Supplementary information

Title: A green synthesis of PEI@nano-SiO_2 adsorbent from coal fly ash: Selective and efficient CO_2 adsorption from biogas

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This supporting information includes:

Figure S4. (a) N_2 adsorption/desorption isotherms and (b) pore size distributions of PEI@nano-SiO_2 adsorbents with different PEI loadings (supported by "SiO_2-6%").

Figure S5. (a) TG and (b) DTG curves of the synthetic PEI@nano-SiO_2 adsorbents with different PEI loadings (supported by "SiO_2-6%").

Figure S6. SEM images of the synthetic PEI@nano-SiO_2 adsorbents with different PEI loadings (supported by "SiO_2-6%").

Figure S7. (a) The thermal stability curves and (b) adsorption curves of the "40%-PEI@SiO_2-6%" adsorbent and the "40%-PEI@Commecial SiO_2"; (c) and (d) the breakthrough curves of CO_2/CH_4 adsorption using the "40%-PEI@SiO_2-6%" adsorbent and the "40%-PEI@Commecial SiO_2" (adsorption at 90 °C; total flow rate: 30 mL/min; inlet CO_2 concentration: 40 vol. %).

Figure S8. FT-IR spectra of fresh PEI@nano-SiO_2 adsorbents (a) with different nano-SiO_2 supports (40% PEI loading), and (b) with different PEI loadings (supported by "SiO_2-6%").

Figure S9. (a) FT-IR spectra of the regenerated "40%-PEI@SiO_2-6%" in pure CO_2 atmosphere at different temperature of 120−165 °C; (b) cyclic performance of "40%-PEI@SiO_2-6%" regenerated under pure CO_2 atmosphere for 15 min at different temperatures of 135−165 °C (adsorption at 90 °C for 30 min).

Figure S10. FT-IR spectra of the regenerated PEI@nano-SiO_2 adsorbents after 50 cycles (a) under pure Ar atmosphere at 120 °C for 15 min; (b) under pure CO_2 atmosphere at 150 °C for 15 min (adsorption at 90 °C for 30 min). (c) cyclic performance of "40%-PEI@SiO_2-6%" and "40%-PEI@Commercial SiO_2" regenerated under pure CO_2 atmosphere for 15 min at 150 °C (adsorption at 90 °C for 30 min).

1.1 Synthesis of nano-SiO_2 supports from coal fly ash

Preheated and sieved 10 g CFA and 5 g NaOH were mixed with 15 mL of ultrapure water in a 100mL sealed Teflon-lined reactor (BeiLun, China) and then the mixture reacted at 110 °C for 0.5 h with stirring (300 rpm). Immediately after the experiment, the reacted suspension was filtered several times with ultrapure water to obtain the leaching solution (Na_2SiO_3 solution). A certain quantity of leaching solution was placed in the Teflon-lined reactor, and the concentration of Na_2SiO_3 ($C_{Na2SiO3}$, $g \cdot L^{-1}$) in the mixture was diluted to 80, 70, 60, 50, 40, 30 and 20 $g \cdot L^{-1}$ by adding ultrapure water, respectively. A constant flow of 40 $mL \cdot min^{-1}$ (15 vol % CO_2 and 85 vol % N_2) was injected to purify the mixture and assist the silica precipitation. The purification process was conducted at 80 °C with

stirring (300 rpm) until the pH value decreased to 10.8-11.3 (~15 min); the purified mixture was then obtained through filtration. Subsequently, the precipitation process was conducted using the purified mixture under the same conditions for another 3-7 h. Finally, the precipitation was filtered, washed and dried at 105 °C for 12 h under vacuum (<1 mmHg) to obtain nano-SiO_2 supports.

1.2 Calculation of silanol content and -OH density

Figure S2(b) showed the thermogravimetric analysis of nano-SiO_2 in the range of 50−800 ℃. The weight loss of adsorbents could be divided into three stages: 50−200 ℃, 200−600 ℃ and 600−800 ℃, respectively [1], and the weight loss of each stage was shown in Table 2. Accordingly, the weight loss on the first stage (below 200 ℃) was caused by the release of physical and chemical adsorbed water on nano silica surface [2]. On the second stage (200−600 ℃), the weight loss was mainly attributed to dehydroxylation following the condensation of germinal silanol and vicinal silanol. And the weight loss in the last stage (above 600 ℃) was mainly due to the loss of isolated silanol [3]. Depending on the weight loss, the silanol content (N_{OH}) and the silanol density (C_{OH}) of different nano-SiO_2 supports can be confirmed with formulas (1) and (2), respectively [4].

