Electronic Supplementary Information

Carbon Nanotube-Templated Synthesis of Covalent Porphyrin Network for Oxygen Reduction Reaction.

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Synthesis and representation of the physisorbed MWNT/CoP hybrid.

MWNT/CoP hybrid. A suspension of 15 mg of porphyrin **3** (5,10,15,20-Tetrakis[(trimethylsilyl)ethynyl]porphyrinato Co(II)) and MWNTs (10 mg) in THF (15 ml) were sonicated with sonic bath 160 W max for 35 min (100% for 5 min and then 60% for 30 min). The THF was evaporated with nitrogen stream and the resulting solid was used to prepare the ink as described in the experimental section "***ORR experiments. Sample preparation***"

Estimation of the number of carbon atoms in a 1 nm section of nanotube.

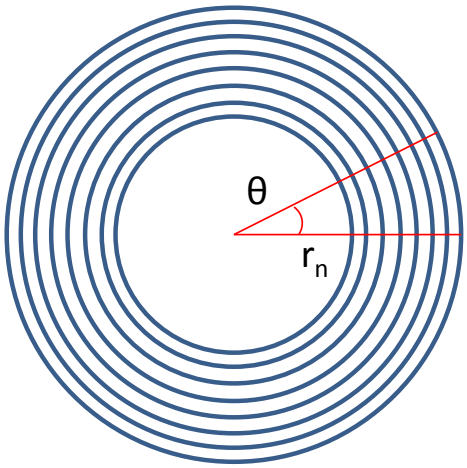
First, we determined by molecular modeling using HyperChem 8.0 software that a tetraethynylporphyrin has an area of 1 nm^2. So for the estimation of the number of carbon atoms, we assume that one porphyrin occupies an arc of 1 nm of the outer shell on a length of 1 nm of nanotube. The outer diameter is 9.5 nm (average diameter from Nanocyl); by TEM, we estimated that the average number of walls in the nanotubes is 8 (each walls being separated of 0.34 nm). In graphene, 1 nm^2 contains 40 carbon atoms.

diameter r_n (nm)	Area[a] (nm^2)	Nb of carbon
9.50	1	40
9.16	0.96	38
8.82	0.93	37
8.48	0.89	36
8.14	0.85	34
7.80	0.82	33
7.46	0.78	31
7.12	0.75	30

[a] Area = $Arc_n \cdot$length; with length = 1 nm and $Arc_n = r_n \cdot \theta$.

$\theta = 1/9.5 = 0.105$ rad (~6°)

The total carbon represents 280 atoms for 1 porphyrin.



For the outer shell:
Arc = 1 nm

$Arc_n = r_n \cdot \theta(rad)$

Figure S1. Representation of the geometry of a 9.5 nm diameter MWNT containing 8 walls.

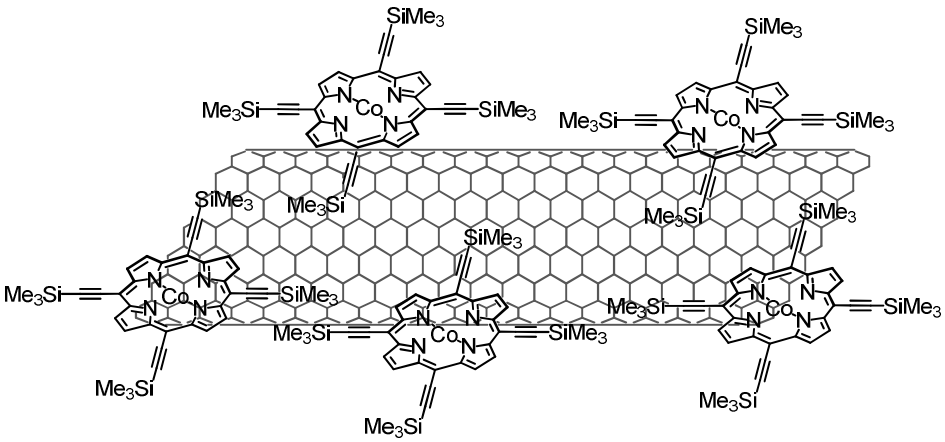


Figure S2. Representation of the physisorbed MWNT/CoP hybrid.

