Surface Tunable Magnetic Nano-sorbents for Carbon Dioxide Sorption and Separation

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ABSTRACT

The increasing level of carbon dioxide (CO₂) in the atmosphere is directly linked to global climate change, which has motivated a number of technological-based mitigation approaches for carbon capture and storage. Among these, CO₂ sorption using solid sorbents is one of the most promising strategies. This report focuses on the development and evaluation of novel, hybrid inorganic-organic magnetic nano-sorbents for advanced, high capacity CO₂ sorption and magnetic separation processes. Magnetic nanocomposites were prepared by grafting various polymers (e.g. polyethylenimine, polyethylene glycol, etc.) onto magnetite nanoparticles (nMAG) through solution-based sonication and evaporation methodologies. Further, we demonstrate that nMAG can be coated with polyethylenimine (PEI) with different molecular weights (Mw) and structures (linear vs. branched), yielding nMAG nanocomposite libraries with varied PEI loadings and combinations of amine types (primary, secondary, and tertiary amines). Surface functionalized nMAG nanocomposites were characterized by TEM, BET, SQUID, and FTIR techniques and evaluated for CO₂ adsorption capacity and recyclability with TGA. Among the as-prepared materials, PEI-nMAG shows the highest CO₂ adsorption capacity with superior selectivity and recyclability.

1. INTRODUCTION

Carbon dioxide (CO₂) is a primary greenhouse gas with anthropogenic sources significantly contributing to global increasing atmospheric levels, which are now above 400 ppm – a 40 % increase compared to the ca. 280 ppm level before industrial revolution.[1-6] Further, driven by continued demand for fossil fuel energy, it is likely that atmospheric CO₂ concentrations will further increase.[1-4] To address this global issue, a wide range of technological options has been explored. Among these, carbon capture and storage (CCS) from large point sources (e.g. fossil fuel based power plants) has attracted broad consideration and attention from government, industry, and academia.[7-12] CCS consists of CO₂ capture and separation followed by compression, transport, and permanent storage in deep oceans and geological reservoirs either in the form of supercritical liquid or solidified carbonates.[5, 11, 13, 14] Given the relative larger energy consumption for CO₂ capture and separation compared to the transport and storage of CO₂, extensive research has been focused on developing new approaches to reduce the cost for CO₂ sorption and separation.[2, 13, 15, 16] Adsorption / absorption with solid / liquid sorbents, cryogenic distillation methods, biological fixation as well as membrane separation have been the most commonly studied CCS techniques for gas mixtures.[5, 17-21] Within the spectrum of CCS technologies, CO₂ adsorption using solid sorbents is considered to be a promising technique compared to typical aqueous (amine-based) sorbents (i.e. monoethanolamine, MEA) due to low energy requirements, high thermal stability, and ease of regeneration for post-combustion / recycling processing.[2, 22-24] Numerous solid sorbents have been investigated for CO₂ capture, including activated carbon, mesoporous silica, zeolites, molecular sieves, metal organic frameworks (MOF), graphene/graphene oxide, and metal oxides, among others.[5, 8, 10, 14, 16, 18, 25, 26] More recently, sorption technologies incorporating surface functionalized engineered

nanomaterials have demonstrated superior physical and chemical properties compared to traditional sorbent strategies, due to their large surface area, and tunable core / surface chemistries, offering unique advantages including low pressure capture, high temperature operation, and superior selectivity.[15, 19, 21, 25, 27, 28]

