Iron oxide nanostructured electrodes for detection of copper(II) ions

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Iron Oxide Nanostructured Electrodes for Detection of Copper(II) Ions

J. G. M. Santos¹, J. R. Souza¹, C. J. Letti², M. A. G. Soler², P. C. Morais²,³, M. A. Pereira-da-Silva⁴,⁵, and L. G. Paterno¹,∗

¹Universidade de Brasília, Instituto de Química, Brasília DF 70910-900, Brazil
²Universidade de Brasília, Instituto de Física, Brasília DF 70910-900, Brazil
³School of Automation, Huazhong University of Science and Technology, Wuhan 430074, China
⁴Instituto de Física de São Carlos, Universidade de São Paulo, São Carlos SP 13560-970, Brazil
⁵Centro Universitário Central Paulista—UNICEP, São Carlos SP 13563-470, Brazil

Iron oxide nanostructured (ION) electrodes were assembled layer-by-layer onto ITO-coated glass substrates and their structure, morphology, and electrochemical properties were investigated, the latter aiming at the development of a chemical sensor for Cu²⁺. The electrodes were built by immersing the substrate alternately into an aqueous colloidal suspension of positively charged magnetite nanoparticles (np-Fe₃O₄, 8 nm) and an aqueous solution of anionic sodium sulfonated polystyrene (PSS). The adsorbed amount of both materials was monitored ex-situ by UV-vis spectroscopy and it was found to increase linearly with the number of deposition cycles. The resulting films feature a densely-packed structure of magnetite nanoparticles, as suggested by AFM and Raman spectroscopy, respectively. Cyclic voltammograms of electrodes immersed in acetate buffer (pH 4.6) displayed three electrochemical events that were tentatively ascribed to the reduction of Fe(III) oxy-hydroxide to magnetite, reduction of maghemite to magnetite, and finally oxidation of magnetite to maghemite. The effect of np-Fe₃O₄/PSS bilayers on the ION electrode performance was to increase the anodic and cathodic currents produced during electrochemical oxidation-reduction of the Fe(CN)₃⁻/⁴⁻ redox couple. With more bilayers, the ION electrode provided higher anodic/cathodic currents. Moreover, the redox couple exhibited a quasi-reversible behavior at the ION electrode as already observed with other working electrode systems. Fitting of voltammetry data provided the apparent electron transfer constants, which were found to be higher in ION electrodes for both redox couples (Fe(CN)₃⁻/⁴⁻ and Cu²⁺/⁰). By means of differential pulsed anodic stripping voltammetry, the ION electrodes were found to respond linearly to the presence of Cu²⁺ in aqueous samples in the range between 1.0 and 8 × 10⁻⁶ mol L⁻¹ and displayed a limit of detection of 0.3 × 10⁻⁸ mol L⁻¹. The sensitivity was ~ 0.6 μA μmol⁻¹ L⁻¹. In standard addition and recovery experiments performed with tap water the recovery was about 102%–119%. In similar experiments conducted with ground and instant coffee samples the recovery was 92.5% and 103%, respectively. Furthermore, the ION electrodes were almost insensitive to the presence of common interfering ions, such as Zn²⁺, Mn²⁺, Ni²⁺, and Fe³⁺, even at concentrations ten times higher than that of Cu²⁺.

Keywords: Iron Oxide Electrodes, Magnetite Nanoparticles, Layer-by-Layer Deposition, Cu(II), Chemical Sensor.

1. INTRODUCTION

The electrochemistry of iron oxide nanoparticles (ION) has been playing a main role in energy conversion, storage and chemical sensing devices. ION ally easy and low cost preparation to a wide range of nanostructures and (photo)electrochemical properties. Photoelectrodes of hematite (α-Fe₂O₃) nanoparticles have taken advantage on their enhanced surface area and semiconducting behavior to reach, via water splitting, a 2.1% conversion efficiency of solar light into molecular hydrogen. The perspective
of a 16.8% theoretical efficiency for such electrodes has attracted the attention of several research groups worldwide and has established itself as an exciting new research field. In chemical sensing, ION have been employed to improve the properties of nanostructured electrodes towards detection of some biochemical analytes, including hydrogen peroxide, dopamine (DA), urea, and glucose.\textsuperscript{2-10} In this type of devices, ION may act in different ways such as an electro catalyst, anchoring matrix for enzymes or hemoglobin, or even in the improvement of the electrode’s life-time. ION have also been used as active elements for sensing of reducing gases and metal cations in solution.\textsuperscript{11-14}

Adekunle et al.\textsuperscript{2} have employed magnetite nanoparticles (np-Fe\textsubscript{3}O\textsubscript{4}, ∼ 30 nm) electrochemically deposited onto single-walled carbon nanotubes (SWCNT)-modified electrodes to improve DA detection. They have found that these nanoparticles are responsible for an electrocatalytic effect enabled by the electronic interaction with SWCNT as well as by their specific interaction (chelate formation via Fe\textsuperscript{3+}) with DA molecules. Cao and Hu\textsuperscript{5} and Zhao et al.\textsuperscript{9} have observed that np-Fe\textsubscript{3}O\textsubscript{4} can act on the direct electron transfer between hemoglobin and pyrolytic graphite electrodes, thus improving the biocatalytic activity towards the reduction of oxygen, hydrogen peroxide, trichloroacetic acid, and nitrite. They have also found that np-Fe\textsubscript{3}O\textsubscript{4} provide a more compatible matrix for proteins such as hemoglobin while preventing their denaturation. Cummings et al.\textsuperscript{7} have found that an ITO-coated electrode modified with maghemite nanoparticles (γ-Fe\textsubscript{2}O\textsubscript{3}, ∼ 10 nm) may exhibit Fe(IV) surface species that are reactive towards oxidation of glucose to gluconolactone in carbonate buffer medium. McKenize et al.\textsuperscript{8} have shown that hydrous ferric oxide nanoparticles adsorbed onto borondoped diamond electrodes act as an efficient electrocatalyst in a heterogenous Fenton-type process that drives the oxidation of hydroxide to dioxygen.

