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Supporting information

Sustainable Synthesis of Alkaline Metal Oxide-Mesoporous Carbons via Mechanochemical Coordination Self-Assembly

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Chemicals: Pluronic F-127 and P-123, PEG-4000 (poly(ethylene glycol), average Mn 4000), hexadecyltrimethylammonium bromide (CTAB, >99%) were supplied by Sigma Aldrich Co. Ltd.; magnesium acetate tetrahydrate ($Mg(OAc)_2$-$4H_2O$ >98%), magnesium chloride ($MgCl_2$, 99%), magnesium sulfate ($MgSO_4$, 97%), calcium acetate hydrate ($Ca(OAc)_2$-H_2O, 98%) were supplied by Alfa Aesar. Tannins were purchased from Silva Team Co. Ltd. Other common solvents and reagents were obtained from other commercial sources and all chemicals in this work were used without further purification.

Synthesis of alkaline-metal-oxide-doped mesoporous carbons: In a typical run for the synthesis, tannin (0.5 g) and copolymers F127 (0.4 g) were mixed and added into a 3.5 cm (diameter) and 6.5 cm (height) screw-capped stainless steel reactor along with two stainless steel ball (diameter:1.5cm). The reactor was then ball milled in a high-speed vibrating ball miller (frequency: 30(1/s)) for 0.5 h. Afterwards, $Mg(OAc)_2$ or $Ca(OAc)_2$ (1.5mmol) was added into the reactor and ball milling for another 0.5 h. The obtained brown gel-like products were washed with deionized water and ethanol, followed by drying in vacuum oven (313 K) overnight. The resultant product were then carbonized at 450 ºC (at a heating rate of 5 ºC min, holding time: 2 h), or further thermally treated at 600/800 ºC (heating rate: 5 ºC /min) for another 2 h under flowing N_2 (flowing rate fixed at 200ml/min). Mg-MC-800 represents a mesoporous carbon material based on tannin, magnesium acetate and F127 mixed by ball milling and then pyrolyzed at 800 ºC. The tannin-F127 polymers with no or various metal salt species ($MgCl_2$, $MgSO_4$), as well as tannin-$Mg(OAc)_2$ polymer with no or different soft templates (P123, PEG-4000, CTAB) were also prepared through ball-milling and subsequently carbonized at 800 ºC using the same experimental process (denoted as C-800(no metal salt), Mg-MC-800(MgCl2), Mg-C-800(no template), Mg-MC-800(P123) etc.).

Synthesis of pure mesoporous carbons: In a typical synthesis, defined amount of alkaline metal oxide-doped mesoporous carbon were mixed with excess hydrochloric acid solution (1 M) and stirring at 50 ºC for 12 h. After filtration, the obtained carbon materials were washed with water and ethanol several times, and then dried under vacuum for further use and characterization.

Dye removal experiment: The adsorption experiments of methylene blue (MB) and methyl orange (MO) were carried out in a batch process by stirring 10 mg of adsorbent in 20 mL of corresponding dye solution. Working solutions of MB and MO were both prepared from the stock solution (1000 mg L^{-1}) to the designed concentration for each experimental run. After stirring for 24 h, 5 ml of dye solution was withdrawn using a syringe, filtered through a 0.45 μm membrane and diluted for the later measurement of dye concentration. The residual concentration of dye solution was determined using a calibration curve prepared at corresponding maximum wavelength (465 nm for methyl orange, and 664 nm for methylene blue) using an UV spectrometer. The amount of adsorbed dye was calculated by

$$Q_e = \frac{(C_0 - C_e)V}{W}$$

where C_0 and C_e are the initial and equilibrium concentrations (mg/L), respectively. V is the volume of dye solution (L), and W is the weight (g) of adsorbent. The Langmuir model can be used to analyze the relationship between the equilibrium adsorption capacity (Q_e, mg g^{-1}) of dye solution and its equilibrium solute concentration (C_e, mg L^{-1}) by the following equation:

$$\frac{C_e}{Q_e} = \frac{1}{Q_m K_L} + \frac{1}{Q_m} C_e$$

where K_L is the Langmuir adsorption constant (L/mg), and Q_m is the theoretical maxiumum adsorption capacity (mg/g).

