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Supercritical Fluid Growth of Porous Carbon Nanocages

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Abstract

Carbon nanocages, with remarkably large mesoporous volumes, have been synthesised by the deposition of p-xylene over a Co/Mo catalyst in supercritical carbon dioxide. Nanocages with diameters ranging between 10 to 60 nm were synthesised at temperatures between 650 to 750 ^{o}C. The surface area and pore volume of the nanocages produced was found to depend on the reaction temperature and pressure employed. In particular, carbon nanocages with a pore volume of up to 5.8 cm^3 g^{-1} and a BET surface area of 1240 m^2 g^{-1} were readily synthesised at a temperature of 650 ^{o}C and pressure of 10.34 MPa. The high pore volume and surface area of the carbon nanocages synthesised makes them ideal materials for use as inert adsorbents and catalytic supports.

Introduction

High purity carbon-based materials, including nanohorns, nanorods, nanofibers and nanocages, have a number of potential uses including their application in electrical and thermal devices, as adsorbent and storage media, including H_2 storage, and as catalytic supports due to their unique chemical and physical properties.[1-9] The discovery of carbon nanohorns was first reported by Iijima et al.[10] in the soot produced by the laser ablation of graphite. Recently, Saito and Matsumoto [11] synthesized multi-walled graphitic carbon nanocages (CNCs), with between 5 to 20 layers of carbon, in a helium atmosphere using a direct-current arc discharge method employing an alkaline-earth metal catalyst, such as calcium or strontium. Small quantities of CNCs have also been produced by the thermal reduction of ethanol in a closed autoclave.[12] Cage-like carbons have also been fabricated by a template method where carbon shells encapsulated with Fe particles were first generated by laser-induction complex heating evaporation, followed by removal of the catalyst with an inorganic acid.[13] However, CNCs produced by these methods are generally only present as the by-product of carbon nanotube formation and a complex post-treatment process is often required to isolate the CNCs from the nanotubes.

Supercritical fluid (SCF) processes have been used to synthesize a number of nanoscale materials, including Si and Ge nanowires, nanorods and carbon nanotubes, due to their unique and tunable properties.[14-19] In particular, the high penetrating power and negligible surface tension of SCFs have been successfully utilized to deposit ordered mesoporous carbon nanofilaments within the pores of mesoporous silica templates.[20] In this paper, we report for the first time the formation of CNCs, with large mesopore volumes, as the major product from a SCF deposition process. p-Xylene was used as the carbon source and decomposed over a

Co/Mo catalyst, supported on MgO, in supercritical carbon dioxide (sc-CO_2) to form CNCs. The BET surface area, and pore volume of the CNCs synthesised was found to depend on the reaction temperatures and pressures employed.

Experimental

CNCs were synthesised by the catalytic decomposition of p-xylene over a MgO supported Co and Mo catalyst. Briefly, MgO was prepared by the decomposition of $Mg_2(OH)_2CO_3$ at 450 ^oC for 6 hr.[21] An aqueous solution of $Co(NO_3)_2.6H_2O$ and $(NH_4)Mo_6O_{24}.H_2O$ were mixed with the MgO support, followed by sonication for 30 minutes and drying. The dried precursor powder was sintered at 500 ^oC for 6 hr. In a typical SCF deposition experiment, a quartz boat containing 0.5 g MgO supported 3 wt.% Co and 4 wt.% Mo catalyst was placed in the centre of a high pressure stainless steel reactor (Inconel 625 GR2- Snap-tite, Inc.). The catalyst was then heated in a reducing atmosphere of H_2/Ar (V/V=20/180 ml min^{-1}) at a flow rate of 200 ml min^{-1} for 30 min. p-Xylene was first added into a 450 ml stainless steel reservoir and charged with CO_2 at 40 ^oC. The gaseous mixture was maintained above the critical temperature and pressure of CO_2 (T_c =31 ^oC, P_c = 7.38 MPa) at 40 ^oC in a temperature controlled water bath. A flow through system was established by connecting the inlet and outlet valves of the carbon source reservoir, which included a piston, to a 260-ml ISCO syringe pump (Lincoln, NE) and the reaction vessel respectively. A back pressure regulator maintained the system at constant pressure and controlled the flow rate of the p-xylene/CO_2 mixture through the system. The reaction time was 1 hr. When the experiment had finished, the reactor was cooled to room temperature under an Ar flow and the powder was treated with 6M HNO_3.

Transmission electron microscopy (TEM) was performed on a JEOL 2000FX microscope operating at 200 kV and high-resolution TEM images were recorded on a JEM 2010 microscope operating at 200 kV. The TEM samples were prepared by dispersing the samples onto copper grids. Scanning electron microscopy (SEM) was conducted on a LEO 530 scanning microscope.

