

Innovative nano-layered solid sorbents for CO₂ capture

Materials and Methods

Materials

The chemical structures of PEI, polystyrene sulfonate (PSS), and polymethylmethacrylate (PMMA) are shown in **Fig. S1**. PEI ($M_n=10,000$) and PSS ($M_n=70,000$) were purchased from Sigma Aldrich Co. (St. Louis, MO) and individually dissolved in deionized water at a concentration of 10 mg/ml. Porous support, PMMA particles (HP-2MG), was obtained from Sigma Aldrich Co. with the following manufacturer specifications: effective particle size - 0.5 mm, pore volume - 1.2 ml/g, specific surface area - 470 m²/g, and density - 0.29 g/ml. N₂ and CO₂ of high purity (>99%) were used. The PMMA sheet was purchased from United States Plastic Corp. (Lima, OH). Rhodamine B labeled PEI (RhoB-PEI) was synthesized by mixing the solutions in 50 mM phosphate buffer solution at a molar ratio of 1:100 of PEI to rhodamine B, stirring for 2 h at room temperature, and dialyzing in deionized water using a cellulose dialysis sack with a cutoff of 10 kDa for 2 days.

Preparation of PEI/PSS nano-layered solid sorbents

To facilitate the deposition of PEI/PSS multilayers within porous particles, a setup (**Fig. S2**) was built where a vacuum pump was used to remove air and permit driving the deposition solutions into the porous evacuated particles. The deposition process included repeated penetration of PEI, water, PSS, and water solutions under vacuum (380 torr). In brief, vacuum was applied to PMMA particles for 30 min. The PEI solution was run through the particles for 15 min followed by vacuum and water washing twice for 15 min each time. After vacuum, the PSS solution was then passed through the particles for 15 min and rinsed with water twice. This process led to the deposition of PEI and PSS, which was designated as one bilayer of PEI/PSS. Repeating this process resulted in the deposition of desirable numbers of PEI/PSS bilayers in the PMMA particles. Finally, sorbents were dried under vacuum at 80°C overnight and stored until further use. RhoB-PEI, instead of PEI, and PSS were also deposited in PMMA particles for fluorescent examination.

Characterization of PEI/PSS nano-layered solid sorbents

The morphology and nitrogen/carbon (N/C) ratio of the inner surfaces of PMMA particles were examined using scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analysis. PMMA particles were cut into half using a thin, sharp blade under optical microscopy. Samples were mounted on stainless steel supports and sputtered with gold, and the sample cross-sections were examined. A Hitachi S-4700 field emission scanning electron microscope was operated at 5.0 keV. Samples with different bilayers of PEI/PSS were studied and their N/C ratio vs. PEI/PSS bilayers was obtained. The data of five randomly selected particles were averaged. The cross-sections of PMMA particles, deposited with RhoB-PEI and PSS, were also examined under confocal laser scanning microscopy (CLSM). In addition, PEI/PSS bilayers were also deposited on a planar PMMA sheet substrate under similar deposition conditions and the thickness was determined using ellipsometry (M-2000, J.A. Woollam., Lincoln, NE).

CO₂ capture properties of PEI/PSS nano-layered solid sorbents

The adsorption and desorption performance of nano-layered solid sorbents was determined using thermogravimetric analysis (TGA).¹ The weight gain and loss from the sorbent particles were recorded, and the weight change in percentage was defined as the ratio of the amount of the gas adsorbed or desorbed over the total amount of gas adsorbed. In a typical adsorption/desorption process, 50 mg of the nano-layered PMMA particles was placed in the microbalance quartz sample cell, heated to 105°C in N₂ atmosphere at a flow of 200 ml/min, and kept at that temperature for about 60 min until no weight loss was observed. The temperature was then adjusted to 40°C and 100% dry CO₂ was introduced at a flow rate of 200 ml/min. After adsorption, the gas was switched to pure N₂ at a flow rate of 200 ml/min to perform CO₂ desorption. Adsorption capacity in mol·CO₂/(kg sorbent) was calculated from the weight change of the samples during the adsorption/desorption process.

