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Supporting Information

Energy efficient synthesis of highly ordered mesoporous carbon nitrides with uniform rods and their superior CO_2 adsorption capacity

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1. Experiment-Synthesis of silica template SEW-SBA-15-T and SEW-MCN-1-T

In a typical synthesis, 4 g of non-ionic surfactant Pluronic P-123 which is a triblock copolymer (EO_{20} PO_{70} EO_{20}), Avg. mwt ~5800, Sigma-Aldrich) was added to 30 g of water in a polypropylene (PP) bottle with a cap and the solution was stirred for 4 hr at room temperature followed by the addition of 120 g of 2 M HCl. Simultaneously, the temperature was raised to 40 ^{o}C and the mixture was stirred for 2 hr. After this, 9 g of tetraethyl orthosilicate (TEOS, 98% Sigma-Aldrich) was added and the mixture was stirred for just 20 minutes after which stirring was stopped completely and the sample was left unagitated for the next 24 hr with the temperature in the water bath maintained at 40 ^{o}C. The solution mixture is now transferred to a Teflon lined autoclave and kept in an oven at 100 ^{o}C for 48 hr. The product is filtered in hot and washed three times with water. The filtered product was dried in an oven at 100 ^{o}C for 6-8 hr and then washed twice with ethanol, each time stirred with ethanol for 3 hr at room temperature. Finally filtered sample is dried again in an oven overnight before use. SEW-SBA-15-130 and SEW-SBA-15-150 silica templates were prepared following the above procedure except that autoclaving was done at 130 and 150 ^{o}C respectively. These samples were labelled as SEW-SBA-15-T (where T = 100, 130 and 150 ^{o}C and denotes the hydrothermal temperature).

Mesoporous carbon nitride was prepared using a hard templating approach involving a polymerization reaction between the carbon source CTC (CCl_4) and nitrogen source ethylenediamine inside the mesopores of the ethanol washed silica template material. In a typical synthesis, 0.5 g of SEW-SBA-15-100 was mixed with 3 g of CCl_4 and 1.35 g of EDA in a round bottom flask fitted with water cooled condenser. The mixture was refluxed at 90 ^{o}C for 6 hr under constant stirring. The temperature was increased in steps of 10 ^{o}C from 60 to 90 ^{o}C. After 6 hr, the unreacted CCl_4 and EDA in the composite polymer were removed in rotavapor at 55 ^{o}C. The sample was then dried at 100 ^{o}C for 6 hr and then crushed into powder using a mortar and pestle. The crushed powder was then carbonized in a tubular furnace at 600 ^{o}C for 5h under nitrogen flow. The carbonized sample was then treated with 5% HF and the sample was washed

three times with excess ethanol and then kept for drying at 100 ^{o}C for 6 hr before characterization. The samples were labelled as SEW-MCN-1-T (where T = 100, 130 and 150 ^{o}C) and SEW abbreviated as above.

2. Characterization

The pore tuned silica templates, SEW-SBA-15-T, and the MCN materials, SEW-MCN-1-T (T= 100,130 and 150 ^{o}C), were characterized with low angle powder XRD. The Powder X-ray diffraction measurements were carried out on a *Bruker Advance D8-III* diffractometer using Bragg-Brentano geometry. The measurements were collected on using Cu K_{α} radiation from a sealed tube source operating at 40 kV and 40 mA, a fixed divergence slit of 0.1 ^{o} and a *Lynxeye* multi-pixel detector. The scan rate used was 0.01 ^{o}/sec. Nitrogen adsorption and desorption isotherms were measured at -196 ^{o}C on a Micromeritics ASAP 2420 surface area and porosity analyser. All the samples were degassed for 8 hr at 250 ^{o}C under a vacuum ($p < 1 \times 10^{-5}$ pa) in the degas port of the adsorption analyser. The specific surface area was calculated using the standard BET model. Pore size distribution was obtained from the adsorption branches of the nitrogen isotherms using the BJH model.

