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Reversible Hydrogen Storage in Electrospun Composite Nanofibers

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Composite nanofibers containing single-walled carbon nanotubes (SWNT) were prepared by using electrospinning technique and hydrogen adsorption/desorption isotherms were carried out by a Sieverts apparatus at room temperature. The SEM analysis of the nanofibers revealed that the deformation of the nanofiber increases with increasing SWNT concentration. The diameter of neat nanofibers was below 200 nm and had smooth surface. The surface of the composite nanofibers was rough even by adding low quantity of SWNT. The hydrogen storage results showed an improvement in the adsorption capacity with increasing the SWNT content in composite nanofibers. These nanofibers were evacuated again to remove the adsorbed hydrogen at room temperature. Moreover, even though specific surface area and total pore volume were important factors for increasing the capacity of hydrogen adsorption. Finally, maximum adsorption capacity was 0.29 wt % in case of nanofibers with 10 wt % SWNT under 30 bar at 298 K.

1. INTRODUCTION

Hydrogen is a globally accepted as clean energy source for mobile and stationary applications in the future. The benefits of using hydrogen as a future fuel are both strategic and environmental arising from decreased reliance on petroleum and major reduction greenhouse gasses in air. The use of hydrogen fuel in various purposes requires lightweight hydrogen storage technology. One of the main challenges facing hydrogen fuel is the development of viable storage systems [1-3]. There are four methods to store hydrogen, including high-pressure gas compression, liquid hydrogen, metal hydrides, and physisorption [4]. Among them, physisorption is one of the most potential candidates for hydrogen storage under normal conditions of pressure and temperature in recent years. Various physisorbent hydrogen storage media have been investigated, which includes carbon nanotube (CNT) [5], metal organic frameworks (MOFs) [6], clathrate hydrates [7], and conductive polymers [8]. Among mentioned media, hydrogen storage on CNT has been of great concern.

Carbon nanotubes possess a unique hollow tubular structure, large surface area, and desirable mechanical and thermal stability. CNT are classified in two general types, namely single-walled carbon nanotubes (SWNTs) and multi-walled carbon nanotubes (MWNTs). Both SWNT and MWNT have been explored as potential candidates for hydrogen storage. Comparing to other form of CNT, SWNT have extraordinary hydrogen storage properties due to high surface area and cylindrical structure [9, 10].

Several experimental and theoretical studies, using different techniques, have been focused on hydrogen physisorption on SWNT with controversial results [11]. Currently, there are few studies in the literature regarding the use of SWNTs in composite structure for improving their hydrogen storage [12, 13]. In the present study, we report the synthesis of novel polyacrylonitrile (PAN) / polyvinylpyrrolidone (PVP) / SWNT composite nanofibers by electrospinning process. The hydrogen adsorption and desorption behavior in these composite nanofibers have been investigated using high-pressure Sieverts apparatus. Also the effect of SWNT amounts on adsorption capacity of composite nanofibers was investigated.

2. EXPERIMENTAL

The SWNTs were purchased from Research Institute of Petroleum Industry (purity: 95%, diameter: 0.8–1.1 nm). PAN ($M_w = 100,000$ g/mol) and PVP ($M_w = 40,000$ g/mol) were supplied with Polyacryl Co. and Sigma-Aldrich, respectively. The solvent used for dissolving polymers was N,N-dimethylformamide (DMF, Merck).

The solutions were prepared by dissolving 1 w/v% of PVP in DMF separately via magnetic stirrer at 298 K for 1 hr. Different amounts of SWNTs were dispersed in the PVP/DMF solutions by the use of a high power ultrasonic homogenizer (UP200, Germany) at 273 K for 40 min. The solutions have also been found to be stable at room temperature for over several weeks without precipitation. Finally, the electrospinning solutions were prepared by dissolving 12 w/v% of PAN in sonicated solutions via magnetic stirrer at 313 K for 24 hr.

The experimental setup used for electrospinning is shown in Fig. 1. These composite nanofibers are collected and then dried in oven at 313 K for 8 hr. In the next step, the dried sample was annealed at 398 K for 3 hr. Finally, the composite nanofibers (CNF) products were coded as CNF-0 (0 wt % SWNT), CNF-1 (1 wt % SWNT), CNF-2 (2 wt % SWNT) and CNF-10 (10 wt % SWNT).

