

## Electronic Supporting Information

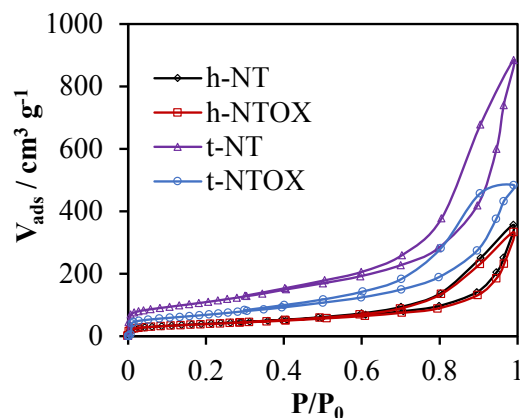
### EFFECT OF SURFACE CHEMISTRY AND STRUCTURE OF CARBON NANOTUBES ON THE COATING OF GLUCOSE OXIDASE AND ELECTROCHEMICAL BIOSENSORS PERFORMANCE

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#### *S.1.1 Physicochemical characterization*

Fig. S1 shows the N<sub>2</sub> adsorption isotherms for the h-NT and t-NT (with and without oxidation treatment). All materials present type II isotherms with a hysteresis loop. The surface area in these nanostructured materials is mainly defined by their external surface area, but they also have the contribution of the porosity generated by the empty spaces between the tubes.



**Fig. S1** N<sub>2</sub> adsorption isotherms at -196 °C of h-NT, h-NTOX, t-NT and t-NTOX

Table S1 presents the atomic composition of the samples obtained by XPS. Pristine carbon nanotubes are composed mainly by carbon, with a very small amount of oxygen in their structures. The oxidized materials show an increase in the amount of oxygen, due to the oxidation treatment. As it was expected, the herringbone structure of the h-NT with higher amount of defects in the edges allows the higher oxidation degree, evidenced in a higher oxygen content of the h-NTOX. Finally,

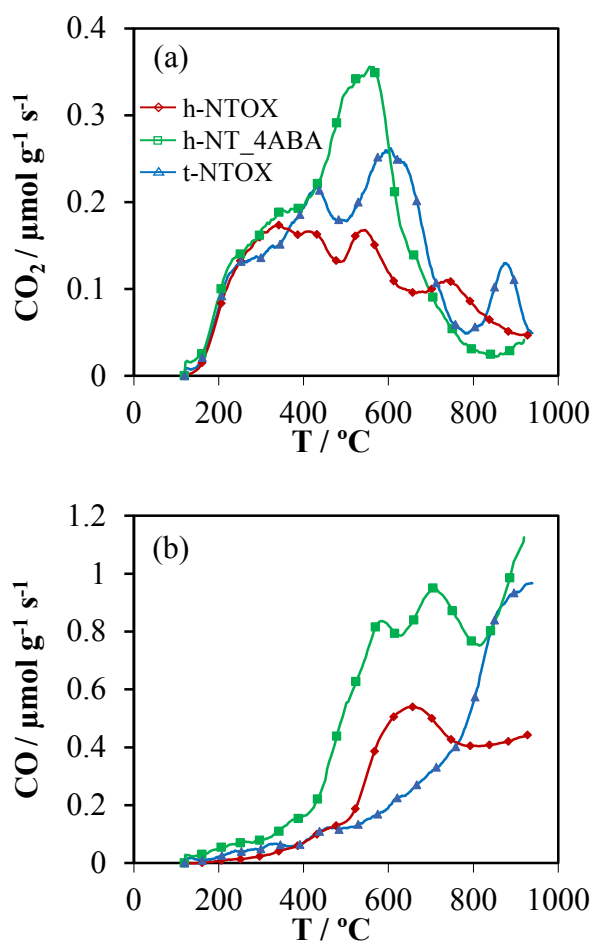
electrochemical functionalization of NT with 4-ABA results in an increase in the oxygen and nitrogen contents. The oxygen content is higher than for the oxidized samples, which is attributed to the electrochemical oxidation as well as the inclusion of the 4-ABA molecule that contains a carboxylic group in its structure. Additionally, 2.3 at.% is found in these samples, related to the 4-ABA functionalities, and the N1s spectrum reveals that the anchorage of the molecule was through the amino group of the 4-ABA molecule.

**Table S1** Atomic composition of the samples obtained by XPS

Sample	C / at. %	O / at. %	N / at. %
<b>h-NT</b>	99.3	0.7	--
<b>h-NTOX</b>	94.2	5.8	--
<b>h-NT4ABA</b>	83.5	14.2	2.3
<b>t-NT</b>	98.1	1.9	--
<b>t-NTOX</b>	96.6	3.4	--

Fig. S2 shows the CO and CO<sub>2</sub> evolution profiles for all samples. The evolution of CO is related to the decomposition of neutral and basic groups such as carbonyl, quinones, phenols and ethers. Likewise, CO<sub>2</sub> evolution is mainly associated to the decomposition of carboxylic, anhydrides and lactones groups. In the case of 4-ABA modified CNTs, previous studies has demonstrated that the obtained functionalities decompose thermally at around 400-500 °C producing the release of CO<sub>2</sub> due to the cleavage of the carboxylic acid found in the starting 4-ABA.