Single crystal magnetite (Fe_3O_4) nanoparticles have the ability to respond to an external magnetic field, allowing for potentially simple placement/recovery, thus lower separation energy and material input requirements.[29] Further, magnetite is abundant and relatively stable in the environment.[6] Due to low cost and high biocompatibility (i.e. relatively low toxicity), magnetite based (nano)materials have been widely used in fields of biomedical research, physics, data storage, catalyst, and environmental engineering.[29-31] Magnetic-based nanocomposites have also been developed and evaluated for their sorption performance toward CO_2 capture. By decorating commercial carbon black with magnetite nanoparticles, Alfe et al. demonstrated a cost-effective method to synthesize magnetic sorbents with high CO_2 uptake capacities and good regeneration properties.[24] Mishra et al. have systematically investigated the performance of magnetic carbon materials functionalized with Fe_3O_4 nanoparticles, such as multi walled carbon nanotubes (MWNTs), graphene, and graphite nanoplatelets.[3, 11, 26] Under high pressure, each of the magnetic nanocomposites demonstrated a large enhancement in CO_2 adsorption capacity, resulting from sorption processes to both the functional groups (from the carbon substrates) and the iron oxide nanoparticles. Recently, Liu et al. reported the functionalization of magnetic Fe_3O_4 nanoparticles prepared from co-precipitation methods with PEI through solution-based reaction pathways.[29] The material exhibits high CO_2 sorption capacity of 0.373 mol/L, albeit system performance was only tested at 40 °C and in the aqueous phase. The functionalization or incorporation of magnetite with either amine containing polymers or carbon-based materials can

greatly improve the CO₂ adsorption capacity.[1] For these, the higher sorption capacities are mainly due to the large surface area and specific interaction between CO₂ and amine-based functional groups.[1, 32] These types of magnetic sorbents offer several advantages, including high sorption capacity, low capital cost, and easy separation compared to traditional aqueous amine solvents.[29] For industrial application, solid amine-based sorbents are usually evaluated in fixed bed or fluidized bed processes.[7, 22, 24] While, easy to imagine for both, magnetic cores have an obvious advantage in highly fluidized bed technologies, especially in newly developed magnetic assisted fluidized bed, due to potentially addressing/alleviating attenuated slugging, channeling, plugging, and agglomeration.[24, 33]

In this work, we have methodically designed, synthesized, and evaluated novel core-shell nanocomposites, comprised of a magnetite (Fe₃O₄) nanoparticle core and tunable surface functionalized organic coatings (shell) as a platform material for advanced CO₂ capture, separation, and reuse. Commercial magnetite nanoparticles (nMAG) were chosen due to their ability to respond to an external magnetic field, allowing for potential low-energy placement/recovery in addition to broad material availability needed for scale-up employment. Through methods described, nMAG can be surface coated with PEI, an excellent organic CO₂ polymeric sorbet, with varied molecular weights (Mw) and structures (linear vs. branched), yielding nanocomposites with tunable coating thickness (PEI loading %) and combinations of different amine types (primary, secondary, and tertiary amine). Besides PEI-based polymers, other surface polymers were similarly demonstrated and explored, such as poly(acrylic acid) (PAA), poly(sodium 4-styrenesulfonate) (PSS), etc. This methodology provides a simple, green and environmentally friendly procedure to produce scalable, surface tunable, and solid-state magnetic nano-sorbents for CO₂ capture. For all, surface coating(s) thermodynamic stability,

polymer loading percentage, specific surface area, and CO₂ adsorption/desorption performance were characterized using Fourier transform infrared spectroscopy (FTIR), Brunauer-Emmett-Teller (BET), and thermogravimetric analysis (TGA) instrument. This work, for the first time, systematically evaluates and compares the CO₂ capture performance of nMAG with a series of tailored surface coatings. Presented data sets clearly demonstrate the critical role of the outer polymer(s) in determining material performance - providing informative direction(s) to further surface (optimized) modification.

