Evaluation of the synergistic effects of a novel organic-inorganic nickel hybrid nanocomposite as electrocatalyst toward glucose oxidation

Ana L. Rinaldi, María Celina Bonetto, Santiago Sobral, Romina Carballo

PII: S1572-6657(20)30222-8

DOI: <https://doi.org/10.1016/j.jelechem.2020.114039>

Reference: JEAC 114039

To appear in: *Journal of Electroanalytical Chemistry*

Received date: 29 November 2019

Revised date: 4 March 2020

Accepted date: 5 March 2020

Please cite this article as: A.L. Rinaldi, M.C. Bonetto, S. Sobral, et al., Evaluation of the synergistic effects of a novel organic-inorganic nickel hybrid nanocomposite as electrocatalyst toward glucose oxidation, *Journal of Electroanalytical Chemistry*(2020), <https://doi.org/10.1016/j.jelechem.2020.114039>

This is a PDF file of an article that has undergone enhancements after acceptance, such as the addition of a cover page and metadata, and formatting for readability, but it is not yet the definitive version of record. This version will undergo additional copyediting, typesetting and review before it is published in its final form, but we are providing this version to give early visibility of the article. Please note that, during the production process, errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Evaluation of the synergistic effects of a novel organic-inorganic nickel hybrid nanocomposite as electrocatalyst toward glucose oxidation.

Ana L. Rinaldi^{a,b}, María Celina Bonetto^a, Santiago Sobral^a, Romina Carballo^{a,b§*}

^aUniversidad de Buenos Aires. Consejo Nacional de Investigaciones Científicas y Técnicas. Instituto de Química y Fisicoquímica Biológica (IQUIFIB). Buenos Aires, Argentina.

^bUniversidad de Buenos Aires. Facultad de Farmacia y Bioquímica. Departamento de Química Analítica y Fisicoquímica. Buenos Aires, Argentina.

Abstract

A novel organic-inorganic hybrid nanocomposite obtained by electro-copolymerization of multi-walled carbon nanotubes and [Ni-(Protoporphyrin IX)], and then decorated with nickel metal nanoparticles (NiPPIX/CNT/NiNp) has been successfully prepared for its use in the non-enzymatic oxidation of glucose.

The structural characterization and the electrochemical evaluation of the charge transport mechanisms for NiPPIX/NTC/NiNp were performed by SEM-EDX, cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements.

The combination of two classes of electron hopping sites, nickel nanoparticles and the nickel atom of the porphyrin, embedded in an environment of high electronic delocalization and optimal film permeability, contributed to the electronic transfer processes, in terms of heterogeneous electron transfer rate constant ($k^0=1.6 \times 10^{-4} \text{ cm s}^{-1}$ for NiPPIX/CNT/NiNp vs $2.4 \times 10^{-5} \text{ cm s}^{-1}$ for NiNp).

NiPPIX/CNT/NiNp glassy carbon electrode shows the best linear response for glucose determination up to 6 mmol L^{-1} , with a 0.9953 correlation coefficient and a slope of $0.2689 \text{ mA L mmol}^{-1} \text{ cm}^{-2}$.

Lastly, the association of homogeneously distributed catalytic centers is an interesting strategy for the design of nanomaterials for sensing purposes.

Keywords: electron hopping; [Ni-(Protoporphyrin IX)]; organic-inorganic hybrid; electrocatalysts.

§ CONICET permanent staff

* Corresponding author. E-mail: rocar@ffybio.uba.ar

1. Introduction

Over the last few years, nanomaterials have greatly contributed to improving current analytical methods and making progress in new developments for the determination of challenging (bio)analytes, mainly in the field of electrochemical sensors. In some cases, the advances in nanotechnology produce significant increases in the effective electrodes area, enhance electrocatalytic activity or facilitate the immobilization of structures of specific molecular recognition [1,2]. In particular, carbon nanomaterials (single or multi-walled carbon nanotubes, and graphene) are usually incorporated as actuators for their ability to provide a high heterogeneous electron transfer rate between analyte and electrode surface [3-6].

For electroanalytical purposes, carbon nanotubes (CNTs) can be deposited on electrode surfaces using different strategies, including directly growing materials on a substrate, drop-casting, incorporating CNTs into polymers and co-deposition of CNTs and metal nanoparticles [7-10]. The direct growth of CNTs onto the electrodes provides a more homogenous coating than conventionally used dip-coating or drop-casting methods, where the evaporation velocity may lead to the formation of a film with a non-uniform distribution of CNTs and low reproducibility. Moreover, the integration of these carbon nanomaterials in a polymer matrix confers benefits that facilitate the bulk fabrication steps of a final device: better carbon nanotubes dispersion, increased conductivity, stable responses, low ohmic resistance, printability for miniaturizing, among others [11].

Various non-covalent approaches and conducting polymers have been used to the functionalization of CNTs [3]. For example, poly(3,4-ethylenedioxythiophene) (PEDOT), polyethylenimine (PEI), polyaniline (PANI), poly(o-anisidine) (POA) or poly(vinyl alcohol) (PVA) doped CNT were applied for the detection of catecholamines, neurotransmitters, ascorbic acid [12,13]. However, the combination of the polypyrrole (PPy) with carbon nanotubes has been the most frequently applied in (bio)sensors design [14]. Carbon nanotubes/poly [Ni-(Protoporphyrin IX)] composites successfully combine the porosity of the pNiPP films with the high conductivity of multi-walled carbon nanotubes and it has been seen that the oxide-reduction events of electroactive derivatives of long chain aliphatic amines is also improved [15]. In addition to the previously discussed advantages, the copolymerization and functionalization strategies of the CNTs give them a high degree of specificity to the detection, especially when they are deposited together with DNAs, aptamers, enzymes, antibodies, magnetic nanoparticles [16-18]. The incorporation of metal nanoparticles into of these composites can also act as an electron transfer mediator to improve the overall conductivity and selectively catalyze the reactions. In particular, in the field of non-enzymatic glucose sensors (NEGs), various catalysts have been explored, composed of one or more types of metal nanoparticles [19-21]. Ni-based sensors present excellent electrocatalytic activity toward glucose oxidation mediated by $\text{Ni}^{2+}/\text{Ni}^{3+}$ redox couples in alkaline medium. Although there are some drawbacks of Ni-based electrodes, such as low sensitivity and poor reproducibility, these can be overcome by modifying the morphological structure of the electrodeposited Ni or $\text{Ni}(\text{OH})_2$. For this reason, a large number of strategies have been employed to get a better performance of glucose sensors based on Ni

and its $\text{Ni}(\text{OH})_2$ and NiOOH forms, and electrodeposition solutions of different compositions have been tested [22, 23].

