* Zeolite (ZT), functionalized carbon nanotube (fCNT), graphene oxide (GO), few layer graphene (FLG), effective medium analysis (EMA)

Dimensionality Effects of Carbon-Based Thermal Additives for Microporous Adsorbents

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Supporting Information Available

ABSTRACT

We present a systematic study of carbon nanomaterials with different geometries and thermal properties, including few-layer graphene (FLG), graphene oxide (GO), and functionalized carbon nanotubes (fCNT) as additives to enhance the thermal conductivity of microporous adsorbent materials. The dimensionality and intrinsic thermal conductivity of the additives were found to be critical for both maximizing the thermal conductivity enhancement, and minimizing the reduction in the adsorption capacity of the active materials. We demonstrated that two-dimensional (2D) FLG was the most effective thermal additive for zeolite (ZT) adsorbents due to its high thermal conductivity and preferential 2D geometry. Meanwhile, negligible enhancement was observed from one-dimensional (1D) additives such as fCNTs,

which is consistent with the predictions from a modified effective medium analysis (EMA). Our work provides insights for the development of additives to enhance the thermal performance of porous materials in applications such as adsorption heat pumps, gas storage, and separation processes.

KEYWORDS

THERMAL CONDUCTIVITY, MICROPOROUS ADSORBENT, ZEOLITE, METAL ORGANIC FRAMEWORKS, GRAPHENE, GRAPHENE OXIDE, CARBON NANOTUBE

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1. Introduction

Modern adsorbent materials including zeolites (ZTs) and metal organic frameworks (MOFs) have the potential to impact a range of applications, from gas and thermal energy storage to separation processes and climate control.[1-3] However, the low thermal conductivity of these materials presents a major barrier to their wide-scale adoption in industry. The heat generated by the adsorption process can cause local temperature spikes that can both reduce total adsorption capacity (Figure S1), and degrade or destroy the adsorbent material.[4-6] For adsorption-based thermal systems such as heat-pumps and chillers, the high heat of adsorption involved make adsorbent thermal conductivity a performance limiting factor.

Thermally conductive additives are a natural solution for problems associated with low adsorbent conductivity. Ideally, a small volume fraction of thermal additives could be mixed with the bulk microporous adsorbent material to enhance the overall effective thermal conductivity. A similar approach for including these conductive additives has been used in composite epoxy adhesives[7-10] and silicon nitride (Si_3N_4) ceramics.[11] On the other hand, many microporous adsorbents such as ZTs and MOFs have open pore structures and high total pore volumes, which present unique challenges in both additive

percolation and the ability to maintain vapor transport and high active material fraction. As a result, significant improvements in thermal conductivity of microporous adsorbent materials have been limited to high additive fractions (>10 wt%), compromising the total adsorption capacity.[12] Alternatively, the graphene coating method demonstrated considerable improvements in thermal conductivity,[13-15] but requires high temperature growth, restricting the type of microporous adsorbents due to temperature stability, *i.e.*, MOFs.[4] In addition, a cohesive understanding of the interrelated effects of intrinsic thermal conductivity, percolation effects, and small scale additive-adsorbent interactions is needed that is essential for engineering next generation high-performance adsorption systems.

In this paper, we present a parametric study of thermally conductive nanomaterials, including 1D carbon nanotubes (CNTs, $2000 \sim 3000$ W/mK)[16-18], 2D few-layer graphene (FLG, $1000 \sim 3000$ W/mK)[19, 20] and 2D graphene oxide (GO, $8.8 \sim 18$ W/mK)[21, 22], as thermal additives to microporous adsorbent materials. ZTs were used as the microporous adsorbent in this study because it is widely used in various adsorption applications.[23-27] Carbon nanomaterials were selected over other thermal additives due to their high intrinsic thermal conductivity, low molecular weight, and excellent stability at high working temperatures. In addition, the carbon surface can be functionalized to control the hydrophilicity in order to tailor both carbon-carbon and carbon-ZT adhesion. The adsorption characterizations were performed using water since it is widely used in adsorption heat pumps due to its abundance and high heat of adsorption with several adsorbent materials. Accordingly, we experimentally demonstrated that FLG is the most effective thermal additive for ZTs among the carbon nanomaterials used in this work due to its high intrinsic thermal conductivity and preferential 2D geometry. These experimental results were also consistent with predictions made with our modified effective medium analysis (EMA).

