
This is the **accepted version** of the journal article:

Muñoz, Jose; Álvarez Prada, Luis Ignacio; Lopez-Lopez, Eric; [et al.]. «Synthesis of 0D to 3D hybrid-carbon nanomaterials carrying platinum(0) nanoparticles : towards the electrocatalytic determination of methylparabens at ultra-trace levels». Sensors and Actuators, B: Chemical, Vol. 305 (Feb. 2020), art. 127467. DOI 10.1016/j.snb.2019.127467

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Synthesis of 0D to 3D hybrid-carbon nanomaterials carrying platinum(0) nanoparticles. Towards the electrocatalytic determination of methylparabens at ultra-trace levels

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Abstract

A generic synthetic methodology has been applied for functionalizing four conducting carbon nanoallotropes, such as 0D carbon nanohorns (CNHs), 1D carbon nanotubes (CNTs), 2D reduced graphene oxide (rGO) and 3D graphite (GP) with platinum(0) nanoparticles (Pt-NP), and exploited towards the electrocatalytic determination of methylparaben (MeP), which has been classified as a potential endocrine-disrupting chemical. After an accurate physical, electrochemical and electroanalytical characterization, the hybrid Pt-NP@CNTs yields detection limits at nM levels, rather than the μM levels obtained with the rest of carbon homologous because of the optimum carbon/nanoparticle composition ratio. The proposed electrochemical sensing system has also been successfully validated by comparison with the standard bench-top chromatographic tool (HPLC), demonstrating its feasibility for MeP quantification in real cosmetic samples at ultra-trace levels. According to the outstanding performance of the hybrid Pt-NP@CNTs electrochemical platform, it can be regarded as a potential alternative to the conventional HPLC technique for the development of rapid, straightforward, cost-effective, reproducible and highly sensitive electrochemical sensors to be exploited in pharmacological, biomedical and environmental fields.

Keywords: Electrode, Sensor, Carbon Nanomaterial, Metal Nanoparticles, Catalysis

1. Introduction

Parabens (PBs) are a class of synthetic alkyl esters of *p*-hydroxybenzoic acid widely used as preservatives in food, pharmaceutical agents and cosmetic formulations due to their excellent antimicrobial activity, stability over a wide pH range and optimum solubility in water.^{1,2} However, recent studies have demonstrated that exposure to PBs can exhibit a hazardous effect similar to estrogen-like endocrine disrupting chemicals, implying that they can potentially interfere with the normal balance of the living beings' endocrine system, as it has been detected in human breast tumors.^{3,4,5,6,7} Therefore, owing to their alarming increase in the aquatic environment and adverse health effects, several organizations, including the EU Commission Cosmetics Directive, has restricted the usage of these preservatives in cosmetics, limiting to 0.8% (w/w) the maximum allowable concentration of a mixture of PBs.⁸ Accordingly, the development of rapid, simple and sensitive analytical methodologies for screening PBs at low concentrations is a must.

The standard technique for PBs quantification builds on using high-performance liquid chromatography (HPLC), a bench-top instrumentation which is quite tedious since require time-consuming enrichment, extraction and clean-up steps.^{9,10,11} In this regard, electrochemical equipment can overcome these drawbacks since they are easy-to-use, low-cost, require a reduced response time, and can be easily miniaturized for the development of at-point-of-use devices because of its electronic transduction method.^{12,13,14} Nonetheless, electrochemical devices are not commonly sensitive enough to determine these compounds at ultra-low concentrations.

The astonishing development of highly sensitive electrochemical sensors utilizing conducting nanomaterials has led to an increase of the analytical signal, which depends

