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CdS quantum dots as a scattering nanomaterial of carbon nanotubes in polymeric nanocomposite sensors for microelectrode array behavior

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Abstract This work is focused on evaluating the direct electrochemical effect of semi-conducting nanocrystals when they are integrated in bulky nanocomposite sensors based on multiwalled carbon nanotubes (MWCNTs). For this aim, MWCNTs have successfully been functionalized with CdS quantum dots (CdS-QDs@MWCNTs) and then dispersed within an insulating polymeric matrix, as epoxy resin, for electroanalytical sensing purposes. After an accurate voltammetric and impedimetric characterization, some electrochemical parameters were surprisingly enhanced regarding the non-modified sensors, such as peak current height, electroactive area, and emphasizing the double-layer capacitance. These results can be explained since CdS-QDs confer to the nanocomposite sensor a microelectrode array behavior, dispersing the conductive microzones through the polymeric matrix, as revealed by morphological experiments. The feasibility of this approach was amperometrically evaluated for ascorbic acid and hydrogen peroxide, both used as reference analytes. Electroanalytical results demonstrated that this approach provides to the CdS-QDs-modified nanocomposite sensors the capability to determine low concentrations of analytes and improved sensitivities.

Introduction

Over the past decade, nanostructuring of surfaces has evolved as an interesting research target. Electrochemical sensors have benefited from this new technology mainly

due to modified diffusion characteristics, an increase in roughness, new electrocatalytic properties, and sensitivity enhancement [1–3].

Currently, high interest is focused on nanocomposites based on carbon nanotubes (CNTs) [4–6], due to their remarkable electrical, chemical, mechanical, thermal, and structural properties [7–9], particularly in electrochemistry and sensor development [10–12]. Among others, CNT and concretely multiwalled carbon nanotubes (MWCNTs) are also capable of increasing electrode roughness and electroactive area, improving electron transfer, enhancing signal-to-noise ratio, and providing electrocatalytic activity toward a wide variety of molecules [13, 14].

Some physical parameters, such as the bulk resistivity, the heterogeneous electron transfer rate, the material stability, and the background capacitance current, are strongly influenced by the distribution of the conducting filler material through the insulating polymeric matrix [15]. Thus, depending on the distance between the conductor microzones, nanocomposites can behave as microelectrode arrays. Microelectrode arrays are known to provide efficient mass transport of the electroactive species due to radial diffusion on the spaced carbon particles, favoring the sensitive electroanalysis of a wide range of analytes [16]. Literature shows works where the amperometric behavior of composite-based electrodes compared to microelectrode arrays is studied [17, 18]. In these cases, it is important to optimize the distance between microelectrodes (conductive microzones) in order to obtain an optimal signal-to-noise ratio. However, due to the random structure of the bulky nanocomposites, the distance between conductive microzones is not easy to control. Recent studies have demonstrated that it is possible to slightly control the distance between the conductive microzones by a decrease or an increase of the filler loading in the final nanocomposite electrode [19, 20].

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Regarding QDs, these semi-conducting nanocrystals have unique photophysical properties that offer significant advantages as optical labels for biosensing. Typical for semiconductor QDs are high fluorescence quantum yields, stability against photobleaching, and size-controlled luminescence properties [21–23]. These properties enable the use of QDs as optical labels for the multiplex analysis of immunocomplexes, DNA hybridization process [24], or electrical coding of single nucleotide polymorphisms [25]. Semiconductor nanoparticles are also used as labels for the electrochemical detection of DNA or proteins. For example, QDs functionalized with nucleic acids or proteins bind to biorecognition complexes, and the subsequent dissolution of the QDs allows the voltammetric detection of the related ions, and the tracing of the recognition events [26].

In addition, QDs can be also applied for the surface modification of CNTs, which led to explore the application of these nanocrystals to the field of electrochemical (bio)sensors and bioassays [27–29]. However, QDs are usually integrated in the (bio)sensor as either optical marker [30] or platform for amplifying the analytical signal [31, 32]. Despite these benefits, the concrete electrochemical effect of QDs when they are integrated in electrochemical nanocomposite sensors based on filler/polymer has not been studied in detail yet.

