Thermal and viscosity properties of inhomogeneous fluids with suspended graphene nanoparticles

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Abstract

The use of nanofluids in a wide variety of applications is promising, but poor suspension stability of nanoparticles in the solution hinders the further development of nanofluids applications. The present study aims to provide a fundamental understanding of the thermal and viscosity properties of inhomogeneous fluids with suspended graphene nanoparticles. A graphite material is exfoliated to form graphene particles, and the effect of nanoparticle volume fraction on the material properties of inhomogeneous fluids with suspended graphene nanoparticles is investigated at different temperatures or under oxidation conditions. Particular emphasis is placed upon the effect of nanoparticle volume fraction on the material properties of inhomogeneous fluids with suspended graphene nanoparticles. The results indicate that the bottom-up approach produces low quantities with high quality and large flakes whereas the top-down approach yields a high concentration of suspended flakes with a low yield of mono-layer graphene. Smaller dispersions result in ease of addition of graphene to other desirable emulsions to enhance the uniform coating matrix for protection attributes graphene can provide to the coating. The pressure drop allows the liquid precursor to flow and homogenizes the pass-through liquid of the liquid precursor that contains thin layers of graphene. The phonon Raman scattering changes are correlated with structural changes and defects associated with the hydroxyl and epoxy groups in the basal plane and a variety of alkyl and oxygen-containing functional groups terminating the edges. Graphene-containing nanofluids provide several advantages over the conventional fluids, including thermal conductivities far above those of traditional solid-liquid suspensions, a nonlinear relationship between thermal conductivity and concentration, strongly temperature-dependent thermal conductivity, and a significant increase in critical heat flux. Stability of the nanoparticle suspension is especially essential for practical industrial applications. Introduction of nanoparticles to the fluid changes density, thermal conductivity viscosity, and specific heat. The functionalization process decreases enhancements in thermal conductivity due to formation of surface oxides. In development of nanofluids for heat transfer a fine balance needs to be obtained between increases in thermal conductivity and viscosity.

Keywords: Graphene; Nanoparticles; Thermal properties; Viscosity properties; Fluids; Graphite

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1. Introduction

Graphene has better electrical conductivity [1, 2], thermal conductivity [3, 4], and mechanical strength than such metals as copper and aluminum [5, 6], and exhibits optically transparent nature [7, 8]. Graphene has a structure of stacking honeycomb layers. In order to maintain ideally the characteristics, it should be formed with single layer and have large area. Graphene has such good characteristics, so it is suitable for semiconductors [9], nuclear fusion reactors [10], base material of secondary batteries [11], base material of clear electrodes for displays and cellphones [12], and it is expected that applications of graphene will be broadened [13, 14]. In particular, since graphene has good electrical conductivity and transparency, it is an ideal material for transparent electrodes of display devices.

Chemical vapor deposition is a general method for manufacturing large-area graphene [15, 16]. However, there have been difficulties in commercializing the manufacturing method because it requires high-cost despite of low productivity [17, 18]. Nevertheless, research for applying graphene to transparent electrodes is widely progressed [19, 20], because graphene manufactured by chemical vapor deposition is suitable for transparent electrodes of displays and cellphones which require high conductivity and visible ray transparency [21, 22]. On the other hand, graphene having single layer and large area has not only good electrical conductivity but also good thermal conductivity [23, 24]. However, it has low thermal capacity because it is thin. Therefore, graphene is difficult to use as a heat radiator for radiating high heat.

Graphite having a graphene structure is suitably applicable to heat radiators [25, 26]. Graphite has a structure of stacking honeycomb layers and is abundant in nature. In recent years, graphite is widely applied to heat radiators for electrical devices [27, 28]. However, there are many technical difficulties in acquiring the same characteristics of graphene from the natural graphite [29, 30]. Graphite must be exfoliated to be thin and large-area, in order to have characteristic of thermal radiation similar to graphene [31, 32]. More specifically, for the sake of using graphite as a heat radiator, it is required to make the graphite powder as thin and wide as possible and manufacture the heat radiator using the graphite powder in such a large volume as to appropriately maintain the temperature of the heat radiator [33, 34]. A conventional method of manufacturing graphite powder is mechanically grinding graphite into fine powder [35, 36]. Another method is a chemical method that involves oxidizing graphite powder at high temperature to obtain an expanded graphite structure [37, 38]. However, there are technical limitations in obtaining graphite powder as thin and wide as graphene according to the mechanical grinding method or the chemical method.

Since graphite powder for heat radiator as manufactured by the mechanical grinding method depends on the particle size of the graphite, the shape of particle is generally irregular and similar to stone fragments. Generally, the graphite powder manufactured by the mechanical grinding method is used as its particle size is 40 microns or less [39, 40]. As such, the graphite powder mechanically ground has various advantages that high density is guaranteed when it is spread or molded and that the size of particle can be controlled according to its use purpose [41, 42]. However, it is difficult to control the thickness of the particle, that is, the thickness of a honeycomb layer, which is stacked layer by layer [43, 44]. Also, the method has the advantage that proportion of pores is low owing to high density [45, 46]. On the other hand, the method has the disadvantage that electrical conductivity and thermal conductivity decrease with an increase in the contact resistance between powder particles.

The chemical method of manufacturing graphite powder for heat radiator using oxidation-reduction reaction has advantage in terms of high productivity [47, 48]. However, it has such a disadvantage that it may cause environmental pollution [37, 38]. Further, it is difficult to produce high purity graphite because of poor manufacturing environment [39, 40]. Graphite oxidized under high temperature condition by the chemical method become powder that is bulky and has very low density in the case of expansion. This powder form of graphite is used as a sheet for heat radiation of electronic devices. The expanded graphite powder of which particle size is 300 microns or less is mainly used for heat radiation purpose [41, 42]. The expanded graphite powder is microscopically similar to bellows in shape. Macroscopically, the expanded graphite is cotton-shaped and light-weighted [33, 34]. However, when the graphite powder expands in volume by the oxidization process under high temperature condition, the gaps between layers crack like bellows to generate many pores [35, 36]. Therefore, the particles of the expanded graphite powder are bigger and thinner than those of the graphite powder manufactured by grinding natural graphite. Consequently, the expanded graphite powder has high electronic conductivity and thermal conductivity [49, 50] but contains many pores between particles to cause deterioration in the thermal conductivity.

In order to solve such a problem as deterioration in the characteristics of the expanded graphite powder caused by the abundance of pores, there have been applied improvement methods such as compressing the expanded graphite powder with high pressure or using the expanded graphite powder in combination with a graphite powder of small particle size or a conductive metal powder [39, 40]. Those methods, however, have an insignificant effect of improving the characteristics [39, 40]. For the sake of making efficient heat radiators using a graphite material, it is required to exfoliate the graphite material as thin and wide as possible to secure good characteristics in terms of electrical conductivity and thermal conductivity as similar to graphene and also to adopt a method of minimizing generation of pores that greatly deteriorate electrical conductivity and thermal conductivity [27, 28]. In particular, the conventional methods such as the mechanical grinding method and the chemical method have technical difficulties in obtaining a graphite powder thin and, wide like graphene [27, 28] and limitations in solving the problem with the abundance of pores between particles.

Currently, the application thickness of the graphite powder is normally 25 microns or greater for radiant sheets used to radiate heat from cellphones and one millimeter or greater for radiant sheets used to radiate heat from electronic devices [41, 42]. In order to reduce the thickness of the radiant sheets used for those electronic devices and enhance the efficiency of heat radiation, it is necessary to make the graphite powder thin and wide and minimize the existence of pores between the particles of the graphite powder [41, 42]. For this purpose, there is a demand for a technique to exfoliate the graphite powder thin and wide like graphene [51, 52]. Contrived in consideration of the problems, it is necessary to provide a method for manufacturing graphene and a method for manufacturing a conductor that solve the problems regarding insufficient exfoliation of the graphite powder and deterioration in the electrical conductivity and thermal conductivity caused by the small particle size [53, 54]. It is also necessary to provide a method for manufacturing graphene and a method for manufacturing a conductor that solve the problem regarding deterioration in the electrical conductivity and thermal conductivity caused by the pores existing between the particles and the environmental problem [55, 56]. It is therefore of great importance to provide a method for manufacturing graphene and a method for manufacturing a conductor that improve the characteristics of the graphite material, in comparison with the conventional methods such as the mechanical grinding method and the chemical method.

Conventional heat transfer fluids play an important role in many industries including power generation, chemical production, air conditioning, transportation, and microelectronics. However, their inherently low thermal conductivities have hampered the development of energy-efficient heat transfer fluids that are required in a plethora of heat transfer applications. However, the heat transfer properties of these conventional fluids can be significantly enhanced by dispersing nanometer-sized solid particle and fibers, namely nanoparticles, in fluids. This new type of heat transfer suspensions is known as nanofluids. Such nanofluids may be engineered by dispersing metallic or nonmetallic nanoparticles in traditional base fluids. The thermal conductivity of heat transfer fluids can be enhanced by adding highly conductive particles. Depending on the application, nanofluids are generally classified such as heat transfer nanofluids, anti-wear nanofluids, metalworking nanofluids, coating nanofluids, and chemical nanofluids. Nanofluids can significantly improve heat transfer characteristics compared with the base fluids. Nanofluids have the potential to improve heat transfer and energy efficiency in thermal systems in applications such as microelectronics, power electronics, transportation, nuclear engineering, heat pipes, refrigeration, air-conditioning, and heat pump systems. The use of nanofluids in a wide variety of applications is promising, but poor suspension stability of nanoparticles in the solution hinders the further development of nanofluids applications. The present study aims to provide a fundamental understanding of the thermal and viscosity properties of inhomogeneous fluids with suspended graphene nanoparticles. Particular emphasis is placed upon the effect of nanoparticle volume fraction on the material properties of inhomogeneous fluids with suspended graphene nanoparticles.

2. Methods

A technical feature of the method for manufacturing graphene is that the method includes exfoliating or transferring a graphite material onto at least one structure to form graphene particles on the surface of any one of the at least one structure, releasing the graphene particles from the structure, and combining the released graphene particles to form graphene. The step of forming graphene particles includes: exfoliating the graphite material onto a first structure of the plural structures to form first graphene particles on the surface of the first structure; and transferring the first graphene particles to a second structure disposed opposite to the first structure out of the plural structures to form second graphene particles. The step of forming graphene particles may include exfoliating or transferring the graphite material onto the surface of rollers used as the structures to form the graphene particles, the rollers being different in diameter from each other and rotating in contact with each other. Preferably, the step of forming graphene particles may include exfoliating or transferring the graphite material onto the surface of rollers and a plate used as the structures to form the graphene particles, the rollers being different in diameter from each other and rotating in contact with each other, the plate moving in a linear reciprocating motion in contact with the rollers. The step of forming graphene particles includes: applying the graphite material between first and second structures making a pair out of the plural structures; exfoliating the graphite material onto the first and second structures to form first graphene particles on the surface of the first and second structures, respectively; and transferring the first graphene particles to third and fourth structures disposed opposite to the first and second structures out of the plural structures, respectively, to form second graphene particles on the surface of the third and fourth structures, respectively. The step of forming graphene includes injecting an adhesive liquid for constraining the released graphene particles and then applying pressure on the released graphene particles to combine the graphene particles. An adhesive layer for exfoliation, transfer or release of the graphene particles may be provided on the surface of the structure. A rubber elastomer may be applied or mounted as the adhesive layer on the surface of the structure. The rubber elastomer may be silicone rubber. The method may further include applying the graphite material together with an adhesive liquid or solid onto the structure. A technical feature of the method for manufacturing a conductor is that the method includes: applying or forming the graphene manufactured by the graphene-manufacturing method on a sheet or a film to make an electrical conductor or a thermal conductor.

In the present study, the term nanofluid describes a homogeneous dispersion of at least a nanomaterial with at least one dimension in a nanoscale in a conventional base fluid. In the present study, the nanomaterial refers to graphene-based compounds or composites. The present study relates to a nanofluid characterized in that it comprises a liquid medium selected from an organic solvent or a water solution of acidic, neutral or basic compounds and said liquid medium optionally comprising a surfactant, and a graphene-based compound or composite, homogenously dispersed in the liquid medium, and the graphene-based compound or composite optionally comprising a material associated to the graphene-based compounds. The term graphene-based compound or composite refers herein to graphene, graphene oxide, reduced graphene oxide or a combination thereof forming either compounds or composites with any other molecule, polymer or solid phase in extended or nanoparticulate form. The graphene-based compound of the nanofluid is in a nanoparticle volume fraction between 0.0008 percent and 0.008 percent based on the total weight of the electroactive nanofluid. Nanofluids are prepared by direct mixing of the graphene-based compound or composite and the liquid medium. The graphene-based compound or composite optionally comprises substances either attached to the graphene-based compounds or forming a mixture by dispersion in the base fluid. The nanofluid may further comprising carbon materials such as activated carbons or carbon nanotubes aside from graphene. Each of these present specific advantages such as low cost or anisotropy which expand the possible applications of the nanofluids. Graphene oxide is synthesized from natural graphite using the modified Hummers method. Graphene oxide nanosheets exhibits pores in mesopores as well as macro-porous region. Enhancements in the thermal conductivities of nanofluids, for the most part, follow the predictions based on Maxwell's mean field theory assuming low concentrations and spherical nanoparticles or the effective medium theory. Thermal conduction in nanofluids is attributed to a variety of mechanisms, including Brownian motion interactions between the nanoparticles and the fluid, clustering and agglomeration. There is no clear consensus on a specific mechanism; however, the general belief is that a combination of mechanisms may be operating and would be specific to a nanoparticles-fluid system and test conditions. Further, the effect of interface layers on the nanoparticles on thermal conductivity is not clearly understood. A metal particle with surface oxidation, for example, continuously increases the interfacial resistance and consequently reduce the thermal conductivity. Some of these nanofluids also can include a surfactant additive to stabilize particle suspensions. Because thermal conductivity of surfactants is very poor compared to water, often more preferred water-based nanofluids are comprised of functionalized graphene wherein as received graphene is treated by oxidation, such as by mixing with concentrated sulfuric and nitric acids. Such oxidized, or functionalized, graphene is disposed in fluids without need of surfactants to achieve greatly improved thermal properties for the nanofluids.

3. Results and discussion

The scanning electron micrographs are illustrated in Figure 1 for the graphene that solves the problems regarding insufficient exfoliation of the graphite powder and deterioration in the electrical conductivity and thermal conductivity. Graphite is a stack of graphene sheets bound by van der Waals interactions, each graphene layer being made ofsp^2 carbons distributed in a hexagonal crystal structure. Graphene has superior mechanical, electrical, and thermal properties. In bottom-up methods to produce graphene, for example, chemical vapor deposition, graphene is synthesized. In top-down methods, for example liquid-phase exfoliation, graphene sheets are separated from bulk graphite material. The bottom-up approach produces low quantities with high quality and large flakes. The top-down approach using graphite is low in cost and yields a high concentration of suspended flakes, but fabricates limited-size sheets with a low yield of mono-layer graphene. Existing commercially available graphene products usually contains precipitates of graphene due to the presence of thick layers of graphene and are not stable. The method of the exfoliation of graphene from graphite using multilayer coextrusion is described herein. Graphite is dispersed within a first processing material, and the first processing material and a second processing material are co-extruded through a plurality of series coupled layer multiplication dies to exfoliate graphene from the graphite. The graphene is separated from the resulting multi-layered material. Graphite flake and expanded graphite may be dispersed within the first processing material. The process uses an organic solvent and silica under high pressure sheer force to create a liquid intermediate containing thin layers of graphene that allows for easy dispersion of graphene in a liquid organic solvent system. High sheer processing of graphene and silica together in a liquid organic solvent system result in stable graphene platelets. During the process, thick layers of graphene can break down to smaller layers of graphene that is more usable. The silica forms a gel simultaneously as graphene platelet multiple stacks are sheered into smaller platelet stacks through the organic solvent carrier. The small platelet stacks are dispersed in the gel and held by the network of the gel stably. In the process, both a graphene raw material and silica are mixed in an organic solvent to form a liquid precursor. Preferably, the graphene raw material is a graphene powder. The graphene raw material may be obtained commercially. Commercially available graphene usually contains thick layers. Thus, when commercially available graphene is used as an additive or is added to a liquid product, the commercially available graphene may precipitate in the liquid product.

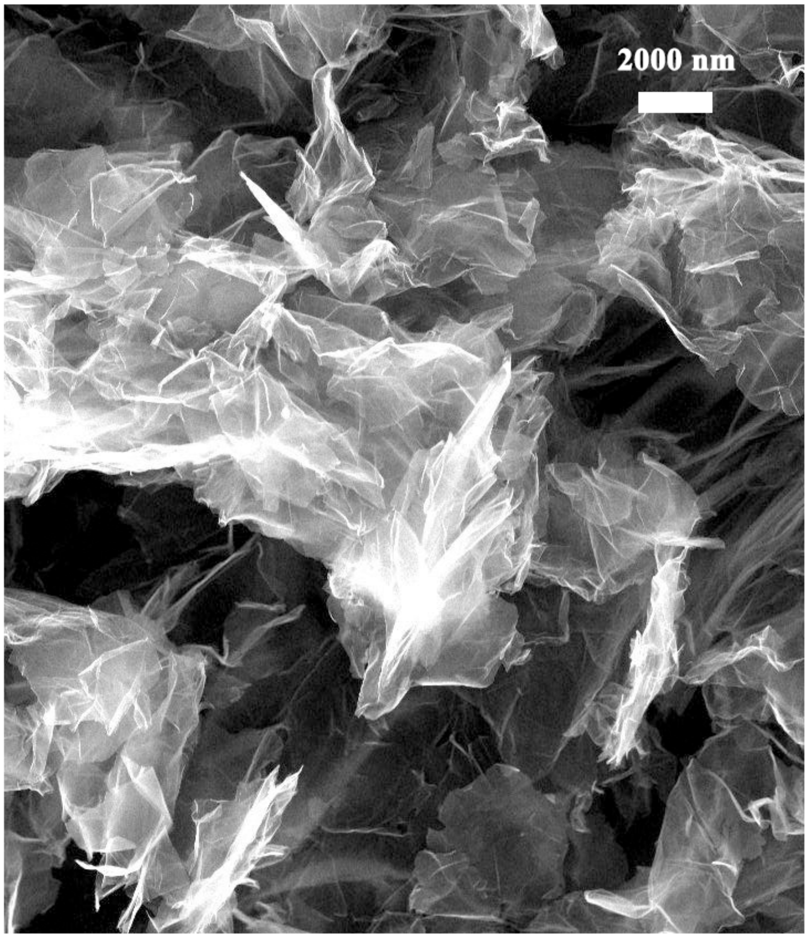

Figure 1. Scanning electron micrographs of the graphene that solves the problems regarding insufficient exfoliation of the graphite powder and deterioration in the electrical conductivity and thermal conductivity.

