



Facile nano-templated CO₂ conversion into highly interconnected hierarchical porous carbon for high-performance supercapacitor electrodes



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ABSTRACT

Hierarchical porous carbon materials have been derived through CO₂ conversion by using NaBH₄ as a reducing agent and CaCO₃ as a nano-template. The CaCO₃-templated porous carbons (CPCs) feature an interconnected three-dimensional structure with hierarchical pores favorable for electrochemical energy storage. Notably, CPC1_700 prepared with an identical mass of CaCO₃ and NaBH₄ at 700 °C shows a very high capacitance of 270 F/g at 1 A/g and retains its capacitance up to 170 F/g at 20 A/g in 6 M KOH aqueous electrolyte. Moreover, it presents an outstanding normalized capacitance of 21.4 μF/cm² even in the absence of pseudocapacitive behavior, and a fast frequency response with a low relaxation time constant of 0.27 s. Concerning the cycle stability, more than 90% of the initial capacitance is maintained after 10000 consecutive cycles at high current densities (20 A/g and 30 A/g). The major fundamental insights underlying this performance are closely related to the interconnected hierarchical pore architecture generated by the concurrent template and CO₂ activation effect, which leads to increased surface area, fast ionic transport, and efficient ionic storage. The proposed route of CO₂-to-carbon with the template affords a facile, efficient, and sustainable strategy to synthesize hierarchical porous carbon for high-performance supercapacitors.

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1. Introduction

As global warming is an issue of great concern, renewable energy is attracting attention as a potential alternative to fossil fuels [1,2]. In addition, the emerging market of numerous electronic devices such as cell phones, cameras and hybrid electric vehicles has generated strong demand for reliable and sustainable energy sources [3]. To meet the requirements, various types of electrochemical systems including fuel cells, lithium-ion batteries, and supercapacitors are considered promising candidates. Among them, the supercapacitors offer many benefits such as high power density, fast charge-discharge rate, and stable life cycle [4–6].

Electrode materials for supercapacitors are typically classified into transition metal oxides, conductive polymers, and porous carbon based materials. The former two materials provide the advantage of high capacitance but also have drawbacks of low rate

capability, short life cycle, and high cost, limiting practical applications for commercialization. On the other hand, porous carbon based materials have attracted a great deal of attention due to their long-term and stable life cycle, as well as large surface area, high conductivity, low production cost, and superior thermal, mechanical, and chemical stabilities [5,7–10]. The specific capacitance of carbon based materials is mainly determined by the specific surface area and the porosity of the structure [11]. Micropores contribute to the improved surface area of the porous material, mesopores provide a transport channel through which ions can readily pass [5,12,13], and macropores function as a reservoir for the ion storage and shorten the transport distance [14,15]. Thus, the optimal porous carbon structure is an interconnected network of the variously sized pores to increase the effective ion storage area and lower the ion migration resistance [16].

Recently, CO₂ conversion into porous carbon materials has emerged as a key technology since CO₂ is an abundant carbon source, and this CO₂ utilization can contribute to the mitigation of global warming [17]. Numerous CO₂ transformation strategies have been proposed to produce CNTs (at 70 MPa) [18], porous carbon (at 32 MPa) [19], and graphene [20] using supercritical CO₂ or dry ice.

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However, these extreme conversion conditions require large energy consumption, and cause the reproduction of CO₂. For a more energy efficient CO₂ conversion process, sodium borohydride (NaBH₄) has been used as a CO₂ reducing agent to produce boron doped porous carbon at atmospheric pressure and 500 °C [17,21–24]. Moreover, porous carbon materials were derived from a reaction of synthetic flue gas (85% N₂ and 15% CO₂) with NaBH₄, followed by KOH activation [25]. Although these studies demonstrated promising technologies for CO₂ conversion into porous carbon materials, the suggested approaches still have some disadvantages of limited electro-capacitive performance and multi-step preparation.

In this study, we propose a single step CO₂ conversion into hierarchical porous carbon by using NaBH₄ as a reducing agent and CaCO₃ as a nano-template. The CaCO₃ nanoparticles have been previously investigated for application as a hard template in carbon precursors such as melamine-formaldehyde resin and sucrose [26,27]. However, the combination of a nano-template with CO₂ conversion has never been explored for the production of hierarchically porous carbon materials. It will be shown that without any chemical treatment such as KOH activation [8,25], the as-prepared hierarchical porous carbons possess a large surface area (1262 m²/g), a high pore volume (3.35 cm³/g), and an interconnecting pore structure, leading to enhanced electrochemical properties. From various electrochemical analyses, it will be demonstrated that the porous carbons exhibit excellent supercapacitive performance in terms of specific capacitance, rate capability, and cycle stability. This study opens up a new way of connecting CO₂ utilization and the production of hierarchical porous carbon via a facile one-step templating method for effective supercapacitive energy storage.

