

High surface area graphene-related materials for hydrogen storage.

Alexandr Talyzin, Guillaume Mercier, Alexey Klechikov

Department of Physics, Umeå University, SE-901 87 Umeå, Sweden
alexandr.talyzin@umu.se

Abstract

Ultra-high surface area graphene scaffold materials were prepared using thermal exfoliation of graphite oxides to produce reduced graphene oxide (rGO) which was modified using KOH activation and high temperature high pressure hydrogen annealing. Using optimized procedure we prepared highly porous graphene scaffold materials with specific surface area (SSA) values up to 3400 m²/g and pore volume up to 2.2 cm³/g. The pore volume of activated graphene scaffold samples is superior compared to other nanoporous materials. For example, comparable pore volume of ~2 cm³/g is achieved in Metal Organic Framework (MOF) materials with about twice higher SSA values (~5000-7000 m²/g). Graphene scaffolds are chemically inert and stable even after weeks of on air storage which is significant advantage compared to most of MOF materials.

The “graphene scaffold” structure created using the KOH activation procedure shows essentially microporous nature in contrast to pristine r-GO obtained by thermal exfoliation as revealed by both SEM imaging (**Figure 1**) and analysis of nitrogen sorption isotherms. Two peaks are typically observed in the pore size distribution plots simulated using slit pore QSDFT: first peak approximately at 0.7-0.8 nm and second at ~1.5 nm. The KOH activation of rGO helps to create 3D packing consisting of disordered, interconnected and highly defective graphene sheets, while hydrogen annealing broadens smallest pores and removes most of the residual oxygen (C/O=35 is achieved) [1].

Hydrogen uptakes were evaluated for rGO and of activated graphene samples with broad range of SSA values 300-3300 m²/g which allowed to establish SSA vs H₂ uptake trends for ambient and liquid nitrogen temperatures (**Figure 2**) [1-2]. Temperature dependence of hydrogen sorption was evaluated in a broad temperature interval (77-296 K). The maximal excess H₂ uptake of 7.5 wt% at 77 K was achieved for samples with SSA over 3000 m²/g which is among highest ever reported for carbon materials. A hydrogen storage value as high as 4 wt% was observed already at 193 K (120 bar H₂), temperature of solid CO₂, which can be easily maintained using common industrial refrigeration methods. The SSA values achieved in our experiments are still below 4000-5000 m²/g theoretically predicted for highly porous perforated ordered graphene multilayers [3] which provides a promise for even further improved hydrogen storage of graphene scaffolds.

The hydrogen sorption trends revealed in our experiments for graphene-related materials demonstrate that H₂ uptakes of “graphene” samples follow standard for all carbon materials trends and can predicted using BET SSA values extracted by analysis of nitrogen sorption isotherms [2]. Thus, the exceptional hydrogen storage properties of “graphene” (reduced graphene oxides) reported in some earlier studies are not confirmed. The same trends are found also for samples of so called “Graphene Oxide Framework” materials prepared using reaction of graphite oxides with benzene-1,4-diboronic acid (DBA) following procedure described in Ref [4]. Optimization of synthesis procedures allowed us to increase SSA of this material up to ~1000 m²/g. The structure of GO/DBA samples cannot be considered to be framework with graphene sheets interconnected by DBA molecules as it is not compatible with revealed swelling of GO/DBA samples in polar solvents. Alternative models with graphene oxide structure pillared (but not linked) by DBA-derived molecular units are proposed [5].

Using swelling in polar solvents and expanded graphite/graphene oxide structures obtained by solution based insertion of various organic molecules for preparation of porous materials will be discussed.

