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CERAMICS INTERNATIONAL
Ceramics International 39 (2013) 3885–3891
www.elsevier.com/locate/ceramint

The effect of functionalisation method on the stability and the thermal conductivity of nanofluid hybrids of carbon nanotubes/gamma alumina

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Received 14 September 2012; received in revised form 21 October 2012; accepted 22 October 2012
Available online 23 November 2012

Abstract

Based on our previous studies that focused on the synthesis of a nanohybrid of multi-walled carbon nanotubes (MWCNTs) and gamma alumina (γ-Al_2O_3) particles, this paper reports the heat transfer properties and dispersion behaviour of the hybrid. In this study, functionalised CNTs were synthesised via a solvothermal process with various concentrations of carboxylic acid groups (–COOH). The microstructure of the synthesised nanohybrids was characterised via high-resolution transmission electron microscopy (HRTEM), transmission electron microscopy (TEM), and energy-dispersive X-ray spectroscopy (EDX). The MWCNT/γ-Al_2O_3 nanofluid was prepared using a two-step method. The thermal conductivities of different nanohybrids were measured with a KD2 probe using a modified transient hot wire method. The zeta potential and particle size distribution were determined to investigate the stability of the nanofluid.

The results showed that the functional groups had a significant influence on the thermal conductivity of the hybrid nanofluid. The data showed that the enhancement in thermal conductivity reached up to 20.68% at a 0.1% volume fraction of hybrid, for a gum arabic (GA) based nanofluid.

Keywords: C. Thermal conductivity; Nanofluid; Hybrid; Multi-walled carbon nanotubes

1. Introduction

Multi-walled carbon nanotubes (MWCNTs) have attracted substantial interest since 1991 due to their unique electrical and mechanical properties, which can be exploited in many technological applications. To enhance or change the properties of MWCNTs, nanotubes have been treated using different methods, such as functionalising, coating, doping or filling pristine nanotubes, thereby obtaining a so-called nanohybrid [1]. Solvothermal synthesis provides favourable conditions for the functionalisation of nanotubes without generating large numbers of defects. During solvothermal synthesis, carboxylic acid (COOH) and hydroxyl (OH) groups, which are obtained from the decomposition of ethanol, attach to the surface and along the inner wall of MWCNTs, effectively resulting in the functionalisation of the MWCNTs [2,3].

Nanofluids are a new class of heat fluids consisting of nanometre-sized particles (less than 100 nm) dispersed in convectional fluids. The advantages of nanofluids are (1) higher thermal conductivity than that predicted by currently available macroscopic models, (2) excellent stability, and (3) low penalty due to an enhancement in the pressure drop and the pipe wall erosion experienced by suspensions of micrometre- or millimetre-sized particles [4]. Several studies, including the earliest investigations of nanofluids, used a two-step method in which either nanoparticles or nanotubes are first produced as a dry powder and then dispersed in a fluid in a second processing step. In contrast, the one-step method synthesises the nanoparticles directly in the heat transfer fluid. The two-step process is commonly used for synthesis of carbon nanotube-based nanofluids [4,5]. Because nanopowders can be commercially obtained in large quantities, some economic advantage

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0272-8842/$ - see front matter
http://dx.doi.org/10.1016/j.ceramint.2012.10.232

exists in using two-step synthesis methods that rely on the use of such powders [6]. Thermal conductivity measurements of nanofluids were the main focus in the early stages of nanofluid research [7]. However, most of the later research has focused on concentrated dispersions of nanoparticles.

These studies have demonstrated that the particle concentration, size and shape, as well as the aggregation structure of nanoparticles, will affect the rheological behaviour of particle dispersions [7,8]. The large intrinsic thermal conductivity of carbon-based nanostructures combined with their low densities compared with those of metals, makes them attractive for use in nanofluids [9]. Moreover, particles with a high aspect ratio are more effective than those with a low aspect ratio and much more attractive than spherical particles [9]. In the present work, a new type of hybrid, γ-Al_2O_3/MWCNT has been developed to promote heat transport in fluids. The main goal of this paper is the preparing of a stable and homogeneous suspension of nanohybrid particles with carboxylate MWCNTs and characterization of nanofluids by comparison of the carboxylic group concentration effect on the thermal conductivity of suspension.

This work focuses on optimising the treatment of MWCNTs and investigates both the stability and the thermal conductivity of this nanofluid for the first time.