2. MATERIALS AND METHOD

2.1 Materials

Nanoscale magnetite powder (nMAG, catalog # 637106, iron (II, III) oxide, < 50 nm, 98+ %), polyethylenimine (PEI, branched, Mw 25,000), poly(acrylic acid) (PAA, Mw 100,000), poly(sodium 4-styrenesulfonate) (PSS, Mw 70,000), poly(allylamine hydrochloride) (PAH, Mw 17,500), poly(ethylene glycol) (PEG, Mw 35,000), and polyvinylpyrrolidone (PVP, Mw 40,000) were all purchased from Sigma-Aldrich. Polyethylenimine (PEI, branched, Mw 1,800), polyethylenimine (PEI, branched, Mw 10,000), and polyethylenimine (PEI, linear, Mw 25,000) were purchased from Polysciences. Reagent grade of ethanol were used without further purification.

2.2 Preparation of surface functionalized nMAG

nMAG nanoparticles were prepared using a modified polymer impregnation-vaporization method through probe sonication, extensive mixing, and solvent evaporation.[9] For a typical sample preparation, a certain amount of polymer (0.4-2.0 g) was dissolved in 25 mL ethanol, and then slowly added under stirring to 5.0 g of nMAG suspended in 25 mL ethanol. Upon completely mixing, the solution was then probe sonicated (UP 50H, Dr. Hielscher, GMHB) for

an extended period of time under vacuum until almost dry. The mixture was subsequently transferred to a vacuum oven overnight at 50 °C. The obtained polymer impregnated nMAG was brown in color and further ground to fine powder with a mortar and pestle for material characterizations. As-prepared nano-sorbents were dried at 80 °C in a vacuum oven before use. The final magnetic nanoparticles are denoted as PEI-nMAG, PAA-nMAG, PSS-nMAG, PAH-nMAG, PEG-nMAG, and PVP-nMAG.

2.3 Material characterization

nMAG nanoparticle size was characterized using transmission electron microscopy (TEM, FEI Tecnai G2 Spirit) operated at 120 kV. In order to prepare the TEM sample, nMAG nanoparticles were first dispersed in hexane and then a small drop of the NPs suspension was placed on a carbon coated copper grids (Electron Microscopy Sciences) and dried overnight. X-ray powder diffraction (XRD) was performed on a Bruker D8 Advance from 20 to 80 2 θ degree at room temperature. The measurement was obtained with a LynxEye XE detector and a Cu K α X-ray source (1.54 Å) generated at 40 kV and 40 mA. The magnetization hysteresis loop was analyzed with a superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS 5XL SQUID) at 300 K (up to 5 T) using powders of pristine and polymer grafted nMAG. Solid-state Fourier transform infrared spectra were obtained on a Nexus 470 FTIR spectroscopy (Thermo Nicolet, NC). To prepare the pristine nMAG and polymer functionalized nMAG powders for IR analysis, each sample was mixed with KBr powder (Spectrograde, International Crystal Lab, NJ) in an optimal 1:3 ratio to achieve a total amount of 40 mg. Before each measurement, a KBr background spectrum was collected and subtracted thereafter. All spectra were performed from 400-4000 cm⁻¹ with a resolution of 2 cm⁻¹. Brunauer-Emmett-Teller (BET) surface area was characterized by N₂ adsorption/desorption isotherm measurements on a

Quantachrome NOVA 2000e instrument. The surface area was determined by the multipoint BET method.[28, 34] TGA was performed on a Q5000IR (TA Instruments, USA) with temperature ranging from room temperature to 1000 °C under an ultra-pure N₂ flow with a heating rate of 10 °C /min.

