How to Teach an Old Dog New (Electrochemical) Tricks: Aziridine-Functionalized CNTs as Efficient Electrocatalysts for the Selective CO_2 Reduction to CO

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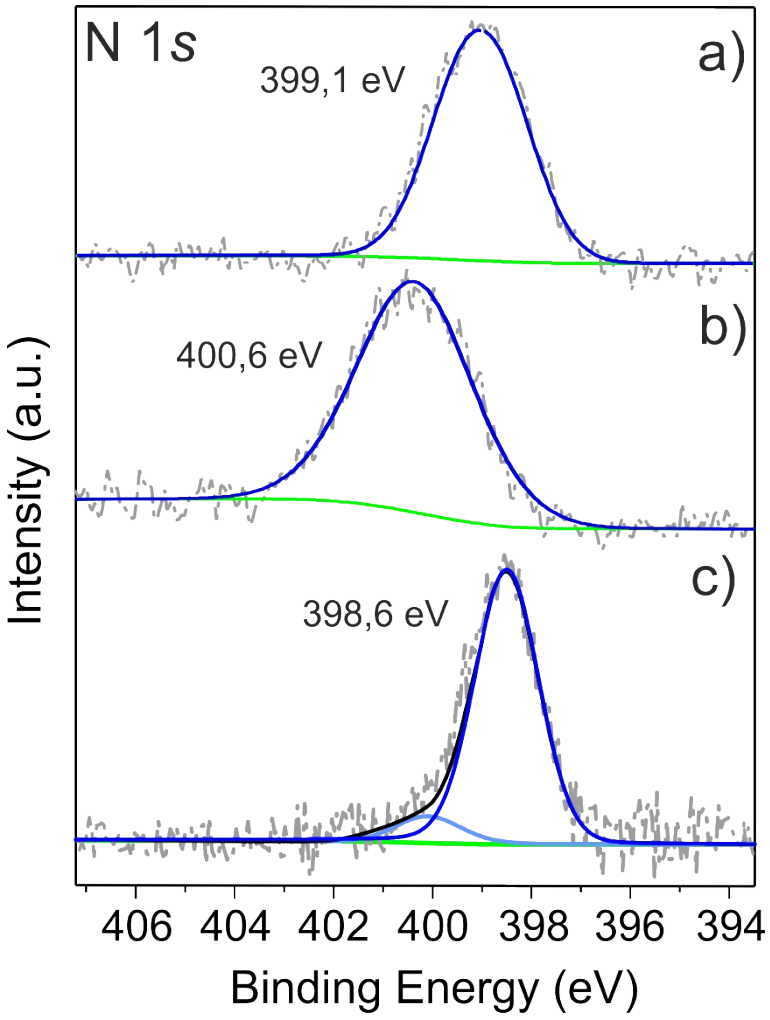


Fig. S1. N 1s core regions and relative fits for the high resolution XPS spectrum of N^{Az}-MW (**1**), N^{AzBoc}-MW (**2**) and N^{Acr}-MW (**3**). A minor shoulder in **3** (at higher binding energy) is ascribed to commonly observed surface contaminations.[1-3]

