



## Nanocomposites of iridium oxide and conducting polymers as electroactive phases in biological media



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### ABSTRACT

Much effort is currently devoted to implementing new materials in electrodes that will be used in the central nervous system, either for functional electrostimulation or for tests on nerve regeneration. Their main aim is to improve the charge capacity of the electrodes, while preventing damaging secondary reactions, such as peroxide formation, occurring while applying the electric field. Thus, hybrids may represent a new generation of materials. Two novel hybrid materials are synthesized using three known biocompatible materials tested in the neural system: polypyrrole (PPy), poly(3,4-ethylenedioxythiophene) (PEDOT) and iridium oxide (IrO<sub>2</sub>). In particular, PPy–IrO<sub>2</sub> and PEDOT–IrO<sub>2</sub> hybrid nanocomposite materials are prepared by chemical polymerization in hydrothermal conditions, using IrO<sub>2</sub> as oxidizing agent. The reaction yields a significant ordered new hybrid where the conducting polymer is formed around the IrO<sub>2</sub> nanoparticles, encapsulating them. Scanning electron microscopy and backscattering techniques show the extent of the encapsulation. Both X-ray photoelectron and Fourier transform infrared spectroscopies identify the components of the phases, as well as the absence of impurities. Electrochemical properties of the final phases in powder and pellet form are evaluated by cyclic voltammetry. Biocompatibility is tested with MTT toxicity tests using primary cultures of cortical neurons grown in vitro for 6 and 9 days.

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### 1. Introduction

The study of hybrid organic–inorganic materials is a recent but very fruitful and prolific enterprise. In particular, hybrid nanocomposites consist of two or more nanosized objects, resulting in materials with unique physical properties, outperforming the mere addition of the properties of the components [1,2]. The composite properties can be controlled by the synthesis procedures, as well as the features of each material involved [3]. They have a wide application. For example, hybrid nanocomposites of conducting polymers and nanoparticles (e.g. Pt, Au, Pd, Zr(HPO<sub>4</sub>)<sub>2</sub>, MoO<sub>3</sub>, MnO<sub>2</sub>, Mo<sub>3</sub>Se<sub>3</sub>,  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>, Fe<sub>3</sub>O<sub>4</sub> and IrO<sub>2</sub>) have applications in different fields such as electrocatalysis [4], energy storage devices such as electrochemical supercapacitors [5], sensors [6], battery cathodes [7,8], microelectronics [2], magnetic materials [9] and electrochemical devices [10]. As observed in the examples mentioned, most of these hybrids contain metals or metal oxides, which could suffer from air or moisture sensitivity if they were not entrapped in an organic material matrix, forming the core/shell nanostructures [11].

Biomedical applications involving implants in soft tissues could also benefit from the use of hybrid organic–inorganic structures if the final material is also conducting and may be used as electrode. An example can be found in composites of polypyrrole (PPy) and carbon nanotubes, which have performed well as electrodes for neural interfaces in chronically implantable neural probes [12]. Iridium oxide (IrO<sub>2</sub>) is an interesting inorganic component for a hybrid material to be used in biomedical applications, since it has served as a substrate for culture, growth and electrical stimulation of neural cells [13–15] and as a coating in medical electrostimulation electrodes and sensors [15–18]. However, the organic part of a hybrid material could consist of conducting polymers such as poly(3,4-ethylenedioxythiophene) (PEDOT) and PPy, which have shown good biocompatibility [19–23]. Therefore, these phases, PEDOT, PPy and IrO<sub>2</sub>, may turn out to be the most indicated components for nanocomposites to be used in biological electrode applications. IrO<sub>2</sub> by itself can be mechanically too rigid, so mixing it with polymers should add mechanical flexibility, making the final hybrid self-standing and more appropriate for implantation into the human body or any other living system.

