

Supporting Information

Mesoporous Carbon Stabilized MgO Nanoparticles Synthesized by Pyrolysis of MgCl₂-Preloaded Waste Biomass for Highly Efficient CO₂ Capture

Wu-Jun Liu,[†] Hong Jiang,^{†,*} Ke Tian,[†] Yan-Wei Ding,[‡] Han-Qing Yu[†]

[†]Department of Chemistry, University of Science and Technology of China, Hefei
230026, China

[‡]Hefei National Laboratory for Physical Sciences at Microscale, University of Science
and Technology of China, Hefei 230026, China

Corresponding author:

Dr. Hong Jiang, Fax: +86-551-63607482; E-mail: jhong@ustc.edu.cn

The following is included as additional **Supporting Information** for this paper

Remark S1;

Tables S1-S4;

References S1-S11;

Figures S1-S10.

Text S1: More Experimental Details

Materials. The biomass used in this work was sawdust, a naturally abundant lignocellulosic biomass waste obtained from a local timber treatment plant in Hefei, China. The biomass was first crushed using a high-speed rotary cutting mill, and the produced particles with the particle size smaller than 0.12 mm (120 mesh) were collected and then dried in an oven at 378 K overnight. The proximate analysis and elemental composition of the biomass was analyzed and shown in our previous work.^{S1} Magnesium chloride hexahydrate ($\text{MgCl}_2 \bullet 6\text{H}_2\text{O}$, 99% purity) was purchased from Sinopharm Chemical Reagent Co., Ltd., China and used without further purification.

The MgCl_2 loaded biomass was prepared in an adsorption process using the biomass as an adsorbent at room temperature. Briefly, 5.0 g of biomass and 1000 mL of MgCl_2 solution with an Mg concentration of 1540 mg L^{-1} (the average Mg content in the sea water) were mixed in a flask and shaken in a constant temperature oscillator at 200 rpm for 300 min. Then the water in the mixture was filtrated, and the solid residue was dried at 378 K till constant moisture was reached, then sieved again to collect the particles with size smaller than 120 mesh for further use.

Pyrolysis experiment. A certain amount of MgCl_2 loaded biomass was first placed in the feed pipe under a nitrogen flow (400 ML/min), and the nitrogen flow was maintained for 20 min to remove air from the pyrolysis system. Soon after the temperature of the heating zone reached the setting value (773-973 K), the MgCl_2 loaded biomass was fed into the quartz tubular reactor via a piston. The volatiles

formed during the fast pyrolysis process were swept out by a nitrogen flow (200 mL/min), and condensed by cold ethanol to obtain bio-oil.

Characterization of the mesopores carbon stabilized MgO NPs (mPC-MgO).

The elemental compositions (C, H, and O) of the mPC-MgO were determined by an elemental analyzer (VARIO EL III, Elementar Inc., Germany), while their Mg contents were analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES, Optima 7300 DV, Perkin-Elmer Co., USA). XRD analysis of the mPC-MgO was performed in an 18 kW rotating anode X-ray diffractometer (MXPAHF, Rigaku, Japan) using nickel-filtered Cu K α radiation source (30 kV/160 mA, $\lambda = 1.54056 \text{ \AA}$). The samples were scanned from 20° to 80° with a scan rate (2θ) of $0.02^\circ \text{ s}^{-1}$, and the diffraction peaks were assigned to the corresponding crystalline phases by comparison with the powder diffraction files from Joint Committee on Power Diffraction Standards (JCPDS). The thermal stability of mPC-MgO was characterized with a DTG-60H/DSC-60 thermogravimetric analyzer (Shimadzu Co., Japan) under N₂ atmosphere, with a heating rate of 5 K min^{-1} from room temperature to 773 K. The structural features of the mPC-MgO were analyzed by nitrogen adsorption-desorption isotherms, which were measured at 77 K on a Micromeritics Gemini apparatus (ASAP 2020 M+C, Micromeritics Co. USA) after degassing the samples at 573 K under vacuum for 4 hours. Specific surface areas of the samples were obtained by the Brunauer, Emmett, and Teller (BET) method, while their pore volumes were calculated by the amount of nitrogen adsorbed at a relative pressure of 0.99. The surface morphology of the mPC-MgO was analyzed using scanning

