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An Aqua Based Reduced Graphene Oxide Nanofluids for Heat Transfer Applications: Synthesis, Characterization, Stability Analysis, and Thermophysical Properties

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Abstract- In the recent years, the engineered colloidal fluids called nanofluids plays a vital role in many heat transfer systems due to its excellent thermophysical properties, and heat transfer rate. However, most of the research studies purchased the nanomaterials from the suppliers and this involves higher cost which further increases the cost of the heat transfer devices. Hence, a low cost graphite powder is converted into reduced graphene oxide (rGO) and detailed characterizations have been done in this work. An aqua based rGO nanofluids with 0.0005, 0.001, and 0.002 wt. % is then prepared by two step method. The nanofluids are found to be stable up to 10 days because of oxygenated groups on the edge of rGO flakes. The rGO nanofluids show an enhancement in thermal conductivity and surface tension in comparison with the base fluid. Viscosity of nanofluids increases with concentrations and Newtonian behavior is also observed for all the tested concentrations.

Keywords Nanofluids, graphene, stability, thermophysical properties.

1. Introduction

Graphene – An atomically thin sheet of SP2 hybridized carbon in 2-D form and honeycomb lattice structure have identified as one of the new material in the recent years, mainly because of its exceptional thermal transport properties. The application of graphene can be found in many diverse areas such as batteries, chemical detectors, composite materials, etc. [1, 2]. However, a limited literature is available in heat transfer applications with graphene based nanofluids [3, 4]. In general, graphene behaves as hydrophobic and hence, the stability of graphene based nanofluids is poor. On the other hand, graphene with functional groups called reduced graphene oxide (rGO) has better stability due to the hydrogen bonding in water medium [5]. Also, the thermal conductivity of rGO (with the order of hundreds of W/m K) is higher than common conductive materials such as aluminum and copper [6]. This powerful merit can be utilized in preparing rGO flakes through reliable and feasible synthesis methods. Hence, the rGO is believed to be an influential candidate in solar applications. A number of research work is seen in flat plate solar collectors [7 – 12]. However, the working fluid in their experimens were water. On the other hand, the nanofluids are used in solar collecters by Subramaniyan et al. [13] and Ajay et al. [14]. They found better performance as compared with conventional fluids. Since the thermal conductivity of rGO is much better than metal/metal oxide nanomaterials, the rGO will be a promising one for the solar collectors.

Although one step method has better stability than two step method, the most of the studies used two step method for the preparation of nanofluids [13, 15]. This is mainly because of its simplicity in preparing the nanofluids and low cost. However, the dispersion stability of the formulated nanofluids must be ensured with different stability analysis viz. Isoelectric Point (IEP), sedimentation, and Zeta potential [5]. Kwark et al. [16] found that the pH value of different nanofluids is far away from the IEP and hence, they are colloidally stable. Recently, Kamatchi et al. [5] evaluated the dispersion stability of aqua based rGO nanofluids by sedimentation analysis and found to be stable even after 7 days.

The thermophysical properties such as thermal conductivity, surface tension, density, and viscosity of nanofluids influence the heat transfer performance and hence, they are found either experimentally or analytically by different research groups [14, 15]. Thermal conductivity shows an enhancement with concentrations and/or temperature. This is due to the Brownian motion of nanoparticles in base fluid [17]. Kim and Kim [18] concluded the density of nanofluids and base fluid is same and similar results are also reported by various authors [19, 20]. Recently, viscosity of nanofluids is considered as one of the major factor in heat and fluid flow problems. With regard to the viscosity of nanofluids, most of the research work showed an enhancement in viscosity with concentrations. However, the viscosity decreases with the increase of temperature [5, 21]. On the other hand, a negligible change in viscosity between base fluid and nanofluid is observed by Kwark et al. [16]. The surface tension of rGO nanofluids increases with concentrations and temperature. Further, it is reported that the Van der Wall force is the main reason for the observed enhancement [5].

Synthesis of nanomaterial is an effective way to minimize the cost involved for the procurement [22]. In the present study, the rGO flakes are synthesized from the commercially available graphite powder. Various studies are conducted in order to confirm the prepared rGO. It is then dispersed in Millipore water to obtain the different concentrations such as 0.0005, 0.001, and 0.002 wt. % respectively. Further, its stability and thermophysical properties are analyzed.

