Aziridine Functionalized Multi-Walled Carbon Nanotubes: a Robust and Versatile Catalyst for the Oxygen Reduction and Knoevenagel Condensation†

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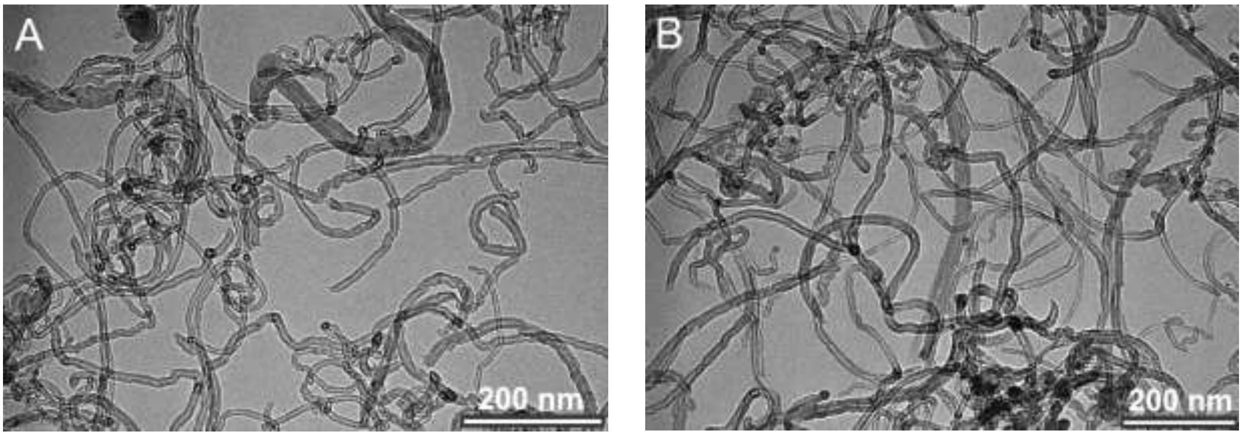

Fig. S1. TEM images of **A**) MWCNTs and **B**) the aziridine-functionalized **MW@N^{Az}**.

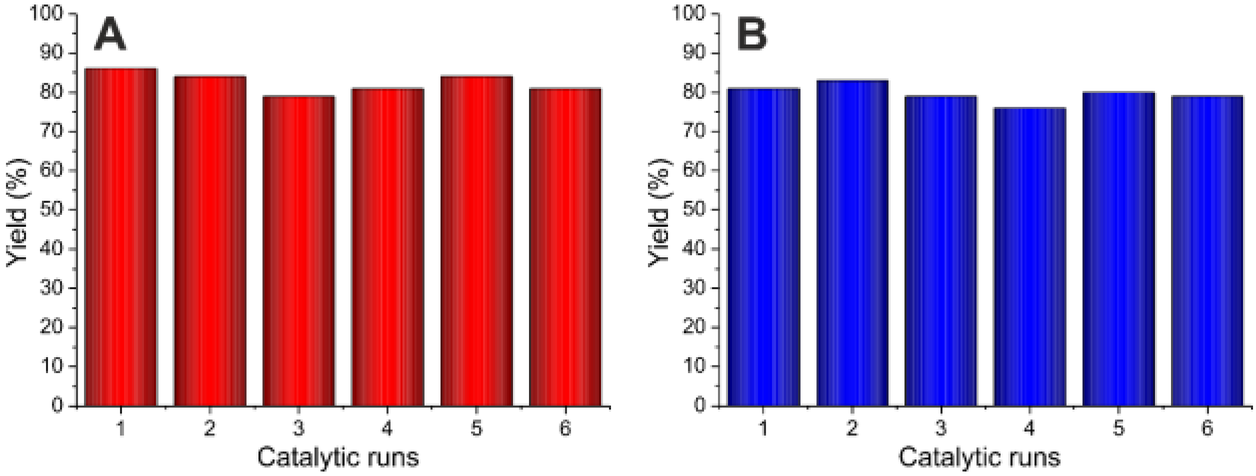

Fig. S2. Catalytic performance of **MW@N^{Az}** in the Knoevenagel condensation in a six-fold catalyst recovery and re-use. A) Reaction of **1a** with **2**; B) reaction of **1b** with **2**.

Electrochemical data processing.

