Invited paper – Rapid

Hydrogen storage in sonicated carbon materials

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Abstract. The hydrogen storage in purified single-wall carbon nanotubes (SWNTs), graphite and diamond powder was investigated at room temperature and ambient pressure. The samples were sonicated in 5 M HNO_3 for various periods of time using an ultrasonic probe of the alloy Ti-6Al-4V. The goal of this treatment was to open the carbon nanotubes. The maximum value of overall hydrogen storage was found to be 1.5 wt %, as determined by thermal desorption spectroscopy. The storage capacity increases with sonication time. The sonication treatment introduces particles of the Ti alloy into the samples, as shown by X-ray diffraction, transmission electron microscopy, and chemical analysis. All of the hydrogen uptake can be explained by the assumption that the hydrogen is only stored in the Ti-alloy particles. The presence of Ti-alloy particles does not allow the determination of whether a small amount of hydrogen possibly is stored in the SWNTs themselves, and the fraction of nanotubes opened by the sonication treatment is unknown.

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The use of hydrogen for fuel cell systems requires an adequate hydrogen storage medium. Solid state storage, as a safe and efficient handling of hydrogen, attains commercial interest if the amount of reversible adsorbed hydrogen is more than 6.5 wt %. Therefore the lightweight novel carbon materials seemed to be ideal candidates. The experimental situation was initially promising, but it is confusing and incomplete. In [1, 2] a high hydrogen storage capacity of single-wall carbon nanotubes (SWNTs) is reported at moderate temperatures and ambient pressures. Other publications [3, 4] imply that useful storage densities can be achieved only at cryogenic temperatures and/or high pressures.

Typically, the ends of SWNTs are closed with fullerene-like caps. In order to enable easier access of hydrogen to the interior volume of the tubes, opening and cutting of the tubes

may be necessary [4–6]. One often-applied technique to cut the SWNTs is to expose the material in suspension to a vigorous ultrasonic treatment [2, 3]. In this paper we investigated the influence of sonication on carbon materials and the resulting hydrogen storage.

1 Experimental

SWNTs produced by laser ablation were purchased from Tubes@Rice in the purified form. Furthermore, SWNTs obtained by arc discharge from University of Montpellier II were purified using the method developed by Holzinger et al. [7]. For comparison we used graphite with a powder size of 50 μm (Merck) and diamond powder with a particle size of less than 1 μm (Alfa Aesar). For sonication, 10 mg of these carbon materials were suspended in 100 ml 5 M HNO_3. The suspension was sonicated with a probe for a range of different times between 1 h and 24 h at a power of 50 W/cm². During sonication the flask was cooled in a cold bath at about 10 °C. The suspension containing the SWNTs was collected on a polycarbonate filter (0.4 μm pore size), rinsed several times with distilled water to remove the acid and dried in air. The ultrasonic probe was made of a Ti alloy with a composition of 90 wt % Ti, 6 wt % Al, and 4 wt % V, which is the typically used material. In addition, a stainless steel ultrasonic probe was used.

The hydrogen storage capacity was analysed with thermal desorption spectroscopy (TDS). Within the TDS apparatus, the sample is heated to 900 K by a radiation furnace in high vacuum (10^{-5} Pa), while the gas desorption can selectively be analysed utilizing mass spectrometry. Without air contact, the samples are exposed in the TDS apparatus to a deuterium atmosphere (0.08 MPa, purity 99.7%) for deuterium uptake. The loading time of the sample was 15 min at room temperature. The use of deuterium instead of hydrogen increases the sensitivity of the TDS apparatus, and, more or less, no background disturbance is observed (for details see [8]). However, the values of the storage capacity in this paper are given in weight percent of hydrogen in order to compare the hydrogen

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storage capacity with other publications. The sample masses used for the TDS experiments were typically between 5 to 10 mg. The TDS apparatus is calibrated by heating a Pd-Gd alloy loaded with a known amount of deuterium. The total deuterium content can be determined with a relative error of about 5%.

The samples were analysed with X-ray diffraction (XRD) utilizing a STOE Transmission Powder Diffractometer STADIP (Cu K_α radiation, Ge monochromator and position sensitive detector (38°)). Furthermore, transmission electron microscopy (TEM) investigations were performed on the sonicated samples to check the influence of the sonication procedure on the length and structure of the SWNTs. Raman spectra were recorded using a Jobin–Yvon Raman microscope operating at a wavelength of 632.8 nm under ambient conditions. Usually the spectra were measured at several positions within the sample to confirm their reproducibility. Chemical analysis of metals was performed on samples dissolved in HCl + HF by inductive coupled plasma (ICP) using an optical emission spectrometer (ARL-3580). By this method the metal content can be determined with a relative error of about 2%.

