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Solvent evaporation mediated preparation of hierarchically porous metal organic framework-derived carbon with controllable and accessible large-scale porosity

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ABSTRACT

We report a template-free and easy solvent evaporation method during carbonizing a metal–organic framework (MOF) for the construction of large-scale meso- and macropore. While the direct thermal evaporation method of non-volatile solvent captured in micropore of a MOF is believed to reduce overall porosity of the resultant MOF, this method unprecedentedly directs the reorganization of MOFs toward the production of ultrahigh porous carbon materials. The obtained porous carbon materials possess a unique interconnected three-dimensional wormhole-like structure, high specific surface area (3000 $m^2 g^{-1}$), and exceptionally high pore volume (5.45 $cm^3 g^{-1}$). The micropores, along with accessible meso- and macropores, provide ion storage site and ion transport channel, respectively, that contributes to a rapid elimination of large amounts of salt within a very short period of time.

1. Introduction

Nanoporous carbon materials have been a crucial component in a variety of energy- and environment-based applications, including gas storage, separation, catalysis, electronics, water treatment, and biochemistry [1–5]. Recently, nanoporous carbon materials with hierarchical pore architectures possessing three-dimensional (3D) interconnected micro-, meso-, and macropores have provided new insights into the advanced utilization of nanoporous carbon materials [5–7]. Hierarchical pore architectures can extend the molecular selectivity and accessibility of a catalytic application and facilitate ion transport in electrochemical applications. These architectures therefore overcome the drawbacks associated with catalyst deactivation and slow reaction kinetics [5,7,8].

To address these pore characteristics, a host of synthetic techniques have been developed to create mesoporous features in microporous materials and vice versa [6,9,10] or to simultaneously evolve hierarchical porosity by removable a template material with features on multiple length scales [5,11]. These approaches include the incorporation of a self-assembled mesopore structure-directing molecule into a

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microporous carbon material synthesis procedure [12], chemical activation of a mesoporous carbon material [10], or nanocasting (or nano-replication) using colloidal silica, polymer beads, or zeolites [11,13,14]. Although synthetic technologies can serve as a conceptually versatile alternative for obtaining hierarchically porous carbon materials, their complicated synthesis and removal from the original template remains a challenge for practical applications. Importantly, the porosity generated by such techniques does not fulfil the demands for the pore characteristic (a high surface area with a hierarchical pore architecture) because adoption of such techniques can sacrifice the original pore characteristics of the starting carbon materials [9,10,15].

Xu et al. proposed a new type of nanoporous carbon material in which a metal–organic framework (MOF) and a furfuryl alcohol were used as the template and carbon precursor, respectively [3,16]. The resultant carbons exhibited intrinsically hierarchical porosity with a relatively high specific surface area (SSA > 2000 $m^2 g^{-1}$). Consequently, outstanding performances were obtained in an evaluation of the materials as electrodes for high-rate electrochemical capacitors [3,16]. Recently, the direct carbonization of MOFs without the use of additional carbon sources was found to be more effective at increasing the overall porosity [17,18]. Despite recent progress in the use of hierarchically porous MOF-derived carbons (MDCs), the lack of systematic control over the pore characteristics continues to hinder the construction of designed pore architectures and the extension of these novel hierarchically porous carbon materials to applications.

Here, we demonstrate a template-free novel carbonization method by which hierarchically porous MDCs with a controlled-macroporosity and an ultrahigh pore volume can be realized. Solvent evaporation during heat treatment can lead to the formation of defect cracks on the surfaces of an MOF, and these cracks play an important role in the introduction of large-sized meso- and macropores within the MDC without the detriments associated with microporosity [19]. The direct thermal evaporation of a non-volatile solvent captured in the micropores of a MOF tends to slightly reduce the overall porosity and is often regarded as a process to be avoided [20–22]. We attempted to utilize this unfavorable effect to direct the reorganization of MOFs toward the production of ultrahigh porous carbon materials featuring micro-, meso-, and macropores as shown in Fig. 1. The new porous carbon material produced through this process can be used as a substitute for capacitive deionization (CDI) electrodes based on conventional porous carbon for the desalination of brackish water. The unique hierarchical porosity facilitated swift ion transport and, hence, large amounts of salt could be eliminated within a short period of time. The CDI performances of the benchmark materials suggested that the novel hierarchical porosity of the MDC could guide the development of new porous carbons-based desalination materials with improved kinetics relative to the current standard.

2. Experimental

2.1. Reagents and chemicals

Zinc nitrate tetrahydrate (Merck), terephthalic acid (Aldrich), N,N′-diethylformamide (DEF, Merck), N,N′-dimethylformamide (DMF, Daejung, Korea), and anhydrous chloroform (Aldrich) were used without further purification.

2.2. Synthesis of isoreticular MOF-1 (IRMOF-1)

Zinc nitrate tetrahydrate (0.78 g, 3 mmol) and terephthalic acid (0.17 g, 1 mmol) were dissolved in DEF (30 ml) in a vial. The reaction mixture was heated in a furnace at 105 °C for 24 h to yield large cubic crystals of IRMOF-1. The reaction vessel was removed from the furnace and allowed to cool to room temperature.

2.3. Preparation of MDC-A, -C, and –D

The prepared IRMOF-1 was transferred to a tube furnace and heat-treated at a target temperature (900 °C) under nitrogen with a heating rate of 5 °C min^{-1} to pyrolyze the MOFs. After

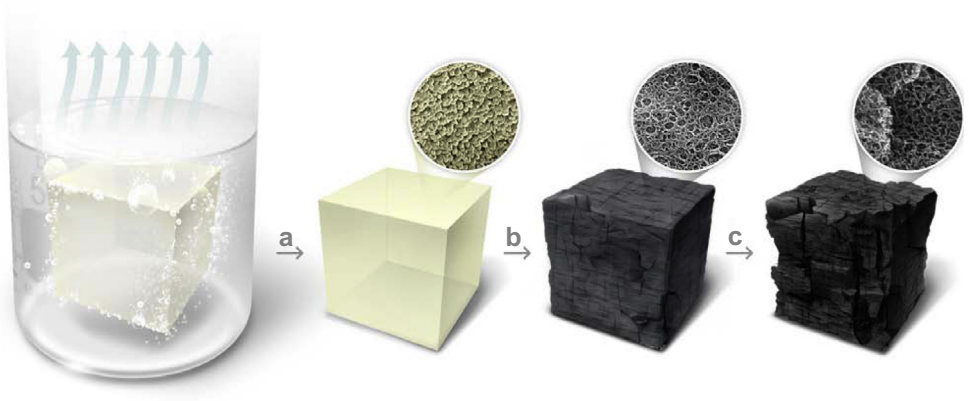

Fig. 1 – Schematics showing the formation of hierarchically porous carbon with an ultrahigh pore volume from MOFs; (a) The structural evolution of the large-sized pore seeds with micrograin boundaries by non-volatile solvent evaporation; (b) The formation of a mesoporous metal oxide@carbon hybrid; (c) Micro- and macropores were introduced by continuously reducing the metal oxide, evaporating the metal, and carbonizing the material. (A colour version of this figure can be viewed online.)