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Multiwalled carbon nanotube cryogels with aligned and non-aligned porous structures

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ABSTRACT

Multiwalled carbon nanotube (MWCNT) cryogels were fabricated with aligned and non-aligned porous structures. The MWCNT cryogels contained a major fraction of MWCNTs with a minor fraction of silk fibroin as the structure binder. The morphology of the porous structures was controlled using a sol–gel process of silk fibroin to form the network structures. Microchannel structures were formed by ice-templating. The MWCNT cryogels contained mesopores and formed as monoliths. The MWCNT cryogels with aligned porous structures showed better thermal stability and electrical conductivity than the MWCNT cryogels with non-aligned porous structures due to the advantageous MWCNT interconnections. The morphology of the porous structures was examined by field emission scanning electron microscopy and transmission electron microscopy. The structure–property relationships of the MWCNT cryogels and the performance of the MWCNT cryogels as electrodes were investigated.

1. Introduction

Porous carbon materials, such as carbon aerogels, have many interesting properties, such as high surface area, high electrical conductivity, interconnected porous network structure and extremely low densities. These materials have potential applications in a variety of areas, including catalysts [1], adsorbents [2], electrodes [3] and template materials [4]. Carbon aerogels can be synthesized using a sol–gel process to form gel structures. This process can be monitored by special drying and carbonization processes in an inert atmosphere [5]. Freeze-drying methods are a special drying method that maintains the gel structures, and aerogels prepared using freeze-drying methods are generally known as cryogels. This method is economical, practical and useful. Recently, Yodh et al. synthesized carbon nanotube (CNT) aerogels [6]. CNT aerogels were reported to support at least 8000 times their weight [6] and exhibited good electrical conductivity, 10^{-2} S/cm [7]. In addition, del Monte et al. produced a macroporous 3D architecture of self-assembled CNT using ice-templating [8].

The morphology of the porous materials is an important factor because the nanostructures, pore properties and microstructure have a significant effect on their applications [9,10]. Coasne et al. synthesized ordered and disordered porous carbon by freezing argon, and reported differences between ordered and disordered porous carbon [9]. The most suitable structure morphology of a porous material must be selected for optimal applications. A porous structure can control the formation of aligned/ordered structures or non-aligned/disordered structures. Aligned/ordered porous structures can be synthesized using an ice-segregation-induced self-assembly (ISISA) method using ice-templating or unidirectional freezing techniques [7,8,10,11]. In this method, ice is used as the template. Ice templates are not only formed in situ but are also formed in the microchannels and aligned/ordered porous structures. In addition, they can be easily removed, and are inexpensive and environmentally friendly. On the other hand, non-aligned/disordered porous structures can be synthesized using sol–gel methods, which is termed gelation [12,13]. This forms interconnected solid structures to three-dimensional (3D) network porous structures.

In this study, aligned or non-aligned multiwalled carbon nanotube (MWCNT) cryogels with silk fibroin were fabricated as either a structure binder or solid structure. MWCNT cryogels can be used as biomaterial scaffolds [11,14,15]. Oxidized MWCNTs are quite soluble in water. Therefore, they can be dispersed in an aqueous silk fibroin solution [16]. For this reason, a stable MWCNT-dispersed silk fibroin solution was prepared as a precursor to create aligned and non-aligned porous structures. Aligned MWCNT cryogels were prepared by ice-templating with silk fibroin as the structure binder. Non-aligned MWCNT cryogels were prepared using a gelation method by employing the sol–gel reaction of silk fibroin. This study also examined the morphological, textural and electrical properties of the fabricated aligned or non-aligned MWCNT cryogels.

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2. Experimental

2.1. Preparation of stable MWCNT dispersed in a silk fibroin aqueous solution

MWCNTs (purity of 95%; supplied by Iljin Nanotech, Korea) were produced by thermal chemical vapor deposition (CVD). The as-received MWCNTs were treated with acid to remove the impurities, such as metallic catalysts, using a procedure reported elsewhere [17]. The MWCNTs were treated with an acid mixture (sulfuric acid/nitric acid = 3:1 (v/v)) at 60 °C for 6 h. As a result, carboxylic functional groups were introduced to the surface of the MWCNTs [18]. Cocoons of *Bombyx mori* silkworm silk were supplied by the Boeun Sericulture Farm in Korea. Pure silk fibroin was obtained by boiling the cocoons for 30 min in an aqueous solution of 0.02 M sodium carbonate (Na_2CO_3, 99.5%+, Aldrich), and rinsing them thoroughly with deionized water to extract the glue-like sericin proteins. The extracted silk fibroin was dried at room temperature for 72 h, and then dissolved in 9.3 M lithium bromide (LiBr, ≥99%, Aldrich) at 55 °C for 2 h [16]. The solution was dialyzed in deionized water using Slide-A-Lyzer® dialysis cassettes (Pierce, MWCO 3500, USA) for 36 h. After dialysis, the final concentration of the aqueous silk fibroin solution was 7–8 wt%, which was determined by weighing the remaining solid after drying. Appropriate amounts of the acid-treated MWCNTs were then dispersed in water using an ultrasonic generator (Kodo Technical Research Co., Korea) with a nominal frequency of 28 kHz and a power of 600 W for 1 h at 25 °C. The MWCNT dispersed in water was added at the appropriate amounts to the silk fibroin aqueous solution. Stable MWCNT (0, 3, 6, and 9 wt%) dispersions in an aqueous silk fibroin (2 wt%) solution were prepared [16].