The structural morphology of SEW-MCN-T samples was observed in JEOL FE-SEM 7001. The sample preparation for HR-SEM was involved sprinkling of a small quantity of powder sample on the carbon tab. The stub is kept in a vacuum oven at 70 ^{o}C for 7 hr before insertion into the SEM. The samples were coated with 5 nm layer of Iridium using Baltek coater using a nominal current of 15.5 mAps and coating time 60 sec. The HR-TEM images were taken using Tecnai F20 FEG TEM equipped with EDAX EDS and Gatan Image Filter (GIF). The preparation of the samples for HR-TEM imaging involved dissolution of a very small quantity about 10-15 mg of the sample in ethanol followed by sonication for 5-8 min. One drop from micro pipette is dropped on the holey carbon film supported on a copper grid and dried in open air before insertion in the TEM machine.

X-ray photoelectron spectroscopy was carried out using a Kratos Axis ULTRA X-ray Photoelectron Spectrometer incorporating a 165 mm hemispherical electron energy analyser.

Survey and multiregion spectra were recorded at C_{1S} and N_{1S} photoelectron peaks. Each spectra region of photoelectron of interest was scanned several times to obtain good signal to noise ratios. The spectrometer used had the following operating configuration. The incident radiation was Monochromatic Al Kα X-rays (1486.6 eV) at 225 W (15 kV, 15 ma). Survey (wide) scans were taken at analyser pass energy of 160 eV and multiplex (narrow) high resolution scans at 20 eV. Survey scans were carried out over 1200-0 eV binding energy range with 1.0 eV steps and a dwell time of 100 ms. Narrow high-resolution scans were run with 0.05 ev steps and 250 ms dwell time. Base pressure in the analysis chamber was $1.0x10^{-9}$ torr and during sample analysis $1.0x10^{-8}$ torr. Atomic concentrations were calculated using the CasaXPS version 2.3.14 software and a Shirley baseline with Kratos library Relative Sensitivity Factors (RSFs). Peak fitting of the high-resolution data was also carried out using the CasaXPS software.

High pressure CO_2 adsorption was carried out on Quanta chrome Isorb HP1 equipped with temperature controlled circulator. The CO_2 adsorption was carried out at 30 bar and different analysis temperatures of 0, 10 and 25 ^{o}C were used. Prior to CO_2 adsorption, samples were degassed for 10 hr at 250 ^{o}C. The isosteric heat of adsorption was calculated using Clausius-Clapeyron equation.

