Supporting information.

Hydrogen storage in high surface area graphene scaffolds.

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1. Experimental details: materials, sample preparation and characterization methods.

Graphite samples supplied by Alfa Aesar (natural flake, 325mesh, 99.8%) and Graphitwerk Kropfmühl (natural ultrafine graphite powder, 10-15µm, 99%) were used as starting material for the preparation of graphite oxide (GO) samples by following the Hummers synthesis method.[1] Thermal exfoliation of graphite oxide at ambient air conditions was used to prepare r-GO.[2] Briefly, the GO powder loaded in 70-1000 ml size containers was rapidly inserted into hot furnace (573 K) for 3-5 minutes and removed immediately after explosive exfoliation. The r-GO prepared using this way showed typical SSA of ~450 m^2/g.

To produce samples with higher SSA we used KOH activation procedure from ref.[3] modified for more precise control of r-GO/KOH ratio and better mixing of components prior to annealing. A solution of KOH/methanol (MeOH) 2.85 M (20 mL) was added to the r-GO sample (400 mg) in a round-bottom flask. The optimal KOH/r-GO weight ratio of 8 (K/C %at.≈1.7) was used to prepare samples with highest SSA. Test experiments with higher KOH to r-GO ratio of 8.5 and 9 were also performed. The mixture solution was magnetically stirred for 1 to 2 h and dried under vacuum at room temperature or 313 K for 12-24 h to evaporate all methanol. The precursor r-GO/KOH mixture was annealed in 5 ml alumina boat placed in horizontal alumina tube under argon flow (130 ml/min). Note that quartz tubes used in ref.[3] chemically react with vapours evolving from annealed material and break after 1-2 experiments. The temperature was first increased to 100°C and maintained at this temperature for 15 minutes. Then the furnace was heated to 1073 K (heating rate of 5 K/min), kept for 1 hour at this temperature and cooled back to ambient temperature. Powder obtained as a result of annealing was washed in an acetic acid solution 10% (100 mL) under stirring conditions for 30min. It was followed by filtration on a PTFE membrane (1µm) and a 3 time washing with deionized water (500mL). The drying step was done by heating the r-GO sample at 323 K under vacuum for at least 12h. The weight loss observed as a result of gasification of r-GO in process of KOH activation was about 75-80 % for samples with maximal surface area of ~3000-3300 m^2/g. Annealing was performed using ~¼ of precursor mixture, yielding 20-30 mg of material. Each of these samples was washed individually and BET surface area verified. Samples with high SSA values were selected and 3-4 samples mixed to make larger 70-100 mg samples required for H_2 sorption tests. Small impurity of sulfur (0.4 %) detected in the precursor GO by XPS, was not found in reduced and activated samples.

Attempts to achieve even higher surface areas using increased KOH amount in the KOH/r-GO mixture were not successful. Higher load of KOH results in higher percent of gasification in process of annealing and smaller yield of a-r-GO material. However, SSA values become smaller (Fig. 2S below). Note that too high KOH load results in complete evaporation of all carbon material.

Somewhat surprisingly, using r-GO prepared by thermal exfoliation as a precursor for KOH activation appeared to be crucial. Attempt to use commercial r-GO with comparable BET surface area provided by Graphenea (prepared using chemical reduction of GO) have not resulted in significant increase of SSA as a result of KOH activation procedure described above. The r-GO prepared exfoliation of Brodie graphite typically has higher surface area (~700-800 m^2/g). However, identical activation procedure applied to r-GO produced using Brodie graphite oxide as a precursor also resulted in much smaller SSA values (~1000 m^2/g) either because of different, presumably less defect structure of this material, or simply because activation procedure needs to be individually tuned for each type of precursor.