The resulting CNCs were characterized by nitrogen adsorption at -196 ^{o}C using a Quantachrome Autosorb-1 analyzer. Before measurement, all samples were degassed at 200 ^{o}C for 6 h. The surface area was calculated using the BET method based on the adsorption data in the relative pressure (P/P_0) of 0.05-0.2. Single-point pore volume was evaluated by converting the amount adsorbed at p/p_o=0.99 to the volume of liquid nitrogen. Pore size distribution (PSD) was calculated by using the Kruk-Jaroniec-Sayari (KJS) method, which employs the BJH algorithm together with Kelvin-type relation calibrated for cylindrical mesopores using MCM-41 silicas,[22] and the statistical film thickness established for the carbon black surface.[23] Adsorption branches of the isotherms were used for the calculation of PSD curves for the carbons studied. Integration of the PSD curves up to 4 nm and from 4 to 60 nm was used to estimate the volumes of fine pores and primary mesopores, respectively. In addition, the α_s-plot analysis[24] was used to estimate the volume of micropores, i.e., pores with widths below 2 nm. In the latter analysis, nitrogen adsorption isotherm on Cabot BP280 nongraphitized carbon black was used as the reference isotherm.[25]

X-ray diffraction (XRD) analysis of the carbons was carried out using a Philips X'Pert PW3207 diffractometer equipped with a Cu K_a source. Raman spectra were recorded on a Renishaw 1000 Raman system in an ambient atmosphere using a 5 mW He-Ne laser (λ = 514.5 nm) and a CCD detector. Thermogravimetric analysis (TGA) of the carbon sample was

performed at a heating rate of 10 ºC min^{-1} up to 900 ºC in air flow of 75 ml min^{-1}.

Near Edge X – ray Absorption Fine Structure (NEXAFS) measurements were carried out at the PM-3 beam-line of the BESSY Synchrotron Radiation Facility in Germany. Thin films of nanocages were prepared by dropping drying iso-propanol suspension of material onto a gold coated silicon substrate. The sample was introduced into the ultrahigh vacuum experimental chamber and treated with rapid annealing cycles of 2 min at increasing temperatures up to a maximum temperature of 700 °C. After each annealing cycle NEXAFX spectra at the carbon K edge were measured. The data were acquired using surface sensitive total-electron yield TEY mode and were normalized to the signal from a gold-covered grid recorded simultaneously. The angle of incidence (the angle between the sample surface and the X-ray beam of the light beam) was kept at 45°. After subtracting the respective ionization jumps at both C K and O K edges, the resulting spectra were decomposed into several Gaussian peaks.

Results and discussion

Figure 1 shows TEM images of the as-synthesized carbons formed at different temperatures and pressures. At a reaction pressure of 10.34 MPa, amorphous carbon is formed at 600 ºC (figure 1a), while cage-like carbons are produced when the temperature is increased to 650 ºC (figure 1b-1d). The diameters of these cage-like carbons range in size from 10 to 60 nm for the samples prepared over a temperature range from 650 to 750 ºC. HRTEM images reveal that the walls of the carbon cages prepared at 700 ºC are very thin and are composed of a curved carbon structure consisting of 5 to 10 layers. It should be noted that similar cage-like carbon were produced although p-xylene/CO_2 with different molar ratios ranging from 0.13 % to 1.3 % were used.

Information on the electronic structure of the CNCs prepared at 700 ^{o}C, was provided by NEXAFS analysis of the core level excitations from the C1s level. The measured core edge structure in the NEXAFS spectra corresponds directly to electronic C 1s transitions into unoccupied states with π^* ($1s\rightarrow\pi^*$) and σ^* ($1s\rightarrow\sigma^*$) character. Figure 2a compares the NEXAFS spectra of CNCs at various temperatures and HOPG (highly oriented pyrolitic graphite). CNCs were deposited on a gold coated Si substrate. Similar to graphite, the CNC spectrum at RT exhibits a smooth edge, consistent with a disordered sp^2 matrix. Moreover the splitting of the C1s π^* peak, observed in the $1s\rightarrow\pi^*$ pre edge region (284.1-284.4 and 286 eV), indicates the presence of two unequal sp^2 carbons, with the lower energy peak attributed to a sizeable density of distorted sp^2 bonds.[26,27] The feature at 288.5 eV in the CNC spectra has been assigned to the presence of hydrogen and oxygen functional groups included in the nanocages after incomplete pyrolysis of the hydrocarbon precursor and reaction of carbon with CO_2. With increasing temperature, up to 700 ^{o}C, the band diminishes significantly due to out-diffusion of oxygen and hydrogen. The low energy $1s\rightarrow\pi^*$ pre-edge structure (284.1-284.4 eV) associated with distorted sp^2 bonds diminishes with increasing temperature, but remains in the spectrum highlighting the presence of some residual disordered phase. The CNC structure can be described as a predominantly sp^2 hybridized carbon network co-existing with a sizable amount of amorphous carbon (distorted sp^2 bonds), and minor sp^3 phase related to the presence of oxygen and hydrogen.