Under this context, the goal of this work is studying if the introduction of semi-conducting nanocrystals, as CdS-QDs, affects the electroanalytical performance of MWCNT-based electrochemical nanocomposite sensors. For this aim, CdS-QDs were previously synthesized in situ on the MWCNT walls and then dispersed as conducting fillers in epoxy resin for nanocomposite sensors fabrication. Afterwards, CdS-QDs-modified sensors were characterized by various electrochemical techniques and compared with those non-modified. Then, some morphological experiments were carried out in order to explain the surprising results, showing a superb dispersion of the conductor microzones through the insulating polymeric matrix, similar to a microelectrode arrays behavior. Finally, the direct effect of these semi-conducting nanocrystals on the electroanalytical response of MWCNT/epoxy nanocomposite sensors containing CdS-QDs was verified by hydrodynamic amperometry, using hydrogen peroxide and ascorbic acid as model analytes.

Experimental

Chemicals and reagents

Raw MWCNTs were provided by SES Research (Houston, TX, USA) whose physical properties are >95 % of carbon purity, 10–30 nm of outer diameter, and 5–15 μm of

length. They were produced using chemical vapor deposition (CVD) method. Epotek H77A and its corresponding hardener Epotek H77B were obtained from Epoxy Technology (Billerica, MA, USA) and were used as polymeric matrix. Quantum Dots were synthesized using inorganic salts (NaBH_4 , $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and Na_2S) which were supplied by Sigma-Aldrich (St. Louis, MO, USA) and did not require any further treatment. All dissolutions were prepared using deionised water from a Milli-Q system (Millipore, Billerica, MA, USA). Potassium ferri-cyanide/ferrocyanide (99.8 %), potassium chloride (99.5 %), potassium phosphate dibasic anhydrous (>99.0 %), and potassium phosphate monobasic (>99.0 %) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Finally, sodium borohydride (96 %) and acetone (99.5 %) were provided by Panreac (Castellar del Vallès, Barcelona, Spain).

Microscopy characterization

Scanning electron microscopy (SEM) images were taken using Zeiss[®] MERLIN FE-SEM. High-resolution scanning transmission electron microscopy (HR-(S)TEM) images and energy-dispersive X-ray spectroscopy analysis (EDS) were obtained by FEI Tecnai G2 F20 S-TWIN HR-(S)TEM field emission of 200 kV with analytical EDS. Sample preparation: Approximately, 1 mg of sample was dispersed in 5 mL of acetone as organic solvent and then placed in ultrasound bath for 1 h. Finally, a drop of the solution was placed on a grid and it was dried before HR-(S)TEM analysis. The CdS-QDs distribution was evaluated with the study of at least 200 nanoparticles from different TEM images. Measurements of nanocomposites topography were made by Confocal Microscopy 3D (CM3D). A Leica DCM 3D unit was used at 150 $\times$ magnifications for measuring fifty-seven profiles in three different areas for each optimum composite electrode (ISO 4287). Finally, measurements of topography and current were obtained simultaneously by means of an Atomic Force Microscopy (AFM) (PicoSPM, Molecular Imaging, USA) equipment.

Surface measurements were done using the current sensing mode: CSAFM and rectangular diamond coated tips (Nanoworld, Switzerland) with an estimated constant spring of 72 N m^{-1} .

QDs content in MWCNTs by thermogravimetric analysis

Thermogravimetric analysis (TGA) was performed on a Netzsch instrument, model STA 449 F1 Jupiter[®] (Selb, Bavaria, Germany), with a flow of air. A ~ 20 mg sample was heated to 1000 $^{\circ}\text{C}$ at 10 $^{\circ}\text{C}/\text{min}$, using air flow. The mass of the sample was continuously measured as a

function of temperature, and the rate of weight loss (d.t.g.) was automatically recorded.