Effect of water on the stability of PEI/PSS nano-layered sorbents

Rhodamine B-labeled PEI was used to monitor the weight loss of nano-layers from 10-bilayered PEI/PSS sorbents. A standard curve was obtained by recording the peak absorbance at 552 nm of labeled PEI solutions of known concentrations. 100 mg of the sorbents was suspended in 2 ml deionized water and then incubated in a water bath (40°C). At predetermined time periods, 0.4 ml of the supernatant was taken for UV-vis measurements to quantify possible disassembly or destruction of PEI from the sorbents. An equal volume of fresh deionized water was added to keep a constant volume of the medium. All measurements were conducted in duplicates. Sorbent stability in water was calculated from the following equation:

$$\text{Sorbent stability (\%)} = [(\text{Loaded PEI in sorbents} - \text{Disassembled PEI from sorbents}) / \text{Loaded PEI in sorbents}] \times 100\%$$

PEI/PSS sorbents were found to be stable in water and, within 14 days, approximately 1% of PEI was diffused out of the sorbents in water (**Fig. S3**).

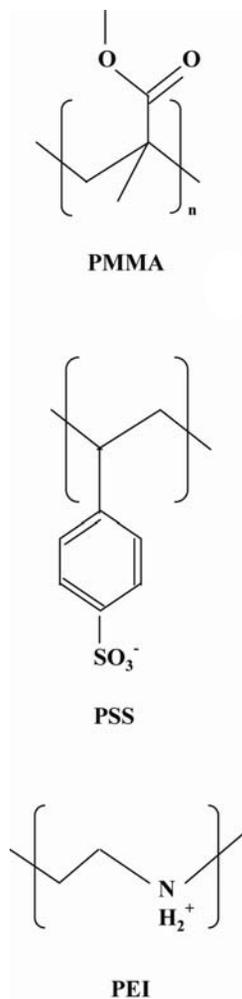


Fig. S1 Structures of polymers studied.

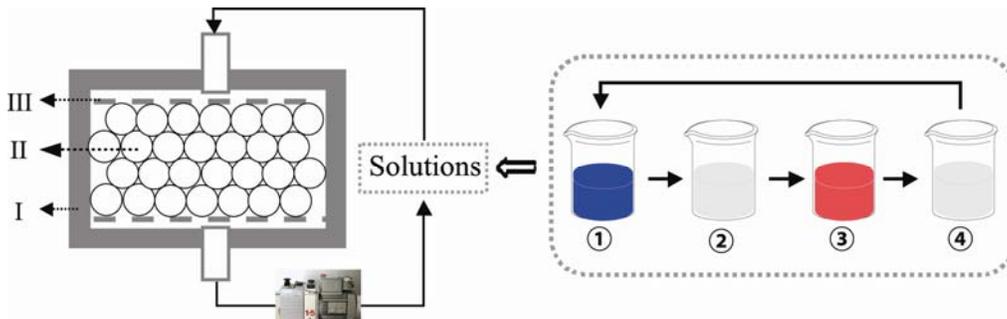


Fig. S2 Formation of nano-layered solid sorbents. I). LBL nanoassembly chamber; II). Porous sorbent substrate; III). Filter support. Solutions of 1, 2, 3, and 4 (representing PEI, water, PSS, and water solutions, respectively) penetrated through the sorbent substrates alternately. A vacuum pump was used to facilitate the running of solutions.

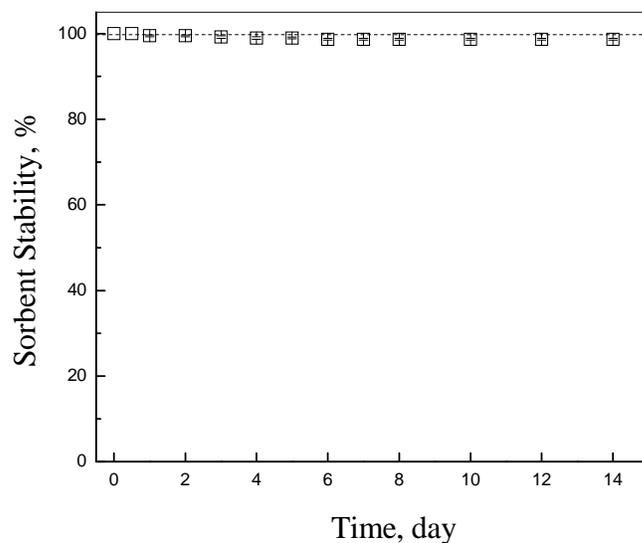


Fig. S3 Stability of PEI/PSS sorbents in water.

Reference

1. Gray, M.L., Hoffman, J.S., Hreha, D.C., Fauth, D.J., Hedges, S.W., Champagne, K.J., Pennline, H.W., 2009. Parametric study of solid amine sorbents for the capture of carbon dioxide. *Energy & Fuels* 23, 4840-4844.