Figure 2b shows the room temperature oxygen K-edge NEXAFS spectrum of a CNC sample in the energy region from 520 to 560 eV. The spectrum contains two characteristic peaks, one at 532.5 eV, which is assigned to a π^* C=O transition and broader asymmetric peaks at 537.5-542.6 eV, associated with σ^* C–O resonances.[28] The formation of oxygen-contained groups

in the carbon is attributed to the reaction between CO_2 molecule and the carbon formed by p-xylene decomposition.

Figure 3 shows SEM images of the CNCs prepared by SCF deposition. The results clearly indicate that these carbon samples are constructed of dense spherical carbon particles. The diameter of CNCs prepared at 700 ^oC and 10.34 MPa is between 10-60 nm. Cage-like carbons are also produced at higher pressures, up to 24.12 MPa. In particular, no obvious morphological difference was found between the two samples by SEM, suggesting that SCF technique is a reproductive technique for the formation of cage-like carbons.

N_2 adsorption–desorption isotherms of the CNCs prepared at different temperatures and pressures are shown in figure 4. The isotherms for the resulting carbons are type IV with capillary condensation steps located in the range of P/P_0 from ~0.48 to 0.99, suggesting the presence of large-size cages. The pore size distributions for the CNCs studied, determined by the KJS method,[22] from adsorption branches of the isotherms, reveal the presence of fine pores, with a mean diameter of about 2.3 nm and large mesopores, with a mean diameter of approximately 20 nm, probably arising from the inter-particle space between and inside the CNCs (Table 1). This is in a good agreement with the TEM results which show the presence of cages with sizes of about 20 nm. Aggregation of these cages affords materials analogous to mesoporous carbons.

Table 1 shows the pore characteristics of the carbons produced at different temperatures and pressures. The α_s-plot analysis of nitrogen adsorption isotherms for the CNCs prepared within temperature range from 650 ^oC to 750 ^oC, and at 10.34 MPa almost does not show micropores, i.e., pores below 2 nm, for the CNCs studied except carbon prepared at 700 ^oC and 24.12 MPa; however, the PSD analysis shows the presence of small mesopores in CNCs, the volume of

which varies depending on the synthesis conditions. It seems that high reaction pressures and lower temperatures favour the formation of fine pores in the shells of CNCs.

With increasing temperature, under the same reaction pressure, the CNCs produced exhibit a decreasing surface area. For example, the BET surface areas of CNCs prepared at 650 ^{o}C, 700 ^{o}C, 750 ^{o}C and 10.34 MPa are 1240, 698 and 680 m^2 g^{-1}, respectively. The highest total pore volume, up to 5.84 cm^3 g^{-1}, was obtained for CNCs prepared at 650 ^{o}C. However, high reaction pressures of 24.12 PMa increase the surface area and microporosity; the latter reaches volume of about 0.2 cm^3 g^{-1}. This result is possibly due to decomposition rates of the carbon precursor as a function of temperature and pressure.[19,29] Korgel et al. [19] suggested that toluene is stable even at 600 ^{o}C without using a catalyst in the reaction, while the pyrolysis rate of toluene was promoted at elevated temperatures and carbon was produced when Fe or Fe/Pt catalyst was added into the reaction.

In the reaction, p-xylene pyrolysis occurred on the surface of metal nanoparticles of catalyst when temperature was higher than 650 ^{o}C, where formed hydrocarbon species may move to the surface of support and covered the support. After the removal the catalyst particles using HNO_3, empty cage-like carbons are finally left. Additionally, CO_2 may interact with support MgO to form $MgCO_3$ in the reaction. However, the bulk $MgCO_3$ phase is unstable at high temperature and easily decomposes again into MgO and CO_2 at temperatures higher than 660 ^{o}C at 0.1 MPa. Thus, it is expected that the production and decomposition of the $MgCO_3$ at high temperatures result in the size difference of the supported catalyst. It should be noted that the Y zeolite supported Co/Fe metals were also investigated as the catalysts for the formation of CNCs, but only non-structured carbons were produced instead of nanocages. Hence, the catalyst also plays a key role in the formation of CNCs.

