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Supporting Information

CNT/Al_2O_3 core-shell nanostructures for the electrochemical detection of dihydroxybenzene isomers

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Water samples analysis.

The developed sensor, fabricated and stored in room temperature in a dry and dark place, was used for the monitoring of DHB isomers in water samples. To account for any matrix effect occurring from the water samples, standards were prepared using tap-water and mineral-water. The collected water samples are used without pretreatment; 0.1 M PBS was used to maintain the pH at pH = 7.4.

Preliminary tests have confirmed that no sensor responses corresponding to DHB isomers were observed. The standard addition method has been then used for the accurate determination of DHB isomers in this present study, adding know amounts of HQ, CC and RS to the real sample water solutions and the respective SWVs were recorded in five replicate measurements for each addition. The tests of the real water samples were done in the lab at room temperature (25±1°C). Table 2 shows sensing measurement results taken from the sensor with their known spiked concentrations.

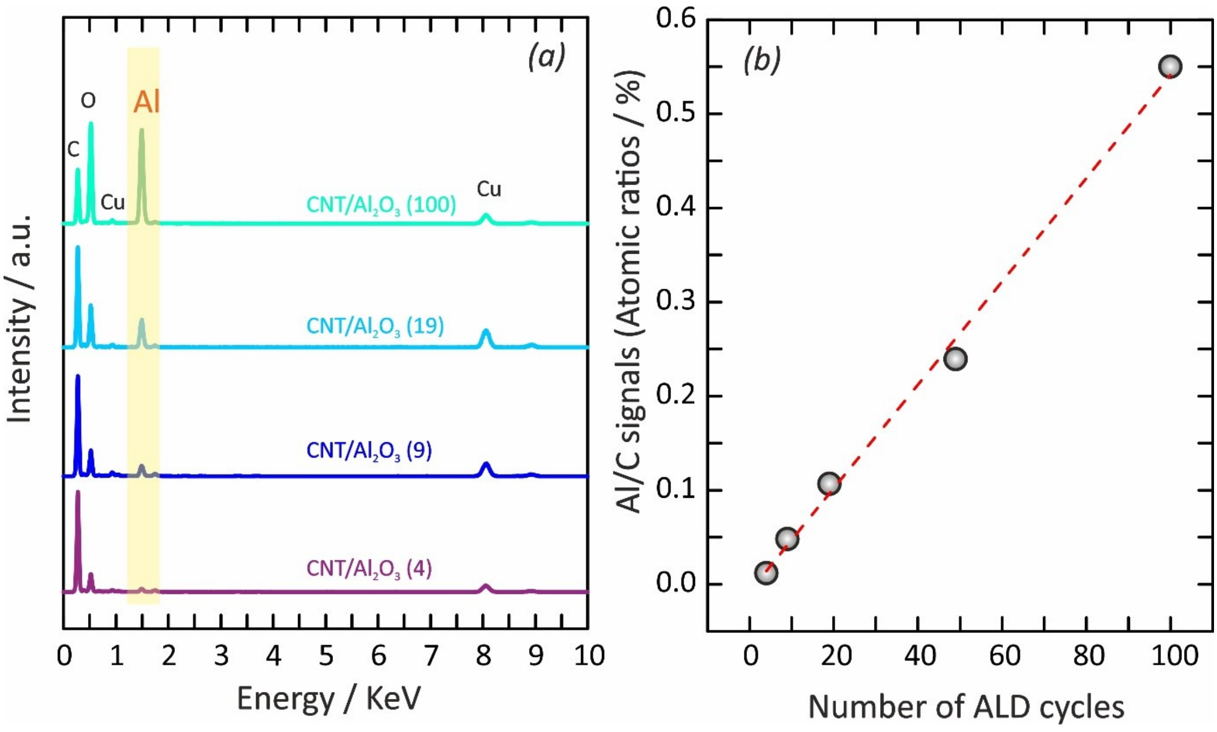

Figure S1. *(a) The energy dispersive X-ray (EDX) spectra's for the elemental mappings in Figure 3 for CNT/*Al_2O_3 *core-shell heterostructures, (b) Al-C signals ratios (%) to the number of ALD cycles, showing a linear increase of the aluminium contents with the number of ALD cycles in the CNT/*Al_2O_3 *heterostructures.*

Table S1. Atomic ratios of elements of interest for the EDX spectra shown in Figure S1.

