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A Highly N-Doped Carbon Phase "Dressing" of Macroscopic Supports for Catalytic Applications

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Content:

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Methods

General procedure for the synthesis of highly N-doped mesoporous carbon-based coating (N@C) on macroscopically shaped supports. In a typical procedure, 2 g of D-Glucose and 3 g of citric acid were added to 10 mL of ultrapure Milli-Q water at room temperature. A proper amount of ammonium carbonate (i.e. 0.75, 1.5 or 2.3 g) was then added in a single portion to the solution at r.t. and an instantaneous effervescence due to CO_2 evolution was observed. The obtained clear solution was exploited as an aqueous pre-catalytic phase for the soaking/impregnation of a series of suitable supports (2 g): SiC extrudates (29 $m^2 \cdot g^{-1}$; SICAT) and powder (25 $m^2 \cdot g^{-1}$; SICAT), SiC foams (30 $m^2 \cdot g^{-1}$; SICAT) and α-Al_2O_3 beads (6 $m^2 \cdot g^{-1}$; Sasol). The wet solids were slowly heated (10 °C min^{-1}) in air from room temperature to 130 °C and kept at this temperature for 1 h. The as obtained dry solids were further impregnated with the same three component solution for several times at will, until the desired loading is achieved. The solids underwent a thermal treatment in air at 450 °C (2 °C·min^{-1}) for 2 h during which the macroscopic host support was coated with a highly N-doped mesoporous carbon phase. The as-prepared solids can be further heated in He atmosphere at 900 °C (10 °C·min^{-1}) for 2 h in order to increase the graphitization/conjugation degree of the final materials.

Materials characterization

^{1}H and ^{13}C{^{1}H} NMR spectra were obtained on either a Bruker Avance DRX-400 spectrometer or a Bruker Avance 300 MHz instrument. Chemical shifts are reported in ppm (δ) relative to TMS.

Thermogravimetric analyses (TGA) were performed under air (100 mL·min^{-1}) on an EXSTAR thermogravimetric analyzer (TG/DTA) Seiko 6200.

The specific surface area of the different samples was measured by the BET method using N_2 as adsorbent at liquid nitrogen temperature (TriStar sorptometer). Before measurement, the samples were outgassed at 200 °C overnight.

XPS measurements were performed on a MULTILAB 2000 (THERMO VG) spectrometer equipped with Al Kα anode (hν = 1486.6 eV) with 10 min of acquisition. Peak deconvolution has been accomplished with "Avantage" program from Thermoelectron Company. The C1s peak at 284.6 eV was used to correct charging effects. Shirley backgrounds were subtracted from the raw data.

The gross morphology of the materials was observed by scanning electron microscopy (SEM) on a JEOL F-6700 FEG with an accelerating voltage of 10 kV.

Transmission electron microscopy (TEM) measurements were performed using a JEOL 2100F operating at 200 kV, equipped with GATAN Tridiem imaging filter and an aberration-corrected condenser.

Electron energy-loss spectroscopy (EELS) analysis was performed in the scanning mode (STEM) with 30 mrad convergence angle and 25 mrad collection angle. The spectral image was acquired in 20×33 pixels with an exposure time of 1 s for each pixel. The energy resolution was 1.7 eV. Elemental signals were extracted from the Si-L, C-K, N-K and O-K edges, respectively.

Energy-filtered TEM (EFTEM) measurements were acquired by a three-window method with energy slits of 8 eV, 30 eV and 20 eV and acquisition times of 10 s, 30 s and 40 s for Si,

C and N, respectively. Prior to the analysis the sample was covered by a thin layer of gold in order to reduce charging during the analysis.

Catalytic Reactions

Oxygen Reduction Reaction (ORR).

Electrochemical studies were performed at 25 °C in a three-electrode cell in 0.1 M KOH supporting electrolyte, using an Autolab PGSTAT30 (Eco Chemie, The Netherlands) potentiostat equipped with an analogue linear sweep generator at a scan rate of 10 mV s^{-1}. Mercury oxide (Hg/HgO) electrode and Pt-wire electrode were used as reference and counter electrode, respectively. Unless otherwise stated, all potentials hereinafter are referred to the reversible hydrogen electrode (RHE). The electrochemical impedance spectroscopic (EIS) is used to determine the resistance of the electrolyte solution.

RRDE (rotating-ring disk electrode) measurements were performed on a Pine electrode (PINE AFE6R2GCPT, glassy carbon disk: 5.5 mm diameter and 0.2376 cm^2 geometrical area, Pt ring: 0.234 cm^2). 10.0 mg of catalyst, 5 mL isopropanol and 50 μL Nafion solution (5 wt.%) were ultrasonically mixed to form a homogenous catalyst ink that was drop-casted onto the GC electrode and dried at room temperature. The reference Pt curve was recorded with a 20 wt.% Pt/VXC-72 (Sigma) catalyst with a loading of 25 μg$_{Pt}$ cm^{-2}.

All aqueous solutions were prepared using ultrapure water (18MΩcm, < 3 ppb TOC) and supra-pure KOH (Sigma-Aldrich). In O$_2$-reduction experiments oxygen was constantly bubbled through the solution in order to maintain the saturation level and the ring potential was set at 1.2 V *vs*. RHE. Collection efficiency (N) was calculated from the experimental data obtained

in 10 mM K_3FeCN_6 in 0.1 M NaOH at standard measurement conditions (potential sweep rate 10 mV s^{-1}, 25°C). The collection efficiency for the Pt(20%)/VXC-72 electrode was found to be 37 % which displays the same value as reported by Chlistunoff [1]

The catalyst four-electron selectivity was evaluated on the basis of the H_2O_2 yield, calculated from the following equation (Eq. [1]):

$$H_2O_2(\%) = 200(J_R/N)/(J_R/N\text{-}J_D) \qquad [1]$$

Here, J_D and J_R are the disk and ring currents density, respectively, and N is the ring collection efficiency.

