Electronic performance of polymer carbon-paste nanoallotropes from 0D to 3D as novel gate electrodes in Water-Gated Organic Field-Effect Transistors

*Adrián Tamayo, Jose Muñoz and Marta Mas-Torrent**

Institut de Ciència de Materials de Barcelona (ICMAB-CSIC) and Networking Research Center on Bioengineering Biomaterials and Nanomedicine (CIBER-BBN) Campus de la UAB, 08193 Bellaterra, Spain

E-mail: mmas@icmab.es

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Water-gated organic field-effect transistors (WGOFETs) are expected to have a strong impact in the field of electronic bio-sensors owing to the synergism between the transduction function of the transistors with the fact that they can be operated in physiological media. Nonetheless, a limited library of gate electrodes has currently been explored for this aim. Herein, different polymer nanocomposite carbon paste gate electrodes (NC-CPgEs) have been successfully exploited for the first time as unusual non-metal gate electrodes in WGOFET devices employing four types of carbon nanoallotropes with dimensionality ranging from 0D to 3D (i.e., carbon nanohorns, carbon nanotubes, reduced graphene oxide and graphite, respectively). Interestingly, after an accurate electrochemical and electrical characterization, it is demonstrated that the WGOFETs with the developed NC-CPgEs reveal excellent behaviors comparable to that achieved with conventional metal gate electrodes, such as gold or glassy carbon electrodes. Further, depending on the carbon nature the device performance can be tuned, being the devices based on reduced graphene oxide the ones showing a better electrical response. Accordingly, this work can pave the way for widespread applications of NC-CPgEs for the development of a new generation of WGOFET devices based on carbon nanostructures.

1. Introduction

Organic field-effect transistors (OFETs) are one of the key components of modern organic electronics due to their great malleability to be integrated into flexible substrates and their potential to be fabricated employing low-cost printing techniques.^[1–4] Such outstanding features endow them with potential for broad applications in the field of physical, chemical and biological sensors.^[5–8] Concretely, the field of point-of-care medical diagnostics require the development of water-compatible electronics as highly sensitive bio-sensing platforms for *in situ* screening. In this regard, water-gated organic field-effect transistors (WGOFETs) have demonstrated to be potential candidates for a new generation of electronic bio-recognition systems, taking advantage of their high interface sensitivity and electrical transduction properties together with the device compatibility with physiological media, where biological targets remain active.^[9–14]

As depicted in Scheme 1, the operation principle of a WGOFET relies on tuning the current following between two electrodes (source, S, and drain, D) connected along a thin organic semiconductor (OSC) in contact with a third electrode (gate, G) through an aqueous-based electrolyte solution by the application of a gate voltage.^[15] The electric field created by the G–S voltage (V_{GS}) modulates the current flowing between S–D electrodes (I_{DS}) and thus, a high mobility is a must to guarantee that a small V_{GS} variation in the transistor (input signal) yields a large response in the I_{DS} (output signal). In comparison to conventional OFETs in which inorganic or organic non-electrolytic dielectrics are used, the much higher capacitance achieved in WGOFETs due to the formation of electrical double layers (EDLs) at the electrolyte/OSC and gate/electrolyte interfaces ($10^2 - 10^3$ times higher), enables to operate the devices at much smaller biasing voltages (< 1 V vs. > 10 V). This ensures a water-stable operation window while the achieved I_{DS} is high enough for further signal processing.^[10,16] Despite impressive progress has been made over the last few years,^[17] the versatility of this

technology still allows plenty of room for testing alternative materials and device architectures.

The WGOFET transistor technology has received therefore considerable attention for application as highly sensitive tool for biological applications.^[9,18–22] Since the vast majority of WGOFET devices are currently focused on using pure metals as gate electrodes (i.e., Au or Pt), wide alternative strategies associated with the gate surface engineering remain open.^[23]

The integration of conductive carbon nanoallotropes within a polymeric matrix for polymer nanocomposite carbon-paste electrodes (NC–CPEs) fabrication has played a leading role in analytical electrochemistry.^[24–28] The resulting non-toxic and environmentally friendly type of electrodes present a series of desirable benefits, such as: *i)* robustness, *ii)* convenient electrical conductivity which can be easily tailored by modifying the filler/polymer composition ratio, *iii)* stable response in aqueous media, *iv)* high specific surface area, *v)* printability for lab-on-a-chip integration, *vi)* facile tunability with a wide range of bio-recognition elements (biocompatibility) and *vii)* surface reset by a simple polishing step (renewability), among others. However, the use of such electrodes has hardly been explored in the field of OFET. Only very recently, our research group reported the use of a NC–CPE made by dispersing carbon nanotubes (CNTs) within an insulating epoxy resin, offering an appealing alternative to be used as carbon-based gates in WGOFETs, permitting to modulate the device response depending on the carbon loading and allowing an easy and reproducible bio-functionalization for sensing applications.^[29]