$$N_{OH} = \frac{2\times(W_{200}-W_{800})}{M_{H_2O}}\times 1000 \quad (1)$$

$$C_{OH} = \frac{2\times(W_{200}-W_{800})}{M_{H_2O}}\times\frac{N_A}{S_{BET}\times 10^{18}} \quad (2)$$

Where W_{200} and W_{800} are the weight of nano-SiO_2 samples at the temperature of 200 and 800 °C, respectively; M_{H2O} is the molecular weight of water; N_A is the Avogadro constant; S_{BET} is the specific surface area of nano-SiO_2 samples.

Table S1 Chemical composition of coal fly ash.

Samples	SiO_2 (wt. %)	Al_2O_3 (wt. %)	Fe_2O_3 (wt. %)	Na_2O (wt. %)	CaO (wt. %)	TiO_2 (wt. %)	MgO (wt. %)	K_2O (wt. %)	Others (wt. %)
CFA	52.00	36.51	5.03	0.14	2.61	1.80	0.33	0.77	0.81

Table S2 Structural properties of the synthetic PEI@nano-SiO_2 adsorbents with different PEI loadings (supported by "SiO_2-6%").

Samples	S_{BET} [a] ($m^2 \cdot g^{-1}$)	V_{pore} [b] ($cm^3 \cdot g^{-1}$)	D_{BJH} [c] (nm)
10%-PEI@SiO_2-6%	47.0	0.47	36.74
20%-PEI@SiO_2-6%	30.6	0.39	47.50
30%-PEI@SiO_2-6%	17.2	0.16	34.00
35%-PEI@SiO_2-6%	8.99	0.062	25.74
40%-PEI@SiO_2-6%	7.7	0.034	16.46
45%-PEI@SiO_2-6%	3.35	0.018	20.08

[a] S_{BET}, specific surface area; [b] V_{pore}, total pore volume; [c] D_{BJH}, average pore size.

