



Short communication

Effects of post-treatments on microstructure and hydrogen storage performance of the carbon nano-tubes prepared via a metal dusting process

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ABSTRACT

Preparation of multi-wall carbon nano-tubes (CNTs) is successfully demonstrated via a metal dusting (MD) process, in which a steel coupon and CO–CO₂ mixed gas are the only reactants needed. During the process, fresh Fe–Ni nano-particles are produced spontaneously and continuously from the steel, and consequently catalyze the growth of the CNTs. Post-treatments, including heating in air at 550 °C and etching in boiling nitric acid, are used to purify the as-prepared multi-wall CNTs. The microstructure modification due to the post-treatments are examined with a transmission electron microscopy. The possibility of utilizing the MD-produced CNTs as a hydrogen storage material is also explored in this study.

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1. Introduction

Carbon nano-tubes (CNTs), which were first observed by Iijima [1] in 1991, have attracted a lot of attention because of their unique physical and mechanical properties [2,3]. The applications of CNTs are widespread in many fields, such as field emission sources [4], electric nano-conductors [5], Li ion secondary batteries [6], electric double-layer capacitors [7], fuel cells [8], and molecular sieves [9]. In addition, CNTs have been recently used to adsorb hydrogen [10] since they are highly porous, stable, light, and inexpensive. Hydrogen, owing to its high energy content and non-polluting nature, is considered as an ideal energy carrier, which may be widely utilized in the near future [11]. However, it has been found that the morphology and microstructure of CNTs, governed by the preparation procedures, significantly affect their hydrogen storage capability [12]. The known synthesis methods of CNTs include arc-discharge [13], laser vaporization [14], and chemical vapor deposition (CVD) [15] techniques. Finding a more favorable and efficient preparation process to mass produce high-quality CNTs with satisfactory hydrogen storage performance is of great importance and interest.

Metal dusting (MD) is a catastrophic form of corrosion, which leads to the disintegration of alloys into a powdery mixture of graphite and metal dusts. It is known that these nano-sized metal dusts can catalyze the deposition of carbon filaments from the atmosphere [16,17]. MD occurs in strongly carburizing atmospheres

(with carbon activity, $a_c > 1$) and predominantly at intermediate temperatures of 400–800 °C. The reaction mechanism was first reported by Hochman [18] and refined later by Grabke et al. [19,20] and Chun et al. [21,22]. However, while corrosion phenomenon beneath the metal surface has been extensively investigated, little work has been done on the characteristics of the deposited nano-sized carbon materials (NCMs). The MD process is expected to be an efficient route to prepare NCMs since it is quite simple and low-cost. Besides the reaction gas, a steel coupon is the only substance needed. Large-scale production should be achievable. Most importantly, fresh catalyst nano-particles are constantly provided during the process, and thus high yield of NCMs can be anticipated. Grabke [20] has indicated that the metal wastage rate and carbon deposition rate for several selected systems are approximately 1 and 10 mg cm⁻² h⁻¹, respectively, at 600 °C.

In this investigation, a novel CNTs preparation approach via MD process is developed. Moreover, the possibility of using the obtained CNTs as a hydrogen storage material, which has never been explored in the literature, is studied. The effects of post-treatments on microstructure and the hydrogen storage performance of the CNTs are also evaluated.

2. Experimental

304L austenitic stainless steel coupons, with a dimension of 10 mm × 10 mm × 1 mm and the chemical composition shown in Table 1, were used. The coupons were first blasted by Al₂O₃ powders, which had their particle size in a range of 200–250 μm. The blasted samples were then placed into a tube furnace filled with a

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Table 1
Chemical composition of the 304L stainless steel used in this study

Element	wt%
C	0.026
Cr	17.92
Ni	8.12
Si	0.46
Mn	1.19
Cu	0.12
S	0.002
P	0.04
Fe	Bal.

