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3rd International Conference on Nanotechnology (ICN2015), 27-28 August 2015, Istanbul, Turkey

Synthesis of silica/multi-walled carbon nano tube hybrid nano-structure and evaluate the thermal conductivity

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***Abstract*— Carbon nanotube (CNT)–inorganic hybrid materials are a new class of functional materials that has gained tremendous interest in recent years due to their exceptional optical, mechanical, electrical and thermal properties. In this study, firstly, the silica-multiwall carbon nanotube (MWCNT) hybrid nano-structures were synthesized using the sol-gel method in the aquatic environment, and also MWCNT were functionalized using the acidic method. Then the hybrid nanostructures were synthesized by different levels of silica and MWCNTs ratio. They were analyzed using the FT-IR, SEM and XRD test methods. The results showed that the hybrid made of 60% MWCNTs and 40% silica with 64 nm diameter can be selected as the best type of structures. A nanofluid was also made of optimal nano-structured hybrid based water with 0.02% wt. The experimental results confirmed that the thermal conductivity was enhanced up to 11.6% of the base fluid at 25°C.**

Keywords- hybrid material; solgel; carbon nano tubes; silica; Nanofluid; thermal conductivity

I. Introduction

Currently, carbon nanotubes (CNTs) play an essential role in various fields of nano based science and technology. CNTs are difficult to disperse homogeneously in different solvents, which greatly limit the application of CNTs. Therefore, extensive research is focused on surface modification of carbon nanotubes mainly to enhance their compatibility and dissolution properties. On the other hand, hybrid of organic/inorganic materials is of interest due to their unique physical and chemical properties, nowadays [1]. Silica surfaces are well-known insulating properties, biocompatible, and can be easily functionalized for bio-conjugation purposes [2]. So, the hybrid structures are considered by various researchers to detoxify problems related to the CNTs. One of the hybrid structures can be include a combination of silice-metal oxide, silice-polymer or slice-carbon which has optical, magnetic, mechanical, electrical and thermal properties. One way to improve the physical and chemical properties of CNTs is synthesis of CNTs@SiO_2 hybrids [2]. So the functionalization of carbon compounds is significant to enhance the surface activity, attractive interaction with other molecules and improvement of physical properties such as optical, mechanical and thermal. In the hybrid structure of carbon-silica, part of porous silica improves the mechanical, dielectric, thermal and chemical properties. Min Zhang et al (2010) [3] synthesized CNTs and silica using the sol-gel method and SDS surfactant as anionic type, in the alcoholic medium. Dominik Eder (2008) [4] synthesized a variety of CNTs and different oxide hybrids such as TiO_2 to Study the effective parameters on the hybrid synthesis of CNT@TiO_2. He concluded that the effect of Benzyl alcohol on the formation of nanostructured hybrid is very important so that the CNT surface is covered with TiO_2. He also studied the effects of their use on photocatalysts [5]. Su-Wen Cheni and colleagues (2012) [6] have synthesized the CNT@SiO_2 hybrid in the alcoholic medium using the benzyl alcohol as surfactant. Their results showed that the SiO_2 coating on the surface of CNT has heavily effect on increasing the diameter of the CNT.

Various investigations [7-10] have shown the most important factors to achieve the best properties as possible

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as are the pH control, temperature during synthesis, the formation of a uniform silica layer on CNTs with a controllable thickness in nanometer scale, The use of suitable ionic or nonionic surfactants, the use of suitable methods to functionalize of silica based on noncovalently (using π–π interaction) or covalently (by forming σ bond). In recent years, using the different methods and materials are proposed to make SiO_2 in the alcoholic mediums using the cationic or anionic surfactants like sodium dodecyl sulfate (SDS), and also using tetraethoxysilane (TEOS) or aminopropyltriethoxysilane (ATPES) as precursor materials [7,9]. Studies show that some of the carbon structures have high thermal conductivity; therefore, they can be used in making nanofluids. Therefore, many researches have been conducted on the thermal properties of nanofluids containing carbon nanostructures, such as graphite, fullerenes, single-wall and multi-wall CNTs and graphene.

Harish et al (2012) [11], studied the thermal conductivity of nanofluid made of single-walled nanotubes based ethylene glycol. They reported that the thermal conductivity increased to 2% volume fraction of single-walled nanotubes i.e., 14.8%. They used the transient hot wire technique to measure the thermal conductivity of nanofluids.

