Supporting Information

Graphene-enhanced Nanorefrigerants

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Materials and Experimental Methods

Preparation of Nanomaterial Suspensions

The materials used in suspension preparation are summarized in Table 1 of the main text. The host fluid consisted of the refrigerant 2-trifluoromethyl-3-ethoxydodecafluorohexane (Novec 7500 Engineered Fluid (I.D. No. 98-0212-2932-85); 3M, St Paul, MN). This formulation displays a boiling point of 128 °C, placing it in the liquid phase under ambient conditions. Data characterizing the refrigerant's temperature dependence of thermal conductivity and viscosity are available from the manufacturer, however we note that the conductivity data are based on a single point measurement using the transient hot wire method which is then extrapolated based on data from a chemically similar fluid. Krytox 157 FSL (1 vol%) was employed as a stabilizer in all suspensions. Nanomaterials were obtained in dry powder form at volume concentrations determined as follows

$$\varphi_v = \frac{1}{\left(100/\varphi_m\right)\left(\rho_p/\rho_f\right)+1}\times 100(\%)$$

where ρ_p and ρ_f are the densities of particle and host fluid respectively, and ϕ_v and ϕ_m are the suspension volume and weight percentages.

Suspensions were prepared by combining appropriate amounts of all components to a final volume of 300 ml, followed by mixing for 5 h using a magnetic stirrer, another 5 h of agitation in an ultrasonic bath (Model 3510DTH, Branson Ultrasonics Corp., Danbury, CT), and a final 30 min of agitation using a probe sonicator (Vibracell VCX 750, Sonics & Materials Inc., Newtown, CT). Ice was periodically added to the ultrasonic bath to offset the temperature increase during the 5 h sonication period. We found that we were able to consistently obtain highly stable suspensions following this protocol.

Thermal Conductivity Measurements

Thermal conductivity measurements were performed using a KD2 Pro thermal property analyzer (Decagon Devices, Inc., Pullman, WA). This device operates according to the transient hot wire method and is capable of measuring conductivities in the range from 0.02 to 2.00 W m^{-1} K^{-1} with an accuracy of ± 5% or 0.01 W m^{-1} K^{-1} over a span of 0 to 50 °C. This instrument measures thermal conductivity by applying a parameter-corrected version of the transient temperature model of Carslaw and Jaeger for an infinite line heat source with constant heat output in a homogeneous, isotropic and infinite medium. [1] The temperature response during heating can be defined as

$$\Delta T = T - T_0 = \frac{-q}{4\pi k} Ei\left(\frac{-r^2}{4Dt}\right), \qquad 0 < t < t_1 \qquad (1)$$

where q is the heat dissipated per unit length (W m^{-1}), k is the thermal conductivity (W m^{-1} K^{-1}), r is the radial distance from the heat source (m), D is the thermal diffusivity (m^2 s^{-1}), t_1 is the heating time (s), and Ei is the exponential integral. The temperature rise after the heat source is turned off can be expressed as

$$\Delta T = T - T_0 = \frac{-q}{4\pi k}\left[-Ei\left(\frac{-r^2}{4Dt}\right) + Ei\left(\frac{-r^2}{4D(t-t_1)}\right)\right], \qquad t > t_1 \qquad (2)$$

Each 90 s measurement cycle consisted of an initial 30 s temperature equilibration stage, followed by 30s of heating and 30 s of cooling. The temperature versus time response during the heating and cooling periods was recorded at 1 s intervals, and the data were fit by applying equations (1) and (2) to obtain the suspension thermal conductivity. The probe response is calibrated to account for finite length and diameter effects. All measurements were replicated at least 3 times, with at least 20 min elapsed between successive measurements.

Measurements were performed by placing the nanosuspension samples in 250 ml glass jars with open-top polypropylene screw caps bonded with Teflon/silicone septa (Cat. No. S121-0250, I-Chem, Rockwood, TN). Free convection was minimized by forming a hole in the center of the septum through which the thermal probe (60 mm long, 1.3 mm diameter) was inserted vertically into the suspension without touching the sidewalls of the jar. The probe was calibrated using glycerin and water standards, and consistently yielded results in good agreement with literature.[2] The sample temperature was controlled by fully immersing each jar in a circulating water bath (Lauda Model RE106, LAUDA-Brinkmann, Delran, NJ) and allowed to equilibrate at the measurement temperature for at least 20 min. All measurements were performed on an optical table, and the water bath was switched off during data acquisition to eliminate vibration effects. Measurement variability was greatly reduced by performing a complete series of experiments in a single session. For example, a typical series of experiments included measurements on control samples of the pure refrigerant and refrigerant-surfactant mixture, in addition to the dispersions of interest. All conductivity data reported here (Figs. 2a, 3a, and 5a)

are therefore normalized by the pure refrigerant values acquired during the same measurement session to minimize systematic variations between experiments performed at different times.

