



CHAPTER IV

PREPARATION OF AN INTERCONNECTED MACROPOROUS RESORCINOL-FORMALDEHYDE (RF) GEL AND CARBON MONOLITH BY ULTRASONIC IRRADIATION DURING GEL-FORMATION FOLLOWED BY CARBONIZATION WITH N₂

An investigation for the preparation of a resorcinol-formaldehyde (RF) monolithic gel synthesized from reaction of sol-gel polycondensation with the assistance of ultrasonic irradiation during gel-formation stage is reported here. Gel-formation time, volume shrinkable after drying, the effect of ultrasonic irradiation time on the interconnected macroporous structure and chemical functional groups of the RF monolithic gel is focused for the investigation. Furthermore, the results in the macropores size of the carbon monolith, which is obtained by carbonization the RF monolithic gel with N₂, by adjustments of the several synthesis parameters in the gel-formation stage are presented and discussed.

4.1 Experimental

4.1.1 Preparation of RF monolithic gel by ultrasonic irradiation during sol-gel polycondensation

4.1.1.1 Preparation of RF solution

At first, the resorcinol (R) was dissolved into the de-ionized water (W) and stirring it with magnetic stirrer until dissolution completely. Then, the resorcinol solution was added with sodium carbonate (C) and followed continuously by adding the formaldehyde solution (F). Next, the mixture was stirred with magnetic stirrer for 5 min at the room temperature.

4.1.1.2 Gel formation stage

The experimental detail in this stage was divided into two sections; the first section is to investigate the effect of ultrasonic irradiation on the gel-formation time,

volume shrinkable after drying, the macropore structure and chemical functional groups of the RF monolithic gel, and the second section is to study the synthesis parameters in the gel-formation step affecting the macropores size of the carbon monolith. The experimental details in each section are described as followed.

An investigation the effect of ultrasonic irradiation on the gel-formation time, volume shrinkable after drying, the macropore structure and chemical functional groups

Prior to experiment, the reactant ratios of resorcinol to formaldehyde, R/F, resorcinol to water, R/W, and sodium carbonate to water, C/W, were fixed at 0.5 mol/mol, 0.15 mol/mol, and 10 m³/g, respectively. Then, the RF solution under mentioned condition was irradiated with high intensity ultrasonic wave at the frequency and power of 20 kHz and 22 W, respectively, during gel formation stage by controlling the temperature during gel-formation stage at 30 °C. As above condition, the complete gel-formation time was success at around 8 hr in order to investigate the role of ultrasonic irradiation time, t_{US} , the RF solution was irradiated by ultrasound at the initial stage to 3 hr, 6 hr, 7 hr, and around 8 hr. While the RF monolith gel synthesized without ultrasonic irradiation was used as a blank. All above experimental were performed with the ultrasonic reactor apparatus as shown in Figure 3.1. When the ultrasonic irradiation was terminated at above mentioned time, the RF solution was transferred into the cylindrical glass tube, sealed the open ends and followed by keeping at the room temperature until the gel was set completely. After the removal of RF wet-monolith gels from the tube, the monolith gels were washed by distilled water daily for 3 day and followed by drying with hot air at 75 °C until the weight was constant. Finally, the RF dried-monolith gels were obtained.

A study on synthesis parameters in the gel-formation step affecting the macropores size of the carbon monolith

The synthesis conditions of the initial pH value of the RF solution, pH_{Int} , the gel-formation temperature during ultrasonic irradiation, T_{US} , and the ultrasonic power, P_{US} , as shown in Table 4.1 were investigated. Prior to experiment, the molar ratios of R/F and R/W of the RF solution were fixed at 0.5 mol/mol and 0.15 mol/mol,

respectively, whereas the ratios of C/W was varied from 3 to 15 mol/m³ for changing pH_{int} in the range of 4.8 to 6.9.

During gel-formation stage, the RF solution was irradiated with high intensity ultrasonic wave at the frequency of 20 kHz until nearly complete gel-formation. The synthesis conditions of T_{US} and P_{US} were varied in this stage. All above experimental were performed with the ultrasonic reactor apparatus as shown in Figure 3.1

After the ultrasonic irradiation was stopped, the RF solution was transferred into the cylindrical glass tube (inner diameter = 3 mm, length = 40 mm) where RF gel was formed. After that the gel was sealed at the ends of the tube, followed by 3 days for aging in the oven at temperature of 75 °C. After the removal of RF wet-monolith gels from the tube, the monolith gels were washed by distilled water daily for 3 day and followed by drying with hot air at 75 °C until the weight was constant.

4.1.2 Carbonization of the RF monolithic gel with N₂

The carbon monolith gels were prepared by carbonizing the RF monolithic gel in a quartz tube of the horizontal furnace as shown in Figure 3.2. N₂ was used as the carrier gas and flowed through a quartz tube containing the RF monolithic gels at 50 cm³ (at STP) /min. The furnace was heated at the heating rate of 10 °C/min by starting from room temperature to the temperature of 850 °C. Then it was maintained at this temperature for 30 min and cooled down to the room temperature. Finally the carbon monoliths were obtained. The carbonization process was carried out for the RF monolithic gels that were synthesized for study in the second experimental as above mentioned.

4.1.3 Characterizations

The macroporous structure of both RF gels and carbons are revealed by scanning electron microscope (JEOL, JSM-6700F). The macropore size distribution of the macroporous monolithic carbon is obtained by mercury porosimeter (Micromeritics, Pore-Sizer-9320). The micro/meso porosities are obtained from the adsorption and desorption isotherms of N₂ at 77 K measured by adsorption apparatus (BEL, mini-BEL Sorp.). A decrease in weight of the obtained carbon monoliths, % burn-off, was measured after carbonization and both physical and chemical

activations. Fourier Transform Infrared (FTIR) spectra were recorded using spectrometer (Perkin Elmer 1615), and the samples for analysis is formed as pellets made by crushing and mixing the samples with spectroscopy grade of KBr.