2. Experimental

2.1 Synthesis of materials

2.1.1 Synthesis of functionalized CNT

CNTs were synthesized in our lab using cobalt-molybdate (Co-Mo as catalyst), magnesium oxide (MgO as support) and methane (as carbon source). Synthesized CNTs were functionalized by the method reported by Bozena et al.[28] Briefly, 5 mg of CNTs was added to 5 ml of oleum acid (sulfuric acid, fuming, reagent grade, 20% free SO₃ basis) in a three neck flask, followed by 24 hours stirring at room temperature under argon gas. CNTs were well-dispersed in oleum acid due to the intercalation of CNTs. The temperature was raised to 65°C before 2.0 ml of nitric acid (Certified ACS Plus, 70%) was added. Intercalation of oleum between bundled CNTs enabled a homogeneous reaction by equally exposing all of the CNT outer surfaces to the oxidants. After two hours of oxidation, the solution was cooled down to room temperature. The degree of functionalization was controlled by the amount of nitric acid added, oxidation time, and oxidation temperature. The solution was diluted with water and vacuum filtered by using an Isopore Membrane Filter (Millipore, 1.2 µm pores). As a result, fCNTs were obtained. The desired amounts of fCNTs, then, were added in deionized water followed by tip sonication for 5 minutes. They were very well-dispersed as expected.

2.1.2. Synthesis of GO

To synthesize GO, graphite flakes were oxidized using Hummers' method.[29] An appropriate amount of concentrated H₂SO₄ was added to a mixture of graphite flakes and NaNO₃, followed by the drop-wise addition of KMnO₄ in an ice bath to keep the reaction temperature below 20 °C. The reaction was heated to 35 °C and stirred for 30 min, followed by adding water slowly. This exothermal step produced a large amount of heat. External heating was introduced to maintain the reaction temperature at 98 °C

for 15 min. The reaction was cooled for 10 min and additional water and 30% H₂O₂ were added. After cooling, the synthesized GO was collected after multiple steps of sonication, filtration and washing. The desired amount of GO was added in deionized water followed by sonication for 5 minutes. They were well-dispersed in water, as expected.

2.1.3. Synthesis of FLG

FLG was synthesized following Chabot's method.[30] 10 g of graphite powder (flake, 332461, Sigma Aldrich) was added in a gum arabic (G9752, Sigma Aldrich) aqueous solution (5 wt%). The gum arabic, a surfactant, was used to separate FLG from bulk graphite layers. FLG dispersion was generated using an extended low power ultrasonication bath (5510, Branson) for 1 week. Upon completion, the dispersion was left to sit two days to enable separation of large unstable graphite aggregates. The supernatant of dispersed FLG solution was collected, followed by centrifugation at 3000 rpm for 5 minutes. The supernatant was once again collected and stirred with nitric acid (5 vol %) for 1 hour to remove the gum arabic. The solution was filtered and washed with plenty of fresh water (> 20 times) to remove the nitric acid.

2.1.4. Synthesis of composite disks

Composite disks were fabricated for thermal conductivity measurements. The synthesized carbon nanomaterials, e.g., fCNT, GO or FLG, were dispersed in water, followed by adding ZTs (molecular sieves, 13X, 283592, Sigma Aldrich, ~ 2 µm average particle size, NaX type, composition - 1 Na₂O: 1 Al₂O₃ : 2.8 ± 0.2 SiO₂ : xH₂O) by a sonicator (Vibra Cell, SONICS, 45 W for 5 mins). The amount of water was controlled to create a uniform solution with appropriate viscosity. This composite solution was directly placed in the die set (13 mm Evacuatable Pellet Die with two die pellets (5mm thickness),

