Alignment of Different Functional Single Wall Carbon Nanotubes using Fe_2O_3 Nanoparticles under External Magnetic Field

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ABSTRACT

In this paper we describe a new approach to align functionalized single walled carbon nanotubes (SWNTs) by γ-Fe2O3 in the presence of an external magnetic field without using chemical surfactant. Three different functionalized SWNTs are studied. SWNT-SO_2OH dissolves completely. SWNT-COOH disperses well and shows the clear alignment. SWNT-PABS disperses poorly and exhibits some kind of alignment. The high entanglement of PABS chain decreases the alignment of SWNT-PABS. The results demonstrate that as long as the charges fit, the functional nanotubes alignment could be reached without chemical surfactant.

Keywords: Functionalized SWNT, alignment, γ-Fe2O3, magnetic field

1 INTRODUCTION

Nanotubes are expected to be very good thermal conductors along the tube. Measurements show that single wall nanotubes have a thermal conductivity as high as 2000–6000 W/mK [1]. Nanofluids containing carbon nanotubes are very important and can be used for variety of applications such as heat transfer coolant and lubricant [2-6]. Alignment of single walled carbon nanotubes (SWNTs) under external magnetic field is also very promising. Electrical and thermal properties of nanofluids can be highly enhanced if all nanotubes are aligned due to the anisotropic nature of carbon nanotubes [7]. Carbon nanotubes tend to aggregate into groups due to the large surface energy (strong Van der Waals attractions between individual tubes). Different approaches have been suggested to decrease the nanotubes agglomeration. Modifying the surface chemistry of the tubes through non-covalently (adsorption) by using surfactant [8-12], covalently (functionalization) by using chemical modification [13-19] and metal coated like Ni-coated SWNTs [5] are considered as the appropriate approaches.

2 LITRITURE REVIEW

Hong et al., [20] found that an electrostatic attraction between the nanotubes, surfactant and metal oxide causes aggregation. (NaDDBS) surfactant with a negative charge attracts to Fe_2O_3 which has positive zeta potential charge. When cationic surfactant, Cetyltrimethyl ammonium bromide (CTAB), was used instead of the anionic surfactant NaDDBS, no alignment was found because the surfactant and Fe_2O_3 have the same positive charge. Kim et al., [21] tethered carboxylic functionalized MWNTs with γ-Fe_2O_3 nanoparticles in a solid phase. Sodium dodecylbenzenesulfonate (NaDDBS) was introduced into the suspension to prevent the formation of an iron oxide 3D network. Surfactants are used to modify the surface of carbon nanotubes and prevent agglomeration successfully [22-24]. However, it has many disadvantages. One of these disadvantages is the weak forces between surfactant and medium which can decrease the load transfer ability of the fluid. Another disadvantage is the decrease in the electrical and thermal conductivity of the materials due to the presence of a non-conductive surfactant [25].

3 EXPERIMENTAL PART AND METHOD

Single wall carbon nanotubes (SWNT) were purchased from Beijing Boda Green High Tech Co LTD. Single walled polyaminobenzene sulfonic acid functionalized (SWNT- PABS) with average diameter of individual SWNT = 1.4nm ± 0.1nm. Bundle dimensions 1.1 nm × 0.5-1.0 μm and average Mw 400-600 g/mol (PABS) were all purchased from sigma Aldrich. Single walled sulfonated functionalized (SWNT-SO2OH) and single walled hydroxyl acids functionalized (SWNT-COOH) were purchased from Rice University and CheapTubes.com. The magnetically sensitive γ-Fe2O3 nanoparticles with an average diameter of 5–25 nm, and chemical surfactant sodium dodecyl benzene sulfonate (NaDDBS) were purchased from Sigma–Aldrich. Sonication was performed using a Branson Digital Sonifier, model 450. A magnetic field was provided by a pair of spaced, Ba–ferrite magnet plates (4 in. ×6 in. ×1 in.). The sample was placed in the middle of gap between the magnets. The magnetic field intensity was recorded by F.W. Bell Gaussmeter model 5060. A Redlake Model PCI 2000S Motion Scope (MASD Inc, San Diego, CA) was used to observe the behavior of nano particles mixture. The detection parameters used were: record rate 250, Shutter 1/250, and trigger 70%. The lens were a WHB 10×/20 and MPlan 10×/0.25. Also Microscope image was taken by Leica Z16 APO, Zoom microscope. For nanofluids preperation, 0.016 g functionalized SWNTs were dispersed in 100 g DI water by using ultrasonicator for 30 min at 35% intensity until good dispersion was achieved, then 0.016 g of γ-Fe2O3 nanoparticles were added to the mixture and sonicated twice in 15 minute intervals. The fluids were put in a glass dish and microscopic images were taken.

