Three-Dimensional Graphene with Preserved Channeling as a Binder Additive for Zeolite 13X for Enhanced Thermal Conductivity, Vapor Transport, and Vapor Adsorption Loading Kinetics

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Abstract: Atmospheric water vapor extraction through adsorption to highly porous materials holds promise for its incorporation into broader technologies, including potable water generation. These technologies require breakthroughs in synthesis and design. Here, we demonstrate a composite of zeolite 13X sorbent for high adsorption capacity infiltrated with a light-weight three-dimensional graphene binder, which effectively networks a substrate structure into the sorbent. The composites described maintained fidelity when passing through the pore structure. This was accomplished by the utilization of a sacrificial polymer for safeguarding channel networking during sorbent infiltration of the binder for the extension of substrate networking. The performance measures for adsorbate loadings and thermal flux are evaluated with additional measurements taken for considering compactions of sorbent/substrates. Graphene/Zeolite 13X with preserved channeling demonstrated specific heat flux at 7664 W/kg, while samples without preserved channeling measured 4206 W/kg. A 0.6 g/cm\(^3\) compaction resulted in a 412% and a 368% improvement in mass transport while compaction at 1.2 g/cm\(^3\) resulted in a 333% and a 290% improvement in mass transport.

Keywords: zeolite; vapor adsorption; water harvesting; heat and mass transfer

1. Introduction

Much of our world is built with the expectation that water will return to us through natural systems and in abundance. Population growth, untreated industrial wastewater, and climate change have resulted in daunting cleanup challenges, rivers with reduced flow, and reservoirs with depleting supplies [1]. In a growing number of regions, the expectation of unstrained access to potable water requiring minimal energy input is untenable for agricultural, residential, and industrial planning [2]. Atmospheric Water Harvesting (AWH) is a wide field of research with a long past. Beautiful ancient rainwater collecting structures known as Khadins, Ahars, and Kattas effectively supported large populations in India. In the 14th century, Chittorgarh Water Fort, utilizing 84 reservoirs and water bodies, had enough capacity to endure a year without rain [3]. In many parts of the world, rain- and dew-collecting structures can be found atop residences with markedly little improvement in the centuries-old engineering underlying their design. AWH dew-collector research, such as the WarkaWater tower, inverted pyramid designs [4], multiscaled curvatures [5], pore-controlled synthesis [6], metal–organic framework adsorbent synthesis [7,8], and macrotexturing [9], seek game-changing performance improvements by incorporating modern advances. Decades of water restrictions in the American West are seeing the installation of Atmospheric Water Extraction (AWE) by way of optimized electric chillers with accompanying cisterns, a modern option for those who can afford it [10]. Such water chiller technologies require a highly resourced infrastructure and could not be used alongside energy conservation efforts. Other techniques of AWE, such as cloud seeding and solar stills,
are active areas of research [11]. The holy grail of AWE is a low-energy input device with sorbents designed for rapid vapor uptake/release cycling across a wide range of humidities and temperature environs. A sorbent-based AWE device meeting such requirements designed in consideration of advances in passive radiative cooling has the potential to be a breakthrough technology [12]. Sorbent-based AWE relies upon the surface attractive forces of highly porous materials wherein an optimized sorbent/substrate structure presents the limiting design hurdle. The structure of a sorbent/substrate composite will directly affect the vapor loadings, the mass diffusivities, and the thermal conductivities. All of which require precise engineering to achieve the rapid uptake/release cycling required for AWE. Compositing of Graphene for the formation of sorbent/substrate structures with Zeolite was demonstrated for the removal of various pollutants from water; for removal of Methyl Orange and Cu(II) [13], for removal of Arsenic [14], for removal of Lead [15], and for removal of Fe(III) [16]. Compositing of Graphene–Zeolite has received attention from a wide array of adsorption-driven applications, for the adsorption of Ethane [17], for Hydrogen [18], and for Carbon capture [19]. The use of functionalized Zeolites for compositing was demonstrated to improve adsorption kinetics with water vapor [20,21]. Our prior research effort in compositing includes Zeolite-driven adsorption with binder additives for climate control and thermal energy storage systems [22], with this publication directly building on a functionalized Graphene–Zeolite compositing synthesis protocol for heat pump applications, which investigates the Zeolite–Water dynamic. Efforts to advance adsorption-based heat pump performance by compositing Graphene with Zeolite has continued to receive attention by researchers [23]. In this publication, the performance of an integrated material “composite” with preserved channeling by sorbent/substrate synthesis with steps for utilization of a sacrificial polymer is considered for use in AWE. The sorbate–sorbent pair were selected in the hope of demonstrating this accelerated uptake/release. The substrate/binder’s higher thermal conductivity and micro-channel pore dimensions are intended to desirably manage the enthalpies of adsorption while facilitating vapor transport. In this study, we demonstrate enhanced heat and mass transfers which function to keep high heat and mass transfer with increasing volumetric adsorption capacity via compaction. We synthesized zeolite composites with three-dimensional graphene-embedded hollow micro-channels (3dGRCh) that enable adsorption stacks to overcome inherent thermal and mass transport limitations simultaneously.

