

Hydrogen storage by KOH-modified multi-walled carbon nanotubes

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Received 3 March 2006; received in revised form 27 March 2006; accepted 29 March 2006

Available online 11 July 2006

Abstract

Potassium hydroxide (KOH) was employed to modify multi-walled carbon nanotubes (MWNTs), which were annealed at high temperatures to evaluate the properties of hydrogen storage in this study. Experimental results revealed that the structure of carbon nanotubes (CNTs) became destructive after being activated by KOH at 823 K in H₂ atmosphere. It was also found that the capacity of hydrogen storage onto the unmodified and KOH modified CNTs were 0.71 and 4.47 wt%, respectively, under ambient pressure and at moderate temperature. In addition to alkali-metal, both the residual metal such as cobalt and the defect structure were also considered as important keys to be used to improve hydrogen adsorption in the CNTs. The cause of which suggested that residual metal such as cobalt may be acting to dissociate hydrogen molecule into its atom state to spread out to the surface and inner layer through defect sites of the CNTs.

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Keywords: Hydrogen storage; Carbon nanotubes; Chemical activation

1. Introduction

Hydrogen is one of the most cleanest and idealized energy sources. In the past few years, several different technologies including compression, liquefaction, metal hydride, and adsorbent material were developed to be used for hydrogen storage. Among these present technologies, the application of adsorbent material is safer and more efficient than any other technologies in terms of controlling hydrogen storage. Generally speaking, the capacity target of hydrogen storage on automotive application requires over than 6.5 wt% of gravimetric density as far as the specification from the US department of energy (D.O.E.) is concerned. Recently, the carbon nanotubes (CNTs) have become one of the most promising materials for hydrogen storage.

In 1997, Dillon et al. [1] first found that single-walled carbon nanotubes (SWNTs) possess excellent hydrogen storage property with gravimetric density of 5–10 wt%. Ye et al. [2] reported that crystalline ropes of SWNTs adsorb hydrogen to exceed 8 wt% at high pressure of about 120 bar and at 80 K. Furthermore, the hydrogen adsorption using SWNTs was claimed to be 4.2 wt% by Liu et al. [3] with pressure under 100 bar

and at room temperature. Also, other than CNTs, the graphite nanofibers are attracting carbon nanomaterials for hydrogen storage. Chambers et al. [4] claimed that the herringbone type of graphite nanofibers can adsorb hydrogen up to 67 wt% at 100 atm and 300 K. However, this storage capacity has been unable to be duplicated so far by other researchers. Upon application of replicating the experiment, Ahn et al. [5] reported that when using the same conditions as performed previously by Chambers et al. [4], there was only ~ 5 wt% of hydrogen uptake after graphite nanofibers were utilized. In disagreement with what have reported beforehand, in recent publications [6–9], almost all experimental results indicated that hydrogen storage using carbon nanomaterials was only 0.1–2 wt%, which is strikingly smaller than those that were reported previously [1–5]. This difference could be attributed to the facts that the dissimilarities may be caused by either the experimental errors or the slight disparity of the characterization of carbon nanomaterials.

In 1999, Chen et al. [10] used alkali-doped CNTs as sorbents to obtain high capacity for hydrogen adsorption. In their report, under ambient pressure, hydrogen adsorption capacity of 20 or 14 wt% was achieved by Li-doped CNTs at 653 K or K-doped CNTs at room temperature, respectively. Nevertheless, the result reported by Yang [11] indicated that the increment of hydrogen adsorption capacity was caused by the moisture

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contained in the gas flow. Actually, hydrogen adsorption capacity for Li-doped or K-doped CNTs is 2.5 or 1.8 wt%, respectively. In fact, the report from Pinkerton et al. [12] found out that K-intercalated graphite has only 1.3 wt% of hydrogen adsorption. Further, there was no evidence to support that Li-modified CNTs could adsorb hydrogen. In fact, they concluded that the weight gain of H₂ was strikingly significant at 653 K using Li-modified CNTs even without the presence of H₂, which is caused by the moisture that leads to the conversion of LiO₂ from LiOH (i.e., 2LiOH \rightleftharpoons Li₂O + H₂O). Therefore, when using the thermogravimetric analyzer to measure the capacity of H₂, the presence of moisture needs to be considered as an impurity in the gas flow to accurately measure the capacity of hydrogen adsorption. However, the usage of chemically modified CNTs to improve the hydrogen storage property is a practical way to increase its storage capacity.

KOH is a common activated reagent to be used in the activation process as a method for activated carbons preparation [13]. Recently, CNTs and nanofibers activated with KOH were also reported [14–16]. After activation, the specific surface area and pore volume of carbon nanomaterials are increased significantly due to the defective structure formed by KOH etching. In some cases [17–20], the CNTs after annealed at high temperature (\sim 3273 K) are considered not only to provide CNTs of higher purity but also to enhance its degree of crystallization. Furthermore, higher crystallization degree of the CNTs can improve the interaction between the hydrogen molecules and the graphite walls to increase hydrogen storage capacity [17].

In this study, the multi-walled nanotubes (MWNTs) annealed at high temperature and modified by KOH reagent were used to enhance the capability of hydrogen storage. In particular, we investigated the hydrogen adsorption behavior of the CNTs with respect to their structural and property changes after considering both the annealing treatment and KOH modification in order to find out the main effective factors for hydrogen storage in the CNTs.

2. Experiments

2.1. Catalyst preparation

In this study, the Co/MgO functioning as catalyst was prepared by using impregnation method to synthesize the MWNTs. The molar ratio of Co/Mg was 0.05/0.95. Preparation procedure of catalyst is described as follows: Co(NO₃)₂ · 6H₂O was dissolved in a solution that was prepared by mixing the ethanol solution with magnesium oxide (MgO) powder. Next, the Co/MgO mixture solution was sonicated for 1 h, stirred strongly at 373 K to become a concentrated state and dried at 403 K for 12 h. Finally, the Co_{0.05}Mg_{0.95}O catalyst was obtained.