Characterizations: Before the measurement, the samples were pretreated at 150 ºC under flowing N_2 for 12 h. The N_2 sorption isotherms at 77 K were measured on a Micromeritics Gemini 2390t system to determine the textural properties of synthesized carbon materials. CO_2 and N_2 adsorption isotherms at 0 and 25 °C were also measured on a Micromeritics Gemini 2390t surface area analyzer. The residue content of carbon materials were measured on a Mettler-Toledo TGA/SDTA851e system under air. X-ray diffraction (XRD) patterns were measured on a Rigaku D/Max-2550 diffractometer using Cu-kα radiation. Fourier transform infrared (FTIR) spectra were recorded using an Excalibur Series instrument with an MVPPro ATR accessory. Scanning electron microscope (SEM) images were taken on a Zeiss Auriga Crossbeam SEM at an acceleration voltage of 5 kV. Transmission electron microscopy (TEM) images were taken on a Tecnai30 field-induced electron microscope. The scanning TEM in high angle angular dark field (STEM-HAADF) images were taken on a Nion UltraSTEM 200 microscope operated at 200 kV. Small-angel X-ray Scattering (SAXS) were measured on a Bruker D8 diffractometer equipped with scintillation counter. A Renishaw 1000 Raman spectrometer with a Leica microscope were used to collect the Raman data.

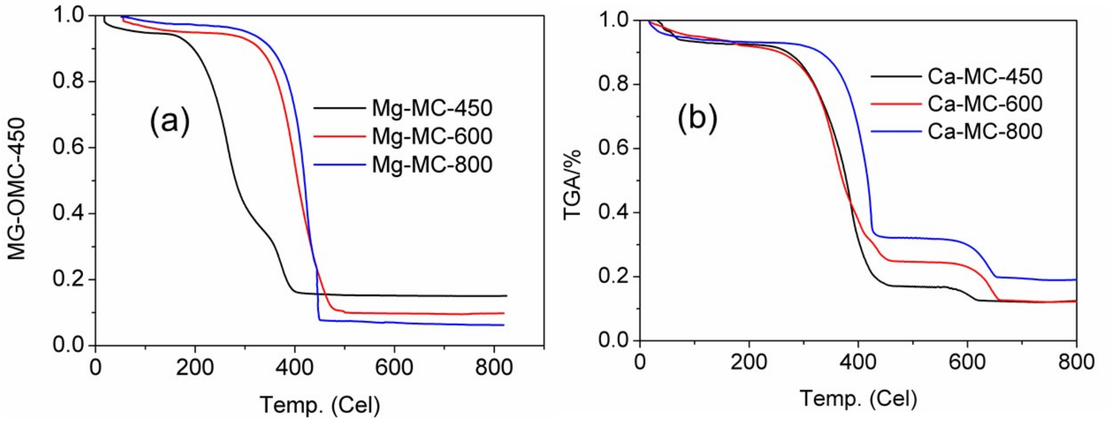

Figure S1. TGA results of Mg-MCs and Ca-MCs carbon materials.

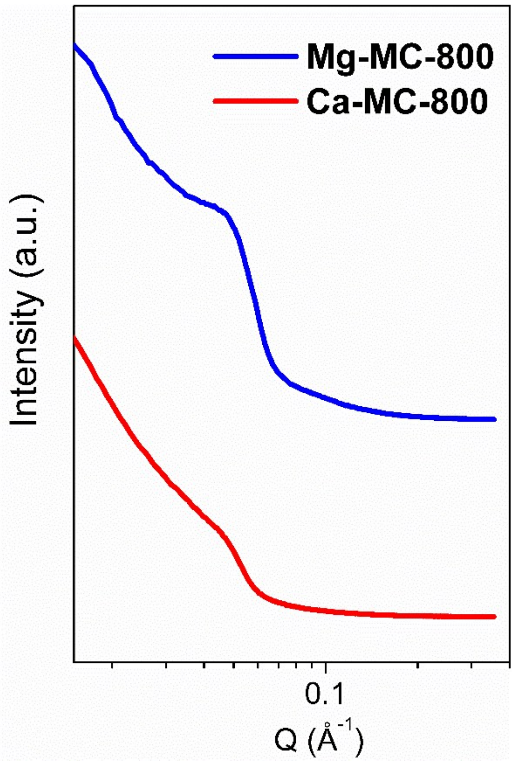

Figure S2. Small angle X-ray scattering (SAXS) patterns of the mesoporous carbons carbonized at 800 °C.

