Innovative nano-layered solid sorbents for CO_2 capture†

Bingyun Li,*[abcd] Bingbing Jiang,[c] Daniel J. Fauth,[b] McMahan L. Gray,[b] Henry W. Pennline[b] and George A. Richards*[a]

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Nano-layered sorbents for CO_2 capture, for the first time, were developed using layer-by-layer nanoassembly. A CO_2-adsorbing polymer and a strong polyelectrolyte were alternately immobilized within porous particles. The developed sorbents had fast CO_2 adsorption and desorption properties and their CO_2 capture capacity increased with increasing nano-layers of the CO_2-adsorbing polymer.

The emission of fossil fuel CO_2 to the atmosphere is implicated as the predominant cause of global climate change; therefore, advanced CO_2 capture technologies are of the utmost importance. Fossil fuels are the main energy supply in the world. The U.S. Department of Energy's Energy Information Agency projects that the more than 300 GW of coal-fired electricity generating capacity currently in operation in the U.S. will continue to increase and may reach 450 GW by 2030.[1] However, the emission of CO_2 from fossil fuel combustion has raised great concerns about the relation between anthropogenic CO_2 and global warming.

According to the Energy Information Agency, approximately 40% of the U.S. CO_2 emission is associated with electricity generation.[2] Consequently, the capture and sequestration of CO_2 from power-plant flue-gas streams is an essential scenario for carbon management. Current post-combustion CO_2 capture and sequestration technologies require three main steps: (i) capture CO_2 from the stack gas, (ii) compress the nearly pure CO_2 to about 2000 psi, and (iii) permanently "bury" or store the CO_2 in certain geological structures deep in the earth. These processes can require up to one-third of the produced power-plant energy, which would otherwise be used as electrical energy for customers. Most of the energy cost of the three steps lies with step (i), *i.e.* CO_2 capture.[3–5] Monoethanolamine (MEA), used as a major aqueous wet scrubbing solvent, has high operating costs due to their heat of sorption plus the sensible and latent heating of the solution. The latent and sensible heating accounts for approximately $\frac{1}{2}$ of the total regeneration energy for conventional liquid solvent systems.[5] The presence of H_2O, ~70 wt% in the MEA-based solvent, is a major cause of energy usage above that required for simple desorption of CO_2. The energy penalty associated with solvent regeneration can be reduced by concentrating the amine solution, thereby reducing the sensible and latent energy needs connected with the water. However, highly concentrated MEA may lead to equipment-corrosion problems and unwanted foaming. Facing these facts and challenges researchers have recently proposed the concept of solid sorbents for CO_2 capture.[3,4,6–10] Compared to liquid amines dissolved in water, the solid sorbents may avoid much of the latent heat duty connected with aqueous solvent regeneration. Studies have indicated that solid sorbents may have the potential to require substantially less energy (*e.g.* a reduction of 30–50%) for regeneration than the current MEA-based CO_2 scrubbing processes.[11]

While solid sorbents may reduce regeneration energy, it is advantageous that the sorbent structure be tailored to minimize diffusion resistance, during both the CO_2 capture and subsequent regeneration. Minimal diffusion resistance will insure that the highest CO_2 capacity is achieved in the shortest time—reducing the needed size of reactors and materials handling. Thus, it would be desirable to develop a technique where adsorbent chemistry could be deposited on high surface area supports, while creating uniform layers of desired thickness.

Here, we conducted a proof-of-concept study showing that advanced solid sorbents can be fabricated using a recently evolved nanotechnology, *i.e.* electrostatic layer-by-layer (LBL) nanoassembly. The LBL technique in principle could be scaled to very large quantities.[12] In this work, a CO_2-adsorbing amine compound, polyethylenimine or PEI, was successfully nano-layered into a porous supporting substrate, and the developed solid sorbents showed advanced CO_2 capture properties. Results show that layers of desired thickness can be deposited such that equilibrium adsorption capacity is proportional to the number of layers, demonstrating excellent control of the deposition process. Sorbents produced in this manner should allow careful evaluation of diffusion resistance limits in experimental development of new sorbents, as well as provide a potential method for larger scale production of highly-efficient sorbents.