on the intrinsic electron transfer capabilities of the transducer.^{15,16,17} Concretely, carbon nanomaterials (CNMs) are composed entirely of sp^2 bonded graphitic carbon, and can be found in all reduced dimensionalities from 0D to 3D. In this sense, CNMs can play an important role in new bio-sensor developments, since they allow a personalized and improved electrochemistry due to the large surface area, good biocompatibility, chemical and electrochemical stability, easy tunability and excellent electrical conductivity, leading to an increase in the Faradaic current derived from electrochemical reactions.^{12,18,19,20,21,22} Among the different types of conducting CNMs, 0D carbon nanohorns (CNHs), 1D carbon nanotubes (CNTs), 2D reduced graphene oxide (rGO) and 3D graphite (GP) are some of the most widely-used carbon nanoallotropes in electroanalysis and electrocatalysis. Further, the decoration of CNMs with some transition metal nanoparticles (*i.e.*, Au, Ag and Pt) has also been extensively applied in electrochemical sensors.^{23,24,25,26,27} The synergic effects of the resulting hybrid-CNMs lead to an effective gate for catalyzing the electron transfer process, and therefore, the ability of the sensor to detect specific compounds at low levels (including PBs) is increased.^{28,29} In particular, platinum(0) nanoparticles (Pt-NPs) in combination with CNTs have shown a remarkably improved sensitivity toward different (bio)analytes.^{30,31,32,33}

Herein, motivated by the possibility of developing a highly sensitive electrochemical sensing platform for the ultra-low quantification of PBs in real samples, and taking into account the synergic effect attained by combining the enhanced electrochemical capabilities of CNMs with the catalytic properties of Pt-NPs, it is reported: *i*) a generic and straightforward organometallic synthesis of platinum(0) nanoparticles integrated on four different CNMs substrates from 0D to 3D (Pt-NP@CNMs) and *ii*) their incorporation on the top of a glassy carbon electrode (GCE) for the electrocatalytic

determination of methylparabene (MeP) as a model PB analyte (see **Scheme 1**). After an accurate physical, electrochemical and analytical characterization, the Pt–NP@CNTs material interestingly exhibited the best electrocatalytic performance, yielding to detection limits at the nM range for the MeP target (rather than the μM concentrations achieved by the rest of hybrid-CNMs). This result demonstrates that an accurate choice of the hybrid-CNM is an essential step prior to achieving sensitive electrochemical devices for sensing purposes. Thereafter, the feasibility of using the Pt–NP@CNT-based electrochemical platform as an alternative to the conventional standard HPLC method has been also validated by intercalibrating comparison employing real samples.

Scheme 1

2. Materials and methods

2.1. Chemicals and Reagents

Carbon Nanohorns (CNHs) and flaked graphite (GP) were purchased from Sigma-Aldrich (St. Louis, MO, USA). GO was synthesized from GP according to our previous methodology.³⁴ Raw single-walled CNTs were provided by SES Research (Houston, TX, USA). Tris(dibenzylideneacetone)platinum(0) ([Pt(dba)₃]) is the organometallic precursor used for the Pt–NPs incorporation on the CNM walls, which was furnished by Strem Chemicals, Inc. (Boston, MA, USA). Hydrogen gas was purchased from Air Liquide (Alphagaz). Other chemical reagents were of the highest grade available and used as received. All organic solvents were of HPLC grade and supplied by Teknokroma, except for THF and hexane used for Pt–NP synthesis, which were dried, distilled and then degassed prior to their use according to a freeze-pump-thaw process. The aqueous solutions were prepared using deionized water 18.2 M Ω ·cm from a Milli-Q system

(Millipore, Billerica, MA, USA). The real MeP sample comes from a commercial shampoo (*Natural HoneyTM*). MeP solutions were prepared in ethanol and stored at 4 °C.

2.2. Synthesis of hybrid Pt–NP@CNMs

The synthesis of Pt–NP upon the four different CNM substrates was carried out using standard Schlenk tubes techniques and in a glovebox under argon atmosphere, following the organometallic approach (see **Scheme 2**).³⁵ Briefly, 5 mg of CNM (CNHs, CNTs, rGO or GP) were introduced into a Fisher-Porter bottle containing 20 mL of anhydrous and degassed tetrahydrofuran (THF) and then sonicated into a water bath for 20 min. Afterwards, 57 mg of [Pt(dba)₃] were incorporated into the Fisher-Porter bottle as the Pt–NPs precursor. The mixtures was pressurized under 3 bar of H₂ and stirred overnight. The resultant hybrid-CNMs (Pt–NP@CNHs, Pt–NP@CNTs, Pt–NP@rGO and Pt–NP@GP) were centrifuged at 2000 rpm for 10 min and washed several times with THF and hexane.

