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A novel signal-off electrochemiluminescence biosensor for the determination of glucose based on double nanoparticles

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In this work, a novel facile signal-off electrochemiluminescence (ECL) biosensor has been developed for the determination of glucose based on the integration of chitosan (CHIT), CdTe quantum dots (CdTe QDs) and Au nanoparticles (Au NPs) on the glassy carbon electrode (GCE). Chitosan displays high water permeability, hydrophilic property, strong hydrogel ability and good adhesion to load the double nanoparticles to the glassy carbon electrode surfaces. Au NPs are efficient glucose oxidase (GOx)-mimickess to catalytically oxidize glucose, similar to the natural process. Upon the addition of glucose, the Au NPs catalyzed glucose to produce gluconic acid and hydrogen peroxide (H_2O_2) based on the consumption of dissolved oxygen (O_2), which resulted in a quenching effect on the ECL emission. Therefore, the determination of glucose could be achieved by monitoring the signal-off ECL biosensor. Under the optimum conditions, the ECL intensity of CdTe QDs and the concentration of glucose have a good linear relationship in the range of 0.01–10 mmol L^{-1}. The limit of detection for glucose was 5.28 μmol L^{-1} ($S/N=3$). The biosensor showed good sensitivity, selectivity, reproducibility and stability. The proposed biosensor has been employed for the detection of glucose in human serum samples with satisfactory results.

Contents

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1. Introduction

Glucose is the primary energy source of the body. The level of glucose in blood has been used for diagnosis of diabetes or hypoglycemia. Besides the need for glucose monitoring in the case of diabetes patients, it is also essential for non-diabetic acute care patients in order to control glucose levels (Matz et al., 2006). Therefore, a huge amount of glucose biosensors have been reported, such as those based on optical techniques (Barone et al., 2005), color metric measurement (Morris et al., 1992) and capacitive detection (Cheng et al., 2001). In recent years, a tremendous amount of attention and effort has been paid to develop ultrasensitive glucose biosensors including electrochemical (Si et al., 2013), surface enhanced Raman scattering (Wu et al., 2006), chemiluminescence (Li et al., 2000), electrochemical transistor biosensor (Liu et al., 2008) and potentiometric biosensor (Liao et al., 2007). However, many approaches suffer from limitations of complicated pretreatment steps, equipment costs and expensive labor resources and time are consuming. Obviously, an effective analytical method for rapid determination of glucose is urgently needed.

Electrochemiluminescence (ECL) is a versatile analytical technique that combines the simplicity of electrochemistry with inherent sensitivity and wide linear ranges of the chemiluminescence method. Most importantly, ECL biosensors have lots of advantages, including high sensitivity, low backgound, ease of control and simple equipments (Zheng et al., 2001; Chovin et al., 2004). Semiconductor quantum dots (QDs) have attracted great attention in the past decade, due to their remarkable optoelectronic properties, such as narrow, symmetrical and size-tunable emission spectrum, broad excitation spectrum, large Stokes shift, high photo-bleaching threshold and good chemical stability (Hanif et al., 2002; Ma and Su, 2011). Uptil now, numerous reviews about QDs-based ECL have been published (Lei and Ju, 2011; Huang et al., 2011; Li et al., 2012). Further, QDs have been widely used to detect various substances via ECL methods. At the same time, great effort has been focused on the QD-based ECL behavior and mechanism. The thin-film technique has provided an effective way for the construction of QD-based ECL biosensors in aqueous solutions (Jie et al., 2008). Chitosan is a polysaccharide biopolymer, which displays excellent film-forming ability, high water permeability and hydrophilic property, strong hydrogel ability and good adhesion with the functional nanoparticles to the electrode surfaces (Kumar et al., 2004; Zhang et al., 2004). Furthermore, the previous research works demonstrated that the CHIT had strong adsorbing ability (Luo et al., 2005).

