Electronic Supplementary Information (ESI)

for

Amine-impregnated silica monolith with a hierarchical pore structure: enhancement of CO_2 capture capacity

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Synthesis of silica monolith. A silica monolith was prepared based upon the method of Smatt et al..[1] Tetraethoxysilane (TEOS, Aldrich) was added to a mixture of polyethylene glycol (PEG, Merck, 35000 g/mol) dissolved in an aqueous nitric acid solution. The sol was subsequently stirred at room temperature until a clear solution was obtained. After adding cetyltrimethylammonium bromide (CTAB) to the sol, stirring was continued until the surfactant was completely dissolved. The TEOS / HNO_3 / H_2O / PEG / CTAB molar ratio was 1.00: 0.25: 14.69: 0.54: 0.0899. The sols were left to gel at 40 ^oC and subsequently aged for at least 48 h at 40 ^oC. The monolith was then kept in a 1 M NH_4OH solution for 9 h at 90 ^oC. The monolith was subsequently acidified with a 0.1 M HNO_3 solution and washed with ethanol (25 wt%). The monolith was dried for 3 days at 60 ^oC in an open beaker and then calcined at 550 ^oC for 5 h under air. The heating rate was 1 ^oC/min.

PEI and TEPA impregnation. PEI was introduced into mesoporous silica support materials prepared by wet impregnation, as reported by Xu et al..[2] In a typical preparation, PEI (Aldrich, average molecular weight of 600 by GPC, linear type, b.p of 250 ^oC) was dissolved in methanol under stirring for about 15 min, after which pieces of monolith were added to the PEI/methanol solution in a glove box. Solvent was evaporated at 70 ^oC for 16 h under reduced pressure (700 mmHg).

TEPA was introduced as a CO_2 capturing agent to the silica monolith according to the procedure reported by Yue et al..[3] A given amount of TEPA was dissolved in 10 g of ethanol under stirring for 0.5 h, and a silica support was then added to the solution. After

stirring and refluxing for 2 h, the solvent was evaporated at 80 ^{o}C, followed by drying at 100 ^{o}C for 1 h.

Characterization Methods. The monolith samples prepared were characterized by N_2 adsorption/desorption and mercury porosimetry. The XRD patterns were obtained on a Rigaku diffractometor using CuKα(λ=1.54 Å) radiation. Nitrogen adsorption-desorption isotherms were obtained on a Micromeritics ASAP-2000 sorptometer at liquid nitrogen temperature. The specific surface areas of these samples were calculated by the BET method and the pore size distributions were obtained by the BJH method using desorption branches of the isotherms. Mercury porosimetry was carried out with an AutoPore IV 9500 V1.03 apparatus. The amount of PEI and TEPA introduced to the mesoporous silica samples was measured by a thermogravimetric analysis (TGA, SCINCO thermal gravimeter S-1000); PEI/monolith samples were heated at 5 ^{o}C /min to 600 ^{o}C under N_2 flow. High-resolution TEM images were obtained on a JEM-2100F model operated at 200 kV. SEM investigation of morphological features was carried out with a Hitachi S-4200 instrument.

CO_2 sorption/desorption study. The same TGA unit (SCINCO thermal gravimeter S-1000) connected to a flow panel was used for CO_2 sorption/desorption measurement. A sample weight of ca. 10 mg was loaded into an alumina sample pan and subjected to CO_2 sorption studies. N_2 (ultra high purity, U-Sung) was used as a purge gas in this study. The sorption run was carried out using high purity CO_2 (99.999%) and 5% CO_2 (N_2 as balance gas). A feed flow rate of 30 mL/min was controlled with a MFC to the sample chamber. Fig. S1 depicts the TGA experiment procedure. Initially, we pretreated the sample at 100 ^{o}C to remove moisture. N_2 was used as a purge gas. When there was no