All of the CNCs produced at different conditions exhibit two characteristic Raman peaks at approximately 1345 and 1595 cm^{-1} corresponding to the D- and G-bands of polycrystalline graphite, as shown in figure 5. In contrast, only one peak at 1580 cm^{-1} is observed for graphite. The D-band is attributed to defects, curved graphite sheets and lattice distortions in carbon structures and the G-band is characteristic of graphite.[30,31] Therefore, the shifted G-band and broad D-band centred at approximately 1345 cm^{-1} indicates the presence of defects in the as-prepared CNCs when compared to that of graphite. This is consistent with the results obtained from HR-TEM images (figure 1e). The ratio of these peaks, in the range of G/D = 45/55, indicates that CNCs formed exhibit a rather defective structure, which is quite common for carbon products prepared by catalytic chemical vapor deposition (CCVD).[32,33] The cause of the disordered structure can possibly be attributed to the etching of carbon by sc-CO_2 during the reaction, as well as by incomplete conversion of non-organised carbon into graphitic structures over the supported Co/Mo catalyst at the employed temperatures.[32]

Figure 6 shows XRD patterns of the synthesized CNCs formed at different temperatures and under different pressures. XRD patterns in figure 5a clearly show two peaks at about $2\theta = 26^{o}$ and 44^{o}, corresponding to the (002) and (100) diffraction peaks of graphite for the four samples prepared at temperatures of 650 and 750 ^{o}C and pressures of 10.34 and 24.12 MPa.[35,36] The position of the carbon peak at $2\theta = 26^{o}$, prepared at 750 ^{o}C, shifts to a narrower angle, $2\theta = 24.6^{o}$, compared to that of the CNCs synthesized at 650 ^{o}C, where a broad peak is observed. At 750 ^{o}C, the spacing between planes of carbon d(002) is about 0.341 nm, which is smaller than that of carbon synthesized at 650 ^{o}C with a plane space of 0.362 nm. The appearance of broad peaks and peaks shifting to a wider angle indicates that the amorphous structure of the as-synthesized samples are present in CNCs synthesized at 650 ^{o}C and

somehow become more ordered upon synthesising at a high temperature. The effect of pressure on the structure of the CNCs formed at 700 ^{o}C was also investigated, but no shift in the peak position was observed, indicating that temperature is the main factor in determining the structure of the as-produced carbons.

Figure 7 shows the TGA data measured for two samples prepared at 650 ^{o}C and 750 ^{o}C under a CO_2 pressure of 10.34 MPa. The weight loss of the sample in air occurs at about 450 °C and continues to about 600 ^{o}C. Comparing curves A and B, an increase in temperature of 110 ^{o}C is observed in curve B, indicating that a more crystalline structure is favoured at higher temperature. Additionally, the residues of the two carbon samples prepared at 650 ^{o}C and 750 ^{o}C are about 3.7 and 5.5 % respectively, possible due to carbon encapsulation of catalyst particles.[37,38]

Conclusions

In summary, we have demonstrated the formation of CNCs with large pore volumes and high specific surface area using a SCF technique. CNCs with a surface area as high as 1240 m^2 g^{-1} and a pore volume of up to 5.8 cm^3 g^{-1} were prepared at 650 ^{o}C. The pore size and pore volume of the CNCs could readily be controlled by changing the reaction temperature or pressure. The nanocage structure contains extended sp^2 co-ordinated domains with a sizeable degree of amorphous carbon. NEXAFS studies of the oxygen K-edge confirmed the presence of π^* and σ^* transitions, corresponding to C=O and C–O oxygenated groups on the surface of CNCs, respectively.

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Table 1 Adsorption characteristics of the CNCs prepared at various temperatures and pressures.

Carbon	Temperature (°C)	Pressure (MPa)	S_{BET} (m^2g^{-1})	V_t (cm^3g^{-1})	V_s (cm^3g^{-1})	V_{me} (cm^3g^{-1})	W_{me} (nm)	W_s (nm)	Vα (cm^3g^{-1})
1	650	10.34	1240	5.84	0.16	3.9	9-20**	2.5	~0
2	700	10.34	698	3.70	0.06	2.48	19.5	2.3-3.3*	~0
3	750	10.34	680	3.64	0.06	2.40	19.5	2.4	~0
4	700	24.12	1087	2.43	0.33	1.26	16.7	2.3	0.20

* no distinct maximum; flat maximum between 2.3-3.3 nm

** no distinct maximum; flat maximum between 9-20 nm

V_t : single-point total pore volume obtained by converting the amount adsorbed at p/p_o=0.99 to the volume of liquid nitrogen