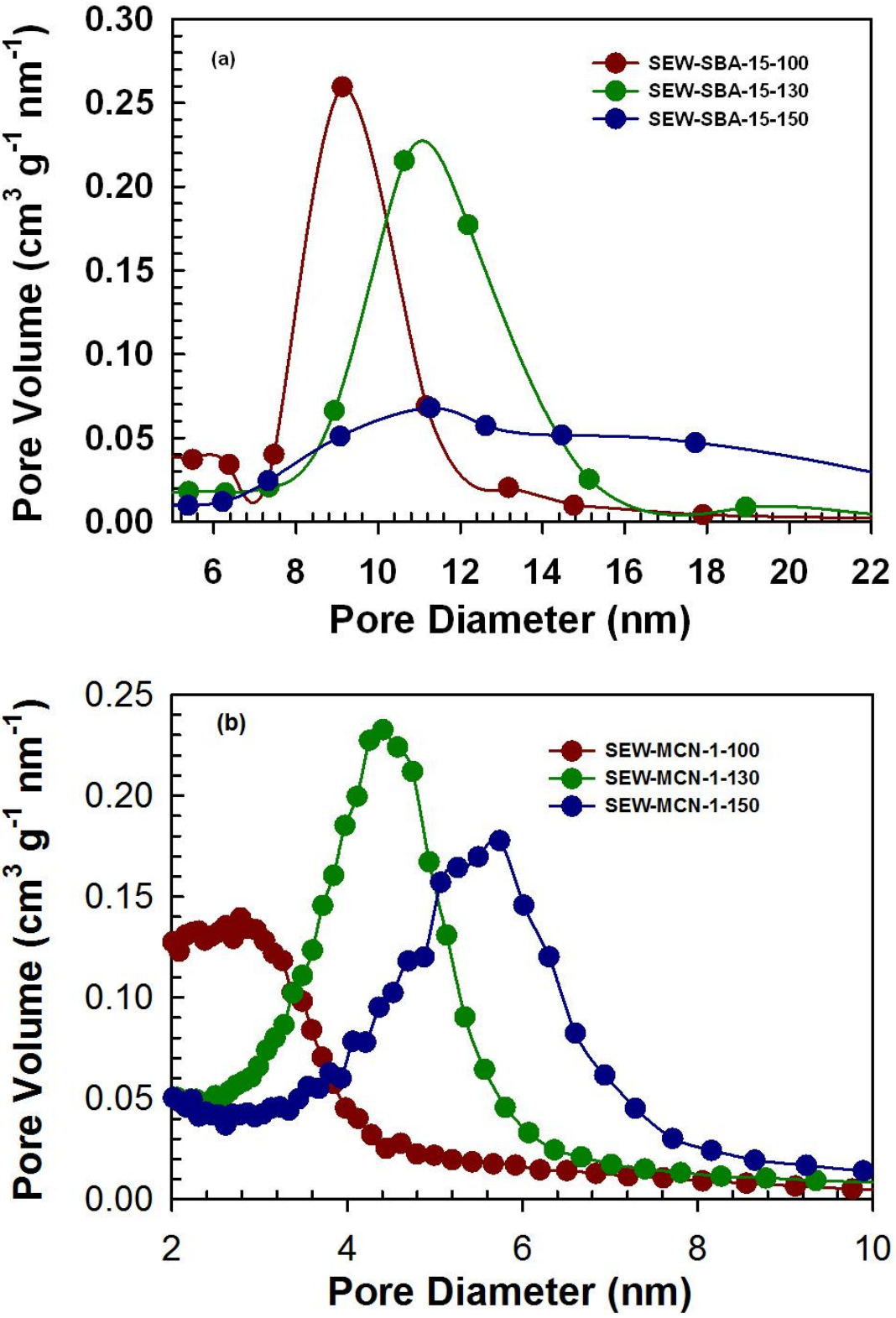
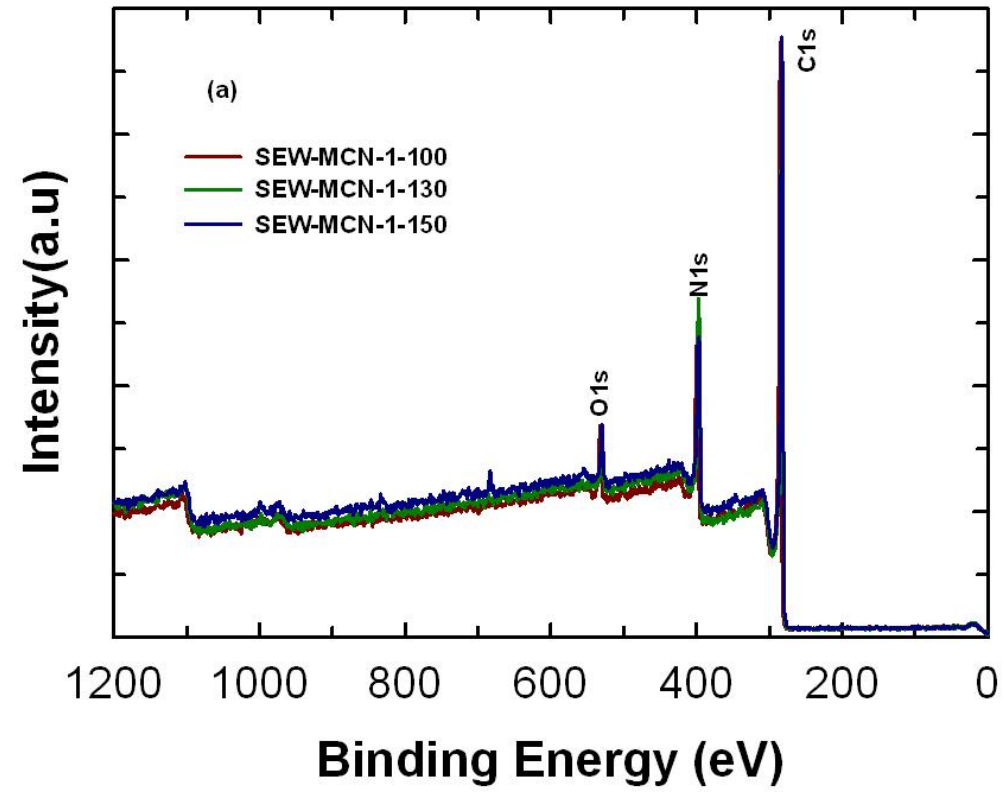