weight loss, the temperature was decreased to the sorption temperature and CO_2 was flowed into the chamber. After the CO_2 sorption run, a desorption step was followed using N_2 as a purge gas. Finally, temperature was increased to 600 ^oC to decompose amines inside the monolith pores in order to measure the amount of PEI or TEPA introduced. In order to examine the moisture effect on the sorption capacity of CO_2, the following procedure was taken: (i) initial thermal regeneration under dry N_2 purge (100 ^oC, 60 min); (ii) decreasing the temperature to 75 ^oC under dry N_2 purge; (iii) conducting humid N_2 sorption to equilibrium (75 ^oC, H_2O/N_2 = 1/9); and finally (iv) humid CO_2 sorption to equilibrium (75 ^oC, H_2O/CO_2 = 1/9). Moisture (10 vol%) was introduced through a syringe pump. The corresponding CO_2 sorption performance of the 65PEI/monolith in the dry and moisture conditions was shown in Fig. S6. CO_2 sorption capacity was found to increase by ca. 24% after moisture was introduced compared with the dry case.

References

1. J. H. Smått, S. Schunk and M. Linden, *Chem. Mater.* 2003, **15**, 2354.

2. X. Xu, C. S. Song, J. M. Andresen, B. G. Miller and A. W. Scaroni, *Micropor. Mesopor. Mater.* 2003, **62**, 29.

3. M. B. Yue, Y. Chun, Y. Cao, X. Dong and J. H. Zhu, *Adv. Funct. Mater.* 2006, **16**, 1717.

Figures

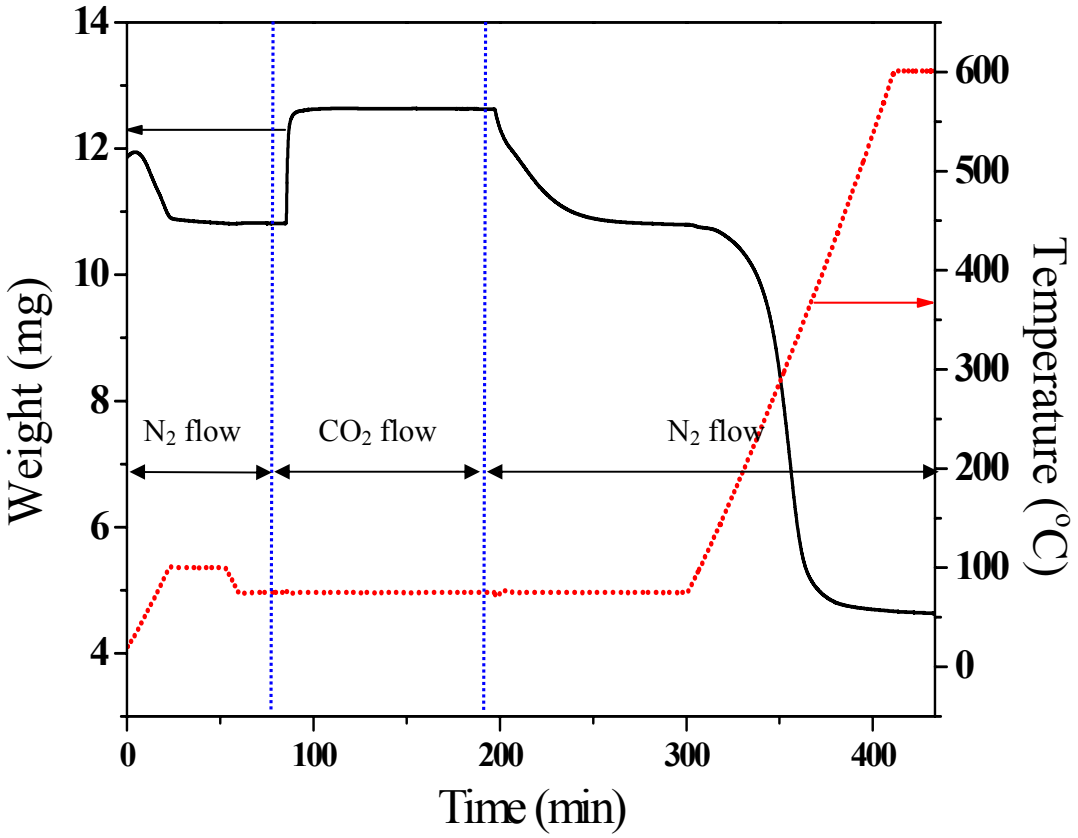

Fig. S1 Temperature steps programmed in TGA for CO_2 sorption/desorption runs.