Electrodes based on ION can be made by different deposition procedures. Among them, the layer-by-layer (LbL) assembly of colloidal ION with different polyelectrolytes has proven to be a quite simple yet very effective strategy for the production of multilayered nanocomposite films with predefined volume fraction and spatial distribution of ION.\textsuperscript{15} The LbL deposition procedure consists on transferring one-by-one colloidal ION and polyelectrolytes layers to a solid substrate that is immersed alternately into their respective solutions/dispersions. The electrostatic mode of adsorption implies that a same amount of material is adsorbed per layer (deposition cycle) so that film thickness and mass loading can be controlled by setting the number of layers at a previously defined value.\textsuperscript{15,16} In previous contributions, we have observed that the LbL assembly permits one to control the volume fraction and, consequently, inter-particle distances in nanocomposite films made of polyaniline or sodium sulfonated polystyrene (PSS) with γ-Fe\textsubscript{2}O\textsubscript{3} nanoparticles.\textsuperscript{17-19} This feature made it possible to tune the electrical conductivity and the strength of magnetic dipolar interactions (in a wide range of energy) within the nanocomposite. The LbL assembly has also been used to control of the ion sensitivity of chemical sensors based on nanocomposite films made with cobalt ferrite nanoparticles and conducting polyelectrolytes.\textsuperscript{12}

In the present contribution, we have engineered iron oxide nanostructured electrodes for detection of Cu\textsuperscript{2+}. The electrodes were built on top of ITO-coated glass substrates by LbL deposing nanocomposite films of positively-charged np-Fe\textsubscript{3}O\textsubscript{4} (8 nm) and anionic PSS, or else (np-Fe\textsubscript{3}O\textsubscript{4}/PSS)\textsubscript{n}, where \(n\) stands for the number of deposited bilayers. The structure of electrodes was assessed by UV-vis and Raman spectroscopy whereas the morphology was investigated by atomic force microscopy. Cu\textsuperscript{2+} is known for its importance as a micronutrient as well as an active component in fungicides for the protection of crops from fungal attacks.\textsuperscript{20,21} For example, coffee trees are rather susceptible to fungal diseases, such as coffee berry disease (Colletotrichum coffeanum) and leaf rust (Hemileia vastatrix), which are protected with Cu-based fungicides.\textsuperscript{22} Nonetheless, the spraying of such fungicides in coffee plantation contaminates the upper soil as well as coffee berries and leaves.\textsuperscript{23} Indeed, higher concentration of Cu\textsuperscript{2+} ions may pose serious risk to human consumers. Measuring of Cu\textsuperscript{2+} contents in coffee also determines its geographical growing location.\textsuperscript{24} Therefore, detection and quantification of Cu\textsuperscript{2+} ions in coffee, either in coffee leaves or berries and ground coffee are key issues for the improvement of food safety and tracking of this food product. As far as we know, ION-based electrodes have never been tested for this purpose. The use of LbL ION-based electrodes in chemical sensing is potentially promising once they are easily produced at low cost and can have their performance tuned by the electrode’s supramolecular assembly.

The electrochemical parameters of the ITO-(np-Fe\textsubscript{3}O\textsubscript{4}/PSS), electrodes, including Δ\(E\textsubscript{f}\), and apparent electron transfer constants as a function of the number of np-Fe\textsubscript{3}O\textsubscript{4}/PSS bilayers (\(n\)) were assessed by cyclic voltammetry (CV). Their analytical application was evaluated by differential pulsed anodic stripping voltammetry (DPASV) with artificially contaminated water samples as well as ground and instantaneous coffee.

2. EXPERIMENTAL DETAILS

2.1. Materials

Sodium sulfonated polystyrene (PSS, M\textsubscript{w} 70,000 g mol\textsuperscript{-1}), FeCl\textsubscript{2}·4H\textsubscript{2}O, FeCl\textsubscript{3}·6H\textsubscript{2}O, NaOH, HClO\textsubscript{4}, and 3-mercaptopropanesulfonic acid sodium salt (3-MPS) were purchased from Sigma-Aldrich (Brazil). K\(_2\)Fe(CN)\textsubscript{6}, CuSO\textsubscript{4}·5H\textsubscript{2}O, acetic acid, nitric acid, hydrogen peroxide 30%, and sodium acetate were purchased from Merck (Germany) and Vetec (Brazil). All chemicals were
analytical grade or better and used as received. Standard solutions of Zn\(^{2+}\), Mn\(^{2+}\), Ni\(^{2+}\), and Fe\(^{3+}\) at 1000 mg·L\(^{-1}\) purchased from Fluka were employed as source of interfering ions. Optical (BK7 type) and ITO-coated (30 ohm·sq) glass slides (1 × 10 × 25 mm) were employed as substrates for nanocomposites film depositions, and for UV-vis spectroscopy characterization and electrochemical measurements, respectively. BK7 slides with a gold-sputtered coating layer (Au-coated) were used to prepare samples for Raman spectroscopy. All experiments (nanoparticle synthesis, solutions preparation, and substrate cleaning) used exclusively ultra-pure water (18 MΩ cm) provided by a Milli-Q Millipore water purification system.