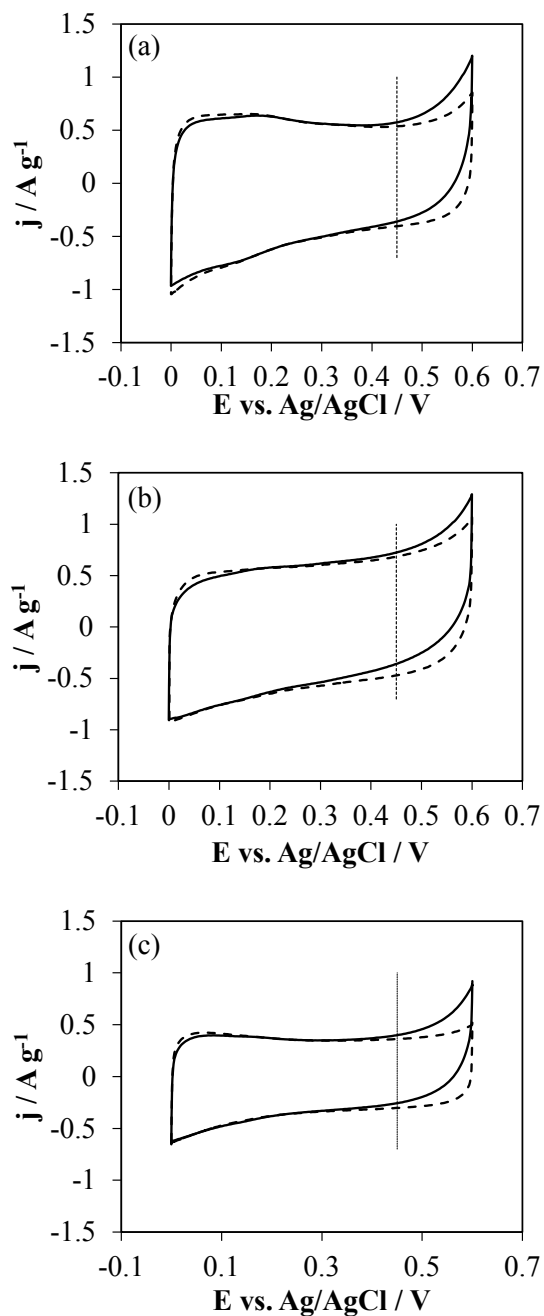
The CO<sub>2</sub>-TPD profiles in Fig. S3a confirm the presence of anhydrides (desorption in the 400 - 600° C range) and lactones (600 - 800 °C range) in the original h-NT sample, and the generation of a small amount of carboxylic acid moieties (200 - 400 °C range) after the mild HNO<sub>3</sub> treatment <sup>1,2</sup>, which ensures the preservation of the h-NT structure and the valuable electrical properties derived from it. In the case of the t-NTOX, it seems that the formation of anhydrides is favored, a difference that could be caused by the longer functionalization time employed for the HNO<sub>3</sub> treatment. The h-NT\_4ABA sample also shows a desorption peak at low temperatures, starting in 200°C, which is attributed to the carboxylic groups generated during the electrooxidation. Additionally, a desorption peak at slightly higher temperatures (450 - 500 °C) can be seen in this sample. It has been associated with the decomposition of the carboxylic acid from the ABA oligomers attached to the carbon surface <sup>3</sup>.



**Fig. S2** (a) CO and (b) CO<sub>2</sub> TPD profiles of h-NTOX, h-NT\_4ABA and t-NTOX

The CO desorption profiles are shown in Fig. S3b. The CO evolution seen at temperatures higher than 600 °C for h-NTOX and t-NTOX points out the existence of phenols (thermal decomposition at temperatures between 650 - 750 °C) and quinones/carbonyls (which desorbs as CO at temperatures higher than 800°C) groups in these samples<sup>1,2</sup>, with a larger amount of the latter in the case of t-NTOX. The nitric acid treatment seems to remove these metal traces, as depicted by the decrease in CO evolution observed at that temperature. In the case of the h-NT\_4ABA sample, a slight increase of CO evolution is observed in all the temperature range. This can be attributed to the presence of anhydride groups which decompose as CO and CO<sub>2</sub> at temperatures lower than 600 °C, and also to the formation of CO-evolving functions, which is known to occur during electrochemical oxidation of carbon materials<sup>3,4</sup>.