CO–CO₂ mixed reaction gas (the volume ratio was 35:1). The MD experiments were performed at 600 °C for 30 and 500 h, while the gas flow rate was 60 sccm and the pressure in the reaction chamber was 1 atm. Fig. 1 shows a schematic of the experimental setup. Carbon activity (a_c) of the atmosphere can be calculated according to the following reaction:



with $a_c = (P_{\text{CO}})^2 K / P_{\text{CO}_2}$, where P_{CO} and P_{CO_2} are the partial pressures of carbon monoxide and carbon dioxide, respectively, and K is the equilibrium constant. For the given reaction conditions, the a_c was 440. After the reaction at 600 °C, the samples were then cooled down to room temperature in inert argon gas to avoid any undesired reaction.

Surface morphologies of the specimens were examined with scanning electron microscopy (SEM). The nano-sized carbon mate-

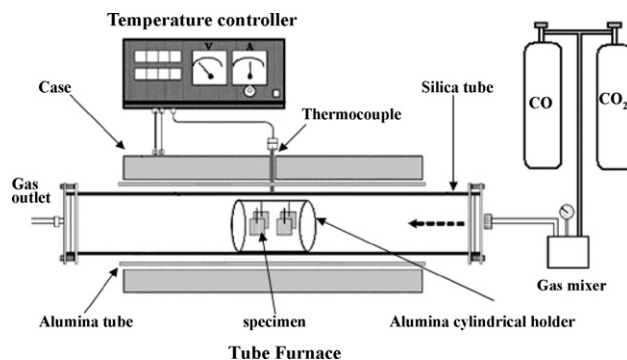


Fig. 1. Configuration of the reaction chamber for the metal dusting experiments.

rials deposited on the steel coupons were then detached from the substrates and dispersed in anhydrous alcohol solution with ultrasonic sonication before they were collected on a Cu grid, which was covered with a lacy carbon film. After that, microstructures of the deposited carbon were further analyzed with a high-resolution transmission electron microscope (HRTEM) operated at 200 kV. Chemical compositions of the catalyst nano-particles were analyzed with an auxiliary X-ray energy dispersive spectroscopy (EDS) attached to the HRTEM. In addition, a Setaram TGA 92 analyzer was used to perform thermogravimetric analyses. The samples were heated from 25 to 1000 °C at a rate of 10 °C min⁻¹ under a flowing air atmosphere.

