



Mesoporous carbon nitride synthesized by nanocasting with urea/formaldehyde and metal-free catalytic oxidation of cyclic olefins

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ABSTRACT

Mesostructured carbon nitride has been synthesized by nanocasting method with urea/formaldehyde as carbon and nitrogen sources by using disk-shaped 2D hexagonal mesoporous silica (INC-2) as a hard template. The resulted mesoporous carbon nitride (UF-MCN) was characterized as a graphitic structure with hexagonal pores of 3–4 nm and short channels in the submicron range. The catalytic oxidation ability of UF-MCN was demonstrated in the metal-free oxidation of cyclic olefins with hydrogen peroxide. The conversions for cyclopentene, cyclohexene and cis-cyclooctene were obtained in the range of 65–80% and selectivities onto epoxides were 40–90%, respectively. The UF-MCN could illustrate the considerable catalytic oxidation activities due to the existence of surface oxygen species.

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1. Introduction

Porous carbon nitride materials have drawn immense attention as metal-free heterogeneous catalyst due to their versatile properties such as porosity, surface functionalities, mechanical strength, intercalation abilities and thermodynamic stability [1]. In recent decades its potential as metal-free catalyst in Friedel–Crafts type reactions using sustainable electrophiles derived from alcohols, quaternary amines, urea and formic acid [2], Knoevenagel condensation of benzaldehyde with ethylcyanoacetate/malononitrile [3–5], trimerization of nitriles and alkynes [6], cycloaddition of CO₂ with epoxide and oxidation of cyclic olefins with O₂/CO₂ [7] have been reported.

Owing to the wide applicability of carbon nitrides in catalysis, design and development of facile synthetic method using economic precursor has been challenged for achieving better activity, selectivity and stability. Many groups have succeeded in synthesizing mesoporous carbon nitrides (MCN) via condensation of C-, N-, and H-containing precursors using hard [1,7,8] or soft templating [9,10] agents. Antonietti et al. reported the synthesis of mesoporous carbon nitride (MCN) with random connected spherical pores using cyanamide as C, N source and “Ludox HS40” as a hard template [2]. Wang and co-workers have demonstrated the synthesis of ordered mesoporous carbon nitride using SBA-15 as a hard template and cyanamide as C/N source [11]. In general cyanamide,

dicyandiamide and melamine are employed as C, N precursor in hard templating method. However, the cyanamide and dicyandiamide are expensive, toxic and potential carcinogens which restrict their use in large-scale production. The use of melamine also creates problems in the synthesis process; due to its low sublimation temperature (300 °C) [12].

Nanocasting of hard templates with safe and economic carbon and nitrogen precursor via polymerization can be regarded as an alternative method for synthesis of mesoporous carbon nitrides. So far, there are only few reports on the synthesis of ordered mesoporous carbon nitride using such methodology. Vinu et al. reported the synthesis of mesoporous carbon nitride using ethylenediamine (EDA) and carbon tetrachloride (CTC) as precursors and SBA-15 as a template [8,13]. Similar precursors have been used by Zhao and co-workers for synthesis of carbon nitride hollow spheres with mesostructured silica foams as a hard template [12]. Although the precursors were economic and the synthetic methods were facile but the carbon nitride matrices consist of pyridine- and benzene-ring building blocks which resemble much like nitrogen doped carbon.

Herein we report the preparation of well-ordered mesoporous carbon nitride (MCN) using urea and formaldehyde as carbon and nitrogen sources with the disk-type mesoporous silica (INC-2) as a hard template. The choices of these precursors were based on their appreciable solubility in water moreover, due to the abundance, economic and non hazardous nature. The INC-2 has been used as template due to its short channel and hexagonal platelet morphology which can be casted in the accessible manner with urea–formaldehyde resin and moreover, the carbon nitride replica

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obtained from INC-2 was presumed to have short channels morphology which could provide efficient diffusion of product and reactants molecules [14].

In continuation of our previous studies on oxidation catalysis with surface oxygen containing carbon nitride [7], in here we address the catalytic abilities of carbon nitride with surface oxygen functionalities for oxidation of cyclic olefins using H_2O_2 as an oxidant.

2. Experimental

2.1. Chemicals

All chemicals were of analytical grade and were used without further purification. The urea and all cyclic olefins were purchased from Sigma–Aldrich Company. Formaldehyde solution in water (35 wt%) was purchased from DC chemical and solvents from “SAM-CHUN” and “DAE JUNG” chemical. The water used during synthetic process was deionized by aqua MaxTM basic water purification system, Young Lin, Korea.

2.2. Catalyst preparation

The UF-MCNs were synthesized by nanocasting with urea–formaldehyde by polymerization over the disk shaped mesoporous silica (INC-2) as a hard template.

2.2.1. Preparation of INC-2

The hard template INC-2 was synthesized with little modification of our prior reported procedure [14]. In a typical synthesis of INC-2, 11 g 10 wt% aqueous solutions of Pluronic P123 were poured into 245 g of distilled water and stirred vigorously using mechanical stirrer. To this mixture 0.096 mole of sodium metasilicate and 1.74 g of 3-aminopropyl triethoxysilane was added dropwise. The mixture was stirred to homogeneity followed by addition of 81 g of concentrated HCl and maintained for 1 h at 35 °C. The resultant mixture was subjected to microwave treatment at 373 K for 2 h with operating power of 300 W. The crystallized products were filtered, washed with warm distilled water and ethanol and finally dried at 333 K. The surfactant was then removed by the soxhlet extraction over ethanol for 24 h.

2.2.2. Preparation of UF-MCN

The typical procedure for preparation of UF-MCNs involves following steps. The urea (U) was added to the formaldehyde (F) solution (molar ratios U/F = 0.7, 1 and 1.3 which were denoted as UF-MCN-0.7, UF-MCN-1.0 and UF-MCN-1.3) to form precursor gel. To this precursor gel, 0.5 g of INC-2 was added and stirred using mechanical stirrer followed by nanocasting and polymerization at 363 K for 9 h to yield urea–formaldehyde-INC-2 nanocomposite. The obtained white colored nanocomposite powder was carbonized at 873 K for 6 h under 50 ml/min of N_2 flow. After carbonization, the black powder was treated for 24 h with 5 wt% HF aqueous solution for removing silica, followed by filtration and overnight drying at 110 °C to obtain mesoporous disk shaped UF-MCN replica.

2.2.3. Preparation of UF-SBA-15

Instead of INC-2, conventional SBA-15 [15] was used as a template for synthesizing UF-SBA-15. The urea and formaldehyde molar ratio was U/F = 1. The procedure for synthesis of UF-SBA-15 was similar to that of UF-MCN (Section 2.2.1).