2. Materials and Methods

Three-dimensional graphene (3dGR) was synthesized by way of Chen’s template-directed chemical vapor deposition (CVD). Nickel foam (American Elements, PPI 110, Los Angeles, CA, USA) acted as catalyst [24]. Methane/hydrogen gasses were used as carbon sources for growth. For the pre-annealing process Ni foam was annealed for about 24 h at 1100 °C under flowing H₂ (40 standard cubic centimeters per minute, sccm) and cooled down to room temperature at 0.5 °C min⁻¹ before conducting CVD growth to enlarge Ni grain size resulting in higher thermal conductivity of 3dGR than without the pre-annealing process. The Ni foam was cut into strips of the desired size (25.4 × 25.4 × 5 mm³), and then placed in a furnace (Thermo Scientific™, BlueM®/Lindburg, Waltham, MA, USA). The temperature of the furnace was ramped to 1000 °C in 1 h under a flowing Ar (40 sccm) and H₂ (10 sccm) mixture and held at 1000 °C for an additional 30 min. To coat graphene on the Ni foam, the mixture of CH₄ (50 sccm), H₂ (50 sccm) and Ar (400 sccm) was introduced for 1 h at 1000 °C. After the growth, the furnace was quickly cooled to room temperature (20 °C min⁻¹). After the growth of 3dGR on nickel foam in a furnace at 1000 °C, the nickel foam template was removed by placing the sample in a diluted HCl acid solution for 3 days at 50 °C, followed by washing with water. As the synthesized 3dGR is hydrophobic, we functionalized the surface of 3dGR to maximize the interaction with zeolite 13X (NaX, Sigma Aldrich, St. Louis, MO, USA 283,592, molecular sieves, 13X, 2 µm), which is hydrophilic. The synthesized 3dGR was oxidized by a mixture of HNO₃ and H₂SO₄ solutions which was described by Menna et al. [25] As shown in Figure 1a, we used poly(methyl methacrylate)
(PMMA) to protect channels inside functionalized 3dGR (f3dGR) while we integrated with zeolites. f3dGR was placed in PMMA solution (PMMA 950, MicroChem, Round Rock, TX, USA) for 30 min, followed by drying with Kimwipes to remove unnecessary PMMA between macro-pores of f3dGR. After curing of PMMA at 170 °C for one-hour, aqueous zeolite solution (50 wt%) was slowly poured. Zeolite particle macro-pores were infiltrated with f3dGR and solidified after 12 h. After drying at 100 °C for overnight, the composite was placed in acetone to remove the PMMA in the micro-channels of the f3dGR. To fabricate the 3dGR-zeolite composite without micro-channels (3dGR/NaX), the zeolite suspension (50 wt% zeolite in H₂O) was directly dropped on the top of the wet f3dGR in a beaker, followed by similar solidifying and drying procedures described above.