Surface area and pore volume of graphene samples were determined by nitrogen adsorption using Quantachrome Nova1200e instrument. Beforehand, r-GO samples were degassed under vacuum at 423 K (temperature increased in steps of 293 K until 373 K) for at least 12h. The relative pressure range for the calculation of (BET) specific surface area was determined by plotting the adsorption isotherm as $V(1-P/P_0)=f(P/P_0)$.[4] The selected relative pressure range should correspond to the part for which $V(1-P/P_0)$ continuously increases with P/P_0. A slit-cylindrical pore-NLDFT (non local DFT) and a slit pore-QSDFT (quenched state DFT) equilibrium models were applied to evaluate the cumulative pore volume and pore size distribution as well.

Rubotherm gravimetric system was used for hydrogen adsorption measurements at room temperature, see details elsewhere[5]. Isotherms were recorded under H_2 pressures up to 120 bar with typical weight of samples 100-300 mg. Degassing of samples prior to H_2 tests was usually performed at high vacuum conditions at 423-573 K for 12-16 hours. Adsorption tests were also performed using Hiden Isochema Intelligent Manometric Instrument (IMI) volumetric system[6] at ambient temperatures and 77 K using immersion cell. Immersion cell was also used for several tests performed using ice bath at 273 K and solid CO_2 bath at 193 K. Temperature dependence of H_2 sorption was recorded using measurement cell cooled using circulating liquid nitrogen, vacuum degassing steps were used between different temperature points. Prior to H_2 sorption tests the samples were degassed under high vacuum conditions at 150°C. Several samples were also heated in-situ under H_2 gas at 673-723 K to verify effect of hydrogen annealing on sorption properties. These samples were studied for H_2 sorption without exposure to air.

2. Analysis of nitrogen isotherms for a-r-GO samples

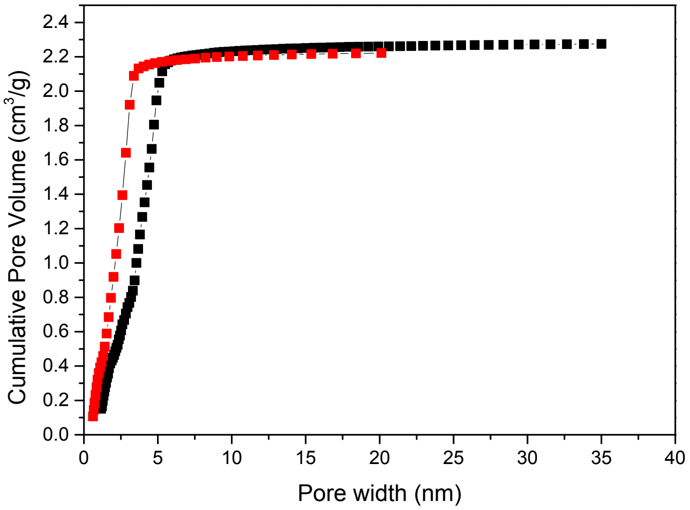


Figure 1S. NLDFT (slit/cylindrical pore model) Cumulative pore volume = 2.27 cm^3/g (black), QSDFT (slit pore model) Cumulative pore volume = 2.22 cm^3/g (red).

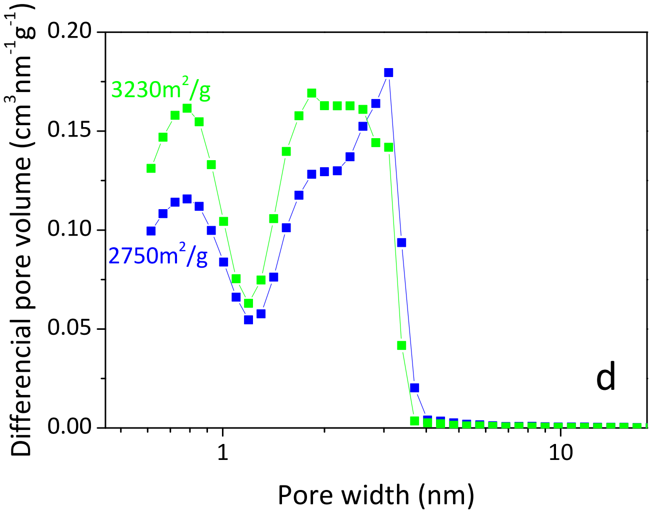


Figure 2S Pore size distribution of a-r-GO samples after annealing at 723 K under 50 bar of H2

