HYDROGEN STORAGE IN TUBULAR AND HERRINGBONE CARBON NANOFIBERS
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INTRODUCTION
Hydrogen provides more energy than fossil fuel on a weight basis and without pollution. However, there is still no cost-effective method combining of both volume and weight limitations for hydrogen-powered vehicles. Carbon materials are being investigated as an inherently safe, high energy density hydrogen storage material, which can be more efficient than metal hydrides and compressed gas storage. Recently, reports of very high, reversible adsorption of molecular hydrogen in nano-carbon materials, i.e., pure carbon nanotubes, alkali-doped graphites, and pure and alkali-doped graphite nanofibers (GNFs) have generated tremendous interest in the research community, stimulating much experimental work and many theoretical studies worldwide1. The validity of many of these results has been questioned. In the present study, we have synthesized a series of graphitic nano fibers (GNFs) with different morphologies and measured their hydrogen uptake.

EXPERIMENTAL
Carbon fibers of different morphology were synthesized by a method described previously in the literature2. The yield of carbon fiber was determined by carbon weight increase relative to the growth catalyst. To remove the catalyst particles, carbon fibers were soaked in HCl for 48-72 hours. The fibers were characterized by N2, Raman, SEM and TEM. Low temperature (77K) and room temperature hydrogen adsorption studies were carried out in a IGA-003 gravimetric adsorption unit (HIDEN Analytical, UKs). The mass uptake due to the hydrogen adsorption was calculated after the bouncy correction. Also LaNi5 was used as a standard for hydrogen adsorption (LaNi5H0.8).

RESULTS AND DISCUSSION
In Fig.1, TEM images of “tubular” and “herringbone” fibers are shown. All samples, however, included a range of microstructures; “tubular”, “herringbone” and “spiral”. The diameters of the fibers were determined using electron microscopy and ranged between 50-250nm, depending on preparation conditions. All samples exhibited two Raman bands at about 1595 and 1345 cm\(^{-1}\), respectively, corresponding to the Raman-allowed E\(_{2g}\) “G-band” and to the defect-induced band called the “D-band”. These bands are typical for GNFs3,4. The N\(_2\) isotherms for all these different carbon nanofibers show type IV character with a H3 hysteresis loop, indicating the presence of slit-shape pores or plate-like particles. The surface area of the GNF increases with the post-synthesis treatments, e.g., in the case of “herringbone”, this GNF shows 370 m\(^2\)/g for as-prepared material, and 578 m\(^2\)/g for oxidized samples. Ash analysis and EDX after the post-synthesis treatments show no trace of catalyst particles remaining in the GNFs.
Figure 2 shows the hydrogen isotherms for herringbone (a) and tubular (b) carbon fibers at room temperature. It is obvious that post synthesis treatment has a significant impact on hydrogen uptake. The increase in surface area correlates with the hydrogen uptake. Preliminary measurements of hydrogen adsorption at 77 K for post synthesis treated samples also has shown that the hydrogen uptake can be improved considerably. In the case of “herringbone” samples, we have observed 1.8 wt% under 15 atm. pressure at T=77K.

CONCLUSIONS

Different morphologies of carbon nanofibers (Herringbone and Tubular) were synthesized. Specific surface area (average pore size) was modified by post-synthesis oxidative treatments. The correlation of the specific surface area with the hydrogen uptake amount shows that postsynthesis treatment is very important. So that, the hydrogen uptake was maximized by a 500°C heat treatment in 5 % O₂ in He and achieved ~1.0 wt% at room temperature under 15 atm. pressure and about 1.8 wt% at 77K under 15 atm. We observed complete reversibility in the hydrogen adsorption and desorption isotherms, so we rule out any possible chemisorbed hydrogen at RT or at 77 K.

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Reference:

Figure 1. TEM images for (a) “Herringbone” and (b) “tubular” carbon fibers.

Figure 2. Hydrogen uptake on different carbon fibers at 300 K.