2.3. Characterization

Fourier transform infrared (FTIR) spectroscopy (Nicolet 6700) and Raman spectroscopy (HR 800, Horiba/Jobin-Yvon) were employed to analyze the chemical structure of catalyst. The nuclear magnetic resonance (NMR) spectra were recorded on Varian Unity NOVA solid state 600 MHz spectrometer. The nitrogen adsorption–desorption isotherms were measured using Micromeritics porosimeter (ASAP-2020) at 77 K. Prior to the measurement, all samples were degassed at 433 K for 5 h. The surface area was calculated by using Brunauer–Emmett–Teller (BET) method. Scanning electron microscopic (SEM) images were collected by using the JEOL 630-F microscope. The aliquot of reaction mixture was analyzed by GC and GC–MS (Agilent technologies 5975).

2.4. Catalytic oxidation of cyclo-olefins with H_2O_2

2.4.1. Oxidation of cyclohexene with different solvents

50 mg of UF-MCN-1.0, 10 mmol of cyclohexene and 5 ml of solvent such as ethanol or acetone or acetonitrile or N,N-dimethylformamide (DMF) were stirred in a glass reactor (Chemistation II, Japan) and heated to 75 °C. The 40 mmol of hydrogen peroxide was introduced through the septum to the reactant mixture. After the reaction was completed, the filtrate was collected and the reaction mixture was diluted with acetone and subjected to GC and GC–MS analysis.

2.4.2. Oxidation of cyclic olefins

50 mg of UF-MCN-1.0, 5 ml of acetone and 20 mmol of reactant such as cyclopentene, cyclohexene and cyclooctene were stirred in a glass reactor (Chemistation II, Japan) and heated to 75 °C followed by dropwise addition of 40 mmol of hydrogen peroxide. After completion of the reaction, the catalyst was separated by filtration and reaction mixture was diluted by acetone and analyzed by GC and GC–MS.

3. Results and discussion

3.1. Catalyst preparation and characterization

3.1.1. Urea to formaldehyde molar ratio optimization

The UF-MCNs, were synthesized by nanocasting of disk shaped silica, INC-2, as a hard template with different molar ratio of urea to formaldehyde (U/F = 0.7, 1, 1.3). The nanocasted samples were carbonized and then subjected to HF treatment in order to remove the silica. The UF-MCNs were subjected to the elemental analysis (C, H and N) which depicted decrease in carbon [UF-MCN-0.7 (56.16%), UF-MCN-1.0 (54.17%), and UF-MCN-1.3 (52.56%)] and nitrogen [UF-MCN-0.7 (24.44%), UF-MCN-1.0 (23.23%), and UF-MCN-1.3 (22.9%)] contents with increase in U/F ratio. Whereas, the hydrogen content was revealed to be less in case of U/F ratio 1.0 compared with UF-MCN-0.7 and UF-MCN-1.3 [UF-MCN-0.7 (2.49%), UF-MCN-1.0 (1.74%), UF-MCN-1.3 (2.13%)] this indicated the existence of higher amount of sp^2 bond in UF-MCN-1.0.

In order to further investigate chemical or electronic states of nitrogen and carbon in UF-MCNs XPS (X-ray photoelectron spectroscopy) analysis (Fig. 1) was carried out. The C 1s binding energy of UF-MCNs was deconvoluted into different components and the peak assignments were made based upon their chemical shifts. The C 1s spectra of UF-MCN-0.7 showed peak at 284.7 eV invariably assigned to sp^2 C–C bonds [16,17]. This peak shifted to lower 284.3 eV in UF-MCN-1.0 and 284.2 eV in case of UF-MCN-1.3 [18]. The peaks assignable to C–N bonds are observed at binding energy (BE) 285.5, 285.4 and 285.3 eV corresponding to U/F ratios of 0.7, 1.0 and 1.3, respectively. These observations were in consonance

