Hydrogen storage in microwave-treated multi-walled carbon nanotubes

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Abstract

Multiwalled carbon nanotubes (MWCNTs) treated by microwave and heat treatment were used for hydrogen storage. Their storage capacity was measured using a quadruple quartz crystal microbalance in a moisture-free chamber at room temperature and at relatively low pressure (0.5 MPa). Deuterium was also used to monitor the presence of moisture. The hydrogen storage capacity of the microwave-treated MWCNTs was increased to nearly 0.35 wt% over 0.1 wt% for the pristine sample and increased further to 0.4 wt%, with improved stability after subsequent heat-treatment. The increase in the storage capacity by the microwave treatment was mostly attributed to the introduction of micropore surfaces, while the stability improvement after the subsequent heat treatment was related to the removal of functional groups. We also propose a measurement method that eliminates the moisture effect by measuring the storage capacity with hydrogen and deuterium gas.

1. Introduction

Hydrogen gas has been recognized as an ideal fuel in fuel cells because it is lightweight, abundant, and produces an environmentally friendly oxidation by-product (water) [1–5] but a storage material with a high storage capacity is required for its practical application [6]. Carbon nanotubes (CNTs), having empty inner spaces and inter-tube spaces that can store hydrogen gas, have been suggested as a potential storage material [7,8]. CNTs have been examined extensively under various conditions. Several experimental methods have been used to test hydrogen storage in CNTs and the reported storage capacity of singlewalled CNTs (SWCNTs) varies widely from 0.03 to 20 wt% from various groups [9–19]. High storage capacity has been predicted by Monte Carlo simulations [20] and density-functional calculations [21–24] which consider the empty intra- and inter-tube spaces as the main factors. The measurement of hydrogen storage in MWCNTs has also been carried out under high pressure (~10 MPa), and these results have also varied from 0.1 to ~5 wt%, as shown in Table 1 [25–33]. Different methods have been used to modify MWCNTs to improve their hydrogen storage capacity [34–36].

The reason for the poor reproducibility of hydrogen storage capacity measurements in CNTs has been debated, and may arise from sample preparation and measurement methods [15,16,37]. The number of CNT walls, presence of defects and
functional groups, and pore sizes are important parameters [2,38]. Purification assisted by a microwave treatment brought about a significant efficiency improvements with minimal CNT damage [39,40]. The purification treatment had a large effect on the adsorption characteristics of the CNTs [41], and a high specific surface area of CNTs can be obtained by the thermal treatment [42]. The enhancement of the hydrogen storage capacity at low pressures is also a crucial factor for practical applications. The presence of moisture in the working chamber has been a serious issue, causing poor reproducibility [43–46]. Since CNTs are very sensitive to ambient moisture [47], special care must be taken to eliminate the moisture effect, so that the hydrogen storage capacity can be measured precisely and reproducibly.

In this report, the MWCNTs treated by microwave and an additional heat treatment were used for hydrogen storage. Their storage capacity was measured by using a quadruple quartz crystal microbalance (QCM) which was modified from a dual QCM [48]. This method has been approved for the precise evaluation of hydrogen storage with a minimal number of CNTs in a moisture-free chamber at room temperature and at a relatively low pressure (0.5 MPa). This approach was necessary to improve the accuracy of the measurement and the reproducibility of the samples. Deuterium (D₂) was also used to monitor the presence of moisture. We propose a measurement method to eliminate the moisture effect by measuring storage capacity with hydrogen and deuterium gas.

<table>
<thead>
<tr>
<th>Material process</th>
<th>Capacity (Wt%)</th>
<th>Temperature (K)</th>
<th>Pressure (MPa)</th>
</tr>
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<tbody>
<tr>
<td>NaOH treated [a]</td>
<td>~ 5</td>
<td>RT</td>
<td>~ 10</td>
</tr>
<tr>
<td>Annealed [c]</td>
<td>3.0</td>
<td>RT</td>
<td>10</td>
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<tr>
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<tr>
<td>Purified [g]</td>
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<td>7.5</td>
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<tr>
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<td>298</td>
<td>9</td>
</tr>
</tbody>
</table>

Table 1 – Hydrogen storage capacity of multi-walled carbon nanotubes.