electron microscope (SEM, Sirion 200, FEI Co., USA) and transmission electron microscope (TEM, JEOL-2100F, Japan) coupled with energy dispersive X-ray (EDX) spectrometer. The chemisorption analysis was conducted with temperature-programmed desorption (TPD) apparatus, which composed of a fixed-bed flow reactor and a QIC20 mass spectrometer. The procedure for the CO₂ chemisorption analysis is described as follows: 100 mg of the mPC-MgO material was placed into the fixed-bed flow reactor, and heated at 500 °C under an Ar flow of 30 mL min⁻¹ for 120 min to remove the gas adsorbed on the material. After the temperature decreased to 80 °C, the CO₂ adsorption was performed under a CO₂ flow of 30 mL min⁻¹ for 60 min, then the gas flow was switched to Ar at 25 °C to sweep the remaining CO₂ and desorb the physically adsorbed CO₂ for 18 h. Afterwards, the temperature was increased from 25 to 500 °C with a rate of 10 °C min⁻¹ to desorb the chemisorbed CO₂. The desorbed CO₂ species were analyzed by the QIC20 mass spectrometer. For comparison, the carbon material without MgO (mPC-773) was also analyzed with the same method.

After CO₂ capture, the used mPC-MgO was further characterized by FTIR and XPS. For the FTIR analysis, the sample was first mixed with KBr at a ratio of 1:100 and compressed into films, then analyzed using an FTIR spectrometer (EQUINOX55 IR spectroscopy, Bruker, Germany). The XPS characterization was carried out through an X-ray photoelectron spectrometer (ESCALAB250, Thermo-VG Scientific Inc., UK) using monochromatized Al K α radiation (1486.92 eV).

References

- (S1) Liu, W.-J.; Tian, K.; Jiang, H.; Zhang, X.-S.; Ding, H.-S.; Yu, H.-Q., Selectively Improving the Bio-Oil Quality by Catalytic Fast Pyrolysis of Heavy-Metal-Polluted Biomass: Take Copper (Cu) as an Example. *Environ. Sci. Technol.* **2012**, *46*, 7849-7856.

Table S1. The texture features and elemental compositions of the mPC-MgO

mPC-MgO	Surface area (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Average pore size (nm)	MgO crystals size (nm) ^a	Elemental composition (wt.%)			
					C	H	O ^b	Mg
mPC-MgO-773	279	0.140	2.01	17.1	56.3	1.1	21.5	21.1
mPC-MgO-873	306	0.156	2.03	18.6	56.7	1.1	21.7	20.5
mPC-MgO-973	298	0.152	2.04	17.8	57.0	1.6	22.0	19.4
mPC-773	14.0	0.067	33.2	-	76.7	3.5	19.8	-

^a calculated from the (2 0 0) diffraction peak of XRD patterns using the Scherrer equation.

^b calculated by difference: O = 100- C- H- Mg

Table S2. Analysis of the main peaks in the XPS spectra of the fresh and regenerated catalysts

Elements	Before CO ₂ capture			After CO ₂ capture		
	Peak B.E. (eV)	FWHM (eV)	At. %	Peak B.E. (eV)	FWHM (eV)	At. %
C 1s	284.8	1.26	72.1	284.8	1.24	74.3
O 1s	532.6	3.72	14.7	532.6	3.67	15.9
Mg 2p	50.9	2.99	6.21	50.9	2.94	6.01

Table S3. Comparison of the different CO₂ capture trappers reported in literature with the trapper in this work

CO ₂ trapper	Maximum capture capacity (mol kg ⁻¹) ^a	Total cycle number	Capture temperature (K)	Regeneration temperature (K)	Reference
Al ₂ O ₃ supported MgO	1.36	5	333	623	S2
K ₂ CO ₃ activated MgO	1.98	17	748	748	S3
Mesoporous carbon supported MgO	2.09	6	298	623-723	S4
Mesoporous MgO	2.27	3	373	1073	S5
K ₂ CO ₃ promoted MgO	4.49	5	323	423-723	S6
Mesoporous carbon stabilized MgO NPs	5.45	19	353	673	This work
Surfactant promoted amine sorbents	3.22	10	303	383	S7
CaO–Ca ₁₂ Al ₁₄ O ₃₃	~6.0	45	963	1163	S8
Mesoporous amine-modified SiO ₂	6.97	Not mentioned	298	Not mentioned	S9
Al ₂ O ₃ , CaO, and MgO composites	7.73	65	923	1123	S10
Amine-functionalized mesoporous capsules	7.90	50	348	383	S11