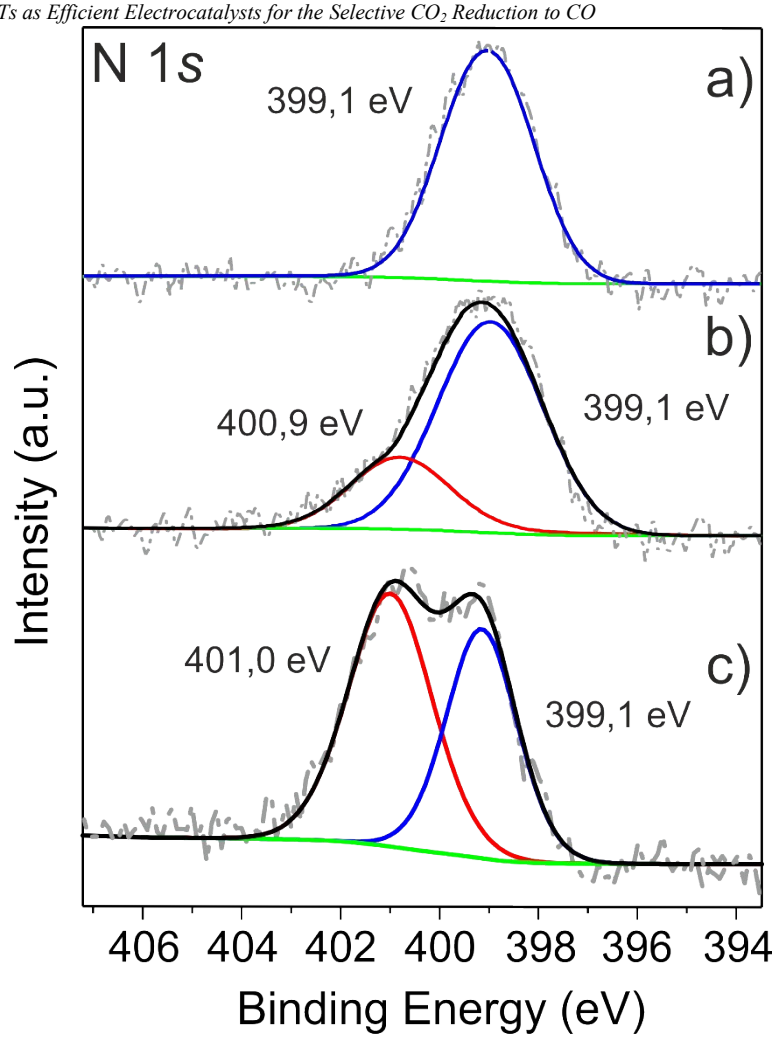


Fig. S2. N 1s core region and relative fit for the high resolution XPS spectrum of N^{Az}-MW sample as freshly prepared (a), after sample exposure on air for few minutes (b) and after a forced exposure to a stream of CO_2 (atm. press.) for 1 h (c). N 1s components at higher binding energies (400.9 and 401.0 eV) in Fig. S2b and S2c are attributed to the formation of amine-carbonate whereas components at 399.1 eV belong to free aziridine groups.

	(*Elemental analyses*)		(*acid-base titration*)	N%[a]
	N%	C%	N%	
N^{Az}-MW (**1**) (1° run)	0.69	95.2	0.71	
N^{Az}-MW (**1**) (2° run)	0.86	95.8	0.64	**0.73**
N^{Az}-MW (**1**) (3° run)	0.83	94.9	0.66	
N^{AzBoc}-MW (**2**) (1° run)	0.86	91.0	-	
N^{AzBoc}-MW (**2**) (2° run)	0.79	91.5	-	**0.81**
N^{AzBoc}-MW (**2**) (3° run)	0.77	91.1	-	
N^{Acr}-MW (**3**) (1° run)	1.64	93.1	1.32	
N^{Acr}-MW (**3**) (2° run)	1.52	92.5	1.30	**1.42**
N^{Acr}-MW (**3**) (3° run)	1.56	93.2	1.20	
MWCNTs	-	97.2	-	-

Table S1. Elemental analyses and acid-base titrations on N^X-MW samples (X = Az, AzBoc, Acr) for the determination of the N^X loading. Values are determined for each sample through three independent runs. [a] Final N^X content measured as average value from Elemental analysis and acid-base titration.