As-purchased MWCNTs was heat-treated at 1500 °C for 2 hrs

Raw-MWCNTs

NaClO₃ (0.2 M) + HNO₃ (100ml), stirring 10 min for melting, 100 mg Raw-MWCNTs was added

Microwave treatment for 4 min

Filtration 3 times with DI water

Dry in oven at 80 °C for 12 hr

600 °C heat treatment for 1 hr

Scheme 1 – Sample preparation for microwave treated and heat treated MWCNTs.

2. Experimental

Highly purified MWCNTs synthesized using the chemical vapor deposition method were purchased from Iljin Co., Korea. The procedure for preparing the MWCNT samples for hydrogen storage is shown in Scheme 1. The choice of MWCNTs was necessary due to the severe microwave treatment which will be explained later. The singlewalled CNTs were easily disintegrated during microwave treatment. On the other hand, defects can be controlled on the surface of MWCNTs while retaining the surface morphology [49]. Then, the purchased MWCNTs were first heat-treated at 1773 K for 2 hrs to remove the amorphous carbons and the catalyst, and to increase the crystallinity of the nanotube walls [50]. The product of this first step is hereafter denoted as Raw-MWCNTs. Second, 0.2 M NaClO₃ powder was added to 100 ml HNO₃ (70%) and stirred for 10 min for melting. The 100 mg of Raw-MWCNTs were added into the prepared oxidizing solution. The mixture was transferred to a home style microwave oven (KR-U20AB, 2.45 GHz, 700W) and treated for 4 min. This condition was optimized to generate a large number of defects on the MWCNT walls and micropores. After the microwave treatment, the mixed solution was filtrated three times and rinsed with deionized water to remove the acidic solution. The filtrated MWCNTs were then dried in an

![Fig. 1](https://via.placeholder.com/150)

Fig. 1 – Partial pressure of the residual gas inside the chamber (a) before and (b) after baking. PP stands for partial pressure.
oven at 353 K for 12 h. The product at this step is hereafter referred to as Mic-MWCNTs. The Mic-MWCNTs underwent further heat treatment at 873 K for an hour to remove the functional groups and increase the crystallinity of the CNT walls. The product at this step is hereafter designated as HT-MWCNTs. The prepared Raw-, Mic-, and HT-MWCNTs were dispersed in dichloroethane (DCE) under the same conditions using a bath sonicator (Power sonic 505). The MWCNT solution was sprayed onto the active area of the quartz crystal (6 MHz, Inficon) and the DCE was evaporated, so only MWCNTs were deposited onto the quartz crystal.

The dual QCM method for evaluating hydrogen storage in CNTs was introduced in our previous work [48]. For this work, we have successfully modified our system to a quadruple QCM system with one reference QCM to eliminate environmental effects such as pressure and temperature changes, and the other three for hydrogen storage measurement. Four QCMs were mounted inside the same chamber. This approach may be beneficial in examining a greater variety of samples in the same environment. After loading the QCMs with test samples into the chamber, the chamber was then pumped out using a mechanical pump and a turbo-molecular pump to maintain a base vacuum of \(~10^{-8}\) Torr. The chamber was baked at to around 403 K for one day to remove the moisture inside the chamber and gas pipes. Hydrogen gas was introduced through the liquid-nitrogen trap to minimize the moisture flow into the chamber.

Fig. 2 – FESEM (left) and TEM (right) images of (a) the Raw-MWCNTs, (b) Mic-MWCNTs, microwave-treated for 4 min, and (c) HT-MWCNTs after further heat-treated for 1 h at 873 K.
the chamber during hydrogen uptake. The hydrogen pressure was limited to within 0.5 MPa to protect the quartz. A second cryotrap was also used on the venting line to capture water vapor that might be introduced into the chamber during ventilation. After exhausting the hydrogen gas through the venting line, the line was closed and the chamber was opened to the turbo-molecular pump that was already running. To minimize the effect of temperature influence, the four QCMs were mounted on a water-circulating substrate where the temperature was controlled by a chiller. The temperature was consistently monitored using a thermocouple mounted on the QCM substrate.