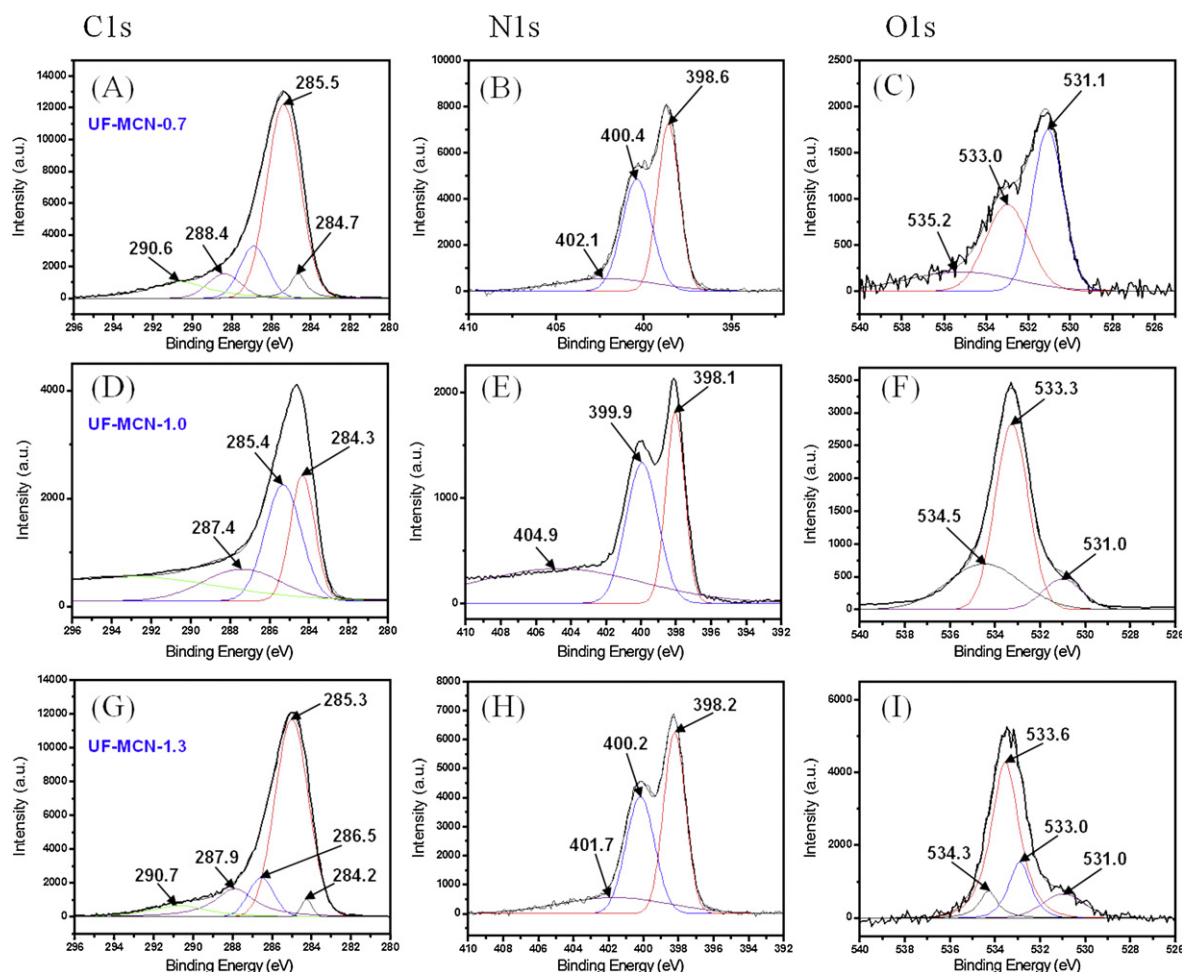


Fig. 1. XPS C 1s, N 1s and O 1s spectra of UF-MCNs (U/F = 0.7 (A–C), 1.0 (D–F), 1.3 (G–I)).

with Li et al. [19] on nitrogen implanted carbon films and also with that of Zhang et al. on carbon nitride nanobells [20]. Whereas, Jama et al. reported that these sp^2 C–N bonds were in close proximity with the neighboring nitrogen similar to pyrrole or pyridine [17]. The peaks at 286.4 and 286.9 eV are related to sp^2 C–N bonds, whereas the peaks at 287.4 and 287.9 eV corresponded to sp^3 C–N bonds [17]. Apart from these, additional peaks were observed at higher BE values 288.4, 290.6 and 290.7 eV which were related with oxygen binding with carbon motif. The deconvoluted N 1s of UF-MCNs showed signals corresponding to sp^3 C–N bonds at 398.6,

398.1 and 398.2 eV [21]. The peaks in the 400.4, 399.9 and 400.2 eV corresponded to sp^2 –C=N as reported earlier [22,23]. The additional peak observed at 402.1 eV was assigned by Yang and Sacher [24] and Das et al. [25] for “NO” species. A peak at 401.7 eV in U/F = 1.3 is due to quaternary N in UF-MCN framework, whereas the peak at 404.9 eV in the U/F = 1 could be assigned to N–N bonds. The O 1s binding energy revealed existence of quinone type C=O bond at 531 and 531.1 eV. The peaks at 533 and 533.6 eV correspond to OH and peak at 533.3 eV to C–O [26–28]. The peak in U/F = 0.7 at 535.2 eV could be assigned to transition of oxygen in

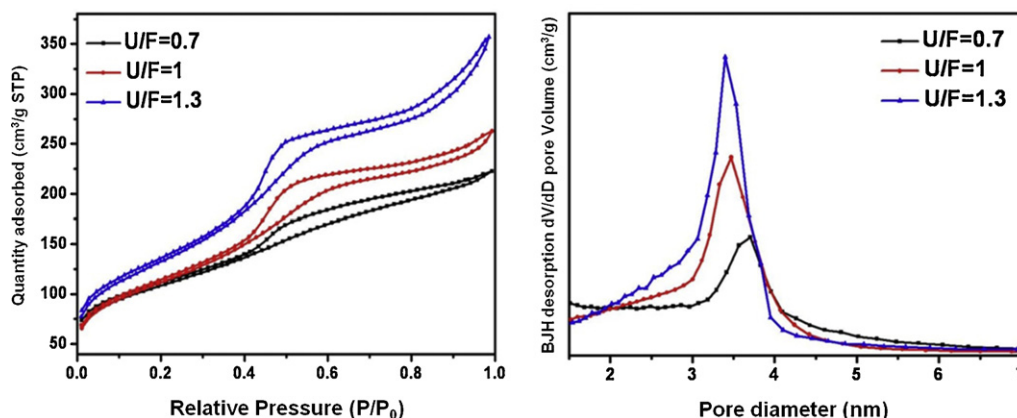


Fig. 2. (A) Nitrogen adsorption–desorption isotherms and (B) pore size distributions of UF-MCNs.

carboxylic group whereas, the peak in the 534.3 eV in U/F = 1.3 is assigned to hydroxyl of carboxylic group [29]. Another component of the O 1s transition of minor intensity was observed at 534.5 eV in U/F = 1.0 which may be associated to physically adsorbed molecular H₂O (533.3 eV). The existences of these oxygen functionalities on the UF-MCN surfaces intrigued us to perform oxidation catalysis.

In order to understand the role of U/F ratios on the surface areas and porous properties of UF-MCNs, the nitrogen adsorption–desorption isotherms (Fig. 2) were measured. The adsorption isotherm of all UF-MCNs showed type IV isotherm with H1 hysteresis loop indicating the replica of INC-2. The surface areas of UF-MCNs were calculated by Brunauer–Emmet–Teller (BET) method and are in range of 350–500 m²/g. The pore size and pore volume were calculated by Barrett–Joyner–Halenda (BJH) method, the pore diameter were in between 2.5 and 3.5 nm with total pore volume in range of 0.3–0.6 cm³/g. The BJH pore size distribution calculated from the adsorption branch of the nitrogen isotherm confirms that the pores of UF-MCNs were highly uniform and had a narrow pore size distribution around 3.5 nm. The adsorption–desorption studies also revealed that increases in U/F ratios gave the increases in BET surface areas, pore volumes and BJH pore diameters as the pore size remains unaffected by the change in ratio this suggests that the pore imprinted in all UF-MCNs is from silica template (INC-2).

