Electrochimica Acta 55 (2010) 1265–1271

Contents lists available at ScienceDirect

Electrochimica Acta

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

Direct electrochemiluminescence of CdTe quantum dots based on room temperature ionic liquid film and high sensitivity sensing of gossypol

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ARTICLE INFO

Article history:
Received 19 July 2009
Received in revised form 13 October 2009
Accepted 14 October 2009
Available online 21 October 2009

Keywords:
Room temperature ionic liquids
Electrochemiluminescence
CdTe
Quantum dots
Gossypol

ABSTRACT

A new method with high sensitivity was developed to determine gossypol content using CdTe quantum dot (QD) electrochemiluminescence (ECL) with a room temperature ionic liquid (RTIL) modified glassy carbon (GC) electrode. It was found that use of RTIL film on the GC electrode can greatly enhance the ECL intensity of CdTe QDs, and the ECL peak potential and ECL onset potential were both shifted positively. Under optimal conditions, the quenching effect of gossypol on the ECL emission of CdTe QDs was observed, and ECL intensity showed a good linear relationship in the gossypol concentration range of 5.0×10^{-7} to 5.0×10^{-9} M with a detection limit of 5.0×10^{-9} M. The proposed method was used to detect gossypol in cottonseed oil with satisfactory results. As a result, the introduction of an RTIL-modified electrode can extend the analytical applications of QD ECL systems.

1. Introduction

Gossypol ($C_{30}H_{30}O_8$) is a polyphenolic compound that has been associated with a wide range of important applications, including use as a male oral contraceptive [1], an anticancer agent [2,3], and in other biological functions [4,5]. It contains a yellow pigment and is most likely the major toxic ingredient extracted from cottonseeds [6]. Cottonseed and cottonseed meal are widely used as protein supplements in animal feed, and cottonseed oil has been consumed as edible oil. Cottonseed oil soapstock is the principal byproduct of cottonseed oil refinement and is increasingly used in animal feed additives; cottonseed hulls are used as a source of additional fiber in animal feeds and usually contain much lower gossypol concentrations than do whole cottonseeds. Gossypol occurs in these cottonseed products in both protein-bound and free forms; the free form is toxic. Signs of acute gossypol poisoning are breathing difficulty, violent and labored respiration, weakness and death. The food and animal agricultural industries must manage gossypol levels to avoid this toxicity, and cottonseed oil must therefore be carefully refined. An analysis of free gossypol levels may be useful in supporting a diagnosis of gossypol poisoning. However, to date, HPLC [7–9] and UV–vis [10] methods have been used for its quantitatively analytical measurement. Therefore, the development of a more simple and sensitive method for gossypol detection is of great importance.

Electrochemiluminescence (ECL), which is developed from chemiluminescence (CL), not only retains the advantages of CL but also has other fascinating features, such as the use of simple equipment, an electrochemically triggered process with ultra low optical background and excellent temporal and spatial controllability, and this method has been employed in a number of fields [11–16]. Recently, ECL research involving quantum dots (QDs) has received considerable momentum because of optical, electrical, electrochemical and luminescent properties that make QDs an attractive material for application in ECL, beginning when Bard and coworkers [17] first reported ECL of Si QDs in an organic solvent. Subsequently, ECL of other QDs in organic solutions [18–22] and in aqueous [23–37] systems has been quickly developed. The latter research has been of more interest since it can vastly enrich strategies for potential applications and has been subsequently designed for H_2O_2 [24,26], glucose [27], amino acid [28] and proteins [29,30]. Previously, the QD ECL method has not been used for gossypol detection. In these cases, ECL research was carried out with bare electrodes or by modifying QDs with electrodes. Studies using direct ECL of QDs and using chemically modified electrodes are rare. Our previous work has introduced the CNT-modified electrode into ECL of CdTe QDs and found this to be an effective approach to optimization of the ECL of QDs [32]. Further studies regarding the direct ECL of CdTe QDs with RTIL-modified electrodes were therefore conducted and are reported here.

Ionic liquids (ILs) are ionic compounds consisting of large organic cations and various kinds of anions that exist in the liquid state over a wide temperature range [37]. Investigation of ILs has gained increasing attention because of their unique chemical

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0013-4686/$ – see front matter © 2009 Published by Elsevier Ltd.
doi:10.1016/j.electacta.2009.10.038

and physical properties, such as high chemical and thermal stabilities, negligible vapor pressure, high ionic conductivity, low toxicity, and the ability to dissolve a wide range of organic and inorganic compounds [38]. Recently, as a new kind of chemically modified electrode, IL-modified electrodes have aroused great interest [39–41] due to characteristics such as a simple preparation procedure, wide potential windows, high rates of electron transfer, and good anti-fouling ability. The electrochemical behaviors of different kinds of IL-modified electrodes have been reported previously. For example, Safavi et al. reported the direct electrochemistry of Hb and its electrocatalytic effect based on direct immobilization on a carbon IL electrode [42]. Sun et al. studied the electrochemical behaviors of guanosine on an IL-modified carbon paste electrode, and furthermore used it for guanosine detection [43]. However, to the best of our knowledge, ECL studies with an RTIL-modified electrode have been rarely reported, and there is no previous report on the ECL of QDs using RTIL-modified electrodes.