The MWCNTs were characterized by field-emission scanning electron microscopy (FE-SEM, JEOL 6700F), transmission electron microscopy (TEM, JEOL 2010F HRTEM, 200 KeV), Raman spectroscopy (Renishaw, RM1000), and X-ray photoelectron spectroscopy (XPS, ESCA2000, VG Microtech, England). The pore structures were determined using the BET method with the adsorption of N2 at 77 K on volumetric equipment (Micromeritics ASAP2020), after pre evacuation for 12 h at 473 K, while maintaining the base pressure at 10⁻⁹ Pa. Pore structure parameters were obtained using the subtracting-pore-effect (SPE) method. We employed the Horvath-Kawazoe (HK) method to determine the micropore size distribution [51–53].

The weight of the loaded MWCNTs on an active area of QCM was limited to satisfy the linear approximation of the frequency shift to the mass change [54]. When a small mass $m_f$ is uniformly added onto a quartz-crystal plate of mass $m_q$, its resonant frequency will change from the original value of $y_q$ to the value of $y_c$. The relation between the frequency shift $\Delta y = y_c - y_q$ and the deposited mass is given as follows:

$$m_f/m_q = -c(\Delta y/y_q).$$  \hspace{1cm} (1)

where $c$ is a constant which depends on the physical configuration of the quartz crystal. If the added mass is uniformly distributed over the entire active area of the crystal surface, $c$ is found to be unity. The significance of Eq. (1) is that the resultant frequency shift is only dependent on the added mass. This was the original justification for the use of quartz-crystal resonators as mass-sensing devices. After spraying MWCNTs on the quartz crystal, the QCMs with MWCNTs were heat-treated at 423 K for 1 h to remove the presumably any remaining DCE and were then transferred into the chamber. The frequency changes of the QCMs were measured in vacuum at 297 K before and after loading the MWCNTs with mass $m_{CNT}$. High purity of hydrogen (99.999%) and deuterium (99.995%) gas were used to crosscheck the gas storage capacity in MWCNT samples. Highly pure hydrogen (99.999%) and deuterium (99.995%) gases were used to crosscheck the gas storage capacity of the MWCNT samples. For hydrogen gas and a frequency change, $\Delta y_{H2}$, corresponding to the adsorption amount of hydrogen gas with mass, $m_{H2}$, the capacity of hydrogen storage, $C_{H2}$, converted from Eq. (1) is given by:

$$C_{H2} = \frac{m_{H2}}{m_{H2} + m_{CQ}} \times 100\% = \frac{\Delta y_{H2}}{\Delta y_{CQ} + \Delta y_{D2}} \times 100\% \hspace{1cm} (2)$$

If the frequency change of hydrogen, $\Delta y_{H2}$, is much less than the frequency change of the CNTs, $\Delta y_{CQ}$, the storage capacity of hydrogen gas is proportional to the frequency change of the adsorption amount.

### 3. Results and discussion

In the procedure used to measure storage capacity with quadruple QCMs in the chamber, the hydrogen uptake/release

| Table 2 – Element atom percentage (at%) of the MWCNT samples. |
|-----------------|-----------------|-----------------|-----------------|
| Elements        | Raw-MWCNTs      | Mic-MWCNTs      | HT-MWCNTs       |
| C K             | 95.11           | 80.75           | 91.45           |
| O K             | 4.89            | 19.25           | 8.55            |

Fig. 3 – Raman spectra at 633 nm laser excitation energy of (i) Raw-MWCNTs, (ii) Mic-MWCNTs, and (iii) HT-MWCNTs.

Fig. 4 – XPS data of (a) Raw-MWCNTs, (b) Mic-MWCNTs, and (c) HT-MWCNTs.

Fig. 4 – Binding energy vs. intensity of (a) C 1s, (b) O 1s, and (c) N 1s.
cycle was repeated several times, followed by a baking of the whole system at 403 K for one day. Fig. 1 shows the partial pressure of the residual gases measured by a residual gas analyzer (SRS RGA-200) before and after baking. The presence of moisture in the chamber before baking is clear (Fig. 1a). After baking and cooling to room temperature, we ran the RGA again, which showed the moisture (as indicated by the partial pressure of water) in the chamber was reduced by about 100 times, as shown in Fig. 1b. This will give accuracy in the measured hydrogen storage capacity to within a 10% error. The effect of the moisture will be alleviated even further for hydrogen uptake.

