Research Article

Thermophysical Properties And Heat Transfer Performance Of N-Doped Carbon-Metal Oxide Nanocomposite Nanofluids

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Abstract

Nanofluids, made by dispersing solid nanoparticles in a base fluid such as water or ethylene glycol, raise the thermal conductivity of ordinary coolants but come with two familiar penalties: the viscosity rises with loading, and the particles tend to settle or clump over time. Nitrogen-doped carbon combined with a transition metal oxide is one of the more promising particle chemistries for getting round these penalties. The carbon phase (graphene, graphene oxide or nanoplatelets) carries a high intrinsic thermal conductivity and, once nitrogen is doped into its lattice, improved wettability and dispersibility in polar base fluids; the metal oxide (Fe_3O_4, Al_2O_3, TiO_2, CuO and related oxides) adds mass, magnetic or optical function, and anchoring sites that keep the carbon sheets from restacking. This review gathers what is known about these hybrid nanofluids. We first cover how they are prepared, the two-step and one-step routes, the choice of base fluid, and the surfactant or functionalization strategies that decide stability. We then treat the thermophysical properties one at a time: thermal conductivity and the mechanisms proposed for its enhancement (Brownian motion, the interfacial nanolayer and particle aggregation), dynamic viscosity, specific heat capacity, density and electrical conductivity, with reported enhancement figures drawn from the experimental literature. The heat-transfer section covers convective performance in laminar and turbulent flow, the Nusselt-number and heat-transfer-coefficient gains reported for nitrogen-doped graphene and carbon-metal oxide hybrids, entropy generation, and device-level results in heat exchangers and solar collectors. We close with the problems that still limit use: the trade-off between conductivity gain and pumping penalty, long-term stability, the gap between property measurements and full-system performance, and the shortage of data specific to nitrogen-doped carbon-metal oxide hybrids as opposed to their single-component parents.

Keywords: nanofluid; nitrogen-doped carbon; metal oxide; hybrid nanofluid; thermal conductivity; viscosity; convective heat transfer; thermal management

1. Introduction

Every system that moves heat, a car radiator, a data-centre cold plate, a solar collector, a power-electronics module, is limited in part by the fluid that carries the heat away. Water, ethylene glycol and thermal oils conduct heat poorly compared with solids, so engineers have long looked for ways to make the working fluid itself carry more. Suspending solid particles is the oldest idea, but micron-sized particles settle and erode surfaces. Nanofluids, which use particles below about 100 nm, largely solved the settling problem and reopened the approach, because even a small volume fraction of a high-conductivity solid can lift the effective thermal conductivity of the base fluid noticeably [1,2].

Two families of nanoparticle dominate the field, and each has a weakness. Metal oxides such as Al_2O_3, TiO_2, CuO and Fe_3O_4 are cheap, chemically stable and easy to disperse, but their own thermal conductivity is modest, so the conductivity gain they give a fluid is limited [1]. Carbon nanostructures, especially graphene, graphene oxide and graphene nanoplatelets, have very high in-plane thermal conductivity and low density, so on paper they are the better filler; in practice they are hydrophobic, restack into graphitic aggregates, and need surfactants or chemical functionalization to stay suspended in water [7,14]. Neither family on its own gives both a large conductivity gain and good long-term stability.

Combining a carbon phase with a metal oxide addresses this directly, and doping the carbon with nitrogen sharpens the benefit. Anchoring an oxide such as Fe_3O_4 onto graphene sheets keeps the sheets separated so they cannot restack, and the oxide adds functions the carbon lacks, mass and magnetic response for magnetically controllable fluids, or optical absorption for direct-absorption solar collectors [16,20]. Nitrogen doping changes the carbon in a way that matters for a fluid rather than a solid device: the doped sites raise the polarity and wettability of the sheet surface, which improves dispersion in polar base fluids and cuts the amount of surfactant needed, and they do so while keeping most of the carbon's conductive character [5,7]. The result is a class of hybrid nanofluids that reach large conductivity enhancements at low loading while dispersing more readily than undoped carbon fluids.