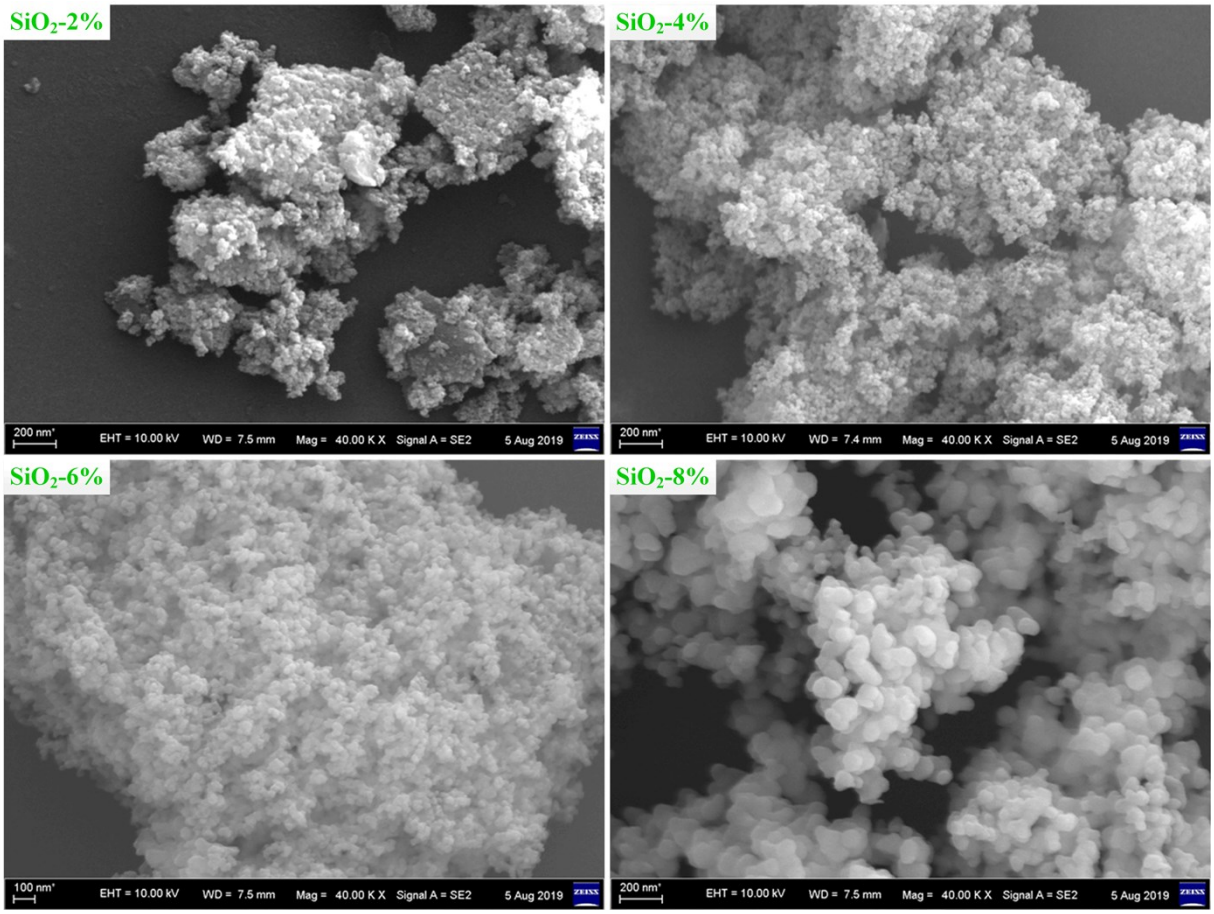
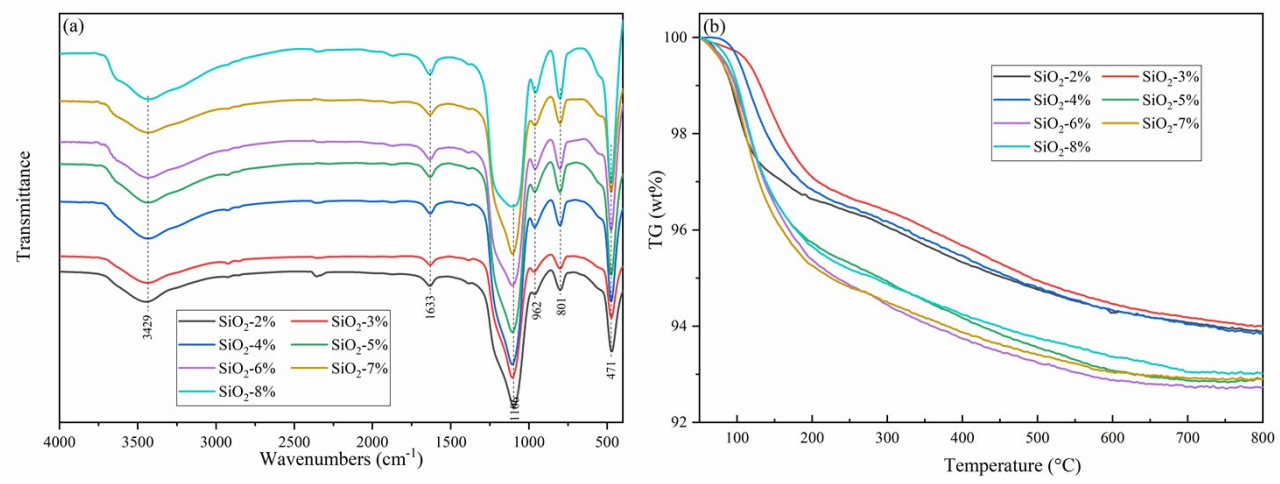


Figure S1. SEM images of the nano-SiO_2 supports synthesized from different Na_2SiO_3 concentrations of 20−80 $g \cdot L^{-1}$.