2.2. Fabrication of non-aligned or aligned MWCNT cryogels

The MWCNTs dispersed in the aqueous silk fibroin solution was poured into cylinder-shaped glass molds (diameter 12 mm). Non-aligned MWCNT cryogels (GEL-series) were fabricated using a gelation method, as shown in Fig. 1a. To prepare GEL-3, 15 ml of stable MWCNT (3 wt%) dispersions in an aqueous silk fibroin (2 wt%) solution were left to stand for a few days at 60 °C at pH ~7 to allow setting in the form of an elastic hydrogel through silk fibroin gelation [19]. The prepared MWCNT-dispersed silk fibroin elastic hydrogel was flash-frozen in liquid nitrogen (−196 °C) for a few seconds to freeze the pore liquid, and immediately freeze-dried in a lyophilizer (LP3, Jouan, France) at −50 °C and 0.045 mbar for 48 h. Aligned MWCNT cryogels (ICE-series) were fabricated using ice-templating according to the procedure described elsewhere, as shown in Fig. 1b [11]. The silk fibroin solution with dispersed MWCNTs (2 wt%) was collected in glass molds, which were dipped into a cold bath at a constant rate of 10 cm/h and a constant temperature (−196 °C). The unidirectionally frozen MWCNTs dispersed in the silk fibroins were then freeze-dried in a lyophilizer under steady conditions used in the gelation process. When the freeze-drying process was complete, the aligned or non-aligned MWCNT cryogels were obtained in monolithic form with both the size and shape of the glass molds maintained, as shown in Fig. 1. The aligned and non-aligned MWCNT cryogels prepared with different concentrations of MWCNTs are denoted as ICE-*x* and GEL-*x*, respectively, where *x* indicates the dispersed MWCNT concentration. As control experiments, silk fibroin cryogels were prepared using either ice-templating or gelation methods, as described above, but without the MWCNTs.

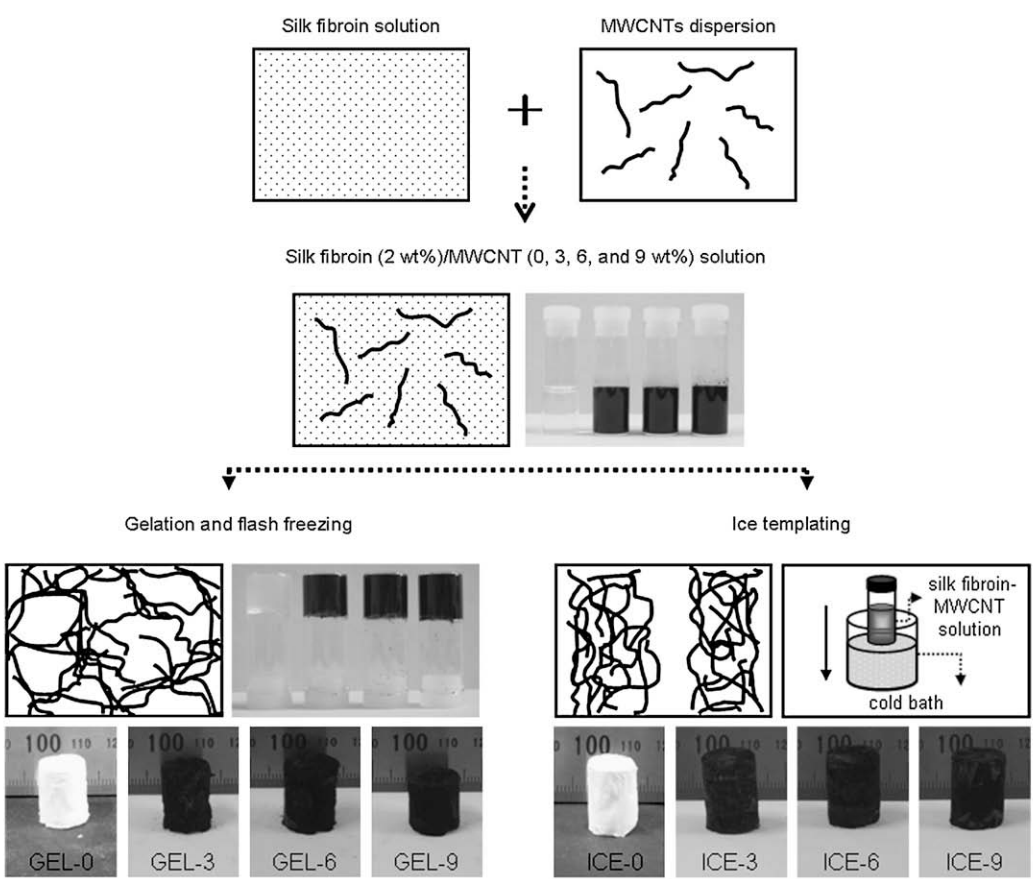

Fig. 1. Schematic diagram of the formation of porous structure with (a) the gelation and flash freezing and (b) ice-templating.