CHAPTER II
THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Nanoporous Carbon

Porous carbon materials can be synthesized by various method :

1. Chemical activation, Physical activation, and a combined physical/chemical activation process.

2. Carbonization of carbon precursors consist of thermosetting and thermally unstable component.

3. Catalytic activation of carbon precursors with metal(oxide) or organometallic compounds.

4. Carbonization of carbon aerogel, cryogel, or xerogel.

5. Presynthesized of hard templates through impregnation, carbonization, and template removal.

6. Self-assembly by using soft templates through cocondensation, and carbonization.

Methods 1 to 4 are less attractive because they can produced porous carbon material with broad pore-size distributions.

Methods 5 and 6 are the recent developments in synthesizing mesoporous carbon materials with well-controlled mesopores. These two method can be called template synthesis method, which can be classified in to two modes; hard-templating and soft-templating method. (Liang et al., 2008)

2.1 Template Synthesis Method

2.2.1 Hard-template Synthesis Strategy for Mesoporous Carbon Material

The template acts as a mold to form mesoporous carbon material, and no chemical reaction between carbon precursors and templates. Preparation of porous carbon are shown in Fig. 2.1: (a) carbon precursor and the inorganic template were mixed together by wet impregnation, chemical vapour deposition or a combination of both methods; (b) polymerization and carbonization of carbon precursor; (c) the

removal of inorganic templates by using strong acid or strong base to yield a porous carbon.
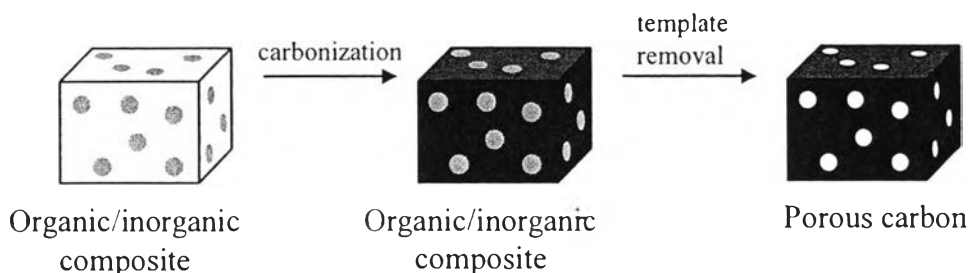

Organic/inorganic composite   Organic/inorganic composite   Porous carbon

Figure 2.1 Preparation of porous carbon by using hard-templating method.

Ryoo *et al.* (1999) prepared mesoporous carbon by using mesoporous silica molecular sieves (MCM-48) as a template and sucrose as a carbon source. Sucrose and sulfuric acid were impreged into the pores of silica molecular sieve. After the impregnation, the silica material was heated to 1073-1373 K under vacuum or in an inert atmosphere. Finally, the silica framework was removes by dissolution typically in aqueous solution containing NaOH and ethanol. The resulting porous carbon material was referred to CMK-1. The argon adsorption-desorption isotherm and the corresponding pores size distribution for CMK-1 reported the pores of 3.0 nm in diameter.

Lee *et al.* (1999) synthesized mesoporous carbon material with regular three-dimensionally interconnected pore channels. A mesoporous MCM-48 aluminosilicate has been used as a template. Aluminium was implanted onto MCM-48 to generate strong acid catalytic sites for the polymerization of phenol and formaldehyde. Phenol and formaldehyde were incorporated into the pores of aluminium-implanted MCM-48 (AlMCM-48) by heating for 12 h at 90 °C under reduced pressure. The polymerization of phenol and formaldehyde to obtain the phenol resin inside AlMCM-48 was carried out by heating the mixture under a nitrogen atmosphere at 125 °C for 5 h. The resulting AlMCM-48–phenol resin composite was heated under an N2 flow at a heating rate of 5 °C/min, 21 to 700 °C and held there for 7 h to carbonize phenol resin inside the MCM-48 channels. The dissolution of MCM-48 frameworks using 48% aqueous hydrofluoric acid (HF)

generated mesoporous carbon, designated SNU-1 (Seoul National University).

