



Rapid Fabrication of Monolithic Carbon Aerogels Based on Resorcinol-Formaldehyde by Ambient Pressure Drying

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New synthesis conditions to rapidly fabricate monolithic carbon aerogels based on resorcinol and formaldehyde were developed using ambient pressure drying. The resorcinol-formaldehyde aerogel network synthesized under strong basic conditions not only dramatically reduced the gelation time but also exhibited better particle connectivity. This also allowed for the rapid drying of the wet-gels and subsequent carbonization in an inert atmosphere to yield carbon aerogels. Monolithic carbon aerogels possessing both microporous and macroporous characteristics were synthesized. It was shown that the microstructure of the carbon aerogels was comprised of spherical particles that could be tailored by control of sol-gel preparation parameters, such as volume ratios of formaldehyde, deionized water and ammonium hydroxide with the resorcinol. The synthesized carbon aerogels had a tapping density as low as 0.11 g/cm³ and a specific surface area as high as 551 m²/g.

Key Words: Carbon aerogels, Ambient pressure drying, BET surface area, TGA-DTA analysis, FE-SEM.

INTRODUCTION

In the last two decades, highly cross-linked organic aerogels have attracted a great deal of attention due to their capability to be transformed into electrically conducting carbon aerogels in the form of monolithic, powders, microspheres or thin films by pyrolysis¹⁻⁵. Carbon aerogels are novel nanoporous materials with many fascinating properties such as low bulk density, continuous porosity, high specific surface area and high electrical conductivity⁶⁻⁹. These properties are derived from the aerogel microstructure which is a network of interconnected primary particles. Owing to their unique textural properties carbon aerogels are considered to be suitable as electrode materials for supercapacitors and rechargeable batteries, advanced catalyst supports, adsorbents and chromatographic packing¹⁰⁻¹⁷.

Carbon aerogels are traditionally prepared through sol-gel polymerization of resorcinol with formaldehyde in an aqueous solution followed by supercritical drying with liquid CO₂ and subsequent carbonization at elevated temperatures under N₂ atmosphere¹, which requires tremendous processing time. Recently, several attempts have been made to reduce the processing time by ambient pressure drying of the resorcinol-formaldehyde wet-gels¹⁸⁻²⁰.

Our approach to rapidly synthesize carbon aerogels is to introduce strong base catalyst such as ammonium hydroxide (13.36 M) during the sol-gel polymerization of resorcinol with formaldehyde to reduce gelation time. Furthermore the resorcinol-formaldehyde wet-gels were able to be rapidly dried and subsequently carbonized in an inert atmosphere. The resulting carbon aerogel network exhibited better particle connectivity.

EXPERIMENTAL

In a typical synthesis the mixture of 5 mL resorcinol and 100 mL formaldehyde was stirred for 15 min to obtain a homogeneous reaction mixture. After 50 mL of deionized water with 0.9 mL of ammonium hydroxide was added to the mixture, the sol was kept at 80 °C for 2 h for gelation. The wet-gels subsequently were immersed in acetone for 5 h at 40 °C for solvent exchange. The wet-gels were then dried for 5 h at 80 °C and for 2 h at 150 °C to form resorcinol-formaldehyde aerogels. The resorcinol-formaldehyde aerogels were carbonized in an inert atmosphere by heating them for 1 h at each elevated temperature of 100, 200, 400 and finally for 3 h at 800 °C. The effects of various sol-gel parameters on the physical and textural properties of the carbon aerogels were investigated by varying the volume ratios of resorcinol to form-

TABLE-1
SYNTHESIS CONDITIONS AND TEXTURAL PROPERTIES OF THE CARBON
AEROGELS PREPARED VIA AMBIENT PRESSURE DRYING ROUTE

Sample ID	Resorcinol (mL)	Form-aldehyde (mL)	D.I. water (mL)	NH ₄ OH (mL)	Tapping density (g/cm ³)	BET surface area (m ² /g)	S _{micro} (m ² /g)	P _d (nm)
CA ₇	5	100	50	0.9	0.14	358	360	20
CA ₈	5	120	50	0.9	0.17	401	335	4
CA ₉	5	130	50	0.9	0.18	551	464	3.2
CA ₁₀	5	140	50	0.9	0.15	362	330	7.28
CA ₁₁	5	150	50	0.9	0.13	365	371	1.8
CA ₁₂	5	100	10	0.9	0.11	462	381	2.11
CA ₁₃	5	100	20	0.9	0.13	520	521	11.5
CA ₁₄	5	100	30	0.9	0.15	423	380	4.51
CA ₁₅	5	100	40	0.9	0.13	335	363	1.73

aldehyde and ammonium hydroxide to resorcinol from 1:20 to 1:30 and from 0.06 to 0.26, respectively.