Metalloporphyrins are metal-organic compounds with a high degree of conjugation of the aromatic structure and chemical versatility conferred by the central metal and the substituents of the porphyrinic ring. Certain metals such as Co, Ru, Cu or Fe show great tendency to incorporate axial ligands [24-27], whereas Mn, Zn, Ni, Co, Pt result excellent catalysts for specific reactions [28-30].

The polymeric structures of metalloporphyrins should be highlighted in terms of their functionality. $[\text{Ni}-(\text{Protoporphyrin IX})]$ polymers (NiPPIX) show permselectivity properties, which depend largely on the method of preparation (potential, supporting electrolytes, solvents), and the movement of the ions and of fixed charges in the films [31]. NiPPIX has a good ability to incorporate aromatic structures, due to π - π interaction during the generation of the conductive films. Thus, multi-walled carbon nanotubes can be immobilized by electro-copolymerization with NiPPIX prior to nickel nanoparticle (NiNp) deposition to enhance the charge transfer processes and the sensitivity of the electrochemical response. We propose the incorporation of an additional nickel atom, in the environment of highly conjugated porphyrin rings with unique electronic properties, as an interesting strategy for the development of a new nanomaterial for glucose determination.

In this work, we studied the effect of combining nickel metal nanoparticles (NiNp), multi-walled carbon nanotubes (CNT) and poly $[\text{Ni}-(\text{Protoporphyrin IX})]$ (NiPPIX) for the modification of glassy carbon electrodes (GCE), named NiPPIX/CNT/NiNp, for their use as non-enzymatic glucose sensors (NEGs). The morphological characterization and the electrochemical evaluation of charge transport mechanisms for the novel NiPPIX/CNT/NiNp nanocomposite were performed by SEM-EDX, cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements. The analytical performance, considering reproducibility in carbon nanotubes immobilization and the sensitivity of the response to glucose determination, is also included.

2. Experimental

2.1. Materials

The chemicals used for this work were of analytical grade. All chemicals were purchased from Merck and Sigma-Aldrich, used as received without any purification or treatment. The aqueous solutions were prepared with deionized water.

Multi-walled carbon nanotubes (CNT) (diameter 15 ± 5 nm; length 1-5 μm) were purchased from Nano-Lab. [Ni-(Protoporphyrin IX)] (NiPPIX) was prepared according to standard procedures [32].

2.2. Apparatus

A glassy carbon electrode (GCE with an area of 0.07 cm^2), an Ag/AgCl KCl 3 mol L^{-1} reference electrode (BAS), a platinum wire auxiliary electrode, and a potentiostat with electrochemical impedance module (nanoTeq-Argentina) were used for electrochemical experiments.

Data analysis was performed with the program ZView® (Scribner Associates, USA).

Scanning electron microscopy (Zeiss DSM982 GEMINI SEM with Field Emission Gun) was used to characterize the morphology and structure of the NiNp, CNT_{dc}/NiNp made by drop-casting, and NiPPIX/CNT/NiNp electrodes. Since gold electrodes were required for these images, the peaks of gold were also observed in the spectrum.

2.3. Electrochemical measurements

All electrochemical experiments were carried out at room temperature in 0.1 mol L^{-1} KOH. The scan rate range used in cyclic voltammetry (CV) experiments was 0.001 V s^{-1} to 1 V s^{-1} and the CV measurements were performed in a glucose concentration range of $0.5\text{--}6\text{ mmol L}^{-1}$ cycling between 0.00 and $+0.80\text{ V}$. Blood samples were diluted five times in 0.1 mol L^{-1} KOH solution. Electrochemical Impedance Spectroscopy (EIS) was used to evaluate the performance of the sensor. The EIS measurements were made in a frequency range of $100\text{ kHz--}0.1\text{ Hz}$, with an amplitude of oscillation (V_{AC}) set to 10 mV_{RMS} . The optimal working potentials (V_{DC}) were set to $+0.350\text{ V}$ and $+0.250\text{ V}$ for measurements in alkaline medium (0.1 mol L^{-1} KOH) and in 0.1 mol L^{-1} KCl containing 5 mmol L^{-1} $[\text{Fe}(\text{CN})_6]^{3-/4-}$, respectively. The amperometric responses of the NiPPIX/CNT/NiNp/GCE in the presence of interferents were evaluated in 0.1 mol L^{-1} KOH, at $+0.40\text{ V}$, under a stirring condition.

2.4. Preparation of the modified electrodes

1 mg of multi-walled carbon nanotubes was ultrasonically dispersed in 4 mL of 3 mmol L^{-1} NiPPIX solution for 30 minutes before electro-copolymerization onto a GCE, polished first with 0.3 and $0.05\text{ }\mu\text{m}$ diameter alumina particles and rinsed with deionized water afterwards. The electropolymerization of NiPPIX/CNT onto the GCE was carried out by five cycles of potential sweep between 0.00 and $+1.80\text{ V}$ (vs. Ag/AgCl) at 0.05 V s^{-1} , in 0.1 mol L^{-1} tetrabutylammonium perchlorate (TBAP)/ CH_2Cl_2 .

Alternatively 25 μL of a CNT dispersion, made ultrasonically in water for 30 minutes, were drop-casted onto a GCE (4 mg mL^{-1}) and left to dry in air.

The electrochemical deposition of NiNp onto the working electrodes were made using non-deaerated solutions of $0.010 \text{ mol L}^{-1} \text{ Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $1 \text{ mol L}^{-1} \text{ NH}_4\text{Cl}$ at pH 5. Ni electrodeposition was carried out by applying for 60 s a potential step of -1.30 V vs Ag/AgCl. Finally, all the electrodes were activated by cycling between 0.00 and $+0.80 \text{ V}$ in aqueous $0.1 \text{ mol L}^{-1} \text{ KOH}$ solution for at least 15 cycles at 50 mV s^{-1} until reproducible peak shape was achieved.

3. Results and discussion

3.1. Morphological and electrochemical characterization of the modified electrode surfaces

For the design of a novel non-enzymatic glucose sensor, glassy carbon electrodes (GCE) were modified using different techniques and nanomaterials/nanocomposites combinations. The NiNp electrodes were prepared by reductive electrodeposition of Ni nanoparticles onto bare GCE, according to previous procedures [33]. The $\text{CNT}_{\text{dc}}/\text{NiNp}$ electrodes were prepared by drop-casting of a multi-walled carbon nanotube dispersion onto a bare GCE and NiNp electrodeposition afterwards. The NiPPIX/CNT/NiNp electrodes were prepared by electro-copolymerization of NiPPIX/CNT onto bare GCE first, and then NiNp electrodeposition. Each modified electrode was produced in triplicate. The control electrodes, only NiPPIX, NiPPIX/CNT, and NiPPIX/NiNp, were also obtained and evaluated.