The high-resolution scanning electron micrographs are illustrated in Figure 2 for the graphene that solves the problems regarding insufficient exfoliation of the graphite powder and deterioration in the electrical conductivity and thermal conductivity. The raw graphene powder can contain graphene nanoparticles consisting of stacks of graphene sheets having a platelet shape. The graphene particles may have an average thickness of about 6-8 nm and a typical surface area of about 80 to 200 square meters per gram. The graphene particles have an average particle diameter of about 8-20 microns. Graphene nanoplatelets may have naturally occurring functional groups like ethers, carboxyl, or hydroxyls that can react with atmospheric humidity to form acids or other compounds. These functional groups are present on the edges of the particles and their weight fraction varies with particle size. The liquid precursor is a suspension containing graphene solids. The amount and concentration of the graphene raw material liquid precursor can depend on the desired amount, concentration, and use of the resultant product of the process. A smaller distribution of graphene, for example, from about 0.05 percent by weight to about 60 percent by weight relative to the total weight of a liquid dispersion containing the graphene, would more easily disperse at the submicron level in the liquid dispersion, when compared to a greater weight fraction of graphene in the liquid dispersion. Smaller dispersions result in ease of addition of graphene to other desirable emulsions, for example, to enhance the uniform coating matrix for protection attributes graphene can provide to the coating. A non-limiting example of the silica that can be used is fumed silica. Silica fume is an ultrafine powder collected as a by-product of the silicon and ferrosilicon alloy production. It may consist of amorphous spherical particles with an average particle diameter of about 80-280 nm, for example, about 200 nm, without the branching of the pyrogenic product. The concentration of silica, for example, fumed silica, can be in the range of about 0.08 percent by weight to 28 percent by weight in the liquid precursor or any subrange thereof, for example, about 0.2-20 percent by weight, about 3-6 percent by weight, or about 4-6 percent by weight. A concentration of fumed silica in the range of about 0.2-20 percent by weight can modify nonpolar solvents to have a viscosity of higher than 80 Sabol seconds, for example, to form ringing gels.

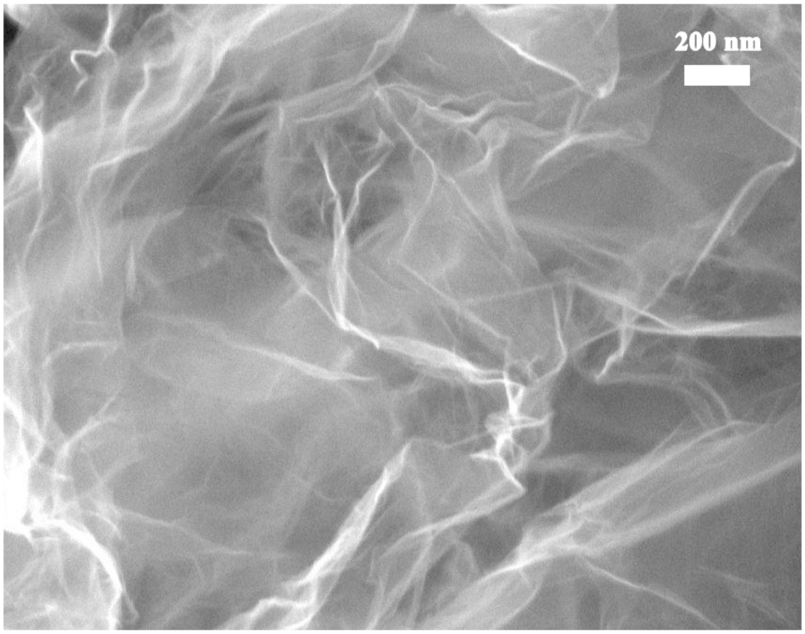

Figure 2. High-resolution scanning electron micrographs of the graphene that solves the problems regarding insufficient exfoliation of the graphite powder and deterioration in the electrical conductivity and thermal conductivity.

The high-resolution transmission electron micrographs are illustrated in Figure 3 for the graphene that solves the problems regarding insufficient exfoliation of the graphite powder and deterioration in the electrical conductivity and thermal conductivity. The organic solvent preferably has a viscosity of less than 80 Sabol seconds. Non-limiting examples include nonpolar organic solvents. The metal cylinder may be pressed against the flat metal plate by an extreme pressure. The pressure applied on the metal cylinder may be in the range of about 2000-6000 psi. This high pressure ensures graphene sheers to a stable form in the resultant nonpolar liquid dispersion. A pressure of below about 2000 psi leads to a wider platelet particle size distribution curve and larger stacks of graphene platelets, which will settle in the non-polar dispersion. The liquid precursor may be forced through an opening on the flat metal plate. The liquid precursor may then pass between the metal cylinder and the flat metal plate. The pumping pressure applied on the liquid precursor may be higher than the pressure between the metal plate and metal cylinder such that the feed of the liquid precursor can be directed through the opening and then between the metal cylinder and the flat metal plate. When the liquid precursor passes between the metal cylinder and the flat metal plate, the thick layers of graphene may be broken into thin layers by the high shear pressure between the metal cylinder and the flat metal plate. The greater the pressure between the metal cylinder and the flat metal plate, the smaller the graphene platelet particle size. When the liquid precursor is directed, for example, forced by the pumping pressure, through the opening on the flat metal plate and between the metal cylinder and the flat metal plate, and then exits from between the metal cylinder and the flat metal plate, the pressure on the liquid precursor drops significantly. This pressure drop allows the liquid precursor to flow and homogenizes the pass-through liquid of the liquid precursor that contains thin layers of graphene such that the smaller graphene platelet particle is well dispersed in the resultant fluid product. The greater the pressure drop is, the greater the level of homogenization. The process thus reduces the particle size of the graphene and creates more uniform graphene platelets. Further, when the liquid precursor passes between the metal cylinder and the flat metal plate, fumed silica undergoing sheer pressure may swell and expand in the nonpolar solvent to form a gel comprising a three-dimensional structure and with a higher rheology and viscosity than the organic solvent. The viscosity of the resultant silica gel can range from about 200,000 to about 600,000 centistokes. The graphene platelet particles are dispersed in the three-dimensional network of the silica gel and held therein stably in the silica gel matrix. The organic solvent keeps the graphene particles apart from each other in the silica web, breaking up the Van der Waals forces between them, so that the graphene particles do not aggregate and maintain their thin layers of two-dimensional configuration. When the graphene suspension additive is added to a product, such as a painting or coating, and when the product is applied on to a surface and allowed to dry, the organic solvent may evaporate, and upon evaporation of the solvent, the graphene nanoparticles can come together in the polymeric matrix of the silica gel and other components, thus strengthening the coating. The graphene can keep metals at uniform temperatures.

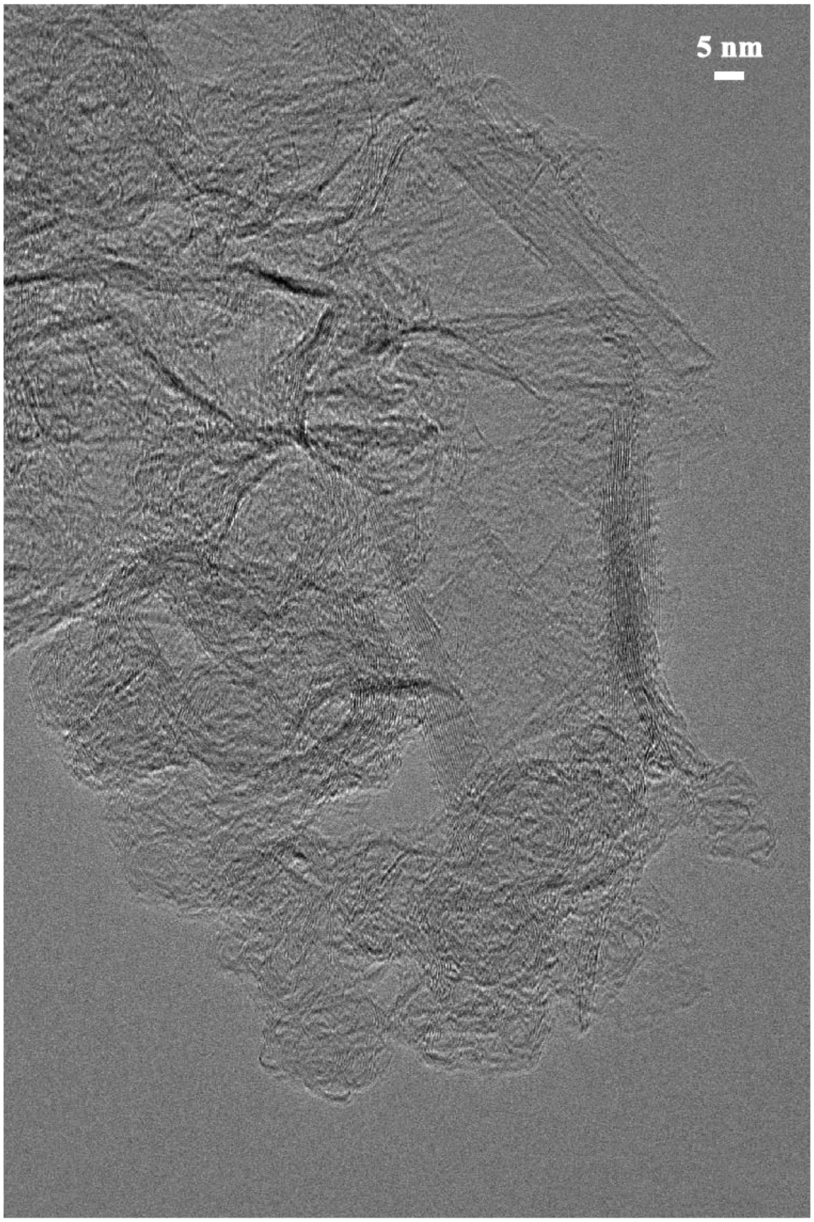

Figure 3. High resolution transmission electron micrographs of the graphene that solves the problems regarding insufficient exfoliation of the graphite powder and deterioration in the electrical conductivity and thermal conductivity.

The Raman spectra are illustrated in Figure 4 for the graphene that solves the problems regarding insufficient exfoliation of the graphite powder and deterioration in the electrical conductivity and thermal conductivity. These laser-induced graphene features may be characterized by the presence of a distinct 2D-band in the Raman spectra. This can be fit with a single Lorentzian and is very similar to that observed for single layer exfoliated graphene and epitaxial graphene. The 2D mode results from a two-phonon resonant scattering process and is normally considered an overtone of the defect mediated D-band. The 2D feature is always observed with widths defined by the thickness and stacking order along the c-axis. For single layer graphene, a single Lorenztian line shape centered at 2690 per centimeter can indicate electronic structure that is dominated by Dirac-Weyl dispersion. It is therefore accepted as one of better optical signatures regarding the presence of graphene. It is different than that from highly oriented pyrolytic graphite. Specifically, the G-band is much broader and blue shifted, there is a strong D-band at 1345 per centimeter, and the 2D-band is nearly absent. These changes are correlated with structural changes and defects associated with the hydroxyl and epoxy groups in the basal plane and a variety of alkyl and oxygen-containing functional groups terminating the edges. The 2D-band is observed and there is a narrowing of the G-band as well as diminution of the D-band. When using nitrogen background gas, the 2D-band is further enhanced, the G-band is much narrower and the D-band is nearly removed. Formation of the 2D-band and G-band narrowing also occurs. However, the D-band feature, though reduced relative to untreated graphene, remains independent of the laser flux. This indicates an intrinsic difference in the defect density and material quality relative to that formed using continuous-wave excitation. When using 355 nm photons, the 2D-band is produced at the lowest powers and the integrated D and 2D peak intensity ratio is about 0.8-2.0. Though sample surface non-uniformity causes variability, this ratio remains close to 0.8 even at the highest power. On the contrary, the integrated D and 2D peak intensity ratio is usually dependent on the power when using 532 nm photons and discernable 2D-band features are not evident. The 355 nm light excites single-photon mediated valence-to-conduction band transitions. This produces electron-hole plasmas in the material at all pulse energies studied. Since at least two 532 nm photons are required to exceed the band-gap, a coherent multiphoton or incoherent multiple photon process may be required to create a similar electron-hole plasma. This is consistent with the 532 nm 2D-band formation threshold of 2.8 megawatts per square centimeter which is below the pre-ablation threshold of graphite.

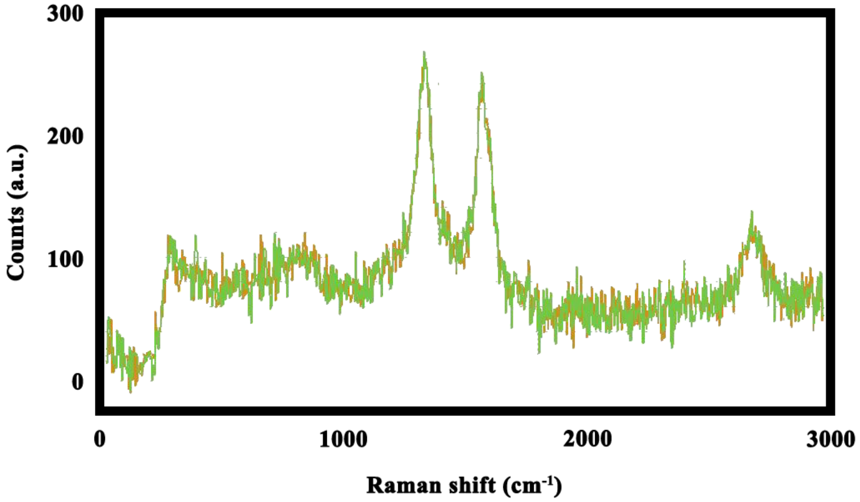

Figure 4. Raman spectra of the graphene that solves the problems regarding insufficient exfoliation of the graphite powder and deterioration in the electrical conductivity and thermal conductivity.

The effect of temperature on thermal conductivity of the graphene in purified water is illustrated in Figure 5 for which the material consists of stacks of graphene sheets having a platelet shape. The quest for thermal systems that are more efficient in removing heat is never ending, with design improvements of heat exchangers being one of the main areas of focus. Water is the working fluid of choice for years for several reasons; it is clean, readily available and has fairly good thermal properties for heat removal. Over a century ago, micro-sized particles with high thermal conductivity are used as a way to increase the thermal characteristics of working fluids [57, 58]. However, micro-sized particles can be abrasive and can precipitate out due to their higher density. Once the nanoparticles settle, the nanofluid loses its property enhancement. Nano-sized particles introduced into a base liquid are also used and called nanofluids. This concept of using copper, aluminum, or carbon nanoparticles to create colloidal suspension fluids has been accepted as a new avenue for enhancing the thermal characteristics [59, 60]. Since heat transfer can be enhanced due to particle size and dispersion isometry, the key technical challenge in implementing this technology is to understand the fundamental physics responsible for enhancing the transport of heat, which can lead to the knowledge-based development of a stable nanofluid with maximum thermal conductivity. Due to the necessity of compact thermal management systems, many researchers have begun to investigate the benefits of the nanofluids on the heat transfer in the thermal management system [61, 62]. Scientists have reported varying degrees of increase in thermal performance with the addition of the nanoparticles to the thermal fluid [63, 64]. The earlier studies are primarily on the enhancements of the thermal conductivity [65, 66]. Most studies report very good enhancements of the thermal conductivity even with small volume percent concentrations [67, 68]. Researchers have investigated the addition of nanoparticles made of highly conductive materials such as aluminum, carbon, diamond, and copper with varying positive results [69, 70]. Many prior researchers have focused on the use of copper oxide nanoparticles to form the nanofluid due to the favorable thermal properties of copper oxide powders [71, 72]. However, nanofluids formed with copper oxide suffer from several drawbacks that can impede its commercial use in a thermal management system [73, 74]. For example, fluids containing copper oxide nanoparticles have a tendency to mix with and retain air and oxygen within the fluid, which adversely affects the thermal properties of the fluid and can create problems in the thermal system [75, 76]. Additionally, the copper oxide nanoparticles tend to agglomerate and stick to the container of the fluid in the thermal system, which can lead to impairment and fouling of fluid flow in the system [77, 78]. In the present study, the nanofluid includes graphene nanoparticles suspended in a base liquid at a nanoparticle concentration in the nanofluid of about 0.008 percent by volume. Graphene nanoparticles are an excellent method to improve thermal conductivity in water. Graphene-containing nanofluids provide several advantages over the conventional fluids, including thermal conductivities far above those of traditional solid-liquid suspensions, a nonlinear relationship between thermal conductivity and concentration, strongly temperature-dependent thermal conductivity, and a significant increase in critical heat flux. Each of these features is highly desirable for thermal systems and together makes nanofluids strong candidates for the next generation of heat transfer fluids. The observed substantial increases in the thermal conductivities of nanofluids can have broad industrial applications and can also potentially generate numerous economic and environmental benefits. Enhancement in the heat transfer ability could translate into high energy efficiency, better performance, and low operating costs. The need for maintenance and repair can also be minimized by developing a nanofluid with a better wear and load-carrying capacity. Consequently, classical heat dissipating systems widely used today can become smaller and lighter, thus resulting in better fuel efficiency, less emission, and a cleaner environment. Nanoparticles of various materials can be used to make heat transfer nanofluids, including copper, aluminum, copper oxide, alumina, titania, and graphene. Of these nanoparticles, graphene shows greatest promise due to their excellent chemical stability and extraordinary thermal conductivity.