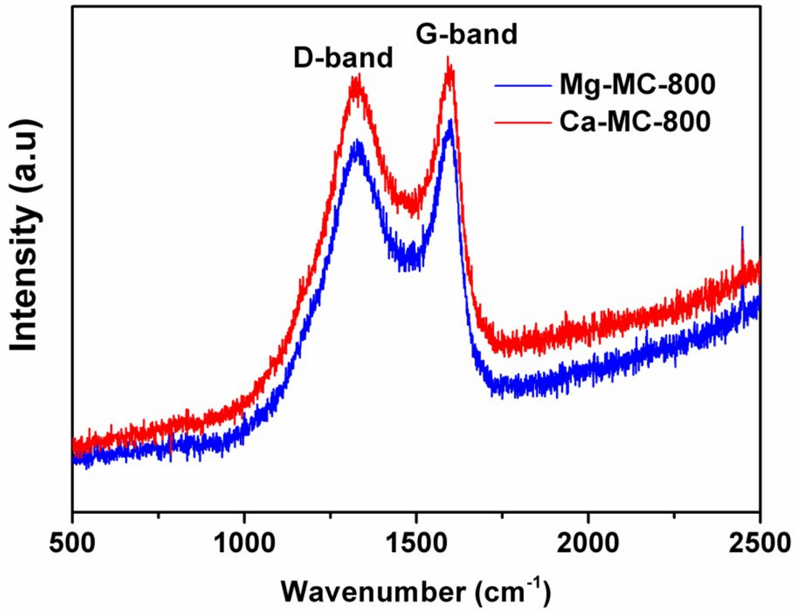

Figure S3. Raman spectra of the mesoporous carbons carbonized at 800 °C.

Table S1. Textural properties of synthesized carbon materials

Samples	Textual Properties					
	S_{BET}[a] (m^2g^{-1})	S_m[b] (m^2g^{-1})	V_t[c] (cm^3g^{-1})	V_m[d] (cm^3g^{-1})	D_{BJH}[e] (nm)	Yield (%)
Mg-MC-450	352	100	0.45	0.04	8.9	43
Mg-MC-600	512	207	0.65	0.09	8.5	38
MG-MC-800	520	273	0.53	0.12	7.4	32
Mg-MC-800(HCl)	707	409	0.70	0.18	7.9	30
Ca-MC-450	440	149	0.58	0.06	9.8	40
Ca-MC-600	273	100	0.43	0.04	9.0	34
Ca-MC-800	436	186	0.49	0.08	8.1	30
Ca-MC-800(HCl)	676	414	0.69	0.17	9.0	29
C-800 (no metal salt)	269	194	0.23	0.09	-	25
Mg-MC-800 (MgCl2)	571	357	0.61	0.16	9.9	28
Mg-MC-800 (MgSO4)	455	227	0.59	0.10	8.9	27
Mg-C-800 (no template)	278	260	0.13	0.12	-	29
Mg-C-800 (CTAB)	258	237	0.12	0.11	-	28
Mg-MC-800 (P123)	461	260	0.45	0.11	5.6	33
Mg-MC-800 (PEG-4000)	522	284	0.47	0.13	4.6	30

[a] Surface area calculated from the BET equation in the relative pressure range of 0.05–0.20. [b] Micropore surface area calculated using the t-plot method. [c] Single point total pore volume calculated at a relative pressure of 0.97. [d] Micropore volume calculated by the t-plot method [e] Pore width obtained from the distribution maxima calculated according to the Barrett–Joyner–Halenda (BJH) method.

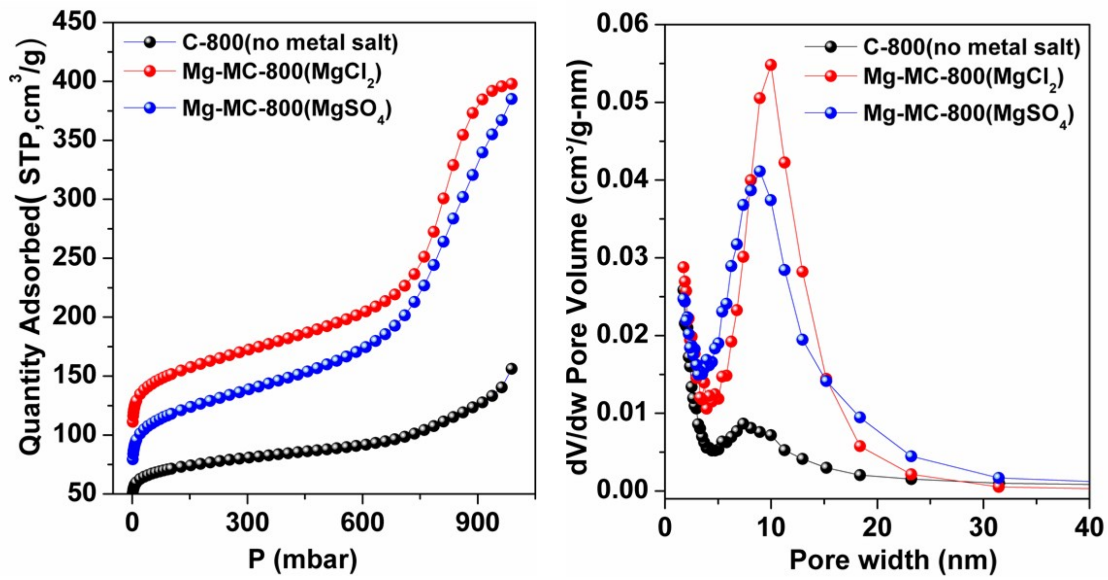

Figure S4. N_2 adsorption isotherms (77K) and Barrett–Joyner–Halenda (BJH) pore size distributions of as-synthesize carbons using no metal salt, $MgCl_2$ or $MgSO_4$, respectively.

