

Electronic Supplementary Information (ESI)

Immobilize amino acid ionic liquid into nanoporous microspheres as robust sorbents for CO₂ capture

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Experimental details

Materials

1-ethyl-3-methylimidazolium bromide ([EMIM][Br], ≥97.0%), glycine (Gly), alanine (Ala), arginine (Arg), anion exchange resin (Amberlite® IRA400 hydroxide), and ethanol were purchased from Sigma Aldrich Co. (St. Louis, MO) Polymethylmethacrylate (PMMA) microparticles were purchased from Supelco Co. (Bellefonte, PA) 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 were used for thermogravimetric analysis (TGA).

Synthesis of [EMIM][AA]

The [EMIM][AA] was prepared using a neutralization method reported previously.¹ Briefly, [EMIM][Br] was dissolved in deionized water to prepare an aqueous solution and passed through the anion exchange resin-Amberlite® IRA400 (OH-type) to prepare the [EMIM][OH] solution. Then, the [EMIM][OH] solution was added in slight excess of an equimolar amino acid solution while stirring at room temperature for 24 h. After evaporation of water and then drying at 50°C in vacuum for 12 h, a crude product containing the desired IL and unreacted amino acid was obtained. Ethanol was then added to recrystallize and remove solvents. The mixture was centrifuged at 3750 rpm for 15 min to remove the insoluble AAs. The ethanol in the resultant solution was removed by rotating evaporation. After drying at 80°C under vacuum for 12 h, [EMIM][AA] was obtained at an overall yield of ~75%.

Preparation of [EMIM][AA]-impregnated PMMA sorbents

Immobilization of [EMIM][AA] into porous PMMA support was carried out with the aid of ethanol solvent according to a well-studied wet impregnation-vaporization method.²⁻⁵ In brief, [EMIM][AA] was dissolved in ethanol at a concentration of 50 mg/mL under a rotary evaporator (RV 10 basic plus D, Wilmington, NC) using a stirring rate of 100 rpm. After 30 min, PMMA microparticles were added. The suspension was continuously stirred for about 30 min under vacuum and subsequently dried at 50°C for 6 h. [EMIM][AA]-PMMA sorbents with various

loadings (i.e. 0, 20, 40, 50, 60, 80, 100 wt.%) of immobilized [EMIM][AA] to the PMMA support were prepared.

Characterization

The thermal stability of [EMIM][AA] was performed on an SDT Q600 (V20.9 Build 20) instrument (Artisan Technology Group, Champaign, IL) under N₂ atmosphere with a heating rate of 10 °C/min. The chemical structures of [EMIM][AA]-impregnated PMMA sorbents before adsorption and after five adsorption/desorption tests were characterized using FTIR (FTS 7000 with UMA 600 microscope). The morphology of PMMA microparticles was observed using scanning electron microscopy (SEM) (Hitachi S-4700, Tokyo, Japan). PMMA microparticles were cut into half using a thin, sharp blade under an optical microscope. Samples were glued onto stainless steel supports sputtered with gold, and examined with SEM.

CO₂ sorption and desorption

The CO₂ capture performance of [EMIM][AA]-impregnated PMMA sorbents was determined using TGA. Approximately 30 mg of PMMA based sorbent was placed in the TGA microbalance quartz sample cell and heated to 105°C in N₂ atmosphere at a flow of 200 ml/min for about 60 min. The temperature was then adjusted to 40°C (or 25, 60, 80°C, for determining the effect of temperature on CO₂ capture performance) and pure dry CO₂ was introduced at a flow of 200 ml/min until no obvious weight gain was observed. The desorption progress was conducted by introducing pure N₂ into the sample cell at 105°C for 60 min. The weight change in mg of the PMMA sorbents was 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 CO₂ adsorbed.

Adsorption capacity in mmol CO₂/(g sorbent) was calculated from the weight change of the samples during the adsorption/desorption cycles.