2. Experimental procedure: materials, preparation and characterisation

To prepare the hybrid γ-Al_2O_3/MWCNT nanoparticles using a solvothermal process, multi-walled carbon nanotubes (MWCNTs), aluminium acetate ($Al(OH)(C_2H_3O_2)_2$) (Sigma Aldrich), ammonia (25%, Merck), Triton X_{100} ($C_{14}H_{22}O$ $(C_2H_4O)_n$) (Merck), nitric acid (65%, Merck) and absolute ethanol (C_2H_5OH) (99.5%, Merck) were used as starting materials.

The carbon nanotubes used in this study were synthesised using a Co–MgO-based catalyst (Research Institute of Petroleum Industry (RIPI) of Iran). The inner diameter, outer diameter and mean length of the MWCNTs were measured by transmission electron microscopy (TEM, Philips) and were 6–20 nm, 10–50 nm and 100 nm, respectively. Following synthesis, the carbon nanotubes were treated with a multi-step purification process [10]. Two methods were used both to introduce functional groups and to open the caps of the MWCNTs. For each run using the first method, pure MWCNTs were added to nitric acid (65%) in a round bottom flask. The nitric acid–MWCNT suspension was refluxed with stirring for 4 h. The suspension was ultrasonicated in an ultrasonic water bath at 60 °C for 4 h. Then, the resulting solid was washed until neutral pH was attained, and the sample was dried at 90 °C for 24 h. The acid treatment of pure MWCNTs in the second method was performed with a solution of concentrated sulphuric acid (98%) and nitric acid (65%) in a 3:1 (V/V) ratio. Pure MWCNTs were suspended in the acid solution and then ultrasonicated at 60 °C for 6 h. The MWCNTs were filtered from the acid solution and washed with deionised water to until reaching a neutral pH; the products were then dried overnight at 90 °C.

Hybrid γ-Al_2O_3/MWCNTs (1:1 wt%) were prepared using a solvothermal process in ethanol. Aluminium acetate powder was dissolved in absolute ethanol under vigorous stirring at room temperature for 30 min until the aluminium acetate powder was dispersed completely. Both the pristine MWCNTs and the functionalised MWCNTs (prepared using both methods) were added to this suspension and dispersed using an ultrasonic water bath at room temperature until no black agglomerates could be observed in the suspension; the prepared samples were labelled PS50, S50 and SF50. The mixture was then placed under vacuum (50 cm Hg) at room temperature. Under these conditions, only capillary forces can cause the tubes to fill with the mixture. After 24 h, a 25% ammonia solution was slowly added to the mixture to adjust the pH above 9 and thus obtain fine boehmite particles. The solution was then transferred to a 350 ml Teflon-lined stainless steel autoclave chamber, after which solvothermal synthesis was performed at 200 °C for 24 h. The autoclave pressure for all synthesis runs was approximately 16 bar. The autoclave was subsequently allowed to cool to room temperature. The collected precipitate was washed with absolute ethanol several times to obtain a neutral pH and then vacuum-dried at 60 °C for 6 h. The resulting powders were calcined at 500 °C for 1 h under an argon atmosphere.

Following synthesis and analysis via FT-IR spectroscopy (Bruker, Vertex70, Germany), the processing conditions and the microstructure of the nanohybrid were characterised by XRD (PHILIP, with Co Kα, λ = 1.789010 Å, X'pert Pro, Netherlands), EDX (INCA, Oxford Instruments), TEM and HRTEM (FEG, Philips, CM200).