Even if electrochemical intensive properties are not improved, a significant charge capacity increase is expected from the presence of both components in the new material because of their faradaic

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behavior, which entails increased charge capacity compared with other materials such as noble metals and their alloys, permitting minor damage in biological tissues. All the cited reasons make them promising materials for implantable electrodes for recording or stimulating neurons [24,25]. Thus, a hybrid material that mixes the properties of conducting polymers and IrO<sub>2</sub> may become a good candidate for bioelectrode applications.

Other fields could also benefit from the development of new hybrid phases, whatever the final form, coating or powder, since PEDOT, PPy and IrO<sub>2</sub> all have applications in energy devices (e.g. solar and fuel cells), electrochromic devices and sensors [18,26–36].

It has been described elsewhere how nanomaterials could induce oxidative stress and inflammation in biological systems [37]. Therefore, a study of the cytotoxic properties of this type of materials was performed. Several other research groups have described PPy and PEDOT composites and nanoparticles toxicity tests, revealing good biocompatibility of the conducting polymer [38–40], but indicating a dependence on the polymer concentration [41].

The present work presents two novel organic–inorganic nanocomposites consisting of IrO<sub>2</sub> encapsulated in either PPy or PEDOT, and the first study on their toxicity. Their syntheses took place through a facile hydrothermal reaction using a one-pot suspension of the IrO<sub>2</sub> and the monomer as precursor. These composites have promising properties in numerous scientific areas because of the wide range of applications of their components. This work focuses on the first stage for biological applications: the study of their biocompatibility. Thus, the toxicity of these composites for cortical neuron cells was assessed, and was compared with IrO<sub>2</sub> and PPy–ClO<sub>4</sub> single phase toxicity, as a prior step for the further development of these materials, and the results indicate that they are promising materials for use in the neural system.

## 2. Materials and methods

### 2.1. Materials synthesis

Pyrrole (Sigma–Aldrich, 98%) was vacuum-distilled until it became a colourless liquid, and was then stored at –10 °C until use. EDOT (3,4-ethylenedioxythiophene) (Sigma–Aldrich, 97%) was used as purchased, but stored at 5 °C until use. Iridium (IV) oxide (IrO<sub>2</sub>, Sigma–Aldrich, 99.9%, 12030-49-8 CAS number) was stored at room temperature in a desiccator. In all experiments, 75 mg of IrO<sub>2</sub> was placed in a 25 ml Pyrex bottle containing 20 ml of high-purity milli-Q water (Millipore, 18.2 MΩ cm resistivity). The resulting mixture was stirred for 1 h. Then, either pyrrole or EDOT was added. The resulting dispersion was stirred for 1 h more. The desired conditions for this oxidation reaction were investigated in a series of experiments using different monomer/IrO<sub>2</sub> molar ratios, with the purpose of obtaining the maximum amount of encapsulated hybrid material: either 1.0, 4.5, 18.0 or 36.0 for pyrrole/IrO<sub>2</sub> molar ratios or 1.0, 4.5, 5.3 or 10.0 for EDOT/IrO<sub>2</sub> molar ratios. Finally, the optimal molar ratios regarding the results found were 18.0 for pyrrole/IrO<sub>2</sub> and 5.3 for EDOT/IrO<sub>2</sub>, which corresponded to 415 μl of pyrrole and 185 μl of EDOT. The resulting suspensions were placed in 25 ml Pyrex bottles, using 80% of their total volume, hermetically sealed with a Teflon screw-cap, and heated at 100, 150 or 200 °C for 96, 168 and 240 h. In the case of experiments at 200 °C, a Parr pressure vessel was used instead of a Pyrex bottle, to avoid pressure problems. The resulting solid was vacuum filtered, rinsed with milli-Q water five times and dried in air at room temperature.

