



Cathodic electrogenerated chemiluminescence of luminol on glassy carbon electrode modified with cobalt nanoparticles decorated multi-walled carbon nanotubes



Behzad Haghighi^{a,b,*}, Azam Tavakoli^a, Somayyeh Bozorgzadeh^a

^a Department of Chemistry, Institute for Advanced Studies in Basic Sciences, P.O. Box 45195 - 1159, Gava Zang, Zanjan, Iran

^b Department of Chemistry, College of Sciences, Shiraz University, Shiraz 71454, Iran

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ABSTRACT

Cobalt nanoparticles with a typical size of 5 nm were decorated on multi-walled carbon nanotubes by the use of a simple, rapid, solvent less thermal decomposition method. The cathodic electrogenerated chemiluminescence (ECL) behavior of luminol was investigated on a glassy carbon electrode modified with cobalt nanoparticles decorated multi-walled carbon nanotubes. The prepared sensor exhibited excellent electrocatalytic activity towards production of reactive oxygen species (ROSSs) and consequently oxygen reduction reaction. Sweep of potential in cathodic direction produced an ECL signal at the potential about -0.5 V versus Ag|AgCl|KCl_{sat} due to the reaction between deprotonated form of luminol and ROSSs. The produced cathodic ECL signal intensity was linear towards luminol in the concentration range between 5 and 770 μM ($r=0.9984$) with a detection limit of 110 nM. Also, under optimal conditions, the ECL signal intensity of luminol was linear towards dissolved O₂ in the concentration range between 0.08 and 0.94 mM ($r=0.9914$) with a detection limit of 0.04 mM. The relative standard deviations (RSD) for repetitive measurements of 20 μM luminol ($n=10$) and 0.50 mM oxygen ($n=10$) at pH = 9.0 were of 3.0 and 3.9%, respectively. A possible mechanism for cathodic ECL reaction of luminol has been discussed.

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1. Introduction

Electrogenerated chemiluminescence, so called ECL, as one of the most empowerment analytical techniques is a combination of the electrochemical and luminescence techniques. As a result of this combination superior advantages such as high sensitivity, low background signal, wide dynamic range, and simple and inexpensive instrumental set up [1–3] have been introduced for ECL.

A great deal of attention has been paid to the anodic ECL reaction of luminol on the surface of various electrodes. Luminol is one of the most efficient and widely used luminophors which its anodic ECL usually appears around +0.5 V vs. Ag|AgCl|KCl_{sat} [4–10]. But the cathodic ECL reaction of luminol has been rarely explored in comparison with its anodic ECL reaction. The cathodic ECL which is commonly known as a hot-electron-induced ECL [11,12] can be observed on the oxide covered metal electrodes such as aluminum, tantalum, magnesium, gallium or indium [13–15].

The cathodic ECL despite of the common anodic ECL is extremely considered to promote the fabrication of ECL based biosensors due to its special features such as high sensitivity, wide dynamic range, low detection limit and good biocompatibility. Since the first study on cathodic ECL reaction of luminol on indium-tin oxide (ITO) electrode [16] several articles have been published on this topic. Kulmala et al. obtained strong ECL response for luminol during cathodic pulse polarization of oxide-covered aluminum electrode in aqueous solution. Concentration of luminol was determined in sub-nanomolar level in a wide linear range covering several orders of magnitude [14].

By the sweep of potential in negative direction, oxide covered metal electrodes can inject electron into the electrolyte solution and cause generation of reactive oxygen species (ROSSs). ROSSs are strong oxidizing radicals and generally highly reactive species due to the presence of unpaired valence shell electron. Singlet oxygen (¹O₂), superoxide hydrogen (HO₂[•]), superoxide radical (O₂^{•-}), hydroxyl radical (OH[•]) and inorganic or organic peroxides are the most well-known ROSSs [17,18]. The performance of cathodic ECL is restricted by the applied reduction potential and by the instability of intermediates. Applying very high negative potential causes hydrogen evolution and consequently instability of ECL response. A

* Corresponding author. Tel.: +98 241 4153 126; fax: +98 241 4153 232.

E-mail address: haghighi@iasbs.ac.ir (B. Haghighi).

large number of electrode materials such as oxide-covered tantalum [12], bismuth [19], AuSb alloy [20], graphene [21], niobate semiconductor [22] and different chemically modified electrodes including C-doped titanium oxide amorphous semiconductor electrode [23], nafion-nano-TiO₂ modified glassy carbon electrode [24], polyaniline/ordered mesoporous carbon (CMK-3) as an organic-inorganic hybrid electrode [25], and Pd and Pt nanoparticles decorated graphene [26] have been examined to eliminate the limitation of reduction potential.

Nowadays, nanoscale science and engineering hold great promise for the fabrication of novel nano-(bio) sensors which offer faster response and higher sensitivity. Nanostructured materials which used for the (bio) sensor fabrication show better physical, electrical and catalytic properties in comparison with their bulk counterparts. They provide higher effective surface area for mediator and biomolecule loadings. They improve the rate of electron transfer and enhance the response time of (bio) sensor [9,25,27,28]. In cathodic ECL reaction, nanomaterials not only increase the effective surface area of the electrode but also improve the rate of electron injection from the electrode interface to the electrolyte solution for ROSs production. Among of various types of nanostructured materials, gold nanoparticles (Au NPs) [29] and carbon nanotubes (CNTs) have been widely used for ECL measurements because of their excellent enhancement effect on ECL responses [30]. Carbon nanotubes have great potential for specific surface engineering applications owing to their unique tunable properties such as conductivity and high tensile strength. The surface of CNTs can be decorated with metal NPs to create a new class of nano-hybrid material with the integrated properties of two components. CNTs decorated with metal nanoparticles show integrated electrochemical, mechanical and catalytic properties which are not available to the respective components alone [28,31]. There are many reports on the application of Co and cobalt oxide NPs decorated electrodes for the biological and environmental analysis [32–36]. But to the best of our knowledge, the application of Co NPs for ECL measurements has not yet been reported.

