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Short communication

A general strategy for the preparation of aligned multiwalled carbon nanotube/inorganic nanocomposites and aligned nanostructures

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ABSTRACT

A general strategy for the preparation of aligned multi-walled carbon nanotube (AMWCNT)/inorganic composites and aligned nanostructures was realized by synthesizing materials within an AMWCNT/hydrogel composite template. Chemical reactions that could damage the AMWCNT structure are not necessary in this strategy. AMWCNT composites of many materials were synthesized. Three typical and popularly used materials were present to show the versatility of the strategy: hydroxyapatite, alumina, and silver. The morphologies of the materials formed on the nanotube surface include continuous layers, nanoparticles, and microspheres. The structures formed after the removal of AMWCNTs include aligned nanofibers, aligned nanotubes, and particles.

1. Introduction

AMWCNT forests possess significant anisotropic properties compared to nonaligned nanotubes, and can easily be incorporated into device configurations due to their orientation texture. Surface functionalization of AMWCNTs can endow them with special properties, thus extending their potential applications in many fields, such as electronic devices [1–4], sensors [5,6], and catalysis [7]. Both inorganic and organic precursors have been used in various methods (e.g. plasma activation, photochemical reaction, electrochemical deposition, chemical functionalization and doping, and polymer masking) to functionalize the surface of AMWCNTs [8,9]. However, in most cases any particular method is only suitable for a few specific AMWCNT functionalization routines. Methods involving conventional solution chemistry – which have been used extensively in modifying nonaligned carbon nanotubes – must be performed carefully as AMWCNT alignment can easily be disrupted by the harsh conditions necessary for oxidizing the carbon atoms on carbon nanotubes.

Functionalizing the surface of AMWCNTs can greatly improve their functional properties for use in various applications. However, unmodified AMWCNTs do have some important properties, for example they possess a unique ability to provide a nano-template for other materials to form aligned structures. Anodic aluminium oxide (AAO) has proved a popular template for synthesizing aligned materials [10]. Here, aligned nanofibers or nanotubes are obtained by material growth within the cylindrical shaped pores, followed by subsequent removal of the template. In contrast, when AMWCNTs are used as a template, material deposition happens inside or on the surface of individual nanotubes, leading to AMWCNT nanocomposites [8,9,11]. Despite their promise, AMWCNTs are not regularly used for synthesizing aligned structures, primarily because of the lack of advanced methods for synthesizing AMWCNT nanocomposites. Thus a general and robust strategy for the synthesis of AMWCNT nanocomposites is desirable.

In this work, we report a general strategy that a simple AMWCNT/hydrogel composite can be used for synthesizing AMWCNT nanocomposites and aligned structures of many materials without AMWCNT support by the sol–gel process, or by pyrolysis of nitrates. The materials synthesized without removal of AMWCNT templates include AMWCNT nanocomposites of titania, silica, and hydroxyapatite (HA) (by sol–gel process), alumina, iron oxide, copper oxide, nickel oxide (by pyrolysis of nitrates), and silver (by pyrolysis of nitrates). Herein we present the results for three typical and popularly used materials to show the versatility of the strategy: hydroxyapatite (HA), alumina, and metal silver.

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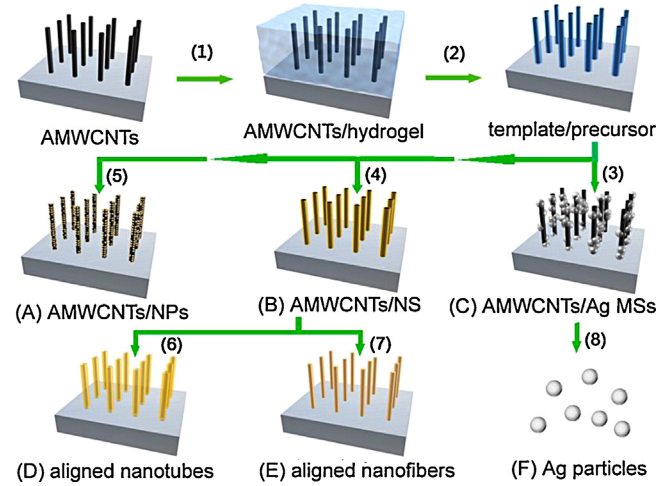

Fig. 1. The general strategy to synthesize AMWCNTs/oxides or metal nanocomposites.

