



# Facile and fast polyaniline-directed synthesis of monolithic carbon cryogels from glucose

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## ARTICLE INFO

### Keywords:

Carbon gels  
Polyaniline  
Hydrothermal carbonization  
CO<sub>2</sub> capture

## ABSTRACT

The development of simple, rapid and sustainable synthesis for carbon cryogels with controllable properties is highly desired in various applications fields. Herein, a template-free hydrothermal synthesis of monolithic nitrogen-doped carbon cryogels was developed, where glucose was used as the carbon precursor and polyaniline (PANI) as nitrogen source and a novel crosslinking agent. The monolithic hydrogels can be formed in only 2 h at a low hydrothermal temperature (140 °C), the shortest time and the lowest temperature for the hydrothermal synthesis of monolithic hydrogels up to now. During the hydrothermal process, the crosslinking effect of PANI resulted in the formation of a 3D hydrogel network composed of interconnected coral-like fibers. The structural properties and surface chemistry can be tuned easily by changing the aniline concentration and carbonization temperature, making carbon cryogels a hierarchically porous structure with nanofiber diameter of 60–200 nm and a high specific surface area of  $\sim 900 \text{ m}^2 \text{ g}^{-1}$ . The resulting carbon cryogels exhibited an excellent CO<sub>2</sub> uptake capacity of  $4.12 \text{ mmol g}^{-1}$  at 25 °C under 1 atm (higher than most of the hydrothermal carbons reported without activation and comparable to those with KOH activation), good recyclability and CO<sub>2</sub>/N<sub>2</sub> selectivity of 9.2.

## 1. Introduction

Due to excellent features in electrical conductivity, chemical and thermal stability, carbon-based nanomaterials have been proven to be promising in many application fields [1–4]. As a class of three-dimensional (3D) carbon nanomaterials, carbon gels possess many unique properties, such as low mass density, continuous porosity and high surface area, which make CAs attractive candidates for a variety of applications including energy storage, adsorption and catalysis [4–8]. Traditionally, preparation of resorcinol-formaldehyde (RF) carbon gels usually undergo three steps: 1) the preparation of the wet gel via a sol-gel process (hydrogels); 2) the drying of the wet gel (organic gels); 3) the carbonization of the dried gel (carbon gels) [9]. A controllable nanostructure and the corresponding macroscopic performance can be achieved by changing the synthesis and processing conditions [10]. However, traditional RF carbon gels need the utilization of carcinogenic chemicals and a long period of gelation process (about a week), which

limits the further practical applications. In the context of sustainability, it is necessary to find a simple method to fabricate carbon gels from environmentally friendly carbon precursors.

Recently, the hydrothermal carbonization (HTC) of biomass-derived precursors has received increasing attention due to its green and sustainable process. Using a well-established HTC process carbohydrate or biomass can be directly transformed into carbonaceous materials in environmentally friendly aqueous medium at a relatively low temperature of 180–200 °C [11–13]. It is found that the HTC process first experience dehydration of sugar to form furan-based intermediate (furfural or 5-hydroxymethylfurfural (HMF)) and then carbonaceous materials are formed via a sol-gel type process [14], which probably provides a new approach to the synthesis of carbon gels. Indeed, several carbon gels have been prepared by the HTC of carbohydrates or biomass. For example, Fellinger et al. found a simple synthesis to obtain monolithic carbon gels by the HTC of glucose in the presence of borax [15]. Brun et al. recently reported the design of porous carbon gels from

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<https://doi.org/10.1016/j.micromeso.2018.01.035>

Received 25 October 2017; Received in revised form 28 January 2018; Accepted 29 January 2018

Available online 02 February 2018

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phloroglucinol-monosaccharide mixtures without a catalyst or additive in hydroalcoholic media [16]. Moreover, Wu et al. Reported the synthesis of sponge-like carbon gels directly from the hydrothermal treatment of watermelon [17]. Considering practical applications, developing more sustainable carbon gels with controllable structure and properties are still highly desirable.

Additionally, the nitrogen incorporation into the carbon nanomatrix can further enhance the electronic and mechanical properties [18,19]. Nitrogen-doped carbons have shown superior performance in a wide range of applications such as oxygen reduction reactions, CO<sub>2</sub> capture, and heavy metal adsorption [20–22]. However, traditional post-modification strategies to nitrogen-doped carbon gels require the thermal treatment with ammonia or amines [23], which leads to corrosion of equipment and waste of nitrogen source that violates the principle of green chemistry. Several researches on the one-pot hydrothermal synthesis of sustainable nitrogen-doped carbon gels have been reported [24–28].

As a known functional polymer, polyaniline (PANI) has many advantages such as low cost monomer, tunable properties, and thermal stability [29]. The PANI hydrogels were even formed with phytic acid (biomass-derived product) gelator [30]. Herein the one-pot synthesis of monolithic nitrogen-doped carbon cryogels by the HTC of glucose at a low hydrothermal temperature (140–160 °C) was presented, where PANI was employed for the first time as a crosslinking agent to create a stable nitrogen-doped carbon scaffolds. The structure property and surface chemistry of the nitrogen-doped carbon cryogels were also tuned by the aniline concentration and carbonization temperature. The as-prepared monolithic nitrogen-doped carbon cryogels exhibited an extraordinarily high CO<sub>2</sub> uptake of 4.12 mmol g<sup>-1</sup> at 25 °C under 1 atm. The resulting carbon cryogels will be a potential absorbent for CO<sub>2</sub> capture, and CO<sub>2</sub>/N<sub>2</sub> separation.