Electrochemical experiments

Cyclic voltammetry (CV), linear sweep voltammetry (LSV), and electrochemical impedance spectroscopy (EIS) measurements were performed using a computer controlled Autolab PGSTAT30 potentiostat/galvanostat (EcoChemie, Utrecht, The Netherlands) using GPES (v.4.9) software package provided by the manufacturer. A three electrode configuration cell was used for impedimetric and voltammetric measurements. An AgCl-covered silver wire reference electrode and a platinum-based electrode 52-671 (Crison Instruments, Alella, Barcelona, Spain) were used as reference and auxiliary electrodes, respectively. CdS-QDs-modified and non-modified nanocomposite electrodes were used as working electrodes. EIS and CV measurements were made in a 10.0 mL of 0.1 M potassium chloride (KCl) solution containing 0.01 M potassium ferricyanide/ferrocyanide, $[\text{Fe}(\text{CN})_6]^{3-/4-}$, under quiescent condition. The experiments were performed at room temperature (25 °C). The impedance spectra were recorded in the frequency range 0.1 Hz to 100 kHz at the redox equilibrium potential. The signal amplitude to perturb the system was 10 mV. The scan rate used for CV and LSV experiments was 10 mV s⁻¹. For LSV measurements, different concentrations of analytes were added in 10.0 mL either phosphate buffer solution in 0.1 M KCl (PBS) at pH 7.0 (for hydrogen peroxide) or 0.01 M HNO₃/KNO₃ solution (for ascorbic acid). Both solutions were used as the background electrolytes.

Amperometry measurements were made using an amperimeter LC-4C (Bio Analytical Systems INC., West Lafayette, IN, USA). A single junction reference electrode Ag/AgCl Orion 900100 (Thermo Electron Corporation, Beverly, MA, USA) and a platinum-based electrode 52-671 were used as reference and auxiliary, respectively. MWCNT-based nanocomposite electrodes (containing CdS-QDs or none) were used as working electrodes. Amperometric measurements were carried out at fixed potential under force convection by stirring the solution with a magnetic stirrer (rotation speed: 1100 rpm). Oxidation potentials were previously evaluated by SLV for modified and non-modified sensors, obtaining 900 mV versus Ag/AgCl for hydrogen peroxide and 600 mV versus Ag/A for ascorbic acid. A freshly prepared 0.01 M hydrogen peroxide solution and 0.10 M ascorbic acid solution were used as stock solutions. Standard solutions were prepared by the dilution of the stock solution. 10.0 mL PBS buffer solution at pH 7.0 and 10.0 mL 0.01 M HNO₃/KNO₃ solution were used as a background

electrolyte for hydrogen peroxide and ascorbic acid, respectively.

Limit of detection (LOD) was estimated three times ($n = 3$) by the $S/N = 3$ criterion [33]. Limit of quantification (LOQ) was determined three times ($n = 3$) as the lowest concentration of the lineal response range.

Nanocomposite preparation methodology: synthesis and incorporation of CdS-QDs

Firstly, the MWCNTs surface was activated with carboxylic groups by 2.5 M nitric acid treatment in ultrasound bath for 2 h, and then, the carboxylic groups on the MWCNTs were converted to Na⁺ form by their immersion in 1.0 M NaCl solution with mechanical stirring, as shown in Eq. (1).

Afterwards, the synthesis of CdS-QDs on MWCNTs surface was carried out by Intermatrix Synthesis (IMS) technique [34, 35] resulting the hybrid nanomaterial CdS-QDs@MWCNTs. IMS can be described as follows:

Stage 1: Loading of Cd²⁺ ions (QDs precursors) onto the carboxylic groups of MWCNTs, see Eq. (2).

Stage 2: Precipitation of CdS-QDs on the MWCNTs surface by adding Na₂S as precipitating agent, see Eq. (3).

