# Carbon-paste nanocomposites as unconventional gate electrodes for Electrolyte-Gated Organic Field-Effect Transistors: Electrical modulation and Biosensing

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#### **Experimental Procedures**

#### Chemicals and reagents

Multiwalled carbon nanotubes (CNTs, > 95% of carbon purity, 10–30 nm of outer diameter and has about 5–15 µm of length) were provided by SES Research (Houston, TX, USA). The Epotek H77 polymeric matrix was obtained from Epoxy Technology (Billerica, MA, USA). Au–NPs were synthesized using the HAuCl<sub>4</sub> salt precursor (> 99.99%, Sigma-Aldrich). Per-6-thio- $\beta$ -cyclodextrin ( $\beta$ –CD-SH) was synthesized following the established methodology and used as the chiral biorecognition element [1]. L–Tryptophan (> 98%), dibenzotetrathiafulvalene (DB-TTF, 97%), polystyrene (PS, analytical standard M<sub>w</sub> ~ 3250) and chlorobenzene (CB, ≥ 99.5%) were purchased from Sigma Aldrich and used as received. All the rest of reagents were of at least analytical grade and used as received. Deionized water (18.2 MΩ·cm) from a Milli-Q system (Millipore, Billerica, MA, USA) was used throughout all the experimental part.

## NC-CPE fabrication

Hand-made working NC–CPEs were fabricated by dispersing different composition ratios of CNTs (either functionalized or not) within an insulating epoxy resin through manually homogenization for 60 min. The carbon-paste was placed into a cylindrical polyvinyl chloride (PVC) tube (6 mm of internal diameter and 20 mm of length) containing a copper disk (5 mm of diameter and 1 mm of thickness) soldered to an electrical connector end (2 mm of diameter) [2]. Prior to soldering, the copper disk was treated with a 5% HNO<sub>3</sub> solution v/v for 2 min in order to remove the oxide layer. The mixture was then incorporated in the hollow end of a PVC tube to form the body of the electrode. The final paste-filled cavity was 3 mm long inside the PVC tube. Then, the nanocomposite paste electrodes were allowed to harden during 24 h at 80 °C.

Afterwards, electrode surfaces were polished with different sandpapers of decreasing grain size (800 and 1200) in order to obtain a reproducible electrochemical surface. The resultant geometric area for the final NC–CPE was 28 mm<sup>2</sup>. It is important to highlight that the developed nanocomposite material is mainly stable in aqueous electrolyte media due to the solubility of the epoxy polymer in some organic solvents.

## **Device** fabrication

Source (S) and drain (D) electrodes were patterned through photolithography (MicroWriter ML Laser Lithography System) on kapton foil (Kapton® HN DuPont, thickness  $\approx 75 \ \mu\text{m}$ ). A Cr/Au (5 and 40 nm) metal layer was subsequently evaporated (Evaporation System Auto 360 from BOC Edwards). The channel width and length were 20700 and 30  $\mu$ m, respectively (W/L = 690). Prior to organic semiconductor deposition, all the substrates were sonicated in acetone and isopropanol for 15 minutes each. The active material was prepared by mixing DBTTF and PS in a 1:2 ratio in CB (4 wt %) and afterward the solution was kept at 105° for 10 minutes in order to ensure the complete dissolution of the material. Afterwards, the solution was deposited by bar assisted meniscus shearing (BAMS) technique at a fixed speed of 1 cm s<sup>-1</sup> and keeping the base plate temperature at 105 °C. As previously reported by the authors, BAMS is a meniscus-assisted method that guarantees the fast deposition of thin films with large-scale crystallinity and homogeneity [3].

## Functionalization of the NC-CPE-based recognition platform

Scheme 1 summarizes the different steps carried out to synthesize the CNT-based recognition platform. Briefly, CNTs were previously activated with carboxylic groups by immersing them in an aqueous solution containing 2.5 M HNO<sub>3</sub> for 2 h.<sup>[2]</sup> Afterwards, CNTs were functionalized with Au–NPs (*step i*)) following the

environmental friendly Intermatrix Synthesis (IMS) technique, as was previously reported.<sup>[4]</sup> Then, Au–NP@CNTs were dispersed in an aqueous (9:1 water/ethanol, v/v) 1.0 mM suspension of  $\beta$ –CD-SH (*step ii*)). Finally, the resultant hybrid-nanomaterial was dispersed within the polymeric epoxy resin (20% w/w in carbon filler), resulting in the functionalized NC–CPE, which was used as the gate for TRP biosensing.

#### *Electrochemical measurements*

The percolation curve of CNTs/epoxy nanocomposite electrodes was carried out through measurement of the electrical resistance, which was performed using a digital multimeter (Fluke, Everett, WA, USA). The electrical resistance was measured between the copper piece of the connector and the NC–CPE surface. Three equal electrodes were fabricated and evaluated for each composition ratio (3% to 20% (w/w) in CNTs) in order to estimate the reproducibility of the hand-made fabrication. The repeatability of the measurement was obtained by testing five different points for each NC–CPE. All experiments were performed at room temperature (25 °C).

Electrochemical characterization was carried out by means of Cyclic Voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS), using a Novocontrol Alpha-AN impedance analyzed with a potentiostat POT/GAL 30V/2A electrochemical interface. Cyclic voltammograms were obtained using a scan rate of 10 mV·s<sup>-1</sup>. For impedance measurements, it was employed a frequency range of 100 kHz to 0.1 Hz at redox equilibrium potential and 50 mV as a signal amplitude to perturb the system (equilibrium time: 10 s). Measurements were performed in a three-electrode configuration cell filled with a 0.1 M KCl solution containing 10 mM  $[Fe(CN)_6]^{3-/4-}$  as the benchmark redox marker. The electrode configuration was: a single junction Ag/AgCl (sat. KCl) as reference electrode, a platinum wire as auxiliary electrode and the different CNT-based NC–CPEs (either functionalized or not) as working electrodes.

