



Modified multiwalled carbon nanotube/epoxy amperometric nanocomposite sensors with CuO nanoparticles for electrocatalytic detection of free chlorine



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ABSTRACT

The benefit of using copper (II) oxide nanoparticles (CuO-NPs), which have catalytic activity for the decomposition of hypochlorite solutions, for the amperometric detection of free chlorine is reported. Cyclic voltammetry and electrochemical impedance spectroscopy have been applied for the electrochemical characterization of nanocomposite materials. If the amperometric detection of free chlorine was determined previously using multiwall carbon nanotube (MWCNT) based epoxy nanocomposite sensors, the electrocatalytic reduction of hypochlorite using modified MWCNT/epoxy nanocomposite sensors with CuO-NPs to obtain sensitive devices capable to amperometrically determine traces of free chlorine in water is demonstrated here. The CuO-NPs were incorporated in the nanocomposite electrode in two different ways i) on the MWCNT surface, Route A and ii) in the nanocomposite matrix in powder form, Route B. Both modified-nanocomposite sensors have shown a fast electron transfer exchange, high electroactive area and an enhancement on the electroanalytical signal. Accordingly, a greater sensitivity compared to raw MWCNT/epoxy nanocomposite sensors has been observed, obtaining the lowest limit of detection for the CuO-NPs modified nanocomposite sensors obtained by Route B.

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1. Introduction

Carbon nanotubes (CNTs) represent an important group of nanomaterials, which are used in a variety of applications since their discovery in 1991 [1,2,3] mainly due to their unique mechanical [4], chemical [5], electrical [6], thermal [7] and structural properties [8]. Currently, significant interest is focused on nanocomposites based on CNTs, especially in multiwalled carbon nanotubes (MWCNTs), because of their electrocatalytic activity.

The unique qualities of MWCNTs make them highly attractive for the development of MWCNT-based chemical (bio)sensors, in general, and electrochemical detection, in particular. In this way, these sensors have shown extensive use for the detection of compounds such as glucose, hydrogen peroxide, ascorbic acid and free chlorine, among others [9,10,11,12]. MWCNTs dispersed in an inert matrix provide attractive electrochemical properties since the polymeric matrix, together with the MWCNTs, confers mechanical robustness and high electric conductivity to the final nanocomposite electrode. Furthermore, its high malleability before being hardened permits an easy incorporation of a variety of nanoparticles (NPs), [13,14] enzymes [15] and chemical recognition agents [16]. Compared to other carbon allotropic forms,

CNTs offer to the composite a higher area to volume ratio, lower resistivity and higher mechanical and chemical stability.

Some parameters, such as the composite resistivity, the heterogeneous electron transfer rate, the material stability and the background capacitance current are strongly influenced by the raw MWCNT nature (such as purity, diameter and length), which in turn also affects the ratio of MWCNT/polymer nanocomposite materials [17,18]. Then, the optimization of the raw MWCNT load is mandatory to obtain nanocomposite electrodes which have a similar behavior to a microelectrodes array. In this context, an exhaustive study regarding the characterization and optimization of the MWCNT loading in a polymeric matrix (epoxy resin, Epotech H77) was previously performed to improve its electrochemical properties [17,19]. The optimal nanocomposite composition, which was 10% (w/w) in carbon loads for the MWCNTs used in this work, combined easy manipulation during the fabrication procedure, low background current and an improved response compared to the conventional conducting composite electrodes used in the vast majority of works reported using a higher carbon load (20%, w/w in carbon loads) [20,21]. Afterwards, the feasibility of these optimum MWCNT-based nanocomposite sensors was evaluated for the amperometric reduction of hypochlorite (ClO^-) for the determination of free chlorine in aqueous solution [22].