The low angle XRD patterns (Fig. 3) were recorded in order to know the optimum ratio required for formation of hexagonal mesostructured replica of INC-2 with *p6mm* space group [14]. All UF-MCNs showed a strong diffraction peak indexed as (1 0 0) plane corresponding to $2\theta = 0.82\text{--}0.90^\circ$. The distinctive orderliness have been only observed in the UF-MCN with ratio U/F = 1. All the UF-MCNs showed a broad diffraction peak at $2\theta = 25.8^\circ$ [8], corresponding to interlayer *d* spacing, 3.42 Å which is also in consonance with earlier reports on hexagonal ordered replica of carbon nitride. These studies revealed that the ratio of U/F = 1.0 would be the optimized ratio which would give ordered hexagonal replica

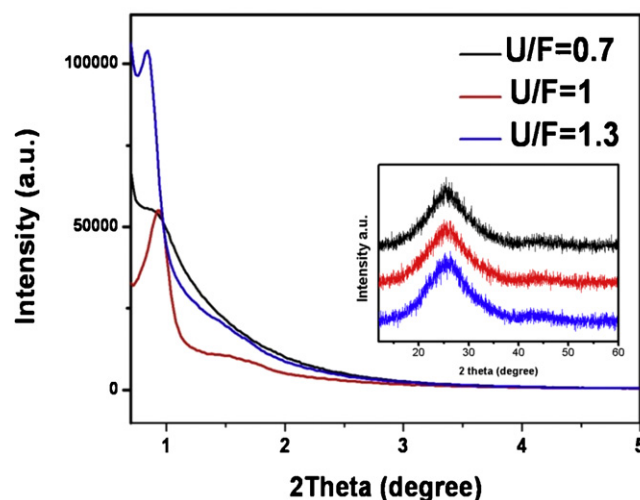


Fig. 3. Low and wide angle XRD patterns of UF-MCNs.

with *p6mm* space group. Furthermore we verified the formation of the disk type hexagonal UF-MCN-1.0 by using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The SEM images (Fig. 4a and b) depicted the morphology of synthesized UF-MCN to be hexagonal disk-type with size in range of 3.5–5 μm which is in agreement with the particle size of used template. The TEM images (Fig. 4c and d) indicated that the materials have highly ordered 1D mesopore structures with a 2D hexagonal arrangement with short 1D ordered mesopore channels of submicrometer length (100–300 nm). The channel directions are perpendicular to the larger surface of hexagonal platelet and parallel to the thickness. These results suggest that the UF-MCN formed with ratio U/F = 1.0 is exact replica of the template INC-2.

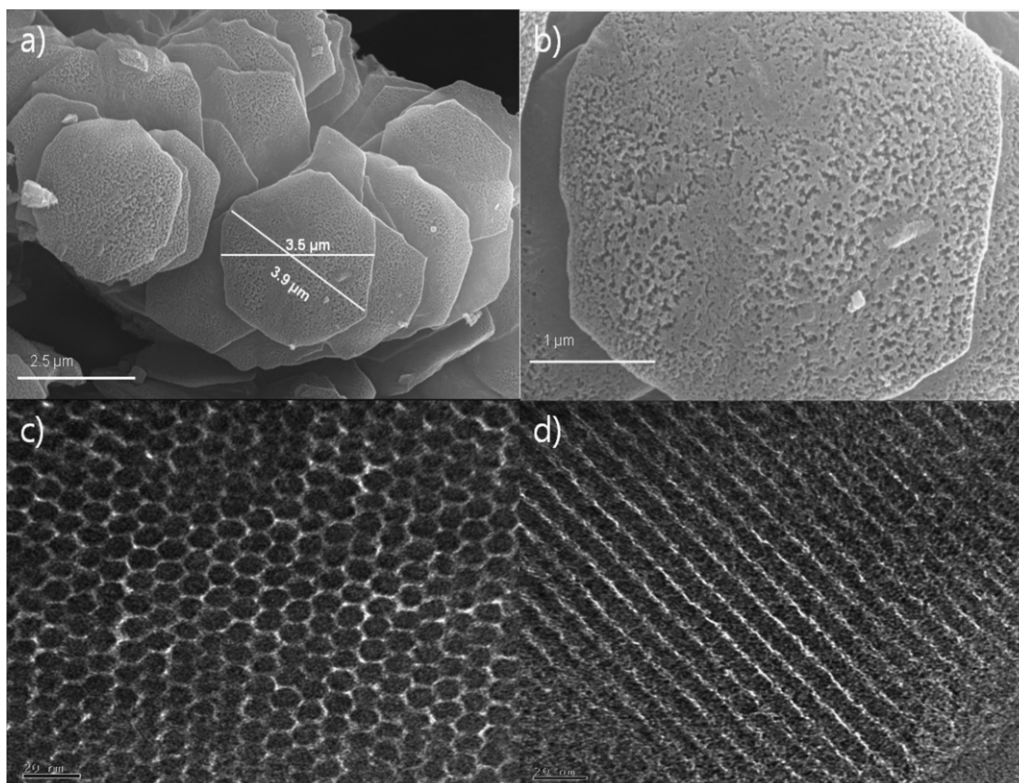


Fig. 4. SEM and TEM images of UF-MCN-1.0.

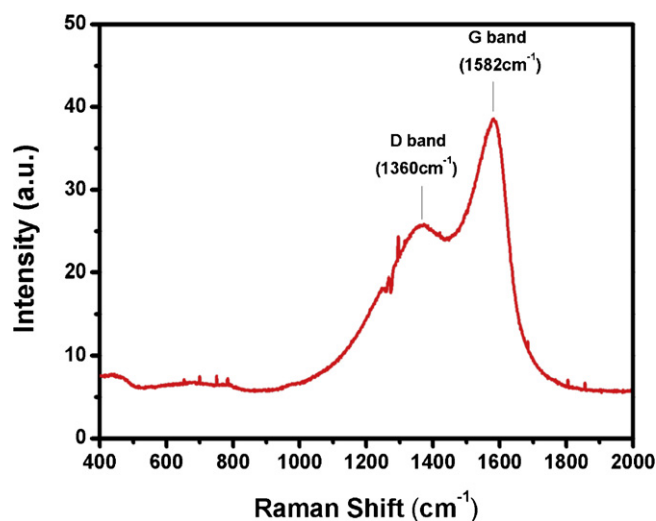


Fig. 5. Raman spectrum of UF-MCN-1.0.

UF-MCN-1.0 with equimolar urea and formaldehyde ratio was chosen as an optimized ratio and further analysis of structural properties were performed by Raman spectroscopy, electron energy loss spectroscopy (EELS), nuclear magnetic resonance (NMR) spectroscopy and Fourier transform infrared (FTIR) spectroscopic studies. The Raman frequencies of mesoporous carbon nitrides possess two distinctive bands namely D band and G band (Fig. 5). The G band lie in the range of $1560\text{--}1600\text{ cm}^{-1}$ and is related to the variation of optically allowed zone associated with E_{2g} in-plane stretching motions of pairs or chains of $C\text{-}sp^2$ bonded atoms [30,31]. Whereas, the D band is associated with the disordered-allowed optical zone mode around 1350 cm^{-1} and it relates to A_{1g} breathing mode of six fold aromatic rings and only becomes active in presence of disorder. The Raman spectra have confirmed the graphitic structure of UF-MCN-1.0 but could not give clear distinction between the carbon and the nitrogen states as the frequency of skeletal bond stretching and ring modes is very similar in benzene, pyridine and pyrrole.

