

Electronic Supplementary Information (ESI)

Nano-inclusion in one step: Spontaneous ice-templating of porous hierarchical nanocomposites for selective hydrogen release.

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Synthesis of Graphene Oxide (GO) via modified Hummers method (Tour's method)

360 mL of sulfuric acid (analytical reagent grade, as received from Fisher) and 40 mL of phosphoric acid (85% aq. as received from Alfa Aesar) were mixed and cooled in an ice bath (0 °C, mix of water and ice). 18 g of potassium permanganate (ACS reagent >99.0%; Sigma-Aldrich) was mixed with 3 g of graphene agglomerates (graphene nanoplatelet aggregates; Alfa Aesar). The powder was then slowly added to the acid mixture once cooled to room temperature, ensuring that the solution does not overheat. The solution was removed from the ice bath and left to warm naturally to room temperature (RT) before heating to 50 °C for 16 h. On heating, the black solution became brown in colour. The mixture was poured into 400 mL of cold deionised water (surrounded by an ice-bath) followed by addition of 7 mL hydrogen peroxide (Hydrogen peroxide 30%; VWR). The final mixture is left to warm naturally to RT. The mixture was centrifuged to separate the dispersed GO followed by the exchange of the supernatant solution with DI water. At least 10 such washes were performed.

Fabrication of nanocomposite structures by ice templating

A GO suspension (10-40 mg of GO per mL of DI water) was poured into a Teflon cylindrical mould (Ø 30 mm and 35 mm tall). The mould was loosely attached to a stainless-steel metallic plate with vacuum grease. The plate was suspended above liquid nitrogen (Figure S1 a). The volume of liquid nitrogen was regularly adjusted to maintain contact between the metallic plate and the liquid nitrogen surface. The temperature gradient was therefore vertical and relatively constant (-196 °C at the cold side and ~20 °C (RT) at the "hot" side). Under unidirectional solidification conditions, the long axis of the hexagonal ice crystals is approximately aligned with the temperature gradient, leading to a lamellar morphology. As the solubility limit of the sample (here only GO) in ice is low, the species present in the initial suspension (here only GO) will be "expelled" by the growing ice crystals. Once frozen, the monolith was removed from the mould and freeze-dried (Schlenk line at ca. 3.10⁻¹ mbar and -196 °C to RT). The monoliths have a typical diameter of 30 mm (from the mould) and variable length (typically 25 mm) with a unidirectional lamellar structure (Figure S1 a).

Alternatively, 3D structures without moulds can be prepared by ice templating as beads. GO beads were synthesised by dropping the GO suspension (e.g. using a syringe and needle) into liquid nitrogen (Figure S1 b) and subsequently freeze-dried.

The temperature gradient is thus radial, leading to a radial lamellar structure. The beads show a relatively homogeneous size distribution with a mean 2.8±0.2 mm diameter (Figure S1 b; a 0.8 mm inner diameter needle was used).

Reduction of Graphene Oxide to reduced Graphene Oxide (rGO)

GO can be reduced to rGO in the TG-DTA under Ar, but on a larger scale a typical pre-treatment involves heating GO beads in an alumina crucible in a box furnace. The temperature is set to 250 °C with a 5 °C.min⁻¹ heating ramp and 3 h dwelling time. The resulting reduced graphene oxide beads (SSA of 20.7±1.2 m².g⁻¹ measured via BET) are then re-dispersed into de-ionised water to obtain a 20 mg.mL⁻¹ rGO solution. (Partially) reduced graphene oxide (rGO) beads and monoliths (and resulting composites) were prepared in a similar way to GO although rGO is notably more hydrophobic than GO itself and so the aqueous treatment required for ice-templating is typically extended.

Calculations of hydrogen gravimetric density (wt. %)

Multiple analyses on GO matrix samples reveal an average mass loss of 34 % (as CO_x) for the batches used to prepare composites. To consider the 1:1 by wt. 1:1 AB:GO composites as an example, the materials exhibit an average mass loss of 22.5 % from RT-250 °C (Figure S19). Given the mass ratio 1:1, 34/2 = 17 wt. % is the mass loss expected from CO_x release. Subtracting this from the total mass loss of the composites gives 22.5-17=5.5 wt. % of gaseous products from AB decomposition. The only gases detected are hydrogen and trace ammonia (which is ca. 4 orders of magnitude less than H₂ and considered negligible). Comparing the 5.5 wt. % yield of H₂ in the 1:1 composite with the theoretical value at 250 °C (13.1 % / 2 = 6.55 %) then 84 % of the theoretical yield of hydrogen at 250 °C from AB is obtained.