2.3. Preparation of modified GCEs

The naked GCE was firstly gently smoothed by polishing on a piece of aluminum sandpaper just prior to use. The modified GCE was prepared by dripping 5 µL of a 0.1 mg·mL⁻¹ ethanolic dispersion of Pt–NP@CNMs. The same methodology was carried out using raw CNMs for comparison (blank experiments).

2.4. Apparatus and procedures

Images of both raw CNMs (CNHs, CNTs, GO and GP) and synthesized hybrid-CNMs (Pt–NP@CNHs, Pt–NP@CNTs, Pt–NP@rGO and Pt–NP@GP) were acquired by High-Resolution Transmission Electron Microscopy (HR–TEM), using a JEM-2011 unit with an acceleration voltage of 200 kV. Thermogravimetric Analysis (TGA) tool was carried out using a Netzsch instrument (STA 449 F1 Jupiter®) to quantify the total amount of metal deposited on the CNM walls. Samples were heated to 1000 °C at 10 °C·min⁻¹ in air. The phase structure and purity of the prepared hybrid-nanomaterials were characterized

by X-Ray Diffraction (XRD), using a PANalytical X'Pert Pro Powder Diffraction with Cu K α radiation and PIXcel^{1D} detector.

Electrochemical measurements were performed by Cyclic Voltammetry (CV), Electrochemical Impedance Spectroscopy (EIS) and Differential Pulse Voltammetry (DPV) means employing an AutoLab Metrohm PGSTAT128N potentiostat/galvanostat equipped with NOVA 2.1.2 software, coupled with a conventional three-electrode configuration cell. The electrode configuration consists of: glassy carbon electrode as the working electrode, Ag/AgCl (sat. KCl) as the reference electrode and a Pt wire as the counter electrode. A 0.1 M KCl solution containing 10 mM [Fe(CN)₆]^{3-/4-} was utilized as the redox marker for CV and EIS characterization. A phosphate-buffered saline (PBS) solution at pH 7.0 was the electrolyte used for DPV electroanalysis.

The HPLC-UV analysis was recorded using an Agilent model 1260 Infinity II equipped with a C18 column (250 x 4.6 mm ID, 5 μ m particle) from Kromasil Eternity.

2.5. Preparation and analysis of MeP

A daily-fresh stock solution of 1.0 mM MeP in EtOH was prepared for calibration curves construction at different dilutions. The quantification was carried out through DPV and HPLC-UV. For the real sample preparation, an accurately weighed portion (~ 0.25 g) of the commercial shampoo containing MeP was transferred into a 20 mL centrifuge supplemented with 10.0 mL of acetonitrile (ACN). The mixture was placed into an ultrasonic bath for 15 min and then centrifuged at 3000 rpm for 15 min. A 10 μ L supernatant volume was analyzed by HPLC in order to quantify the concentration of MeP present in the shampoo ([MeP]_{found} = 196.2 \pm 0.4 μ M).

Electroanalytical measurements were run by DPV, which is known to be a much more sensitive electrochemical tool than its CV homologous, using the aforementioned three-electrode configuration cell filled with 20 mL PBS solution (pH 7.0). Then, consecutive

volume additions of the standard MeP solution were directly added into the electrochemical cell, where it was stirred for a few seconds for homogenization. The repeatability of the method was statistically studied per triplicate ($n=3$), carrying out different calibrates after refreshing the GCE surface by a simple polishing step. Detection limits (LOD) were calculated per triplicate ($n=3$) as the first analytical signal measured by the equipment,³⁴ and they are presented with their respective 95% confidence interval. HPLC-UV measurements were isocratically recorded per triplicate ($n=3$) using a MeOH-ACN-H₂O (15:27:58 v/v/v) mobile flowing at 1 mL·min⁻¹ (injection volume: 10 µL). The column temperature was 25 °C and peaks were recorded at the maximum absorbance wavelength of MeP ($\lambda = 256$ nm).

3. Results and discussion

3.1. Synthesis and characterization of Pt-NP@CNMs

The hybrid-CNMs presented in this study (Pt-NP@CNHs, Pt-NP@CNTs, Pt-NP@rGO and Pt-NP@GP) have been prepared following the organometallic approach.³⁵ It consists on the overnight decomposition of [Pt(dba)₃] complex (dba = dibenzylideneacetone) under 3 bar of H₂ pressure in the presence of the selected carbon support (CNHs, CNTs, GO or GP) in THF and at room temperature (**Scheme 2**).