In regard of this viewpoint we have performed (EELS) electron energy loss spectroscopy, NMR and FTIR studies. The EELS study can reveal the element-specific energy losses due to the inelastic interaction with the C:N atoms during the penetration in carbon nitride. The EELS spectrum (Fig. 6) indicates that the first near-edge

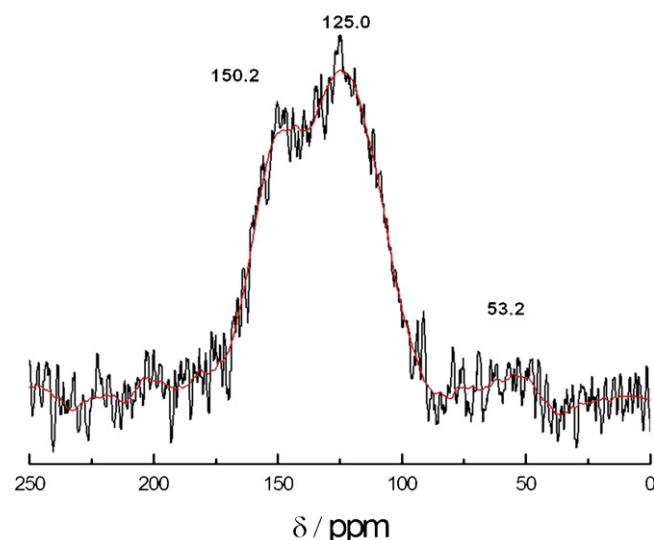


Fig. 7. ^{13}C cross-polarization magic angle spinning NMR spectrum of UF-MCN-1.0.

structure peak (C K-edge) at 284 eV is attributed to $1s \rightarrow \pi^*$ electronic transitions and is a fingerprint of a sp^2 -hybridized carbon bonded to nitrogen [1]. The corresponding π^* and σ^* transitions in the N K-edge appear at 398.5 and 403.5 eV, respectively. Close similarities were observed between the carbon and nitrogen K edges which explains there is occurrence of strong covalent bonding between C and N atoms [32]. The ^{13}C cross-polarization magic angle spinning (CP-MAS), NMR (Fig. 7) spectrum showed resonances at 125 150.2 and 53.2 ppm. The peak at 125 ppm is assignable to the sp^2 carbon atoms present in the graphitic materials, while the signal at 125 ppm correspond to sp^2 carbon atom attached to nitrogen [33]. The broad signal centered at 53.2 ppm is due to resonance of sp^3 carbon atoms. Gammon et al. reported that the broad nature of this band is due to obscurement by the spinning sidebands [34]. The FTIR spectrum (Fig. 8) depicted a broad peak around $3200\text{--}3500\text{ cm}^{-1}$ corresponding to O–H (H-bonded), a well distinct vibration for free OH group at 3670 cm^{-1} , $\text{N}=\text{C}=\text{O}$ vibrations at 2223 cm^{-1} , N–H amide II band at 1595 cm^{-1} , $\text{--CH}_2\text{--O--CH}_2\text{--}$ vibrations at 1187 cm^{-1} , --O--H bending at 1385 cm^{-1} and ring quadrant vibrations in finger print region [35].

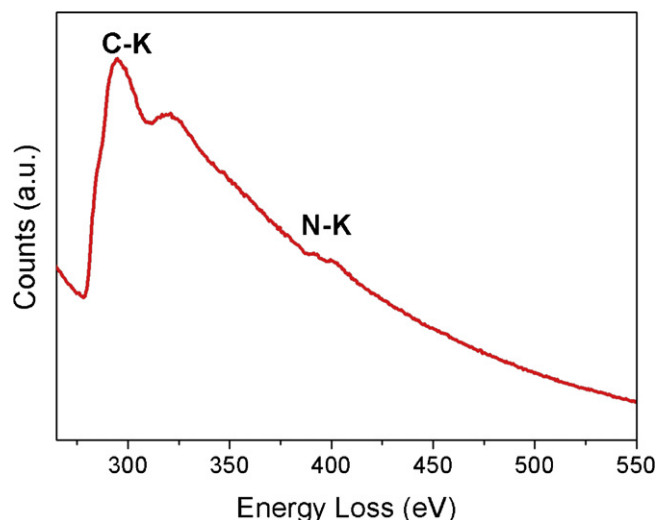


Fig. 6. Electron energy loss spectrum of UF-MCN-1.0.

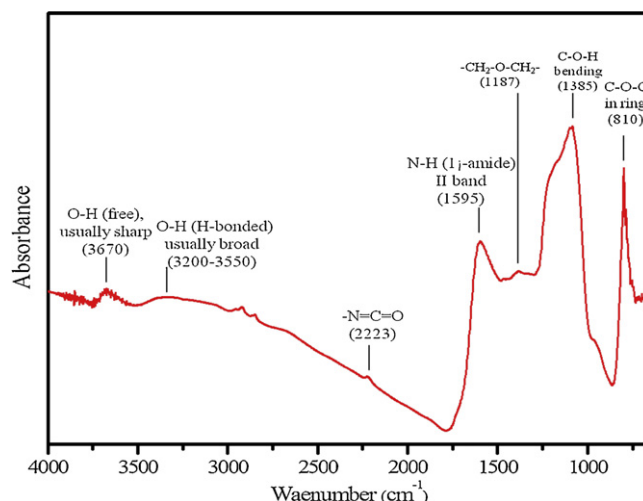


Fig. 8. Fourier transform infrared spectrum of UF-MCN-1.0.

