed as a powerful analytical tool for glucose detection due to its inherent sensitivity and selectivity. In an enzymatic ECL glucose biosensor, glucose oxidase (GOx) catalyzes the oxidation of glucose to gluconic acid by the reduction of molecular oxygen to the hydrogen peroxide. The enzymatically produced H_2O_2 reacts with luminol radical anion, the oxidation product of luminol at the electrode surface, and gives the excited state 3-aminophthalate anion which its light emission at about 425 nm is used for quantification of hydrogen peroxide or indirectly for glucose detection. Various nano-structured materials such as CNTs film [17], CNTs paste [31] and Au-NPs self-assembled onto a silica sol–gel network [20], Fe_3O_4-NPs [32], Au-NPs and Pd-NPs decorated CNTs [13,30], graphene Pt nanoflower/graphene oxide [33], C_{60} embedded in tetraoctylammonium bromide [34], poly(luminol-aniline) nanowires [35] and hollow gold nanospheres [36] have been applied for the fabrication of glucose biosensor based on the monitoring of ECL signal of luminol.

Nano-structured Co and cobalt oxide have been widely used for the determination of biological and environmental species such as glucose [37], cysteine [38], methanol [39,40], arsenic [41], nitrite [42] and hydrogen peroxide [43]. Our previous study revealed that cobalt nanoparticles decorated multi-walled carbon nanotubes (nanoCo-MWCNTs) is an effective nanohybrid material for the cathodic ECL measurement of luminol and dissolved oxygen [44]. In the present work, the electrocatalytic activity of nanoCo-MWCNTs on luminol ECL reaction is explored to show the feasibility of the proposed nanohybrid material for the fabrication of novel ECL (bio)sensors for luminol, H_2O_2 and glucose detection.

2. Experimental

2.1. Reagents and chemicals

All chemicals were of analytical reagent grade and used without further purification. Nafion perfluorinated ion-exchange (5% solution in 90% light alcohol) was obtained from Fluka (Buchs, Switzerland). Luminol, Cobalt (II) acetate, sodium hydroxide, dimethylformamide (DMF) were obtained from Merck (Darmstadt, Germany). Multi-walled carbon nanotubes (95% purity, OD = 10–30 nm, ID = 5–10 nm and length = 0.5–500 μm) was purchased from Aldrich (Steinheim, Germany). Co-NPs decorated MWCNTs nanohybrid (nanoCo-MWCNTs) was prepared according to the method reported previously via manual mixing without modifications [27].

A 1.0×10^{-2} M stock solution of luminol (3- aminophthalhydrazide) was prepared by dissolving luminol in a small amount of 0.1 M NaOH. Working solutions of luminol were prepared by diluting the stock solution with phosphate buffer solution (PBS, 0.1 M, pH = 7.4). Analytical grade O_2 and Ar gases were used for the preparation of solutions saturated with oxygen and argon gases, respectively. Phosphate buffer solution (0.1 M, pH = 7.4) saturated with oxygen and argon gases were prepared separately by sparging of O_2 and Ar into the PBS for at least 30 min.

2.2. Apparatus and procedure

Electrochemical and ECL measurements were carried out in a 4 mL homemade Teflon ECL cell [30]. The working electrode was mounted in the horizontal position in the ECL cell where its surface was exactly in front of the window of a Hamamatsu photomultiplier module (H7468) (Hamamatsu city, Japan). The photodetector and ECL cell were enclosed in a light-tight black box. The electrochemical system consisted of a conventional three-electrode set-up in which nanoCo-MWCNTs modified glassy carbon electrode, a platinum wire, and an $Ag|AgCl|KCl_{sat}$ electrode served as the working, auxiliary and reference electrodes, respectively. The working potential was applied to the working electrode in the standard way using an Autolab potentiostat-galvanostat model PGSTAT30 (Utrecht, The Netherlands) and the output cyclic voltammograms and ECL signals were acquired using Autolab NOVA software and a home-written data acquisition program, respectively. A Metrohm 691 pH meter was used for pH adjustments. All measurements were performed at room temperature.

2.3. Fabrication of luminol, H_2O_2 and glucose ECL based (bio)sensor

The surface of a glassy carbon electrode (GCE) was polished with 0.3, 0.1 and 0.05 μm alumina paste (Struers, Copenhagen, Denmark), consecutively to obtain a mirror like surface and then cleaned in water-ethanol mixture using ultrasonic agitation for 3 min. One milligram of nanoCo-MWCNTs was dispersed in 1 mL DMF with ultrasonic agitation to achieve a well-dispersed suspension. 2 μL of the prepared nanoCo-MWCNTs suspension was cast on the surface of GCE and dried in an oven at 50 °C to prepare GCE modified with nanoCo-MWCNTs (GCE/nanoCo-MWCNTs). The prepared sensor, GCE/nanoCo-MWCNTs, was directly used for luminol detection. Then, 5 μL of Nafion solution (0.1%) was cast on the surface of GCE/nanoCo-MWCNTs to fabricate H_2O_2 sensor (GCE/nanoCo-MWCNTs/Nafion). The prepared sensor was stored at room temperature in air when not in use. Furthermore, 2 μL of PBS containing desired amount of GOx (2.11 U μL^{-1}) was placed on the surface of GCE/nanoCo-MWCNTs and allowed to dry at room temperature. Then, 5 μL of Nafion solution (0.1%) was cast on the surface of GCE/nanoCo-MWCNTs/GOx to fabricate glucose biosensor (GCE/nanoCo-MWCNTs/GOx/Nafion). The prepared glucose biosensor was stored at 4 °C in PBS when not in use. For comparison GCE/MWCNTs, GCE/Nafion and GCE/MWCNTs/Nafion were prepared through similar procedures.

Nafion solution was used for the fabrication of H_2O_2 sensor and also for the immobilization of GOx at the electrode surface because of its outstanding biocompatibility and excellent thermal and mechanical properties. Moreover, Nafion can induce permselectivity property against some compounds such as ascorbic acid, uric acid and dopamine which co-exist in the biological fluids and may interfere with glucose determination. Also, Nafion film prevents the passivation of electrode surface by side products of ECL reaction and improves the reproducibility of the ECL system.

3. Results and discussion

3.1. Characterization of GCE/nanoCo-MWCNTs

Energy dispersive X-ray spectroscopy (EDS) and transmission electron microscopy (TEM) were used to characterize the prepared nanoCo-MWCNTs (Fig. S1). The analysis of EDS profile revealed that the calculated atomic levels of carbon and cobalt were approximately similar to the applied amounts of MWCNTs and cobalt for the preparation of nanohybrid. Also, the formation of Co-NPs with an average diameter of 5 nm on the outer surface of MWCNTs was approved by TEM images.

The presence of Co-NPs in the prepared nanohybrid material was approved by cyclic voltammetry (CV) studies in alkaline solution (pH = 12) at a scan rate of 20 mV s^{-1}. Noticeable redox peaks were observed for GCE/nanoCo-MWCNTs and no redox peaks for GCE/MWCNTs and GCE (Fig. S2). The appearance of several redox peaks at different potentials was attributed to the conversion between different forms of cobalt which were stable at alkaline pH [38,39,43,45–47].