2.2.2 Soft-template Synthesis Strategy for Mesoporous Carbon Material

Produce nanostructures by self-assembly of organic molecules. Pore structures are determined by synthetic conditions such as mixing ratios, solvents, and temperature.
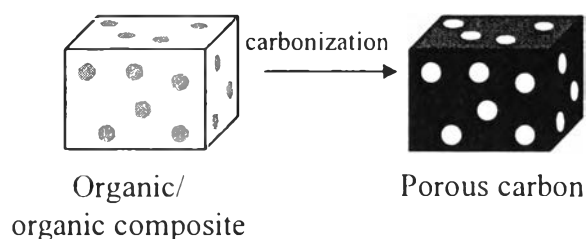

Organic/
organic composite   Porous carbon

Figure 2.2 Preparation of porous carbon by using soft-templating method.

Dai *et al.* (2004) first successfully prepared highly ordered and well-oriented mesoporous carbon films through self-assembly of polystyrene-block-poly(4-vinylpyridine) (PS-P4VP) and carbonization of a nanostructured resorcinol-formaldehyde resin composite.

The basis of this methodology is to first preorganize the resorcinol monomers into a well-ordered nanostructured film with the assistance of polystyrene-block-poly(4-vinylpyridine) self-assembly and solvent-induced structural annealing, which is followed by the in situ polymerization of the resorcinol monomers with formaldehyde vapor to form ordered nanostructured resorcinol-formaldehyde resin. Upon carbonization, the nanostructured resorcinol-formaldehyde resin is transformed into a highly ordered nanoporous carbon film with the concomitant decomposition of the PS-P4VP template to gaseous species.

The resulting mesoporous carbon thin films possess oriented cylindrical pores perpendicular to the substrate with dimension of 35 nm.
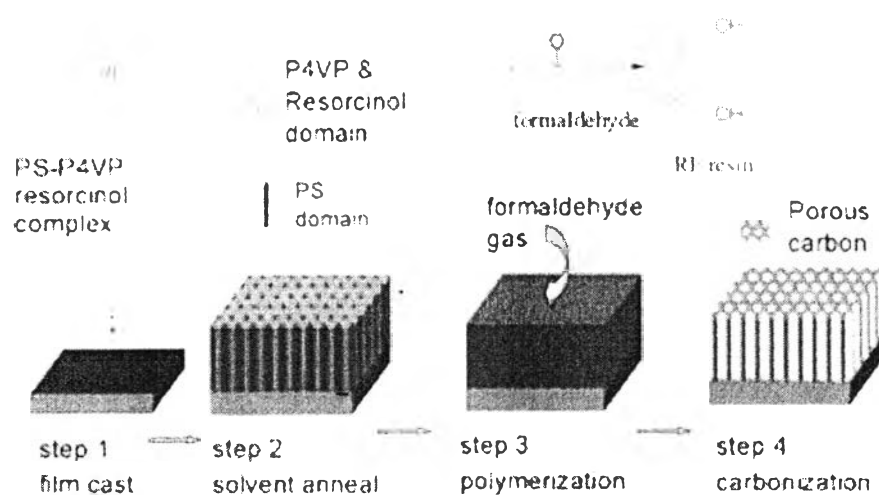
Figure 2.3 Preparation of porous carbon by using polystyrene-block-poly(4-vinylpyridine) as a soft template. (Dai *et al.*,2004)

Tanaka *et al.* (2005) fabricated mesoporous carbons with ordered channel structure (COU-1) via a direct carbonization of an organic-organic nanocomposite.

They used this method to avoids the use of hard templates, reduce cost and the number of preparation steps. In this work, they use an organic-organic interaction between a thermosetting polymer (resorcinol-formaldehyde) and a thermally decomposable surfactant (Triblock copolymer Pluronic F127) to form an ordered nanocomposites. The thermosetting polymer is carbonized by heating under N_2, after which process it remains as a carbonaceous pore wall. Resorcinol/formaldehyde (RF) and triethyl orthoacetate (EOA) were used as the carbon co-precursors and Pluronic F127 was used as template. The resultant materials are referred to as COU-1. The result mesoporous carbon materials shown the pore diameters of 7.4, 6.2, and 5.9 nm., which is carbonized at 400, 600 and 800 °C, respectively.
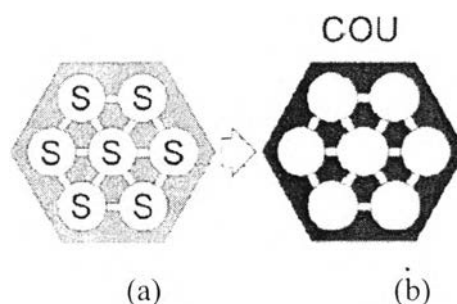
COU