In this research, sodium silicate (Na_2SiO_3) is used instead of other precursors i.e., ATPES and TEOS to save production costs. Also, the experiments were carried out in the aqueous environment using non-ionic surfactants and sol-gel technique. Additionally, MWCNT@SiO_2 hybrid is used as nanoparticles suspended in the fluid to study the thermal properties.

II. Materials and Method

A. *Materials*

The synthesized Multi-wall CNTs which were made by CVD method (with a diameter of 60–100 nm) were obtained from Nanotechnology Research Center, Research Institute of Petroleum Industry (RIPI). Benzyl alcohol (C_7H_8O), Sodium silicate (Na_2SiO_3) (28%), Sulfuric acid (H_2SO_4) and Nitric acid (HNO_3) were all purchased from Merck. It was also used the Gum Arabic and deionized (DI) water.

B. *Functionalization of MWCNT*

The MWCNTs were mixed with sulfuric acid and nitric acid in a ratio of 3:1, and was placed in the ultrasonic bath for 3 hours. Then, the mixture was cooled quickly. In the next step, the mixture was washed with DI water and filtered as long as the pH reached to 7. Finally, the prepared mixture was put in an oven at 120°C for 4 h.

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C. *Synthesis of silica/MWCNTs hybrid*

The functionalized MWCNTs with benzyl alcohol (2:1) were mixed with 50 ml DI water by sonication for 2h in ultrasonic bath. Next, the sodium silicate solution (0.16 M) was prepared, and during 3 hours, MWCNTs was slowly added to this solution (drop by drop) with the mixing rate of 750 rpm rate, at 80°C. The acidic medium was adjusted at about pH=5 by sulfuric acid (0.16 M). After finishing the addition of sodium silicate, a colloidal solution was obtained. Then, this colloidal solution was aged at room temperature for 13 h until the gel was formed. Finally, the produced gel was recovered by filtration, washed with DI water, and then the calcination process was carried out at 550°C for 6 h with a heating rate of 2°C/min in nitrogen atmosphere. The obtained, silica coated MWCNTs were prepared and characterized

D. *Preparation of nanofluid*

In a typical method, 0.01 g MWCNTs@SiO_2 hybrid and 1 g gum arabic surfactant were dispersed into 50 mL water. Then, this solution was sonicated for 30 min in order to stabilize the nanofluids. In this research we used the KD2 Pro. (Decagon Devices, Inc.) to measure the thermal conductivity of nanofluids.

III. Results and Discussion

The morphology of the as-prepared MWCNTs@SiO_2 composites is examined by SEM method. FT-IR spectrum of the MWCNTs@SiO_2 (Fig.1) shows an absorption peak at 3444.65 cm^{-1} assigned to the –COOH group. Additionally, peaks at 2924 cm^{-1} and 2854 cm^{-1} related to N-H and C-H group, respectively. On the other hand, the FT-IR analysis shows that C = O and C = C groups are also formed at 1632 cm^{-1} and 1526 cm^{-1} peak points, respectively.

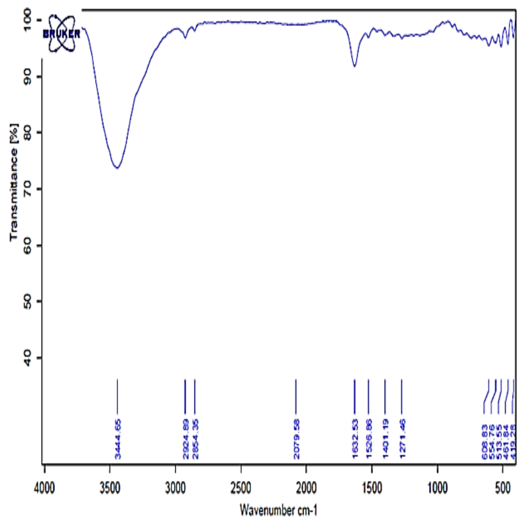

Figure 1. The FT-IR analysis of CNTs functionalized with acidic techniques

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In Fig.2, X-ray diffraction patterns are characterized to compare the structure of the synthesized hybrid composites. For the raw MWCNTs in Fig. 2a, the peaks are observed at the angles 2theta = 25.5◦ and 43.38◦. The angle 2theta at 25.5º corresponds to the (002) reflection for the feature peak of raw MWCNTs. For silica coated MWCNT (40% and 60%, respectively) in Fig. 2b, the feature peak of MWCNTs at 26.7◦ disappeared because the raw MWCNTs were perfectly coated with amorphous silica.