## 2. Experimental

### 2.1. Synthesis of monolithic nitrogen-doped carbon cryogels

In a typical synthesis, 10 g glucose was first dissolved in 25 mL 1 M HCl solution at room temperature (20 ± 1 °C). Then 0.306 g ammonium persulfate (APS) (as the oxidant) and 0.125 g aniline were added sequentially into the solution under stirring (the molar ratio of APS and aniline was 1:1) for the preparation of PANI [31]. When the solutions turned dark and sticky in 5 min, they were transferred to a quartz tube, placed in a 100 mL Teflon-lined autoclave and then kept at 160 °C for 10 h. Brown-colored and mechanically stable monolithic hydrogels were then obtained. The obtained hydrogels were washed by deionized water and then by ethanol. After purification and changing the solvent back to water, the samples were freeze-dried to obtain the light brown cryogels. To obtain carbon cryogels, cryogels were calcined at a high temperature (≥800 °C) under flowing nitrogen gas for 2 h. The as-prepared carbon cryogels were denoted as CA-x-y, where x and y correspond to the concentration of aniline used (g/L) and carbonization temperature (°C), respectively. In addition, the influences of the

hydrothermal time (0, 0.5, 1, 2, 5 and 10 h) and temperature (130–160 °C) on the morphology were also studied.

### 2.2. Characterization

Scanning electron microscopy (SEM) images were obtained with ZEISS MERLIN Compact instrument. Transmission electron microscopy (TEM) images were taken on a JEOL (JEM-2000 FX) operating at 200 kV. Particle diameter was measured using Nano Measurer software based on the SEM/TEM images. Nitrogen adsorption-desorption analysis was performed at 77 K using Micromeritics ASAP 2460 Surface Area and Porosity Analyzer. Before the analysis, the samples were degassed under vacuum at 250 °C for 12 h. Elemental analysis was measured using the EA3000 analyzer (Leeman). Fourier transform infrared spectra (FTIR) were collected on a Bruker (Tensor 37) instrument. X-ray diffraction (XRD) patterns were carried out with Ulitma IV X-ray diffractometer. Raman spectra were recorded on a Renishaw inVia Raman microscope. In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was recorded on a ThermoFisher (Nicolet iS50) instrument. X-ray photoelectron spectroscopy (XPS) was performed on a Kratos AXIS Ultra DLD system under UHV conditions with Al Kα X-ray to investigate the composition and chemical states. XPS data were analyzed with Kratos Vision and CasaXPS software.

### 2.3. Gas uptake measurements

The CO<sub>2</sub> adsorption isotherms of carbon cryogels were measured using Micromeritics ASAP 2460 Surface Area and Porosity Analyzer at 25 °C. All samples were degassed under vacuum at 250 °C for 12 h before analysis. N<sub>2</sub> adsorption isotherm at 25 °C was also measured on this instrument to investigate the CO<sub>2</sub>/N<sub>2</sub> selectivity.

## 3. Results and discussion

### 3.1. Preparation of monolithic carbon cryogels

The fabrication process for the monolithic nitrogen-doped carbon cryogels is demonstrated in Fig. 1. After aniline was added into the solution containing glucose and APS, a change in the color of the solution from colorlessness to dark green (the color of PANI) was observed, which indicated the formation of PANI. The FTIR spectrum of PANI was identical to emeraldine salt form of PANI (Fig. S1) [30]. Subsequently, the mixture were hydrothermally assembled to form dark brown monolithic hydrogels with the water content of 93%. After the freeze-drying process, the light brown cryogels with low density ( $\rho \sim 0.1 \text{ g cm}^{-3}$ ) were obtained. Finally, carbon cryogels with low density ( $\rho \sim 0.05 \text{ g cm}^{-3}$ ) but a certain contraction ( $\sim 40\%$ ) were obtained after carbonization at 800 °C.

### 3.2. Morphologies of hydrogels and cryogels

During the hydrothermal process, gradual change took place on the

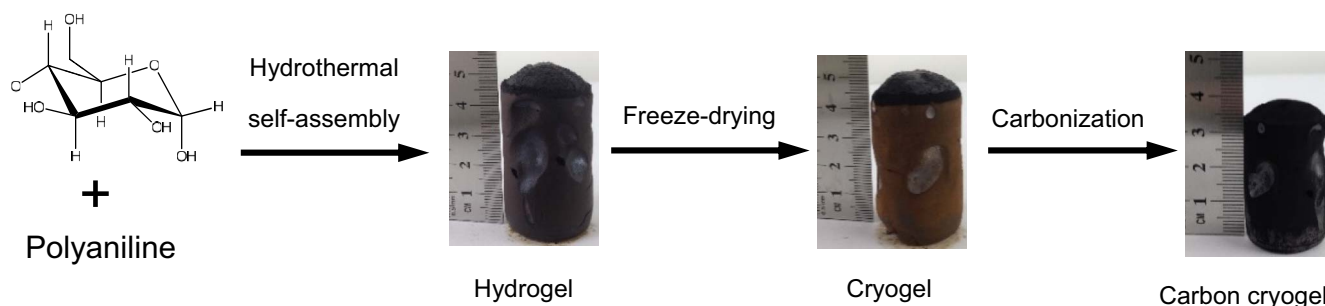


Fig. 1. Synthesis process of nitrogen-doped carbon cryogels.

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