

Organic acid-assisted soft-templating synthesis of ordered mesoporous carbons

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Abstract A series of soft-templated ordered mesoporous carbons (OMCs) was synthesized by using resorcinol and formaldehyde as carbon precursors, triblock copolymer Pluronic F127 as a soft-template, and an organic acid (acetic, benzoic, citric, oxalic, or succinic) as a polymerization reaction catalyst. The aforementioned organic acids were strong enough to facilitate the formation of ordered mesophases by the block copolymer template used and to catalyze the polymerization reaction of resorcinol and formaldehyde in this template. The use of weak organic acids instead of strong inorganic acids such as HCl eliminated inorganic anions from the reaction environment and resulted in high surface area OMCs. Basically, the resulting carbons showed the surface areas and pore volumes comparable to those reported for the carbons prepared under similar conditions but in the presence of strong inorganic acids. Electron microscopy analysis proved the presence of ordered mesopores, whereas thermogravimetric analysis showed a good thermal stability of these carbons.

Keywords Adsorption properties · Soft-templating synthesis · Mesoporous carbons · Organic acid-assisted synthesis · Block copolymers

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1 Introduction

Within the last decade, the research devoted to the development of ordered mesoporous carbons (OMCs) has been intensified. The reason for this growing interest is a high demand for applications of OMCs ranging from adsorption (Jun et al. 2000), catalysis (Chai et al. 2004), and separations (Liang et al. 2003) to energy storage and conversion (Kalbour et al. 2006). OMCs have been mainly prepared by hard and soft-templating. The former method makes the use of ordered mesoporous silica materials (Joo et al. 2001; Ryoo et al. 1999, 2001; Lee et al. 2004), colloidal silica (Han and Hyeon, 1999; Li and Jaroniec, 2001; Jaroniec et al., 2008), and colloidal crystals (Zakhidov et al. 1998; Yoon et al. 2005) as templates. The latter method employs triblock copolymers (Liang and Dai, 2006; Meng et al. 2006; Jaroniec et al. 2009; Gorke et al. 2009; Choma et al. 2010) as soft templates, phenol derivatives (such as phenol, resorcinol, or phloroglucinol) and formaldehyde as carbon precursors along with HCl or NaOH used to catalyze polymerization of carbon precursors. In the first stage of soft-templating, a mesostructured polymer–polymer composite is formed by the self-assembly of carbon precursors and block copolymer. Subsequent thermal treatment at elevated temperatures yields a mesoporous polymer, which subjected to carbonization yields a mesoporous carbon. Soft-templating is a simple and effective method for controlling the mesoporous structure of carbons; for instance, pH of the synthesis mixture influences the average pore size of the resulting carbons. The initial synthesis conditions, basic or acidic, affect the average pore size (which is about 4 or 8 nm, respectively) as well as the cross-linking and thickness of pore walls that determine chemical, mechanical, and thermal stability of the resulting carbons (Meng et al. 2006; Wang et al. 2008).

The synthesis of OMCs under basic conditions requires a precise pH control during the entire process. In addition, this recipe requires an additional step of pre-polymerization of phenol and formaldehyde to obtain resol, which is self-assembled with a block copolymer template. The base-catalyzed soft-templating was introduced for the first time by Zhao and co-workers (Meng et al. 2005, 2006; Zhang et al. 2005). Liang and Dai (2006), Wang et al. (2008) developed an alternative recipe under acidic conditions, which is less sensitive to pH changes. One of the disadvantages of the latter recipe is a high concentration of chloride ions introduced to the reaction environment along with HCl. The presence of these ions is not desirable in certain applications of OMCs. That is why more and more efforts have been made to develop the feasible and more environmentally friendly routes for the synthesis of OMCs. Lu et al. (2008) proposed the soft-templating synthesis of OMCs by using resorcinol and formaldehyde, triblock co-polymer Pluronic F127, and glutamic acid. The resulting mesoporous carbons possessed the specific surface area over 700 m²/g, total pore volume of ca. 0.60 cm³/g, and the thickness of pore walls of about 7 nm. In addition, Liu et al. (2011) synthesized soft-templated OMCs by using citric acid as a polymerization catalyst of resorcinol and formaldehyde. The resulting carbon materials were found to possess good thermal stability, hexagonally ordered mesoporous structure with the mean pore size of ca. 5.2 nm. The specific surface area varied in the range between 612 and 851 m²/g, and the total pore volume between 0.46 and 0.62 cm³/g. It was reported (Liu et al. 2011) that the aforementioned carbon materials can be useful for CO₂ adsorption and/or sequestration.