Hybrid samples with various oxidation states were also achieved by adding reducing (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>·5 H<sub>2</sub>O, sodium thiosulfate pentahydrate (ACS reagent, 99.5%, Merck)) and oxidizing (K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>,

potassium persulfate (ACS reagent, ≥99.0%, Aldrich)) agents in molar ratio 1:1 with respect to iridium after hydrothermal treatment. This part of the reaction was carried out on previously prepared powders by mixing both the material and the reducing or oxidizing agent in water dispersions for 96 h at room temperature in a 25 ml Pyrex bottle. The resulting solid was vacuum filtered, rinsed with milli-Q water five times and dried in air at room temperature. Thus, three different types of powder were obtained for each hybrid composition: as prepared, oxidized and reduced samples.

Moreover, with the purpose of comparing the cytotoxicity results of PPy–IrO<sub>x</sub> with pure IrO<sub>2</sub> and non-hybrid PPy, the latter was synthesized in exactly the same experimental conditions as polymer–IrO<sub>x</sub> (Pyrex bottle, 150 °C, 96 h) using sodium perchlorate (NaClO<sub>4</sub>, ACS reagent, ≥98.0%, Sigma–Aldrich) as counterion (18.0 pyrrole/NaClO<sub>4</sub> molar ratio), which corresponded to 41 mg of NaClO<sub>4</sub> and 415 μl of pyrrole dissolved in the Pyrex bottle.

### 2.2. Electrochemical analysis

Electrochemical characterization measurements of the final materials in aqueous suspensions were carried out using a PAR VMP3 potentiostat. A two-compartment electrochemical cell was used for the linear sweep voltammetry to prevent secondary reactions from the counter-electrode. A glass frit was used as separator. A platinum foil was used as the working electrode, and a platinum wire (0.5 mm diameter, 78.54 mm<sup>2</sup> exposure) as the pseudo-reference electrode on one compartment and a coiled platinum wire (0.5 mm diameter, 78.54 mm<sup>2</sup> exposure) in the counter-electrode compartment. The pseudo-reference platinum was previously shown to be stable vs. Ag/AgCl during cyclic voltammeteries, possibly owing to the formation of an oxide at the surface, and was used successfully as such [42]. The main compartment containing the working electrode was bubbled with argon for 30 min prior to reaction, which was also performed in an argon environment. Voltammetry was performed from open circuit potential, near 0 V to –0.75 V vs. Pt. at a scan rate of 2 mV s<sup>–1</sup>. The electrolyte used was a 0.1 M sodium phosphate buffer solution at a pH of 7.21, using 50 mg of the material powder for every voltammetry, and with permanent stirring at 500 rpm. Teflon™ material disks were also prepared for an additional electrochemical study. For that purpose, 85 mg of the material, 10 mg of Super P Carbon (Csp hereafter from Timcal) and 5 mg of polytetrafluoroethylene (Aldrich, 60 wt.%, dispersion in water) were mixed in ethanol, and heated at 60 °C for 5 h in a glass beaker with continuous stirring. The resulting slurry was cut into disks 1.2 cm in diameter and vacuum dried for 12 h at 80 °C. Disks voltammeteries were performed in an open Swagelok-type carbon cell with the Teflon–carbon–material cylinder as the working electrode and two platinum rods as counter and reference electrodes. The same phosphate buffer was used as the electrolyte, and argon was bubbled for 10 min prior to every experiment to eliminate oxygen. The CV were performed in this case at 20 mV s<sup>–1</sup> in the –1 to 1 V vs. Pt potential window.

### 2.3. Physicochemical characterization

Further characterization of the samples was done by scanning electron microscopy (SEM), using a Quanta FEI 200 FEG-ESEM instrument, equipped for energy-dispersive X-ray (EDX) analysis and backscattered electron imaging (BSE) analysis. Typical operating parameters were 10–20 keV accelerating voltage and 2.5–3.0 nm spot size. X-ray photoelectron spectroscopy (XPS) measurements of the samples were performed at room temperature with a SPECS EA10P hemispherical analyzer using non-monochromatic Al K<sub>α</sub> (1486.6 eV) radiation as the excitation source at a base pressure of ~10<sup>–9</sup> mbar (binding energies estimated

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