The measured performance of these fluids has been encouraging. Nitrogen-doped graphene nanofluids have shown thermal conductivity enhancements above 30% and convective heat-transfer-coefficient gains in the tens of percent in laminar tube flow [6]. Hybrid carbon-metal oxide fluids such as MWCNT-Fe_3O_4 in water have improved the effectiveness of compact heat exchangers and the efficiency of solar collectors [17,18]. This review organizes that body of work around the physics rather than around individual papers. Section 2 covers preparation and stability. Section 3 treats the thermophysical properties one at a time, with the mechanisms behind thermal-conductivity enhancement. Section 4 covers convective heat transfer and device-level results. Section 5 isolates what nitrogen doping and hybridization each contribute. Section 6 is a candid account of the open problems, and Section 7 concludes.

2. Preparation and stability of the nanofluids

2.1 The nanocomposite and the role of nitrogen

The particle itself is a nitrogen-doped carbon phase carrying, or decorated with, a metal oxide. Nitrogen enters the carbon lattice during synthesis, most simply by annealing graphite oxide with a nitrogen-rich precursor such as melamine, or hydrothermally treating graphene oxide with ammonia, which installs pyridinic, pyrrolic and graphitic nitrogen at the sheet edges and basal plane [9]. For nanofluid use the important consequence is not electronic but colloidal: the doped nitrogen and the residual oxygen groups make the sheet surface more polar, so it wets and disperses in water and ethylene glycol far better than pristine graphene, which is strongly hydrophobic [5,7]. Growing or precipitating a metal oxide such as Fe_3O_4 onto the doped sheets, usually by co-precipitation or an in-situ hydrothermal step, both adds the oxide's function and keeps the sheets physically apart so they resist restacking [16,17]. Nitrogen-doped carbon can also be grown directly on a metal support, as in the chemical-vapour-deposition growth of nitrogen-doped graphene on copper nanowires used for thermal-interface materials, which shows the same pairing in a solid rather than a fluid [10].

2.2 Two-step and one-step routes and the choice of base fluid

Almost all of these nanofluids are made by the two-step method: the nanocomposite powder is synthesised first, then dispersed into the base fluid by stirring and ultrasonication, sometimes with a surfactant. The route is simple and scalable, which is why most experimental studies use it, including the nitrogen-doped graphene fluids that established the field [5,6]. Its weakness is that a dry powder wants to re-agglomerate as soon as it is wetted, so dispersion quality depends heavily on sonication time and surfactant choice. The one-step method, which produces and disperses the particles in the fluid in a single operation, gives better dispersion and less aggregation but is harder to scale and constrains the choice of base fluid. Water is the most common base fluid, followed by ethylene glycol and water-ethylene glycol mixtures for sub-zero and automotive coolant use, where the crumpled nitrogen-doped graphene coolant of Amiri and co-workers is a representative example [7].

2.3 Stability, surfactants and functionalization

Stability decides whether a nanofluid is useful, because a fluid that sediments loses its conductivity gain and can foul a channel. Dispersion is governed by the balance between van der Waals attraction between particles and the repulsion supplied by an electrical double layer or by adsorbed molecules; when repulsion wins, the particles stay separated and the fluid is stable [2,4]. Three levers control that balance. Surfactants add steric or electrostatic repulsion but can foam and degrade at high temperature. Covalent or non-covalent functionalization of the carbon surface, attaching polar groups directly, gives more durable stability than physisorbed surfactant, and covalently modified carbon nanotubes have shown some of the best long-term stability reported [1]. Adjusting pH away from the particle's isoelectric point raises the zeta potential and the electrostatic repulsion. Nitrogen doping helps here too, because it builds polarity into the sheet rather than relying on an added dispersant, which is one reason nitrogen-doped carbon fluids need less surfactant than their undoped counterparts [5,7]. Stability is assessed by sedimentation photographs, zeta-potential measurement and UV-visible absorbance over time, and the aggregation state that these track feeds directly back into the thermal conductivity and viscosity discussed next [4].

3. Thermophysical properties

3.1 Thermal conductivity and the mechanisms behind its enhancement

Thermal conductivity is the property nanofluids are built to raise, and carbon-metal oxide hybrids raise it substantially. Nitrogen-doped graphene aqueous nanofluids reported by Mehrali and co-workers reached enhancements in the range of roughly 22% to 37% over water depending on concentration and temperature, larger than most metal-oxide fluids at comparable loading [5,6]. Graphene oxide nanosheet fluids showed similar behavior, with conductivity rising with both loading and temperature [11]. Hybrid fluids that pair carbon with an oxide add the oxide's contribution and the benefit of better dispersion: a graphene-Fe_3O_4 water fluid gave about a 6% rise at very low mass fraction, and an MWCNT-Fe_3O_4 fluid reached about 28% enhancement at 0.3 vol% and 60 degrees C [16,18]. The enhancement in every case grows with particle loading and, for most systems, with temperature.

