NO titration for the estimation of H_2-storage capacity of carbon nanotubes

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Since the discovery of carbon nanotubes (CNTs) in 1991, scientists have devoted a lot of attention to this material for H_2 storage. Dillon et al. [1] speculated that the H_2-storage capacity of pure single walled CNTs (SWCNTs) was 5–10 wt% (133 K, 0.04 MPa); there was only 0.1 wt.% SWCNTs in their samples and they reported that H_2 could be desorbed at room temperature. Since then, various hydrogen storage capacities were reported by Chambers et al. [2] (67 wt.%, 25 °C, 120 atm, carbon nanofibers), Ye et al. [3] (8.25 wt.%, 80 K, 100 atm, SWCNTs), Liu et al. [4] (4.2 wt.%, 25 °C, 10 MPa SWCNTs), and Chen et al. [5] [20 wt.%, 473–653 K, ambient pressure, Li-multi-walled CNTs (MWCNTs); 14 wt.%, room temperature, ambient pressure, K-MWCNTs] (1 atm = 101325 Pa). However, Yang [6] pointed out that the results of Chen et al. should be treated as unreliable due to the presence of H_2O. The causes for discrepancies in H_2-storage measurements are: (i) the CNT materials studied were different in diameter, and (ii) experimental error is usually large in determination methods based on weight or pressure changes. Since the CNT samples examined were in small quantities (a few mg), trace amounts of impurities in the H_2 source would cause large errors in gravimetric methods; this is especially so if water is the impurity. For methods based on pressure measurements, error could be large as well and the use of a suitable sensor is crucial. In view of the above concerns, we have established the NO-titration method for better measurement of CNT H_2-storage capacities. The method was derived from our previous $DeNO_x$ studies conducted over CNT-supported metal catalysts [7]. We found that H_2-storage capacity can be determined according to the stoichiometric reaction:

$$NO + H_2 \text{ (or 2H)} = H_2O + 1/2N_2 \tag{1}$$

The method is not affected by impurities; a minute amount of other oxidant or reductant in the H_2 or NO source would not be a problem. Here, we report the H_2-storage of MWCNTs synthesized by catalytic decomposition of CH_4 over $LaNiO_3$ (perovskite) and La_2NiO_4 (K_2NiF_4-type) precursors [8]. After CH_4 catalytic CVD reaction (750 °C, flow rate 60 ml min^{-1}, 8 h), MWCNTs were obtained. By nitric acid washing, most of the catalyst could be removed. By means of oxidation at 400 °C in air, the presence of amorphous carbon could be dismissed. Our TGA study has demonstrated that MWCNTs could only be oxidized in air at temperatures above 600 °C [8]. After purification, the purity of CNTs can reach 95 wt.%; there is a La–Ni impurity of around 5 wt.%. Transmission electron microscopy (TEM; JEOL JEM-100CX, 50 kV) images indicated that the MWCNTs obtained over reduced $LaNiO_3$ had an average inner diameter of 25 nm and a wall thickness of 18 nm (referred to as MWCNTs-1); those grown over reduced La_2NiO_4 had an average inner diameter of 12 nm and a wall thickness of 9 nm (referred to as MWCNTs-2). For MWCNTs-1, the BET specific surface area was 50.2 m^2 g^{-1} and there was a narrow pore size distribution at 22.5 nm (measured on a NOVA 1200 system); for MWCNTs-2, they were 75 m^2 g^{-1} and 15.0 nm, respectively. The measured pore diameters are consistent with the results of TEM imaging. It is apparent that besides the hollow tubes, there was very little microporosity in the MWCNTs.

Hydrogen adsorption behavior was monitored by temperature-programmed adsorption (H_2-TPA; 10H_2–90He%; 50 ml min^{-1}, 10 mg of MWCNTs, heating rate = 10 °C min^{-1}). For MWCNTs-1, hydrogen consumption during H_2-TPA studies occurred at 200 to 400 °C and maximum consumption occurred at ca. 320 °C. For MWCNTs-2, there was hydrogen consumption from 260 to 420 °C and maximum consumption at ca. 370 °C. For both MWCNTs samples, H_2 adsorption thus takes place between 200 and 450 °C, and 350 °C is the temperature for maximum adsorption.