The electron transfer number can be calculated in two ways. The first is to use the ring current and the disk current (Eq. [2]):

$$n = \text{-}4J_D/(J_R/N\text{-}J_D) \qquad [2]$$

The second way to calculate n is by using the first-order Koutecky-Levich equation (Eq. [3]):

$$1/J_D = 1/j_k + 1/j_d \qquad [3]$$

where j_k is the kinetic current density and j_d *is* the diffusion-limited current density through the expression $j_d = Bf^{1/2} = 0.2nF\gamma^{-1/6}D_{O2}{}^{2/3}C_{O2}f^{1/2}$. Here n is the average electron transfer number; F is the Faraday constant; γ is the kinematic viscosity of the electrolyte; D_{O2} is the oxygen diffusion coefficient (1.95×10^{-5} cm^2/s); C_{O2} is the bulk oxygen concentration in the electrolyte (1.15×10^{-3} mol/dm^3); f is the angular velocity of the electrode. The kinetic current density (j_k) and the Koutecky-Levich slope ($1/B$) can be obtained from a plot of $1/j$ versus $1/f^{1/2}$.

Partial Oxidation of H_2S into Elemental Sulfur.

The catalytic selective oxidation of H_2S by oxygen [Eq. 4] was carried out in an all glass tubular reactor working isothermally at atmospheric pressure.

$$H_2S + \tfrac{1}{2} O_2 \rightarrow 1/n\ S_n + H_2O \qquad \Delta H = -222 \text{ kJ/mol} \qquad [4]$$

A proper amount of catalyst (300 mg) was placed on silica wool in a tubular Pyrex reactor (inner diameter: 16 mm) located inside a vertical tubular electrical furnace. The temperature was controlled by a K-type thermocouple and a Minicor regulator. The gas mixture of the reactant feed including H_2S (1 vol.%), O_2 (1 to 2.5 vol.%), H_2O (30 vol.%) and He (balance) was passed downward through the catalyst bed. The gases flow rates were monitored by Brooks 5850TR mass flow controllers linked to a control unit. The weight hourly space velocity (WHSV) was fixed at 0.3 - 0.6 h^{-1} and the O_2/H_2S molar ratio was settled to 2.5, unless otherwise stated.

The reaction was conducted in a continuous mode. The sulfur formed in the reaction was vaporized (because of the high partial pressure of sulfur at the adopted temperatures) and then condensed at the exit of the reactor in a trap maintained at room temperature. The analysis of the inlet and outlet gases was performed online using a Varian CP-3800 gas chromatograph (GC) equipped with a Chrompack CP-SilicaPLOT capillary column and a thermal catharometer detector (TCD), which allowed the detection of O_2, H_2S, H_2O and SO_2.

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Table S1. Physico-chemical characterization of N@C phases of various SiC/Al$_2$O$_3$-based composites.[a]

Entry	Sample[b] [Cat. label]	1st impregn. cycle (NH$_4$)$_2$CO$_3$ (g)	2st impregn. cycle (NH$_4$)$_2$CO$_3$ (g)	Thermal treatment/ atmosphere	N@C wt % loading from TGA	N wt % from EA[c]	N wt % at the N@C phase[d]	SSA (m^2/g)	Nitrogen species (%)[e] Pyridinic	Pyrrolic	Graphitic	Oxidized
1	N@C/(SiC)$_E$^{2} [**I**]	2.3	0.75	450 °C/Air	10.3	3.34	32.4	108	55.2	28.8	11.2	4.8
2	^{A}N@C/(SiC)$_E$^{2} [**II**]	2.3	0.75	900 °C/He	10.4	2.12	20.4	109	43.2	7.5	37.2	12.1
3	^{A}N@C/(SiC)$_P$^{2} [**III**]	2.3	0.75	900 °C/He	15.2	3.55	23.4	112	44.6	17.4	32.4	5.6
4	N@C/(SiC)$_E$^{2} [**IV**]	2.3	1.5	450 °C/Air	17.1	5.11	29.9	138	45.9	27.6	19.6	6.9
5	^{A}N@C/(SiC)$_E$^{2} [**V**]	2.3	1.5	900 °C/He	10.4	1.61	15.5	144	38.9	10.5	37.9	12.7
6	^{A}N@C/(αAl$_2$O$_3$)$_B$^{2} [**VI**]	2.3	0.75	900 °C/He	13.0	1.47	12.9	91	40.6	11.2	35.6	12.6