2.4 Adsorption measurements

CO₂ adsorption/desorption performance of polymer functionalized nMAG nanoparticles was analyzed using TGA (Q5000IR, TA Instruments) under atmospheric pressure. Ultrahigh purity of CO₂ was used for thermogravimetric analysis (TGA). For a typical test, the dried nMAG powder sample (10-50 mg) was placed into a platinum pan and heated up to 105 °C under N₂ flow (25 mL/min) for 2 hours until no obvious weight change was observed. This step was to remove trace moisture and any background sorbed CO₂ from the sample. The temperature was then lowered to the desired values (20-100 °C) and the gas flow was switched to CO₂ (up to 1 hour). The flow rate of the CO₂ gas was maintained at 25 mL/min. The change in mass of the sample was recorded continuously during the entire measurement. The CO₂ adsorption capacity in mg·CO₂/ g·sorbent was calculated based on the weight change of the samples in the adsorption processes. Regeneration of the nMAG was performed at an elevated temperature (105 °C) using a temperature-swing approach by introducing pure N₂ into the sample cell. Cyclic adsorption-desorption studies were performed to evaluate the recyclability of these materials for potential real-world application. Sorption measurements of O₂ and N₂ were carried out similarly.

3. RESULTS AND DISCUSSION

3.1 Material preparation and characterization

The general preparation process for nMAG nanoparticles is shown in Figure 1a. Polymer grafting onto nMAG nanoparticles was successfully carried out through a sonication method

followed by evaporation of solvent.[9] The sonication-mixing-evaporation strategy explored here allows for homogeneous and complete incorporation of polymers onto the nMAG surfaces. The primary particle diameter ranged from 10-50 nm for pristine nMAG nanoparticles as shown in a TEM micrograph (Figure 1b). Figure 1c shows XRD diffraction patterns of pristine nMAG and PEI-nMAG. The diffraction peaks at 30.2°, 35.3°, 43.0°, 53.4°, 56.9°, and 62.5° correspond to the magnetite crystal planes of (220), (311), (400), (422), (511), and (440), respectively. These patterns precisely match the typical cubic spinel magnetite (Fe₃O₄) structure (JCPDS card # 19-0629). The crystal domain size of pristine nMAG is derived from the (311) plan refraction using Scherrer equation:

$$d = K\lambda / \beta \cos\theta \quad (1)$$

where θ is the reference peak position, λ is the X-ray wave length (0.154 nm for Cu K α line), β is the full width at half maximum of the reference peak and K is the shape factor (0.9 in this case).[32, 35, 36] For samples tested, average particle size calculated was 22.7 nm. Diffraction patterns of nMAG before and after PEI coating were similar, indicating the high crystallinity of magnetite nanoparticles is preserved during polymer grafting. The magnetic properties of pristine nMAG and PEI-nMAG were characterized with SQUID at 300 K and the hysteresis loops are shown in Figure 1d. The pristine nMAG and PEI-nMAG are paramagnetic with the coercivity of 97.0 Oe and 82.5 Oe. The saturation magnetization (M_{sat}) values were 81.1 and 60.7 emu/g for pristine nMAG and PEI-nMAG (branched, Mw 25,000), respectively. Compared to pristine nMAG, PEI-nMAG demonstrated relatively lower M_{sat} , possibly due to the incorporation of PEI layer on the nMAG surface,[29] as surface polymers on nMAG surface likely impede the tendency of direct particle-particle contact. Such magnetic properties allow for simple separation processes for material collection and recycling while also saving energy, compared to other

separation technologies.[29] As shown in Figure 1e, nMAG nano-composites are strongly attracted to a small magnet (< 1.5 T).

