Improved hydrogen storage capacity of CNTs synthesized in presence of iron catalyst using arc discharge method in air atmosphere

N. Ismail[1*], R. Joshi[2], J. Engstler[2], J. J. Schneider[2]

[1]Physical Chemistry Department, National Research Centre, Dokki 12311, Cairo, Egypt
[2]Department of Chemistry, Inorganic Chemistry, Darmstadt University of Technology, Darmstadt, Germany

Arc discharge method is used to prepare carbon nanotubes (CNTs) in air atmosphere with high yield. Multiwall-CNTs are produced in absence of catalyst. When 10wt% of Fe and amorphous FeB are used as catalysts during the synthesis process, the quality of produced CNTs is improved and the number of walls tends to decrease. The XRD structural study records the graphite 002pattern accompanied with the main peaks of Fe structure. Scanning electron microscopy showed high yield of CNTs distributed all over the soot when catalysts are used. High transmission electron microscopy is utilized to investigate the local microstructure of the CNTs. The growth mechanism of CNTs in presence of amorphous FeB is discussed. After removal of the catalyst, the hydrogen storage capacity is measured at 80K under applied hydrogen pressure up to 20 bar. The storage capacity is improved to 3.25 wt% when CNTs are prepared in presence of catalysts.

Key words: Hydrogen storage, Carbon nanotubes, Catalyst

INTRODUCTION

Since their discovery in 1991 [1], CNTs draw the attention of the researchers, as they possess unique mechanical, electronic, thermal, chemical and optical properties. Scientists classified them according to the number of walls assingle-walled nanotubes (SWNTs), double-walled nanotubes (DWNTs) and multi-walled nanotubes (MWNTs). The most popular methods of CNTS preparation are arc discharge, chemical vapor deposition and laser ablation [2-7]. Other methods have been reported, e.g., electrolysis [8,9], hydrothermal[10] and ball milling [11,12].Arc discharge is considered as the most successful preparation method for quantitative production. However, the atmosphere used is mostly hydrogen [13], noble gas like argon or helium [14]or a mixture of hydrogen with noble gas [15]. Carbon nanotubes have been found promising for several applications like hydrogen energy storage. This is due to theirinteresting rolling graphene sheets. The tube hollow cavity is considered a possible site for hydrogen to occupy along withits possible adsorption on the outer surface as a result of Van der Waals forces. Several publications reported the adsorption of hydrogen by CNTs either electrochemically [16-18] or from the gas phase [19-21].Additionally, CNTs were used as a catalyst to overcome the slow kinetics of Mg hydride.Chen *et al*. [22] added CNTs to Mg hydride during ball milling which enhanced the formation of Mg hydride

nanoparticles. They detected remarkable improvements of kinetics of Mg hydride absorption/desorption cycling. When TiO_2-Co nanoparticles decorated the CNTs using electrophoretic deposition, Bordbar *et al.*[23] recorded atwo-fold increase in the hydrogen discharge capacity(305 mAh/g) compared to CNT alone. Another study claimed an enhancement in hydrogen storage capacity of Ag-CNTs when CNTs have been deposited on Ag microporous foam by electrophoretic deposition [24]. The researchers believed that the interconnections between the CNTs and the Ag increased and became more stable, and in return, the charge transfer process through the electrode was facilitated. This was believed to be the reason for the remarkable increase in the hydrogen storage capacity to reach 5.2 wt%.When 10 mol% of CNTs were mixed with $NaAlH_4$ the hydrogen storage capacity reported was 3.3wt% [25], a further increase up to 4.2 wt% was achieved by rehydrogenation.

In this work we report a convenient method of preparation of CNTs by arc discharge method in air atmosphere. Fe and amorphous FeB alloy were used as catalysts for the synthesis process and the hydrogen storage capacity wasenhanced in case of CNTS prepared using acatalyst.