In this study, multi-walled carbon nanotubes (MWCNTs) was decorated with cobalt nanoparticles (nanoCo) to prepare a nano-hybrid material (nanoCo-MWCNTs) by a simple, low cost and solvent-less method. After that, the surface of a glassy carbon electrode (GCE) was modified with nanoCo-MWCNTs and a layer of Nafion to fabricate a new sensor (GCE/nanoCo-MWCNTs/Nafion). The electrochemical and cathodic ECL behaviors of GCE/nanoCo-MWCNTs/Nafion were investigated towards luminol and dissolved oxygen. The proposed sensor exhibited excellent electrocatalytic activity towards oxygen reduction. A stable and intense ECL response was observed for luminol under sweeping potential in cathodic direction without the use of any additional common co-reactant such as hydrogen peroxide or peroxydisulfate ion. The proposed GCE/NanoCo-MWCNTs/Nafion sensor showed improved analytical performance in terms of linear dynamic range, reproducibility and stability.

2. Experimental

2.1. Chemicals, apparatus and procedure

All chemicals were of analytical reagent grade and used without further purification. Luminol, cobalt (II) acetate tetrahydrate, 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). Nafion perfluorinated ion-exchange (5% solution in 90% light alcohol) was obtained from Fluka (Buchs, Switzerland).

The hybrid of nanoCo-MWCNTs with 1 mol% Co loading (0.08 mmol Co ~ 4.72 mg Co ~ 19.92 mg Co(CH₃COO)₂·4H₂O per 100 mg MWCNTs ~ 8 mmol carbon equivalent) was prepared according to the method reported previously via manual mixing without modifications [37].

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 9). Analytical grade O₂ and Ar gases were used for the preparation of solutions saturated with oxygen and argon gases, respectively.

Analytical grade argon and oxygen gases were used for the preparation of solutions saturated with Ar and O₂ gases, respectively. Phosphate buffer solution (0.1 M, pH 9.0) saturated with Ar and O₂ gases were prepared separately by sparging of Ar and O₂ into the PBS for at least 30 min. The working phosphate buffer solutions (0.1 M, pH 9.0) containing different amounts of O₂ were prepared by mixing different ratios of Ar and O₂ saturated phosphate buffer solutions.

Electrochemical and ECL measurements were carried out in a 4 mL homemade Teflon ECL cell [7] using an Autolab potentiostat-galvanostat model PGSTAT30 (Utrecht, The Netherlands) with a conventional three-electrode set-up and a Hamamatsu photomultiplier module (H7468) (Hamamatsu city, Japan). The photodetector and ECL cell were enclosed in a light-tight black box. The working potential was applied to the working electrode in the standard way using the potentiostat and the output electrochemical and ECL signals were acquired using Autolab NOVA software and a home-written data acquisition program, respectively. All measurements were performed in a phosphate buffer solution (PBS, 0.1 M, pH 9) and at room temperature.

2.2. Fabrication of GCE/nanoCo-MWCNTs/Nafion

A 4 μL suspension of nanoCo-MWCNTs in DMF (1 mg mL⁻¹) was cast on the polished surface of a GCE and the solvent was evaporated in an oven at 60 °C. Then, 5 μL of Nafion solution (0.1%) was cast on the surface of the prepared GCE/nanoCo-MWCNT to fabricate a luminol sensor (GCE/nanoCo-MWCNTs/Nafion). Nafion layer prevented the passivation of electrode surface by side products of ECL reaction and improved the reproducibility of the luminol ECL system. For comparison, GCE/MWCNTs/Nafion and GCE/Nafion were also prepared through similar procedures.

3. Results and discussion

3.1. Characterization of nanoCo-MWCNTs

The prepared nano-hybrid, nanoCo-MWCNTs, was characterized by transmission electron microscopy (TEM), energy dispersive X-ray spectroscopy (EDS), electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV). TEM images of nano-hybrid (Fig. 1) obviously showed the formation of cobalt nanoparticles with a typical size 5 nm on the surface of walls of MWCNTs. The analysis of EDS profile of nanoCo-MWCNTs showed a similar ratio between calculated atomic level of cobalt and carbon and added amounts of cobalt and MWCNTs in the preparation step i.e. 1 mol% Co (Fig. S1). CV studies in alkaline solution (pH = 12) using GCE/nanoCo-MWCNTs with the scan rate of 20 mV s⁻¹ approved the presence of cobalt nanoparticles on MWCNTs surfaces. (Fig. S2). Noticeable redox peaks in cyclic voltammograms of GCE/nanoCo-MWCNTs were attributed to the conversion between four different cobalt oxidation phases of Co(OH)₂, Co₃O₄, CoOOH and CoO₂ which they were almost stable in alkaline solution. The obtained results were in good agreement with those reported previously [38,39].

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