In the current work, organic acid-assisted soft-templating synthesis of OMCs is studied. A series of carbon samples was prepared by using resorcinol and formaldehyde as carbon precursors, triblock copolymer Pluronic F127 as a soft-template, and either: acetic, benzoic, citric, oxalic, or succinic acid as a polymerization catalyst of the carbon precursors. It is shown that the resulting carbons possess the surface areas and pore volumes, which are comparable to those of the block copolymer-templated carbons prepared in the presence of strong inorganic acids.

2 Experimental

2.1 Chemicals

Poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) triblock copolymer (EO₁₀₆PO₇₀EO₁₀₆, Pluronic F127) was generously provided by BASF Corp. (Germany). Resorcinol (C₆H₄(OH)₂; 98 %), and formaldehyde (HCHO, 37 %), were acquired from Sigma–Aldrich (Germany).

Citric, acetic, oxalic, succinic, and benzoic acid were purchased from POCh (Poland), while ethanol (96 %) from Chempur (Poland).

2.2 Synthesis of mesoporous carbons

Mesoporous carbons were prepared by extending the soft-templating recipe reported by Liu et al. (2011). Approximately 2.5 g of Pluronic F127 and 1.65 g of resorcinol were dissolved in 20 cm³ of ethanol and 20 cm³ of deionized water. After complete dissolution, the reaction mixture was supplied with 6.3 g of either: citric, acetic, oxalic, succinic or benzoic acids and stirred vigorously for 1 h. Then, 2.5 cm³ of formaldehyde was added to the solution and stirred for additional 80 min. The resulting solution was homogeneous and yellowish; it was transferred into a Teflon-lined autoclave and heated at 60 °C for 72 h. The polymeric monolith was collected by filtration, washed with water, and dried in an oven at 80 °C for 12 h; finally, an orange-red monolith was obtained. Thermal treatment and carbonization of this monolith were performed in a tube furnace under flowing nitrogen (20 dm³/h) using a heating rate of 1 °C/min up to 600 °C and keeping the sample at that temperature for 3 h. The procedure yielded 0.6–1.2 g of each mesoporous carbon obtained with different organic acid. The final products were denoted as ST-(organic acid) where (organic acid) denotes the name of organic acid used during synthesis.

2.3 Characterization

Low-temperature nitrogen adsorption/desorption isotherms were measured at –196 °C on ASAP 2020 volumetric analyzer manufactured by Micromeritics Inc. (Norcross, GA, USA). Prior to measurements, all samples were degassed at 200 °C for at least 2 h.

High-resolution thermogravimetric (TG) analysis was conducted using Q500 thermogravimetric analyzer manufactured by TA Instruments (New Castle, DE, USA). TG and DTG curves were recorded from 30 to 800 °C in air with a heating rate of 5 °C/min.

Scanning electron microscopy images were taken using LEO1530 scanning electron microscope manufactured by Zeiss (Germany) operated at 2 kV accelerating voltage.

Transmission electron microscopy images were taken using 200 kV FEI Tecnai F20 TEM equipped with a field emission gun. The samples for TEM analysis were first suspended in ethanol, and then a droplet of the sample was put onto a carbon-coated copper TEM grid (400-mesh). TEM specimens were allowed to air-dry and kept in vacuum for a few hours to minimize the contamination during TEM observation.