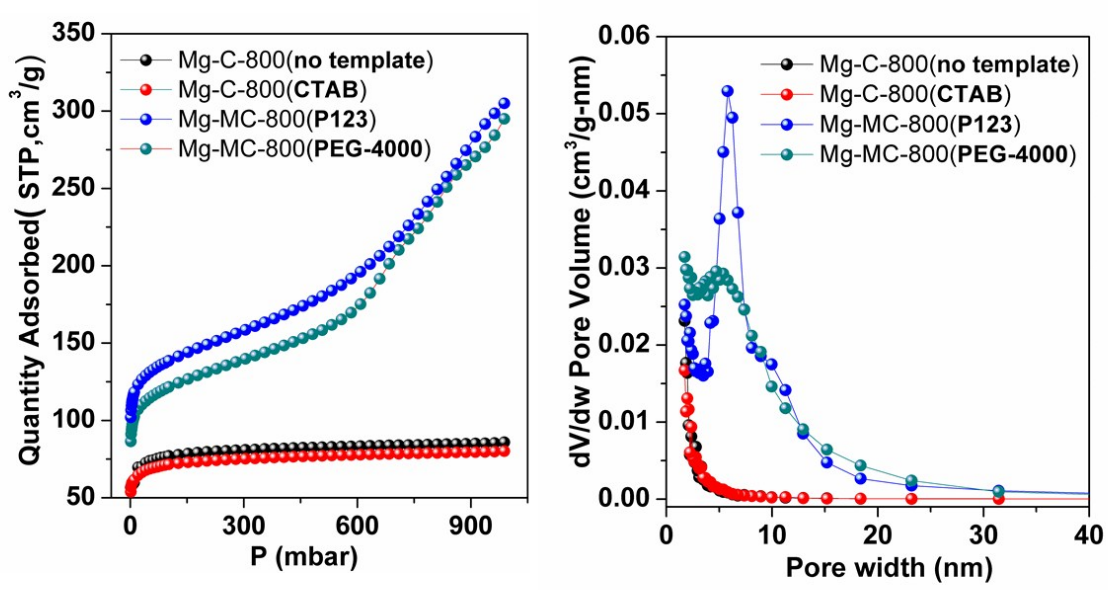

Figure S5. N_2 adsorption isotherms (77K) and Barrett–Joyner–Halenda (BJH) pore size distributions of as-synthesized carbons using no or various soft template, respectively.

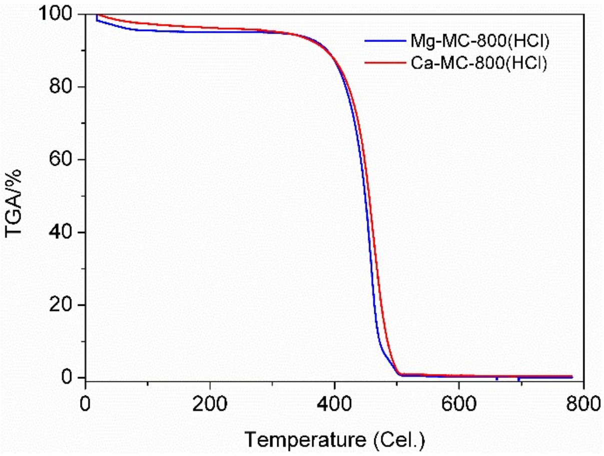

Figure S6. Thermo-gravimetric analysis (TGA) results of Mg-MC-800(HCl) and Ca-MC-800(HCl).

