



Dimensionality effects of carbon-based thermal additives for microporous adsorbents



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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.

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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 (Fig. 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 makes 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, 2000–3000 W/mK) [16–18], 2D few-layer graphene (FLG, 1000–3000 W/mK) [19,20] and 2D graphene oxide (GO, 8.8–18 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

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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 h 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 2 h 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 min. 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 min. The supernatant was once again collected and stirred with nitric acid (5 vol%) for 1 h 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 min). 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 (5 mm thickness), REFLEX Analytical Corporation) and pressed using a hydraulic press maintained at desired pressure for approximately 6 h, followed by drying at 200 °C for 6 h. 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 ~1.18 g/cm³ and ~1.33 g/cm³ 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 ~3.0 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 (~3.0 wt%), the volume fractions of CNT, GO and FLG in the composites were 2.1, 2.0 and 1.6 vol%, respectively, estimated by

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

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/cm³, 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 (1.19–1.35 g/cm³) 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), respectively. 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 thermo-gravimetric 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 Fig. 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 h 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

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