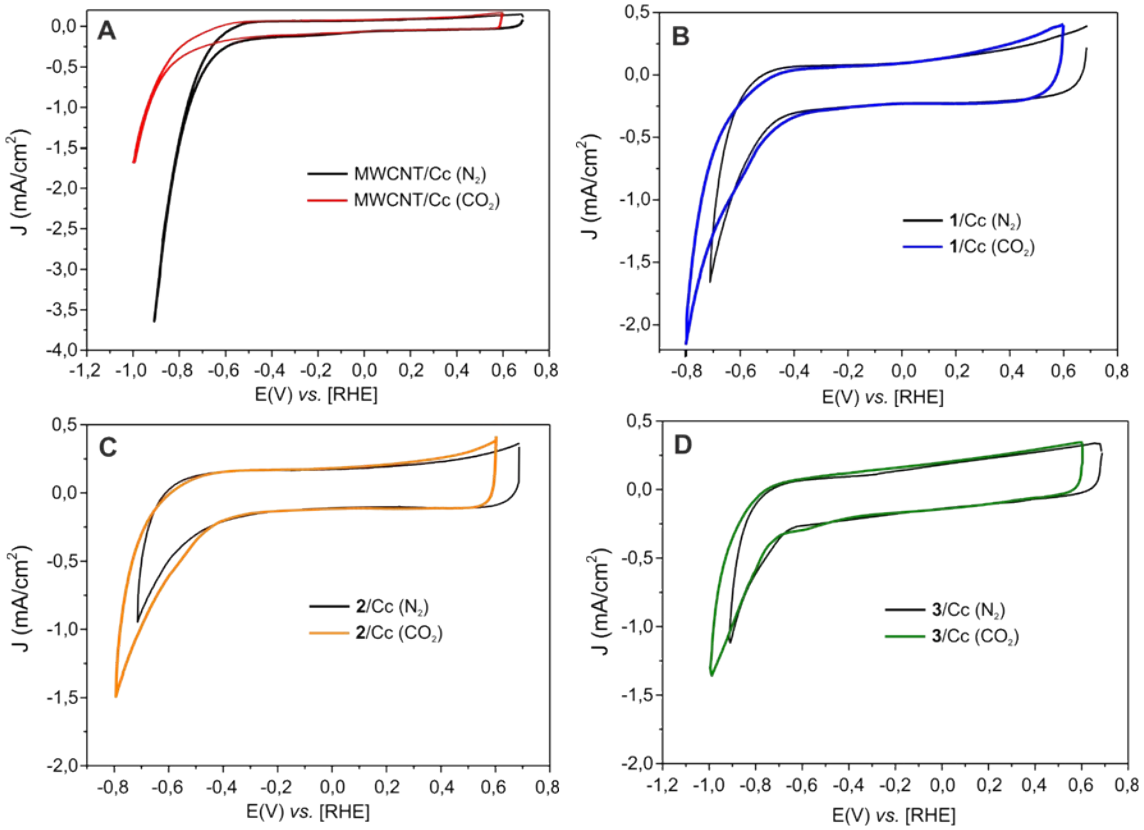


Fig. S3. Cyclic voltammograms for electrocatalysts MWCNT/Cc (**A**), **1**/Cc (**B**), **2**/Cc (**C**) and **3**/Cc (**D**) under a CO_2-saturated 0.1 M $KHCO_3$ solution (colored curves). For the sake of completeness, CV profiles recorded under N_2 saturated environment are also outlined (black curves). Potentials were linearly swept in the −1.6 to 0.0 V at a scan rate of 10 mV s^{-1} *vs*. Ag/AgCl/$KCl_{sat.}$ and then re-scaled towards the reversible hydrogen electrode (RHE) taking into account the pH value of the respective solutions. *E* (vs. RHE) = *E* (vs. Ag/AgCl) + 0.197 V + 0.0591*pH. pH of the N_2 saturated 0.1 M $KHCO_3$ solution: 8.3; pH of the CO_2 saturated 0.1 M $KHCO_3$ solution: 6.8.