^a determined at first cycle

References

- (S2) Li, L.; Wen, X.; Fu, X.; Wang, F.; Zhao, N.; Xiao, F.; Wei, W.; Sun, Y. MgO/Al₂O₃ Sorbent for CO₂ Capture. *Energy Fuels* **2010**, *24*, 5773-5780.
- (S3) Xiao, G.; Singh, R.; Chaffee, A.; Webley, P. Advanced adsorbents based on MgO and K₂CO₃ for capture of CO₂ at elevated temperatures. *Int. J. Greenhouse Gas Contr.* **2011**, *5*, 634-639.
- (S4) Bhagiyalakshmi, M.; Hemalatha, P.; Ganesh, M.; Mei, P. M.; Jang, H. T. A direct synthesis of mesoporous carbon supported MgO sorbent for CO₂ capture. *Fuel* **2011**, *90*, 1662-1667.
- (S5) Bhagiyalakshmi, M.; Lee, J. Y.; Jang, H. T. Synthesis of mesoporous magnesium oxide: Its application to CO₂ chemisorption. *Int. J. Greenhouse Gas Contr.* **2010**, *4*, 51-56.

- (S6) Lee, S. C.; Chae, H. J.; Lee, S. J.; Choi, B. Y.; Yi, C. K.; Lee, J. B.; Ryu, C. K.; Kim, J. C. Development of regenerable MgO-based sorbent promoted with K_2CO_3 for CO_2 capture at low temperatures. *Environ. Sci. Technol.* **2008**, *42*, 2736-2741.
- (S7) Wang, J.; Long, D.; Zhou, H.; Chen, Q.; Liu, X.; Ling, L. Surfactant promoted solid amine sorbents for CO_2 capture. *Energy Environ. Sci.* **2012**, *5*, 5742-5749.
- (S8) Martavaltzi, C. S.; Lemonidou, A. A. Development of new CaO based sorbent materials for CO_2 removal at high temperature. *Microporous Mesoporous Mater.* **2008**, *110*, 119-127.
- (S9) Cui, S.; Cheng, W.; Shen, X.; Fan, M.; Russell, A.; Wu, Z.; Yi, X. Mesoporous amine-modified SiO_2 aerogel: a potential CO_2 sorbent. *Energy Environ. Sci.* **2011**, *4*, (6), 2070-2074.
- (S10) Li, L.; King, D. L.; Nie, Z.; Li, X. S.; Howard, C. $MgAl_2O_4$ Spinel-stabilized calcium oxide absorbents with improved durability for high-temperature CO_2 capture. *Energy Fuels* **2010**, *24*, 3698-3703.
- (S11) Qi, G.; Wang, Y.; Estevez, L.; Duan, X.; Anako, N.; Park, A.-H. A.; Li, W.; Jones, C. W.; Giannelis, E. P. High efficiency nanocomposite sorbents for CO_2 capture based on amine-functionalized mesoporous capsules. *Energy Environ. Sci.* **2011**, *4* (2), 444-452.

Table S4. Band positions for the function groups of mPC-MgO before and after CO ₂ capture		
Functional groups	Band positions (cm ⁻¹)	
	Before CO ₂ capture	After CO ₂ capture
O-H or O-Mg configurations stretching	3439	3434
-CH symmetric stretching	2921	2916
CO ₂ stretching	-	2317
C=O asymmetric stretching	-	1631
O-H deformation vibration	1592	1550
O-Mg configurations deformation vibration	1447	1442
C-O stretching	1119	1127
Finger print of O-Mg vibration	687	685
	633	637
	496	498