The activation energy (E_a) of CO₂ adsorption was calculated from Fig. 4 based on the Arrhenius law. The following equation was used:

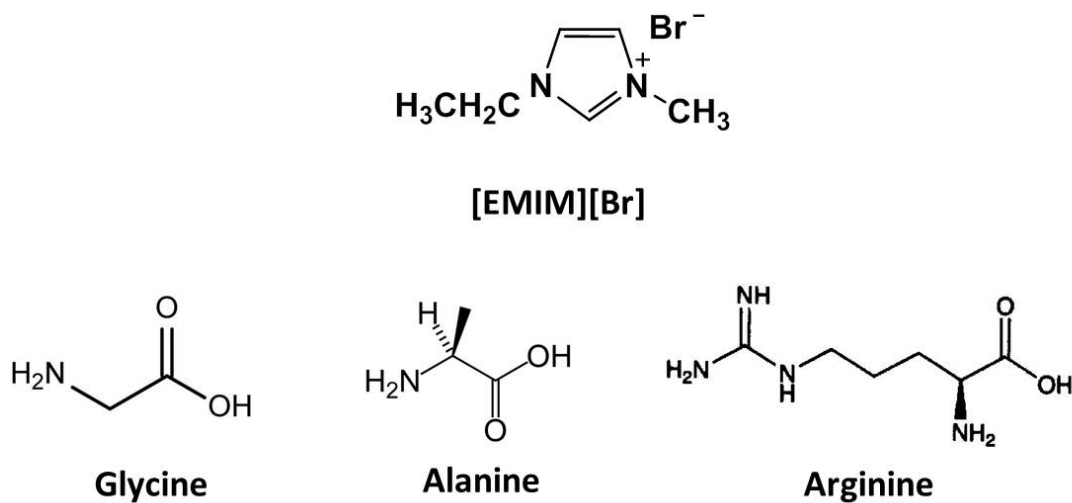
$$\ln(C_1/C_2) = \ln(k_1/k_2) = E_a/R(1/T_1 - 1/T_2)$$

Where C_1 and C_2 were the capacity at two different temperatures (T_1 and T_2) and $R=8.314$ J/mol·K. The calculated E_a was 6.8 kJ/mol.

Table S1. CO₂ sorption capacity (C) of the three sorbents with [EMIM][AA] loading of 50 wt.%.

Sample	C_{theo} (mol/mol)	C_{exp} (mol/mol)	C_{exp} (mmol/g IL)	C_{exp} (mmol/g sorbents)
[EMIM][Gly]-PMMA	0.5	0.49	3.06	1.53
[EMIM][Ala]-PMMA	0.5	0.45	2.76	1.38
[EMIM][Arg]-PMMA	1.5	0.52	2.02	1.01

C_{theo} : Theoretical CO₂ sorption capacity; C_{exp} : Experimental CO₂ sorption capacity



Scheme S1. Structure of [EMIM][Br], glycine, alanine, and arginine.

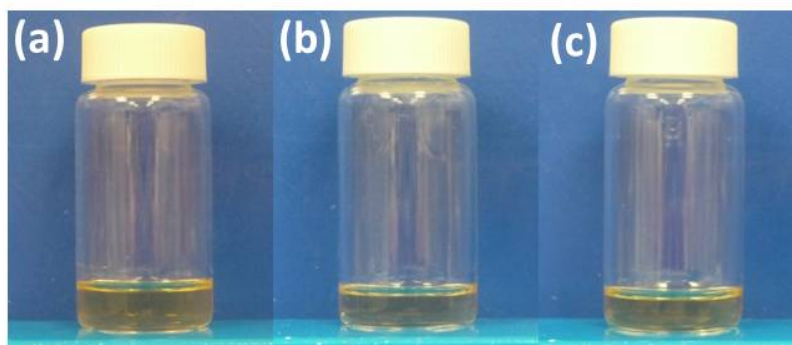


Fig. S1. Prepared amino acid ionic liquids: (a) [EMIM][Gly], (b) [EMIM][Ala], and (c) [EMIM][Arg].