2.4 Calculations

The BET (Brunauer–Emmett–Teller) specific surface area S_{BET} was calculated from nitrogen adsorption isotherms in the range of relative pressures from 0.05 to 0.2 using cross-sectional area of 0.162 nm² per nitrogen molecule (Brunauer et al. 1938). Single-point total pore volume V_t (Gregg and Sing, 1982) was estimated from the amount adsorbed at a relative pressure of ~ 0.99 . Micropore volume V_{mi} was calculated by the α_s plot method (Gregg and Sing, 1982; Jaroniec et al., 1989) in the range of α_s from 0.8 to 1.2. Mesopore volume V_{me} was obtained by subtraction of the micropore volume V_{mi} from the total pore volume V_t . Pore size distribution (PSD) curves were calculated based on the adsorption branch of nitrogen isotherm using the improved Kruk–Jaroniec–Sayari (KJS) method for cylindrical pores smaller than 12 nm (Kruk et al. 1997b). The statistical film thickness (t curve) calculated by fitting the low-temperature (-196 °C) nitrogen adsorption isotherm measured on the nonporous carbon Cabot BP280 (Kruk et al. 1997a) to the multilayer region of the t curve derived for ordered mesoporous silica materials MCM-41 (Choma et al. 2002), and the modified Kelvin equation, were used in the KJS method. Maxima of PSD curves were used to determine the micropore and mesopore widths, w_{mi} and w_{me} accordingly. Mesoporosity, expressed in %, was calculated as the ratio of the mesopore volume V_{me} to the total pore volume V_t .

3 Results and discussion

The main focus of the conducted studies was to investigate the feasibility of the organic acid-assisted soft-templating synthesis of OMCs. The secondary goal was to study the impact of the organic acid used on adsorption properties of the resulting carbon materials. Figure 1 depicts a general synthetic path of the soft-templating synthesis of mesoporous carbons carried on in the presence of an organic acid. The first step of this synthesis is to introduce triblock copolymer and organic acid into an aqueous–alcoholic solution.

Resorcinol and formaldehyde, used as carbon precursors, were introduced subsequently into the reaction solution and underwent organic acid-catalyzed polymerization in hydrophilic domains of the ordered mesophase of block copolymer. Next, the resulting polymer–polymer mesostructured composite was subjected to the thermal treatment in flowing nitrogen. The initial treatment at elevated temperatures resulted in the cross-linking of phenolic resin and the creation of mesopores due to the decomposition of block copolymer template; further heating of the resulting mesoporous phenolic resin in nitrogen at higher temperatures (so-called carbonization) afforded OMC.

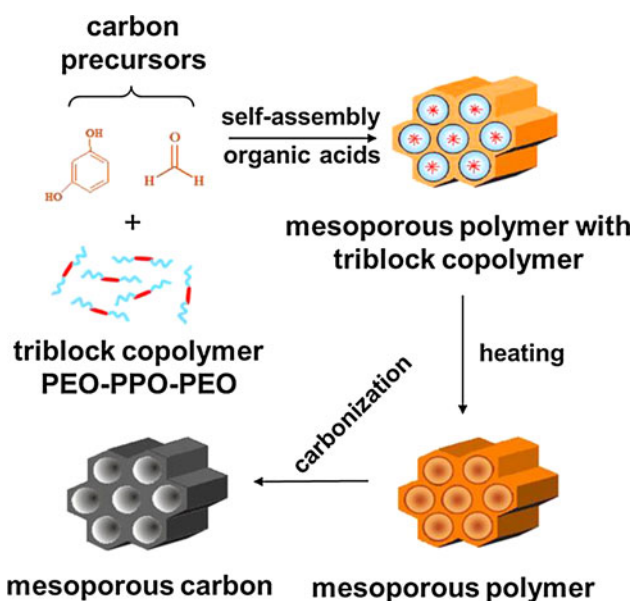


Fig. 1 Schematic illustration of the soft-templating synthesis of mesoporous carbons in the presence of organic acids; scheme analogous to that in Gorka dissertation (2010)