Uncertainty was estimated by considering the errors associated with the thermal conductivity, weight, and temperature measurements[3]. The conductivity and temperature accuracies of KD2 thermal property analyzer are ± 0.01 W m^{-1} K^{-1} from (0.02 to 0.2 W m^{-1} K^{-1}) and ± 0.5 °C, respectively. Samples were weighed using a Mettler Toledo AB analytical balance (Model. AB204-S) with ± 0.0001 g accuracy. The overall uncertainty is estimated to be

$$u_{m,k} = \pm\sqrt{\left(\left(\frac{\Delta k}{k}\right)^2 + \left(\frac{\Delta W}{W}\right)^2 + \left(\frac{\Delta T}{T}\right)^2\right)} = \pm 5.5\%.$$

Viscosity Measurements

Steady shear viscosity measurements were performed using a MCR 300 Modular Compact Rheometer (Anton Paar, Ashland, VA) with a cone and plate fixture (CP 50-1, 50 mm diameter, 0.05 mm gap, 0.987 angle, ~ 0.5 mL sample volume). The instrument was programmed for constant temperature and equilibration followed by a two-step shear ramp in which the shear rate was increased from 10 to 500 s^{-1} and immediately decreased from 500 to 50 s^{-1}. A solvent trap was used to minimize evaporation. All measurements were repeated at least 3 times.

Uncertainty was estimated by considering the errors associated with the viscosity, weight, and temperature measurements [3]. The viscosity and temperature accuracies of MCR 300 rheometer are ± 0.5% and ± 0.1 °C, respectively. Samples were weighed using a Mettler Toledo

AB analytical balance (Model. AB204-S) with ± 0.0001 g accuracy. The overall uncertainty is estimated to be $u_{m,t} = \pm\sqrt{\left(\left(\frac{\Delta\mu}{\mu}\right)^2 + \left(\frac{\Delta W}{W}\right)^2 + \left(\frac{\Delta T}{T}\right)^2\right)} = \pm 0.68\%$.

Transmission Electron Microscopy (TEM) Characterization

Transmission electron microscopy (TEM) images of our metal oxide and nitride nanoparticles, multiwall carbon nanotube (MWCNT) and graphene nanosheet (GNS) samples were taken by high-resolution TEM instrument (FEI Tecnai G2 F20ST) equipped with a field emission gun at a working voltage of 200kV. The dilute nanopowder suspensions were prepared with ethanol using ultrasonication (~5 mins). The carbon film coated square mesh copper grids (3 mm, 300 mesh, Pelco) were glow discharged using Pelco easiGlow (Ted Pella Inc., Redding, Ca). Then a small volume of sample was dropped onto a holey carbon film coated grid and allowed to dry by evaporation under ambient conditions overnight. The images were taken in high vacuum (10^{-5}-10^{-6} bar).

Cryogenic Transmission Electron Microscopy (Cryo-TEM)

Cryo-TEM images of our nanomaterial suspensions were obtained using an FEI Tecnai G2 F20 instrument. MWCNT-based refrigerant suspensions were diluted from 0.25 vol% to 0.0025 vol%. Before characterization, all of the diluted suspensions were subjected to 1 hr sonication in an ultrasonic cleaner (Model 3510DTH; Branson Ultrasonics Corp.). TEM grids with 2 μm hole size (C-Flat^{TM} samples CF 2/2-2C, Electron Microscopy Sciences, Hatfield, PA) were glow discharged using Pelco easiGlow (Ted Pella Inc., Redding, CA). Specimens were prepared by quench freezing thin films of the refrigerant suspensions in liquid ethane using a

vitrification robot (Vitrobot, FEI, Hillsboro, OR) equipped with a controlled humidity chamber (100% RH, 22^{o}C). A 3 μL droplet of the sample solution was placed on a grid then automatically blotted with a filter paper (blot offset was -2 mm, and blot time was 3.5 s) and plunge-frozen in liquid ethane. The grids were then mounted in dedicated cartridges and stored under liquid nitrogen until data collection. The vitrified specimens were then transferred into the electron microscope operated at 200 kV under a liquid nitrogen environment with Gatan 626 cryo specimen holder and observed at liquid nitrogen temperature (~ −180 °C). Images were recorded with a Gatan Tridiem GIF-CCD (2k x 2k CCD camera and post column energy filter) attached to the microscope.