The properties of the MWCNT samples used in our study were examined with several characterization tools. The morphologies of the three MWCNT samples were determined by FESEM and TEM images, as shown in Fig. 2. The Raw-MWCNTs, after high temperature treatment, showed a clear and smooth wall structure and good crystallinity without obvious amorphous carbons on the wall surfaces. Their diameter distribution was wide, ranging from 5 to 30 nm as determined from TEM images and one sample shown in Fig. 2. However, the wall structures of the Mic-MWCNTs after a 4 min microwave treatment with the oxidizing agents NaClO3 and HNO3 were severely deteriorated due to oxidative etching, and some parts were transformed into amorphous carbons (Fig. 2b). This phenomenon is similar to that seen in KOH-modified MWCNTs [25]. With subsequent heat treatment at 873 K for 1 h, the wall structure of the HT-MWCNTs again became clearer again than that of the Mic-MWCNTs, but was still not as clear as that of the Raw-MWCNTs. The crystallinity of the HT-MWCNTs increased but small defects and some micropores remained on the CNT walls, as shown in Fig. 2c. Table 2 shows the main elemental atomic percentage of the MWCNT samples as determined by energy dispersive spectroscopy (EDS). The Raw-MWCNTs were mainly composed of carbon atoms with a very small quantity of oxygen atoms. With microwave treatment, the carbon atoms in the MWCNTs were oxidized by the oxidants NaClO3 and HNO3, and therefore defects and oxygen-based functional groups such as –COOH and –OH were likely to be introduced on the side walls of CNTs [52]. Thus, the oxygen content was significantly increased to the Raw-MWCNTs. When the Mic-MWCNTs underwent further heat treatment at 873 K for 1 h, some functional groups were decomposed, so the oxygen contents in the HT-MWCNTs are obviously decreased compared to that in the Mic-MWCNTs. Nevertheless, a large amount of the strong covalent bonds of oxygen atoms with defective carbons remained in the sample, consistent with the defective CNT walls in Fig. 2c.

Fig. 3 shows the Raman spectra of the MWCNT samples at the 633 nm laser excitation wavelength. The spectra are normalized with respect to the G-band at about 1572 cm$^{-1}$ with the same background. The D-band near 1322 cm$^{-1}$ represents the contributions of defects and/or amorphous carbon on the nanotube walls [55]. The intensity ratio of the D-band to the G-band, the $R_{D/G}$ value, represents the severity of defects. The Raw-MWCNTs had the lowest $R_{D/G}$ value of the three MWCNT samples, indicating that the Raw-MWCNTs were less defective than the other two samples. The highest $R_{D/G}$ value was observed in the Mic-MWCNTs, indicating a large number of defects were generated during the microwave treatment with the oxidant. The $R_{D/G}$ value of the HT-MWCNTs was decreased by heat treatment at 873 K for 1 h, indicating the reduction of the disordered degree or the recovery of crystallinity of the CNT walls. All of these characteristics are consistent with the morphologies observed in the SEM and TEM images.

Fig. 4 shows C1s XPS data of each sample to confirm the presence of functional groups related to the D-band in Raman spectra. The main sp$^2$ peak was maintained in all the three samples, indicating a robust preservation of carbon nanotube backbones. On the other hand, tail groups near high energy side were developed in the mic-MWCNTs (Fig. 4b) and this tail groups were recovered to the similar level of the pristine sample after heat treatment (Fig. 4c). Table 3 shows the summary of each peak obtained from the deconvoluted peak. The peak was deconvoluted into five peaks (sp$^2$/sp$^3$, –C=O, >C=O, –COO, and π–π* plasmon) depending on the curve [56]. The sp$^2$/sp$^3$ peak position near 284.9 eV in the raw-MWCNTs consisted of 70%, which is the most abundant species with 26% some residual functional groups. About 3.5% was contributed from the π plasmon. On the other hand, in the Mic-MWCNTs, sp$^2$/sp$^3$ contribution was significantly reduced.