[a] All SiC/α-Al$_2$O$_3$-composites are prepared by repeating the soaking/impregnation step of the pristine SiC support twice and using impregnating solutions prepared dissolving 2g of D-Glucose, 3g of citric acid and (NH$_4$)$_2$CO$_3$ (from 0.75 to 2.3 g) in 10 mL of ultrapure Milli-Q water. [b] Composites are designated as follows: ^{A}N@C/SiC$_x$^{y} where superscript "A" denotes "annealead samples" (treatment at 900 °C under inert atmosphere), "N@C/SiC" or "N@C/α-Al$_2$O$_3$" stand for the SiC/α-Al$_2$O$_3$ material coated with the (N@C) active-phase, "X" subscript illustrates the pristine support form (P = powder; E = extrudates; B = beads) while "Y" superscript displays the number of impregnation cycles. [c] Elemental analysis: average values calculated over three independent runs per sample. [d] N wt.% normalized to the N@C content (active phase) calculated by TGA analysis. [e] Estimated from fitting of the N 1s XPS profile.
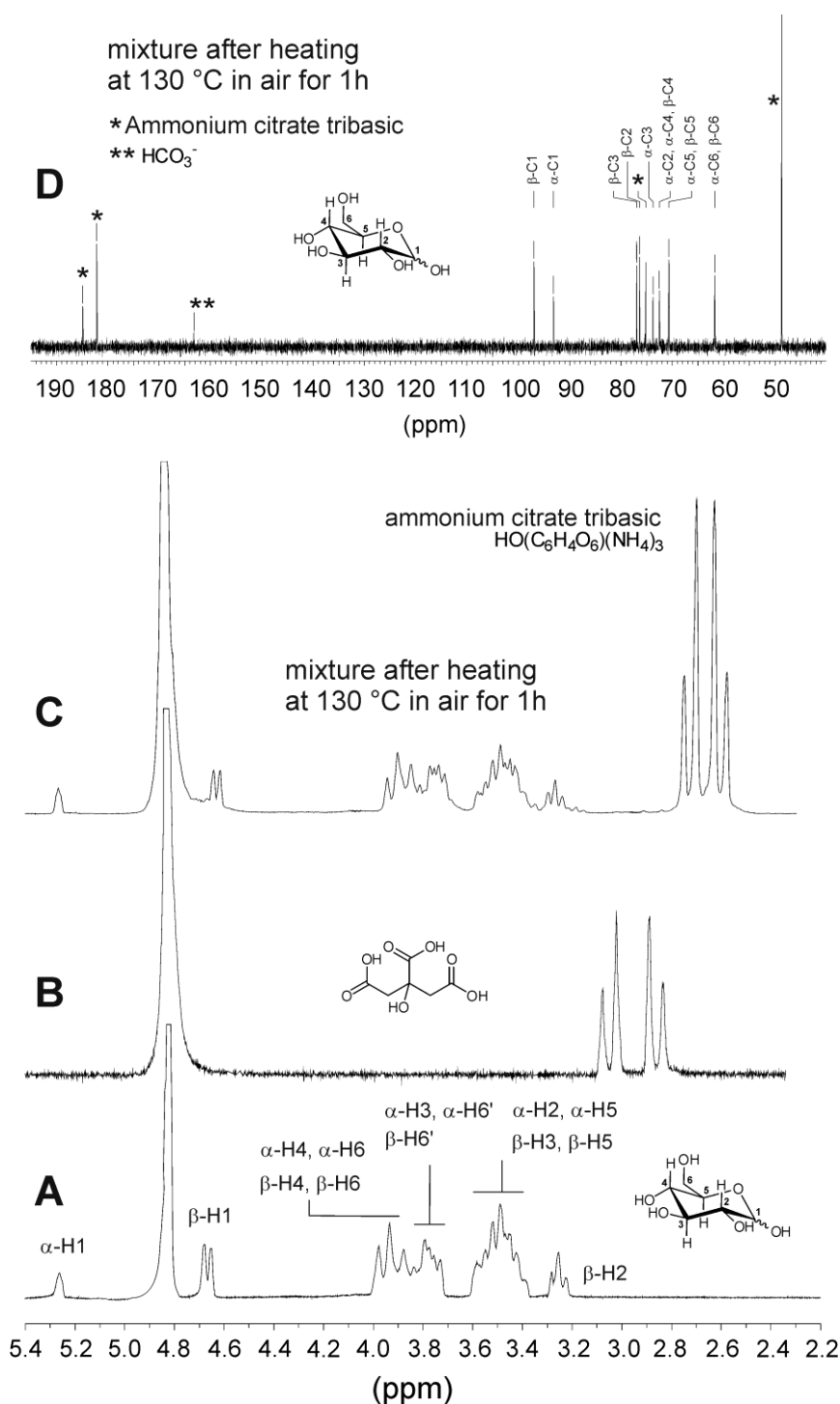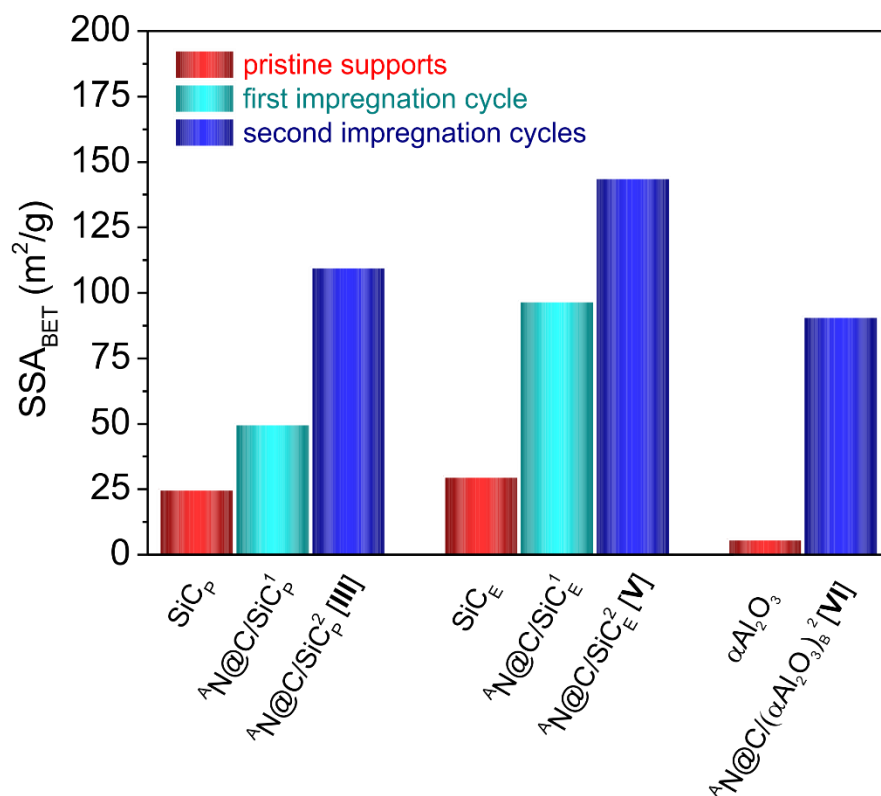
Fig. S1. ^{1}H and ^{13}C{^{1}H} NMR spectra (D$_2$O, 298 K) of the three component mixture after heating at 130 °C for 1h (C, D) and ^{1}H NMR spectra (D$_2$O, 298 K) of the two separate components, D-Glucose (A) and citric acid (B). From a close inspection of the NMR spectra, the first thermal treatment at 130 °C of the three-component aqueous solution results into a homogeneous solid mixture of α,β-D-glucopyranose and ammonium citrate tribasic. Traces of either CO$_3^{2-}$ or HCO$_3^-$ are observed after this phase (D).