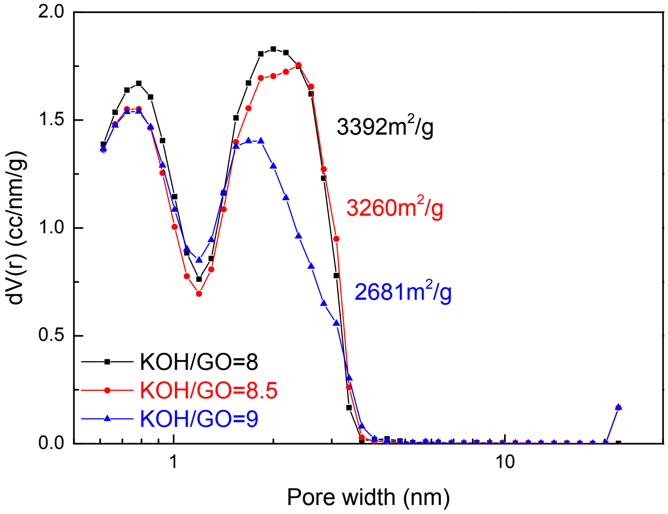


Figure 3S. Pore size distributed simulated using slit pore model (QSDFT) for samples obtained using variation of KOH/r-GO load for activation annealing.

2. XPS characterization of precursor GO, r-GO and KOH activated r-GO.

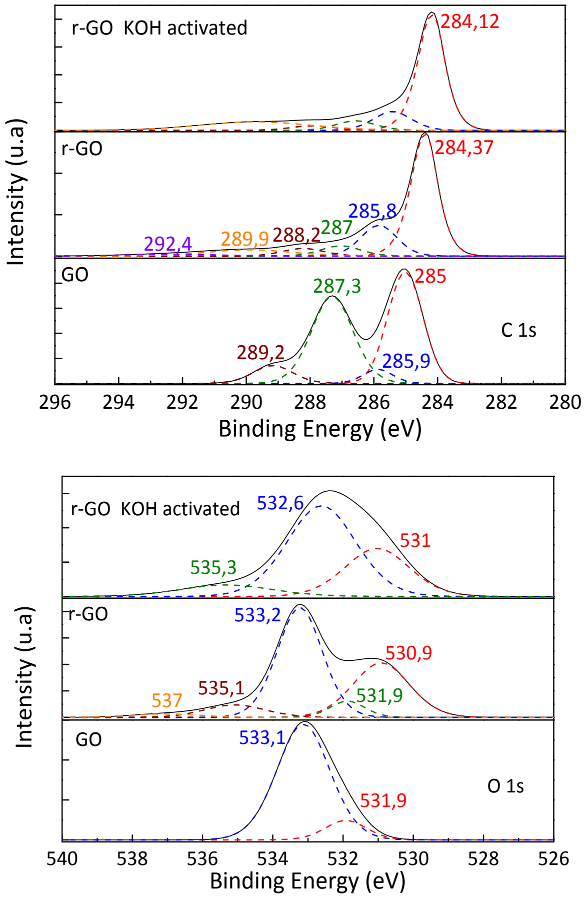


Figure 5S. XPS spectra recorded from samples of precursor GO, r-GO prepared using thermal exfoliation and KOH activated r-GO sample.