The research herein is devoted to electrically explore the WGOFET capability using nanocomposite carbon-paste gate electrodes (NC–CPgEs) employing four different carbon fillers with dimensionality ranging from 0D to 3D, such as 0D carbon nanohorns (CNHs), 1D CNTs, 2D reduced graphene oxide (rGO) and 3D graphite (G). These materials have been used as conducting fillers and dispersed throughout an inert polymeric matrix in an optimum filler/polymer composition ratio for NC–CPgE engineering. The influence of the carbon

allotrope nature on relevant figures of merit of the transistor performance have been analyzed and compared with the performance when using conventional gate electrodes, verifying the feasibility and potential of such carbon-based NC–CPgEs to be applied in field-effect transistors.

2. Results and Discussion

Four types of conducting carbon materials, including CNHs, CNTs, rGO and G have been employed as carbon fillers for NC–CPgEs fabrication. The dispersion of these carbon nanoallotropes throughout an inert polymeric matrix (as an epoxy resin) leads to a nanocomposite that combines the electrical properties of the carbon component with the mechanical robustness and malleability of the polymer. However, it is well-known that such properties strongly depend on the nature of each component, their relative quantities and their distribution. The percolation theory is a valid approximation to determine the optimum composition ratio (named as near-percolation composition, NPC) to ensure the maximum conductivity value with the minimum conductive particle loading to guarantee the perseverance of the mechanical properties.^[30] Hence, the four different carbon-based NC–CPgEs have been engineered by choosing their respectively near-percolation composition ratios (6%, 10%, 13% and 16% w/w in CNHs, CNTs, rGO and G, respectively), which gives rise to electrodes with very similar electroactive areas (A).^[31] In this way an accurate comparison can be realized.

2.1. Morphological studies of the NC–CPgEs

Prior to electrochemical studies, scanning electron microscopy (SEM) and atomic force microscopy (AFM) techniques were employed in order to gain an insight of the surface characteristics of the different carbon-based NC–CPgEs. The structure and morphology of the

surface in such type of electrodes can affect their electrical properties due to the formation of the EDLs.^[32]

Figure 1 and Figure S1 depicts, respectively, the backscattered electrons (BSE) and large field detector (LFD) images of the carbon-based NC–CPgEs recorded by SEM. A quite similar microscopic morphology can be observed for all NC–CPgEs (Figure 1). The different morphologies inside the conductor domains are attributed to the different self-aggregation of the carbon allotropes (Figure S1). Further, AFM provided information about the surface roughness using the root mean square (Rms) values (see Figure S2). Importantly, as presented in Table 1, the optimized NC–CPgEs ranging in the near-percolation composition zone exhibited similar Rms values, fact that might lead to similar electroactive areas (A). Additionally, conductive AFM measurements (Figure S3) provided information about conductor material distribution, where a major dispersibility of the conducting areas with decreasing the dimensionality of the carbon nanostructure was observed, fact that could be ascribed to the lower amount of conducting filler necessary to achieve the near-percolation composition.

2.2. Electrochemical characterization of NC–CPgEs

The electrochemical behaviour of the four developed NC–CPgEs was interrogated *via* CV and EIS (Figure 2). The widely used benchmark $[\text{Fe}(\text{CN})_6]^{3-/4-}$ redox marker was utilized to investigate the electrochemical performances of the electrode surfaces. The more conventional electrodes gold (Au) and glassy carbon electrode (GCE) were also studied used for comparison.

CV provides information about the accessibility and reversibility of the redox marker to be oxidized or reduced at the electrode surface by analyzing the peak currents (I_p) and peak-to-peak separation (ΔE), respectively.^[33] As shown in Figure 2A, both NC–CPgEs and conventional electrodes exhibited similar electrochemical performances by means of I_p . In concordance with the morphological characterization, similar A values were achieved by

simply optimizing the electrically conductive networks *via* tuning the filler/polymer composition ratio, making possible to avoid its influence on the device performance (see Table 1) since this value is known to be directly related to the current (I_p) through Equation (1).^[29] However, it is important to note the larger capacitive behavior of the 2D-NC-CPgEs, resulting in a significant ΔE increase.

