Electronic Supplementary Information

Growth and dissolution of NaO_2 in an ether-based electrolyte, as the discharge product in the Na-O_2 cell

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Experimental Methods

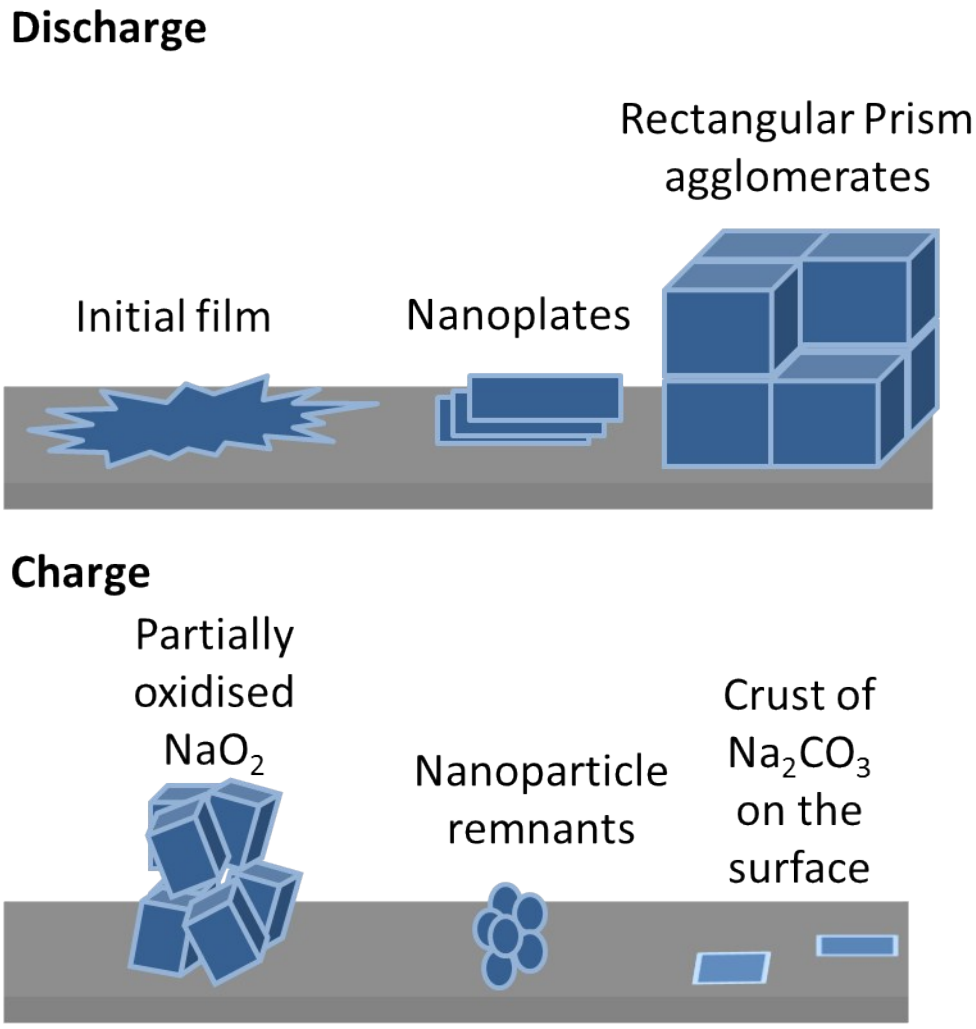
Sodium perchlorate ($NaClO_4$) (Aldrich, 98%), was dried under vacuum at 120°C overnight. Anhydrous diethylene glycol dimethyl ether (DEGDME) (99.9% Romil <10 ppm H_2O) was stored over activated molecular sieves (4 Å) (Aldrich) until the water content was <5 ppm, whereby after O_2 purge H_2O content increased slightly to <20 ppm (Karl Fischer Coulometer (Mettler-Toledo C20)). All electrolytes were prepared in an Ar glovebox (Innovative Technologies, < 0.1 ppm H_2O and O_2).

HOPG (Bruker AFM probes) of quality of ZYB grade (grain size up to 1 μm) was cleaved using the scotch tape method before use.[26] HOPG was used as the working electrode and mounted within a glass cell in 0.5 M $NaClO_4$/DEGDME. Ag wire pseudo-reference electrode and Pt wire coil counter electrodes were used to complete the setup. The measurements were taken via CV at 100 mVs^{-1} to a specified potential and held there for one minute until current had diminished below -0.01 mA cm^{-2}. All samples were then transferred to the AFM glovebox without exposure to atmosphere. The AFM images of HOPG were collected via a Bruker Multimode 8 system. The HOPG surface was then scanned in the liquid electrolyte (Scanasyst fluid and Scanasyst+ fluid tips, spring constant 0.7 N m^{-1}, resonant frequency 150 KHz) using quantitative nanomechanical mapping (QNM). Image analysis was performed using nanoscale analysis software (Bruker).

Raman spectroscopy (Renishaw in via spectrometer with inverted microscope) was carried out on samples in a hermetically sealed measurement cell using a 633 nm laser (max power 2 mW cm^{-2}). FTIR spectroscopy was performed on a Nicolet IS50 ATR that was contained within an inert atmosphere glove box (0.1 ppm O_2, 0.0 ppm H_2O) allowing for the analysis of samples without exposure to atmosphere.

Table S1 Charge passed and calculated mass of NaO_2 produced during various stages of the discharge process in DEGDME.