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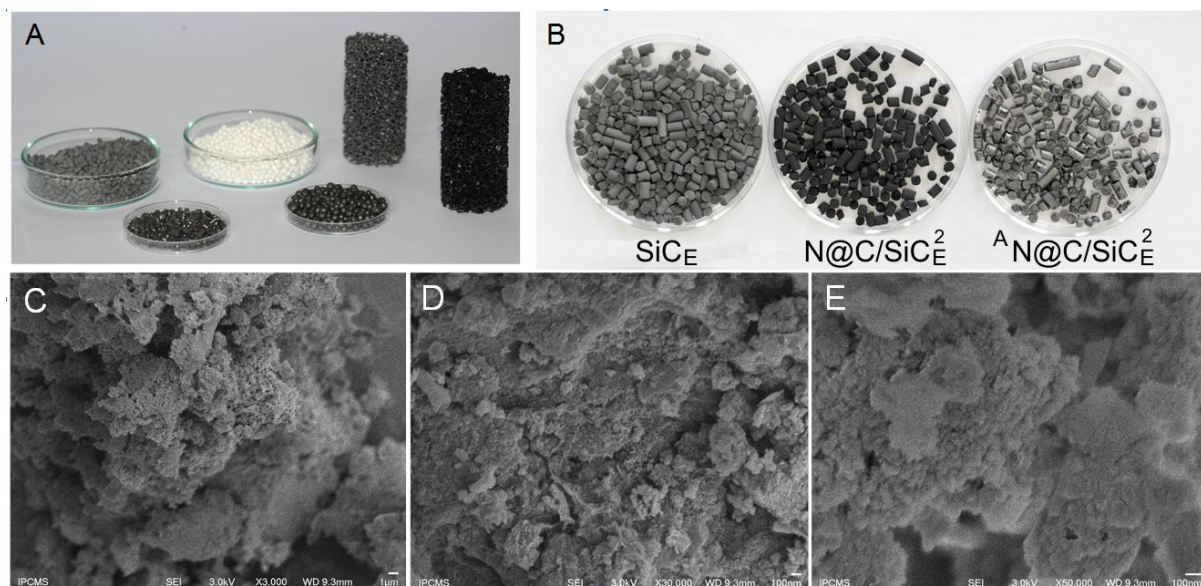
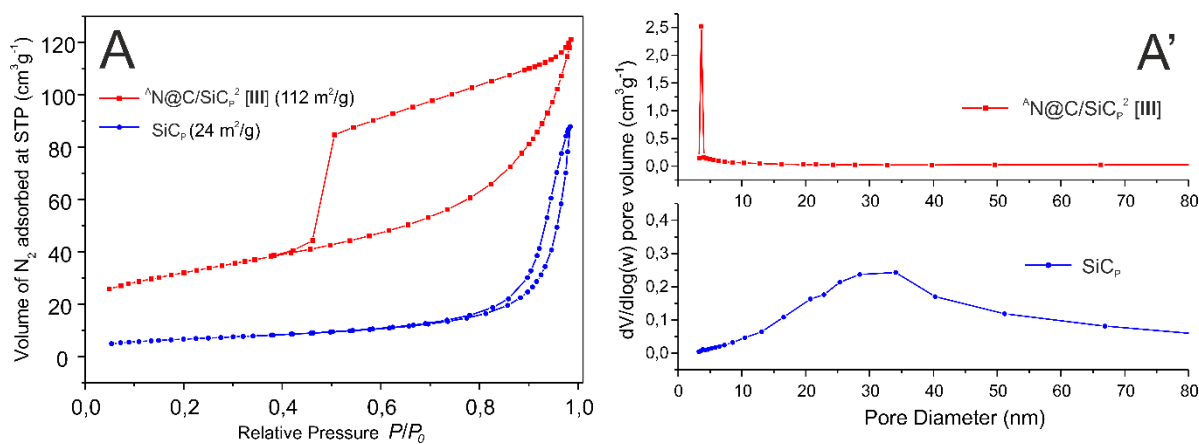