Scheme 2

The successful synthesis of the hybrid Pt-NP@CNMs was confirmed by HR-TEM. **Figure 1** shows the representative TEM images of the four different hybrid Pt-NP@CNMs: A) Pt-NP@CNHs, B) Pt-NP@CNTs, C) Pt-NP@rGO and D) Pt-NP@GP. Insets show the corresponding raw CNMs without modification for comparison. Overall,

it is evident that CNMs are homogeneously decorated by a large quantity of spherical Pt-NPs on their surface with rather good mean size distribution, demonstrating that the organometallic method employed is generic independent of the CNM nature. As depicted in the histograms from **Figure S1**, the Pt-NPs display an average diameter around 2.3 – 2.7 nm (2.7 ± 0.5 , 2.5 ± 0.5 , 2.3 ± 0.4 and 2.4 ± 0.6 nm for Pt-NP@CNHs, Pt-NP@CNTs, Pt-NP@rGO and Pt-NP@GP, respectively). The similarity on the average diameter of the four hybrid systems confirms a comparable effect on the stabilization of the Pt-NPs by the different CNMs. Finally, the phase purity and crystal structure of the different Pt-NP@CNMs were investigated by XRD (see **Figure S2**). The XRD patterns shows the Bragg peaks (111), (200), (220), (311) and (222) reflections, which corresponds to the face centered cubic (fcc) structure of Pt, demonstrated an optimum formation of crystalline Pt-NPs. Additionally, a peak decrease together with a shift in the graphite (002) framework to lower angles was also observed owing to the encompassed amorphous graphite on the 0D to 2D CNM walls.

Figure 1

Importantly, it is clearly observable a lower amount of Pt-NP on the CNTs walls compared to the rest of hybrid-CNMs, which are fully plenty of nanoparticles. This fact was also corroborated by TGA experiments, which were used to quantify the *wt %* of Pt-NPs on the CNM walls. TGA analyses demonstrated the functionalization of the raw CNMs, with an amount of 57.5%, 37.6%, 53.6% and 56.4% in Pt-NP for the 0D to the 3D CNM, respectively.

3.2. Electrochemical behavior of Pt–NP@CNMs

The electrochemical performances of the synthesized Pt–NP@CNMs casted on a GCE surface (Pt–NP@CNM/GCE) were studied by CV and EIS, using the well-known benchmark $[\text{Fe}(\text{CN})_6]^{3-/4-}$ redox marker. Raw CNMs were also studied as the blank. **Figure 2** shows the electrochemical characteristics of the (a) GCE, (b) CNTs/GCE and (c) Pt–NP@CNTs/GCE as a model CNM.

While the peak currents (I_p) derived from CV (**Figure 2A**) supplies information about the accessibility of the redox probe to be oxidized or reduced at the electrode surface, the reversibility of the redox couple is defined by means of peak-to-peak separation (ΔE).³⁶ Thus, a clearly I_p increase accompanied by an ΔE decrease was achieved when raw CNTs were incorporated upon the GCE surface due to the intrinsic conducting nature of the CNM together with an enhanced electroactive area (higher roughness). The same trend, but even more emphasized, was observed when the hybrid Pt–NP@CNTs was casted on the GCE surface, resulting in an improved electrochemical behavior.

Nyquist plots (imaginary impedance, Z_{imag} vs. real impedance, Z_{real}) from **Figure 2B** represent the electronic transfer capabilities in the frequency domain. The semicircular portion at higher frequencies corresponds to the charge transfer resistance (R_{CT}) value, an indicator reflecting the resistance at the electrode-solution interface.¹⁷ As it was expected from CV performances, a significant R_{CT} decrease after casting the GCE with both raw CNTs (4.43 to 1.58 k Ω) and Pt–NP@CNTs (4.43 to 1.21 k Ω) was observed because of the conducting nature of both CNTs and Pt–NPs.

Surprisingly, although the rest of raw CNMs also improved the charge transfer capabilities after being casted on the GCE surface, this effect was reversed using their corresponding hybrid-CNMs (Pt–NP@CNHs, Pt–NP@rGO and Pt–NP@GP) (see **Figure S3**). This fact could be ascribed to the huge amount of Pt–NPs covering the CNMs

(see **Figure 1**), concealing the CNM exposed on the electrode surface and hindering their intrinsic electronic transfer potential.