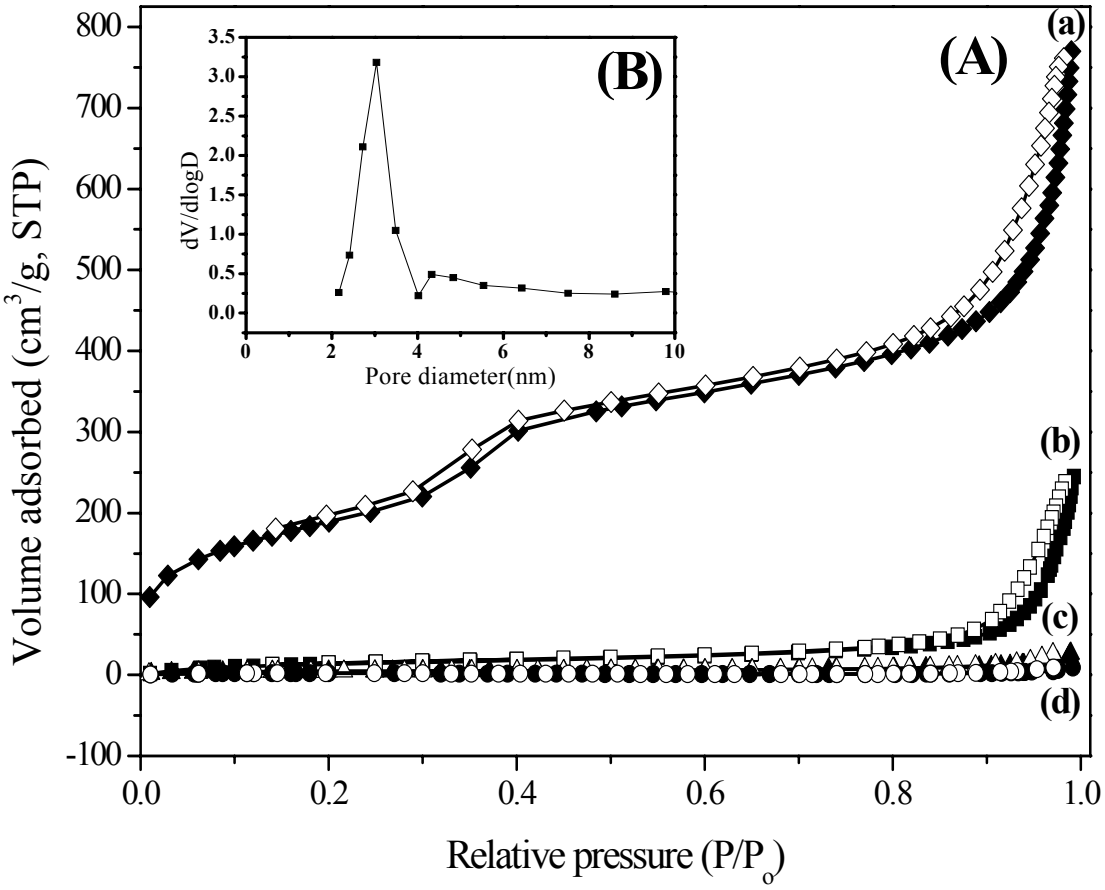

Fig. S2 (A) N_2 adsorption-desorption isotherms of: (a) monolith, (b) 45PEI/monolith, (c) 65PEI/monolith, (d) 70PEI/monolith and (B) pore size distribution curve of the monolith.