(a)   (b)

Figure 2.4 Preparation of porous carbon. (a) Self-assembly of carbon precursor and surfactant. (b) Obtaining of COU-1 via removal of surfactant by direct carbonization. (Tanaka *et al.*,2005).

2.2 Polybenzoxazine

Polybenzoxazine, a new high performance phenolic resin. Unlike traditional phenolic resin, polybenzoxazine provides some characteristics such as excellent dimension stability, high heat resistance, flame retardance, low moisture adsorption, and good dielectric properties (S. Rimdusit, 2012).

Benzoxazine resin can be easily synthesized by a combination of phenolic derivative, formaldehyde, and a primary amine without using strong acid or basic catalysts. Since the polymerization takes place via thermally activated ring-opening mechanism; as a result, no by product is generated (Ishida, 2011).
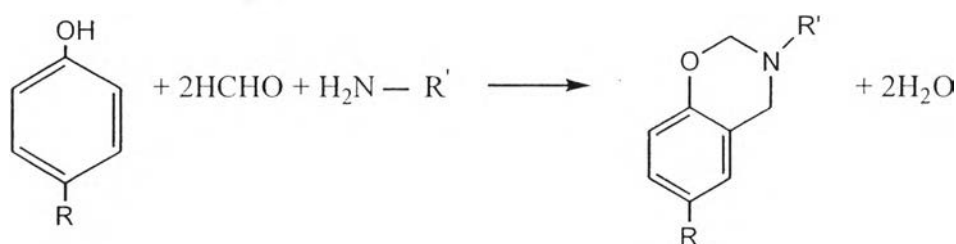

Figure 2.5 Synthesis of benzoxazine resin, where X and R are subtituents. R includes a group such as benzene, CH_3, and C_2H_5 (Ishida, 2011).

Polybenzoxazines have been applied in many fields such as protective coatings for circuits in television studios and computer chips, materials for airplane interiors, curing agents for other synthetic resins, and varnishes which form films with a good resistance to water, alkali and solvent.

2.3.1 Chemical Methodologies for Synthesis of Benzoxazine Monomers

The typical way to synthesis benzoxazine monomer is using phenol, formaldehyde and amine (aliphatic or aromatic) as starting materials either by employing solution or solventless methods. Various types of benzoxazine monomer can be synthesized using various phenols and amines with different substitution groups attached (Ghosh et al., 2007).

2.3.1.1 Mono-functional Benzoxazine Monomers

Holly et al. (1944) first reported the condensation reaction of primary amines with formaldehyde and substituted phenols for the synthesis of well defined benzoxazine monomers. According to the reported procedure, this reaction was performed in a solvent in two-steps. Later, Burke (1949) found that the benzoxazine ring reacts preferentially with the free ortho positions of a phenolic compound and forms a Mannich bridge. The synthetic procedure of the Mannich condensation for benzoxazine synthesis in a solvent proceeds by first addition of amine to formaldehyde at lower temperatures to form an N,N-dihydroxymethylamine derivative, which then reacts with the labile hydrogen of the hydroxyl group and ortho position of the phenol at the elevated temperature to form the oxazine ring.
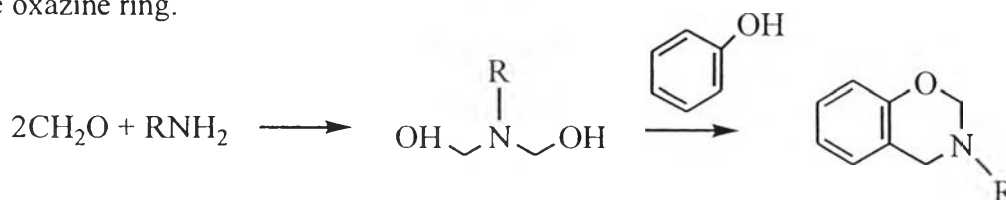
$$2CH_2O + RNH_2 \longrightarrow OH \smile N \smile OH \longrightarrow$$

Figure 2.6 Synthesis of 3,4-dihydro-2H-1,3-benzoxazines (Ghosh et al., 2007).