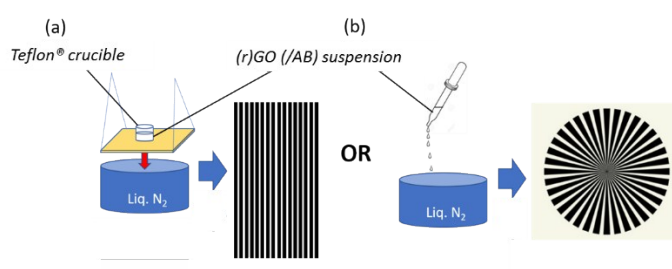


Figure S1: Set up used to fabricate: (a) (r)GO monoliths with vertical porosity and (b) (r)GO beads with radial porosity. The same process was performed with (r)GO/AB suspensions to prepare composite structures.

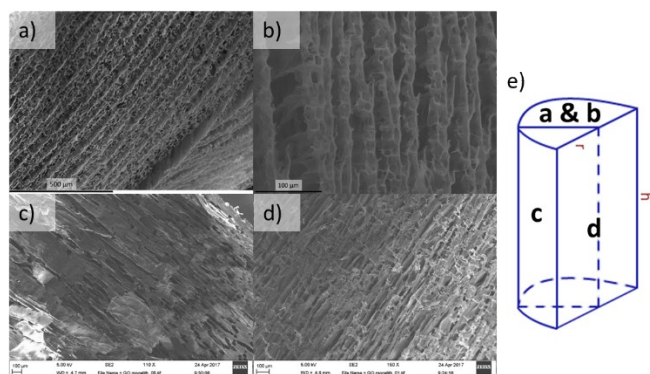


Figure S2: (a)-(d) Micrographs of sections of GO monoliths made via ice-templating. (e) is a representation of the faces of the monolith where a, b, c and d refer to the points where the monolith was taken. (a) and (b) are plan views from the top surface, whereas (c) and (d) represent side views of the monolith. r is the radius of the monolith (typically, 1.4 ± 0.1 mm) and h its height (typically, 25 mm).

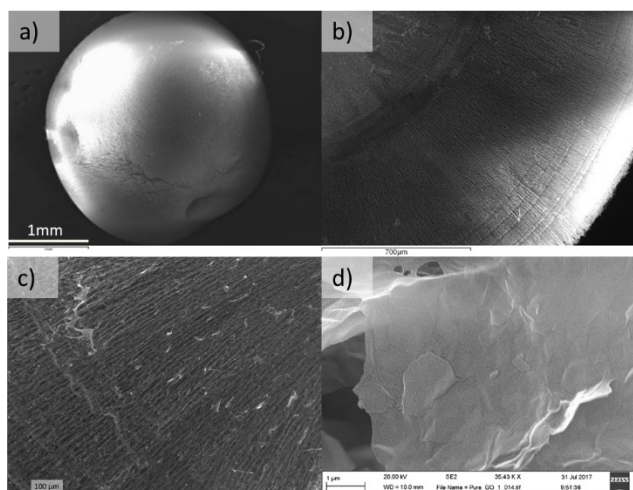


Figure S3: Micrographs of (a) entire GO beads, (b, c) cross sections of GO beads and (d) GO sheets within bead layers.