Preparation of np-Fe\(_3\)O\(_4\) was carried out by co-precipitation of Fe(II) and Fe(III) ions with NaOH.\(^{25}\) In a typical run, an aqueous solution containing iron ions in a 1:2 mole ratio of Fe(II)/Fe(III) was added drop wise to a solution of NaOH kept stirred by a magnet bar at room temperature. After the complete addition of the iron ions solution, the reaction mixture was kept stirring for additional 30 minutes at the same temperature. The black precipitated of np-Fe\(_3\)O\(_4\) was then isolated from the supernatant reaction mixture by decantation and washed (3 times) with ultra-pure water. The stoichiometry for the co-precipitation reaction synthesis is as follows:\(^{25}\)

\[
\text{Fe}^{2+} (aq) + 2\text{Fe}^{3+} (aq) + 8\text{OH}^- (aq) \rightarrow \text{Fe}_3\text{O}_4(s) + 4\text{H}_2\text{O}(l)
\]

The isolated particles were dispersed in aqueous \(\text{HClO}_4\) solution (pH 3) with magnetic stirring for 18 h. After the stirring step, the as-obtained colloidal dispersion was sonicated for more 10 min. and then centrifuged (4500 rpm, 10 min.) to remove insoluble and aggregated particles. This final colloidal dispersion of np-Fe\(_3\)O\(_4\) was employed as source of nanoparticles for film depositions. The acidic medium protonates nanoparticles’ surface and thus ensures the colloidal stability through electrostatic repulsion forces. The iron concentration (in mg·mL\(^{-1}\)) of colloidal dispersions was determined by combining atomic and UV-vis absorption spectrophotometries.

2.2. Nanocomposites Film Depositions

The optical glass slides were previously cleaned in a two-step cleaning procedure with piranha solution and RCA solution, as described elsewhere.\(^{26}\) ITO-coated slides were gently rubbed with neutral detergent soap and left soaked into diluted detergent solution for 20 min in an ultrasonic bath. The detergent was removed with plenty of water. The substrates were then soaked into ultra-pure water and left in ultrasonic bath for more 20 min. Au-coated slides were functionalized with sulfonic groups by soaking them into a 3-MPS aqueous solution (0.02 mol·L\(^{-1}\)) overnight. A colloidal suspension of positively-charged np-Fe\(_3\)O\(_4\) (0.1 mg·mL\(^{-1}\)) and the anionic PSS solution (1.0 mg·mL\(^{-1}\), pH 3.0 H\(_2\text{ClO}_4\)) were used for all nanocomposites’ depositions. The depositions were performed via the LbL procedure in which the substrate was alternately immersed into the np-Fe\(_3\)O\(_4\) suspension and the PSS solution, followed by washing and drying steps in between. The time of immersion of substrates (adsorption time) was set in 3 min. for both materials with a washing step of 20 s. Drying was performed with a N\(_2\) gas flow. The deposition cycles resulted in multilayered nanocomposites with the repeating unit (np-Fe\(_3\)O\(_4\)/PSS), where \(n\) stands for the number of deposition cycles (= number of bilayers). The conditions here employed for depositions followed those used in previous studies.\(^{19}\) This deposition procedure was equally employed for all types of substrates (optical glass, ITO-coated, and Au-coated glass slides). All depositions were performed by hand at 25 °C.

2.3. Characterization

The size and morphology of the as synthesized np-Fe\(_3\)O\(_4\) was evaluated by TEM (Jeol Jim 1011, 80 kV). TEM samples were prepared by dropping a highly diluted suspension of positively charged np-Fe\(_3\)O\(_4\) onto copper grids (TedPela) and allowing them to dry in a silica-filled borosilicate glass desiccator. The np-Fe\(_3\)O\(_4\) were approximately spherical with a diameter of 8.7 ± 0.1 nm according to the log-normal fitted size distribution presented in Figure 1. The co-precipitation route invariably leads to polydisperse samples. A typical micrograph of the np-Fe\(_3\)O\(_4\) sample is shown as the inset of Figure 1.

The zeta potential of np-Fe\(_3\)O\(_4\) in the colloidal suspension was measured with a Malvern Zetasizer Nano series Nano ZS90 and the value found was +46 mV. The adsorption of each (np-Fe\(_3\)O\(_4\)/PSS) bilayer was measured \textit{ex situ} by UV-vis spectroscopy (Varian Cary 5000). The vibrational structure of np-Fe\(_3\)O\(_4\) in the nanocomposites was
evaluated by Raman spectroscopy (Jobin Yvon T 64000, laser line at 514 nm). The morphology of nanocomposites was assessed by AFM (Digital MultiMode Nanoscope IIIa, tapping mode).