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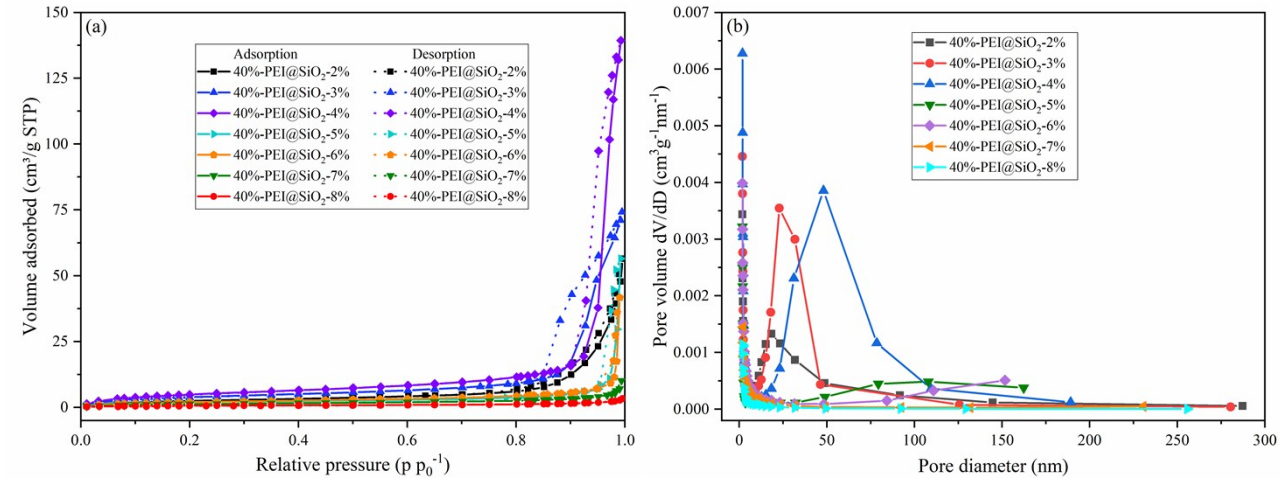
83 **Figure S2.** (a) FT-IR spectra and (b) TG curves of nano-SiO_2 supports synthesized from different Na_2SiO_3

84 concentrations of 20−80 g·L^{-1}.



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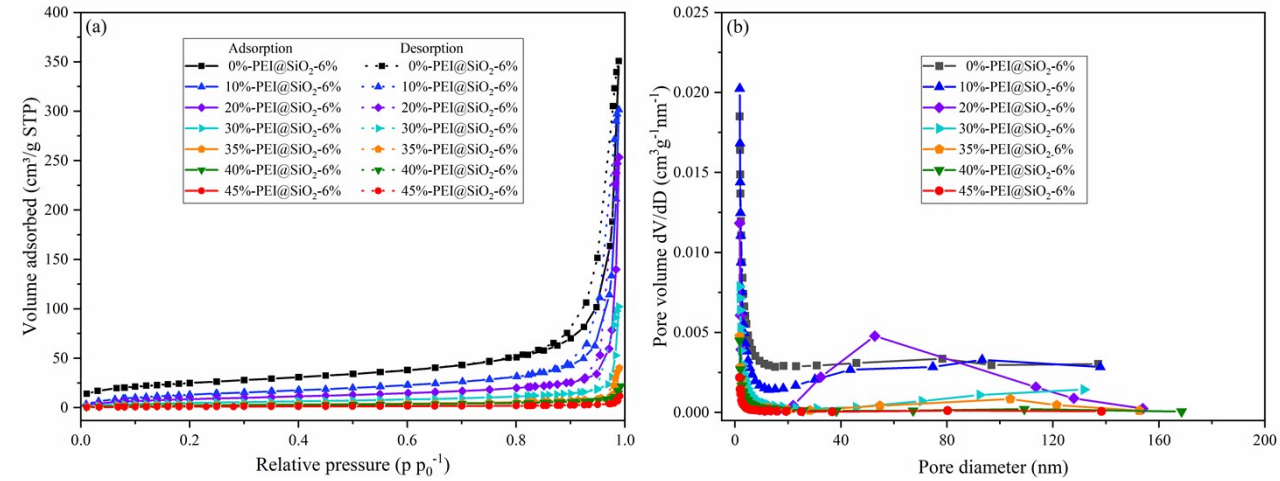
86 **Figure S3.** (a) N_2 adsorption/desorption isotherms and (b) pore size distributions of PEI@nano-SiO_2 adsorbents

87 with different nano-SiO_2 supports (40% PEI loading).