Why the conductivity rises by more than simple mixing rules predict is still debated, and several mechanisms are proposed rather than one settled cause [2,3]. The interfacial nanolayer model attributes part of the gain to an ordered layer of base-fluid molecules that forms on the particle surface and conducts better than the bulk liquid; this matters most for high-surface-area sheets like graphene. Brownian motion of the particles is argued to drive micro-convection in the surrounding fluid and to bring particles into transient contact, though its quantitative role is contested. Particle aggregation cuts both ways: loose, percolating clusters can form conductive pathways and raise conductivity, while dense settled clusters remove particles from suspension and lower it, which is why stability and conductivity are linked [3,4]. For carbon-metal oxide hybrids a further, synergistic effect is reported, where the oxide keeps the carbon dispersed and the carbon bridges between oxide particles, so the pair conducts better than either component alone at the same total loading [16,17]. No single mechanism explains all systems, because the balance shifts with particle shape, base fluid and temperature [2].

3.2 Viscosity

Viscosity is the property that limits how much particle a fluid can carry, because a thicker fluid costs more pumping power and can wipe out the benefit of higher conductivity. Adding nanoparticles always raises viscosity, and the rise steepens with loading. For the MWCNT-Fe_3O_4 solar-collector fluid the viscosity increases over water climbed from about 8% at 0.05 vol% to about 28% at 0.3 vol% at 20 degrees C, and reached about 50% at 0.3 vol% when the fluid was heated to 60 degrees C [18]. Unlike thermal conductivity, viscosity of most nanofluids falls with temperature, following the base fluid, which is helpful because the hottest part of a loop is where low viscosity is most wanted. The practical figure of merit is not conductivity or viscosity alone but their ratio, since a fluid is only worth using if the heat-transfer gain outweighs the pumping penalty; hybrid formulations are attractive partly because a well-dispersed hybrid can raise conductivity strongly while keeping the viscosity rise moderate [16,17].

3.3 Specific heat capacity and density

Specific heat capacity and density are the two properties that usually move the wrong way when particles are added, and both are needed to compute convective performance. Solid nanoparticles have lower specific heat than water or ethylene glycol, so a nanofluid stores slightly less heat per unit mass than its base fluid, and the specific heat falls as loading rises. Density rises with loading, following a simple mixing rule closely, because the solid is denser than the liquid. Most experimental studies measure specific heat by differential scanning calorimetry and density by a vibrating U-tube, or estimate both from mixing correlations for the hybrid particle, as done for the MWCNT-Fe_3O_4 fluids [15,18]. These two properties, together with conductivity and viscosity, are what feed the Nusselt-number and heat-transfer-coefficient calculations, so a complete thermophysical characterizations reports all four across the working temperature range rather than conductivity alone [15].

3.4 Electrical conductivity

Electrical conductivity is less often reported but matters for two reasons: it signals how charged and therefore how well dispersed the particles are, and it constrains use near electronics. Nitrogen-doped graphene fluids carry measurable electrical conductivity that rises with loading, and the doped nitrogen contributes to it; a combined experimental and numerical study of nitrogen-doped graphene nanofluids tracked this behavior and linked it to particle concentration and the surrounding double layer [8]. Where a coolant must be electrically insulating, this property sets a limit that a purely thermal characterization would miss.

3.5 Property summary

Table 1 collects representative reported enhancements. The values come from different fluids, loadings and temperatures, so they show what has been reached rather than a controlled comparison.

Nanofluid	Base fluid	Property change (reported)	Ref.
N-doped graphene	Water	Thermal conductivity +22 to +37%	[5,6]
N-doped graphene	Water	Convective HTC +7 to +50% (laminar)	[6]
Graphene oxide nanosheets	Ethylene glycol / water	Thermal conductivity rises with loading and T	[11]
Graphene-Fe3O4	Water	Thermal conductivity up to +6% (low wt%)	[16]
MWCNT-Fe3O4	Water	k +28.5%; viscosity +50.4% (0.3 vol%, 60 C)	[18]
Graphene nanoplatelets	Water	Nusselt number up to +83% (constant flux)	[14]
Crumpled N-doped graphene	Water-ethylene glycol	Coolant conductivity gain over base fluid	[7]

Table 1. Representative reported thermophysical and heat-transfer enhancements for carbon and carbon-metal oxide nanofluids. Values are from the cited studies under each study's own conditions and are not directly comparable across rows. HTC = heat-transfer coefficient; k = thermal conductivity.