Further electrochemical parameters, such as ohmic resistance (R_Ω), charge transfer resistance (R_{CT}) and double-layer capacitance (C_{dl}), were also evaluated through the frequency domain by EIS (see Table 1).^[34] Nyquist plots from Figure 2B (and Figure S4) reveal a general trend: a significant R_Ω decrease with increasing the nanostructured dimension of the carbon material. The R_Ω parameter is dependent on the ionic concentration, the type of electrolyte, the geometric electrode area and the bulk resistance of the nanocomposite. Accordingly, this resistance is the one that has a direct relation with the bulk resistance taken from the percolation plot.^[30] The fact that R_Ω decreases with increasing the dimensionality of the carbon nanostructure can be explained since at lower carbon loads, the ohmic resistance is more dominated by the bulk resistance, whereas at higher carbon loads, this parameter decreases to low values and therefore, it is more dominated by the solution resistance. In a more ideal behaving Au electrode, the extracted R_Ω could be more directly attributed to the solution resistance (Figure S5). In this sense, this trend is in concordance with the carbon loading contained in each NC-CPgE to achieve the near-percolation composition ratio, which decreases with the nanostructured dimension of the carbon filler. Comparing with the conventional electrodes, higher R_Ω parameters were found for NC-CPgEs as expected due to the insulating nature of the polymeric matrix. R_{CT} is a parameter inversely proportional to the electron transfer rate, whereas C_{dl} is directly related to the background current. In general, no significant impedimetric changes between 0D-, 1D- and 3D-NC-CPgEs were observed by means of R_{CT} and C_{dl} values because of their similar A. However, it is important to point out

the much higher values found for the 2D-NC-CPgE, which is in agreement with the capacitive behavior of this material exhibited by CV.

Thus, and according to the morphological and electrochemical results summarized in Table 1, similar NC-CPgE surfaces were achieved using the different carbon allotropes by using their corresponding near-percolation composition ratios, which gives electrodes with similar A . The only difference observed was the more pronounced capacitive behaviour in the case of 2D-NC-CPgE. Although rGO is an excellent conductive material, its dispersion throughout an insulating polymeric matrix can lead the resulting nanocomposite to act as a good capacitor.^[32]

2.3. Electrical performance of WGOFETs

The next step was focused on studying the electrical response of such unconventional gates in the WGOFET device, employing also the Au and GCE as conventional electrodes. The devices were prepared by depositing on Si/SiO₂ substrates with pre-fabricated interdigitated source/drain Au electrodes, a solution of the organic semiconductor diF-TES-ADT and polystyrene (PS) by bar-assisted solution shearing as previously reported (see Experimental Section for further details)^[35]. It has been previously reported that this methodology leads to highly crystalline thin films that exhibit a robust WGOFET performance.^[12,36] As illustrated in Scheme 1, the different gate electrodes were connected to the electrical device through immersing them in a 300 μ L Milli-Q water solution that acted as dielectric.

Figure 3A (Figure S6, S7 and S8) shows the I - V transfer characteristics of the NC-CPgEs recorded in linear regime ($V_{DS} = -0.2$ V), which mainly evidence: *i*) the leakage current values are low enough to guarantee that parasite faradaic processes or electrochemical doping is not occurring, and therefore, the current modulation is due to the field-effect, and *ii*) the low hysteresis observed point towards a good formation and disruption of the electrochemical double layers at the gate electrode/electrolyte and electrolyte/OSC interfaces. In general, all

NC-CPgEs based on the different carbon composites presented similar electrical characteristics that the ones obtained by the conventional gate electrodes. Further, the output characteristics depicted in Figure S9 also presented good I_{DS} modulations and no significant contact resistance effects at low V_{DS} .

Some electrical parameters, such as the V_{TH} (fitted interpolation value) and the slope of the curve, which is proportional to the device mobility ($\sigma \propto C \cdot \mu$, where μ is the field-effect mobility and C is the electrolyte capacitance per unit area), were extracted from the transfer curves and are summarized in Table 2. NC-CPgEs demonstrated consistent σ values in the same order of the conventional electrodes and as in agreement with the values previously reported ($\sigma \sim 5\text{-}10 \mu\text{S}$, in devices with μ values in the range $0.1\text{-}0.2 \text{ cm}^2/\text{Vs}$).^[36] Additionally, the stability of the CPgE was also studied. Figure S10 shows the response of two different devices employing a fresh 2D-NC-CPgE electrode and the same one aged 8 months, demonstrating that the performance is very similar and, thus, the electrodes are very stable. Interestingly, while conventional electrodes presented similar V_{TH} values, the transfer characteristics of the NC-CPgEs displayed a marked V_{TH} shift depending on the nature of the carbon filler (see Figure 3B). Previously, it has been shown that the electrode work function ($\phi_{electrode}$) can be directly related to the V_{TH} ,^[37,38] although such correlation has not always been observed.^[23,39] In some cases, other aspects such as the impact on the EDL capacitance in functionalised electrodes has been found to be a more important parameter. In order to study the influence of the $\phi_{electrode}$ on these devices, we characterised the NC-CPgEs by Kelvin Probe Force Microscopy (KPFM). However, it was observed that the $\phi_{electrode}$ could not be correlated with the V_{TH} shift (Figure S11 and S12). We believe that in such unconventional gate electrodes, other effects are having a major impact. In fact, the trend of the V_{TH} shift follows the carbon material dimensionality accordingly to: CNHs (0D) > CNTs (1D) > rGO (2D) > G (3D). Further, is it important to note that since the gate surface electroactive area A is similar in all cases, the modulation of the V_{TH} should indeed be caused