EXPERIMENTAL

Preparation of amorphous FeB

Intermetallic iron boride alloy of 99% purity was purchased from CHEMPUR, Poland. Mechanical alloying was performed using a planetary ball mill

* To whom all correspondence should be sent:
E-mail:nahlaismail24@yahoo.com

Fritsch Pulverisettein order to convert it from crystalline to amorphous state. A mass of 20 g of FeB alloy was transferred to a stainless steel vial. The ball to powder ratio was kept 10:1 in argon atmosphere. The powder was milled for 50 h at a constant rotation speed of 700 rpm. Figure 1 shows the XRD pattern of the amorphous structure of FeB alloy after ball milling.
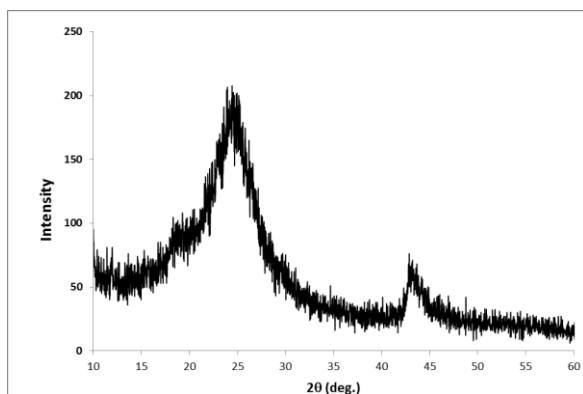
**Fig. 1.** XRD pattern of FeB alloy after ball milling

Setup of arc discharger

To synthesize CNTs the power was adjusted at 40V constant potential usingM30-TP305E DC power supply.The two electrodes used for arc discharge are of graphite of 99.7%purity.The anode is a hollow rod of 11 mm diameter facing the cathode disc of 2.5 cm diameter mounted on a rotating copper plate. The hollow space is centered in the middle with 6 mm diameter and 6 cm depth filled with the catalyst. Filling the anode with Fe and amorphous FeB catalyst is performed in a glove box in argon atmosphere. A schematic diagram of the experimental setup is shown in ref. [26]. The copper disc rotates at a slow speed adjusted at 5 rpm and is cooled during the experiment by water running through a tube coil surrounding the cathode. All experiments were carried out in air atmosphere. Soot deposited on the cathode disc was removed using a thin blade during rotation.

Phase identification was performed by X-ray diffraction (XRD) EMPY REAN diffractometer operated at 30 mA and 45 KV, using Cu Kα radiation. Phillips XL30 FEG scanning electron microscope (SEM) was utilized to study the soot morphology and Phillips CM 20 FEG transmission electron microscope (TEM) was used with an acceleration voltage of 200 KV for local microstructure investigations of the nanotubes. A volumetric Sieverts method was used to estimate the weight percentage of the amount of hydrogen adsorbed by the CNTs, as previously mentioned in [2, 28].

RESULTS AND DISCUSSION

The anode was filled with 10wt% of Fe in argon atmosphere, then arc discharge was operated for few minutes in air and the chamber was left to cool down before repeating the process. The soot deposited on the cathode disc was collected. Its physical properties are: hard grey from the outside andblack from inside where bundles of CNTs exist. The SEM image of the soot (Fig. 2) reveals its hard, brittle properties.
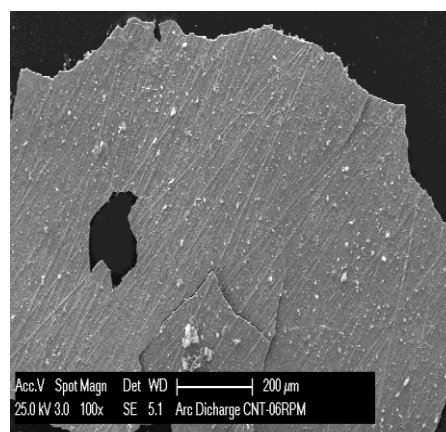
Fig 2. SEM image of the soot