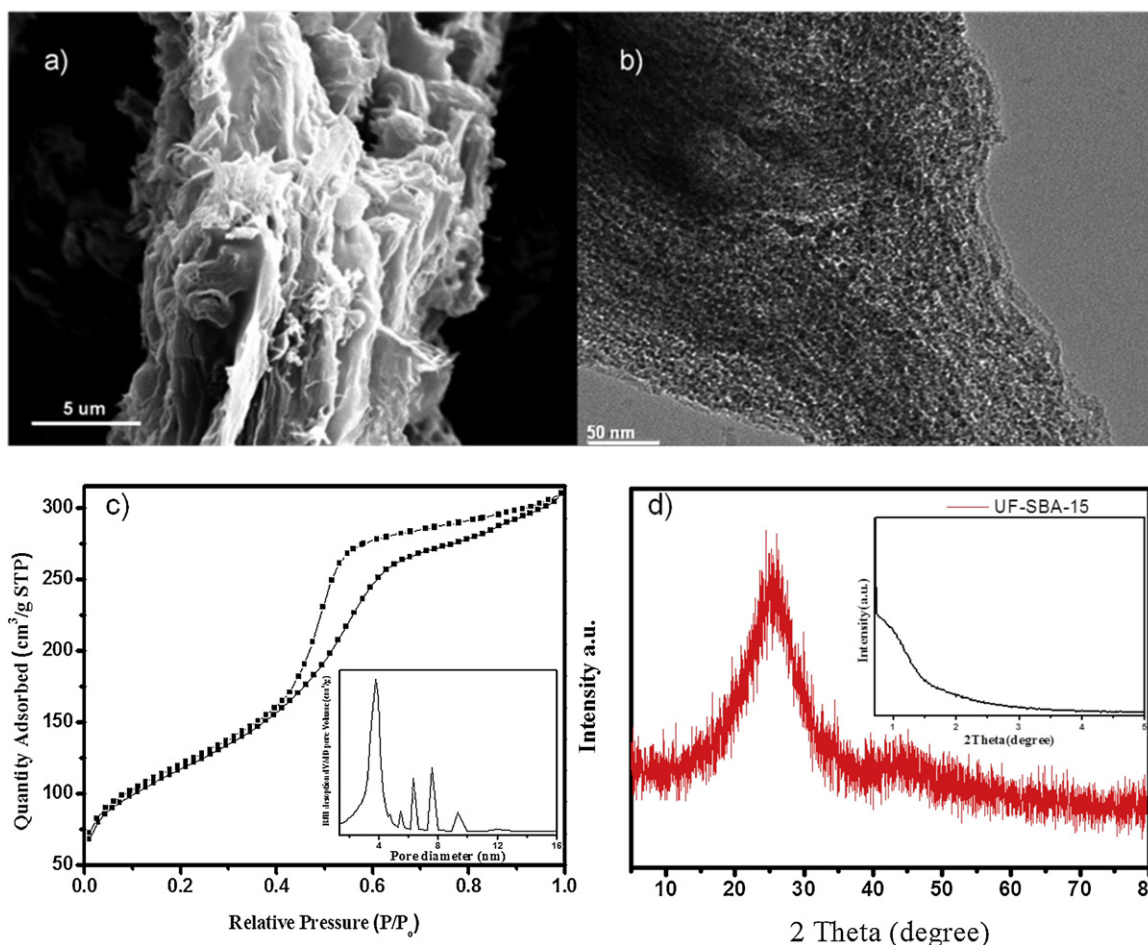


Fig. 9. SEM (a) and TEM (b) images, (c) nitrogen adsorption-desorption isotherm and pore size distributions and (d) XRD patterns of UF-SBA-15.

3.1.2. UF-MCN vs. UF-SBA-15

The morphological features of UF-SBA-15 synthesized by nano-casting method have been compared with that with UF-MCN. The SEM image (Fig. 9a) of UF-SBA-15 was not clear and depicted fibrous shape. Moreover, no often distinct morphological feature was observed by SEM and mesopore distribution was found to be random by the TEM image (Fig. 9b). It might be due to uneven polymerization over the SBA-15 prior to coating and pore filling of urea and formaldehyde into long 2D-channels of SBA-15. The N₂ adsorption-desorption isotherm of the UF-SBA-15 (Fig. 9c) showed type IV isotherm with H1 hysteresis. The surface area of the material was found to be 418 m²/g and the pore size distribution showed pores in range from 4 to 12 nm. The wide angle XRD pattern of UF-SBA-15 (Fig. 9d) showed a broad diffraction peak at $2\theta = 25.8^\circ$, corresponding to interlayer *d* spacing (3.42 Å) of graphitic materials [8]. The absence of peak in low angle XRD pattern of the UF-SBA-15 revealed the lack of orderness and replication of SBA-15 structure.

These results are contradictory to that of UF-MCN synthesized by INC-2 which shows uniform hexagonal disk shaped morphology with hexagonal mesopores and short 1D mesopore channels of submicrometer length.

3.2. Catalytic results

In our previous report, the oxidation of cyclic olefins over MCNs was investigated by using O₂/CO₂ or O₂/N₂ as an oxidant. The maximum conversion of cyclic olefin was found to be 40% under CO₂/O₂ with 37% epoxide selectivity [7]. The reaction conditions adopted were harsh such as high pressure of 80 psi and high

temperature 100 °C. In continuation to our prior findings on the role of carbon nitride as oxidation catalyst, herein we investigate the catalytic performance of UF-MCN in oxidation of cyclic olefins due to existence of surface oxygen functionalities as confirmed by XPS and IR spectroscopy. We presumed that such oxygen functionalities may serve as active site and could facilitate the oxidation at mild condition using H₂O₂ as an oxidant. The catalytic activity

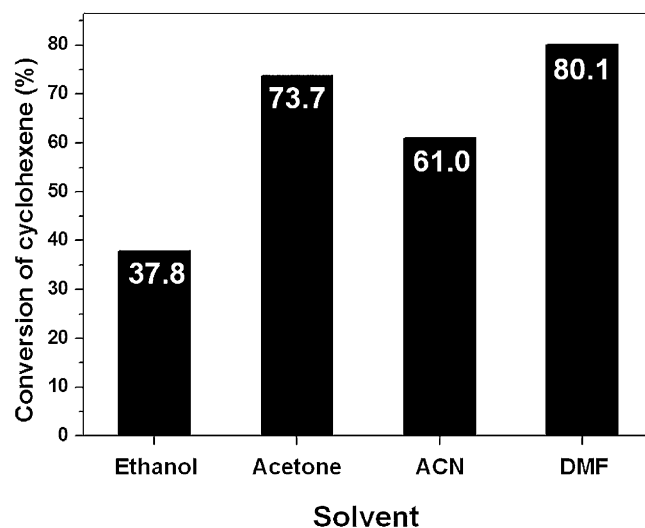
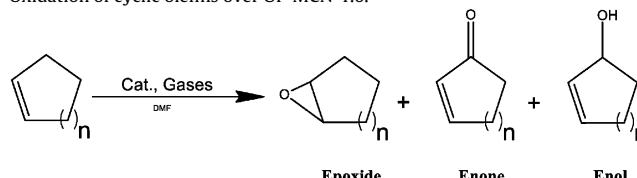


Fig. 10. The solvent effect at the oxidation of cyclohexene.