NO desorption was investigated by NO temperature programmed desorption (NO-TPD). The CNT sample was first exposed to an NO flow (5000 ppm with He as the carrier) at 400 °C and cooled to room temperature; then the sample was heated in helium at 10 °C min^{-1}. In NO-TPD studies, the desorption profile over MWCNTs-1 ranged from 90 to 320 °C and peaked at 270 °C. Over MWCNTs-

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2, it ranged from 90 to 410 °C and peaked at 290 °C. We did not detect any signals of N_2 and O_2; the observation confirmed that NO did not decompose below 500 °C. Above 550 °C, however, NO reacted with MWCNTs-1 and MWCNTs-2 to produce CO_2. Before H_2 adsorption and below 550 °C, the pulsing of NO (65.7 μl, 25 °C, 1 atm) onto MWCNTs-1 and MWCNTs-2 did not result in N_2 generation and NO signal intensity remained intact. In other words, below 550 °C and in the absence of adsorbed hydrogen, NO was not consumed over the MWCNTs. The results indicated that NO titration could be suitably performed below 500 °C.

For H_2-storage, 0.005 g of CNTs was first treated in helium (purity = 99.999%, 10 ml min^{-1}) at 600 °C in a micro-quartz tube reactor. After being cooled to room temperature, the CNT sample was exposed to pure hydrogen (purity = 99.999%) at various combinations of temperature and pressure for 3 h. The NO-titration experiment was carried out in a quartz tube micro-reactor (I.D. 2 mm) by means of NO-pulsing and temperature-programmed surface reaction (NO/H-TPSR). For accurate MS measurement of N_2 content during NO titration, we first pulsed NO and N_2, respectively, into an empty quartz tube to obtain the corresponding peaks for area calibration. The NO-pulsing experiment was conducted by pulsing NO (purity = 99.99%) into the reactor with helium (10 ml min^{-1}) being the carrier gas at a desired temperature; the outlet was analyzed by a mass spectrometry (MS) system (HP G-1800A). During pulsing, N_2 was generated and there was a decrease in NO intensity. When N_2 generation ceased and NO pulses remained intact, NO-H titration was complete. For the NO/H-TPSR experiment, the CNT sample with stored hydrogen was heated in a flow of NO (5000 ppm, He being the carrier) and the generation of N_2 was recorded continuously. From the area under the curve, one can estimate the exact amount of hydrogen storage.

If MWCNTs-1 and MWCNT-2 were exposed to H_2 at temperatures below 200 °C and at a pressure of 0.101 MPa, there was no N_2 detection during NO titration; we hence chose 250, 300, 350, and 400 °C and 0.101 MPa for H_2 adsorption. Titration of MWCNTs-1 at 100 °C, with hydrogen adsorbed at 250 °C, resulted in an uptake of 0.55 wt.%. Since NO only interacted with weakly adsorbed hydrogen below 100 °C, the titration of the strongly adsorbed hydrogen was conducted at 100, 200, 300, 400, and 450 °C (see Table 1). Another titration step at 480 °C gave no N_2 signals, indicating that there was no more hydrogen left. The overall hydrogen storage at a 250 °C H_2-exposure was 2.10 wt.% for MWCNTs-1. At a H_2-exposure temperature of 300 °C, the maximum hydrogen storage was 2.88 wt.%; at 350 and 400 °C, the values were 2.62 wt.% and 1.87 wt.%, respectively. As for MWCNTs-2, the maximum hydrogen storage was 3.76 wt.% at a H_2-exposure temperature of 350 °C. During NO/H-TPSR of MWCNTs-2 with hydrogen adsorbed at 300 °C, N_2 was generated from 70 to 450 °C and reached its highest abundance at 330 °C. According to the area under this curve, we estimated a hydrogen storage of 3.62 wt.%. The NO/H-TPSR results are a little bit higher than the corresponding NO-pulsing data. This is reasonable because NO-pulsing steps were conducted at intervals and there would be hydrogen desorption between measurements. Since, compared to MWCNTs-1, MWCNTs-2 is smaller in inner tube diameter and wall thickness but higher in hydrogen storage capacity (per unit weight), we deduce that hydrogen is not stored between the folding walls but rather inside the tubes of MWCNTs. Furthermore, the chemisorption of hydrogen at ambient pressure may be a result of hydrogen dissociation on La–Ni impurities and subsequent diffusion into CNTs by means of spillover.

