

Hydrogen storage in high surface area graphene scaffolds.

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Abstract.

The ability to adsorb and desorb gases reversibly makes high surface area (SSA) carbon materials of great interest for hydrogen storage. Theoretically predicted value of SSA for graphene is 2630 m²/g. However, recent theoretical modelling results demonstrate that SSA can be further increased up to about 5000 m²/g for imperfect perforated graphene[1]. One of the best known methods to prepare highly defective porous carbon materials is KOH activation.

We established optimized synthesis parameters required to achieve highest surface area “graphene scaffold” (Figure 1) by varying type of precursor graphite oxides (GO), KOH/carbon ratio, activation temperature, washing and drying procedures. As a result we prepared highly porous graphene materials with broad range of SSA [2, 3].

Sample with maximum SSA value of 3400 m²/g shows extraordinary high pore volume (2.2 cm³/g), which were evaluated using DFT models (Figure 1 b), applied to nitrogen sorption isotherms. Comparable pore volume of ~2 cm³/g is achieved in Metal Organic Framework (MOF) materials with about twice higher SSA value (~5000-7000 m²/g).

Hydrogen uptake of graphene scaffold samples was evaluated using both gravimetric and volumetric methods. We used immersion thermostat for measuring hydrogen uptake by volumetric method to ensure high thermal stability in used temperature interval of 77-296 K. The maximal H₂ uptake of 7.04 wt% was achieved for 77 K (40 bar), whereas at 296 K adsorption is not saturated and reaches 1.13 wt% at 120 bar. Further increase of hydrogen uptake was achieved after additional hydrogen annealing activation step (1.25 wt% at 296 K and 7.48 wt% at 77 K, Figure 1 d) performed under 50 bar H₂ at 450 °C during 2 hours. The isosteric heat of adsorption (Q_{st} ~ 6.2-6.4 kJ/mol) was calculated for the sample with maximal storage capacity and it's in a good agreement with other high surface area carbon materials.

Hydrogen uptake vs. SSA (300-3300 m²/g) trend was evaluated for various graphene-related materials: reduced graphene oxide (r-GO) and KOH activated r-GO (Figure 1 c) [2, 3]. The correlation of hydrogen uptakes with SSA values observed in our experiments is very similar to trends previously reported for other carbon materials. Exceptional hydrogen storage values reported for r-GO in some earlier studies are not confirmed in our experiments.

Maximal SSA value achieved in our experiments is still below ~5000 m²/g predicted for perforated graphene stacks which gives a promise for further improving of hydrogen properties of graphene scaffolds. An advantage of graphene scaffold compared to MOFs is stability to pressure and air exposure. Experiments with the sample stored on-air for 9 weeks demonstrated only rather minor decrease in hydrogen sorption.

References

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Figures

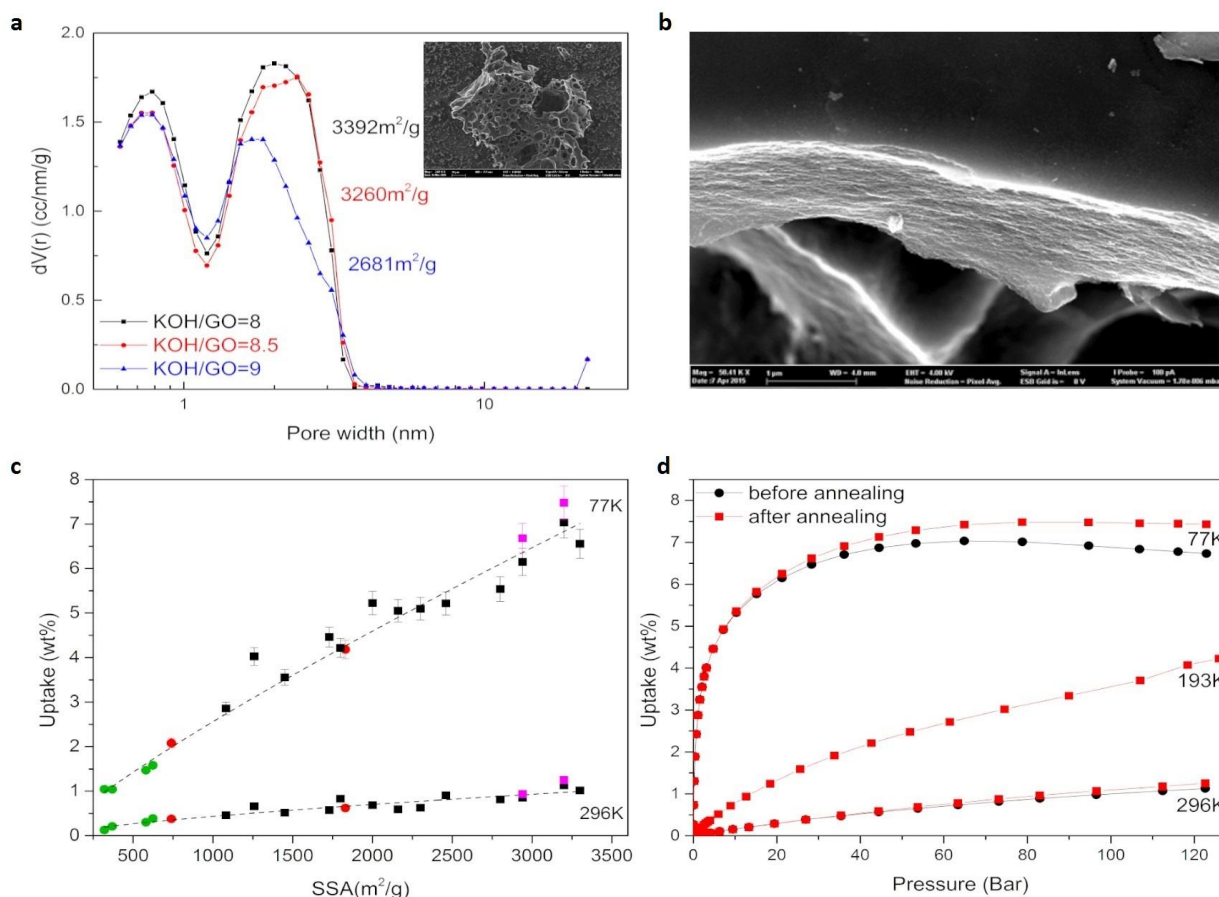


Figure 1. **a**. Pore size distribution simulated using slit pore model (QSDFT) for samples obtained using variation of KOH/r-GO load for activation annealing. **b**. SEM image. **c**. Hydrogen uptake vs. SSA relation for carbon materials **d**. Hydrogen isotherms for the sample with SSA = 3300 m²/g