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3 **Electronic Supplementary Information:**

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5 **Crystallized glass tailored by controlled heat treatment for carbon dioxide capture under**
6 **mild conditions**

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24 **I. Materials and Methods**

25 Materials

26 The following chemicals were used as received without further purification. Strontium carbonate
27 (SrCO_3 , 98% Aldrich), silicon dioxide (SiO_2 , extra pure, Junsei), boron trioxide (B_2O_3 , Junsei),
28 and sodium carbonate anhydrous (Na_2CO_3 , extra pure, Samchun) were used for amorphous glass
29 fabrication. Carbon dioxide gas (CO_2 , 99.5% purity, Daesung Industrial Gases Co.) and nitrogen
30 gas (N_2 , 99.999% purity, Daesung Industrial Gases Co.) were used for CO_2 capture and N_2
31 physisorption, respectively. Inductively coupled plasma (ICP) multielement standard solution IV
32 (Merck Millipore) was used for concentration calibration. Deionized (DI) water (18.2 $\text{M}\Omega$ cm at
33 298 K) obtained from a Millipore Direct-Q[®] water purification system was used for CO_2 capture
34 media.

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36 Fabrication of amorphous alkaline earth oxide-containing glass adsorbent

37 Amorphous alkaline earth oxide-containing glass adsorbent was fabricated using the same
38 procedure as our previous work.^[1] A powder mixture with the specific molar composition of 35
39 $\text{SiO}_2:20 \text{ B}_2\text{O}_3:5 \text{ Na}_2\text{CO}_3:40 \text{ SrCO}_3$ was homogeneously mixed in a Nalgene[®] bottle with zirconia
40 balls for 30 min and then transferred to a platinum crucible. SrCO_3 and Na_2CO_3 were used as an
41 alkaline earth oxide and a network modifier, respectively, while SiO_2 and B_2O_3 were used as
42 network formers. Subsequently, the powder mixture was melted in an electric furnace at 1573 K
43 for 2 h. The molten glass was poured on a graphite plate and rapidly cooled to room temperature.
44 Broken glass pieces were collected and the prepared sample was denoted as Sr-glass- Na_2O .

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46 Crystallization of amorphous alkaline earth oxide-containing glass adsorbent

47 The crystallized glass was prepared by an additional heat treatment step using an electric furnace.
48 In order to convert the amorphous glass into a crystalline structure, the glass was slowly cooled
49 after the heat treatment above its crystallization temperature (T_c , Sr-glass- Na_2O = 1073 K), which
50 was confirmed by thermogravimetric analyzer & differential scanning calorimetry (TGA & DSC,
51 TA instrument SDT Q600). Sr-glass- Na_2O was heated from 298 K to 1173 K at a rate of 10 K
52 min^{-1} and allowed to stay at 1173 K for 1 h, followed by cooling at a rate of 15 K min^{-1} to 298 K.
53 After the controlled heat treatment, the formed glass was collected and pulverized utilizing a
54 planetary mill (SPEX SamplePrep 8000M). An automatic shaker with sieve attachments (Orto
55 Alresa OASS 203) was then used to separate glass powders sub-45 μm in size. The prepared
56 sample was denoted as crystallized-Sr-glass- Na_2O .

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58 Characterization

59 The X-ray diffraction (XRD) patterns of the adsorbents were obtained using a Bruker D2
60 PHASER. The XRD patterns were collected in the range of 2θ from 10 to 80° at a rate of 0.02° per
61 step with a counting time of 0.2 s per step using Cu-K-alpha source radiation. Fourier transform
62 infrared spectroscopy coupled with attenuated total reflection (FT-IR/ATR, Nicolet iS5 with iD5
63 ATR accessory, Thermo Scientific) and X-ray photoelectron spectroscopy (XPS, Nexsa, Thermo
64 Fisher Scientific) were used to analyze the chemical structures of the adsorbents. For the textural
65 properties, N_2 physisorption isotherms and Brunauer–Emmett–Teller (BET) surface areas were
66 determined at 77 K using an ASAP 2020 (Micromeritics). Before measurement, the solidifications
67 were degassed overnight at 423 K under vacuum to remove the physically adsorbed moisture. The
68 pore size distributions were calculated based on the N_2 physisorption isotherm by the Broekhoff-
69 deBoer–Frenkel-Halsey-Hill (BdB–FHH) method.^[2] An SDT Q600 thermogravimetric analyzer