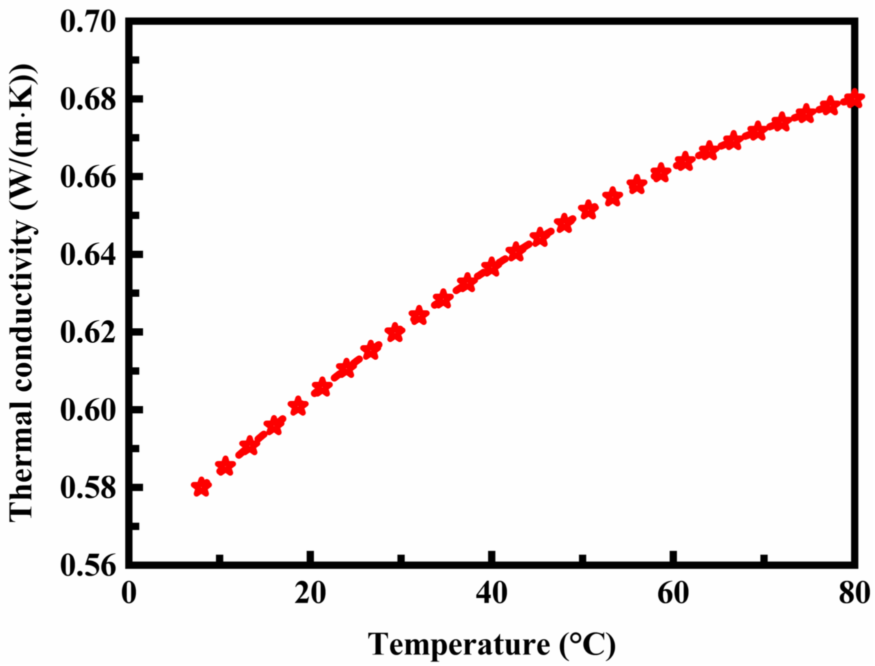

Figure 5. Thermal conductivity of the graphene in purified water at different temperatures for which the material consists of stacks of graphene sheets having a platelet shape.

The effect of nanoparticle volume fraction on the thermal conductivity enhancement ratio is illustrated in Figure 6 for the nanofluid with suspended graphene nanoparticles. Improved thermal conductivity enhancement of 4.8 percent or more can be achieved with only a 0.008 percent volume fraction of graphene nanoparticles. Despite those extraordinary promising thermal properties exhibited by graphene suspensions, it remains to be a serious technical challenge to effectively and efficiently disperse graphene into aqueous or organic mediums to produce a nanoparticle suspension with a sustainable stability and consistent thermal properties. Due to hydrophobic natures of graphitic structure, graphene is not soluble in any known solvent. They also have a very high tendency to form aggregates and extended structures of linked nanoparticles, thus leading to phase separation, poor dispersion within a matrix, and poor adhesion to the host. However, stability of the nanoparticle suspension is especially essential for practical industrial applications. Otherwise, the thermal properties of a nanofluid, such as thermal conductivity, will constantly change as the solid nanoparticles gradually separate from the fluid. Accordingly, there is a great need for the development of an effective formulation which can be used to efficiently disperse different forms of graphene into a desired heat transfer fluid and produce a nanofluid with a sustainable stability and consistent thermal properties. Therefore, the nanofluid may comprise a conventional heat transfer fluid, graphene nanoparticles, metal oxide nanoparticles and a surfactant. The metal oxide nanoparticles in combination with the surfactant are used to facilitate the dispersion of the graphene nanoparticles and to increase the stability of the nanofluid. There is a charge attraction between the nonpolar region of the surfactant molecules and the graphene nanoparticles. This interaction forms a shell around the graphene nanoparticles, with the charged head region of the surfactant molecules oriented towards the outside. This facilitates the dispersion of the graphene nanoparticles in the fluid thus preventing precipitation from the fluid, which in turn enhances thermal conductivity. To further enhance thermal conductivity, metal oxide nanoparticles are also added to the thermal transfer fluid. These positively charged metal oxide nanoparticles repel one another and further enhance stability and thermal conductivity of the nanofluid. The term surfactant refers to a molecule having surface activity, including wetting agents, dispersants, emulsifiers, detergents, and foaming agents. A variety of surfactants may alternatively be included in the present study as a dispersant to facilitate uniform dispersion of nanoparticles in a desired thermal transfer fluid, and to enhance stabilization of such a dispersion as well. Typically, the surfactants used in the present study contain a lipophilic nonpolar hydrocarbon group and a polar functional hydrophilic group. The polar functional group may be a carboxylate, ester, amine, amide, imide, hydroxyl, ether, nitrile, phosphate, sulfate, or sulfonate. The surfactants that are useful in the present study may be used alone or in combination. Accordingly, any combination of surfactants may include anionic, cationic, nonionic, zwitterionic, amphoteric and ampholytic surfactants, so long as there is a net positive charge in the head regions of the population of surfactant molecules. In most instances, a single negatively charged surfactant is used in the preparation of the nanofluids of the present study.

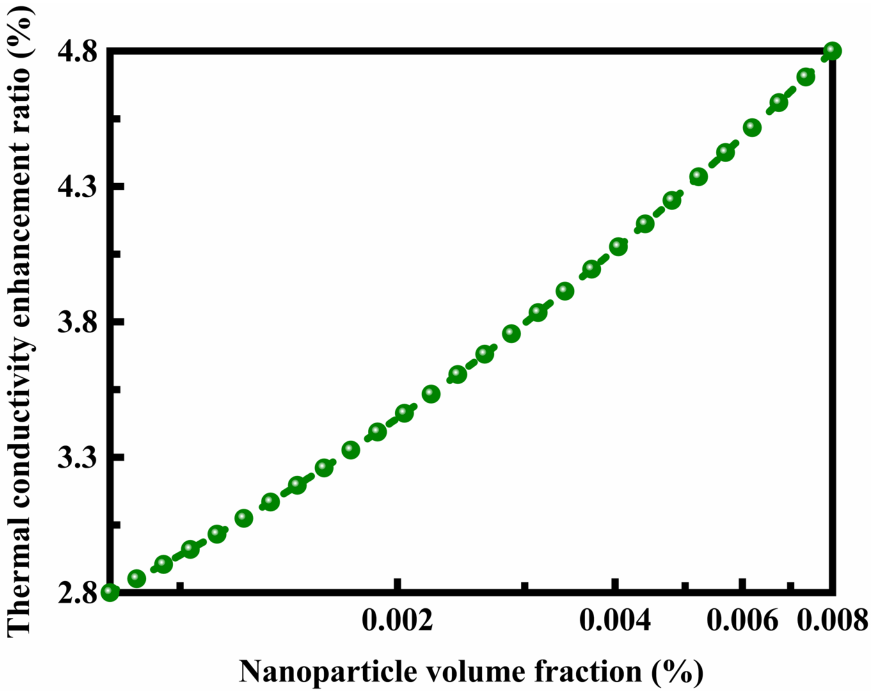

Figure 6. Thermal conductivity enhancement ratio of the nanofluid with suspended graphene nanoparticles at different nanoparticle volume fractions.

The effect of nanoparticle volume fraction on the viscosity enhancement ratio is illustrated in Figure 7 for the nanofluid with suspended graphene nanoparticles.

Production of metal containing nanofluids faces some major challenges, such as stability towards agglomeration and surface oxidation, availability, cost of materials and manufacturing issues. Dramatic increases in thermal conductivity of nanofluids are most likely due to the unique nature of such highly anisotropic graphene nanomaterials that allows engaging multiple heat transfer mechanisms in suspensions, arising from the effective medium theory, percolation, and plasmon resonances. The drawback of carbonaceous nanofluids with high aspect ratio particles is very high viscosity, up to about 14 percent higher than viscosity of the base fluid. Such viscosity increases result in pumping power penalties that are much higher than the benefits in thermal conductivity of suspensions. Industrial applications for nanofluid technology are in an embryonic state. However, today, the nanofluid field has developed to the point where it is appropriate to look to the next level, namely nanofluids that show substantial heat transfer enhancement over their base fluids and are candidates for use in a variety of industrial and commercial systems. For example, potential use of nanofluids for cooling systems such as power electronics and also for radiators in vehicles, will require not only enhanced thermal properties, but also minimal negative mechanical effects of the nanofluids in a closed system. In this regard, reduced viscosity of the nanofluid for instance is a contributing factor to reducing pumping power needed for the circulation of the nanofluid. Since the cooling efficiency of the heat transfer fluids is the main consideration in the current nanofluid development, the ratio of heat transfer coefficients for the suspensions and the base fluid is estimated for fully developed, laminar and turbulent flow regimes using conventional fluid dynamic equations. The ratio of heat transfer coefficients is a convenient measure for comparison of two fluids flowing in the same geometry and at the same flow rates. In a laminar flow regime, the heat transfer coefficients are proportional to the thermal conductivity, but in a turbulent flow regime the heat transfer coefficients depend on a set of thermo-physical properties. Introduction of nanoparticles to the fluid changes density, thermal conductivity viscosity, and specific heat of the fluid. In the case of hydrodynamically and thermally fully developed laminar flow, the heat transfer coefficient is proportional to the thermal conductivity, and within the acceptable range of inlet and outlet temperature difference is independent of the flow velocity. The comparison of two liquids flowing in fully developed turbulent flow regime over or through a given geometry at a fixed velocity reduces to the ratio of changes in the thermo-physical properties. Suspensions with larger diameter and thickness of nanoparticles provide the highest increase in thermal conductivity; however, viscosity increase of up to about 14 percent makes this fluid impractical for heat transfer applications. The optimization of viscosity and thermal conductivity increases in nanofluids is required for development of practical nanofluid with advanced heat transfer. Segregation of surfactants at liquid-nanoparticle interface creates additional thermal resistance for heat flow. Thus, organic surfactants are detrimental for the thermal conductivity of water-based suspensions. Use on non-surfactant approach to stabilizing dispersions of nanoparticles involves an additional surface functionalization step as described hereinafter.

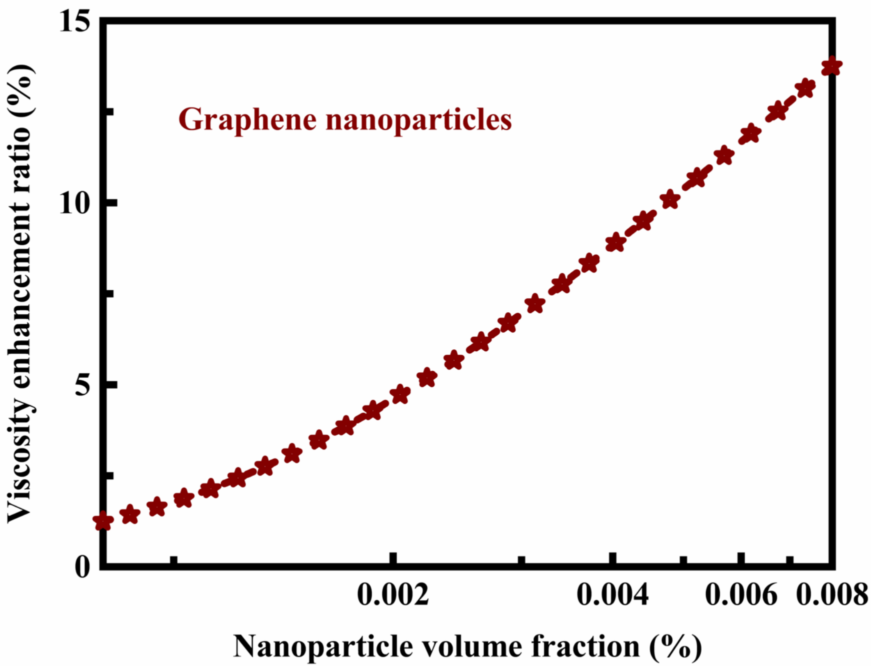

Figure 7. Viscosity enhancement ratio of the nanofluid with suspended graphene nanoparticles at different nanoparticle volume fractions.

The effect of nanoparticle volume fraction on the viscosity enhancement ratio is illustrated in Figure 8 for the nanofluid with suspended graphene oxide nanoparticles.

Surface functionalization can convert oxidized sp^2 graphitic layers into a variety of hydroxy- and carboxylic ionic groups. These groups can carry electrostatic charge and are miscible with water-based fluids. Thus, core-shell structures of graphitic gore and graphene oxide shell are formed. On one hand, surface oxidation helps increasing the stability and decreasing viscosity of nanofluids; but, on the other hand, thermal conductivity of graphene oxides is much smaller than that of graphite and graphene. Therefore, the functionalization process decreases enhancements in thermal conductivity due to formation of surface oxides. In development of nanofluids for heat transfer a fine balance needs to be obtained between increases in thermal conductivity and viscosity. For graphitic nanoparticle suspensions, advanced thermal conductivity is observed when nanoparticle percolation threshold is achieved. The concentration of the percolation threshold will vary with particle morphology, and both platelet diameter and thickness are important for that matter. Besides the important role of surface charges in nanoparticle agglomeration and viscosity of nanofluids, particle shape effect can also play a role in abnormally increased viscosity of graphitic nanofluids. Shear rate dependence of viscosity in suspensions indicates some restriction in fluid movement due to particle alignment and agglomeration. In a steady state, a rod-like particle or elongated agglomerate can have two types of motion due to the Brownian movements: rotational motion around the mid-point, and translational motion in parallel or perpendicular to the long axis. When the average spacing between particles is much larger than the longest dimension of the particle, the rotational and translational motions are not restricted by each other; hence very weak shear thinning behavior is expected. In suspensions of cylinders with higher volume fractions nanoparticles start to interact, so the viscosities at zero shear rate can be much greater than the base fluid viscosity and be very sensitive to the shear. At concentrations of nanomaterials that are significantly above the percolation threshold, an extended microstructure will be created in a nanofluid, obstructing the fluid flow and producing high viscosities. Such enhancements are possible with graphitic nanoparticles that are commercially available at reasonable costs. Surface chemistry and functionalization provides better dispersion stability, lower viscosity, and higher thermal conductivity, enhanced performance with temperature.

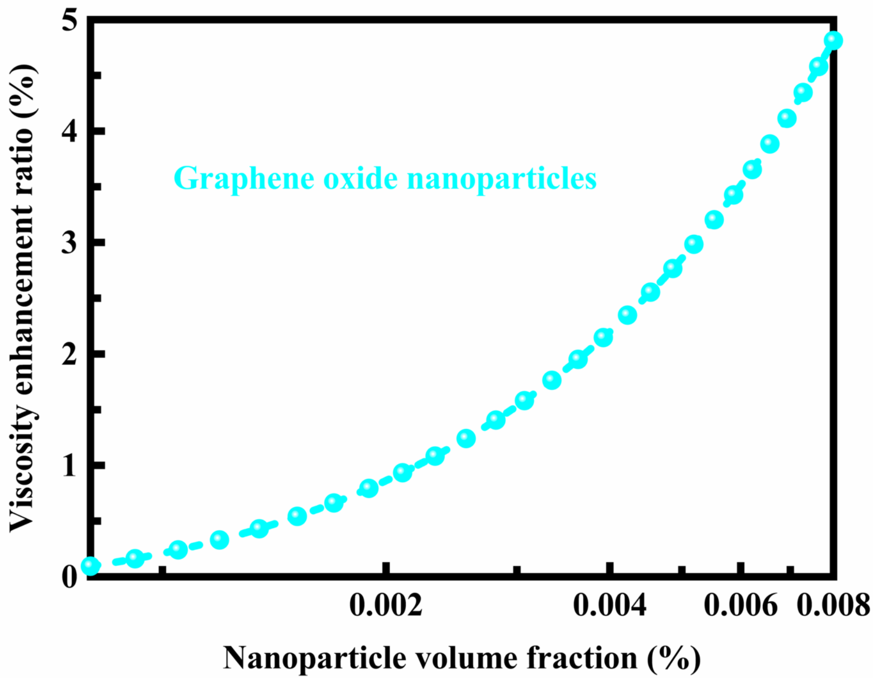

Figure 8. Viscosity enhancement ratio of the nanofluid with suspended graphene oxide nanoparticles at different nanoparticle volume fractions.

4. Conclusions

A graphite material is exfoliated to form graphene particles, and the effect of nanoparticle volume fraction on the material properties of inhomogeneous fluids with suspended graphene nanoparticles is investigated at different temperatures or under oxidation conditions. The present study aims to provide a fundamental understanding of the thermal and viscosity properties of inhomogeneous fluids with suspended graphene nanoparticles. Particular emphasis is placed upon the effect of nanoparticle volume fraction on the material properties of inhomogeneous fluids with suspended graphene nanoparticles. The major conclusions are summarized as follows:

- The bottom-up approach produces low quantities with high quality and large flakes. The top-down approach using graphite is low in cost and yields a high concentration of suspended flakes, but fabricates limited-size sheets with a low yield of mono-layer graphene.
- Smaller dispersions result in ease of addition of graphene to other desirable emulsions to enhance the uniform coating matrix for protection attributes graphene can provide to the coating.
- The pressure drop allows the liquid precursor to flow and homogenizes the pass-through liquid of the liquid precursor that contains thin layers of graphene such that the smaller graphene platelet particle is well dispersed in the resultant fluid product.
- The phonon Raman scattering changes are correlated with structural changes and defects associated with the hydroxyl and epoxy groups in the basal plane and a variety of alkyl and oxygen-containing functional groups terminating the edges.
- Graphene-containing nanofluids provide several advantages over the conventional fluids, including thermal conductivities far above those of traditional solid-liquid suspensions, a nonlinear relationship between thermal conductivity and concentration, strongly temperature-dependent thermal conductivity, and a significant increase in critical heat flux.
- Stability of the nanoparticle suspension is especially essential for practical industrial applications.
- Introduction of nanoparticles to the fluid changes density, thermal conductivity viscosity, and specific heat.
- The functionalization process decreases enhancements in thermal conductivity due to formation of surface oxides. In development of nanofluids for heat transfer a fine balance needs to be obtained between increases in thermal conductivity and viscosity.