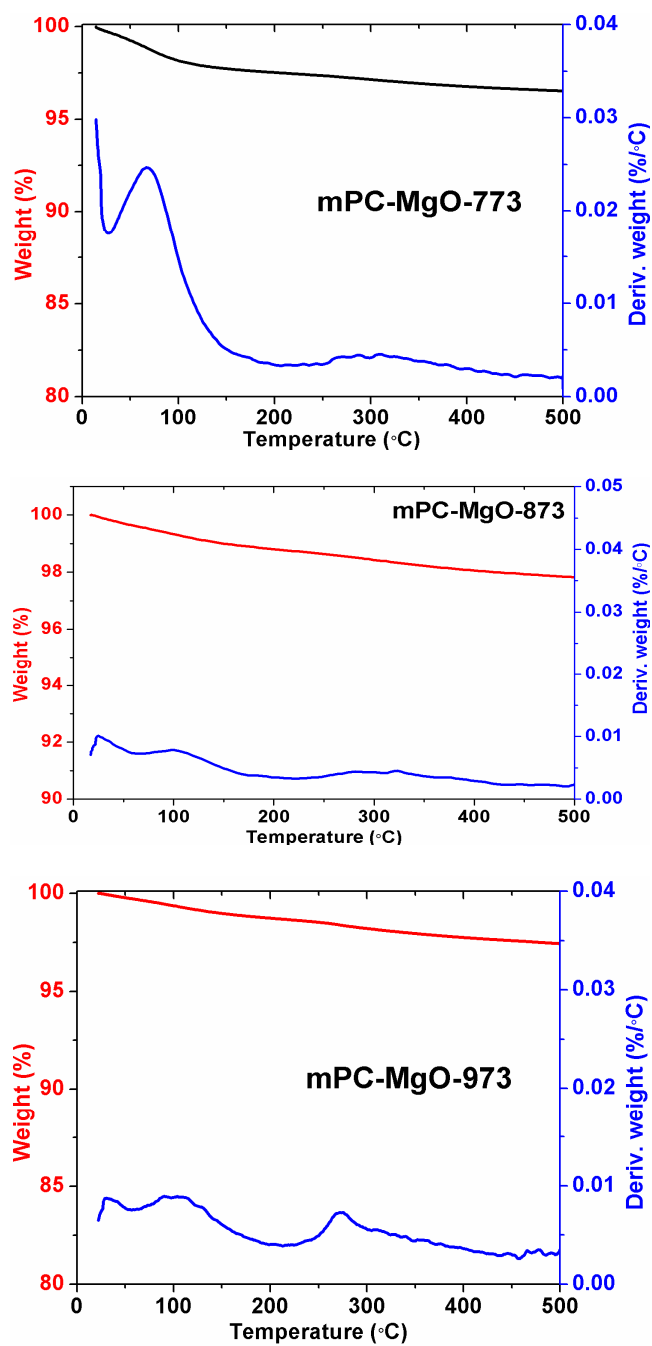


Fig. S1. Thermal stability of the mPC-MgO materials prepared at different temperatures.

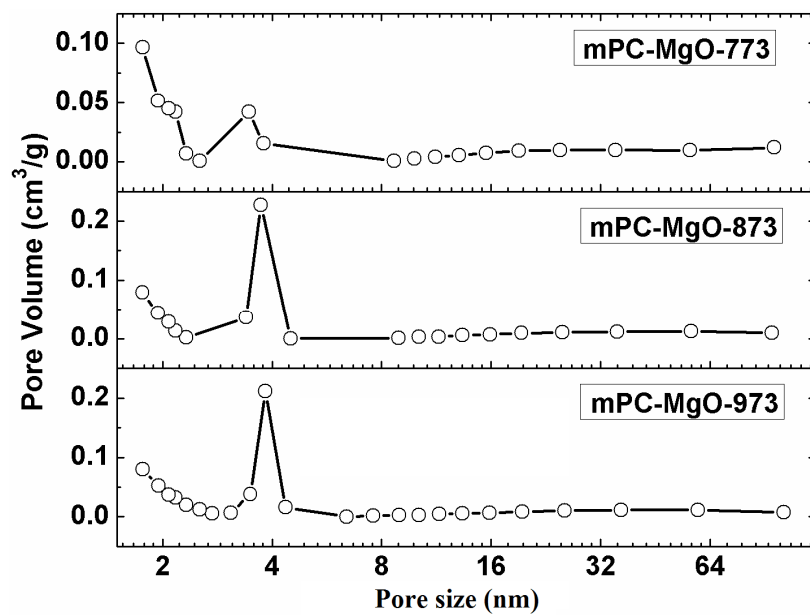


Fig. S2. Pore size distributions of the mPC-MgO NPs prepared at different temperatures