2.2. Synthesis of MWNTs

MWNTs were synthesized by catalytic decomposition of acetylene over Co_{0.05}Mg_{0.95}O catalyst. The prepared Co_{0.05}Mg_{0.95}O powders were loaded at the center of quartz reactor tube with a flow of H₂, and then heated up to 973 K for 30 min. On reaching this temperature, the flow of

C₂H₂/H₂(30/70) mixture was introduced into the quartz reactor for 30 min. The total flow rate was 100 ml/min. The raw MWNTs samples were obtained after the temperature of the reactor was cooled down to room temperature. For the procedure of purifying MWNTs, the raw samples were immersed using 37% of HCl solution to dissolve impurities such as metal catalyst. After the samples were filtered, they were washed using de-ionized water and then dried at 373 K in the air. Finally, the CNTs with high purity (> 90%) can be obtained (known as P).

2.3. Annealing treatment

The aforementioned pre-purified CNTs samples were heated up to 1273 K (1000 °C) in N₂ (known as P + A1000) and to other higher temperatures (e.g., 2173 K (1900 °C), as P+A1900 and 2873 K (2600 °C), as P+A2600) in vacuum, and then held at these temperatures for 60 min.

2.4. KOH-modified CNTs

In this study, CNTs was annealed at various temperatures and then modified by KOH to evaluate hydrogen storage property. Several hundred mini-grams of CNTs with four different types of annealing conditions (P, P + A1000, P + A1900 and P + A2600) were impregnated with 1 M KOH solution by magnetically stirring them for 24 h at room temperature. The K-modified CNTs were obtained after filtering and drying them at 373 K (known as P + K, P + A1000 + K, P + A1900 + K and P + A2600 + K). The amount of K deposited onto the CNTs samples was analyzed by using atomic absorption spectroscopy (A.A.) after the impregnation process.

2.5. Hydrogen storage measurement

Hydrogen adsorption/desorption experiments were performed by the thermogravimetric analyzer (Cahn, TG2121) within a vacuum system. In this study, ‘ultrahigh purity grade’ hydrogen (99.9995%) was used through moisture trap (packed SICAPENT powder, Merck) to eliminate moisture impurities. Ten milli-grams of CNTs samples were loaded into quartz sample holder in a close system of TG. Before performing hydrogen uptake measurement, the TG system was evacuated in order to eliminate possible contamination within the system. Then, hydrogen was introduced into the TG system to pump the pressure back to ambient condition. A flow of hydrogen (20 ml/min) was maintained to purge the system for several hours in order to ensure its cleanliness and weight stability in the TG system. For hydrogen adsorption/desorption measurement, we adopt two-step thermal programs and they were carried out as follows: (1) the first step of thermal programs: the CNTs sample was initially heated up to 823 K at a heating rate of 5 K/min, and then held for 1 h in a flow of H₂ at 20 ml/min. Afterwards, it was cooled down to room temperature until weight stability. (2) The second step of thermal programs: the temperature was heated again from 303 to 773 K at a heating rate of 5 K/min, and then cooled down to 303 K. In order to obtain accurate values of hydrogen uptake,

buoyancy effect was considered for heating/cooling of temperature. All weight changes with respect to adsorption/desorption data were corrected by a quartz blank calibration [11].

2.6. Material characterizations

The crystallographic data of CNTs through annealing treatment were analyzed by X-ray diffractometer (XRD, MAC SCIENCE, MXP-3 type, CuK target). The CNTs samples were mixed with the powder of standard silicon at a ratio of 4:1 (w/w) prior to the analysis. The structure of CNTs was characterized by a high-resolution transmission electron microscope (HRTEM, JEOL, JEM-2010 type) and a Raman spectrometry (Tokyo Instruments, NANOFINDER 30). The nitrogen adsorption isotherm of CNTs samples was measured by a gas adsorption meter (QUANTACHROME, AUTOSORB-1) at 77 K. The specific surface area and pore size distribution were calculated by using BET and BJH method, respectively.

3. Results and discussion

3.1. Material characterizations

Fig. 1 shows the TEM micrographs of the prepared CNTs in this study. As shown in Fig. 1a, it was clearly demonstrated that most of catalyst particles were removed from the CNTs after purification process. The caps of CNTs were opened. Moreover, the residual catalyst of cobalt was found on the CNTs' sample by EDS analysis (data no shown). The size of tubes ranges from 5 to 25 nm, and its length was at a range of several micrometers. The structure of as-prepared CNTs was found with no significant defect, as shown in Fig. 1b. In this study, the CNTs samples were impregnated with 1 M KOH solution, and then both thermal treatment and hydrogen storage measurement were carried out by using TG system. The TG thermal programs consist of two steps. The first step was involved with the activation and the removal of impurities, and