The electrochemical characterizations (CV and DPASV) of ION electrodes were all conducted in a Autolab potentiostat system (EcoChimie, PGSTAT 30) with a three electrode configuration cell comprised by a Ag/AgCl reference electrode, a platinum wire counter-electrode and the working electrode being the ITO-coated glass modified with the (np-Fe₃O₄/PSS) bilayers. ION electrodes with \( n = 1, 3, 5, 7, \) and \( 10 \) bilayers were built and characterized. The electrolyte was an acetate buffer solution (pH 4.6), which was chosen to ensure Cu\(^{2+} \) solubility and nanocomposites’ stability. Before each measurement run, the electrochemical cell was purged with \( \text{N}_2 \)-gas flow for 300 s and then followed by a rest period of 120 s. CV scans were performed at different scan rates in pure acetate (to identify working potential window) and in Fe(CN)\(_{6}^{3−/4} \) redox pair solution (1 mmol \( \cdot \) L\(^{-1} \)). From these measurements the thermodynamic and kinetic parameters of ION electrodes were determined; the formal reduction potential (\( E^\circ \)), the apparent electron-transfer rate constant (\( k_{\text{app}} \)), separation peak potentials (\( \Delta E_p \)), and electron transfer coefficient (\( \alpha \)).

The analytical application of ION electrodes was evaluated by DPASV in Cu\(^{2+} \) aqueous solutions (0.49; 0.98; 2.0; 3.9 and 7.9 \( \mu \text{mol} \cdot \text{L}^{-1} \)) and coffee samples. Ground (GC) and instant coffee (IC) samples were purchased in the local market and digested according to the following procedures: (1) 45 min. at 40 W; (2) 6 min. at 650 W; (3) 6 min. at 850 W; (4) 5 min. at 800 W. After this treatment, the sample was transferred to a volumetric flask (25.0 mL) to which 10.0 mL of sodium acetate 2.0 mol \( \cdot \) L\(^{-1} \) was added. The remaining volume was completed with ultrapure water. In a typical DPASV measurement run, the working electrode was initially (and before each measurement step) conditioned at +0.3 V for 90 s, followed by an accumulation step at -0.4 V for 180 s, and finally, the determination step was performed by applying a differential pulse from -0.4 V to +0.3 V (pulse amplitude: 50 mV; scan rate: 5 mV \( \cdot \) s\(^{-1} \); pulse time: 40 ms). Standard addition and recovery experiments were performed with tap water and coffee samples. These experiments allowed estimation of the sensitivity and the limit of detection (LD) of ION electrodes to Cu\(^{2+} \). The LD was determined from the analytical curve, according to Eq. (1):

\[
LD = \frac{s_i \cdot r}{a_i} \sqrt{\frac{1}{N} + 1 + \frac{(\bar{y} - \bar{y})^2}{a_i^2 \sum_{i=1}^{N} (x_i - \bar{x})^2}}
\]

where \( s_i \) is the standard deviation, \( r \) is the Student distribution, \( a_i \) is the slope for the linear regression of the analytical curve, \( N \) is the number of measurements, \( y \) is the superior limit of the confidence interval, \( \bar{y} \) is the analytical signal, and \( x \) is the analyte concentration.

The amount of Cu\(^{2+} \) in tap water and coffee samples was also determined by atomic absorption spectroscopy (Varian, model AA240FS) performed under the following conditions: air/acetylene flame (air flow 13.5 L \( \cdot \) min\(^{-1} \), acetylene flow: 2.0 L \( \cdot \) min\(^{-1} \); Cu\(^{2+} \) concentration range: 7.9 to 94.1 \( \mu \text{mol} \cdot \text{L}^{-1} \); UV detection at 324.8 nm.

The influence of some interfering ions was also investigated. For that purpose, standards of Zn\(^{2+} \), Mn\(^{2+} \), Ni\(^{2+} \), and Fe\(^{3+} \) were separately added to a 2.5 \( \mu \text{mol} \cdot \text{L}^{-1} \) Cu\(^{2+} \) aqueous solution. The standards were added at three concentration levels of interference: 0.25, 2.5, and 25.0 \( \mu \text{mol} \cdot \text{L}^{-1} \). The analytical signal (height peak) was calculated as relative to the analytical signal of pure Cu\(^{2+} \) solution (2.5 \( \mu \text{mol} \cdot \text{L}^{-1} \) in the absence of the interfering ion).

3. RESULTS AND DISCUSSION

3.1. Deposition, Structure and Morphology of Nanocomposites

The deposition of nanocomposites (np-Fe\(_3\)O\(_4\)/PSS) onto BK7 glass slides was monitored \textit{ex situ} by UV-vis spectroscopy. The spectra were recorded after every deposited (np-Fe\(_3\)O\(_4\)/PSS) bilayer. As shown in Figure 2, spectra of nanocomposites are rather structureless and display two subtle shoulders at 480 nm and 360 nm. These features are typical of magnetite and are ascribed to the Fe\(^{2+} \) → Fe\(^{3+} \) electron transfer process in the inverse spinel crystal structure. Those bands have been also referred to as the indirect band gap transition. PSS absorbs only at 270 nm due to the π → π* transition of its sulfonated...
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benzene rings and, therefore, it does not contribute to the nanocomposites’ absorption in the measured wavelength range (from 800 to 300 nm). After inspecting the inserted graphic in Figure 2 it is clearly noted that the absorbances of these two shoulders increase linearly with the number of bilayers. Therefore, it can be concluded that each bilayer contributes with a constant amount of np-Fe3O4, as already reported for similar systems.12, 18, 19, 26, 28 Since the adsorption process is electrostatically driven, it depends on the mutual charge compensation between depositing electrolyte materials. Therefore, it can be assumed that the amount of adsorbed of PSS is also constant at each bilayer.