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The surface morphology of the electrospun nanofibers was examined by SEM (Philips, XL-30) at an accelerating voltage of 25 kV under magnification of 10000X, and the average fiber diameter was measured with the SEM images using Image J software (National Institute of Health, USA) from 200 fibers/sample. The orientation of SWCNTs in the SWCNT/PAN/PVP nanofibers was characterized using a TEM (Philips, EM 208). The BET surface area, total pore volume, pore diameter of the CNF composite nanofibers were determined in a static volumetric system (Belsorp mini II, Japan) using N_2 adsorption/desorption isotherm at 77 K up to 1 bar pressure. Prior to adsorption measurements the samples were activated by heating at a rate of 1 K.min^{-1}, to 423 K under vacuum for 4 h. Hydrogen storage test was carried out under high pressure up to 40 bar at room temperature using an experimentally Sieverts apparatus and the capacity of adsorbed hydrogen was calculated by measuring volumetric change.
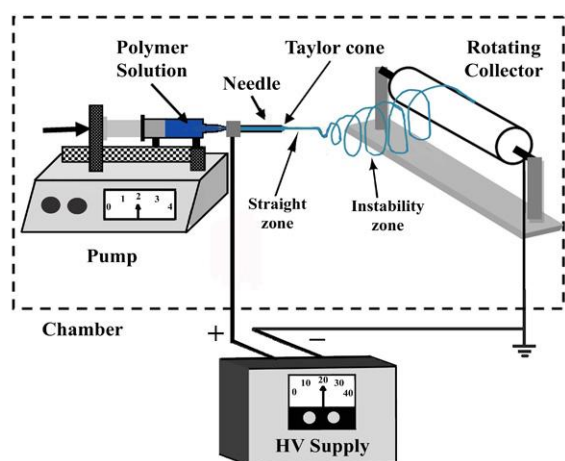

Fig. 1 – Schematic diagram of a general type of electrospinning apparatus in this work

3. RESULTS AND DISCUSSION

3.1 Surface Morphology of Composite Nanofibers

Fig. 2(a-d) shows SEM images of electrospun composite nanofibers with various concentration of SWNT. As can be seen, the surface morphology of CNF composite nanofibers is uniform. The average diameter of the neat nanofibers (CNF-0) was about 163 nm and the surface morphology is very smooth. In CNF-1 and CNF-2 samples despite the SWNT were well embedded in the nanofibers, but it seem that the presence of SWNT made the nanofiber surface rough and uneven. The CNF-10 sample surface is quite rough, comparing to other nanofiber samples. As can be seen from Fig. 2d, some aggregates and local irregularities were observed as the SWNT content increased to 10 wt %. Changes in the average diameter of CNF composite nanofibers versus the SWNT concentration is shown in Fig. 2e. As it can be seen, with increasing the concentration of SWNT in the solution from 0 to 2 wt %, the mean diameter of nanofibers increased from 163±19 to 307±34 nm. However, when SWNT concentration was increased to 10 wt % the average diameter decreased to 148±22 nm.
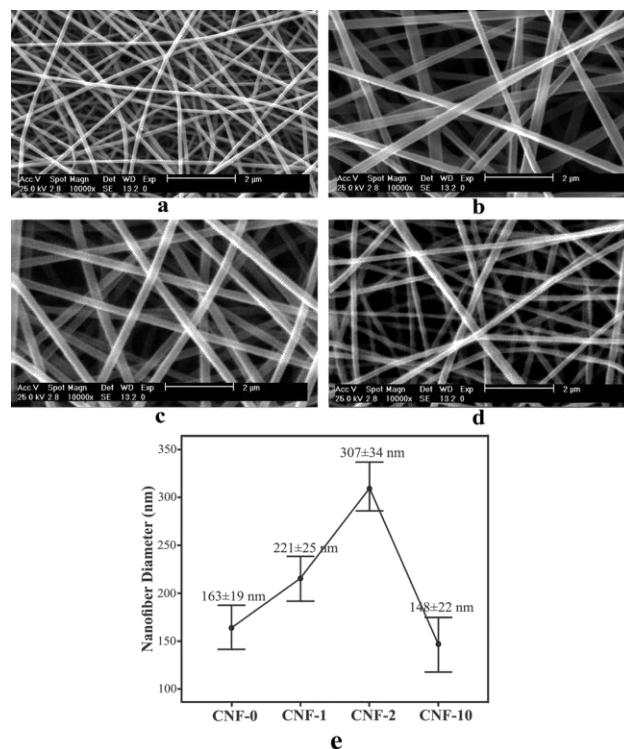

Fig. 2 – SEM images of electrospun nanofibres: (a) CNF-0, (b) CNF-1, (c) CNF-2, (d) CNF-10 and (e) Error plot of composite nanofibers average diameter versus samples

3.2 TEM analysis of Composite Nanofibers

Fig. 3 show the TEM photographs of the composite nanofibers. The electrospun nanofibers with the SWCNT content of 1 wt % (CNF-1), are shown in Fig. 3a. As it can be seen, the SWNT in this sample was aligned and almost fully extended. However, as the SWNT content in the electrospun nanofibers increased to 10 wt % (see SNF-10 sample), the nanofibers surface was irregular and rough, which can be related to SWNT aggregation and bundling during the electrospinning process (Fig. 3b). Also, the alignment of the SWNT within the nanofibers structure can influence the mechanical properties of the composite samples.