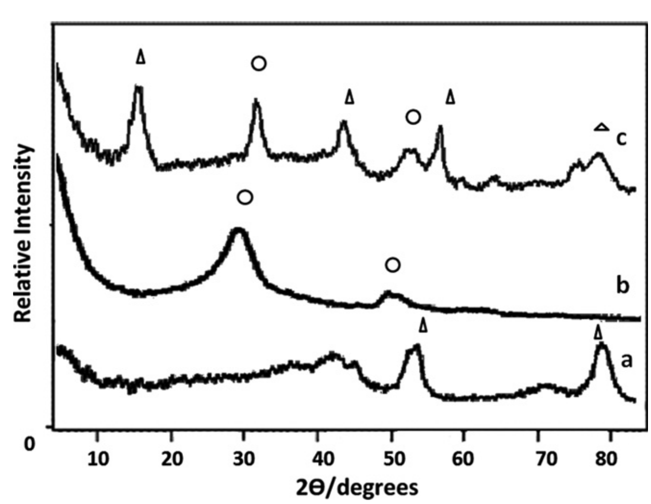


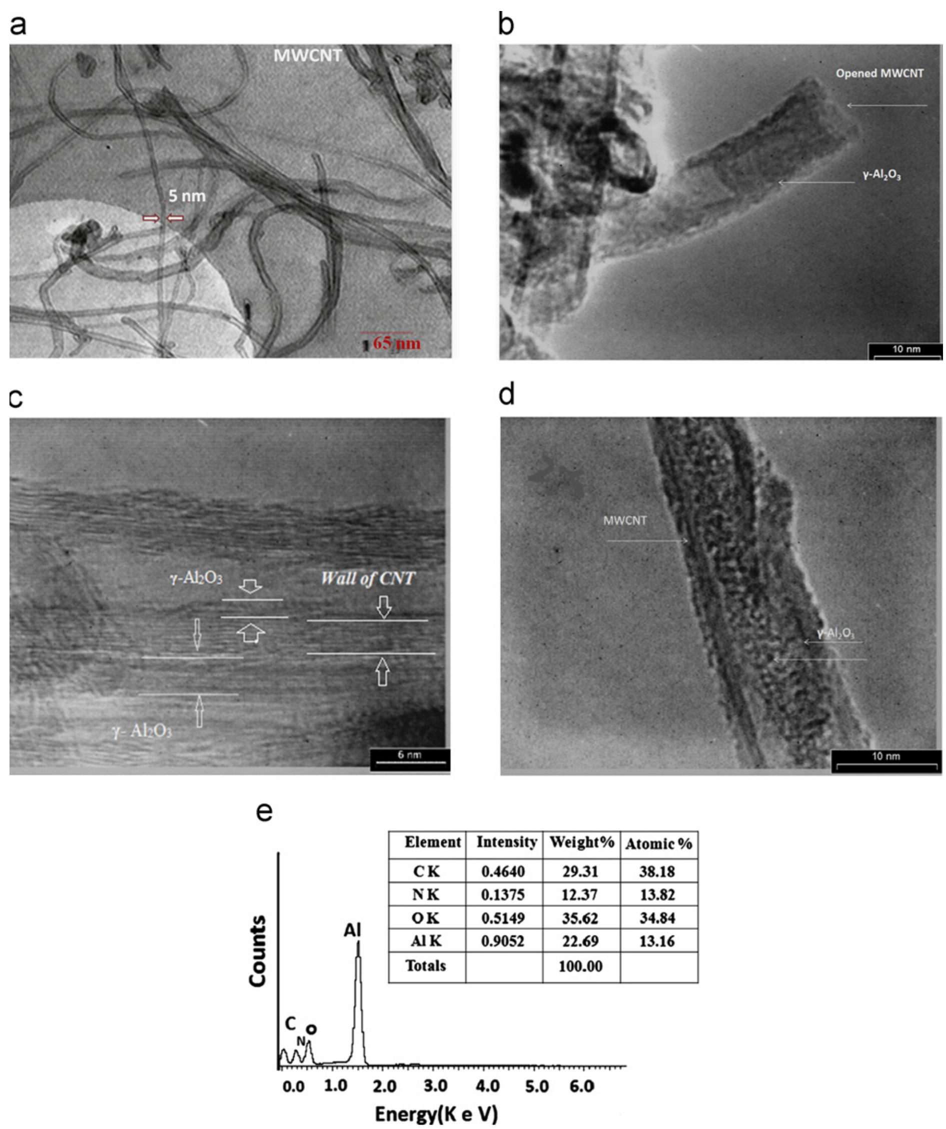
Fig. 1. XRD patterns of (a) the calcined boehmite at 500 °C for 1 h, (b) the pre-opened MWCNTs and (c) the synthesised hybrid MWCNTs calcined at 500 °C for 1 h under an Ar atmosphere (Δ γ-Al2O3, ○ MWCNT).

A two-step process was used to prepare the nanofluid. First, the necessary amount of gum arabic (GA) was added to deionised water and then ultrasonicated in an ultrasonic water bath at room temperature for 1 h. Next, 0.1 wt% of the hybrid was added to the suspension and dispersed using an ultrasonic water bath at room temperature until no black agglomerates could be observed in mixture.