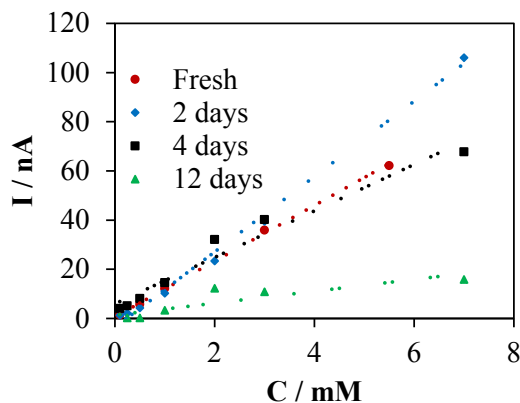
### S.3.2.2. Sensitivity towards glucose oxidation



**Fig. S3** Cyclic voltammograms for electrodes (a) h-NTOX-G6.3, (b) t-NTOX-G6.3 and (c) h-NT4ABA-G6.3 in 0.1 M PBS solution in absence (dashed line) and in presence of 3 mM  $\text{H}_2\text{O}_2$  (solid line)

The stability of the electrodes was tested at different times after their preparation. The electrodes were prepared at the same time under the same conditions. The sensitivity to glucose detection was studied at different times since the preparation of the electrode. One electrode was analyzed the day of its preparation, applying 0.45 V as working potential. The electrodes that

were not tested were stored at 4 °C, then they were tested after 2, 4 and 12 days. Fig. S5 shows the calibration curves for h-NTOX-G3.1 electrodes and Table S2 presents the values of the sensitivity and correlation coefficient obtained from these experiments. It is possible to observe that the electrodes freshly prepared and until 4 days of preparation did not show a significant variation in the same working range, with good correlation coefficients. In the case of the electrode tested after 12 days, the sensitivity decreases 78.6 % compared to the initial activity.

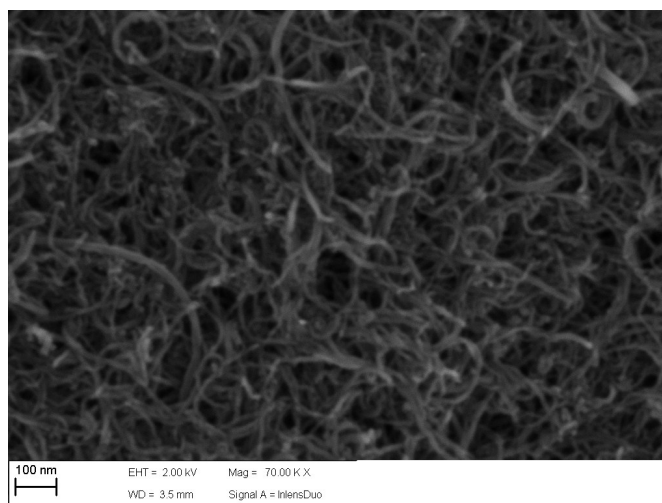


**Fig. S4** Calibration curves of h-NTOX-G6.3 tested at different times from their preparation

**Table S2** Sensitivity, correlation coefficient and working range from chronoamperometric experiments at 0.45 V of different electrodes tested in different times from their preparation

Sample	Sensitivity nA mM <sup>-1</sup>	Correlation coefficient R <sup>2</sup>	Working range (mM)
h-NTOX-G6.3 Fresh	11.3	0.999	1 – 7
h-NTOX-G6.3 After 2 days	15.3	0.995	1 – 7
h-NTOX-G6.3 After 4 days	9.45	0.960	1 – 7
h-NTOX-G6.3 After 12 days	2.42	0.778	1 – 7

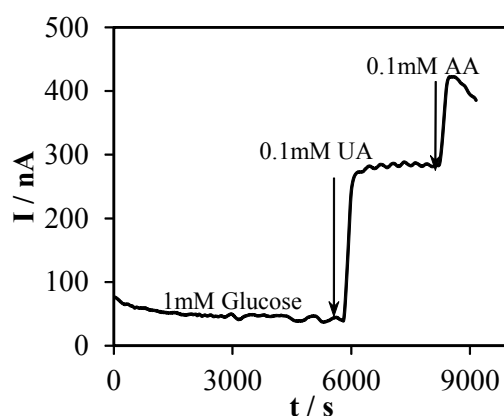
Fig. S5 displays FE-SEM image of the pristine multiwall carbon nanotubes (t-NTOX) for comparison purposes.



**Fig. S5** FE.SEM images of t-NTOX

### S.3.3.3. Interference study

The evaluation of the effect of the presence of different interferents was also performed in these biosensors. Fig. S6 presents the chronoamperometric experiments with the addition of uric (UA) and ascorbic acids (AA) using a working potential of 0.45 V. The experiments show clear interferences with the two analytes, attributed to the high potential used during the measurements. Experiments performed at -0.4 V did not show any interference problems with these two analytes.



**Fig. S6** Chronoamperometric response to successive additions of uric acid (UA) and ascorbic acid (AA) into an initial concentration of 1 mM of glucose of h-NTOX modified electrode at 0.45V

## REFERENCES

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