Table 1
Oxidation of cyclic olefins over UF-MCN-1.0.^a



Cycloalkene	Con. (%) ^b	Selectivity (%) ^b			
		Epoxide	Enone	Enol	Others
Cyclopentene	67.8	41.4	6.4	30.2	22.0 ^c
Cyclohexene	75.1	53.5	0.8	28.6	17.0 ^d
Cyclooctene	80.6	92.0	–	8.0	–

^a Reaction conditions: 20 mmol reactant; 5 g acetone; 50 mg UF-MCN for 10 h at 75 °C with 40 mmol H₂O₂.

^b Determined by GC; identified by GC–MS.

^c 6-Oxabicyclo[3.1.0]hexan-2-one (14.6%); 1-penten-3-ol (7.3%); 3,4-dihydrocyclopentadiene (0.1%).

^d Cyclohexanol (1.0%); 2-hydroxycyclohexan-1-one (5.9%); 7-oxabicyclo[4.1.0]heptan-2-one (2.3%); 7-oxabicyclo[4.1.0]heptan-2-ol (2.2%); 1,2-cyclohexanediol (5.1%); bi-2-cyclohexen-1-yl (0.5%).

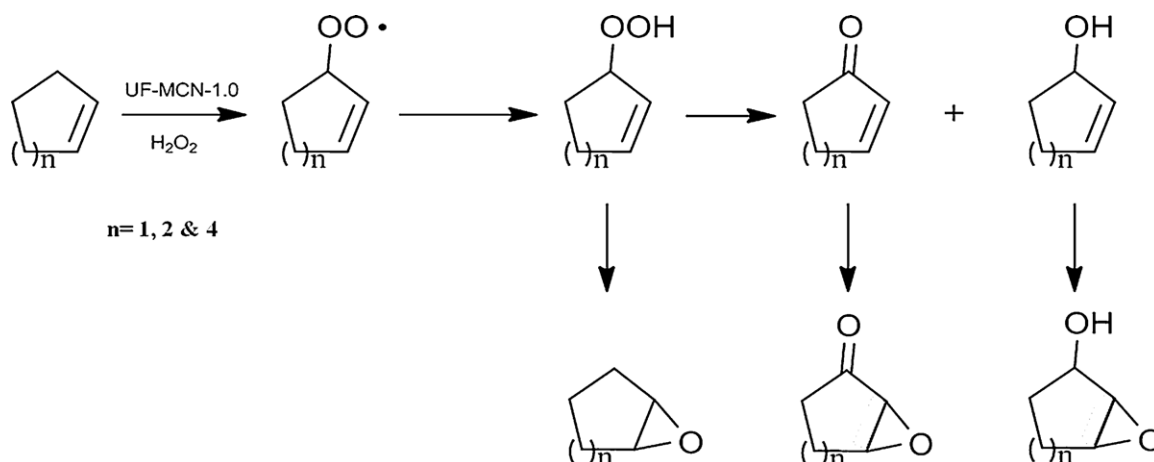


Fig. 11. The reaction pathway for oxidation of cyclic olefins.

of UF-MCN-1.0 was investigated in different polar solvents such as ethanol, acetone, acetonitrile and dimethylformamide (DMF) (Fig. 10). In ethanol least conversion of cyclohexene (37.8%) was observed due to its protic nature and low dipole moment (1.69 D). Moreover, in case of protic solvents with non polar solute (cyclic olefin) the solvophobic effects play an important role as the solvent/solvent interactions are much stronger than solute/solvent interactions. Such solvent/solvent association leads to a diminution of the catalytic effect by protic solvents [36]. In polar aprotic solvent like acetone, acetonitrile and DMF there is absence of such effects which leads to optimum conversion. The conversion in dimethylformamide was found to be highest 80.1% whereas, in case of acetone and acetonitrile 73.7% and 61% conversion was observed, respectively (Fig. 10).

The effect of ring size in relation with catalytic activity for oxidation was investigated using different cyclic olefins such as cyclopentene, cyclohexene and cyclooctene (Table 1). With increase in ring size of cyclic-olefin increase in conversion was observed [37]. The best catalytic performance was observed in case of cyclooctene with 80.6% conversion and 92% selectivity for epoxide. In case of cyclopentene and cyclohexene lower conversion and low selectivity for epoxide were observed. The conversion is dependent on the conformation, the bond angle strain and the torsional strains of cyclic olefins [37]. With respect to these viewpoints the reactivity of cyclic olefins increased in the following order: cyclopentene < cyclohexene < cyclooctene.

The selectivity of epoxide is increased with increase in ring size, cyclooctene showed highest selectivity for epoxide (92%) whereas in case of cyclohexene and cyclopentene the selectivities for epoxide 53.5% and 41.4%, respectively.

3.3. Plausible mechanistic pathway

It has been well understood fact that carbonaceous material with nitrogen containing molecules can form radical which have been evidenced by us over graphitic melamine glyoxal resin system and moreover the oxidation abilities of carbon nitride toward cyclic olefins have been well demonstrated by us earlier [38]. Based upon these observations we proposed that cyclic olefin on reaction with hydrogen peroxide forms cyclic olefin peroxyradical which further transform into cyclic olefin peroxide [39]. This cyclic olefin peroxide serves as an intermediate for other oxidized products like epoxide, enone or enol. The byproducts in the reaction are formed by reaction of hydrogen peroxide with enone and enol forming corresponding epoxides (Fig. 11).

4. Conclusions

The UF-MCN was synthesized by a hard templating method using urea and formaldehyde as C, N source and INC-2 as a template. A unimolar ratio of urea and formaldehyde was found to be optimum for synthesis of ordered mesopores with disk type hexagonal

platelet morphology. The formed UF-MCN showed pore size of 3 nm and short channel of 250 nm. In contrast the nanocasting of conventional SBA-15 showed fibrous morphology, uneven distribution of pores and lack of orderliness.