The slow reaction rate, large amount of solvent required for the synthesis and, in some cases, the poor solubility of the precursors are the major disadvantages associated with this procedure. The use of an organic solvent also increases the cost of the products and causes environmental problems. In addition, the solvent residue in the precursors also leads to problems during processing of the benzoxazine resins (Brunovska, 1999). To overcome these shortcomings, Ishida *et al.* (1996) developed a solventless synthesis in the melt state.

Liu (1995) proposed the reaction mechanism and kinetics of solventless synthesis. In this method, aldehyde, amine and phenolic precursors were physically mixed together, heated to their melting temperature, and maintained at a temperature sufficient to complete the interaction of reactants to produce the desired benzoxazine. In this connection, formaldehyde is not typically used as it evaporates easily and loss stoichiometry quickly. Instead, paraformadehyde was used. The choice of amines and phenols provided the flexibility in designing monomer structure for tailoring the properties of the resulting polybenzoxazine. The main advantages of the solventless method are the improvement of reaction times compared with the traditional synthetic rout and the formation of fewer unwanted intermediates and by-products.

2.3.1.2 Di-Functional and Multifunctional Benzoxazine Monomers

Ishida *et al* (1994 and 2002) have developed a novel type of difunctional or multifunctional benzoxazine monomers, and their curing with ring opening reactions into phenolic materials being initiated by dimers and higher oligomers in the resin composition. The precursor synthesized by using formaldehyde, bisphenol-A, and methyl amine in different solvent and refered to as B-m (figure 2.7), as a reference to two of its original ingredient : methylamine and bisphenol-A. The main component of products was a monomer with difunctional benzoxazine ring structure at both side of bisphenol-A. The rest of composition compose of a mixture of dimmers and oligomers, with both benzoxazine rings and free phenol structure.
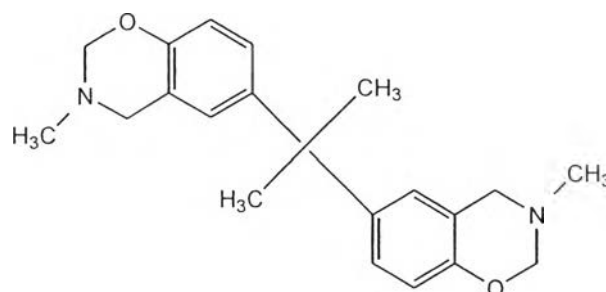
Figure 2.7 Chemical structure of benzoxazine (B-m) monomer (Ghosh *et al.*,2007).

2.3.2 Preparation of High-Molecular-Weight Benzoxazine Precursors

Takeichi *et al.* (2005) prepared a high molecular weight polybenzoxazine precursors containing cyclic benzoxazine groups in backbone from bisphenol-A, various diamimes, and paraformaldehyde (Figure 2.8). They reported that, partially ring-opened structure was observed, but the ratio of the ring-closed structre in the precursor was high enough to be used as polybenzoxazine precursors. They also found that, the polybenzoxazine films from the high molecular weight precursors exhibited significantly improved toughness than the typical polybenzoxazine, PB-a, due to the long linear backbone and high crosslink density. The Tg values of polybenzoxazines from the high molecular weight precursors were 238–260 °C, much higher than the Tg of the typical PB-a (171 °C). Thermal stability of the polybenzoxazine depended on the aromatic content, and polybenzoxazine from aromatic diamine showed higher thermal stability than that of PB-a.
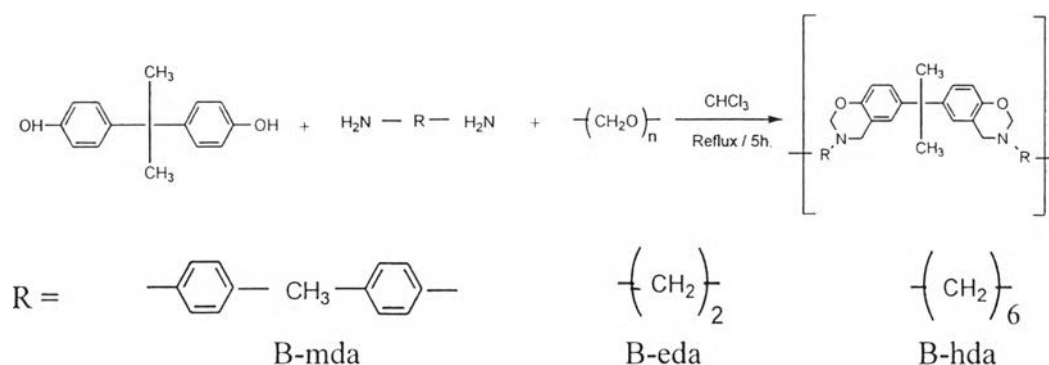
R =   B-mda   B-eda   B-hda