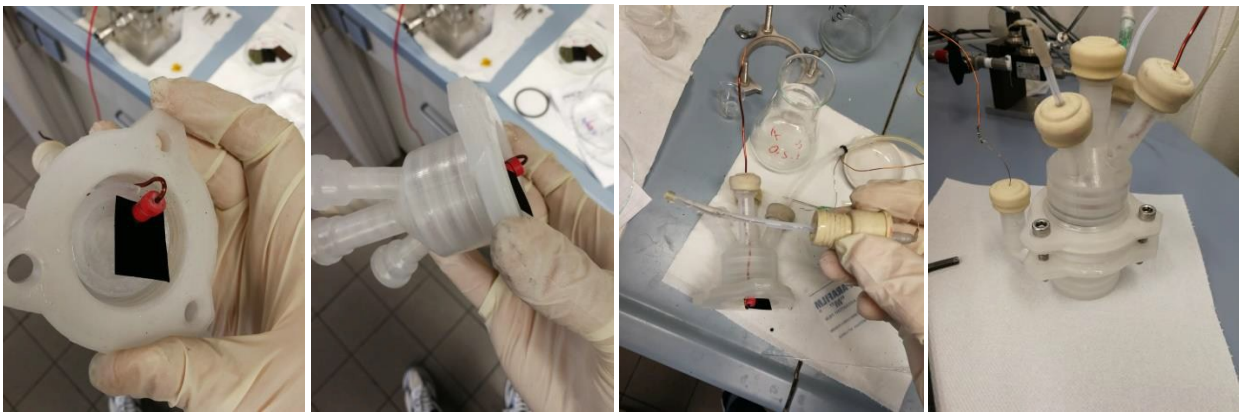
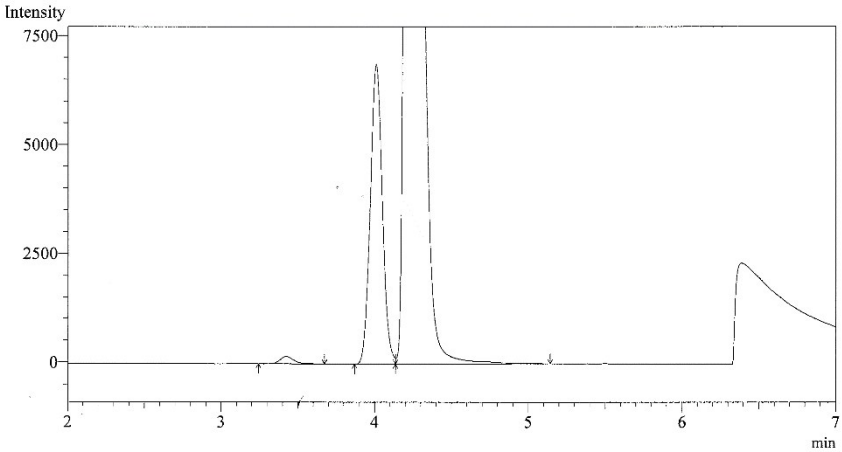


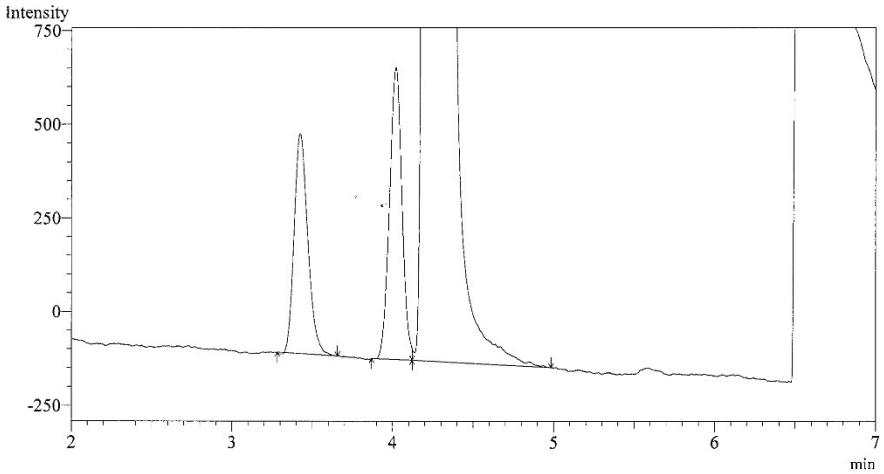
Fig. S4. Home-made 3D-printed *ABS*[4] three-electrode cell operating in a 0.1M $KHCO_3$ solution, equipped with an [Ag][AgCl][KCl_{sat}] reference electrode, a Pt counter electrode and a gas collector cone on the top for the sampling of the produced volatiles.

