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Preparation of MWNT/TiO_2 Nanofluids and Study of its Thermal Conductivity and Stability

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Abstract

In this study, functionalized multi-walled carbon nanotubes using mixed acid treatment were synthesized using solvothermal method by $TiCl_4$ as a precursor and the thermal conductivity enhancement of MWNT-TiO_2 nanofluids in various temperatures were compared. The treated nanotubes have been characterized using Fourier Transform Infrared Spectroscopy (FTIR). Hybrid materials were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The results showed that MWNTs are uniformly decorated with anatase nanocrystals. Temperature effects on thermal conductivity of MWNT-TiO_2 nanofluids at different concentrations have been studied. The best result showed enhancement of thermal conductivity around 12.1% for the sample with 0.08 wt% of MWNT-TiO_2 compared to distilled water at 36°C and 13. 71% at 52°C. Also, zeta potential of 0.02 wt% nanofluids and particle size distribution of nanoparticle were measured.

Keywords: *Nanofluids, CNT, Hybrid, Thermal Conductivity*

1. Introduction

The efficiency of the heat transfer fluids can be enhanced by increasing their thermal conductivity and heat transfer properties. Since nanostructures show higher thermal conductivity than routine fluids (water, ethylene glycol, transformer oil, etc.) and microstructures, the use of nanostructures fluids has been recommended [1].

Heat transfer performance of fluids can be improved by adding up nanostructures which have to be stable on the fluids. For increasing the stability of nanoparticles in fluids, a variety of techniques has been applied [2]. Use of hybrid nanoparticles is one proposed way to improve the efficiency of nanofluids. Their excellent mechanical, electrical and optical properties support CNTs as an ideal building block in hybrid materials. The high thermal conductivity of CNTs enables them

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to behave as a heat sink during calcination and activation treatments, thereby stabilizing small inorganic moieties that can decorate the sidewalls of the CNTs. This results in producing materials with higher specific surface areas that could allow the use of fewer materials and reduction in cost as well as toxicity [3]. Ex-situ and in-situ techniques are the main synthesis methods for inorganic CNT hybrids. The ex-situ (building block) approach first produces the inorganic component in the desired dimensions and morphology (typically spherical nanoparticles), then modifies and attaches this component to the surface of CNTs via covalent, noncovalent, or electrostatic interactions. In contrast, the in-situ approach carries out the synthesis of the inorganic component in the presence of pristine or functionalized CNTs, onto which the inorganic material grows as particles, nanowires, or thin film [3]. In this study, MWNT-TiO$_2$ hybrids were synthesized using solvothermal method and the thermal conductivity enhancement of MWNT-TiO$_2$ nanofluids was compared in various temperatures. Nanofluids have been prepared for a wide range of weight concentrations (0. 02, 0.04, 0.06 and 0.08 wt%) and temperatures (36, 44, 52 and 60°C).

2. Experimental

2-1. Materials

The multiwalled carbon nanotube was purchased from the Research Institute of Petroleum Industry (RIPI). Sulfuric acid (H_2SO_4), Nitric acid (HNO_3), titanium chloride ($TiCl_4$) and Ethanol were purchased from Merck KGaA (Darmstadt, Germany).

2-2. Functionalization of multiwall carbon nanotube

For introducing oxygen containing functional groups on the raw-MWNTs surface, a mixture of H_2SO_4 and HNO_3 (v/v, 3:1) was added to MWNTs and sonicated in an ultrasonic bath at 60°C for 3 h. The load of MWNTs was 1 g for 80 mL of the blended acid solution. Then the mixture was diluted by distilled water, it was filtered and washed repeatedly till the washing showed no acidity. The clean MWNTs were dried in the oven at 60°C for 12 hours [4].

2-3. Synthesis of MWNT-TiO$_2$ hybrid and preparations of nanofluids

The MWNT-TiO$_2$ hybrid nanostructures were prepared using solvothermal method and titanium chloride as precursor. Briefly, 0.5 mL $TiCl_4$ (4.55 mmol) was slowly dropped into 40 mL ethanol and stirred magnetically to provide a completely clear yellow solution. A desired amount of MWNTs was dissolved, placed in the ultrasonic bath for 45 min and dispersed in the solution. Then it was transferred into a Teflon-lined, stainless autoclave and stored at 120°C for 24 h to produce the gray or dark precipitate for separating the precipitate. The solution was centrifuged and then washed with ethanol to remove organic species. The collected materials were left to dry in an oven at 60°C for 12 h, then calcined at 400°C for 2 h [5]. In this paper, all samples contain 50 wt% MWNT.