Figure 2.8 Preparation of polybenzoxazine precursors (Takeichi *et al.*, 2005).

Agag *et al.* (2007) synthesized AB-type benzoxazine precursors a high molecular weigh polybenzoxazine precursors from aminophenols and formaldehyde (figure 2.9). They obtained self-standing thin film from the precursors before curing by casting the precursor solutions onto glass plates. Furthermore, both viscoelestic analysise and TGA indicated that the thermoset derived from novel AB precursors have excellent thermomechanical properties as well as high thermal stability. This can be attributed to the increase in crosslinking density and hence suggests that the use of AB precursors were an effective ways to obtained the excellent thermomechanical properties.
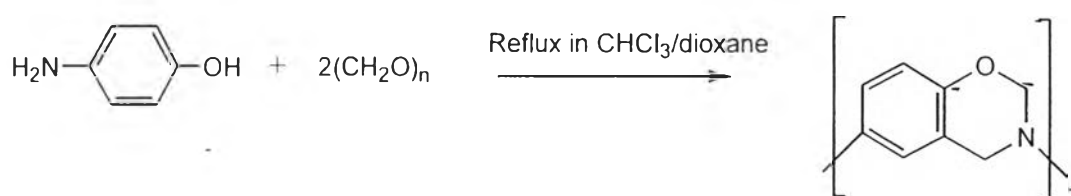

Figure 2.9 Preparation of AB-ρ-aminophenol (AB-PAP) as a polybenzoxazine prepolymer (Agag *et al.*, 2007).

Katanyoota *et al.* (2010) prepared carbon aerogel electrode for supercapacitors from two types of polybenzoxazine with two difference amines; aniline (BA-a), and triethylenetetramine (BA-teta). These precursors were prepared from the main chemicals shown in Table 1 The BA-teta consisted of a partially cured

state similar to the traditional preparation of polybenzoxazine precursors by Takeichi et al. (2005), but had a lower thermal stability than BA-a due to no presence of aromatic group at (C) position after the fully cured stage in Fig 2.10. Nevertheless, a char yield of the BA-teta was higher because crosslinking density might be higher which result from H-bonding of the secondary amines in the chain.

Table 2.1 The molar ratio of bisphenol-A (BA), amines, and aldehydes in each precursor (Aniline is abbreviated as "a" and triethylenetetramine as "teta") (Katanyoota *et al.*, 2010)