The modified electrodes were characterized by SEM and energy dispersive X-ray microanalysis (EDX); the morphological differences are observed in Fig. 1. Fig. 1a shows a continuous surface of nickel with some dispersed agglomerates for NiNp electrode, although the presence of nanostructures is not clearly observed. Conversely, Figs. 1b ($\text{CNT}_{\text{dc}}/\text{NiNp}$) and 1c (NiPPIX/CNT/NiNp) reveal a highly nanoporous structure, determined by the presence of a carbon nanotube network, where heterogeneous mass transport processes will be described later. In both cases, the NiNp are well dispersed throughout the carbon nanotube lattice. However, it is possible to observe that the electrodeposition at 60 s of nickel nanoparticles in the NiPPIX/CNT/NiNp electrode leads to NiNp with higher size ($\sim 100 \text{ nm}$) than in the $\text{CNT}_{\text{dc}}/\text{NiNp}$ case ($\sim 50 \text{ nm}$). It can be thought that the high conductivity of the polymeric nanocomposite (NiPPIX/CNT) contributes to a better coating and homogeneous growth of the nickel metal nanoparticles [3, 9, 15].

These results are clearly quantified in the EDX analysis (Figs. 1d, e, f), where the percentage of nickel atoms (atomic %) is four times higher in both NiNp (Fig. 1d, 45.03%) and NiPPIX/CNT/NiNp (Fig. 1f, 44.13%) electrodes, than in the $\text{CNT}_{\text{dc}}/\text{NiNp}$ case (Fig. 1e, 10%). Thus, the NiNp electrodeposition onto the CNT_{dc} (Fig. 1e) is less efficient than the nickel metal nanoparticles electrodeposition onto a bare electrode (Fig. 1d) or onto the NiPPIX/CNT (Fig. 1f).

As we have already discussed in a previous work [24], the electrochemical polymerization of the NiPPIX in the presence of multi-walled carbon nanotubes leads to the

formation of a network of porous semipermeable interconnected fibrils. The CVs corresponding to this electropolymerization process, through which the NiPPIX/CNT organic nanocomposite on GCE is obtained, are presented in Fig. S1. These show the minor reversible signals due to $\text{Ni}^{2+}/\text{Ni}^{3+}$ of the porphyrin in a $\text{Cl}_2\text{CH}_2/\text{TBAP}$ medium, at +0.900/+0.850 V vs. Ag/AgCl. However, when this modified electrode is activated in alkaline medium in order to generate $\text{Ni}(\text{OH})_2/\text{NiOOH}$ [23, 34], the $\text{Ni}^{2+}/\text{Ni}^{3+}$ redox couple becomes much more reversible and it appears at much lower potentials (+0.340/+0.250 V, Fig. 2a). Similar behaviors are observed for the other systems that we can consider as controls: NiPPIX (Fig. 2b); NiPPIX/NiNp (Fig. 2c), NiNp (Fig. 2d); $\text{CNT}_{\text{dc}}/\text{NiNp}$ (Fig. 2e), although with lower nickel coating values than for NiPPIX/CNT/NiNp (Fig. 2f). On the other hand, Fig. 2c (NiPPIX/NiNp) and Fig. 2f (NiPPIX/CNT/NiNp) show very significant differences in the $I_{\text{pa}}/I_{\text{pc}}$ peaks corresponding to nickel sites (Table S1). That is, the presence of both nickel containing structures, [Ni-Protoporphyrin IX] (organic) and nickel metal nanoparticles (inorganic), is not enough to obtain a major and more efficient amount of $\text{Ni}(\text{OH})_2 / \text{NiOOH}$ catalytic sites. Instead, there must be a remarkable synergistic effect between [Ni-(Protoporphyrin IX)] polymer and the carbon nanotubes, due to the high conjugation and the strong electronic interactions of both semiconductors, contributing to the electronic delocalization [35, 36].

Fig. 2 also shows that NiPPIX/CNT/NiNp electrode presents the lowest ΔE_p (60 mV at 50 mV s^{-1}). This result is consistent with the idea that this organic-inorganic hybrid nanocomposite facilitates the electronic transfer processes onto GCE. Moreover, both, the nickel nanoparticles and the nickel center of the porphyrin, may be acting as electron hopping sites, favoring the charge transfer mechanism, through the movement of electrons between the different redox centers and the compensating flow of ions. Thus, the inclusion of transition metals, the orbital overlay, the nature of the supporting electrolyte (tetrabutylammonium cations), and the π - π interactions into the nanostructured polymer could explain the improvements in charge propagation for NiPPIX/CNT/NiNp modified GCE [37]. According to this discussion, Scheme 1 represents the main contributions of each component of the organic-inorganic hybrid nanocomposite and how they are enhanced.

3.2. Analysis of the electrochemical behavior of NiNp, $\text{CNT}_{\text{dc}}/\text{NiNp}$ and NiPPIX/CNT/NiNp glassy carbon electrodes, in alkaline medium.

The analysis of CVs at different scan rates (v) can be used to evaluate diffusion-controlled redox reactions for NiNp, $\text{CNT}_{\text{dc}}/\text{NiNp}$ and NiPPIX/CNT/NiNp modified electrodes, in 0.1 mol L^{-1} KOH. In all cases, it is observed that the anodic (E_{pa}) and cathodic (E_{pc}) peak potentials of the $\text{Ni}^{2+}/\text{Ni}^{3+}$ redox couple shift toward more positive and negative values, respectively, as the scan rate increases (Fig. S 2a, b,c). These shifts are higher for the modified GCE with multi-walled carbon nanotubes deposited by drop-casting ($\text{CNT}_{\text{dc}}/\text{NiNp}$). As can be seen, the ΔE_p values are larger than 60 mV at all scan rates in the range of 0.001 to 1 V s^{-1} . In Fig. 3a, these peak separations (ΔE_p) as a function of the logarithm of scan rate depict the typical trumpet plots for three modified electrodes, and since all curves converge at different v , the electron-transfer

rates are not the same in the three systems. Thus, the electron-transfer processes between the substrate and the $\text{Ni}^{2+}/\text{Ni}^{3+}$ sites are relatively slow, being less favorable for $\text{CNT}_{\text{dc}}/\text{NiNp}$ [38].