AFM Image (E/V vs. Na^+/Na)	Q(C)	Q(eV)	Moles of NaO_2	Mass of NaO_2 (g)	Mass in mg of NaO_2 (mg)	Idealised film thickness (nm)
Fig1c $NaClO_4$ 2.1 V	2.58	1.61×10^{-19}	2.68×10^{-5}	1.04×10^{-3}	1.04	4.7
Fig1d $NaClO_4$ 1.6 V	13.54	8.45×10^{-19}	1.40×10^{-4}	5.47×10^{-3}	5.47	25
Fig 1e $NaClO_4$ 1.1 V	23.99	1.50×10^{-20}	2.49×10^{-4}	9.69×10^{-3}	9.69	44
FigS11 NaTFSI 1.1 V	27.70	1.73×10^{-20}	2.87×10^{-4}	1.12×10^{-3}	11.20	51



Schematic 1. Growth and dissolution of NaO_2 rectangular prisms as discharge product in the Na-O_2 cell on HOPG in 0.5 M $NaClO_4$ DEGDME

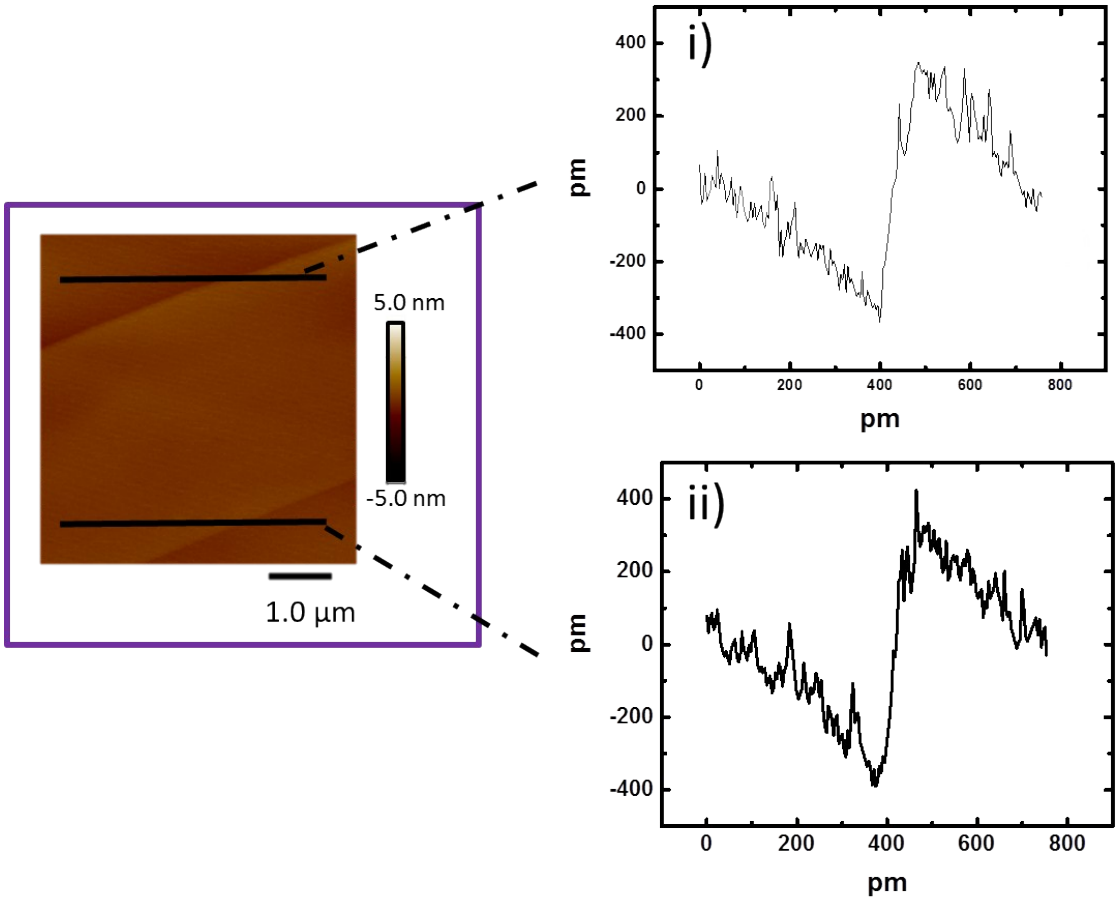


Figure S1. Line profiles of figure 1b showing the step edges height on a clean, cleaved HOPG surface at 2.8 V vs. Na^+/Na. This shows the step edges are 500 pm in height.

