energies

MDPI

Supplementary Materials

CO_2 Electrochemical Reduction by Exohedral N-Pyridine Decorated Metal-Free Carbon Nanotubes

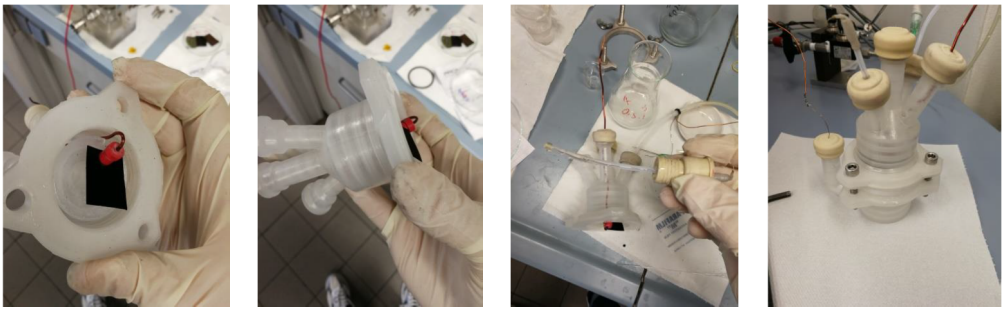

Figure S1. Home-made 3D-printed *ABS* [1] three-electrode cell operating in a 0.1 M $KHCO_3$ solution, equipped with an [Ag][AgCl][KCl_{sat}] reference electrode, a Pt counter electrode and a gas collector cone on the top for the sampling of the produced volatiles. These photos are reproduced from Ref. [2] with permission from The Royal Society of Chemistry.

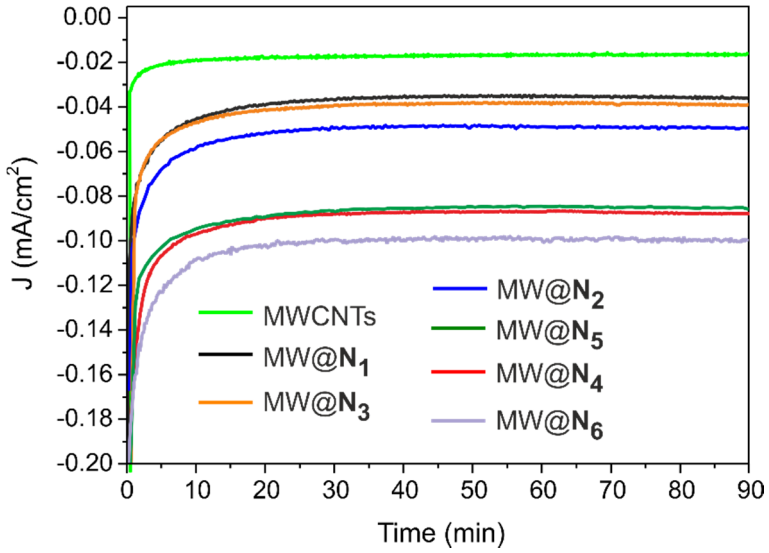

Figure S2. Total current density values (J_{tot}) and their stability vs. time, measured for each electrocatalytic material MW@$N_{1\text{-}6}$ at the potential value where they present the highest FE_{CO}.

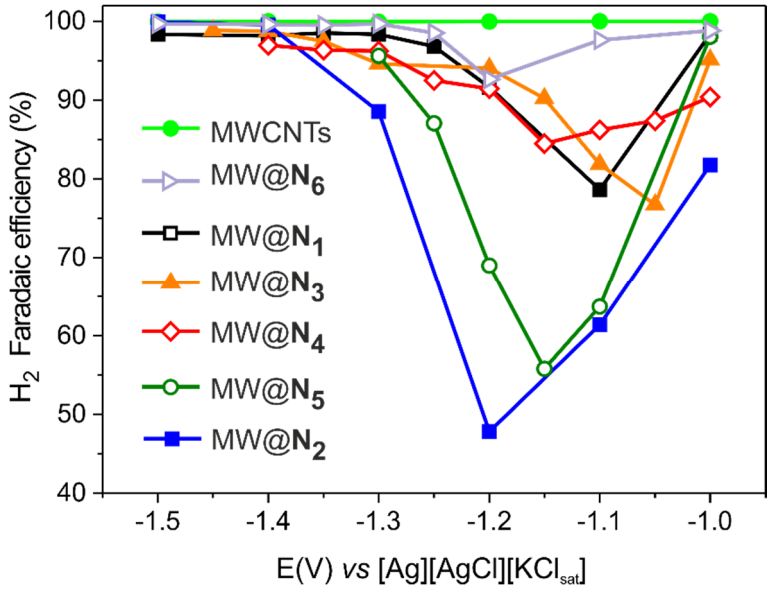

Figure S3. H_2 faradaic efficiency as a function of the applied potential (−1.0 ÷ −1.5 V range).