The thermal conductivity was measured using a KD2 Pro Thermal Properties Analyzer (Decagon Devices Inc., USA), which operates based on the transient hot wire method. The KD2 meter has a probe length of 60 mm and diameter of 1.3 mm; the meter contains both a heating element and a thermistor, and also has a specified accuracy of 5%, which meets both ASTM D5334 and IEEE 442-1981 standards. The KD2 meter was calibrated with deionised water before each set of measurements. The zeta potential and particle size of the nanohybrids were measured on a Malvern (ZEN 3600, Instrument Inc., London, UK) with $V=10$ V, $T=25$ °C and switch time $t=50$ s. Each experiment was repeated at least 10 times to calculate the mean value of the experimental results.

3. Results and discussion

Fig. 1 shows the XRD patterns of boehmite calcined at 500 °C for 1 h, gamma alumina, pre-opened MWCNT, and hybrid γ-Al_2O_3/MWCNT prepared using a solvothermal method at 200 °C for 24 h and calcined at 500 °C for 1 h under an Ar atmosphere. In pattern (a), the diffraction peaks at 16.845°, 32.882°, 44.855°, 57.491° and 58.002° were attributed to the (0 2 0), (1 2 0), (0 3 1), (0 5 1) and (2 0 0) planes of Al_2O_3, respectively, obtained from boehmite (JCPDS card no. 01-076-1871). In pattern (b), the peaks at 5.750°, 30.785° and 50.167° were identified as the (0 0 3), (0 0 2) and (1 0 0) reflections of graphite, respectively



Element	Intensity	Weight%	Atomic %
C K	0.4640	29.31	38.18
N K	0.1375	12.37	13.82
O K	0.5149	35.62	34.84
Al K	0.9052	22.69	13.16
Totals		100.00	

Fig. 2. HRTEM and TEM micrographs of (a) pristine MWCNTs, (b) opened-tip MWCNTs, (c, d) γ-Al_2O_3/MWCNTs hybrids and (e) EDX spectrum of the hybrids.

(marked with "C"). As shown in Fig. 1(c), the two peaks from the MWCNTs are much lower than that of the pre-opened MWCNTs, and a small shift in the peaks was observed compared with the peaks of the pre-opened MWCNTs. Based on these data and the observed microstructures, the synthesised nanohybrids can be considered to be nanosized MWCNTs that are coated and filled with γ-Al_2O_3.

As it was mentioned earlier, HRTEM and TEM were used to detect possible morphological changes in the MWCNTs. Fig. 2(a) shows TEM micrographs of a pristine carbon nanotube. Following oxidation with nitric acid (Fig. 2(b)), it is evident that the cap of the nanotube is open. Fig. 2(c, d) shows HRTEM micrographs of the γ-Al_2O_3/MWCNT nanohybrid, which reveal the periodic multiwall of the MWCNTs and the γ-Al_2O_3 coating layers. In Fig. 2(e), the EDX spectrum of the nanohybrid is shown in which C, O and Al are detected.

Fourier transform infrared spectroscopy (FT-IR) was employed to analyse the surface of the MWCNTs following functionalisation. Representative FT-IR spectra of the hybrids are shown in Fig. 3. The broad band at 1637 cm^{-1} was attributed to the bending mode of adsorbed water [11].