2 Results and discussion

SWNTs from Tubes@Rice were sonicated in 5 M HNO₃ for different times (1, 5, 10, 16, and 24 h) using a Ti-alloy ultrasonic probe. Additionally, purified SWNTs from Montpellier were treated by sonication in 5 M HNO₃ for 16 h. Directly after this treatment some of these samples were exposed in the TDS equipment to a deuterium atmosphere ($p(D_2) = 0.08$ MPa) at room temperature for 15 min. In the following TDS run up to 900 K, no release of deuterium was measured. However, after heating in high vacuum up to 900 K, a further loading procedure at room temperature performed under the same conditions ($p(D_2) = 0.08$ MPa for 15 min) causes a significant deuterium uptake. In Fig. 1 the deuterium desorption spectra are shown for purified SWNTs from Tubes@Rice sonicated for different times. In the inset the total hydrogen content desorbed is plotted versus the sonication time (note that for a better comparison with literature the storage capacity is given in wt % hydrogen). The amount of deuterium stored increases with increasing sonication time. Figure 2 shows two TEM bright-field images with different magnification of SWNTs sonicated in 5 M HNO₃ for 16 h using a Ti-alloy probe. At lower magnification, metal particles with varying sizes up to 1 μm are visible surrounded by carbon material. For higher magnification, nanotubes and smaller metal particles as small as 10 nm can be seen. Some of these smaller particles may be catalyst still remaining from the tube production process. XRD measurements yield diffraction maxima of titanium (Fig. 3). Furthermore, chemical analysis of the samples yielded increasing Ti content with increasing sonication time (Table 1). In addition to Ti, typically traces of Al and V were detected, yielding an alloy composition of about 90 wt % Ti, 6 wt % Al, and 4 wt % V. After deuterium loading, the samples show, in the XRD spectra, no more Ti maxima, while the peaks of Ti deuteride are clearly visible (Fig. 3), indicating an atomic ratio of deuterium to Ti of about 1.5 D/Ti or even higher.
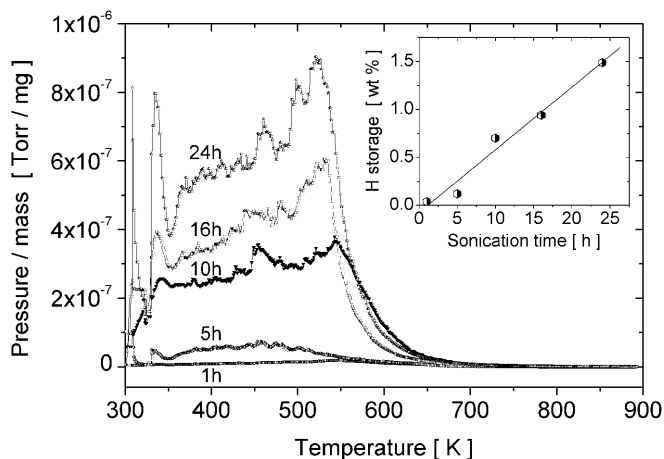

Fig. 1. Thermal desorption rate of deuterium in high vacuum plotted against temperature (heating rate 4.9 K/min) for SWNTs sonicated in 5 M HNO₃ for different times using a Ti-alloy probe, heated to 900 K in high vacuum and then deuterium loaded (0.08 MPa D₂ at room temperature for 15 min). The *inset* shows the total hydrogen content (note that storage capacity is given in wt % hydrogen) plotted versus the sonication time
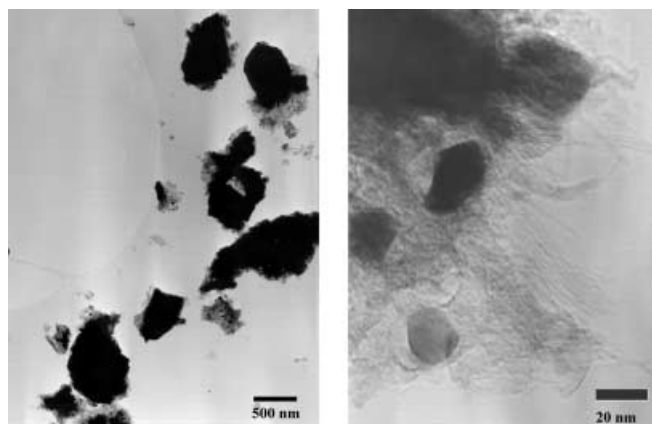