Samples	**Atomic Fraction (%) Al, O, C**	**Atomic Error (%) Al, O, C**	**Fit Error (%) Al, O, C**	**Al/O atomic ratio**
CNT/Al_2O_3 (4)	1.05, 9.39, 89.56	0.21, 1.92, 3.81	0.45, 1.43, 0.90	0.12
CNT/Al_2O_3 (9)	4.03, 11.84, 84.13	0.84, 2.51, 6.14	1.69, 1.93, 2.92	0.34
CNT/Al_2O_3 (19)	8.23, 17.70, 74.07	1.77, 3.88, 6.20	0.86, 3.31, 0.59	0.46
CNT/Al_2O_3 (49)	13.93, 27.81, 58.26	3.25, 6.55, 7.26	0.83, 0.67, 0.36	0.50
CNT/Al_2O_3 (100)	23.68, 33.27, 43.05	6.05, 8.60, 6.97	1.41, 2.66, 1.29	0.71

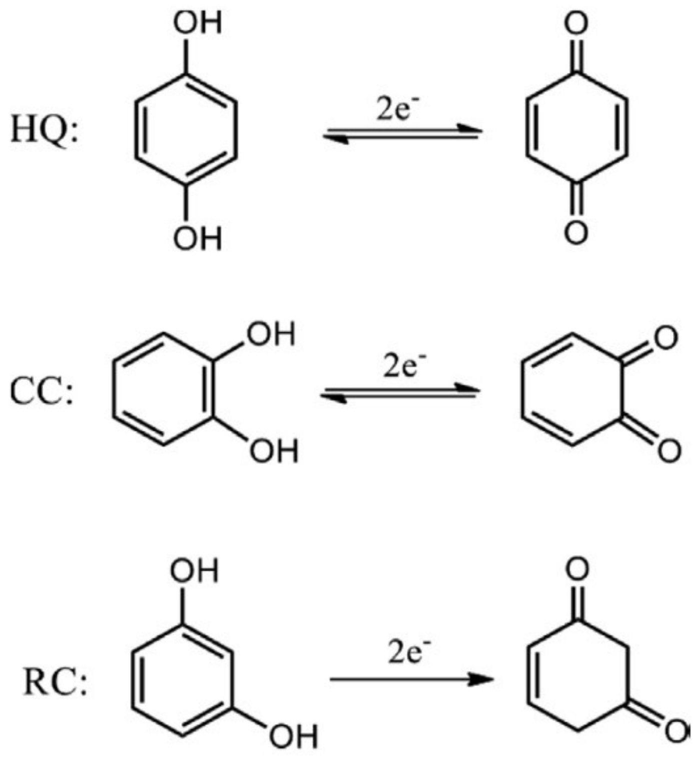

Figure S2. *Electrochemical redox reactions for the three DHB isomers. S. Meng, Y. Hong, Z. Dai, W. Huang, and X. Dong, ACS Appl.Mater. Interfaces,9, 12453–12460 (2017).*

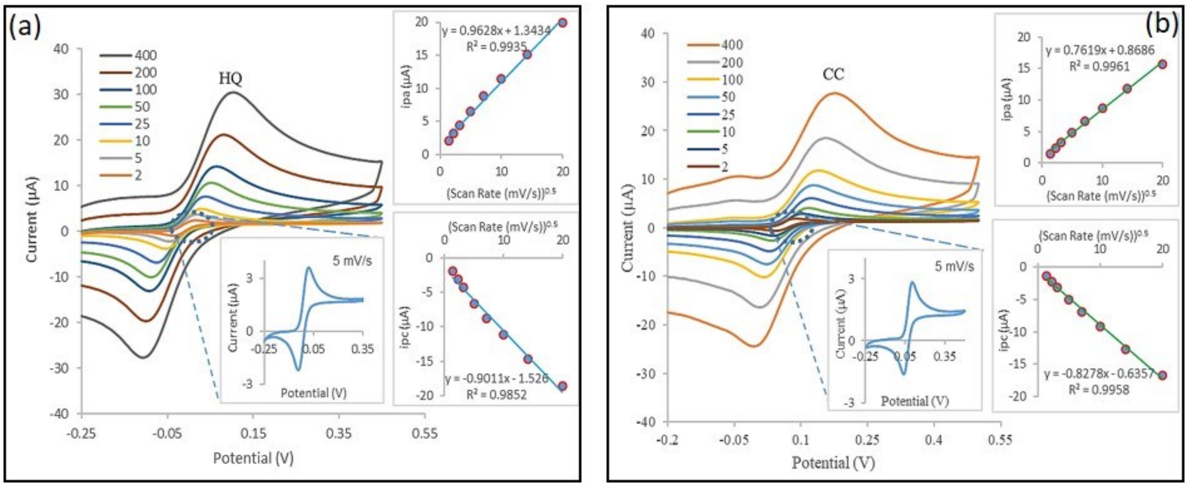

Figure S3. *Cyclic voltammograms of CNT/Al_2O_3(9)-SPCE in a solution containing 100 µM (a) HQ and (b) CC in PBS at pH=7.4 at scan rates from 2 to 400 mV/s. Insets depict the variation of the baseline corrected anodic peak currents (Ipa) and cathodic peak currents (Ipc) versus the square rate of scan rate.*