2. Experimental Methods

2.1 Synthesis of rGO

In the present study, graphite powder, concentrated sulfuric acid, ethanol, hydrogen peroxide, hydrazine, potassium permanganate, sodium nitrate, and sodium borohydride are directly purchased from the supplier (Merck, India) and used as procured without purification. The preparation of rGO flakes is followed in two steps, which is shown in Fig. 1.

2.1.1 Conversion of graphite into graphite oxide

Graphite oxide (GO) is synthesized from graphite by the most widely used method called modified Hummer method [23]. Graphite (5 g), concentrated sulphuric acid (200 ml), and sodium nitrate (2.5 g) are poured in a glass vessel and stirred for about 20 min. After that, the glass vessel is placed in a beaker containing ice cubes and successively, potassium permanganate (12 g) is added under constant stirring. The reaction is continued for another 30 min. Once, the glass vessel is removed from the beaker containing ice cubes, it is placed in a magnetic stirrer and the process is continued for 48 h at room temperature. It is seen that the mixture becomes pasty with a brownish color. Now, 250 ml of Millipore water is added and the solution is agitated for about 15 min. Successively, 350 ml of hot water of about 50°C and hydrogen peroxide (25 ml) are added. The color of the diluted solution is turned to brilliant yellow. The solution is undergone centrifuged followed by washing with HCl, water and ethanol for several times to remove ions and impurities. The powder is then kept in a vacuum at 60°C for periods of 40 h to get dry GO.

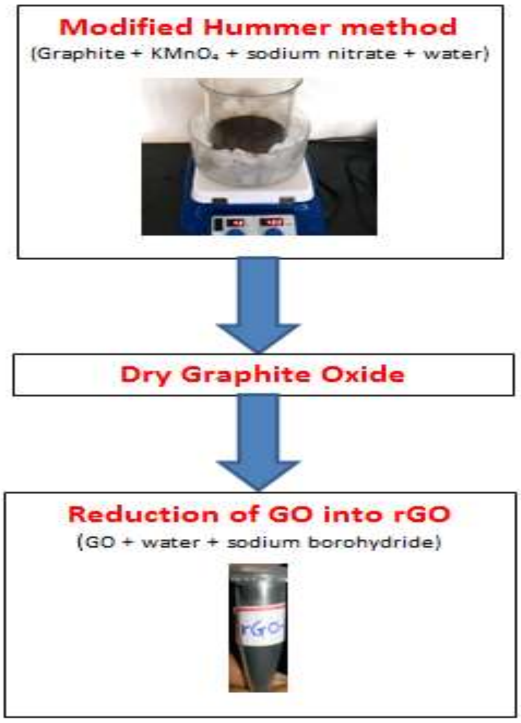

Fig 1. Synthesis of rGO

2.1.2 Reduction of GO into rGO

The equal amount of hydrazine solution (98%) and GO solution are mixed in a beaker and the suspension is added with ammonia solution during constant stirring in order to adjust the pH of the solution is by ~10. The reduction process is then held at 60°C for 18 h. After that, the flakes are taken away with filtration. Finally, the rGO is cleaned with water for several times and placed in an oven at 80°C to obtain dry flakes. Various characterization techniques are used to study the size, thickness, number of layers, oxygenated groups and are explained in results and discussion.

2.2 Preparation and Thermophysical Properties of rGO-Water Nanofluids

Fig. 2 depicts the methodology of preparation, stability and thermophysical properties of aqua based rGO nanofluids. As a first step, 1 mg/ml concentration of rGO-water solution with 35 ml in quantity is prepared by dispersing the flakes in Millipore water using two step method.

Fig. 3 shows the rGO-water solution after keeping in an ultrasonic bath of about 1 h. It is then divided into 5, 10, and 20 ml and added with the appropriate quantity of base fluid to prepare 0.0005, 0.001, and 0.002 wt. % concentrations of aqua based rGO nanofluids. An ultrasonic homogenizer and probe sonicator is used to sonicate the nanofluids of about 3 h to obtain stable nanofluids. After that, various studies on stability have been conducted to find the possibility of using this in heat transfer applications and discussed in sec. 3.2.

