ARTICLE IN PRESS
JID: JTICE [m5G;May 3, 2017;6:51]
Journal of the Taiwan Institute of Chemical Engineers 000 (2017) 1–9
Contents lists available at ScienceDirect
Journal of the Taiwan Institute of Chemical Engineers
journal homepage: www.elsevier.com/locate/jtice

Thermophysical and rheological properties of water-based graphene quantum dots nanofluids

Ahmad Amiri[a,*], Mehdi Shanbedi[b,*], Hossein Dashti[c]

[a] Department of Mechanical Engineering, University of Malaya, Kuala Lumpur, Malaysia
[b] Department of Chemical Engineering, Faculty of Engineering, Ferdowsi University of Mashhad, Mashhad, Iran
[c] Department of Chemical Engineering, School of Chemical and Petroleum Engineering, Curtin University, WA, Australia

ARTICLE INFO

Article history:
Received 18 January 2017
Revised 6 April 2017
Accepted 7 April 2017
Available online xxx

Keywords:
Graphene quantum dots
Nanofluid
Stability
Viscosity
Density
Thermal conductivity

ABSTRACT

Application of the suspended solid particles in the base fluids is one of the novel methods to increase the thermal performance of heat transfer fluids. However, the major problems with this technique are the short time colloidal stability, low thermal conductivity of additive as well as significant negative effects on rheological properties once loading nanoparticles. The present study explores, for the first time, the impacts of graphene quantum dot (GQD) on the colloidal stability and thermophysical properties of water-based GQD suspensions as a new generation of heat transfer fluid. To this end, amine-treated GQD (A-GQD) were synthesized with a novel method. Surface functionality groups on A-GQD were analyzed by XPS. Atomic-force microscopy (AFM), UV–vis spectrometry, zeta potential and average particle size techniques have been used in order to measure and evaluate the colloidal stability, size and thickness of A-GQD. After applying A-GQD as an additive, colloidal stability results indicate no sedimentation after a 30-day period. In addition, all the thermophysical properties *e.g.* thermal conductivity, density and viscosity were measured experimentally. The viscosity of the water-based A-GQD samples was tested at various shear rates, concentrations and temperatures. Further, it has shown that by loading A-GODs in the water, the increasing rate of the density and viscosity is not significant. Interestingly, the water-based A-GQD nanofluids at very low concentration significantly increase the thermal conductivity in comparison with that of pure water.

1. Introduction

The poor thermal conductivity of conventional heat transfer fluids such as air, deionized (DI) water, ethylene glycol (EG) and engine oil is one of the biggest problems in high heat transfer application in mechanical equipment and engineering processes. The addition of ultrafine solids particles suspended in the base fluid could enhance the thermal conductivity of fluids [1–5]. The early studies indicated that the low dispersion stability of suspended particles with sizes in the range of millimeters or micrometers could have an adverse influence on the effective thermal conductivity. Their poor stability suspension leads to abrasion and channel clogging [6]. However, recently it was found that nanosized particles (1–100 nm) suspensions in a common fluid can result in more stable and high thermal conductivity as well as improved rheological properties [7,8]. The term of “nanofluid” was first used by Choi in 1995 [9]. Several studies have shown an increased interest in nanofluids in order to improve heat transfer, stability and thermophysical properties performance [10,11].

Several types of additives have been identified in the research community: metals, metal oxides *e.g.* titanium oxide (TiO_2), aluminum oxide (Al_2O_3) and carbon-based nanostructures *e.g.* carbon nanotubes, graphene. The main problem of metal- and metal oxide-based nanoparticles is their sedimentation in the common base fluid. Carbon-based nanostructures are capable to be functionalized covalently and non-covalently to change from a hydrophobic structure to hydrophilic one. Recently, researchers have shown an increased interest in development of different carbon-based nanostructures to prepare nanofluids like single-walled carbon nanotubes, double-walled carbon nanotubes, multi-walled carbon nanotubes, graphene, graphene nanoplatelets and graphene oxide [12–16]. Graphene as a single atomic plane of graphite has high electrical and thermal conductivity, high specific surface area (SSA), high fracture strength and highly ordered graphitic carbon those attract lots of attention for the application in processes with high heat flux such as coolant technology [17]. The thermal conductivity of graphene has been measured to be in the range of 2000–5350 W/m K at room temperature [18–23]. The

* Corresponding authors.
E-mail addresses: ahm.amiri@gmail.com (A. Amiri), mehdi.shanbedi@stu-mail.um.ac.ir (M. Shanbedi).

http://dx.doi.org/10.1016/j.jtice.2017.04.005

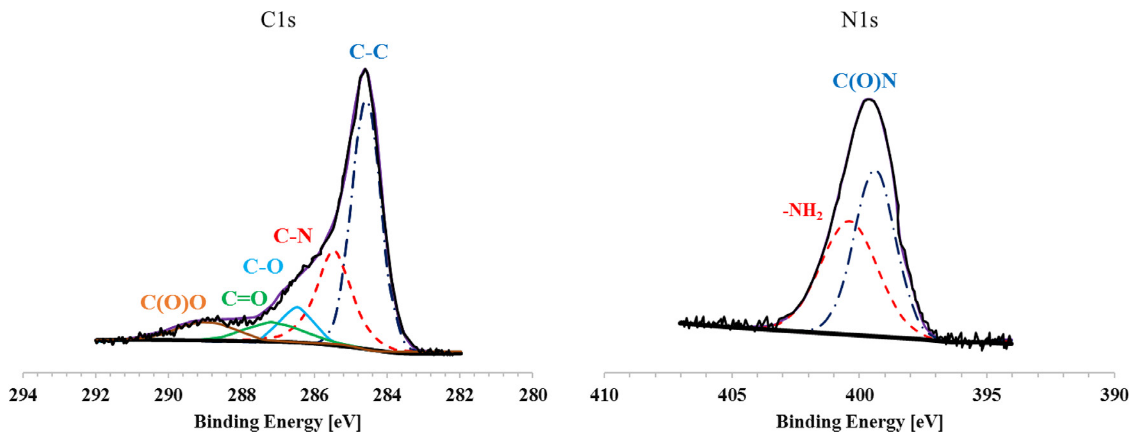

Fig. 1. The C1s and N1s XPS spectra of A-GQDs.