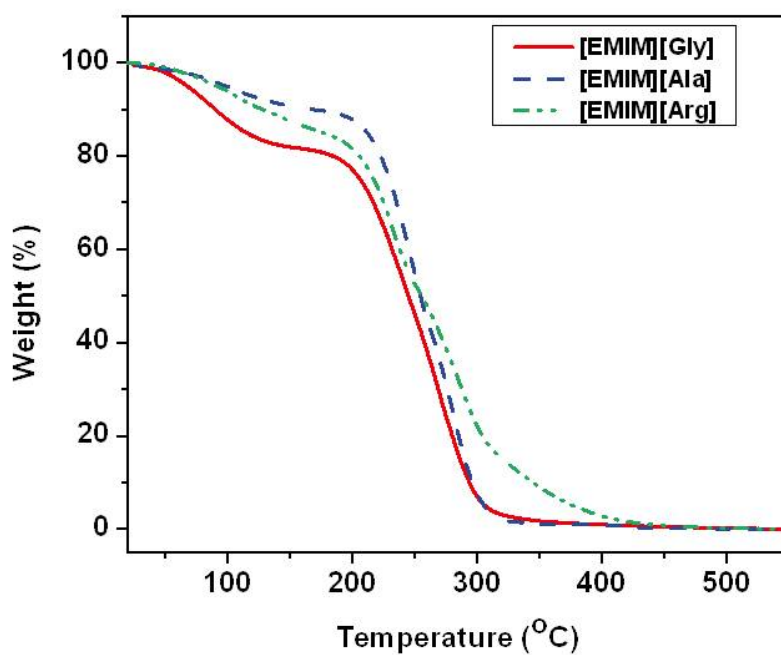


Fig. S2. Thermogravimetric analysis traces of as-prepared [EMIM][AA] (N_2 atmosphere, heating rate of $20^\circ C/min$).

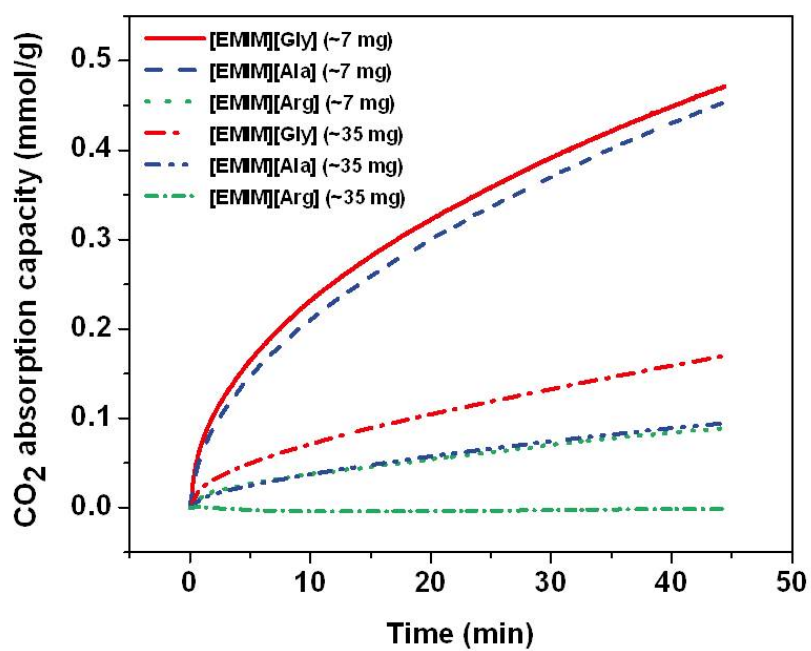


Fig. S3. CO₂ absorption of [EMIM][AA] (i.e. [EMIM][Gly], [EMIM][Ala] and [EMIM][Arg]) solvents at 40°C.