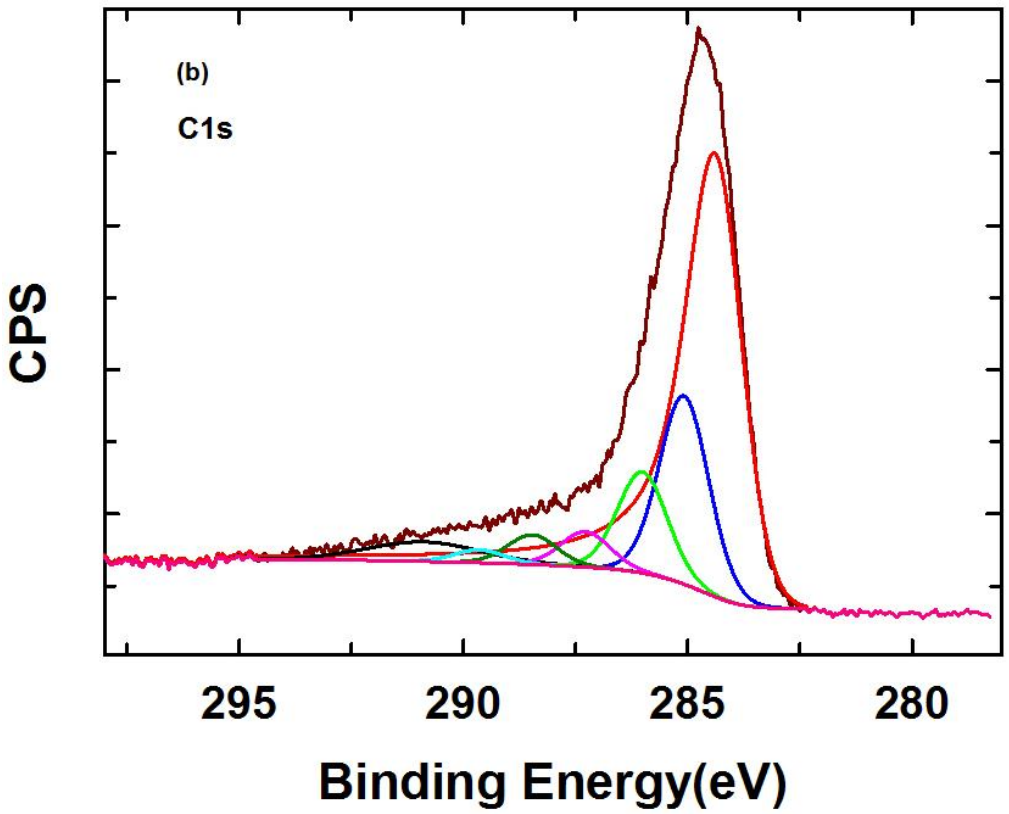