In Fig. 3b, the dependency between peak current (I_p) and the first power of the scan rate reveals some limitations in the mass transport, mainly studied for $\text{NiPPIX}/\text{CNT}/\text{NiNp}$. Indeed, for the latter, the $I_{p,a,c}$ values are proportional to the square root of the scan rates, which is in agreement with diffusion controlled processes (Fig. S2). Moreover, for $\text{NiPPIX}/\text{CNT}/\text{NiNp}$ (Fig. S2 c) the highest slope value is obtained, as compared to the other electrodes, interpreted as a higher diffusion coefficient in terms of Randles-Sevcik equation [39]. In this organic-inorganic hybrid nanocomposite, the diffusion-controlled processes can be understood through the fixed charges and the characteristic permselectivity of the NiPPIX film that facilitates the movement of ions, the porous framework constructed by a suitable dispersion of multi-walled carbon nanotubes, the presence of numerous organic and inorganic redox hopping centers and the consequent reduction of the space between those sites [40].

3.3. Characterization of the redox processes in NiNp and $\text{NiPPIX}/\text{CNT}/\text{NiNp}$ modified GCE by EIS measurements.

Previously discussed effects of charge transport and electron transfer, as well as the propagation of charge by electron hopping or ion mobilities, can also be studied by Electrochemical Impedance Spectroscopy (EIS) measurements. This is a very powerful technique, largely applied to characterize the electrochemical redox processes carried out onto the surface of modified electrodes [41]. Furthermore, EIS allows to investigate the kinetics of rapid electrode reactions and to calculate the heterogeneous electron transfer rate constants (k°).

Fig. 4 shows the Nyquist plots for $\text{Ni}(\text{OH})_2/\text{NiOOH}$ inner redox couple in $0.1 \text{ mol L}^{-1} \text{ KOH}$ at $+0.350 \text{ V}$ vs Ag/AgCl , corresponding to both the NiNp (Fig. 4a) and the $\text{NiPPIX}/\text{CNT}/\text{NiNp}$ GCE (Fig. 4b). The experimental data are best fitted to two different equivalent circuits depicted in each inset. As can be seen, EIS experiments confirmed the presence of a Warburg impedance element (W , diffusional impedance) only for $\text{NiPPIX}/\text{CNT}/\text{NiNp}$, attributed to the predominant mass transport mechanism through the porous network in this nanocomposite modifier. Whereas for NiNp , there is no Warburg impedance in the fitted circuit. Rather, CPE_{ads} and R_{ads} are the electrical elements related to the adsorption of the OH^- ions in the activation of the electrocatalyst, as we have described in previous works [33]. Clearly, the differences in the response mechanisms revealed by the EIS experiments in alkaline medium, are linked to the structural characteristics of both organic-inorganic hybrid nanocomposite and nickel nanoparticles electrocatalysts.

In order to evaluate the kinetic characteristics of the modified electrodes, EIS measurements toward a fast transfer external redox couple were carried out (Fig. 5). The impedance data were fitted to Randles' equivalent circuit. The model employed consists of the solution resistance (R_s) in series with a constant phase element corresponding to the double

layer capacitance (CPE_{DL}) in parallel to the Faradaic charge transfer resistance (R_{CT}) and a Warburg impedance element (W).

The heterogeneous electron transfer rate constants (k^0) for the reaction between $Fe(CN)_6^{3-/4-}$ and both NiNp and NiPPIX/CNT/NiNp modified surfaces were calculated using Eq. (1), usually applied to evaluate the high frequency part of EIS spectra, where electrochemical reaction is kinetically controlled [42, 43],

$$k^0 = \frac{RT}{n^2 F^2 A C R_{ct}} \quad (1)$$

where A is the electrode area; n is the number of electrons involved in the oxidation/reduction of $Fe(CN)_6^{3-/4-}$; R is the ideal gas constant, T is the temperature in Kelvin degrees; F is Faraday constant; C is $Fe(CN)_6^{3-/4-}$ concentration in $mol\ cm^{-3}$, and R_{ct} is the charge transfer resistance obtained from Randles circuit.

From these R_{ct} values, the k^0 constants are estimated to be 2.4×10^{-5} and $1.6 \times 10^{-4}\ cm\ s^{-1}$ for NiNp and NiPPIX/CNT/NiNp, respectively. As it can be observed, the NiPPIX/CNT/NiNp electrode shows the highest k^0 value. These results suggest that the interaction between the porphyrin ring and the multi-walled carbon nanotubes truly facilitates the electronic transfer due to a strong interaction between both materials, reducing the Fermi energy [44]. This high degree of electronic delocalization, along with the increase in the number of catalytic sites (capacitance values of 48.5 and $8.7\ \mu F\ cm^{-2}$ for NiPPIX/CNT/NiNp and NiNp, respectively) and the reduction of distances between active redox sites, effectively lead to a lower value of the charge transfer resistance ($4670\ \Omega$ for NiPPIX/CNT/NiNp vs $31731\ \Omega$ for NiNp) and improvement of the kinetic and charge transport properties of the proposed organic-inorganic hybrid nanostructured catalyst [45].

3.3. Analytical performance of non-enzymatic glucose sensors toward glucose determination.

The electrochemical properties formerly compared and discussed for the $Ni(OH)_2 / NiOOH$ based systems, combined or not with nanostructures and conductive polymers, motivate their evaluation for the application in the final NEG's design.

The electrocatalytic performance of the new nanocomposite, NiPPIX/CNT/NiNp glassy carbon electrode, toward glucose oxidation was investigated by cyclic voltammetry in the range of 0.5 to $6.0\ mmol\ L^{-1}$ of glucose. A plot of the scan rate normalized current ($I_p/v^{1/2}$) versus v (Fig. S3) depicts the characteristic curve of a catalytic controlled process for the electrooxidation of glucose. The results of comparing the electrochemical response to glucose for the three systems, NiNp, CNT₆₀/NiNp and NiPPIX/CNT/NiNp, are shown in Fig. 6.

Although the three modified electrodes could certainly be used for glucose quantification, the sensitivity of the electrochemical response of the organic-inorganic hybrid nanocomposite turns out to be much higher than that presented by the other modifiers assayed (Fig. S4). In terms of reproducibility, the replicate measurements employing different

NiPPIX/CNT/NiNp sensors also show lower dispersion when compared with the simpler systems (slope RSD value of 10.1; $n=3$) (Fig. S4a, b and c). Furthermore, there is no good correlation between current values and glucose concentration using the CNT_{dc}/NiNp modifier (Fig. S4c).

Selectivity of Ni-based NEG's has already been evaluated in our previous works. In this case, the sensor with the best analytical performance, NiPPIX/CNT/NiNp, was applied to the direct quantification of the glucose in whole blood samples. Two blood samples, diluted five times with 0.1 mol L⁻¹ KOH solution, were evaluated using two different NiPPIX/CNT/NiNp glassy carbon electrodes, one for each sample. The obtained currents correspond to 6.1 (123 mg dL⁻¹) and 13.8 (276 mg dL⁻¹) mmol L⁻¹ of glucose, for each sample. A satisfactory agreement between the results achieved by the organic-inorganic hybrid nanocomposite sensor and those measured by a commercial glucose biosensor was also noticed (Table 1). In addition, signals due to other interferents of the biological matrix, such as proteins, were not detected (Fig. S5).