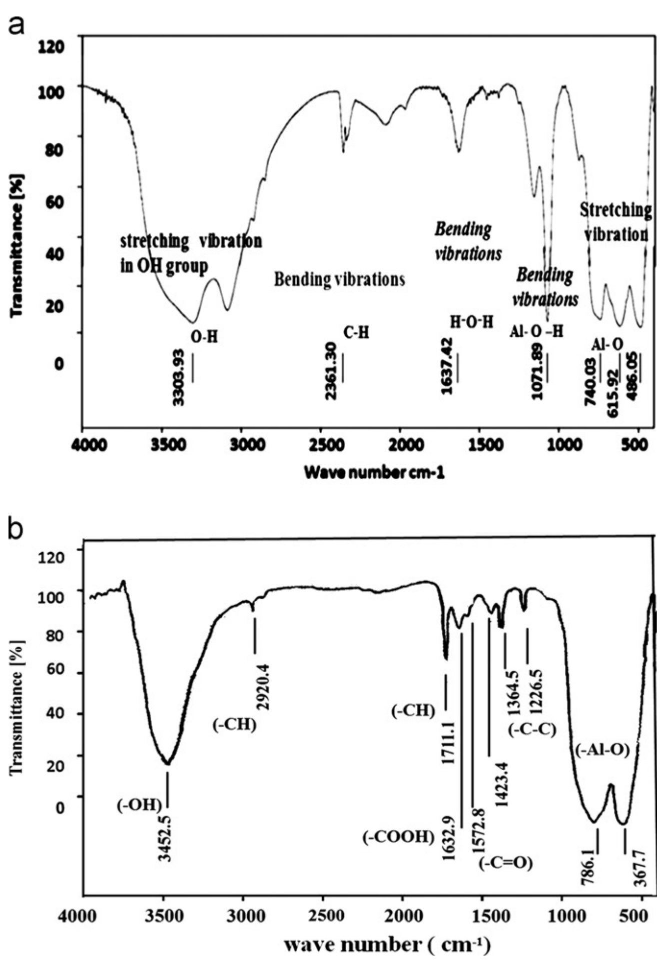


Fig. 3. FT-IR spectra of the as-synthesised nanohybrids (a) with the first method of functionalisation (S50) and (b) with the second method of functionalisation (SF50).

The intense band at 1071 cm^{-1} was attributed to the symmetric bending vibrations in the Al–O–H group [12]. The three strong bands at 740, 615 and 486 cm^{-1} were ascribed to the vibration of AlO_6, the peak at 740 cm^{-1}could be due to an Al–O stretching vibration [12]. These results confirm the formation of γ-Al_2O_3 in calcined nanohybrid powders. The bands at 2361 cm^{-1} correspond to the C–H stretch and bending vibration, which originate from the pre-treatment of the $MWCNT_S$ [13]. The detectable transmission bands approximately 1600 cm^{-1} are strongly linked to the C=O stretching vibrations of carboxylic acid groups (–COOH), and extra peaks approximately 800 cm^{-1} can be assigned to the stretching vibration of C–O–C groups [13,14]. The FT-IR results clearly show that hydrophilic groups, such as hydroxyls and carboxylic acid moieties, have been introduced onto the treated MWCNT surfaces.

Approximately 45 days after preparation, the particle size distribution and the zeta potentials of the hybrids synthesised with both functionalisation methods were examined at neutral pH to investigate their dispersion behaviour, shown in Fig. 4.

For MWCNTs synthesised using the first functionalisation method (S50), the average particle size is approximately 804 nm, with a low range of dispersion; for MWCNTs synthesised using the second functionalisation method (SF50), the average particle size is approximately 335 nm, and for the unfunctionalized MWCNTs (PS50), the average particle size is approximately 37 μm.

The zeta potential is the potential difference between the dispersion medium and the stationary layer of fluid attached to the dispersed particle. The significance of the zeta potential is that its value can be correlated to the stability of colloidal suspensions [15]. The zeta potential indicates the extent of the repulsion between particles, which regulates the extent of dispersion. For particles that are sufficiently small, a high zeta potential confirms stability, i.e., the suspension will resist aggregation [15,16].When the zeta potential is low, attraction overcomes repulsion, and the dispersion will destabilise and flocculate. Consequently, the zeta potential values of the suspensions of MWCNTs with the first functionalisation method (S50), are about -22.3 (ζ- nanohybrid γ-Al_2O_3/$MWCNT_S$/H_2O -1 = -22.3); the zeta potential value for the suspensions of MWCNTs using the second functionalisation method (SF50) is about -21.1 (ζ- nanohybrid γ-Al_2O_3/$MWCNT_S$/H2O -2 = -21.1) and the zeta potential values for the unfunctionalized MWCNTs (PS50) are about -16.8 (ζ- nanohybrid γ-Al_2O_3/$MWCNT_S$/H2O -3 = -16.8). Because the zeta potential of the S50 MWCNT suspensions is higher than that of the other suspensions, the S50 MWCNT suspension is more stable.