In this paper, the RTIL of 1-butyl-3-methylimidazolium hexafluorophosphate ($BMIMPF_6$) was used as a new type of binder to construct a chemically modified glassy carbon (GC) electrode, and the direct ECL of CdTe QDs was studied. The RTIL-modified electrode is capable of improving the electrochemistry reaction in the process of CdTe QD ECL and further increasing the intensity of ECL. Such a property would promote the application of QD ECL with RTIL-fabricated sensors for chemical analysis. The ECL emission of CdTe QDs is quenched by gossypol, and the ECL intensity decreases linearly in the concentration ranges of 5.0×10^{-7} to 5.0×10^{-9} M. Finally, a highly sensitive method for the detection of gossypol was proposed, which shows satisfactory results for detection of the gossypol in cottonseed oil. As a result, the introduction of an RTIL-modified electrode can extend the analytical application of QDs ECL systems.

2. Experiment

2.1. Chemicals and materials

Nafion solution (5.0% in methanol with an equivalent weight of about 1100; Aldrich Chemicals Co.), $BMIMPF_6$ (99.0%) were purchased from Alfa Aesar Chemical Reagent Co., Ltd. and used without further purification (American). Gossypol was bought from Sigma–Aldrich Chemie (American). $CdCl_2 \cdot 2.5H_2O$ (99.0%), Tellurium powder (99.9%) and $NaBH_4$ (96.0%) were obtained from Tianjin Chemical Reagent Plant (Tianjin, China). Thioglycolic acid (TGA) and Na_2TeO_3 were obtained from Sinopharm Chemical Reagent Co., Ltd. (American). L-Isoleucine (L-Ile), L-threnine (L-Thr), L-alanine (L-Ala), L-proline (L-Pro) and L-glutamic (L-Glu) were purchased from Shanghai Boao Biotechnology Co., Ltd. (Shanghai, China). All other reagents were of analytical grade and ultrapure water was used throughout. A 0.1 M phosphate buffer solution (PBS, pH 7.5) was used, and the buffer pH was adjusted by changing the ratio of Na_2HPO_4 to NaH_2PO_4. The stock solution of 10 mM gossypol was freshly prepared with a 0.5 M NaOH solution from which dissolved oxygen had been removed. Cottonseed oil was obtained from Huazhong Agricultural University.

2.2. Instrumentation

Ultraviolet–visible (UV–vis) absorption and the photoluminescence (PL) spectrum were recorded on a Nicolet Evolution 300UV-Vis spectrophotometer (America) coupled with a 1.0 cm quartz cell and a Perkin-Elmer Model LS-55 luminescence spectrometer equipped with a 20 kW xenon discharge lamp as a light source, respectively. The excitation wavelength of PL was fixed at 390 nm. A high-resolution transmission electron microscopy (HRTEM) image of the CdTe QDs was acquired on a JEM2010FEF HRTEM (Japan). ECL emission was detected using a Model MPI-B ECL analytical system (Xi'An Remax Electronic Science & Technology Co. Ltd., Xi'An, China) with an 800 V photomultiplier (PMT) tube voltage. The lab-built electrochemical cell consisted of a Ag/AgCl reference electrode (saturated KCl), a platinum wire counter electrode, and an RTIL-modified electrode as the working electrode.

2.3. Synthesis of thiol-capped CdTe QDs

The CdTe QDs capped with thiols were synthesized according to the literature [44] with little modification. Briefly, 38 ml of ultrapure water and 10 ml of 0.01 M $CdCl_2$ were transferred to a small flask under N_2 atmosphere and held for about 15 min. Then, 10 μl of TGA was added quickly, followed by adjustment of the pH to 11.0 by dropwise addition of 1 or 0.5 M NaOH, until the mixture became clear. A 55.5 mg quantity of tri-sodium citrate and 2 ml of 0.01 M Na_2TeO_3 were injected into the above mixture solution. Finally, 3.0 mg of $NaBH_4$ was added, and the solution was de-aerated by highly pure N_2 bubbling for 10 min. After mixing, about 25 ml of this mixture was transferred to a reaction kettle, heated to 180 °C and refluxed for 60 min; thus, thiol-capped CdTe QDs could be obtained. Afterward, the resulting products were precipitated by acetone, and superfluous TGA and Cd^{2+} were removed by centrifugation at 3000 rpm for 5 min. The resultant precipitate was redispersed in water, reprecipitated three times by a copious amount of acetone, and then kept in the dark for further use.

2.4. Fabrication of RTIL-modified electrode

Prior to modification, the GC electrode was carefully polished mechanically with a 1, 0.3, and 0.05 μm Al_2O_3 slurry on different polishing cloths, rinsed with ultrapure water, and then sonicated in nitric acid (1:1), NaOH (1 M), anhydrous alcohol, and doubly distilled water for about 4 min in turn. The clean electrode was allowed to dry at room temperature.

About 0.5 ml of RTILs were transferred to a 5 ml measuring flask, and Nafion (0.5% v/v) was added to constant volume. Then, 8 μl of the RTIL/Nafion was cast onto the surface of a clean GC electrode with a microsyringe and allowed to dry at room temperature to form a stable film. The final electrode produced was an RTIL/GC electrode. If not used immediately, it was stored at 4 °C in a refrigerator.

2.5. Sample preparation

An amount of 5 g of cottonseed oil was collected in a sample tube, and 30 ml of methanol was added. The mixture was shaken for about 7 h at 30 °C. After quiescence, the insoluble substances were filtered from the solution under normal pressure. Then, 5 ml of filtrate was kept bubbling with highly pure N_2, until a yellow powder was finally obtained. The yellow powder was dissolved and diluted with 0.5 M NaOH solution, from which dissolved oxygen had been removed. The diluted samples were spiked with selected amounts of gossypol standard solution and detected with the proposed method.

3. Results and discussion

3.1. Characterization of water-soluble CdTe QDs

From Fig. 1A, the UV–vis absorption spectrum shows that the CdTe QDs solution possesses a well-resolved absorption