Table 4.1: Synthesis conditions of RF monolith gels and carbon monoliths

<i>^aSample name</i>	<i>Synthesis conditions</i>				
	R/F [mol/mol]	R/W [mol/mol]	pH _{Int}	T _{US} [°C]	P _{US} [Watt]
<u>Carbon monolith gel varied pH_{Int}</u>					
s-C1	0.5	0.15	4.8	30	22
s-C2	0.5	0.15	5.5	30	22
s-C3	0.5	0.15	6.0	30	22
s-C4	0.5	0.15	6.4	30	22
s-C5	0.5	0.15	6.9	30	22
<u>Carbon monolith gel varied T_{US}</u>					
s-C6	0.5	0.15	6.4	20	22
s-C7	0.5	0.15	6.4	25	22
s-C8	0.5	0.15	6.4	30	22
s-C9	0.5	0.15	6.4	45	22
<u>Carbon monolith gel varied P_{US}</u>					
s-C10	0.5	0.15	6.4	30	12
s-C11	0.5	0.15	6.4	30	22
s-C12	0.5	0.15	6.4	30	30

Remark: ^a The sample name in the series of s-Cx are denoted to the carbon monoliths derived from carbonization of RF monolith gels, obtained from several synthesis conditions, with N₂ at the flow rate, temperature, time and heating rate at 50 cm³/min, 850 °C, 30 min and 10°C/min, respectively.

4.2 Results and discussion

4.2.1 Investigation influence of ultrasonic irradiation on the RF monolithic gel

4.2.1.1 Gel-formation time and volume shrinkable resistance for drying

Table 4.2: Effect of ultrasonic irradiation on gel-formation time and %volume shrinkage after drying of the RF monolithic gels

Samples	Synthesis conditions			Results	
	pH _{Int}	T _{US} [°C]	P _{US} [Watt]	Gelation time [hr]	% volume shrinkage after drying
n-RF1	6.4	30	0	31	24
s-RF1	6.4	30	22	8	1

According to Table 4.2, the gel-formation time and %volume shrinkage of the RF monolithic gel synthesized via sol-gel polycondensation only, n-RF, and combination of ultrasonic irradiation and sol-gel process, s-RF, were compared. It is clear that the gel-formation time is shortened outstandingly with ultrasonic irradiation. The time obviously decreases from 31 hr to 8 hr. Hence, the irradiation of ultrasonic wave during gel-formation play role as the catalysis for the acceleration of RF gel synthesis. The %volume shrinkages of n-RF and s-RF after drying are 24% and 1% respectively. It is obvious that the role of ultrasonic irradiation during gel-formation leads to small shrinkage in volume of the RF monolithic gel.

4.2.1.2 Influence of ultrasonic irradiation time on macropore texture

The ultrasonic irradiation time, t_{US} , are varied at 0 hr (without using ultrasonic irradiation), 3 hr, 6 hr, 7 hr, and 8 hr (complete gel-formation) for investigation of the porous structure in the range of micrometer of the RF monolithic gels. It is noticed that all of obtained RF gels in monolithic shape can be obtained as shown in Figure 4.1 (a). According to Figure 4.1 (b) to (f), the SEM images which reveal the internal structure in the range of micrometer scale of the RF monolithic gels synthesized under

several t_{US} are shown. One can see that when t_{US} is extended to 7 hr, the interconnected macroporous structure is started to form as shown in Figure 4.1 (e). As t_{US} is terminated at nearly complete gel-formation ($t_{US} = 8$ hr), the fully interconnected macroporous structure is obtained as shown in Figure 4.1 (f). However, the porous structure of the RF monolithic gel synthesized under t_{US} at 3 hr and 6 hr, Figure 4.1 (c) and (d) respectively, are not different from the RF monolithic gel without using ultrasonic irradiation during gel-formation, Figure 4.1 (b). These results clearly suggest that the irradiation of high intensity ultrasonic wave from initial stage to nearly complete gel-formation can play an importance role to form the interconnected macroporous structure in the RF monolith gel.

Unfortunately, the role of the ultrasonic irradiation for the formation of the interconnected macropores structure in the RF monolith gel can not precisely be understood at the present time. However, it is possible to suppose that the cavitation cloud, which is occurred from a series of rapid growth and collapse in continuous cycle of the cavity during irradiation with ultrasound, may be the key factor in making the interconnected macroporous structure. Because the macropore size of the RF monolith gel consistent agrees with the average size distribution of the cavity in water, which have been reported from several authors who determined and investigated these dynamic phenomena by several techniques, for instance, using high-speed photography and holography [32], using simultaneously a fiber optics laser knife and a laser-Doppler anemometer [33], using the laser phase-Doppler technique [34, 35], and so on. They have reported that the average cavity diameter is found to be at a few micrometer scales up to the several hundred micrometer scale depending on several factors such as power, temperature etc.