In order to prepare the MWNT-TiO$_2$ nanofluids samples, a two-step process was used. MWNT-TiO$_2$ with wide range of concentrations (0.02, 0.04, 0.06 and 0.08 wt%) were mixed in a base fluid distilled water and placed in the ultrasonic (BANDELIN SONOPULS HD 3200, 140 W, 20 kHz) for 45 min. Sodium dodecylbenzenesulfonate surfactants were used to ensure better stability and proper dispersion.

2-4. Thermal conductivities measurement

A transient short hot-wire technique was applied to measure the thermal conductivities of the samples from the temperature range of 36 to 60°C. In addition, a temperature-controlled bath was used to preserve different temperatures of nanofluids during the measurement process. The experimental apparatus was calibrated by measuring the thermal conductivity of deionized water [6]. In this device, the vessel containing the tested sample was placed in the bath and a thermocouple inside the vessel was used to control the sample temperature. Before measuring, to ensure heat equilibrium the sample temperature was maintained for a further 30 min at the bath temperature. Three separated measurements were repeated and the average value of thermal conductivity was reported [7]. The set-up consisted of a circulator and KD_2 Pro device.

3. Results and discussion

3-1. FTIR spectroscopy

The functionalization and chemical structure of MWNT were identified by FTIR (BRUKER TENSOR 27). Typically, 100 scans over the range 500–4000 cm^{-1} were taken from each sample with a resolution of 1cm^{-1} and summed to provide the spectra. The results are shown in Fig. 1.

The broad band of FTIR spectra between 3000 and 3700 cm^{-1} is attributed to the presence of the oxygenated groups [8]. The presence of carboxyl functional groups can be detected at around 1768 cm^{-1} and OH group around 3454 cm^{-1} [9]. The peak at 1647 cm^{-1} can correspond to C=C banding vibrations of aromatic structures and in the 1225 cm^{-1} related to C-O banding [10].

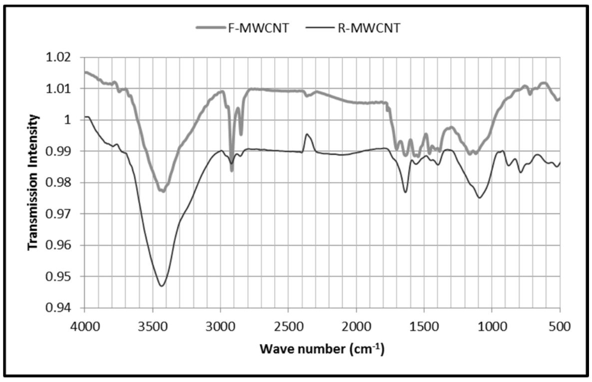


Figure 1. FTIR of raw-MWNT and func-MWNT.