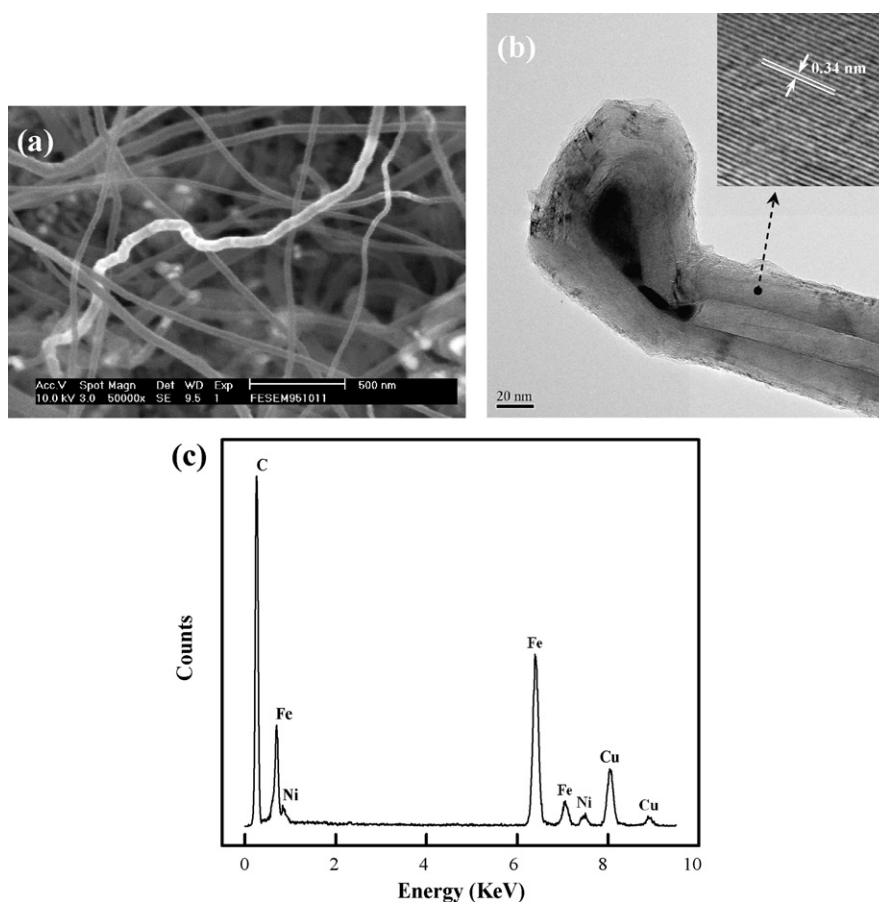


Fig. 2. (a) SEM observation of the steel after exposure in the 600 °C CO–CO₂ mixed gas for 30 h. (b) HRTEM micrograph of the multi-wall CNT shown in (a). (c) EDS spectrum taken from the catalyst particle.

The hydrogen storage performance of the samples was evaluated by an electrochemical method at 25 °C. The CNTs obtained were mixed with nickel powder (with a diameter of $\sim 1 \mu\text{m}$) in a weight ratio of 1:10 and then pressured to pellets, which were 10 mm in the diameter and 1 mm in thickness. A pellet was then connected to a nickel wire and used as the working electrode. A Pt foil and a Hg/HgO (in 6 M KOH) electrode were assembled to be the counter and reference electrodes, respectively. The electrolyte used was 6 M KOH aqueous solution. Before testing, the electrodes were immersed in the electrolyte for at least 1 day to ensure they were completely wetted. The working electrode was cathodically charged hydrogen at a current density of 300 mA g^{-1} (based on the weight of CNTs) for 1 h and subsequently discharged at the same rate to a cut-off potential of -0.4 V . The hydrogen charge–discharge conditions were controlled with an EG&G Model 263 potentiostat.

3. Results and discussion

Fig. 2(a) shows the surface morphology of the 304L stainless steel after exposure in the CO–CO₂ mixed gas at 600 °C for 30 h. It was found that the sample surfaces were covered with nano-sized carbon filaments with an average diameter of approximately 65 nm and the length of typically a few micrometers. Some metal particles, which were produced via MD from the 304L substrate, were also observed on the sample. The microstructure of the carbon filaments can be further characterized with a HRTEM. The micrograph obtained is shown in Fig. 2(b), and the filament is clearly identified as a multi-wall nano-tube. A catalyst nano-particle with a size of $\sim 30 \text{ nm}$ was recognized on the top of the CNT, and thus the tip-catalyzed growth model of the CNT is suggested in this case [23]. The chemical composition of the catalyst particle was analyzed with EDS and the results, shown in Fig. 2(c), indicate that the metallic particle is composed of 89 wt% Fe and 11 wt% Ni. However, no Cr is detected within the particle (it should be 18 wt% in the 304L substrate, as shown in Table 1), since it could be fixed by the formation of spinel oxide and/or stable carbide near the sample surface [22]. The enlarged micrograph on the wall of the CNT shows that the long-range ordered carbon layers are virtually parallel with the tube axis. Moreover, the spacing between each layer is found to be approximately 0.34 nm, which is consistent with the ideal basal plane distance of a graphite structure.