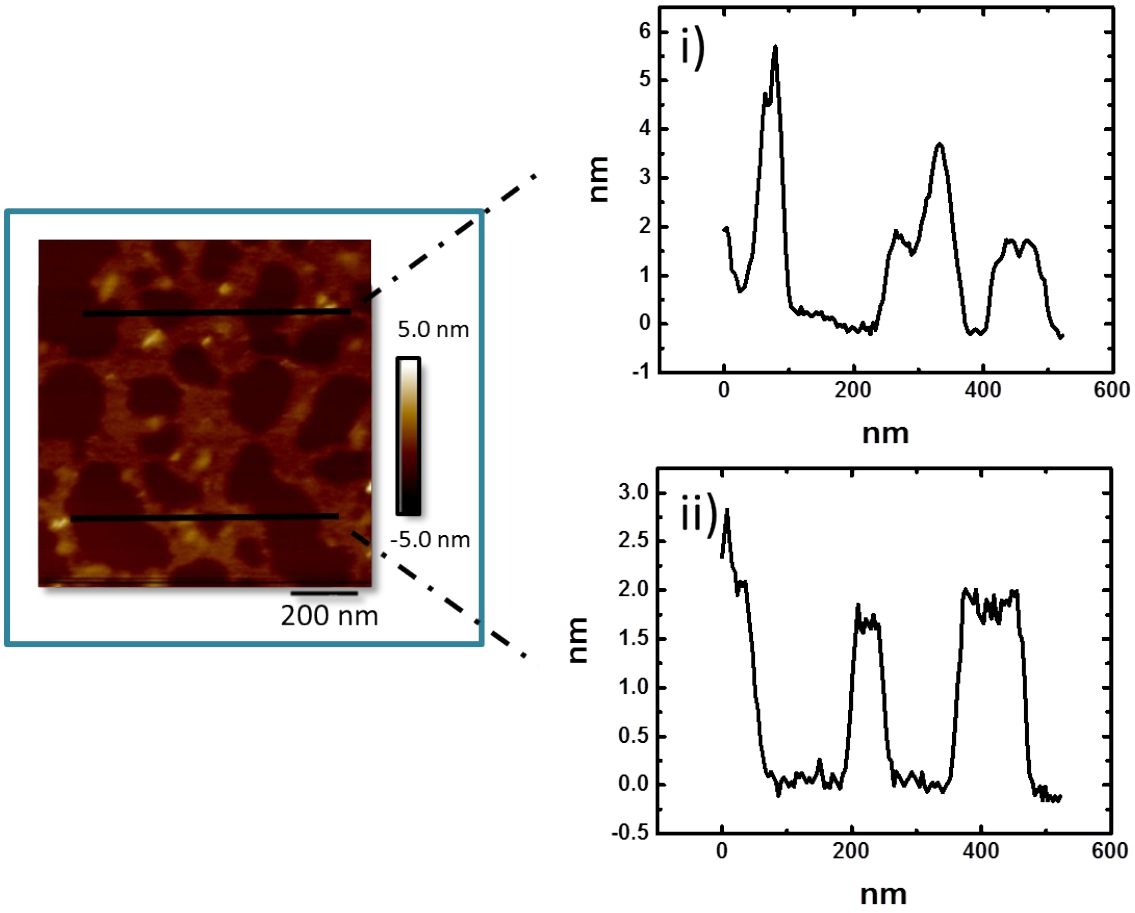


Figure S2. Line profiles of figure 1c showing the film formed at 2.1 V vs. Na^+/Na. The film is patchy and inhomogeneous. From the height profiles in i) and ii) it can be seen that these features are between 3 and 5 nm in height.

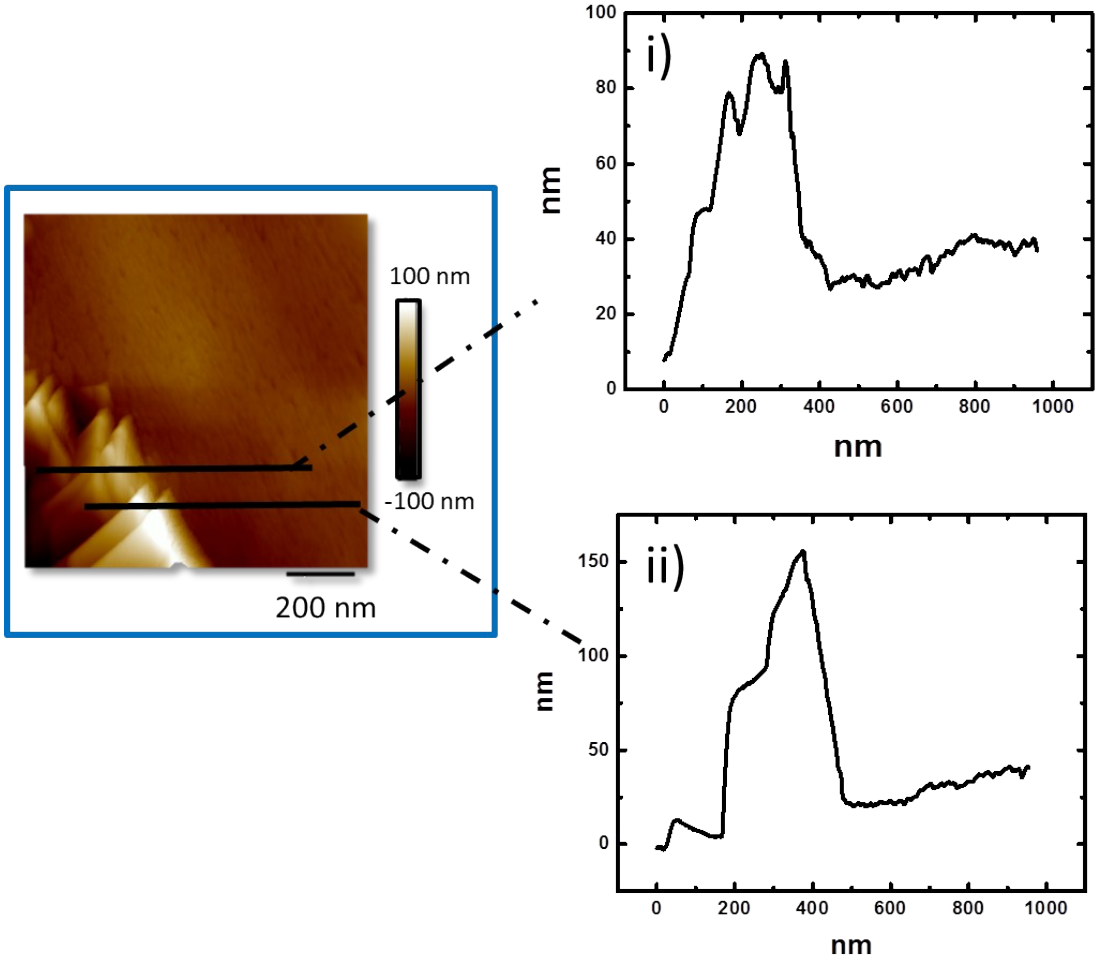


Figure S3. Line profiles of figure 1d showing the nanoplates formed at 1.5 V vs. Na^+/Na. The plates are grouped together and vary in height and morphology. i) shows features 100 nm in height and with a roughened top. ii) is a smoother part of the feature showing one major step and a peak that is again 100 nm in height.