Fig. 5 shows images of nanohybrid/deionised water suspensions (nanofluid) 24 h after sonication. All of the functionalised MWCNTs remained well-dispersed colloidal suspensions for several weeks. Based on these results, it is evident that the presence of functional groups in the

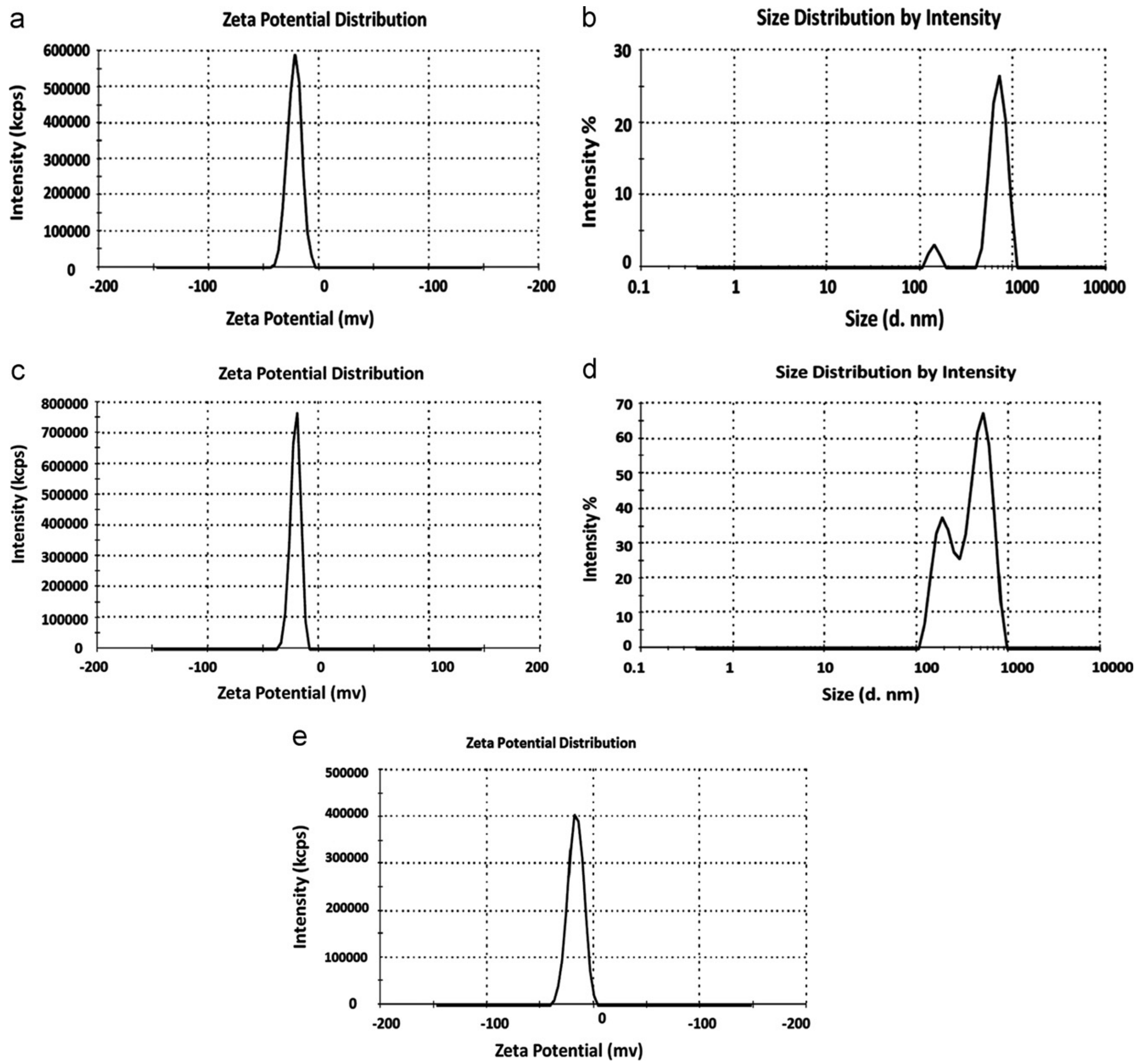


Fig. 4. The particle size distribution (PSD) and the zeta potentials for the as-synthesised nanohybrids (a, b) S50, (c, d) SF50 and (e) PS50.

oxidised $MWCNT_S$ led to a reduction of attractive van der Waals interactions among them, thereby promoting their separation and dispersion in deionised water. Additionally, these images show that when the unfunctionalized MWCNT sample (SP50) is dispersed in deionised water, it is prone to aggregation and sedimentation at the bottom of the container, even following a lengthy sonication. After a few hours, almost all of the nanohybrids sedimented, thereby leaving the dispersion medium transparent.