by topological differences of the carbon materials^[29] combined with the $\phi_{electrode}$ shift, although the latter effect is less prevailing. Thus, the V_{TH} shift can be related in this case to the bulk properties of the electrode, and hence, to the intrinsic bulk electronic properties of the NC-CPgE, which seems to play a more dominant effect on the V_{TH} than the $\phi_{electrode}$.^[32] Analysing the electrochemically extracted R_Ω , and considering that the electrolyte employed is always the same, we can affirm that the differences in this parameter come from the different electrode resistance. As shown in Figure 3C, a clear correlation can be found between V_{TH} and R_Ω , which is in agreement with the carbon load used (the NPC composition ratio) required in each case to achieve NC-CPgEs with similar A (see inset graph).

Importantly to highlight is the fact that the devices in which 2D-NC-CPgE was used showed a negligible hysteresis indicative of the high capability of this gate electrode to fast form and annihilate the electrochemical double layer. Figure 3D shows the V_{TH} extracted from the forward and reverse sweeps of different devices, which are plotted together. As can be clearly observed, the lowest dispersion in values was found with the 2D-NC-CPgE, which exhibited a performance similar to the one of the Au electrode. This fact could be ascribed to the more capacitative behaviour of this electrode. Thus, the devices response using rGO in the nanocomposite gate electrode gives rise to more robust and stable performances with a higher device-to-device reproducibility. This is of particular relevance for the application of these devices for sensing purposes, where the changes in performance should be correlated solely with the variations coming from the presence of a specific analyte.

According to the electrical studies, transfer and output characteristics of the developed NC-CPgEs displayed a general field-effect behaviour working in a regime of electric double layer capacitance, with low leakage currents and slight hysteresis comparable to the conventional gate electrodes. Beyond this general trend, the 2D-NC-CPgE has also presented the best electrical improvement by means of EDL formation and annihilation. Importantly, the

physical and inherent electrochemical and electrical properties of the different carbon-based composite materials seem to rule the NC–CPgE performances, being possible to customize the WGOFET operation voltage window by changing the nature of the carbon allotrope included in the gate electrode.

3. Conclusions

Four different types of conducting carbon allotropes with dimensionality ranging from 0D to 3D have been dispersed within an insulating polymeric matrix in an optimum composition ratio for the fabrication of NC–CPgEs and tested for the first time as unconventional non-metal gate electrodes in WGOFET devices. After an accurate physical and electrochemical characterization to fix the A parameter for an optimal comparison, the electrical feasibility of such alternative gate electrodes in the transistor has been validated. Remarkably, the performances achieved are comparable to those obtained with conventional gate electrodes such as Au or glassy carbon. Interestingly, the WGOFET capabilities can be tailored by changing the nature of carbon nanomaterial, resulting in an operation voltage window shift. In this sense, the dimensionality of the carbon allotrope has demonstrated to be the most pivotal parameter affecting the electrical transistor response since influences the polarization ability of the gate electrode, and therefore, the V_{TH} . In addition, the best electrical performance in terms of robustness and reproducibility was exhibited by the 2D-NC–CPgE, probably due to its higher capacitive features. Finally, this work opens up the exploitation of NC–CPgEs, taking into account the synergism benefits of the carbon nanoallotropes with the polymeric matrix, as potential non-metal gate alternatives for widespread applications in the field of WGOFET devices.

4. Experimental Section

Chemicals and reagents: CNHs (0D), CNTs (1D), rGO (2D) and G (3D) carbon nanoallotropes were used as the conducting filler materials. CNHs and G powder were

purchased from Sigma-Aldrich (St. Louis, MO, USA), while multi-walled CNTs were provided by SES Research (Houston, TX, USA). rGO was successfully synthesized and characterized according to our previous work.^[30] Briefly, Graphene Oxide (GO) was synthesized from the flaked G via Hummers method and then reduced using ascorbic acid to obtain the conducting graphene form (rGO). CNHs, CNTs and G were used without further purifications. The Epotek H77 polymeric matrix was obtained from Epoxy Technology (Billerica, MA, USA). 2,8-difluoro-5,11-bis(triethylsilyl-ethynyl)anthradithiophene (diF-TES-ADT, 99%) was purchased from Lumtec and used as received. Polystyrene (PS, analytical standard, Mw ~10000 g·mol⁻¹), 2,3,4,5,6-pentafluorothiophenol (PFBT, 97%) and anhydrous chlorobenzene (CB, ≥99.5%) were purchased from Sigma Aldrich and used as received. Kapton® substrates (Kapton®HN, 75 mm thick) for transistor fabrication were delivered by DuPont (Wilmington, DE, USA). Polydimethylsiloxane (PDMS) was purchased from Dow Corning Corporation (Barry, UK) and prepared according to the standard protocol. All organic solvents were of HPLC grade. Deionized water (18.2 MΩ·cm) was obtained from a Milli-Q system (Millipore, Billerica, MA, USA). All the rest of reagents were of at least analytical grade and used as received.