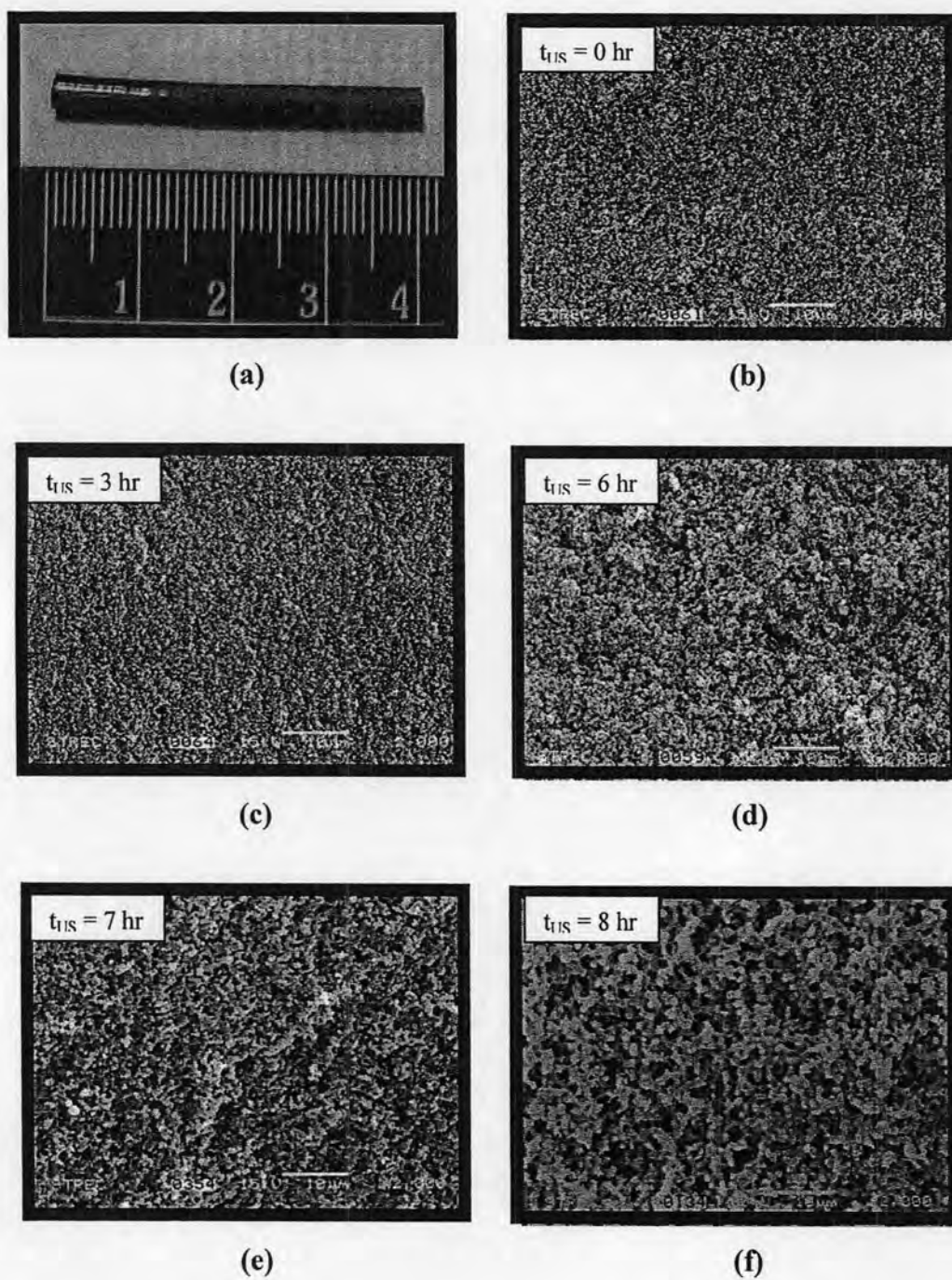


Figure 4.1: (a) Photograph of the resorcinol-formaldehyde (RF) monolithic gels, (b) to (f) SEM images of the macroporous structure of the RF monolithic gel synthesized under ultrasonic irradiation time, t_{US} , of 0 (b), 3 (c), 6 (d), 7 (e) and 8 hr (f).

4.2.1.3 Influence of ultrasonic irradiation on surface chemistry

According to Figure 4.2, there are no different of infrared spectra of RF monolith gels prepared form ultrasonic irradiation and without. They suggest that the ultrasonic irradiation has no effect on the surface functional groups of the RF monolith gel.

The infrared spectra for the both gels are in good agreement with many literatures [36 - 38]. These literatures have proposed the functional groups on the surface of the RF gels as shown in Figure 4.3. The broad bands around 3400 cm^{-1} , in this case at 3398 and 3410 cm^{-1} for n-RF1 and s-RF1 respectively, is assigned to hydroxyl groups (-OH) stretching vibrations owing to hydrogen bonding. They may be either -OH groups bonded to the benzene rings or -CH₂OH groups connected to the resorcinol molecule, which did not take path in network formation. The peaks at 2970 , 2942 and 1476 cm^{-1} for n-RF and at 2974 , 2940 and 1476 cm^{-1} for s-RF can may be attributed to the stretching of -CH₂ in methylene bridge. The aromatic skeleton stretching bands at around 1620 , 1480 and 1445 cm^{-1} [39, 40], in this case at 1618 , 1476 and 1442 cm^{-1} for n-RF1 and at 1116 , 1476 and 1442 cm^{-1} for s-RF1 respectively, are readily visible in the spectrum. The peaks at 1220 and 1098 cm^{-1} for n-RF and at 1218 and 1096 cm^{-1} for s-RF can be attributed to C-O-C linkage stretching between two resorcinol molecules. The peaks at 1370 and 1366 cm^{-1} for n-RF and s-RF can be assigned to phenolic-OH in-plane deformation. The peaks at 1296 and 1294 cm^{-1} for n-RF and s-RF, respectively, can be attributed to alkyl-phenol C-O stretching. The peaks at 900 and 998 cm^{-1} for n-RF1 and at 900 and 994 cm^{-1} for s-RF1 can be assigned to out-of-plane deformation vibrations of C-H groups mono-substituted to aromatic rings [40]. The peak bands in the region below 850 cm^{-1} is difficult to interpret because of several peaks overlapping. These peaks may be, however, due to C-C out-of-plane bending vibrations at substituted positions in aromatic rings [40 - 42].

