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A bio-based, facile approach for the preparation of covalently functionalized carbon nanotubes aqueous suspensions and their potential as heat transfer fluids

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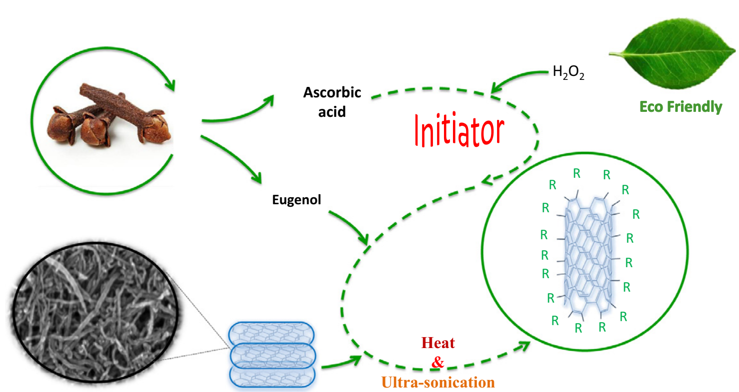
HIGHLIGHTS

- A novel, green method for covalent functionalization of MWCNTs was introduced.
- Highly stable clove-treated MWCNTs aqueous suspension was synthesized.
- The success of functionalization process was validated by characterization techniques.
- The solubility of the synthesized MWCNTs nanofluid was verified by zeta potential and UV–vis spectra.
- The synthesized clove-treated MWCNTs nanofluid showed remarkable thermo-physical properties.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, we propose an innovative, bio-based, environmentally friendly approach for the covalent functionalization of multi-walled carbon nanotubes using clove buds. This approach is innovative because we do not use toxic and hazardous acids which are typically used in common carbon nanomaterial functionalization procedures. The MWCNTs are functionalized in one pot using a free radical grafting reaction. The clove-functionalized MWCNTs (CMWCNTs) are then dispersed in distilled water (DI water), producing a highly stable CMWCNT aqueous suspension. The CMWCNTs are characterized using Raman spectroscopy, X-ray photoelectron spectroscopy and transmission electron microscopy. The electrostatic interactions between the CMWCNT colloidal particles in DI water are verified via zeta potential measurements. UV–vis spectroscopy is also used to examine the stability of the CMWCNTs in the base fluid. The thermo-physical properties of the CMWCNT nano-fluids are examined experimentally and indeed, this nano-fluid shows remarkably improved thermo-physical properties, indicating its superb potential for various thermal applications.

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1. Introduction

The electrical, thermal and mechanical properties of carbon nanotubes (CNTs) combined with their small size, low density and high toughness [1–3], give these materials great potential for a wide range of applications including heat transfer and supercapacitors [4–8]. However, CNTs are known to have weak dispersibility in many solvents as a consequence of strong intermolecular π–π interactions. This hinders the processability of CNTs in industrial applications [9,10]. In order to tackle this issue, various techniques have been developed over the years to modify the surface of CNTs in order to improve their stability and solubility [7,11]. This enhances processing and manipulation of insoluble CNTs, rendering them useful for synthesizing innovative CNT nano-fluids with impressive properties that are tuneable for a wide range of applications.

Chemical routes such as covalent functionalization have been studied extensively, which involves the oxidation of CNTs via strong acids (e.g. sulfuric acid, nitric acid or a mixture of both) in order to set the carboxylic groups onto the surface of the CNTs as the final product or for further modification by esterification or amination [12–14]. Free radical grafting is a promising technique among covalent functionalization methods, in which alkyl or aryl peroxides [15], substituted anilines, and diazonium salts are used as the starting agents [12]. Free radical grafting of macromolecules (as the functional group) onto the surface of CNTs can improve the solubility of CNTs compared to common acid treatments which involve the attachment of small molecules such as hydroxyl onto the surface of CNTs. Indeed, the solubility of CNTs can be improved significantly by free radical grafting because the large functional molecules facilitate the dispersion of CNTs in a variety of solvents, even at a low degree of functionalization [16]. Even though these chemical routes are generally reliable to synthesize functionalized CNTs, these techniques are not environmentally friendly because the reagents used for synthesis are toxic and detrimental to the environment. More importantly, some of these chemical routes may cause defects in the lattice which will degrade the inherent characteristics of CNTs [12].

Hence, there is a critical need to develop a simple, efficient and environmentally friendly technique for the dispersion of CNTs, which will be greatly beneficial in the long term since it helps reduce pollution resulting from the use of toxic reagents during syntheses [17].