The textural properties of the carbon aerogels were investigated by the standard N₂ gas adsorption method using a surface area analyzer (Quantachrome, Autosorb-1). The adsorption-desorption isotherm was obtained at 77 K after degassing the samples. The specific surface area was evaluated using the standard Brunauer-Emmett-Teller (BET) method. The micropore surface area (S_{micro}) was determined by the Horvath-Kawazoe method. The average pore diameters (P_d) and pore size distributions (PSD) were estimated by the Barrett-Joyner-Halenda (BJH) method. The microstructure of the carbon aerogel was probed by a field emission scanning electron microscope (FE-SEM, JSM 6700 F microscope, JEOL). The tapping density, generally used to describe the bulk density of powders, was estimated by the mass to volume ratio of the carbon aerogels and the thermal behaviour was identified by thermogravimetric and differential thermal analysis (TG-DTA) in an argon atmosphere.

RESULTS AND DISCUSSION

Physical properties of the carbon aerogels: The major disadvantage in the classical synthesis of carbon aerogels is the long gelation time which ultimately increases total processing time. In present studies this bottleneck was overcome by using a strong base catalyst which could result in the dramatic reduction of the gelation time from a few days to 2 h. The physical properties of the carbon aerogels such as density, surface area and average pore diameters at various synthetic conditions are summarized in Table-1. The aerogels obtained by our rapid processing approach including ambient pressure drying and subsequent carbonization in an inert atmosphere were monolithic *i.e.* crack-free as shown in the Fig. 1a. This is due to the fact that the carbon aerogel networks developed under strong basic conditions were capable of withstanding the stresses developed during the ambient pressure drying in a furnace. From the FE-SEM image shown in Fig. 1b, it can be found the aerogels were comprised of interconnected spherical particles forming a porous three dimension network. As a consequence the carbon aerogels exhibited high specific surface area ranging from of 335 m²/g to 551 m²/g. Furthermore the significant values of the S_{micro} imply that the carbon particles comprising the aerogel network are microporous. The aerogels also exhibited low densities ranging from 0.11 g/cm³ to 0.18 g/cm³ though they were rapidly dried at the ambient pressure.

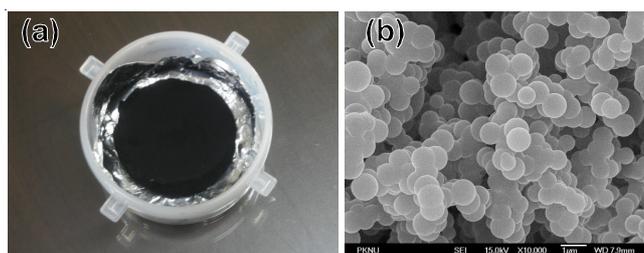


Fig. 1. Carbon aerogel synthesized by ambient pressure drying: (a) photograph showing monolithic carbon aerogel (b) microstructure of the aerogels showing network with spherical particles

The effect of NH₄OH/resorcinol volume ratio on the tapping density of the carbon aerogels was also investigated as summarized in Table-2. The ratio was varied from 0.06 to 0.26 while the amounts of resorcinol, formaldehyde and deionized water were fixed at 5, 100 and 50 mL, respectively. As the NH₄OH/resorcinol volume ratio increased from 0.06 to 0.26, the density exhibited a tendency to slightly increase but still maintained at the low level ranging from 0.12 g/cm³ to 0.16 g/cm³. Thus it is conjectured that the NH₄OH/resorcinol ratio has an adverse effect on the connectivity of the particles which decreases the bulk modulus of the network, in turn the network shrinks a bit more during drying, ultimately causing the bulk density slightly increased.

TABLE-2
EFFECT OF THE NH₄OH/RESORCINOL VOLUME RATIO
ON THE TRAPPING DENSITY OF THE SYNTHESIZED
CARBON AEROGELS

Sample ID	NH ₄ OH/resorcinol volume ratio	Tapping density (g/cm ³)
CA ₂₁	0.06	0.13
CA ₂₂	0.10	0.12
CA ₂₃	0.12	0.14
CA ₂₄	0.18	0.16
CA ₂₅	0.22	0.16
CA ₂₆	0.26	0.15