NaClO is a compound registered in the Toxic Substances Control Act (TSCA) Chemical Substance Inventory that is frequently used for water

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disinfection and purification, including drinking water, swimming pool water, treated wastewater for non-potable reuse and others. Normally it is handled as concentrated aqueous solutions and needs periodical control of its concentration to adjust dosages due to the possibility of decomposition and the formation of undesirable byproducts [23].

Chlorine and hypochlorite are related by following chemical equation:



The sum of ClO^- , Cl_2 and HClO is known in hydrochemistry as free chlorine and its concentration can be expressed as mass of Cl_2 per liter. This criteria has also been followed in this paper.

NaClO slowly self-decomposes in solution [24] but can rapidly decompose in the presence of different metal ion catalysts, such as Ni, Co and Cu [25,26]. Recently, CuO -NPs, NiO -NPs and Co_3O_4 -NPs have demonstrate a higher catalytic activity to decompose the NaClO [23,27]. While CuO -NPs and NiO -NPs do not show any degradation in catalytic performance for the decomposition of hypochlorite during repeated uses, Co_3O_4 catalyst continuously decreased with repeated use [27]. In addition, it is known the catalytic activity of the CuO -NPs for the amplification signal of different analytes, such as glucose, hydrogen peroxide, rhodamine B (RhB) and different carbohydrates [28,29,30,31].

Accordingly, in this work the catalytic properties of CuO -NPs for their incorporation as a catalytic support in the optimum MWCNT/epoxy nanocomposite composition to develop sensitive amperometric nanocomposite sensors for the analysis of free chlorine have been exploited. CuO -NPs were synthesized by an environmentally friendly technique (Intermatrix Synthesis, IMS) and were incorporated in the nanocomposite electrode by two different routes: i) on the MWCNT surface (Route A) and ii) in the nanocomposite matrix in powder form (Route B). Then, the nanocomposite electrodes containing CuO -NPs were characterized by cyclic voltammetry and electrochemical impedance spectroscopy in order to study their electrochemical behavior. Finally, the obtained results have been compared with the ones obtained by the raw MWCNT/epoxy nanocomposite sensors.

2. Experimental

2.1. Chemicals and reagents

All solutions were prepared using deionized water from a Milli-Q system (Millipore, Billerica, MA, USA). Sodium hypochlorite (NaClO , 10–15%), potassium chloride (KCl , 99.5%), potassium ferricyanide/ferrocyanide ($\text{K}_3[\text{Fe}(\text{CN})_6]/\text{K}_4[\text{Fe}(\text{CN})_6]$, 99.8%), potassium phosphate dibasic anhydrous (K_2HPO_4 , >99.0%) and potassium phosphate monobasic (KH_2PO_4 , >99.0%) were obtained from Sigma-Aldrich (St. Louis, MO, USA). L-purified multiwalled carbon nanotube (MWCNT) growth using the chemical vapor deposition process (purity >95%, length 5–15 μm , outer diameter 10–30 nm) was purchased from SES Research (Houston, TX, USA). Resin Epotek H77A and its corresponding hardener Epotek H77B, supplied by Epoxy Technology (Billerica, MA, USA), were used as polymeric matrix. Copper (II) nitrate trihydrate ($\text{Cu}(\text{NH}_3)_2 \cdot 3\text{H}_2\text{O}$, 99%) and sodium hydroxide (NaOH >98%) and the different salts used for the interfering experiments were purchased from Sigma-Aldrich and were used as-received.

2.2. Apparatus and procedure

Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) studies were carried out using a computer controlled AUTOLAB PGSTAT 30 and FRA boards (Eco Chemie, Utrecht, The Netherlands). EIS and CV measurements were made in a 10.0 mL of 0.1 M KCl solution containing 0.01 M $\text{K}_3[\text{Fe}(\text{CN})_6]/\text{K}_4[\text{Fe}(\text{CN})_6]$, using a three-electrode configuration. Moreover, CV studies in the presence of