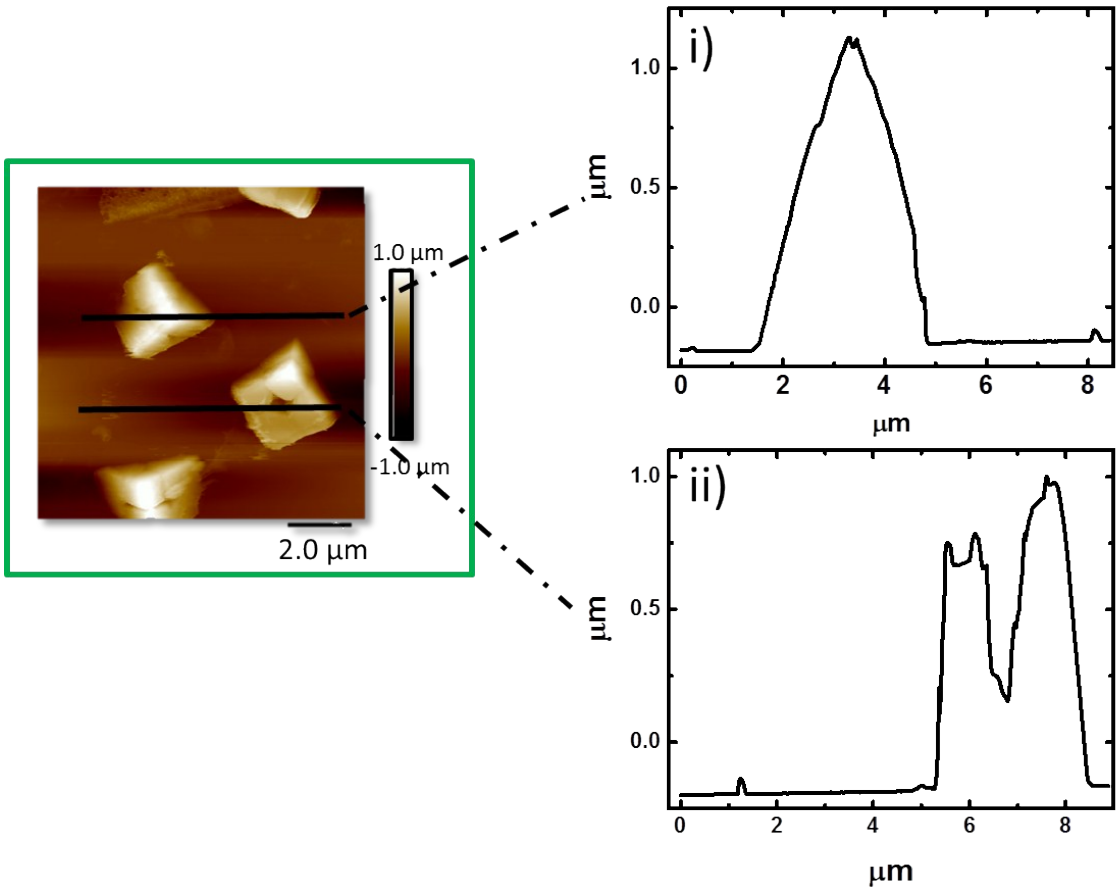


Figure S4. Line profiles of figure 1e showing the step edges height at 1.1 V vs. Na^+/Na. Here line profile i) shows the triangular or pyramidal shape of the deposit growing out from the surface to 1.0 µm and ii) a line profile of the height of a rectangular prism orientated straight out of the picture in the z direction. This shows the hole or defect of the cube is half way into the NaO_2 crystal.

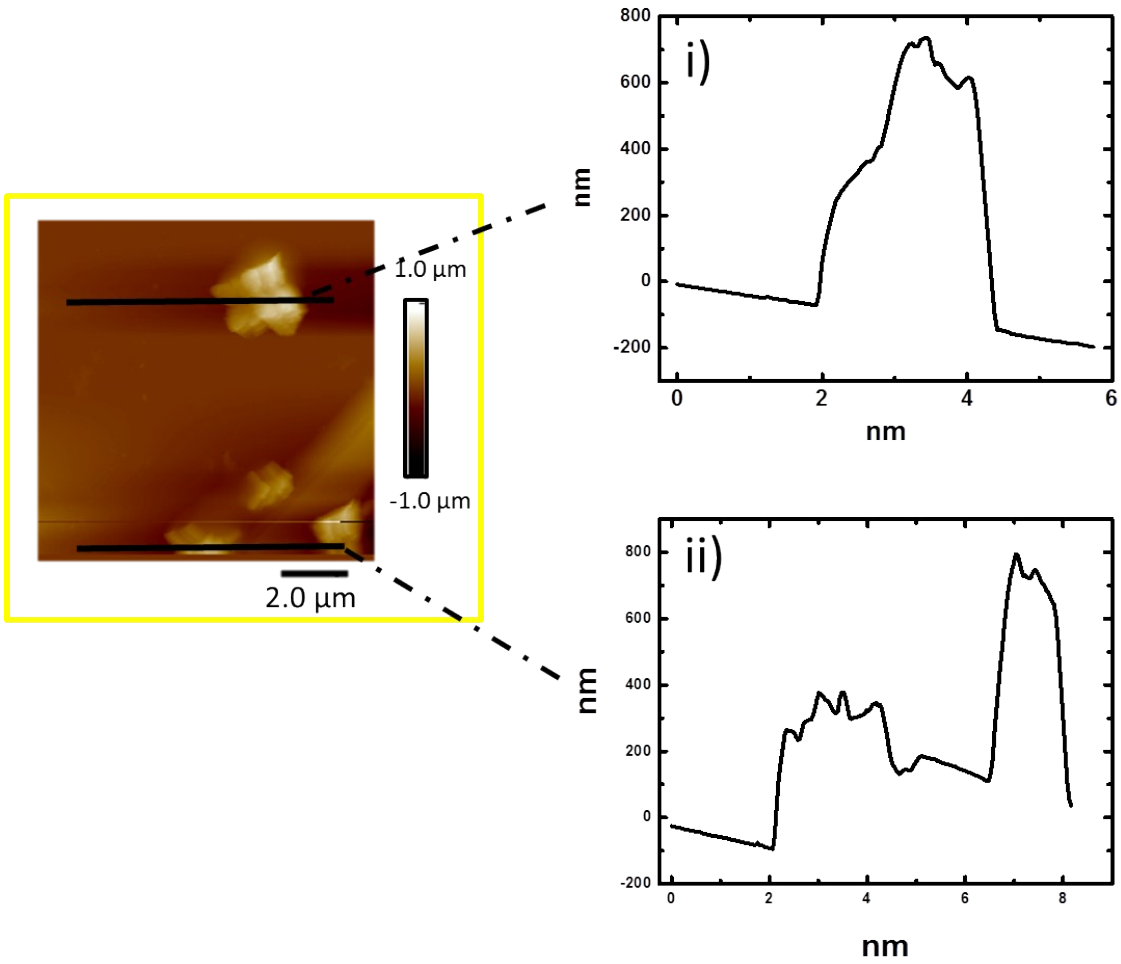


Figure S5. Line profiles of figure 1f showing the step edges height at 2.8 V vs. Na^+/Na. This shows the height profiles in i) and ii) that show partially oxidised NaO_2 crystals that are more rounded in shape, the edges being oxidised first, and diminished in size from the formed NaO_2 rectangular prisms.