Electronic device fabrication: S- and D-electrodes were patterned on Kapton® via photolithography (MicroWriter ML Laser Lithography System).^[13] Briefly, a 5/40 nm metallic layer of Cr/Au layer was deposited through thermal evaporation (Evaporation System Auto 306 from BOC Edwards). The channel width (W) and length (L) was 5 mm and 50 μm, respectively (W/L = 100). Prior to the organic thin-film layer deposition, substrates were cleaned in an ultrasonic bath containing acetone and then isopropanol for 15 min. Afterwards, Au-based electrode surfaces were firstly activated using an ultraviolet ozone cleaner for 25 min and then chemically modified by immersing them in a 15 mM PFBT solution in isopropanol for 15 min. The diF-TES-ADT and PS were mixed in a 4:1 diF-TES-ADT:PS volume ratio in a CB solution (2 wt%) and deposited in ambient conditions by applying the

bar-assisted meniscus shearing (BAMS)^[35,40] technique as previously reported (coating speed: 10 mm·s⁻¹, base plate temperature: 105 °C).^[36]

NC-CPgE fabrication: Hand-made carbon-pastes were prepared by mixing the conducting carbon material and the insulating epoxy resin in an optimized composition ratio through manually homogenization for 30 to 60 min, depending on the carbon nanoallotrope nature. As previously reported,^[31] the near-percolation composition ratios are 6%, 10%, 13% and 16% (w/w) for CNH, CNT, rGO and G, respectively, and have been chosen as the optimum ones in order to ensure a very similar electroactive area. For NC-CPgE fabrication, a copper disk (5 mm of diameter and 1 mm of thickness) was soldered to a female connector (2 mm of diameter) and then introduced into a polyvinylchloride (PVC) tube (6 mm of internal diameter and 20 mm of length). Afterwards, the electrode body gap was fully filled with the carbon-paste, tightly packed and cured at 80 °C for 24 h. Finally, the resulting carbon-based NC-CPgEs (CNH-, CNT-, rGO- and G-based NC-CPgE, named as 0D-, 1D-, 2D- and 3D-NC-CPgE, respectively) were polished with different sand-papers of decreasing grain size until obtaining a totally flat surface (geometric area: 28 mm²), and then used as gate electrodes in the WGOFET devices. Three equal NC-CPgEs were fabricated for each carbon material in order to estimate the reproducibility of the hand-made fabrication.

Apparatus and characterisation procedures: Electrochemical characterizations by means of cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were recorded with an AutoLab Metrohm PGSTAT128N potentiostat/galvanostat equipped with NOVA 2.1.3 software. CV and EIS experiments were carried out using a three-electrode configuration cell filled with 20 mL of 0.1 M KCl aqueous solution containing 10 mM [Fe(CN)₆]^{3-/4-} as a redox marker. A single junction reference electrode Ag/AgCl (3 M) and a platinum wire were used as reference and auxiliary electrodes, respectively. The developed NC-CPgEs were employed as working electrodes. The electroactive area (A , cm²) was efficiently calculated from the peak current (I_p , A) according to the modified Randles-Sevcik

equation (1),^[41] where n is the number of electrons (in this case, $n = 1$), α represents the symmetry factor which was taken approximately as 0.5, D_{red} corresponds to the diffusion coefficient of the reduced species ($D_{red} = 6.32 \cdot 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$), ν is the scan rate ($0.05 \text{ V} \cdot \text{s}^{-1}$) and C_{red}^* is the bulk concentration of the electroactive species ($C_{red}^* = 0.01 \text{ M}$).

$$I_p = 3.01 \cdot 10^5 n^{3/2} (\alpha D_{red} \nu)^{1/2} A C_{red}^* \quad (1)$$

For EIS measurements, a frequency range of 100 kHz to 0.1 Hz was employed at redox equilibrium potential (+150 mV). The signal amplitude to perturb the system was 5 mV and the equilibrium time was 10 s. Impedimetric values were determined by fitting the Nyquist plots (Z_{real} vs. Z_{imag}) with a typical Randles equivalent circuit,^[31] which was sufficiently suitable to interpret the values of ohmic resistance (R_{Ω}), charge transfer resistance (R_{CT}) and double-layer capacitance (C_{dl}) in terms of the interfacial phenomena that occur at the electrochemical cell. An additional element, the Warburg impedance (Z_W), was incorporated to the equivalent circuit because of the mass-transfer limitations.