Having synthesized the hybrid nanomaterial, it was used as conducting fillers for electrodes construction. Handmade working nanocomposite electrodes were prepared by mixing polymer Epotek H77A and its corresponding H77B hardener in a 20:3 (w/w) ratio and adding 10 % (w/w) of either raw MWCNTs or CdS-QDs@MWCNTs, which was found as the optimum filler/polymer composition ratio [15]. Then, the filler nanomaterials were dispersed through the polymeric matrix and hardener agents by manually homogenization. The composites were homogenized for 1 h. The mixture was blended thoroughly and placed in the hollow end of a PVC tube to form the electrode body. Two electrode series with modified MWCNTs (CdS-QDs@MWCNTs) and non-modified MWCNTs were constructed. The composite paste electrodes (3 mm thickness) were allowed to harden during 24 h at 80 °C. Then, electrode surfaces were polished with different sandpapers of decreasing grain size. The final electrode dimensions were 28 mm² of physic area.

Finally, it is important to highlight that the raw MWCNTs were also activated with carboxylic groups following Eq. (1) because they were used as a blank for the characterization studies of the raw MWCNTs/epoxy nanocomposite electrodes.

Results and discussion

CdS-QDs nanocrystals characterization

IMS technique provided a favorable distribution of CdS-QDs on the MWCNTs surface, as shown in the HR-(S)TEM images, Fig. 1. Moreover, QDs are well separated from each other and do not form any visible agglomerates. The identification and quantification of the metal content in each case was accomplished by EDS spectra (Fig. 1d) and TGA analysis, respectively, differentiating the QDs from the catalyst remaining from the industrial synthesis of the raw MWCNTs. While TGA analysis of raw MWCNTs

showed metal impurities content of 2.0 %, TGA analysis of the hybrid nanomaterial determined that IMS technique provides 11.0 % of CdS-QDs content. As TGA provides only quantitative information on the presence of total metal content in CNT material, EDS analysis is needed for the qualitative determination of the metal composition. EDS spectra determined that the raw MWCNTs contain different catalyst particles, mainly Fe and Ni.

These catalysts are located into the walls of the MWCNTs. The QDs nanocrystals were differentiated from the catalyst particles by the EDS analysis of CdS-QDs@MWCNTs. After a study of 200 nanoparticles, the average diameter of CdS-QDs nanocrystals obtained was 2.3 ± 0.4 nm (see Fig. 1e).

According to the characterization of CdS-QDs, the fact that these nanocrystals are well distributed over the surface of the MWCNTs leads to the idea of studying the electrochemical characteristics of this nanomaterial as a component of electrochemical sensors, concretely as amperometric CdS-QDs@MWCNTs/epoxy nanocomposite sensors.

Fig. 1 **a** HR-(S)TEM of raw MWCNTs (in the *inset* is shown a catalyst particle); **b** HR-(S)TEM of different CdS-QDs@MWCNTs; **c** HR-(S)TEM of a single modified carbon nanotube with CdS-QDs;

d and its corresponding EDS spectrum and **e** size distribution histogram for CdS-QDs on MWCNTs

Hydrogen peroxide and ascorbic acid were chosen as the model analytes for this aim.

Electrochemical characterization of CdS-QDs@MWCNTs/epoxy nanocomposite electrodes

In order to probe the electrochemical behavior of the CdS-QDs in MWCNT-based electrochemical nanocomposite sensors, various electrochemical techniques, including CV and EIS, were carried out in a 0.01 M $[\text{Fe}(\text{CN})_6]^{3-/4-}$ solution. The obtained results were also compared to the bare electrodes (MWCNTs/epoxy nanocomposite electrodes).

On the one hand, Fig. 2a shows the typical cyclic voltammograms of the CdS-QDs-modified and non-modified MWCNTs nanocomposite electrodes. Different parameters such as peak height (I_p), peak separation potential (ΔE), and electroactive area (A) have been extracted from the cyclic voltammograms, and are shown in Table 1.