Fig. 2. Transmission electron microscopy bright-field images of SWNTs sonicated in 5 M HNO₃ for 16 h using a Ti-alloy probe
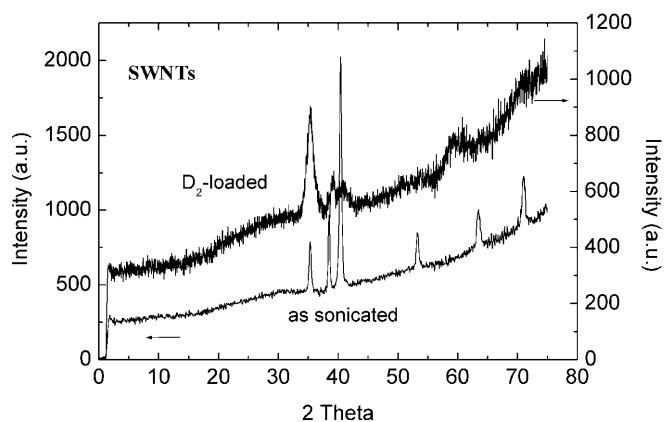

Fig. 3. X-ray diffraction spectrum (Cu K_α radiation) of SWNTs sonicated in 5 M HNO₃ for 16 h using a Ti-alloy probe, as-sonicated and after deuterium loading (0.08 MPa D₂ at room temperature for 15 min)

For comparison, an ultrasonic treatment was performed using a stainless steel probe. Figure 4 shows the TDS spectrum of SWNTs from University of Montpellier II each

Table 1. List of different carbon materials sonicated using a Ti-alloy probe: Total hydrogen storage capacity (TDS) an Ti content (ICP) an hypothetical H/Ti-6Al-4V content under the assumption that all hydrogen is absorbed by Ti-alloy particles

Sample	Sonication time [h]	Total H [wt %]	Ti [wt %]	H/Ti-6Al-4V [wt %]
SWNTs Rice	1	0.04	8.5	0.42
SWNTs Rice	5	0.12	16.6	0.65
SWNTs Rice	10	0.74	36.0	1.85
SWNTs Rice	16	0.94	45.5	1.86
SWNTs Rice	24	1.47	59.6	2.22
Graphite powder	16	1.4	≈ 50	2.52
Diamond powder	1	0.05	2.0	2.25
Diamond powder	5	0.19	7.8	2.19
Diamond powder	16	0.67	20.3	2.97
Diamond powder	24	0.94	25.9	3.27

Fig. 5. Thermal desorption rate of deuterium in high vacuum plotted against temperature (heating rate 4.9 K/min) for diamond powder sonicated in 5 M HNO_3 for different times using a Ti-alloy probe, heated to 900 K in high vacuum and then deuterium loaded (0.08 MPa D_2 at room temperature for 15 min). The *inset* shows the total hydrogen content (note that storage capacity is given in wt % hydrogen) plotted versus the sonication time
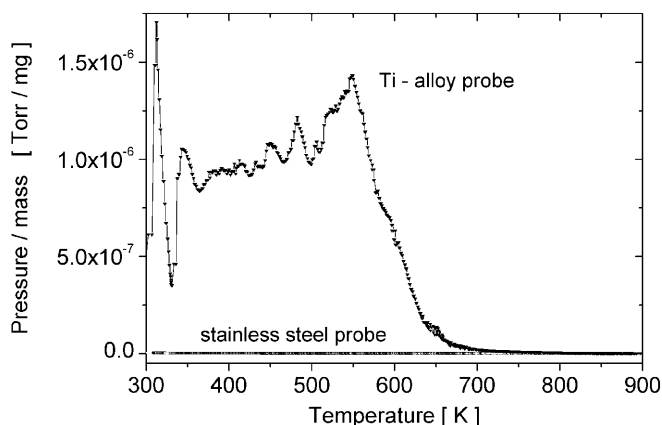

Fig. 4. Thermal desorption rate of deuterium in high vacuum plotted against temperature (heating rate 4.9 K/min) for SWNTs sonicated in 5 M HNO_3 for 16 h using a Ti-alloy probe and a stainless steel probe and after deuterium loading (0.08 MPa D_2 at room temperature for 15 min)

Fig. 6. Raman spectra (wavelength 632.8 nm) of SWNTs sonicated in 5 M HNO_3 for different times

sonicated in 5 M HNO_3 for 16 h using Ti-alloy and stainless steel probes. SWNTs treated by the stainless steel probe showed no appreciable hydrogen storage (below 0.005 wt %). Using a stainless steel probe, sonication in 5 M HNO_3 also incorporates metal particles, e.g., a Fe content of 34 wt % was determined by chemical analysis after a sonication time of 5 h.