To increase the amount of the CNTs produced, the reaction time was increased. In fact, Grabke [20] has indicated that the carbon deposition rate during the MD process is proportional to the square of time. Fig. 3(a) shows a SEM micrograph of the sample exposed in the CO–CO₂ mixed gas at 600 °C for 500 h; numerous carbon filaments with the diameter of approximately 90 nm are observed. As

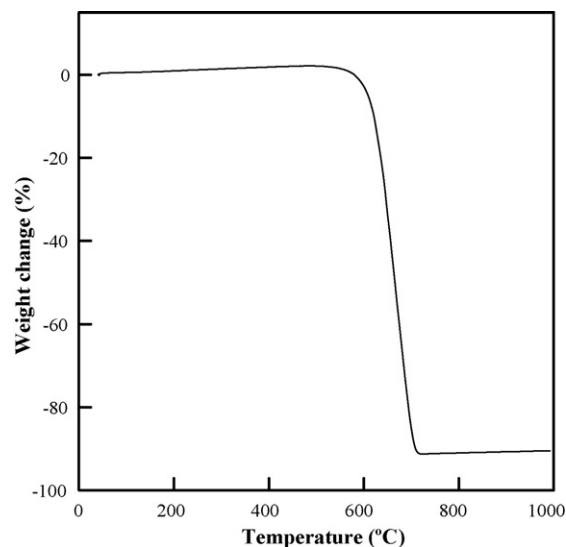


Fig. 4. Thermogravimetric analysis of the as-prepared CNTs performed in air atmosphere at a heating rate of $10^\circ\text{C min}^{-1}$.

compared to Fig. 2(a), the yield of the carbon filament does indeed increase with reaction time, indicating the feasibility of mass production exploiting the MD process. However, it is found that the surface of the filaments is rather rough (compared to that of the 30-h sample), and many carbon blocks (i.e. non-tubular carbon aggregation) coexist on the specimen. A high level of amorphous carbon may be present as the exposure time was quite long. Fig. 3(b) shows a HRTEM picture of the carbon filament shown in Fig. 3(a). It is confirmed that it is still a multi-wall CNT, revealing the tubular structure of deposited carbon did not change with reaction time during the MD process. As can be also seen in Fig. 3(b), the CNT are decorated with many tiny metal particles (typically less than 5 nm), which were produced from the MD process. It is believed that the tiny particles are attached to the tube wall via the deposited amorphous carbon, which acts as a binder; as a result, an impurity layer covers the surface of the CNT. Therefore, proper post-treatment is needed to purify the as-prepared multi-wall CNTs before they can be practically used in various applications.

Fig. 4 shows the thermogravimetric data for the CNTs, produced by the MD process for 500 h, in an air atmosphere at a heating rate of $10^\circ\text{C min}^{-1}$. The weight change as a function of temperature is depicted in this figure. It is found that the mass of the sample is almost constant at temperatures below 550 °C, suggesting the CNTs could be immune (or stable) in this temperature range. However, a

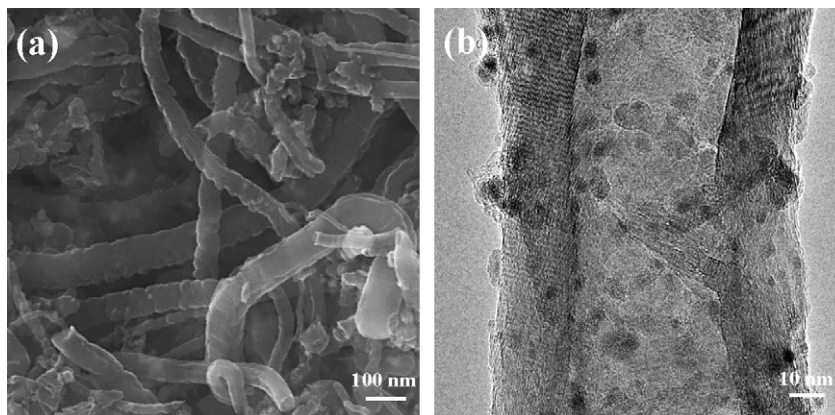


Fig. 3. (a) SEM observation of the steel after exposure in the 600 °C CO–CO₂ mixed gas for 500 h. (b) HRTEM micrograph of the multi-wall CNT shown in (a).

