Synthesis and Characterization of SiO_2-Carbon Nanotube Hybrides Using a Sol-Gel Method

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Abstract

This work is focused on synthesis of SiO_2- CNT hybrides via sol-gel method. Homogeneous distribution of carbon nanotubes within silicon matrix was obtained by mixing the functionalized carbon nanotube (CNT-COOH) with active silicic acid followed by titration to the solution of sodium silicate (Na_2SiO_3) under the average temperature condition of 80ºC. Different ratios of multi-walled carbon nanotubes and various concentrations of colloidal silica were used for synthesis of SiO_2-CNT. Powder X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) used for studying the structure and morphological characteristics of the synthesized SiO2-CNT hybrids. The results showed that the various morphologies of SiO_2-CNTs are obtained with different ratio of precursors. The SEM images indicated the formation of uniform nanoparticles, nanowires and nanotube structures in various samples. In addition, the hydrogen storage capacity and thermal conductivity of SiO_2-CNT hybrides were determined and presented in this article. Also total pore volume and BET surface area were calculated for these composites.

Keywords: SiO_2-CNT; nanohybride; crystal size; morphology; hydrogen storage capacity; thermal conductivity; BET surface area

1. Introduction

Carbon nanotubes (CNTs) as nanosized carbon structures (nanocarbons), have been promising materials in new researches. They are important due to their remarkable properties such as high chemical and thermal stability, low mass density, superior surface property, high mechanical flexibility and strength, resistance to strong acids and high electron conductivity [1-3]. Among the limitations for CNTs is their inability to survive in high-temperature, harsh-environment applications, CNTs have many potential applications such as hydrogen storage, nanoelectronic and nanomechanical devices and elective absorption agents.[3] They can also be used as conductive nanofilters, conductive additives to polymers and nanoreactor to carry out catalytic reactions [4, 5].

In recent years, the synthesis of nanocarbon/ base hybrids has been studied seriously. The novel hybride material with enhanced physical, chemical and electronic characteristics such as large surface area, extensive porous structure and rapid absorption capability, can be used in important applications like catalysis, energy storage, water desalination and pollution control [3].

SiO_2 is an excellent dielectric material with outstanding thermal properties and this enables one to overcome the drawbacks of CNT-based polymers, such as limited operating temperature range [6]. Due to the predicted good chemical interaction of CNTs with silica matrix without altering their original properties [7], CNTs–SiO_2 composites have many potential applications including optical materials or opto-electronic devices, as well as electromagnetic interference shielding devices. According to the previous work of Gavalas et al. [8] on CNTs–silica xerogel composites, there have been several reports on CNTs–SiO_2 dense composites. In most cases, multi-walled CNTs (MWCNTs) were preferably used probably due to their higher disposability and

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lower costs in comparison to single-walled (SWCNTs) or double-walled CNTs (DWCNTs) [9].

Hydrogen has been recognized as an ideal energy carrier, but it cannot be used widely because of several reasons. One of the main problems is that, it is difficult to find efficient storage materials. One of the materials which can be used for its high hydrogen storage capacity is carbon nanotubes. Numerous experimental and theoretical works have been carried out in order to improve the storage capacity of carbon nanotubes. Giannis et al. [10] found that point charges upon the material surface can improve the storage capacity because they increase the binding energy of hydrogen. Results also showed that the hydrogen capacity of SiO_2-CNTs is more than double compare to that of CNTs at low pressures [11]. It is obvious that the amount of adsorption has an opposite relation with temperature. So the thermal conductivity of the solid can be so impressive in the adsorption. If the conductivity be high enough that the adsorbent be able to remove the heat of adsorption easily, the gas uptake will be improved. This will be more visible in larger scale of adsorbent. SiO_2-CNTs also show the high thermal conductivity in comparison with carbon nanotubes [3].