The amount of the **MW@N^{Az}** deposited on RRDE is maintained constant and fixed to the optimal value [catalyst loading (μg of N-MWCNTs cm^{-2})] of n_E transferred in the process per O_2 molecule.

Table S1. Number of exchanged electrons n_E for RRDE measurements carried out at different catalyst loadings (288, 336 and 384 μg cm^{-2}).

Catalyst loading (mg of ink)	2.4	2.8	3.2
Catalyst loading (μg cm^{-2})	288	336	384
Catalyst loading (μg)[a]	56	66	75
Exchanged electrons (*n*)	3.36	3.53	3.29

[a] 0.196 cm^2 GC rotating-disk electrode

The ORR is studied through the RRDE measurements as described in the bodytext. The Pt Ring electrode potential is kept constant at a value of 0.5 V *vs*. Ag/AgCl/KCl sat. while the potential of the Disk electrode is swept from -1.1 V to 0.2 V and reversed against an Ag/AgCl/KCl sat. as reference electrode with a scan rate of 5 mVs^{-1}. The Ring potential value is chosen to allow only the oxidation of H_2O_2. While the total Disk current I_D is the sum of the O_2 reduction current to H_2O (I_{H2O}) and to H_2O_2 (I_{H2O2}) (eq.1), the Ring current I_R is due to the H_2O_2 oxidation (I_{H2O2}) exclusively (eq.2).

$$I_D = I_{H_2O} + I_{H_2O_2} \quad \text{(eq. 1)}$$

$$I_R = I_{H_2O_2}N \quad \text{(eq. 2)}$$

N is the Collection Efficiency and it is the fraction of the material from the disk which subsequently flows at the ring electrode. It can be expressed as a fraction between 0.0 and 1.0 and depends on the electrode geometry. In this work we make use of the theoretical Collection Efficiency of 0.256 as reported for the employed Pine RRDE electrode.

Accordingly, the molar fraction of H_2O_2 (X_{H2O2}) produced in the process is calculated from the number of moles of H_2O (n_{H2O}) and H_2O_2 (n_{H2O2}) using the following equations:

$$n_{H_2O} = \frac{I_{H_2O}}{4F} \quad \text{(eq. 3)}$$

$$n_{H_2O_2} = \frac{I_{H_2O_2}}{2F} \quad \text{(eq. 4)}$$

$$X_{H_2O_2} = \frac{n_{H_2O_2}}{n_{H_2O_2} + n_{H_2O}} \quad \text{(eq. 5)}$$

Replacing moles with the experimental currents (I_D and I_R) as calculated from eqs. 1 and 2 we obtain eq. 6:

$$X_{H_2O_2} = \frac{2I_R/N}{I_D + I_R/N} \qquad \text{(eq. 6)}$$

The number of electrons transferred per O_2 molecule in the ORR for the different catalysts has been calculated by the Koutecky-Levich equation applied to the ORR curves obtained at different rotation rates (rpm). The Koutecky-Levich equation is given by eq 7:

$$\frac{1}{j} = \frac{1}{j_{cc}} + \frac{1}{nK_f\sqrt{f}} \qquad \text{(eq. 7)}$$

With:

$$K_f = 0{,}2FC_0{D_0}^{2/3}\nu^{-1/6}$$

Where, j is the current density, j_{cc} is the kinetic current density, n is the number of exchanged electrons, F is the Faraday constant, D_0 is the oxygen diffusion coefficient (1.95 x 10^{-5} cm^2 s^{-1}), f is the angular rotation rate of the electrode (rpm), ν is the kinematic viscosity of the solution (0.008977 cm^2 s^{-1}) and C_0 is the O_2 concentration in solution (1.15 x 10^{-3} mol dm^{-3}). With these parameters, the value of K_f constant is 0,03538. The average number of electrons n exchanged during the ORR has been extrapolated from the slop of the plot of j^{-1} versus $f^{-1/2}$ at a specific potential value. We have recorded cyclic voltammetries from -1.0 V to 0.2 V at different rotation rates (from 400 to 2000 rpm) and calculated the n values at -0.70 V.

