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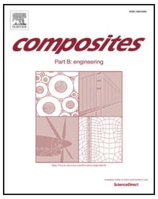

Carbon nanotube-poly(vinyl alcohol) hybrid aerogels: Improvements in the surface area and structural stability by internal morphology control

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ABSTRACT

In this study, carbon nanotube (CNT) hybrid aerogels with high mechanical properties were fabricated by interconnecting structural networks of CNTs using poly(vinyl alcohol) (PVA) through amine-functionalized iron oxide (NH_2-Fe). Consequently, Fe-CNT-PVA hybrid aerogels exhibited good structural stabilities, even under repeated loads due to the interconnection bonding with PVA between neighboring CNTs. Furthermore, compared to the Fe-CNT aerogels, the Fe-CNT-PVA hybrid aerogels showed ~3 times higher specific surfaces due to the tuning of the internal morphology by controlling electromagnetic interactions between NH_2-Fe on the surface of the CNTs and the applied magnetic field. These results clearly show that CNT aerogels with both improved structural stabilities and specific surface areas can be fabricated by the method proposed in this study.

1. Introduction

Carbon nanotubes (CNTs) are tubular nanostructures composed of carbon atoms that have good mechanical (tensile strength of ~1 TPa) [1], electrical (conductivity of ~10^4 S/cm) [2], and thermal properties (conductivity of ~3000 W/m K) [3,4]. Furthermore, CNTs have low specific densities (0.2 ± 0.01 g/cm^3) [5], high surface areas (> 100 m^2/g) [6], good thermal resistances in an inert atmosphere, as well as high chemical stabilities. Therefore, assembly of CNTs into bulk materials with desired structures and properties hold the key to realizing their higher value-added industrial applications, which can open new application fields for carbon-based materials [7–12]. Assembling CNTs into aerogels creates new CNT-based bulk materials that integrate the intriguing properties of CNTs with the unique structural properties of the aerogels, such as low densities, large specific surface areas, high porosities, as well as extraordinarily low thermal conductivities [13–16].

In fact, research into CNT-based aerogels/hydrogels has already attracted much attention due to their potential applications in the fields of lightweight multi-functional composites, drug-release materials, acoustic insulation, energy storage/conversion electrode materials, and gas/oil absorbents [14–16]. However, their practical uses still suffer from many limitations, particularly from low mechanical strengths. In general, carbon-based three-dimensional (3D) bulk materials are very vulnerable to external impact, due to weak interfacial interactions forces between the constituents forming the 3D carbon-based structures. Consequently, the preformed 3D carbon-based structures collapse upon external impact, which result in significant losses in the surface areas, pore distributions, and mechanical properties of the final products. Due to this problem, these 3D carbon-based materials, despite having the high initial pore distribution and specific surface area, do not show dramatic improvement in performance when applied as energy storage/conversion electrode materials or gas/oil absorbents. As a result, commercial applications of these materials are still limited.

In the present work, we propose a simple and efficient method to fabricate ultra-lightweight CNT aerogels with structural stabilities against external impact, using poly(vinyl alcohol) (PVA) as an adhesive material between individual CNTs in the 3D architecture.

PVA is a polymer resin that is generally capable of forming hydrogen bonds with hydroxyl (-OH) or carboxylic (-COOH) functional groups [17–19]. On mixing with oxidized-CNTs (O-CNTs), PVA can act as an effective adhesive connecting CNTs via hydrogen bond formation, with the -OH groups present on the surface or edges of the O-CNTs.

In addition, we use iron oxide modified with an amine functional group to connect adjacent CNTs and try to control the orientations of CNTs during the lyophilization process by electromagnetic interactions between the attached iron oxide on the CNT surface and the applied magnetic field [20–22]. Consequently, the internal structure of the aerogel changed, leading to an increase in the surface areas of the resulting CNT aerogels. Because of the interconnectivity between the