The soot was purified from undesired carbonaceous materials by calcination in an oven at 550°C for 1 h. After that, the soot wasre-weighed and the difference in weight was considered as undesired carbonaceous materials which became oxidized to CO_2. The remaining product was CNTs. In absence of a catalyst, the undesired carbonaceousmaterials were found to be 7wt. % of the soot. When Fe and amorphous FeB were used as catalysts, the undesired carbonaceous materials were reduced to 1.3 wt. % and 1.7 wt. %, respectively.
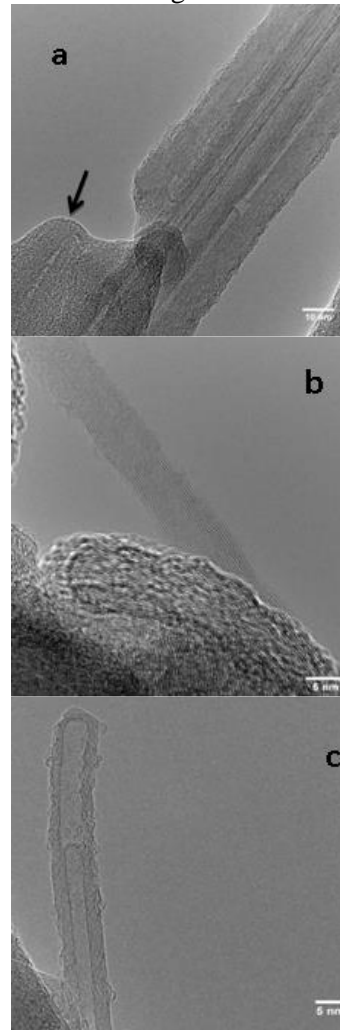
The SEM image of the CNTs synthesized without a catalyst is shown in Fig 3a. Long nanotubes which look like needles are observed in different areas of the image, their lengths are in micrometers. The image shows the graphitized materials covering the major parts of the image. Figs.3b and c present the image of the crushed soot formed in presence of Fe and amorphous FeB, respectively. These images justify the high yield of CNTs calculated in presence of catalyst. The formation of bundles of CNTs is seen all over the soot samples and few graphitized materials are observed. The length of CNTs observed is in micrometers. The rotating cathode disc promoted the formation of μm long CNTs both in presence and absence of the catalyst. Certainly, the presence of Fe and amorphous FeB remarkably promotes the CNTs yield and the distribution of the CNTs all over the soot, and also minimizes the formation of graphitized materials.
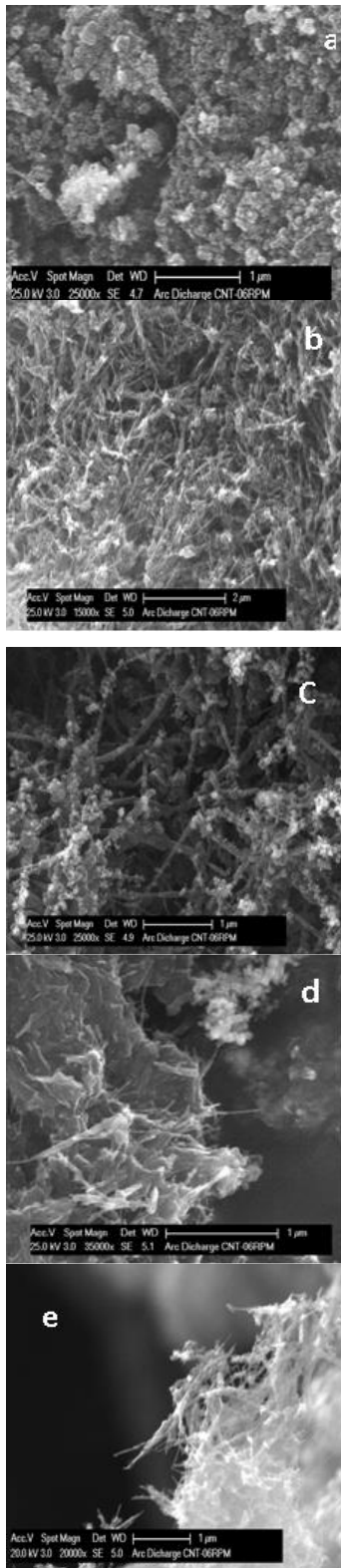
Fig 3. SEM images of the prepared CNTs

The soot formed in presence of Fe and FeB was purified by stirring in boiling 6M HCl for 2 h, then ultrasonicated in ethanol for 10 min. The SEM images of purified CNTs are presented in Figs 3 d and e. The images illustrate the formation of lumps of CNTs.

For local microstructure investigations to identify the type and size of CNTs, HR-TEM was utilized. The images of CNTs synthesized without a catalyst and in presence of Fe and amorphous FeB as catalysts, are shown in Fig 4.


Fig 4. SEM images of CNTs formed a) without a catalyst, b) in presence of Fe, c) in presence of amorphous FeB.