3. Raman spectra of r-GO and a-r-GO samples.

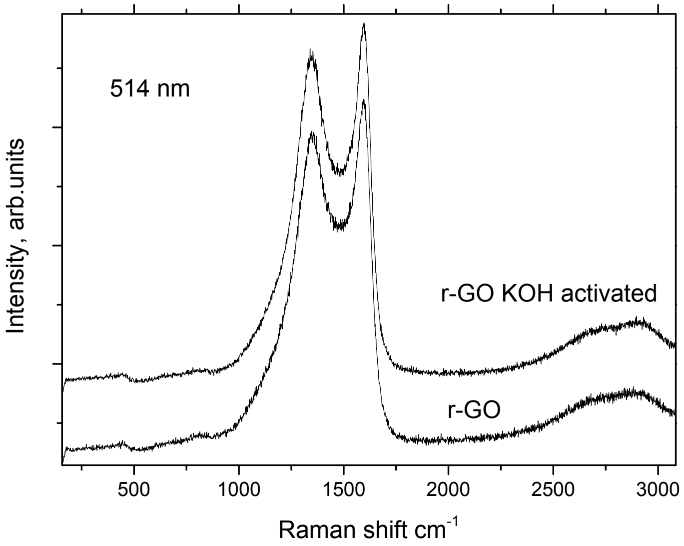


Figure 3S. Raman spectra recorded using 514 nm excitation laser for samples of r-GO before and after KOH activation. Both materials exhibit spectra typical for amorphous carbon with two strong and broad features assigned to D- and G- modes

4. Details of hydrogen uptake measurement results.

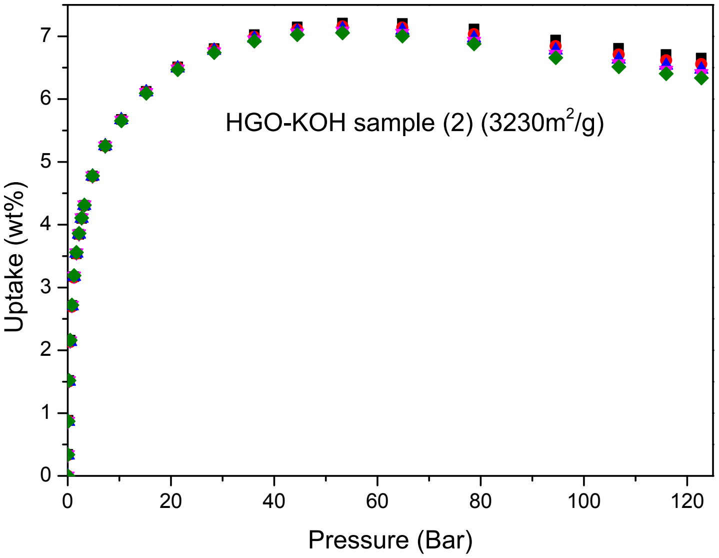


Figure 4S Hydrogen uptake measured in five consecutive adsorption cycles separated by short vacuum degassing. Measurements were performed using sample 2 (Table 1S) after air exposure for 9 weeks and degassed using standard procedure (without hydrogen annealing). Despite long air exposure the sample showed only slightly lower maximal uptake at 77K (7.2 wt% in the first cycle and 7.02 wt% in the fifth cycle). The remarkable stability of the graphene scaffold samples is an advantage compared to MOF's known to be rather sensitive to air exposure.

Table 1 H_2 uptake measured in immersion reactor at 296 K (120 bar), 273 K (120 bar), 193 K (120 bar) and 77 K (saturation pressure ~35 bar) for high-surface area a-r-GO samples before and after annealing (at 723 K under 50 bar of H_2).