Fig. 2 Electrochemical experiments carried out in a 0.01 M $[\text{Fe}(\text{CN})_6]^{3-/4-}$ for *a* raw MWCNTs/epoxy and *b* CdS-QDs@MWCNTs/epoxy nanocomposite electrodes. **a** Cyclic voltammograms recorded at 10 mV s⁻¹. **b** Nyquist plots; inset shows the equivalent circuit used for the impedance spectra fitting

The electroactive area was estimated from the peak-shaped voltammograms by the following for electron transfer-controlled processes [14]:

$$I_p = 3.01 \times 10^5 \cdot n^{3/2} (\alpha D_{\text{red}} \nu)^{1/2} \cdot A \cdot C_{\text{red}}^*$$

where α represents the charge transfer coefficient ($\alpha = 0.5$), D_{red} corresponds to the diffusion coefficient of the reduced species ($D_{\text{red}} = 6.32 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$), ν represents the scan rate ($\nu = 0.01 \text{ V s}^{-1}$), A is the electroactive area, and C_{red}^* is the bulk concentration of the electroactive species ($C_{\text{red}}^* = 0.01 \text{ M}$).

According to CV results presented in Fig. 2a, CdS-QDs@MWCNTs/epoxy nanocomposite electrodes exhibited an enhancement of I_p , which was around 73 % for I_{pa} and 75 % for I_{pc} , indicating that the CdS-QDs well enhanced the surface area as well as the electroactivity of the nanocomposite. As can be observed from Table 1, the present modified system exhibits a good reversibility, with an I_{pc}/I_{pa} ratio close to 1. Moreover, the inclusion of CdS-QDs in the nanocomposite electrode also increased the electroactive area (A) from 0.25 cm² to 0.84 cm². Figure 2a also shows a change in ΔE from 0.48 to 0.62 V for the CdS-QDs-modified electrodes, which can be explained by the incorporation of semi-conducting nanocrystals in the nanocomposite matrix. This increase of ΔE turns into partial decrease in the system reversibility. Finally, a well-defined pair of redox peaks and quasi-reversible redox peaks was observed for both electrodes.

On the other hand, EIS is a powerful tool for studying the interface properties of the modified MWCNTs/epoxy nanocomposite electrodes and can provide information on the impedance changes of the interface of the electrode surface-electrolyte solution. The Nyquist plots of the EIS consist on a semicircular portion and a linear part, which corresponds to the electron transfer limited process (kinetic control) and the diffusion limited process (mass transfer control), respectively [36]. From Fig. 2b, it is possible to observe how the impedance spectra are dominated by the semicircle feature, indicating that the electrochemical systems are limited by the electron transfer rate. Accordingly, the impedance spectra were fitted to a simple equivalent circuit: $R_\Omega \cdot (R_{ct} \cdot C_{dl})$. This circuit was sufficiently suitable to interpret the ohmic resistance (R_Ω), charge transfer resistance (R_{ct}), and double-layer capacitance (C_{dl}) values in terms of the interfacial phenomena that occur at the electrochemical cell (see Fig. 2b, inset). It is important to highlight that the error values were lower than 5 %, fact that evidences a goodness fit.

R_Ω parameter consists in the solution resistance in series with the contact or the ohmic composite resistance. R_Ω depends basically on the ionic concentration and the type of ions present in solution, which were kept constant during the measurements. Then, the obtained R_Ω values were

Table 1 Voltammetric and impedimetric characterization of modified and non-modified electrodes with CdS-QDs

Electrode containing	I_{pa} (mA)	I_{pc} (mA)	I_{pc}/I_{pa}	A (cm ²)	ΔE (V)	R_{Ω} (Ω)	R_{ct} (Ω)	C_{dl} (μF)
Raw MWCNTs	0.139	0.121	0.871	0.25	0.48	138.0	530.0	9.02
CdS-QDs@MWCNTs	0.509	0.483	0.949	0.84	0.62	141.9	858.5	1.55

Experiments were recorded in a 0.01 M $[Fe(CN)_6]^{3-/4-}$ solution; CV scan rate: 10 mV s⁻¹

similar (about 140 Ω) for non-modified and modified MWCNTs/epoxy nanocomposite electrodes with CdS-QDs, see Table 1.