First, nano-layered solid sorbents were formed using LBL nanoassembly. PEI, a common CO_2-adsorbing polymer, was adsorbed into porous supporting substrates, *i.e.* polymethylmethacrylate (PMMA) particles, using LBL nanoassembly technology. Upon each bilayer deposition of a CO_2-adsorbing polymer (*i.e.* PEI) and an oppositely-charged polyelectrolyte (*i.e.* polystyrene sulfonate or PSS), the nitrogen/carbon (N/C) ratio (Fig. 1a) and the fluorescent intensity of Rhodamine B labeled PEI (RhoB-PEI) (Fig. 1b) increased approximately linearly with increasing number of PEI/PSS bilayers. Also, thickness of the polymer nano-layers increased with increasing

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[a] *National Energy Technology Laboratory, U.S. Department of Energy, Morgantown, WV 26505, USA*
[b] *National Energy Technology Laboratory, U.S. Department of Energy, Pittsburgh, PA 15236, USA. E-mail: bli@hsc.wvu.edu, george.richards@netl.doe.gov; Fax: +1 304-293-7070; Tel: +1 304-293-1075*
[c] *School of Medicine, West Virginia University, Morgantown, WV 26506, USA*
[d] *WVNano Initiative, Morgantown, WV 26506, USA*

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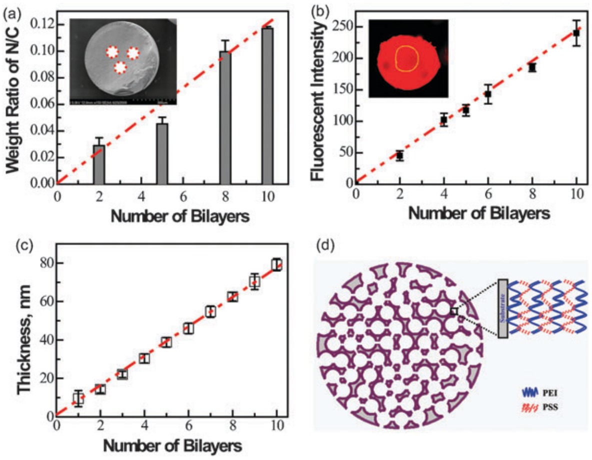

Fig. 1 (a) N/C ratio *vs*. number of PEI/PSS bilayers inside PMMA sorbents. The inset is an SEM image and the N/C ratio data were obtained from the circled areas. (b) Fluorescence intensity of RhoB-PEI *vs*. number of PEI/PSS bilayers inside PMMA sorbents. The inset shows the circled area that was used for fluorescence measurements. (c) Thickness *vs*. number of PEI/PSS bilayers on planar substrates. (d) The schematic diagram of nano-layered PEI/PSS solid sorbents.

number of PEI/PSS bilayers (Fig. 1c); each bilayer was found to be approximately 8 nm thick.

LBL nanoassembly has been widely studied to prepare multiple nano-layers on planar or spherical surfaces, and the formation of multiple layers is mainly due to the reversal of surface charge after each polyelectrolyte deposition.[13–27] The formation of multiple nano-layers has been determined using a variety of techniques including ellipsometry, UV-vis spectrometry, circular dichroism spectrometry, zeta potential analyzer, *etc*.[20,26,28–31] In this study, formation of the nano-layered solid sorbents (Fig. 1d) was confirmed using energy dispersive X-ray analysis (Fig. 1a), confocal laser scanning microscopy (Fig. 1b), and ellipsometry (Fig. 1c), where an increase in PEI deposition was found with increasing PEI/PSS bilayer formation. The applied LBL nanoassembly procedure involves repetitive sequential penetration of oppositely charged polyelectrolyte solutions (*i.e.* PEI and PSS) in porous PMMA particles. Electrostatic attraction is believed to be the main driving force of the multiple nano-layer formation, although other forces, *e.g.* hydrophobic, van der Waals, and acid–base type, may also play a role in the multiple nano-layer formation.

The developed nano-layered solid sorbents could be used for CO_2 removal, and the CO_2 adsorption capacity was found to increase with increasing number of PEI/PSS bilayers (Fig. 2a). The 5- and 10-bilayered PEI/PSS sorbents had a capacity of 0.8 and 1.7 mol CO_2/(kg sorbents), respectively. Replacing the strong polyelectrolyte, PSS, using a weak polyelectrolyte such as poly(acrylic acid) or PAA, however, led to low CO_2 adsorption capacity. The capacity of 10-bilayered PEI/PAA sorbents was 0.1 mol CO_2/(kg sorbents).