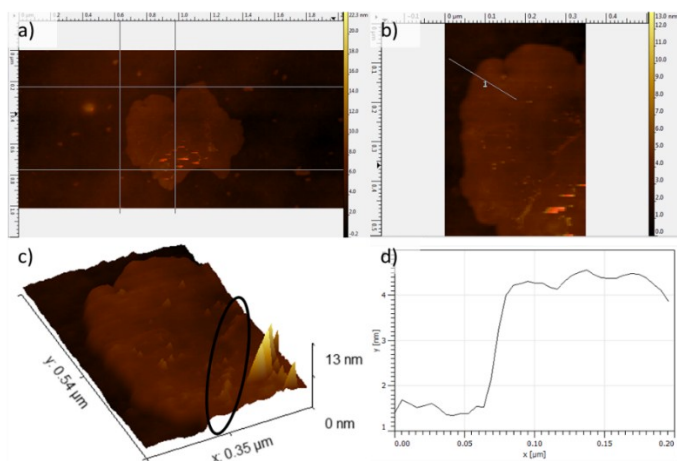


Figure S4: AFM imaging of GO prepared by Tour's method: (a, b) A GO full particle showing the zoomed area defined by the white rectangle (in (b)); (c) 3D representation of the selected area shown in (b) highlighting a wrinkle and (d) profile analysis taken through the white line in (b). Considering reported values for the thickness of GO (0.6-1.2 nm),²⁻⁶ this analysed particle is <5 layers thick. Particles were 3.5 nm thick on average across the AFM samples (<6 layers thick).

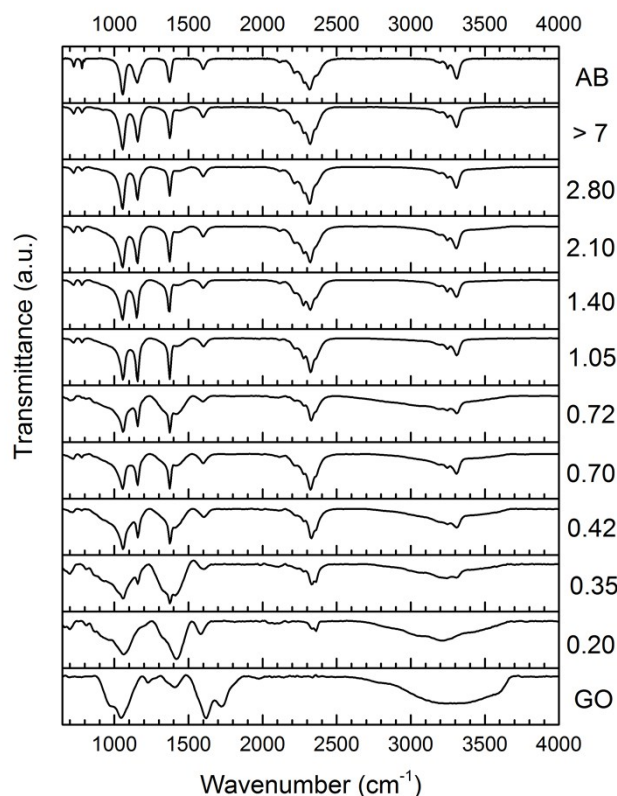


Figure S5: IR spectra of GO and composite materials across a range of weight ratios from the pure matrix (GO) to as-received AB. The AB:GO ratio by wt. is annotated on each spectrum.

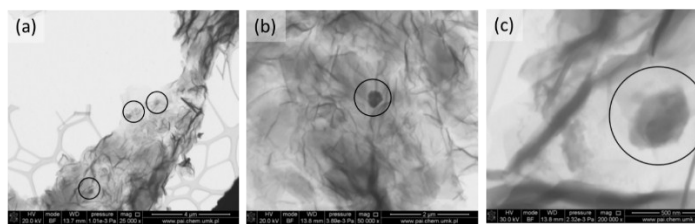


Figure S6: STEM images of (a, b) a 1:1 by wt. AB:GO composite and (c) a 1:2 by wt. AB:rGO composite. Circles highlight the larger AB clusters within the GO/rGO matrices.

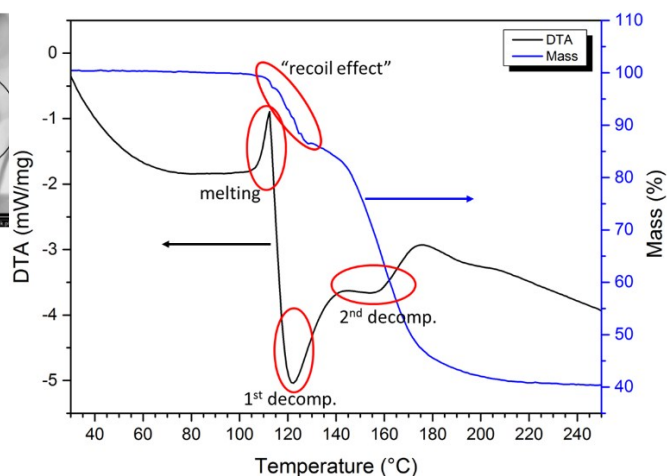


Figure S9: TG-DTA profiles of neat AB on heating from RT to 250 °C at 5 °C.min⁻¹ under argon flow.