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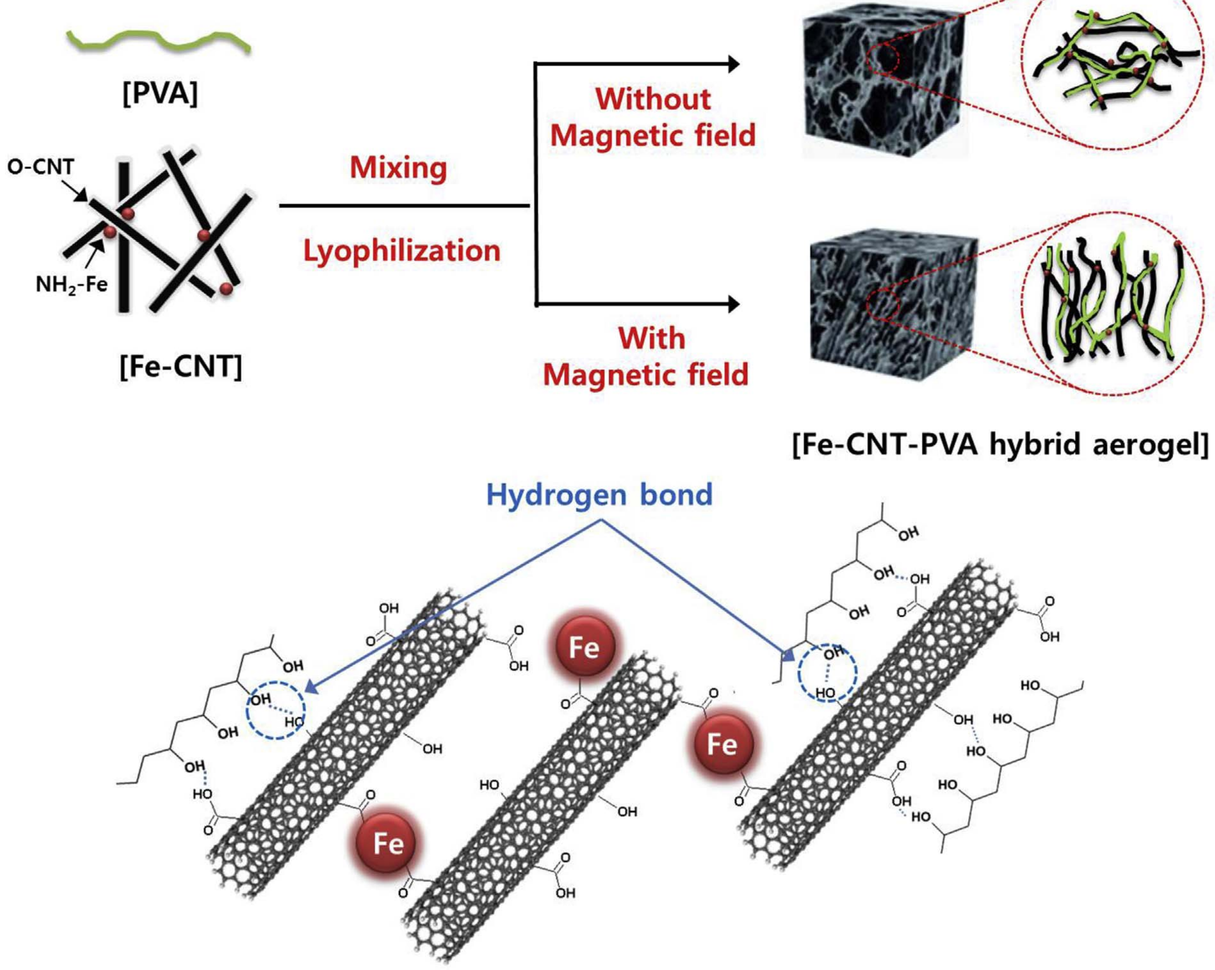

Fig. 1. (a) Methods of preparation of the Fe-CNT-PVA hybrid aerogel with and without a magnetic field and scheme of the network structure of Fe-CNT-PVA hybrid aerogels.

structure and the orientation of CNTs, the 3D hybrid CNT aerogels are shown to have enhanced the specific surface areas and mechanical properties than those of Fe-CNT aerogels. Consequently, this work provides a simple and effective fabrication method for versatile CNT aerogels, which have great potential in the fields of oil/gas absorption and energy storage/conversion electrode materials.

2. Materials and methods

2.1. Materials

The carbon nanotubes (CNTs) were purchased from Nanocyl, Belgium. The type of CNTs are multi-walled carbon nanotube (MWCNTs), and the diameters of the CNTs were about > 10 nm. Iron oxide (α-Fe_2O_3), 3-amino propyltrimethoxysilane, potassium permanganate ($KMnO_4$), and poly(vinyl alcohol) (PVA, Mw: 100,000 g/mol) were purchased from Sigma Aldrich (St. Louis, MO, USA). In this study, we used glutaraldehyde solution (50 wt% in H_2O), resorcinol and sodium tetraborate for binders between the individual CNTs [23]. These chemicals were purchased from Sigma Aldrich (St. Louis, MO, USA). All reagents were used without further purification. Sulfuric acid (H_2SO_4), ethanol, hydrochloric acid (HCl), tetrahydrofuran (THF) were obtained from PFP Matunoen Chemicals Ltd, Japan.

2.2. Preparation of oxidized carbon nanotube (O-CNTs)

CNTs (1 g) was added to 200 mL of 1 N sulfuric acids (H_2SO_4) and sonicated for 1 h at room temperature. Potassium permanganate (19.8 g, $KMnO_4$) was dissolved in 200 mL of 1 N H_2SO_4. The mixture was heated to 150 °C with vigorous stirring. Then, the $KMnO_4$ solution was added drop by drop through the side arm of a flask. The solution was refluxed for 5 h. The mixture was then cooled to room temperature and filtered. The filtrate was washed with deionized water (DI-water) and then with 30% hydrochloric acid (HCl) to remove the manganese (IV) oxide. The residual filtrate containing the oxidized CNTs was collected and dried for 24 h at 60 °C.

2.3. Preparation of aminosilane-modified iron oxide (NH$_2$-Fe)

Iron oxide (0.25 g) was added to 150 mL ethanol and sonicated for 1 h, followed by vigorous stirring for 1 h at room temperature. 3-amino propyltrimethoxysilane (10 mL) was added to the iron oxide solution followed by stirring for 24 h at room temperature. The resulting suspension was washed 5 × with methanol (200 mL) and filtered. The aminosilane end-product was functionalized with iron oxide (NH_2-Fe) and was dried at 50 °C for 24 h.

2.4. Preparation of networked hybrid materials (Fe-CNTs)

NH_2-Fe (20 mg) and 0.1 g of O-CNTs were added to 80 mL of THF, and the mixture was sonicated for 1 h, and then stirred for 24 h at room temperature. The resulting solution was washed 5 × with DI-water (200 mL), and the precipitate was dried at 50 °C for 24 h. The iron oxide content of Fe-CNTs was investigated by comparing the TGA results of O-