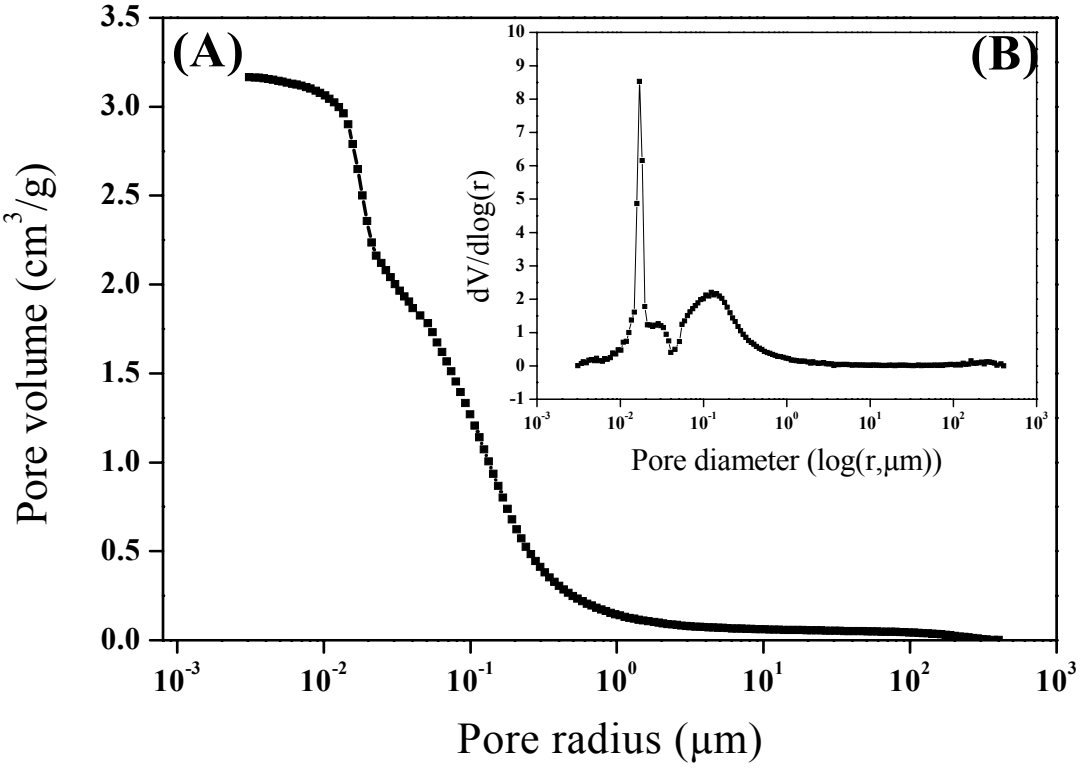

Fig. S3 (A) Cumulative pore volume and (B) pore size distribution for the silica monolith determined by Hg porosimetry.