Image (a) shows the CNTs synthesized without a catalyst - MWCNTs with a large number of walls, outer diameter larger than 10 nm and inner diameter about 2.5 nm. They coexist with ellipsoidal polyhedral particles (see the arrow) which are considered as embryonic state of CNTswhich may grow under constant ion supply [29]. Figs. 4b and c present the local microstructure of the CNTs grown in presence of Fe and amorphous FeB, respectively. From image 4b it is seen that the synthesized CNTs inner diameter is 2.5 nm and the outer diameter is 6.3 nm, the number of walls is 5-7. Image 4c shows that the CNTs inner diameter is 3.9 nm, the outer diameter is 6.7 nm and the same number of walls is observed in the case of Fe.The statistical error of the measurement is ± 0.2. From these results we deduce

that the presence of the catalyst tends to reduce the number of walls and this agrees with another conformation [30] that the catalyst favors the growth of single- and double-wall CNTs rather than MWCNTs. During arc plasma discharge the catalyst metal atoms vaporize along with the carbon atoms and at the cathode the metal liquid redistributes its temperature in a way that it suppresses the formation of multi-walls during the nucleation of the carbon nanotubes. For the binary catalyst FeB the nonmetal is added as a promotor, during plasma arc discharge, the difference between the metal and nonmetal melting points leads to the formation of a core/shell on the cathode [31, 32]. It forms active sites on the catalyst surface so that CNTs nucleation occurs at these sites. Thus, the type of catalyst controls the number of walls and the diameter of the nanotubes. In case of metallic Fe asa catalyst, the tube diameters were relatively smaller than those of the tubes formed in presence of amorphous FeB; in both cases of catalysts the number of walls was almost the same. This observation confirms the suggestion that core/shell active sites (of logically larger diameter) are formed and that nucleation occurs on these sites.

The structural investigation of the sootwascarried out using XRD (Fig. 5). The plots show the 002 graphitic reflections of pyrolytic graphite [33, 34], which indicates a high degree of crystallinity. The CNTs formed in presence of Fe as a catalyst, record additional peaks of Fe pattern.
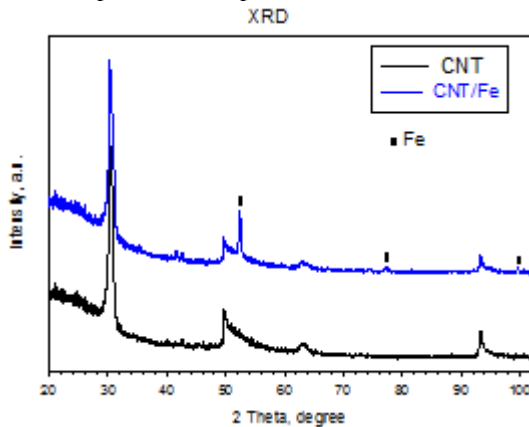
Fig 5. XRD patterns of the CNTs soot in presence of Fe as a catalyst and without a catalyst.

The hydrogen sorption capacity in weight percentage was estimated by the computer programmed volumetric Sievertsdevice. At 80K, the pressure composition isotherm (PCI) of CNTs formed in absence of the catalyst is shown in Fig.6. Theplotdisplays typeIIisotherm so that at relatively low applied hydrogen pressure (up to 13 bar), the CNTsadsorb hydrogen linearly, then the rate of adsorption decreases by increasing the applied

hydrogen pressure. At 20 bar, the amount of sorbed hydrogen is 2.5 wt%.
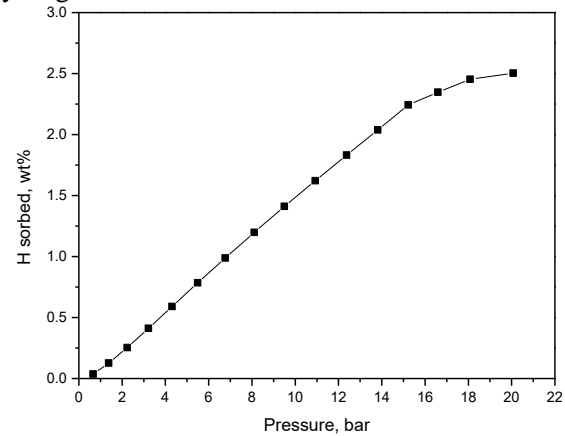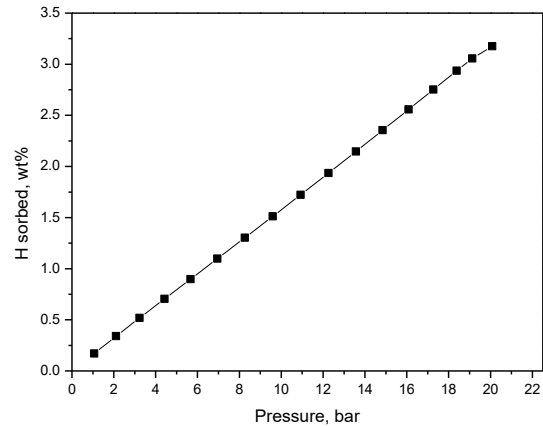

Fig 6. PCT isotherm of the CNTs prepared in absence of a catalyst.

