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Synergistic effect of Fe and Al_2O_3 layers on the growth of vertically aligned carbon nanotubes for gecko-inspired adhesive applications

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ABSTRACT

This study focused on the application of vertically aligned carbon nanotubes (VACNTs) grown by thermal chemical vapor deposition as a gecko-inspired dry adhesive material. The adhesive properties of VACNTs comprising Fe and Al_2O_3 layers of different thicknesses were evaluated by scanning electron microscopy, Raman spectroscopy, transmission electron microscopy, and atomic force microscopy. Owing to the surface energy difference between metallic Fe and alumina, the wetting influence of the latter enabled the conversion of the iron film into metal islands (nanoparticles) at high temperature. The bionic morphological characteristics of the produced VACNTs (e.g., alignment, density, diameter, growth rate, and defects) and thus their adhesive properties were determined by the size and distribution of the catalyst particles. With respect to variable adhesion test angles, VACNTs were sensitive to peeling angles and showed high tangential but low normal adhesion strength, thereby providing controlled strong adhesion characteristics in combination with easy peel-off.

1. Introduction

The unique biological adhesive system evolved on gecko feet endows these animals with extraordinary climbing ability, allowing them to suspend by a single toe and achieving an adhesive force of ~10 N/cm^2 [1]. Gecko feet feature a large number of keratinous aligned microscopic hairs, called setae, split at the end into even smaller spatulae which come into close contact with the surface to induce strong van der Waals interactions [2,3]. The unique micro-nano structure of gecko feet enables strong adhesion to rough surfaces, inspiring the development of various synthetic polymer and carbon nanotube arrays as dry adhesive materials [4–9]. Although the limitations associated with polymer array manufacturing have precluded their utilization on the nanoscale, vertically aligned carbon nanotubes (VACNTs) are considered better candidates for this purpose owing to their nanostructure and outstanding mechanical properties [10–13]. Recently, VACNTs were reported to exhibit a macroscopic adhesive strength exceeding that of the natural array of setae on gecko feet [14,15]. Despite a sufficient number of studies investigating VACNTs as dry adhesive materials, the factors influencing their adhesion are not fully understood, with the controlled synthesis of such materials still being a big challenge.

Chemical vapor deposition (CVD) is commonly used to synthesize VACNTs, requiring lower reaction temperatures and providing the benefits of easily controlled parameters and easy scalability [16]. In systems employing Fe as catalyst, Si/SiO_2 is commonly used as a growth substrate, with a layer of Al_2O_3 deposited on its surface serving to extend the lifetime of such catalysts [17,18]. According to the classical vapor–liquid–solid theory, VACNT growth features the following steps: Carbon source capture and cracking by catalyst particles, incorporation of carbon atoms into the catalyst, precipitation of supersaturated carbon atoms, and carbon nanotube generation [19]. At high temperatures, Fe thin films are fragmented into catalytically active nanoparticles, with different film thicknesses affecting the structure and morphology of the produced VACNTs by influencing the size and distribution of the formed nanoparticles [20,21]. Xu et al. [22] achieved controllable VACNT growth (producing random to super-aligned structures) by changing the thickness of the Fe layer and obtained double-walled VACNTs by adjusting the density of the active catalyst. Herein, we study the macroscopic adhesive properties of VACNTs synthesized using various thicknesses of the Fe and Al_2O_3 layers to increase their adhesive force. In catalytic systems containing Al_2O_3 as a buffer layer, the role of Al_2O_3 has been interpreted in a number of ways, e.g., alumina has been reported to impart long-term stability to the metal clusters in its pores [23]. During the catalytic process, the alumina support has been reported to play a vital role in promoting the formation of nanoparticles, increasing their density beyond a level sufficient for vertical alignment and restricting the surface migration of Fe required to produce nanoparticles suitable for VACNT growth [24].

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Moreover, some researchers have found that the Al_2O_3 layer is mostly amorphous, probably aiding the deposition of more uniform Fe films by increasing the wettability of Fe on its surface [25,26]. Other correlation studies also support the hypothesis that the porous structure of alumina significantly contributes to the homodispersion and fixation of catalytically active nanoparticles [27–29].

Although there has been encouraging progress in the growth of VACNTs for adhesion-related applications, their controlled, repeatable, and stable growth for practical applications is still a significant challenge. VACNT synthesis involves complex phenomena, such as interactions of the Fe catalyst and the Al_2O_3 buffer layer, which are still not well understood. Herein, we reveal that the size and distribution of catalytic nanoparticles can be tuned by adjusting the thicknesses of the Fe and Al_2O_3 layers, leading to VACNTs with different structures and morphologies, and, hence, different adhesive properties. Thus, understanding the growth mechanism of VACNTs is crucial for enhancing their adhesive properties.

2. Experimental

VACNTs were grown in a tubular furnace (Nano 160, Tytan, USA) by thermal CVD on a Si/SiO_2 wafer. The Al_2O_3 buffer layer and Fe catalytic film were deposited on the Si/SiO_2 substrate using an electron beam system. Catalytic systems with Fe layer thicknesses of 0.5, 1, 2, and 3 nm and alumina thicknesses of 10, 15, 20, and 30 nm were fabricated as described below.

Growth was achieved under a low pressure (100 Torr), using ethylene (C_2H_4, 270 sccm) as the carbon source, H_2 (180 sccm) as the reducing gas, and Ar (740 sccm) as the protective gas. H_2 was injected into the furnace for catalyst pretreatment and the growth of VACNT was achieved after 40-min heating at 750 °C in the presence of C_2H_4.

