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Stability investigation of water based exfoliated graphene nanofluids

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Abstract. Until now stability is a crucial technical challenge to prepare a homogeneous dispersion. The main purpose of this work is to experimentally investigate the suspension stability of the exfoliated Graphene (Gr) suspension in deionized water (DW) (Gr/DW). Five different samples were prepared by varying the exfoliated Gr volume fraction from 0.11 to 0.30 % in deionized water. For the observation of sedimentation photo capturing was used as a primary technique. Finally stability of the exfoliated Gr/DW nanofluids were monitored quantitatively with the aid of optical absorbance measurements using ultra violet-visible absorbance spectroscopy. The wavelength range of light was varied from 200 to 800 nm. Digital photographs of Gr/DW nanofluid samples after preparation of about 25 days shown homogeneous and visibly there was no sedimentation in the suspensions. The peak absorbance of Gr/DW nanofluids was appeared at the wavelength of 280 nm. For a certain volume fraction, absorbance was decreased monotonically with the increasing wavelength. The relative concentration of the Gr/DW samples was decreased due to slight agglomeration by the increasing concentration of precipitation with time. After 600 hours (~25 days), the lowest and maximum precipitation rate were appeared ~ 6 and ~ 10 % for the Gr/DW samples with the volume fraction of 0.11 and 0.30 % respectively. Different amount of exfoliated Gr loading affect the rate of sedimentations of exfoliated Gr/DW nanofluids.

1. Introduction

Stability is a crucial technical challenge to prepare a homogeneous dispersion because of the strong van der Waals interactions among the nanoparticles which always leading to the generation of aggregates. Sometimes sedimentation, clogging and aggregation phenomenon are the main cause for the stability of suspension which results in hampering of valuable properties of the suspension such as thermal conductivity and viscosity. There are some physical or chemical approaches such as surfactant addition, modification of particles surface or application of strong forces on the aggregated nanoparticles are implemented to achieve the stable nanofluids [1].

Even though, suspension stability of a nanofluid is an important concern for its application, there are inadequate studies on assessing the suspension stability of the nanofluids. Photo capturing is used as a primary technique to observe the sedimentation in nanofluids. Mehrali et al., (2014) [2] have investigated the Gr nanoparticle dispersed nanofluids by capturing the photos of the prepared different samples after 600 hours of preparation. Many other techniques such as, addition of surfactant [3], surface modification of Gr [4], chemical functionalization [5] and sonication [6] are commonly used for monitoring the suspension stability. However, these are not recommended techniques to monitor

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the stability of the nanofluids because of the consumption of longer time and qualitative accuracy of the stability results [7].

Ultra Violet-Visible (UV-Vis) spectrophotometer is the most widely used approach to estimate the rate or percentage of sedimentation of the nano-suspension [7]. It has been used to illustrate the colloidal stability of the nano-dispersions quantitatively.

At the wavelength from 200 to 800 nm, the UV-Vis spectrophotometer took the absorption by liquid and is used to analyze various dispersions in the fluid. Usually, stability of the suspension is determined by estimating the sediment concentration against the sedimentation time. However, for the high concentration (such as more than vol. 1%) this technique is shows some incompatibility for estimating dispersion stability of nanofluids [7, 8, 9].

2. Materials and Methods

Graphene nano-flakes were fabricated using a simple and direct technique sonication assisted liquid phase exfoliation (LPE) of graphite powder in organic solvent N-Methyl-2-Pyrrolidone (NMP). Preparation process and characterization are explained elsewhere [10]. After the dispersion of exfoliated Gr flakes in DW, it was bath sonicated using BRANSONIC ultrasonic cleaner for 10 minutes and then stirred about 1 hour using magnetic stirrer for the homogenization purpose. Gr/DW nanofluid samples were prepared by varying the Gr volume fraction in DW base fluid. Five different samples were prepared with the volume fraction of 0.10, 0.15, 0.20, 0.25 and 0.30 % of as produced Gr flakes.

2.1. Photograph Capturing

To see the sedimentation of produced Gr/DW nanofluid samples photo capturing was used as a primary technique. Some amounts of the suspension were to put aside after preparation to capture photos after a certain time. By comparing these photos of nanofluids, apparent sedimentation of suspension was observed.

2.2. Relative Stability Estimation by UV-vis Spectroscopy

The stability of the produced Gr/DW nanofluid samples were monitored quantitatively with the aid of optical absorbance measurements using UV-vis absorbance spectroscopy. The Beer-Lambert law (A = α IC) provides a linear relationship between an absorbance of light and the properties of a material through which light is passing. A is the absorbance, α is the absorption coefficient (ml mg⁻¹m⁻¹), 1 (m) the distance that light travel through material and C is the concentration (mg ml⁻¹) of absorbing types in the material. Beer-Lambert law shows that at fixed volume fraction optical path and absorptivity, the absorbency is relative to the percentage amount of the particles inside the suspension.