To clarify the influence of the SWNTs on hydrogen storage, diamond powder was used instead of tubes. Figure 5 shows the TDS spectra of diamond powder sonicated by a Ti-alloy probe for different times (the fluctuations in the TDS spectrum after 24 h sonication are due to instabilities of the temperature control, which have no influence on the measurement of the total hydrogen content). After first heating in high vacuum up to 900 K, the samples were deuterium loaded (0.08 MPa D_2 at room temperature for 15 min). The inset displays the hydrogen storage versus the sonication time.

From the hydride database [9] it is known that after removing the natural oxide layer of Ti by heating to 400–600 °C, Ti readily takes up hydrogen at room temperature. For all carbon samples treated by sonication, Table 1 gives the total hydrogen storage capacity, the Ti content and the hypothetical hydrogen content in Ti-6Al-4V alloy assuming that all hydrogen is stored in these alloy particles. The hydrogen content in the Ti-alloy particles, obtained
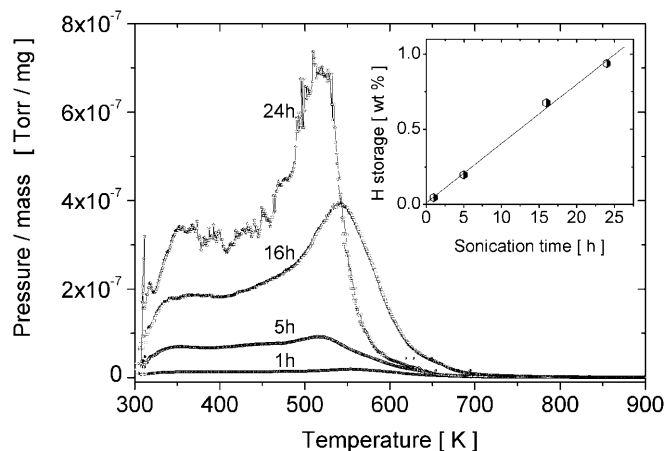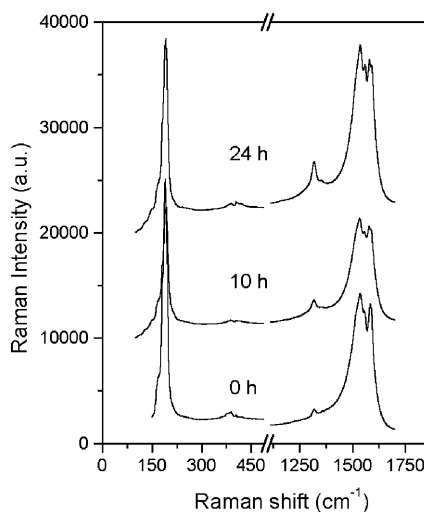
under this assumption, is in the range of 0.4 to 3.3 wt %, which may be compared to the maximum storage capacity of pure Ti of 3.98 wt % [9]. The hydrogen storage capacity of the Ti alloy was checked on Ti-6Al-4V powder with a particle size of 45 μm (Goodfellow); it was treated with the same method as the carbon materials (heated up to 900 K in high vacuum, 0.08 MPa D_2 at room temperature for 15 min) and then measured by TDS to have a hydrogen uptake of 3.5 wt %. All data can be reasonably explained by assuming that only the Ti alloy is responsible for the hydrogen storage. The presence of Ti-alloy particles does not allow the determination of whether a small amount of hydrogen is stored in the SWNTs themselves. Furthermore, the fraction of SWNTs opened by our treatments is unknown.

The existence of SWNTs after sonication is proved by Raman spectroscopy (Fig. 6). The radial breathing mode around 192 cm^{-1} as well as the graphitic mode around 1580 cm^{-1} are seen for all sonication times. The intensity of the defect

line at $1320\,\mathrm{cm}^{-1}$ increases with sonication time as defects are induced.

3 Conclusions

The present experiments show that ultrasonic treatment in $5\,\mathrm{M}$ HNO_3 incorporates metal particles from the ultrasonic probe material into the sonicated carbon materials. The fraction of incorporated particles increases with increasing sonication time. The most commonly used probe material is a Ti-6Al-4V alloy. After removing the oxide layer of these Ti-alloy particles, the material readily takes up hydrogen at room temperature and ambient pressure. In the present investigation, the majority of hydrogen storage can be ascribed to the incorporated Ti-alloy particles. SWNTs treated by sonication using a stainless steel ultrasonic probe showed no hydrogen storage. The fraction of nanotubes opened by the used treatment is unknown. (Estimates on possible hydrogen storage in SWNTs at high pressure or lower temperatures cannot be based on these findings.)

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