Experimental nitrogen adsorption–desorption isotherms for the carbon studied are shown in Fig. 2. All isotherms are Type IV according to IUPAC classification (Sing et al. 1985) with well-developed hysteresis loops classified as Type H1 (Sing et al. 1985). Microporosity of all samples was evaluated by the α_s plot method from nitrogen adsorption isotherms (Gregg and Sing, 1982). Four samples, which were synthesized with citric, succinic, acetic, and benzoic acid, possess well-developed, and fairly similar microporosity, whereas microporosity of the carbon sample obtained with use of oxalic acid is less developed as compared to other samples. The mesopore volume of the samples was obtained by subtracting the micropore volume from the single-point pore volume; of course, its value is larger for the samples having higher step of capillary condensation. Thus, the carbon obtained in the presence of citric acid possessed the most developed mesoporous structure among all samples studied. A comparable mesoporosity was found for the carbon obtained in the presence of succinic acid. The least developed mesoporous structure was observed for the carbon prepared with the help of oxalic acid.

Basic structural parameters of the carbon materials studied were calculated based on experimental nitrogen adsorption isotherms shown in Fig. 2. The resulting parameters are shown in Table 1.

The BET specific surface area (S_{BET}) values varied from 601 m²/g for the ST-Oxalic acid sample to 746 m²/g for the ST-Acetic acid sample, whereas the single-point pore volume (V_t) values ranged from 0.40 cm³/g for the ST-Oxalic acid to 0.59 cm³/g for the ST-Citric acid. Since

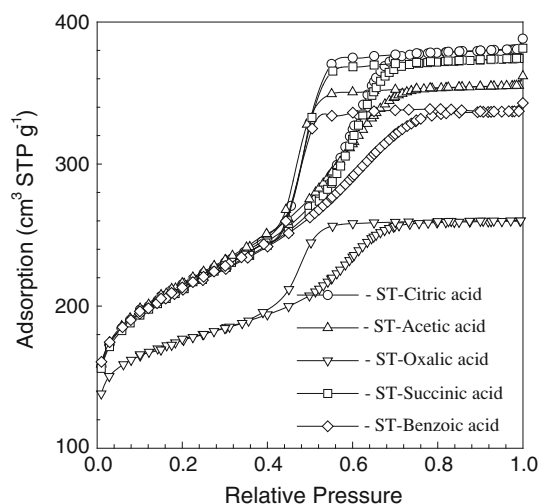


Fig. 2 Nitrogen adsorption–desorption isotherms measured for the mesoporous carbons synthesized in the presence of organic acids

the target of this study was to obtain carbon materials with the well-developed mesoporosity, therefore the volumes of mesopores (V_{me}) should be dominant. The micropore volumes do not exceed $0.1 \text{ cm}^3/\text{g}$ except those for the ST-Oxalic acid and ST-Benzoic acid samples, having micropore volumes of 0.14 and $0.13 \text{ cm}^3/\text{g}$, respectively. The mesopore volumes recorded for the ST-Citric acid and ST-Succinic acid samples are 0.51 and $0.49 \text{ cm}^3/\text{g}$, respectively.

The highest mesoporosity value of 86% was observed for the ST-Citric acid sample, whereas the lowest value of 65% was for the ST-Oxalic acid sample. The mesoporosity values reported in Table 1 show that in all carbon samples mesopores dominate over micropores.