Finally, and according to the objective of this work, Table 2 summarizes some examples of nickel carbon-materials polymeric nanocomposites used for the construction of NEG's. The most relevant analytical parameters are compared. Thus, our organic-inorganic hybrid nanocomposite sensor, NiPPIX/CNT/NiNp, should be a competitive proposal.

4. Conclusions

In the design of a novel electrocatalyst applied to the development of non-enzymatic glucose sensors, NiPPIX/CNT/NiNp has been proposed. Two classes of nickel catalytic centers, homogeneously distributed as electron hopping sites in a network of multi-walled carbon nanotubes were evaluated. The morphological characteristics evaluated by SEM-EDX reveal that the method of preparation of the nanocomposite generates a very stable, and reproducible dispersion of carbon nanotubes in the [Ni-(Protoporphyrin IX)] film, along with a high percentage of nickel electrodeposition (approximately, 44%).

The CV experiments for $\text{Ni}^{2+}/\text{Ni}^{3+}$ redox couple in alkaline medium show $\text{Ip}_{\text{a,c}}$ values five times higher for NiPPIX/CNT/NiNp compared to NiPPIX/NiNp. Lower ΔE_{p} values have also been obtained for the first system. These results suggest that the processes of electronic transfer are more favored in the NiPPIX/CNT/NiNp sensor. For this nanocomposite, limitations in the mass transport due to the diffusion-controlled reactions are evaluated by CV and EIS measurements.

In this work, we demonstrate that the electrocatalytic activity and analytical performance of NEG's can be effectively improved. Both, appropriate structural characteristics of a polymeric nanocomposite and the combination of redox centers in an environment with high electronic delocalization contribute to the flow of electrons and the kinetics of the reaction under study. NiPPIX/CNT/NiNp GCE shows the best linear response for glucose determination up to 6 mmol L^{-1} , with a 0.9953 correlation coefficient and a slope of 0.2689 mA $\text{L mmol}^{-1} \text{cm}^{-2}$. The highest electron transfer rate constant (k°), $1.6 \times 10^{-4} \text{ cm s}^{-1}$, was estimated for the proposed organic-inorganic hybrid nanocomposite.

Acknowledgements

Financial support from the University of Buenos Aires (UBACyT 2018 20020170100155BA), and CONICET (11220130100029CO) are gratefully acknowledged. A.L. Rinaldi would like to thank CONICET for her doctoral fellowship. The authors thank Andrea Rinaldi for providing language help.

References

- [1] D. Shcharbin, I. Halets-Bui, V. Abashkin, V. Dzmitruk, S. Loznikova, M. Odabaş, Ö. Acet, B. Önal, N. Özdemir, N. Shcharbina, Hybrid metal-organic nanoflowers and their application in biotechnology and medicine, *Colloids Surf. B Biointerfaces* 182 (2019) 110354. <https://doi.org/10.1016/j.colsurfb.2019.110354>
- [2] H. Huang, L. Chen, S. Wang, P. Kang, X. Chen, Z. Guo, X.-J. Huang, Electrochemical monitoring of persistent toxic substances using metal oxide and its composite nanomaterials: Design, preparation, and application, *TrAC-Trend. Anal. Chem.* 119 (2019) 115636. <https://doi.org/10.1016/j.trac.2019.115636>.

- [3] C. Yang, M.E. Denno, P. Pyakurel, B.J. Venton, Recent trends in carbon nanomaterial-based electrochemical sensors for biomolecules: A review, *Anal. Chim. Acta* 887 (2015) 17-37. <https://doi.org/10.1016/j.aca.2015.05.049>.
- [4] Z. Li, L. Wang, Y. Li, Y. Feng, W. Feng, Carbon-based functional nanomaterials: preparation, properties and applications, *Compos. Sci. Technol.* 179 (2019) 10-40. <https://doi.org/10.1016/j.compscitech.2019.04.028>
- [5] A. Martín, M.Á. López, M.C. González, A. Escarpa, Multidimensional carbon allotropes as electrochemical detectors in capillary and microchip electrophoresis, *Electrophoresis* 36 (2015) 179-194. <https://doi.org/10.1002/elps.201400328>
- [6] R. Zhang, W. Chen, Recent advances in graphene-based nanomaterials for fabricating electrochemical hydrogen peroxide sensors, *Biosens. Bioelectron.* 89 (2017) 249-268. <https://doi.org/10.1016/j.bios.2016.01.080>
- [7] M. Karakoti, Sandeep, S. Dhali, S. Rana, S.R.V.S. Prasanna, S.P.S. Mehta, N.G. Sahoo, Surface modification of carbon-based nanomaterials for polymer nanocomposites in: A.F. Ismail and P.S. Goh (Eds.), *Carbon-based polymer nanocomposites for environmental and energy applications*, Part I, Ch. 2, Elsevier, Amsterdam, 2018, pp. 27-56. <https://doi.org/10.1016/B978-0-12-813574-7.00002-2>
- [8] C. Janáky, E. Kecszenovity, K. Rajeshwar, Electrodeposition of inorganic oxide/nanocarbon composites: opportunities and challenges, *ChemElectroChem* 3 (2016) 181-192. <https://doi.org/10.1002/celc.201500460>
- [9] A. Martín, L. Vázquez, A. Escarpa, Carbon nanomaterial scaffold films with conductivity at micro and sub-micron levels, *J. Mater. Chem. A* 4 (2016) 13142-13147. <https://doi.org/10.1039/C6TA04870F>
- [10] K. Chaisiwamongkhon, C. Batchelor-McAuley, S.V. Sokolov, J. Holter, N.P. Young, R.G. Compton, Optimising carbon electrode materials for adsorptive stripping voltammetry, *Appl. Mater. Today* 7 (2017) 60-66. <https://doi.org/10.1016/j.apmt.2017.02.003>
- [11] J. Muñoz, M. Baeza, Customized bio-functionalization of nanocomposite carbon paste electrodes for electrochemical sensing: A Mini Review, *Electroanalysis* 29 (2017) 1660-1669. <https://doi.org/10.1002/elan.201700087>
- [12] Q. Cao, P. Puthongkham, B.J. Venton, Review: New insights into optimizing chemical and 3D surface structures of carbon electrodes for neurotransmitter detection, *Anal. Methods* 11 (2019), 247-261. <https://doi.org/10.1039/C8AY02472C>
- [13] D. Sangamithirai, S. Munusamy, V. Narayanan, A. Stephen, Fabrication of neurotransmitter dopamine electrochemical sensor based on poly(o-anisidine)/CNTs nanocomposite, *Surfaces and Interfaces* 4 (2016), 27-34 <https://doi.org/10.1016/j.surfin.2016.09.003>

