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Electrochemical, spectroscopic and electrochemiluminescent characterization of self-assembled 3-aminopropyltriethoxysilane/CdTe quantum dots hybrids on screen-printed electrodes

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ABSTRACT

This work describes the electrochemical, spectroscopic and electrochemiluminescent (ECL) characterization of graphite screen-printed electrodes (SPE) modified with a multilayer electrostatic assembly between 3-aminopropyltriethoxysilane (APTES) and CdTe quantum dots stabilized with glutathione (GSH) as the cationic and the negative layers, respectively. The characterization of the obtained system was performed by cyclic voltammetry, electrochemical impedance spectroscopy, scanning electron microscopy and Raman spectroscopy, which confirm the homogeneous presence of CdTe quantum dots on the multilayer assembly. The electrochemiluminescent properties were measured in a potentiostat coupled with a photodiode detector, showing stable and repetitive electrochemiluminescent signals. The ECL response was studied using potassium persulfate and hydrogen peroxide as co-reactants, and the measurements were carried out at different scan rates, pH values and concentrations. The ECL properties of the studied system at specific experimental conditions demonstrated different mechanisms by changing the co-reactants associated with the electrochemical step to generate the radical species and its interaction with the SPE/APTES/CdTe (GSH) reduced system, obtaining a more intense ECL signal with H_2O_2 than with $S_2O_8^{2-}$. Some analytical parameters, such as the linear range and the limit of detection for SPE/APTES/CdTe (GSH) in ECL H_2O_2 detection, were obtained.

1. Introduction

Electrochemiluminescence (ECL) is defined as the generation of light activated by an electrochemical process. Compared to fluorescence techniques, the former can be easily miniaturized, made portable, and the optical noise can be minimized [1–4]. ECL has gained great interest for applications such as sensors [5], biosensors [6,7], bipolar sensors [8,9], and microscopy [10]. ECL signal can be generated by different electrochemical techniques, including cyclic voltammetry, square wave voltammetry, and chronoamperometry, with different light detectors and different configurations of electrochemical cells [11,12].

A relevant material with ECL properties are semiconductor nanoparticles, such as quantum dots, which have also gained great interest since the work of Bard and collaborators [4,6,13–16]. ECL properties, similar to the optical properties of quantum dots, can be modulated by changing the size of nanoparticles, with interesting applications in sensors and biosensors [15,17–21]. Several works have reported the use of specific stabilizing agents to synthesize quantum dots, inducing properties such as charge, disposable functional groups to crosslink reactions, etc. [1,21–24], or by using electrostatic interactions with convenient counterions [23,25]. However, to our knowledge, there is only one study about the ECL

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of quantum dots immobilized on screen-printed electrodes [26].

The ECL properties of quantum dots, by employing the typical bulk one compartment, three electrode configuration cell, have been reported to depend on the surface states of the semiconductor, and the key process to generate light has been proposed to be associated with the ability to recombine the electron/hole pair on the surface [1,27]. In these studies, cathodic ECL of quantum dots was observed; for example, the working electrode donates an electron from a high energy level toward the conduction band of the semiconductor nanoparticles. At the same time, in the majority of cases, sacrificial radical species with highly oxidative character are electrochemically generated from the co-reactant. Such radical species can take an electron from the valence band of the semiconductor, thus generating an excited state of the quantum dots, characterized by the electron/hole pair configuration. At this point, recombination must take place, returning the quantum dots to the ground state and yielding light as a product [16,27].

More specifically, the ECL properties of CdTe stabilized with glutathione (GSH) have been described to be poor in colloidal suspension using indium tin oxide (ITO) electrodes as the working electrode. Results have shown poor ECL, presumably due to the lack of flexibility of the glutathione compared to other less rigid stabilizing agents, such as thioglycolic acid, that desactives the excited state generated for ECL process of quantum dots [4,28]. Other work has focused in the study of the optimization of co-reactants in the presence of quantum dots immobilized on polymeric platforms and have proposed that the near-infrared ECL properties of quantum dots are improved if persulfate is the coreactant [16]. Zhang et al. have studied the ECL of ITO electrodes modified with CdTe/ZnS nanoparticles in anodic scans because, at these potentials, the working electrodes can be oxidized and take part in the ECL process cooperatively with CdTe quantum dots, avoiding the use of a co-reactant in solutions and giving reproducible results [20].

Specifically, in the case of screen-printed electrodes (SPE), the most typical electrochemical process to generate ECL signal is by the oxidation of $[Ru(bpy)_3]^{2+}$ in the presence of tripropylamine as the co-reactant [29,30] or 3-aminophthalhydrazide (luminol) in the presence of hydrogen peroxide as the co-reactant [12,31]. In these examples, the species that generates light are obtained toward positive scans, yielding an oxidizing state of the initial compound and radical species from the co-reactant with a high reducing capability to induce an excited species that finally relaxes to yield the original compound and light as products.