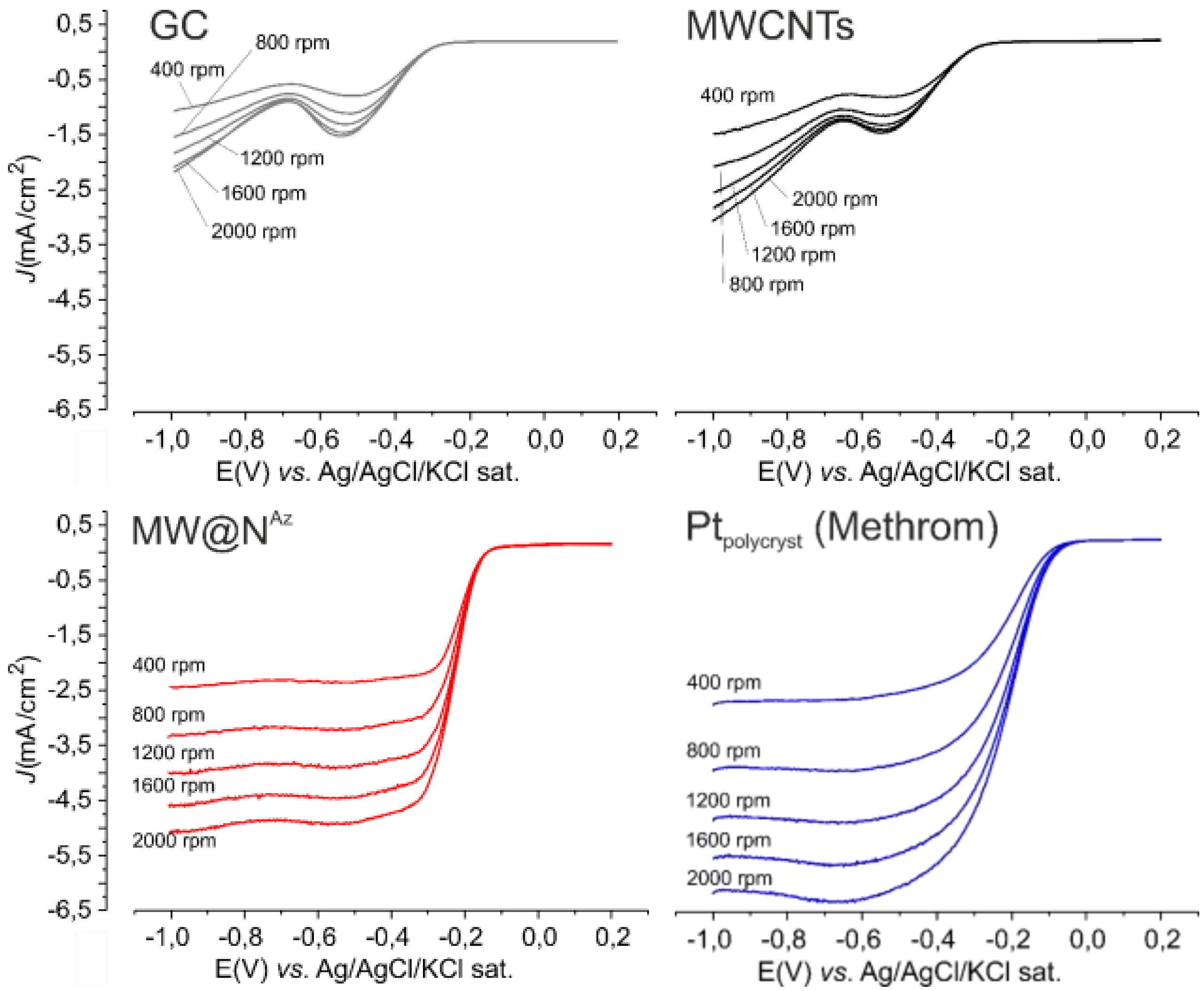

Fig. S3. Linear sweep voltammograms (LSVs) for ORR in O_2-saturated 0.1 M KOH solution for **MW@N^{Az}**, GC, pristine MWCNTs and the Pt-based reference electrode, at variable spin rates (400, 800, 1200, 1600 and 2000 rpm). Scan rates: 5 mV s-1, catalyst loading 336 µg cm^{-2}.