REFLEX Analytical Corporation) and pressed using a hydraulic press maintained at desired pressure for approximately 6 hours, followed by drying at 200°C for 6 hours. To increase the packing density of ZT adsorbents per volume, the composites were densified using a hydraulic press at between 100 MPa and 350 MPa corresponding to $\sim 1.18 \text{ g/cm}^3$ and $\sim 1.33 \text{ g/cm}^3$ composite densities, respectively. Upon completion, the composite disks were removed from the die for thermal conductivity measurements. Because these thermal additives adsorb minimal vapor compared to ZTs, the vapor adsorption of the composite samples was reduced in proportion to the thermal additive fraction, as observed in a previous study.[12] Therefore, to minimize the decrease of vapor adsorption even after the inclusion of the thermal additives, in this study, the net mass of all thermal additives was limited to $\sim 3.0 \text{ wt\%}$, unlike in previous studies where more than 10% thermal additives were typically used. Even though the net mass of all thermal additives was similar ($\sim 3.0 \text{ wt\%}$), the volume fractions of CNT, GO and FLG in the composites were 2.1, 2.0 and 1.6 vol%, respectively, estimated by

$$vol\%_{add} = \frac{\frac{wt\%_{add}}{\rho_{add}}}{\frac{wt\%_{ZT}}{\rho_{ZT}} + \frac{wt\%_{add}}{\rho_{add}}}$$

where, $vol\%_{add}$, $wt\%_{add}$ and ρ_{add} represent the volume fraction, weight fraction and density of the additives, respectively. The density of CNT, GO and FLG was 1.74, 1.8 and 2.25 g/cm^3 , respectively. [31-33] The $wt\%_{ZT}$ and ρ_{ZT} are the weight fraction and effective density of the ZT disk. The effective density of the ZT disk increased ($1.19 \sim 1.35 \text{ g/cm}^3$) with compression. Note that the volume fraction of these thermal additives slightly increased as the effective density of the ZT disk increased.

2.2 Characterization

Scanning electron microscope (SEM) and transmission electron microscope (TEM) images were obtained using models SEM (6010LA, JEOL) and TEM (2010 Advanced High Performance, JEOL), re-

spectively. Moreover, x-ray diffraction (XRD) patterns of the samples were acquired on a high-resolution diffractometer (X'Pert PRO MRD, PANalytical) with Cu K radiation. In order to determine the Brunauer–Emmett–Teller (BET) surface area, the micropore volume and pore size distribution of the samples, nitrogen adsorption-desorption isotherm measurements were conducted at 77 K (ASAP 2010, Micromeritics system). The amount of carbon in the composite was measured using a thermogravimetric analyzer (TGA Discovery, TA Instruments) by determining the weight loss of carbon upon oxidation. To differentiate the weight loss from the water and the carbon additives in the composites, N₂ gas was used first to remove the adsorbed water from the composites, followed by O₂ gas to oxidize the carbon in the sample. For example, as shown in Figure S2, the concentration of GO in the GO-ZT composite obtained by TGA was approximately 3.0 wt%. Raman spectra (HR800, Horiba Jobin Yvon) were obtained from the dried CNT, fCNT, GO and FLG samples on a glass substrate using a 532 nm laser.

The thermal diffusivity of various composites was evaluated using the laser flash method (LFA 457, NETZSCH Instruments).[5, 6] In addition, the specific heat capacity was measured by using the differential scanning calorimetry (Polymer DSC R, METTLER). The measured specific heat of the dry ZT and the composites was ~ 0.9 J/g K, which agrees well with the reported value by Hirasawa *et al.*[34] In order to calculate the sample weight of the dried samples, the pressed composite disk was dried at 450°C for 24 hours under N₂ gas prior to measuring its dry weight. The thermal conductivity was the average of measured results (at least 9 times or more), and the error was based on the standard deviation of the measurements. On the other hand, the amount of vapor adsorption was measured with a vapor adsorption analyzer (Q5000 SA, TA Instrument), which precisely controls nitrogen gas and vapor flow to control the humidity at the sample. Each composite sample was completely dried at 450°C for 24 hours under N₂ gas, followed by immediate transfer to the vapor adsorption analyzer.