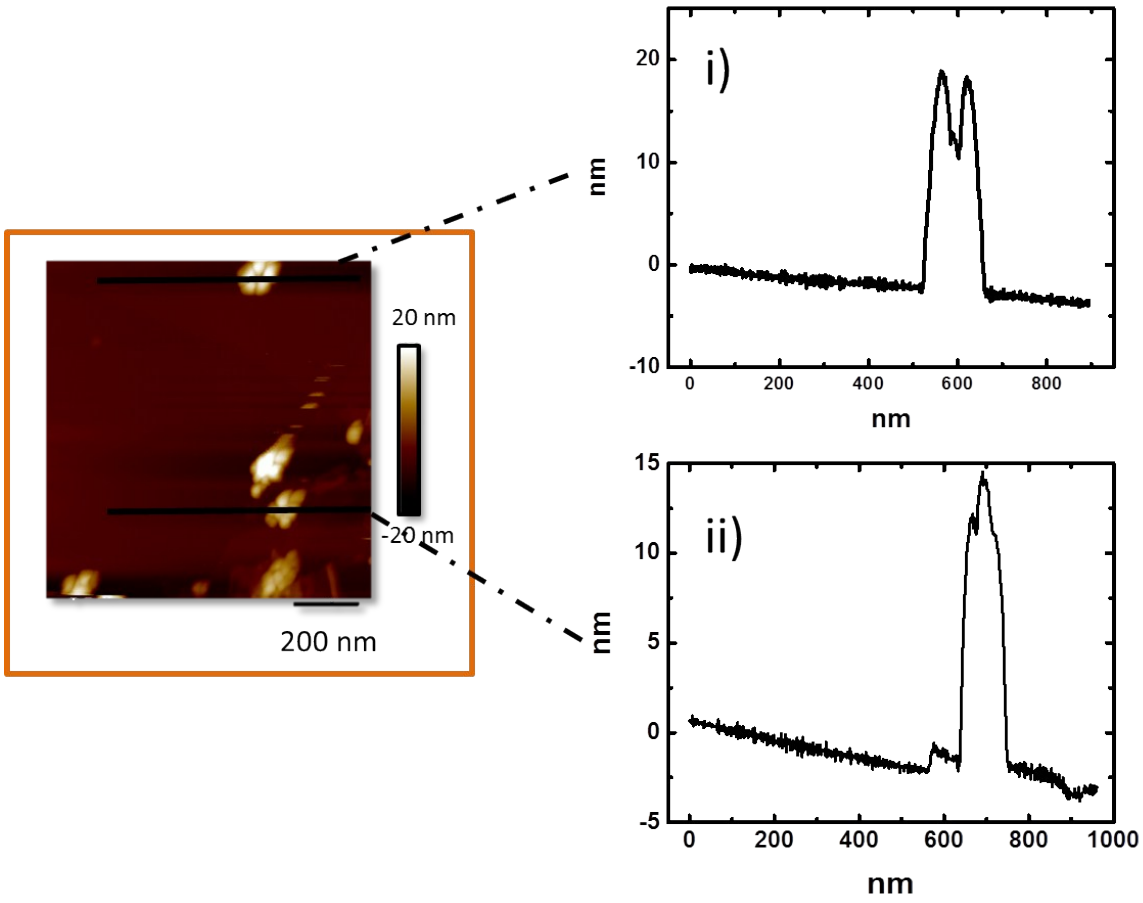


Figure S6. Line profiles of figure 1g showing the step edges height at 3.25 V vs. Na^+/Na. The features are now 20 nm in size as in i) and ii). These features are wider than they are in height. Again they appear to be rounded from the height profiles.