Sample №	SSA, m²/g	Uptake (wt%), before annealing				Uptake (wt%), after annealing			
		296K	273K	193K	77 K	296K	273K	193K	77 K
1	2940	0.85	1.21	3.36	6.14	0.94	1.13	4.21	6.68
2	3230	1.13			7.03	1.25	1.61	4.23	7.48
3	3300	1.01	1.25	3.83	6.55				
4	1800	0.82	0.98	2.24	4.21				

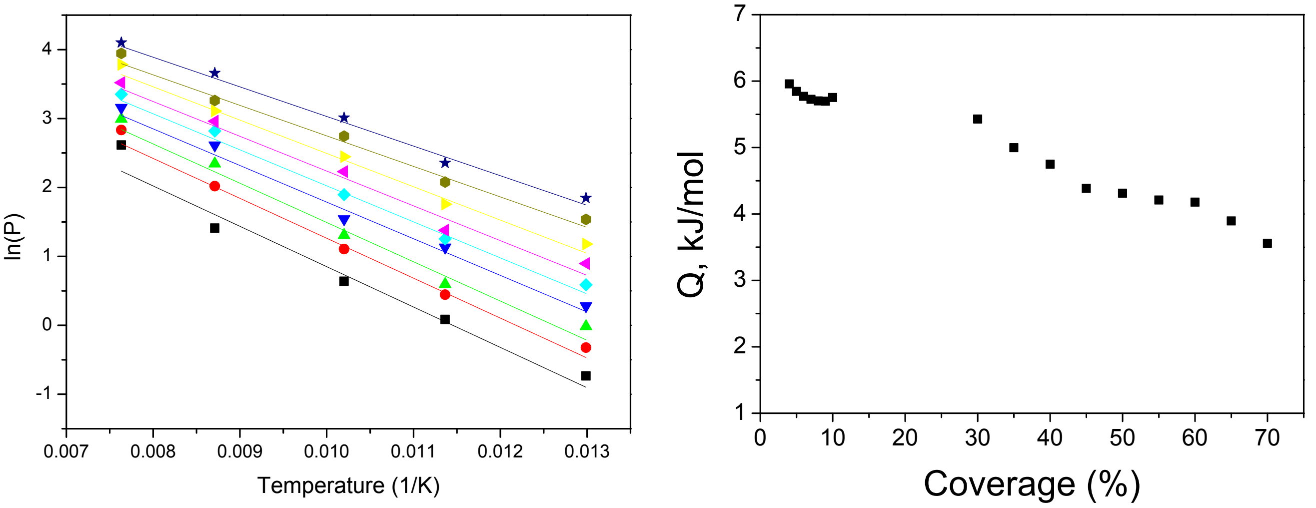
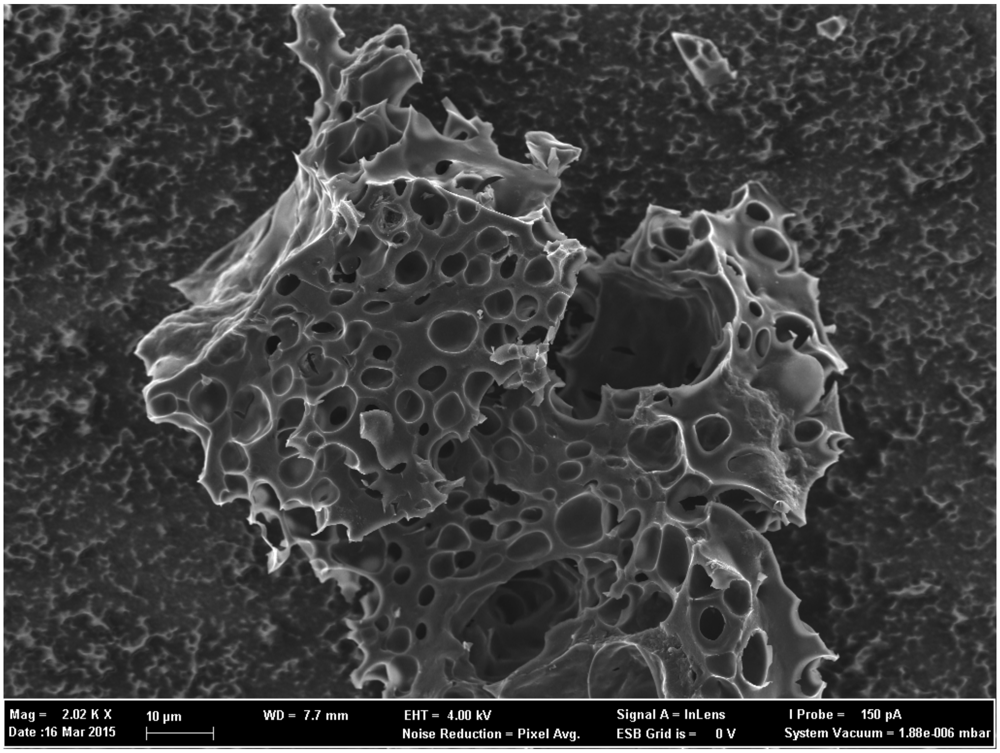
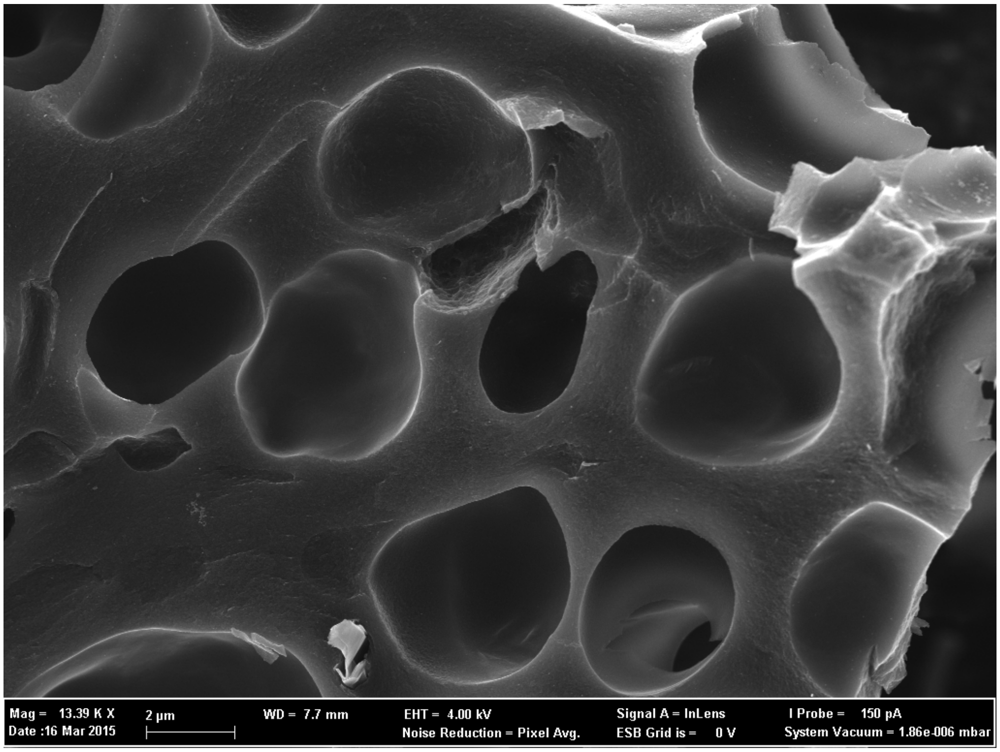