2. Experimental

2.1. Sample preparation

All the reagents here were purchased from Beijing Chemical Reagent Company (Beijing, China). The strategy is illustrated by Fig. 1: (1) AMWCNTs with a length of 4 mm were prepared in our lab by a CVD method. AMWCNT/hydrogel composites were prepared by polymerizing an ethanol and water (1:1 wt/wt) solution (acrylic acid (AA), dimethylacrylamide (DMAA), methylenebisacrylamide (MBAA), and ammonium persulfate in 1:1:0.02:0.01 weight ratios, with a total monomer content of 25 wt%) inside the AMWCNT forest; (2) the formed hydrogel shrunk, broke and enveloped the individual nanotube by losing water, and reabsorbed reaction solution in the hydrogel layer; (3), (4), and (5) sol–gel process and/or pyrolysis reactions were performed in the hydrogel layer, forming AMWCNT nanocomposites with morphology of nanoparticles (A, NPs), or nanoshell (B, NS), or microspheres (C, MSs) on the surface of the nanotubes; (D) aligned nanotubes, (E) aligned nanofibers, and (F) dispersed particles can be prepared by removing AMWCNTs in air flow at high temperature. The morphologies obtained depended on the materials and the synthesis processes of the nanocomposites were the same.

2.2. Sample characterization

A field-emission scanning electron microscope (SEM, LEO-1530) was used to observe the morphologies of specimens, and the acceleration voltage was 10 kV during measurements. AMWCNT/HA nanocomposites were sputtered Cr_2O_3 before characterized by energy-dispersive X-ray spectroscopy (EDX) and other samples were characterized by EDX directly. The transmission electron microscope (TEM) used was a JEOL-200CX, and the acceleration voltage was 100 kV. The powder X-ray diffraction (XRD) patterns were recorded with a D/MAX-RB X-ray diffractometer.

3. Results and discussion

3.1. Preparation of AMWCNT/HA nanocomposites and aligned HA structure

HA is an extensively studied bioceramic due to its similarity with the inorganic component of human bone. As the extracellular matrix of human tissues has a rich architecture of nanoscale features, such as aligned nanofibers, interconnected pores, and ridges [12], many materials with advanced topographies, including AMWCNTs [13], porous materials [14,15], and colloidal crystals [16], are being used to study cell-substrate interactions. AMWCNT/HA nanocomposites and aligned HA nanofibers may thus find applications in bone regeneration [17]. The synthesis of AMWCNT/HA nanocomposites and aligned HA nanofibers by a process using the AMWCNT/hydrogel template and combining a sol–gel reaction and pyrolysis of nitrate is a perfect example for application of the AMWCNT/hydrogel template synthesis strategy. Comparing with the nanotubes in pure AMWCNTs (Fig. 2A), the nanotubes in the AMWCNT/hydrogel template showed larger diameters and rougher surfaces due to the hydrogel enveloping them (Fig. 2B). As shown in Fig. 3A, the AMWCNT/HA nanocomposite retained the aligned structure of the AMWCNTs after pyrolysis of hydrogel at 500 °C, forming a rough NS on the surface of AMWCNTs (Fig. 3B). After removal of AMWCNTs by calcination in air, the HA partially fused but retained a nanofiber texture inside the materials (Fig. 3C). When a dilute HA sol was used, HA NPs as illustrated by Scheme 1(A) formed on the nanotube surface (Fig. 3D). The formed HA nanoshell on the nanotubes was confirmed by EDX and XRD (Fig. 4).

3.2. Preparation of AMWCNT/alumina nanocomposite and aligned alumina nanotubes

It is well known that the pyrolysis of metal nitrates depends on the activity of the metal. In the metal active order, nitrates from K

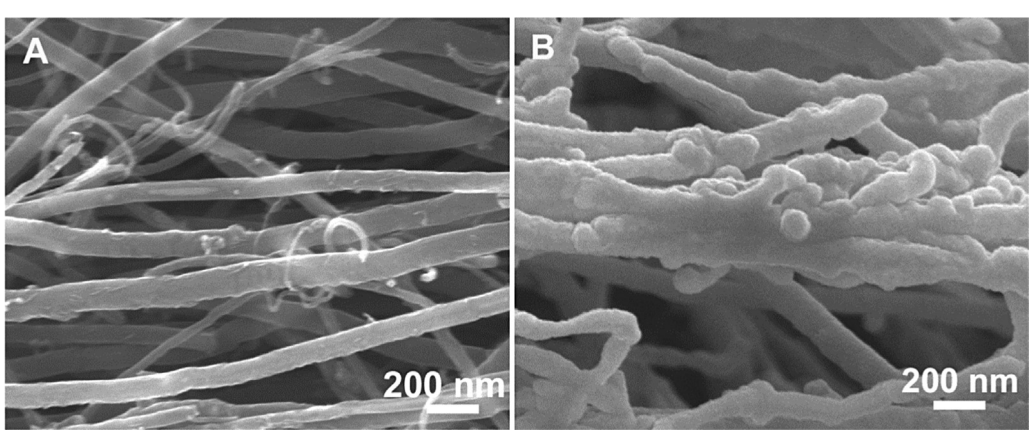

Fig. 2. SEM images of AMWCNT templates: (A) AMWCNTs; (B) AMWCNT/hydrogel template.