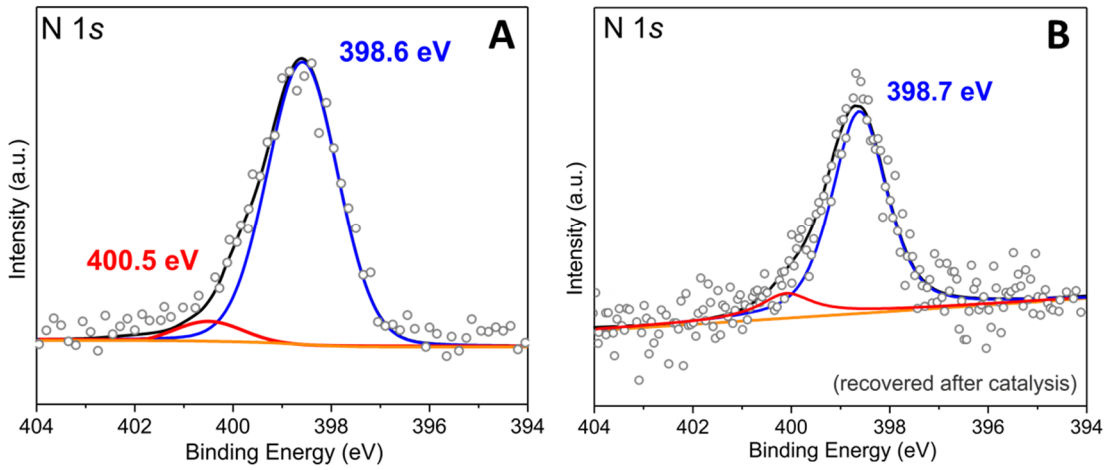

Figure S4. N 1s core regions and relative fits for the high resolution XPS spectrum of MW@N_2 before (A) and after (B) CO_2RR. Sample B has been recovered from MW@N_2/Cc after 90 min of electrocatalytic run.

Table S1. J_{tot}, J_{CO}, CO and H_2 faradaic efficiency (FE) and productivity as obtained with MW@**N**$_{1\text{-}6}$/Cc and MWCNT/Cc as electrodes at different potential values: (a) −1.1 V, (b) the V value where each electrocatalyst offers the highest FE_{CO} (ranging from −1.05 to −1.2 V) and (c) the highest potential values (up to −1.5 V) applied to the electrochemical cell. Electrolysis time were comprised between 1.5–2 h and 0.5 h, for tests in (a–b) and (c) respectively, using a 0.1 M $KHCO_3$ solution as electrolyte.

Entry	Electrode	*E* (V)	*N*%[a]	$\lvert J_{tot}\rvert$ (mA cm^{-2})	FE_{CO} (%)	$\lvert J_{CO}\rvert$ (mA cm^{-2})	Prod. $NL^{CO}g_N^{-1}h^{-1}$	FE_{H2} (%)	Prod. $NL^{H2}g_N^{-1}h^{-1}$
1	MWCNT/Cc	−1.10	-	0.01	-	-	-	100	0.05[b]
2	"	−1.20	-	0.02	-	-	-	100	0.1[b]
3	"	−1.50	-	4.15	-	-	-	100	1.2[b]
4	MW@N_1/Cc	−1.10	1.49	0.04	21.4	0.009	0.18	78.6	0.65
5	"	−1.50	"	3.27	1.7	0.055	1.25	98.3	271.0
6	MW@N_2/Cc	−1.10	1.28	0.04	38.7	0.015	0.48	61.3	0.76
7	"	−1.20	"	0.05	52.2	0.026	0.70	47.8	0.64
8	"	−1.50	"	6.00	0.1	0.006	0.11	99.9	168.7
9	MW@**N**$_3$/Cc	−1.05	1.09	0.05	23.3	0.012	0.48	76.7	1.57
10	"	−1.10	"	0.06	18.1	0.011	0.47	81.9	2.13
11	"	−1.45	"	2.54	1.1	0.028	1.25	98.9	112.4
12	MW@**N**$_4$/Cc	−1.10	1.75	0.05	13.8	0.007	0.15	86.2	0.93
13	"	−1.15	"	0.09	15.5	0.014	0.27	84.5	1.49
14	"	−1.40	"	1.02	3.7	0.037	0.75	96.3	19.4
15	MW@**N**$_5$/Cc	−1.10	1.24	0.08	36.3	0.029	0.68	63.7	1.19
16	"	−1.15	"	0.09	44.2	0.040	0.96	55.8	1.21
17	"	−1.30	"	0.35	4.4	0.015	0.37	95.6	8.04
18	MW@**N**$_6$/Cc	−1.10	2.69	0.03	2.4	0.001	0.01	97.6	0.38
19	"	−1.20	"	0.10	7.3	0.007	0.08	92.7	1.04
20	"	−1.50	"	2.08	0.3	0.006	0.08	99.7	26.1

[a] Average value determined from elemental analysis and acid-base titrations (if applicable) on each material (see Table 1 on the manuscript). [b] Expressed as NL^{H2} *per* g of catalyst *per* h; no N is present in pristine MWCNTs.

References

1. *ABS* (Acrylonitrile-Butadiene-Styrene) is a common base-resistant thermoplastic polymer for 3D-printing.
2. Tuci, G.; Filippi, J.; Ba, H.; Rossin, A.; Luconi, L.; Pham-Huu, C.; Vizza, F.; Giambastiani, G.; How to Teach an Old Dog New (Electrochemical) Tricks: Aziridine-Functionalized CNTs as Efficient Electrocatalysts for the Selective CO_2 Reduction to CO. *J. Mater. Chem. A* **2018,** *6*, 16383–16389.