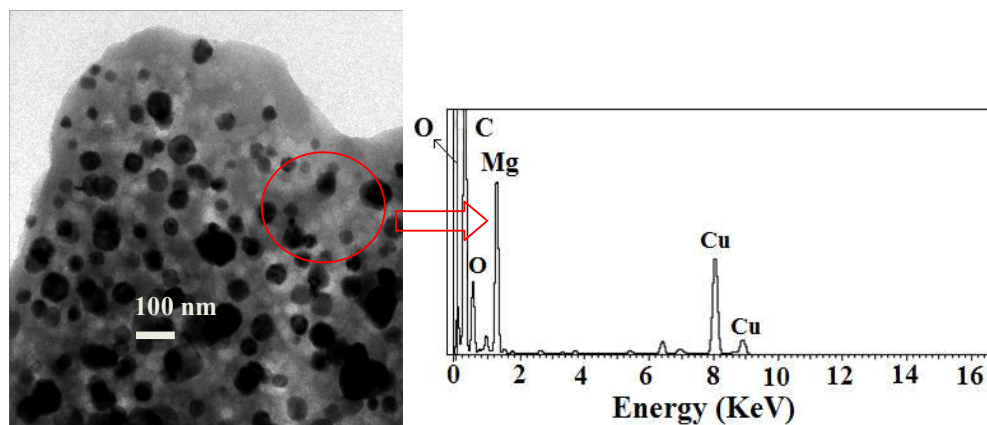


Fig. S3. TEM-EDX analysis of the mPC-MgO-873. The Cu is present because copper wire mesh is used to support the samples in TEM analysis