A



Peak#	Ret.Time	Area	Height	Cmpd Name	Area%
1	3,421	1023	168		0,3448
2	4,009	37303	6859		12,5733
3	4,223	258361	42821		87,0819
Total		296687	49848		100,0000

B



Peak#	Ret.Time	Area	Height	Cmpd Name	Area%
1	3,423	3477	588		1,4754
2	4,019	4192	777		1,7792
3	4,232	227974	38255		96,7454
Total		235643	39620		100,0000

Fig. S5. GC-MS traces of volatile products for two CO_2RR runs with **1**/Cc as electrocatalyst at -1.25 and -1.50 V *vs*. [Ag][AgCl][KCl_{sat}] after 45 min and 15 min electrolysis time, respectively, at constant potential value. Peaks (from left to right) are: H_2 (ret. time ≈ 3.4 min), N_2 (ret. time ≈ 4.0 min), CO (ret. time ≈ 4.2 min); CO_2 (ret. time ≈ 6.4 min). Peak areas are corrected according to calibration curves registered previously for each gas (H_2 correction factor: 138.8, CO correction factor: 7189.3).

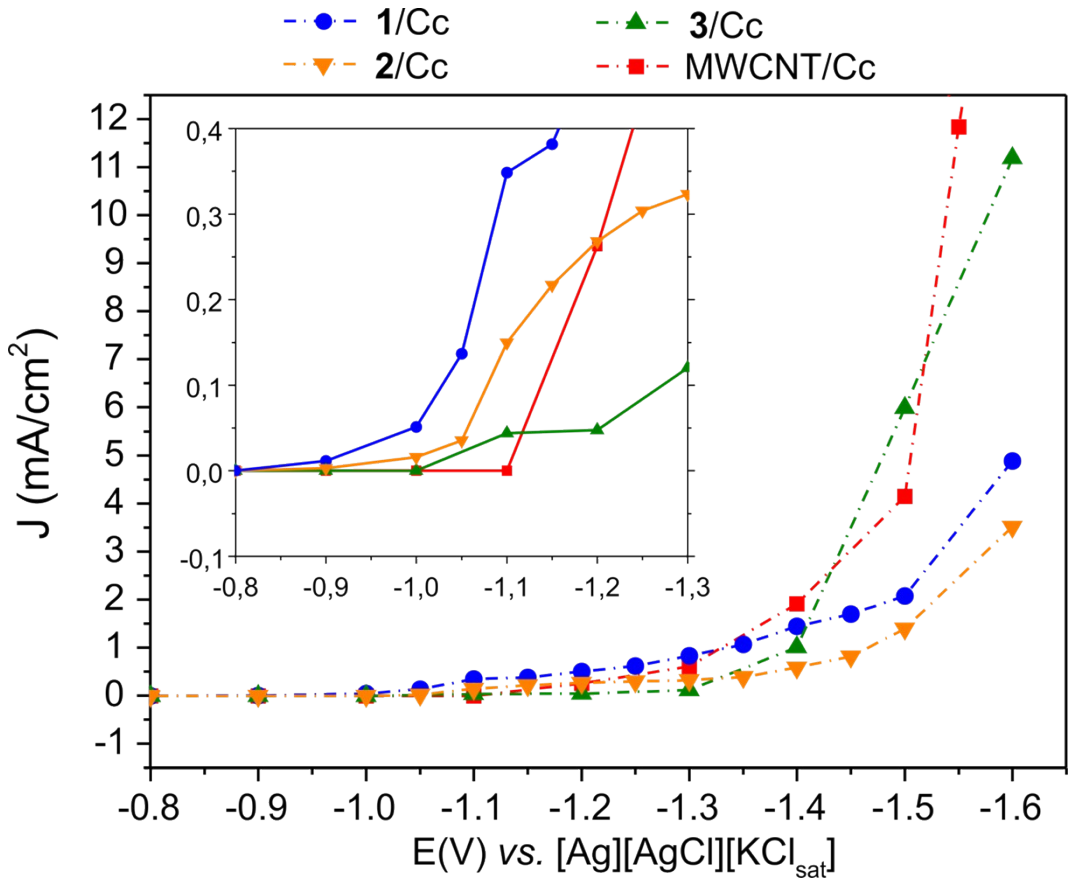


