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Fabrication of Electrospun Composite Nanofibers Containing Carbon Nanotubes for Reversible Hydrogen Storage Applications

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A B S T R A C T

In this research, composite nanofibers containing carbon nanotubes (CNT) 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 increased with increasing CNT 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 CNT. The hydrogen storage results showed an improvement in the adsorption capacity with increasing the CNT content in composite nanofibers. These nanofibers were evacuated again to remove the adsorbed hydrogen at room temperature. Specific surface area and total pore volume were important factors for increasing the capacity of hydrogen adsorption. Maximum adsorption capacity was 0.29 wt % in case of nanofibers with 10 wt % CNT under 30 bar at 298 K.

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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 highpressure 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 include 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 singlewalled carbon nanotubes (SWNTs) and multiwalled carbon nanotubes (MWNTs) [9]. Both SWNT and MWNT have been explored as

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potential candidates for hydrogen storage. Comparing to other form of CNT, SWNT has extraordinary hydrogen storage properties because of its high surface area and cylindrical structure [10, 11].

Polyacrylonitrile (PAN) fibers have been used in industrial applications such as precursors for the production of carbon fibers, water absorbents, and ion exchange materials. One of the main reasons for versatility of these fibers in wide range of applications is because of the presence of high thermal stability [12, 13]. Even though conventional fiber forming process such as wet spinning and dry spinning produces fibers, electrospinning technique has come out as advantage in the hand of the researchers to produce nanofibers. The electrospun nanofibers layers have large surface area per volume ratio, high porosity along with small pore sizes, flexibility, and superior mechanical properties, so they are excellent candidates for applications in filter media, scaffolds for tissue engineering, sensor, reinforcement in composite materials, protective clothing, fuel cell, and hydrogen storage media [14, 15].

Several experimental and theoretical studies, using different techniques, have been focused on hydrogen physisorption on SWNT with controversial results [16]. Currently, there are few studies in the literature regarding the use of SWNTs in composite structure for improving their hydrogen storage [17, 18]. In the present study, we report the synthesis of novel polyacrylonitrile/ polyvinylpyrrolidone/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 Procedure

The SWNTs were purchased from Research Institute of Petroleum Industry (purity: 95%, diameter: 0.8-1.1 nm). Polyacrylonitrile (PAN, M_w =100,000 g/mol) and polyvinylpyrrolidone (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 h. 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 24h (see flow chart in Figure 1).

The experimental setup used for electrospinning is shown in Figure 2. the electrospinning process is connected to a high- voltage power supply to create an electric field between two electrodes: needle and collector that raise the electrostatic potential of polymer drop that comes from a tip of a needle. Increasing the electrostatic potential, leads to increase the surface charge of the liquid. Normally, the shape of a volume of fluid is dictated by its surface tension.



Fig.1. Flow chart for the synthesis of composite nanofibers



Fig.2. Schematic diagram of a general type of electrospinning apparatus in this work

However, when the fluid is charged, the surface charge acts in the opposite way to surface tension, resulting in the fluid changing shape, forming the structure known as the Taylor cone. In a tip of Taylor's cone, concentration of electric stresses leads to the ejection of a fluid jet. This fluid jet carries a charge, so it will be drawn in the direction of the local electrostatic field. After a certain amount of flight time this jet will become vulnerable to a number of instabilities, included in the bending instability that is largely responsible for the narrow diameter of nanofiber obtained during electrospinning [19, 20]

In present study, the prepared solutions were added to a glass syringe with a needle tip (22G, L=34 mm and D=0.7 mm). The feeding rate of the polymer solutions was 0.25ml/h and electrospinning voltage of 16 kV was applied to the needle, while the distance between the needle tip and the drum collector was chosen at 18 cm and the take-up speed was set on 100 RPM [21]. The electrospinning of composite solutions were performed at 295±2 K and constant relative humidity (30-35 %). These composite nanofibers are collected and then dried in oven at 313 K for 8hr. In the next step, the dried sample was annealed at 398 K for 3 h. Finally, the nanocomposites products were designated as CNF-0 (0 wt % SWNT), CNF-1 (1 wt % SWNT), CNF-2 (2 wt % SWNT) and CNF-10 (10 wt % SWNT). 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. The orientation of SWNTs in the 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 (10⁻⁶ Torr) for 4 h. Hydrogen storage test was carried out under high pressure up to 40 bar at room temperature using a experimentally Sieverts apparatus and the capacity of adsorbed hydrogen was calculated by measuring volumetric change based on the method described elsewhere [22]. Prior to each measurement, the experimental setup was evacuated to $\sim 10^{-8}$ Torr, and samples were heated at 423 K for 3 h or longer. After the temperature of the sample cell became constant at 298 K, the adsorption measurement was started. A high purity hydrogen (>99.9999 %) was used for hydrogen storage study. Hydrogen absorption at different times was executed at a medium pressure (~30 bar) with a pre-calibrated reservoir.

3.Results and Discussion

Figure 3 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 was about 163 nm and the surface morphology is very smooth. In CNF-1 and CNF-2 samples the SWNT were well embedded in the nanofibers, but it seems 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 Figure 3d, 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 are shown in Figure 4. 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. With increasing of SWNT concentration of the polymer solutions from 0 wt % (CNF-0) to 2 wt% (CNF-2), a slight increase in the viscosity and conductivity were obtained.



Fig.3. SEM images of electrospun nanofibers: (a) CNF-0, (b) CNF-1, (c) CNF-2, and (d) CNF-10



Fig.4. Error plot of composite nanofibers average diameter versus samples

However, when the SWNT concentration was increased to 10 wt%, the viscosity and conductivity decreased noticeably. This result was in good agreement with others [23, 24].

Figure 5 shows the TEM photographs of the composite nanofibers. The nanofibers with the SWNT content of 1 wt% are shown in Figure 5a were well aligned and almost fully extended. However, as the SWNT content in electrospun nanofibers increased to 2 wt%, the surfaces of nanofibers were irregular and rough which can relate to the SWNT aggregation during the electrospinning process (Figure 5b). It was clearly visible that individual and aligned SWNT (except for a small curvature at the junction point) occurred in the inner surface of the electrospun nanofiber. As shown in Figure 5, much lower SWNTs aggregation degree in CNF-1 and CNF-2 comparison with CNF-10 leading to some SWNT bundles that exposed to the outer surface of CNF-10 nanofibers. However, considerable aggregation and local irregularities in nanofibers structure by incorporating low concentrations of CNT (<1 wt%) have been also reported by other researchers [25].Figure 6 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 Figure 7.



Fig.5. TEM photographs of electrospun composite nanofibers: (a) CNF-1, (b) CNF-2, (c) and (d) CNF-10



Fig.6. Hydrogen adsorption curves samples at 30 bar and 298 K for synthesis composite nanofibers



Then all samples were evacuated again to remove the adsorbedhydrogen at 298K. Accordingly, it can be concluded that the synthesis composite nanofibers were adsorbing hydrogen physically.

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 Figure 8. 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 m^2/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.

The nanocomposite samples studied in this paper were not modified with any catalyst for increasing the capacity of hydrogen storage,



Fig.8. (a) Nitrogen adsorption/desorption isotherms and (b) Pore size distributions for various CNF composite nanofiber samples

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

Sample	Surface area (m ² /g)	Total pore volume (cm ³ /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

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 [17], the Pt/SWNT nanostructures were found to adsorb up to 3.03 wt% of hydrogen under 78 bar at 125 K. In other work [18], 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 [18], 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.

2. 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 30bar at 298 K.

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