At the same temperature, the hydrogen sorption plots of the CNTs prepared in presence of Fe and amorphous FeB are shown in Figs. 7 and 8, respectively. Both diagrams display linear first order plots so that the rate of hydrogen sorption is almost constant all over the range of the applied hydrogen pressure.
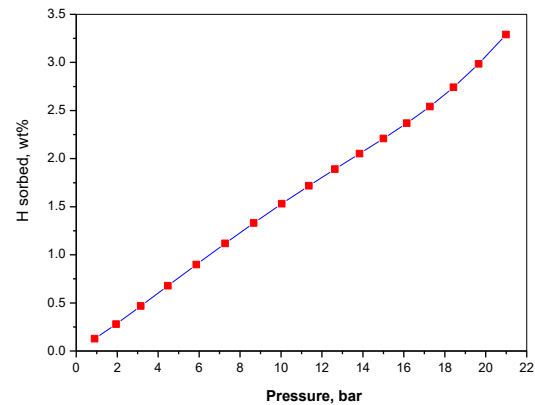
Fig 7. PCT isotherm of the CNTs prepared in presence of Fe.

Fig 8. PCT isotherm of the CNTs prepared in presence of amorphous FeB.

The amounts of hydrogen stored by the CNTs at 20 barare 3.25 and 3.2 wt % respectively. The

enhancement of the amount of hydrogen sorbed by the CNTs prepared in presence of the Fe catalysts is related to the quality of CNTs produced in presence of the catalysts. The regularity of the produced CNTs and the reduction of the number of walls may have increased the possibility of the CNTs to uptake more hydrogen.

CONCLUSIONS

Carbon nanotubes were prepared by arc discharge in an air atmosphere. Contrary to other research reports [35], CNTs can be prepared without a catalyst, but the presence of the catalyst, in our case Fe and amorphous FeB, improved the quality of the CNTs. Regular tubes were produced. In addition, the presence of Fe and FeB tended to reduce the number of walls to reach penta to hepta walls. The improved quality of the CNTs in presence of the catalysts had enhanced, on its turn, the hydrogen sorption capacity under the same conditions.

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ПОДОБРЕН КАПАЦИТЕТ НА ВЪГЛЕРОДНИ НАНОТРЪБИ (CNT) ЗА СКЛАДИРАНЕ НА ВОДОРОД ПРИ ДЪГОВО ИЗПРАЗВАНЕ ВЪВ ВЪЗДУХ В ПРИСЪСТВИЕ НА ЖЕЛЕЗЕН КАТАЛИЗАТОР

Н. Исмаил[1], Р. Джоши[2], Й. Енгстлер[2], Й.Й. Шнайдер[2]

[1]Департамент по физикохимия, Национален изследователски център, Докки 12311, Кайро, Египет
[2]Департамент по химия, Неорганична химия, Технологичен университет в Дармщадт, Германия

(Резюме)

Използване е метод на дъгово изпразване във въздушна атмосфера за изготвянето на въглеродни нанотръби (CNTs) с висок добив. Многостенните CNTs се получават в отсъствие на катализатор. Когато се добавят 10 % (тегловни) желязо и аморфен FeB като катализатор по време на синтезата качеството на получените CNTs се подобрява и броят на стените намалява. Рентгено-структурният анализ показва наличието на графит 002, придружени от главни пикове на желязна структура. Сканиращата електронна микроскопия показа висок добив на CNTs, разпределени по целите сажди когато се използва катализатор. Високо-трансмисионна електронна микроскопия е използвана за изследването на локалната микроструктура на CNTs. Обсъден е механизма на израстване на CNTs в присъствие на FeB. След отстраняването на катализатора е измерен капацитета за складиране на водород при 80 K при налягане на газа до 20 бара. Капацитетът на складиране се подобрява до 3.25 % (тегловни), когато CNTs се изготвят в присъствие на катализатор.