Fig. S2. Digital photos of pristine SiC supports with different macroscopic shapes (A) and SiC extrudate (SiC$_E$) samples (B) after N@C-coating and thermal treatment at 450 °C in air (N@C/SiC$_E^2$) (Table S1†, entry 1) and annealing at 900 °C under He atmosphere (^{A}N@C/SiC$_E^2$). Typical SEM images illustrating the N@C porous texture of the ^{A}N@C/SiC$_E^2$ sample (Table S1†, entry 2) at different magnifications.
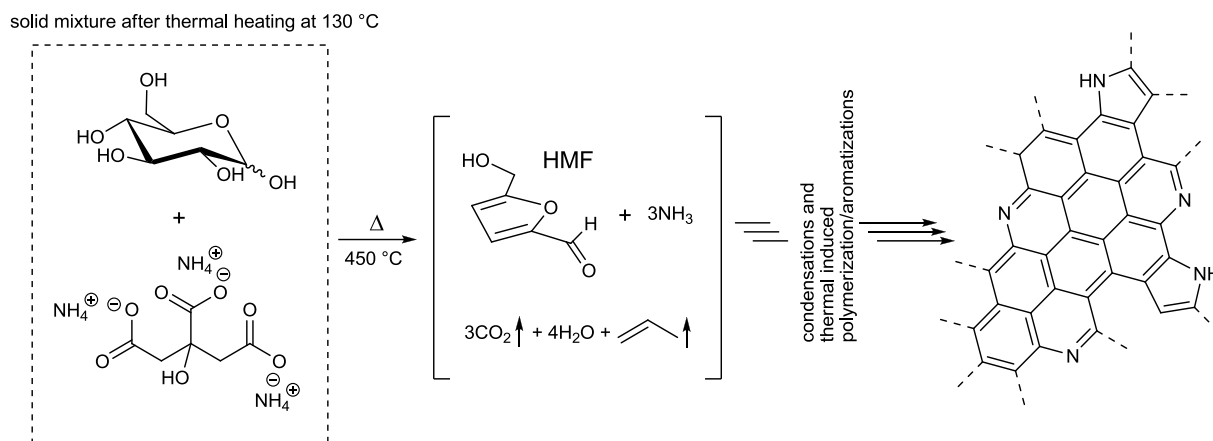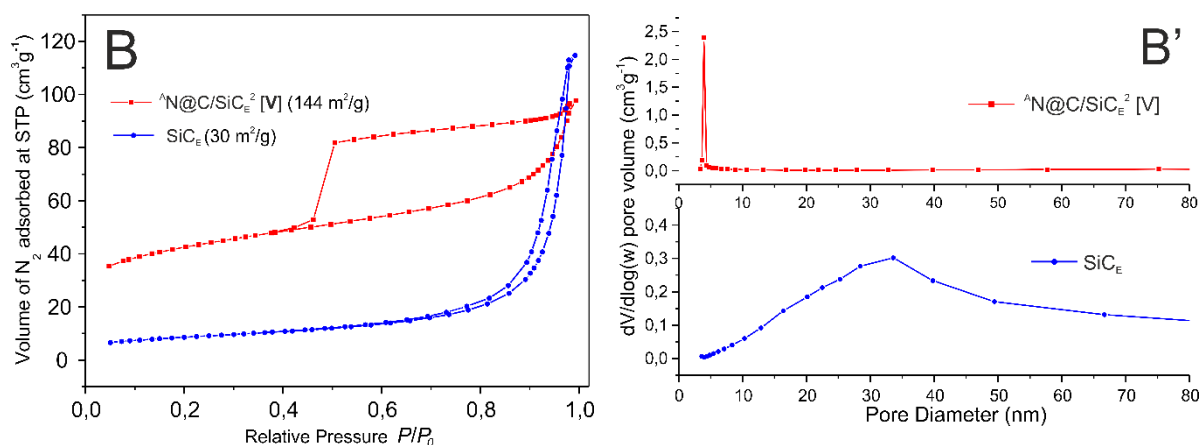

Fig. S3. Proposed mechanism for the thermal transformation of α,β-D-glucopyranose and ammonium citrate tribasic (pre-catalyst phase) into a N-rich, heteroaromatic, graphene-like network (N@C - catalytically active phase). The thermal treatment at 450 °C is supposed to start the progressive dehydration of the sugar into the 5-hydroxymethyl-furfural (5-HMF)[2]. Under these conditions, ammonium citrate tribasic, is expected to act as both a N-reservoir for the generation of N-containing heterocycles[3,4] and a pore-forming agent (due to its complete decomposition into volatiles like NH_3, CO_2, H_2O and propene) thus contributing to the ultimate material mesoporosity.

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Fig. S4. BET Specific Surface Area of annealed composites after one or two impregnation cycles of differently shaped SiC and αAl_2O_3 matrices. For samples [**III**], [**V**] and [**VI**, refer to Table S1†.