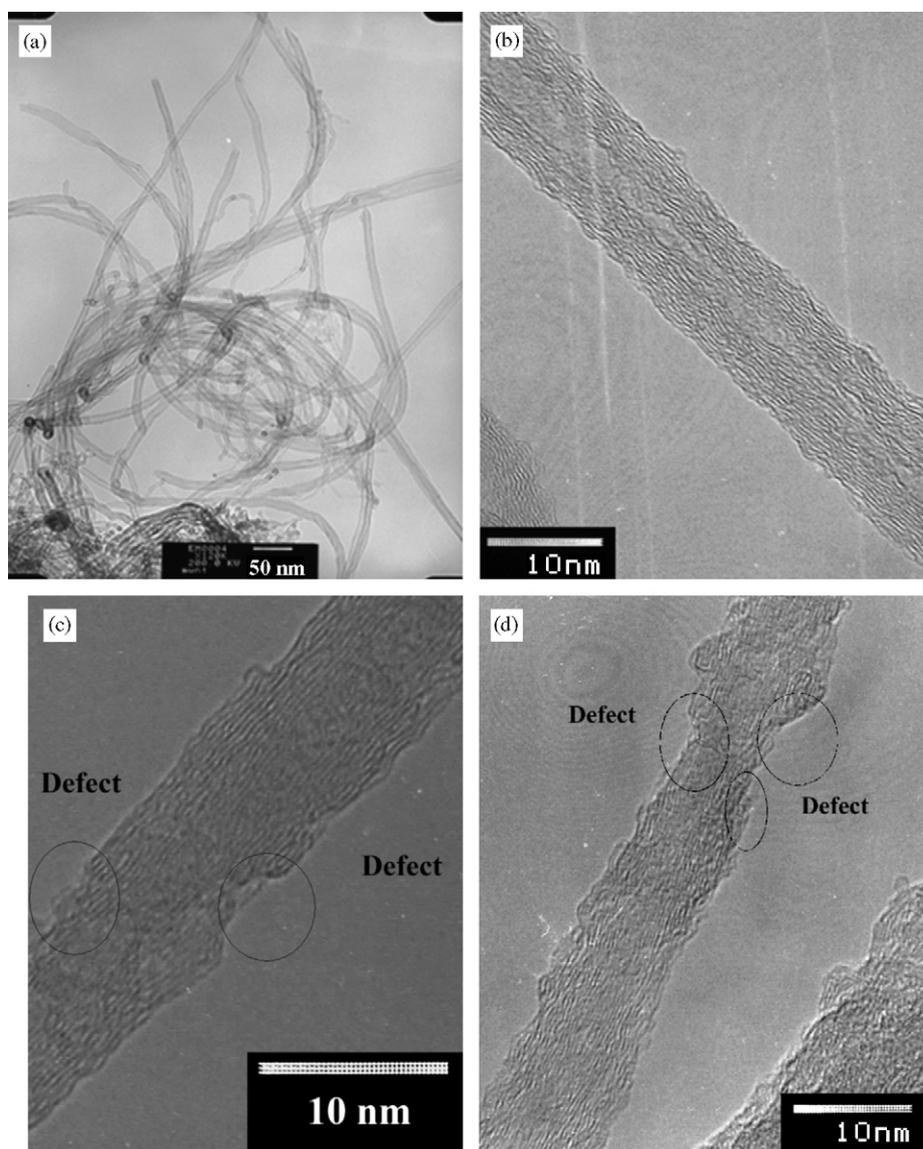


Fig. 1. TEM micrographs of CNTs: (a) and (b) as-prepared CNTs samples (P), (c) P + K samples after the first step of thermal programs, (d) P + A1000 + K samples after the first step of thermal programs.

