



Facile synthesis of hierarchical triazine-based porous carbons for hydrogen storage



Xin-Ming Hu ^{a,b}, Qi Chen ^a, Yan-Chao Zhao ^a, Bo W. Laursen ^b, Bao-Hang Han ^{a,*}

^a CAS Key Laboratory of Nanosystem and Hierarchical Fabrication, National Center for Nanoscience and Technology, Beijing 100190, China

^b Nano-Science Center and Department of Chemistry, University of Copenhagen, Universitetsparken 5, DK-2100 København Ø, Denmark

ARTICLE INFO

Article history:

Received 7 May 2015

Received in revised form

19 November 2015

Accepted 25 November 2015

Available online 8 December 2015

Keywords:

Cyclotrimerization of nitrile

Carbonization

Triazine-based porous carbon

Hierarchical

Hydrogen uptake

ABSTRACT

Triazine-based porous carbon materials (TPCs) have been synthesized via cyclotrimerization of aromatic tetranitriles and *in situ* carbonization. The resulting TPCs have high surface area (above 1200 m² g⁻¹), large pore volume (above 1.4 cm³ g⁻¹), and hierarchical pore structures with micropores (0.63–1.24 nm) and mesopores (2.4–20 nm). Gas adsorption experiments demonstrate their promising hydrogen uptake capacity, up to 2.34 wt% at 77 K and 1.0 bar, due to the hierarchical porosity that facilitates the diffusion and adsorption of gas molecules.

© 2015 Elsevier Inc. All rights reserved.

1. Introduction

The development of efficient and safe methods for hydrogen storage is still an essential prerequisite for utilization of hydrogen energy. One conventional approach is to chemisorb hydrogen as metal or chemical hydrides, which has been comprehensively investigated and proved fairly efficient [1,2]. However, the high discharge temperature and poor cycle performance remain the bottleneck for their practical applications [2]. An alternative approach to store hydrogen is through physisorption in porous media, which has advantages of fast kinetics and complete reversibility [3]. Of various porous materials, porous carbons are of particular interest thanks to their easy availability and excellent stability.

A simple approach to achieve high hydrogen uptake in porous carbons is to increase the specific surface area [4]. Particular efforts have also been devoted to enhancing hydrogen uptake by creation of micropores, and ultramicropores (<0.7 nm) in particular, where improved interactions between carbon and hydrogen molecules are present [3,5]. This approach seems more essential as micropores contribute dominantly to the high surface area and are most

suitable for trapping of small gas molecules. On the other hand, purely microporous materials may have some limitations due to low permeability and restricted access to active sites for hydrogen adsorption. Mesopores, though they do not adsorb hydrogen efficiently, facilitate hydrogen transport in the porous media. To achieve fast and efficient hydrogen storage, an interconnected porous architecture with both micro- and mesoporosity (hierarchical structure) is thus essential.

To create hierarchical porous carbons, sacrificial-template-based method is typically employed [6,7]. This method requires introduction and removal of templates and seems somewhat complicated and cost-ineffective. Thus, simple synthesis strategies are still highly desirable. Cyclotrimerization of aromatic nitriles has been proved highly efficient for construction of porous covalent triazine-based frameworks (CTFs) [8]. In such reaction, zinc chloride acts as both catalyst and solvent. Note that zinc chloride has also been widely used as activating reagents for synthesis of various carbon materials [9,10]. Pushing the nitrile cyclotrimerization reaction further to the carbonization stage is expected to produce carbon materials with both microporosity and mesoporosity. A systematical study by Kuhn and co-workers has demonstrated that cyclotrimerization of nitriles in zinc chloride at 400 °C produces microporous polymers and that higher reaction temperatures (>600 °C) induce the formation of additional mesopores via carbonization [11]. Their subsequent work indicates that more

* Corresponding author. Tel.: +86 10 8254 5576.

E-mail address: hanbh@nanoctr.cn (B.-H. Han).

equivalents of zinc chloride can also induce the carbonization (at 400 °C) and lead to the formation of mesopores, though micropores are still dominant in the final materials [12,13].

Recently, we introduced a combined cyclotrimerization and carbonization process that allows the formation of a nitrogen-rich porous carbon (TPC-1) from a perfluorinated aromatic nitriles [14]. TPC-1 exhibits dominant micropores, though mesopores are present as well [14]. By use of different precursors and increasing amount of zinc chloride, triazine-based porous carbons (TPCs) with varying porosities and chemical compositions could be expected. Herein, we report two more TPCs that are prepared by combined cyclotrimerization and carbonization of two aromatic tetranitriles in twenty equivalents of zinc chloride. Both TPCs prove to be nitrogen-free and feature well-defined bimodal pore structure, thereby exhibiting exceptionally high hydrogen uptake capacities.

2. Experimental

2.1. Materials

All chemicals were purchased from commercial suppliers and used without further purification unless otherwise stated. Anhydrous zinc chloride was further dried at 120 °C in vacuo overnight prior to use. Tetra(4-bromophenyl)methane [15] and tetra(4-bromophenyl)ethene [16] were synthesized according to reported procedures. Ultra-high-purity grade gases were used for all gas adsorption experiments.