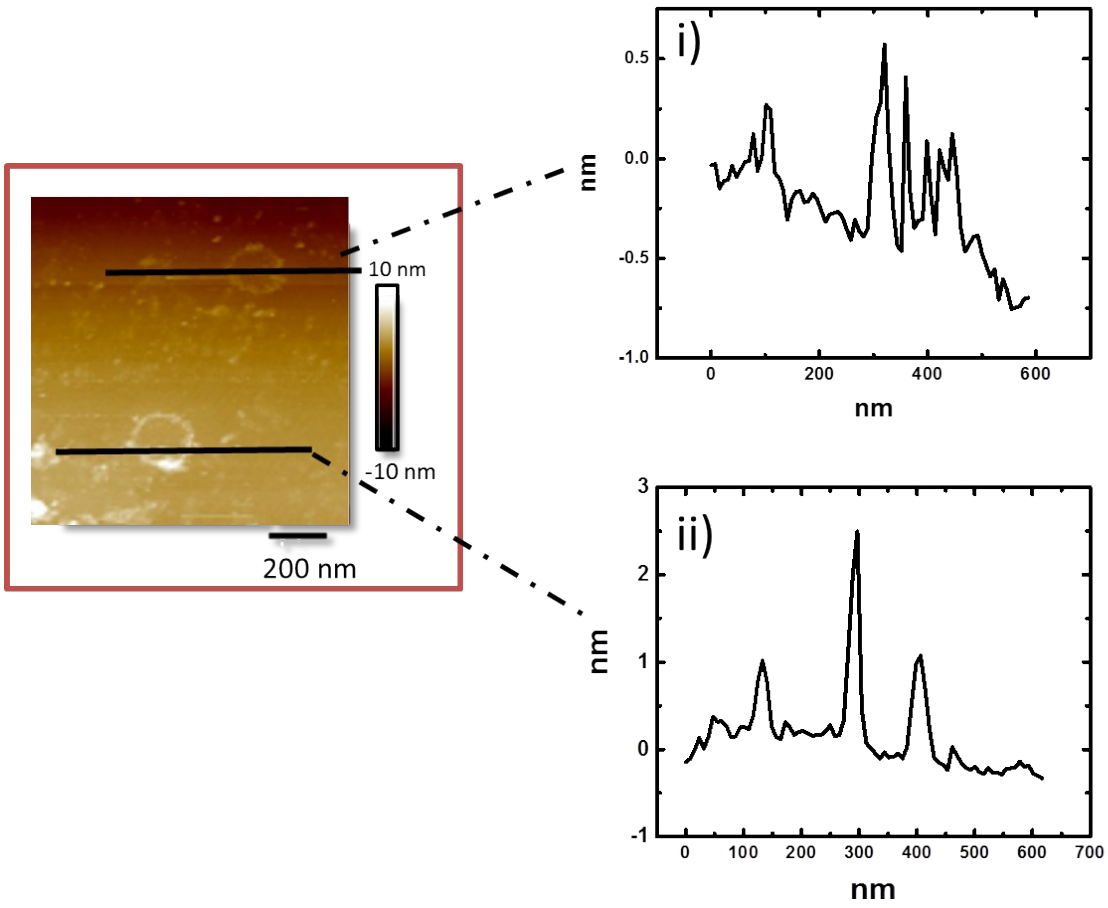


Figure S7. Line profiles of figure 1h showing the step edges height at 4.0 V vs. Na^+/Na. i) and ii) show the height profiles of the Na_2CO_3 crusts that are left on the surface. The rings have a height of 1-3 nm. The ring in i) is rougher in the centre whereas the ring in ii) is smoother between peaks.

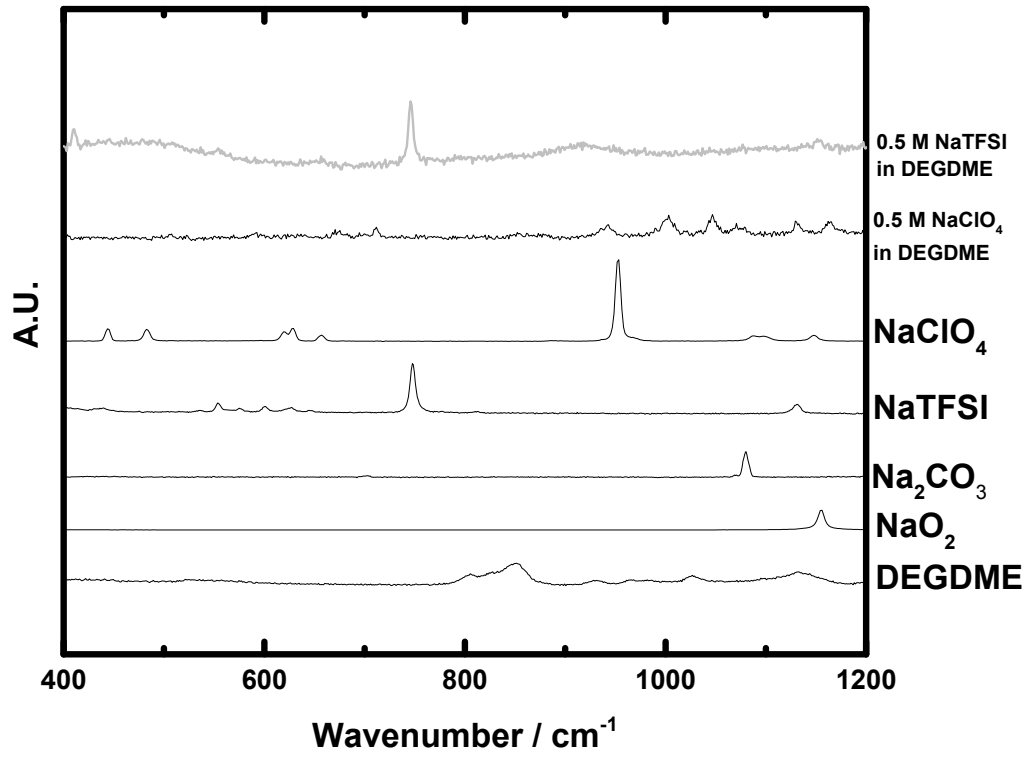


Figure S8 Showing Raman data of the AFM image of HOPG at 1.1 V vs. Na^+/Na in 0.5 M $NaClO_4$ (Figure 1e) and NaTFSI (Figure S12) in DEGDME compared to the standards of $NaClO_4$, NaTFSI, NaO_2 and $NaClO_4$ and DEGDME. This shows the presence of NaO_2 at 1165cm^{-1} for $NaClO_4$, and 1154 cm^{-1} for NaTFSI. In the 0.5 M $NaClO_4$ in DEGDME, sodium carbonate (Na_2CO_3) is also detected at 1078 cm^{-1}. Additional bands can be tentatively assigned to trace electrolyte solvent and salt.