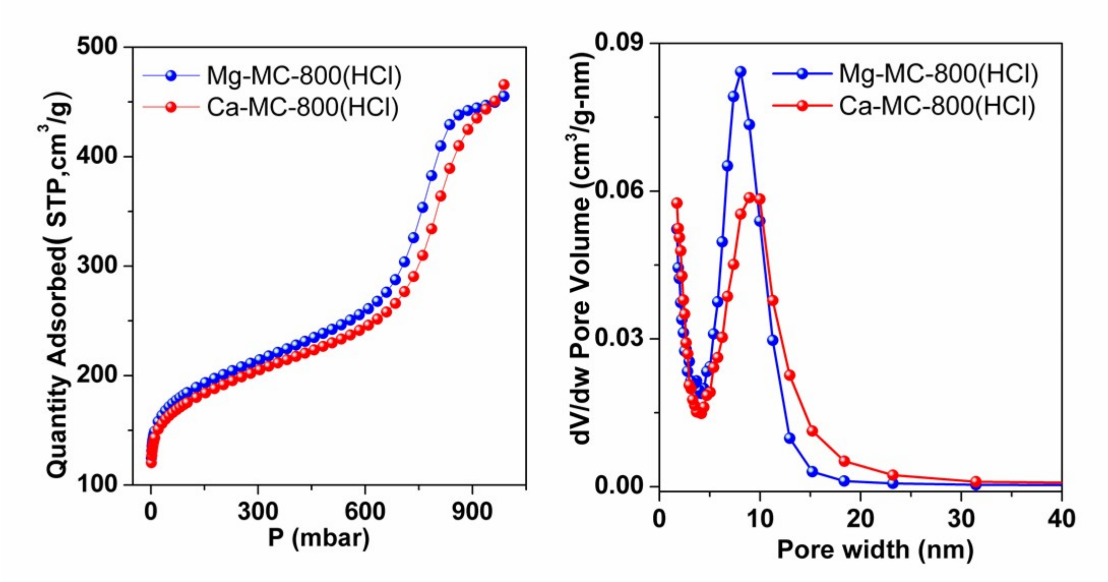

Figure S7. N_2 adsorption isotherms (77K) and Barrett–Joyner–Halenda (BJH) pore size distributions of as-synthesize carbons after the removal of alkaline-metal-oxide NPs.