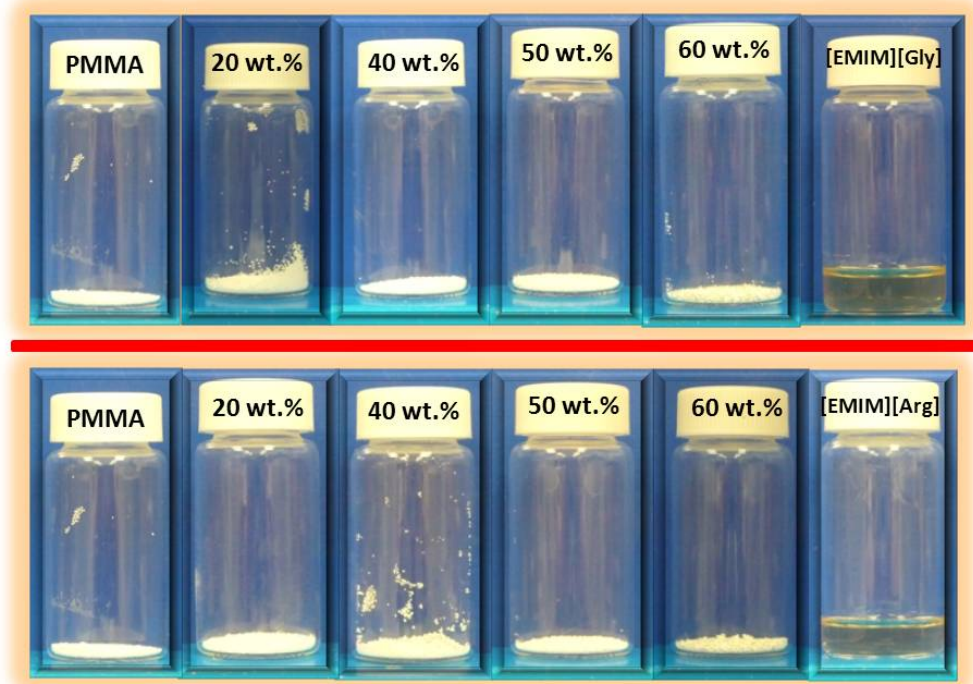


Fig. S4. Photograph images of [EMIM][AA] sorbents with various AAIL loadings. Top: [EMIM][Gly]; Bottom: [EMIM][Ala].

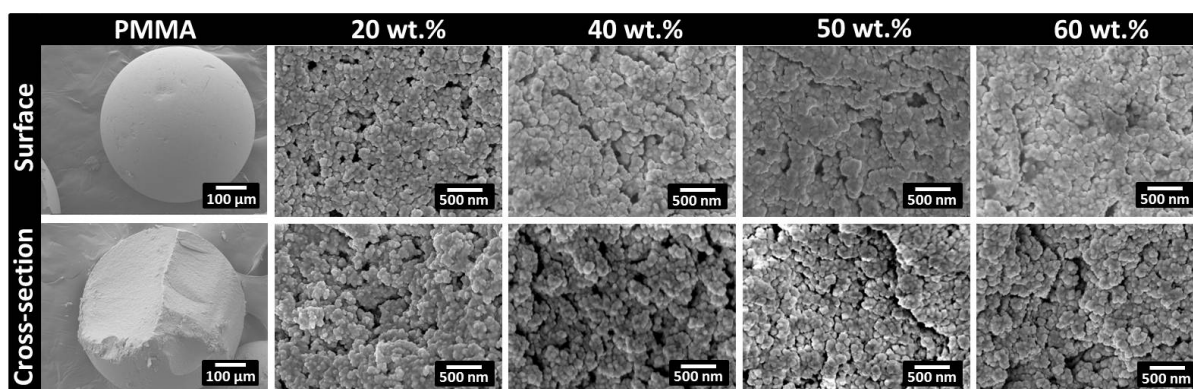


Fig. S5. SEM images of PMMA particles and as-prepared [EMIM][Gly]-PMMA sorbents with different [EMIM][Gly] loadings (20, 40, 50, and 60 wt.%). Top: Surface structures; Bottom: Cross-section structures.