As pointed out previously,29 Raman as well as FT-IR spectra30 give unique fingerprints for each iron oxide phase so that discrimination and identification of phases can be accomplished unequivocally. The Raman spectrum of a (np-Fe3O4/PSS) nanocomposite film, recorded under 0.3 mW power excitation intensity, is presented in Figure 3. The spectrum displays three main bands that are then adjusted by five Lorentzians ascribed to magnetite vibration modes, as follows:31

- Figure 3. The spectrum displays three main bands that are then adjusted by five Lorentzians ascribed to magnetite vibration modes, as follows:31

\[ T_{2g}^l \quad (193 \text{ cm}^{-1}) \]

\[ E_g \quad (328 \text{ cm}^{-1}) \]

\[ T_{2g}^h \quad (470 \text{ cm}^{-1}) \]

\[ T_{2g}^f \quad (540 \text{ cm}^{-1}) \]

\[ A_{1g} \quad (670 \text{ cm}^{-1}) \]

It is worth mentioning that the maghemite phase, indicated by a vibrational mode at 720 cm\(^{-1}\), is absent in the nanocomposite.

The AFM images (topography and phase) of the (np-Fe3O4/PSS) nanocomposite film are shown in Figure 4. The topography image (Fig. 4(a)) shows a densely-packed layer of np-Fe3O4. The featured sizes in AFM images corroborate the sizes of np-Fe3O4 in the colloidal suspension as measured by TEM. Some np-Fe3O4 aggregates are also present. The phase image (Fig. 4(b)) reveals that np-Fe3O4 (lighter features) are surrounded by a softer PSS layer (darker contours). As already observed in previous investigations, in the LbL assembly the ION readily adsorb onto the plain substrate as well as onto already adsorbed bilayers.17, 32 They prefer to adsorb into the voids left between particles of the underneath layer to form more compact layers instead of adsorbing on top of them. These voids, as well as the nanoparticles’ surfaces, are coated with polyelectrolyte that serves as an anchoring site for the upcoming nanoparticles. In fact, the rms surface roughness of nanocomposite films increased from 7.5 nm for the very first np-Fe3O4 single layer to 12.1 nm (5 np-Fe3O4/PSS bilayers) and finally to 15 nm for 10 bilayers. Thereafter, the roughness remained constant what corroborates the assumption made before that upcoming nanoparticles set into the voids left around nanoparticles from the previous layers.

3.2. Electrochemical Properties

The electrochemical properties of (np-Fe3O4/PSS) electrodes were studied by CV. The CV enables one the observation of redox reaction dynamics and provides data for determination of the electrochemical window and the kinetics and thermodynamics parameters of electrodes, such as electron transfer rate constants and formal potentials. Figure 5 shows the electrochemical behavior of electrodes with different number of (np-Fe3O4/PSS) bilayers investigated in acetate buffer (pH 4.6) at 50 mV \(\cdot\) s\(^{-1}\) scan rate. The voltammograms shown in Figure 5(a) share similar features, including two cathodic waves set at around 192 mV and +41 mV and an anodic one at +360 mV, all for the three bilayer electrode. For the electrodes with different number of bilayers, the potentials are slightly different from the previous ones, as quoted in Table I. According to the literature, the first cathodic wave is ascribed to the reduction of Fe(III) oxy-hydroxide to magnetite (Fe3O4)33, 34 These Fe(III) containing species are located at the nanoparticles’ surface as a result of oxidation. Oxidation of ION is hardly avoided, especially because of their great reactivity due to the enhanced surface to volume ratio. On the other hand, these oxidized surface groups are readily protonated in acidic medium (or deprotonated in basic medium) and in this way they are key for the preparation of colloidal dispersions as stabilized by repulsive electrostatic forces.35 The second cathodic wave at +41 mV for the three bilayer electrode (for other number of bilayers please refer to Table I) is ascribed to the reduction of γ-Fe2O3 (maghemite) to Fe3O4. The respective oxidation reaction (Fe3O4 \(\rightarrow\) γ-Fe2O3) is related to the anodic
Figure 5. (a) Cyclic voltammograms and (b) peak currents for the three redox events of ION-based electrodes as a function of the number of (np-Fe₃O₄/PSS) bilayers. \(I_{pc1}\) and \(I_{pc2}\) correspond to peak currents for the first and second cathodic waves, respectively. \(I_{pa1}\) corresponds to the peak current for the first anodic wave. Electrolyte: acetate buffer pH 4.6; scan rate: 50 mV·s⁻¹.

Wave peak at +360 mV. The process is itself practically irreversible. In Figure 5(b) one can see that the peak currents for the three redox events (\(I_{pc1}\), \(I_{pc2}\), peak currents for the first and second cathodic waves; \(I_{pa1}\), peak current for the first anodic wave) in the ION-based electrodes change as a function of the number of (np-Fe₃O₄/PSS) bilayers. It is interesting to note that in all electrochemical events, the current reaches a maximum at about three bilayers and thereafter remains almost constant. This behavior is due to the densification of ION electrodes as more bilayers are being deposited, which limits electron transfer between ION film surface and the underlying ITO substrate.