Different dispersion methods and densification techniques have been used to prepare these composites. Sol–gel technique is an innovative route for the fabrication of CNTs-reinforced ceramic bulks and coatings because of its effectiveness for obtaining homogeneous dispersion of CNTs in the matrix and higher interfacial strength between matrix and reinforcement [12]. Hence, the aim of this paper is to study the sol–gel based manufacturing route to produce MWCNT-silica nanohybrides. Structures and morphologies of samples were studied using XRD and SEM. The surface area was also determined using nitrogen adsorption apparatus (Autosorp-1 Quantachrome Ltd., American) via BET approach. Also hydrogen storage capacity and thermal conductivity of these structures were investigated with absorbance measurement instrument of Sivert and KD2, respectively.

2. Experimental

Commercial sodium silicate (water glass) (SiO_2=25.5-28.5%, Na_2O=7.5-8.5%) with density of about 1.296-1.396 in 20°C and -COOH functionalized multi-wall carbon nanotube with diameters in the range of 2-5 nm, and lengths of about 10μm were used for SiO_2-CNT hybride synthesis in this work. The CNTs are insoluble in any organic solvent because of the pure carbon element and their stable structure, which limits its usage in the sol–gel preparation. To improve the solubility of CNTs in organic solution, the functionalized CNT (CNTs-COOH) were used. Functionalized CNT was prepared by dissolving 5 g of MWCNT in 400 ml sulfuric acid and 100 ml nitric acid, which mixture was agitated thoroughly by ultrasonic for 3 hours in a glass vial. While Acids may generate heat upon neutralization ice was used to cool the solution. So the solution was filled with ice-cold water and aged for 24 hours in an ambient temperature. Afterwards, it was washed with distilled water for several times and neutralized up to PH=3. Finally it was dried at 60 °C in an electric oven. SiO_2-CNT nanohybrides were synthesized by passing 200 ml of sodium silicate solution with 4 and 8 % wt. SiO2 through a column filled by a cation exchange resin (Amberlite 120, pH= 2.3), which silicic acid solutions (H_2SiO_3) were obtained. 0.1 wt% and 0.3 wt% of MWCNT-COOH were mixed with 200 ml silicic acid and agitated by ultrasonic for 30 min. In the second raw of experiments, four alkaline sodium silicate solutions were prepared through diluting 1.3 (1 wt% SiO_2) sodium silicate up to 30ml by DI water. These four solutions were heated under the average temperature condition of 80 °C. Then the alkaline soduim silicate solutions were titrated by mixture of MWCNT-COOH and silicic acid at constant rates of 5 ml/min. During particle formation, the homogenous nucleation of functionalized carbon nanotube that was dispersed in active silicic acid was occurred. It should be noticed that titration and evaporation rate must be approximately equal to form the colloidal particles and pH value of the solution must be controlled during the process not to decrease below 8, otherwise it would lead the solution to be gelled. It must be mentioned, for all solutions the total time of the reaction was the same (240 minutes). The mixture consisting of nano silica and carbon nanotube particles, was heated and dried in an oven with temperature around 80 °C. Calcinations of the prepared sample were carried out in the furnace, at 400 °C for 4 hours with heating rate of 5 °C/min in N_2 atmosphere. Carbon/ silica composites were formed in the end of carbonization. XRD measurements (PW1840, Philips) were carried out using Cu Kα radiation with a step scanning technique. The microstructure was measured by SEM (XL30, Philips). Also thermal conductivity of the samples was measured by KD2 based on transient hot wire mechanism. Hydrogen storage capacity was also measured by absorbance measurement system based on volumetric method. The surface area was determined using nitrogen adsorption apparatus (Autosorp-1 Quantachrome Ltd., American) via BET method.

3. Results and discussion

The neutralization to silicic acid must be considered in the context of the polymeric or monomeric condition of the starting silicate. The neutralization of sodium metasilicate may naively be written as Eq. (1) and (2):

$$Na^+ \xrightarrow{\text{Substitution}} H^+ \qquad (1)$$

$$Na_2SiO_3 + 2H^+ \rightarrow H_2SiO_3 + 2\,Na^+ \qquad (2)$$

yielding a monomeric species with the empirical formula H_2SiO_3 [13].