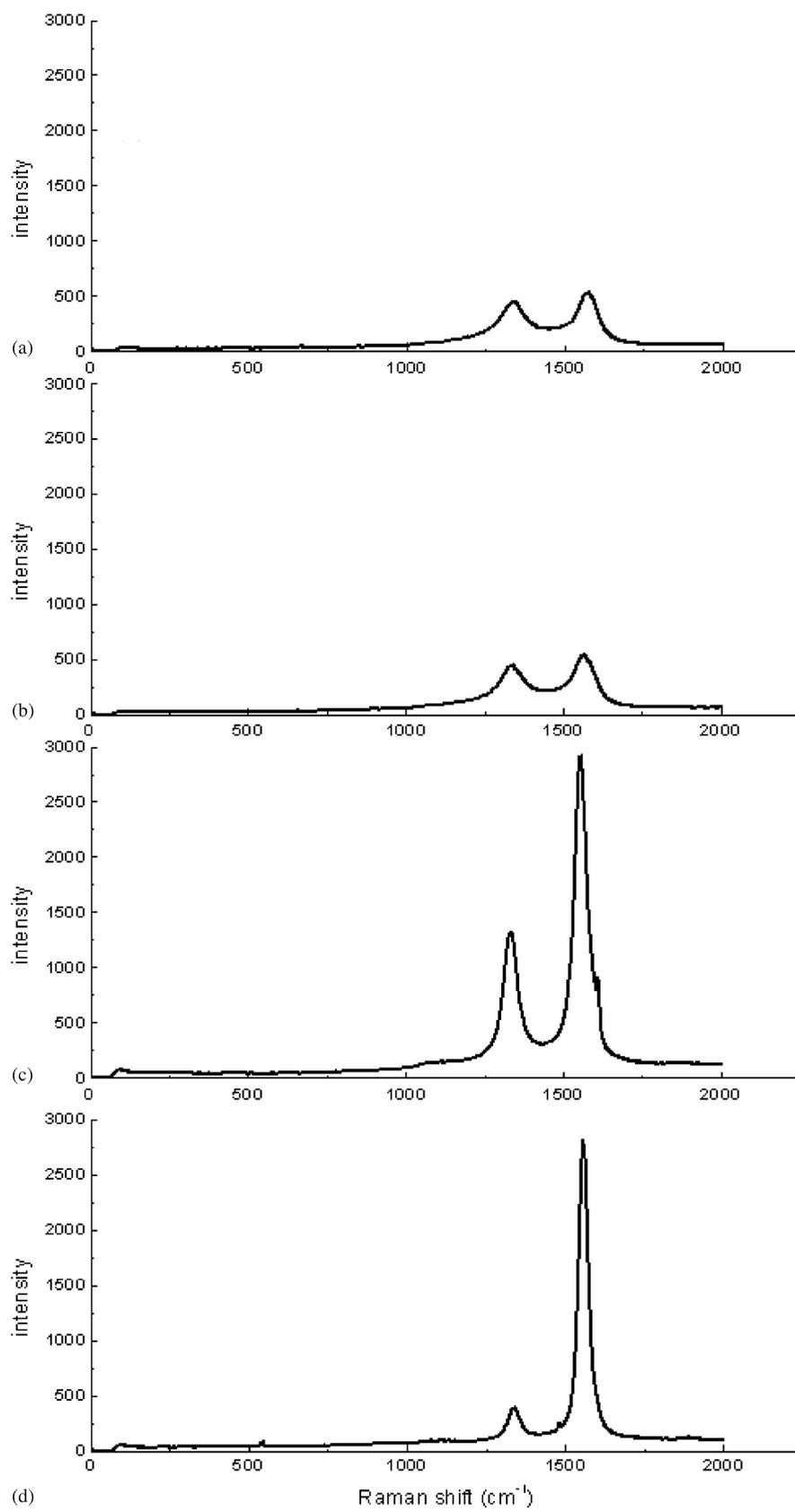


Fig. 2. Raman spectra of the CNTs annealed at different temperatures: (a) as-prepared, (b) 1273 K, (c) 2173 K, (d) 2873 K.

the second step was to run the adsorption/desorption cycle. When observed under TEM micrographs (see Fig. 1c and d), the structure of KOH-modified CNTs samples after the first step of thermal programs was found to have considerable surface defects. This finding suggests that the surface of CNTs was attacked by KOH, thus forming pores with size ranging from 2 to 15 nm due to the destruction of CNT's structure.

After the purification and annealing treatments, Raman spectra of the CNTs samples were taken as shown in Fig. 2. Two main peaks were observed in the high-frequency region, at $\sim 1580\text{ cm}^{-1}$ (G peak) and $\sim 1350\text{ cm}^{-1}$ (D peak). The G peak indicates an original graphitic structure, and the D peak reflects the presence of either disordering feature or amorphous carbon [21–23]. As can be seen from Raman spectra, the intensity of G peak of P samples was similar to that of D peak. Also, the intensity ratio of G band to D band is increased with increasing annealing temperature. It revealed that the degree of crystalline perfection of CNTs was improved after the annealing treatment. As for the P + A2600 samples, the intensity ratio of G peak to D peak was about seven times higher than the rest of other samples. It implied that the P + A2600 samples possess high graphitic structure with fewer defective features on the graphitic wall.

Fig. 3 shows XRD pattern of the CNTs samples that were annealed at various high temperatures. It was found that the 002 peak for P samples appeared broad and weak. After annealing at 1273 K, the graphitic structure revealed no significant change

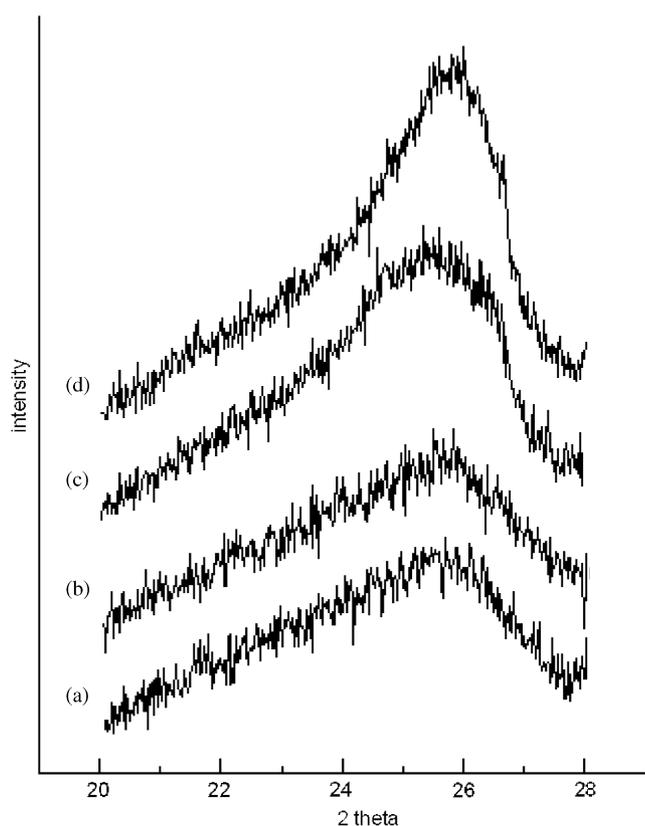


Fig. 3. XRD pattern of the CNTs annealed at different temperatures: (a) as-prepared, (b) 1273 K, (c) 2173 K, (d) 2873 K.

Table 1
Specific surface area of the unmodified and KOH-modified CNTs' samples

Samples	Specific surface area (m^2/g)
P	307.7
P + K	162.1
P + K after the first step of thermal programs	208.3