| Table 2 – XPS data of C1s of each samples deconvoluted into five peaks; Binding energies and area percentages. |
|-----------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Raw-MWCNTs                 | Mic-MWCNTs      | HT-MWCNTs       |
| sp$^2$/sp$^3$              | –C=O            | >C=O            | –COO            | π–π*            |
| 284.9 (70.1%)              | 286.31 (15.5%)  | 287.6 (6.6%)    | 289.2 (4.3%)    | 290.9 (3.5%)    |
| 284.8 (58.7%)              | 286.3 (17.2%)   | 287.5 (13.1%)   | 289.3 (8.4%)    | 291.1 (2.6%)    |
| 284.85 (69.8%)             | 286.2 (14.2%)   | 287.7 (6.8%)    | 289.4 (4.9%)    | 291.1 (4.3%)    |

Fig. 5 – BET isotherms of MWCNT samples. The solid and open symbols indicate adsorption and desorption branches, respectively; Raw-MWCNTs (□), Mic-MWCNTs (○), and HT-MWCNTs (◆).
to ~59%, and in turn the functional groups increased to 39%. As discussed in the Raman spectra, the D-band was increased after microwave treatment, which is in congruent with the increased functional groups shown here. With subsequent heat treatment, both the sp²/sp³ and the functional groups were recovered to the level of the pristine sample. This is again in good agreement with the Raman spectra, where the D-band was reduced.

Fig. 5 shows the N₂ adsorption isotherms of the Raw-, Mic-, and HT-MWCNTs. The SPE method was employed to determine the exact porosity using high-resolution αₛ plots for the N₂ adsorption isotherms (77 K) of these MWCNT samples. The pore-structure parameters of the samples are summarized in Table 4. The mesopore volume was calculated by subtracting the micropore volume from the total pore volume, which was determined from the amount of N₂ adsorbed at P/P₀ = 0.98.

The microwave treatment enhanced the micropore surface area by two times, but the total BET surface area remained unchanged. The micropore volume was increased but the external surface area and the mesopore volume were significantly reduced by about 4 times. After heat treatment, the BET surface area was increased by about two and a half times which was mostly contributed by the increased micropores. The correlation of these parameters to hydrogen storage capacity will be discussed later.

The HK method was also used to obtain the micropore size distribution (Fig. 6). The pore size distribution (PSD) of the Raw-MWCNTs ranged of from 0.5 to 1.0 nm with a peak at 0.5 nm and a shoulder in the range of 1.0–2.0 nm. After microwave treatment, the peak intensity between 0.5 and 1.0 nm decreased slightly but its position was downshifted to 0.9 nm. After heat treatment, both the sp²/sp³ and the functional groups increased to 39%. As discussed in the Raman spectra, the D-band was increased after microwave treatment, which is in congruent with the increased functional groups shown here. With subsequent heat treatment, both the sp²/sp³ and the functional groups were recovered to the level of the pristine sample. This is again in good agreement with the Raman spectra, where the D-band was reduced.

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To evaluate the hydrogen storage capacity, QCMs loaded with MWCNT samples were transferred into the chamber. After the chamber was vacuumed for one day, the system was heated to ~403 K to remove the moisture and then cooled to room temperature. Hydrogen gas was introduced slowly into the chamber until the pressure reached 0.5 MPa. This pressure was maintained for a certain adsorption time, then the gas was slowly vented for desorption. The pressure in the chamber decreased from 0.5 MPa to 0.1 MPa and was then vacuumed to ~10⁻⁷ Torr. This was repeated for several uptake/release cycles. When hydrogen gas was introduced into the chamber through a liquid-nitrogen trap, the four QCMs responded in distinctively different ways. The resonant frequency of the reference QCM abruptly increased (not shown here). This response to pressure was reproducible. In contrast with the reference QCM, a significant frequency drop in the MWCNT-loaded QCM was observed. The reference frequency also fluctuated with a slight temperature variance. The frequency shifts of the MWCNT-loaded QCMs during hydrogen and deuterium uptake/release and their storage capacities determined using Eq. (1) were recorded and plotted in Fig. 7 after subtracting the reference shift and deducting pressure and temperature effects measured on the reference QCM. The temperature during the entire experiment was maintained at about 297 ± 0.3 K. Three MWCNT samples, the Raw-, Mic-, and HT-MWCNTs, were recorded simultaneously with time, thus improving the reliability of the measurement, which is an advantage of using quadruple QCMs. The down arrows indicate an initiation of uptake of either H₂ or D₂ gas and the up arrows indicate the beginning of gas release. The effects of the uptake/release of H₂ (D₂) gas in the Raw-MWCNTs is shown in Fig. 7a. With an increase in hydrogen pressure up to 0.5 MPa, the resonant frequency decreased rapidly due to the adsorption of hydrogen molecules on the CNTs. The frequency should then be constant with constant pressure [57]. However, this constant frequency region was narrow and instead the frequency increased gradually. The pressure in the chamber was reduced by pumping out during the release process, and the frequency was slightly shifted