Note that the thermal conductivity of the base fluid is nearly constant for different concentrations of electrolyte salt, acid and base. The enhancement in the thermal conductivity of base fluid is related only to the particles [16,17]. When the nanoparticles are dispersed in water, the overall behaviour of the particle–water interaction depends on the properties of the particle surface [17]. Table 1 shows the thermal conductivity of a water-based nanohybrid γ-Al_2O_3/MWCNT nanofluid. There is some concern that the thermal conductivity is reduced by a defect (e.g., a vacancy defect or an isotope impurity) generated during either the MWCNT synthesis or the functionalisation process [18]. In addition, the length and morphology of the $MWCNT_S$, the aspect ratio and the extent of aggregation play key roles in the thermal transport properties of the MWCNT nanofluid [19].

Substantial increases in the thermal conductivity are observed in all measured nanofluids, with enhancements in the thermal conductivity of up to 20.68%, 17.24% and 3.45% observed for the first method functionalised sample (S50), second method functionalised sample (SF50) and third method functionalised sample (PS50), respectively.

The volume fraction and the morphology of CNTs play important roles in the thermal transport properties of the

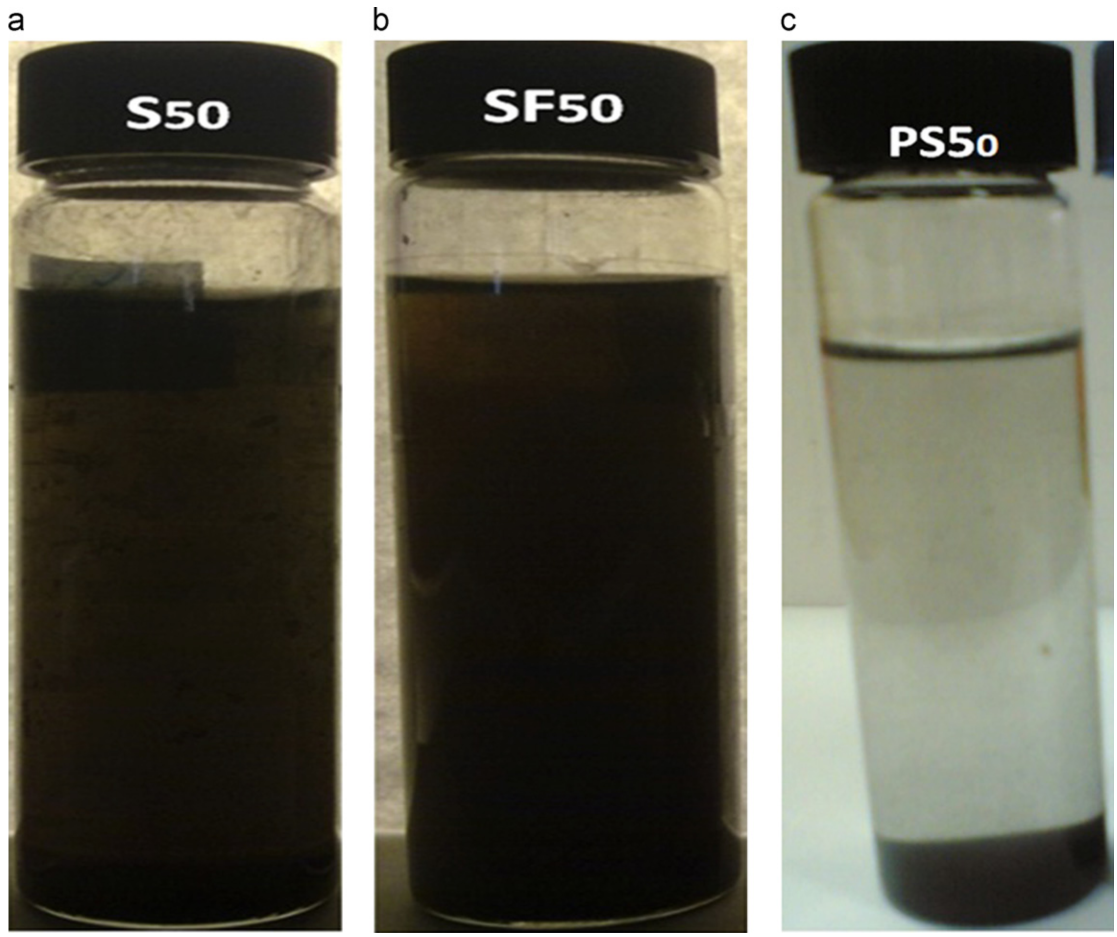


Fig. 5. Digital images of the hybrid suspensions: (a) a suspension of hybrids (synthesised using the first method of functionalisation) in DW (S50), (b) a suspension of hybrids (synthesised using the second method of functionalisation) in DW (SF50), and (c) a suspension of hybrids (unfunctionalized MWCNTs) in DW (PS50).

Table 1
Experimental data for the thermal conductivity of the hybrid γ-Al_2O_3/MWCNT nanofluid.

Loading volume fraction %	Thermal conductivity of base fluid (W/m. K)	Thermal conductivity of first method (S50) (W/m. K)	Thermal conductivity of second method (SF50) (W/m. K)	Thermal conductivity of third method (PS50) (W/m. K)
0.1	0.58	0.70	0.68	0.60