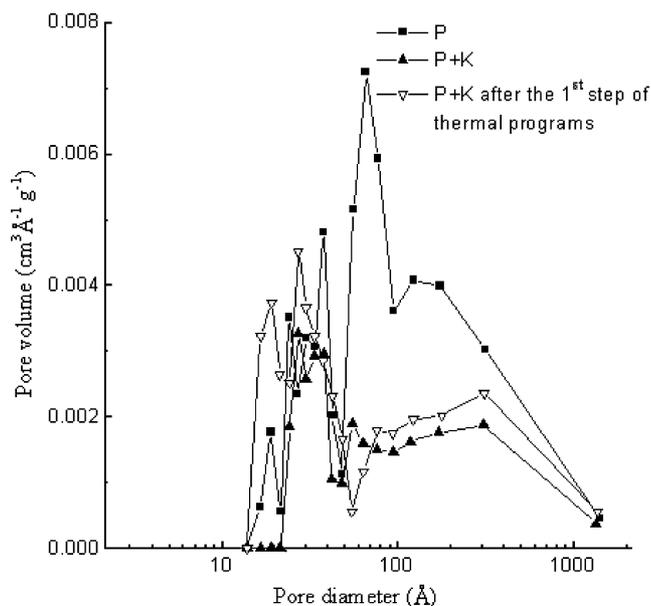


Fig. 4. Pores size distribution of the unmodified and KOH-modified CNTs samples.

until the thermal treatment above 2173 K, which is in agreement with the previous papers [19,20]. Therefore, these results shown above demonstrated that the graphitic domains and crystalline size of CNTs could be enhanced after the annealing treatment. Table 1 lists the specific surface area of the unmodified and KOH modified CNTs samples. It was found that the specific surface area of the P + K samples increased from 162.1 to $208.3\text{ m}^2/\text{g}$ after the first step of thermal programs, due to the formation of defect structure. The pores size distributions of the unmodified and KOH modified CNTs samples are shown in Fig. 4. The new formative pores of the P + K samples after the first step of thermal programs were found to locate in 2–3 nm ranges, which was then confirmed by TEM monograph (Fig. 1c).

3.2. The first step of thermal programs: activation and outgas

Fig. 5 shows the TG profiles of various CNTs samples during the first step of thermal programs. It was observed that the weight losses have two different gradations for all KOH-modified CNTs samples from 303 to 823 K. There was only a slight weight decrease with respect to the P samples. For KOH-modified CNTs, the first gradation of weight losses at about 373 K was moisture that was vaporized from moisture absorbed onto KOH particle. For the second gradation from

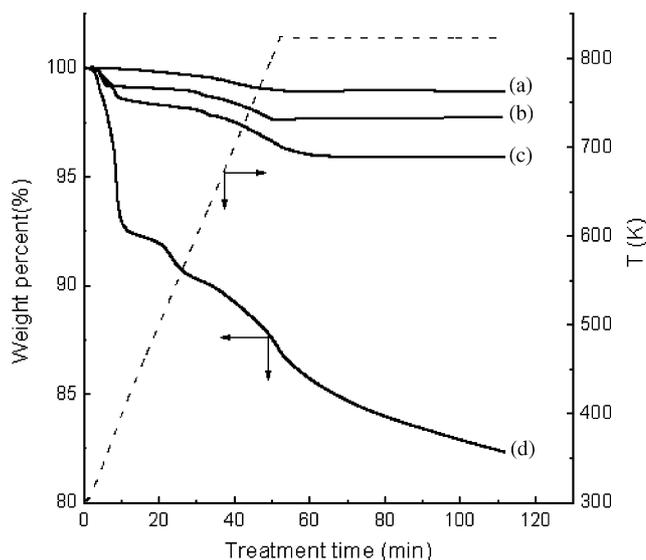


Fig. 5. TG profiles of the CNTs samples during the first step of thermal programs: (a) P, (b) P + K, (c) P + A1900 + K, (d) P + A2600 + K.

373 to 823 K, the weight losses of the P + K samples were about 10% larger than that of other KOH-modified CNTs. In addition, the mass ratio of W/K was decreased slightly with increasing annealing temperature, as shown in Table 2. In other words, the higher crystalline size structure was difficult to be etched through KOH activation.

Carbonaceous materials activation by KOH reagent was reported by many research papers [24–29]. What they proposed was that K_2CO_3 and C–O–K metal salts were considered as products after the activation of KOH in N_2 or Ar atmosphere, and hydrogen and CO_2 were found to exist in the effluent gas. Furthermore, KOH was able to form K_2O by dehydration during activation process. The potassium oxide was reduced possibly to metallic potassium when the activation temperature was above 973 K. For activation in H_2 atmosphere at 823 K, the reactions such as the formation of K_2CO_3 and C–O–K metal salt were considered unfavorably to follow according to the Le Chatelier's principle. Therefore, we believed that K_2O was the final product that remained onto the CNTs after activation

process. The cause of weight losses was due to the emission of CO_2 or CH_4 in forming defect structure (as shown in Eqs. (1) and (2)). Furthermore, the potassium intercalation into inner layers of the CNTs might take place through the defect sites of CNTs



3.3. The second step of thermal programs: hydrogen adsorption and desorption

A comparison of the hydrogen storage capacity, the amount of K loaded, and weight losses of all CNTs samples is listed in Table 2. The results indicated that the capacity of hydrogen adsorption of the P and P + A1000 samples were 0.71 and 0.74 wt%, respectively, which were higher than that of other unmodified samples after annealing at 2173 and 2873 K. This finding suggested that the amount of residual catalyst onto the CNTs was capable of affecting the property of hydrogen storage. Lueking and Yang [30,31] reported that residual metal oxide as active site was able to dissociate hydrogen, and there was spillover from metal oxide to the surface of MWNTs. Furthermore, the purity of CNTs during high-temperature annealing (above 2273 K) can be improved due to the fact that residual metal was vaporized [18,20]. Li et al. [17] reported that high crystalline structure can improve hydrogen uptake on the CNTs under 10 MPa. But, in this study, high crystalline samples such as P + A1900 and P + A2600 samples were found to reveal weak hydrogen adsorption property. This finding can be attributed to the facts that the effect of high crystallization on hydrogen storage was insignificant under atmospheric pressure.