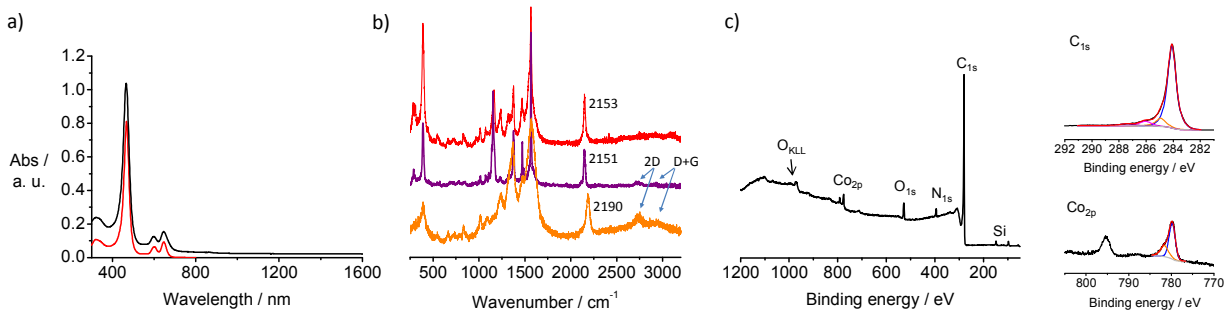


Figure S3. a) Absorption spectra of the physisorbed MWNT/CoP hybrid (in black) and of *meso*-tetra(trimethylsilylethynyl)-porphyrinato cobalt (II) 3 (in red) in NMP. b) Raman spectra of MWNT/CoP hybrid (purple) and of MWNT-CoP **1** (orange) and CoP monomer **3** (red), for comparison. The position of the bands corresponding to the stretching mode of the triple bonds is given in cm^{-1}. c) XPS spectrum of the physisorbed MWNT/CoP hybrid and deconvoluted XPS core level spectra of carbon C_{1s}, and Co_{2p}.

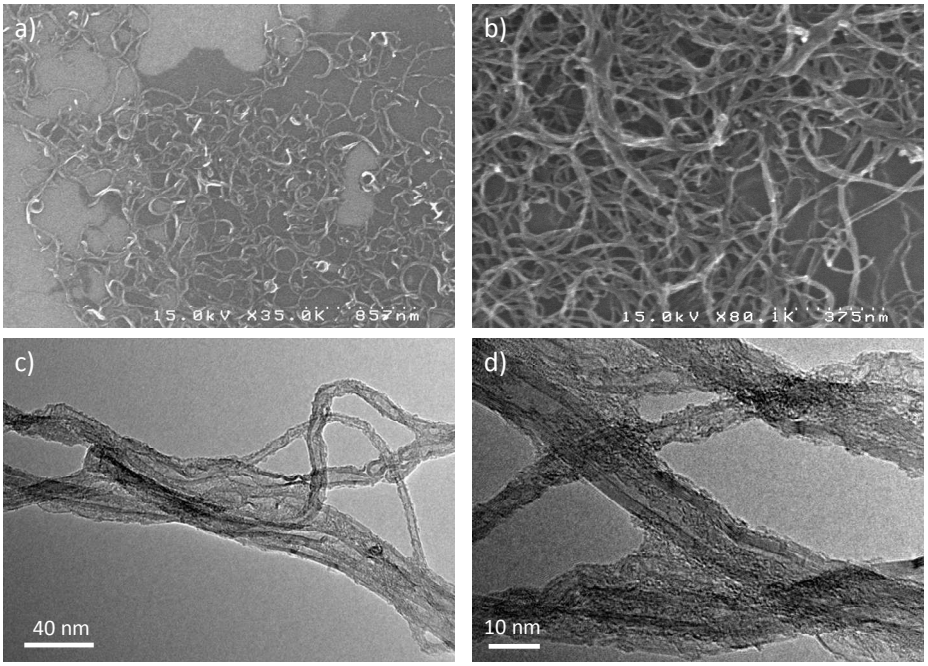


Figure S4. SEM (a-b) and TEM (c-d) micrographs of the physisorbed MWNT/CoP hybrid. SEM images show that upon drying the porphyrins form a puddle on the surface around the nanotubes. Conversely to MWNT-CoP **1**, in the physisorbed hybrid, the porphyrins are not bound to each other around the nanotubes. The TEM images show the presence of a thin and discontinuous layer of porphyrins around the nanotubes.