R_{ct} is a parameter inversely proportional to the heterogeneous charge transfer rate and affects the sensitivity and response time of the electrode. Nyquist plots presented in Fig. 2b showed an optimum kinetically controlled response for both nanocomposite electrodes, demonstrating a fast electron exchange. An increase of R_{ct} with the incorporation of CdS-QDs on the MWCNTs surface was also observed because of the incorporation of semi-conducting nanocrystals, confirming again the modification of the electrode.

C_{dl} is directly related to the charging or background current and inversely proportional to the signal-to-noise ratio [19]. The increase of the background current smears the Faradaic signal response, especially when the electroactive species are present in low concentration. In this case, an evident decrease of the C_{dl} value was observed for the CdS-QDs@MWCNTs/epoxy nanocomposite electrodes (from 9.02 to 1.55 μF), which corresponds to a decrease around 80 %, as is also shown in Table 1. This important decrease of C_{dl} value allows the increase of the signal-to-noise. Consequently, the analyte detection limits may improve.

Based on EIS results, the electrochemical parameters of CdS-QDs@MWCNTs/epoxy nanocomposite electrodes enhanced electrochemical properties comparing to those obtained for the bare electrodes. The electrochemical enhancement of CdS-QDs@MWCNTs/epoxy nanocomposite electrodes showed by CV and EIS seems to provide the properties that a (bio) sensor must have, such as rapid response time, low limit of detection, and high sensitivity.

In order to explain the enhanced in the electrochemical performance on modified nanocomposite electrodes with semi-conducting nanocrystals, different morphological experiments were carried out by CSAFM and CM3D.

Morphological characterization of nanocomposite electrodes

CSAFM and CM3D techniques were used to understand the electrochemical results obtained for the MWCT-based electrodes containing CdS-QDs. Under this context, CSAFM technique was applied to obtain qualitative information about the size, shape, and distribution of the

conducting nanomaterial in the modified nanocomposite structure. Results were also compared with those obtained by the non-modified nanocomposite electrodes.

On the one hand, Fig. 3 presents the most significant images obtained during the surface study of CdS-QDs@MWCNTs/epoxy (Fig. 3a, c) and raw MWCNTs/epoxy (Fig. 3b, d) nanocomposite electrodes. Figure 3 shows that while non-modified nanocomposite material shows closer conductive channels, a further dispersion of the conductor microzones through the insulating polymeric matrix is observed when CdS-QDs were incorporated on the MWCNTs walls. These results determine that the presence of CdS-QDs in the nanocomposite increases the spaces between conductive channels, conferring on them a behavior much closer to a microelectrode array, with the benefits they exhibit, such as lower background currents and therefore, improved detection limits.

According to conductive results, while the non-modified material has a behavior more similar to a macroelectrode (Fig. 3b, d), CdS-QDs-modified materials present many separated and thin conductive microzones on the electrode surface, where the electronic transfer is produced (Fig. 3a, c). The separation between conductor microzones offers the electrode the capability to improve the electrochemical performance, as shown in Table 1. In addition, the separation between conductive microzones allows the electrode to generate radial diffusion in which the electroactive species diffuse on its surface by the Edge effect [37]. However, in non-modified electrodes, only the linear diffusion is contemplated. Such radial diffusion provides an increase of the mass transfer which must favor positively the electroanalytical response because C_{dl} decreases (see Table 1), and consequently, the limit of detection improves.

Due to the random structure of bulky nanocomposite materials, the distance between conductive microzones is not easy to control. In this way, the presented results open a new strategy to obtain advanced home-made electrodes where the dispersion of the conductive microzones can be generated by the incorporation of a scattering nanomaterial, as CdS-QDs, on the MWCNT surface. These semi-conducting nanocrystals may remove some chemical interactions between MWCNTs, and thus, they allow them to be more distance one with other. Thereby, after CdS-QDs incorporation, a behavior much closer to a microelectrode array is obtained.