<table>
<thead>
<tr>
<th>Samples</th>
<th>BET Total surface area (m² g⁻¹)</th>
<th>BET Micropore surface area (m² g⁻¹)</th>
<th>BET Micropore volume (mL g⁻¹)</th>
<th>BET External surface area (m² g⁻¹)</th>
<th>BET Mesopore volume (mL g⁻¹)</th>
<th>BET Total pore volume (mL g⁻¹)</th>
<th>SPE Micropore surface area (m² g⁻¹)</th>
<th>SPE Micropore volume (mL g⁻¹)</th>
<th>SPE External surface area (m² g⁻¹)</th>
<th>SPE Mesopore volume (mL g⁻¹)</th>
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<tr>
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Table 4 – Pore structure parameters of MWCNT samples determined by BET and SPE methods.

Fig. 6 – HK method for micropore size distribution by BET adsorption isotherm of the MWCNT samples. Raw-MWCNTs (□), Mic-MWCNTs (○), and HT-MWCNTs (◇).
from the original value. This might be related to the removal of functional groups on the CNTs during hydrogen uptake and release. Similar behaviors were observed in the next cycle of uptake/release cycle. Deuterium gas was introduced in the third cycle followed by another cycle of hydrogen uptake/release. In the last hydrogen cycle, a constant frequency was maintained after hydrogen uptake. It is intriguing to note that the storage capacity of deuterium gas ($w_{D_2} = 0.2$ wt%) was double that of hydrogen gas ($w_{H_2} = 0.1$ wt%), i.e., $C_{D_2} = 2C_{H_2}$, as described in Eq. (1) and Eq. (2). The resultant frequency shift of the QCM was dependent only on the added mass. The weight of the loaded MWCNTs was linearly proportional to the adsorbed gas on the QCM. Since the storage capacity of deuterium is twice that of hydrogen, this strongly implies that the moisture effect is negligible. Otherwise, the proportionality of a factor of two would not be maintained.

The absorption and desorption behaviors of Mic-MWCNTs and HT-MWCNTs similar to those seen with Raw-MWCNTs were also observed, as shown in Fig. 7b and c. In the case of HT-MWCNTs, the storage capacity slightly increased to 0.32 and 0.63 wt% for hydrogen and deuterium gases, respectively. This is not consistent with the doubling of micropore surface area, as listed in Table 4. One possible reason for this result is the removal of oxygen-based functional groups after heat treatment. The reduction of the binding strength between hydrogen molecules and the CNT surface with fewer functional groups alleviated the effect of the increased micropores. Therefore, the critical parameters for hydrogen storage are i) micropore formation and ii) the presence of functional groups or the enhancement of the binding strength between hydrogen molecules and the surface of the host material. Another intriguing finding is that the frequency fluctuation was greatly reduced after heat treatment. During hydrogen uptake and release, a constant frequency was well maintained in the HT-MWCNTs. This is ascribed to the reduction of functional groups, as indicated in Table 2. The reproducibility of the Mic- and HT-MWCNTs measurements was much better than that of the Raw-MWCNTs, even after 12 repetitions.

To see the influence of water molecules on hydrogen storage capacity, we carried out experiments without baking.
out the system. Hydrogen gas was introduced into the chamber without a liquid-nitrogen trap. Typical results for Mic- and HT-MWCNTs are shown in Fig. 8. The behavior of the frequency change in the case of the Mic-MWCNTs film was similar to that in the previous case, as shown in Fig. 7b. However, the absorption storage capacity with deuterium grew to 0.94 wt% from 0.52 wt% when using hydrogen gas, a slight deviation from the proportionality factor of two. Similarly, the proportionality was not maintained for the HT-MWCNTs film, which is ascribed to the presence of moisture. Thus, the monitoring of the proportionality is a good guideline for the presence of moisture in the system and therefore the reliability of the measurement’s accuracy.