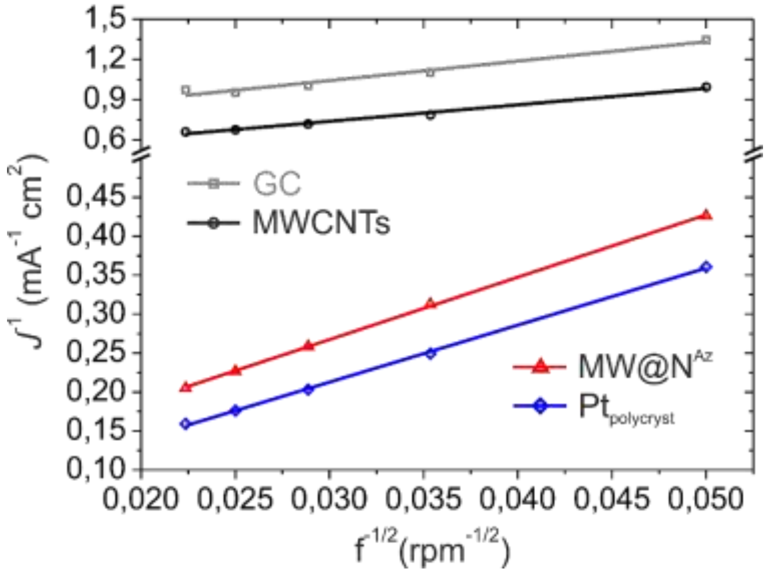

Fig. S4. K-L plots for **MW@N^{Az}**, GC, MWCNTs and Pt catalysts as obtained from the respective LSVs at -0.7 V. Parameters used: O_2 concentration (C), 1.15 10^{-3} mol L^{-1}; O_2 diffusion coefficient (D), 1.95 10^{-5} cm^2 s^{-1}; kinematic viscosity (*v*) of the electrolyte solution, 0.008977 cm^2 s^{-1} (see also the Experimental section).

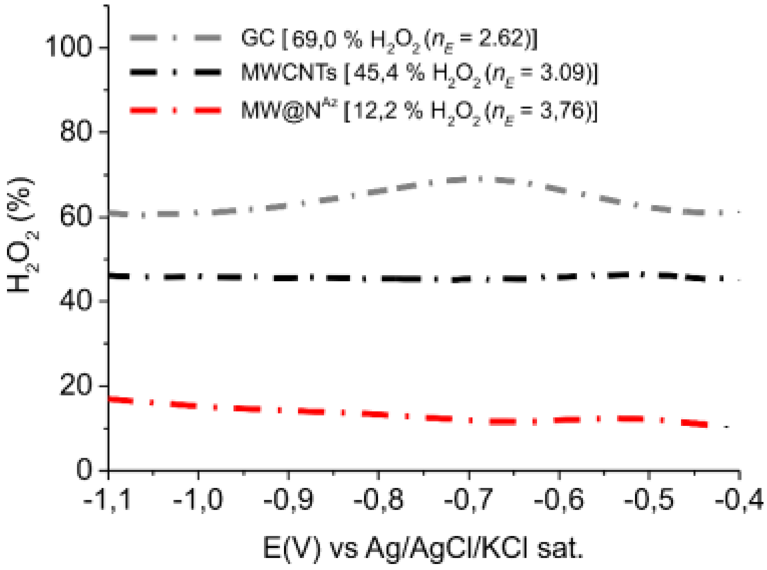

Fig. S5. H_2O_2 production (%) for all carbon based (N-doped and undoped) catalysts. Number of exchanged electrons for mol of O_2 is measured at -0.7V.