Fig. S6. Total current densities measured for CO_2RR with **1-3**/Cc and MWCNT/Cc in the -0.8 ÷ -1.6 V range *vs*. Ag/AgCl/$KCl_{sat.}$ as the reference electrode. Inset refers to the magnification of J_{tot} profiles at the lower overpotentials where electroreduction starts.

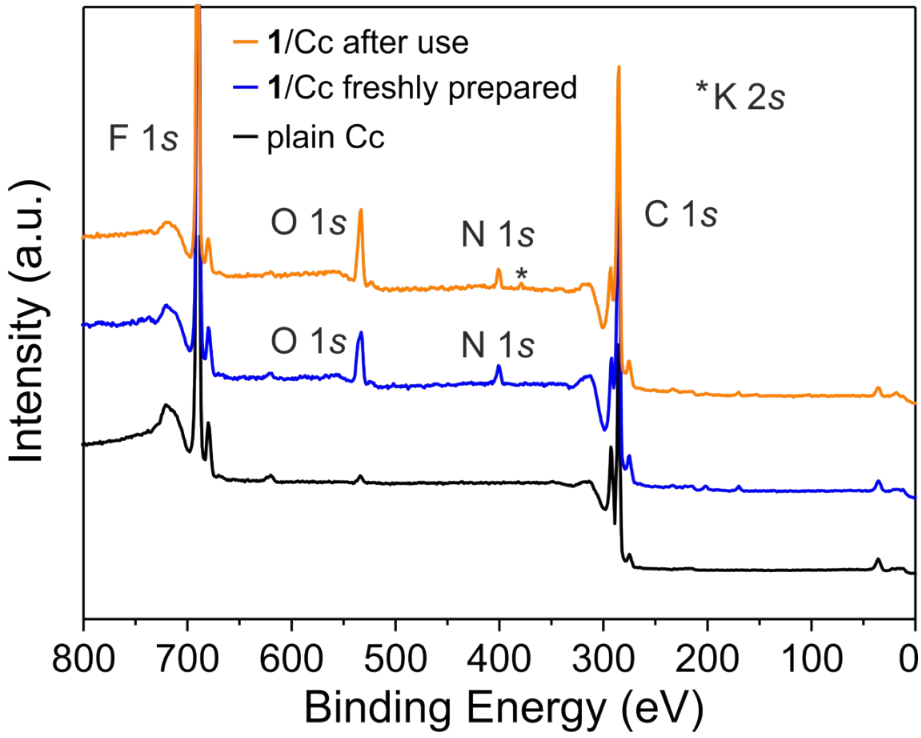


Fig. S7. XPS survey spectra of plain Teflonised carbon cloth (Cc) (black line), the freshly prepared **1**/Cc (blue line) and used **1**/Cc (orange line). The minor component at 379 eV in the spectrum of **1**/cc after use is ascribed to K 2*s* component due of residual $KHCO_3$ traces. The primary K 2*p* component overlaps with C 1*s* region.[5, 6]

Sample	O (at.%)	N (at.%)	C (at.%)	F (at.%)	O/C ratio	N/C ratio
Carbon cloth **(Cc)**	0.9	0	59.4	39.7	-	-
1/Cc – freshly prepared	4.3	2.2	71	22.5	0.06	0.03
1/Cc – after use	6.8	1.9	73.2	18.1	0.09	0.03

Table S2. Relative at.% of main elements from the XPS survey spectra of plain carbon cloth (Cc), the freshly prepared **1**/Cc and the **1**/Cc after use.