3.2 FTIR analysis

The FTIR spectra of the pristine and polymer functionalized nMAG are reported in Figure 2. The peak at 598 cm^{-1} is assigned to the stretching vibration of Fe-O-Fe in pristine nMAG (Fe_3O_4) (Figure 2a). We found the characteristic peaks of PEI from the PEI-nMAG (Figure 2b), such as the -N-H stretching at 3272 cm^{-1} , -C-H stretching at 2940 cm^{-1} and 2815 cm^{-1} , -N-H bending at 1576 cm^{-1} , -C-H bending at 1465 cm^{-1} , and -C-N stretching at 1300 cm^{-1} . [37] For PAA-nMAG, a strong band is shown at 1720 cm^{-1} , which is the characteristic peak of C=O stretching (Figure 2c). [38, 39] The weaker band at 1451 cm^{-1} is associated with $-\text{CH}_2$ deformation. Response at 1413 , 1248 and 1178 cm^{-1} are attributed to C-O stretching coupled with O-H in-plane bending. [40] Two peaks at 1600 and 1503 cm^{-1} are from the asymmetric and symmetric bending vibrations of $-\text{NH}_3^+$ in the PAH-nMAG (Figure 2d). [41] For PEG-nMAG (Figure 2e), the absorption band at 2878 cm^{-1} is due to C-H stretching. Two peaks at 1464 cm^{-1} and 1343 cm^{-1} are ascribed to C-H bending vibrations. O-H and C-O-H stretching can be found at 1279 cm^{-1} and 1094 cm^{-1} , respectively. [42] For PSS-nMAG, two bands at 1000 cm^{-1} and 1040 cm^{-1} are attributed to the S=O stretching vibration (Figure 2f). [43] For PVP-nMAG, characteristic peaks of pyrrolidinyl group are shown at 1463 cm^{-1} and 1424 cm^{-1} . The peak at 1678 cm^{-1} is due to C=O vibrations and the peak at 1290 cm^{-1} is assigned to C-N vibrations in PVP (Figure 2g). [44, 45] FTIR spectra confirm all polymers (e.g. PEI, PAA, PAH, etc.) were successfully coated onto nMAG surface though intensively mixing and sonication as described above.

3.3 Thermal stability

218 Thermal stability of the sorbents is an important factor to be considered for real-world
219 applications, especially in power plant related CCS technologies. Here, the thermal stabilities of
220 different polymer grafted nMAG nanoparticles were quantified by thermogravimetric analysis
221 (TGA) under an ultra-pure N₂ atmosphere. Figure 3a depicts the TGA thermal stability curves
222 for pristine nMAG and PEI-nMAG with different PEI loading and PEI types (low vs. high Mw;
223 branched vs. linear). Pristine nMAG shows high stability with negligible weight loss (0.6 %) up
224 to temperature of 1000 °C.[29] Four PEI-nMAG samples with different PEI loadings (same Mw
225 of 25,000 and branched structure) were prepared and evaluated here. These samples did not start
226 to decompose until ca. 160 °C, indicating good thermal stability. The slight weight loss (< 1 %)
227 below this temperature is attributed to loss of adsorbed water or other associated, small volatiles.
228 Observable weight loss starts from ca. 200 °C, until all the coatings were completely
229 decomposed and released around 700 °C. The amount of PEI in the PEI-nMAG was calculated
230 based on the weight loss curve. TGA profiles indicate that ca. 6 %, 12 %, 16 %, and 26 % of
231 (wt/wt %) PEI (branched, Mw 25,000) was grafted onto the four PEI-nMAG samples,
232 respectively. This result confirms that the higher PEI loading amount can be obtained through
233 the addition of additional PEI polymer during preparation. The PEI loading was between 16-17
234 % for functionalized nMAG prepared using lower molecular weight PEI (Mw 1,800 and 10,000)
235 and linear PEI (Mw 25,000). The sonication-mixing-evaporation strategy also allowed for the
236 preparation of surface functionalization nMAG with similar PEI loading (16 %) from different
237 PEI sources, which is important for the direct comparison of their CO₂ capture performance. The
238 thermal stability of other polymer functionalized nMAG was measured in the same way and
239 shown in Figure 3b. TGA curves show all other polymers (PAA-nMAG, PAH-nMAG, PEG-

nMAG, PSS-nMAG, and PVP-nMAG) evaluated were also stable below 200 °C with similar weight percentages ca. 17-18 % mass loading (Figure 3b).