Textural properties of the carbon aerogels: The representative N₂ adsorption-desorption isotherms and pore size distributions are shown in Figs. 2a-d. It is clearly seen from Figs. 2a and 2c that no hysteresis loops are observed in the isotherm curves since the adsorption and desorption branches of each isotherm coincide. This indicates that the isotherms are of Type 1 which exhibits the characteristic feature of microporous materials²⁰. It also observed from Figs. 2b and 2d

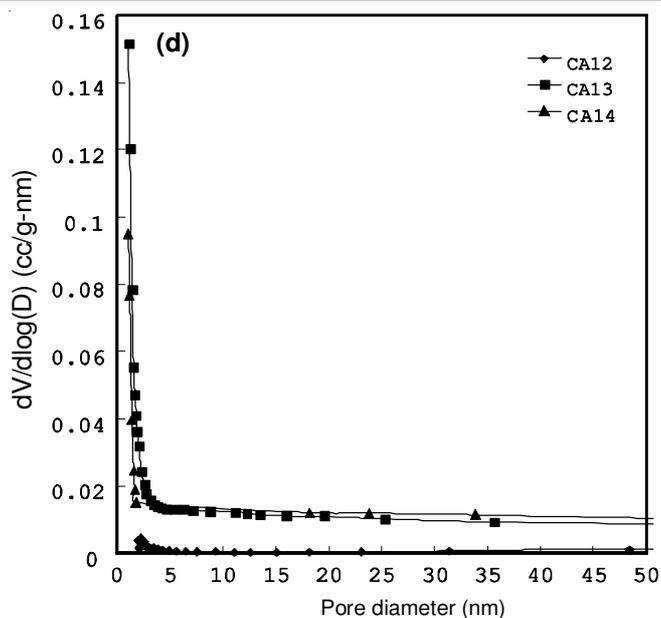
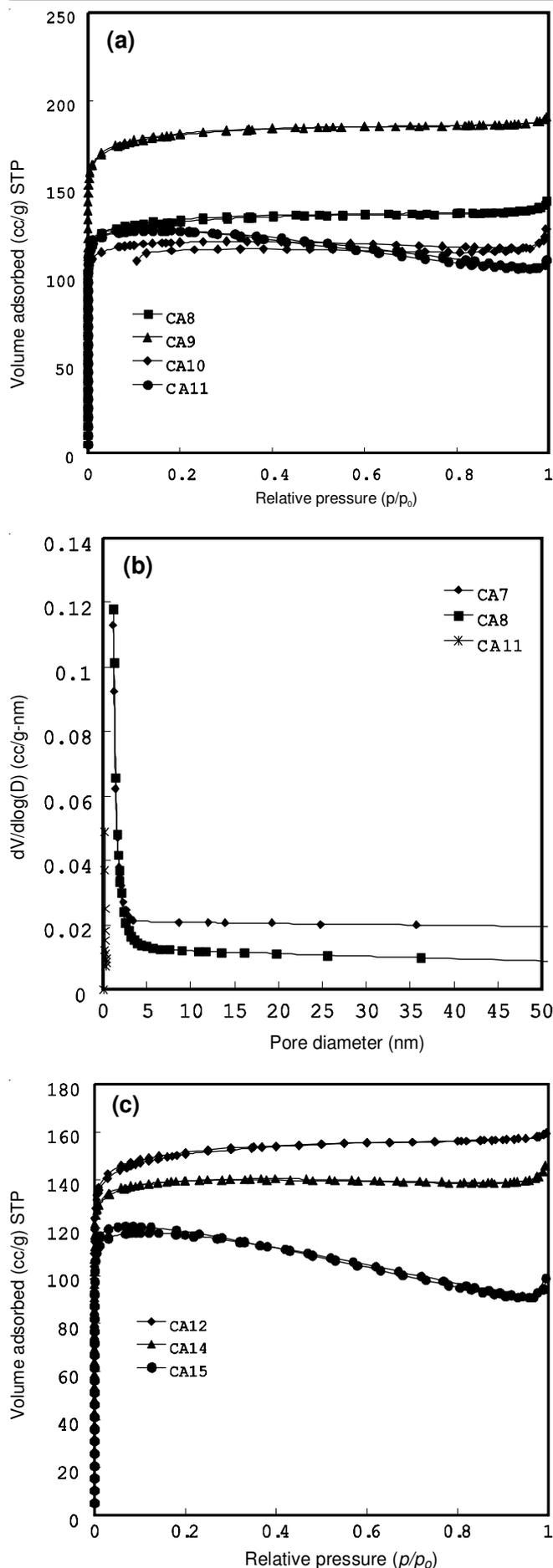


Fig. 2. Plots of N_2 adsorption-desorption isotherms and pore size distributions for carbon aerogels synthesized with different compositions

that the sharp peaks of all pore size distributions reside near 1.5 nm, confirming that the aerogels possess micropores. On the other hand, the FE-SEM images shown in Fig. 3 indicate that the aerogels also have the structures of macropores larger than 50 nm. These results collectively reveal that the carbon aerogel samples prepared by present method are both microporous and macroporous, resulting in high surface areas.