free chlorine were carried out in 10.0 mL of 0.1 M KCl containing phosphate buffer solution (PBS) at pH 5.5. A single junction reference electrode Ag/AgCl Orion 900100 (Thermo Electron Corporation, Beverly, MA, USA) and a platinum-based electrode 52-671 (Crison Instruments, Alella, Barcelona, Spain) and the constructed MWCNT/epoxy nanocomposite electrodes (modified or none with metal oxide nanoparticles) were used as reference, auxiliary and working electrodes, respectively. The voltammograms scan rate was $50 \text{ mV} \cdot \text{s}^{-1}$ and the impedance spectra were recorded in the frequency range of 0.1 Hz–100 kHz at the redox equilibrium potential previously obtained by CV. The resistance parameters were obtained by fitting the impedance spectra to a simple equivalent circuit: $R_\Omega \cdot (R_{ct} \cdot C_{dl})$.

Electroanalytical experiments were carried out in a 10.0 mL PBS solution at pH 5.5. This solution was used as a background electrolyte and the experiments were made using a three-electrode configuration. Amperometric measurements were performed using an amperimeter LC-4C (Bioanalytical Systems, Inc., West Lafayette, IN, USA). Amperometric detection was performed under stirring conditions with a Teflon-coated magnetic stirring bar (working potential: $E_{app} = -0.35 \text{ V vs. Ag}/\text{AgCl}$) and constant agitation. A freshly prepared 1000 ppm NaClO solution was used as a stock solution. Standard solutions were prepared by the dilution of the stock solution. All the experiments were made at room temperature (25 °C). The NaClO solutions were previously analyzed using the standard N,N-diethyl-p-phenylenediamine (DPD) colorimetric method [32,33] which consists in a Kit-commercial colorimeter (HACH, Düsseldorf, Germany) that provides measurements directly in $\text{mg} \cdot \text{L}^{-1}$ of free chlorine.

The metal oxide contained on MWCNT surface was evaluated by thermogravimetric analysis (TGA), using a Netzsch instrument; model STA 449 F1 Jupiter®. Approximately 20 mg of sample was heated to 1000 °C at 10 °C/min, using flow of air. 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.

The presence of CuO -NPs on the MWCNT surface (CuO -NPs@MWCNT) was observed by high resolution transmission electron microscopy (HR-TEM) images and energy dispersive X-Ray spectroscopy (EDS), using a JEM-1400 unit with an acceleration voltage of 120 kV. Approximately 1 mg of sample was dispersed in 5 mL of acetone as organic solvent and then placed in an ultrasound bath for 1 h. Finally, a drop of this solution was placed on a gold grid and let it dry before HR-TEM and EDS analysis.

2.3. Nanocomposite preparation methodology: synthesis and incorporation of CuO -NPs

Handmade working nanocomposite electrodes were prepared following the conventional methodology described in our previous works [13,17]. The working electrodes based on nanocomposites were prepared by mixing polymer Epotek H77A and its corresponding H77B hardener in a 20:3 (w/w) ratio and adding a 10% load of MWCNTs (either modified or none). The (modified-)MWCNTs were dispersed in the resin and hardener agents by manually homogenization for 1 h. For the electrode construction, the mixture was placed into a cylindrical PVC tube (6 mm of internal diameter and 20 mm of length) containing a copper disk soldered to an electrical connector end. The mixture was incorporated in the hollow end of a PVC tube to form the body of the electrode. The final paste-filled cavity was 3 mm long inside the PVC tube. Then, the nanocomposite paste electrodes were allowed to harden during 24 h at 80 °C. Afterwards, in order to obtain a reproducible electrochemical surface, electrode surfaces were polished with different sandpapers of decreasing grain size (800 and 1200 grits) and finally with alumina paper (polishing strips 948201, Orion). The resultant geometric area for the final electrodes was 28 mm^2 .

Two different methodologies were carried out for the modification of the transducer material with CuO -NPs: (i) *in situ* functionalization of MWCNT surface previously to their mixture incorporation and

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