References

1. M. Trushin and J. Schliemann. Minimum electrical and thermal conductivity of graphene: A quasi-classical approach. *Physical Review Letters* , Volume 99, Issue 21, 2007, Article Number: 216602.
2. Y.V. Skrypnyk and V.M. Loktev. Electrical conductivity in graphene with point defects. *Physical Review B* , Volume 82, Issue 8, 2010, Article Number: 085436.
3. M.N. Esfahani, M. Jabbari, Y. Xu, and C. Soutis. Effect of nanoscale defects on the thermal conductivity of graphene. *Materials Today Communications* , Volume 26, 2021, Article Number: 101856.
4. A. Alofi and G.P. Srivastava. Thermal conductivity of graphene and graphite. *Physical Review B* , Volume 87, Issue 11, 2013, Article Number: 115421.
5. M. Taghioskoui. Trends in graphene research. *Materials Today* , Volume 12, Issue 10, 2009, Pages 34-37.
6. F. Guinea, B. Horovitz, and P.L. Doussal. Gauge fields, ripples and wrinkles in graphene layers. *Solid State Communications* , Volume 149, Issues 27-28, 2009, Pages 1140-1143.
7. A.S. Thampy, M.S. Darak, and S.K. Dhamodharan. Analysis of graphene based optically transparent patch antenna for terahertz communications. *Physica E: Low-dimensional Systems and Nanostructures* , Volume 66, 2015, Pages 67-73.
8. D.H. Shin, Y.-J. Kim, S.-K. Lee, S. Bae, and S. Ahn. Atomically thin alkane passivation layer for flexible and transparent graphene electronics. *Applied Surface Science* , Volume 612, 2023, Article Number: 155695.
9. F. Arca, J.P. Mendez, M. Ortiz, and M.P. Ariza. Strain-tuning of transport gaps and semiconductor-to-conductor phase transition in twinned graphene. *Acta Materialia* , Volume 234, 2022, Article Number: 117987.
10. E. Wu, C. Schneider, R. Walz, and J. Park. Adsorption of hydrogen isotopes on graphene. *Nuclear Engineering and Technology* , Volume 54, Issue 11, 2022, Pages 4022-4029.
11. F. Sultanov, A. Mentbayeva, S. Kalybekkyzy, A. Zhaisanova, S.-T. Myung, and Z. Bakenov. Advances

of graphene-based aerogels and their modifications in lithium-sulfur batteries. *Carbon* , Volume 201, 2023, Pages 679-702.

12. M.B. Arvas, M. Gencten, and Y. Sahin. Investigation of supercapacitor properties of chlorine-containing functional groups doped graphene electrodes. *Journal of Electroanalytical Chemistry* , Volume 918, 2022, Article Number: 116438.
13. S. Ghosal, N.S. Mondal, S. Chowdhury, and D. Jana. Two novel phases of germa-graphene: Prediction, electronic and transport applications.*Applied Surface Science* , Volume 614, 2023, Article Number: 156107.
14. H. Assad, I. Fatma, and A. Kumar. An overview of the application of graphene-based materials in anticorrosive coatings. *Materials Letters* , Volume 330, 2023, Article Number: 133287.
15. N. Koosha, J. Karimi-Sabet, M.A. Moosavian, and Y. Amini. Improvement of synthesized graphene structure through various solvent liquids at low temperatures by chemical vapor deposition method. *Materials Science and Engineering: B* , Volume 274, 2021, Article Number: 115458.
16. J. Kulczyk-Malecka, I.V.J.D. Santos, M. Betbeder, S.J. Rowley-Neale, Z. Gao, and P.J. Kelly. Low-temperature synthesis of vertically aligned graphene through microwave-assisted chemical vapour deposition. *Thin Solid Films* , Volume 733, 2021, Article Number: 138801.
17. M. Batzill. The surface science of graphene: Metal interfaces, CVD synthesis, nanoribbons, chemical modifications, and defects.*Surface Science Reports* , Volume 67, Issues 3-4, 2012, Pages 83-115.
18. A. Hussain, S.M. Mehdi, N. Abbas, M. Hussain, and R.A. Naqvi. Synthesis of graphene from solid carbon sources: A focused review.*Materials Chemistry and Physics* , Volume 248, 2020, Article Number: 122924.
19. M.J. Im, S.-K. Hyeong, J.-H. Lee, T.-W. Kim, S.-K. Lee, G.Y. Jung, and S. Bae. High uniformity and stability of graphene transparent conducting electrodes by dual-side doping. *Applied Surface Science* , Volume 605, 2022, Article Number: 154569.
20. J.S. Roh, J.K. Jang, N. Kwon, S. Bok, Y.J. Kim, C. Jeon, H.W. Yoon, H.W. Kim, B. Lim, and H.B. Park. Macroscopic properties of single-crystalline and polycrystalline graphene on soft substrate for transparent electrode applications. *Carbon* , Volume 178, 2021, Pages 181-189.
21. A. Triana, J.J. Olaya, and C. Prieto. Effect of the electrolyte composition on the corrosion resistance of single-layer CVD-graphene.*Surfaces and Interfaces* , Volume 31, 2022, Article Number: 102025.
22. S. Kumar, J. Shakya, T. Mahanta, D. Kanjilal, and T. Mohanty. Substrate-assisted Fermi level shifting of CVD graphene by swift heavy ions. *Surfaces and Interfaces* , Volume 28, 2022, Article Number: 101625.
23. S.R. Joshi, J. Lee, and G.-H. Kim. Low-cost synthesis of high quality graphene oxide with large electrical and thermal conductivities.*Materials Letters* , Volume 292, 2021, Article Number: 129649.
24. A.A. Tarhini and A.R. Tehrani-Bagha. Graphene-based polymer composite films with enhanced mechanical properties and ultra-high in-plane thermal conductivity. *Composites Science and Technology* , Volume 184, 2019, Article Number: 107797.
25. A. Alhusseny, A. Al-Fatlawi, Q. Al-Aabidy, A. Nasser, and N. Al-Zurfi. Dissipating the heat generated in high-performance electronics using graphitic foam heat-sinks cooled with a dielectric liquid.*International Communications in Heat and Mass Transfer* , Volume 127, 2021, Article Number: 105478.
26. K. Rostem, E. Cimpoiasu, K.R. Helson, A.P. Klassen, and E.J. Wollack. Specific heat of epoxies and mixtures containing silica, carbon lamp black, and graphite. *Cryogenics* , Volume 118, 2021, Article Number: 103329.
27. P. Jamzad, J. Kenna, and M. Bahrami. Development of novel plate heat exchanger using natural graphite sheet. *International Journal of Heat and Mass Transfer* , Volume 131, 2019, Pages 1205-1210.
28. D.S. Jang, D. Kim, S.H. Hong, and Y. Kim. Comparative thermal performance evaluation between ultrathin flat plate pulsating heat pipe and graphite sheet for mobile electronic devices at various operating conditions. *Applied Thermal Engineering* , Volume 149, 2019, Pages 1427-1434.
29. B. Bhaduri. Synthesis of Cu catalyzed chemical vapor deposition grown Cu-CNFs on less porous

graphite powder. *Materials Letters* , Volume 305, 2021, Article Number: 130828.

30. J.H. Han, K.W. Cho, K.-H. Lee, and H. Kim. Porous graphite matrix for chemical heat pumps. *Carbon* , Volume 36, Issue 12, 1998, Pages 1801-1810.
31. M. Bonnissel, L. Luo, and D. Tondeur. Compacted exfoliated natural graphite as heat conduction medium. *Carbon* , Volume 39, Issue 14, 2001, Pages 2151-2161.
32. S. Hoshii, A. Kojima, and M. Goto. Rapid baking of graphite powders by the spark plasma sintering method. *Carbon* , Volume 38, Issue 13, 2000, Pages 1896-1899.
33. J.H. Han and K.-H. Lee. Gas permeability of expanded graphite-metallic salt composite. *Applied Thermal Engineering* , Volume 21, Issue 4, 2001, Pages 453-463.
34. R. Janot and D. Guérard. Ball-milling: the behavior of graphite as a function of the dispersal media. *Carbon* , Volume 40, Issue 15, 2002, Pages 2887-2896.
35. E.L. Kitanin, M.S. Ramm, V.V. Ris, and A.A. Schmidt. Heat transfer through source powder in sublimation growth of SiC crystal.*Materials Science and Engineering: B* , Volume 55, Issue 3, 1998, Pages 174-183.
36. A. Yeoh, C. Persad, and Z. Eliezer. Dimensional responses of copper-graphite powder composites to sintering. *Scripta Materialia* , Volume 37, Issue 3, 1997, Pages 271-277.
37. M. Wissler. Graphite and carbon powders for electrochemical applications. *Journal of Power Sources* , Volume 156, Issue 2, 2006, Pages 142-150.
38. C. Natarajan, H. Fujimoto, A. Mabuchi, K. Tokumitsu, and T. Kasuh. Effect of mechanical milling of graphite powder on lithium intercalation properties. *Journal of Power Sources* , Volume 92, Issues 1-2, 2001, Pages 187-192.
39. H.A. Wilhelm, B. Croset, and G. Medjahdi. Proportion and dispersion of rhombohedral sequences in the hexagonal structure of graphite powders.*Carbon* , Volume 45, Issue 12, 2007, Pages 2356-2364.
40. R. Bissessur, P.K.Y. Liu, and S.F. Scully. Intercalation of polypyrrole into graphite oxide. *Synthetic Metals* , Volume 156, Issues 16-17, 2006, Pages 1023-1027.
41. T. Rayment, R. Schlogl, and J.M. Thomas. Low-temperature x-ray powder diffraction studies of antimony pentachloride-intercalated graphite.*Physical Review B* , Volume 30, Issue 2, 1984, Pages 1034-1037.
42. S. Chandrasekaran, T. Basak, and R. Srinivasan. Microwave heating characteristics of graphite based powder mixtures. *International Communications in Heat and Mass Transfer* , Volume 48, 2013, Pages 22-27.
43. F. Bagheri, M. Fakoor-Pakdaman, and M. Bahrami. Utilization of orthotropic graphite plates in plate heat exchangers, analytical modeling. *International Journal of Heat and Mass Transfer* , Volume 77, 2014, Pages 301-310.
44. K. Sultan, C.T. DeGroot, A.G. Straatman, N.C. Gallego, and H. Hangan. Thermal characterization of porous graphitic foam - Convection in impinging flow. *International Journal of Heat and Mass Transfer* , Volume 52, Issues 19-20, 2009, Pages 4296-4301.
45. N. Burger, A. Laachachi, B. Mortazavi, M. Ferriol, M. Lutz, V. Toniazzo, and D. Ruch. Alignments and network of graphite fillers to improve thermal conductivity of epoxy-based composites.*International Journal of Heat and Mass Transfer* , Volume 89, 2015, Pages 505-513.
46. Y. Wen-Jei, H. Takizawa, and D.L. Vrable. Augmented boiling on copper-graphite composite surface. *International Journal of Heat and Mass Transfer* , Volume 34, Issue 11, 1991, Pages 2751-2758.
47. B. Simon, S. Flandrois, K. Guerin, A. Fevrier-Bouvier, I. Teulat, and P. Biensan. On the choice of graphite for lithium ion batteries.*Journal of Power Sources* , Volumes 81-82, 1999, Pages 312-316.
48. A.M. Andersson, K. Edström, N. Rao, and Å. Wendsjö. Temperature dependence of the passivation layer on graphite. *Journal of Power Sources* , Volumes 81-82, 1999, Pages 286-290.
49. S.G. Kim, S.J. Heo, S. Kim, J. Kim, S.O. Kim, D. Lee, S. Lee, J. Kim, N.-H. You, M. Kim, H.C. Kim, H.G. Chae, and B.-C. Ku. Ultrahigh strength and modulus of polyimide-carbon nanotube based carbon and graphitic fibers with superior electrical and thermal conductivities for advanced composite applications. *Composites Part B: Engineering* , Volume 247, 2022, Article Number: 110342.
50. D.W. Kim, K.W. Lee, J.-W. Jang, and C.E. Lee. Dimensional crossover of quantum Hall conductivity in graphite through proton-irradiation.*Carbon* , Volume 187, 2022, Pages 126-132.

51. H. Aghamohammadi, R. Eslami-Farsani, M. Torabian, and N. Amousa. Recent advances in one-pot functionalization of graphene using electrochemical exfoliation of graphite: A review study.*Synthetic Metals* , Volume 269, 2020, Article Number: 116549.
52. J.A. Morton, A. Kaur, M. Khavari, A.V. Tyurnina, A. Priyadarshi, D.G. Eskin, J. Mi, K. Porfyrakis, P. Prentice, and I. Tzanakis. An eco-friendly solution for liquid phase exfoliation of graphite under optimised ultrasonication conditions. *Carbon* , Volume 204, 2023, Pages 434-446.
53. V.P. Vasiliev, A.S. Kotkin, V.K. Kochergin, R.A. Manzhos, and A.G. Krivenko. Oxygen reduction reaction at few-layer graphene structures obtained via plasma-assisted electrochemical exfoliation of graphite.*Journal of Electroanalytical Chemistry* , Volume 851, 2019, Article Number: 113440.
54. J.K. Lynch-Branzoi, A. Ashraf, A. Tewatia, M. Taghon, J. Wooding, J. Hendrix, B.H. Kear, and T.J. Nosker. Shear exfoliation of graphite into graphene nanoflakes directly within polyetheretherketone and a spectroscopic study of this high modulus, lightweight nanocomposite.*Composites Part B: Engineering* , Volume 188, 2020, Article Number: 107842.
55. P. Krawczyk, B. Gurzęda, and A. Bachar. Thermal exfoliation of electrochemically obtained graphitic materials. *Applied Surface Science* , Volume 481, 2019, Pages 466-472.
56. B.D.L. Campéon, M. Akada, M.S. Ahmad, Y. Nishikawa, K. Gotoh, and Y. Nishina. Non-destructive, uniform, and scalable electrochemical functionalization and exfoliation of graphite. *Carbon* , Volume 158, 2020, Pages 356-363.
57. L.A. Pozhar and K.E. Gubbins. Quasihydrodynamics of nanofluid mixtures. *Physical Review E* , Volume 56, Issue 5, 1997, Pages 5367-5396.
58. D.H. Kumar, H.E. Patel, V.R.R. Kumar, T. Sundararajan, T. Pradeep, and S.K. Das. Model for heat conduction in nanofluids. *Physical Review Letters* , Volume 93, Issue 14, 2004, Article Number: 144301.
59. G. Donzelli, R. Cerbino, and A. Vailati. Bistable heat transfer in a nanofluid. *Physical Review Letters* , Volume 102, Issue 10, 2009, Article Number: 104503.
60. M. Bernardin, F. Comitani, and A. Vailati. Tunable heat transfer with smart nanofluids. *Physical Review E* , Volume 85, Issue 6, 2012, Article Number: 066321.
61. L.A. Pozhar. Structure and dynamics of nanofluids: Theory and simulations to calculate viscosity. *Physical Review E* , Volume 61, Issue 2, 2000, Pages 1432-1446.
62. J.K. Percus, L.A. Pozhar, and K.E. Gubbins. Local thermodynamics of inhomogeneous fluids at equilibrium. *Physical Review E* , Volume 51, Issue 1, 1995, Pages 261-265.
63. L.A. Pozhar, K.E. Gubbins, and J.K. Percus. Generalized compressibility equation for inhomogeneous fluids at equilibrium.*Physical Review E* , Volume 48, Issue 3, 1993, Pages 1819-1822.
64. M. Glässl, M. Hilt, and W. Zimmermann. Convection in nanofluids with a particle-concentration-dependent thermal conductivity. *Physical Review E* , Volume 83, Issue 4, 2011, Article Number: 046315.
65. J. Eapen, J. Li, and S. Yip. Beyond the Maxwell limit: Thermal conduction in nanofluids with percolating fluid structures.*Physical Review E* , Volume 76, Issue 6, 2007, Article Number: 062501.
66. S. Kondaraju, E.K. Jin, and J.S. Lee. Investigation of heat transfer in turbulent nanofluids using direct numerical simulations.*Physical Review E* , Volume 81, Issue 1, 2010, Article Number: 016304.
67. M. Rajnak, Z. Spitalsky, B. Dolnik, J. Kurimsky, L. Tomco, R. Cimbala, P. Kopcansky, and M. Timko. Toward apparent negative permittivity measurement in a magnetic nanofluid with electrically induced clusters. *Physical Review Applied* , Volume 11, Issue 2, 2019, Article Number: 024032.
68. P. Ben-Abdallah. Dynamic structure and cluster formation in confined nanofluids under the action of an external force field. *Physical Review E* , Volume 74, Issue 4, 2006, Article Number: 041407.
69. L. Braginsky and V. Shklover. Thermal conductivity of low-particle-concentration suspensions: Correlation function approach.*Physical Review B* , Volume 78, Issue 22, 2008, Article Number: 224205.
70. A. Gupta, P. Magaud, C. Lafforgue, and M. Abbas. Conditional stability of particle alignment in finite-Reynolds-number channel flow.*Physical Review Fluids* , Volume 3, Issue 11, 2018, Article Number: 114302.
71. S.A. Egorov. Interactions between nanoparticles in supercritical fluids: From repulsion to attraction. *Physical Review E* , Volume 72, Issue 1, 2005, Article Number: 010401(R).
72. T. Shende, D. Mangal, J.C. Conrad, V. Niasar, and M. Babaei. Nanoparticle transport within non-

Newtonian fluid flow in porous media. *Physical Review E* , Volume 106, Issue 1, 2022, Article Number: 015103.

73. D.R. Evans, S.A. Basun, G. Cook, I.P. Pinkevych, and V.Y. Reshetnyak.*Physical Review B* , Volume 84, Issue 17, 2011, Article Number: 174111.
74. S. Merabia, P. Keblinski, L. Joly, L.J. Lewis, and J.-L. Barrat. Critical heat flux around strongly heated nanoparticles.*Physical Review E* , Volume 79, Issue 2, 2009, Article Number: 021404.
75. M. Rafique, M.S. Rafique, S.H. Butt, A. Afzal, and U. Kalsoom. Laser nature dependence on enhancement of optical and thermal properties of copper oxide nanofluids. *Applied Surface Science* , Volume 483, 2019, Pages 187-193.
76. S. Rostami, A.A. Nadooshan, A. Raisi, and M. Bayareh. Modeling the thermal conductivity ratio of an antifreeze-based hybrid nanofluid containing graphene oxide and copper oxide for using in thermal systems. *Journal of Materials Research and Technology* , Volume 11, 2021, Pages 2294-2304.
77. I. Zaaroura, M. Toubal, H. Reda, J. Carlier, S. Harmand, R. Boukherroub, A. Fasquelle, and B. Nongaillard. Evaporation of nanofluid sessile drops: Infrared and acoustic methods to track the dynamic deposition of copper oxide nanoparticles. *International Journal of Heat and Mass Transfer* , Volume 127, Part B, 2018, Pages 1168-1177.
78. L. Fu and L. Resca. Exact theory of the electrostatic interaction in electrorheological fluids and the effects of particle structure.*Solid State Communications* , Volume 99, Issue 2, 1996, Pages 83-87.