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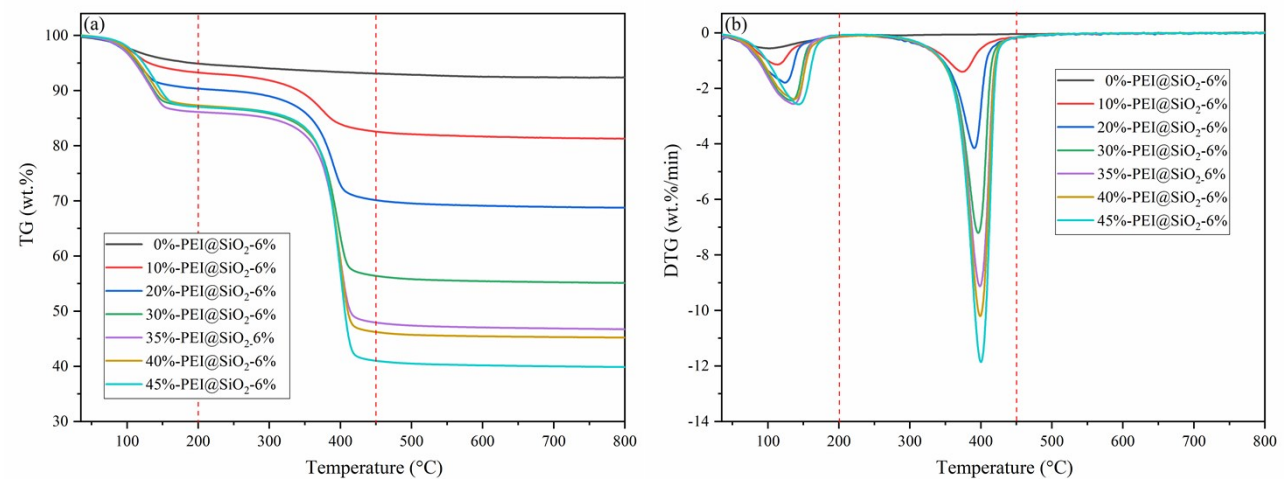
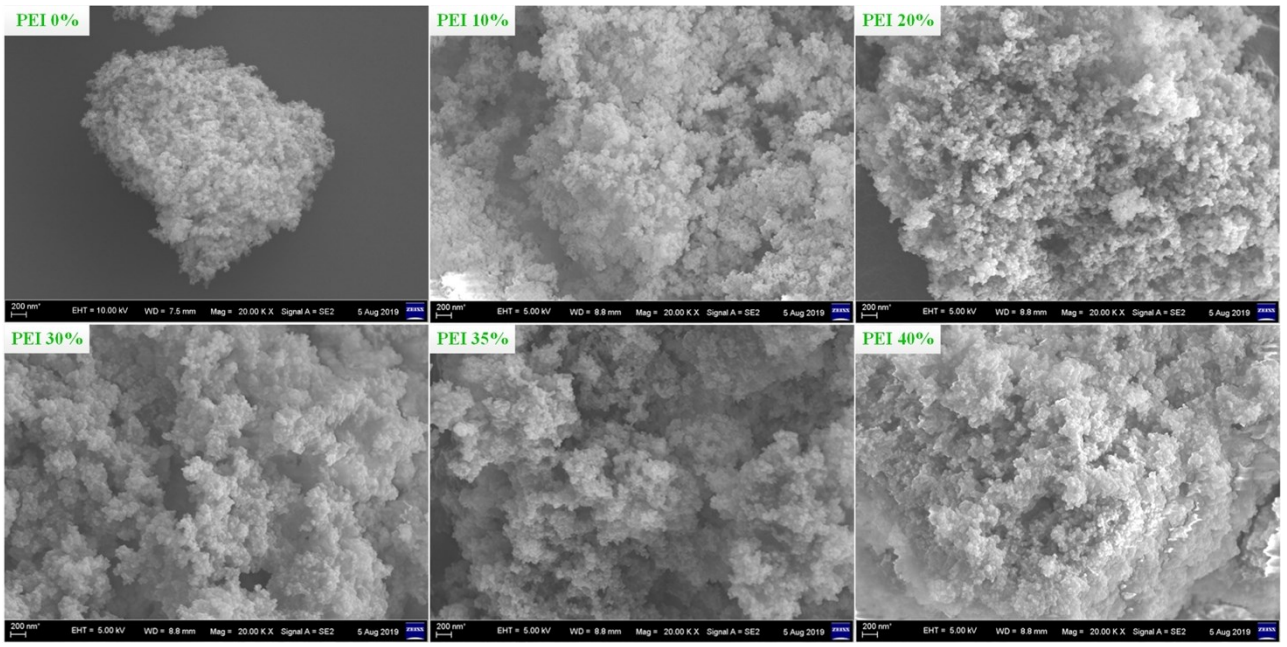


Figure S5. (a) TG and (b) DTG curves of the synthetic PEI@nano-SiO_2 adsorbents with different PEI loadings (supported by "SiO_2-6%").