One thing to note is that once the hydrogen gas was introduced, hydrogen molecules were immediately stored in the first stage and then, in the second stage, additional hydrogen was stored slowly, even after 24 h, as indicated by the gradual decrease in frequency. When hydrogen gas was released, desorption immediately occurred and then stabilized, but the desorption amount decreased to 0.72 wt% compared to an uptake amount of 1.31 wt%. The stored hydrogen gas was not fully released. This behavior was repeated in the subsequent cycles, and recovery eventually saturated. The large size of water molecule may block the entrances of the micropores and delay hydrogen adsorption.

We now explain how the moisture effect can be eliminated for the accurate measurements of hydrogen capacity. The storage capacities of hydrogen and deuterium were measured in the presence of moisture. Each term is expressed as follows:

\[
C_{\text{H}_2} + C_{\text{H}_2O} = C_{\text{H}_2} + C_{\text{H}_2O}
\]

(3)

\[
C_{\text{D}_2} + C_{\text{H}_2O} = C_{\text{D}_2} + C_{\text{H}_2O}
\]

(4)

where \( C_m \) indicates the storage capacity of gas \( m \). Using \( C_{\text{D}_2} = 2C_{\text{H}_2} \) from Eq. (2) and subtracting Eq. (3) from Eq. (4), we obtain:

\[
C_{\text{H}_2} = C_{\text{D}_2} + C_{\text{H}_2O} - C_{\text{H}_2} - C_{\text{H}_2O}
\]

(5)

For example, the net storage capacities of Mic-MWCNTs and HT-MWCNTs are 0.42 and 0.49 wt%, respectively, as shown in Fig. 8. These values are larger than those measured in the clean conditions in Fig. 7. Our results provide a new method to precisely evaluate the hydrogen storage capacity in materials regardless of water content.

Additional experiments were carried out to test the reproducibility of hydrogen storage capacity in our MWCNT samples. The Mic- and HT-MWCNTs showed very good reproducibility. Fig. 9 summarizes the average gas storage capacities with error bars of hydrogen and deuterium at room temperature and a pressure of 0.5 MPa. It is easy to see the hydrogen storage capacity of the Mic-MWCNTs increased to 0.35 wt% on average, as compared to only 0.1 wt% for the Raw-MWCNTs. Furthermore, the hydrogen storage capacity in the HT-MWCNTs increased to 0.4 wt%, four times the average of the Raw-MWCNT results. The storage capacity is expected to increase significantly at the higher pressure of 10 MPa that was often used in the previous studies. Even though the total surface area of the HT-MWCNTs increased about two and a half times that of the Mic-MWCNTs, the hydrogen storage capacity of the HT-MWCNTs did not increase proportionally as expected. This could be due to the
removal of oxygen-based functional groups from the Mic-MWCNTs, which is the crucial factor in strongly binding hydrogen molecules to the CNT walls. The increased storage capacity of the HT-MWCNTs may be due to the hydrogen absorption in deep micropores. Although our results show a significant improvement in the hydrogen storage after microwave treatment, the precise control of micropores is a crucial factor in enhancing the storage capacity and requires a further study.

4. Conclusion

In summary, the hydrogen storage capacity of MWCNTs was examined using quadruple QCMs in a clean system at room temperature and under a pressure of 0.5 MPa. The hydrogen uptake of the raw MWCNTs was about 0.1 wt%. The hydrogen storage capacities of the microwave-treated and further heat-treated MWCNTs increase to 0.35 wt% and 0.4 wt% on average, respectively. This increase is ascribed to the oxygen-based functional groups and micropores generated during the microwave treatment with an oxidant. In addition to micropores, the presence of functional groups is a critical factor for hydrogen storage in addition to the micropores. Thus, the proper functional groups and the presence of abundant sites for physical adsorption could increase the hydrogen storage capacity. We proposed a new method of eliminating the moisture effect by introducing deuterium gas. This method can be used to determine the precise hydrogen storage capacity in other materials as well even in the presence of moisture and therefore minimize their environmental effect.

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