Thermal and viscosity properties of inhomogeneous fluids with suspended graphene nanoparticles

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Abstract

The use of nanofluids in a wide variety of applications is promising, but poor suspension stability of nanoparticles in the solution hinders the further development of nanofluids applications. The present study aims to provide a fundamental understanding of the thermal and viscosity properties of inhomogeneous fluids with suspended graphene nanoparticles. A graphite material is exfoliated to form graphene particles, and the effect of nanoparticle volume fraction on the material properties of inhomogeneous fluids with suspended graphene nanoparticles is investigated at different temperatures or under oxidation conditions. Particular emphasis is placed upon the effect of nanoparticle volume fraction on the material properties of inhomogeneous fluids with suspended graphene nanoparticles. The results indicate that the bottom-up approach produces low quantities with high quality and large flakes whereas the top-down approach yields a high concentration of suspended flakes with a low yield of mono-layer graphene. Smaller dispersions result in ease of addition of graphene to other desirable emulsions to enhance the uniform coating matrix for protection attributes graphene can provide to the coating. The pressure drop allows the liquid precursor to flow and homogenizes the pass-through liquid of the liquid precursor that contains thin layers of graphene. The phonon Raman scattering changes are correlated with structural changes and defects associated with the hydroxyl and epoxy groups in the basal plane and a variety of alkyl and oxygen-containing functional groups terminating the edges. Graphene-containing nanofluids provide several advantages over the conventional fluids, including thermal conductivities far above those of traditional solid-liquid suspensions, a nonlinear relationship between thermal conductivity and concentration, strongly temperature-dependent thermal conductivity, and a significant increase in critical heat flux. Stability of the nanoparticle suspension is especially essential for practical industrial applications. Introduction of nanoparticles to the fluid changes density, thermal conductivity viscosity, and specific heat. The functionalization process decreases enhancements in thermal conductivity due to formation of surface oxides. In development of nanofluids for heat transfer a fine balance needs to be obtained between increases in thermal conductivity and viscosity.

Keywords: Graphene; Nanoparticles; Thermal properties; Viscosity properties; Fluids; Graphite

1. Introduction

Graphene has better electrical conductivity [1, 2], thermal conductivity [3, 4], and mechanical strength than such metals as copper and aluminum [5, 6], and exhibits optically transparent nature [7, 8]. Graphene has a structure of stacking honeycomb layers. In order to maintain ideally the characteristics, it should be formed with single layer and have large area. Graphene has such good characteristics, so it is suitable for semiconductors [9], nuclear fusion reactors [10], base material of secondary batteries [11], base material of clear electrodes for displays and cellphones [12], and it is expected that applications of graphene will be broadened [13, 14]. In particular, since graphene has good electrical conductivity and transparency, it is an ideal material for transparent electrodes of display devices.

Chemical vapor deposition is a general method for manufacturing large-area graphene [15, 16]. However, there have been difficulties in commercializing the manufacturing method because it requires high-cost despite of low productivity [17, 18]. Nevertheless, research for applying graphene to transparent electrodes is widely progressed [19, 20], because graphene manufactured by chemical vapor deposition is suitable for transparent electrodes of displays and cellphones which require high conductivity and visible ray transparency [21, 22]. On the other hand, graphene having single layer and large area has not only good electrical conductivity but also good thermal conductivity [23, 24]. However, it has low thermal capacity because it is thin. Therefore, graphene is difficult to use as a heat radiator for radiating high heat.

Graphite having a graphene structure is suitably applicable to heat radiators [25, 26]. Graphite has a structure of stacking honeycomb layers and is abundant in nature. In recent years, graphite is widely applied to heat radiators for electrical devices [27, 28]. However, there are many technical difficulties in acquiring the same characteristics of graphene from the natural graphite [29, 30]. Graphite must be exfoliated to be thin and large-area, in order to have characteristic of thermal radiation similar to graphene [31, 32]. More specifically, for the sake of using graphite as a heat radiator, it is required to make the graphite powder as thin and wide as possible and manufacture the heat radiator using the graphite powder in such a large volume as to appropriately maintain the temperature of the heat radiator [33, 34]. A conventional method of manufacturing graphite powder is mechanically grinding graphite into fine powder [35, 36]. Another method is a chemical method that involves oxidizing graphite powder at high temperature to obtain an expanded graphite structure [37, 38]. However, there are technical limitations in obtaining graphite powder as thin and wide as graphene according to the mechanical grinding method or the chemical method.

Since graphite powder for heat radiator as manufactured by the mechanical grinding method depends on the particle size of the graphite, the shape of particle is generally irregular and similar to stone fragments. Generally, the graphite powder manufactured by the mechanical grinding method is used as its particle size is 40 microns or less [39, 40]. As such, the graphite powder mechanically ground has various advantages that high density is guaranteed when it is spread or molded and that the size of particle can be controlled according to its use purpose [41, 42]. However, it is difficult to control the thickness of the particle, that is, the thickness of a honeycomb layer, which is stacked layer by layer [43, 44]. Also, the method has the advantage that proportion of pores is low owing to high density [45, 46]. On the other hand, the method has the disadvantage that electrical conductivity and thermal conductivity decrease with an increase in the contact resistance between powder particles.

The chemical method of manufacturing graphite powder for heat radiator using oxidation-reduction reaction has advantage in terms of high productivity [47, 48]. However, it has such a disadvantage that it may cause environmental pollution [37, 38]. Further, it is difficult to produce high purity graphite because of poor manufacturing environment [39, 40]. Graphite oxidized under high temperature condition by the chemical method become powder that is bulky and has very low density in the case of expansion. This powder form of graphite is used as a sheet for heat radiation of electronic devices. The expanded graphite powder of which particle size is 300 microns or less is mainly used for heat radiation purpose [41, 42]. The expanded graphite powder is microscopically similar to bellows in shape. Macroscopically, the expanded graphite is cotton-shaped and light-weighted [33, 34]. However, when the graphite powder expands in volume by the oxidization process under high temperature condition, the gaps between layers crack like bellows to generate many pores [35, 36]. Therefore, the particles of the expanded graphite powder are bigger and thinner than those of the graphite powder manufactured by grinding natural graphite. Consequently, the expanded graphite powder has high electronic conductivity and thermal conductivity [49, 50] but contains many pores between particles to cause deterioration in the thermal conductivity.

In order to solve such a problem as deterioration in the characteristics of the expanded graphite powder caused by the abundance of pores, there have been applied improvement methods such as compressing the expanded graphite powder with high pressure or using the expanded graphite powder in combination with a graphite powder of small particle size or a conductive metal powder [39, 40]. Those methods, however, have an insignificant effect of improving the characteristics [39, 40]. For the sake of making efficient heat radiators using a graphite material, it is required to exfoliate the graphite material as thin and wide as possible to secure good characteristics in terms of electrical conductivity and thermal conductivity as similar to graphene and also to adopt a method of minimizing generation of pores that greatly deteriorate electrical conductivity and thermal conductivity [27, 28]. In particular, the conventional methods such as the mechanical grinding method and the chemical method have technical difficulties in obtaining a graphite powder thin and, wide like graphene [27, 28] and limitations in solving the problem with the abundance of pores between particles.

Currently, the application thickness of the graphite powder is normally 25 microns or greater for radiant sheets used to radiate heat from cellphones and one millimeter or greater for radiant sheets used to radiate heat from electronic devices [41, 42]. In order to reduce the thickness of the radiant sheets used for those electronic devices and enhance the efficiency of heat radiation, it is necessary to make the graphite powder thin and wide and minimize the existence of pores between the particles of the graphite powder [41, 42]. For this purpose, there is a demand for a technique to exfoliate the graphite powder thin and wide like graphene [51, 52]. Contrived in consideration of the problems, it is necessary to provide a method for manufacturing graphene and a method for manufacturing a conductor that solve the problems regarding insufficient exfoliation of the graphite powder and deterioration in the electrical conductivity and thermal conductivity caused by the small particle size [53, 54]. It is also necessary to provide a method for manufacturing graphene and a method for manufacturing a conductor that solve the problem regarding deterioration in the electrical conductivity and thermal conductivity caused by the pores existing between the particles and the environmental problem [55, 56]. It is therefore of great importance to provide a method for manufacturing graphene and a method for manufacturing a conductor that improve the characteristics of the graphite material, in comparison with the conventional methods such as the mechanical grinding method and the chemical method.

Conventional heat transfer fluids play an important role in many industries including power generation, chemical production, air conditioning, transportation, and microelectronics. However, their inherently low thermal conductivities have hampered the development of energy-efficient heat transfer fluids that are required in a plethora of heat transfer applications. However, the heat transfer properties of these conventional fluids can be significantly enhanced by dispersing nanometer-sized solid particle and fibers, namely nanoparticles, in fluids. This new type of heat transfer suspensions is known as nanofluids. Such nanofluids may be engineered by dispersing metallic or nonmetallic nanoparticles in traditional base fluids. The thermal conductivity of heat transfer fluids can be enhanced by adding highly conductive particles. Depending on the application, nanofluids are generally classified such as heat transfer nanofluids, anti-wear nanofluids, metalworking nanofluids, coating nanofluids, and chemical nanofluids. Nanofluids can significantly improve heat transfer characteristics compared with the base fluids. Nanofluids have the potential to improve heat transfer and energy efficiency in thermal systems in applications such as microelectronics, power electronics, transportation, nuclear engineering, heat pipes, refrigeration, air-conditioning, and heat pump systems. The use of nanofluids in a wide variety of applications is promising, but poor suspension stability of nanoparticles in the solution hinders the further development of nanofluids applications. The present study aims to provide a fundamental understanding of the thermal and viscosity properties of inhomogeneous fluids with suspended graphene nanoparticles. Particular emphasis is placed upon the effect of nanoparticle volume fraction on the material properties of inhomogeneous fluids with suspended graphene nanoparticles.

2. Methods

A technical feature of the method for manufacturing graphene is that the method includes exfoliating or transferring a graphite material onto at least one structure to form graphene particles on the surface of any one of the at least one structure, releasing the graphene particles from the structure, and combining the released graphene particles to form graphene. The step of forming graphene particles includes: exfoliating the graphite material onto a first structure of the plural structures to form first graphene particles on the surface of the first structure; and transferring the first graphene particles to a second structure disposed opposite to the first structure out of the plural structures to form second graphene particles. The step of forming graphene particles may include exfoliating or transferring the graphite material onto the surface of rollers used as the structures to form the graphene particles, the rollers being different in diameter from each other and rotating in contact with each other. Preferably, the step of forming graphene particles may include exfoliating or transferring the graphite material onto the surface of rollers and a plate used as the structures to form the graphene particles, the rollers being different in diameter from each other and rotating in contact with each other, the plate moving in a linear reciprocating motion in contact with the rollers. The step of forming graphene particles includes: applying the graphite material between first and second structures making a pair out of the plural structures; exfoliating the graphite material onto the first and second structures to form first graphene particles on the surface of the first and second structures, respectively; and transferring the first graphene particles to third and fourth structures disposed opposite to the first and second structures out of the plural structures, respectively, to form second graphene particles on the surface of the third and fourth structures, respectively. The step of forming graphene includes injecting an adhesive liquid for constraining the released graphene particles and then applying pressure on the released graphene particles to combine the graphene particles. An adhesive layer for exfoliation, transfer or release of the graphene particles may be provided on the surface of the structure. A rubber elastomer may be applied or mounted as the adhesive layer on the surface of the structure. The rubber elastomer may be silicone rubber. The method may further include applying the graphite material together with an adhesive liquid or solid onto the structure. A technical feature of the method for manufacturing a conductor is that the method includes: applying or forming the graphene manufactured by the graphene-manufacturing method on a sheet or a film to make an electrical conductor or a thermal conductor.

In the present study, the term nanofluid describes a homogeneous dispersion of at least a nanomaterial with at least one dimension in a nanoscale in a conventional base fluid. In the present study, the nanomaterial refers to graphene-based compounds or composites. The present study relates to a nanofluid characterized in that it comprises a liquid medium selected from an organic solvent or a water solution of acidic, neutral or basic compounds and said liquid medium optionally comprising a surfactant, and a graphene-based compound or composite, homogenously dispersed in the liquid medium, and the graphene-based compound or composite optionally comprising a material associated to the graphene-based compounds. The term graphene-based compound or composite refers herein to graphene, graphene oxide, reduced graphene oxide or a combination thereof forming either compounds or composites with any other molecule, polymer or solid phase in extended or nanoparticulate form. The graphene-based compound of the nanofluid is in a nanoparticle volume fraction between 0.0008 percent and 0.008 percent based on the total weight of the electroactive nanofluid. Nanofluids are prepared by direct mixing of the graphene-based compound or composite and the liquid medium. The graphene-based compound or composite optionally comprises substances either attached to the graphene-based compounds or forming a mixture by dispersion in the base fluid. The nanofluid may further comprising carbon materials such as activated carbons or carbon nanotubes aside from graphene. Each of these present specific advantages such as low cost or anisotropy which expand the possible applications of the nanofluids. Graphene oxide is synthesized from natural graphite using the modified Hummers method. Graphene oxide nanosheets exhibits pores in mesopores as well as macro-porous region. Enhancements in the thermal conductivities of nanofluids, for the most part, follow the predictions based on Maxwell's mean field theory assuming low concentrations and spherical nanoparticles or the effective medium theory. Thermal conduction in nanofluids is attributed to a variety of mechanisms, including Brownian motion interactions between the nanoparticles and the fluid, clustering and agglomeration. There is no clear consensus on a specific mechanism; however, the general belief is that a combination of mechanisms may be operating and would be specific to a nanoparticles-fluid system and test conditions. Further, the effect of interface layers on the nanoparticles on thermal conductivity is not clearly understood. A metal particle with surface oxidation, for example, continuously increases the interfacial resistance and consequently reduce the thermal conductivity. Some of these nanofluids also can include a surfactant additive to stabilize particle suspensions. Because thermal conductivity of surfactants is very poor compared to water, often more preferred water-based nanofluids are comprised of functionalized graphene wherein as received graphene is treated by oxidation, such as by mixing with concentrated sulfuric and nitric acids. Such oxidized, or functionalized, graphene is disposed in fluids without need of surfactants to achieve greatly improved thermal properties for the nanofluids.

3. Results and discussion

The scanning electron micrographs are illustrated in Figure 1 for the graphene that solves the problems regarding insufficient exfoliation of the graphite powder and deterioration in the electrical conductivity and thermal conductivity. Graphite is a stack of graphene sheets bound by van der Waals interactions, each graphene layer being made of sp^2 carbons distributed in a hexagonal crystal structure. Graphene has superior mechanical, electrical, and thermal properties. In bottom-up methods to produce graphene, for example, chemical vapor deposition, graphene is synthesized. In top-down methods, for example liquid-phase exfoliation, graphene sheets are separated from bulk graphite material. The bottom-up approach produces low quantities with high quality and large flakes. The top-down approach using graphite is low in cost and yields a high concentration of suspended flakes, but fabricates limited-size sheets with a low yield of mono-layer graphene. Existing commercially available graphene products usually contains precipitates of graphene due to the presence of thick layers of graphene and are not stable. The method of the exfoliation of graphene from graphite using multilayer coextrusion is described herein. Graphite is dispersed within a first processing material, and the first processing material and a second processing material are co-extruded through a plurality of series coupled layer multiplication dies to exfoliate graphene from the graphite. The graphene is separated from the resulting multi-layered material. Graphite flake and expanded graphite may be dispersed within the first processing material. The process uses an organic solvent and silica under high pressure sheer force to create a liquid intermediate containing thin layers of graphene that allows for easy dispersion of graphene in a liquid organic solvent system. High sheer processing of graphene and silica together in a liquid organic solvent system result in stable graphene platelets. During the process, thick layers of graphene can break down to smaller layers of graphene that is more usable. The silica forms a gel simultaneously as graphene platelet multiple stacks are sheered into smaller platelet stacks through the organic solvent carrier. The small platelet stacks are dispersed in the gel and held by the network of the gel stably. In the process, both a graphene raw material and silica are mixed in an organic solvent to form a liquid precursor. Preferably, the graphene raw material is a graphene powder. The graphene raw material may be obtained commercially. Commercially available graphene usually contains thick layers. Thus, when commercially available graphene is used as an additive or is added to a liquid product, the commercially available graphene may precipitate in the liquid product.

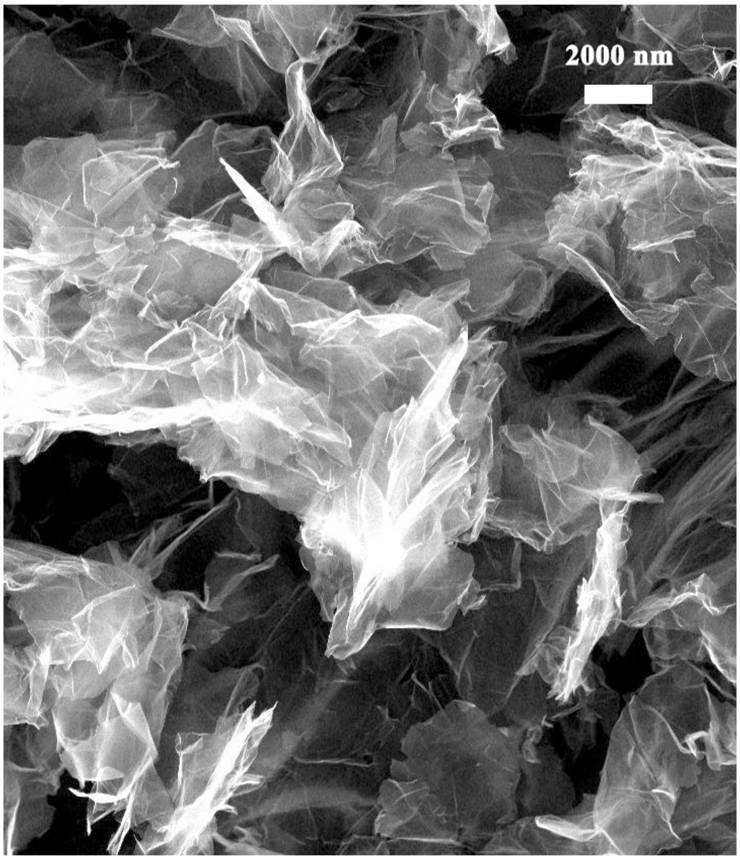

Figure 1. Scanning electron micrographs of the graphene that solves the problems regarding insufficient exfoliation of the graphite powder and deterioration in the electrical conductivity and thermal conductivity.