The thermophysical properties of nanofluids play an essential role for enhancing the performance of heat transfer devices. Therefore, they are measured as a part of the present investigation. The density is measured by a specific gravity bottle. A KD2 Pro analyzer (accuracy: ±5%) is used for the measurement of thermal conductivity of nanofluids.

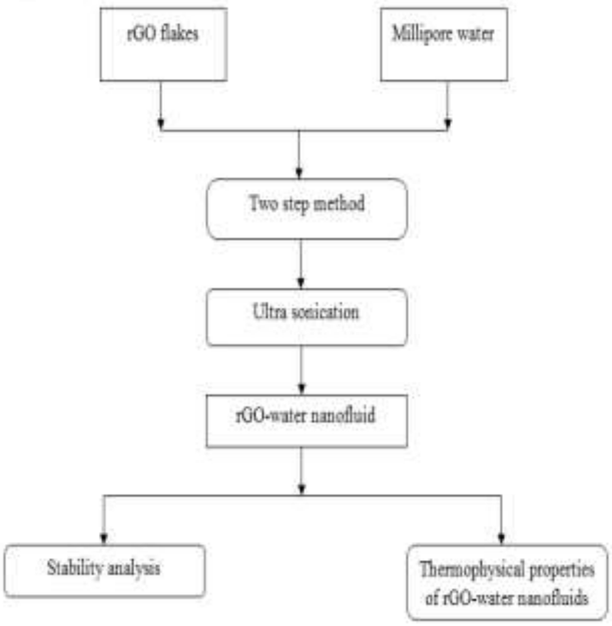

Fig 2. Methodology of preparation of rGO nanofluids

The dynamic viscosity of base fluid and all the tested concentrations are measured by Brookfield DV-II + Pro viscometer (accuracy: ±1%). Surface tension is measured using SITA dynotester (SITA process solutions, Germany; resolution: 0.1%).

Fig 3. Photographic image of aqua based rGO nanofluid

3. Results and Discussion

3.1 Characterization of rGO

Fig. 4 represents the XRD patterns of graphite, GO, and rGO, which is obtained by Rigaku Ultima IV with CuK*α* radiation (λ= 0.154 nm). Graphite exhibits a 2θ value of about 26.4°. In the case of GO, a new typical diffraction peak appears at 2θ = 10.7°, mainly because of insertion of oxygenated functionalities and water molecules during synthesis. For rGO, a new peak is obtained at 2θ = 25.03°. This ensures a smaller crystallite size of rGO in single and/or multilayer structure with oxygenated or functional groups [24]. Using Bragg's law, the d–spacing between the layers is calculated and is found to be respectively 0.337, 0.825, and 0.355 nm for graphite, GO, and rGO. Since the d-spacing value of rGO is low, the reduction of GO to rGO is confirmed.

$$d = \frac{n\lambda}{2\sin\theta} \quad (1)$$

where n – integer, λ - wave length of incident wave (nm), θ - angle between scattering planes and incident ray (°).