At the first step, just after preparation each type of nanofluid samples were scanned in UV-Vis spectrometer (Thermo Scientific, Multiskan GO, Version-1.00.40. 96-grid transparent micro-plates) at room temperature while each measurement was repeated three times to attain a better accuracy. The wavelength range of light was varied from 200 to 800 nm. Peak absorbance was identified for every sample to a certain wavelength. Then, standard graph was fit for the each type of samples with sample concentrations (C_0) against their corresponding peak absorbance's as the concentration of suspension has a linear relation with absorbance. At the last step, relative stability of the as prepared nanofluids was monitored with increasing sedimentation time. In this purpose, UV-Vis spectrometer scanning was conducted on the supernatant of each sample in about 5 days (120 hours) interval for 25 days (600 hours). Supernatant concentration (C) of the samples was estimated for the corresponding absorbance. The relative concentrations (C/C_0) of the samples were plotted against time.

3. Results and Discussion

3.1. Physical Appearance of Gr/DW nanofluids

Figure 1 shows the physical appearance of the exfoliated Gr dispersed Gr/DW nanofluids samples. Digital photographs in Figure 1(a-e) show the representative of Gr/DW samples after preparation of

about 25 days for the five different volume fractions. A homogeneous and uniform dispersion is acquired. It was apparent that there is no sedimentation in the suspensions.



Figure 1. Dispersions of exfoliated Gr dispersion in DW. For the volume fraction of: (a) 0.30, (b) 0.25, (c) 0.20, (d) 0.15 and (e) 0.11 %.

3.2. Stability Investigation of Gr/DW Nanofluids with UV-vis spectroscopy

Figure 2(a) shows the absorbance of exfoliated Gr dispersed Gr/DW nanofluids samples for different amount loading with the variation of wavelengths. The peak absorbance of Gr/DW nanofluids is appeared at the wavelength of 280 nm. For a certain volume fraction the UV-vis spectrum of these Gr/DW nanofluids is featureless with a monotonic decrease in absorbance with increasing wavelength. Moreover, the absorbance of Gr/DW nanofluids decreases with the decreasing amount of Gr in DW; it should be known that the increasing amount of Gr will increase the absorbance that refers to the better nanofluid dispersion.

Figure 2(b) shows the relationships between volume fraction of Gr nanofiller and the corresponding peak absorbance obtained on the Gr/DW samples. There is a good linear relationship between the absorbance and the volume fraction of Gr is perceived, which satisfies Beer's law and indicates that Gr flakes were dispersed well in the DW base fluid [2] (Mehrali et al., 2014).



Figure 2. (a) UV-vis spectrum of Gr dispersed Gr/DW nanofluids samples at different volume fractions and wavelengths; (b) Linear relationship between light absorption and volume fraction of Gr in DW at wavelength of 280 nm.

Using the linear relationship (as shown in Figure 2(b)); Figure 3 shows the relative stability of Gr/DW nanofluids at different loadings as a function of sedimentation time. From the results, it is observed that, the relative concentration of the Gr/DW samples is decreased due to slight agglomeration by the increasing concentration of precipitation with time. Higher loading of Gr in DW leads to more sedimentation. Various forces such as gravitational force on the particles, electrostatic force and van der Waals forces between particles are effect in the nanofluid [2] (Mehrali et al., 2014). It is seen that, within 120 hours (~5 days) concentration decreased by 0.22, 1.46, 2.42, 3.98 and 4.26 % for the

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samples with the Gr loading of 0.11, 0.15, 0.20, 0.25 and 0.30 % respectively. The rate of sedimentation after 600 hours (~25 days) is different among these five samples as different amount of Gr loading are imposed. After this period of time, the lowest precipitation rate is appeared ~ 6 % for the Gr/DW sample with the volume fraction of 0.11%, while maximum precipitation rate is seemed ~ 10 % for the Gr/DW sample with the volume fraction of 0.30 %. These results show that variation of Gr volume fraction in the nanofluids affect the rate of sedimentation, which agree well with the results of previous studies by Mehrali et al. (2014) [2].



Figure 3. Relative supernatant concentrations of DW based exfoliated Gr dispersed nanofluids (Gr/DW) as a function of sedimentation time.

4. Conclusion

Stability of the exfoliated Gr dispersed Gr/DW nanofluids have been successfully investigated. It is found that that volume fraction loading has the effect on the rate of sedimentation as well as properties. Higher loading of Gr in DW leads to more sedimentation. After 600 hours (~25 days), the lowest precipitation rate is appeared ~ 6 % for the Gr/DW sample with the volume fraction of 0.11%, while maximum precipitation rate is seemed ~ 10 % for the Gr/DW sample with the volume fraction of 0.30 %.

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