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3. RESULTS AND DISCUSSION

3.1 SWNT-SO_2OH

Fig. 1 illustrates the microscope images of 0.016 wt% SWNT-SO2OH and 0.016 wt% Fe2O3 nanoparticles in DI water obtained by using a high speed microscope video system (A) 0 min, (B) 4 min and (C) 9 min. Magnetic field (H = 0.14 kG) was applied with an internal reference of 30 μm. As shown in Fig. 1A, it is clearly seen that at 0 min SWNT-SO2OH dissolves completely in water and any particles can barely be seen. No changes were observed when the magnetic field is applied for 2 min. But, after applying the magnetic field for 4 min, the fine particles start to aggregate and very thin lines were observed as seen in Fig 1B. 9 minutes later, the aggregation of the fine particles continued and became larger and longer alignment as shown in Fig 1C. The explanation why SWNT-SO2OH dissolves well in water is that R-SO_2OH is an organic compound containing a sulfur atom attached to the R group which can be aromatic or aliphatic group. The sulfur atom is also connected to three oxygen atoms, two of them connected with a double bond to the sulfur. The other oxygen atom, which has a single bond with the sulfur, connected to the hydrogen atom that gives the compound the acidic behavior as illustrated in figure 2. The compound is considered as a strong acid with acidity much stronger than carboxylic acid. For example, the dissociation constant of benzensulfonic acid is -2.8 which approximately equals to the Pka of the strong acid, sulfuric acid [26]. Sulfonic acid dissociates completely in water as the following reaction

$$R\text{-}SO_2OH + H_2O \longrightarrow R\text{-}SO_2O^- + H^+_3O$$

SO_2OH group transforms the hydrophobic surface of SWNTs to a hydrophilic surface which helps to get well dispersed fluids. The negative charge which carries on the acidic oxygen atom after the dissociation process attracts the Fe_2O_3 nanoparticles which have a positive zeta potential. External magnetic field makes the SWNT-SO_2OH/γ-Fe2O3 nanoparticles mixture align well, as seen in Fig 1C.

3.2 SWNT-COOH

Microscope images of 0.016 wt% SWNT-COOH and 0.016 wt% γ-Fe2O3 in DI water were obtained by using high speed microscope video system (A) 0 min, (B) 0.5 min and (C) 4 min are shown in Fig.4. Magnetic field (H = 0.14 kG) was applied with an internal reference of 30 μm. As shown in Fig. 2A, it is clearly seen that at 0 min the SWNT-COOH, metal oxide Fe_2O_3 mixture is randomly dispersed in the water. It can also be seen from the figure that the mixture is entangled and looks like scattered dots (most of these dots are much less than 30 μm in diameter) in the microscope image. With the application of the external magnetic field, the “scattered dots” start to stretch, vibrate and align, as shown in Fig. 2B, as quickly as 30 s after applying the magnetic field. About 4 min later (Fig. 2C), these randomly dispersed dots form larger and longer lines, indicating that SWNT-COOH/γ-Fe2O3 nanoparticles mixture align under the external magnetic field. The carboxylic acid R-COOH is an organic compound, which has a carboxylic group (C=O) and hydroxyl group (OH), R can be aromatic or aliphatic group. R-COOH is considered as a weak acid, for example, the dissociation constant (Pka) for benzencarboxylic (benzoic acid) is about 4.19 [27], which explains why SWNT-COOH cannot be dissolved completely in water, although it can be dispersed well in water, as seen in fig 2A. The negative charge, which carries on the acidic oxygen atom after the dissociation process, attracts the γ-Fe_2O_3 nanoparticles which have a positive zeta potential. External magnetic field makes the SWNT-COOH/γ-Fe_2O_3 nanoparticles mixture align well, as seen in Fig 2B and 2C.