V_s : pore volume obtained by integration of the PSD curve up to 4 nm

V_{me}: pore volume obtained by integration of the PSD curve from 4 nm to 60 nm

W_{me}: pore width at the maximum of PSD in the range between 4 nm and 60 nm

Ws: pore width at the maximum of PSD in the pore range below 4 nm

Vα: micropore volume calculated by α_s-plot method

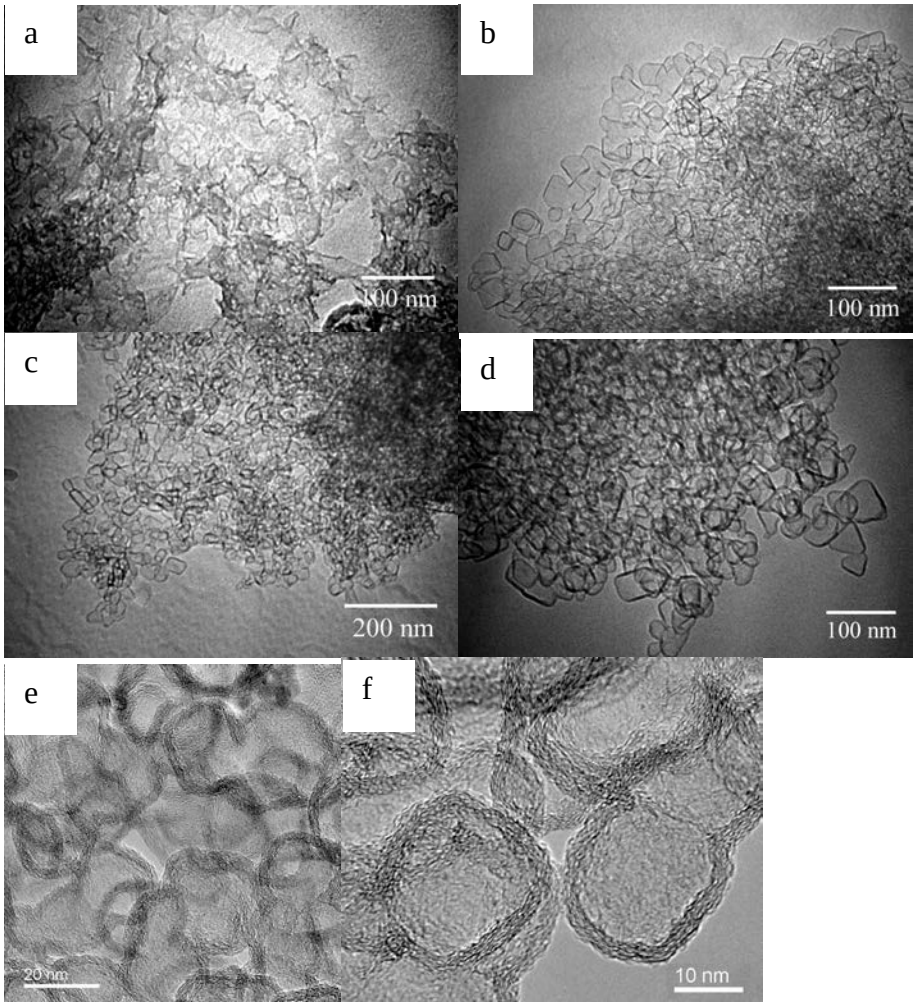


Figure 1 TEM images of carbon products prepared using sc-CO_2 on Co/Mo/MgO at (a) 600 ^oC, (b) 650 ^oC, (c) 700 ^oC, and (d) 750 ^oC. (e, f) HRTEM images of sample (c) reveal curved carbon layers. Molar ratio: p-xylene/CO_2=0.4%, Pco_2=10.34 MPa.