Percolation curve was performed by measuring the electrical resistance of the nanocomposites with a digital multimeter (Fluke, Everett, WA, USA). Microscopy images of carbon materials were obtained by High Resolution Transmission Electron Microscopy (HR-TEM) unit with an acceleration voltage of 120 kV. Topography images of the resulting carbon-based NC-CPgE surfaces were taken by Scanning Electron Microscopy (SEM), using a JEM-1400 unit with and QUANTA FEI 200 FEG-ESEM with an acceleration voltage of 15 kV.

Additional topographic and current measurements were performed by Current Atomic Force Microscopy (AFM) with a current sensing mode employing an Agilent 5500LS combined with a Resiscope and diamond doped DDESP tips. The surface roughness obtained by AFM was determined using the root-mean-square roughness (Rms) through a Gwyddion 2.47 software.

Kelvin Probe Force Microscopy (KPFM) data were obtained with a 5500LS SPM from Agilent Technologies in amplitude mode by applying an AC voltage (V_{AC}) plus a DC voltage (V_{DC}) to the sample. All the measurements were recorded with a platinum tip. The V_{CPD} values extracted for each electrode have been compared with a reference gold substrate.

Electrical characteristics were obtained in top-gate, bottom-contact geometry using an Agilent 5100A connected to the samples with a SÜSS probe station. The system was run on a PC using an Easy Expert software. The transfer and output characteristics were performed at ambient and dark conditions by confining 300 μ L of Milli-Q water on the interdigitated area with a PDMS pool where NC-CPgEs were submerged. Transfer measurements (which were taken per triplicate with three different electrodes ($n = 9$) and they are presented with their respectively 95% confident interval) were recorded in linear regime ($V_{DS} = -0.10$ V or -0.20 V) following Equation (2), where μ^{lin} is the charge-carrier field-effect mobility (in $\text{cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$) and C is the double layer capacitance per unit area.

$$I_{DS} = \mu^{lin} C \frac{W}{L} \left((V_{GS} - V_{TH}) V_{DS} - \frac{V_{DS}^2}{2} \right) \quad (2)$$

Importantly, NC-CPgEs were electrically characterized using the same device by following a random and different order of the electrodes employed to rule out any arbitrary factor (i.e., memory effects, polarized effects, bias stress or accumulated experimental errors) which could affect the properties of the transistor. Electrical experiments, which are represented with their corresponding error bars, were repeated using twenty-four different devices. In this way, both reproducibility and repeatability are evaluated.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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References

- [1] Y. Zang, D. Huang, D. Chong-an, D. Zhu, *Adv. Mater.* **2016**, 28, 4549.
- [2] C. Kotlowski, P. Aspermaier, H. U. Khan, C. Reiner-Rozman, J. Breu, S. Szunerits, J. J. Kim, Z. Bao, C. Kleber, P. Pelosi, W. Knoll, *Flex. Print. Electron.* **2018**, 3, 034003.
- [3] K. Takei, *Flexible and stretchable medical devices*; John Wiley & Sons, **2018**.
- [4] S. Riera-Galindo, A. Tamayo, M. Mas-Torrent, *ACS Omega* **2018**, 3, 2329.
- [5] S. G. Surya, H. N. Raval, R. Ahmad, P. Sonar, K. N. Salama, V. R. Rao, *TrAC - Trends Anal. Chem.* **2019**, 111, 27.
- [6] L. Torsi, M. Magliulo, K. Manoli, G. Palazzo, *Chem. Soc. Rev.* **2013**, 42, 8612.
- [7] X. Wu, S. Mao, J. Chen, J. Huang, *Adv. Mater.* **2018**, 30, 1705642.
- [8] R. Pfattner, A. M. Foudeh, S. Chen, W. Niu, J. R. Matthews, M. He, Z. Bao, *Adv. Electron. Mater.* **2019**, 5, 1800381.
- [9] G. Palazzo, D. De Tullio, M. Magliulo, A. Mallardi, F. Intranuovo, M. Y. Mulla, P. Favia, I. Vikholm-Lundin, L. Torsi, *Adv. Mater.* **2015**, 27, 911.
- [10] D. Wang, V. Noël, B. Piro, *Electronics* **2016**, 5, 9.
- [11] P. Seshadri, K. Manoli, N. Schneiderhan-Marra, U. Anthes, P. Wierzchowiec, K.