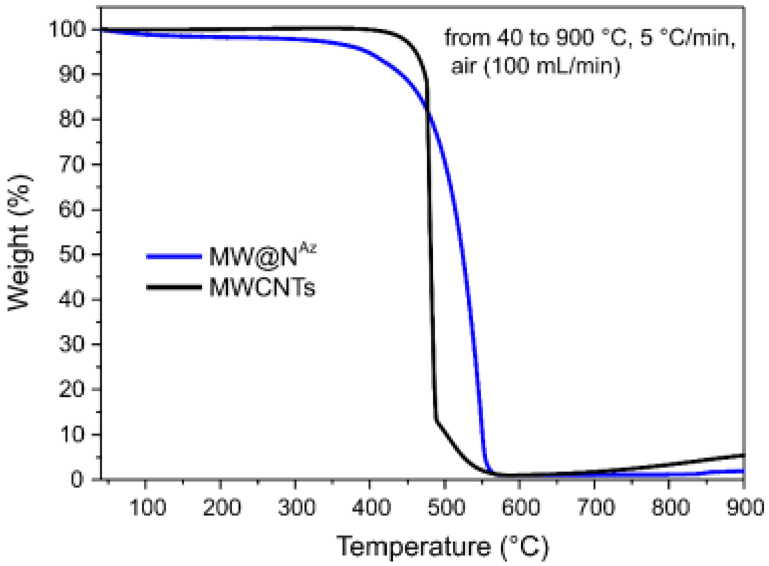

Fig. S6. TG profiles of pristine MWCNT (black line) and **MW@N**$^{\mathbf{Az}}$ (blue line) samples in air (100 mL/min).

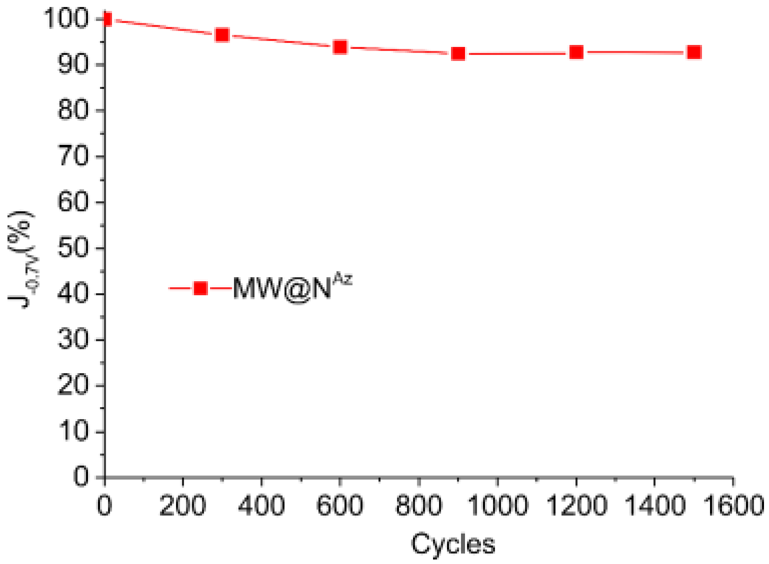

Fig. S7. ORR stability tests on **MW@N**$^{\mathbf{Az}}$ in ORR after 1500 cycles in the -1.1 ÷ 0.2 V range (200 mV s^{-1}, 800 rpm in 0.1 M KOH at 25 °C)

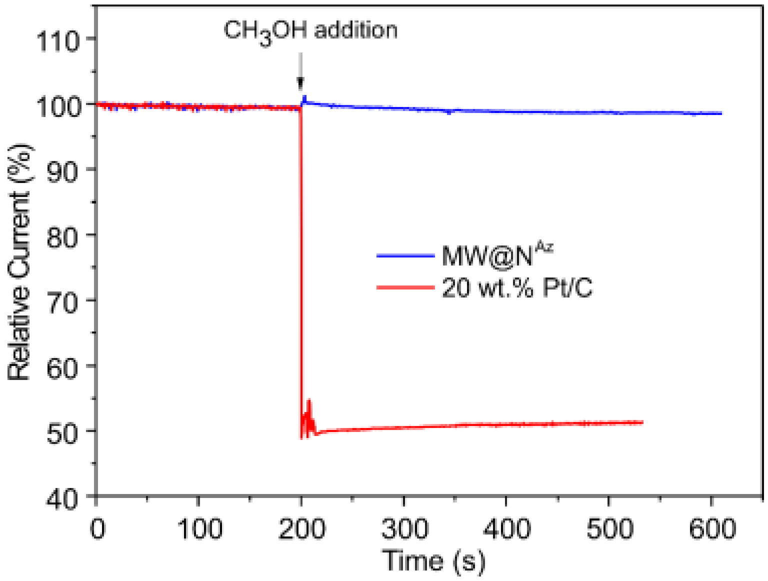

Fig. S8. Chronoamperometric ORR response as measured at -0.35 V *vs.* Ag/AgCl/KCl sat (800 rpm) on **MW@N^{Az}** and 20 wt% Pt/C (Vulcan® XC-72) electrodes in O_2-saturated 0.1 M KOH electrolyte solution upon injection of MeOH (till 1M concentration)