4. Heat transfer performance

4.1 Convective heat transfer in laminar flow

Raising thermal conductivity only helps if it turns into a higher heat-transfer coefficient in a flowing system, and in laminar flow it largely does, because conduction across the fluid dominates there. Nitrogen-doped graphene nanofluids in a laminar tube gave heat-transfer-coefficient gains of roughly 7% to 50% over water, tracking their conductivity enhancement, with the largest gains at the highest loading [6]. Graphene nanoplatelet fluids under a constant wall heat flux reached Nusselt-number increases up to 83% in a horizontal tube [14]. The convective gain generally exceeds the conductivity gain alone, because the particles also flatten the temperature profile and, near the wall, disturb the boundary layer, so a fluid with a 30% conductivity rise can show a larger rise in heat-transfer coefficient [6,13].

4.2 Turbulent flow and the pumping penalty

In turbulent flow the picture is more mixed, because mixing already dominates heat transfer and the added conductivity matters less, while the added viscosity still costs pumping power. Graphene nanoplatelet fluids tested under turbulent conditions still improved the heat-transfer coefficient, but the net benefit has to be judged against the pressure-drop rise [12]. The honest metric for any regime is a performance-evaluation criterion that weighs the heat-transfer gain against the pumping penalty; a fluid clears the bar only when that ratio exceeds one, and hybrid carbon-metal oxide fluids have been shown to exceed it, with a thermal performance factor reported above 1.1 for an MWCNT-Fe_3O_4 fluid in a compact heat exchanger [17].

4.3 Entropy generation

A second-law view adds what the first-law heat-transfer coefficient misses, because it accounts for both the thermal and the frictional losses in one number. Studies of nitrogen-doped graphene and graphene nanoplatelet fluids have computed entropy generation alongside heat transfer and found that the particles cut the thermal component of entropy generation while adding to the frictional component, so an optimum loading exists that minimises total irreversibility [6,13]. This framing is useful because it identifies the concentration beyond which more particle stops helping, which a heat-transfer-coefficient plot alone does not show.

4.4 Device-level performance: heat exchangers and solar collectors

The clearest case for these fluids is in real devices. In compact and plate heat exchangers, hybrid MWCNT-Fe_3O_4 water fluids raised effectiveness by around 12% to 13% and the number of transfer units by around 20% to 24% over de-ionised water, with exergy efficiency about 10% higher at the higher loading and flow rate [17]. Al_2O_3-MWCNT hybrid fluids in a tube-and-shell exchanger raised the heat-transfer rate substantially, with the gain growing with loading and depending on tube geometry [21]. Solar collectors benefit for a second reason beyond convection, because a carbon-metal oxide fluid also absorbs sunlight directly: an MWCNT-Fe_3O_4 fluid in a flat-plate collector under natural (thermosyphon) circulation improved thermal efficiency through its higher conductivity [18], consistent with broader reviews of hybrid nanofluids in flat-plate collectors [22], and in a direct-absorption collector an Fe_3O_4/MWCNT hybrid raised thermal efficiency to about 94%, well above the pure Fe_3O_4 fluid, while storing more energy per unit area [20]. Machine-learning models are now being fitted to this collector data to predict efficiency from loading and flow rate [19]. Electronics and building thermal management use the same fluids in mini- and micro-channels, where graphene nanofluids lowered channel wall temperatures relative to water at equal heating power [24].

Table 2 collects representative device-level results.

Fluid / device	Setting	Reported result	Ref.
MWCNT-Fe3O4 / water	Compact heat exchanger	Effectiveness +11.7 to +13.2%; NTU +21 to +24%	[17]
MWCNT-Fe3O4 / water	Flat-plate solar collector (thermosyphon)	k +28.5%, viscosity +50.4% at 0.3 vol%, 60 C; higher efficiency	[18]
Fe3O4/MWCNT / water	Direct-absorption solar collector	Thermal efficiency ~94% (vs ~85% for Fe3O4)	[20]
Al2O3-MWCNT / water	Tube-and-shell heat exchanger	Heat-transfer rate up strongly with loading and tube shape	[21]
N-doped graphene / water	Laminar tube	HTC +7 to +50%	[6]
Graphene / water	Mini-channel	Wall temperature down ~16% vs water	[24]

Table 2. Representative device-level heat-transfer results for carbon and carbon-metal oxide nanofluids. Conditions differ between studies; values indicate reported performance, not a controlled comparison. NTU = number of transfer units; HTC = heat-transfer coefficient.