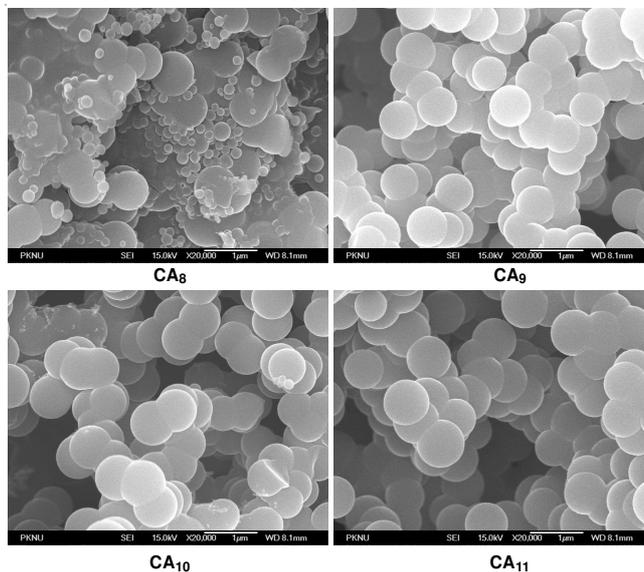


Fig. 3. FE-SEM images of the resorcinol-formaldehyde based carbon aerogel showing wide variations in the microstructure and the size of primary particles

Microstructure analysis: The microstructure of the carbon aerogels synthesized *via* ambient pressure drying could vary significantly depending on the preparation condition of the sol as shown in Fig. 3. As the content of formaldehyde in the sol increased (samples from CA₈ to CA₁₁), the porosity of the network also increased. This is clearly seen from the

FE-SEM images that CA₈ contains relatively denser network than CA₁₁. Though the aerogel particles exhibited spherical morphology, the particle size could strongly depend on the synthesis condition and significantly varied from 500 to 2 μm.

Thermal properties of carbon aerogels: Fig. 4 depicts the TG-DTA curves obtained for the carbon aerogel sample in an argon atmosphere with the heating rate of 10 °C/min. The weight of the aerogel sample slightly decreased until the temperature reached 200 °C due to the evaporation of residual solvent and water and then remained almost constant in the temperature range of 200 to 450 °C. As the temperature increased further, the weight sharply decreased in the temperature range of 450 to 550 °C due to the intense oxidation of carbon. In this temperature range, a strong exothermic peak was also observed.

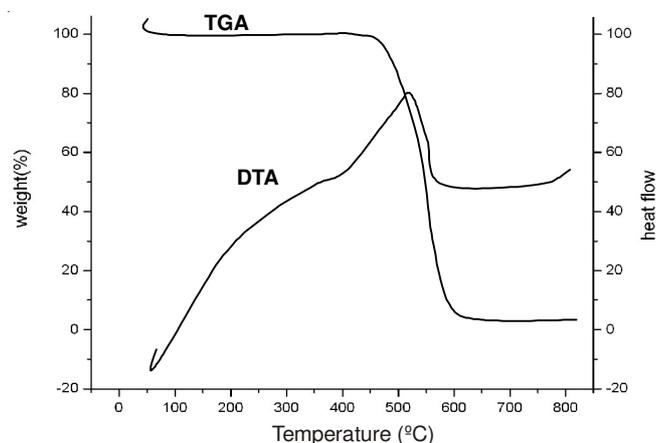


Fig. 4. TG-DTA curves obtained for the carbon aerogel in argon atmosphere

Conclusion

A new strategy for the synthesis of rapid fabrication of monolithic carbon aerogels, based on resorcinol-formaldehyde *via* ambient pressure drying, was developed. The gelation time was dramatically reduced down to several hours by introducing a strong base catalyst in the sol-gel polymerization of resorcinol with formaldehyde. The effects of various sol-gel parameters on the physical and textural properties of the carbon aerogels were investigated. It was also shown that the present method could be utilized in the preparation of organic and carbon

aerogels over a wide range of densities (0.11 g/cm³ to 0.18 g/cm³) by proper control over the sol-gel preparation parameters. The resulting carbon aerogels were both microporous and macroporous, exhibiting high specific surface areas in the range of 335 m²/g to 551 m²/g.

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