3. Results and Discussion

3.1. Carbon nanomaterials as thermal additives

A uniform dispersion of thermal additives in the adsorbent is important to maximize both the thermal conductivity and the adsorption capacity of the composite material. This uniform dispersion minimizes the local temperature gradients during the exothermic adsorption of vapor. As shown in Figure S1, the ZTs showed a lower adsorption capacity at a higher temperature as a result of the increased temperature gradients. Functionalizing the carbon nanomaterials promises to improve the dispersion of the carbon nanomaterials in composites.[35-38] For example, a good dispersion of CNTs in polymer or ceramic based composites has reported higher electrical and thermal conductivity, if a suitable dispersion of thermal additives is ensured.[39, 40] However, CNTs often exist as bundles in a hydrophilic medium due to the strong mutual van der Waals interactions between CNTs. For example, Tapasztó *et al.* reported that CNTs exist in the form of small aggregate structures in a hydrophilic composite.[41] Therefore, to create a suitable dispersion in hydrophilic ZTs, we functionalized the surface of the CNTs using oleum and nitric acid. Figure 1(a) shows a TEM image of CNTs after functionalization. Few-walled carbon nanotubes (FWNTs) were used in this study, since the inner walls of the FWNTs survived the functionalization process without a significant reduction in the intrinsic thermal conductivity. As a result, the presence of carboxyl groups on their surface helped the dispersion of functionalized FWNT (fCNT) solution (Figure S3(b)). The Raman spectra (Figure S3(c)) indicated that the outer walls of the fCNTs were selectively functionalized, while the inner walls remained intact. The ratio between the G-mode (graphite mode around 1600 cm^{-1}) and D-mode (disorder mode around 1300 cm^{-1}) was found to be 25.7 ± 1.9 even after functionalization, indicating high-quality fCNTs (Figure S3(d)). The error was based on the standard deviation of testing five specimens.

Even though the thermal conductivity of GO ($8 \sim 18 \text{ W/mK}$) is notably lower than that of the CNT ($2000 \sim 3000 \text{ W/mK}$), GO was also selected as a promising thermal additive because its 2D geometry could lead to increased contact area with ZTs. Figure 1(b) shows a TEM image of GO (See also Figure S4(a)). The average lateral size of GO was $\sim 2 \mu\text{m}$ (mainly composed of several layers) as estimated from the TEM images. While a single layer of GO shows a 2D peak around 2640 cm^{-1} , several layers of GO show a broadened 2D peak around 2680 cm^{-1} (Figure S4(b)). The 2D peak shift between one and more than five layers of GO was reported to be approximately 40 cm^{-1} . [42] In addition, because GO was synthesized by Hummer's method [29] where strong acids were used to exfoliate graphite, GO had a relatively high intensity D-mode in the red Raman spectra (Figure 1(d)). This Raman spectrum suggests that numerous functional groups on the GO surface enhanced the dispersion of GO in the ZT composite as well as the adhesion to ZTs due to their hydrophilicity.

FLG, with its high intrinsic thermal conductivity ($1000 \sim 3000 \text{ W/mK}$) and 2D geometry was another promising candidate material for enhancing adsorbent thermal conductivity. The synthesized FLG generally consisted of $\sim 2 \mu\text{m}$ with 5-10 individual FLG layers, as determined by TEM images and the Raman spectrum (Figure 1(c), Figure S5(a) and Figure S5(b)). TEM images of the synthesized FLG were used to estimate the average FLG size. While single or double layers of graphene show a 2D peak around 2670 cm^{-1} , 5 $\sim$ 10 layers of graphene show a broadened 2D peak around 2720 cm^{-1} . [43] It is worthwhile noting that higher thermal conductivity can be achieved by reducing the number of layers of GR up to $\sim 4000 \text{ W/mK}$. [20] In addition, as shown in Figure 1(d), the green Raman spectrum of FLG shows that the G/D mode ratio was much higher than that of GO indicating fewer structural defects. Since structural defects act as strong scattering centers for phonons in graphene, these defects can impact the thermal transport properties of graphene. [44] Therefore, our synthesized FLG was expected to have a significantly higher thermal conductivity than GO.