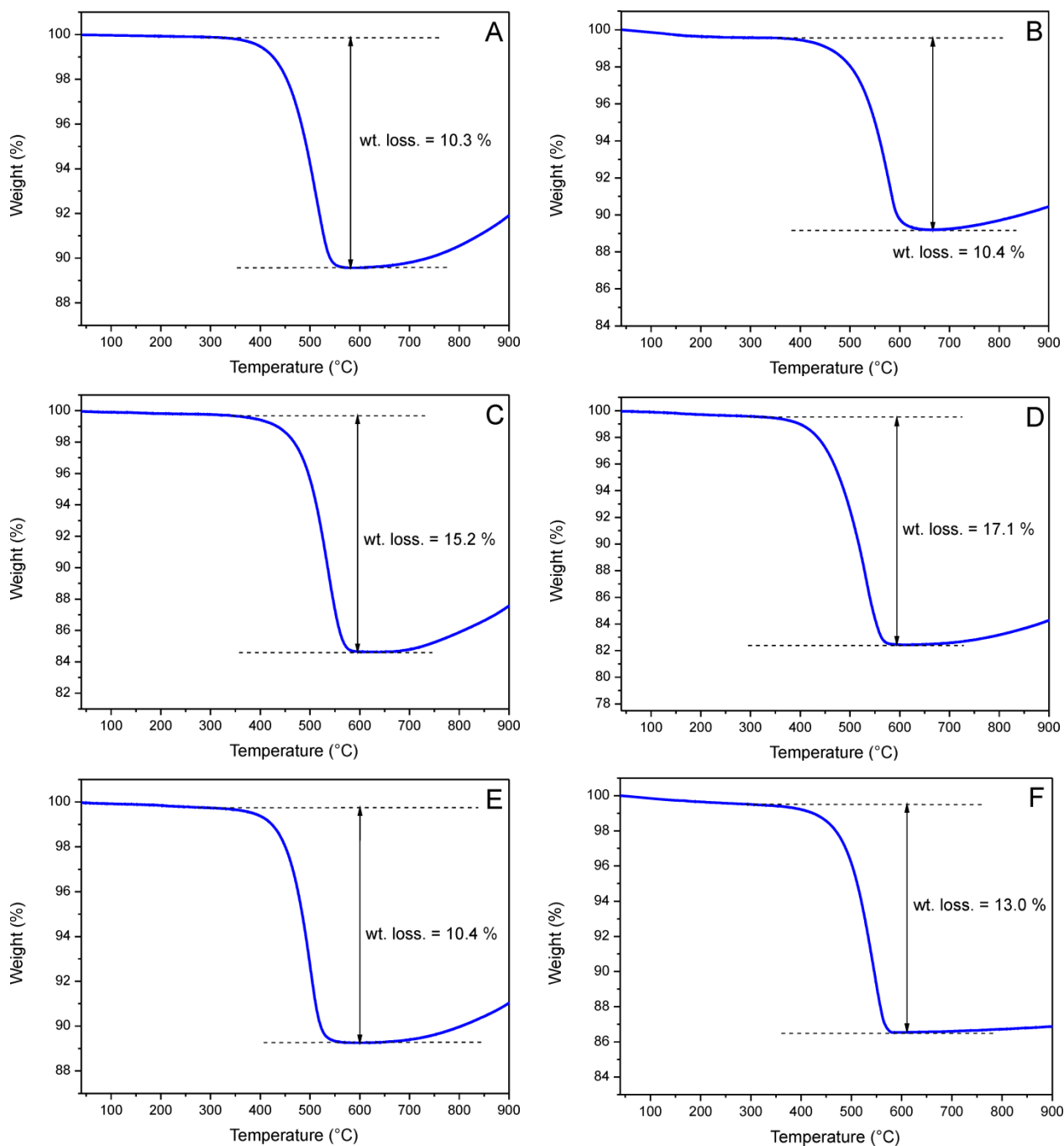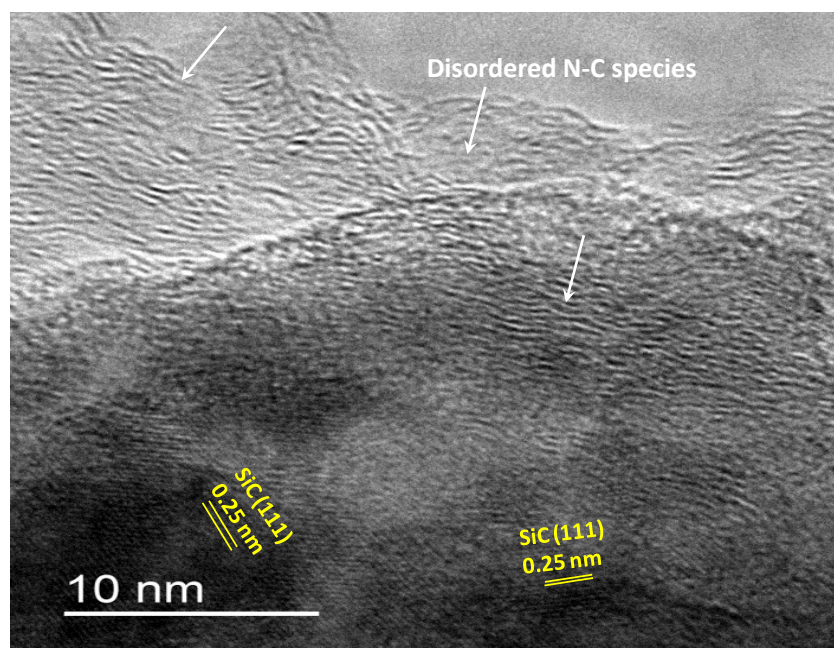*A Highly N-Doped Carbon Phase "Dressing" of Macroscopic Supports for Catalytic Applications*

Fig. S5. (**A** and **B**) Nitrogen adsorption-desorption isotherm linear plot (BET) of N@C/SiC$_{P/E}^2$ samples (red curves) and pristine SiC$_{P/E}$ supports (blue curves) recorded at 77 K. Both N@C/SiC materials present a Type II isotherm with a distinctive H2 hysteresis loop in the range of 0.4–1.0 P/Po, typical for mesoporous structures featured by complex pore networks of ill-defined shape. On the other hand the bare SiC$_{P/E}$ scaffolds present a Type-II isotherm with an almost completely suppressed hysteresis loop. The pore-size distribution curves (**A'** and **B'** - BJH method) for the N@C/SiC$_{P/E}^2$ samples show largely prevalent components (> 80%) between 3 and 10 nm with a maximum centered around 4 nm (small mesopores). On the other hand larger mesopores (prevalently in the 20-40 nm range) are present in the bare SiC$_{P/E}$ supports.
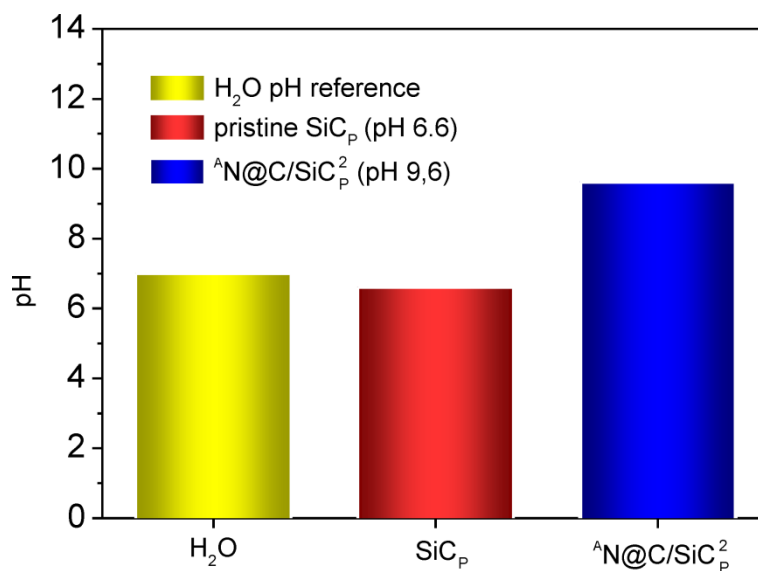

Fig. S6. Acid-basic properties of an aqueous dispersion of [**III**] (Table S1†, entry 3) at comparison with its pristine counterpart (bare SiC$_P$)

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Fig. S7. TGA profiles of N@C/SiC composites (40-900 °C, 5°C/min, air 100 mL/min). All samples are dried at 40°C at 0.05 torr, overnight before each measurement. Weight losses refer to the complete burning of the N@C deposit at the SiC matrices: **A**) N@C/SiC$_E^2$ [**I**], see Table S1†, entry 1. B) ^{A}N@C/SiC$_E^2$ [**II**], see Table S1†, entry 2. C) ^{A}N@C/SiC$_P^2$ [**III**], see Table S1†, entry 3. D) N@C/SiC$_E^2$ [**IV**], see Table S1†, entry 4. E) ^{A}N@C/SiC$_E^2$ [**V**], see Table S1†, entry 5. F) ^{A}N@C/α-Al$_2$O$_{3B}^2$ [**VI**], see Table S1†, entry 6.