- Bonrad, C. Di Franco, L. Torsi, *Biosens. Bioelectron.* **2018**, *104*, 113.
- [12] Q. Zhang, F. Leonardi, S. Casalini, M. Mas-Torrent, *Adv. Funct. Mater.* **2017**, *27*, 1703899.
- [13] F. Leonardi, S. Casalini, Q. Zhang, S. Galindo, D. Gutiérrez, M. Mas-Torrent, *Adv. Mater.* **2016**, *28*, 10311.
- [14] T. Cramer, A. Campana, F. Leonardi, S. Casalini, A. Kyndiah, M. Murgia, F. Biscarini, *J. Mater. Chem. B* **2013**, *1*, 3728.
- [15] H. Sun, J. Gerasimov, M. Berggren, S. Fabiano, *J. Mater. Chem. C* **2018**, *6*, 11778.
- [16] L. Kergoat, B. Piro, M. Berggren, G. Horowitz, M. C. Pham, *Anal. Bioanal. Chem.* **2012**, *402*, 1813.
- [17] E. Macchia, K. Manoli, B. Holzer, C. Di Franco, M. Ghittorelli, F. Torricelli, D. Alberga, G. F. Mangiatordi, G. Palazzo, G. Scamarcio, L. Torsi, *Nat. Commun.* **2018**, *9*, 3223.
- [18] M. D. Angione, R. Pilolli, S. Cotrone, M. Magliulo, A. Mallardi, G. Palazzo, L. Sabbatini, D. Fine, A. Dodabalapur, N. Cioffi, L. Torsi, *Mater. Today* **2011**, *14*, 424.
- [19] M. Magliulo, A. Mallardi, M. Y. Mulla, S. Cotrone, B. R. Pistillo, P. Favia, I. Vikholm-Lundin, G. Palazzo, L. Torsi, *Adv. Mater.* **2013**, *25*, 2090.
- [20] M. Berto, C. Diacci, R. D'Agata, M. Pinti, E. Bianchini, M. Di Lauro, S. Casalini, A. Cossarizza, M. Berggren, D. Simon, G. Spoto, F. Biscarini, C. A. Bortolotti, *Adv. Biosyst.* **2018**, *2*, 1700072.
- [21] M. Y. Mulla, E. Tuccori, M. Magliulo, G. Lattanzi, G. Palazzo, K. Persaud, L. Torsi, *Nat. Commun.* **2015**, *6*, 6010.
- [22] S. Casalini, A. C. Dumitru, F. Leonardi, C. A. Bortolotti, E. T. Herruzo, A. Campana, R. F. De Oliveira, T. Cramer, R. Garcia, F. Biscarini, *ACS Nano* **2015**, *9*, 5051.
- [23] F. Leonardi, A. Tamayo, S. Casalini, M. Mas-Torrent, *RSC Adv.* **2018**, *8*, 27509.
- [24] M. Pumera, A. Merkoçi, S. Alegret, *Sensors Actuators, B Chem.* **2006**, *113*, 617.

- [25] J. Muñoz, M. Baeza, *Electroanalysis* **2017**, 29, 1660.
- [26] I. Švancara, K. Vytrás, K. Kalcher, A. Walcarius, J. Wang, *Electroanalysis* **2009**, 21, 7.
- [27] I. Svancara, K. Kalcher, A. Walcarius, K. Vytras, *Electroanalysis with carbon paste electrodes*; Crc Press: NW, **2012**.
- [28] J. Muñoz, R. Montes, J. Bastos-Arrieta, M. Guardingo, F. Busqué, D. Ruíz-Molina, C. Palet, J. García-Orellana, M. Baeza, *Sensors Actuators, B Chem.* **2018**, 273, 1807.
- [29] J. Muñoz, F. Leonardi, T. Özmen, M. Riba-Moliner, A. González-Campo, M. Mas-Torrent, M. Baeza, M. Mas-Torrent, *J. Mater. Chem. C* **2019**, 7, 14993.
- [30] J. Muñoz, J. Bartrolí, F. Céspedes, M. Baeza, *J. Mater. Sci.* **2014**, 50, 652.
- [31] J. Muñoz, R. Montes, M. Baeza, *TrAC - Trends Anal. Chem.* **2017**, 97, 201.
- [32] J. Muñoz, L. J. Brennan, F. Céspedes, Y. K. Gun'ko, M. Baeza, *Compos. Sci. Technol.* **2016**, 125, 71.
- [33] D. R. Crow, *Principles and applications of electrochemistry*; Routledge: London, **2017**.
- [34] B. A. Mei, O. Munteshari, J. Lau, B. Dunn, L. Pilon, *J. Phys. Chem. C* **2018**, 122, 194.
- [35] I. Temiño, F. G. Del Pozo, M. R. Ajayakumar, S. Galindo, J. Puigdollers, M. Mas-Torrent, *Adv. Mater. Technol.* **2016**, 1, 1600090.
- [36] Q. Zhang, F. Leonardi, S. Casalini, I. Temiño, M. Mas-Torrent, *Sci. Rep.* **2016**, 6, 39623.
- [37] S. Fabiano, S. Braun, M. Fahlman, X. Crispin, M. Berggren, *Adv. Funct. Mater.* **2014**, 24, 695.
- [38] M. Singh, M. Y. Mulla, M. V. Santacroce, M. Magliulo, C. Di Franco, K. Manoli, D. Altamura, C. Giannini, N. Cioffi, G. Palazzo, G. Scamarcio, L. Torsi, *J. Phys. D. Appl. Phys.* **2016**, 49, 275101.
- [39] M. Singh, K. Manoli, A. Tiwari, T. Ligonzo, C. Di Franco, N. Cioffi, G. Palazzo, G. Scamarcio, L. Torsi, *J. Mater. Chem. C* **2017**, 5, 3509.
- [40] F. G. Del Pozo, S. Fabiano, R. Pfattner, S. Georgakopoulos, S. Galindo, X. Liu, S.