Fig. 3 CSAFM images with their corresponding conductance mapping for nanocomposite electrodes containing **a** CdS–QDs@MWCNTs and **b** raw MWCNTs, **c**, **d** correspond to 3D conductance image from **a**, **b**, respectively

On the other hand, roughness surfaces of both nanocomposite electrodes were also compared by CM3D. Figure 4 presents significant images obtained during the electrode surface study. Results, which are summarized in Table 2, also reveal the CdS–QDs effect on the electrode roughness.

The incorporation of these semi-conducting nanocrystals on the filler nanomaterial significantly modified the topography of the MWCNT-based epoxy nanocomposites. Thus, the CdS–QDs@MWCNTs/epoxy nanomaterial (Fig. 4b) exhibited a roughness increment of around 75 % compared with the raw MWCNTs/epoxy nanocomposite (Fig. 4a) surface electrode, fact that can explain the electroactive area (A) enhancement, which was also around 70 % (see Table 1). If the electrode roughness increases, the probability of more conducting material exposed on the electrode surface also increases, and consequently, its electroactive area and I_p value, following the Eq. (1).

Furthermore, it is necessary to emphasize that the enhancement of electrode roughness for CdS–QDs@MWCNTs/epoxy nanocomposite electrodes is only due to the separation of the conductor microzones provided by the incorporation of CdS–QDs on the MWCNT walls, which provides an enhancement of A.

Finally, the potentiality of this approach in terms of electroanalytical response has been evaluated by means of amperometric detection of ascorbic acid and hydrogen peroxide, both used as reference analytes.

Electroanalytical response of CdS–QDs@MWCNTs/epoxy nanocomposite sensors

Different concentrations of hydrogen peroxide and ascorbic acid were added in 10.0 mL of its corresponding background electrolyte solution for hydrodynamic amperometric studies. The polarization potentials obtained by LSV

Fig. 4 Topographic images of **a** raw MWCNTs electrode and **b** CdS-QDs-modified electrode were obtained with the 3D Optical Surface Metrology System Leica CM3D for the roughness study

Table 2 Roughness values collected from surface analysis

Electrode containing	R_a^a (μm)		R_q^b (μm)		R_z^c (μm)	
	Mean	SD	Mean	SD	Mean	SD
Raw MWCNTs	0.555	0.129	0.920	0.271	7.31	2.60
CdS-QDs@MWCNTs	2.24	0.55	3.34	0.97	21.82	6.70

Data are the mean and standard deviation (SD) from 57 profiles of three areas examined in each series (ISO 4287)

^a Arithmetical mean deviation of the assessed profile

^b The root mean square deviation of the assessed profile

^c Maximum height of the profile

and applied for amperometric studies were 900 mV versus Ag/AgCl for hydrogen peroxide detection and 600 mV versus Ag/AgCl for ascorbic acid detection.

If the raw sensors demonstrated a suitable electroanalytical response for the oxidation of both analytes, the modified sensors with CdS-QDs exhibited a clear enhanced of its response, as depicted in Fig. 5. In addition,

this enhanced of sensitivity was translated into an important LOD decrease (see Table 3).

For hydrogen peroxide detection, the LOD obtained with CdS-QDs@MWCNTs/epoxy nanocomposite sensors is $0.040 \pm 0.002 \mu\text{M}$, more than 1.4 decades of concentration less than non-modified sensors, whose LOD was $2.80 \pm 0.06 \mu\text{M}$. LOQ improved as well, obtaining $0.200 \pm 0.003 \mu\text{M}$ for CdS-QDs@MWCNTs/epoxy nanocomposite sensors, compared to $5.59 \pm 0.06 \mu\text{M}$ for raw MWCNTs/epoxy nanocomposite sensors, more than 1.5 decades of concentration better. In regard to ascorbic acid detection, the LOD and LOQ obtained for the CdS-QDs@MWCNTs-modified sensors were 0.067 ± 0.004 and $0.159 \pm 0.001 \mu\text{M}$, respectively. Thereby, the presence of CdS-QDs improved around 2 orders of magnitude the LOD and 1 order of magnitude the LOQ for this analyte (see Table 3), compared to the non-modified sensors. Amperometric results also demonstrated a significant decrease of both LOD and LOQ for the modified sensors containing CdS-QDs because of the significant enhancement of its sensitivity (see Table 3).