3.4 BET surface area

The Brunauer-Emmett-Teller (BET) method was used to determine the specific surface area of nMAG with resulting data presented in Table 1. The specific surface area of the pristine nMAG was 39.6 m²/g and polymer coatings were found to reduce the surface area of the nanocomposites. For PEI-nMAG (branched, Mw 25,000), when PEI loading increases from 6% to 26%, the specific surface area significantly decreases from 32.2 m²/g to 3.61 m²/g. For other samples, nMAG exhibit surface area ranging from 12.4 m²/g to 35.5 m²/g, depending on the coating type and loading.

3.5 CO₂ sorption

The CO₂ sorption measurements were determined by TGA at atmospheric pressure. The effect of PEI (branched, Mw 25,000) loading (weight percentage) on CO₂ sorption performance was evaluated under pure CO₂ atmosphere at 25 °C (Figure 4a). Sorption capacities of 6.1, 11.6, 15.0 and 6.1 mg/g were observed for the PEI-nMAG samples with 6 %, 12 %, 16 %, and 26 % PEI loading, respectively. CO₂ adsorption capacity increased with increasing PEI loading from 6 % to 16 %, and then decreased at higher PEI loading of 26 %. The further increase of PEI loading amount reduced the specific surface area of the nMAG from 39.6 m²/g to 3.6 m²/g, leading to an overall lower CO₂ sorption capacity. In a previous study by Xu et al., the highest sorption capacity for MCM-41-PEI sorbent was obtained when the PEI loading is 50 wt %, due to the combination of increasing CO₂ affinity sites and decreasing surface area and pore size/volume.[8] Labreche et al. also observed a maximum CO₂ capacity of 1.25 mmol/g-fiber when the PEI loading was chosen at a moderate concentration of 10 wt%.[22] The CO₂

capacities were lowered when the PEI concentrations were either decreased or increased. Yu et al. concluded that CO₂ uptake capacity is not directly linked to the amine loading since the aggregation of amine may form on supports, leading to reduced accessibility with regard to CO₂. [10] Overall, in this study, PEI-nMAG with 16 % PEI exhibits the highest adsorption capacity towards CO₂, which was further studied.

Figure 4b shows CO₂ uptake as a function of time for nMAG coated with different PEI types but with similar PEI loadings (ca. 16 wt/wt %). For these, the time needed to absorb 90% of the total CO₂ uptake is ca. 25 min, indicating the sorption processes occur relatively quickly. The CO₂ adsorption capacities were 14.0 mg/g, 14.6 mg/g, and 15.0 mg/g for nMAG with branched PEI 1,800, PEI 10,000, and PEI 25,000, respectively. nMAG coated with linear PEI (Mw 25,000) show a CO₂ sorption capacity of 16.4 mg/g, higher than the nMAG decorated with branched PEI (Mw 25,000). Under dry conditions, only the primary and secondary amines of branched PEI react with CO₂ to form carbamate salts with a molar ratio of 2:1 (carbamate formation: $2R_1R_2NH + CO_2 = R_1R_2NCOO^- + R_1R_2NH_2^+$), however, the tertiary amine (ca. 25 %) from branched PEI does not typically undergo complexation with CO₂. [46] In case of linear PEI, only secondary amines are present.

Figure 5 presents CO₂ sorption capacities of nMAG with varied surface coatings (25 °C). CO₂ adsorption capacities were 0.7 mg/g, 1.1 mg/g, 1.3 mg/g, 2.2 mg/g, and 1.7 mg/g, for PAA-nMAG, PAH-nMAG, PEG-nMAG, PSS-nMAG, and PVP-nMAG, respectively. Compared to PEI-nMAG (branched, Mw 25,000, 16 wt/wt %) sorbents, other surface coating polymers demonstrate substantially lower CO₂ sorption capacities. Similar trends have been reported by others. Jiang et al. found the substantial decrease in CO₂ capture capacity when the

polyelectrolyte was switched to PAA or PAH.[21] For these systems, PEI-nMAG are superior in CO₂ capture, due to the specific chemical bonding between basic amine functional groups and acidic CO₂ molecules compared to other polymers investigated.[1, 10]