This amorphous silica caused the hindrance of MWCNT. characteristic peak due to the interference of the X-ray. Also, the peaks in the range 26.7º, 36.80º and 38.70º are detected related to the silica structure. Crystalline structure of the silica is Cristobalite based on the standard card number JCPD. As seen, the deviation in this figure is mainly related to the impurities included in the MWCNTs.

Fig. 3 shows SEM analysis of MWCNTs and MWCNT@SiO_2 hybrid structure with the average particle diameter of 50 nm. Figure 3b shows that the average diameter of functionalized MWCNTs is 32 nm which has been decreased due to the functionalization of MWCNTs. Figure 3c demonstrates the uniform structure of hybrid MWCNT@SiO_2. It can be concluded that the nano particles of silica with the average particle diameter of 64 nm uniformly coated the surface of MWCNTs. As can be seen, the MWCNT diameter has increased about 32 nm by the growth of silica nanoparticles on the surface of the MWCNT.

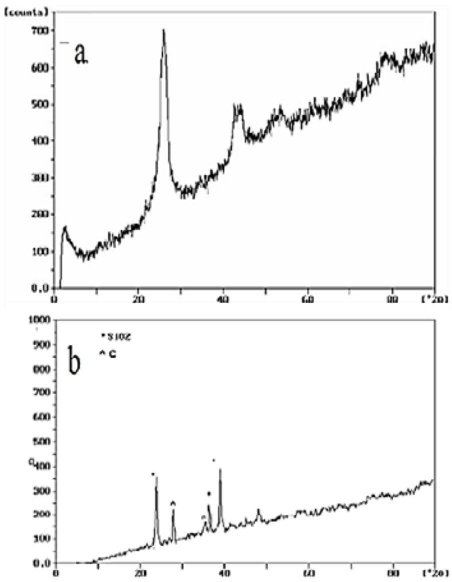
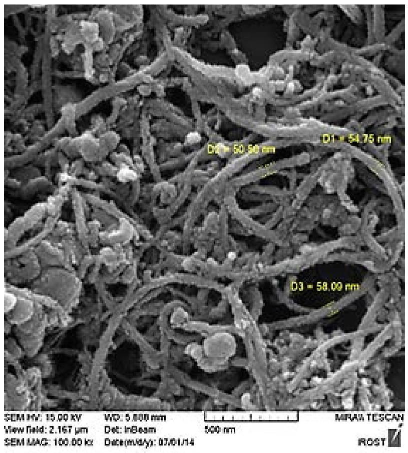
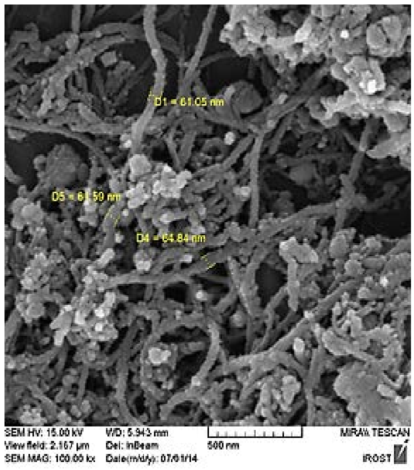


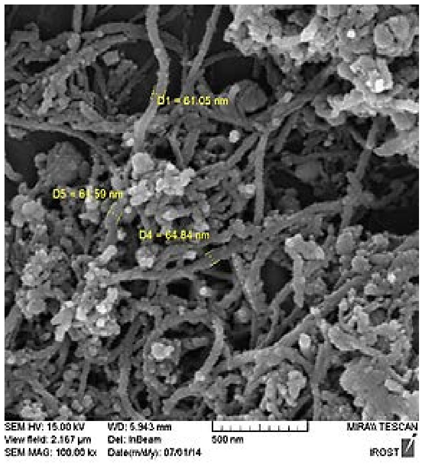
Figure 2. XRD patterns of (a) raw MWCNTs and (b) silica coated MWCNTs.