On the other hand, the use of ethoxysilane derivatives to modify an oxygen-rich surface is a very common silanization process, generating disposable functional groups for a specific requirement. For instance, ITO electrodes have been modified covalently with 3-aminopropyltriethoxysilane (APTES) since the terminal amine group of APTES may link covalently to carboxylate groups in the stabilizing agent present in quantum dots [23] or induce electrostatic interactions to immobilize negatively charged gold-silica nanoparticles [32]. This strategy is achieved considering the pK_a of APTES, generating a cationic layer available for electrostatic assembly. Kyaw and coworkers have proposed that APTES can adopt different self-assembly positions on glass to immobilize gold nanoparticles, achieved by changing the concentration of APTES and the time of deposition, among other parameters [33]. These observations are in agreement with the work of Zhi and coworkers, who demonstrated that the modification of graphene nanoparticles with APTES can increases the number of conductive sites, where APTES reacts with oxygen functional groups present in the carbon nanoparticle [34].

Related to oxygen functional groups, graphite screen-printed electrodes (SPEs) present a highly functionalized working surface and edge regions that contribute to their conductive properties [11,35]. The electroactivity of graphite can be increased with different treatments and studied using typical redox couples, such as $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ or $[Ru(NH_3)_6]^{3+}/[Ru(NH_3)_6]^{2+}$.

This work describes the modification of graphite screen-printed electrodes with APTES, electrostatically assembled with CdTe (GSH) quantum dots. The obtained SPE/APTES/CdTe (GSH) systems were characterized and studied by several techniques, including cyclic voltammetry, electrochemical impedance spectroscopy, scanning electron microscopy and Raman spectroscopy, to gain insights about their ECL process. The ECL properties were studied using $S_2O_8^{2-}$ and H_2O_2 as co-reactants by cyclic voltammetry scanning toward negative potentials, varying pH values, scan rates and concentrations. Some analytical parameters of SPE/APTES/CdTe (GSH) as an ECL sensor for hydrogen peroxide are explored.

2. Experimental

Reagents and solvents were purchased from Sigma-Aldrich or Merck and were used without further purification. Electrochemical impedance spectroscopy and cyclic voltammetry measurements were performed on a CH-Instrument 620B. ECL experiments were carried out by cyclic voltammetry in a μStat-ECL bipotentiostat (DropSens) coupled with a photodiode detector, considering the last five cycles from a total of 10 cycles. All data were collected with DropView 8400 software. Screen-printed electrodes (DRP 110) were purchased from DropSens™, where the working electrode was graphite (4 mm diameter), the pseudo-reference electrode was Ag^+/Ag and graphite was the auxiliary electrode. Tris (hydroxymethyl)aminomethane (tris) was employed in all experiments at a concentration at 0.100 M, by using doubly distilled water, in the presence of 0.100 M KCl as the supporting electrolyte. Solutions were adjusted to the desired pH using concentrated analytical grade 1.0 M HCl.

Scanning Electron Microscopy with Energy Dispersive X-ray spectroscopy (SEM-EDX) analyses were performed on a high-resolution imaging system via a Vegan 3 Tescan microscope coupled to a Bruker Quantax 400 energy dispersive X-ray detector.

Raman measurements were carried out using a Renishaw micro-Raman RM 1000 spectrometer equipped with laser lines at 514, 633 and 785 nm. The spectrometer was coupled to a Leica microscope and a thermoelectrically-cooled CCD detector. The Raman signal was calibrated to the 520 cm^{-1} line of silicon, and a 50× objective lens was used. Spectral recording conditions and the choice of the laser line were selected in order to avoid degradation of the sample; in this case, the 785 nm laser line was used.

2.1. Procedures

2.1.1. Synthesis of CdTe (GSH) quantum dots

The CdTe quantum dots stabilized with glutathione were synthesized according to literature reports [36]. The obtained nanoparticles were carefully purified with 2-propanol to achieve reliable ECL signals. Characterization of the obtained nanoparticles (3.80 nm) was carried out by UV vis, FT-IR, and fluorescence spectroscopy, as described in previous reports [25].

2.1.2. Electrode modification

Graphite SPEs were activated by 10 cyclic voltammetry scans at 100 mV/s in 0.1 M NaOH solution. The activated electrodes were rinsed with doubly distilled water and dried at 70 °C in an oven.

Five microliters of 3-aminopropyltriethoxysilane (APTES) solution at a concentration of 5.0% v/v in water was dropped on the activated surface of the working electrode of the SPE, and then dried at 70 °C for 1 h in an oven. After this procedure, the working electrode was rinsed with doubly distilled water to eliminate the