References

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[3] D. P. Kulkarni, P. K. Namburu, H. Ed Bargar and D. K. Das. "Convective Heat Transfer and Fluid Dynamic Characteristics of SiO2 Ethylene Glycol/Water Nanofluid." *Heat Transfer Engineering* **29** (2008): 1027-1035.

Electronic Supplementary Material (ESI) for Nanoscale

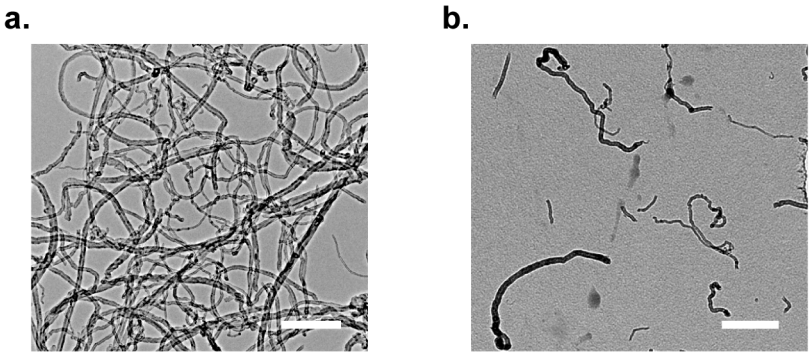

Figure S1. Comparison of nanomaterial morphology before and after preparation of nanorefrigerant suspensions. (a) TEM image of MWCNTs in powder form before suspension preparation. **(b)** Cryo-TEM image of MWCNTs from a 0.0025 vol% refrigerant suspension. Data shown are for nanotubes obtained from Helix Material Solutions, Inc. Scale bars, 400 nm.

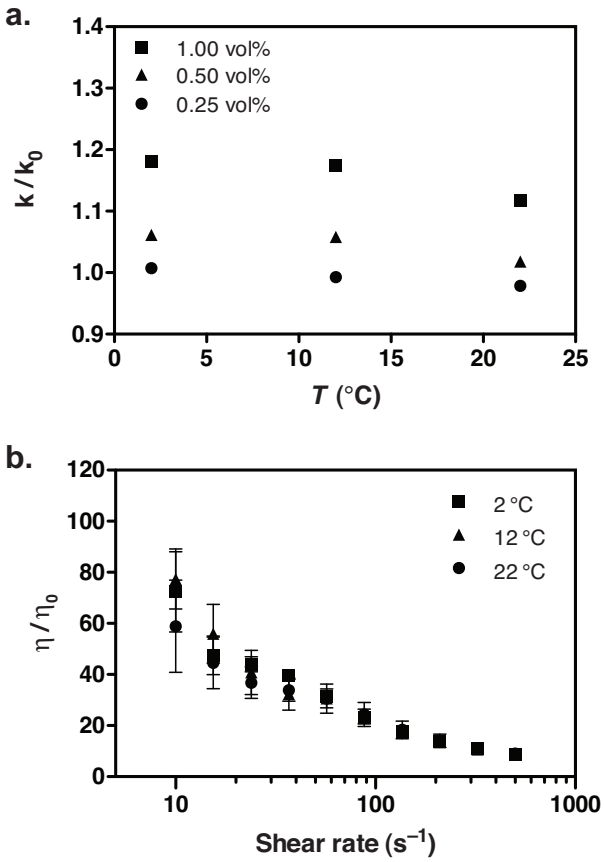

Figure S2. (a) Temperature dependence of thermal conductivity in refrigerant suspensions containing MWCNTs (data are expressed relative to the particle-free case k/k_0, $k_0 = 0.0938$ W m^{-1} K^{-1}). **(b)** Temperature dependence of steady shear viscosity (plotted relative to the pure refrigerant (particle- and surfactant-free) (η/η_0)) in a 1 vol% MWCNT dispersion over a shear rate sweep from 500 to 10 s^{-1} after first ramping up from 10 to 500 s^{-1} to generate a reproducible initial condition. Data shown are for nanotubes obtained from Cheap Tubes, Inc.