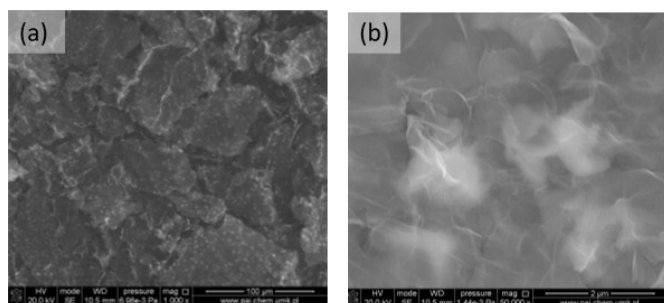


Figure S7: (a, b) SEM images of a 1:1 by wt. AB:GO composite. AB clusters were randomly and relatively well dispersed.

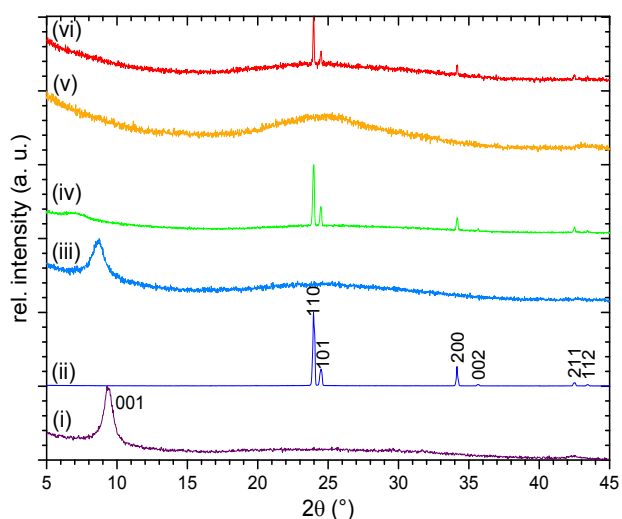


Figure S8: PXD patterns of (i) neat GO, (ii) neat AB and composites of (iii) 1:5 AB:GO, (iv) 3:4 AB:GO, (v) 1:5 AB:rGO and (vi) 3:4 AB:rGO.

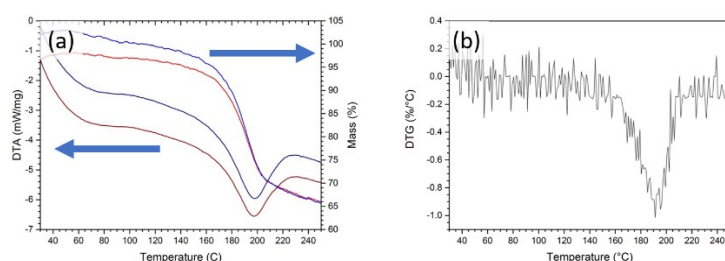


Figure S10: (a) TG-DTA and (b) d(TG)/dT (DTG) profiles of GO beads on heating from RT – 250 °C. A clear mass loss occurs from 150 – 160 °C due to CO₂/CO release.

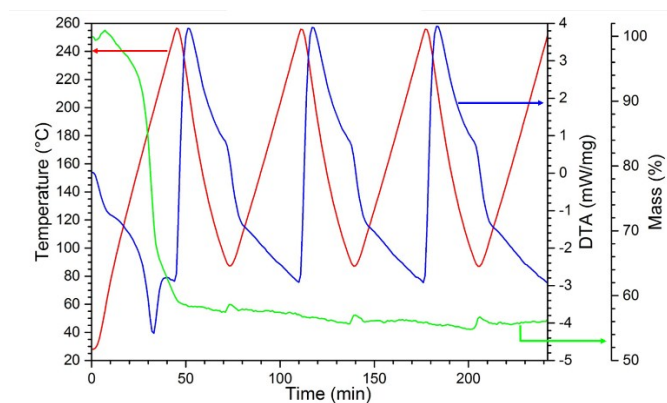


Figure S11: TG-DTA profiles for GO beads over three heating/cooling cycles (RT-250 °C). A mass loss occurs during the first heating ramp (cycle #1) corresponding to release of CO_x. No further mass change is observed on subsequent cycling.