trivial interaction between graphene and other materials, presence of micro-sized dimensions, restacking and agglomeration in different base fluids are the main concerns about the application of graphene as an additive [14]. Owning a micro-sized dimension can be considered as a fundamental limitation for the Brownian motion of graphene in base fluids [22].

Several researchers found that based on the micro-convection model, the Brownian motion of the nanoparticles in the base fluid induced local convection [24–26]. Shima et al. (2009) showed that Reynolds number in Brownian motion has the inverse proportional with the square root of the particle diameter [26]. Consequently, as the particle size decreases the thermal conductivity will increase significantly. So, aggregation and restacking can intensify this problem. To have a carbon-based additive with completely nano-sized dimensions, graphene quantum dots (GQDs) can be applied. GQDs have been produced from various carbon-based materials such as graphene oxides [27–31], carbon fibers [32] and carbon nanotubes [33,34].

This study provides new insights into the application of GQDs to improve the thermal conductivity of nanofluids. To this end, Amine-treated GQDs (A-GQDs) as fully nano-sized dimensions with superior thermal conductivity and capability of functionalization have been applied as additives for the preparation of stable nanofluids. A-GQDs are morphologically characterized to study the size of particles. Finally, the colloidal stability and thermophysical properties of the water-based A-GQD nanofluids are comprehensively ascertained.

2. Methodology

2.1. Nanofluid preparation

In this study, a modified Hummers method was used to produce the graphite oxide sheets from natural graphite powder [35]. The synthesis procedure for GQDs was done by adapting the procedure employed by Zhang et al. (2013) with slight modification [35]:

(1) 2.0 g of the graphite were oxidized under mild ultrasonication in the concentrated HNO_3 (60 mL, 38 wt.%) and H_2SO_4 (180 mL, 28–30 wt.%) for 48 h.
(2) After enough cooling, the mixture was then diluted with 1200 mL of deionized water and centrifuged at 4000 rpm to separate unexfoliated material.
(3) The supernatant was diluted with the deionized water (2000 mL) and sonicated for 30 min at room temperature.
(4) The colloidal suspension was dialyzed using a dialysis bag (Mw cut-off: 3500 Da) overnight. In this step, it is necessary to remove the acidic groups decorated on the edge of GQDs.
(5) Typically, 100 mL of colloidal solution was mixed with deionized water (100 mL) and ammonia solution (120 mL, 28–30%) in a vessel. The black suspension was sonicated in a 300 W probe sonicator for 30 min. Then the mixture was stirred for 4 h at 100 °C. After sufficient cooling to achieve the room temperature, the black suspension centrifuged at 25,000 rpm and the supernatant was collected. In the reaction step, most oxidized GQDs changed to the amine-treated GQDs (A-GQDs).
(6) A rotary evaporator was used to concentrate the A-GQDs solution at 50 °C. Then by drying the solution in a vacuum oven, the dried A-GQDs powder was obtained. A-GQDs were properly dispersed in Distilled water using an ultrasonication probe (Sonics Vibra-Cell, VC 750, Sonics & Materials, Inc., USA) with a power supply of (20 kHz) frequency and output power of (750 W). It is noteworthy that synthesized GQDs are soluble in aqueous solution [36].

2.2. Characterization

The Characterization of the A-GQD dispersions was investigated using atomic force microscopy (AFM, ScanAsyst mode, frequency 1 Hz, Bruker). The thermal conductivity has been determined by a KD2 Pro thermal analyzer (Decagon Devices, USA). The thermal analyzer works according to transient of hot wire technique, and it has the accuracy of about 4%. The rheological behavior of water-based A-GQD nanofluids was determined using a shear-rate controlled Anton Paar rotational rheometer (model Physica MCR301, Anton Paar GmbH) based on the double gap DG 26.7 measuring system. The density of synthesized nanofluids as well as water was measured by Mettler Toledo DE-40 density meter. The accuracy of this device is $\pm 10^{-4}$ g/cm^3. All the density measurements performed in triplicate for each temperature.

In this study, UV–vis spectroscopy is also performed using Shimadzu UV-spectrometer (A Shimadzu UV-2600, Kyoto, Japan), which operates in the range of wavelengths 200–700 nm. The light absorbance of all the samples was determined at specific time intervals for more than 15 days using special quartz cuvettes suitable for UV region. In order to validate the accuracy and reproducibility of the UV–vis spectrophotometer results, each absorbance reading was repeated twice. The maximum difference in the results was about 0.05%. The Zeta potential tests on the synthesized nanofluids were performed using Zetasizer Nano ZS (Malvern Instruments Ltd, Malvern, UK) by the Electrophoretic Light Scattering (ELS) technique. The zeta potential results indicate that the degree of repulsion between adjacent particles is of the same charge in the dispersion.