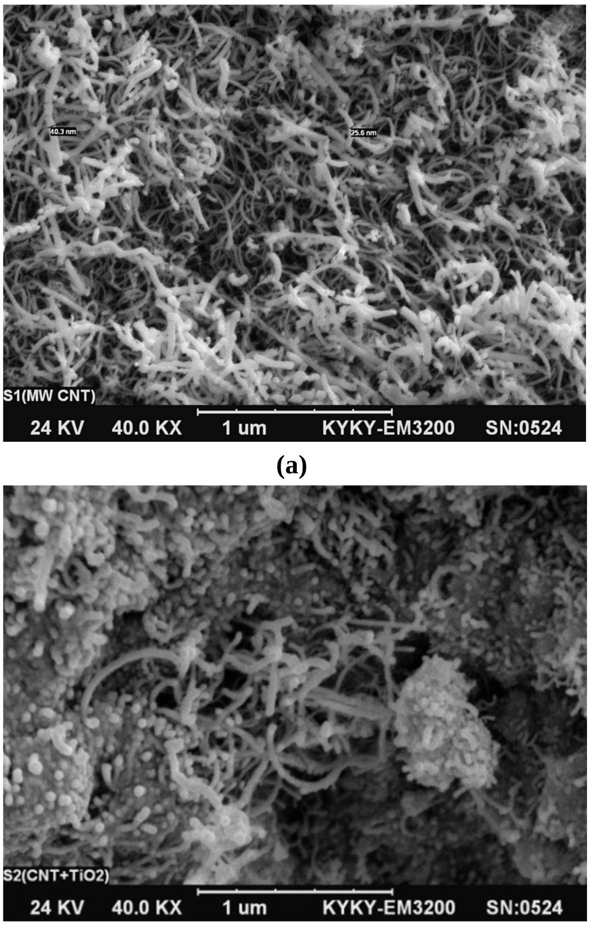
3-2. SEM imaging

The morphology of the TiO_2 on MWNT was examined using SEM image. Scanning Electron Microscope (SEM) was carried out using a KYKY-EM3200 at 40 kV. The SEM image of the functionalized MWNT and MWNT-TiO_2 hybrid was shown in Fig. 2. The MWNTs coated with well-dispersed TiO_2 particles show that the MWNTs and TiO_2 had close contact.

3-3. XRD analysis

X-raydiffraction (XRD) patterns were analyzed using the X-ray diffractometer (Bruker AXS., Germany) and Cu Kα radiation source at 40 kV. The XRD patterns of functionalized MWNT and MWNT-TiO_2 hybrid were shown in Fig. 3.

The XRD patterns reveal that only anatase phase of TiO_2 could be identified. The pristine MWNTs have two typical (002) and



(a)

(b)

Figure 2. SEM image of (a) f-MWNT, (b) MWNT/TiO$_2$ hybrid.

(101) diffraction peaks. For MWNT-TiO$_2$ hybrid, the main diffraction peaks of anatase TiO$_2$ (101, 004, 200, 105, 211, and 204) are clearly shown [11].

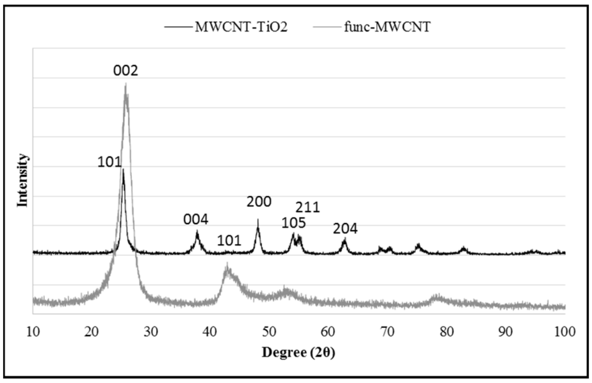


Figure 3. XRD patterns of the f-MWNT and MWNT-TiO$_2$ hybrid.

3-4. Thermal conductivity variations vs. temperature

In general, the thermal conductivity of nanofluids is more sensitive on account of temperature [12]. The effective thermal conductivity of the nanofluids rises with an increase in the temperature [13] but the trends change for different cases. In order to study the temperature effect on thermal conductivity of nanofluids, a thermostat bath was used. All the measurements were taken after calibrating the KD$_2$ Pro instrument with distilled water [14]. Our experimental data show that thermal conductivity of the samples involving MWNT-TiO$_2$ nanofluids increases with temperature and the results are shown in Fig. 4. The comparison of MWNT-TiO$_2$ nanofluid effective thermal conductivity with MWNT nanofluid shows that our nanofluid with the lower percent of MWNT-TiO$_2$ (about one-tenth) with respect to wen and Ding [2] nanofluid is in the same range of effective thermal conductivity.

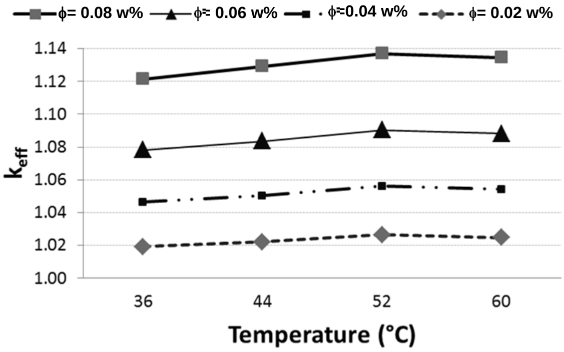


Figure 4. Effective thermal conductivity vs. temperature after preparation for the samples.

According to the Brownian motion of fluids, the dispersed MWNT-TiO$_2$ move fast in the water, so that energy transport inside the liquid becomes strong and thermal conductivity increases [15]. Therefore, thermal conductivity gradually rose by increasing temperature. For example, thermal conductivity of the 0.08 wt% MWNT-TiO_2 nanofluids increases about 3.98% at 36 to 52°C. In moderate temperatures, between 36°C and 52°C, there is a semi-linear dependence of thermal conductivity enhancement in all samples. Although at temperatures over 52°C, efficient thermal conductivity of all nanofluids decreased. This behavior can be explained by the validity of KD_2 technique within the limits 10 to 55°C. Another reason can be decrease of surfactant function at high temperatures which causes reduction of nanofluids stability. For example, efficient thermal conductivity of the 0. 06 wt% MWNT-TiO_2 nanofluids decreases about 0.2% at 52 to 60°C.