nanofluids [14]. As indicated in Fig. 6, enhancement of thermal conductivity in the hybrid nanofluids occurs as a function of the volume fraction of the nanohybrid, yet the thermal conductivity decreased with increasing concentration of carboxylic acid groups. In this article, K_0 and K represent the thermal conductivities of the base fluid and the nanofluid, respectively, $\Delta K= K-K_0$ and is the enhancement in thermal conductivity and $\Delta K/K_0$ refers to the enhancement in thermal conductivity.

The results showed that enhancement of the thermal conductivity noticeably increases with the nanotube aspect ratio [19]. The CNT walls have a structure similar to that of graphene sheets, and the thermal conductivity of CNTs displays highly anisotropic behaviour [19]. When the CNTs were treated, the CNTs were fragmented and cut short with an appropriate average length. The straightness

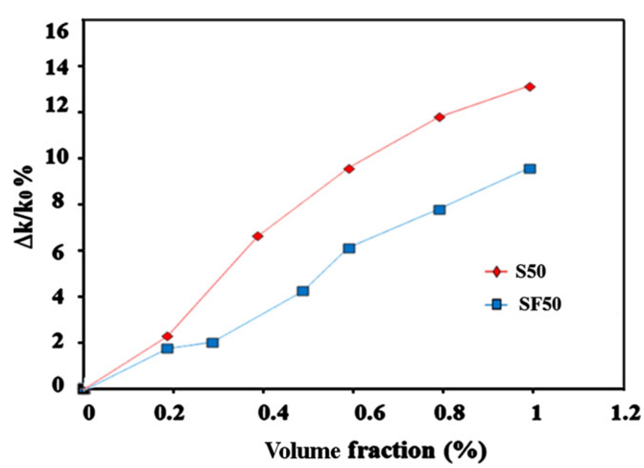


Fig. 6. The thermal conductivity of the hybrid nanofluids as a function of the nanohybrid loading.

ratio significantly increased, and heat transport occurred more effectively both through the CNTs and along the interfaces between the CNT tips and the base fluid [20].

4. Conclusion

The hybrid γ-Al_2O_3/MWCNTs with a lower concentration of carboxylic acid groups on the MWCNT surface have no fragmentation, better stability and higher thermal conductivity compared with the hybrid γ-Al_2O_3/MWCNTs with a higher concentration of carboxylic acid groups that have a lower zeta potential or lower stability. Therefore, further treatment of nanotubes with a relatively high straightness ratio would cause excessive deterioration of the aspect ratio, thereby decreasing the thermal conductivity of nanofluid. Based on the experimental results, a well-dispersed suspension with a high surface charge density was obtained to generate strong repulsive forces; therefore, the lowest zeta potential value may not be stable for combination of hybrid γ-Al_2O_3/MWCNTs with unfunctionalized MWCNTs. Finally, the thermal conductivity of the nanofluid is clearly dependent on the stability of the hybrid nanoparticles in the nanofluid; enhancement of the thermal conductivity can reach up to 14.75% at a volume fraction of 0.01 for a gum arabic (GA)-based nanofluid.

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