The UF-MCN material shows catalytic activity toward oxidation of cyclic olefins such as cyclopentene, cyclohexene and cyclooctene using H_2O_2 as oxidant. The conversion of cyclic olefin and selectivity of epoxide increases with increase in ring size. The conversion of cyclic olefins and selectivity of epoxides were in range 65–80% and 40–90%, respectively

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References

- [1] A. Thomas, A. Fischer, F. Goettmann, M. Antonietti, J.O. Müller, R. Schlögl, J.M. Carlsson, *Journal of Materials Chemistry* 18 (2008) 4893–4908.
- [2] F. Goettmann, A. Fischer, M. Antonietti, A. Thomas, *Angewandte Chemie: International Edition* 45 (2006) 4467–4471.
- [3] M.B. Ansari, H. Jin, M.N. Parvin, S.-E. Park, *Catalysis Today* 185 (2012) 211–216.
- [4] S.N. Talapaneni, S. Anandan, G.P. Mane, C. Anand, D.S. Dhawale, S. Varghese, A. Mano, T. Mori, A. Vinu, *Journal of Materials Chemistry* 22 (2012) 9831–9840.
- [5] F. Su, M. Antonietti, X. Wang, *Catalysis Science and Technology* 2 (2012) 1005–1009.
- [6] F. Goettmann, A. Fischer, M. Antonietti, A. Thomas, *New Journal of Chemistry* 31 (2007) 1455–1460.
- [7] M.B. Ansari, B.-H. Min, Y.-H. Mo, S.-E. Park, *Green Chemistry* 13 (2011) 1416–1421.
- [8] A. Vinu, K. Ariga, T. Mori, T. Nakanishi, S. Hishita, D. Golberg, Y. Bando, *Advanced Materials* 17 (2005) 1648–1652.
- [9] H. Yan, *Chemical Communications* 48 (2012) 3430–3432.
- [10] Y. Wang, X. Wang, M. Antonietti, Y. Zhang, *ChemSusChem* 3 (2010) 435–439.
- [11] X. Chen, Y.S. Jun, K. Takanabe, K. Maeda, K. Domen, X. Fu, M. Antonietti, X. Wang, *Chemistry of Materials* 21 (2009) 4093–4095.
- [12] Q. Li, J. Yang, D. Feng, Z. Wu, Q. Wu, S.S. Park, C.-S. Ha, D. Zhao, *Nano Research* 3 (2010) 632–642.
- [13] A. Vinu, P. Srinivasu, D.P. Sawant, T. Mori, K. Ariga, J.-S. Chang, S.-H. Jhung, V.V. Balasubramanian, Y.K. Hwang, *Chemistry of Materials* 19 (2007) 4367–4372.
- [14] Sujandi, S.-E. Park, D.-S. Han, S.-C. Han, M.-J. Jin, T. Ohsuna, *Chemical Communications* (2006) 4131–4133.
- [15] D. Zhao, J. Sun, Q. Li, G.D. Stucky, *Chemistry of Materials* 12 (2000) 275–279.
- [16] S.M. Lyth, Y. Nabae, S. Moriya, S. Kuroki, M.-a. Kakimoto, J.-i. Ozaki, S. Miyata, *Journal of Physical Chemistry C* 113 (2009) 20148–20151.
- [17] C. Jama, A. Al khawwam, A.S. Loir, P. Goudmand, O. Dessaux, L. Gengembre, J. Grimblot, *Surface and Interface Analysis* 31 (2001) 815–824.
- [18] I. Kusunoki, M. Sakai, Y. Igari, S. Ishidzuka, T. Takami, T. Takaoka, M. Nishitani-Gamo, T. Ando, *Surface Science* 492 (2001) 315–328.
- [19] J. Li, W. Zheng, C. Gu, Z. Jin, Y. Zhao, X. Mei, Z. Mu, C. Dong, C. Sun, *Carbon* 42 (2004) 2309–2314.
- [20] G.Y. Zhang, X.C. Ma, D.Y. Zhong, E.G. Wang, *Journal of Applied Physics* 91 (2002) 9324.
- [21] M. Kim, S. Hwang, J.-S. Yu, *Journal of Materials Chemistry* 17 (2007) 1656–1659.
- [22] Y.H. Cheng, X.L. Qiao, J.G. Chen, Y.P. Wu, C.S. Xie, Y.Q. Wang, D.S. Xu, S.B. Mo, Y.B. Sun, *Diamond and Related Materials* 11 (2002) 1511–1517.
- [23] B. Zhang, Y. Yu, J. Zhang, *Journal of Physics D: Applied Physics* 42 (2009) 185304.
- [24] D.Q. Yang, E. Sacher, *Surface Science* 531 (2003) 185–198.
- [25] D. Das, K.H. Chen, S. Chattopadhyay, L.C. Chen, *Journal of Applied Physics* 91 (2002) 4944.
- [26] M.S. Bhuvaneswari, N.N. Bramnik, D. Ensling, H. Ehrenberg, W. Jaegermann, *Journal of Power Sources* 180 (2008) 553–560.
- [27] D. Yang, A. Velamakanni, G. Bozoklu, S. Park, M. Stoller, R.D. Piner, S. Stankovich, I. Jung, D.A. Field, C.A. Ventrice Jr., R.S. Ruoff, *Carbon* 47 (2009) 145–152.
- [28] W. Zhang, S. Lin, C. Wang, J. Hu, C. Li, Z. Zhuang, Y. Zhou, R.A. Mathies, C.J. Yang, *Lab on a Chip* 9 (2009) 3088–3094.
- [29] W. Zhang, V. Carravetta, O. Plekan, V. Feyer, R. Richter, M. Coreno, K.C. Prince, *Journal of Chemical Physics* 131 (2009) 035103.
- [30] A. Ferrari, J. Robertson, *Physical Review B* 64 (2001) 075414.
- [31] A.C. Ferrari, S.E. Rodil, J. Robertson, *Diamond and Related Materials* 12 (2003) 905–910.
- [32] C.B. Cao, F.L. Huang, C.T. Cao, J. Li, H.S. Zhu, *Chemistry of Materials* 16 (2004) 5213–5215.
- [33] D. Rovnyak, M. Baldus, B.A. Itin, M. Bennati, A. Stevens, R.G. Griffin, *Journal of Physical Chemistry B* 104 (2000) 9817–9822.
- [34] W. Gammon, D. Malyarenko, O. Kraft, G. Hoatson, A. Reilly, B. Holloway, *Physical Review B* 66 (2002) 153402.
- [35] G. Socrates, *Infrared and Raman Characteristic Group Frequencies Tables and Charts*, 3rd ed., Wiley, New York, 2000.
- [36] C. Reichardt, *Solvents and Solvent Effects in Organic Chemistry*, 3rd ed., Wiley, New York, 2002.
- [37] K.M. Jinka, J. Sebastian, R.V. Jasra, *Journal of Molecular Catalysis A: Chemical* 274 (2007) 33–41.
- [38] M.B. Ansari, E.A. Prasetyanto, J. Lee, S.-E. Park, *Research on Chemical Intermediates* 36 (2010) 677–684.
- [39] X. Tong, J. Xu, H. Miao, G. Yang, H. Ma, Q. Zhang, *Tetrahedron* 63 (2007) 7634–7639.