3-5. Measurement of the zeta potential and particle size

In this study 0.02% weight fraction of MWNT-TiO_2 nanofluids was used to measure the zeta potential and particle size distribution. Zeta potential and particle size of nanoparticle were measured by a Malvern ZS Nano S analyzer (Malvern Instrument Inc., London, UK). The measurement was run at voltage of V=10 V and temperature of T= 25°C

With switch time of t= 50 s. To calculate the mean value of the experimental data each experiment was repeated at least 10 times. The pH value of system was adjusted with HCl and NaOH solution by precise pH Meter (PHS-25, China). As shown in Fig. 5, Zeta potential value was reported-47/5 mV for hybrid nanofluids that, according to the ASTM D 4185-82 standard, hybrid nanofluids stability is acceptable.

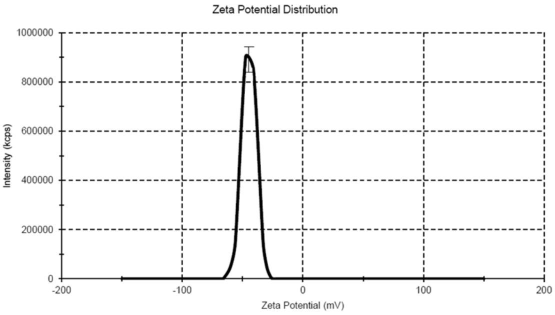


Figure 5. Zeta potential for MWNT-TiO_2 nanofluids.

Fig. 6 illustrates the particle size distributions (measured by a Malvern ZS Nano S analyzer) of MWNT-TiO_2 nanofluids.

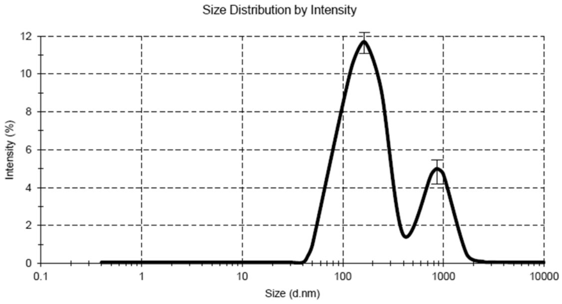


Figure 6. Particle size distributions of MWNT-TiO_2 nanofluids.

According to Fig. 7, average particle size distribution of nanofluids was 164 nm and 859 nm with a portion of 90.1% and 9.9% and PDI index was 0.290. Distinct peak at 860 nm due to the presence of TiO_2 particles has not been linked with CNTs and remains in the environment. Also, differences in the structure of carbon nanotubes with TiO_2 metal nano particles cause larger particles sedimentation to be faster than smaller particles.

4. Conclusions

This study investigates the stability and thermal conductivity of MWNT-TiO_2 nanofluids. The effective thermal conductivities were determined versus temperature for different concentrations of MWNT-TiO$_2$. The raw-MWNTs were functionalized with a mixture of H_2SO_4 and HNO_3 (v/v, 3:1) in ultrasonic bath and characterized by FTIR. Anatase TiO$_2$ nanoparticles were anchored on CNTs surface via solvothermal method and characterized by XRD and SEM techniques. According to FTIR analysis, it can be concluded that function of MWNT in acid media is a suitable method to prepare Hydrophilic MWNT structure in which the carboxyl groups exist on the surface of the nanotubes.

Thermal conductivity of all the samples was improved by increasing temperature in the range of 36 to 52°C and a linear relationship between these two parameters-temperature and thermal conductivity- was observed. The effective thermal conductivity of all samples was decreased at 60°C. Thermal conductivity enhancement is 2.65% and 5.61% for 0.02 wt% and 0.04 wt% nanofluids correspondingly at 36°C, while it increases to 13.71% on 0.08 wt% nanofluids at 52°C.

A Zeta potential value was reported -47/5 mV for hybrid nanofluids which, according to the ASTM D 4185-82 standard, is an acceptable stability. Average particle size distribution of nanofluids was 164 nm and 859 nm with a portion of 90.1% and 9.9% and PDI index was 0.290.

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