3.2. Changes in adsorption capacity of the composites

In most adsorption based applications, higher adsorption per weight or volume is desired. Therefore, the composites were densified to enhance the adsorption energy density. Due to the good mechanical strength of the ZT crystals, almost no deformation was expected in the crystal structure even after the densification process, as indicated by the XRD patterns (Figure S6). However, while densification of the ZT adsorbent enhances the thermal conductivity and adsorption density, it can hinder the mass transport of the adsorbate (*e.g.*, H₂O) through the adsorbent due to the reduction of intercrystalline void volume.[45] Therefore, for a fixed duration of adsorption, a decrease in the net usage of the adsorbent is observed due to several factors. Adsorbent densification, higher adsorption capacities, larger sample thicknesses, and lower operational pressures can lead to lower energy and power densities due to lower vapor penetration into the adsorbent samples. Hence, to address vapor transport limitations for any given operating condition, the adsorbent sample geometry needs to be selected to ensure saturation within the desired operational time. In this study, we aimed to enhance thermal transport without adversely affecting vapor transport and net adsorption after the addition of thermal additives. We characterized the vapor transport and adsorption characteristics of the composite. Figure 2 shows SEM images of compressed (a) ZT, (b) fCNT-ZT, (c) GO-ZT and (d) FLG-ZT composite disks. As shown in Figure 2(b), fCNTs bundled together, with diameters of typically several hundred nanometers, even though they were functionalized. Conversely, Figures 2(c) and 2(d) qualitatively indicate that both GO and FLG, false colorized in red and green for contrast, respectively, were well-dispersed in the ZT particles due to their 2D geometry. This observation is consistent with that of Walker *et al.*, who demonstrated that the FLG wrapped underneath the matrix grain (Si₃N₄) resulted in ~235% (MPa·m^{1/2}) improvements in toughness compared to that of 1D CNTs.[46]

We also confirmed that there was not a significant decrease in vapor transport and net adsorption after adding the thermal additives. Figure 3 shows the change in adsorption capacities at 10% and 20% relative pressure ($RP = P/P_0$) at 40°C. The minor but measurable reduction in vapor uptake of the composites was due to the amount (3.0 wt%) of thermal additives in the composite. The additives also did not delay the adsorption process, which is useful for applications requiring efficient mass transport. Furthermore, the BET surface analysis showed that the decrease in micropore volume and surface area (Table 1) after adding the carbon additive was negligible ($< 1.0\%$), indicating that the thermal additives did not block the micropores in the ZTs. The micropore volume of an adsorbent is important because it determines the vapor adsorption capacity, especially in the low relative pressure region ($RP < 10\%$).^[47] In addition, there was no significant ($< 1.0\%$) change in the pore size distribution after incorporating the thermal additives (Figure S7).

3.3. 2D few-layer graphene enhanced composite thermal conductivity

The thermal conductivity of the composite material was extracted from thermal diffusivity obtained from the LFA (*i.e.*, the thermal conductivity is the product of the measured effective density, specific heat and thermal diffusivity). Figure 4 compares the thermal conductivities of ZT, fCNT-ZT, GO-ZT, and FLG-ZT composites for various composite densities. In general, the thermal conductivity of the composite increased with density since the overall thermal transport is primarily due to conduction through the solid phase, which was further enhanced with the increased solid fraction with increasing sample density. More interestingly, a comparison of different composites shows that while there was a negligible improvement in the thermal conductivity after adding fCNT or GO, the thermal conductivity of the FLG-ZT composite was enhanced $\sim 6.7 - 21.0 \%$ with only $\sim 3.0 \text{ wt\%}$ of thermal additives. While

even more improvement in thermal conductivity can be achieved with more thermal additives added, it consequentially will compromise adsorption capacity.

To explain this variation of thermal conductivity with the addition of different materials, we conducted theoretical analysis using a modified effective medium analysis (EMA) based on Nan's model.[48, 49]. We examined the use of fCNTs and FLG as additives, representing the case of the 1D and 2D geometry, respectively. GO was not considered because the geometry is similar to that of FLG, but with a much lower thermal conductivity.

The modified EMA assumes no percolation of thermal additives in the medium and a constant interfacial resistance (R_k) existing between the carbon thermal additives and the medium, *i.e.*, ZTs. For CNTs, thermal transport is dominated by the longitudinal direction due to the high aspect ratio (~ 1000). Therefore, the effective thermal conductivity of the CNT-ZT composite can be written as

$$k_{eff} = k_m \frac{3+f_c(\beta_x+\beta_z)}{3-f_c\beta_x} \quad (1)$$

where

$$\beta_x = \frac{2(k_x^c - k_m)}{k_x^c + k_m} \text{ and } \beta_z = \frac{k_z^c}{k_m} - 1 \quad (2)$$

$$k_x^c = \frac{k_{CNT}}{1 + \frac{2R_k k_m k_{CNT}}{d k_m}} \text{ and } k_z^c = \frac{k_{CNT}}{1 + \frac{2R_k k_m k_{CNT}}{L k_m}} \quad (3)$$