Table 1
Hydrogen storage capacity of MWCNTs-1 and MWCNTs-2 at 0.101 MPa

Hydrogen storage temperature (°C)	Hydrogen capacity (wt.%) determined by steps of NO titration conduction at various temperature (°C)					Storage capacity[a] (wt.%)	Storage capacity[b] (wt.%)
	100	200	300	400	450		
MWCNTs-1							
250	0.55	1.05	0.24	0.21	0.05	2.10	2.54
300	0.68	1.39	0.37	0.29	0.15	2.88	3.16
350	0.49	1.11	0.45	0.37	0.20	2.62	2.91
400	0.12	0.76	0.38	0.25	0.36	1.87	2.05
MWCNTs-2							
250	0.06	0.45	0.52	0.34	0.26	1.63	1.81
300	0.47	1.16	1.09	0.48	0.24	3.44	3.62
350	0.45	0.98	1.36	0.62	0.35	3.76	3.91
400	0.24	0.73	0.54	0.31	0.40	2.22	2.35

[a] Determined by NO-pulsing.

[b] Determined by NO/H-TPSR.

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Effect of cupped cathode on microstructures of carbon nanotubes in arc discharge

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Arc discharge, as a major synthesis technique for carbon nanotubes (CNTS) [1–4], has been explored extensively. It has a very high temperature and can yield highly graphitized multi-walled CNTs (MCNTs) without being contaminated by a metal catalyst [5]. Most research has focused on investigating the effect of growth conditions (buffer gas, arc current, electrode temperature etc.) on the quality and output of MCNTs in the cathode deposit, and the optimum conditions for preparing high density and loosely entangled MCNTs have been obtained [6–10]. Nevertheless, the effect of growth conditions on the microstructures (diameter, helicity, number of layers, etc.) of MCNTs is still not clear due to the process having a very high temperature.

In the case of the self-sustained stabilized arc discharge, we found there are two regions with different morphologies on the top surface of the cathode deposit: the central region with regular triangular arrangement of locations (~80 μm) and the fringe region (the region around the central region) with no pattern [7,8]. Besides, we also found that the microstructures of MCNTs in these two regions are quite different from each other. In fact, during arc discharge, carbon atoms and heat energy can escape continuously from the fringe of the arc to the outside in all directions, which leads to the differences in growth conditions such as temperature, temperature gradients and density of carbon species between the central region and the fringe region. These differences in microstructures of the MCNTs can perhaps be attributed to the differences of growth conditions. In the present work, we used a cupped cathode instead of a flat cathode for the arc discharge, which possibly can eliminate or reduce the differences of growth conditions between these two regions by preventing carbon atoms and energy from escaping from the fringe of arc. By investigating the changes of morphologies and microstructures of MCNTs, we can get some details about the relationship between growth conditions and microstructures of MCNTs.

Our experiments were carried out in the same apparatus as previously reported [8,15], an 8-mm diameter graphite rod and a 40-mm diameter cupped graphite disk were installed horizontally as anode and cathode, respectively. The diameter and depth of the hole in the center of cathode are 16 and 20 mm, respectively. A self-sustained stabilized

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