70 (TGA, TA Instruments) was used to obtain the continuous on-line records of weight loss and
71 temperature. Prior to the TGA measurement, adsorbents were dried in a vacuum oven at 373 K for
72 12 h to remove physically adsorbed moisture. Each sample was heated from room temperature to
73 1473 K with a heating rate of 10 K min⁻¹ under N₂ gas. Supernatant solution samples obtained
74 during CO₂ capture tests were diluted and filtered using a Millex-GP Filter (0.22 μm pore size) to
75 characterize their compositions. Ion concentrations in the solution were measured using ICP-
76 optical emission spectroscopy (ICP-OES, PQ9000 Elite, Analytikjena), calibrated with standard
77 solutions with ion concentrations ranging from 0 to 3000 ppm.

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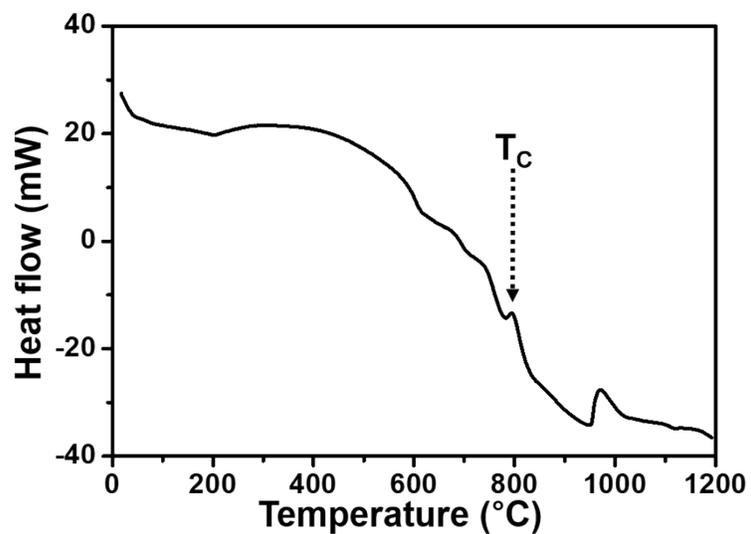
79 CO₂ capacity measurement

80 CO₂ capture using glass adsorbents was performed with the following experimental setup. First,
81 the collection vial (joint size: 24/29) was filled with 3 g of crystallized-Sr-glass-Na₂O and 75 mL
82 of DI water, and the solution was vigorously stirred to obtain a homogenous mixture. Pure CO₂
83 gas was then introduced to the collection vial with a flow rate of 75 mL min⁻¹ at room temperature
84 and allowed to be capture by the glass adsorbent. After a predetermined time, the glass adsorbent
85 was separated from the solution *via* centrifugation and collected by immediate drying at 333 K for
86 12 h. After another 12 h, TGA measurements were performed. The CO₂ capacity of the glass
87 adsorbent was determined as the amount of the CO₂ captured per unit mass of the glass used (*i.e.*,
88 mmol CO₂ per g glass) based on its TGA curve at each specific point of time. Simultaneously, the
89 supernatant solution was also collected to quantify the molar concentration of Sr²⁺ ion under the
90 conditions where CO₂ flows (CO₂ flowing condition) or not (CO₂ non-flowing condition) at same
91 specific point of time.