k_m is the thermal conductivity of the ZT matrix, and k_{CNT} ($=3000 \text{ W/mK}$) and f_c are the thermal conductivity and the effective volume fraction of the CNTs, respectively. Since k_m is a function of the effective density of the ZT disk, it was obtained by a linear interpolation equation ($k_m = -0.4716 + 0.63363 \rho_{ZT}$) based on the measured thermal conductivity of the ZT disks (Figure 4). In addition, d ($\approx 5.0 \text{ nm}$) and L ($\approx 2.0 \text{ }\mu\text{m}$) are the diameter and the length of the CNTs, respectively, estimated from TEM images. R_k ($= 1.0 \times 10^{-7} \text{ m}^2 \text{ K/W}$) is the interfacial resistance, *i.e.*, the Kapitza resistance.[50] k_{eff} is also a

function of the volume fraction. However, unlike Nan's model, we used a modified contact volume fraction, f_c ($\approx 0.11 - 0.15$, which is a function of the effective density of composite), which accounts for the partial contact between the ZTs and CNTs, due to the experimentally observed effect of geometry on the extent of contact between the thermal additives and porous crystals, as shown SEM images in Figure 2. Therefore, f_c was obtained based on the amount of added thermal additives and the contact ratio (=contact area/total area of the additive) determined from image-analysis of numerous SEM images, *e.g.*, Figure 5(a), Figure S8 and S9. The blue colorized region represents the area in contact, and red denotes the area not in contact with the underlying ZT. Accordingly, the contact ratio of fCNT with the ZT medium was estimated to be 0.11, as shown in Figure 5(b), and the contact ratio increased with the composite density. It is worthwhile noting that a composite with ZTs includes both the micropores and macropores. However, the volume fraction of these pores of ZT particles is already accounted for in the EMA model as the thermal conductivity of the ZT matrix. In addition, k_x^c and k_z^c are, respectively, the equivalent thermal conductivities along transverse and longitudinal axes of a composite unit cell.[49]

The effective thermal conductivity of the FLG-ZT composites can be modeled similarly. However, unlike the 1D CNT, thermal transport in 2D FLG is dominated by the transverse direction due to the very high aspect ratio, typically ~ 0.001 . Assuming that FLG is a thin square sheet embedded in the ZT medium, the effective thermal conductivity of FLG-ZT composite is

$$k_{eff} = k_m \frac{1 + \frac{2}{3} f_c \beta_x}{1 - \frac{1}{3} f_c \beta_z} \quad (4)$$

where

$$\beta_x = \frac{k_x - k_m}{k_m} \text{ and } \beta_z = \frac{k_z - k_m}{k_z}, \quad (5)$$

$$k_x^c = \frac{k_{FLG} L}{L + 2 k_{FLG} R_k} \text{ and } k_z^c = \frac{k_{FLG} t}{t + 2 k_{FLG} R_k} \quad (6)$$

k_{FLG} ($=3000 \text{ W/mK}$) is the thermal conductivity of FLG, and L ($\approx 2 \mu\text{m}$) and t ($\approx 5 \text{ nm}$) are the length in the transverse direction and the thickness of FLG, respectively, estimated from TEM images. The contact ratio of FLG with the ZT medium was estimated as $\approx 0.76 - 0.95$ depending on the effective density of the composite as shown in Figure 5(b). Note that the equivalent thermal conductivities along transverse and longitudinal axes of FLG coated with a very thin interfacial thermal barrier layer should be different from what was described by Nan *et al.* for CNTs. Therefore, we developed k_x^c and k_z^c for FLG by modifying k_x^c and k_z^c for CNTs (Figure S10). In addition, as reported in previous studies, R_k of FLG is expected to be close to that of CNTs.[51, 52]

The experimental results and the modified EMA show reasonable agreement. As in the experiments, the modeling results also indicate a significant improvement in thermal conductivity for the FLG-ZT composite, and a negligible improvement for the fCNT-ZT composite (dotted lines in Figure 4 and Figure S11 for GO-ZT). The measured thermal conductivity of the FLG-ZT composite had a larger enhancement with increasing density compared to the predicted values with the modified EMA which is attributed to the assumed constant R_k in the EMA, which in reality decreases with increasing pressure or the extent of densification.[53]