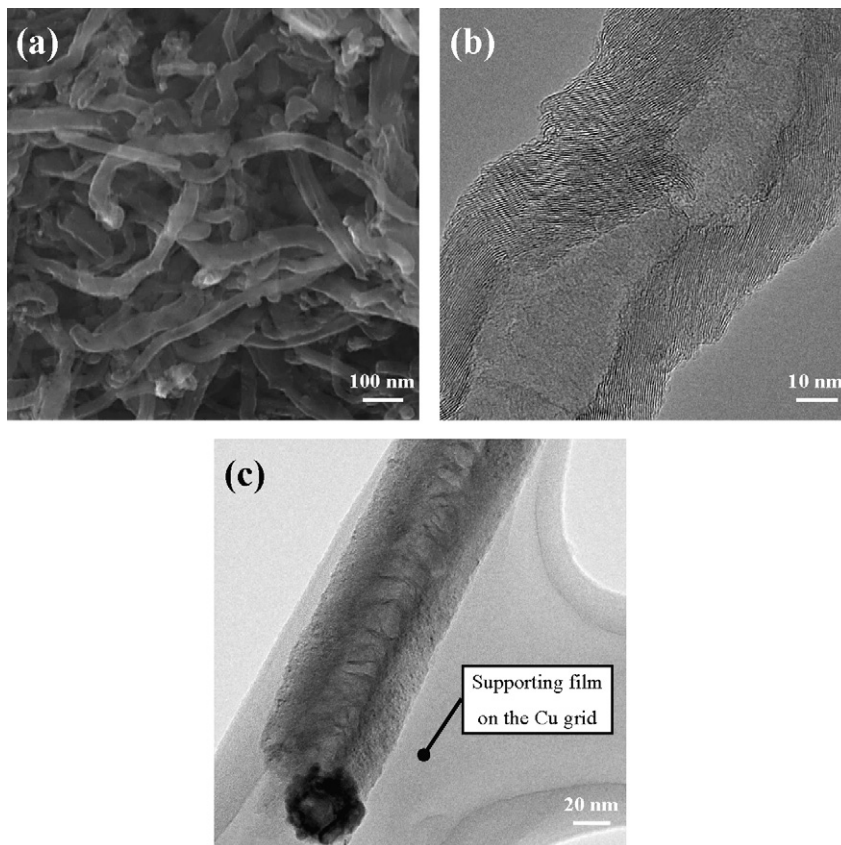


Fig. 5. (a) SEM morphology of the prepared CNTs after a 550 °C heat treatment for 30 min. (b) and (c) The body- and tip-region HRTEM micrographs of the heated CNT.

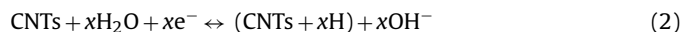
significant weight loss from 550 to 700 °C is observed; it is believed that the amorphous carbon is oxidized to CO and CO₂ at the lower temperature, while the graphitized carbon (CNT) is vaporized during the later stage [24,25]. At temperatures higher than 700 °C, all the carbon species are eliminated and only the metal (or its oxide) particles remain. The analytical result also discloses that the residual particles included in the multi-wall CNTs are approximately 10 wt%. According to the information given in Fig. 4, 550 °C seems to be an appropriate temperature to remove the surface deposited amorphous carbon but preserve the CNTs consisting of graphene layers.