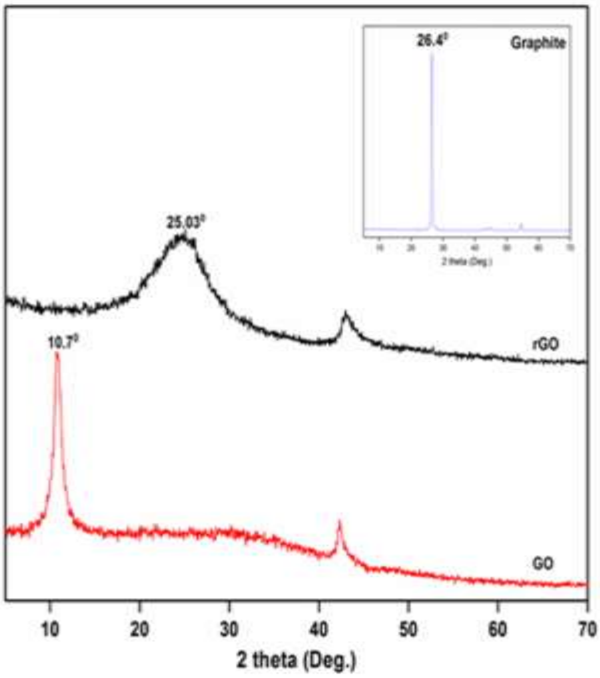

Fig 4. XRD of graphite, GO and rGO

Raman spectroscopy is the powerful tool for ascertaining the structural defects in various carbon based materials. Fig. 5 shows the D, G, and 2D band at 1328, 1573, and 2658 cm^{-1} respectively. The D band is generally termed as defective bond and its location exhibits structural defects in the rGO structure. Also, it is said to be monolayer graphene when the D band appears at 1350 cm^{-1}, reported by Kamatchi et al. [5]. In this study, the peak appears at 1328 cm^{-1}, resulting less structural defects. The in-plane crystallite size (L_a) of rGO flakes is determined using the Eq. (2) and found as 2.35 nm which is in agreement with Subrahmanyam et al. [25]. It is noted that the intensity ratio (I_G/I_D) is calculated after the baseline correction.

$$L_a = 4.4\ (I_G/I_D) \quad (2)$$

where I_D – intensity of D band, I_G – intensity of G band.

Chakrabarti et al. [26] suggested that the rGO has a chance of 7 to 10 layers when the 2D band appears above 2700 cm^{-1}. In Fig. 2 (b), the 2D appears at 2658 cm^{-1} and hence, we confirmed that the synthesized rGO may have 2 to 6 layers. On the other hand, the ratio between I_D and I_G is greater than 1 and thus the existence of some oxygen groups on the edge of the flakes is confirmed [27].

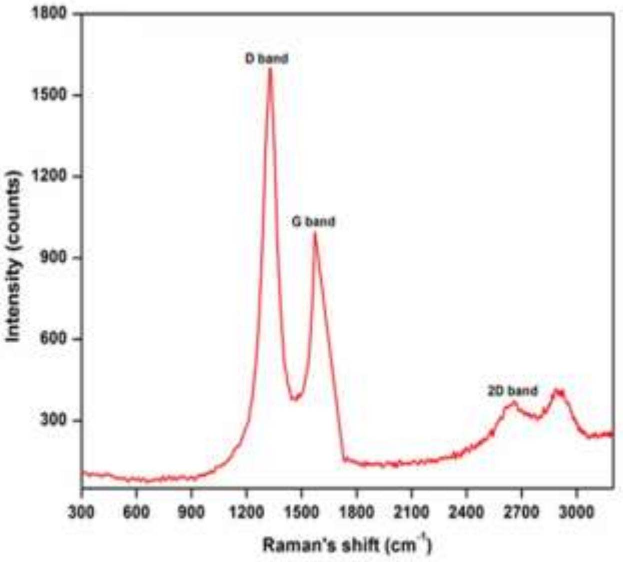

Fig 5. Raman spectrum of rGO

The flakes are then characterized by FT-IR – the most widely used tool for identifying the presence of functional groups (Fig. 6). Absorption bands corresponding to C-O stretching at 1089 cm^{-1}, C-OH stretching peak appears at 1160 cm^{-1}, phenolic O-H deformation vibration exhibits at 1439 cm^{-1}, C=C stretching occurs at 1631 cm^{-1}, C=O carbonyl stretching at 1653 cm^{-1}, and O-H stretching vibration appears at 3432 cm^{-1}.

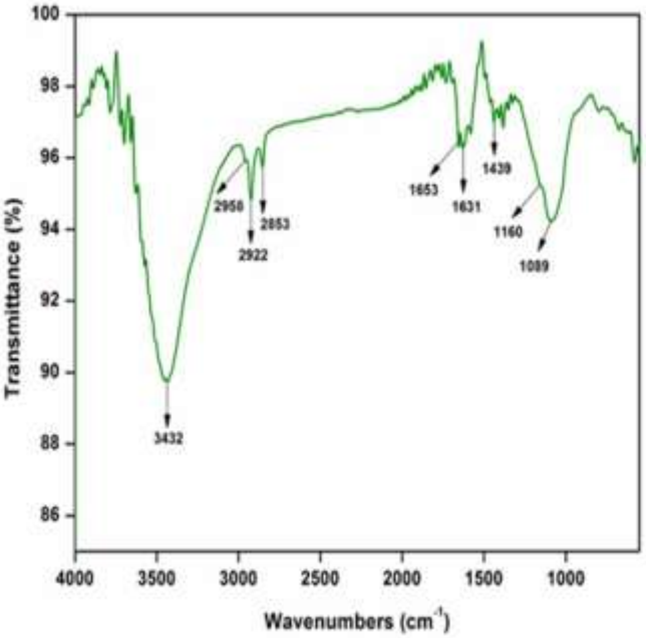

Fig 6. FT-IR pattern of rGO

Additionally, one CH3 and two CH2 - peaks occur at 2958, 2922, and 2853 cm^{-1} respectively [27, 28]. Hence, the presence of OH and C-OH groups on the surface of rGO flakes is evident. In addition, the hydrogen bonding formation aids high dispersion in base fluid and hence, the stability of nanofluids is good.

