



Advanced and economical ambient drying method for controlled mesopore polybenzoxazine-based carbon xerogels: Effects of non-ionic and cationic surfactant on porous structure



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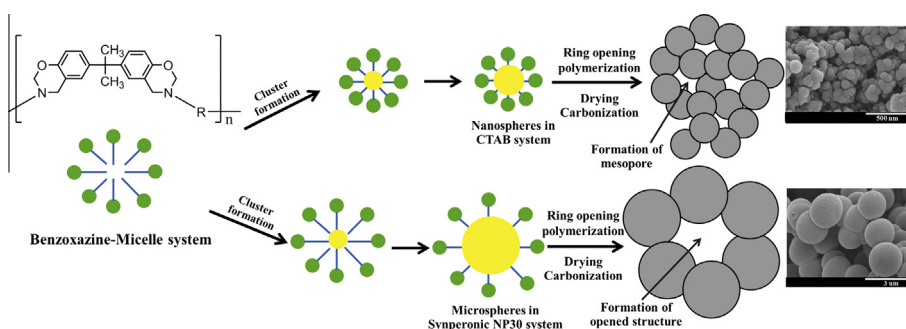
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HIGHLIGHTS

- Polybenzoxazine can be synthesized within the short preparation time.
- Polybenzoxazine is a good candidate for producing carbon xerogel.
- Carbon xerogel nanospheres with different mesopore sizes were obtained for CTAB.
- Microporous carbon xerogel microspheres were obtained for Synperonic NP30 system.

GRAPHICAL ABSTRACT



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ABSTRACT

Polybenzoxazine has been successfully synthesized by a facile quasi-solventless method and used as a precursor for producing carbon xerogels via an ambient drying method, rather than usually used CO₂ critical or freeze drying. In this work, we aim to study the effect of non-ionic (Synperonic NP30) and cationic (CTAB) surfactants on porous structure of polybenzoxazine-based carbon xerogels. Of particular interest is the formation of inter-connected structure of mesoporous carbon xerogels with mesopore diameters in the range of 15–36 nm by using different concentrations of the cationic surfactant. In addition, carbon xerogel nanospheres with the size of 50–200 nm are also obtained through the emulsion process. The mesopore diameters start to decrease when the carbon xerogel nanospheres are formed at the cationic surfactant concentration of equal to or exceeding 0.030 M. By using the non-ionic surfactant, the properties of the obtained carbon xerogels are shifted from mesoporous materials for the reference carbon xerogel (no surfactant added) to microporous materials at higher concentrations of the non-ionic surfactant (0.009–0.180 M). The carbon xerogel microspheres with the diameter size of about 2.5 μm are also obtained through the emulsion process when the concentration of the non-ionic surfactant is at 0.180 M.

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1. Introduction

Resorcinol (R)-formaldehyde (F)-based organic gel and its carbon gel after pyrolysis were first introduced by Pekala [1,2].

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Carbon gel could be mainly classified into three types viz. carbon aerogel, carbon cryogel, and carbon xerogel; depending on the drying method during solvent removal process [1–7]. Carbon gel is a porous material which possess various outstanding properties. Some of these properties are: light weight, high surface area, high porosity, high thermal stability, and low density. According to its outstanding properties, carbon gel has been used in many

applications, such as catalyst supporting material [5,8,9], energy storage [10–12], and molecular sieve material for gas separation technology [13,14].

Recently, development of carbon materials is becoming the great topic of research due to the consumption growth of carbonaceous materials in many applications. The actively studied subjects include understanding the effects of structural and manufacturing parameters on pore size, pore volume, and specific surface area of carbon materials. In general, the pores formed in carbon gel could be classified into two types; micropore (<2 nm) located within the carbon particle and meso–macropore (2–50 nm and >50 nm) formed at interstices of carbon particles during the phase separation phenomena [1,2,15,16]. Microporosity of carbon gel can easily be controlled by various activation processes [16–19]. However, the generation of meso–macroporosity mainly depends on the phase separation mechanism of polymer and solvent in the sol–gel process [1,2]. Many new routes to generate meso–macroporosity of carbon gels have been reported for example: surfactant-templated method [20,21], emulsion method [22,23], and hard-templated method [24,25].

Moreover, many materials have been used as precursors for syntheses of carbon gels [1,2,26–29], especially, resorcinol–formaldehyde (RF) polymer. In this work, polybenzoxazine (abbreviated as PBZ) was used for the production of carbon gel. The particularly attractive properties of polybenzoxazine for obtaining porous carbonaceous materials are: no need of harsh catalyst or initiator for polymerization, no releasing of toxic by-product during polymerization, near zero shrinkage after polymerization, excellent mechanical integrity, high char yield, and great molecular design flexibility [30–34]. In particular, the crosslink density was quite important because high crosslink density not only leads to improvement of thermo-oxidative stability enabling high char yield after carbonization [34], but also results in the preservation of porosity and its dimension, especially, mesoporosity, after the solvent removal process. In addition, polybenzoxazine is a cross-linked polymer with additional extensive hydrogen bonded networks which can withstand pore collapse without the need of supercritical CO₂ drying process. Hence, polybenzoxazine aerogels with more economical ambient drying have been reported in the literature [35–42].