References

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Figures

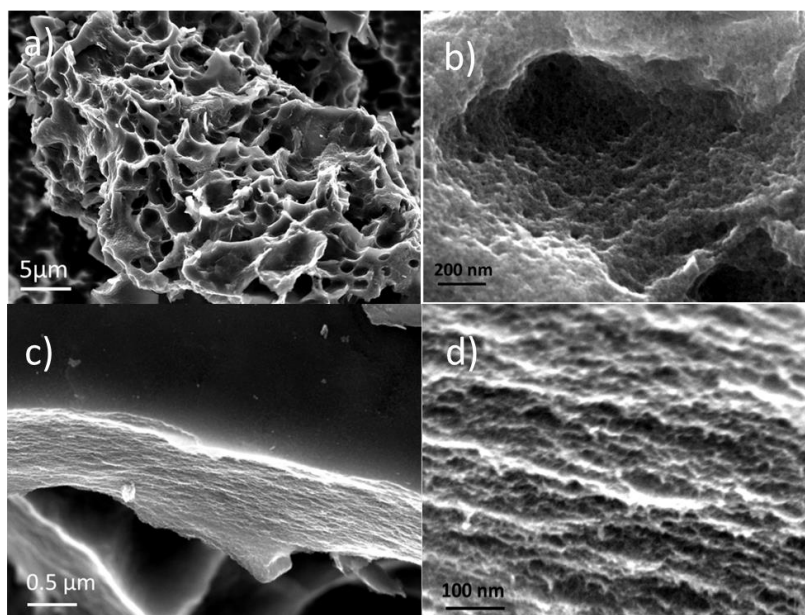


Figure 1. SEM images recorded from a-r-GO sample with BET surface area of $\sim 3300 \text{ m}^2/\text{g}$. The images show hierarchical size pore network (a, b) and also some layered structure on broken grain edge (c, d).

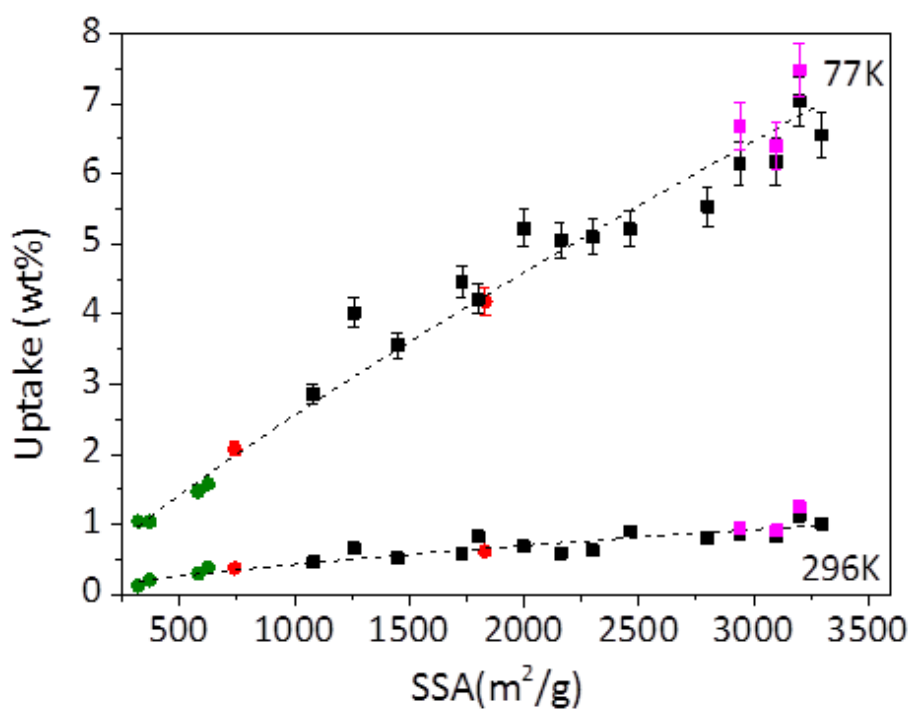


Figure 2. H_2 uptake (wt%) vs SSA trends evaluated using volumetric method and immersion cell for a-r-GO samples at 296 K (120 bar) and 77 K (saturation value) before (■) and after H_2 annealing (■). The trend is extended showing samples of r-GO (●)¹³ and reference points for Mesoporous Carbon and Activated Carbon (●).