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Fig. S8. HR-TEM high-resolution image of the ^{A}N@C/SiC$_p^2$ [**III**] sample (Table S1†, entry 3) showing the N@C coating phase in the form of disordered and crumpled N-doped carbons at the SiC support.
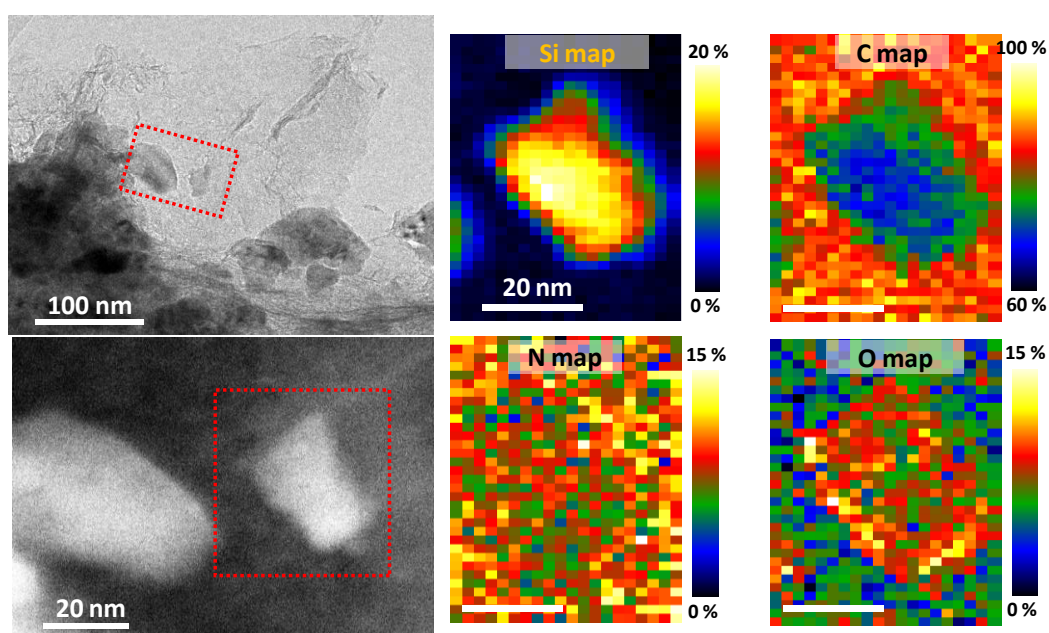

Fig. S9. Morphology of ^{A}N@C/SiC$_p^2$ [**III**] sample (Table S1†, entry 3). An overview bright field TEM image (Top left). A high-angle annular-dark-field image (STEM-HAADF) which was taken from the area marked by the red dashed-line box in the top left image (Bottom left). Elemental maps of Silicon, Carbon, Nitrogen and Oxygen, respectively taken from the area highlighted by the red dashed-line box in the bottom-left image (Four color images on the right side). The colors correspond to the relative atomic composition ratio indicated by the adjacent vertical color bars.