Figure 1. (a) Schematic of the synthesis of 3dGRCh-NaX using PMMA as sacrificial polymer to protect the micro-channels of 3dGR. SEM images of 3dGRCh-NaX and 3dGR-NaX composites; (b) N₂ adsorption–desorption isotherms at 77 K for NaX (black-round) and 3dGRCh-NaX (blue-round) composite. Inset: pore size distribution based on N₂ adsorption–desorption isotherm. y-axis is incremental pore volume (cm³/g) and x-axis is diameter (nm). (c) NaX with infiltrated 3dGRCh thermal additive binder coating, and (d) 3dGR-NaX without preserved channeling. The 3dGR was falsely colorized in green for better contrast.

A composite of zeolite with 3dGR and 3dGRCh of desired dimension (25 × 25 × 5 mm³) was mounted on a heat-flux sensing adsorption platform (HFS) in a pressure-controlled vacuum chamber, which was built to measure the heat released from an adsorption stack via conduction through a thin film heat flux sensor to a temperature-controlled sample holder. To measure heat generated by the adsorption stack, we fabricated the HFS rig shown in the inset of Figure 3c. The HFS was located in the custom environmental chamber where vapor pressure and wall temperature were precisely controlled. A thin film heat flux sensor (HFS-4, OMEGA, Norwalk, CT, USA) was located between the adsorption stack and a copper sample holder. A thin layer of thermal paste (silicone heat sink compound, 340, DOW CORNING, Midland, TX, USA) was applied to bond the adsorption stack and the heat flux sensor. To minimize thermal resistance, it was important to apply a thin but uniform layer of thermal paste. A thermal pad (A15896-02, Laird Technologies, Chesterfield, CT, USA) was placed between the heat flux sensor and the copper sample holder. The use of a thermal pad, rather than additional thermal paste, ensured equivalent thermal contact.
resistance from the sample to the sample holder between subsequent trials. Two resistive heaters (OMEGALUX, Kapton Insulated Flexible Heater, OMEGA, Norwalk, CT, USA) were located in the middle of the copper sample holder to heat the adsorption during the desorption process. A U-shaped tube was inserted in the copper sample holder to cool or maintain its temperature at a constant ~22 °C. The U-shaped tube was connected with a water pump, and a flow meter was installed to monitor the flow of cooling water. During the adsorption process, heat released by the adsorption stack was passed through the heat flux sensor, which generated electrical signals collected by a data acquisition system (34972A LXI Data Acquisition, Agilent, Santa Clara, CA, USA). To convert the electrical signals (mV) to heat flux (W), calibration was conducted using the HFS and a resistive heater with the same dimensions (25.4 × 25.4 mm²). The power (W) provided by the resistive heater was simply the product of voltage (V) and current (I), and corresponding voltage signal from the HFS was recorded. The calibration factor, converting the electrical signal to heat flux, was 349.1 W m⁻¹ V⁻¹. A replacement in the HFS showed a small variation in the calibration factor. Therefore, the calibration experiments were conducted again upon replacing the HFS. The reported uncertainty is based on the standard deviation of multiple measurements. The specific surface area and pore size distribution of the solid were based on the multipoint Brunner–Emmett–Teller theory (BET) and nonlocal density functional theory (NLDF). SEM images were obtained on a JEOL 6010LA SEM. The thermal conductivity of NaX and NaX/3dGRCh composite were measured by laser flash method (NETZSCH, LFA 457 MicroFlash). Pellets of NaX or NaX/3dGRCh were prepared in 12.5 mm diameter for use of laser flash method. Adsorption isotherms were obtained on a DVS Vacuum Surface Measurement System (0.1 µg sensitivity), in which the vapor pressure and temperature was precisely controlled. Typical loading mass of absorbent was ~30 mg. Before adsorption on the DVS Vacuum, all adsorbents were fully dried. The desorption conditions used for zeolite (NaX) were 400 °C and 0.1 Pa for 6 h. To achieve an accurate isotherm, the adsorbent was exposed to vapor at the desired relative pressure until it reached its absorption plateau.