Figure 2

3.3. Electroanalytical assay

The electrochemical responses of the electrodes to oxidation of 20 nM MeP were analyzed by DPV in a comparative way on the Pt–NP@CNM/GCE surfaces, as depicted in **Figure 3**. As it was expected from the electrochemical characterization studies, only the Pt–NP@CNTs/GCE exhibited a well-defined anodic current response (I_{pa}) at +0.89 V vs. Ag/AgCl for MeP oxidation process in the nM range. This fact must be directly attributed again to amount of coverage of Pt–NP on the CNM surface (see **Figure 1**). Thus, if the CNM surface is totally camouflaged by the Pt–NP, the synergistic effect between the enhanced electron transfer capability of the CNM with the catalytic effect of the Pt–NP is lost (note the blank experiment carried out using the CNTs/GCE from **Figure 3**, curve *b*'), and therefore, the electrocatalytic behavior of the hybrid Pt–NP@CNM is practically null.

Figure 3

The DPV responses of the four functionalized-electrodes towards different [MeP] concentrations (**Figure 4**, insets) clearly certified the aforementioned statement, since only the Pt–NP@CNTs/GCE performed a significant electrocatalytic effect towards the determination of MeP at ultra-trace levels. The calibration curves from **Figure 4** show an excellent linear correlation with the [MeP] in the range of 5.00 to 30.0 nM, yielding to a detection limit (LOD) as low as 5.00 ± 0.03 nM (see **Figure 4B**). Blank experiments

carried out using raw CNTs (CNTs/GCE surface) demonstrated the electrocatalytic behavior of the Pt–NPs on the MeP oxidation since no response was observed at such low concentrations (see **Figure S4**).

Figure 4

However, the analytical responses of the rest of hybrid Pt–NP@CNMs fall in the μM linear range (see **Figure 4 A, C-D**), with LODs of $30.0\ \mu\text{M}$, $2.5\ \mu\text{M}$ and $5.0\ \mu\text{M}$ for the Pt–NP@CNHs, Pt–NP@rGO and Pt–NP@GP, respectively. Accordingly, the synergistic effect between the CNM and the Pt–NPs seems to be directly related with an optimum composition ratio, which must be lower than 50% following the TGA analyses.

Additionally, it is important to point out the superb sensitivity (slope) shown by the hybrid Pt–NP@CNTs material ($0.045\ \mu\text{A}\cdot\text{nM}^{-1}$ or $45\ \mu\text{A}\cdot\mu\text{M}^{-1}$), improving $3.75\cdot 10^3 - 5.63\cdot 10^3$ times the homologous carbon nanoallotropes responses. According to such promising analytical results obtained by the hybrid Pt–NP@CNTs, this material was the one exploited as the electrochemical sensing platform for the determination of MeP in real samples.

Finally, it is important to point out the general lack of homogeneity by diameter/length means in the different commercial CNMs, fact that usually leads to a poor electrochemical reproducibility on the bio-sensing performance batch to batch. Accordingly, an accurate characterization of the raw CNM nature before being used for electroanalysis is a must to improve both repeatability and reproducibility.

3.4. Validation of the electrochemical method employing real samples

HPLC-UV technique was employed as the standard reference tool to validate the presented electrochemical sensing approach. Accordingly, a calibration curve was firstly constructed per triplicate in order to quantify the [MeP] in the real sample used. Chromatograms are presented in **Figure 5**, which show a peak area (A) increase with increasing the [MeP], exhibiting a wide linear range from 5.0 nM to 0.5 mM and detection limit of 5.0 ± 0.6 nM derived by the following equation: $A \text{ (mAU)} = 0.053 + 0.011 [\text{MeP}] \text{ (mg}\cdot\text{L}^{-1})$ (see inset plot). Afterwards, 10 μL of the pretreated real sample (see Section 2.5) were interpolated in the calibration curve, obtaining a concentration of 196.2 ± 0.4 μM .