The electrochemical kinetics and thermodynamics of ION electrodes was investigated with the ferricyanide/ferrocyanide system, which is widely used as a model probe to evaluate surface electrochemical reactivities. Figure 6 provides cyclic voltammetry data concerning the electrochemical reactions of ferricyanide/ferrocyanide conducted with the ION electrodes made with different numbers of (np-Fe₃O₄/PSS) bilayers. The electroactive area of ION electrodes was determined by the Randles-Sevcik equation. Table II collects thermodynamic and kinetics parameters of electrodes determined from fitting the voltammetry data with the model proposed by Nicholson.

In Figure 6(a), cyclic voltammograms recorded at a scan rate of 50 mV·s⁻¹ show the well-defined pair of oxidation-reduction waves regarding the \(\text{Fe}^{III}(\text{CN})_6^{3-} + e^{-} \leftrightarrow \text{Fe}^{II}(\text{CN})_6^{4-}\) reaction. The current density is slightly increased by the deposition of (np-Fe₃O₄/PSS) bilayers (Table II, 3rd column). This effect is more pronounced for the very first bilayer, which increases the electroactive surface area of the working electrode in about 32%. This is reflected on the substantial increase of the electron transfer rate, which for the ION electrode with one bilayer is about four times greater than that measured with the plain ITO electrode (Table II, 5th column, 2nd row). However, for the subsequent bilayers, the current density reaches a maximum and remains constant. The electron transfer rate after three bilayers is even smaller than that determined by the plain ITO electrode. By one hand, the increase on the electrode's surface area with (np-Fe₃O₄/PSS) bilayers enhances the adsorption of ferricyanide/ferrocyanide ions and thus increases the concentration of electrons near the electrode. However, more bilayers block the electron path between the electrolytic solution and the ITO substrate underneath. Despite the semiconducting behavior of np-Fe₃O₄ they are still much less conducting than the plain ITO substrate, so that only those ferricyanide/ferrocyanide ions closest to the electrode are detected. Cao and Hu also observed that electrodes based on hemoglobin/np-Fe₃O₄ multilayers reached a current limit after few bilayers were deposited on top of pyrolytic graphite substrates.

In Figure 6(b) it is seen that the current density (anodic and cathodic) increases, but not linearly with the square root of the scan rate \(v^{1/2}\), except for the plain ITO and for ION electrodes with few bilayers. In fact, it is commonly observed that the ferricyanide/ferrocyanide couple is quasi-reversible at many different working electrodes. Figure 6(c) corroborates this observation, since \(\Delta E_p\) increases with the scan rate as well. The first and third bilayer reduce the irreversibility in comparison to plain ITO, but for more bilayers the quasi-reversible regime is reestablished.

Table I. Electrochemical potentials for redox processes occurring in electrodes with different number of (np-Fe₃O₄/PSS) bilayers. Electrolyte: acetate buffer, pH 4.6. Scan rate: 50 mV·s⁻¹.

<table>
<thead>
<tr>
<th>(np-Fe₃O₄/PSS) bilayers</th>
<th>1st cathodic wave (mV)</th>
<th>2nd cathodic wave (mV)</th>
<th>1st anodic wave (mV)</th>
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Cyclic voltammetry of 0.001 mol L⁻¹ K₃Fe(CN)₆ in 1.0 mol L⁻¹ KCl electrolyte as measured with ION electrodes with different number (n) of (np-Fe₃O₄/PSS) bilayers. (a) voltammograms recorded at 50 mV s⁻¹ scan rate, (b) cathodic and anodic peak currents as a function of v¹/₂; and (c) ΔEₚ versus logν.

Despite that (np-Fe₃O₄/PSS) bilayers have been slightly more effective than the plain ITO in driving the electrochemical oxidation-reduction of the ferri/ferrocyanide couple, these ION based bilayers have considerably improved in all electrochemical parameters the electrodes’ response to Cu²⁺, which is indeed our target analyte. According to Figure 6(b), DP voltammograms exhibit two well-defined and separated anodic peaks regarding the Cu → Cu²⁺ + 2e⁻ and Fe → Fe³⁺ + 3e⁻ oxidation reactions. When the concentration of Cu²⁺ is increased, the anodic current at −104 mV has a significant increase. Also, a current due to Fe³⁺ appears, which is associated to a slight shift on the measurement background. As quoted in Figure 7(b), the ION electrode responds linearly (r² = 0.996) to the presence of Cu²⁺ in the range between 1.0 and 8.0 × 10⁻⁶ mol L⁻¹ and presents a limit