Braun, M. Fahlman, J. Veciana, C. Rovira, X. Crispin, M. Berggren, M. Mas-Torrent, *Adv. Funct. Mater.* **2016**, *26*, 2379.

- [41] J. Muñoz, J. Bastos-Arrieta, M. Muñoz, D. Muraviev, F. Céspedes, M. Baeza, *J. Mater. Sci.* **2016**, *51*, 1610.

Scheme 1. Schematic representation of the WGOFET setup employing the four types of carbon filler in the NC-CPgEs from 0D to 3D (inset: HR-TEM images of the employed carbon materials). Au-based *S* and *D* electrodes were deposited through thermal evaporation and diF-TES-ADT:PS thin film layer was incorporated as the OSC film.

Figure 1. BSE images obtained by SEM of A) 0D-, B) 1D-, C) 2D- and D) 3D-NC-CPgEs.

Figure 2. Electrochemical characterization *via* (A) CV and (B) EIS employing the four different NC-CPgEs. Au and GCE were used for comparison. Measurements were carried out in a three-electrode configuration using a 0.1 M KCl solution containing 10 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ as the redox probe.

Figure 3. A) $I-V$ transfer characteristic obtained at the same WGO-FET device using the four types of NC-CPgEs and compared with conventional GCE and Au electrodes ($V_{DS} = -0.2$ V) and B) the hysteresis extracted from the forward and return (inset) $I-V$ transfers. Influence of the C) electroactive area and D) ohmic resistance (inset: influence of the composition ratio) on the threshold voltage of the different NC-CPgEs (inclusion of Au and GCE for comparison).

Table 1. Summary of the composition ratio and the morphological (AFM) and electrochemical (CV and EIS) properties of the four NC-CPgEs investigated and of two conventional electrodes (Au and GCE). NOTE: the numbers in parentheses denote the standard deviation of the sample.

Tool / Electrode	Composition	AFM	CV			EIS			
	NPC	R_{ms}	I_p	ΔE	A	R_Ω (Ω)	R_{CT}	C_{dl}	χ^2
	(w/w)	(nm)	(μA)	(V)	(cm^2)		(Ω)	(μF)	
0D-NC-CPgE	6% in CNHs	268(31)	329(21)	0.30(.03)	0.28(.01)	288(44)	41(12)	31(9)	0.011(5)
1D-NC-CPgE	10% in CNTs	297(66)	296(26)	0.25(.01)	0.25(.01)	245(13)	97(15)	11(7)	0.06(2)
2D-NC-CPgE	13% in rGO	228(67)	283(17)	0.58(.03)	0.24(.01)	197(18)	225(18)	79(6)	0.13(4)
3D-NC-CPgE	16% in G	283(98)	321(22)	0.21(.01)	0.27(.01)	151(20)	115(3)	20(5)	0.18(2)
GCE	-	-	269(24)	0.14(.02)	0.23(.01)	54(5)	120(4)	2(1)	0.12(1)
Au	-	-	278(19)	0.11(.01)	0.23(.01)	35(3)	43(1)	4(1)	0.07(3)

Table 2. Electrical characteristics extracted in the linear regime of the WGOFET employing the four different NC-CPgEs and compared with two conventional electrodes (GCE and Au). NOTE: the numbers in parentheses denote the standard deviation of the sample.

Electrode	V_{TH} (V)	σ (μS)
0D-NC-CPgE	-0.14(.06)	6.8(3.5)
1D-NC-CPgE	-0.17(.06)	6.7(3.4)
2D-NC-CPgE	-0.22(.04)	7.5(2.6)
3D-NC-CPgE	-0.28(.03)	6.7(3.4)
GCE	-0.06(.04)	6.9(2.5)
Au	-0.02(.03)	6.4(3.8)