## Electrical measurements

Transfer and output characteristics were performed under ambient conditions using an Agilent 5100A and Easy Expert software connected to the samples with a SUSS probe station. Transfer and output characteristics were performed by confining 100 µl of Milli-Q water on the interdigitated area with a PDMS pool. Transfer characteristic were recorded in linear ( $V_{DS} = -0.1$  V) and saturation regime ( $V_{DS} = -0.4$  V).

Carbon electrodes were mechanically polished using different sandpapers of decreasing grain size before each sensing experiment in order to regenerate the surface. Pt wire ( $\phi = 0.5$  mm) was purchased from Sigma-Aldrich and was cleaned in hot sulphuric acid (0.1 M) for 30 min and rinsed with Milli-Q water (resistivity: 18.2 M $\Omega$  cm) prior to each electrical and electrochemical measurements. Glassy Carbon Electrode (GCE) was mechanically polished and rinsed abundantly with Milli-Q water before each experiment.

### Microscopy images

Physical characterization of raw CNTs, Au–NP@CNTs and β–CD-SH/Au–NP@CNTs were obtained from High-Resolution Transmission Electron Microscopy (HR–TEM), using a JEM-1400 unit with an acceleration voltage of 120kV coupled to an Energy Dispersive X-Ray Spectroscopy (EDS). Topography images of the bare and functionalized NC–CPEs were taken by Scanning Electron Microscopy (SEM), which were acquired using a QUANTA FEI 200 FEG-ESEM with an acceleration voltage of 15 kV, using secondary electron imaging under high vacuum.

#### Synthesis and characterization of the functionalized gate electrode

HR–TEM was employed to monitor the CNT–based nanomaterials at different functionalization stages. **Figure S2A-B** clearly shows a successful incorporation and homogenous distribution of Au–NPs on the CNT walls, with an average particle size 7.2  $\pm$  0.8 nm. Afterwards, Au–NP@CNTs were used as nanotemplates for grafting the thiolated  $\beta$ –CD. The strength of the gold-thiol interactions was the basis to obtain a robust  $\beta$ –CD-SH/Au@NP@CNTs hybrid-nanomaterial (see **Figure S2C**). The EDS spectrum from **Figure S2D** confirmed both the presence Au–NPs as well as the S peak provided by the thiolated  $\beta$ –CD. Finally, the aforementioned CNT-based hybridnanomaterial was dispersed throughout an insulating epoxy resin for gate electrode fabrication. Electrode surfaces of the bare and functionalized NC–CPEs were also characterized by SEM (see **Figure S1E-F**). Comparing both surfaces, the presence of Au–NPs is clearly observed on the functionalized NC–CPE surface, suggesting the exposure of the recognition agent on the functionalized electrode surface since it is covalently grafted upon the Au–NPs *via* gold-thiol bond formation.



**Figure S1.** A) Output characteristics corresponding to the NC–CPEs electrodes loaded with 3%, 5%, 10% and 20% in CNTs (w/w). B) Comparison between the NC–CPE loaded with 20% in CNTs (w/w) and two standard electrode materials (GC and Pt).



**Figure S2.** I/V transfer characteristics of different gate electrodes ( $V_{DS}$ : -0.4 V): A) NC–CPEs containing from 3% to 20% in CNTs (w/w) and B) electrical comparison between a) a NC–CPE loaded with 20% in CNTs, two standard electrode materials (b) GC and c) Pt) and d) the NC–CPE-based biorecognition platform (20% in  $\beta$ –CD/Au–NP@CNTs, w/w).



**Figure S3.** HR–TEM images of A) raw CNTs; B) Au–NP@CNTs; C)  $\beta$ –CD/Au–NP@CNTs and D) its corresponding EDS spectrum (the Cu peak corresponds to TEM grid).The presence of S demonstrates the successful functionalisation of Au-NPs with  $\beta$ –CD. SEM images of NC–CPEs containing E) raw CNTs and F)  $\beta$ –CD/Au–NP@CNTs (20% *w/w* in conducting filler), where it is clearly observed de Au–NPs exposed on the functionalized gate electrode surface.



**Figure S4.** Stability of the NC–CPE-based biorecognition system before (black line) and after (red line) 20 *I/V* cycles; ( $V_{DS}$  = -400 mV).



**Figure S5.** Impedimetric performances of the bio-recognition gate electrodes before and after being incubated with different [TRP]. A notable  $R_{CT}$  shift with [TRP] is observed due to the supramolecular complex formation that lead to an insulating layer formation on the electrode surface, hindering the interfacial electron transfer reaction from the redox probe to the electrode surface. Inset: Blank experiment using the bare CNT-based NC–CPE exposed to the same [TRP] concentrations, where the impedimetric capability of the bare electrode keeps practically constant due to the absence of the bio-recognition element, and therefore, not supramolecular sandwich formation can be formed on the electrode surface.



**Figure S6.** Regeneration capability of the electrode surface before (*a*) and after (*b*) the last transfer of the sensing experiment. After the polishing procedure, the electrode recovers its initial electrical behavior (*c*);  $(V_{DS}: -400 \text{ mV})$ .

# References

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