3.3 Hydrogen Adsorption/desorption Isotherm

Fig. 4(a) displays the kinetic of hydrogen adsorption on composite nanofibers at 30 bar. It can be seen that the neat nanofibers does not absorb any hydrogen after 10 min. However, the sample can store approximately 0.01 wt % hydrogen at 30 bar and 298 K. It is easy to see the hydrogen storage capacity of the CNF-2 increased to 0.14 wt % on equilibrium condition, as compared to only 0.08 wt % for the CNF-1. Furthermore, the hydrogen storage capacity in the CNF-10 sample with 10 % SWNT increased to 0.29 wt % that is four times higher than the CNF-1 results. At the end of each adsorption process, desorption experiment were examined under atmospheric pressure and room temperature, which are depicted in Fig. 4(b). Then all samples were evacuated again to remove the adsorbed hydrogen at 298K. Accordingly, it can be concluded that the synthesis composite nanofibers were adsorbing hydrogen physically.
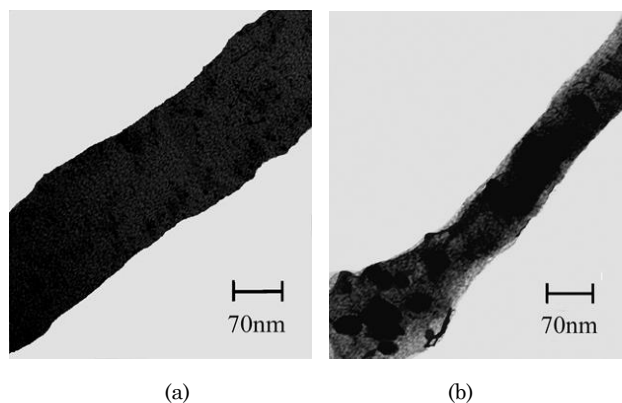
Fig. 3 – TEM photographs of electrospun nanocomposites: (a) CNF-1 and (b) CNF-10
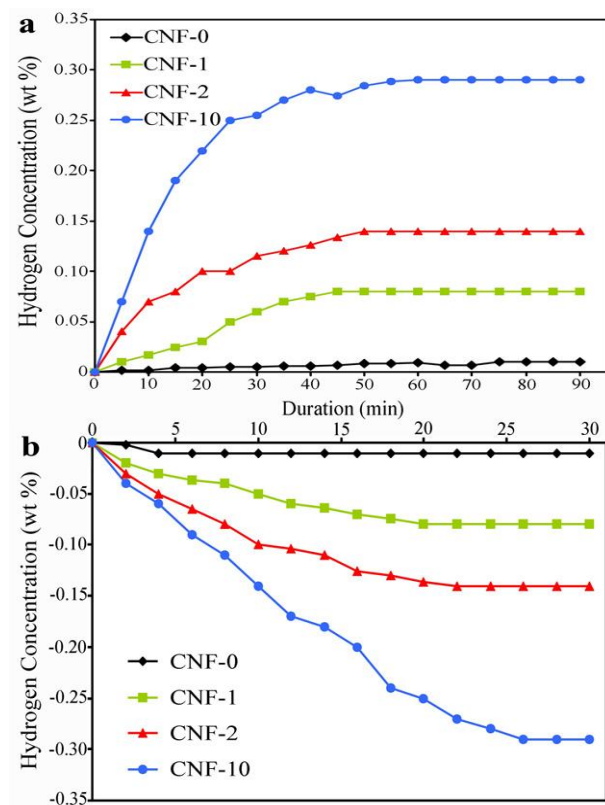

Fig. 4 – (a) Hydrogen adsorption curves samples at 30bar and 298K and (b) Hydrogen desorption curves samples at 298K for synthesis composite nanofibres