Various samples were produced from different ratios of CNT-OOH and sodium silicate solution by using the same reaction time of 4h and temperature of 80-90 °C. The surface growth became important as the active silicic acid was continuously titrated to the solution with the new born seed. It was approved that the mean particle size of colloidal silica formed by slow titration rate are generally larger than that formed by the quick titration rate. It is probably caused by the time difference between the surface growth and titration rate. If titration rate is faster than the surface growth, the added silicic acid might not have enough time to consume itself on the surface of the seeds. It would induce the concentration accumulation of silicic acid, and consequently the homogenous nucleation occurs. The colloidal silica formed in these conditions has small particle size. Otherwise, if titration rate is slower than the surface growth, the time of surface growth seems to be enough. The surface growth would dominate the mechanism of particle formation. During the process, the carbon nanotube particles interconnected the silica particles because of hybridization between C and SiO_2 and existence of a strong covalent bond between these atoms [14].

Colloidal silica particle formation and their reaction with MWCNT mechanism is described as Eq. (3-6).

The molar mixing ratios of the materials are summarized in Table 1. The high formation temperature would accelerate the reaction of surface growth to form the larger particle colloidal silica. It also led the solution to be gelled.

$$2H_2SiO_3 \rightarrow H_4SiO_4 + SiO_2 \qquad (3)$$

$$H_4SiO_4 + NaOH + MWCNT\text{-}COOH \rightarrow NaH_3SiO_4\text{-}MWCNT + H_2O \qquad (4)$$

$$NaH_3SiO_4 + Na_2SiO_3 \rightarrow 3NaOH + 2SiO_2\text{-}MWCNT \qquad (5)$$

Total:

$$Na_2SiO_3 + 2H_2SiO_3 + CNT \rightarrow 3SiO_2\text{-}MWCNT + 2NaOH + H_2O \qquad (6)$$

Table 1. The molar ratio of materials

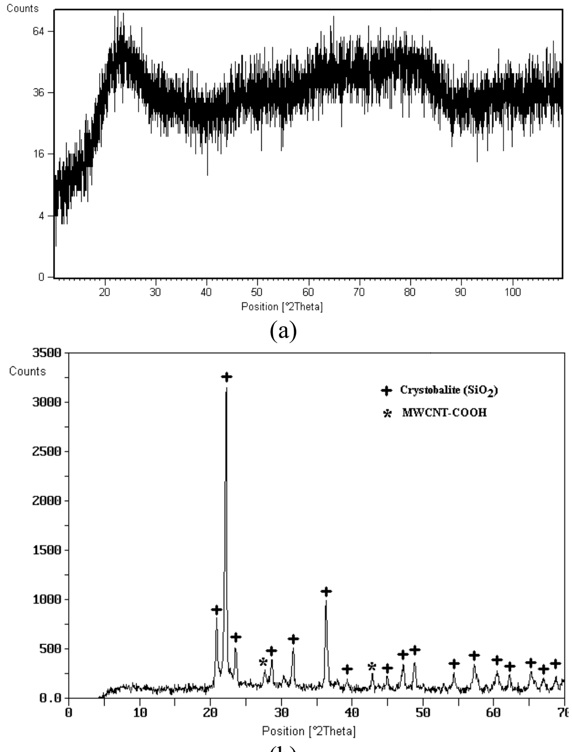
Sample code	Acid silicic concentration	CNT-COOH weight percent	Alkaline solution concentration	Temp.
SiO_2CNT 1	4%	0.3	1%	80
SiO_2CNT 2	4%	1	1%	80
SiO_2CNT 3	8%	0.3	1%	90
SiO_2CNT 4	8%	1	1%	80

Table 2. BET and BJH results for SiO_2-CNT composites

Sample code	Mean pore diameter (nm)	$a_{s,BET}$(m^2 g^{-1})	Total pore volume (cm^3 g^{-1})	V_p (cm^3 g^{-1})	a_p (m^2 g^{-1})	$r_{p,peak}$ (nm)
SiO_2CNT 1	16.826	1.3992E+02	0.5886	0.5781	123.59	10.64
SiO_2CNT 2	20.950	6.5781E+01	0.3445	0.3451	68.538	7.98
SiO_2CNT 3	9.2341	2.4230E+02	0.5594	0.5612	265.55	4.63
SiO_2CNT 4	8.4884	1.4227E+02	0.3019	0.2988	144.79	4.05

X-ray diffraction patterns of the sintered MWCNT/SiO_2 nanocomposites indicated only crystalline SiO_2 (Crystobalite) and CNT phases in any instance. It can be concluded that no reaction took place between SiO_2 particles and CNT as well as that the damage of CNT due to exposures did not occur during sintering. SiO_2 phase was crystallized during sintering because SiO_2 phase is present in form of amorphous for as-received colloidal silica, and identified that the crystalline SiO_2 phase was Crystobalite. Fig. 1 shows the XRD pattern for SiO_2-CNT4 composite before and after calcinations.