Figure 1S. Pore size distribution plot obtained from the adsorption branch of nitrogen adsorption isotherm: (a) SEW-SBA-15-T and (b) SEW-MCN-1-T.


(a)
SEW-MCN-1-100
SEW-MCN-1-130
SEW-MCN-1-150
C1s
N1s
O1s
Intensity(a.u)
1200
1000
800
600
400
200
0
Binding Energy (eV)


(b)
C1s
CPS
295
290
285
280
Binding Energy(eV)

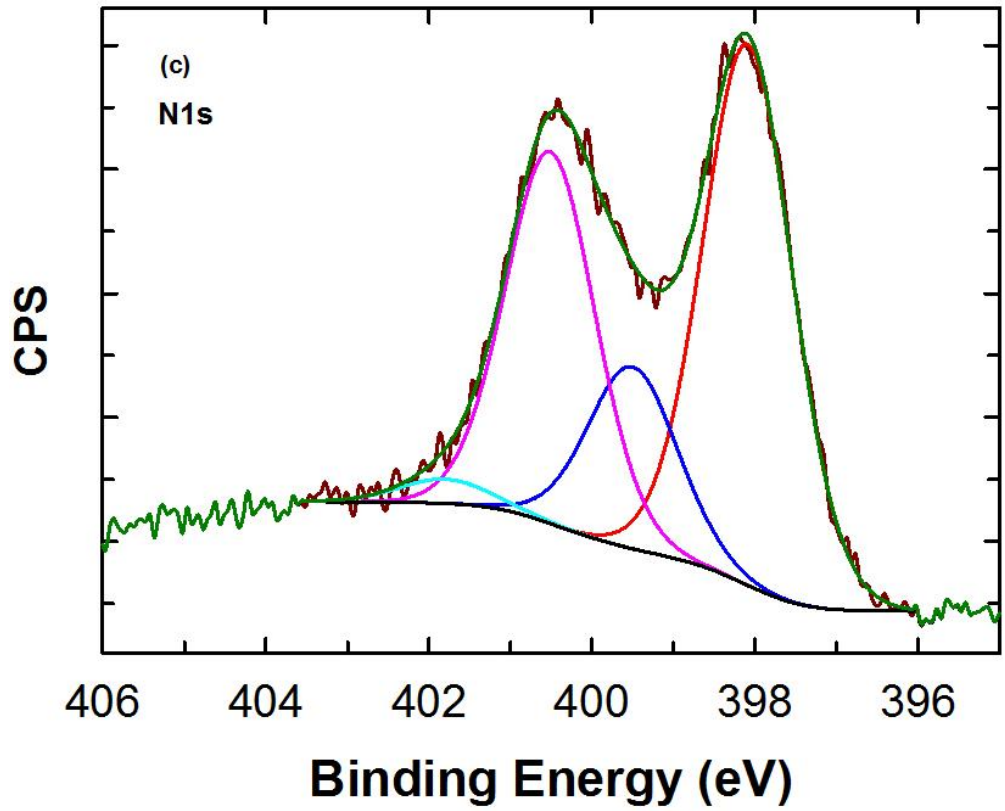
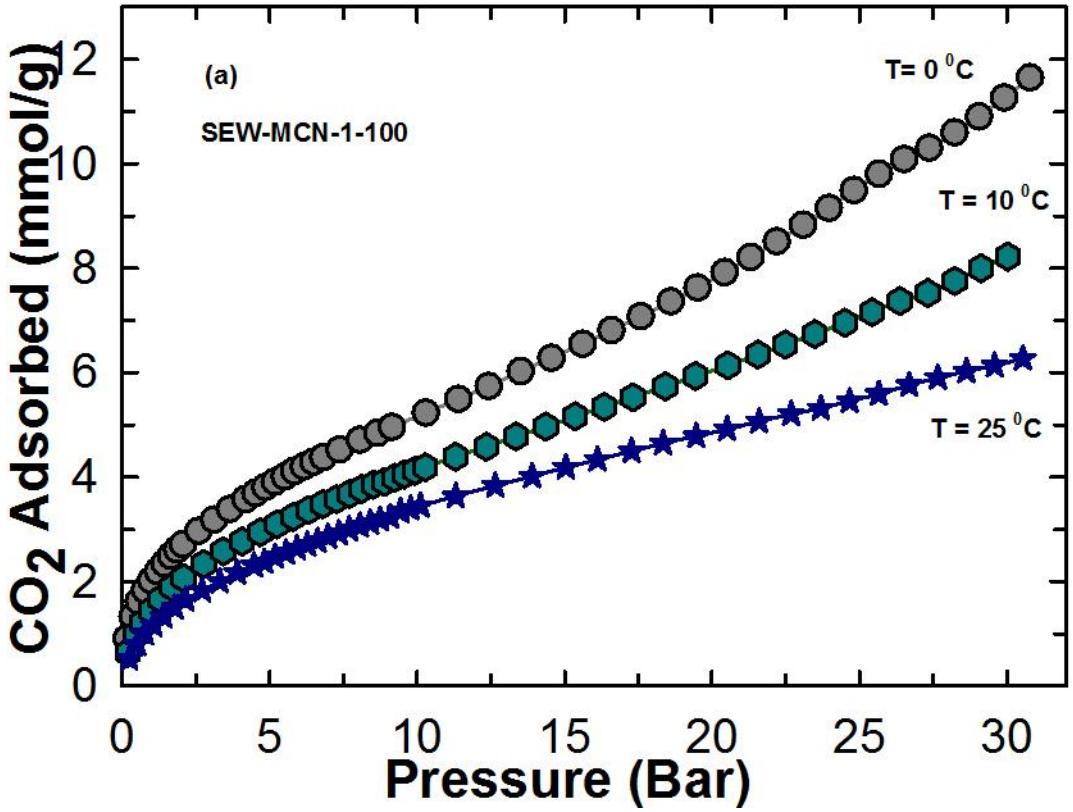
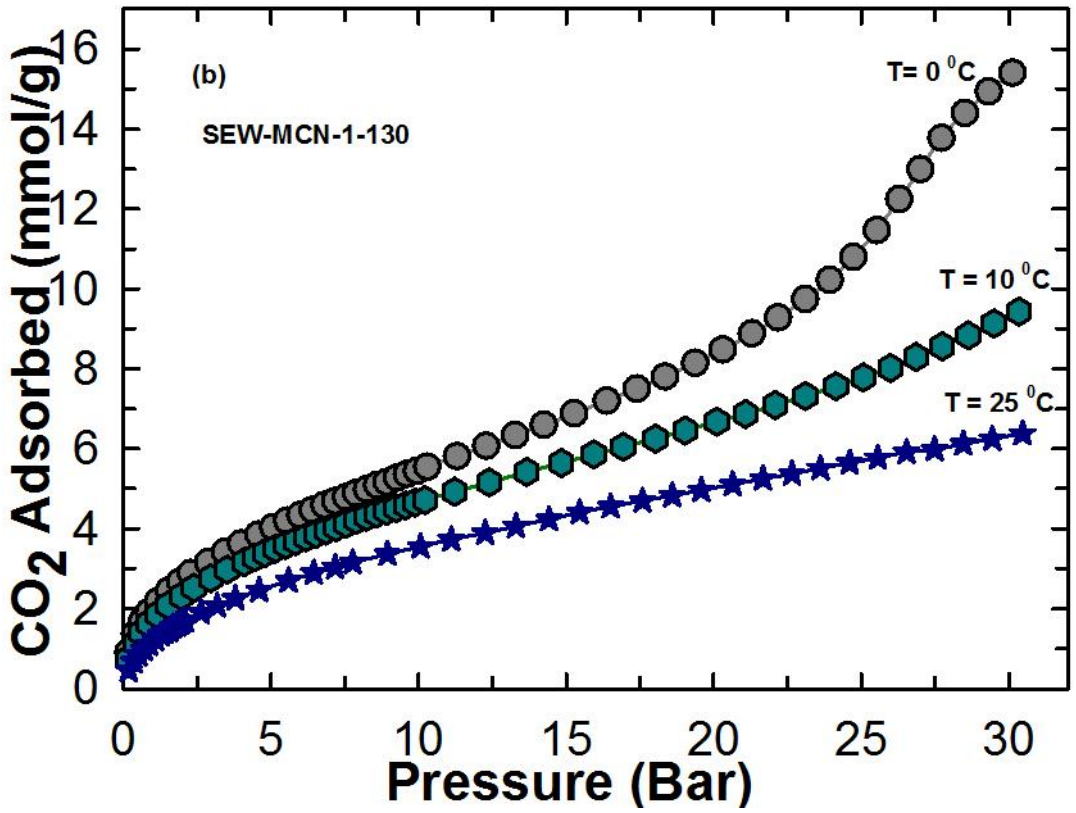