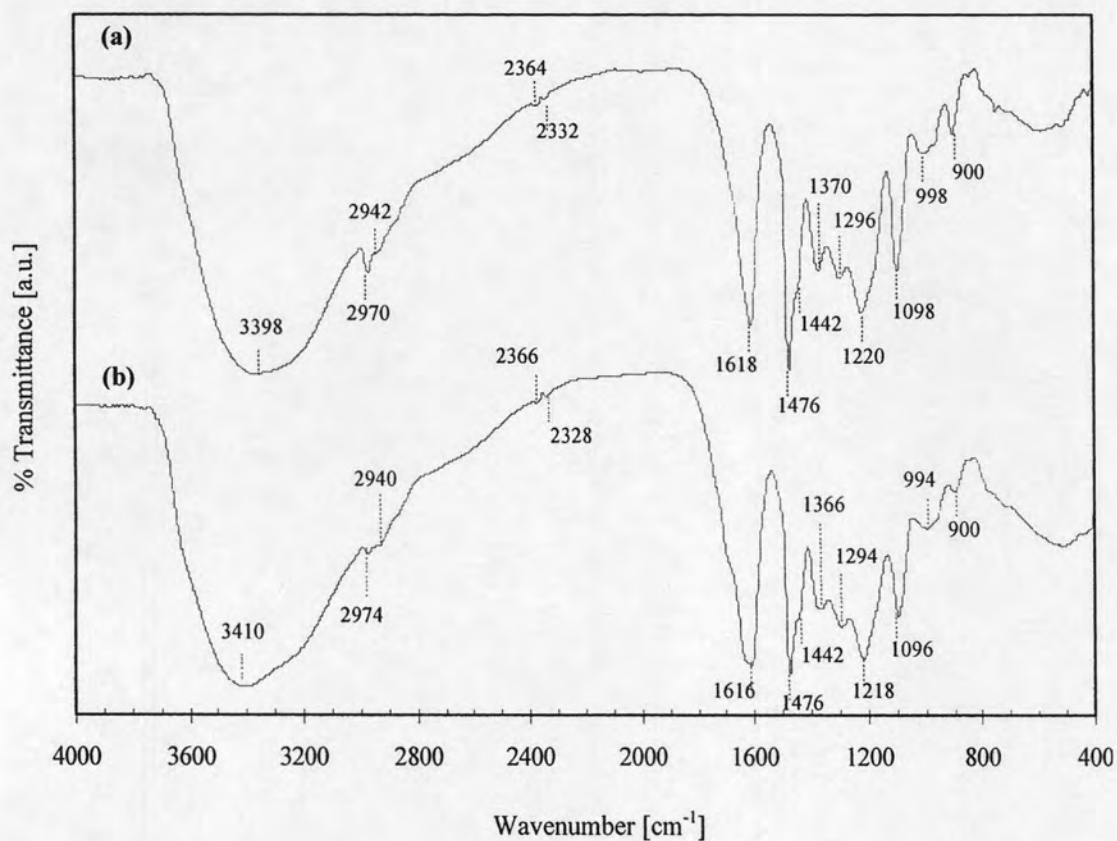


Figure 4.2: FTIR spectra of (a) the RF monolithic gel synthesized from only sol-gel polycondensation, n-RF1, and (b) the RF monolithic gel synthesized by ultrasonic irradiation during gel-formation (8 hr), s-RF1

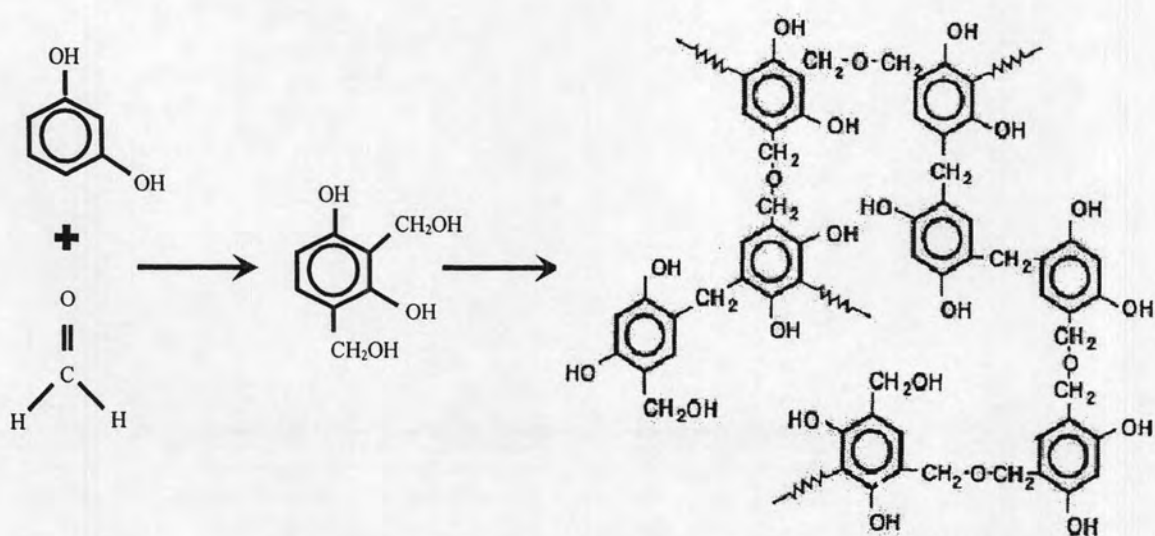


Figure 4.3: Schematic diagram of gel-formation by sol-gel polycondensation of resorcinol with formaldehyde [36]

4.2.2 Preparation of the interconnected macroporous carbon monolith by carbonization with N_2

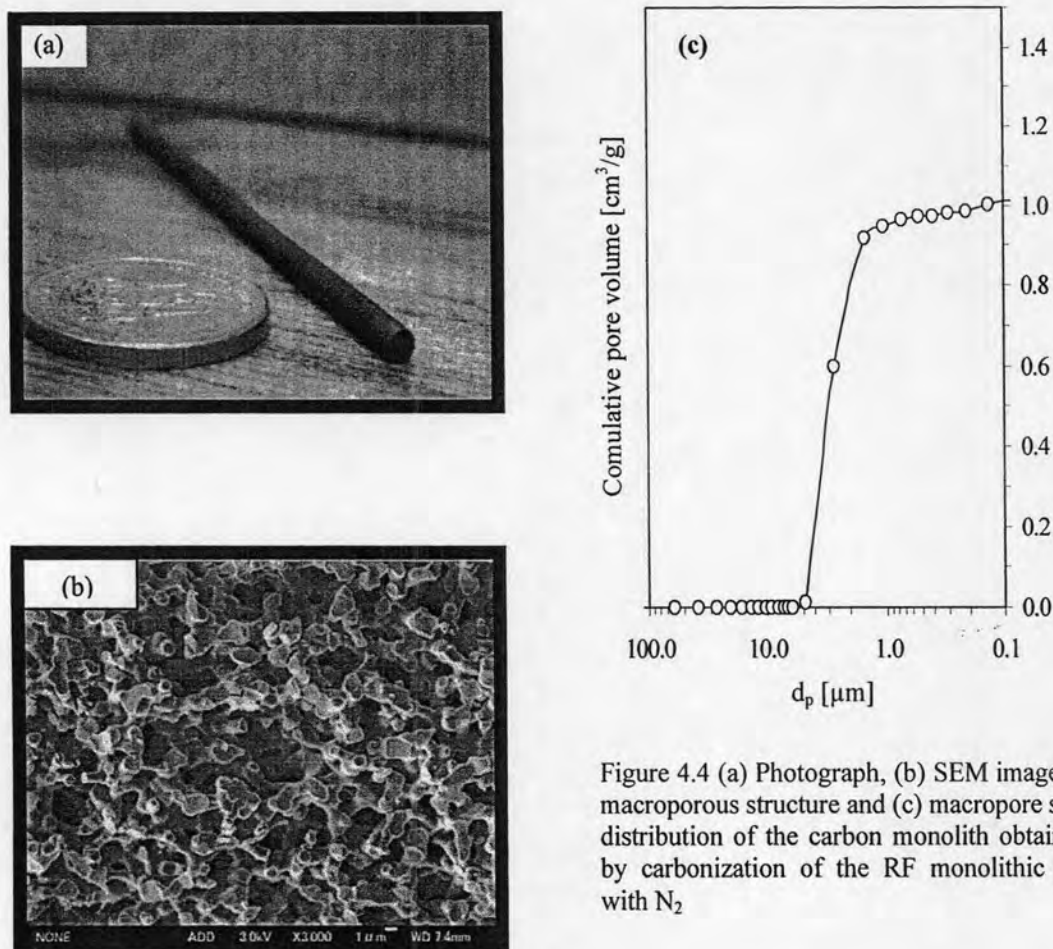


Figure 4.4 (a) Photograph, (b) SEM image of macroporous structure and (c) macropore size distribution of the carbon monolith obtained by carbonization of the RF monolithic gel with N_2