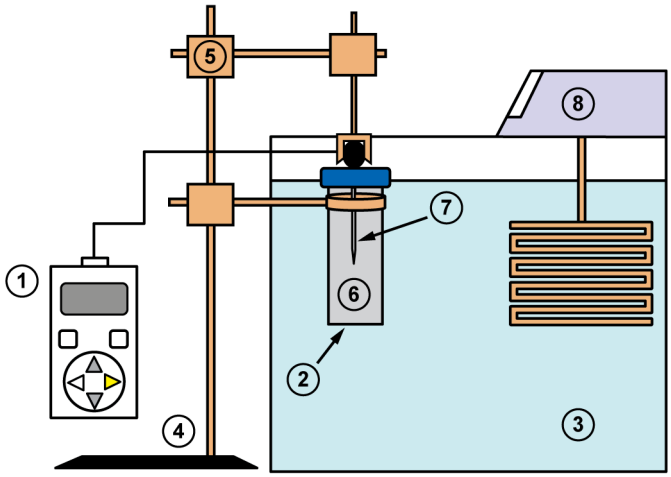

Figure S3. A standardized thermal conductivity measurement protocol for nanorefrigerants. The apparatus employs commercially available components to create a benchmark platform that can be easily assembled in any laboratory. Shown are (1) KD2-Pro thermal conductivity meter, (2) glass jar with septum in cap, (3) isothermal circulating water bath, (4) support stand, (5) clamps, (6) nanorefrigerant sample, (7) KS-1 probe needle, and (8) bath temperature controller. Drawing is not to scale.

Table S1. Effect of added surfactant on refrigerant steady-shear viscosity. Data are shown as a function of shear rate (averaged over an ensemble of 5-10 experiments at each temperature), and as an average over all shear rates at each temperature.

T (°C)	Shear rate (s^{-1})	Viscosity (Pa s)		Percent Change	Average
		HFE 7500	HFE 7500 & Krytox 157		
2	500	0.001798	0.001848	2.78%	**3.90%**
	324	0.001796	0.001846	2.78%	
	210	0.001796	0.001844	2.67%	
	136	0.001798	0.001846	2.67%	
	87.9	0.001798	0.001854	3.11%	
	56.9	0.001808	0.001848	2.21%	
	36.8	0.001832	0.001852	1.09%	
	23.9	0.001712	0.001914	11.80%	
	15.4	0.001904	0.001948	2.31%	
	10	0.001796	0.001932	7.57%	
12	500	0.001496	0.001549	3.52%	**3.25%**
	324	0.001495	0.001551	3.71%	
	210	0.001491	0.001538	3.17%	
	136	0.001488	0.001535	3.18%	
	87.9	0.001487	0.001537	3.36%	
	56.9	0.001495	0.001540	3.04%	
	36.8	0.001503	0.001558	3.69%	
	23.9	0.001464	0.001532	4.66%	
	15.4	0.001464	0.001514	3.39%	
	10	0.001477	0.001489	0.80%	
22	500	0.001290	0.001330	3.10%	**2.91%**
	324	0.001290	0.001330	3.10%	
	210	0.001284	0.001324	3.12%	
	136	0.001282	0.001322	3.12%	
	87.9	0.001280	0.001326	3.59%	
	56.9	0.001304	0.001336	2.45%	
	36.8	0.001302	0.001348	3.53%	
	23.9	0.001312	0.001304	-0.61%	
	15.4	0.001354	0.001442	6.50%	
	10	0.001296	0.001312	1.23%	

Table S2. Effect of added surfactant on refrigerant thermal conductivity. Data shown are average values over the entire ensemble of experiments reported (see main text for details).

T (°C)	Thermal Conductivity (W m^{-1} K^{-1})		Percent Change
	HFE 7500	HFE 7500 & Krytox 157	
2	0.09233	0.09233	**No change**
12	0.09383	0.09317	**–0.71%**
22	0.09300	0.09267	**–0.36%**