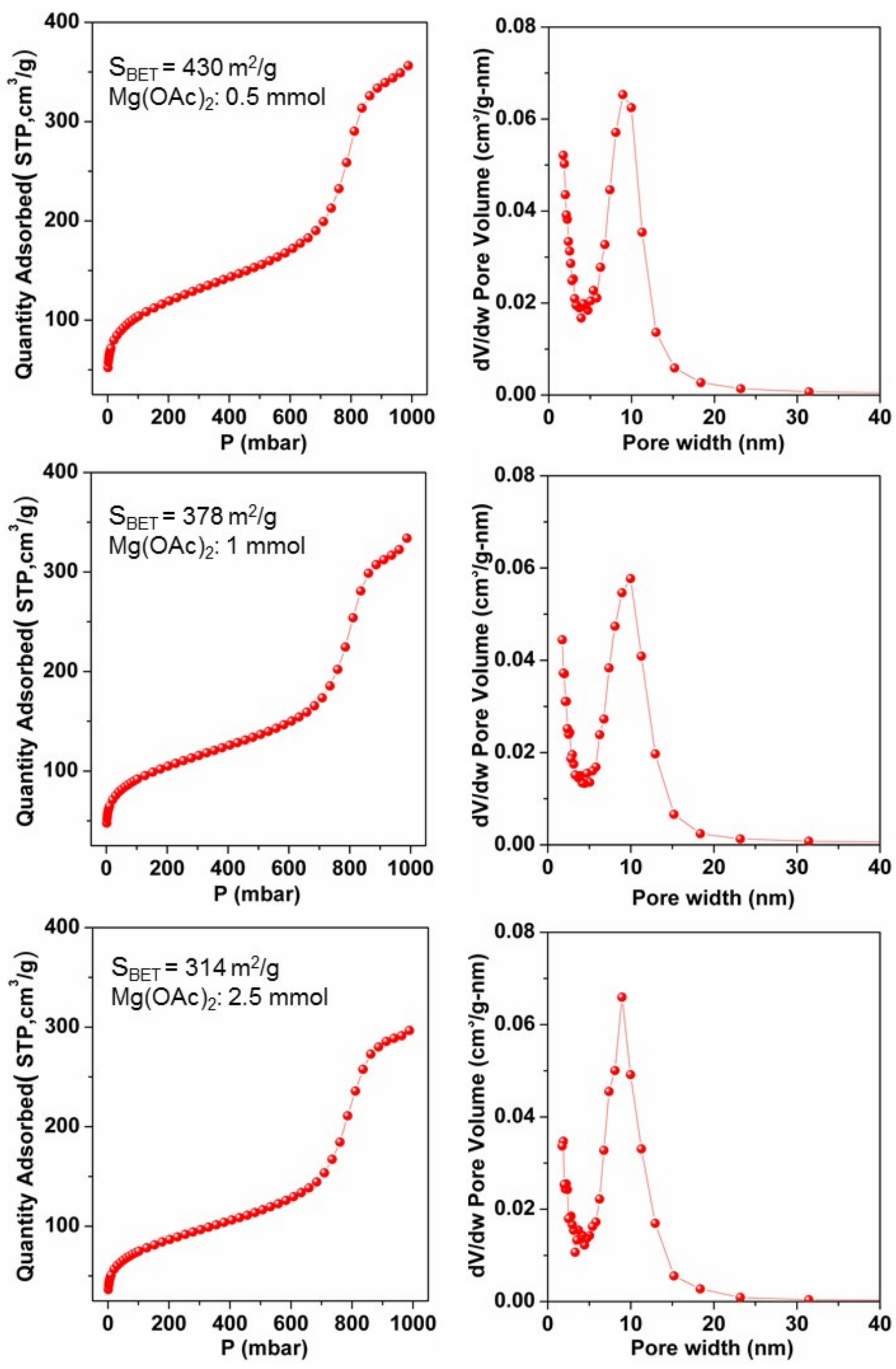

Figure S8. N_2 adsorption isotherms (77K) and Barrett–Joyner–Halenda (BJH) pore size distributions of as-synthesized Mg-OMCs using different amount of $Mg(OAc)_2$.

Table S2. CO2 adsorption capacity of Mg-MCs and Ca-MCs at 273K

Samples	800 ℃		600 ℃		450 ℃	
	0.15bar (mmol/g)	1bar (mmol/g)	0.15bar (mmol/g)	1bar (mmol/g)	0.15bar (mmol/g)	1bar (mmol/g)
Mg-MCs	1.66	2.70	0.96	1.84	0.58	1.24
Ca-MCs	1.24	2.05	0.75	1.41	0.60	1.30
Mg-MC(HCl)	1.47	3.08	-	-	-	-

Table S3. CO2 adsorption capacity of Mg-OMCs and Ca-OMCs at 298K

Samples	800 ℃		600 ℃		450 ℃	
	0.15bar (mmol/g)	1bar (mmol/g)	0.15bar (mmol/g)	1bar (mmol/g)	0.15bar (mmol/g)	1bar (mmol/g)
Mg-MCs	1.20	2.10	0.71	1.45	0.35	0.86
Ca-MCs	0.81	1.54	0.52	1.02	0.37	0.88
Mg-MC(HCl)	0.85	2.16	-	-	-	-

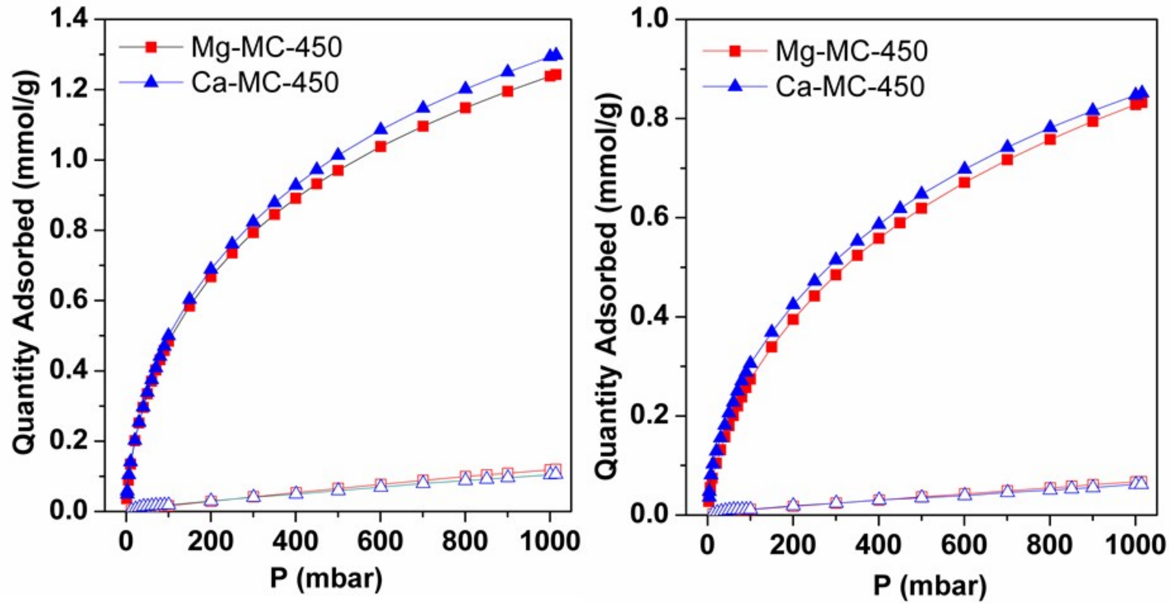

Figure S9. CO_2 (filled symbols) and N_2 (open symbols) adsorption isotherms of synthesized MCs carbonized at 450 ℃ at 0℃ (left) and 25℃ (right).