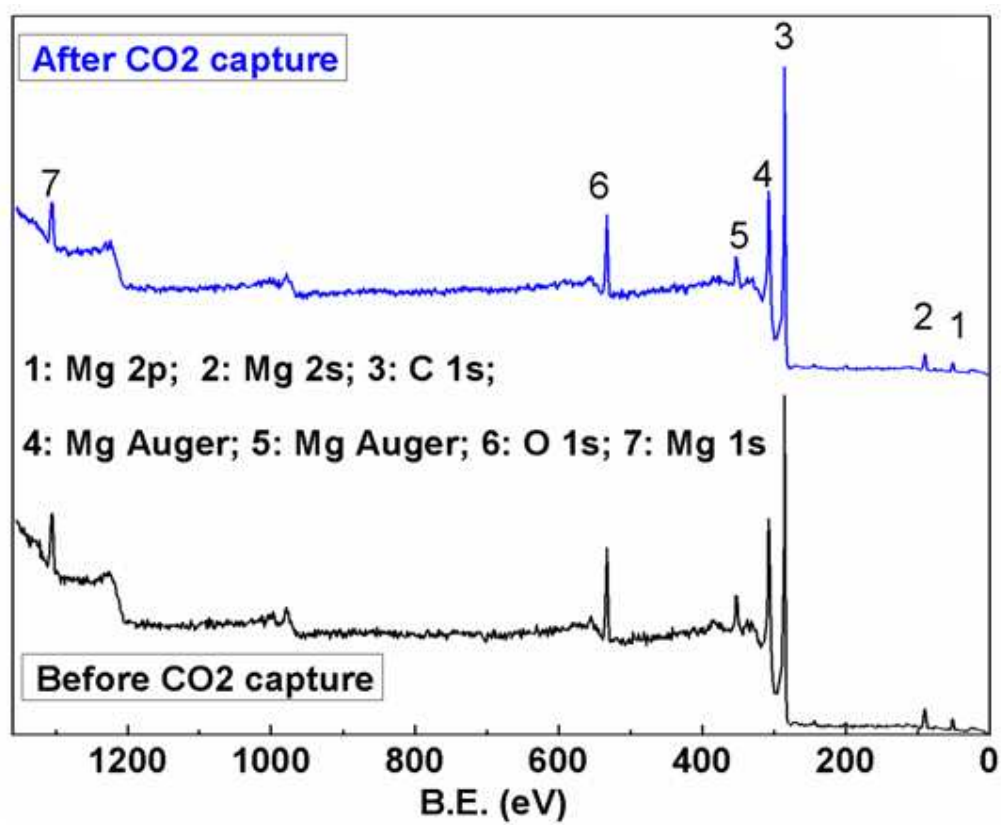


Fig. S4. XPS survey spectra of the mPC-MgO-873 before and after CO₂ capture

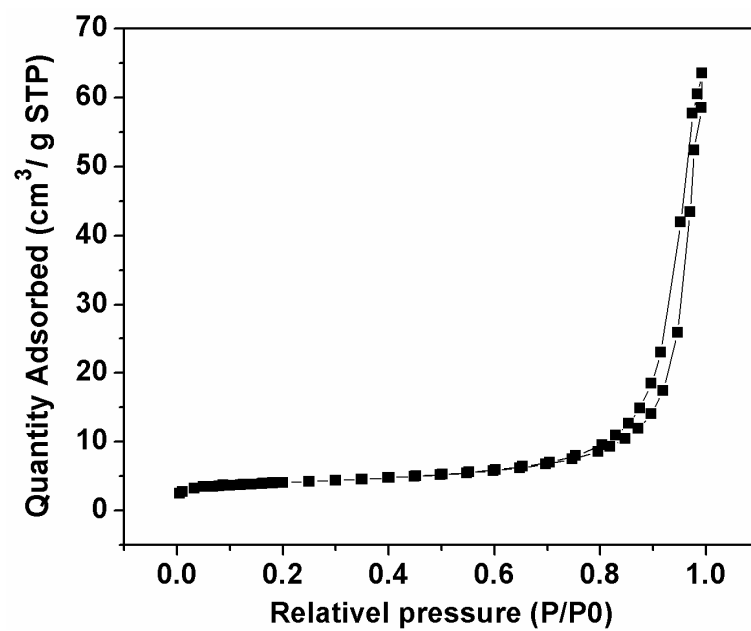


Fig. S5. The adsorption-desorption isotherm of the mPC-773

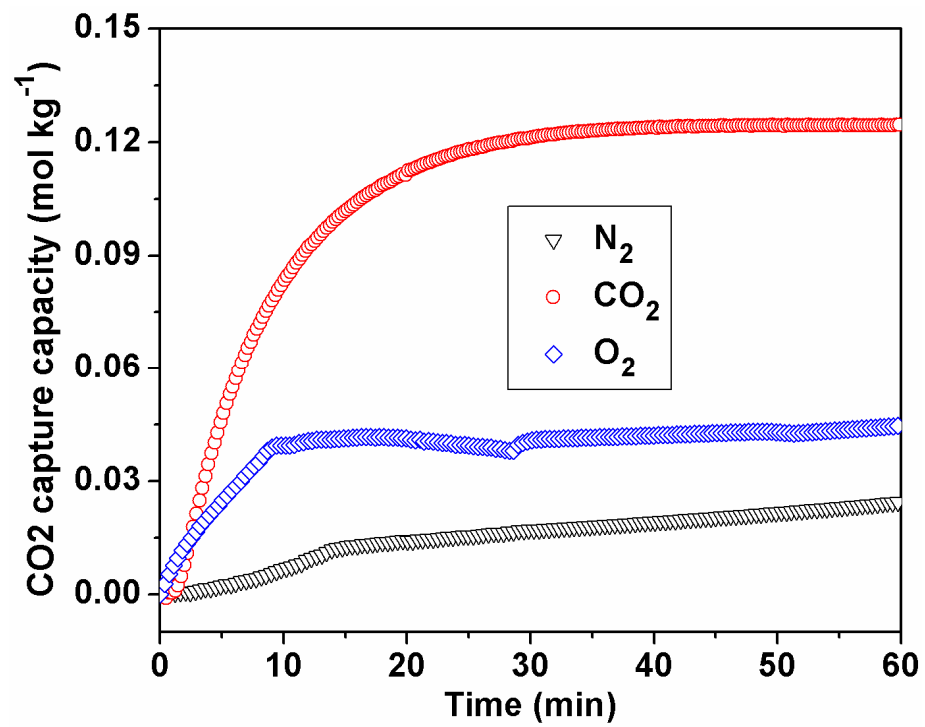


Fig. S6. Comparison of the capture of the CO₂, N₂, and O₂ by the mPC-773