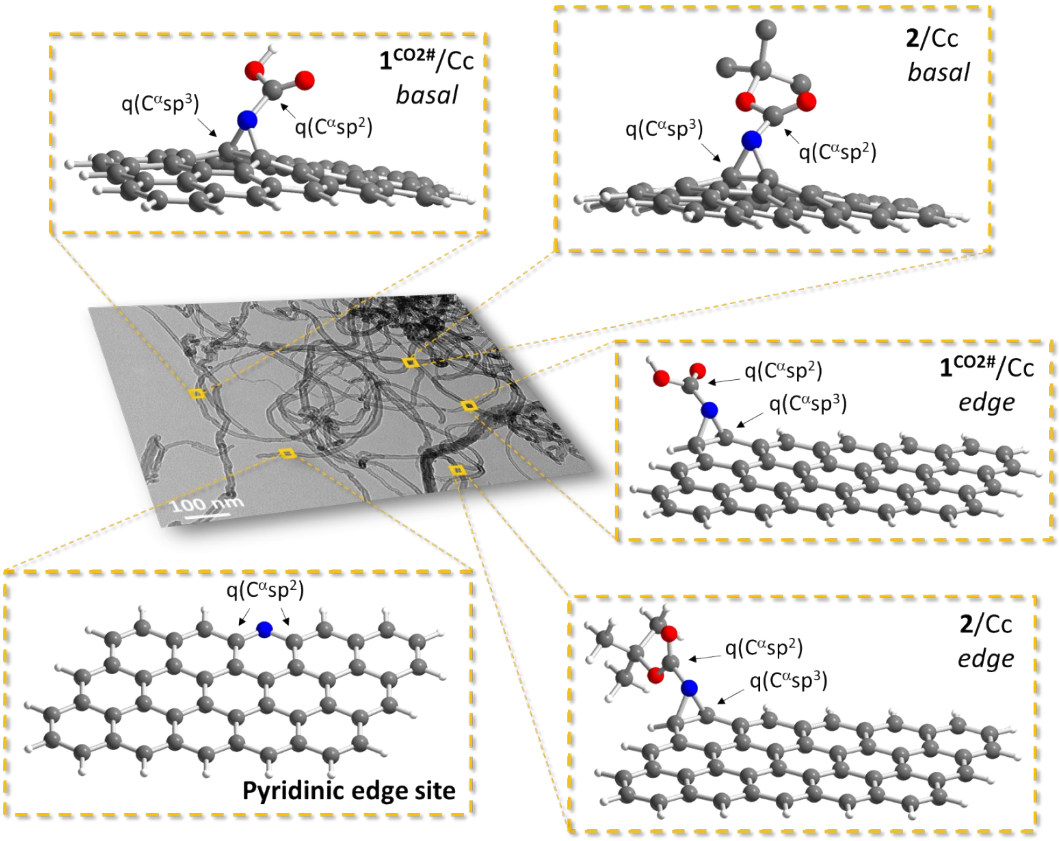


Fig. S8. DFT optimized structures of aziridine NBoc- and NH-carbonate groups as edge or basal plane dangling moieties on a polycyclic aromatic hydrocarbon cluster model. The same cluster with a pyridinic edge N-site has also been optimized to calculate the Bader atomic charges at the neighboring C^{α} atoms. TEM micrograph refers to a bundle portion of sample **1**.

Optimized samples	$q(C^{\alpha}sp^3)$	$q(C^{\alpha}sp^2)$
1$^{CO2\#}$/Cc – basal	+0.83	+3.93
1$^{CO2\#}$/Cc - edge	+0.60	+3.94
2/Cc – basal	+0.87	+3.93
2/Cc - edge	+0.23	+3.18
pyridinic edge group	-	+1.32

Table S3. Net Bader Charges (q) of the $C^{\alpha}sp^3/C^{\alpha}sp^2$ atoms on DFT optimized N-heterocycles as edge or basal-plane dangling fragments of a polycyclic (hetero)aromatic hydrocarbon cluster.

References and Notes.

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