Figure 5S. a) Plot of ln(P) versus 1/T constructed using five isotherms recorded for sample (2) (Table 1S) and used for evaluation of isosteric heat of adsorption according to procedure described in ref.[7] b) Heat of adsorption plotted vs Wt% value. The ΔH_0 value was calculated by extrapolation of the adsorption enthalpy to zero pressure (~6.2 kJ/mol). For low coverage part of this figure we used additionally the 293K isotherm.

5. High resolution SEM images from a-r-GO showing hierarchical pore structure.





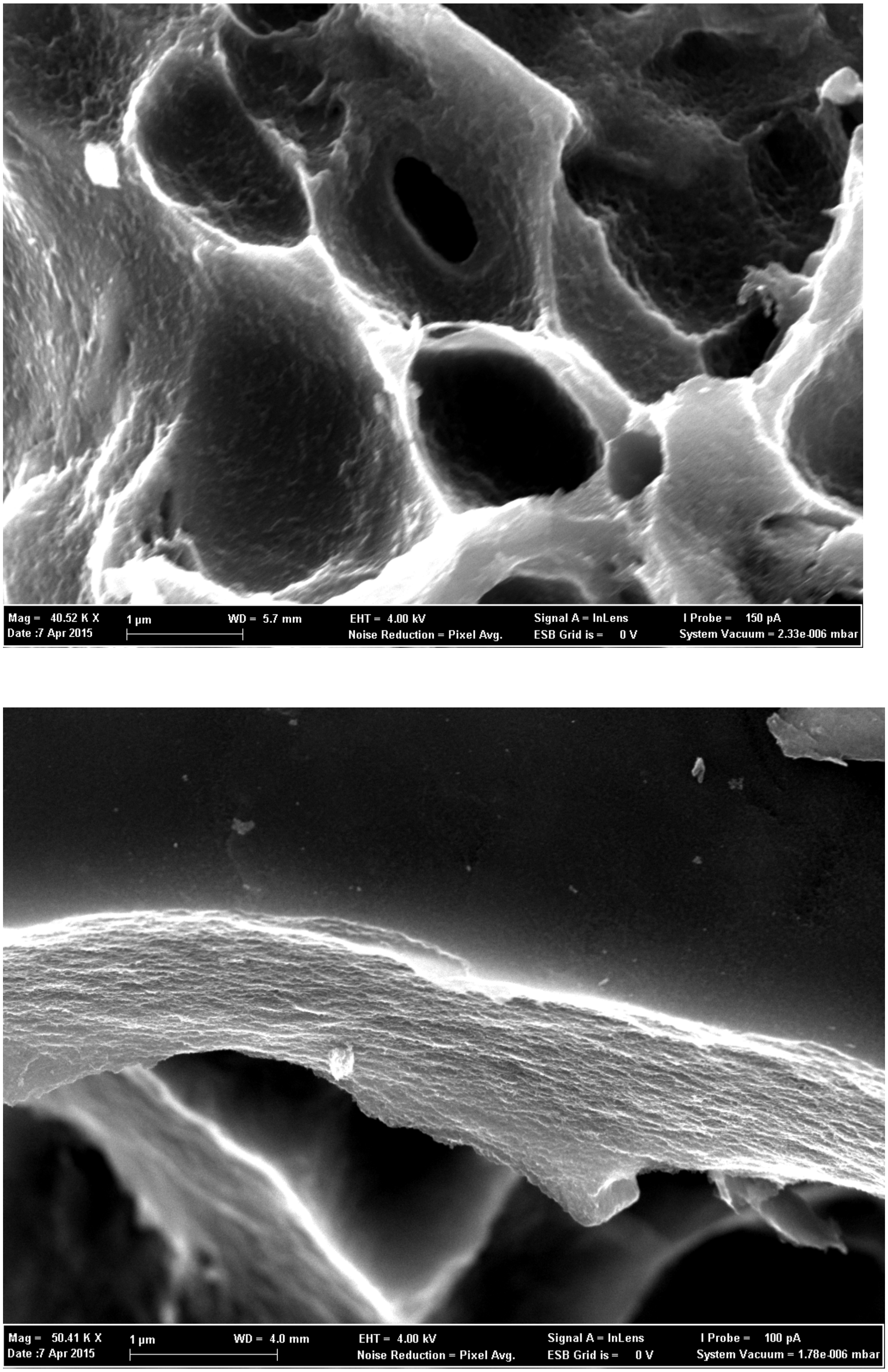


Figure 6S. SEM images from a-r-GO samples showing pores on different magnification scales.

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