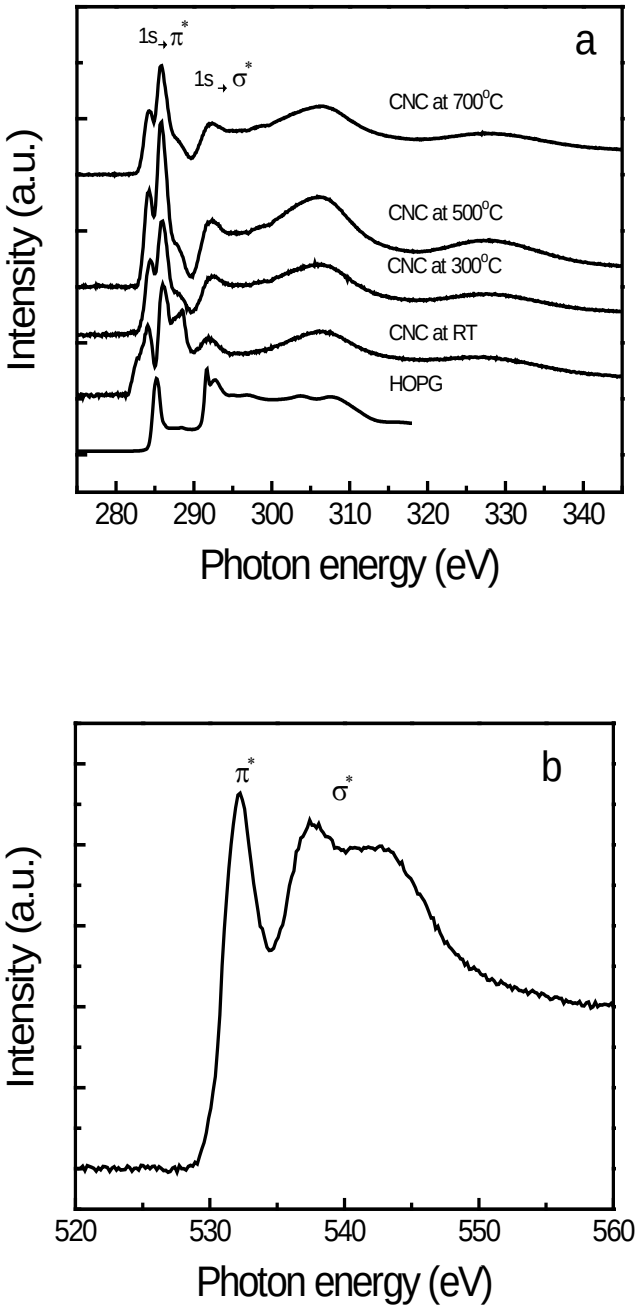


Figure 2 (a) Carbon K-edge NEXAFS spectra of HOPG and carbon nanocages as a function of annealing temperature, (b) Normalized NEXAFS spectra at the oxygen K-edge of a CNC sample.