Figure 2S. (a) Survey spectra of SEW-MCN-1-T samples, (b) high resolution C1s spectrum of SEW-MCN-1-130 sample, and (c) high resolution N1s spectrum of SEW-MCN-1-130 sample.


(a)
SEW-MCN-1-100
T= 0 ^{0}C
T = 10 ^{0}C
T = 25 ^{0}C
CO_2 Adsorbed (mmol/g)
Pressure (Bar)
0
2
4
6
8
10
12
0
5
10
15
20
25
30


(b)
SEW-MCN-1-130
T= 0 ^{0}C
T = 10 ^{0}C
T = 25 ^{0}C
CO_2 Adsorbed (mmol/g)
Pressure (Bar)
0
2
4
6
8
10
12
14
16
0
5
10
15
20
25
30

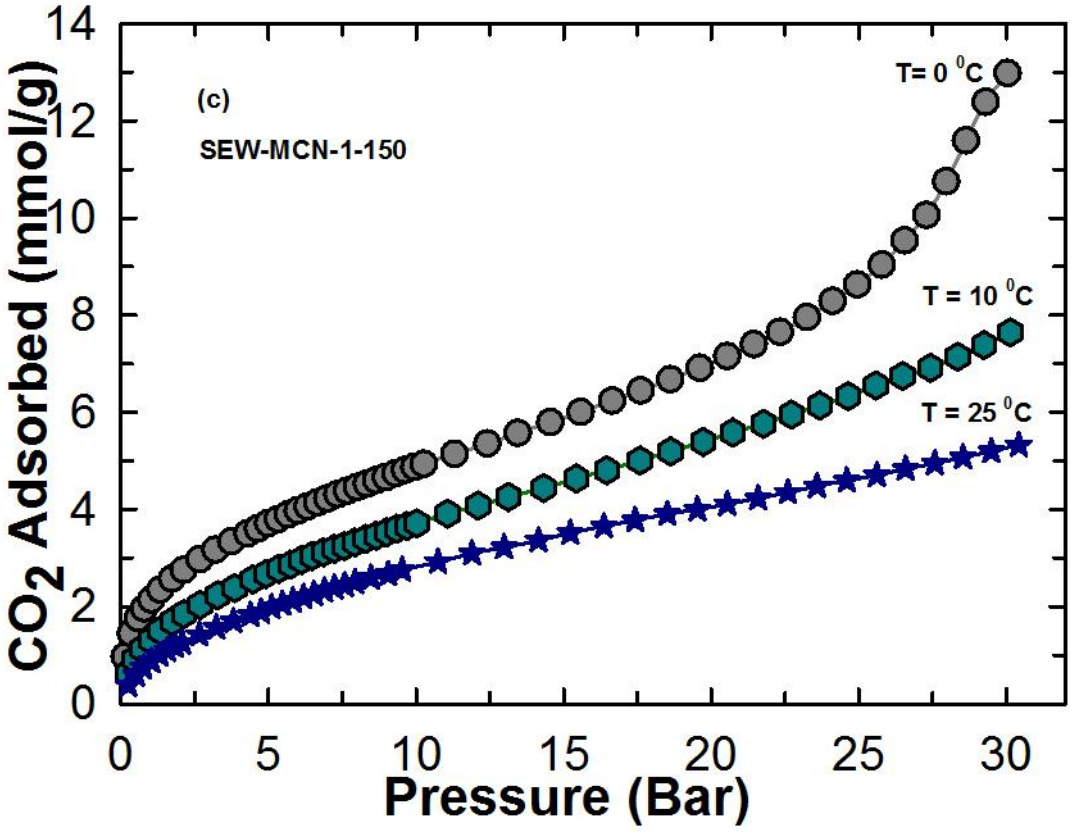


Figure 3S. CO_2 adsorption isotherms of (a) SEW-MCN-1-100, (b) SEW-MCN-1-130, and (c) SEW- MCN-1-150.

Sample	a_0 (nm)	PD (nm)	t^* ($a_0 - P_D$) (nm)
SBA-15-100C	10.63	8.4	2.23
SBA-15-130C	11.32	11.25	0.07
SBA-15-150C	11.74	11.29	0.45
SEW-SBA-15-100	12	9.12	2.88
SEW-SBA-15-130	11.7	10.5	1.2
SEW-SBA-15-150	11.5	11.2	0.3
MCN-1-100C	10.38	3.76	6.62
MCN-1-130C	11.16	4.99	6.17
MCN-1-150C	11.32	5.94	5.38
SEW-MCN-1-100	10.9	2.8	8.1
SEW-MCN-1-130	10.6	4.4	6.2
SEW-MCN-1-150	11.8	5.7	6.1

SI Table 1S. Comparison of the wall thickness of different materials

*t is the calculated wall thickness for a hexagonal p6mm symmetry.

