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Low-temperature grafting of carbon nanotubes on carbon fibers using a bimetallic floating catalyst

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ABSTRACT

The degradation mechanism of CFs experiencing the catalytic growth of CNTs on their surface through high-temperature CVD was revealed using microstructural analysis. Catalysts nanoparticles, if their energy was high enough to diffuse into CFs, generated micro-voids in CFs and reduced their tensile strength. Herein, we report a new low-temperature processing route to grow CNTs on CF surfaces without mechanically degrading the CFs. The use of a Ni–Fe bimetallic catalyst was key to achieving the growth of CNTs at low temperature, e.g., 500 °C. Catalyst diffusion into the CFs during CVD was inhibited at this temperature, which facilitated uniform growth of CNTs on only the CF surfaces and minimized internal structural changes of the CFs.

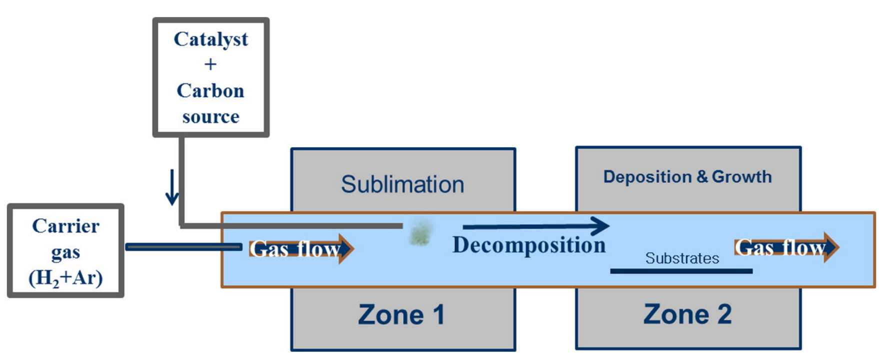

Fig. 1. Schematic diagram of the FCVD process for a two-zone furnace. The catalyst precursors and carbon source supplied into the first zone sublime and vaporize, respectively. These then decompose into the catalyst and carbon atoms in the second zone, where CNTs grow on the substrate.

1. Introduction

The hybridization of carbon nanotubes (CNTs) and carbon fibers (CFs) is a versatile method to develop new and advanced materials by hierarchically combining their excellent thermal, electrical and mechanical properties at the nano- and microscales [1]. CNT-grafted CFs made via direct growth have emerged as a material that can improve the reinforcing effect of CFs in composites and solve the dispersion problems of CNTs [2]. Radially grown CNTs on CFs improve the radial stiffness [3] and axial tensile strength [4,5] of CF-reinforced composites, the interfacial shear strength (IFSS) of polymer composites [6], and the electrochemical performance of CF electrodes [7]. Several issues must be resolved, however, for successful dissemination of CNT-grafted CFs. These issues include the manufacturing method, which degrades

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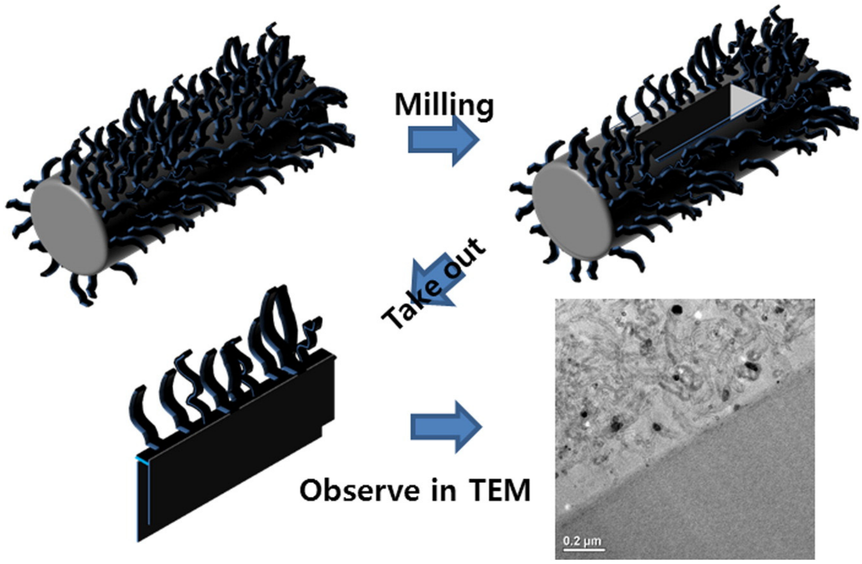