The SEM image of rGO flakes at a different magnification level is depicted in Fig.7. A curled surface morphology and a wrinkled paper-like structure of rGO is seen, which confirms the successful exfoliation of GO into rGO. Moreover, the rGO forms a porous like structure since the curled and wrinkled flakes stacked together disorderly.

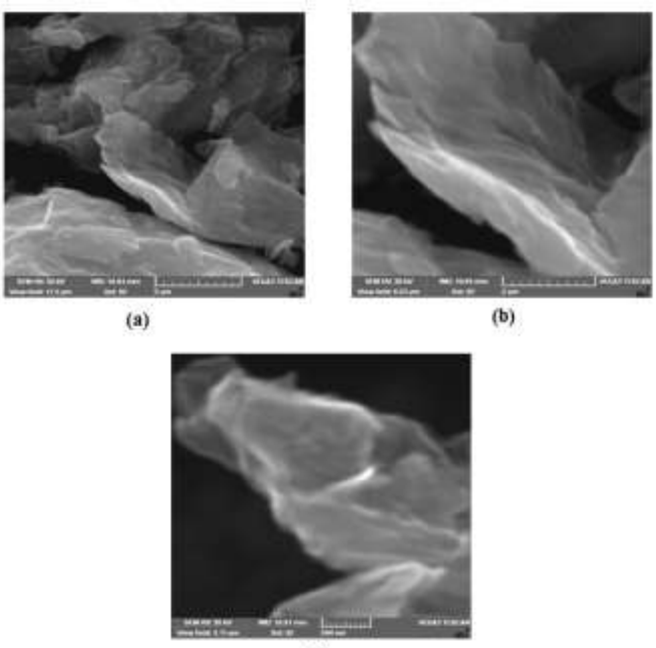
(a) (b) (c)

Fig 7. SEM image of rGO at different magnification level

The surface morphology and thickness are further analyzed by atomic force microscopy (AFM), shown in Fig. 8. The size of the flakes is found to be 200 nm and the thickness is approximately 4 nm, which is greater than the thickness of monolayer graphene (0.7 nm) [29]. Therefore, this indicates formation of few layers of rGO sheets, which is in accordance with SEM micrographs and Raman Spectroscopy.

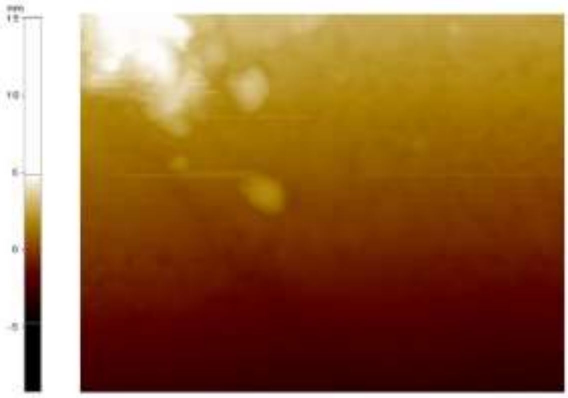

Fig 8. AFM image of rGO

3.2 Stability and Thermophysical Properties of Nanofluids

Kamatchi et al. [5] stated that the stability and thermophysical properties of nanofluids are the major factor, which needs to be investigated before using it in heat transfer applications. Further, they reported the stability depends on its Isoelectric point (IEP) value. If the pH of nanofluids is far away from IEP, they have good stability. Based on this, pH value of aqua based rGO nanofluids is measured using a pH meter after 5th day of preparation. Three trials are performed for each concentration and the average value of pH is respectively ~7.36, ~7.51, and ~7.72 for 0.0005, 0.001, and 0.002 wt. % of rGO-water nanofluids. It is found that they are far away from the IEP of reduced graphene (~4.7), confirming the nanofluids have better stability. The maximum concentration (0.002 wt. %) is chosen in the sedimentation study rather than conducting tests for all the concentrations. Interestingly, no sedimentation is seen for a period of 10 days. A traceable sedimentation is observed from 11th day onwards and the flakes settle at the bottom of the glass tube after 15 days. Hence, it is confirmed that the prepared nanofluids found to be stable for 10 days due to the oxygenated groups at the edge of the flakes, as evident from FT-IR spectroscopy. Further, this oxygenated group helps the flakes to disperse in Millipore water [30].