<table>
<thead>
<tr>
<th>(np-Fe₃O₄/PSS)</th>
<th>ΔEₚ (mV)</th>
<th>ION</th>
<th>(np-Fe₃O₄/PSS)</th>
<th>ΔEₚ (mV)</th>
<th>ION</th>
<th>(np-Fe₃O₄/PSS)</th>
<th>ΔEₚ (mV)</th>
<th>ION</th>
</tr>
</thead>
<tbody>
<tr>
<td>ITO</td>
<td>72</td>
<td>157</td>
<td>253</td>
<td>0.26</td>
<td></td>
<td>72</td>
<td>157</td>
<td>253</td>
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<tr>
<td>1</td>
<td>62</td>
<td>163</td>
<td>253</td>
<td>1.10</td>
<td></td>
<td>62</td>
<td>163</td>
<td>253</td>
</tr>
<tr>
<td>3</td>
<td>69</td>
<td>161</td>
<td>256</td>
<td>0.34</td>
<td></td>
<td>69</td>
<td>161</td>
<td>256</td>
</tr>
<tr>
<td>5</td>
<td>80</td>
<td>162</td>
<td>263</td>
<td>0.15</td>
<td></td>
<td>80</td>
<td>162</td>
<td>263</td>
</tr>
<tr>
<td>7</td>
<td>74</td>
<td>162</td>
<td>262</td>
<td>0.16</td>
<td></td>
<td>74</td>
<td>162</td>
<td>262</td>
</tr>
<tr>
<td>10</td>
<td>87</td>
<td>162</td>
<td>262</td>
<td>0.12</td>
<td></td>
<td>87</td>
<td>162</td>
<td>262</td>
</tr>
</tbody>
</table>

Notes: Obs. All redox analyte concentrations were 0.001 mol L⁻¹. Supporting electrolyte for Fe(CN)₆³⁻⁻ and Cu²⁺/³⁺ was 1.0 mol L⁻¹ KCl and ammonium acetate 0.1 mol L⁻¹ (pH 4.6), respectively. Data shown are for the fifth scan. (a) Oxidation peak was normalized to the electrodes’ geometric area according to Randles-Sevcek equation. The electron transfer coefficient (α) was 0.950, as attained from the slope of E versus logν; (b) Scan rate, 100 mV s⁻¹; (c) Scan rate 20 mV s⁻¹.

3.3. Analytical Application

The analytical application of ION electrodes was evaluated by DPASV in Cu²⁺ aqueous solutions (0.49; 0.98; 2.0; 3.9 and 7.9 μmol L⁻¹) and coffee samples. The idea was to verify the possibility of using ION electrodes to detect copper, since its relevance for agricultural activities and food safety. The experimental conditions are described in the experimental section. Figure 7 displays the DPASV data attained with an ION electrode made with three (np-Fe₃O₄/PSS) bilayers. This electrode was chosen because it is homogeneous (three bilayers were sufficient to coat the ITO substrate with a compact ION layer), displays a steady value for cathodic/anodic currents due to np-Fe₃O₄, which is indeed our target analyte. According to Figure 7(a), DP voltammograms exhibit two well-defined and separated anodic peaks regarding the Cu → Cu²⁺ + 2e⁻ and Fe → Fe³⁺ + 3e⁻ oxidation reactions. When the concentration of Cu²⁺ is increased, the anodic current at −104 mV has a significant increase. Also, a current due to Fe³⁺ appears, which is associated to a slight shift on the measurement background. As quoted in Figure 7(b), the ION electrode responds linearly (r² = 0.996) to the presence of Cu²⁺ in the range between 1.0 and 8.0 × 10⁻⁶ mol L⁻¹ and presents a limit
the linear fitting (solid line) are included in the plot.

Figure 7. (a) Differential pulse voltammograms for Cu²⁺ solutions at different concentrations (in μmol·L⁻¹) recorded with the (np-Fe₃O₄/PSS) ION electrode and (b) analytical curve. Adjusting data for the linear fitting (solid line) are included in the plot.

of detection (LD) of 0.3 × 10⁻⁸ mol·L⁻¹ (or else ∼0.2 ppm). The sensitivity is 5.7 × 10⁻⁷ μA/μmol·L⁻¹. The detection precision exhibited by the ION electrode (three bilayers) was evaluated by means of the standard deviation (sd) calculation of ten consecutive DPASV measurements of a 2.5 μmol·L⁻¹ Cu²⁺ solution. The variation coefficient (sd/IP(average) × 100) was about 3.6%.

The LD exhibited by the ION electrode is quite promising since it is comparable to values reported in the literature for specific electrodes. For example, gold electrodes modified by cysteine, which is recognized for its ability to form a stable complex with Cu²⁺, exhibited LD ranging from ppm to ppt.38-40 Other approaches for attaining specific electrodes for copper, including molecular imprinting with EDTA,41 Schiff bases42 or peptides fragments43,44 have also reached the same range of LD. More recently, Mahendran and Philp,13 and Philip et al.14 have proposed an elegant approach for detection of metallic cations, including Cu²⁺, in which the color of an iron oxide nanoparticle based magnetic fluid is changed by the presence of the ion. The metallic ion shifts the diffraction Bragg peak of the magnetic fluid and the shift linearly scales with Cu²⁺ in the range between 1.5 to 12.0 ppm.

For the ION electrode we have performed standard addition and recovery experiments. According to data presented in Table III, the recovery of Cu²⁺ for tap water sample was about 102%–119%. For ground (GC) and instant coffee (IC) samples, the recovery was 92.5% and 103%, respectively.

The response of ION electrodes to Cu²⁺ was also tested in presence of possible interfering ions in ultrapure water. According to data collected in Table IV, all interfering ions tested (Zn²⁺, Mn²⁺, Ni²⁺, and Fe³⁺) have reduced the sensitivity of the ION electrode (three bilayers) to Cu²⁺. However, this reduction is significantly solely when the interfering ion concentration is ten times higher than that of Cu²⁺, with Zn²⁺ being the most important. In that case, the interfering ion reduces the electrochemical signal to 69% of its original value (in solution absent of interfering ion). For the other ions at this interference level, the electrochemical signal of the ION electrode to Cu²⁺ is reduced less than 20%. In fact, the matrix effect can be suppressed by the standard addition method. Therefore, it is possible to conclude that the ION electrode suffer very little influence of common interfering ions and can be applied to detect Cu²⁺ with great confidence.