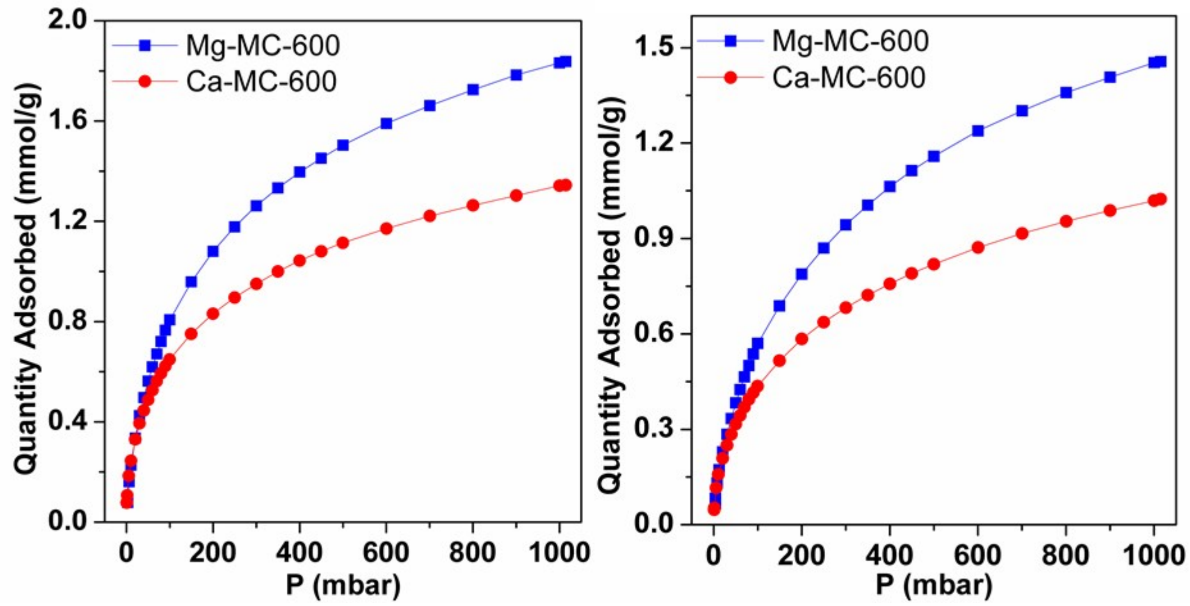

Figure S10. CO_2 adsorption isotherms of synthesized MCs carbonized at 600 ℃ at 0 ℃ (left) and 25℃ (right).

Table S4. Comparison of CO_2 adsorption performance on different adsorbents

sorbents	S_{BET} (m^2/g)	Temperature (℃)	$N(CO_2)$ (mmol/g)		Reference
			0.15 bar	1 bar	
ordered mesoporous carbon	798	25	0.80	1.5	1
CMK-3[a]	1352	30	-	1.6	2
MCM-41[b]	1031	20	0.74	1.0	3
ZIF-8 [c]	1475	25	0.15	0.9	4
MOF-177[d]	4508	25	-	0.8	5
3C-650N	741	25	1.10	2.4	6
PDVB-VP-0.25[e]	489	25	0.82	1.9	7
Carbon-[Bmim-dca][f]	600	25	-	2.2	8
om-ph-MR[g]	256	25	0.84	1.8	9
AC[h]	413	25	0.65	1.7	9
N-OMC[i]	566	25	0.95	2.3	10
Mg-OMC-800	520	25	1.20	2.1	This work
Ca-OMC-800	436	25	0.81	1.5	This work

[a] CMK-3: Mesoporous carbon materials. [b] Amine-tethered mesoporous silica. [c] Zeolite-like imidazole framework (ZIF). [d] metal-organic framework (MOF). [e] Nitrogen-doped porous polymer. [f] N-doped mesoporous carbon. [g] ordered mesoporous phenolic-functionalized melamine resin. [h] Activated carbon (AC). [i] Nitrogen-doped mesoporous carbon.