5. What nitrogen doping and hybridization each contribute

It is worth separating the two design choices in the title, because they act through different routes and a study that changes both at once cannot tell them apart. Nitrogen doping acts mainly on the fluid side. It raises the polarity and wettability of the carbon surface, which improves dispersion in water and ethylene glycol and reduces the surfactant needed, and this better dispersion is itself part of why nitrogen-doped graphene fluids reach high conductivity enhancements and hold them over time [5,7]. The doping has a smaller direct effect on the solid conductivity of the sheet, and can even lower it slightly by adding scattering sites, so its value in a fluid comes from colloidal stability rather than from a more conductive particle [8].

Hybridization with a metal oxide acts on both sides. Physically, the oxide particles sit between the carbon sheets and stop them restacking, which preserves the high surface area that dispersion and the nanolayer effect depend on [16,17]. Functionally, the oxide brings properties the carbon lacks: Fe_3O_4 makes the fluid respond to a magnetic field, useful for pumping or for switching heat transfer on and off, and both Fe_3O_4 and other oxides absorb light, which is what makes these fluids strong candidates for direct-absorption solar collectors [20,23]. The reported synergy, where a hybrid outperforms either component at the same total loading, comes from these two effects together: better dispersion from the pairing, plus the oxide's added function [16,17]. The practical message is that the two choices are complementary, and the strongest fluids use nitrogen doping to fix dispersion and the oxide to fix restacking and add function.

6. Open problems and future directions

Several specific problems stand between these fluids and routine use, and naming them precisely is more useful than a general call for more work.

The conductivity-viscosity trade-off. Every gain in thermal conductivity comes with a rise in viscosity and pumping power, and in turbulent flow the viscosity penalty can cancel the thermal benefit. More studies should report a performance-evaluation criterion or an entropy-generation analysis rather than a bare conductivity number, so the reader can see whether the fluid is a net win at the intended flow regime [13,17].

Long-term stability. Most stability data cover days to weeks, not the years a coolant must survive, and elevated temperature and flow shear both accelerate aggregation and surfactant breakdown. Durable stability, ideally through covalent functionalization or built-in surface polarity rather than added surfactant, is the property most in need of long-duration testing [1,4].

From properties to systems. A large fraction of the literature stops at property measurement or single-tube tests, and the step to full devices under realistic duty cycles often shrinks the headline gains. Device-level and long-run testing, with pumping power and fouling included, is what will decide practical value [17,18].

Data specific to nitrogen-doped carbon-metal oxide hybrids. Much of the evidence here is assembled from nitrogen-doped carbon fluids on one side and carbon-metal oxide hybrids on the other, with fewer studies on the specific combination named in this title. Systematic work that varies nitrogen speciation and oxide type independently, on the same base fluid, would let the two contributions be separated and optimized rather than inferred [5,16].

Modelling and prediction. Existing thermal-conductivity correlations were built for simple nanofluids and fit hybrids poorly, and the active mechanism shifts with system. Physics-based models that include the nanolayer and aggregation together, alongside the machine-learning approaches now being fitted to collector data, are the route to prediction that generalizes beyond the fluid it was trained on [3,19].

7. Conclusions

Nitrogen-doped carbon-metal oxide nanofluids combine two fixes for the weaknesses of single-component nanofluids. The carbon phase supplies high intrinsic conductivity, nitrogen doping makes it disperse and stay dispersed in polar base fluids with less surfactant, and the metal oxide keeps the carbon sheets apart while adding magnetic or optical function. Reported thermal-conductivity enhancements above 30% and convective heat-transfer gains in the tens of percent, together with device-level improvements in heat exchangers and solar collectors, show the approach works.

What stands between these results and deployment is specific: the conductivity-viscosity trade-off, which demands second-law rather than first-law reporting; long-term stability under heat and shear; the gap between property measurement and full-system performance; and a shortage of data on the exact nitrogen-doped carbon-metal oxide combination as opposed to its separate parents. Progress on those points, rather than incremental gains in measured conductivity, is what will move these fluids from the laboratory into working thermal systems.

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Declarations

Conflicts of interest: The authors declare no competing interests.