Pore size distribution functions (PSDs) for the carbon studied were calculated using Kruk–Jaroniec–Sayari method (KJS) (Kruk et al. 1997b) and are shown in Fig. 3. All PSD curves exhibit two maxima. The first, occurring for pore sizes $<2 \text{ nm}$, corresponds to the width of micropores, whereas the

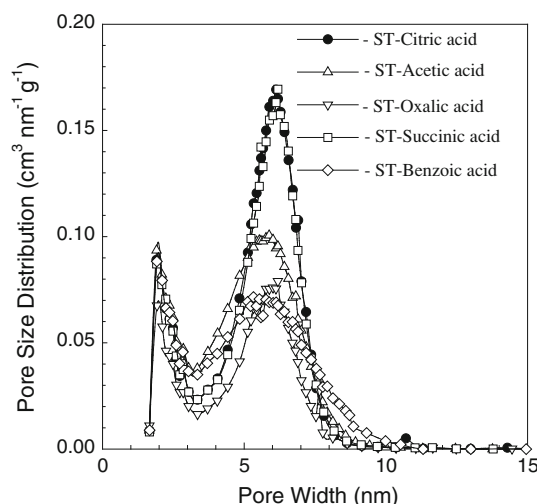


Fig. 3 Pore size distributions (PSDs) calculated by the KJS method for the mesoporous carbons synthesized in the presence of organic acids

letter (about 6 nm), corresponds to the width of mesopores. As can be seen from Table 1, the micropore size, ca. 1.9 nm , is analogous for all the samples studied regardless of the organic acid used. On the other hand, the width of mesopores is changing slightly with the organic acid used during the synthesis. The smallest value, 5.88 nm , was obtained for the ST-Acetic acid sample, whereas the largest mesopores, 6.19 nm , were obtained when succinic acid was used (the ST-Succinic acid sample). Based on above it can be concluded that the organic acids used during soft-templating synthesis affect slightly the mesoporous structure of the resulting carbons; an exception is the sample obtained in the presence of oxalic acid.

It was mentioned in introduction that the initial synthesis conditions, basic or acidic, affect the average size of mesopores; smaller mesopores ($\sim 4 \text{ nm}$) are usually reported for the carbons prepared from resol (basic conditions; Meng et al. 2006) and larger mesopores ($\sim 8 \text{ nm}$) are reported for

Table 1 Adsorption parameters of the mesoporous carbons studied

Mesoporous carbon	S_{BET} (m^2/g)	V_t (cm^3/g)	V_{mi} (cm^3/g)	V_{me} (cm^3/g)	w_{mi} (nm)	w_{me} (nm)	Mesoporosity (%)	pK_a
ST-citric acid	741	0.59	0.08	0.51	1.88	6.12	86	3.1;4.8*
ST-acetic acid	746	0.55	0.09	0.46	1.91	5.88	84	4.8
ST-oxalic acid	601	0.40	0.14	0.26	1.92	6.02	65	1.3;4.3*
ST-succinic acid	733	0.58	0.09	0.49	1.91	6.19	84	4.2;5.6*
ST-benzoic acid	730	0.52	0.13	0.39	1.92	6.10	75	4.2
ST-HCl	694	0.68	0.16	0.51	1.92	7.92	75	

Mesoporosity the percentage of the volume of mesopores to the single-point pore volume, *Acidity* pK_a (*1st number denotes pK_{a1} and 2nd number gives pK_{a2} ; for citric acid $pK_{a3} = 6.4$); adsorption parameters for the carbon sample (ST-HCl) prepared in the presence of HCl have been reported by Choma et al. (2012)

S_{BET} BET specific surface area, V_t single-point pore volume, V_{mi} volume of micropores obtained by the α_s method, V_{me} volume of mesopores obtained by subtraction of the micropore volume V_{mi} from single-point pore volume V_t , w_{mi} micropore diameter at the first maximum of the PSD curve obtained by the KJS method, w_{me} mesopore diameter at the second maximum of the PSD curve obtained by the KJS method

carbons obtained under acidic conditions (Wang et al. 2008). The current study confirms this case. The average mesopore size for the carbon prepared in the presence of citric acid is ~ 6 nm, while the value of about 8 nm was reported for the corresponding sample prepared in the presence of HCl (see a comparison of nitrogen adsorption isotherms and pore size distributions in Fig. 4). It seems that in the case of the block copolymer used, higher acidity favors the formation of larger micelles and consequently, larger mesopores; similar finding was reported by Grant and Jaroniec (2012) for the block copolymer-templated alumina samples.