The high-resolution scanning electron micrographs are illustrated in Figure 2 for the graphene that solves the problems regarding insufficient exfoliation of the graphite powder and deterioration in the electrical conductivity and thermal conductivity. The raw graphene powder can contain graphene nanoparticles consisting of stacks of graphene sheets having a platelet shape. The graphene particles may have an average thickness of about 6-8 nm and a typical surface area of about 80 to 200 square meters per gram. The graphene particles have an average particle diameter of about 8-20 microns. Graphene nanoplatelets may have naturally occurring functional groups like ethers, carboxyl, or hydroxyls that can react with atmospheric humidity to form acids or other compounds. These functional groups are present on the edges of the particles and their weight fraction varies with particle size. The liquid precursor is a suspension containing graphene solids. The amount and concentration of the graphene raw material liquid precursor can depend on the desired amount, concentration, and use of the resultant product of the process. A smaller distribution of graphene, for example, from about 0.05 percent by weight to about 60 percent by weight relative to the total weight of a liquid dispersion containing the graphene, would more easily disperse at the submicron level in the liquid dispersion, when compared to a greater weight fraction of graphene in the liquid dispersion. Smaller dispersions result in ease of addition of graphene to other desirable emulsions, for example, to enhance the uniform coating matrix for protection attributes graphene can provide to the coating. A non-limiting example of the silica that can be used is fumed silica. Silica fume is an ultrafine powder collected as a by-product of the silicon and ferrosilicon alloy production. It may consist of amorphous spherical particles with an average particle diameter of about 80-280 nm, for example, about 200 nm, without the branching of the pyrogenic product. The concentration of silica, for example, fumed silica, can be in the range of about 0.08 percent by weight to

28 percent by weight in the liquid precursor or any subrange thereof, for example, about 0.2-20 percent by weight, about 3-6 percent by weight, or about 4-6 percent by weight. A concentration of fumed silica in the range of about 0.2-20 percent by weight can modify nonpolar solvents to have a viscosity of higher than 80 Sabol seconds, for example, to form ringing gels.

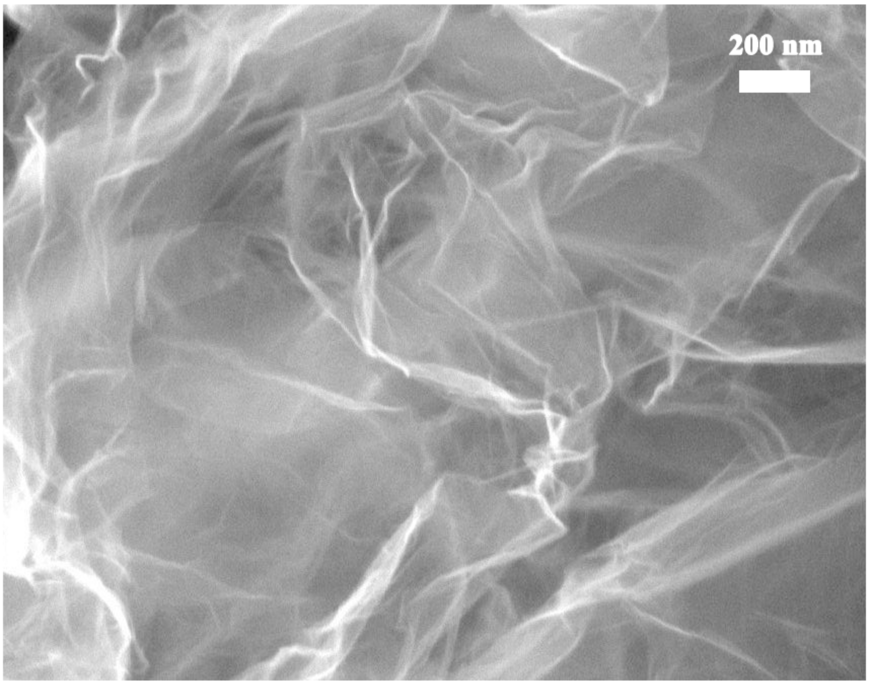

Figure 2. High-resolution scanning electron micrographs of the graphene that solves the problems regarding insufficient exfoliation of the graphite powder and deterioration in the electrical conductivity and thermal conductivity.

The high-resolution transmission electron micrographs are illustrated in Figure 3 for the graphene that solves the problems regarding insufficient exfoliation of the graphite powder and deterioration in the electrical conductivity and thermal conductivity. The organic solvent preferably has a viscosity of less than 80 Sabol seconds. Non-limiting examples include nonpolar organic solvents. The metal cylinder may be pressed against the flat metal plate by an extreme pressure. The pressure applied on the metal cylinder may be in the range of about 2000-6000 psi. This high pressure ensures graphene sheers to a stable form in the resultant nonpolar liquid dispersion. A pressure of below about 2000 psi leads to a wider platelet particle size distribution curve and larger stacks of graphene platelets, which will settle in the non-polar dispersion. The liquid precursor may be forced through an opening on the flat metal plate. The liquid precursor may then pass between the metal cylinder and the flat metal plate. The pumping pressure applied on the liquid precursor may be higher than the pressure between the metal plate and metal cylinder such that the feed of the liquid precursor can be directed through the opening and then between the metal cylinder and the flat metal plate. When the liquid precursor passes between the metal cylinder and the flat metal plate, the thick layers of graphene may be broken into thin layers by the high shear pressure between the metal cylinder and the flat metal plate. The greater the pressure between the metal cylinder and the flat metal plate, the smaller the graphene platelet particle size. When the liquid precursor is directed, for example, forced by the pumping pressure, through the opening on the flat metal plate and between the metal cylinder and the flat metal plate, and then exits from between the metal cylinder and the flat metal plate, the pressure on the liquid precursor drops significantly. This pressure drop allows the liquid precursor to flow and homogenizes the pass-through liquid of the liquid precursor that contains thin layers of graphene such that the smaller graphene platelet particle is well dispersed in the resultant fluid product. The greater the pressure drop is, the greater the level of homogenization. The process thus reduces the particle size of the graphene and creates more uniform graphene platelets. Further, when the liquid precursor passes between the metal cylinder and the flat metal plate, fumed silica undergoing sheer pressure may swell and expand in the nonpolar solvent to form a gel comprising a three-dimensional structure and with a higher rheology and viscosity than the organic solvent. The viscosity of the resultant silica gel can range from about 200,000 to about 600,000 centistokes. The graphene platelet particles are dispersed in the three-dimensional network of the silica gel and held therein stably in the silica gel matrix. The organic solvent keeps the graphene particles apart from each other in the silica web, breaking up the Van der Waals forces between them, so that the graphene particles do not aggregate and maintain their thin layers of two-dimensional configuration. When the graphene suspension additive is added to a product, such as a painting or coating, and when the product is applied on to a surface and allowed to dry, the organic solvent may evaporate, and upon evaporation of the solvent, the graphene nanoparticles can come together in the polymeric matrix of the silica gel and other components, thus strengthening the coating. The graphene can keep metals at uniform temperatures.

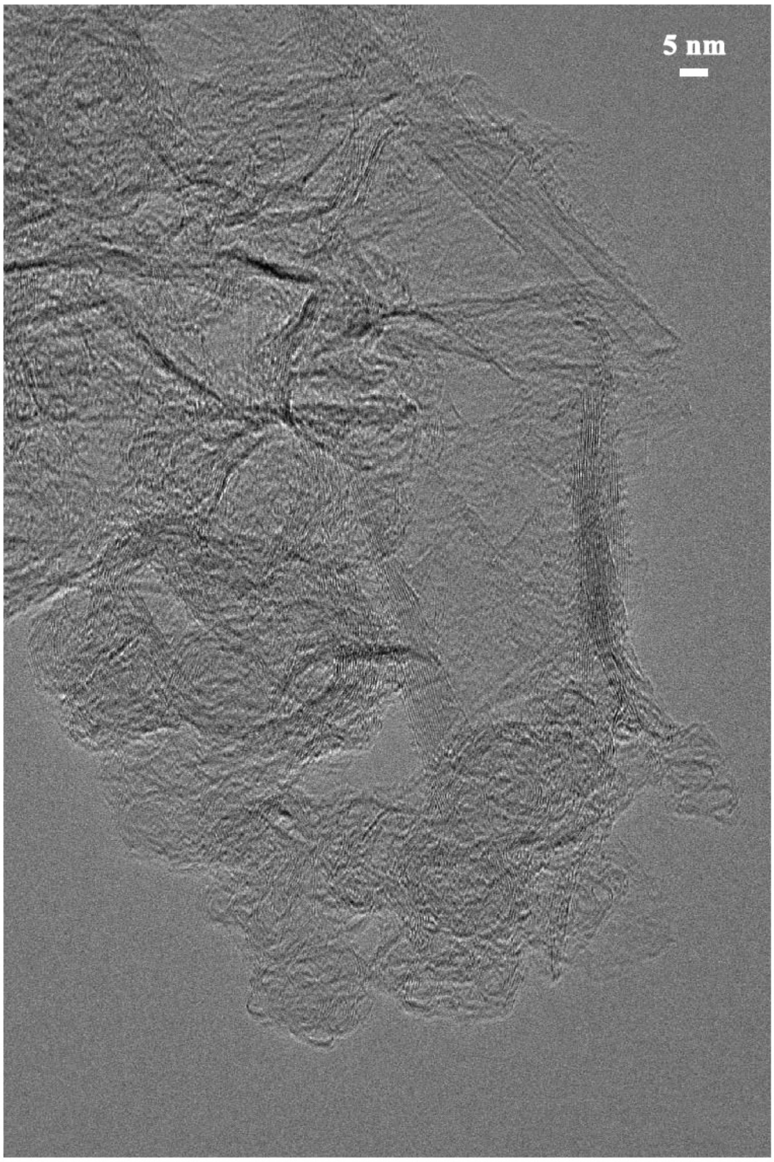

Figure 3. High resolution transmission electron micrographs of the graphene that solves the problems regarding insufficient exfoliation of the graphite powder and deterioration in the electrical conductivity and thermal conductivity.

The Raman spectra are illustrated in Figure 4 for the graphene that solves the problems regarding insufficient exfoliation of the graphite powder and deterioration in the electrical conductivity and thermal conductivity. These laser-induced graphene features may be characterized by the presence of a distinct 2D-band in the Raman spectra. This can be fit with a single Lorentzian and is very similar to that observed for single layer exfoliated graphene and epitaxial graphene. The 2D mode results from a two-phonon resonant scattering process and is normally considered an overtone of the defect mediated D-band. The 2D feature is always observed with widths defined by the thickness and stacking order along the c-axis. For single layer graphene, a single Lorenztian line shape centered at 2690 per centimeter can indicate electronic structure that is dominated by Dirac-Weyl dispersion. It is therefore accepted as one of better optical signatures regarding the presence of graphene. It is different than that from highly oriented pyrolytic graphite. Specifically, the G-band is much broader and blue shifted, there is a strong D-band at 1345 per centimeter, and the 2D-band is nearly absent. These changes are correlated with structural changes and defects associated with the hydroxyl and epoxy groups in the basal plane and a variety of alkyl and oxygen-containing functional groups terminating the edges. The 2D-band is observed and there is a narrowing of the G-band as well as diminution of the D-band. When using nitrogen background gas, the 2D-band is further enhanced, the G-band is much narrower and the D-band is nearly removed. Formation of the 2D-band and G-band narrowing also occurs. However, the D-band feature, though reduced relative to untreated graphene, remains independent of the laser flux. This indicates an intrinsic difference in the defect density and material quality relative to that formed using continuous-wave excitation. When using 355 nm photons, the 2D-band is produced at the lowest powers and the integrated D and 2D peak intensity ratio is about 0.8-2.0. Though sample surface non-uniformity causes variability, this ratio remains close to 0.8 even at the highest power. On the contrary, the integrated D and 2D peak intensity ratio is usually dependent on the power when using 532 nm photons and discernable 2D-band features are not evident. The 355 nm light excites single-photon mediated valence-to-conduction band transitions. This produces electron-hole plasmas in the material at all pulse energies studied. Since at least two 532 nm photons are required to exceed the band-gap, a coherent multiphoton or incoherent multiple photon process may be required to create a similar electron-hole plasma. This is consistent with the 532 nm 2D-band formation threshold of 2.8 megawatts per square centimeter which is below the pre-ablation threshold of graphite.

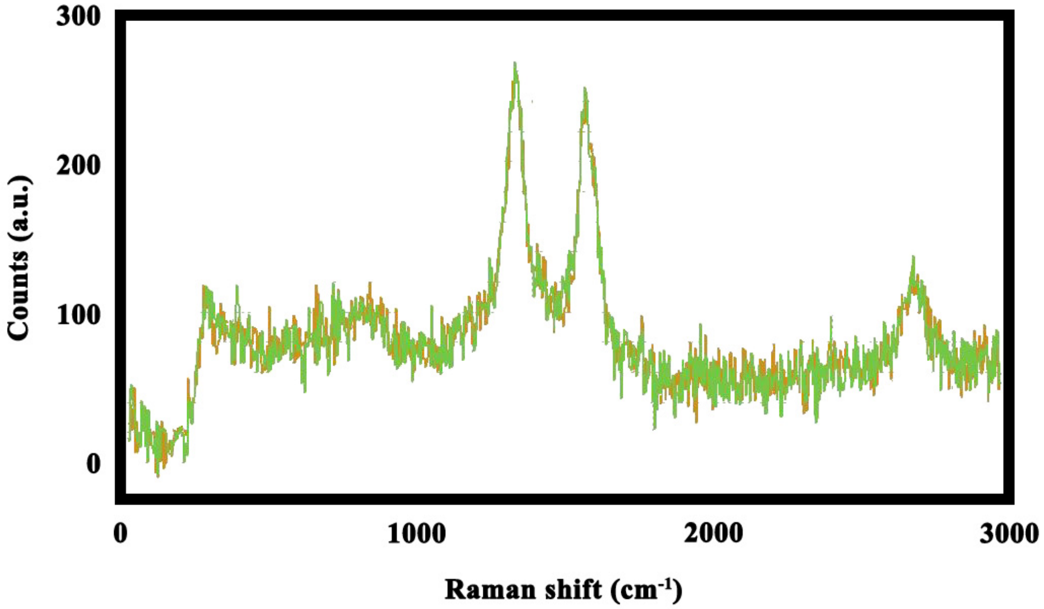

Figure 4. Raman spectra of the graphene that solves the problems regarding insufficient exfoliation of the graphite powder and deterioration in the electrical conductivity and thermal conductivity.

The effect of temperature on thermal conductivity of the graphene in purified water is illustrated in

Figure 5 for which the material consists of stacks of graphene sheets having a platelet shape. The quest for thermal systems that are more efficient in removing heat is never ending, with design improvements of heat exchangers being one of the main areas of focus. Water is the working fluid of choice for years for several reasons; it is clean, readily available and has fairly good thermal properties for heat removal. Over a century ago, micro-sized particles with high thermal conductivity are used as a way to increase the thermal characteristics of working fluids [57, 58]. However, micro-sized particles can be abrasive and can precipitate out due to their higher density. Once the nanoparticles settle, the nanofluid loses its property enhancement. Nano-sized particles introduced into a base liquid are also used and called nanofluids. This concept of using copper, aluminum, or carbon nanoparticles to create colloidal suspension fluids has been accepted as a new avenue for enhancing the thermal characteristics [59, 60]. Since heat transfer can be enhanced due to particle size and dispersion isometry, the key technical challenge in implementing this technology is to understand the fundamental physics responsible for enhancing the transport of heat, which can lead to the knowledge-based development of a stable nanofluid with maximum thermal conductivity. Due to the necessity of compact thermal management systems, many researchers have begun to investigate the benefits of the nanofluids on the heat transfer in the thermal management system [61, 62]. Scientists have reported varying degrees of increase in thermal performance with the addition of the nanoparticles to the thermal fluid [63, 64]. The earlier studies are primarily on the enhancements of the thermal conductivity [65, 66]. Most studies report very good enhancements of the thermal conductivity even with small volume percent concentrations [67, 68]. Researchers have investigated the addition of nanoparticles made of highly conductive materials such as aluminum, carbon, diamond, and copper with varying positive results [69, 70]. Many prior researchers have focused on the use of copper oxide nanoparticles to form the nanofluid due to the favorable thermal properties of copper oxide powders [71, 72]. However, nanofluids formed with copper oxide suffer from several drawbacks that can impede its commercial use in a thermal management system [73, 74]. For example, fluids containing copper oxide nanoparticles have a tendency to mix with and retain air and oxygen within the fluid, which adversely affects the thermal properties of the fluid and can create problems in the thermal system [75, 76]. Additionally, the copper oxide nanoparticles tend to agglomerate and stick to the container of the fluid in the thermal system, which can lead to impairment and fouling of fluid flow in the system [77, 78]. In the present study, the nanofluid includes graphene nanoparticles suspended in a base liquid at a nanoparticle concentration in the nanofluid of about 0.008 percent by volume. Graphene nanoparticles are an excellent method to improve thermal conductivity in water. Graphene-containing nanofluids provide several advantages over the conventional fluids, including thermal conductivities far above those of traditional solid-liquid suspensions, a nonlinear relationship between thermal conductivity and concentration, strongly temperature-dependent thermal conductivity, and a significant increase in critical heat flux. Each of these features is highly desirable for thermal systems and together makes nanofluids strong candidates for the next generation of heat transfer fluids. The observed substantial increases in the thermal conductivities of nanofluids can have broad industrial applications and can also potentially generate numerous economic and environmental benefits. Enhancement in the heat transfer ability could translate into high energy efficiency, better performance, and low operating costs. The need for maintenance and repair can also be minimized by developing a nanofluid with a better wear and load-carrying capacity. Consequently, classical heat dissipating systems widely used today can become smaller and lighter, thus resulting in better fuel efficiency, less emission, and a cleaner environment. Nanoparticles of various materials can be used to make heat transfer nanofluids, including copper, aluminum, copper oxide, alumina, titania, and graphene. Of these nanoparticles, graphene shows greatest promise due to their excellent chemical stability and extraordinary thermal conductivity.