3.3 SWNT- PABS

Fig 3 illustrates the microscope images of 0.02 wt% swnt-pabs and 0.02 wt% Fe_2O_3 in di water. the images were obtained using the optical microscope system (a) 0 min, (b) 2 min, and (c) 8 min. magnetic field (h = 0.14 kg) was applied to the mixtures. it can be seen in fig.3A that, without applying magnetic field, swnt- pabs has a bad dispersion in water and some nanotubes agglomerate and form very big bundles. fig.3B illustrates the microscope images of the mixture after applying the magnetic field for 4 min. it looks like that nanofluids containing swnt-pabs/γ-Fe_2O_3 mixture has some kind of weak and vague alignment. with more time (8 min), no significant changes are observed, as seen in fig 3C. the explanation to the results maybe as follows: pabs functionalized single wall carbon nanotubes have the function group poly (m-aminobenzene sulfonic acid) as shown in fig. 4. (PABS) is a soluble polymer in water and many other organic solvent. it has an electrical conductivity of 5.4 × 10-7 s cm-1. swnt- pabs has an electrical conductivity of 5.6 × 10-3 s cm-1 [29]. the sulfonic group in swnt- pabs may dissociate in water just like the SWNT- SO_2OH and have negative charge. it should assume that as before, the negative charge which carries on the acidic oxygen of SO_2OH should attract the γ- Fe_2O_3 which has the positive zeta potential charge and form good alignment. however, the chains of pabs and relative high molecular weight of SWNT-PABS make the dispersion difficult. without good dispersion, it is hard to get the good alignment. in addition, the resonance structures of an amide and stereo effect of the SWNT-PABS molecule make the less possibility of charges, as discussed previously. overall, those factors hinder (reduce) the negative charges on

SWNT-PABS and no clear alignments are observed on experiments, as shown in fig 4b and 4c.

5. CONCLUSION

In summary five different functionalized SWNTs/ γ-Fe_2O_3 nanofluids were prepared successfully without using surfactant. Negatively charged functionalized SWNTs aligned very well by the application of an external magnetic field. SWNT-SO2OH dissolved completely in water and the alignment was perfect and took few minutes to be observed. The full negative charge on the -SO_2OH tethered to the magnetic guided γ-Fe_2O_3 and very fine chains were seen initially and grew longer and thicker gradually. SWNT-COOH dispersed well in water. The negative charge on the -COOH tethered to the magnetic guided γ-Fe2O3 and made the alignment fast. SWNT-PABS disperse poorly and exhibit some kind of alignment. The highly entanglement of the PABS chain decreases the alignment of SWNT-PABS. This property is attributed to the electrostatic attraction between the partially negative charged, oxygen atoms, and γ-Fe_2O_3. These results demonstrate that as long as the charges fit, the alignment could be reached without chemical surfactant. The use of magnetic guidance for aligning carbon nanotubes in a fluid may open up new routes for the research and applications of nanofluids. Also, it could be applicable to a variety of potential applications, such as reinforced polymer composites, chemical sensors, etc.

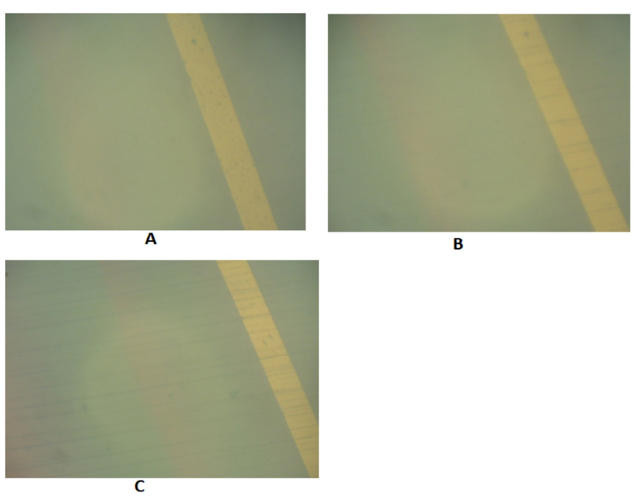

Figure 1: Microscope images of 0.016wt % SWNT-SO_2OH, 0.016wt % Fe_2O_3 in DI water. A: at 0 min, B: after 4 min and C: after 9 min. The Internal reference is 30 µm.

