



Electrochemical detection of quantum dots by stabilization of electrogenerated copper species



Daniel Martín-Yerga, Agustín Costa-García *

Departamento de Química Física y Analítica, Universidad de Oviedo, 33006 Oviedo, Spain

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ABSTRACT

The determination of quantum dots is of particular interest as they are frequently used as labels in electrochemical biosensors. In this paper, we describe a method for the detection of very low concentrations of quantum dots using the voltammetric response of copper in ammonia solution. Copper species electrogenerated on the electrode surface are stabilized by the nanoparticles, preventing their oxidation by dissolved oxygen, and a relationship between the concentration of the nanoparticles and the copper voltammetric response can thus be obtained. The reported method shows a linear range between 0.05 and 2 nM of quantum dots, with a limit of detection in the order of 9×10^7 nanoparticles. This method could be employed to improve the detection limit of electrochemical biosensors using quantum dots as labels.

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1. Introduction

Quantum dots (QDs) are small semiconductor nanoparticles with interesting optical and electronic properties [1]. These properties, and the easy functionalization of the QDs, make them suitable for use as labels in bioassays [2]. Electrochemical detection is usually performed after the metals comprising the nanoparticles have been released to the solution by acid digestion [3,4], providing a large amount of metal for detection. However, this step increases the complexity of the detection process. Some methods have been proposed in order to simplify detection, such as *in situ* digestion and detection on the surface where the bioassay is performed [5,6], or the use of flexible devices in ELISA well plates [7]. Other methods have been proposed which avoid acid digestion of the nanoparticles, thus facilitating electrochemical detection. For example, the direct detection of cadmium from nanoparticles allows their quantification, but with a much lower sensitivity than that obtained by performing acid digestion [8]. Another method that does not require acid digestion involves the selective electrodeposition of silver on the surface of the QDs [9]. The stripping signal of the selectively deposited silver can then be used to determine the concentration of the QDs. In another interesting work, CdSe quantum dots were determined at low concentrations by the voltammetric reduction of borax, which is facilitated at nanoparticle-modified electrodes [10]. This apparent enhancement of the kinetics could be due to the organic capping agent of the nanoparticles, which could alter the mass transport or local solubility of the redox species [11]. The development of simple procedures that

improve sensitivity and reduce analysis times is thus of great interest. In this work, we describe a novel method for the electrochemical determination of CdSe/ZnS quantum dots that uses the voltammetric response of copper in ammonia solution.

2. Materials and methods

2.1. Apparatus and electrodes

Electrochemical measurements were conducted using a μ Stat 8000 (DropSens) potentiostat interfaced to an Apple Macbook Air laptop and controlled by DropView 8400 2.2 software. All measurements were carried out at room temperature. 8-channel screen-printed electrochemical arrays (SPCEs) were purchased from DropSens (ref. 8x110). Each array is formed by eight 3-electrode electrochemical cells with carbon-based working and counter electrodes; the quasireference electrodes and electrical contacts are made of silver. The dimensions of the device are $4.0 \times 7.9 \times 0.06$ cm (length \times width \times height) and the diameter of the circular working electrode is 2.56 mm. The 8-channel arrays were connected to the potentiostat through a specific connector, DRP-CAST8x. All measurements were performed without removing oxygen from the solution, at room temperature, using an aliquot of 25 μ L of the appropriate solution. All indicated potentials are relative to the silver quasireference screen-printed electrode.

2.2. Reagents and solutions

Ammonia solution (25% w/v) and fuming hydrochloric acid were purchased from Merck. Copper nitrate trihydrate and tris(hydroxymethyl)aminomethane (Tris) were purchased from

* Corresponding author at: Departamento de Química Física y Analítica, Universidad de Oviedo, Julián Clavería 8, Oviedo 33006, Spain.

E-mail address: costa@uniovi.es (A. Costa-García).

Sigma-Aldrich. CdSe/ZnS Qdot® 655 Biotin Conjugate (QDs) was purchased from Life Technologies. The supplied material was 2 μM in particle concentration. Ultrapure water obtained using a Millipore Direct Q5™ purification system from Millipore was used throughout this work. All other reagents were of analytical grade. Working solutions of QDs were prepared in 0.1 M pH 7.4 Tris-HCl buffer. Cu(II) solutions were prepared in 1 M NH_3 aqueous solution. Copper ions in ammonia solutions are typically complexed: $[\text{Cu}(\text{NH}_3)_4]^{2+}$ for a + 2 oxidation state, and $[\text{Cu}(\text{NH}_3)_2]^+$ or $[\text{Cu}(\text{NH}_3)_3]^+$ for a + 1 oxidation state [12,13]. To simplify the notation, these species will be referred to as Cu(II) and Cu(I), respectively. The concentration of QDs is always given as a particle concentration. The commercial QDs used have a core-shell structure of CdSe/ZnS and are functionalized with an outer organic/polymeric coating for solubility in aqueous solutions and for conjugation with biomolecules. The total size of the functionalized nanoparticles, which are ellipsoid in shape, is about 10 nm (larger diameter), as stated in the manufacturer's specifications and observed experimentally by transmission electron microscopy (TEM) in a previous work [9]. However, the manufacturer does not provide the exact size of the coating and the nanocrystal and they cannot be differentiated by TEM.