In agreement with the results expected from electrochemical and morphological characterizations, the electroanalytical enhancement of CdS-QDs containing sensors is mainly attributed to the dispersion of the conductive microzones through the insulating polymeric matrix, which decreases the C_{dl} value. This value is directly related to the decrease of the background current and hence improves the signal-to-noise ratio and LODs. Accordingly, the simple incorporation of CdS-QDs in the MWCNT-based bulky system makes possible to obtain advanced electrochemical nanocomposite sensors, with a behavior similar to a microelectrode array.

Conclusions

CdS-QDs have successfully been synthesized on MWCNT surface by an environmentally friendly technique (IMS) for a facile fabrication of amperometric-modified nanocomposite sensors.

CdS-QDs@MWCNTs/epoxy nanocomposite electrodes have been characterized by various electrochemical techniques for the pioneering study of the direct effect of semi-conducting nanocrystals when they are integrated in MWCNT-based electrochemical nanocomposite sensors.

Electrochemical results showed a great enhancement of some physical parameters for CdS-QDs-modified electrodes, such as higher electroactive area and superb decrease of C_{dl} value regarding to non-modified electrodes.

Morphological experiments were key to explaining the surprisingly electrochemical improvements of CdS-QDs-modified electrodes, which are mainly due to the dispersion

Fig. 5 Calibration curves of current vs. concentration of **a** hydrogen peroxide in a PBS solution at pH 7.0 and **b** ascorbic acid in a 0.01 M $\text{KNO}_3/\text{HNO}_3$ solution for CdS-QDs@MWCNTs/epoxy (grey filled

circle) and raw MWCNTs/epoxy (black filled circle) sensors. The calibration curves are represented with their corresponding error bars ($n = 3$)

Table 3 Amperometric performance of CdS-QDs@MWCNTs/epoxy nanocomposite sensors is compared with raw MWCNTs/epoxy nanocomposite sensors

Sensor containing	Hydrogen peroxide			Ascorbic acid		
	LOD (μM)	LOQ (μM)	Sensitivity ($\mu\text{A } \mu\text{M}^{-1}$)	LOD (μM)	LOQ (μM)	Sensitivity ($\mu\text{A } \mu\text{M}^{-1}$)
Raw MWCNTs	2.80 ± 0.06	5.59 ± 0.06	0.002 ± 0.001	0.400 ± 0.003	1.51 ± 0.02	0.003 ± 0.001
CdS-QDs@MWCNTs	0.040 ± 0.002	0.200 ± 0.003	0.0112 ± 0.0004	0.067 ± 0.004	0.159 ± 0.001	0.0080 ± 0.0007

LOD and LOQ are represented with their, respectively, 95 % confidence interval ($n = 3$). Experiments were carried out in a PBS solution at pH 7.0 for hydrogen peroxide analyte and 0.01 M $\text{KNO}_3/\text{HNO}_3$ solution for ascorbic acid

of the conductive microzones provided by the incorporation of semi-conducting nanocrystals, resulting in a behavior much closer to a microelectrode array. This fact was directly involved in improving the electroactivity, conductivity, and signal-to-noise ratio of the CdS-QDs-modified electrodes.

Analytical results verified the feasibility of these advanced amperometric nanocomposite sensors based on modified MWCNTs with CdS-QDs to detect and quantify low concentrations of different model analytes. Accordingly, it has been demonstrated that an optimum dispersion of the conductive microzones is mandatory to obtain a high signal-to-noise ratio and hence, low LODs.

Finally, these results open a new way to use semi-conducting nanocrystals as scattering nanomaterials of MWCNTs through the polymeric matrix for the tunable fabrication of handmade electrochemical nanocomposite (bio)sensors, which present the benefits of a microelectrode array performance.

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