The thermophysical properties of rGO and base fluid are shown in Table. 1. It is seen that an appreciable increase in thermal conductivity and surface tension with concentrations. Also, there is no significant increase in viscosity with concentrations.

Table 1. Thermophysical properties of Millipore water and rGO-water nanofluids at 36˚C.

Properties	**Milli-pore water**	**0.0005 wt. %**	**0.001 wt. %**	**0.002 wt. %**
Thermal conductivity (W/m K)	0.6084	0.6105	0.6165	0.6178
Density (kg/m^3)	996.43	994.58	993.42	993.12
Surface tension (mN/m)	71.6	71.9	72.4	72.7
Dynamic viscosity (mPa s)	0.679	0.683	0.685	0.686

Fig. 9 depicts the ratio of nanofluid properties to the base fluid for different concentrations, measured at 36˚C. The average of three different trails is used for the measurement of properties. Thermal conductivity shows an enhancement with concentrations due to the Brownian motion of rGO flakes in base fluid [17]. It is seen that all the tested concentrations exhibit Newtonian behavior and no significant enhancement in viscosity is observed between base fluid and nanofluids. However, there is an increase in viscosity with concentrations, which is in agreement with Kamatchi et al. [5]. Similarly, surface tension increases with rGO concentrations. This is due to the Van der Walls force between the accumulated particles at the liquid-gas interface [5]. Though density of rGO water nanofluids decreases with concentrations, the changes between the concentrations are negligible.

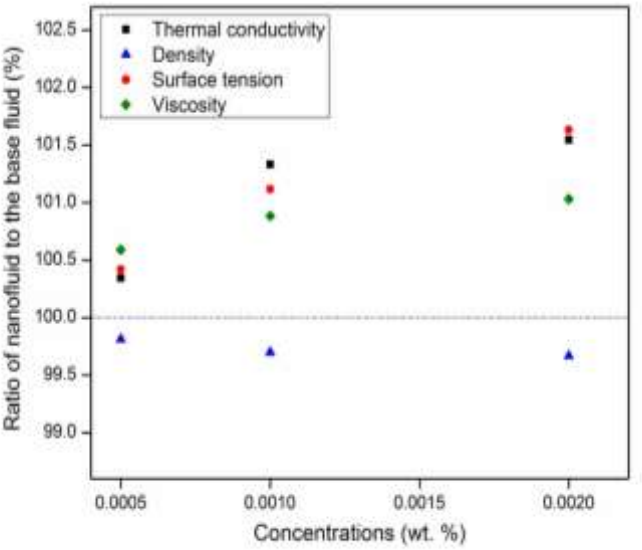

Fig 9. Thermophysical properties of rGO

4. Conclusion

It is widely accepted that the use of nanofluids improves the performance of heat transfer devices. However, the stability of nanofluids and cost involved for the procurement of nanomaterial is the biggest challenge for the research community. It is up to our knowledge that a very few authors used graphene based nanofluids. Hence, this paper presents the new way of synthesizing the reduced graphene oxide nanomaterial for heat transfer applications. The surfactant free rGO is synthesized using low cost method and various characterization techniques confirmed the thus prepared rGO. The aqua based rGO nanofluids reveal that they are stable for a period of 10 days because of the existence of oxygenated groups at defect sites. Due to the Brownian motion of flakes in base fluid, the thermal conductivity of rGO-water nanofluids showed better enhancement than base fluid. The viscosity of nanofluids showed no significant enhancement and all the concentrations exhibit Newtonian behavior. Surface tension increases with concentrations due to the Vander Walls force between the accumulated particles at the liquid-gas interface. Therefore, it is recommended that the aqua based rGO nanofluids will be a better replacement of conventional based fluids with considerable reduction in cost of purchasing the nanomaterials.

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