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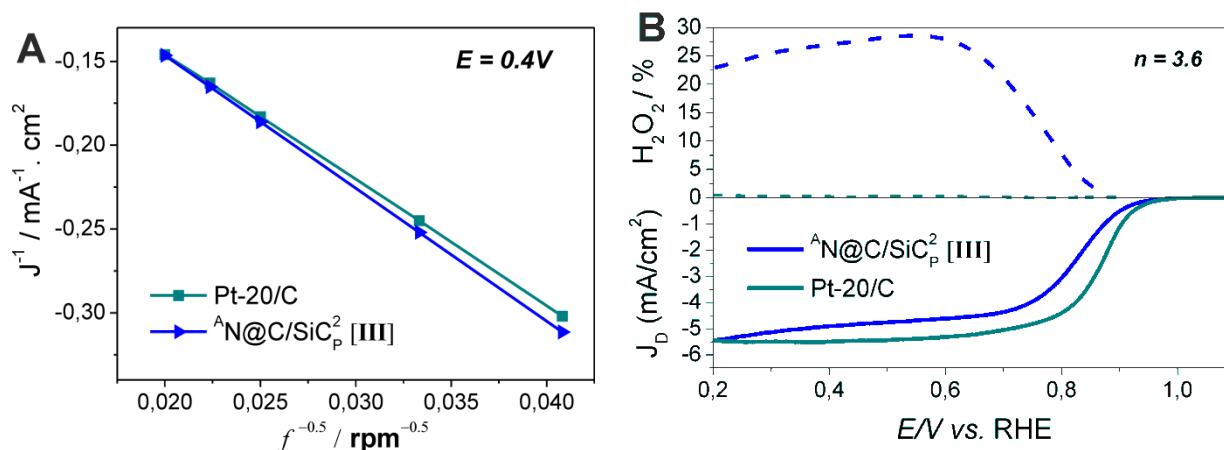
Fig. S10. (A) K-L plots for [**III**] and the reference 20 wt.% Pt/C catalysts as obtained from the respective LSVs at 0.4V (vs. RHE). Parameters used: O_2 concentration (C), 1.15×10^{-3} mol L^{-1}; O_2 diffusion coefficient (D), 1.95×10^{-5} cm^2 s^{-1}; kinematic viscosity (ν) of the electrolyte solution, 0.008977 cm^2 s^{-1}. **(B) [down]** RRDE current −potential curves at 25 °C for ORR in O_2 saturated 0.1 M KOH solution recorded by using a rotating ring-disk GC electrode [GC disk, A = 0.238 cm^2] with **(B) [top]** Pt ring [A = 0.234 cm^2]. Both samples ([**III**] and 20 wt.% Pt/C) are measured at an angular rotation rate (f) of 1600 rpm.
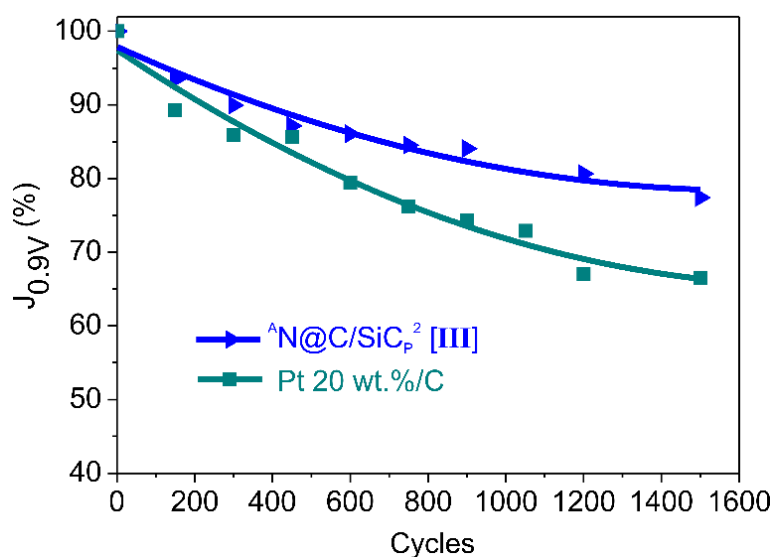
Fig. S11. Long-term stability tests for [**III**] and 20 wt.% Pt/C catalysts at 25 °C and 1600 rpm in O_2 saturated 0.1 M KOH solution; the test was carried out for 1500 cycles between 1.0 and 0.6 mV.
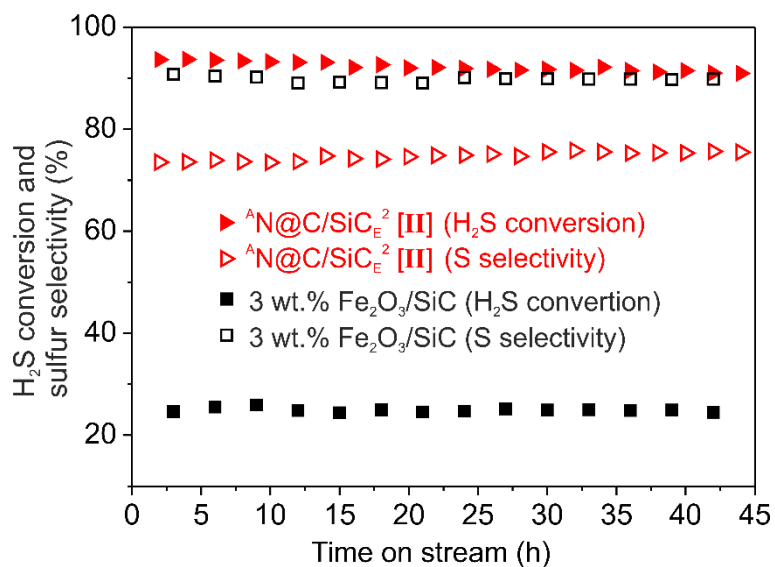
Fig. S12. Comparative study of H_2S conversion and sulfur selectivity over **II** and 3 wt. % Fe_2O_3/SiC catalysts (operative cond.: T = 210 °C, 1g of catalyst, O_2/H_2S molar ratio = 2.5, WHSV = 0.6 h^{-1}).
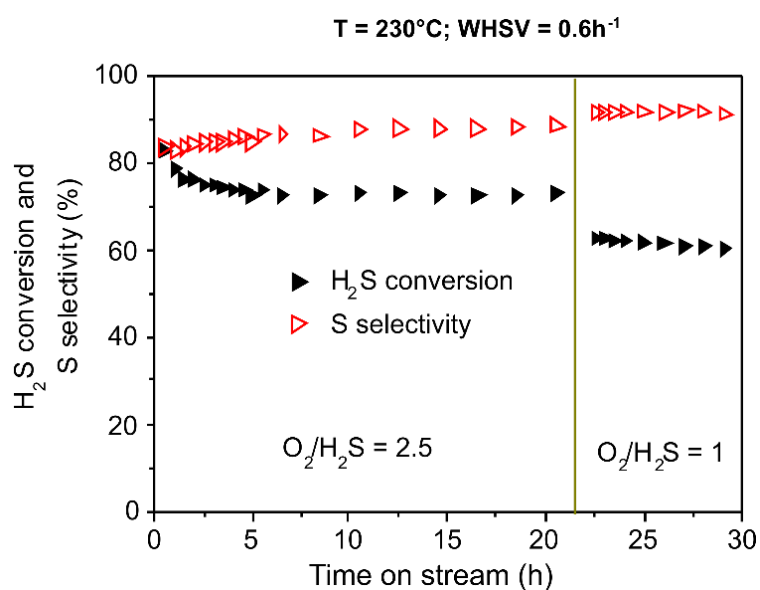
Fig. S13 H_2S conversion and sulfur selectivity on catalyst **VI** under two O_2/H_2S molar ratio. Reaction conditions: M_{catal} = 1 g; T= 230 °C, WHSV = 0.6 h^{-1}

References

1   J. Chlistunoff, *J. Phys. Chem.,* 2011, **C115**, 6496.

2   R.-J. van Putten, J. C. van der Waal, E. de Jong, C. B. Rasrendra, H. J. Heeres, J. G. de Vries, *Chem. Rev.*, 2013, **113**, 1499.

3   F. W. Lichtenthaler, A. Brust, E. Cuny, *Green Chem.* 2001, **3**, 201.

4   F. W. Lichtenthaler, *Accounts Chem. Res.*, 2002, **35**, 728.