Fig. 5(a) shows a SEM micrograph of the 500-h produced CNTs after a 550 °C heat treatment for 30 min, when a weight loss of approximately 30% was detected. In contrast with the morphology of the as-prepared CNTs shown in Fig. 3(a), the heat-treated CNTs are thinner and smoother, suggesting the surface amorphous carbon is effectively removed. Fig. 5(b) demonstrates a HRTEM image of a multi-wall CNT shown in Fig. 5(a), and it clearly confirms that the deposited amorphous carbon and thereby the attached tiny metal particles are eliminated, as compared to Fig. 3(b). This observation result shows that the body of the MD produced CNTs can be successfully purified by the heat treatment performed in air atmosphere. In addition, Fig. 5(c) shows a tip region of the heat-treated CNT observed under a HRTEM; it is found that the graphene cap, covering a catalyst particle (as shown in Fig. 2(b)), is ruptured. This localized destruction could be attributed to two reasons—exothermic reaction and volume expansion of the metal particle upon oxidation. The former process caused thermal damage and the latter caused mechanical damage to the surrounding graphene cap, and thereby led to the fracture [26]. According to our observation, the catalyst particles could either fall away or still adhere on tips of the CNTs (as shown in Fig. 5(c)). Either way,

in both the cases, a post-cleaning procedure is needed to remove the catalyst particles if high-purity multi-wall CNTs are demanded. Since the surface impurity layer is cleaned and the graphene cap is opened, the BET specific surface area of the MD prepared CNTs increased from 170 to 258 m² g⁻¹ through the heat treatment.

Further removal of the Fe–Ni catalyst was attempted by etching the heat-treated CNTs sample in 15 M boiling nitric acid solution for 4 h. It is confirmed by HRTEM observation, as shown in Fig. 6(a), that the metal particle can be completely dissolved. The HRTEM micrograph shown in Fig. 6(b) displays the body region of an etched CNT, revealing its wall thickness of only ~5 nm. As compared to Fig. 5(b), the wall thickness is evidently reduced (from ~20 nm) due to the acid treatment. It is proposed that, besides eliminating the catalyst particles, the concentrated and high-temperature nitric acid can also dissolve (or oxidize) the graphene layers. As a result, the wall of the multi-wall CNT is thinned upon etching in the nitric acid solution.

Hydrogen storage performance of the as-produced and purified CNTs prepared via the MD process was evaluated by an electrochemical method. Essentially, hydrogen was charged (or discharged) into (or from) the CNTs according to the following equation [27]:



By measuring the charges passed through the sample, its hydrogen storage capacity could be estimated from the above reaction. Fig. 7 shows the hydrogen discharging curves of the different CNTs samples at an anodic current density of 300 mA g⁻¹, after they have been fully charged at the same rate (300 mA g⁻¹). A potential plateau, corresponding to the release of hydrogen via Eq. (2), is found at approximately -0.7 V. After most of the stored hydrogen is desorbed, the electrode potential is remarkably polarized (i.e.

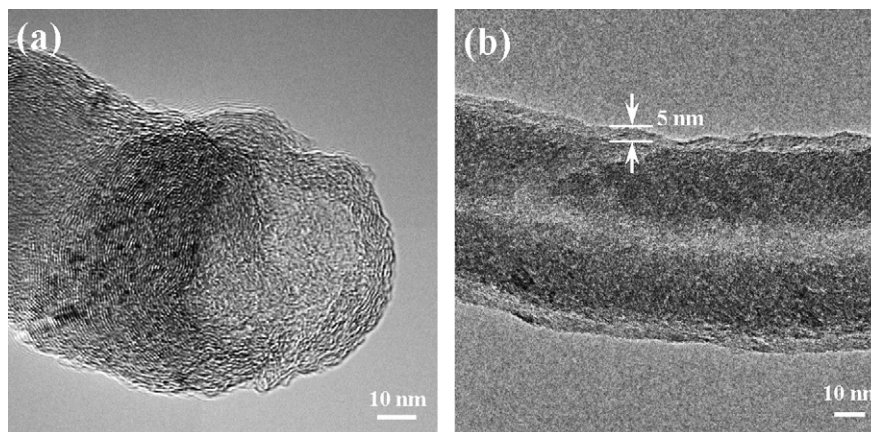


Fig. 6. (a) The tip-region and (b) the body-region HRTEM micrographs of the heated CNT sample after post-etching in 15 M boiling nitric acid solution for 4 h.