Polybenzoxazine was generally synthesized by the Mannich polycondensation reaction of phenol (or phenol derivatives), formaldehyde, and amine (or amine derivatives), via a quasi-solventless route. In 2009, polybenzoxazine-based carbon aerogels were first introduced by Lorjai et al. who found that their carbon aerogel exhibited the properties as a microporous material [35]. In 2010, polybenzoxazine-based carbon aerogels with an average pore diameter of 3.67 nm were used as an electrode in supercapacitors by Katanyoota et al. [36]. As mentioned above, it was found that polybenzoxazine-based carbon shows the pore diameter in a range of small micro–mesopore. This property could affect the utilization of polybenzoxazine-based carbon for various applications that need large pore diameter.

For application as the catalyst supporting material, those small pore sizes of PBZ-based carbon aerogels might limit the catalytic efficiency for reactions that are involved with large molecules due to the limitation of mass transfer of large molecules [43,44].

In this work, we aim to study the effect of cationic and non-ionic surfactant on porous structure of polybenzoxazine-based carbon xerogels, in order to improve the ability to control the pore diameter. The morphological characteristics of the obtained carbon xerogels were also investigated.

2. Experimental

2.1. Materials

Main-chain type benzoxazine polymer (abbreviated as MCBP) with benzoxazine group as part of the chemical repeat unit was synthesized by the Mannich polycondensation reaction of bisphenol-A (abbreviated as BA, 97%, Aldrich), formaldehyde (37%, Merck Limited, Germany), and triethylenetetramine (abbreviated as teta, 85%, Facai Group Limited, Thailand) using dioxane (analytical grade, Labscan Asia Co., Ltd., Thailand) as a solvent. Non-ionic surfactant, Synperonic NP30 (Polyethylene glycol nonylphenyl ether, >99.8%), and cationic surfactant, hexadecyltrimethylammonium bromide [$\text{CH}_3(\text{CH}_2)_{15}\text{N}(\text{Br})(\text{CH}_3)_3$, abbreviated as CTAB, >99.8%], were purchased from Fluka. Ethyl alcohol (>98%) was purchased from J.T. Baker. All chemical were used without further purification.

2.2. Synthesis of polybenzoxazine-based carbon xerogels (PBZ-based carbon xerogels)

MCBP was synthesized by a quasi-solventless method adopted from the solventless method proposed by Ishida [45]. The molar ratio of BA, teta, and formaldehyde, required for synthesizing MCBP, was 1:1:4, respectively. MCBP derived from bisphenol-A and teta was hereinafter abbreviated as MCBP(BA-teta). For the synthesis step, first, BA was dissolved in dioxane and magnetically stirred for 20 min. Then, a surfactant was mixed and stirred for 30 min. The concentrations of the surfactant in the solution are kept at 0.003 M, 0.009 M, 0.030 M, 0.090 M, and 0.180 M. Afterwards, formaldehyde was added and continuously stirred for 20 min. Finally, teta was slowly dropped into the mixture and continuously stirred for 1 h until a transparent pale yellow solution was obtained. Unlike the conventional method which took 5 h, the reaction was completed within an hour [33]. The concentration of MCBP(BA-teta) solution was fixed at 10% w/w. The MCBP(BA-teta) solution was sealed off in a glass vial and left for 24 h. The MCBP(BA-teta) solution was further heated in an oil bath at 80 °C for 1 day to form a white-opaque-MCBP(BA-teta) organogel. The MCBP(BA-teta) organogel was taken out from the glass vial and cut into a cubic shape. The Soxhlet technique was used to remove all residual surfactant in the organogel by using ethyl alcohol as a carrier phase under heating temperature of 100 °C and reflux temperature of 10 °C for 24 h. After that, the MCBP(BA-teta) organogel was taken out from the Soxhlet tube and heated in an oven at 90 °C for 24 h to remove all residual ethyl alcohol. Subsequently, the MCBP(BA-teta) organogel was placed in a temperature-programmed oven for step-polymerization at 160 °C and 180 °C for 3 h at each temperature, and 200 °C for 15 min to achieve the fully-polymerized polybenzoxazine xerogel [36,37]. The possible structure of polybenzoxazine synthesized using teta, BA, and formaldehyde is shown in our previous works [37–39]. After step-polymerization, fully-polymerized polybenzoxazine xerogel was carbonized under nitrogen flow of 600 cc/min using the following cycle step: 30–250 °C for 1 h, 250–600 °C for 5 h, 600–800 °C for 1 h and held at 800 °C for 2 h, and then the oven was cooled to room temperature under nitrogen atmosphere [36,37].

Polybenzoxazine-based carbon xerogels using Synperonic NP30 and CTAB as the surfactants during synthesis of MCBP(BA-teta) solution are denoted as CX-NP30-xx and CX-CTAB-xx where NP30 and CTAB are nomenclatures of Synperonic NP30 (Polyethylene glycol nonylphenyl ether) and CTAB (hexadecyltrimethylammonium bromide) by evaporation drying

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