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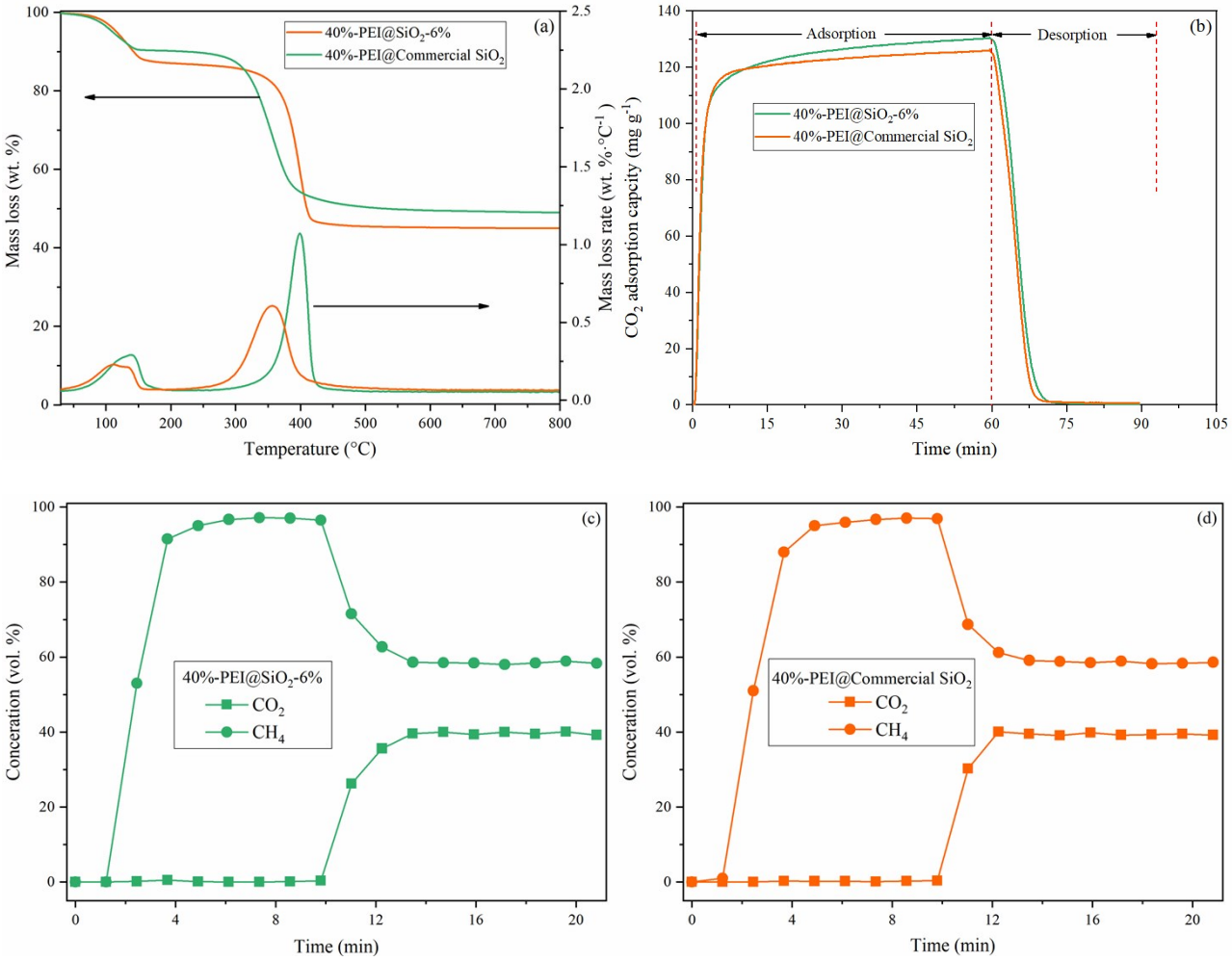