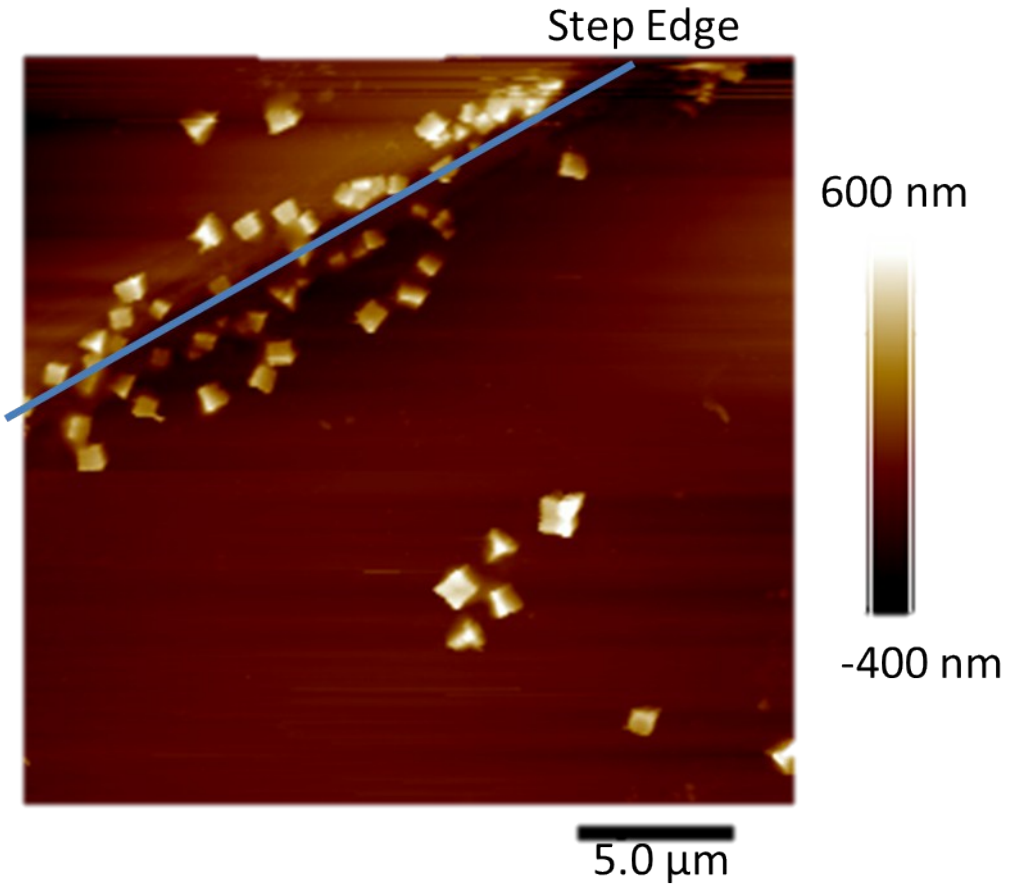


Figure S9. Agglomeration of NaO_2 crystals along a step edge and on the basal plane surfaces of HOPG at 1.1 V vs. Na^+/Na

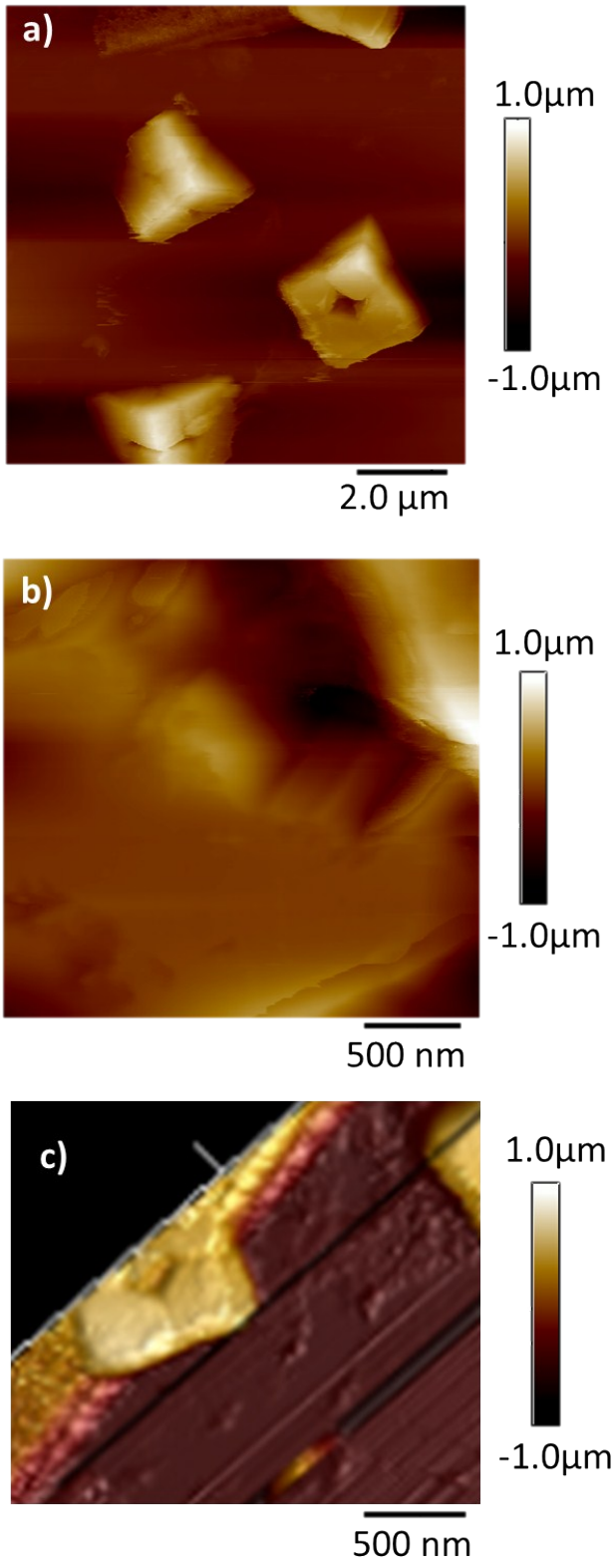


Figure S10. *Ex situ* AFM images of a) of both pyramidal and rectangular prismatic NaO_2 crystals b) Top of NaO_2 cube, b) height profile of cubes on the surface, c) 3D image of a crystal at the interface showing visible bare electrode surface in the hole of the crystal formed at the discharge to 1.1 V vs. Na^+/Na.