The TG profile was recorded for the ST-Citric acid sample. The data were measured in the temperature range from 30 to 800 °C in flowing air. The TG data indicate that the mesoporous carbons are thermally stable in air atmosphere up to 400 °C and start to decompose afterward with a rapid combustion at ~ 430 °C. A very small value of residue, i.e. 0.61 %, shows that the carbons studied contain negligible amount of inorganic impurities.

An important aspect is the morphology of the mesoporous carbons studied. Figures 5 and 6 show SEM images of the ST-Benzoic acid and ST-Succinic acid samples, respectively. These images show that the carbons studied display some kind layered organization at the macroscopic level. This structure can be well seen at the edge of the

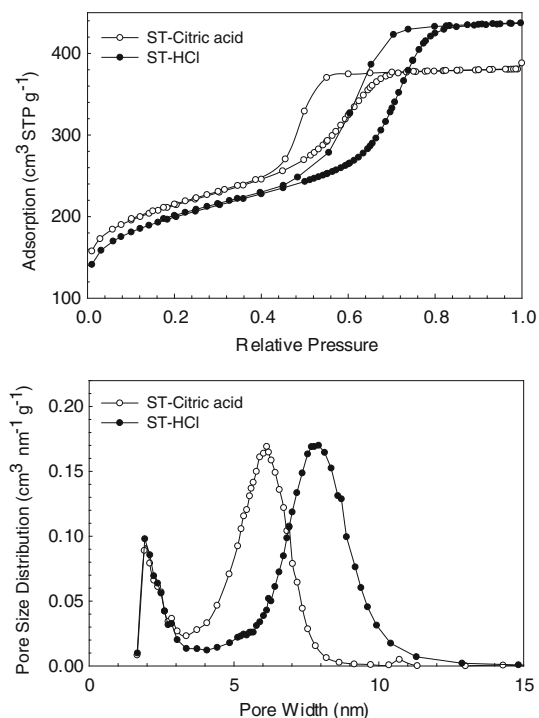


Fig. 4 A comparison of nitrogen adsorption isotherms (*top panel*) and pore size distributions (*bottom panel*) for the carbon samples prepared in the presence of citric acid and HCl; data for the latter sample are reported by Choma et al. (2012)