The experiments and modeling suggest that the overall change in thermal conductivity is a result of both structural geometry and intrinsic thermal conductivity of the thermal additives. In the case of fCNTs, while the thermal conductivity is high ($2000 \sim 3000 \text{ W/mK}$), there was poor contact between fCNTs and ZT, which did not result in a significant improvement in thermal transport. As shown in Figure 2(b), fCNTs mostly occupied the intercrystalline voids between the ZTs even though they were marginally functionalized to promote uniform dispersion. Consequently, the contact area ratio of the fCNT-ZT composite ($\sim 1.2 \text{ g/cm}^3$ effective density) was ~ 0.12 , significantly smaller than that of FLG-ZT composite (~ 0.83). Therefore, the interaction of the hydrophilic ZTs and fCNTs was not considerably

favorable for promoting mutual contact. In contrast to fCNTs, FLG was well-dispersed in the FLG-ZT composite as evidenced by the SEM image in Figure 2(d). Consequently, the contact ratio of FLG (~ 0.83) was significantly higher than that of fCNT (~ 0.12). The preferential contact area ratio and the high intrinsic thermal conductivity of FLG led to the marked thermal conductivity enhancement in Figure 4. In the case of GO, only a minimal improvement in thermal conductivity was observed despite the enhanced contact of ZT with the 2D geometry due to an inherently low GO thermal conductivity.

4. Conclusions

We studied the use of various carbon based nanomaterials with different geometries (1D and 2D) and thermal properties, including fCNT, GO and FLG as additives to enhance the overall thermal conductivity of microporous adsorbents. In order to maximize the thermal conductivity while minimizing the reduction in the adsorption capacity of the adsorbent, the intrinsic thermal conductivities and dimensionality of the additives were both found to be critical. Among all of the additives considered, 2D FLG was the most effective thermal additive. With a 3.0 wt% addition of FLG, the thermal conductivity was enhanced by approximately 25% due to both the high thermal conductivity and preferential 2D geometry. Meanwhile, a negligible enhancement was observed using GO additives due to the lower intrinsic thermal conductivity, despite its preferential 2D geometry to microporous adsorbents. Furthermore, one-dimensional carbon additives such as fCNTs showed no significant increase in the overall thermal conductivity of the composite structures. This negligible enhancement in the composite thermal conductivity was attributed to the poor contact between the constituent particles. These experimental results were also consistent with predictions made with our modified effective medium theory analysis (EMA). These findings give insight into the interplay between intrinsic properties, dimensionality, and adhesive

forces that govern the role that carbon nanomaterials play as conductive additives in various applications. These systematic studies offer a step forward towards improving thermally conductive additives for high performance adsorption-based systems.

Acknowledgements

The authors gratefully acknowledge the support of Advanced Research Projects Agency-Energy (ARPA-E) with Dr. Ravi Prasher and Dr. James Klausner as program managers.

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FIGURE CAPTIONS

Figure 1: TEM images of (a) functionalized few-walled carbon nanotubes (fCNT), (b) graphene oxide (GO) and (c) few-layer graphene (FLG) and their Raman spectra (G and D modes).

Figure 2: SEM images of (a) ZT only, (b) fCNT-ZT, (c) GO-ZT and (d) FLG-ZT composites after densification. Carbon additives were false-colored to highlight them in the SEM images.

Figure 3: Water vapor uptake capacity at 40°C with 10% and 20% relative vapor pressure. While the average sample weight was ~ 50 mg, the balance sensitivity was ~ 0.1 μ g with $\pm 0.1\%$ weighing accuracy.

Figure 4: Thermal conductivity obtained from experiments and modified effective medium analysis (EMA). The ZT conductivity and fCNT-ZT, GO-ZT and FLG-ZT composite thermal conductivities as a function of density are shown with symbols. The concentration of all of the thermal additives was approximately 3.0 wt%. The thermal conductivity from EMA for FLG (green dotted line) and fCNT (blue dotted line) show reasonable agreement with the experiments. FLG increased the composite thermal conductivity while no enhancement was observed with fCNT or GO.

Figure 5: (a) Example SEM images used to determine the contact area ratio of the FLG-ZT (top) and fCNT-ZT (bottom) composites where blue represents contact area and red represents non-contact area. (b) The contact ratio (f_c) FLG-ZT (green) and fCNT-ZT (red) composites with various densities.