- [14] H. Mao, Z. Cao, X. Guo, D. Sun, D. Liu, S. Wu, Y. Zhang, X.-M. Song, Ultrathin NiS/Ni(OH)₂ nanosheets filled within ammonium polyacrylate-functionalized polypyrrole nanotubes as an unique nanoconfined system for nonenzymatic glucose sensors, *ACS Appl. Mater. Interfaces* 11 (2019) 10153–10162. <https://doi.org/10.1021/acsami.8b20726>
- [15] R. Carballo, A.L. Rinaldi, P.C. Dabas, I.N. Rezzano, A carbon nanotube/poly [Ni-(Protoporphyrin IX)] composite for amperometric detection of long chain aliphatic amines, *Bioelectrochemistry* 104 (2015) 51-57. <http://dx.doi.org/10.1016/j.bioelechem.2015.03.002>
- [16] D. Rawtani, M. Tharmavaram, G. Pandey, C.M. Hussain, Functionalized nanomaterial for forensic sample analysis, *TrAC-Trend. Anal. Chem.* 120 (2019) 115661. <https://doi.org/10.1016/j.trac.2019.115661>
- [17] S. Kumar, D. Zheng, K. Al-rubeaan, J.H.T. Luong, F. Sheu, Advances in carbon nanotube based electrochemical sensors for bioanalytical applications, *Biotechnol. Adv.* 29 (2011) 169-188. <https://doi.org/10.1016/j.biotechadv.2010.10.002>
- [18] J. Muñoz, A. González-Campo, M. Riba-Moliner, M. Baeza, M. Mas-Torrent, Chiral magnetic-nanobiofluids for rapid electrochemical screening of enantiomers at a magneto nanocomposite graphene-paste electrode, *Biosens. Bioelectron.* 105 (2018) 95-102. <https://doi.org/10.1016/j.bios.2018.01.024>
- [19] D.-W. Hwang, S. Lee, M. Seo, T.D. Chung, Recent advances in electrochemical non-enzymatic glucose sensors – A review, *Anal. Chim. Acta* 1033 (2018) 1-34. <https://doi.org/10.1016/j.aca.2018.05.051>
- [20] G. vG. Kumar, G. Amala, S.M. Gowtham, Recent advancements, key challenges and solutions in non-enzymatic electrochemical glucose sensors based on graphene platforms, *RSC Adv.* 7 (2017) 36949-36976. <https://doi.org/10.1039/C7RA02845H>
- [21] H. Zhu, L. Li, W. Zhou, Z. Shao, X. Chen, Advances in non-enzymatic glucose sensors based on metal oxides, *J. Mater. Chem. B* 4 (2016) 7333-7349. <https://doi.org/10.1039/C6TB02037B>
- [22] W. Lu, X. Xu, Ni-MOF nanosheet arrays: efficient non-noble-metal electrocatalysts for non-enzymatic monosaccharide sensing, *New J. Chem.* 42 (2018) 3180-3183. <https://doi.org/10.1039/C7NJ04754A>
- [23] D.S. Hall, D.J. Lockwood, C. Bock, B.R. MacDougall, Nickel hydroxides and related materials: a review of their structures, synthesis and properties, *Proc. R. Soc. A* 471 (2015) 20140792. <http://dx.doi.org/10.1098/rspa.2014.0792>
- [24] M. Hamer, R.R. Carballo, N. Cid, I.N. Rezzano, Study of the electron transfer properties of nanostructured bimetallic films of polymerized porphyrins, *Electrochim. Acta* 78 (2012) 302-307. <http://dx.doi.org/10.1016/j.electacta.2012.05.097>

- [25] Z. Valicsek, O. Horváth, Application of the electronic spectra of porphyrins for analytical purposes: The effects of metal ions and structural distortions, *Microchem. J.* 107 (2013) 47-62
- [26] Y. Fang, Z. Ou, K.M. Kadish, Electrochemistry of corroles in nonaqueous media, *Chem. Rev.* 117(2016) 3377-3419. <https://doi.org/10.1021/acs.chemrev.6b00546>
- [27] A. Ziesak, L. Steuer, E. Kaifer, N. Wagner, J. Beck, H. Wadepohl, H.-J. Himmel, Intramolecular metal-ligand electron transfer triggered by co-ligand substitution, *Dalton Trans.* 47 (2018) 9430-9441. <https://doi.org/10.1039/C8DT01234B>
- [28] P. Zhang, J. Hu, B. Liu, J. Yang, H. Hou, Recent advances in metalloporphyrins for environmental and energy applications, *Chemosphere* 219 (2019) 617-635. <https://doi.org/10.1016/j.chemosphere.2018.12.024>
- [29] S.-I. Yamazaki, Metalloporphyrins and related metallomacrocycles as electrocatalysts for use in polymer electrolyte fuel cells and water electrolyzers, *Coord. Chem. Rev.* 373 (2018) 148-166. <https://doi.org/10.1016/j.ccr.2017.09.016>
- [30] C.F. Pereira, M.Q. Simoes, J.P.C. Tomé, F.A.A. Paz, Porphyrin-based metal-organic frameworks as heterogeneous catalysts in oxidation reactions, *Molecules* 21 (2016) 1348 <https://doi.org/10.3390/molecules21101348>
- [31] R. Carballo, I. Rezzano, Approach for modulation of the permselective properties of Ni(II) porphyrin polymers, *Electroanalysis* 29 (2017) 1161-1165. <https://doi.org/10.1002/elan.201600730>
- [32] D.A. Adler, F.R. Longo, F. Kampas, J. Kim, On the preparation of metalloporphyrins, *J. Inorg. Nucl. Chem.* 32 (1970) 2443-2445, <http://dx.doi.org/10.1016/0022-1902>
- [33] A.L. Rinaldi, R. Carballo, Impedimetric non-enzymatic glucose sensor based on nickel hydroxide thin film onto gold electrode, *Sens. Actuators B-Chem* 228 (2016) 43-52. <http://dx.doi.org/10.1016/j.snb.2015.12.101>
- [34] K.E. Toghill, R.G. Compton, Electrochemical non-enzymatic glucose sensors: a perspective and an evaluation, *Int. J. Electrochem. Sci.* 5 (2010) 1246-1301 <http://www.electrochemsci.org/papers/vol5/5091246.pdf>.
- [35] G.A.M. Sáfar, H.B. Ribeiro, L.M. Malard, F.O. Plentz, C. Fantini, A.P. Santos, G. de Freitas-Silva, Y.M. Idemori, Optical study of porphyrin-doped carbon nanotubes, *Chem. Phys. Lett.* 462 (2008) 109-111. <http://dx.doi.org/10.1016/j.cplett.2008.07.093>.
- [36] T. Gu, J. Tao, W. Zhu, J. Mack, R.C. Soy, T. Nyokong, H. Xu, M. Li, X. Liang, Co(II)tetraphenyl tetraphenanthroporphyrin@MWCNTs: Enhanced π - π interaction for robust electrochemical catalysis, *New J. Chem.* 43 (2019) 10631-10636. <http://doi.org/10.1039/C9NJ01707K>

