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Controllable synthesis of core-sheath structured aligned carbon nanotube/titanium dioxide hybrid fibers by atomic layer deposition

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ABSTRACT

Carbon nanotube (CNT)-inorganic hybrids have been extensively investigated due to their potential to become the next-generation materials for applications in energy and environment. However, the random dispersion of CNTs and the low-quality inorganic phases may hinder their use in flexible and multi-functional devices. Herein, we synthesize the multi-functional aligned CNT/titanium dioxide (TiO_2) hybrid fibers involving CNT-based continuous fibers coated by TiO_2 through the atomic layer deposition (ALD). The aligned CNT/TiO_2 hybrid fibers with various thicknesses of TiO_2 layer can be simply obtained by changing the ALD cycles. Microscopic analysis of the surface morphologies and structures of the as-prepared hybrid fibers confirms the conformal oxide coating on the CNT fibers. Furthermore, the tensile strength of the hybrid fiber varies little after the deposition of TiO_2 while its electrical conductivity decreases by 28.3% when the ALD cycle number is increased to 715 cycles. Due to its unique self-limiting characteristic, ALD has precise control in deposition at the atomic level and can facilitate the conformal and uniform coating of TiO_2 on the CNT fibers while preserving the alignment of CNT bundles within the fiber, which may offer a promising solution for fabricating the novel multi-functional fibers.

1. Introduction

Carbon nanotube (CNT)-inorganic hybrids have been extensively investigated due to their potential to become the next-generation materials for applications in energy and environment [1–3]. Combining CNTs with multi-functional inorganic nanomaterials can fully utilize the synergistic effects between the CNT-inorganic interface and bring superior combined properties to the hybrids [1,4–6]. Take the widely studied CNT-titanium dioxide (TiO_2) hybrids for example. The CNTs can not only act as the dispersing agents that prevent the agglomeration of TiO_2, thus providing a higher active surface area, but also act as the electron acceptors that promote the interfacial electron-transfer processes from the attached TiO_2, thus suppressing the recombination of electrons and holes [1,6]. Therefore, the CNT-TiO_2 hybrids have shown improved efficiencies in photovoltaics [6], increased capacitances in supercapacitors [7] and enhanced activities in photocatalysts [8–10]. However, one of the main challenges to manufacture of these hybrids is the random dispersion of CNTs in the resulting hybrids, which leads to much reduced mechanical and electrical properties and further hinders their applications in flexible and multi-functional devices [11,12].

Recently, the development of high-performance macro-assemblies of CNTs, such as CNT arrays, films, and fibers, make it more conveniently to synthesize the CNT-inorganic hybrids with coherent 3D structures than the individual CNTs which are commonly dispersed in the matrix [3,12]. Among these CNT assemblies, CNT based continuous fibers, which combine lightweight, excellent mechanical and electrical properties with large specific surface area, have attracted considerable research interest and may become the desirable scaffolding materials [13–18]. Some attempts have been made to synthesize the CNT-TiO_2 hybrids based on aligned CNT fibers. Neocleus et al. synthesized the hierarchical CNT/TiO_2 hybrid fibers via a vapor-assisted hydrothermal technique, but the fiber shrink was inevitable and there existed many axial folds on the surface of the as-prepared fiber with the increase of the reaction time [3]. Chen et al. coated a layer of TiO_2 nanoparticles onto the CNT fibers by immersing them into the TiO_2 colloid, but the thickness of the TiO_2 layer could only be controlled at the

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micrometer scale [17]. Li et al. also dip-coated the CNT fibers with a thin layer of compact n-TiO_2 by immersing them into a precursor solution, but it was hard to obtain a thin and continuous film of n-TiO_2 without any defects [18]. Therefore, exploring a suitable coating method to preserve the morphology of the CNT structures while achieving desirable inorganic phases is an essential prerequisite to obtain high performance CNT-inorganic hybrids [3,12].

Atomic layer deposition (ALD), which utilizes two sequentially cyclic self-limiting surface reactions to deposit ultrathin films [19–22], may be a potentially effective technique to prepare the CNT-inorganic hybrids. Due to its unique surface reaction mechanism, ALD can deposit precise, uniform and conformal oxide layers on very high-aspect-ratio substrates at low temperatures, and strong covalent linkages can be formed between the ALD layers and the underlying substrate [5,20,22–24]. The highly conformal ALD oxide layers, which can be precisely controlled from several nanometers to hundreds of nanometers, has demonstrated the ability to enhance the efficiency and stability of the photoelectrochemical systems [21,22] and the lithium and sodium ion batteries [25]. While the use of ALD to synthesize the powder form of CNT-inorganic hybrids based on individual CNTs has been extensively explored [7,20,26–28], it has been scarcely reported to utilize ALD to fabricate the 3D structured CNT-inorganic hybrids involving the macro-assemblies of CNTs.

In this study, with the aim of obtaining high-quality 3D structured CNT-inorganic hybrid fibers, we synthesized the multi-functional aligned CNT/TiO_2 hybrid fibers involving CNT-based continuous fibers coated by TiO_2 through the atomic layer deposition. The aligned CNT/TiO_2 hybrid fibers with various thicknesses of TiO_2 layer can be simply obtained by changing the ALD cycles. Microscopic analysis of the surface morphologies and structures of the hybrid fibers confirmed the conformal oxide coating on the CNT fibers. Furthermore, the hybrid fibers exhibited both mechanical robustness and good electrical conductivities, which may offer a promising solution for fabricating the novel multi-functional fibers.