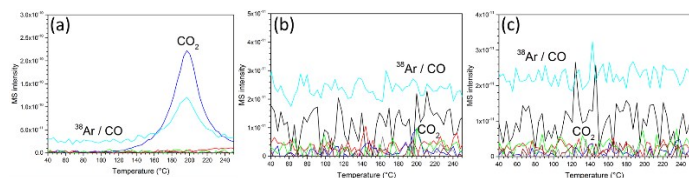


Figure S12: Evolved gas analysis mass spectra as a function of temperature over thermal cycling of GO by TG-DTA (RT- 250 °C) for: (a) cycle #1, (b) cycle #2, (c) cycle #3. No gas evolution is detected after the first heating cycle. CO₂ is represented in blue, ³⁸Ar/CO in light blue (cyan), hydrogen in black, NH₃ in red, O₂ in green, borazine in wine and diborane is represented in grey.

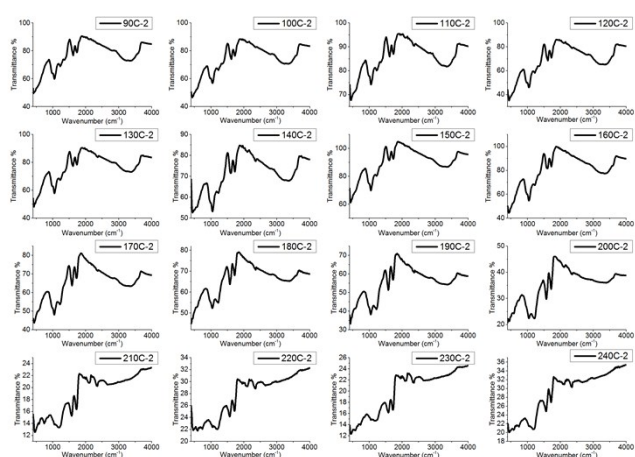


Figure S13: FTIR spectra of GO on heating from 90-240 °C (in 10 °C increments in spectra from the top left to bottom right).

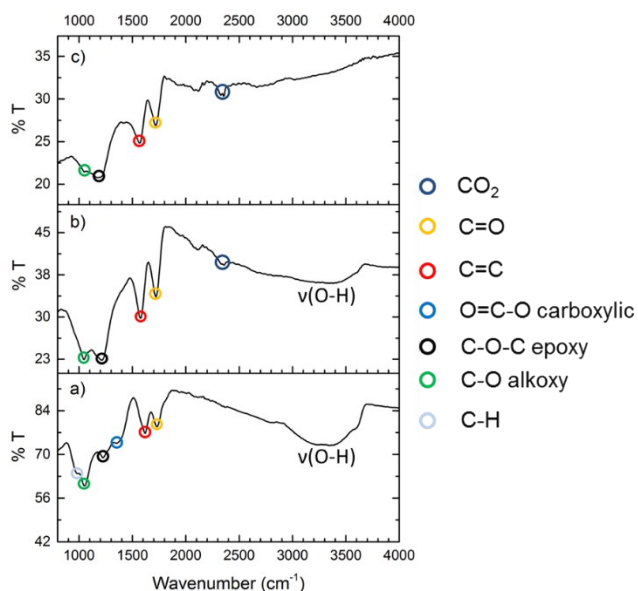


Figure S14: FTIR spectra and assignments for selected GO samples at temperatures at (a) 90°C, (b) 200 °C and (c) 240 °C.

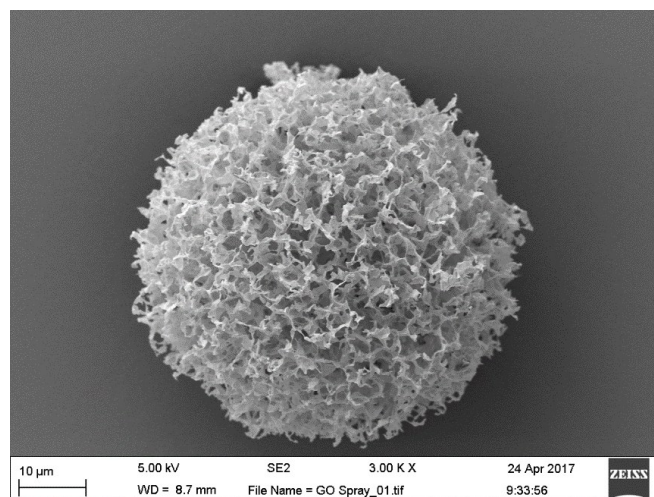


Figure S15: Example of GO matrix size/shape control. SEM micrographs of a smaller GO bead prepared via nebulization of a GO suspension into liquid nitrogen.