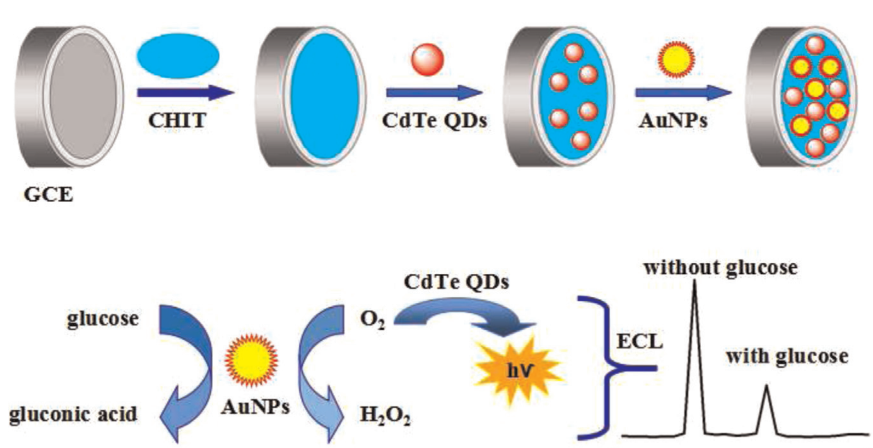
Due to the attractive electronic properties, Au nanoparticles (Au NPs) have a wide range of applications like catalysis and bioanalysis (Gong and Mullins, 2009; Lee et al., 2010; Corma and Garcia, 2008; Hammer, 2006). Recently, Au NPs were found to be efficient GOx-mimickess; they can catalytically oxidize glucose and produce gluconates in a "green" approach, similar to that of the natural enzyme of GOx (Comotti et al., 2004). Au NPs also catalyzed the oxidation of glucose with the cosubstrate oxygen (O_2), producing gluconate and hydrogen peroxide (Beltrame et al., 2006). Comparing with glucose oxidase, Au NPs as biomimetic enzymes possess more advantages, such as providing an easy approach for preparation and purification, having high stability, avoiding degeneration and inactivation.

In this paper, we report a new and simple method for the fabrication of an ECL biosensor by using an Au NPs-CdTe QDs-CHIT/GCE composite film. Scheme 1 describes the preparation of the composite film and the mechanism of the ECL system for analysis of glucose. For the composite films, CHIT can connect CdTe QDs and Au NPs to the glass carbon electrode via powerful adsorption ability. When glucose is added into the system, Au NPs serve as a catalyst and dissolved O_2 acts as a cosubstrate for the glucose oxidation reaction. Dissolved O_2 also worked as coreactant for the cathodic CdTe QDs ECL emission. Due to the consumption of dissolved O_2 , a quenching effect would appear on the CdTe QDs ECL emission. The main features of this biosensor are: (i) chitosan displays excellent film-forming ability, high water permeability, strong hydrogel ability and good adhesion to load the double nanoparticles onto the glassy carbon electrode surfaces; (ii) Au NPs have not only accelerated electrical conductivity but can also oxidize glucose as GOx-mimickers in this green no-enzyme system; and (iii) to the best of our knowledge, the signal-off CdTe QDs ECL biosensor for glucose determination based on Au NPs as GOx-mimickess has not been reported before. The proposed Au NPs-CdTe QDs-CHIT/GCE system is a novel ECL biosensor with good selectivity and stability. Further, it was successfully applied to the determination of glucose in samples of human serum with good accuracy and precision.

2. Experiment section

2.1. Materials and apparatus

All chemicals and reagents were analytical grade and used directly without further purification. 3-Mercaptopropyl acid (MPA) was purchased from J&K Chemical. Tellurium powder (~200 mesh, 99.8%), $CdCl_2$ (99%) and $NaBH_4$ (99%) were purchased from Aldrich Chemical Co. $HAuCl_4$ was purchased from Acros Organics. Glucose and other materials were obtained from Beijing Dingguo Biotechnology Co. Ltd. All reagents were prepared using ultrapure water



Scheme 1. The schematic illustration of the ECL biosensor for determination glucose based on Au NPs-CdTe QDs-CHIT/GCE composite film.