Fig. 2. Sample preparation using focused ion beam (FIB) milling to observe the internal structure of CNT-grafted carbon fibers (CFs) by transmission electron microscopy (TEM).

the mechanical properties of the resulting CFs [1,8], and the high cost of the batch process used for their manufacture, i.e., the pre-process for introducing catalyst nanoparticles on the CF surface [9] and the main process for growing CNTs via chemical vapor deposition (CVD) [10]. Herein, we demonstrate that a bimetallic catalyst and floating catalyst chemical vapor deposition (FCVD) can solve these problems.

As one of the simplest methods to graft CNTs on CFs, FCVD provides carbon sources and catalysts concurrently, inducing the deposition and growth of CNTs on substrates. There have been several studies concerning the grafting of CNTs on various substrates using FCVD [11–15]. When CFs are used as the substrate, the catalyst nanoparticles diffuse into the CFs and become poisoned and deactivated by carbon atoms separated from the CFs because the CFs are porous [16]. Diffused catalysts destroy the internal structure of CFs, while the poisoning and deactivation of catalyst particles hinders CNT growth [17]. Diffused catalysts depopulate the CF surfaces of active catalyst particles, also

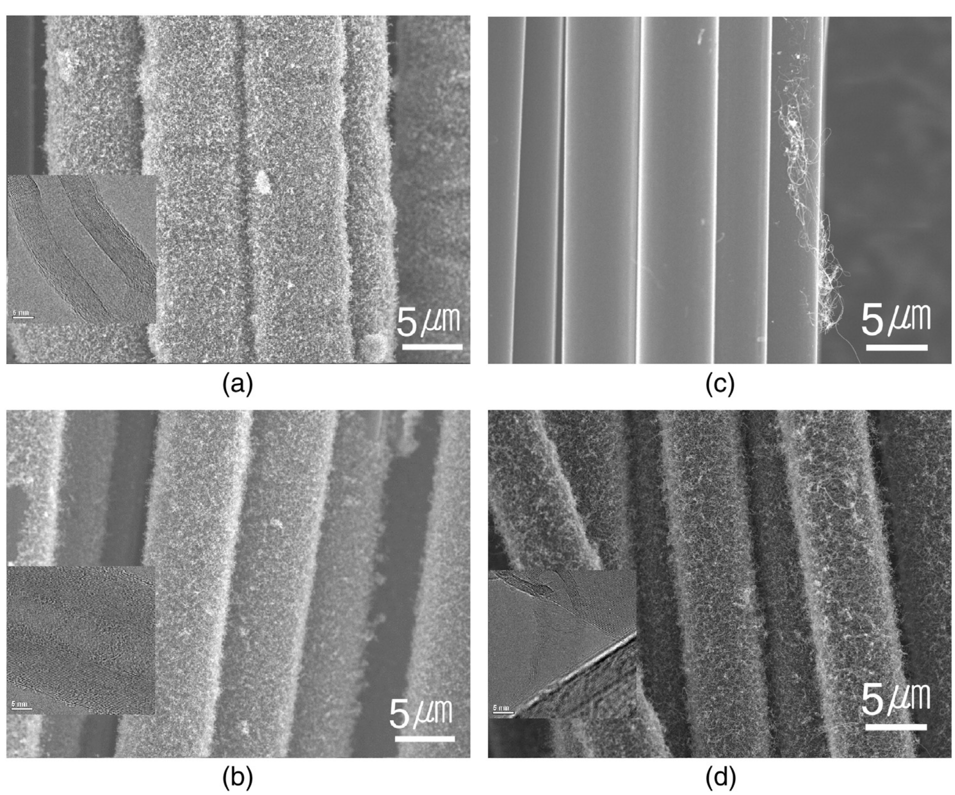

Fig. 3. Morphologies of CNT-grafted CFs prepared from different substrate CFs, catalysts, and CVD temperatures. (a) As-received CFs, bimetallic catalyst, 500 °C; (b) oxidized CFs, bimetallic catalyst, 500 °C; (c) as-received CFs, Fe-only catalyst, 750 °C; (d) oxidized CFs, Fe-only catalyst, 750 °C.