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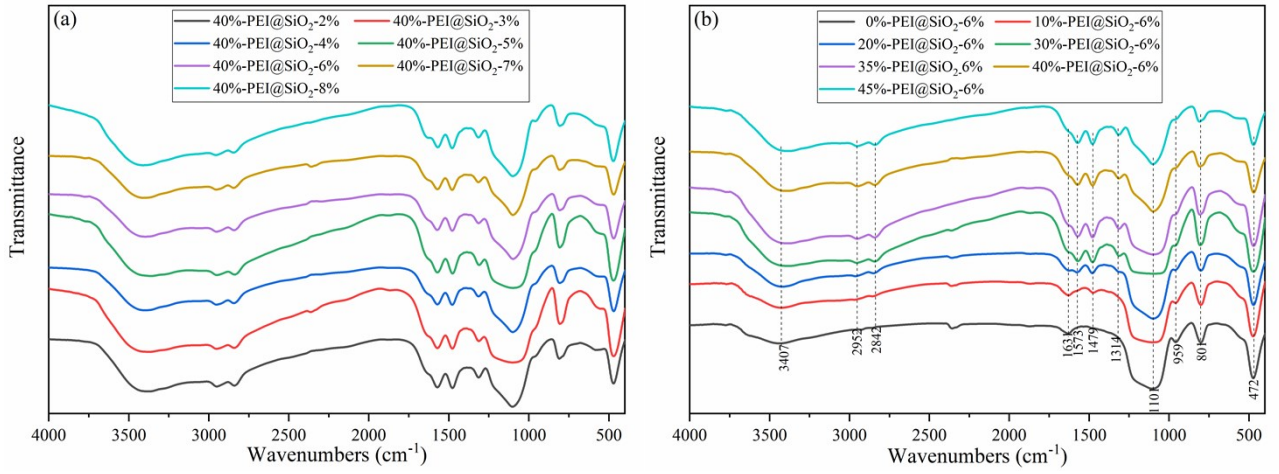

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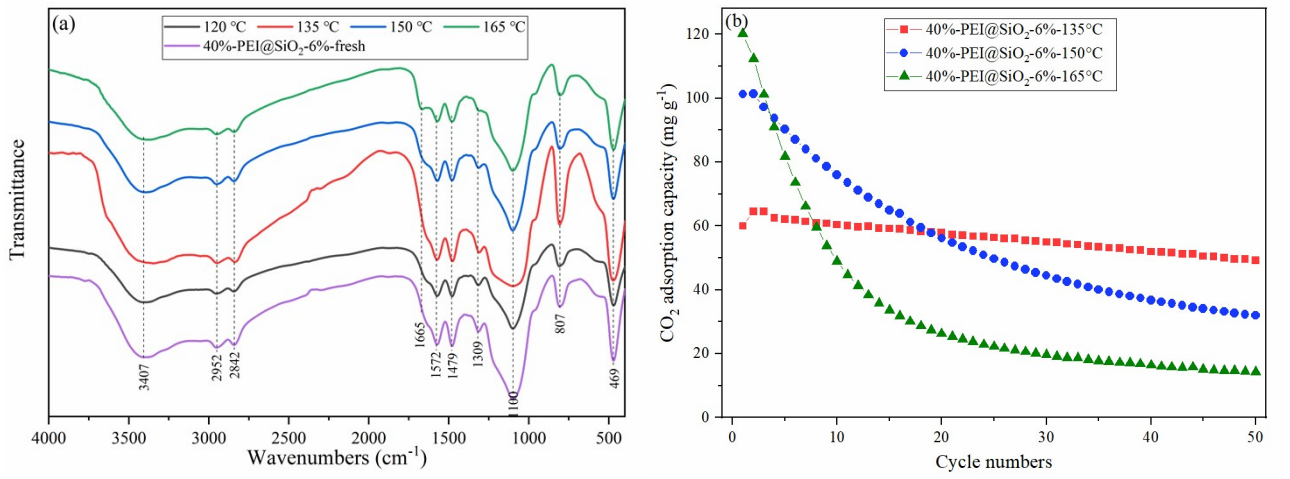