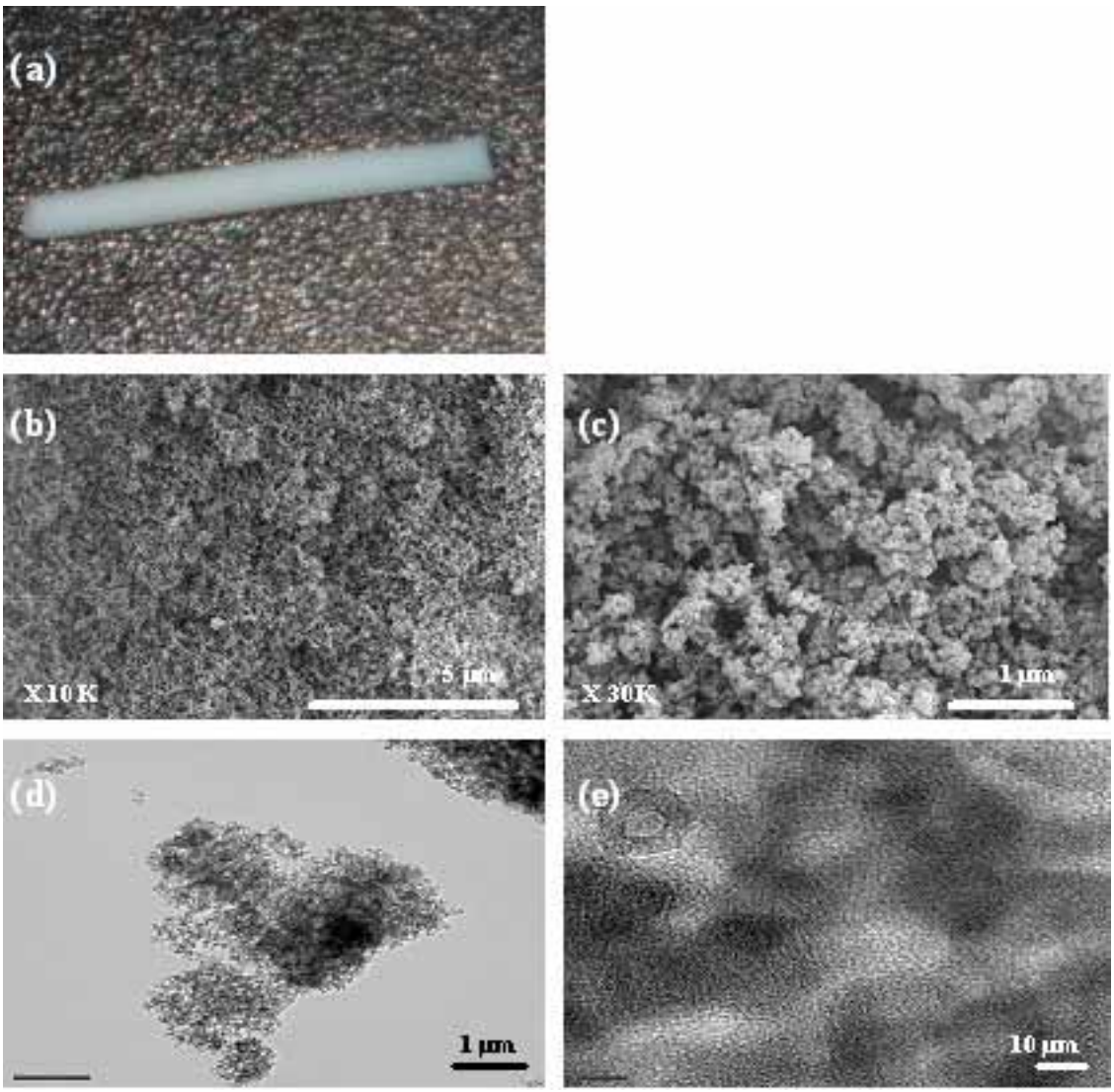

Fig. S4 (a) Photograph of silica monolith, dimension size: 34×4 mm i.d ; (b), (c) SEM images; and (d), (e) TEM images of the monolith.

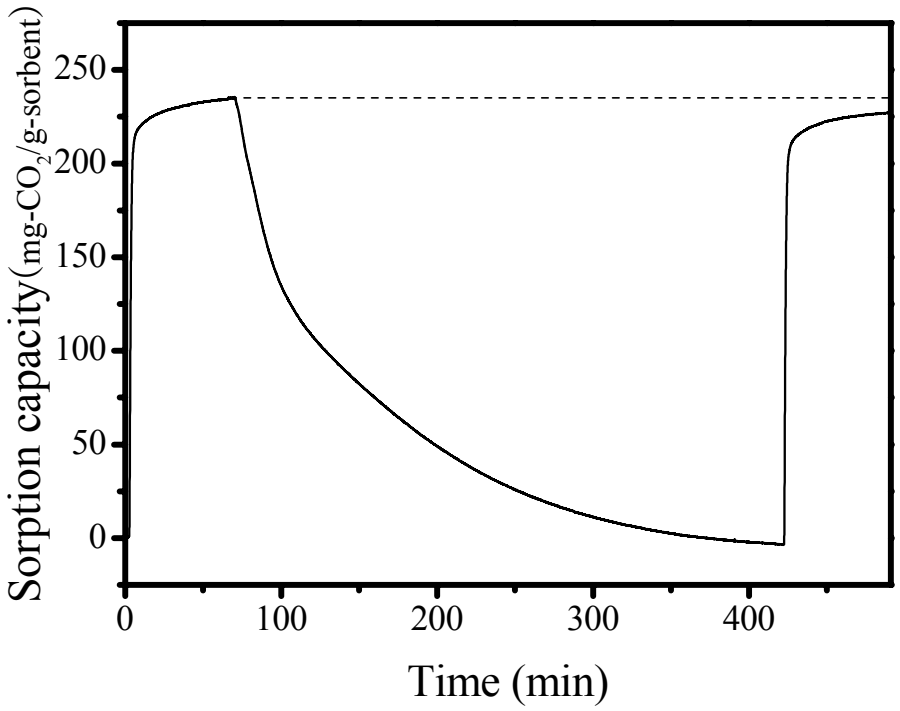

Fig. S5 CO_2 sorption-desorption cycle of 65TEPA/monolith at 65 ^{o}C.