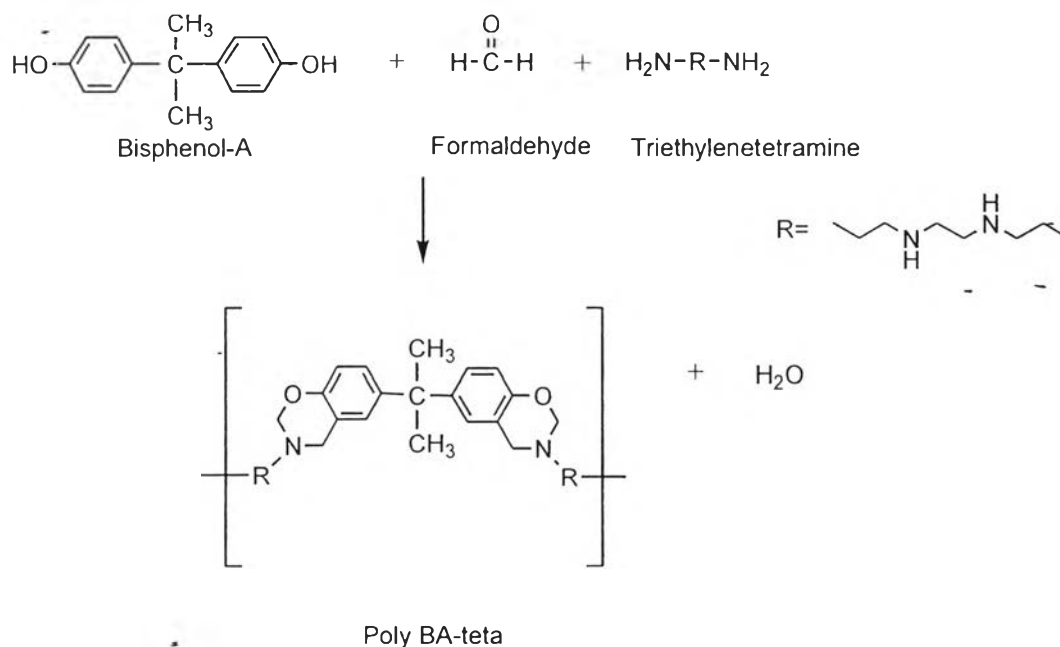| Precursors | The ratio of molar mass | | | | |
| | Bisphenol-A | Aldehydes | | Amines | |
		Paraformal-dehyde	Formalde-hyde	Aniline	TETA
BA-a	1	4	-	2	-
BA-teta	1	-	4	-	1

Poly BA-teta

Figure 2.10 Preparation of poly BA-teta precursor (Katanyoota *et al.*, 2010).
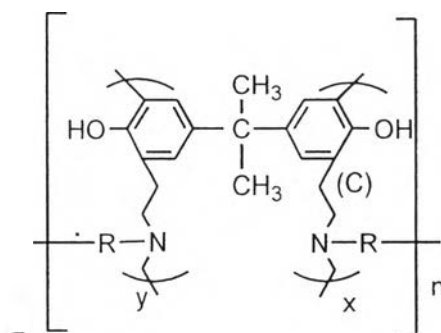
Figure 2.11 The structure of poly BA-teta in the fully cured stage (Katanyoota *et al.*, 2010).

2.3 Morphological Designed Porous Carbon

Carbon material is very useful in daily life. They have been use and still developed in many research group. This is because of their indispensable applications in energy storage and conversion, catalysis, adsorption, and others. The evidence is that a number of new structured carbon materials have been synthesized from molecular level. Nowadays, it has possible to synthesized carbon materials with defined nanostructure and morphology, tunable surface area, and pore size.

Nanoporous carbon have a number of remarkable properties such as ;

1. Carbon is a light element and structure made from carbon tend to be light weight. (C is about six times lighter than Fe)

2. Carbon in tubular form has been shown to be the strongest material synthesized to date.

3. Carbon can act as conductor, semi conductor or insulator depending on the C-C bonding and C structure.

4. The surface of carbon materials can be chemically modified (functionalized), leading to a new generation of reagent that can be used in new applications, for example, in composite materials.

Li and Xue (2012) reported the structural and textural properties of pordered porous carbon nanoparticles with well-controlled morphologies from sphere to rod via a sofe template route by using phenol-formaldehyde as carbon

yielding component and triblock copolymer Pluronic F127 as soft template.