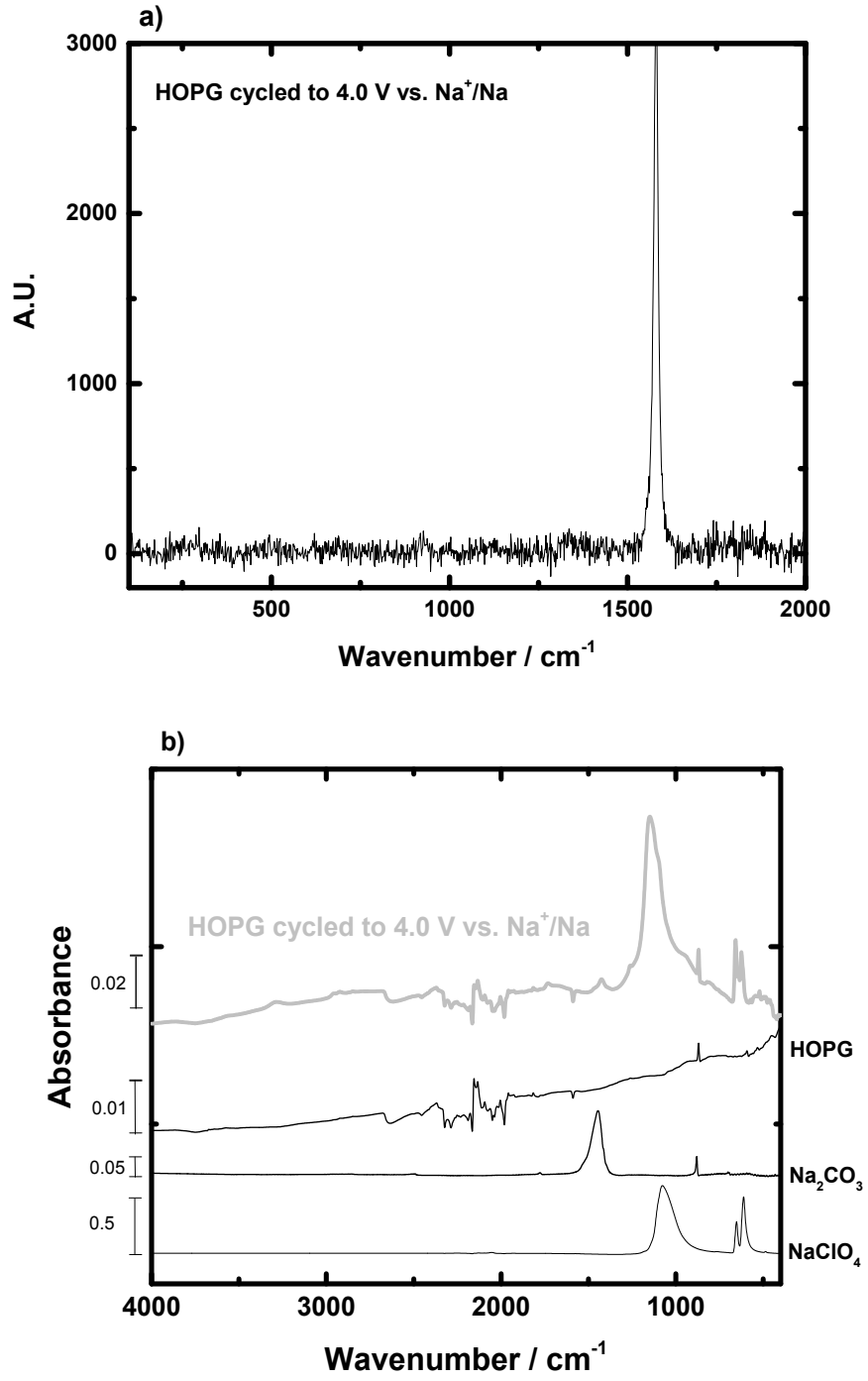


Figure S11. *Ex situ* Raman spectroscopy of HOPG after cycling to and end CV vertex of 4.0 V vs. Na^+/Na after an initial vertex of 1.1 V vs. Na^+/Na b) *Ex situ* FTIR of HOPG after cycling to and end CV vertex of 4.0 V vs. Na^+/Na after an initial vertex of 1.1 V vs. Na^+/Na where 1429 cm^{-1} shows the presence of Na_2CO_3. The other spectral features that are shown in the cycled HOPG spectra are found in both the standard spectra for freshly cleaved HOPG and $NaClO_4$.

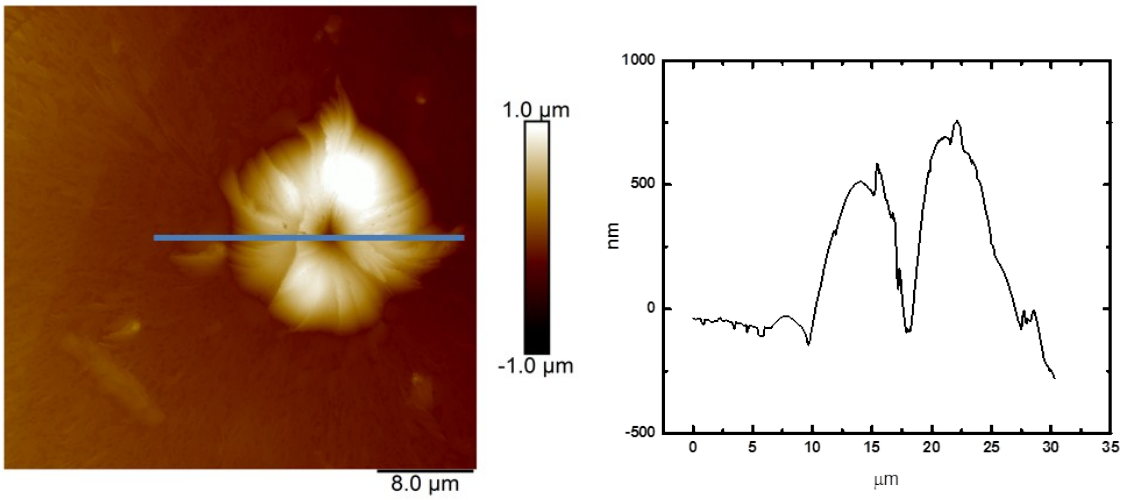


Figure S12. AFM image of HOPG at 1.1 V vs. Na^+/Na in 0.5 M NaTFSI, DEGDME, showing a poorly defined and uneven ring morphology as compared to the more regular cubic features from reduction in 0.5 M $NaClO_4$, DEGDME. The similar crystallographic feature of a central dip or hole is again present. The precipitate dimensions are much larger ca. 16x16 µm vs. 2x2 µm for $LiClO_4$ illustrating the effect of changing the anion from ClO_4^- to $TFSI^-$ on NaO_2 crystal morphology The line scan image (right) presents the height profile of the blue trace shown in the AFM image (left) that shows the hole and that the deposit is only ca. 0.5 micron in height leading to a plate like deposit of 16x16x0.5 µm.