Fig. 6 shows TG profiles of H_2 adsorption/desorption with respect to K-modified and unmodified CNTs samples. It implied that the capacity of hydrogen storage of CNTs was improved after KOH modification. The P + K samples can achieve 4.47 wt% of hydrogen uptake capacity, based on the calculation from adsorption curve. In this study, we obtained the capacity of hydrogen adsorption to be greater than that reported previously [11,12]. It is deduced that the characteristics of CNTs in

Table 2
Comparison of hydrogen storage capacity, K loaded and weight losses for different CNTs' samples

	H_2 storage (wt%)	K loaded (wt%)	H_2 adsorbed/ K^a molar ratio	Weight losses of the CNTs W (wt%)	W/ K loaded mass ratio
P	0.71	—	—	—	—
P + A1000	0.74	—	—	—	—
P + A1900	0.22	—	—	—	—
P + A2600	0.26	—	—	—	—
P + K	4.47	15.36	4.773	10.10	0.66
P + A1000+K	3.98	13.23	4.775	10.50	0.79
P + A1900+K	0.57	4.81	1.419	2.74	0.57
P + A2600+K	0	2.89	0	1.32	0.46

^a $(H_2 \text{ wt}\%_{K \text{ modified}} - H_2 \text{ wt}\%_{\text{unmodified}})/K \text{ loaded wt}\% \times (K \text{ molecular weight}/H_2 \text{ molecular weight})$.

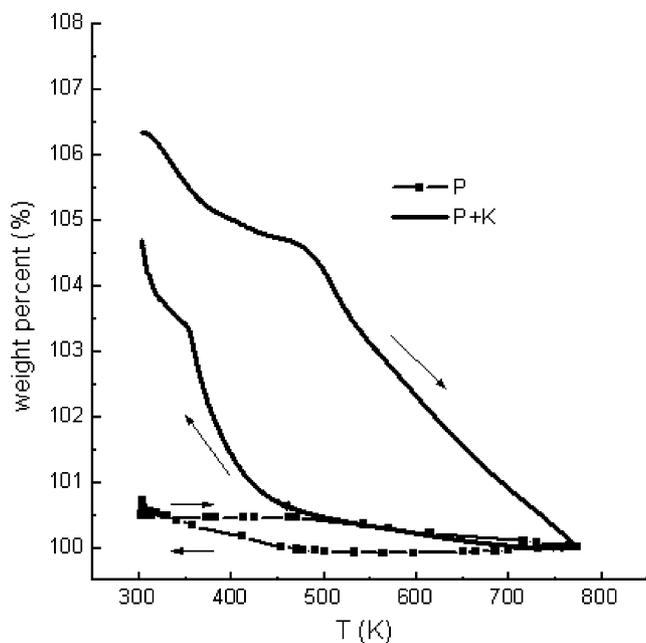


Fig. 6. TG profile of as-prepared (P) and K-modified (P + K) CNTs samples for adsorption/desorption cycle. Operation condition: the temperature was heated up to 773 K and then cooled down to 303 K.

this experiment were different with those reported in previous papers.

Furthermore, the annealing of CNTs samples at different temperatures followed by immersing them with 1 M KOH solution revealed that the amount of K of each samples was different (see Table 2). The K adsorption capacity onto the CNTs was decreased with increasing annealing temperature. The reason was attributed to the facts that the surface of CNTs became inactive after the annealing treatment. Moreover, we also found out that the capacity of hydrogen adsorption was increased with respect to both the increment of amount of K onto the CNTs and the weight losses that occurred during the first step of thermal programs. The molar ratio of adsorbed H_2 to K was to understand clearly the hydrogen storage property for all K-modified CNTs samples (see Table 2), because to the amount of K onto the CNTs was different. The molar ratios of all adsorbed H_2 to K were found to be different, from 4.773 to zero.

3.4. Potassium metal effect

In order to understand the effect of alkali-metal on hydrogen storage, the K-modified CNTs sample was washed after activation to remove alkali-metal and then used to adsorb hydrogen for measurement again, as shown in Fig. 7a. The capacity of hydrogen adsorption was 2.18 wt%. From the graph of adsorption curve, two different weight gradations were observed, that is, point II to III and point III to IV, as shown in Fig. 7. We called these two weight gradations of hydrogen adsorption as the first adsorption gradation (from point II to III), and the second adsorption gradation (from point III to IV). Taking P + K samples as an example (see Fig. 7c), the first and second adsorption gradations were obtained as 3.22 and 1.23 wt%, respectively. However, after P + K samples were washed, the

second adsorption gradation was reduced much higher as compared with the first adsorption gradation, as listed in Table 3. This result can be further interpreted; that is, the second adsorption gradation strongly depended on the presence of potassium metal. If the main reason of improvement of hydrogen adsorption was due to the presence of potassium metal, the capacity of hydrogen adsorption for P + K washed samples should be reduced to approach its original capacity (unmodified CNTs, P) of 0.71 wt%. Consequently, potassium metal was not the main factor to achieve 4.47 wt% of hydrogen uptake for P + K samples. Froudakis proposed [32] that hydrogen should be physisorbed on potassium-metal-doped tubes only. In other words, it was not possible for potassium metal to cause hydrogen dissociative adsorption. In this study, we believed that the defect structure of CNTs was a key factor to improve the capacity of hydrogen storage. In addition, residual metal such as cobalt functioned as a catalyst to dissociate hydrogen and caused it to spread onto the CNTs [33]. The catalyst of cobalt could improve the capacity of hydrogen storage, especially when defects on the structure exist.