They found that, rod-shape nanoparticles was obtained by the concentration of F127 was set at ~12 wt%. By decreasing the F127 concentration to 9 wt%, the rod-shaped porous carbon nanoparticles were evolved to be worm-like. When the F127 concentration was further decrease to 6 wt% and below 3 wt%, spherical porous carbon nanoparticle with different particle size were obtained.
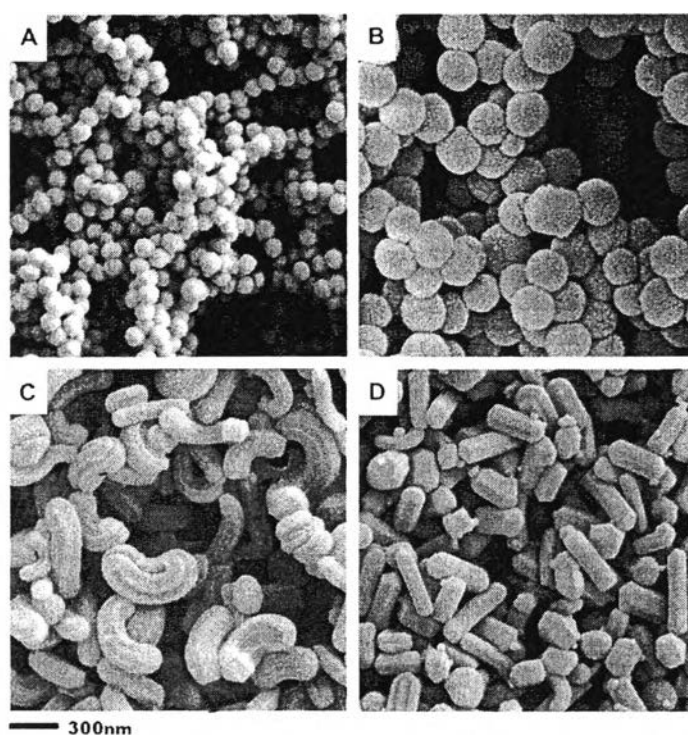

Figure 2.12 SEM images of the ordered porous carbon nanoparticles with different morphologies: (A) 3 wt%, (B) 6 wt%, (C) 9 wt%, (D) 12 wt% F127 (Li and Xue , 2012).

Figure 2.13 TEM images of the ordered porous carbon nanoparticles with different morphologies: (A) 3 wt%, (B) 6 wt%, (C) 9 wt%, (D) 12 wt% F127 (Li and Xue , 2012).
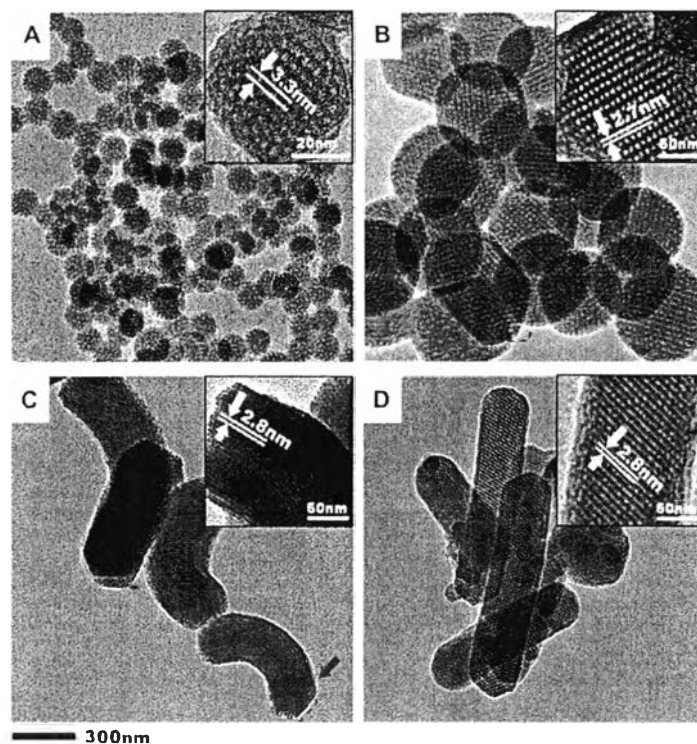
Fig. 2.12 showed the scanning electron microscopy (SEM) images of four typical ordered porous carbon nanoparticles. Porous carbon with low F127 concentration of 3wt% showed a spherical in morphology and had an average particles size of 50 nm. The transmission electron microscopy (TEM) image, as shown in Fig. 2.13, clearly showed their ordered structure. By decreasing the F127 concentration to 6 wt%, spherical carbon nanoparticles with diameter of 200 nm were obtained. When the F127 concentration was increase to 9 wt%, there was a dramatic change in the nanoparticle morphology, that is, worm-like carbon nanoparticles were obtained (Fig. 2.13C). Finally, rod-like carbon nanoparticles were obtained by increasing the F127 concentration to 12 wt%.