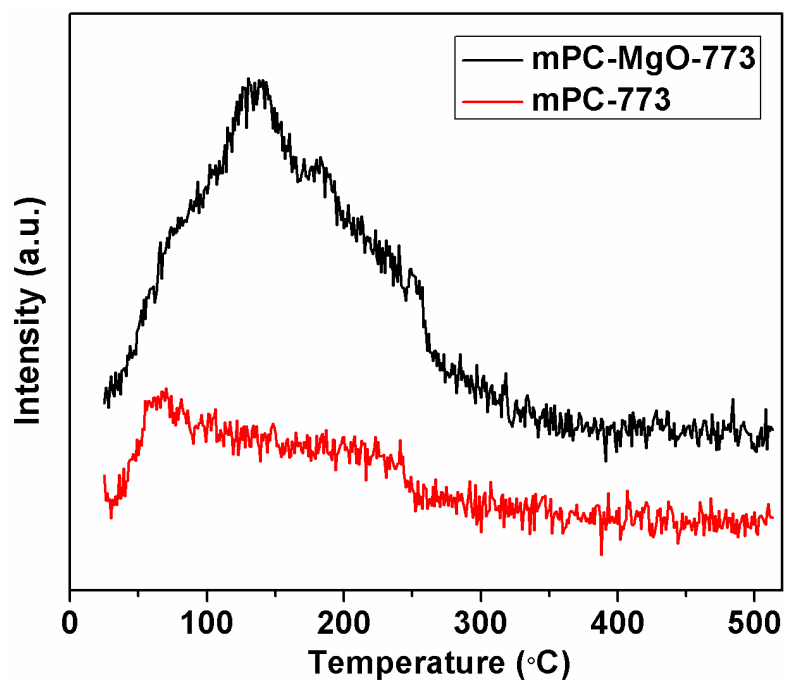


Fig. S7. CO₂-TPD profiles of the mPC-MgO materials and the carbon support

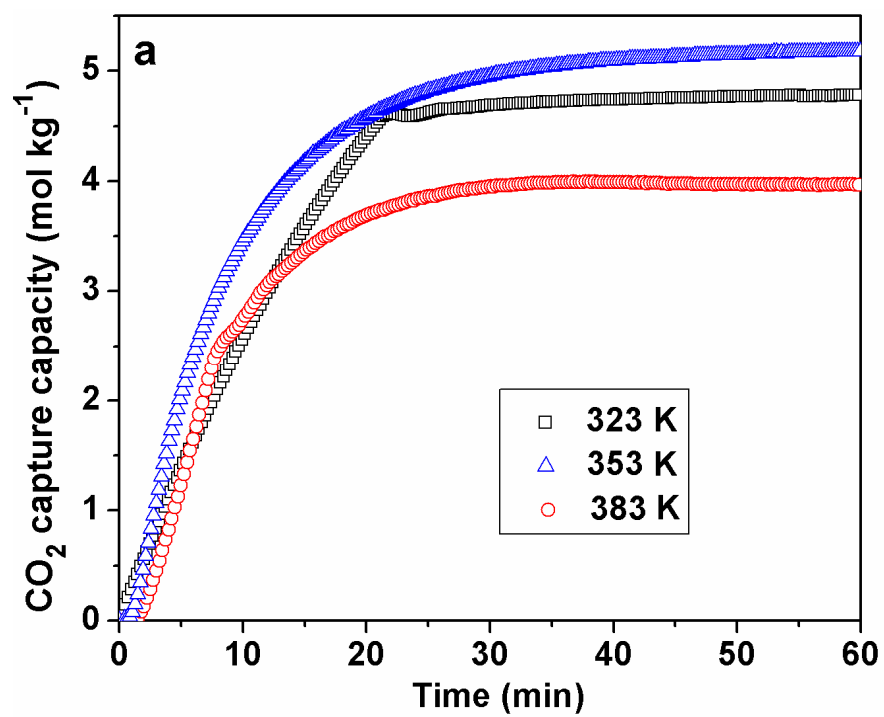


Fig. S8. CO₂ capture at three different temperatures and a fixed time of 60 min

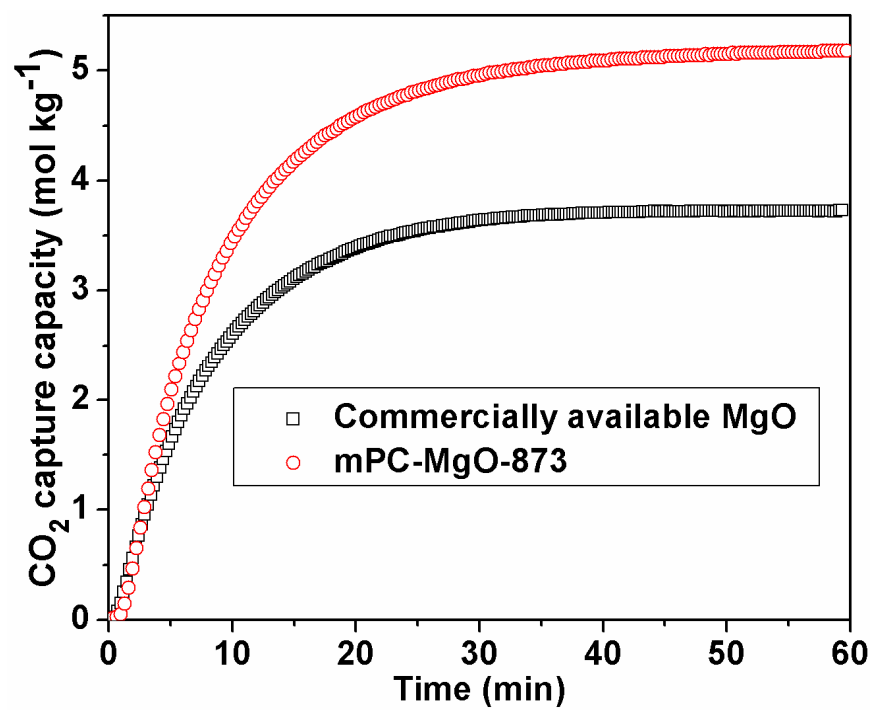