3.5. Desorption temperature effect

From all adsorption/desorption cycle curves, it was found that the initial weight (point I) of samples was larger than the final weight (point IV) of samples. The causes were attributed to the facts that the equilibrium state was not really achieved and part of the carbonaceous material decomposed during the desorption process. Based on the results mentioned above, we reset the maximum desorption temperature and it was decreased from 773 to 673 K, as shown in Fig. 7b and d. The gap between point I and point IV was reduced significantly for P + K-washed samples when the maximum desorption temperature was 673 K. Therefore, in Fig. 7a, the weight losses at nearly 773 K should be ascribed to the decomposition of carbonaceous material. It was noted that the structure of CNTs became weak due to the destruction caused by KOH activation. For P + K samples, the gap between points I and IV shows insignificant change, even with the decrease of maximum desorption temperature. Furthermore, the gap between points I and IV for P + K samples was obtained to be less than that of P + K-washed samples when the maximum desorption temperature was 773 K. It is deduced that the non-reacting KOH particle present continued attacking the surface of CNTs. Moreover, the potassium metal might play a role as a protector to protect CNTs' decomposition at high temperature.

Through the summaries obtained from the aforementioned results, we concluded that hydrogen adsorption capacity of KOH-modified CNTs depends on the degree of surface defect of CNTs, potassium content, and residual metal of cobalt. Fig. 8 shows a schematic representation of KOH-activated CNTs process and hydrogen adsorption onto the CNTs, respectively. The KOH deposited onto the surface of CNTs after the impregnation process. After activation, KOH might transform into K_2O , and K also might intercalate into the inner layer of the CNTs, as shown in Fig. 8a. Moreover, the defect structure of CNTs was formed due to CO_2 or CH_4 emission during the

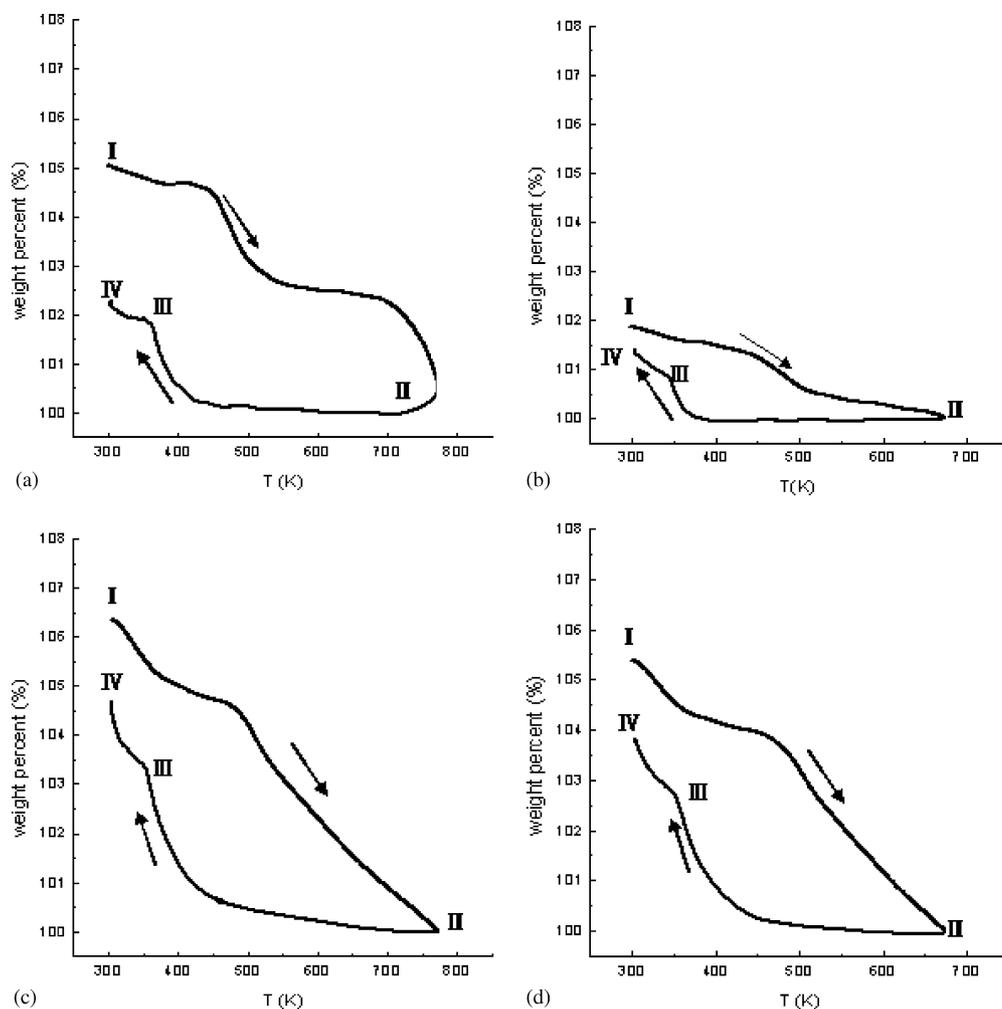


Fig. 7. TG profiles of washed and non-washed K-modified CNTs' samples at different desorption temperatures. (a) and (b) P + K-activated-washed samples, (c) and (d) P + K samples. (a) and (c): The first step of thermal programs: heated up to 823 K and this temperature was maintained for 1 h; the second step of thermal programs: 303–773 K and then cooled down to 303 K. (b): The first step of thermal programs: heated up to 673 K and this temperature was maintained for 1 h; the second step of thermal programs: 303–673 K and then cooled down to 303 K. (d): The first step of thermal programs: heated up to 823 K and this temperature was maintained for 1 h; the second step of thermal programs: 303–673 K and then cooled down to 303 K.