Importantly, the developed solid sorbents had fast kinetics; the CO_2 adsorption occurred within seconds and desorption of 90% of adsorbed CO_2 within 30 min (Fig. 2b). Note that this desorption time was observed when regeneration was conducted by simply exchanging the gas atmosphere from CO_2 to nitrogen—*i.e.*, a "swing" in the partial pressure of CO_2. Practical regeneration systems will likely include thermal swing, providing heat to increase the regeneration temperature. Raising the temperature would provide additional driving potential for CO_2 release from the amine adsorbent and could provide accelerated regeneration. These issues will be reported in subsequent studies on the CO_2 capture performance of sorbents created with the LBL technique.

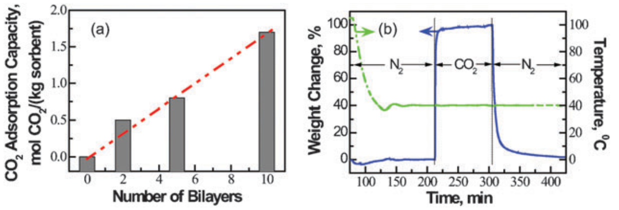

Fig. 2 (a) CO_2 adsorption capacity *vs*. number of PEI/PSS bilayers. (b) Typical CO_2 adsorption/desorption curves of PEI/PSS nano-layered solid sorbents. Weight change (solid blue line), temperature (dashed green line).

The mechanism of CO_2 capture in nano-layered solid sorbents is similar to those of amine solvents, where primary, secondary, and tertiary amines react with CO_2 molecules.[32] In the presence of water,[4] the amine groups react with gaseous CO_2 to form bicarbonate or carbamate. In the absence of water,[6] the main reaction believed to account for CO_2 removal is carbamate formation, where $\frac{1}{2}$ mole of CO_2 is removed for every one mole of amine:

$$CO_2 + 2R_2NH = R_2NH_2^+ + R_2NCOO^-$$

The CO_2 capture capacity increased with increasing PEI/PSS bilayers (Fig. 2a) and a capacity of 1.7 mol CO_2/(kg sorbents) was obtained in the 10-bilayer sorbents; a CO_2 adsorption capacity of >1 mol CO_2/(kg sorbents) was indicated to potentially reduce the cost of CO_2 sequestration.[33] Similarly, newly developed sorbents like silica-supported tetraethylenepentamine (TEPA/SiO_2), polyethylene-glycol-modified TEPA/SiO_2, and tertiary amidine supported on activated carbon had capacities of 2.1, 1.1, and 0.8 mol CO_2/(kg sorbents), respectively.[34,35]

As noted earlier, one important aspect related to CO_2 capture technologies (*e.g.* solvents, sorbents, and membranes) is CO_2 transport kinetics. To be energy-efficient, the adsorption and desorption of CO_2 must be fast; current aqueous amine technologies have low adsorption/desorption rates.[36] In general, solid sorbents have high adsorption/desorption rates due to high gas/sorbent interface area, but it could take hours to adsorb/desorb CO_2 where diffusion resistance is high.[6] In this study, the alternate layering of PSS, a strong polyelectrolyte, may have facilitated the transport of CO_2 within the porous particles leading to fast CO_2 adsorption and desorption (Fig. 2b).

In summary, LBL nanoassembly was used, for the first time, to build nano-layers of CO_2-adsorbing polymers (*e.g.* PEI) within porous particles serving as sorbents for CO_2 removal. The alternate nano-layers of a strong polyelectrolyte (*e.g.* PSS) may have facilitated CO_2 transport within the developed solid sorbents. The formation of nano-layers of PEI and PSS was determined. We found that the N/C ratio and the fluorescent intensity of RhoB-PEI within porous PMMA particles increased almost linearly with increasing deposition of PEI/PSS bilayers. Also, the thickness of PEI/PSS bilayers and the CO_2 capture capacity increased with more bilayers of PEI/PSS. In addition, the nano-layered solid sorbents demonstrated the potential for rapid CO_2 transport kinetics. The developed solid sorbents will potentially reduce corrosion and require substantially less energy (thereby leading to cost reductions) for regeneration than current CO_2 scrubbing. In future studies, the effects of flue-gas contaminants and multiple cycling on CO_2 capture capacity and kinetics will be investigated, and the optimal conditions will be defined to achieve both high CO_2 capture capacity and fast kinetics.

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