After carbonization of the RF monolithic gel, no change in the interconnected macroporous structure and very low shrinkage are observed as shown in Figure 4.4 (a). It can be seen from SEM micrograph in Figure 4.4 (b) that the carbon monolith can keep the interconnected macroporous structures. The macropore size distributions of carbon monolith are narrow, the average macropore size around 1.3 μm as shown in Figure 4.4 (c).

Figure 4.5 shows the adsorption-desorption isotherm of N_2 at 77 K on the monolithic RF gel and the obtained carbon monolith. There is not adsorbs N_2 on macroporous monolithic RF gel. It is indicated that there is not porosities in the range of micropores and mesopores. For the carbon monolith the isotherm is type I. It is indicated that the micropores is developed after carbonization.

Regarding to the porosities determined from the isotherm, the BET specific surface area, S_{BET} , and the micropore volume, V_{mic} , of the carbon monolith increases to $423 \text{ m}^2/\text{g}$ and $0.20 \text{ cm}^3/\text{g}$, respectively, after carbonization whereas the mesopore volume, V_{mes} , cannot be detected from Type I of isotherm.

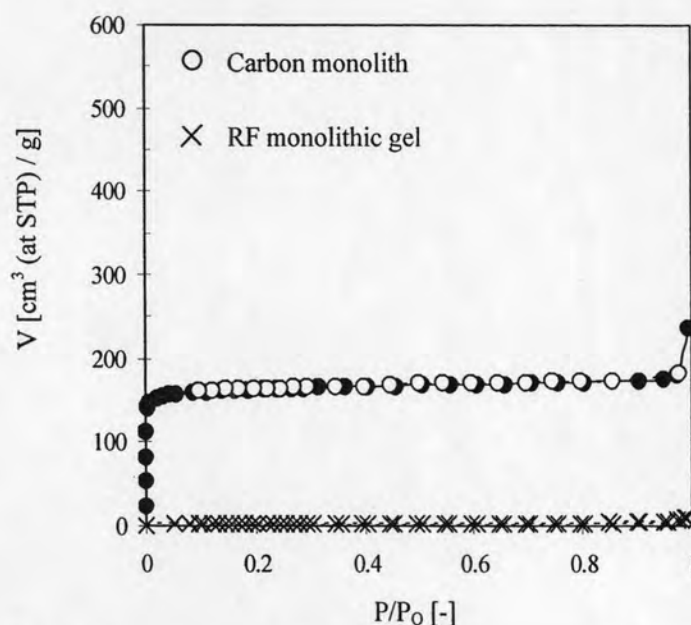


Figure 4.5: N_2 adsorption-desorption isotherm of interconnected macroporous RF monolithic gel and carbon monolith

4.2.3 A study on the influence of the synthesis parameters for changing the interconnected macropore size of the carbon monolith

4.2.3.1 By changing the initial pH value at the gel-formation step

In general, the initial pH value, pH_{Int} , of the RF solution can be directly changed by adjustment of the C/W ratios, and the relationship between these values is shown in Table 4.1. The parameter pH_{Int} , therefore, is discussed here. According to Table 4.1, the parameter pH_{Int} is varied at 4.8, 5.5, 6.0, 6.4 and 6.9, which are denoted as s-C1, s-C2, s-C3, s-C4 and s-C5 respectively, for investigation of the final macroporous structure of the carbon monoliths.

At first, the suitable pH_{Int} range for formation of the interconnected macroporous structure is investigated. It is revealed that the gel-formation at pH_{Int} of 4.8 results in aggregating of carbon particles without monolith formation, while the interconnected macroporous structure cannot be formed in the carbon monolith prepared from higher than pH_{Int} of 6.9. They clearly exhibit that the interconnected macroporous texture depends on the pH_{Int} .

The effect of the pH_{Int} is studied by SEM, and the micrographs of the interconnected macroporous texture of the carbon monoliths, s-C2, s-C3, s-C4 and s-C5, are shown in Figure 4.6 (a), (b), (c) and (d), respectively.

The SEM images clearly indicate that an increase in the pH_{Int} can result in size reduction of the interconnected macropores. The particle size of s-C2 is around 4 μm which each of the particles appears to be globular and connecting with the others. On the contrary, s-C3, s-C4 and s-C5 exhibit the interconnected macroporous structure, and their macropore sizes tend to decrease with an increase in pH_{Int} .

From Figure 4.7, the interconnected macropore size of the carbon monoliths increase with decreasing pH_{Int} , corresponding with the SEM images. The mean pore diameters of the macropore in the structure of s-C2, s-C3, s-C4 and s-C5 are 10.7, 3.1, 1.4 and 0.3 μm , respectively.

4.2.3.2 *By changing the temperature at the gel-formation step*

According to Table 4.1, the temperature at gel-formation step, T_{US} , is varied at 20, 25, 30 and 45 °C, which are denoted as s-C6, s-C7, s-C8 and s-C9 respectively, for investigation of the final macroporous structure of the carbon monoliths.

The SEM images in Figure 4.8 reveal that at the T_{US} of 20, 25 and 30 °C, which are denoted as s-C6, s-C7 and s-C8 respectively, the interconnected macroporous structure of the carbon monoliths are in a range of micrometer, whereas at the T_{US} of 45 °C, s-C9, the interconnected macroporous structure in a range of micrometer cannot be observed but monolith shape can be formed. Therefore, the suitable T_{US} to the formation of interconnected macroporous carbon monolith is not exceeding of 45 °C.