3.6 CO₂ sorption-PEI-nMAG selectivity

For practical application, solid sorbent will need to selectively capture CO₂ from gas mixtures. As an example, N₂ is the major component in typical flue gas.[27] The sorption capacity of PEI-nMAG (16 wt/wt %, branched, Mw 25,000) towards N₂ and O₂ were evaluated and shown in Figure 6. PEI-nMAG shows 0.18 mg/g adsorption capacity for N₂ and 0.13 mg/g adsorption capacity for O₂, thus demonstrating high selectivity for CO₂ over N₂ and O₂. On-going studies are exploring more complicated and real-world gas mixtures.

3.7 Temperature effect

Figure 7 shows CO₂ adsorption capacity as a function of temperature (25 °C to 100 °C) for PEI-nMAG (16 wt/wt %, branched, Mw 25,000) with sorption capacities of 15.0 mg/g, 17.1 mg/g, 18.0 mg/g, 18.8 mg/g, 17.5 mg/g, and 13.1 mg/g at 25 °C, 40 °C, 50 °C, 60 °C, 80 °C, and 100 °C, respectively. CO₂ uptake first increases when the temperature increases to 60 °C and then decreases as temperature is increased to 120 °C. At lower temperatures, bulk phase aggregation of PEI on the nMAG surface results in diffusion-limited adsorption of CO₂ molecules with lower uptake capacity.[47] As reported by others, when temperature is further increased, PEI chains become more flexible as the viscosity of PEI decreases, thus allowing for easier CO₂ access to active sorption sites.[5, 15] Similar observations were also reported by Meth et al. who examined the adsorption capacity of CO₂ vs. temperature ranging from 30-100 °C for fumed silica impregnated with PEI and found the maximum CO₂ uptake at a moderate temperature of 50 °C.[15] The decrease of sorption capacity at higher temperatures is attributed

to the more favorable equilibrium towards desorption processes.[15] These results indicate the PEI-nMAG is also suitable for CO₂ capture, even at the elevated temperatures of flue gas (50-120 °C).[2]

3.8 Recyclability

In addition to high sorption capacities, sorbents with superior regenerative ability (recyclability) to undergo multiple adsorption/desorption cycles are technically and economically preferable. Typically, regeneration of (gas) sorbents can be achieved by either controlled pressure or temperature swings. Here, a temperature swing method was used to regenerate sorbents and test the recyclability of the materials during CO₂ sorption/desorption events. Figure 8 presents CO₂ recyclability of PEI-nMAG sorbents (branched, Mw 25,000, 16 wt/wt %) for 20 cycles. CO₂ sorption capacity is 14.1 mg/g after 20 cycles, with slight (ca. 6%) drop in performance as compared to the initial capacity (15.0 mg/g). Since the desorption was carried out at 105 °C under dry conditions which is lower than the formation temperature of urea (above 135 °C),[48] the slight decrease in CO₂ sorption capacity may result from the loss of outer weakly bound PEI from nMAG surfaces during temperature swing regeneration processes.[9] The overall the excellent regenerative ability of PEI-nMAG nanocomposites can be attributed to the low volatility of PEI, strong interaction between PEI and nMAG, and good thermal stability.[10, 11, 28]

4. Conclusions

nMAG-based, surface tunable, nanocomposite materials demonstrated in this study can be simply and reproducibly prepared from commercially available materials. PEI-nMAG show significantly higher sorption capacity for CO₂ compared to other polymer-based, surface functionalized nMAG composite materials. In addition, PEI-nMAG nanocomposites exhibit

332 enhanced CO₂ capture performance even at elevated temperature (40-80 °C), which is ideal for
333 post-combustion CO₂ capture. Further, PEI-nMAG can be used for multiple sorption / desorption
334 (separation) cycles while maintaining high performance. Taken together, cost effectiveness,
335 facile and scalable preparation routes, high CO₂ sorption capacities, magnetic susceptibility, and
336 good recyclability underpin these hybrid nanocomposites as a potentially attractive CCS material
337 platform. On-going material evaluation includes CO₂ capture experiments for simulated and real
338 flue-gas streams.