SI Table 2S. Atomic compositions of SEW-MCN-1-T samples from XPS and CNS analysis.

Sample	XPS (surface atomic composition)			CNS (bulk composition)	
	C (%)	N(%)	O(%)	C	N
SEW-MCN-1-100	79	17.12	3.89	61.7	18.6
SEW-MCN-1-130	79.32	17.74	2.94	64.6	17.7
SEW-MCN-1-150	76.87	20.45	2.68	62.8	21.4

SI Table 3S. CO_2 adsorption capacities of SEW-MCN-1-T samples at different temperatures and 30 bar pressure.

Sample	CO_2 adsorption capacity(mmol/g)		
	0 ^oC	10 ^oC	25 ^oC
SEW-MCN-1-100	11.6	8.2	6.2
SEW-MCN-1-130	15.4	9.4	6.4
SEW-MCN-1-150	13	7.6	5.3

SI Table 4S. Isosteric heat of adsorption of SEW-MCN-1-T samples and its comparison with other materials.

Sample	Isosteric heat of adsorption[a] (kJ/mol)
SEW-MCN-1-100	38.61 – 19.96
SEW-MCN-1-130	34.44 – 22.21
SEW-MCN-1-150	60.99 – 24.40
MCN-1-100s	31.1 – 22.0[14]
MCN-1-130s	27.9 – 16.3[13]
MCN-1-150s	54.9 – 22.3[13]
MCN-7-130	34.9 – 24.0[3]

SI Table 5S. Area normalized CO_2 adsorption capacity of SEW-MCN-1-T samples**.**

Sample Code	BET S.A (m^2/g)	CO_2 Adsorption (mmol/g) at 273K	% N content	CO_2 Adsorption/ BET S.A (umol/m^2)
SEW-MCN-1-100	557	11.6	17.12	20.8
SEW-MCN-1-130	655	15.4	17.74	23.5
SEW-MCN-1-150	638	13.0	20.45	20.3