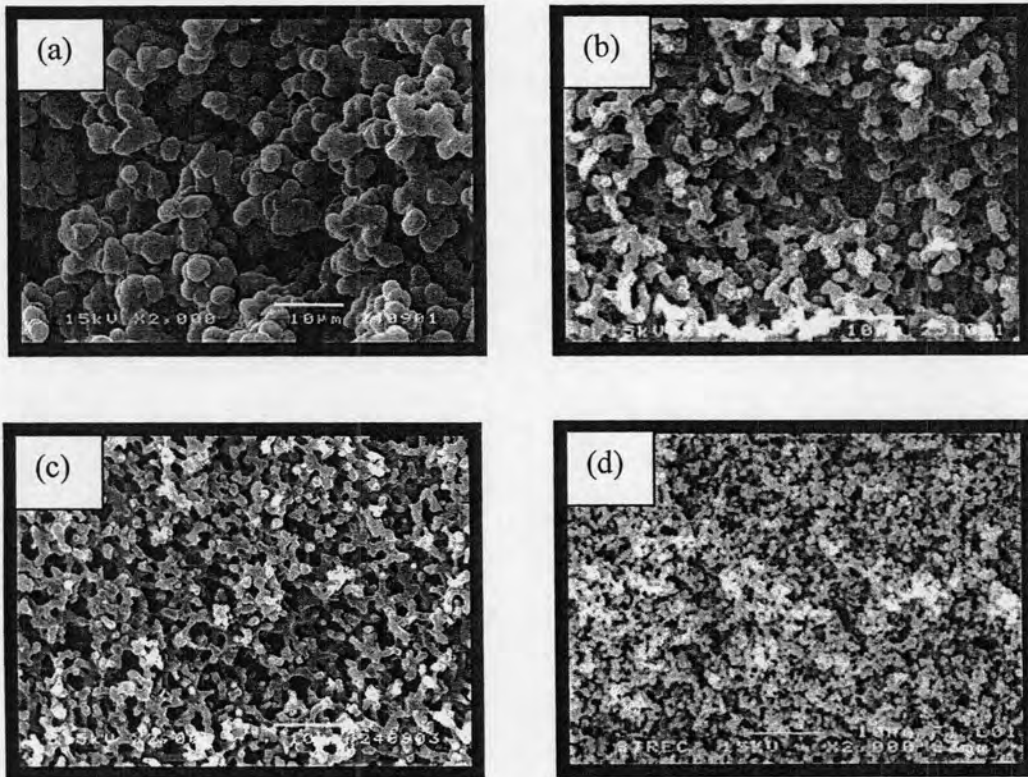


Figure 4.6: SEM images of macroporous structure of the carbon monolith prepared from RF monolithic gels synthesized at various pH_{int} of 5.5 (s-C2), 6.0 (s-C3), 6.4 (s-C4) and 6.9 (s-C5).

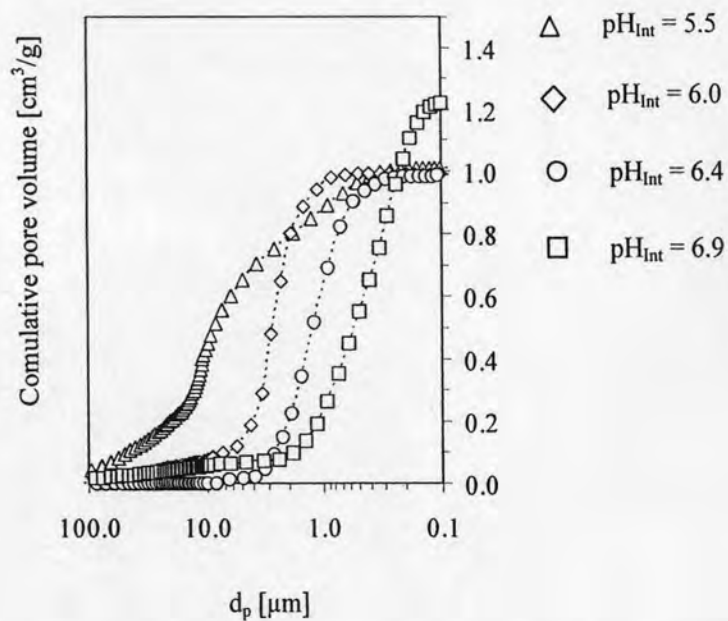


Figure 4.7: Macropore size distribution determination of the carbon monoliths prepared from the RF monoliths synthesized in conditions of pH_{int} at 5.5 (s-C6), 6.0 (s-C7), 6.4 (s-C1) and 6.9 (s-C8).

These results correspond with the macropore size distributions as shown in the Figure 4.9. The macropore size distributions of carbon monoliths get narrower when T_{US} increases. The mean macropore diameter of s-C6, s-C7 and s-C8 are 3.9, 2.3, and 1.4 μm , respectively, while the macroporous structure cannot be observed in s-C9.