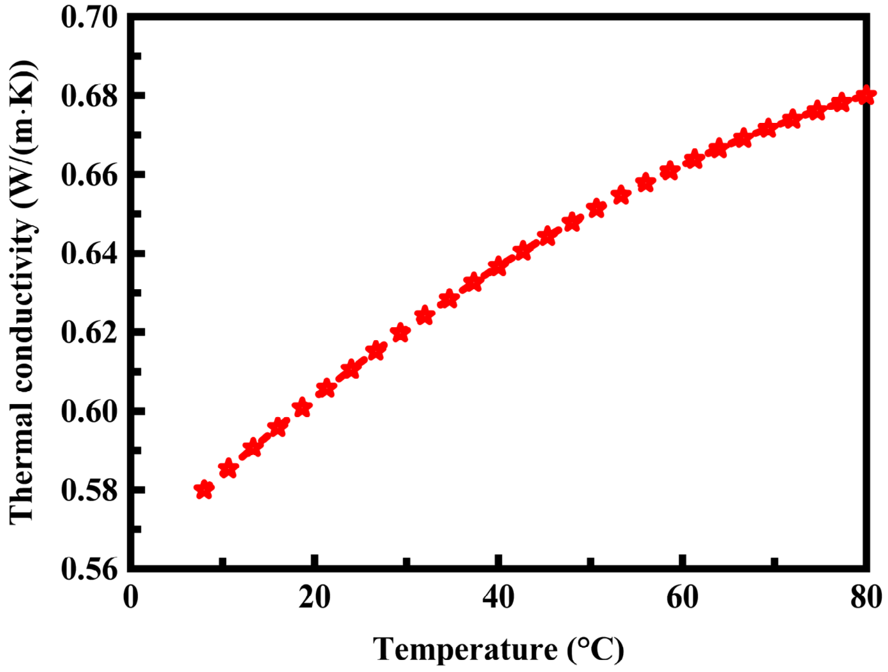

Figure 5. Thermal conductivity of the graphene in purified water at different temperatures for which the material consists of stacks of graphene sheets having a platelet shape.

The effect of nanoparticle volume fraction on the thermal conductivity enhancement ratio is illustrated in Figure 6 for the nanofluid with suspended graphene nanoparticles. Improved thermal conductivity enhancement of 4.8 percent or more can be achieved with only a 0.008 percent volume fraction of graphene nanoparticles. Despite those extraordinary promising thermal properties exhibited by graphene suspensions, it remains to be a serious technical challenge to effectively and efficiently disperse graphene into aqueous or organic mediums to produce a nanoparticle suspension with a sustainable stability and consistent thermal properties. Due to hydrophobic natures of graphitic structure, graphene is not soluble in any known solvent. They also have a very high tendency to form aggregates and extended structures of linked nanoparticles, thus leading to phase separation, poor dispersion within a matrix, and poor adhesion to the host. However, stability of the nanoparticle suspension is especially essential for practical industrial applications. Otherwise, the thermal properties of a nanofluid, such as thermal conductivity, will constantly change as the solid nanoparticles gradually separate from the fluid. Accordingly, there is a great need for the development of an effective formulation which can be used to efficiently disperse different forms of graphene into a desired heat transfer fluid and produce a nanofluid with a sustainable stability and consistent thermal properties. Therefore, the nanofluid may comprise a conventional heat transfer fluid, graphene nanoparticles, metal oxide nanoparticles and a surfactant. The metal oxide nanoparticles in combination with the surfactant are used to facilitate the dispersion of the graphene nanoparticles and to increase the stability of the nanofluid. There is a charge attraction between the nonpolar region of the surfactant molecules and the graphene nanoparticles. This interaction forms a shell around the graphene nanoparticles, with the charged head region of the surfactant molecules oriented towards the outside. This facilitates the dispersion of the graphene nanoparticles in the fluid thus preventing precipitation from the fluid, which in turn enhances thermal conductivity. To further enhance thermal conductivity, metal oxide nanoparticles are also added to the thermal transfer fluid. These positively charged metal oxide nanoparticles repel one another and further enhance stability and thermal conductivity of the nanofluid. The term surfactant refers to a molecule having surface activity, including wetting agents, dispersants, emulsifiers, detergents, and foaming agents. A variety of surfactants may alternatively be included in the present study as a dispersant to facilitate uniform dispersion of nanoparticles in a desired thermal transfer fluid, and to enhance stabilization of such a dispersion as well.

Typically, the surfactants used in the present study contain a lipophilic nonpolar hydrocarbon group and a polar functional hydrophilic group. The polar functional group may be a carboxylate, ester, amine, amide, imide, hydroxyl, ether, nitrile, phosphate, sulfate, or sulfonate. The surfactants that are useful in the present study may be used alone or in combination. Accordingly, any combination of surfactants may include anionic, cationic, nonionic, zwitterionic, amphoteric and ampholytic surfactants, so long as there is a net positive charge in the head regions of the population of surfactant molecules. In most instances, a single negatively charged surfactant is used in the preparation of the nanofluids of the present study.

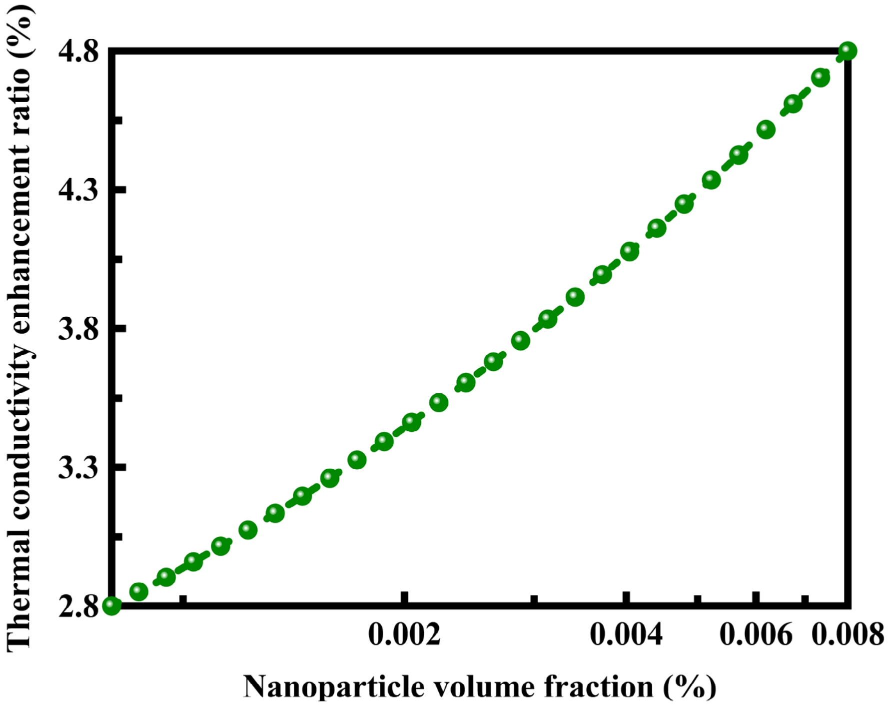

Figure 6. Thermal conductivity enhancement ratio of the nanofluid with suspended graphene nanoparticles at different nanoparticle volume fractions.

The effect of nanoparticle volume fraction on the viscosity enhancement ratio is illustrated in Figure 7 for the nanofluid with suspended graphene nanoparticles. Production of metal containing nanofluids faces some major challenges, such as stability towards agglomeration and surface oxidation, availability, cost of materials and manufacturing issues. Dramatic increases in thermal conductivity of nanofluids are most likely due to the unique nature of such highly anisotropic graphene nanomaterials that allows engaging multiple heat transfer mechanisms in suspensions, arising from the effective medium theory, percolation, and plasmon resonances. The drawback of carbonaceous nanofluids with high aspect ratio particles is very high viscosity, up to about 14 percent higher than viscosity of the base fluid. Such viscosity increases result in pumping power penalties that are much higher than the benefits in thermal conductivity of suspensions. Industrial applications for nanofluid technology are in an embryonic state. However, today, the nanofluid field has developed to the point where it is appropriate to look to the next level, namely nanofluids that show substantial heat transfer enhancement over their base fluids and are candidates for use in a variety of industrial and commercial systems. For example, potential use of nanofluids for cooling systems such as power electronics and also for radiators in vehicles, will require not only enhanced thermal properties, but also minimal negative mechanical effects of the nanofluids in a closed system. In this regard, reduced viscosity of the nanofluid for instance is a contributing factor to reducing pumping power needed for the circulation of the nanofluid. Since the cooling efficiency of the heat transfer fluids is the main consideration in the current nanofluid development, the ratio of heat transfer coefficients for the suspensions and the base fluid is estimated for fully developed, laminar and turbulent flow regimes using conventional fluid dynamic equations. The ratio of heat transfer coefficients is a convenient measure for comparison of two fluids flowing in the same geometry and at the same flow rates. In a laminar flow regime, the heat transfer coefficients are proportional to the thermal conductivity, but in a turbulent flow regime the heat transfer coefficients depend on a set of thermo-physical properties. Introduction of nanoparticles to the fluid changes density, thermal conductivity viscosity, and specific heat of the fluid. In the case of hydrodynamically and thermally fully developed laminar flow, the heat transfer coefficient is proportional to the thermal conductivity, and within the acceptable range of inlet and outlet temperature difference is independent of the flow velocity. The comparison of two liquids flowing in fully developed turbulent flow regime over or through a given geometry at a fixed velocity reduces to the ratio of changes in the thermo-physical properties. Suspensions with larger diameter and thickness of nanoparticles provide the highest increase in thermal conductivity; however, viscosity increase of up to about 14 percent makes this fluid impractical for heat transfer applications. The optimization of viscosity and thermal conductivity increases in nanofluids is required for development of practical nanofluid with advanced heat transfer. Segregation of surfactants at liquid-nanoparticle interface creates additional thermal resistance for heat flow. Thus, organic surfactants are detrimental for the thermal conductivity of water-based suspensions. Use on non-surfactant approach to stabilizing dispersions of nanoparticles involves an additional surface functionalization step as described hereinafter.

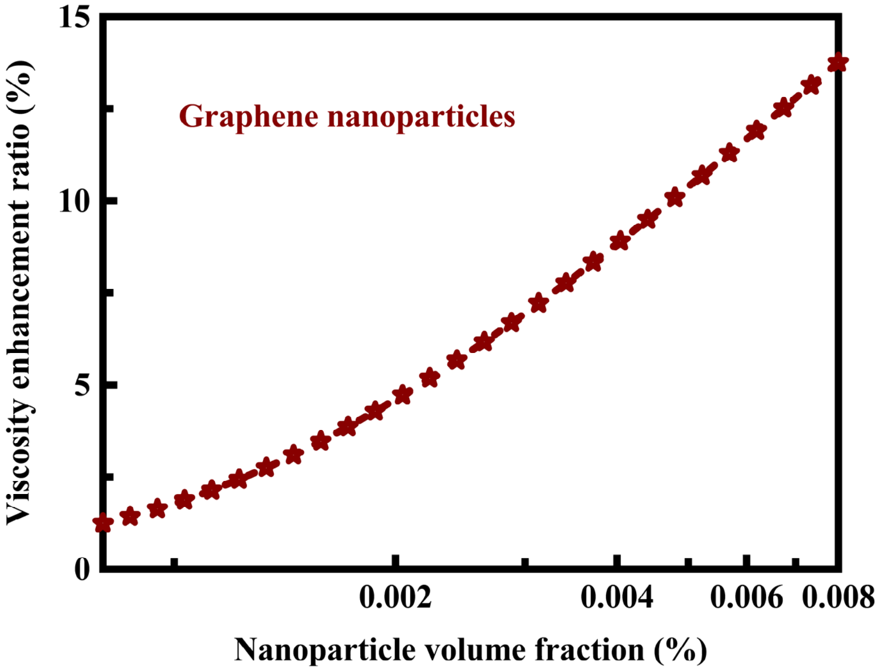

Figure 7. Viscosity enhancement ratio of the nanofluid with suspended graphene nanoparticles at different nanoparticle volume fractions.

The effect of nanoparticle volume fraction on the viscosity enhancement ratio is illustrated in Figure 8 for the nanofluid with suspended graphene oxide nanoparticles. Surface functionalization can convert oxidized sp^2 graphitic layers into a variety of hydroxy- and carboxylic ionic groups. These groups can carry electrostatic charge and are miscible with water-based fluids. Thus, core-shell structures of graphitic gore and graphene oxide shell are formed. On one hand, surface oxidation helps increasing the stability and decreasing viscosity of nanofluids; but, on the other hand, thermal conductivity of graphene oxides is much smaller than that of graphite and graphene. Therefore, the functionalization process decreases enhancements in thermal conductivity due to formation of surface oxides. In development of nanofluids for heat transfer a fine balance needs to be obtained between increases in thermal conductivity and viscosity. For graphitic nanoparticle suspensions, advanced thermal conductivity is observed when nanoparticle percolation threshold is achieved. The concentration of the percolation threshold will vary with particle morphology, and both platelet diameter and thickness are important for that matter. Besides the important role of surface charges in nanoparticle agglomeration and viscosity of nanofluids, particle shape effect can also play a role in abnormally increased viscosity of graphitic nanofluids. Shear rate dependence of viscosity in suspensions indicates some restriction in fluid movement due to particle alignment and agglomeration. In a steady state, a rod-like particle or elongated agglomerate can have two types of motion due to the Brownian movements: rotational motion around the mid-point, and translational motion in parallel or perpendicular to the long axis. When the average spacing between particles is much larger than the longest dimension of the particle, the rotational and translational motions are not restricted by each other; hence very weak shear thinning behavior is expected. In suspensions of cylinders with higher volume fractions nanoparticles start to interact, so the viscosities at zero shear rate can be much greater than the base fluid viscosity and be very sensitive to the shear. At concentrations of nanomaterials that are significantly above the percolation threshold, an extended microstructure will be created in a nanofluid, obstructing the fluid flow and producing high viscosities. Such enhancements are possible with graphitic nanoparticles that are commercially available at reasonable costs. Surface chemistry and functionalization provides better dispersion stability, lower viscosity, and higher thermal conductivity, enhanced performance with temperature.

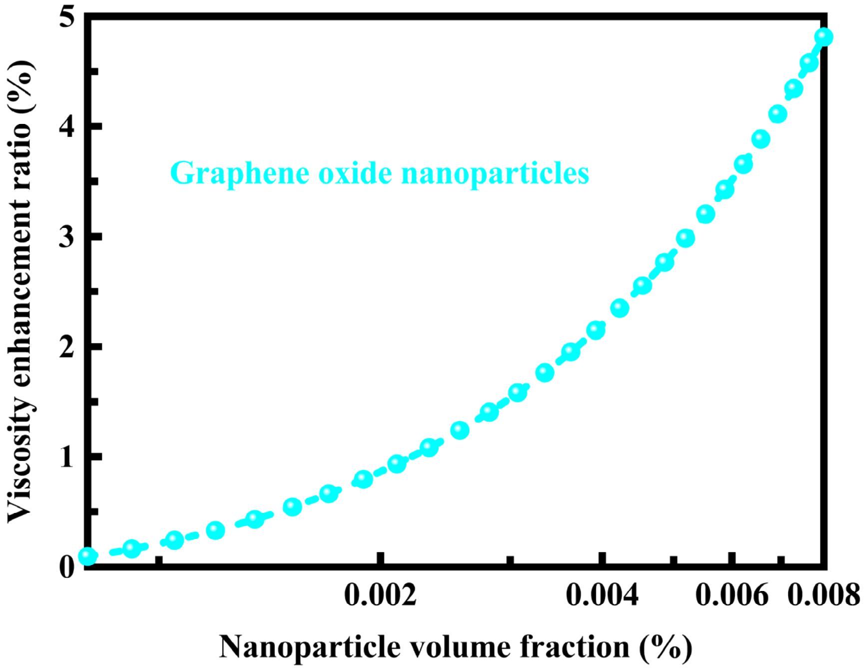

Figure 8. Viscosity enhancement ratio of the nanofluid with suspended graphene oxide nanoparticles at different nanoparticle volume fractions.

4. Conclusions

A graphite material is exfoliated to form graphene particles, and the effect of nanoparticle volume fraction on the material properties of inhomogeneous fluids with suspended graphene nanoparticles is investigated at different temperatures or under oxidation conditions. The present study aims to provide a fundamental understanding of the thermal and viscosity properties of inhomogeneous fluids with suspended graphene nanoparticles. Particular emphasis is placed upon the effect of nanoparticle volume fraction on the material properties of inhomogeneous fluids with suspended graphene nanoparticles. The major conclusions are summarized as follows:

- The bottom-up approach produces low quantities with high quality and large flakes. The top-down approach using graphite is low in cost and yields a high concentration of suspended flakes, but fabricates limited-size sheets with a low yield of mono-layer graphene.
- Smaller dispersions result in ease of addition of graphene to other desirable emulsions to enhance the uniform coating matrix for protection attributes graphene can provide to the coating.

- The pressure drop allows the liquid precursor to flow and homogenizes the pass-through liquid of the liquid precursor that contains thin layers of graphene such that the smaller graphene platelet particle is well dispersed in the resultant fluid product.
- The phonon Raman scattering changes are correlated with structural changes and defects associated with the hydroxyl and epoxy groups in the basal plane and a variety of alkyl and oxygen-containing functional groups terminating the edges.
- Graphene-containing nanofluids provide several advantages over the conventional fluids, including thermal conductivities far above those of traditional solid-liquid suspensions, a nonlinear relationship between thermal conductivity and concentration, strongly temperature-dependent thermal conductivity, and a significant increase in critical heat flux.
- Stability of the nanoparticle suspension is especially essential for practical industrial applications.
- Introduction of nanoparticles to the fluid changes density, thermal conductivity viscosity, and specific heat.
- The functionalization process decreases enhancements in thermal conductivity due to formation of surface oxides. In development of nanofluids for heat transfer a fine balance needs to be obtained between increases in thermal conductivity and viscosity.

References

[1] M. Trushin and J. Schliemann. Minimum electrical and thermal conductivity of graphene: A quasiclassical approach. *Physical Review Letters*, Volume 99, Issue 21, 2007, Article Number: 216602.

[2] Y.V. Skrypnyk and V.M. Loktev. Electrical conductivity in graphene with point defects. *Physical Review B*, Volume 82, Issue 8, 2010, Article Number: 085436.

[3] M.N. Esfahani, M. Jabbari, Y. Xu, and C. Soutis. Effect of nanoscale defects on the thermal conductivity of graphene. *Materials Today Communications*, Volume 26, 2021, Article Number: 101856.

[4] A. Alofi and G.P. Srivastava. Thermal conductivity of graphene and graphite. *Physical Review B*, Volume 87, Issue 11, 2013, Article Number: 115421.

[5] M. Taghioskoui. Trends in graphene research. *Materials Today*, Volume 12, Issue 10, 2009, Pages 34-37.