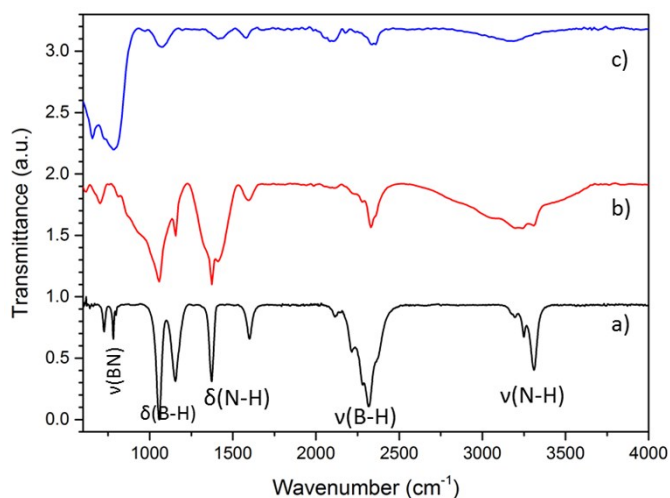


Figure S16: FTIR spectra of (a) neat AB and a 0.35:1 AB:GO composite (b) before and (c) after thermal decomposition at 250 °C. The low frequency ν(BN) band was the only major vibrational mode observed after the thermal decomposition of the composite.

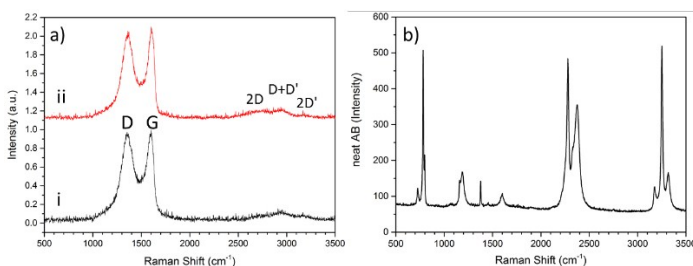


Figure S17: Raman spectra of (a) a 2:3 AB:GO composite (i) before and (ii) after thermal decomposition at 250 °C at 5 °C.min⁻¹ under argon and (b) as received AB.

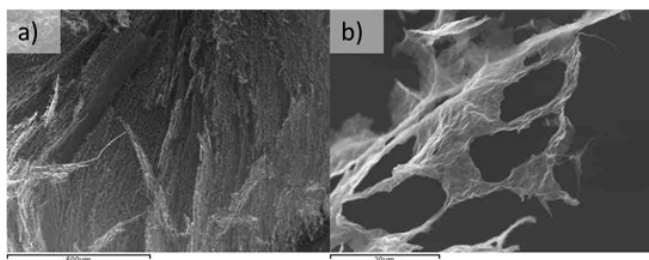


Figure S18: Micrographs of GO beads after heating at 200 °C showing: (a) retention of the layered structure; (b) constituent reduced GO sheets.

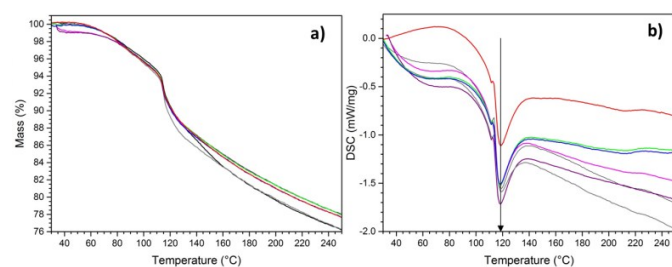


Figure S19: (a) TGA and (b) DTA profiles of a 1:1 wt. AB:GO composite on heating from room temperature to 250 °C. Seven samples (7 curves in each set of plots) were analysed to ensure repeatability and to obtain reliable average values.

References

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