Figure 5

Table 1 displays the added and found values for five different samples. The concentration in sample SA-1 (4.79 μM) corresponds to a dilution of the initially MeP amount present in the commercial shampoo. Then, this sample was spiked with known standard [MeP] solutions (SA-2 to SA-5). Notable recoveries were found *via* HPLC technique, which were very close to 100%. The same methodology was applied using the Pt-NP@CNTs/GCE electrochemical sensing platform, making the proper dilutions for the addition in the electrochemical cell at the nM range (see **Figure S5**). Excellent recoveries were also yielded by DPV between 97.8% and 103.5%, demonstrating the selectivity of the method since the possible matrix effect provided by the extraction of MeP from the real samples did not alter the electrochemical sensing response.

Table 1

Finally, the accuracy of the electroanalytical technique towards the quantification of MeP was also tested through a comparison with the standard HPLC procedure. Thus, a correlation between the concentration values found for the five aforementioned samples (SA-1 to SA-5) through DPV and HPLC techniques were compared ($C_{\text{MeP}}^{\text{HPLC}}/C_{\text{MeP}}^{\text{DPV}}$), as shown in **Table 1**. Nicely values very close to 1 were achieved for the spiked real samples, verifying that the electrochemical sensing platform is accurate. According to these results, it is possible to conclude at this point that the developed electrochemical sensor is validated since no significant differences between DPV and HPLC techniques can be observed, making feasible its exploitation towards the determination of MeP in real samples at ultra-low concentrations.

3.5. Electrochemical comparison with other works

Having demonstrated that the LOD as well as the sensitivity of the electrochemical method is improved by using the hybrid Pt–NP@CNTs as the sensing platform, and taking into account the excellent MeP quantification in real samples, the next step was focused on comparing these results with some additional carbon-based electrochemical sensors previously reported in the literature for MeP determination. Data shown in **Table 2** reveals that the electrochemical platform based on Pt–NP@CNTs, which is fast, straightforward, highly sensitive, reproducible and has been validated by the standard HPLC method, yields one of the lowest LOD found in literature with the best sensitivity. Further, the methodology employed for synthesizing the electrocatalytic hybrid-nanomaterial is much easier than some works that provide LODs in the same nM range.^{37,38} Thus, this superb sensing performance might be ascribed to an optimum Pt–NP loading on CNTs, which significantly enhances the electrocatalytic active area and promote electron transfer in the oxidation of MeP.

Table 2

4. Conclusions

Four different CNMs from 0D to 3D have been successfully functionalized with Pt-NPs employing a generic organometallic synthetic route and used towards the determination of the endocrine disruptor MeP at ultra-low levels. Surprisingly, the electrocatalytic capabilities of the synthesized Pt-NP@CNMs for the MeP oxidation depend on the CNM/Pt-NPs ratio, being the Pt-NP@CNTs material the most appropriate for electrochemical approaches. Excellent electroanalytical performances were achieved by the Pt-NP@CNTs/GCE sensing platform, yielding detection limits as low as 5.00 ± 0.03 nM with the better sensitivity found in literature ($4.5 \cdot 10^{11} \mu\text{A} \cdot \text{M}^{-1}$). Moreover, the present electrochemical method was validated with the standard bench-top chromatographic technique (HPLC), demonstrating that the electroanalytical measurements provide the same results of the conventional HPLC method in different real samples. Accordingly, it is presented a simple, rapid, cost-effective and easily minituarizable electrochemical sensing platform that offers excellent reproducibility, high accuracy and sensitivity as well as superb precision (selectivity) in real samples, which could be exploited in pharmaceutical, biomedical and environmental fields.

Acknowledgments

This work was funded by the national DGI project FANCY CTQ2016-80030-R and the MINECO/FEDER project CTQ2015-64261-R, the Generalitat de Catalunya (2017-SGR-918) and the Spanish Ministry of Economy and Competitiveness, through the “Severo Ochoa” Programme for Centers of Excellence in R&D (SEV-2015-0496). The authors also than the Networking Research Center on Bioengineering, Biomaterials, and

Nanomedicine (CIBER-BBN). Dr. J. Muñoz gratefully acknowledges the “Juan de la Cierva” programme. Dr. J. García-Antón acknowledges the Serra Húnter Program. I. Álvarez-Prada thanks the UAB for the PhD grant. Dr. J. Muñoz and I. Álvarez-Prada contributed equally to this work.

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