2.3. Electrochemical detection of quantum dots

Quantum dots were physisorbed on the electrode surface by placing a drop (4 μL) on the working electrode. The adsorption reached a maximum after 30 min and the analytical signal did not increase even when left overnight at 4 °C. After washing with H_2O , a drop (25 μL) of 25 μM $\text{Cu}(\text{NO}_3)_2$ in 1 M NH_3 was added to the electrochemical cell and a potential of -0.4 V was applied for 30 s to reduce Cu(II) to Cu(I). Square-wave voltammetry (SWV) was then performed between -0.4 and $+0.3$ V using the following parameters: 20 Hz frequency, 25 mV amplitude, 20 mV step potential and 3 s equilibration time.

3. Results and discussion

We first describe briefly the voltammetric response of copper at bare electrodes and compare it with that obtained at electrodes modified with QDs in aqueous ammonia solution. We then optimize our method of detecting QDs using the copper voltammetric response.

3.1. Electrochemistry of copper at bare and QD-modified screen-printed carbon electrodes

We have recently discovered that electrogenerated copper species in ammonia solution are stabilized on QD-modified electrodes (unpublished results [14]). Briefly, there is a clear difference between the voltammograms obtained for the electrochemical processes involving copper species at bare SPCEs and those for SPCEs modified with QDs

(60 μM of Cu(II) in 1 M NH_3 at 50 mV/s) (Fig. 1A). The electrochemical processes found in the cathodic curve can be attributed to the reduction of Cu(II) to Cu(I), the reduction of Cu(I) to Cu(0) and the oxygen reduction reaction (ORR), although the last two appear at a similar potential and are therefore difficult to resolve. The electrochemical processes found in the anodic curve can be assigned to the oxidation of Cu(0) to Cu(I) and the oxidation of Cu(I) to Cu(II) [15,16]. At initial Cu(II) concentrations below the concentration of dissolved O_2 (typically around 100 μM), a chemical reaction coupled to the electrochemical processes has a significant influence on the response obtained. This coupled reaction can be attributed to the oxidation of Cu(I) by O_2 to regenerate the initial Cu(II) at the electrode surface [17–19]. This is shown in the voltammograms as the appearance of a quasi-limiting current for the reduction of Cu(II) to Cu(I), and the disappearance of the anodic process corresponding to the oxidation of Cu(I) to Cu(II). This can be observed at higher resolution in Fig. 1B, where the voltammograms were recorded with a lower switching potential and lower Cu(II) concentration (40 μM). However, for electrodes modified with QDs, well-defined peak-shaped processes are observed. In this case, the influence of the coupled reaction is lower, the initial Cu(II) species is not regenerated as quickly at the electrode surface, and the Cu(I) species are available for the anodic reaction, which appears in the voltammogram as a peak-shaped response. It seems likely that the QDs on the electrode surface are able to stabilize the electrogenerated Cu(I) species, unlike the situation prevailing on bare SPCEs where the coupled reaction with O_2 occurs. The potentials of the electrochemical processes of the Cu(II)/Cu(I) redox couple are similar in the presence and absence of QDs, so it seems that the stabilization is due to weak adsorption of Cu(I) on the surface of the QDs, probably by interaction with the sulphide groups or with the functionalized layer. Something similar can be observed at more negative potentials for the Cu(I)/Cu(0) redox couple (see again Fig. 1A). In the presence of O_2 in NH_3 solution, Cu(0) is typically oxidized to Cu(II) [17], so the stripping process is quite diminished for bare SPCEs since Cu(0) is not stable. However, the response obtained for this same process at SPCEs modified with QDs is significantly higher. This implies that the QDs are also able to stabilize the Cu(0) electrogenerated at the electrode surface, preventing its oxidation by the O_2 present in the solution.

3.2. Electrochemical quantification of quantum dots by detection of stabilized copper species

Because copper shows an enhanced voltammetric response in the presence of QDs, the anodic processes could be used to quantify these nanoparticles. Fig. 2A shows the SWV response obtained for a solution of 40 μM Cu(II) in 1 M NH_3 after reduction at -1 V for 30 s using bare SPCEs and SPCEs modified with 1 nM of QDs. A higher peak current was obtained for both anodic processes when QDs are present on the

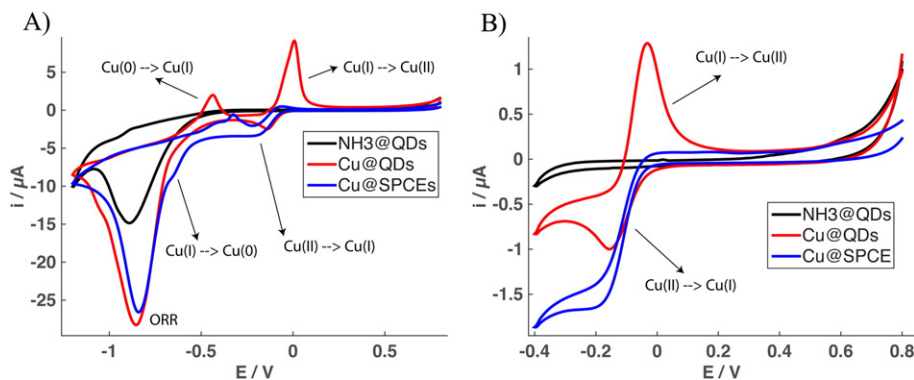


Fig. 1. A) Cyclic voltammograms from $+0.8$ to -1.2 V of a solution of 60 μM Cu(II) in 1 M NH_3 at bare SPCEs and SPCEs-modified with 5 nM of QDs. B) Cyclic voltammograms from $+0.8$ to -0.4 V of a solution of 40 μM Cu(II) in 1 M NH_3 at bare SPCEs and SPCEs-modified with 5 nM of QDs. Voltammetric response from a blank (1 M NH_3) solution at QDs-modified electrodes is shown in both figures as comparison.

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