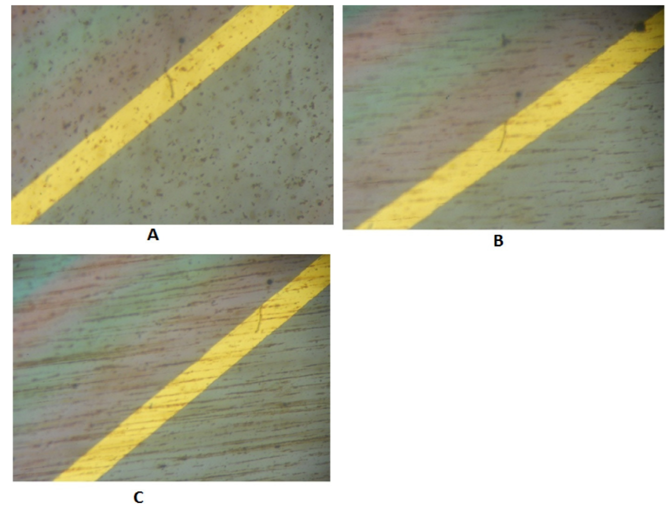

Figure 2: Microscope images of 0.016wt % SWNT-COOH, 0.016wt % Fe_2O_3 in DI water. A: at 0 min, B: after 0.5 min and C: after 4 min. The Internal reference is 30 µm.

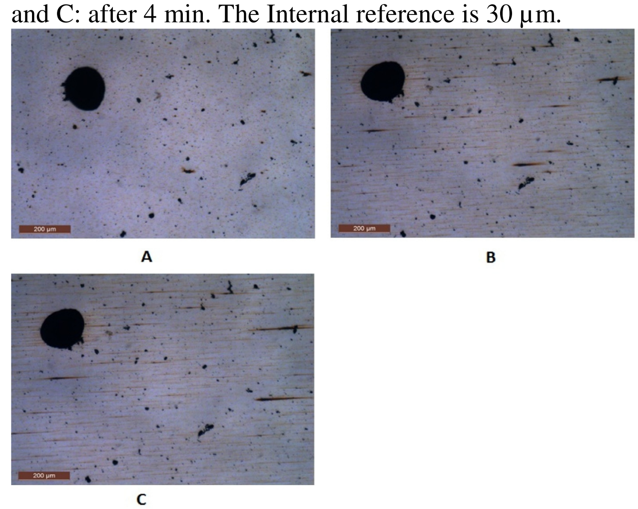

Figure 3. Microscope images of 0.02wt % SWNT-PABS, 0.02wt % Fe_2O_3 in DI water. A: at 0 min, B: after 2 min and C: after 6 min.

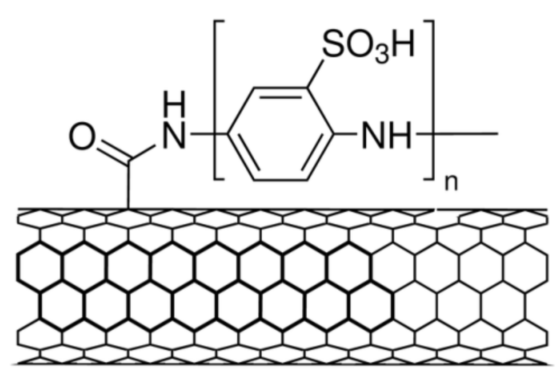

Figure 4 . Polyaminobenzene sulfonic acid functionalized SWNTs with an average of 2~4 Polyaminobenzene sulfonic acid units per molecule.

6. CONCLUSION

In summary five different functionalized SWNTs/ γ-Fe_2O_3 nanofluids were prepared successfully without using surfactant. Negatively charged functionalized SWNTs aligned very well by the application of an external magnetic field. SWNT-SO_2OH dissolved completely in water and the alignment was perfect and took few minutes to be observed. The full negative charge on the -SO2OH tethered to the magnetic guided γ-Fe_2O_3 and very fine chains were seen initially and grew longer and thicker gradually. SWNT-COOH dispersed well in water. The negative charge on the -COOH tethered to the magnetic guided γ-Fe_2O_3 and made the alignment fast. SWNT-PABS disperse poorly and exhibit some kind of alignment. The highly entanglement of the PABS chain decreases the alignment of SWNT-PABS. This property is attributed to the electrostatic attraction between the partially negative charged, oxygen atoms, and γ-Fe_2O_3. These results demonstrate that as long as the charges fit, the alignment could be reached without chemical surfactant. The use of magnetic guidance for aligning carbon nanotubes in a fluid may open up new routes for the research and applications of nanofluids. Also, it could be applicable to a variety of potential applications, such as reinforced polymer composites, chemical sensors, etc.

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