Cloves (i.e. buds of Syzygium aromaticum) are spices commonly used throughout the world and they are known for their valuable medicinal properties due to the presence of active components. The main bioactive compound of cloves is eugenol, which is typically present in concentrations of around 82.6 wt% [18]. Phenolic acid and gallic acid are among the active components of cloves, though at higher concentrations. Previous studies have also shown that ascorbic acid is present in clove flower buds at low concentrations up to 0.08 wt% [19]. The structure and unique properties of clove components make cloves an ideal candidate to enhance the functionalization of CNTs in aqueous media. In this study, we propose a facile, economical, environmentally friendly technique to synthesize highly dispersed multi-walled carbon nanotubes (MWCNTs) in aqueous media using the free radical grafting technique. We characterize the clove-functionalized MWCNT (henceforth designated as CMWCNTs in the remainder of this article) by Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), zeta potential and UV–vis spectra measurements in order to verify the success of the covalent functionalization. Following this, we prepare CMWCNTs nano-fluids by dispersing 0.08 and 0.05 vol% of CMWCNTs in distilled water, which we have selected as the base fluid. Lastly, we measure the thermo-physical properties of the CMWCNT nano-fluid as a function of the fluid temperature and particle concentration to verify the potential of this nano-fluid for thermal applications.

2. Material and methods

2.1. Chemicals and sample preparation

Here, we outline our innovative procedure to prepare the environmentally friendly CMWCNTs. The procedure consists of two primary steps: (1) the preparation of the clove extract solution, and (2) the covalent functionalization of the MWCNTs. In the first step, we purchased the cloves from a local market in Iran and we prepared the clove extract solution (which is a source of eugenol and ascorbic acid [19]) as follows. Firstly, 4 g of ground cloves were added into a vessel filled with 200 ml of distilled water. The process was carried out under heating at 80 °C and the solution was homogenized at 1000 rpm for 30 min. Lastly, the clove extract solution was then filtered through 45 μm PTFE membrane under ambient conditions. Scheme 1 shows a pictorial representation of the clove extract solution preparation procedure.

In the second step, 1 g of pristine MWCNTs (Nanostructured & Amorphous Materials Inc.) was poured into a vessel filled with 200 ml of clove extract solution and then stirred for 15 min. Following this, 7 ml of hydrogen peroxide (30%) (Sigma-Aldrich Co., Selangor, Malaysia) was added drop by drop into the mixture throughout the sonication time. The resultant mixture was ultrasonicated for 10 min, followed by heating up to 80 °C under reflux for 14 h. The suspension was centrifuged at 14,000 rpm and washed with distilled water several times to remove unreacted materials until the solution attained a pH of 7. The functionalized sample was subsequently dried overnight in a vacuum oven at 60 °C. Following this, CMWCNTs-water nano-fluid is prepared by dispersing (10 min ultra-sonication) 0.05 and 0.08 vol.% of covalently functionalized MWCNTs nanoparticles in distilled water. We observed that the CMWCNTs were well-dispersed in the aqueous media.

Scheme 2(a) shows the initiation reaction for the free radical grafting. In the initiation step, the ascorbic acid (*i.e.* vitamin C) reacts with hydrogen peroxide (a free-radical oxidizer that generates non-toxic by-products and leaves no chemical residue), producing hydroxyl radicals [20]. At high temperatures, the hydrogen peroxide becomes unstable and decomposes spontaneously into hydroxyl radicals. These reactions continue to take place at 80 °C in harmless water [21]. Scheme 2(b) shows that most of the generated hydroxyl radicals will attack eugenol to produce free radicals on the eugenol structure, which leads to the linkage of the activated eugenol onto the surface of MWCNTs. In addition, the hydroxyl radicals can attack the MWCNTs directly, leading to formation of hydroxyl groups on the MWCNT surface.

2.2. Instrumentation

Ultrasonication was conducted via ultrasonic liquid processor (Misonix Inc., Farmingdale, New York, NY, USA) having an output of 600 W. We used Axis Ultra-DLD system, Kratos Analytical X-ray photoemission spectrometer (XPS) with Al Kα X-ray source (hν = 1486.8 eV) to recognize the functional groups in Clove-treated MWCNTs nanoparticles. We used the CASA XPS programme with Gaussian-Lorentzian mix function and Shirley background subtraction for deconvolution of the XPS spectra. Hitachi HT7700 transmission electron microscope (high-resolution digital TEM) was used to examine the morphological characteristics of