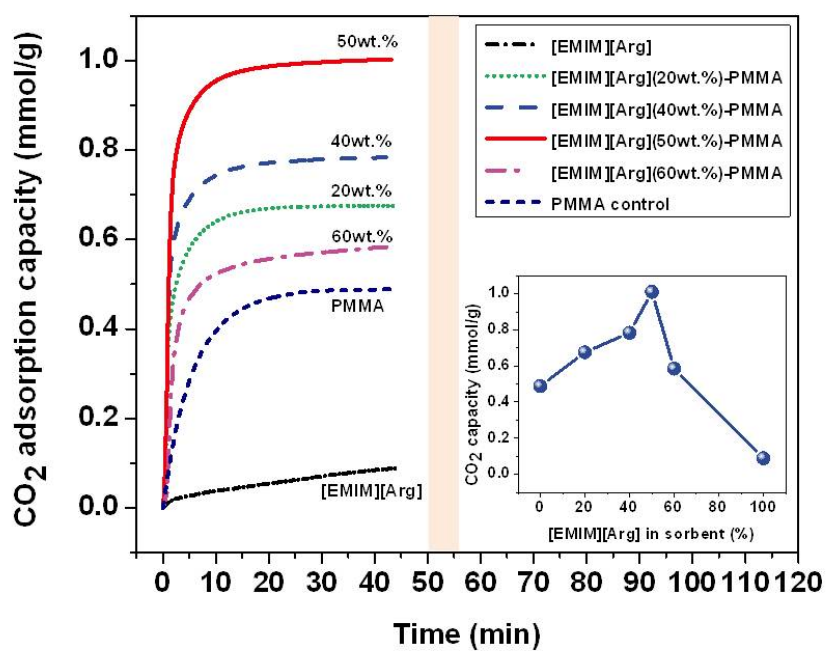


Fig. S6. CO₂ adsorption of [EMIM][Arg]-PMMA sorbent with various [EMIM][Arg] loadings (0 or PMMA, 20, 40, 60, and 100 wt.% or [EMIM][Arg]) at 40°C. Inset shows the CO₂ capacity vs. [EMIM][Arg] loading in sorbents.

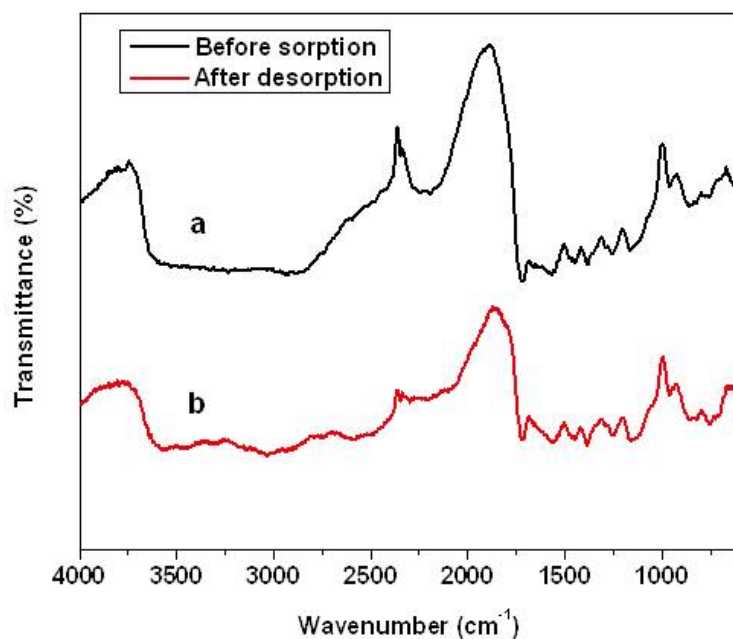


Fig. S7. FTIR spectrum of [EMIM][Gly]-PMMA sorbent (a) before CO₂ adsorption and (b) after CO₂ desorption.

References

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