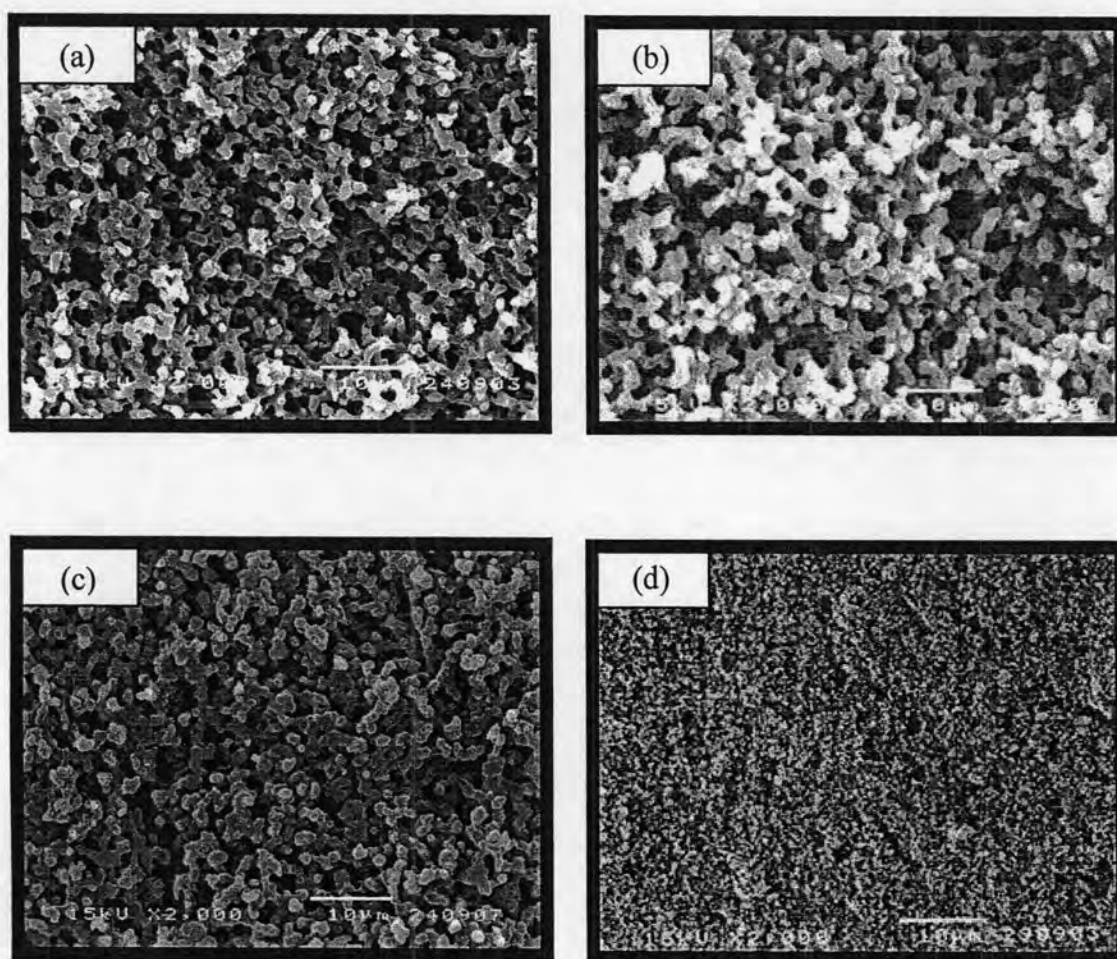


Figure 4.8: SEM images of macroporous structure of the carbon monolith prepared from RF monolithic gels synthesized in condition of T_{US} = (a) 20 (s-C6), (b) 25 (s-C7), (c) 30 (s-C8) and (d) 45 °C (s-C9)

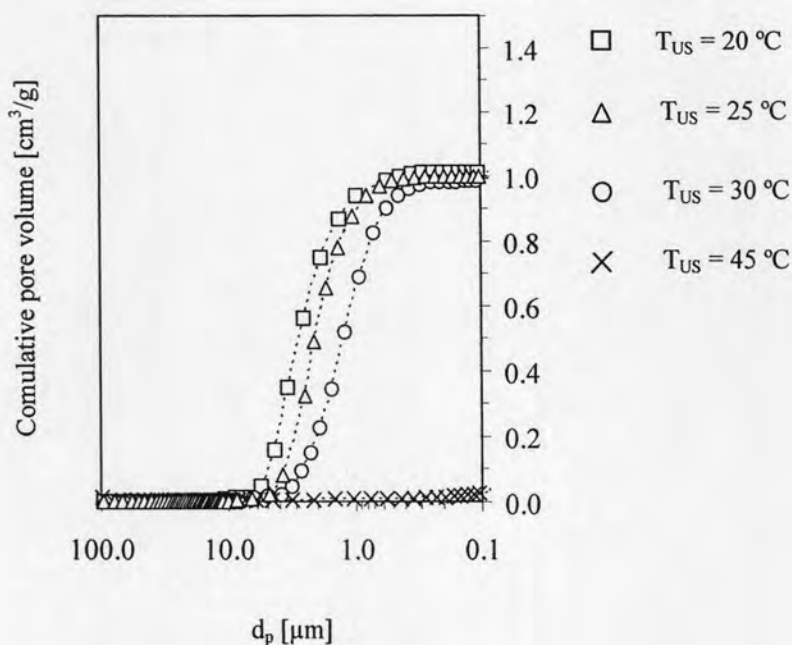


Figure 4.9: Macropore size distribution of the carbon monoliths prepared from the RF monolithic gel with $T_{US} = 20$ (s-C6), 25 (s-C7), 30 (s-C8) and 45 °C (s-C9)

4.2.3.3 By changing the power of ultrasonic irradiation at the gel-formation step

According to Table 4.1, the power of ultrasonic irradiation at the gel-formation step, P_{US} , is varied at 12, 22 and 30W, which are denoted as s-C10, s-C11 and s-C12 respectively, for investigation of the final macroporous structure of the carbon monoliths.

The effect of P_{US} on the interconnected macroporous structure of the obtained carbon monoliths is shown by SEM images in Figure 4.10 (a), (b) and (c). As the result, the internal structure of s-C12 ($P_{US} = 30$ W) exhibits the aggregation of 2 μm size-globular particles. While the carbon sample s-C11 ($P_{US} = 22$ W) exhibits the interconnected macropore throughout in its monolithic form. However, the interconnected macroporous structure of s-C10 cannot be obtained.

Figure 4.10 (d) shows the macropore size distribution of these carbon monoliths which indicates that the macropore size distribution of s-C12 is broader than s-C11. The mean pore diameters are 12.1 and 3.1 μm for s-C12 and s-C11 respectively. In addition, the macropore volume of s-C12 (1.4 cm^3/g) is also higher than s-C11 (1.0 cm^3/g).