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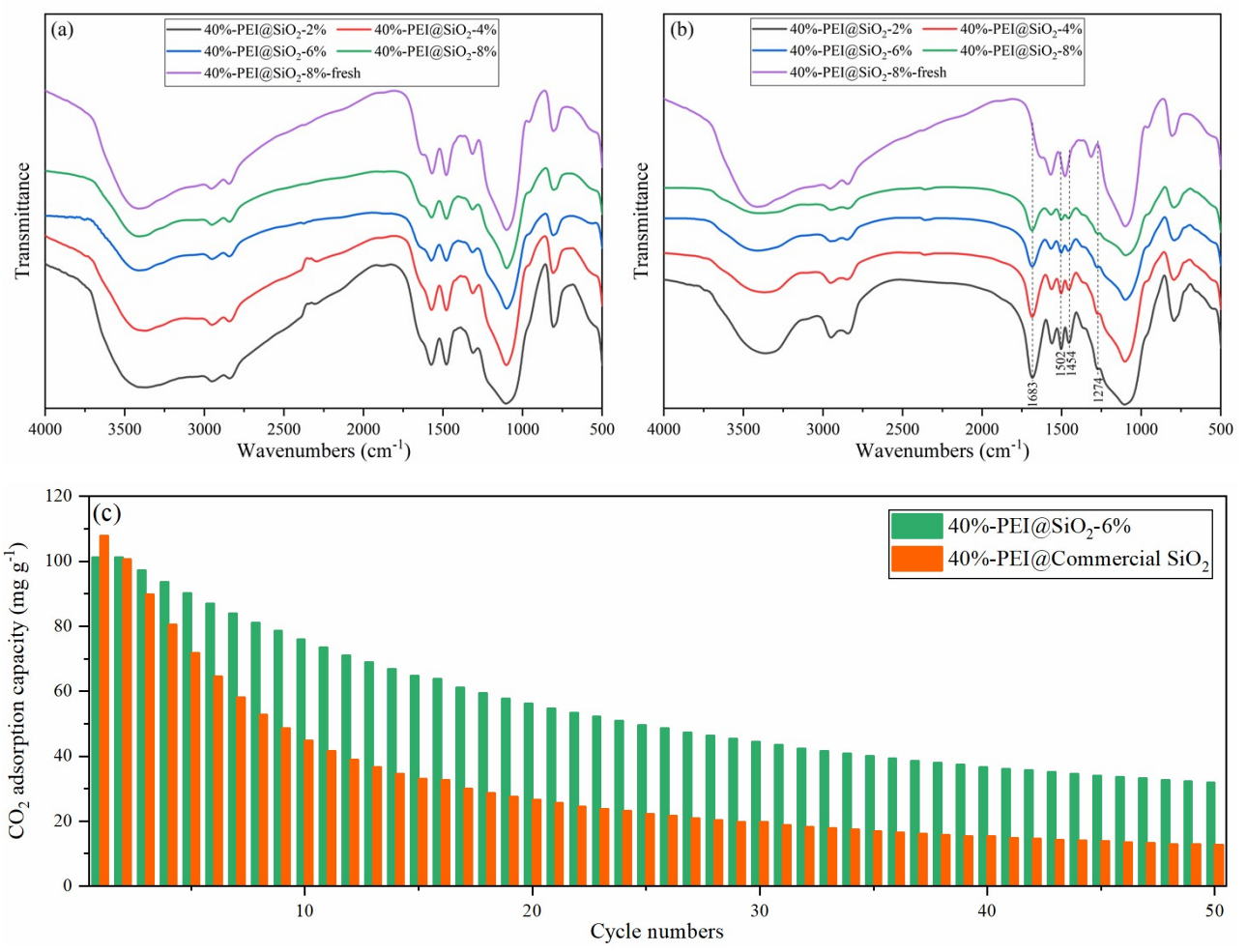

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CO_2 atmosphere for 15 min at 150 °C (adsorption at 90 °C for 30 min).

References

[1] Li K-M, Jiang J-G, Tian S-C, Chen X-J, Yan F. Influence of silica types on synthesis and performance of amine–silica hybrid materials used for CO_2 capture. J Phys Chem C 2014;118(5):2454-62.

[2] Wang L, Yang RT. Increasing selective CO_2 adsorption on amine-grafted SBA-15 by increasing silanol density. J Phys Chem C 2011;115(43):21264-72.

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[4] Ek S, Root A, Peussa M, Niinistö L. Determination of the hydroxyl group content in silica by thermogravimetry and a comparison with 1H MAS NMR results. Thermochim Acta 2001;379(1):201-12.