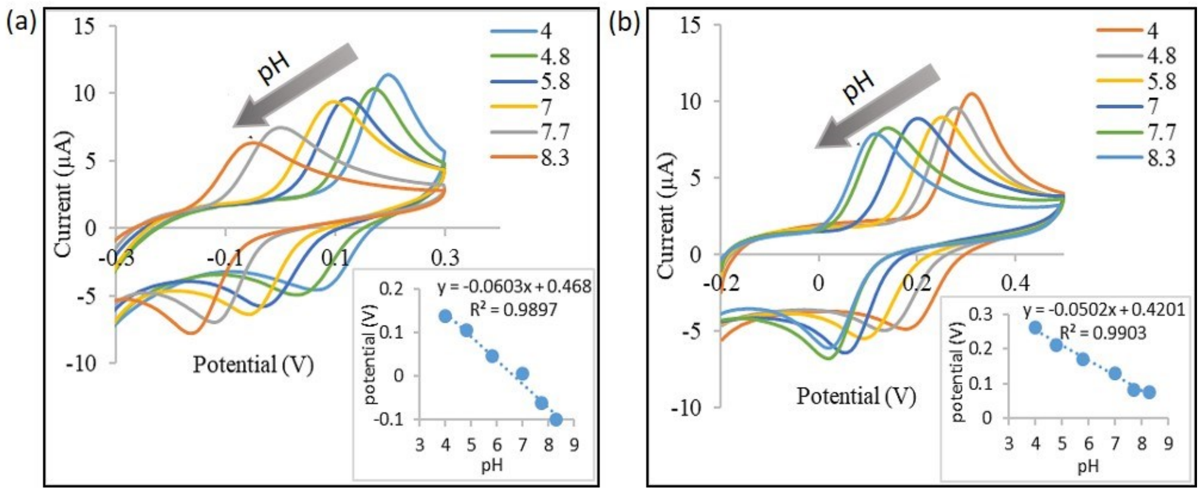

Figure S4. *Cyclic voltammograms for a 200 µM solution of (a) HQ and (b) CC at pHs between 4 and 8.3 using SPCE-CNT/Al_2O_3 (9)-SPCE. Scan rate: 20 mV/s. Insets plots show the variation of the oxidation peak potentials of HQ and CC as a function of pH.*

Table S2. *Performance of the proposed sensor in comparison to previously reported metal oxide based electrochemical sensors for DHB isomers measurements.*

Sensing material	**Overall Linear Range (μM)**			**LOD (μM)**			**Method**	**Real sample**
	HQ	CC	RS	HQ	CC	RS		
Co_3O_4@carbon core/shell nanostructured[1]	0.8-127.1	0.6-116.4	-	0.03	0.03	-	DPV	River water
Mesoporous carbon /CeO_2 composite[2]	0.5–500	0.4–320	-	0.24	0.13	-	DPV	Tap water and lake water
Fe_3O_4 functionalized graphene oxide-gold nanoparticle[3]	2-145	3-137	-	1.1	0.8	-	Amperometry	Tap water
AuNPs/RGO/WO_3 nanocomposite[4]	0.1-10	0.1-10	-	0.036	0.020	-	DPV	River water
Carbon nanofibers–Sm_2O_3 nanocomposite[5]	1-500	1-500	-	0.09	0.07	-	DPV	Tap water and lake water
CuO/carbon nanofragment[6]	3-80	6-150	-	1	2	-	DPV	River water
CNT/TiO_2 nanoparticles[7]	0.4-276.0	0.4-159.0	3.0–657	0.06	0.07	0.52	DPV	River water
NiO/CNT nanocomposite[8]	10-500	10-400	-	2.5	2.5	-	DPV	Tap water
nitrogen-doped MWCNTs modified/nickel nanoparticles[9]	0.3-300	0.1-300	-	0.011	0.009	-	DPV	Pond, tap and river water samples
CNT/Al_2O_3* *This work	*2.0-1000*	*0.5-700*	*3.5-500*	*1.2*	*0.3*	*2.7*	*SWV*	*Tap water and mineral water*

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