2. Experimental

2.1. Materials

Argon (Ar, > 99.9%) and carbon dioxide (CO₂, > 99.9%) were purchased from Deokyang Co., Ltd. Sodium borohydride (NaBH₄, > 99%), polytetrafluoroethylene (PTFE, 60 wt% dispersion in water), and potassium hydroxide (KOH, > 90%) were purchased from Sigma-Aldrich. Hydrochloric acid (HCl, 37 wt% in water) was available in Junsei Chemical Co., Ltd. Calcium carbonate nanoparticles (CaCO₃, 15–40 nm) were acquired from SkySpring

Nanomaterials. All of the chemicals were used without further purification.

2.2. Synthesis of CaCO₃-templated porous carbon (CPC) and non-templated porous carbon (NPC)

In a typical synthesis of CPCs_700 (Fig. 1), 4 g of NaBH₄ was mechanically mixed with CaCO₃ at different mass ratios (CaCO₃/NaBH₄ = 0.5, 1 and 2). The mixture of NaBH₄ and CaCO₃ was heated up to 500 °C (5 °C/min) under a CO₂ flow of 75 ml/min and maintained at this temperature for 2 h. The temperature was then increased up to 700 °C (5 °C/min), in which CO₂ gas was switched to a 50 ml/min Ar flow at 600 °C, and the temperature was held at 700 °C for 2 h. The resultant was transferred into a beaker, and the residue including the template was washed several times with hot aqueous solutions of 5 M HCl, deionized (DI) water, and ethanol in sequence. The sample was dried in an oven at 95 °C for 12 h. The as-prepared carbons were denoted as CPC_x_700, where x indicates the CaCO₃/NaBH₄ weight ratio (x = 0.5, 1 and 2). In the case of CPC1_600, the sample was heated until 600 °C under only a CO₂ flow, and then cooled to room temperature without the Ar treatment. NPC_700 was prepared following the same procedure as CPC_x_700, except for the addition of a CaCO₃ template.

2.3. Characterization

The morphology of the porous carbon was investigated by a scanning electron microscope (SEM, Hitachi SU8230). Transmission electron microscopy (TEM) images were obtained with a JEOL JEM-2100F at 200 kV. The sample for TEM was dispersed in ethanol, followed by dropwise addition of the suspension onto a copper grid. The nitrogen adsorption–desorption isotherms were measured at 77 K using a Micromeritics 3Flex after degassing of the sample under a high vacuum at 200 °C for 8 h. The specific surface area was calculated by the Brunauer-Emmett-Teller (BET) theory by using a relative pressure range of 0.02–0.2. The correlation coefficients for BET plots were above 0.9999. The micropore and mesopore size distributions were determined by the Horvath-Kawazoe (H–K) and Barrett-Joyner-Halenda (BJH) analyses, respectively. The total pore size distributions were obtained from non-local density functional theory (NLDFT). X-ray diffraction (XRD) patterns were measured on a RIGAKU Smart lab with Cu K α

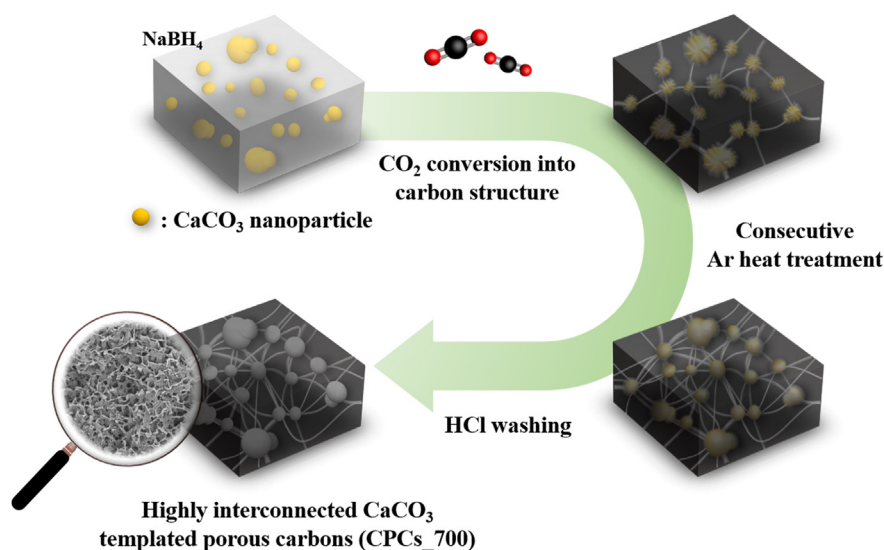


Fig. 1. Schematic diagram for one-step nano-templated CO₂ conversion into porous carbons, CPCs_700. (A colour version of this figure can be viewed online.)

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