Table III. Recovery experiments for determination of Cu²⁺ in tap water and coffee using the (np-Fe₃O₄/PSS) ION electrode.

<table>
<thead>
<tr>
<th>Sample</th>
<th>[Cu²⁺] (μmol·L⁻¹)</th>
<th>Reference (μmol·L⁻¹)</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>–</td>
<td>0.60</td>
<td>–</td>
</tr>
<tr>
<td>A1.1a</td>
<td>6.36</td>
<td>6.25</td>
<td>102</td>
</tr>
<tr>
<td>A1.2a</td>
<td>3.75</td>
<td>3.15</td>
<td>119</td>
</tr>
<tr>
<td>GC1.0</td>
<td>–</td>
<td>0.45</td>
<td>–</td>
</tr>
<tr>
<td>GC1.1a</td>
<td>0.98</td>
<td>1.06</td>
<td>92.5</td>
</tr>
<tr>
<td>IC2.0</td>
<td>–</td>
<td>0.11</td>
<td>–</td>
</tr>
<tr>
<td>IC2.1a</td>
<td>1.37</td>
<td>1.33</td>
<td>103</td>
</tr>
</tbody>
</table>

Notes: (a) sample prepared by adding 6.25 μmol·L⁻¹ of Cu²⁺ to sample A1. The concentration was estimated in 6.96 μmol·L⁻¹ while subtracting 0.60 μmol·L⁻¹ of A1 resulting 6.36 μmol·L⁻¹ de Cu(II). (b) sample prepared by adding 3.15 μmol·L⁻¹ of Cu²⁺ to sample A1. The concentration was estimated in 4.35 μmol·L⁻¹ while subtracting 0.60 μmol·L⁻¹ of A1 and resulting in 3.75 μmol·L⁻¹. (c) sample prepared by adding 0.61 μmol·L⁻¹ of Cu²⁺ to sample GC1.0. (d) sample prepared by adding 1.2 μmol·L⁻¹ of Cu²⁺ to sample IC2.0. (e) determined by DPASV (f) determined by atomic absorption spectrometry.

Table IV. Effect of interfering ions on the analytical signal of Cu²⁺ (2.5 μmol·L⁻¹ in ultrapure water) as measured with the ION electrode (three bilayers) by DPV.

<table>
<thead>
<tr>
<th>Interfering ion</th>
<th>Level of interference/remaining signal</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.25 μmol·L⁻¹</td>
</tr>
<tr>
<td>Zn²⁺</td>
<td>81 (%)</td>
</tr>
<tr>
<td>Mn²⁺</td>
<td>92 (%)</td>
</tr>
<tr>
<td>Ni²⁺</td>
<td>93 (%)</td>
</tr>
<tr>
<td>Fe³⁺</td>
<td>93 (%)</td>
</tr>
</tbody>
</table>
4. CONCLUSIONS

The layer-by-layer assembly of magnetite nanoparticles (np-Fe₃O₄) and sulfonated polystyrene (PSS) on top of ITO substrates enabled the construction of iron oxide nanostructured (ION) electrodes. The electrodes detected Cu²⁺ in tap water as well as in commercially available coffee samples. The assembly of ION electrodes was made possible by the electrostatic attraction between positively-charged np-Fe₃O₄ and anionic PSS after the alternated dipping of the ITO substrate into their respective colloidal suspension/solution. The amount of adsorbed np-Fe₃O₄ increased linearly with the number of immersion cycles, which thus ensured the stepwise growth of ION electrode and, therefore, permitted a great control of the electrode fabrication process.

The presence of np-Fe₃O₄ reflected on the electrochemical behavior of ION electrodes. They exhibited the main redox reactions involving Fe²⁺/Fe³⁺, and hydrous iron oxide surface layers, which corroborated the presence of maghemite phase as earlier evidenced by Raman spectroscopy. The effect of np-Fe₃O₄/PSS bilayers on the ION electrode performance was to increase slightly the anodic and cathodic currents produced during electrochemical oxidation-reduction of the ferricyanide/ferrocyanide redox couple. Moreover, the redox couple exhibited a quasi-reversible behavior on the ION electrode as already observed with other working electrode systems. The apparent electron transfer coefficients for both ferricyanide/ferrocyanide and Cu²⁺/Cu⁺ redox couples were greater with ION electrodes, although current densities reached a maximum after deposition of three np-Fe₃O₄/PSS bilayers. This behavior was ascribed to densification and thickening of ION electrodes that decrease the electron transfer across the electrode/electrolyte interface. Finally, ION electrodes presented a linear response to Cu²⁺ with a limit of detection (LD) of 0.3 × 10⁻⁸ mol·L⁻¹, which can be considered very promising in comparison to values reported in the literature for other electrodes including specific ones. In fact, the ION electrodes appeared almost insensitive to the presence of common interfering ions such as Zn²⁺, Mn²⁺, Ni²⁺, and Fe³⁺. Moreover, the ION electrodes could detect Cu²⁺ in both ground and instant coffee samples with good precision and accuracy.

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References and Notes

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