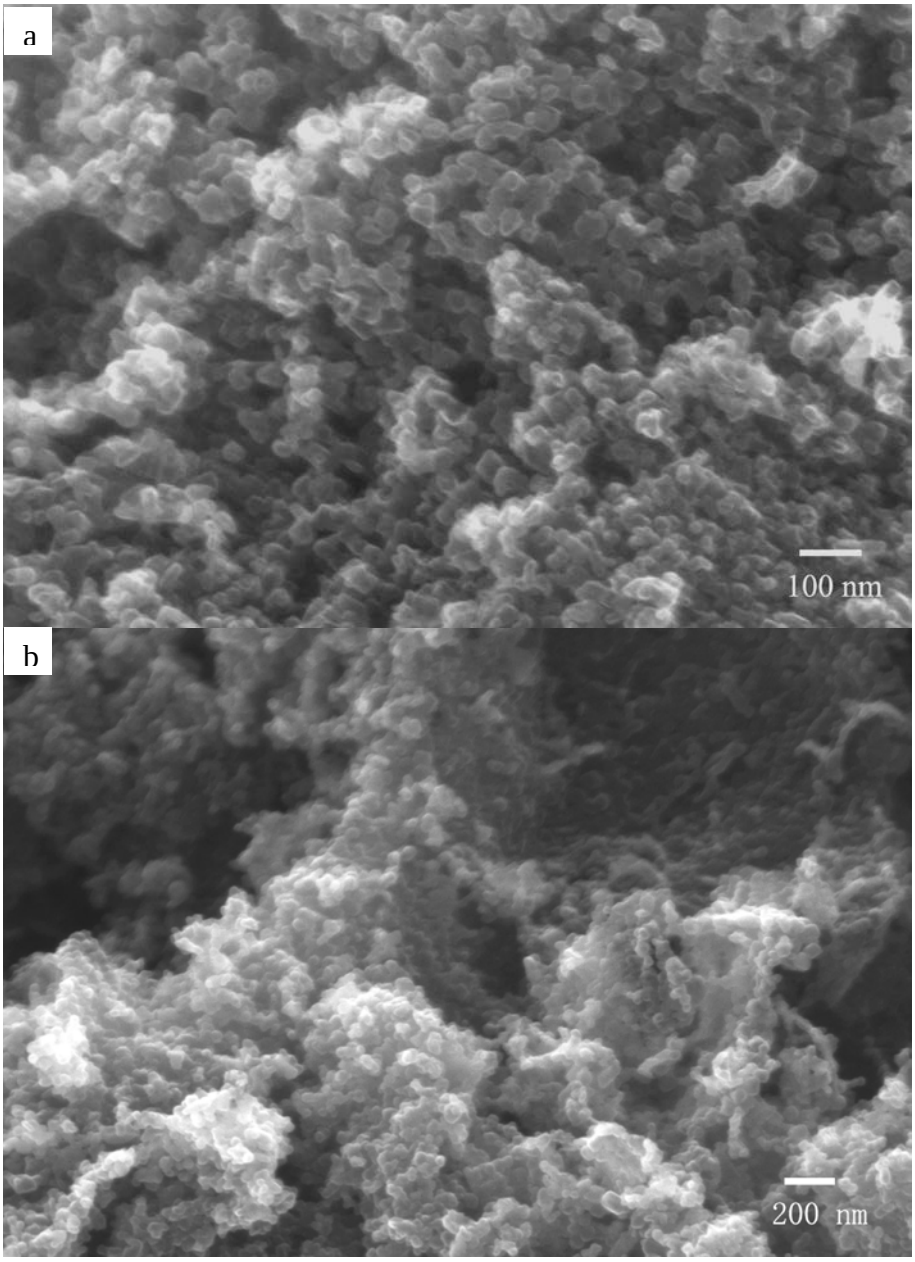


Figure 3 SEM images of carbons prepared by sc-CO_2 on Co/Mo/MgO at 700 ^{o}C and (a) 10.34 MPa, (b) 24.12 MPa.

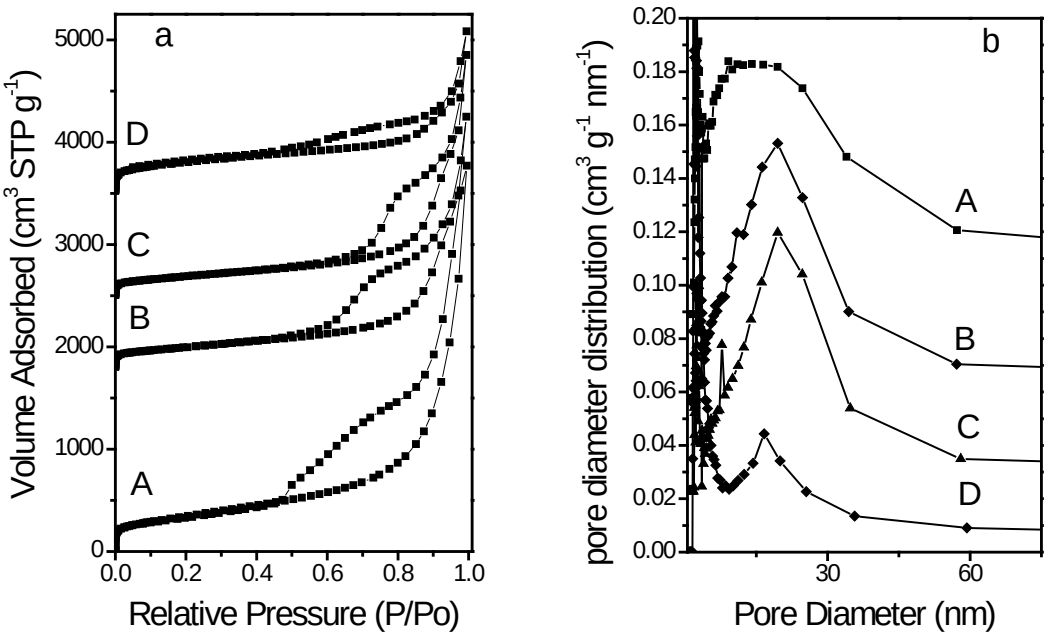


Figure 4 (a) N_2 sorption isotherms and (b) the corresponding pore-size distributions of CNCs prepared by sc-CO_2 on Co/Mo/MgO at (A) 650 ^oC, (B) 700 ^oC, (C) 750 ^oC and 10.34 MPa, (D) 700 ^oC and 24.12 MPa. The isotherms in figure 4a for B, C and D samples are offset vertically by 1800, 2500 and 3500 cm^3 STP g^{-1}.