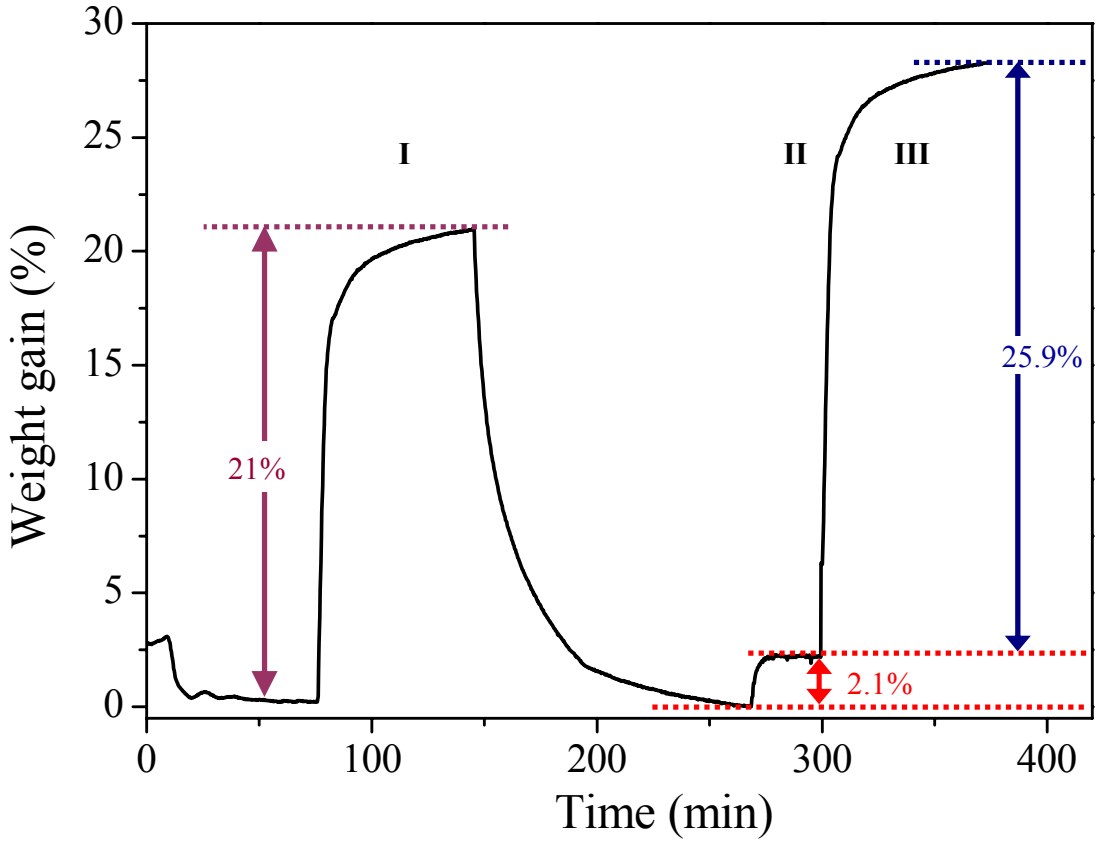

Fig. S6 CO_2 sorption performance of 65PEI/monolith in dry and moisture conditions: (I) dry condition, (II) water sorption only, and (III) moisture condition.

Table S1 Pore properties of monolith samples with different PEI loadings

Samples	BET surface area (m^2/g)	Pore volume* (cm^3/g)
monolith	950	1.17
45PEI/monolith	55	0.29
65PEI/monolith	16	0.04
70PEI/monolith	7	0.01

* BJH desorption