Hot field emission scanning electron microscopy (SEM; SIGMA, Zeiss, Germany) was employed to observe the microstructure of VACNTs, and micro-Raman spectroscopy (λ = 632.8 nm, Labram HR 800, Japan) was used to characterize their quality (graphitic ordering, defects, etc.) Transmission electron microscopy (TEM) was used to determine the number of walls, diameter, and purity of VACNTs. The morphology of the nanoparticles on the alumina-iron surface was characterized by atomic force microscopy (AFM) after heating in an atmosphere of H_2.

A multifunctional material adhesion and friction test platform (IBSS-2, NBIT Co. Ltd., Nanjing, China) was used to analyze the adhesive property of VACNT arrays. The platform contains a 3-dimensional force sensor with a force resolution of ~1 mN and a glass slide mounted on a sample stage for adhesive surface. A side of polymer sheet was attached on the backside of the sample (silicon surface), and its other side was fixed adjustably to change the angle (α) between the polymer sheet and test platform. When the finger-pressed pre-loading was completed, the test platform was moved vertically to investigate the adhesive properties.

3. Results and discussion

3.1. AFM analysis

The morphologies of the catalyst particles in different catalytic systems were characterized by AFM investigation of Fe-Al_2O_3 surfaces after their exposure to H_2 for 40 s at 750 °C, and Fig. 1(a–d) show that the nanoparticle size gradually increased with increasing Fe layer thickness. Specifically, Fig. 1(c) reveals relatively uniform particles for a Fe layer thickness of 2 nm, with all the particles exhibiting integral spherical shapes, uniform distribution, and similar sizes. Conversely, Fig. 1(a) (Fe layer thickness of 0.5 nm, present as sporadic pinpoints on the surface) displays small and sparsely distributed catalytic particles. Moreover, no catalytic nanoparticles are observed for a Fe layer thickness of 3 nm (Fig. 1(d)), with "hills" protruding from the iron film surface instead.

Similarly, Fig. 1(c, e, f, g) display the effect of the thickness of the alumina layer. The nanoparticle morphology observed in Fig. 1(f) (alumina thickness of 20 nm) is similar to that in Fig. 1(c) (alumina thickness of 15 nm), featuring uniformly distributed particles with similar sizes and integral spherical shapes. However, the particle size observed for a 20-nm-thick alumina coating is smaller than that observed for a 15-nm-thick one. Fig. 1(e, g) reveal that 10- and 30-nm-thick Al_2O_3 coatings are not suitable for achieving uniform nanoparticle distribution and size, producing low-quality and sparsely distributed particles. In particular, aggregated particles are observed for an alumina thickness of 30 nm, owing to the obscure and rough topography.

3.2. Structure and morphology analysis

VACNT growth is closely related to the structural and morphological evolution of the metal catalyst, being significantly affected by the choice of the catalytic system. In this case, the variable thicknesses of iron and alumina layers resulted in totally different growth patterns. SEM images in Fig. 2 illustrate the top-view and cross-sectional view of VACNTs grown in different catalytic systems with different iron and alumina layer thicknesses.

According to the collective mechanism of the evolution and self-termination of VACNT growth proposed by Bedewy et al., the initial growth phase consists of randomly oriented self-assembled VACNTs [29], the produced structures of which are depicted in the top-view SEM images showing the top layer (Fig. 2 (a1–g1)). The top section of VACNTs is of considerable importance, as it represents the contact surface for adhesion-related applications. The cross-sectional images of VACNTs demonstrate the various possible orientations, e.g., fluffy "sponges" or vertical "forest." These observations are related to previous AFM results, where serried catalyst particles produced vertically aligned VACNT arrays owing to the "crowding effect" of neighboring carbon nanotubes, which describes the interaction of neighboring carbon nanotubes determining the growth direction [22]. In contrast, sparsely distributed catalytic nanoparticles produce fluffy or poorly aligned arrays. Under this condition, the orientation can also reflect the density of the array, and these characteristics play a crucial role in determining the mechanical properties of the material [30,31].

Fig. 3 shows the heights of the arrays produced at different catalyst layer thicknesses, reflecting the overall catalyst lifetimes and VACNT growth rates. The broad range of observed height (10–800 μm) agrees with the results of AFM observations, indicating that the evolution of the iron catalyst during the growth process determines the structure and morphology of VACNTs. The growth of VACNTs is strongly dependent on the properties of the catalytically active particles, with their grown being terminated if their size and distribution becomes unfavorable. In adhesion tests and applications, the height of the VACNTs array is primarily responsible for their adaptation to the roughness of the target surface.

The TEM images showing the morphologies of single CNTs are shown in Fig. 4, revealing that the number of walls and the diameter of the CNTs increase with increasing thickness of the Fe layer. Moreover, some impurities attached to the nanotube walls are also observed.

Similarly, varying the alumina layer thickness (10, 15, 20, and 30 nm) at a constant Fe layer thickness (2 nm) affected the nanotube diameter and number of walls, as shown in Fig. 4 (c, e, f, g). The thickness of the alumina layer influenced the size and distribution of the catalyst nanoparticles [32,33]. In the chemical vapor deposition of multiwalled CNTs, iron films undergo morphological restructuring at the high temperature used for the growth, causing the iron film to transform into nanoparticles; this process determines the distribution and size of the catalyst and affects the final CNT diameter because the CNT nucleates on the particle. Moreover, according to previous studies, the size of CNTs formed on iron particles depends on the size of the catalytic particles, i.e., the number of walls and diameter of CNTs