2. Experimental

2.1. Preparation of aligned CNT/TiO_2 hybrid fibers

CNT fibers used in this study were spun by drawing and twisting of CNT strips out of vertically well-aligned CNT arrays, whose CNTs were super-aligned and mainly double- and triple-walled with diameter distribution from 4 to 6 nm. Specific details of the preparation of CNT fibers can be found in Ref. [29]. The weight of CNT fibers was measured on an Ultra-microbalance (Sartorius M2P). A typical 13 μm diameter and 100 mm long CNT fiber weighed 10–30 μg, giving a linear density between 0.1 and 0.3 tex (1 tex = 1 μg/mm).

A traveling thermal ALD system (Ensure Nanotech Co., Ltd.) was used for the ALD-TiO_2 coating on the CNT fibers to fabricate the aligned CNT/TiO_2 hybrid fibers. In the ALD-TiO_2 process, several CNT fibers with a length of 10 cm were separately loaded into a commercial 6-inch ALD reactor. Then, tetrakis dimethylamino titanium (Ti $(CH(NH_2)_2)_4$, TDMAT, 99.9999%, Sigma-Aldrich) for the Ti precursor and deionized water (DI H_2O) vapors for the reactant were introduced into the ALD reactor in an alternating sequence to perform the ALD-TiO_2 deposition, as illustrated in Fig. 1. It should be noted that there existed many hydroxyl (>COH) and carboxyl (−COOH) groups attached to the defect sites of CNTs on the fiber surface, and these reactive surface groups can assist in chemisorbing the TDMAT and the H_2O molecules and serve as nucleation sites for the subsequent oxide deposition [20,26]. TDMAT was heated to 65 °C while water was kept at room temperature in order to provide sufficient vapors for the ALD-TiO_2 process. The ALD-TiO_2 growth temperature was set as 120 °C. Additionally, the delivery lines were heated to 150 °C in order to prevent the precursors from condensing. Nitrogen was used as the carrier gas with a flow rate of 20 sccm and the ALD reactor was sustained at a low level of pressure (typically 0.22 Torr) with a vacuum pump.

The sequence of one ALD-TiO_2 cycle was: (i) a 0.4 s supply of TDMAT; (ii) a 60.0 s extended exposure of TDMAT to the CNT fibers; (iii) a 30.0 s purge of oversupplied TDMAT and any by-products; (iv) a 0.1 s supply of water vapor; (v) a 60.0 s extended exposure of water vapor to the CNT fibers; (vi) a 30.0 s purge of oversupplied water and any by-products. The ALD process can be adjustable with different cycling numbers in order to obtain the aligned CNT/TiO_2 hybrid fibers with various TiO_2 thicknesses.

The calcination of the hybrid fibers was conducted in a furnace in argon at 600 °C for 1 h with the fibers mounted on a graphite mold.

2.2. Single-fiber tensile tests

Details of the specimen preparation for single-fiber tensile tests can be found elsewhere [30]. Ten specimens of each type of fiber were tested on a Testometric testing machine (TM-350) with a load cell of 5 N and a tensile rate of 0.5 mm/min. The gauge length of all specimens was fixed to 7 mm, and the average diameter of each specimen was calculated by taking the average of 10 measurements at different locations along the fiber axis in the gauge section using the laser diffraction method.

2.3. Characterizations

The surface morphologies and microstructures of the pure and the as-prepared CNT/TiO_2 hybrid fibers were characterized by scanning electron microscopy (SEM, HITACHI S-4800) and high-resolution transmission electron microscopy (HRTEM, FEI Tecnai G2 F20 S-Twin, 200 KV), respectively. Raman spectra of the fiber specimens were recorded by Raman spectroscopy (Horiba JY Labram HR800). The laser with a wavelength of 632.81 nm was used to excite Raman scattering in the specimen. The laser power was adjusted to 2 mW to avoid the heating effect on the samples. X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250Xi) was performed using a monochromatic Al K α source (1486.6 eV). Specimens for XPS characterization were prepared by tightly aligning the fiber bundles on a central hole of the aluminum substrate with the fiber ends attached to the carbon tapes near the hole. The XPS depth profiling experiment was conducted by using argon ions as the etching beam. The etching rate was estimated as 0.22 nm/s when 2000 eV-ion energy and 1 mm^2-raster size were employed in the experiment. For the pure CNT fiber, a single etch period was used with 10 etches of 30 s each. For the CNT/TiO_2 hybrid fiber (286 ALD cycles), the multiple etch phases were employed with 10 etches of 5 s and 25 etches of 30 s to obtain better depth resolution at the CNT-TiO_2 interface. The electrical resistance of CNT fibers before and after ALD TiO_2 deposition was measured using a Keithley 2000 multimeter. For a better electrical contact, silver paste was used to fix the two ends of the tested fiber on a glass slide. The electrical conductivities of the fibers were calculated based on Ohm's law.

3. Results and discussion

Fig. 2a shows the surface morphology of a pure CNT fiber observed by SEM. It can be seen that the CNT bundles within the fiber are tightly compacted due to the ethanol infiltration during the spinning process. To synthesize the aligned CNT/TiO_2 hybrid fibers, we coated the CNT fibers with various TiO_2 thicknesses by varying the ALD cycles (72, 143, 286 and 715 cycles). Fig. 2b–e shows the