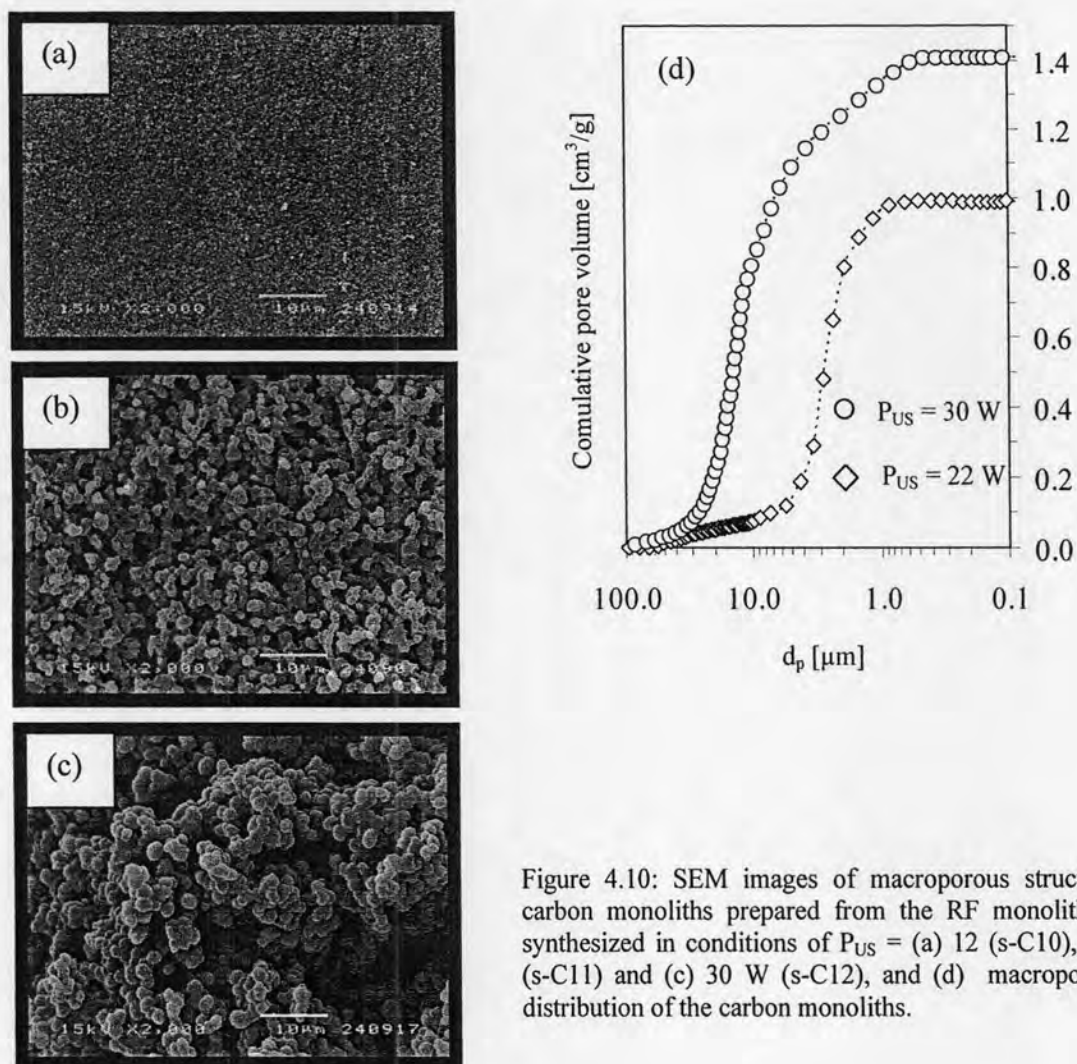


Figure 4.10: SEM images of macroporous structure of carbon monoliths prepared from the RF monolithic gel synthesized in conditions of P_{US} = (a) 12 (s-C10), (b) 22 (s-C11) and (c) 30 W (s-C12), and (d) macropore size distribution of the carbon monoliths.

4.3 Conclusions

Chapter IV focuses on an investigation of the effect of the ultrasonic irradiation during gel-formation on the internal structure of the obtained RF gel. Both monolithic form and interconnected macropores are established in the gel structure. It is found that the RF monolith gel with the interconnected macroporous structure can be achieved when ultrasound with constant frequency of 20 kHz is applied continuously into the RF solution from initial stage to nearly complete gel-formation. N_2 adsorption-desorption isotherm indicates that both micropores and mesopores are not located on the interconnected macropores of the RF monolith gel. Whereas the FT-IR result suggests that the ultrasound can not affect on the chemical compositions of the RF monolith gel because the surface functional groups are similar to the RF gel

synthesized without irradiating the ultrasound. From unique characteristics as mentioned above, the RF monolith gel which synthesized with an assistance of the ultrasonic irradiation during gel formation is a good carbon precursor for the preparation of the carbon monolith gel with hierarchical porous structure by carbonization with N_2 . For more concrete information, an investigation on the suitable preparing conditions and the effect of the preparing conditions on the interconnected macroporous structure are conducted. These preparing conditions are the initial pH value of RF solution, pH_{Int} , the gel-formation temperature, T_{US} , and the power of ultrasonic irradiation, P_{US} . The conclusion can be drawn from this work as followed.

1. The carbon monolith prepared by carbonization with N_2 not only can maintain the interconnected macroporous structure as well as the RF monolith gel but also can generate the micropores on the interconnected macroporous structure. Therefore, the carbon monolith with hierarchical microporous/macroporous structure can be obtained by carbonizing the interconnected macroporous RF monolith gel.
2. Both monolith form and interconnected macroporous structure of the carbon monoliths after carbonization depend strongly on the preparing conditions of pH_{Int} , T_{US} and P_{US} .
3. The suitable pH_{Int} values for the preparation of the carbon monolith with hierarchical porous structure are in the range of 5.5 to 6.9. The monolith form of both RF gel and carbon can not be obtained when the pH_{Int} is lower than 5.5. Whereas the interconnected macroporous structure of both carbon and RF monolith gel can not be obtained when the pH_{Int} is higher than 6.9. Moreover, an increasing pH_{Int} value can affect on a decrease in the interconnected macropores size of the carbon monolith.
4. The suitable T_{US} in preparing the carbon monolith with hierarchical porous structure is less than 45 °C to maintain the interconnected macroporous structure in the carbon monolith. Moreover, an increasing T_{US} can lead to a decrease in the interconnected macropores size of the carbon monolith.
5. The suitable P_{US} in the preparation of the carbon monolith with hierarchical porous structure must be higher than 12 W in order to maintain the interconnected macroporous structure in the carbon monolith.

Moreover, an increasing T_{US} can lead to an increase in the interconnected macropores size of the carbon monolith.

In summary, the ultrasonic irradiation during gel-formation of RF gel synthesis is a new effective method without using any templates for preparation the carbon precursor, in which possess both monolithic shape and interconnected macroporous structure. Such material is a good candidate to continuously preparing the carbon monolith with hierarchical porous structure. Moreover, the interconnected macropore size can easily be adjusted by changing the preparing conditions of the initial pH of RF solution, the temperature of gel-formation and the ultrasonic power.