- [37] S. Lin, P.M. Usov, A.J. Morris, The role of redox hopping in metal–organic framework electrocatalysis, *Chem. Commun.* 54 (2018) 6965-6974. [http://doi.org/ 10.1039/C8CC01664J](http://doi.org/10.1039/C8CC01664J)
- [38] M. Tagliazucchi, E.J. Calvo, Charge transport in redox polyelectrolyte multilayer films: The dramatic effects of outmost layer and solution ionic strength, *Chemphyschem* 11 (2010) 2957-2968. [http://doi.org/ 10.1002/cphc.201000172](http://doi.org/10.1002/cphc.201000172)
- [39] S.R. Ahrenholtz, C.C. Epley, A.J. Morris, Solvothermal preparation of an electrocatalytic metalloporphyrin MOF thin film and its redox hopping charge-transfer mechanism, *J. Am. Chem. Soc.* 136 (2014) 2464-2472. <https://doi.org/10.1021/ja410684q>
- [40] K. Maindan, X. Li, J. Yu, P. Deria, Controlling charge-transport in metal–organic frameworks: Contribution of topological and spin-state variation on the iron–porphyrin centered redox hopping rate, *J. Phys. Chem. B* 123 (2019) 8814-8822. <https://doi.org/10.1021/acs.jpcc.9b07506>
- [41] Z.O. Uygun, H.D.E. Uygun, A short footnote: Circuit design for faradaic impedimetric sensors and biosensors, *Sens. Actuators B-Chem* 202 (2014) 448-453. <http://dx.doi.org/10.1016/j.snb.2014.05.029>
- [42] D. Nkosi, K.I. Ozoemena, Self-assembled nano-arrays of single-walled carbon nanotube–octa(hydroxyethylthio)phthalocyaninato iron(II) on gold surfaces: Impacts of SWCNT and solution pH on electron transfer kinetics, *Electrochim. Acta* 53 (2008) 2782-2793. <http://doi.org/10.1016/j.electacta.2007.10.073>
- [43] E.P. Randviir, A cross examination of electron transfer rate constants for carbon screen-printed electrodes using electrochemical impedance spectroscopy and cyclic voltammetry, *Electrochim. Acta* 286 (2018) 179-186. <https://doi.org/10.1016/j.electacta.2018.08.021>
- [44] S. Gotovac, H. Honda, Y. Hattori, K. Takahashi, H. Kanoh, K. Kaneko, Effect of nanoscale curvature of single-walled carbon nanotubes on adsorption of polycyclic aromatic hydrocarbons, *Nano Lett.* 7 (2007) 583-87. <https://doi.org/10.1021/nl0622597>
- [45] M.E. Tagliazucchi, E.J. Calvo, Surface charge effects on the redox switching of LbL self-assembled redox polyelectrolyte multilayers, *J. Electroanal. Chem.* 599 (2007) 249-259. <https://doi.org/10.1016/j.jelechem.2006.03.014>
- [46] K.C. Lin, Y.T. Hung, S.M. Chen, Facile preparation of a highly sensitive nonenzymatic glucose sensor based on multi-walled carbon nanotubes decorated with electrodeposited metals, *RSC Adv.* 5, (2015) 2806-2812. <https://doi.org/10.1039/C4RA11465E>
- [47] A. Meng, X. Yuan, Z. Li, K. Zhao, L. Sheng, Q. Li, Direct growth of 3D porous (Ni-Co)₃S₄ nanosheets arrays on rGO-PEDOT hybrid film for high performance non-enzymatic glucose sensing. *Sens. Actuators B-Chem.* 291 (2019) 9-16. <https://doi.org/10.1016/j.snb.2019.04.042>

- [48] C. Guo, Y. Hu, Y. Liu, Y. Mu, Y. Miao, X. Hu, Synthesis of MWCNT/nickel glycolate polymer core-shell nanostructures and their nonenzymatic electrocatalytic activity toward glucose, *Mater. Chem. Phys.* 130 (2011), 10-13. <https://doi.org/10.1016/j.matchemphys.2011.07.054>
- [49] Q. Sheng, D. Liu, J. Zheng, NiCo alloy nanoparticles anchored on polypyrrole/reduced graphene oxide nanocomposites for nonenzymatic glucose sensing, *New J. Chem.* 40 (2016) 6658-6665. <https://doi.org/10.1039/C6NJ01264G>
- [50] N. Hui, S. Wang, H. Xie, S. Xu, S. Niu, X. Luo, Nickel nanoparticles modified conducting polymer composite of reduced graphene oxide doped poly(3,4-ethylene dioxythiophene) for enhanced nonenzymatic glucose sensing, *Sens. Actuators B-Chem.* 221 (2015) 606-613. <http://dx.doi.org/10.1016/j.snb.2015.07.011>
- [51] D. Yang, F. Wang, J. Yan, Y. Gao, H. Li, Preparation, characterization, and electrochemical performances of graphene/Ni(OH)₂ hybrid nanomaterials, *J. Nanoparticle Res.* 15 (2013), 1762-1776. <https://doi.org/10.1007/s11051-013-1762-7>
- [52] L. Shahhoseini, R. Mohammadi, B. Ghanbari, S. Shahrokhian, Ni(II) 1D-coordination polymer/C 60 -modified glassy carbon electrode as a highly sensitive non-enzymatic glucose electrochemical sensor, *Appl. Surf. Sci.* 478 (2019) 361-372. <https://doi.org/10.1016/j.apsusc.2019.01.240>
- [53] P.K. Bairagi, N. Verma, Electro-polymerized polyacrylamide nano film grown on a Ni-reduced graphene oxide- polymer composite: A highly selective non-enzymatic electrochemical recognition element for glucose, *Sens. Actuators B-Chem.* 289 (2019) 216-225. <https://doi.org/10.1016/j.snb.2019.03.057>

Legends

Figure 1. SEM images at 50000 X and EDX analysis of (a, d) NiNp, (b, e) NTC_{dc}/NiNp, and (c, f) NiPPIX/NTC/NiNp systems.