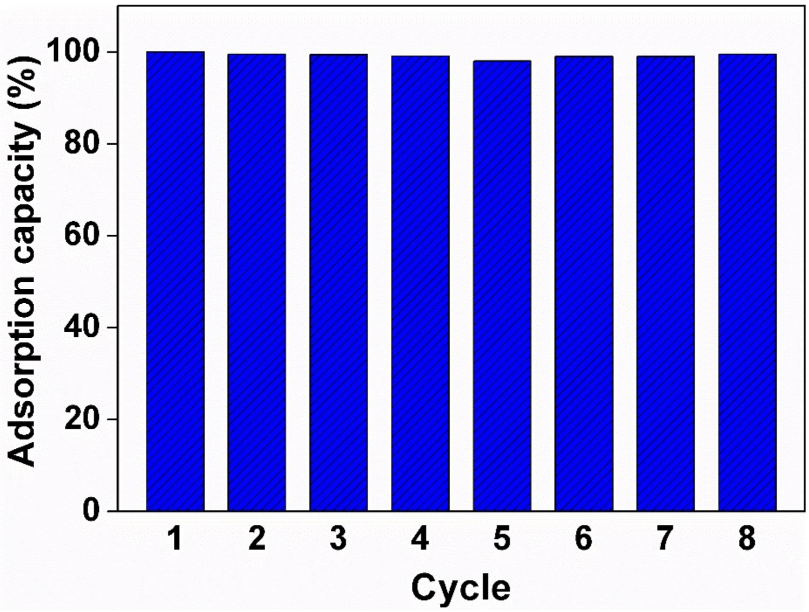

Figure S11. CO_2 adsorption capacity of the Mg-MC-800 sample over eight adsorption-desorption cycles; the isotherms were measured at 0 °C, and desorption process was performed at 473 K for 6 h prior to each measurement.

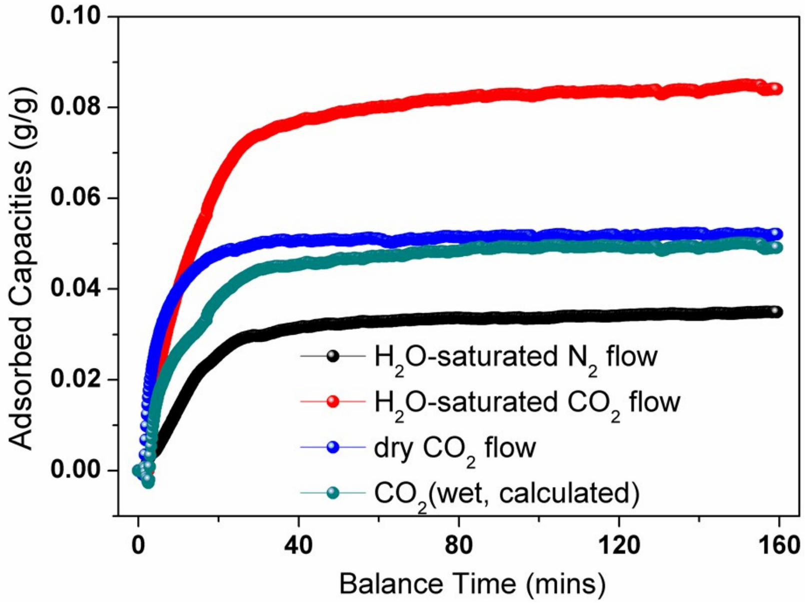

Figure S12. H_2O vapor, dry and wet CO_2 adsorption isotherms of Mg-MC-800 at 323 K, 1 bar. In a typical run, Mg-MC-800 sample was first activated at 150 °C for 3 h and then at 50 °C for 3h under pure dry nitrogen flow (760 mmHg) until no weight change was observed. For H_2O vapor or wet CO_2 adsorption isotherms, dry N_2 or CO_2 was used as carrier gas and effervesced through a vessel filled with deionized water to generate H_2O-saturated N_2 or CO_2 flow. The total gas flow used was controlled at 100 cm^3/min. The results in Figure S12 shows that the H_2O vapor adsorption (water-saturated N_2 flow) increase immediately in the first 20 mins and subsequently reach a plateau (0.03 g/g), and similar adsorption behavior was also observed in the dry and wet CO_2 adsorption isotherms. Notably, compared to dry CO_2 adsorption, the presence of H_2O vapor just slightly lower the CO_2 adsorption capacity (0.050 g/g (wet, calculated) *vs* 0.053 g/g (dry)), indicating that synthesized mesoporous carbon can retain most of its CO_2 adsorption capacities even in the presence of H_2O vapor.

Table S5. Langmuir isotherm parameters of the Mg-MC-800 sample at 298 K.

Dye	Q_e (mg/g)	Q_m (mg/g)	K_L (L/mg)	R^2
Methylene blue (MB)	541	565	0.075	0.994
Methyl orange (MO)	435	446	0.095	0.997

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