92 **II. Supporting Figures**

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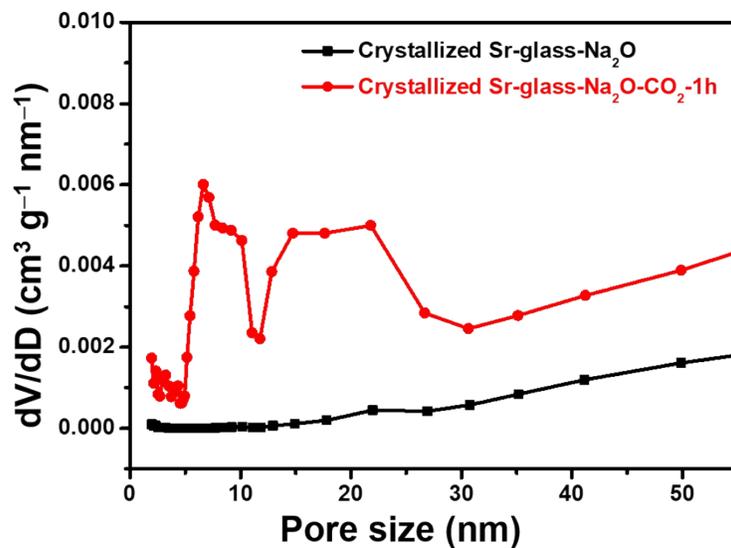
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96 **Fig. S1.** DSC curve for the amorphous Sr-glass-Na₂O (45 μm).

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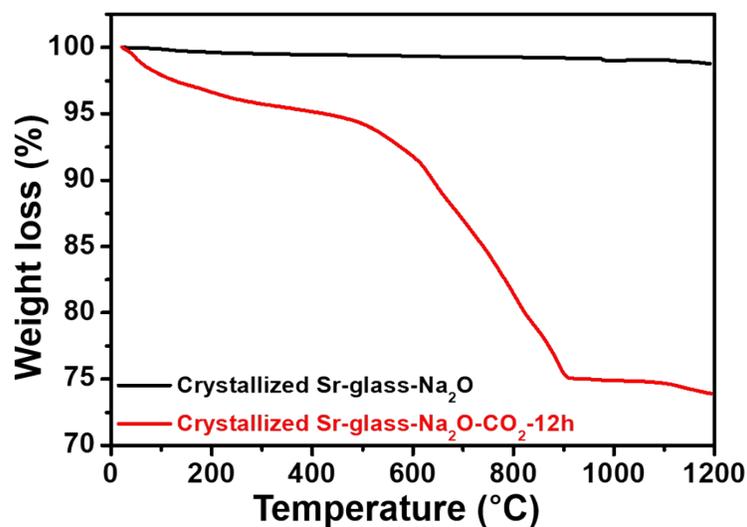
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101 **Fig. S2.** Pore size distributions of crystallized Sr-glass-Na₂O (45 μm) prior and subsequent to 1 h
102 of CO₂ capture at 298 K.

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 105 **Fig. S3.** TGA curves of crystallized Sr-glass-Na₂O (45 μm) prior and subsequent to 12 h of CO₂
 106 capture at 298 K.

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109 III. Supporting Table

110 **Table S1.** Textual properties of crystallized Sr-glass-Na₂O (45 μm) prior and subsequent to 1 h
 111 of CO₂ capture at 298 K.

Samples	BET surface area (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)
Crystallized Sr-glass-Na ₂ O	1.43	0.014
Crystallized Sr-glass-Na ₂ O-CO ₂	51.13	0.117

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114 IV. References

- 115 [1] H.-J. Kim, S.-J. Kim, H.-C. Yang, H.-C. Eun, K. Lee, J.-H. Lee, *J. CO₂ Util.* **2022**, *61*,
 116 102001.
 117 [2] Lukens Wayne W., P. Schmidt-Winkel, D. Zhao, J. Feng, G. D. Stucky, *Langmuir* **1999**,
 118 *15*, 5403.
 119