Figure 2: Cyclic voltammograms plots of each modified electrode in 0.1 mol L⁻¹ KOH solution, 15 cycles, at 50 mV s⁻¹. Each plot corresponds to (a) NiPPIX/CNT, (b) NiPPIX, (c) NiPPIX/NiNp, (d) NiNp, (e) CNT_{dc}/NiNp, (f) NiPPIX/CNT/NiNp,

Figure 3. (a) Peak potential vs log scan rate for (■) NiPPIX/CNT/NiNp, (○) CNT_{dc}/NiNp, and (Δ) NiNp glassy carbon electrodes. (b) Plots of the peak currents vs. scan rate for (■, □) NiPPIX/CNT/NiNp, (●, ○) CNT_{dc}/NiNp, and (▲, Δ) NiNp. The studied scan rates were 0.001; 0.010; 0.020; 0.030; 0.040; 0.050; 0.070; 0.100; 0.200; 0.300; 0.500 y 1.00 V s⁻¹.

Figure 4. Nyquist plots of (a) NiNp and (b) NiPPIX/CNT/NiNp GCE in 0.1 mol L^{-1} KOH solution. The working potential was set to $+0.350 \text{ V}$ (vs Ag/AgCl). The insets show the corresponding equivalent circuit. In black line, fitted data.

Figure 5. Nyquist plots of (a) NiNp and (b) NiPPIX/CNT/NiNp GCE for $5 \text{ mmol L}^{-1} \text{ Fe(CN)}_6^{3-/4-}$ in 0.1 mol L^{-1} KCl solution. The working potential was set to $+0.250 \text{ V}$ (vs Ag/AgCl). In black line, fitted data.

Figure 6. Cyclic voltammetries in 0.1 mol L^{-1} KOH solution using (a) NiNp, (b) NiPPIX/CNT/NiNp, and (c) CNT_{dc}/NiNp after glucose addition in concentrations 0, 0.5, 1, 2, 4 y 6 mmol L^{-1} . (d) Comparison of the calibration curves obtained with the three systems assayed ($n=3$). (e) Amperometric measurements for NiPPIX/CNT/NiNp/GCE corresponding to the addition of 1 mM of uric acid, 0.2 mM of ascorbic acid, 0.1 mM of epinephrine, and six replicates of 1 mM of glucose into 0.1 mol L^{-1} KOH solution, under a stirring condition at $+0.40 \text{ V}$ (vs Ag/AgCl).

Table 1. Determination of glucose in blood samples using two different NiPPIX/CNT/NiNp electrodes and comparison with the measurements obtained by a commercial glucose biosensor.

Table 2. Comparison of the organic-inorganic hybrid nanocomposite, NiPPIX/CNT/NiNp electrode, with different carbon-materials polymeric nanocomposites non-enzymatic glucose sensors based on nickel.

Scheme 1. Representation of the main contributions of each component of the organic-inorganic hybrid nanocomposite.

Credit Author Statement

Ana L. Rinaldi: Methodology, Conceptualization, Writing - Original Draft, Writing - Review & Editing. **Maria Celina Bonetto:** Validation, Visualization. **Santiago Sobral:** Formal analysis, Software, Resources. **Romina Carballo:** Investigation, Conceptualization, Funding acquisition, Writing - Original Draft, Writing - Review & Editing

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Table 1

Blood Sample	NiPPIX/ CNT/ NiNp electrode (mA cm ⁻²)	Glucose concentration by NiPPIX/ CNT/ NiNp (mmol L ⁻¹)	Glucose concentration by commercial glucose biosensor (mg dL ⁻¹)
A	1.53 ^a	13.8 (276 mg dL ⁻¹)	285
B	1.14 ^a	6.1 (123 mg dL ⁻¹)	119

a The blood samples were diluted five times with 0.1 mol L⁻¹ KOH solution for the measurements. Two different NiPPIX/CNT/NiNp glassy carbon electrodes were used, each electrode for each sample.

Table 2

Electrode Material	Sensitivity, $\mu\text{A L mmol}^{-1} \text{cm}^{-2}$	Linear Range, mmol L^{-1}	E_p , V	References
Ni/CuAg/MWCNT/GCE	5007	0.005-0.4	0.58	[46]
(Ni-Co) ₃ S ₄ /rGO- PEDOT/GCE	938400	0.001-5	≈ 0.85	[47]
MWCNT/nickel glycolate polymer nanocomposites	---	1-12	0.55	[48]
NiCo/PPy/rGO/ GCE	2030	1.1-500	0.45	[49]
NiNPs/PEDOT/ rGO/GCE	36.15	0.001-5.1	0.55	[50]
PG/Ni(OH) ₂ /GCE	-----	0.0003-0.750	0.54	[51]
Ni(II)-Cp/C ₆₀ /GC	614	0.01-11	0.57	[52]
NiS/Ni(OH) ₂ /NH ₄ PA/PPy NTs/GCE	-----	0.5-600	0.52	[14]
PAA-Ni-rGO/P	1724.58	0.0017-13.8	0.22	[53]
NiPPIX /CNT/ NiNp/GCE	268.9	0.5-6	0.40	This work

rGO: reduced graphene oxide; PEDOT: poly 3,4-ethylenedioxythiophene; PPy: polypyrrole; P: poly (3,4-ethylene dioxythiophene) polystyrene sulfonate; NH₄PA/PPyNTs: ammoniumpolyacrylate-functionalized polypyrrole nanotubes; PAA: polyacrilamide; Cp: coordination polymer; C₆₀: fullerene; PG: polymer-functionalized graphene oxide.

HIGHLIGHTS

Novel organic-inorganic hybrid nanocomposite is applied to glucose electrooxidation.

Nickel nanoparticles and nickel center of porphyrin act as electron hopping sites.

Stable dispersion of carbon nanotubes in NiPPIX facilitates the electronic transfer.

Highest sensitivity ($0.2689 \text{ mA L mmol}^{-1} \text{ cm}^{-2}$) is achieved with NiPPIX/CNT/NiNp.

The highest k^0 , $1.6 \times 10^{-4} \text{ cm s}^{-1}$, was obtained for NiPPIX/CNT/NiNp.

Figure 1ac

Figure 1df

a) NiPPiX/CNT

b) NiPPiX

c) NiPPiX/NiNp

d) NiNp

e) CNT_{dc}/NiNp

f) NiPPiX/CNT/NiNp

Figure 2

Figure 3

Figure 4

a

b

Figure 5

Figure 6