Table 1: Surface area and micropore volume change of fCNT-ZT, GO-ZT and FLG-ZT composites measured by BET. The results indicate that the thermal additives were not blocking the micropores of the ZTs.

Figure S1: Change in water vapor uptake of the ZT and the composites at 10% relative vapor pressure with various temperatures between 25°C to 80°C. While the average sample weight was ~ 50 mg, the balance sensitivity was ~ 0.1 μ g with $\pm 0.1\%$ weighing accuracy.

Figure S2: Example TGA results with GO-ZT composite where the sample was dried first under N_2 gas to remove vapor first, followed by carbon oxidation under O_2 gas to determine the carbon concentration

in the composite. The 1st weight loss around 20 minutes was due to drying water vapor and the 2nd one around 170 minutes was due to oxidizing GO (2.23%). The concentration of GO in the GO-ZT composite, then, was estimated around 3.0% ($= 2.23/75.8$).

Figure S3: TEM images of FWNTs (a) before and (b) after functionalization, and Raman (c) radial breath mode (RBM) and (d) GD mode of before (black lines) and after (red lines) functionalization. The RBM and GD modes correspond to radial expansion-contraction and the quality of the nanotube, respectively. Inserted digital images in Figure S3(a) and (b) show the dispersion of FWNT and fCNT in ethanol, respectively.

Figure S4: TEM image of GO showing its number of layers.

Figure S5: TEM image and (b) Raman spectra of FLG showing its number of layers. While single or double layers of graphene shows 2D peak around 2670 cm^{-1} , 5 ~ 10 layers of graphene shows broaden 2D peak around 2720 cm^{-1} . [43]

Figure S6: XRD patterns of ZT before (black) and after (red) densification using hydraulic press showing that there was no loss of crystallinity even after densification, indicating that the ZT micropores remained intact.

Figure S7: Pore-size distribution (mesopores) of fCNT-ZT (blue), GO-ZT (red) and FLG-ZT (green) composites. There was no significant change in adsorption capacity and micropore volume of the composites as shown in Table 1.

Figure S8: Example SEM images of fCNT-ZT composites (a and b) where the contact (c and d) and non-contact area (e and f) used for the contact ratio analysis. The contact and non-contact area were colored in blue and red, respectively. The fCNTs were observed to bundle together even after functionalization, resulting in relatively high non-contact area (red) compared to contact area (blue).

Figure S9: Examples of the contact ratio analysis based on the SEM images of FLG-ZT composites (a and b) where the contact (c and d) and non-contact area (e and f) were extracted from SEM images by using Matlab code. Contact and non-contact area are colored in blue and red, respectively. FLG were observed to be well-dispersed resulting in relatively high contact area (blue) compared to non-contact area (red).

Figure S10: Schematic of a composite unit cell of a graphene coated with a thin interfacial thermal barrier layer. The case of CNT was reported by Nan et al. [49]

Figure S11: Thermal conductivity obtained from modified effective medium analysis (EMA). The ZT conductivity and fCNT-ZT, GO-ZT and FLG-ZT composite thermal conductivities as a function of density are shown with symbols. The thermal conductivity from EMA show reasonable agreement with the experiments. FLG increased the composite thermal conductivity while no enhancement was observed with fCNT or GO.

FIGURES AND TABLE

Figure 1: TEM images of (a) functionalized few-walled carbon nanotubes (fCNT), (b) graphene oxide (GO) and (c) few-layer graphene (FLG) and their Raman spectra (G and D modes).

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Table 1: Surface area and micropore volume change of fCNT-ZT, GO-ZT and FLG-ZT composites measured by BET. The results indicate that the thermal additives were not blocking the micropores of the ZTs.

	ZT only	fCNT-ZT	GO-ZT	FLG-ZT
Surface area	$661 \pm 12.3 \text{ m}^2/\text{g}$	$667 \pm 14.3 \text{ m}^2/\text{g}$	$668 \pm 13.7 \text{ m}^2/\text{g}$	$659 \pm 11.8 \text{ m}^2/\text{g}$
Micropore volume	$0.280 \pm 0.019 \text{ cm}^3/\text{g}$	$0.281 \pm 0.023 \text{ cm}^3/\text{g}$	$0.288 \pm 0.015 \text{ cm}^3/\text{g}$	$0.278 \pm 0.013 \text{ cm}^3/\text{g}$