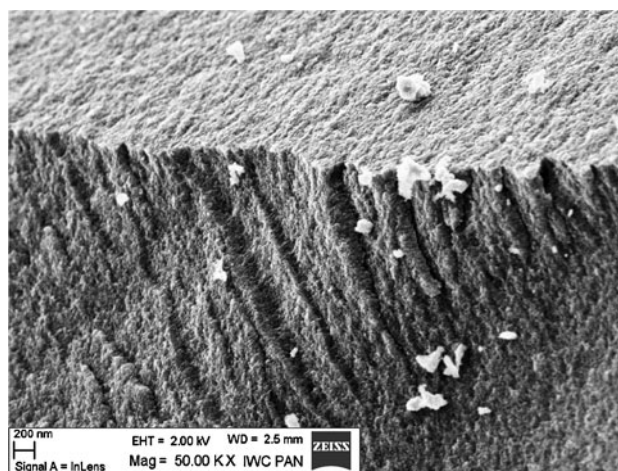


Fig. 5 SEM image of carbon synthesized in the presence of benzoic acid

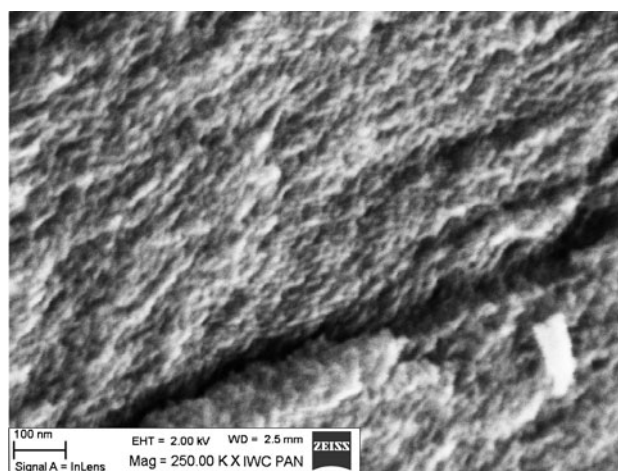


Fig. 6 SEM image of the carbon synthesized in the presence of succinic acid

ST-Benzoic acid sample shown in Fig. 5. In addition, ordered nature of uniform mesopores can be noticed in Fig. 6 showing the SEM image of the ST-Succinic acid sample. The convincing evidence of mesostructural ordering is provided by TEM analysis, which is presented below.

As it was previously mentioned, the main focus of the current study was to obtain mesoporous carbon materials with ordered and uniform mesoporosity through an organic acid-assisted soft-templating synthesis. TEM studies were conducted to prove the ordered and uniform nature of mesopores in the carbon materials prepared in the presence of organic acids. Figure 7 shows the TEM image of the mesoporous carbon obtained using citric acid (the ST-Citric acid sample). The well-ordered mesopores of this

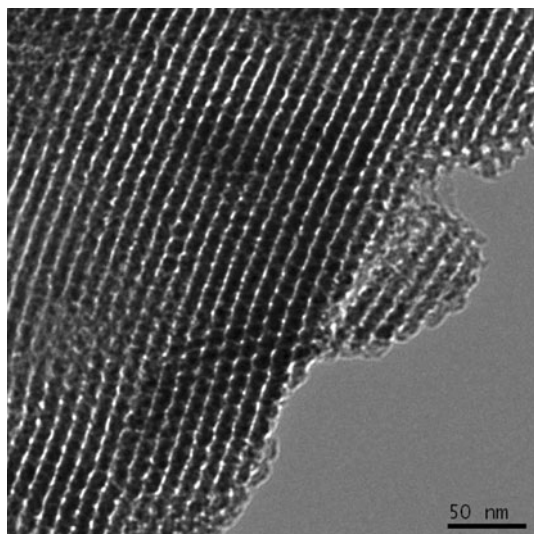


Fig. 7 TEM image of the carbon synthesized in the presence of citric acid

carbon are clearly seen in Fig. 7 and their size is in a good agreement with adsorption-based pore size analysis.

4 Conclusions

The current work shows that the organic acid-assisted soft-templating represents a feasible route for the synthesis of well-ordered mesoporous carbon materials. Citric, acetic, oxalic, succinic, and benzoic acids were successfully employed in this soft-templating synthesis as catalysts for the polymerization of resorcinol and formaldehyde carbon precursors. The use of the aforementioned organic acids was sufficient for the preparation of mesoporous carbons with good structural properties, i.e., specific surface area reaching $700 \text{ m}^2/\text{g}$, total pore volume of about $0.60 \text{ cm}^3/\text{g}$, and the mesopore width of about 6 nm. It is noteworthy that the organic acid-assisted synthesis eliminated chloride ions from the reaction environment because HCl catalyst was not used. Acidity values of the organic acids used, expressed in terms of pK_a (Table 1) show that pK_a in the range of 3–4 is sufficiently strong to catalyze the polymerization reaction of resorcinol and formaldehyde during soft-templating synthesis of mesoporous carbons. In addition, it was shown that triblock copolymer Pluronic F127 works well as a soft template, in the presence of not only a strong acid such as HCl but also in the presence of weak organic acids such as citric, acetic, succinic, or benzoic acids. The resulting mesoporous carbon materials possess the well-developed mesoporous structures and relatively large volumes of mesopores.

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