Table 3
Hydrogen adsorption behaviors of KOH-modified CNTs' samples

Samples	Hydrogen storage capacity (wt%) point II to point IV ^a	The first weight increase (wt%) point II to point III ^a	The second weight increase (wt%) point III to point IV ^a	The gap between point I to point IV (%) ^b
P + K-activated-washed ^c	2.18	1.85	0.33	2.72
P + K-activated-washed ^d	1.40	0.88	0.52	0.44
P + K ^c	4.47	3.22	1.25	1.58
P + K ^e	3.81	2.26	1.14	1.41

^aweight increase/ final weight (point IV).

^b(initial weight – final weight) / initial weight (point I).

^cThe first step of thermal programs: heated up to 823 K and this temperature was maintained for 1 h, the second step of thermal programs: 303–773 K and then cooled down to 303 K.

^dThe first step of thermal programs: heated up to 673 K and this temperature was maintained for 1 h, the second step of thermal programs: 303–673 K and then cooled down to 303 K.

^eThe first step of thermal programs: heated up to 823 K and this temperature was maintained for 1 h, the second step of thermal programs: 303–673 K and then cooled down to 303 K.

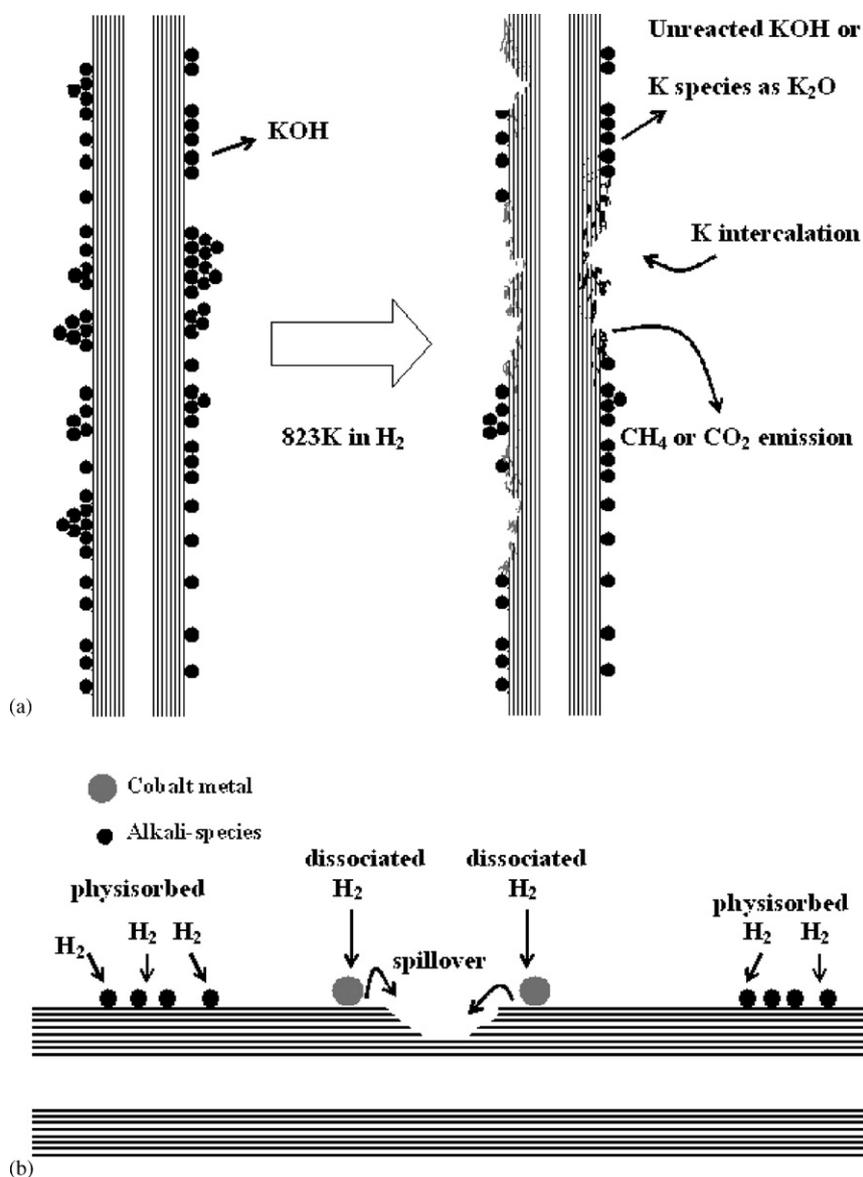


Fig. 8. Schematic representation of (a) KOH-activated CNTs process; (b) the mechanism of hydrogen uptake onto the CNTs.

activation process. As shown in Fig. 8b, hydrogen physisorption and hydrogen dissociative adsorption may be attributed to the fact that the hydrogen possible uptake onto K modified CNTs' samples. Hydrogen molecule physisorbed onto the surface of CNTs and potassium metal deposited onto the CNTs. Moreover, the residual catalyst of cobalt can dissociate hydrogen and it can also spread from metal particle to the surface or inner layer of CNTs.

4. Conclusion

In this study, the graphitized MWNT was modified by KOH impregnation to improve hydrogen storage property. The hydrogen uptake of 4.47 wt% was achieved for P + K samples. The experimental results revealed that CNTs samples after the annealing treatment were unfavorable to enhance hydrogen storage capability. There are three main factors that can be

attributed to have an impact on the effect of hydrogen storage using KOH-modified CNTs:

1. The potassium metal can be used to promote hydrogen storage capacity of the CNTs, but it was the existence of physisorption.
2. The defect structure of CNTs was formed via KOH activation in enhancing hydrogen spilling into the inner layers of CNTs.
3. Residual metal of cobalt onto the CNTs sample can enhance hydrogen adsorption due to hydrogen spillover.

Acknowledgment

This work was financially supported by the National Science Council, Taiwan, Republic of China, under contract (NSC 91-2212-E-224-014).

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