(a)



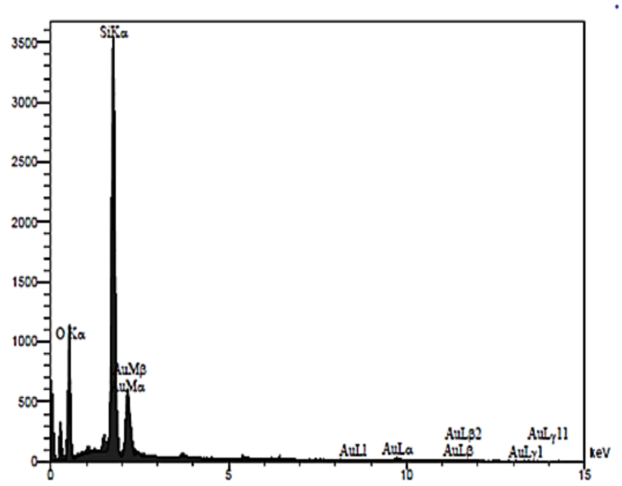
(b)



(c)

Figure 3. SEM images of uncoated MWCNTs (a) and functionalized MWCNTs (b); and MWCNTs@SiO2 composites (c).

In Fig. 4, EDX analysis of functionalized MWCNTs and silica is presented. This figure confirms that the impurities of MWCNTs have been removed, and there is only pure silica on the structure of MWCNT.



Quantitative Results

Elt	Line	Int	Error	K	Kr	W%	A%	ZAF	Formula	Ox%	Cat#
C	Ka	57.2	38.1891	0.1022	0.0471	22.48	36.13	0.2096		0.00	0.00
O	Ka	297.8	38.1891	0.2650	0.1222	38.04	45.89	0.3212		0.00	0.00
Si	Ka	1358.6	10.9637	0.4432	0.2043	23.94	16.45	0.8534		0.00	0.00
Au	La	5.5	0.5139	0.1895	0.0873	15.54	1.52	0.5619		0.00	0.00
				1.0000	0.4609	100.00	100.00			0.00	0.00

Figure 4. The EDX analysis of MWCNTs@SiO_2 hybrid

The thermal conductivity of MWCNTs@SiO_2 based DI water measured to analyze the thermal properties of hybrid materials and detect the impact of using MWCNTs@SiO_2 as nanoparticles on thermal conductivity enhancement. Table 1. shows the thermal conductivity measurement results of MWCNT@SiO_2 as hybrid nanostructure which dispersed in DI water to prepare nanofluid. As expected, by adding nanoparticles to the base fluid, heat transfer properties of that has been improved significantly. As seen, in comparison to the thermal conductivity of Raw MWCNT water), that of MWCNT@SiO_2 hybrid increases by 11.6%.

Table 1. Thermal conductivity measurement of DI water, raw MWCNT and MWCNT@SiO_2

Material	DI water	Raw MWCNT	MWCNT@ SiO_2 hybrid
Thermal conductivity (W/m.K)	0.578	0.614	0.697

IV. Conclusion

In this study, the MWCNT@SiO_2 hybrid materials have been produced via a typical sol–gel process using Benzyl alcohol as a surfactant, which enable SiO_2 to interact with the hydrophobic surface of the MWCNTs. Initially, the MWCNTs were functionalized with acidic method. In this method, the -COOH functional groups and the C = O with σ-σ bound were active on the MWCNT surface by break off π-π bounds. Then SiO_2 nanoparticles coated the MWCNT surface through the van der Waals forces in the aquatic environment at 80°C. As well as, the benzyl alcohol was as a link between the MWCNT surface and the SiO_2. It also controlled the growth of nanoparticles on the surface of the MWCNT. The results showed that the SiO_2 coating on the surface of MWCNT has heavily effect on increasing the diameter of the MWCNT. The results showed that the hybrid made of 60% MWCNT and 40% SiO_2 with 64 nm diameter can be selected as the best type of structures. Therefore, its thermal characteristics were analyzed. The concentration of 0.02% wt. of hybrid nano-structure dispersed in DI water as base fluid confirmed that the thermal conductivity was enhanced up to 11.6% of the base fluid at 25°C. Hence the key achievement of this study is the variation of morphology of CNT–SiO2 hybrid materials, which is crucial to design novel carbon–inorganic hybrid materials suited for the desired photochemical, catalytic and sensor application.

Acknowledgment

We would like to express our great appreciation to Mr. F. Noorbakhsh and Mr. M.A. Fatemi for their valuable and constructive suggestions during the planning and development of this research work. We would also like to thank Nitel Pars Company a subsidiary of Fateh Group for the financial support and technical assistance.

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