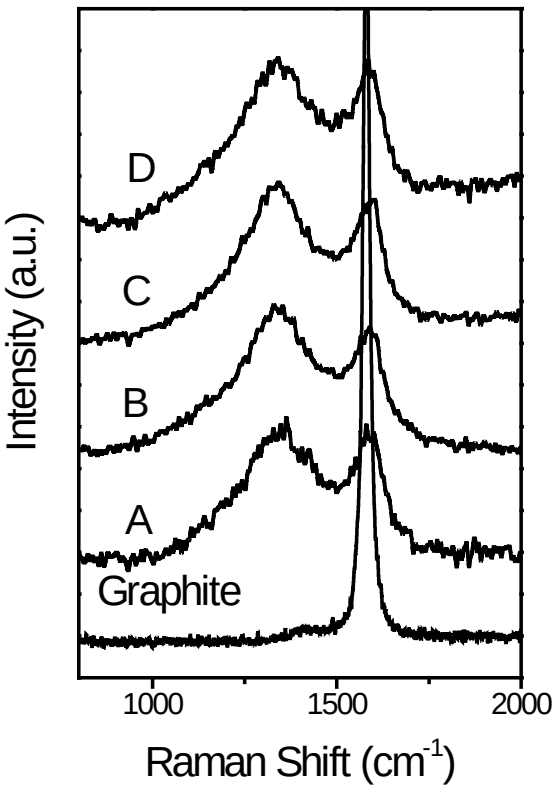


Figure 5 Raman spectra of graphite and carbon products over Co/Mo/MgO catalyst after decomposition of p-xylene at (A) 650 ºC, (B) 700 ºC, (C) 750 ºC and 10.34 MPa, (D) 700 ºC and 24.12 MPa.

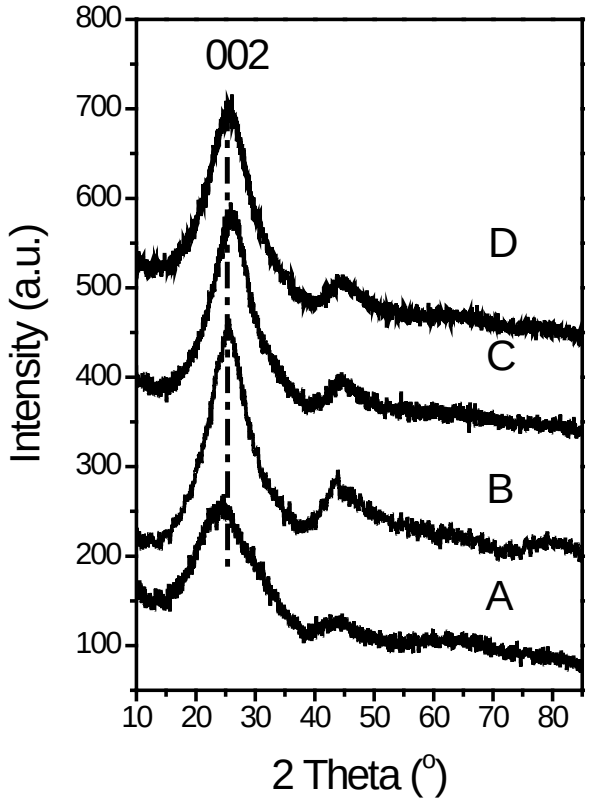


Figure 6 XRD patterns of carbon cages prepared on Co/Mo/MgO at (A) 650 °C, (B) 700 °C, (C) 750 °C and 10.34 MPa, respectively. (D) Carbons are prepared at 700 °C and 24.12 MPa.

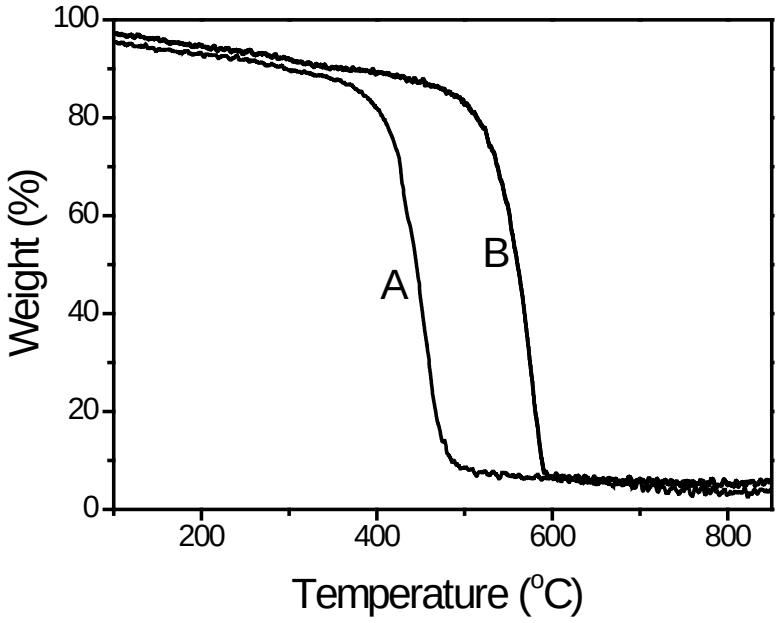


Figure 7 TG profiles of the synthesized CNCs on Co/Mo/MgO. (A) 650 ºC, (B) 750 ºC and 10.34 MPa.