[6] F. Guinea, B. Horovitz, and P.L. Doussal. Gauge fields, ripples and wrinkles in graphene layers. *Solid State Communications*, Volume 149, Issues 27-28, 2009, Pages 1140-1143.

[7] A.S. Thampy, M.S. Darak, and S.K. Dhamodharan. Analysis of graphene based optically transparent patch antenna for terahertz communications. *Physica E: Low-dimensional Systems and Nanostructures*, Volume 66, 2015, Pages 67-73.

[8] D.H. Shin, Y.-J. Kim, S.-K. Lee, S. Bae, and S. Ahn. Atomically thin alkane passivation layer for flexible and transparent graphene electronics. *Applied Surface Science*, Volume 612, 2023, Article Number: 155695.

[9] F. Arca, J.P. Mendez, M. Ortiz, and M.P. Ariza. Strain-tuning of transport gaps and semiconductor-to-conductor phase transition in twinned graphene. *Acta Materialia*, Volume 234, 2022, Article Number: 117987.

[10] E. Wu, C. Schneider, R. Walz, and J. Park. Adsorption of hydrogen isotopes on graphene. *Nuclear Engineering and Technology*, Volume 54, Issue 11, 2022, Pages 4022-4029.

[11] F. Sultanov, A. Mentbayeva, S. Kalybekkyzy, A. Zhaisanova, S.-T. Myung, and Z. Bakenov. Advances of graphene-based aerogels and their modifications in lithium-sulfur batteries. *Carbon*, Volume 201, 2023, Pages 679-702.

[12] M.B. Arvas, M. Gencten, and Y. Sahin. Investigation of supercapacitor properties of chlorine-containing functional groups doped graphene electrodes. *Journal of Electroanalytical Chemistry*, Volume 918, 2022, Article Number: 116438.

[13] S. Ghosal, N.S. Mondal, S. Chowdhury, and D. Jana. Two novel phases of germa-graphene: Prediction, electronic and transport applications. *Applied Surface Science*, Volume 614, 2023, Article Number: 156107.

[14] H. Assad, I. Fatma, and A. Kumar. An overview of the application of graphene-based materials in anticorrosive coatings. *Materials Letters*, Volume 330, 2023, Article Number: 133287.

[15] N. Koosha, J. Karimi-Sabet, M.A. Moosavian, and Y. Amini. Improvement of synthesized graphene structure through various solvent liquids at low temperatures by chemical vapor deposition method. *Materials Science and Engineering: B*, Volume 274, 2021, Article Number: 115458.

[16] J. Kulczyk-Malecka, I.V.J.D. Santos, M. Betbeder, S.J. Rowley-Neale, Z. Gao, and P.J. Kelly. Low-temperature synthesis of vertically aligned graphene through microwave-assisted chemical vapour deposition. *Thin Solid Films*, Volume 733, 2021, Article Number: 138801.

[17] M. Batzill. The surface science of graphene: Metal interfaces, CVD synthesis, nanoribbons, chemical modifications, and defects. *Surface Science Reports*, Volume 67, Issues 3-4, 2012, Pages 83-115.

[18] A. Hussain, S.M. Mehdi, N. Abbas, M. Hussain, and R.A. Naqvi. Synthesis of graphene from solid carbon sources: A focused review. *Materials Chemistry and Physics*, Volume 248, 2020, Article Number: 122924.

[19] M.J. Im, S.-K. Hyeong, J.-H. Lee, T.-W. Kim, S.-K. Lee, G.Y. Jung, and S. Bae. High uniformity and stability of graphene transparent conducting electrodes by dual-side doping. *Applied Surface Science*, Volume 605, 2022, Article Number: 154569.

[20] J.S. Roh, J.K. Jang, N. Kwon, S. Bok, Y.J. Kim, C. Jeon, H.W. Yoon, H.W. Kim, B. Lim, and H.B. Park. Macroscopic properties of single-crystalline and polycrystalline graphene on soft substrate for transparent electrode applications. *Carbon*, Volume 178, 2021, Pages 181-189.

[21] A. Triana, J.J. Olaya, and C. Prieto. Effect of the electrolyte composition on the corrosion resistance of single-layer CVD-graphene. *Surfaces and Interfaces*, Volume 31, 2022, Article Number: 102025.

[22] S. Kumar, J. Shakya, T. Mahanta, D. Kanjilal, and T. Mohanty. Substrate-assisted Fermi level shifting of CVD graphene by swift heavy ions. *Surfaces and Interfaces*, Volume 28, 2022, Article Number: 101625.

[23] S.R. Joshi, J. Lee, and G.-H. Kim. Low-cost synthesis of high quality graphene oxide with large electrical and thermal conductivities. *Materials Letters*, Volume 292, 2021, Article Number: 129649.

[24] A.A. Tarhini and A.R. Tehrani-Bagha. Graphene-based polymer composite films with enhanced mechanical properties and ultra-high in-plane thermal conductivity. *Composites Science and Technology*, Volume 184, 2019, Article Number: 107797.

[25] A. Alhusseny, A. Al-Fatlawi, Q. Al-Aabidy, A. Nasser, and N. Al-Zurfi. Dissipating the heat generated in high-performance electronics using graphitic foam heat-sinks cooled with a dielectric liquid. *International Communications in Heat and Mass Transfer*, Volume 127, 2021, Article Number: 105478.

[26] K. Rostem, E. Cimpoiasu, K.R. Helson, A.P. Klassen, and E.J. Wollack. Specific heat of epoxies and mixtures containing silica, carbon lamp black, and graphite. *Cryogenics*, Volume 118, 2021, Article Number: 103329.

[27] P. Jamzad, J. Kenna, and M. Bahrami. Development of novel plate heat exchanger using natural graphite sheet. *International Journal of Heat and Mass Transfer*, Volume 131, 2019, Pages 1205-1210.

[28] D.S. Jang, D. Kim, S.H. Hong, and Y. Kim. Comparative thermal performance evaluation between ultrathin flat plate pulsating heat pipe and graphite sheet for mobile electronic devices at various

operating conditions. *Applied Thermal Engineering*, Volume 149, 2019, Pages 1427-1434.

[29] B. Bhaduri. Synthesis of Cu catalyzed chemical vapor deposition grown Cu-CNFs on less porous graphite powder. *Materials Letters*, Volume 305, 2021, Article Number: 130828.

[30] J.H. Han, K.W. Cho, K.-H. Lee, and H. Kim. Porous graphite matrix for chemical heat pumps. *Carbon*, Volume 36, Issue 12, 1998, Pages 1801-1810.

[31] M. Bonnissel, L. Luo, and D. Tondeur. Compacted exfoliated natural graphite as heat conduction medium. *Carbon*, Volume 39, Issue 14, 2001, Pages 2151-2161.

[32] S. Hoshii, A. Kojima, and M. Goto. Rapid baking of graphite powders by the spark plasma sintering method. *Carbon*, Volume 38, Issue 13, 2000, Pages 1896-1899.

[33] J.H. Han and K.-H. Lee. Gas permeability of expanded graphite-metallic salt composite. *Applied Thermal Engineering*, Volume 21, Issue 4, 2001, Pages 453-463.

[34] R. Janot and D. Guérard. Ball-milling: the behavior of graphite as a function of the dispersal media. *Carbon*, Volume 40, Issue 15, 2002, Pages 2887-2896.

[35] E.L. Kitanin, M.S. Ramm, V.V. Ris, and A.A. Schmidt. Heat transfer through source powder in sublimation growth of SiC crystal. *Materials Science and Engineering: B*, Volume 55, Issue 3, 1998, Pages 174-183.

[36] A. Yeoh, C. Persad, and Z. Eliezer. Dimensional responses of copper-graphite powder composites to sintering. *Scripta Materialia*, Volume 37, Issue 3, 1997, Pages 271-277.

[37] M. Wissler. Graphite and carbon powders for electrochemical applications. *Journal of Power Sources*, Volume 156, Issue 2, 2006, Pages 142-150.

[38] C. Natarajan, H. Fujimoto, A. Mabuchi, K. Tokumitsu, and T. Kasuh. Effect of mechanical milling of graphite powder on lithium intercalation properties. *Journal of Power Sources*, Volume 92, Issues 1-2, 2001, Pages 187-192.

[39] H.A. Wilhelm, B. Croset, and G. Medjahdi. Proportion and dispersion of rhombohedral sequences in the hexagonal structure of graphite powders. *Carbon*, Volume 45, Issue 12, 2007, Pages 2356-2364.

[40] R. Bissessur, P.K.Y. Liu, and S.F. Scully. Intercalation of polypyrrole into graphite oxide. *Synthetic Metals*, Volume 156, Issues 16-17, 2006, Pages 1023-1027.

[41] T. Rayment, R. Schlogl, and J.M. Thomas. Low-temperature x-ray powder diffraction studies of antimony pentachloride-intercalated graphite. *Physical Review B*, Volume 30, Issue 2, 1984, Pages 1034-1037.

[42] S. Chandrasekaran, T. Basak, and R. Srinivasan. Microwave heating characteristics of graphite based powder mixtures. *International Communications in Heat and Mass Transfer*, Volume 48, 2013, Pages 22-27.

[43] F. Bagheri, M. Fakoor-Pakdaman, and M. Bahrami. Utilization of orthotropic graphite plates in plate heat exchangers, analytical modeling. *International Journal of Heat and Mass Transfer*, Volume 77, 2014, Pages 301-310.

[44] K. Sultan, C.T. DeGroot, A.G. Straatman, N.C. Gallego, and H. Hangan. Thermal characterization of porous graphitic foam - Convection in impinging flow. *International Journal of Heat and Mass Transfer*, Volume 52, Issues 19-20, 2009, Pages 4296-4301.

[45] N. Burger, A. Laachachi, B. Mortazavi, M. Ferriol, M. Lutz, V. Toniazzo, and D. Ruch. Alignments and network of graphite fillers to improve thermal conductivity of epoxy-based composites. *International Journal of Heat and Mass Transfer*, Volume 89, 2015, Pages 505-513.

[46] Y. Wen-Jei, H. Takizawa, and D.L. Vrable. Augmented boiling on copper-graphite composite surface. *International Journal of Heat and Mass Transfer*, Volume 34, Issue 11, 1991, Pages 2751-2758.

[47] B. Simon, S. Flandrois, K. Guerin, A. Fevrier-Bouvier, I. Teulat, and P. Biensan. On the choice of graphite for lithium ion batteries. *Journal of Power Sources*, Volumes 81-82, 1999, Pages 312-316.

[48] A.M. Andersson, K. Edström, N. Rao, and Å. Wendsjö. Temperature dependence of the passivation layer on graphite. *Journal of Power Sources*, Volumes 81-82, 1999, Pages 286-290.

[49] S.G. Kim, S.J. Heo, S. Kim, J. Kim, S.O. Kim, D. Lee, S. Lee, J. Kim, N.-H. You, M. Kim, H.C. Kim, H.G. Chae, and B.-C. Ku. Ultrahigh strength and modulus of polyimide-carbon nanotube based carbon and graphitic fibers with superior electrical and thermal conductivities for advanced composite applications. *Composites Part B: Engineering*, Volume 247, 2022, Article Number: 110342.

[50] D.W. Kim, K.W. Lee, J.-W. Jang, and C.E. Lee. Dimensional crossover of quantum Hall conductivity in graphite through proton-irradiation. *Carbon*, Volume 187, 2022, Pages 126-132.

[51] H. Aghamohammadi, R. Eslami-Farsani, M. Torabian, and N. Amousa. Recent advances in one-pot functionalization of graphene using electrochemical exfoliation of graphite: A review study. *Synthetic Metals*, Volume 269, 2020, Article Number: 116549.

[52] J.A. Morton, A. Kaur, M. Khavari, A.V. Tyurnina, A. Priyadarshi, D.G. Eskin, J. Mi, K. Porfyrakis, P. Prentice, and I. Tzanakis. An eco-friendly solution for liquid phase exfoliation of graphite under optimised ultrasonication conditions. *Carbon*, Volume 204, 2023, Pages 434-446.

[53] V.P. Vasiliev, A.S. Kotkin, V.K. Kochergin, R.A. Manzhos, and A.G. Krivenko. Oxygen reduction reaction at few-layer graphene structures obtained via plasma-assisted electrochemical exfoliation of graphite. *Journal of Electroanalytical Chemistry*, Volume 851, 2019, Article Number: 113440.

[54] J.K. Lynch-Branzoi, A. Ashraf, A. Tewatia, M. Taghon, J. Wooding, J. Hendrix, B.H. Kear, and T.J. Nosker. Shear exfoliation of graphite into graphene nanoflakes directly within polyetheretherketone and a spectroscopic study of this high modulus, lightweight nanocomposite. *Composites Part B: Engineering*, Volume 188, 2020, Article Number: 107842.

[55] P. Krawczyk, B. Gurzęda, and A. Bachar. Thermal exfoliation of electrochemically obtained graphitic materials. *Applied Surface Science*, Volume 481, 2019, Pages 466-472.

[56] B.D.L. Campéon, M. Akada, M.S. Ahmad, Y. Nishikawa, K. Gotoh, and Y. Nishina. Non-destructive, uniform, and scalable electrochemical functionalization and exfoliation of graphite. *Carbon*, Volume 158, 2020, Pages 356-363.

[57] L.A. Pozhar and K.E. Gubbins. Quasihydrodynamics of nanofluid mixtures. *Physical Review E*, Volume 56, Issue 5, 1997, Pages 5367-5396.

[58] D.H. Kumar, H.E. Patel, V.R.R. Kumar, T. Sundararajan, T. Pradeep, and S.K. Das. Model for heat conduction in nanofluids. *Physical Review Letters*, Volume 93, Issue 14, 2004, Article Number: 144301.

[59] G. Donzelli, R. Cerbino, and A. Vailati. Bistable heat transfer in a nanofluid. *Physical Review Letters*, Volume 102, Issue 10, 2009, Article Number: 104503.

[60] M. Bernardin, F. Comitani, and A. Vailati. Tunable heat transfer with smart nanofluids. *Physical Review E*, Volume 85, Issue 6, 2012, Article Number: 066321.

[61] L.A. Pozhar. Structure and dynamics of nanofluids: Theory and simulations to calculate viscosity. *Physical Review E*, Volume 61, Issue 2, 2000, Pages 1432-1446.

[62] J.K. Percus, L.A. Pozhar, and K.E. Gubbins. Local thermodynamics of inhomogeneous fluids at equilibrium. *Physical Review E*, Volume 51, Issue 1, 1995, Pages 261-265.

[63] L.A. Pozhar, K.E. Gubbins, and J.K. Percus. Generalized compressibility equation for inhomogeneous fluids at equilibrium. *Physical Review E*, Volume 48, Issue 3, 1993, Pages 1819-1822.

[64] M. Glässl, M. Hilt, and W. Zimmermann. Convection in nanofluids with a particle-concentration-dependent thermal conductivity. *Physical Review E*, Volume 83, Issue 4, 2011, Article Number: 046315.

[65] J. Eapen, J. Li, and S. Yip. Beyond the Maxwell limit: Thermal conduction in nanofluids with

percolating fluid structures. *Physical Review E*, Volume 76, Issue 6, 2007, Article Number: 062501.

[66] S. Kondaraju, E.K. Jin, and J.S. Lee. Investigation of heat transfer in turbulent nanofluids using direct numerical simulations. *Physical Review E*, Volume 81, Issue 1, 2010, Article Number: 016304.

[67] M. Rajnak, Z. Spitalsky, B. Dolnik, J. Kurimsky, L. Tomco, R. Cimbala, P. Kopcansky, and M. Timko. Toward apparent negative permittivity measurement in a magnetic nanofluid with electrically induced clusters. *Physical Review Applied*, Volume 11, Issue 2, 2019, Article Number: 024032.

[68] P. Ben-Abdallah. Dynamic structure and cluster formation in confined nanofluids under the action of an external force field. *Physical Review E*, Volume 74, Issue 4, 2006, Article Number: 041407.

[69] L. Braginsky and V. Shklover. Thermal conductivity of low-particle-concentration suspensions: Correlation function approach. *Physical Review B*, Volume 78, Issue 22, 2008, Article Number: 224205.

[70] A. Gupta, P. Magaud, C. Lafforgue, and M. Abbas. Conditional stability of particle alignment in finite-Reynolds-number channel flow. *Physical Review Fluids*, Volume 3, Issue 11, 2018, Article Number: 114302.

[71] S.A. Egorov. Interactions between nanoparticles in supercritical fluids: From repulsion to attraction. *Physical Review E*, Volume 72, Issue 1, 2005, Article Number: 010401(R).

[72] T. Shende, D. Mangal, J.C. Conrad, V. Niasar, and M. Babaei. Nanoparticle transport within non-Newtonian fluid flow in porous media. *Physical Review E*, Volume 106, Issue 1, 2022, Article Number: 015103.

[73] D.R. Evans, S.A. Basun, G. Cook, I.P. Pinkevych, and V.Y. Reshetnyak. *Physical Review B*, Volume 84, Issue 17, 2011, Article Number: 174111.

[74] S. Merabia, P. Keblinski, L. Joly, L.J. Lewis, and J.-L. Barrat. Critical heat flux around strongly heated nanoparticles. *Physical Review E*, Volume 79, Issue 2, 2009, Article Number: 021404.

[75] M. Rafique, M.S. Rafique, S.H. Butt, A. Afzal, and U. Kalsoom. Laser nature dependence on enhancement of optical and thermal properties of copper oxide nanofluids. *Applied Surface Science*, Volume 483, 2019, Pages 187-193.

[76] S. Rostami, A.A. Nadooshan, A. Raisi, and M. Bayareh. Modeling the thermal conductivity ratio of an antifreeze-based hybrid nanofluid containing graphene oxide and copper oxide for using in thermal systems. *Journal of Materials Research and Technology*, Volume 11, 2021, Pages 2294-2304.

[77] I. Zaaroura, M. Toubal, H. Reda, J. Carlier, S. Harmand, R. Boukherroub, A. Fasquelle, and B. Nongaillard. Evaporation of nanofluid sessile drops: Infrared and acoustic methods to track the dynamic deposition of copper oxide nanoparticles. *International Journal of Heat and Mass Transfer*, Volume 127, Part B, 2018, Pages 1168-1177.

[78] L. Fu and L. Resca. Exact theory of the electrostatic interaction in electrorheological fluids and the effects of particle structure. *Solid State Communications*, Volume 99, Issue 2, 1996, Pages 83-87.