Figure 1. (a) Scheme for the preparation of polymer impregnated nMAG through sonication, (b) TEM micrograph of pristine nMAG, (c) XRD patterns of nMAG and PEI-nMAG, the blue vertical lines correspond to JCPDS card of Fe_3O_4 (JCPDS card # 19-0629), (d) The magnetization curves of nMAG and PEI-nMAG, and (e) photograph of PEI-nMAG response to a magnet.

345

346 **Figure 2.** FTIR spectra of the pristine and functionalized nMAG: (a) pristine nMAG, (b) PEI-

347 nMAG (branched, Mw 25,000), (c) PAA-nMAG, (d) PAH-nMAG, (e) PEG-nMAG, (f) PSS-

348 nMAG, and (g) PVP-nMAG. The right column of the figure shows the chemical structure of

349 each polymer used in this study.

350

351 **Figure 3.** TGA thermal stability curves of different nMAG (N₂ atmosphere, 10 °C /min heating
 352 rate): (a) the pristine nMAG and various PEI-nMAG, and (b) PAA-nMAG, PAH-nMAG, PEG-
 353 nMAG, PSS-nMAG, and PVP-nMAG.

354 **Table 1.** Specific surface area of the pristine and functionalized nMAG used in this study as
 355 measured by BET.

Sample	Surface area (m ² /g)	Sample	Surface area (m ² /g)
Pristine nMAG	39.6	PSS-nMAG	35.5
PEI-nMAG (branched, Mw 25,000, 6 %)	32.2	PAA-nMAG	19.4
PEI-nMAG (branched, Mw 25,000, 12 %)	25.9	PAH-nMAG	33.7
PEI-nMAG (branched, Mw 25,000, 16 %)	16.5	PVP-nMAG	19.2
PEI-nMAG (branched, Mw 25,000, 26 %)	3.6	PEG-nMAG	23.8
PEI-nMAG (branched, Mw 1,800, 16 %)	12.4		
PEI-nMAG (branched, Mw 10,000, 16 %)	13.1		
PEI-nMAG (linear, Mw 25,000, 16 %)	18.9		

356

Figure 4. Effect of PEI loading and type on CO₂ sorption. (a) CO₂ adsorption of PEI-nMAG sorbents with various PEI loading amount (branched, Mw 25,000, loading amount from 6 % to 26 %) at 25 °C, 1 atm CO₂, (b) CO₂ sorption onto different PEI-nMAG sorbents, and (c) CO₂ adsorption capacity of various PEI-nMAG sorbents with similar PEI loading (16 wt/wt %).

Figure 5. Adsorption of CO₂ at 25 °C for PEI-nMAG (branched, Mw 25,000, 16 %), PAA-nMAG, PAH-nMAG, PEG-nMAG, PSS-nMAG, and PVP-nMAG.

365
 366 **Figure 6.** Selective adsorption of CO₂ over N₂ and O₂ for PEI-nMAG (branched, Mw 25,000, 16
 367 %) at 25 °C.

368
369 **Figure 7.** CO₂ adsorption of PEI-nMAG (branched, Mw 25,000, 16 %) sorbent at 25, 40, 50, 60,
370 80, and 100 °C.

371
 372 **Figure 8.** CO₂ adsorption-desorption cycles of PEI-nMAG (branched, Mw 25,000, 16 %). For
 373 each cycle, nano-sorbents were flushed with CO₂ at 25 °C for 60 min and then flushed with N₂ at
 374 105 °C for 15 min. The gas flow rate was set at 25 mL/min and 1 atm CO₂ or N₂ was used under
 375 dry condition.

376 ASSOCIATED CONTENT

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