2.2. Synthesis of monomers

Tetra(4-cyanobiphenyl)methane (M-2). To a round-bottom flask were added tetra(4-bromophenyl)methane (1.0 g, 1.57 mmol), 4-cyanophenylboronic acid (1.39 g, 9.43 mmol), potassium carbonate (4.35 g, 31.5 mmol), and *N,N*-dimethylformamide (30 mL). The mixture was degassed by the freeze–pump–thaw cycles. Tetraakis(triphenylphosphine)palladium (80 mg) was then added and the formed mixture was heated at 100 °C under nitrogen atmosphere for 24 h. The reaction mixture was cooled down to room temperature and poured into deionized water with stirring. The precipitate was dissolved in dichloromethane and washed with deionized water and brine. The organic phase was collected and the solvent was evaporated. The residue was purified by column chromatography on silica gel (dichloromethane/methanol, v/v = 100:1) to afford a white solid (0.51 g, 45%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.74–7.69 (m, 16H), 7.57 (d, *J* = 8.0 Hz, 8H), 7.44 (d, *J* = 8.0 Hz, 8H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 146.7, 144.9, 137.2, 132.8, 131.74, 127.7, 126.84, 119.0, 111.3, 64.6. MS (MALDI-TOF) *m/z*: calcd for C₅₃H₃₂N₄ 724.26 [M], found 724.21.

Similarly, *tetra(4-cyanobiphenyl)ethene (M-3)* was synthesized from tetra(4-bromophenyl)ethene. Purification by column chromatography on silica gel (dichloromethane/methanol, v/v = 150:1) afforded a yellow solid (0.64 g, 56%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.71–7.64 (m, 16H), 7.42 (d, *J* = 8.0 Hz, 8H), 7.22 (d, *J* = 8.0 Hz, 8H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 144.9, 143.8, 140.8, 137.6, 132.7, 132.3, 127.6, 126.9, 119.0, 111.1. MS (MALDI-TOF) *m/z*: calcd for C₅₄H₃₂N₄ 736.26 [M], found 736.66.

2.3. Preparation of TPCs

TPC-2. To a glass ampoule were added tetra(4-cyanobiphenyl)methane (M-2, 150 mg, 0.21 mmol) and anhydrous zinc chloride (564 mg, 4.14 mmol) under nitrogen atmosphere. The ampoule was evacuated, sealed, and heated to 400 °C over 1 h. After keeping at this temperature for 40 h, the ampoule was cooled down to room temperature. The reaction mixture was washed thoroughly with

water and diluted aqueous hydrochloric acid solution to remove zinc chloride. The resulting black product was further purified by Soxhlet extraction with water, tetrahydrofuran, and dichloromethane. After drying in vacuo at 150 °C, 125 mg of black powder was obtained, corresponding to 83% of the starting material by mass.

Similarly, *TPC-3* was prepared from M-3 in 75% yield.

2.4. Characterization and measurement

¹H and ¹³C NMR spectra were recorded on a Bruker Avance DMX-400 NMR spectrometer (Bruker, Germany) using the residual solvent as internal reference. MALDI-TOF mass spectra were recorded on a Bruker Autoflex vertical reflector instrument (Bruker, Germany). IR spectra were measured on a Bruker ALPHA FT-IR spectrometer (Bruker, Germany) with an attenuated total reflection accessory. Field emission scanning electron microscopy (SEM) observations were carried out on a JSM-6320F scanning electron microscope (JEOL, Japan) at an accelerating voltage of 10 kV. The powder of the as-prepared materials was placed on a silica wafer before measurement. Raman spectroscopy, X-ray diffraction (XRD), thermogravimetric analysis (TGA), X-ray photoelectron spectroscopy (XPS), and gas adsorption experiments were performed according to previously reported procedures [14].

3. Results and discussion

3.1. Synthesis and characterization of TPCs

The synthesis routes to TPCs are presented in [Scheme 1](#). The two aromatic tetranitrile monomers (M-2 and M-3) are synthesized via fourfold palladium-catalyzed Suzuki coupling reaction between tetra(4-bromophenyl)methane/-ethene and 4-cyanophenylboronic acid. Heating the mixture of the monomer and zinc chloride in a sealed glass ampoule at 400 °C produces the desired porous carbon materials (TPC-2 and TPC-3, from M-2 and M-3, respectively). Note that Ren et al. [17] and Bhunia et al. [18] have reported respectively porous frameworks made from tetra(4-cyanophenyl)methane/-ethene, similar tetranitriles to ours. In their reports the final materials prepared in ten equivalents of or less zinc chloride are claimed to be either porous aromatic frameworks (PAF-2) or CTFs (PCTF-1), rather than the desired TPCs. Thus, to ensure the efficient carbonization of the resulting polytriazine networks, twenty equivalents of zinc chloride are used. Analogous to the synthesis of CTFs, the reaction is carried out at autogenic pressure and no apparent pressure is detected when the ampoule is opened [8]. Black monolith that can be grounded to powder is obtained in the yield of ca. 80% by successive washing away the salt from the final mixture with aqueous hydrochloric acid solution and deionized water followed by Soxhlet extraction. It is noteworthy that overpressure is detected and the yield is only 54% for the synthesis of TPC-1 [14], implying that the carbonization process for TPC-2/-3 and TPC-1 occurs through different pathways that will be discussed after structural and porosity characterization.

The as-prepared TPCs were characterized by IR spectroscopy ([Fig. 1a](#)). The IR spectra of both monomers exhibit intense carbonitrile band around 2220 cm⁻¹, which is not detected anymore for TPCs. The disappearance of such band indicates the complete transformation of the nitriles. Unlike the synthesis of CTFs, the triazine vibration band around 1360 cm⁻¹ is not observed [8,18,19]. More significantly, no obvious vibration bands can be detected for the TPCs. Even the original strong bands between 1490 and 1600 cm⁻¹ that are assigned to skeleton vibration of the aromatic rings in monomers are extinguished. The most likely reason for the

Download English Version:

<https://daneshyari.com/en/article/6532876>

Download Persian Version:

<https://daneshyari.com/article/6532876>

[Daneshyari.com](https://daneshyari.com)