Fig. S9. Comparison of the CO₂ capture performance between the mPC-MgO-873 and the commercially available MgO NPs

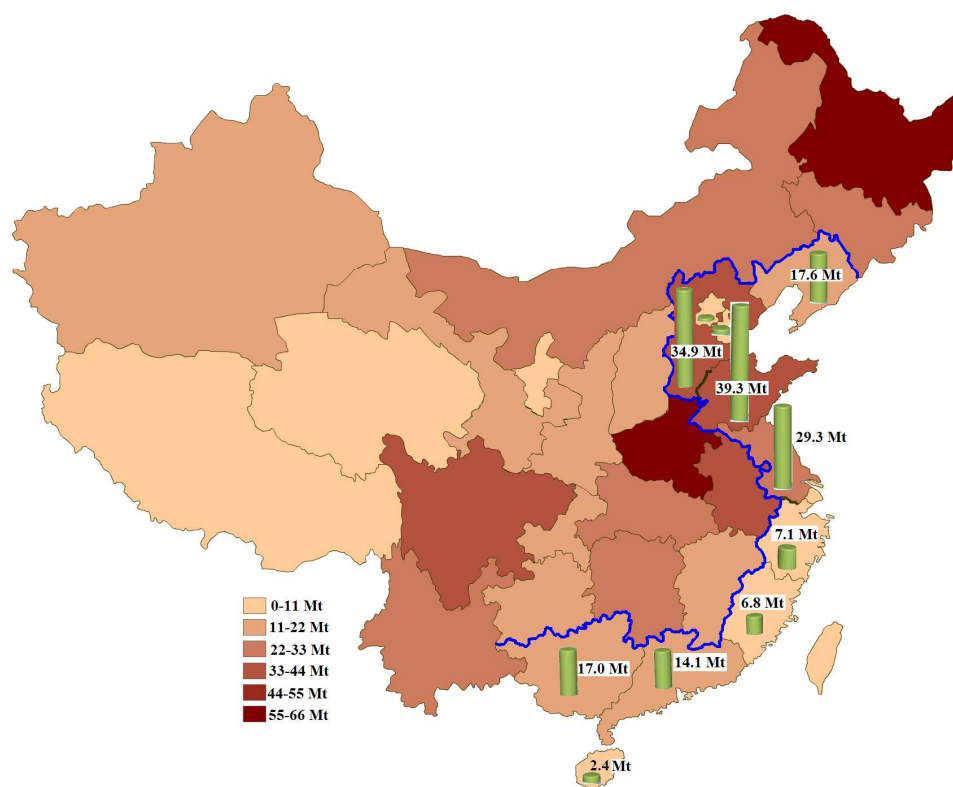


Fig. S10. Potential reduction of the CO₂ emission in the coastal areas of China by mPC-MgO synthesized by pyrolysis of MgCl₂-preloaded biomass