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Surface tunable magnetic nano-sorbents for carbon dioxide sorption and separation

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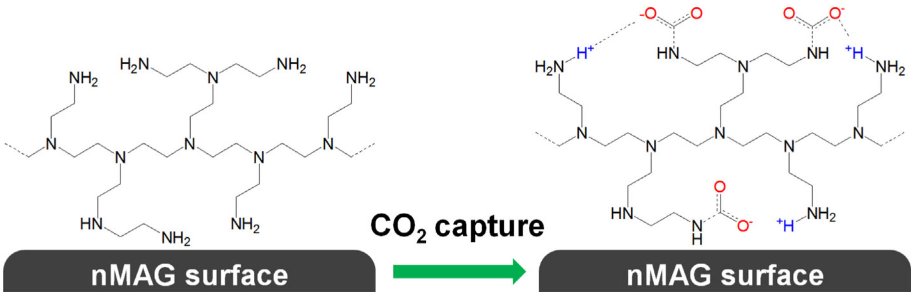
HIGHLIGHTS

- Magnetic, surface tunable nano-sorbents were prepared from commercially available materials.
- Polyethylenimine coated nano-sorbents exhibit both high CO_2 sorption capacity and selectivity.
- As prepared, nano-sorbents show excellent recyclability.

GRAPHICAL ABSTRACT



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ABSTRACT

The increasing level of carbon dioxide (CO_2) 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, CO_2 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 CO_2 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 CO_2 adsorption capacity and recyclability with TGA. Among the as-prepared materials, PEI-nMAG shows the highest CO_2 adsorption capacity with superior selectivity and recyclability.

1. Introduction

Carbon dioxide (CO_2) 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 CO_2 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

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CO_2 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 CO_2 capture and separation compared to the transport and storage of CO_2, extensive research has been focused on developing new approaches to reduce the cost for CO_2 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, CO_2 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 CO_2 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 CO_2 adsorption capacity [1]. For these, the higher sorption capacities are mainly due to the large surface area and specific interaction between CO_2 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 (Fe_3O_4) nanoparticle core and tunable surface functionalized organic coatings (shell) as a platform material for advanced CO_2 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 CO_2 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 CO_2 capture. For all, surface coating(s) thermodynamic stability, polymer loading percentage, specific surface area, and CO_2 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 CO_2 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 1800), 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.