Isotherm absorption/desorption curves for the SiO_2 –CNT composites are demonstrated in Fig 2. In this figure the adsorption/ desorption isotherm of a nonreactive gas (N_2 at 77 K) and at the temperature of 300 °C with 1 hour heat treatment is determined as a function of the relative pressure, i.e. ratio of the applied pressure and the saturation pressure of the gas. It shows a departure of absorption and desorption plot, forming a so called “absorption circuitry” at relatively high pressure region (92.816 kPa) which is due to the attribution of mesoporous structure. It starts at low relative pressure. At a certain minimum pressure, the smallest pores will be filled with liquid nitrogen. As the pressure is increased further, larger pores are filled, and near the saturation pressure, all pores are filled. The total pore volume is determined by the quantity of gas absorbed near saturation pressure. Desorption occurs when the pressure is decreased from the saturation pressure downward [15]. Mean pore diameter, BET surface area and total pore volume of the composites was calculated by BET method from isotherm curves. Results show that BET surface area increases from 65.8 to142 m^2/g^{-1} at first and then decreases to 140 m^2/g^{-1} in 0.26 ratio of silicic acid/CNT and finally increases up to 242 m^2/g^{-1}. Also it can be seen that the total pore volume shows the opposite trend on contrary to BET surface area.



(a)

(b)

Fig. 1. X-Ray diffraction pattern of SiO_2-CNT4 (a) before calcinations and (b) after calcinations.

Pore size contribution of composites was calculated by BJH method from the corresponding isotherm curves, which is presented for SiO_2-CNT composites in Fig 3. The calculated values for composites are summarized in Table 2. The SEM images of SiO_2-CNTs synthesized in different ratios are shown in Fig. 4. These images indicates the formation of various structures consist of nano particles, nanowires and nanotubes in these composites. Also this figure can clearly show the formation of SiO_2 spherical particles on carbon nanotubes and shows the hybridization between SiO_2 and CNTs for SiO_2-CNT3 and confirms the XRD results for these composites. Hydrogen storage capacity and thermal conductivity of the samples were also determined. The higher amounts were reported for SiO_2-CNT3 composite.

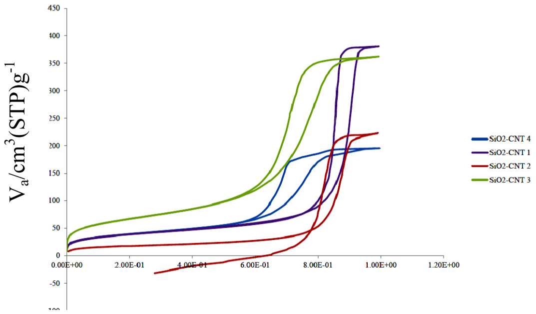


Fig. 2. Isotherm curves of the SiO_2-CNT composites with different silicic acid concentration/CNT weight percent ratios.