3.4 Porosity of Composite Nanofibers

Generally, the specific surface area and total pore volume are two very important parameters in adsorption phenomenon, there are still some other factors influencing the storage capacity. The nitrogen adsorption/desorption isotherm and pore size distributions for composite samples are presented in Fig. 5. A summary of the textural and hydrogen adsorption properties is presented in Table 1. The CNF-0 and the CNF-1 had low surface area within the 11 and 12 m²/g, respectively. According to the results, the CNF-10 sample presented the highest specific surface area, total pore volume and hydrogen adsorption values of 27 m²/g, 0.142 cm³/g, and 0.29 wt %, respectively. It is concluded that

the actual order of the hydrogen storage capacities is very similar to that of the SWNT content, specific surface area and total pore volume in composite nanofibers.
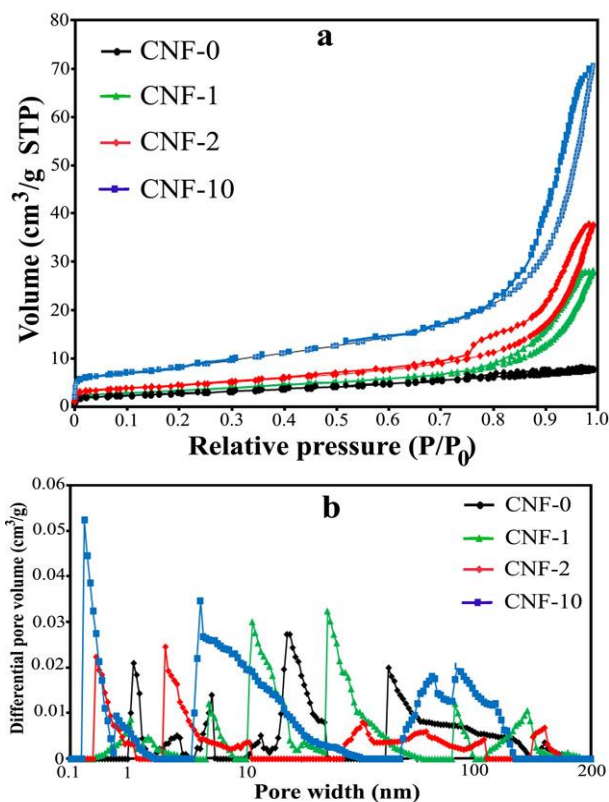

Fig. 5 – (a) Nitrogen adsorption/desorption isotherms and (b) Pore size distributions for various CNF composite nanofiber samples

The nanocomposite samples studied in this paper were not modified with any catalyst for increasing the capacity of hydrogen storage, because the purpose of our study is to compare the capacity of hydrogen storage using various kinds of SWNT composite materials. But, other groups have used low temperature and very high pressure for hydrogen storage in SWNT composite structure. It has been reported in the literature [12], the Pt/SWNT nanostructures were found to adsorb up to 3.03 wt% of hydrogen under 78 bar at 125 K. In other work [13], the MOF/SWNT nanocomposite with 10 wt% SWNT was found to hydrogen uptake up to 8.24 wt% under 60 bar at 77 K. Although, simultaneous cooling down during physisorption process can rise up the hydrogen storage capacity, it is not convenient for mobile and automotive applications. In other results reported in the literature [13], the MOF/SWNT sample with 10 wt% SWNT was found to adsorb up to 0.21 wt% of hydrogen under 60 bar at 298 K. Accordingly, the hydrogen storage capacity in the CNF-10 sample with 10 wt% SWNT increased to 0.29 wt% that is 38% higher than the MOF/SWNT nanocomposite results.

Table 1 – The textual properties and hydrogen sorption capacity of composite nanofibers

Sample	Specific surface area (m²/g)	Total pore volume (cm³/g)	Amount of hydrogen adsorption (wt %)
CNF-0	11	0.058	0.01
CNF-1	12	0.061	0.08
CNF-2	14	0.096	0.14
CNF-10	27	0.142	0.29

4. CONCLUSION

Composite nanofibers containing SWNT have been produced by electrospinning technique for improved hydrogen storage. The SWNT concentration was varied from ~1 wt % to 10 wt %. The morphological analyses of the composite nanofibers revealed that the surface morphology of the nanofibers changes with increasing SWNT concentration. By rising SWNT amounts in the nanocomposite, the surface roughness of nanofibers was increased. The hydrogen storage results showed an improvement in the adsorption capacity with increasing the SWNT content in composite nanofibers. These nanofibers were evacuated again to remove the adsorbed hydrogen at room temperature. Finally, maximum adsorption capacity was 0.29 wt % in case of nanofibers with 10 wt % SWNT under 30 bar at 298 K.

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