greatly deviated from the plateau potential); the discharging process is thus terminated at a cut-off potential of -0.4 V to avoid any undesired damage to the sample. As illustrated in Fig. 7, the hydrogen discharging capacities of the as-prepared, heat-treated, and heat-treated plus etched CNTs are 57, 85, and 93 mAh g^{-1} , respectively. The experimental results indicate that due to the removal of the amorphous carbon and the tiny metal particles attached to the CNTs, the hydrogen storage performance of the heat-treated CNTs is significantly improved by approximately 50%, as compared to that of the as-prepared CNTs. It is also found that the post-etching by nitric acid, which can dissolve the catalyst particles and thin the wall thickness of the CNTs, is able to further enhance the hydrogen storage performance, as the capacity is increased by 63% compared to the as-prepared sample. The uplift in hydrogen storage capability of the CNTs, due to the post-purification treatments, is attributed to the elimination of the metal particles and amorphous carbon which are considered to be unable to adsorb hydrogen, and the increase in the active hydrogen adsorption sites (on the surface of the bare and tubular graphene layers [28,29]). The open-end and thin-wall characteristics of the etched CNTs could facilitate the electrolyte to penetrate inside the tubes, and thereby be beneficial for electro-

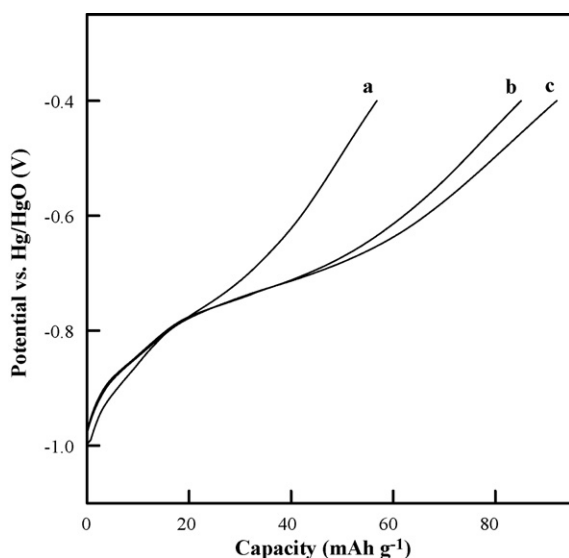


Fig. 7. Hydrogen discharging curves of the as-prepared (curve a), heat-treated (curve b), and heat-treated plus etched (curve c) CNTs electrodes. The applied anodic current density is 300 mA g^{-1} until a cut-off potential of -0.4 V.

chemically gathering hydrogen (via Eq. (2)). The optimum specific hydrogen storage capacity in this study, evaluated under room temperature and pressure, is about 0.35 wt%, which is in the same order as those measured in a similar electrochemical method for other multi-wall CNTs reported in the literature [30–32]. Although further measuring of the storing performance under high pressure of hydrogen gas (or low temperature) is still in progress, the data presented herein has clearly indicated that the CNTs prepared by the MD process are promising materials for hydrogen storage applications.

4. Conclusions

A promising CNTs fabrication method, namely a metal dusting process, has been successfully developed. Since a steel coupon and CO-CO_2 mixed gas are the only reactants needed and the fresh catalyst nano-particles are produced spontaneously and continuously from the steel, this process is considered to be low-cost, simple, and easily scaled up. However, the as-prepared multi-wall CNTs have to be purified before their practical use. Heat treatment in 550°C air atmosphere for 30 min can effectively remove the amorphous carbon deposited on the CNTs and thus detach the tiny metal particles that adhere on their surface. It is also found that the heat treatment is able to open the caps in the tips of the CNTs. Thereby, the catalyst particles are easily dissolved by the subsequent etching procedure in boiling nitric acid; as a result, further purification of the CNTs is achieved. The hydrogen discharging capacities of the as-prepared, heat-treated, and heat-treated plus etched CNTs are 57, 85, and 93 mAh g^{-1} , respectively, indicating that these materials are potential candidates for use in hydrogen storage applications.

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