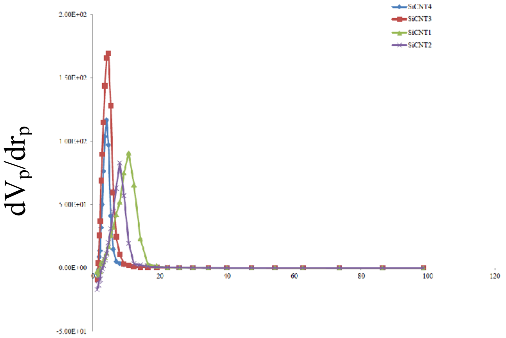
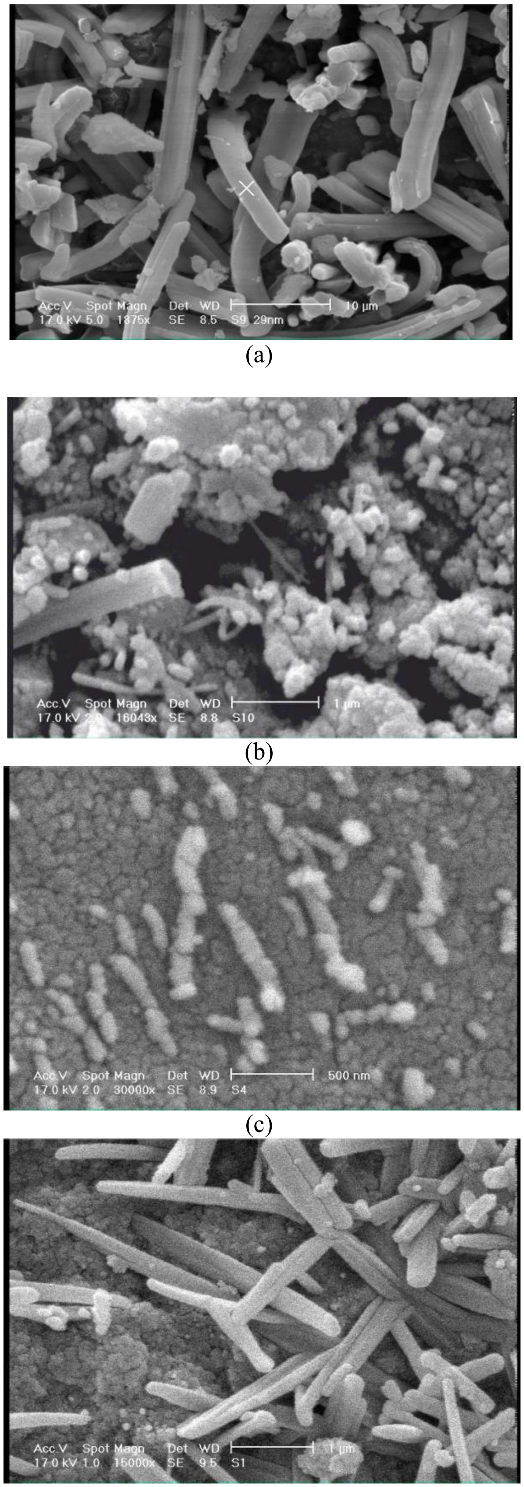


Fig. 3. Pore size distribution of the SiO_2-CNT composites with different silicic acid concentration/CNT weight percent ratios.



(a)

(b)

(c)

(d)

Fig. 4. SEM images of SiO_2-CNTs synthesized at different ratios: (a) SiO_2-CNT1, ratio 4:0.3 (1875×), (b) SiO_2-CNT2, ratio 4:1 (16043×), (c) SiO_2-CNT3, ratio 8:0.3 (30000×) and (d) SiO_2-CNT4, ratio 8:1(15000×).

The amount of hydrogen absorbed on SiO_2-CNT3 was about 0.23 Wt% which was increased compared with MWCNT and SiO_2 itself and was measured at 298K over the hydrogen pressure range of 0-40 bar. Also thermal conductivity for SiO_2-CNT3 was calculated by KD2 and showed the amount of about 0.76 W/m.k for this sample.

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4. Conclusions

In this study inexpensive precursors such as sodium silicate (watergalss) and multi-walled carbon nanotube (MWCNT) were used to synthesis colloidal silica via sol-gel method for commercial production of SiO_2-CNT composite. The effect of the process parameters such as silicic acid concentration/CNT weight percent ratios at constant formation temperature and equal calcination conditions on morphology, BET surface area and total pore volume were investigated.

It can be seen that these composites have mesoporous structures. Results showed SiO_2-CNT hybride formation for sample with silicic acid concentration of about 8% and 0.3Wt% CNT. Also the high amount of surface area ($243m^2g^{-1}$), hydrogen storage capacity and high thermal conductivity were obtained for these composites in comparison with MWCNTs.

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