3. Results and Discussion

We created micro-channels inside of the 3dGR as vapor transport channels to enhance vapor transport through adsorption composite stack, while a percolated graphene network of 3dGR ensures effective thermal transport without compromising adsorption uptake due to light weight of 3dGR. Figure 1a shows a schematic of the synthesis of the 3dGR with micro-channels (3dGRCh). Details of the procedure can be found in the experimental section above. Figure 1c,d show SEM images of (3dGRCh-NaX) composite with micro-channels and (3dGR-NaX) composite without micro-channels. Figure 1a shows the purpose of the sacrificial polymer (PMMA) in preserving the 3dGR microchannels, which is critical to maximize the mass transport of water vapor while enhancing thermal transport through a maximized binder 3dGR network to the substrate. Once the NaX particles were successfully incorporated with 3dGRCh, the sacrificial polymer was removed via acetone washing. Figure 1c,d show the 3dGRCh and 3dGR networking formed on NaX. The 3dGR was falsely colorized in green for better contrast. The BET specific surface area of the NaX and 3dGRCh-NaX composite were estimated using the multipoint BET method based on adsorption–desorption isotherms at 77 K, as shown in Figure 1b. The surface area of the NaX and 3dGRCh-NaX composite was 657.5 m²/g and 644.8 m²/g, respectively. In addition, the inset of Figure 1b shows the pore-size distribution. Micropore volumes of NaX and 3dGRCh-NaX composite were estimated at 0.282 cm³/g and 0.285 cm³/g, respectively. This isotherm analysis demonstrated that the surface area and micropore volume of the samples remained relatively constant, even after the addition of 3dGRCh. The relatively unaffected surface area and pore-volume suggests that the effect of the addition of thermal additive (3dGRCh) was not significant and the pores of the NaX particles stayed open during the synthetic process of 3dGRCh-NaX. The vapor adsorption dynamics (Figure 2)
and the heat-flux sensing adsorption results below (Figure 3c,d) also support preserved micropores in the 3dGRCh-NaX composite.

Figure 2. (a) Adsorption dynamics comparison between NaX powder (black), and compacted 3dGR-NaX (red) and 3dGRCh-NaX (blue) composites in time. The inset shows a schematic of sample loading in DVS. (b) Thermal conductivity comparison between NaX (black squares), 3dGR-NaX (red rounds), and 3dGRCh-NaX (blue triangles) in different density.

Figure 3. (a) Thermal conductivity comparisons of NaX (black), 3dGR-NaX (red) and 3dGRCh-NaX (blue). (b) A schematic side view of the heat-flux sensing adsorption platform (HFS) to measure specific heat flux responses and gravimetric energy density of the adsorption heat. (c) Specific heat flux responses and (d) gravimetric energy density adsorption stacks with 3dGRCh (blue triangle) and 3dGR (red rounds), and without binder (black square). The inset of (c). shows an image of experimental set up. The 3dGRCh-NaX composite exhibits increased thermal power density as its higher thermal conductivity increases the proportion of heat that is delivered to the substrate, rather than lost to the vapor ambient. The inset is an image of the experimental setup.

To compare the adsorption dynamics of the 3dGRCh-NaX to the composite 3dGR-NaX, 3dGR-NaX and 3dGRCh-NaX composites were pressurized at 50 Mpa and samples were
taken (3 × 3 × 1 mm³) which were then loaded into a vapor adsorption analyzer (DVS Vacuum, Surface Measurement Systems). The desorption condition was characterized at ~10⁻⁴ Pa and 400 °C and the adsorption condition was characterized at 25 °C with 1% relative pressure. Figure 2a shows that adsorption dynamics of the 3dGR-NaX composite after densification was similar to that of the NaX disk. However, vapor transport of the 3dGRCh-NaX was faster than that of 3dGR-NaX. This is attributed to the small weight fraction (<2%) of 3dGR in the composite of 3dGRCh-NaX, minor reduction of adsorption capacity was observed after adding 3dGR. Figure 2b presents the moisture diffusion coefficients in the composites by measuring adsorption isotherms on the thin films in a DVS instrument. The diffusion constants for the composites were estimated by utilizing the diffusion equation employed by Crank and Park [26]. The initial kinetics of sorption into a bulk adsorbent can be described as:

\[
\frac{M_t}{M_\infty} = \frac{4}{\pi} \left( \frac{D t}{d^2} \right)
\]

where \( M_t \) is amount adsorbed at time \( t \), \( M_\infty \) is amount adsorbed at thermodynamic equilibrium, \( d \) is the thickness of a sample, and \( D \) is diffusion constant. The equation is generally accepted for values of \( \frac{M_t}{M_\infty} < 0.4 \), where a plot of \( \frac{M_t}{M_\infty} \) against \( \frac{t^2}{d} \) is linear. The diffusion constant, \( D \), was calculated from the slop of the line. Sorption data points were collected every 2 s for the experiment, and a minimum \( R^2 \) value of 99.9% was applied for the diffusion constant characterization.

Figure 2b presents a general trend for diffusion coefficients calculated for each discrete step in humidity. The diffusion constants from the composites increased with increasing partial vapor pressure of water. In addition, the diffusion constants of the composite with micro-channels (3dGRCh-NaX) were higher than those without micro-channels (3dGR-NaX). The diffusion constants of the NaX disk were the lowest. The diffusion data suggest enhanced diffusion coefficient by adding micro-channels.

While 3dGRCh showed enhanced mass transport, it exhibits comparable enhancement in thermal conductivity to that of 3dGR, as shown in Figure 3a. The improvements of 3dGRCh and 3dGR were approximately 412% and 368%, respectively, at a low composite density (~0.6 g/cm³), and approximately 333% and 290%, respectively, at a high composite density (~1.2 g/cm³). The amount of enhancement decreased with densification as the thermal conductivities of the zeolite without the binders increased. In addition, the composite of 3dGR and NaX without channels shows higher thermal conductivity compared to those with channels. Figure 3b shows a schematic side view of the heat-flux sensing (HFS) adsorption platform to measure specific heat flux responses and gravimetric energy density of the adsorption heat. A thermal paste and a thermal pad were applied to ensure the heat flow of the adsorption heat generated by the adsorption bed. Figure 3c presents thermal responses from a sample without any thermal additive (NaX) and composites with micro-channels (3dGRCh-NaX) and without (3dGR-NaX). A water vapor step input was from ~1 Pa to ~2500 Pa, comparable to the operating conditions in practical adsorption chillers. The released heat was normalized by the total weight of the adsorption stack. The sample without any thermal additive (NaX) not only showed slowest thermal energy release among the three samples but also experienced significant heat loss to its surroundings due to low thermal conductivity. This is because the thermal resistance from the adsorbent stack without thermal additive to the sample base was comparable to the thermal resistance to the surroundings, resulting in thermal loss to the ambient. The 3dGRCh-NaX showed higher specific heat flux (7664.0 W kg⁻¹) than that of 3dGR-NaX (4206.7 W kg⁻¹). Figure 3d shows that the 3dGRCh-NaX and 3dGR-NaX composites released 99% of their thermal energy in 632 s and 1046 s, respectively, while energy release from the NaX sample without additives was clearly slower. These results demonstrate the enhancement in thermal transport using the micro-channels of the 3dGRCh.
4. Conclusions

In summary, 3dGR with micro-channels (3dGRCh) appears to be a promising thermal and mass transport additive to simultaneously enhance thermal and mass transports. The percolated structure of the 3dGR provides effective heat transfer through the adsorbent stack while the reduction of adsorption capacity was minimal due to it being light weight. The micro-channels inside of the 3dGR, created by PMMA as a sacrificial material, enhanced mass transport through the adsorption stacks compared to the samples without the micro-channels. This work demonstrates that heat and mass transports were simultaneously improved by the 3dGR, light weight thermal additive, and the micro-channels of 3dGRCh. Significant improvement in thermal additives and mass transport channels is expected to result in enhanced water harvesting. While the micro-channels demonstrated a way for simultaneous improvement of thermal and mass transports, the investigation of a new class of thermal and mass additives is clearly needed in consideration of improving its flexibility, weight, and cost.

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