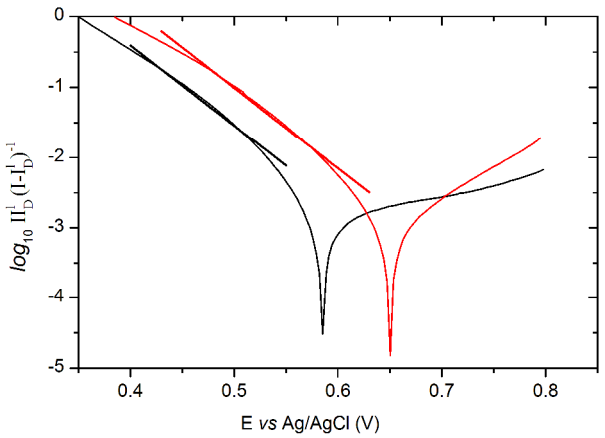


Figure S5. Mass transfer corrected Tafel plots Log_{10} ($I_D II^{-1} I_D^{-1}$) *vs* potential for predeposited MWNT-CoP **1** (red) and physisorbed MWNT/CoP (black) catalysts on GC. The polarization curves have been recorded at 400 rpm in O_2-saturated 0.5 M H_2SO_4 solution (scan rate = 5 $mV.s^{-1}$, 25°C). The loading is 155 $\mu g.cm^{-2}$, which corresponds to the same amount (17 nmol) of porphyrins in both samples. I^l_D = experimental diffusion limited current. The fittings of the linear parts in figure S5 lead to a ratio of 3.6 between the exchange currents of the MWNT-CoP **1** and the MWNT/CoP.

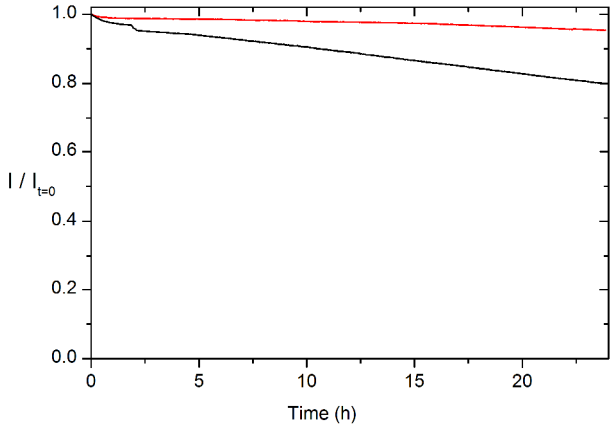


Figure S6. Normalized chronoamperometry recorded for ORR in O_2-saturated 0.5 M H_2SO_4 solution (rotating speed 60rpm, 25°C) on GC with predeposited MWNT-CoP 1 (red line) and physisorbed MWNT/CoP (black line). The loading is 155 $\mu g.cm^{-2}$. Ew=0.2 V *vs* Ag/AgCl. The recording started after stabilization at 0.2 V *vs* Ag/AgCl for 10 min.

Table S1 Summary of the XPS data for C_{1s}, N_{1s} and Co_{2p}.

Compound	Binding energy eV (area CPS·eV)	Number of porphyrin[a]
MWNT-CoP **1**	C_1 284.0 (8735)	
	C_2 284.8 (3546)	
	C_3 286.0 (1991)	
	C_4 287.6 (1796)	
	C_{tot} (16068)	
	N_{1s} 398.4 (1312)	1 CoP for 90 C
	$Co_{2p3/2}$ 780.5 (1528)	1 CoP for 130 C
MWNT/CoP physisorbed	C_1 284.1 (13064)	
	C_2 284.9 (1537)	
	C_3 286.0 (960)	
	C_4 287.5 (601)	
	C_{tot} (16162)	
	$Co_{2p3/2\ tot}$ (1509)	1 CoP for 135 C

[a]Scofield factor used for the calculation: C_{1s}=1; N_{1s}=1.8; $Co_{2p3/2}$=12.62; for Al Kα X-rays; estimated with the ratio (corrected by the Scofield factor) $C_{tot}/0.25N_{1s}$ and $C_{tot}/Co_{2p3/2}$.