Diamond & Related Materials 86 (2018) 87–97

Contents lists available at ScienceDirect

Diamond & Related Materials

journal homepage: www.elsevier.com/locate/diamond

Multi-walled carbon nanotubes enhanced superhydrophobic MWCNTs-Co/a-C:H carbon-based film for excellent self-cleaning and corrosion resistance

Xiaobo Zhu[a], Shengguo Zhou[a,*], Qingqing Yan[a], Shuncai Wang[b]

[a] School of Materials Science and Engineering, Jiangxi University of Science and Technology, Ganzhou 341000, PR China
[b] National Centre for Advanced Tribology at Southampton (nCATS), School of Engineering Sciences, University of Southampton, SO17 1BJ, UK

ARTICLE INFO

Keywords:
Superhydrophobic
MWCNTs-Co/a-C:H
Corrosion resistance
Self-cleaning

ABSTRACT

A robust superhydrophobic MWCNTs-Co/a-C:H carbon-based film was successfully fabricated for the first time by a safe technology, namely electrochemical deposition. The multi-walled carbon nanotubes (MWCNTs) and Co nano-particles were confirmed to tailor a micro-nanoscale hierarchical surface and nanocrystallite/amorphous microstructure. The resulting MWCNTs-Co/a-C:H carbon-based film exhibited complete water repellency with the contact angle (158.1°) and much smaller sliding angle (2.98°), fairly strong mechanical property, excellent corrosion resistance and self-cleaning ability. This research highlights a promising route for the preparation of robust superhydrophobic film, providing potential uses including self-cleaning, antifouling and anti-corrosion applications such as ship hulls and aeroplane wings.

1. Introduction

Superhydrophobic surfaces with a minimum 150°. contact angle (CA) and a maximum 10°. sliding angle (SA) for water droplets have attracted extensive attention due to their great significance in both fundamental research and potential applications in the fields of oil-water separation [1–4], water collection [5], anti-fogging [6], anti-icing [7], energy conversation [8], self-cleaning [9,10], anti-corrosion [11,12], and friction drag reduction [13], etc. In general, there are two key points to equip surfaces with superhydrophobicity: creating a suitable surface roughness with micro-nanoscale hierarchical structures and low surface energy material modifications, which derived from the phenomenon of superhydrophobicity in nature [14,15]. Therefore, the combination of appropriate surface roughness and materials with low surface energy is a successful way to prepare superhydrophobic surfaces, for instance, advanced materials including carbon nanotubes [16,17], carbon nanofibers [18,19], graphene [20], graphene oxide [21] and so on. Among these nanomaterials, Carbon nanotubes (CNTs) have attracted much attention in fabricating films because of their intrinsic 1-dimensional pore structure and unusual chemical and physical properties, including high surface area, good lubricity, hardness and toughness for superior transport capability [22,23]. Since carbon nanotubes were fist observed by Iijima in 1991, a variety of them have become available, such as single, double, few, and multi-walled carbon nanotubes (MWCNTs) [24,25]. Besides, the MWCNTs are more active than single-walled carbon nanotubes because of it contain a large amount of hydroxyl groups. It was reported that the presence of hydroxyl groups could enhance the superhydrophobic properties [26,27].

Li et al. synthesized a superhydrophobic bionic surface, this bionic surfaces were fabricated by depositing CNTs on PS colloidal crystals by the wet chemical self-assembling technique and the subsequent chemical treatment of the surface with fluoroalkylsilane [16]. Losic et al. prepared 3D graphene-carbon nanotube aerogels via a reaction, which exhibit superior adsorption performance [28]. Mokarian et al. fabricated a superhydrophobic composite comprising multi-walled carbon nanotubes and silicone rubber by etching, the contact angle of de-ionized water droplets on the prepared surface was measured with the larger value [29]. As a result, MWCNTs could be a promising candidate to effectively improve the micro-nanoscale hierarchical structures so as to increase the surface roughness, which should be conducive to the formation of superhydrophobicity. However, most of those methods could include severe conditions, such as expensive materials, strict deposition conditions and complex multi-step processing, and those could limit its practical application immensely. In contrast, electrochemical deposition, having the benefits of facile operation, moderate costs and reproducibility, is a more appropriate technique to produce water-repellent surfaces for engineering applications. At present, our group has obtained a compact superhydrophobic carbon-based film via the incorporation of cobalt by simple one-step high-voltage electrochemical deposition method, and this method presents a simple, efficient and less energy-consuming features. Cobalt has good hardness, strength and wear resistance. The dispersion of cobalt particles into the

* Corresponding author.
E-mail address: zhousg@jxust.edu.cn (S. Zhou).

https://doi.org/10.1016/j.diamond.2018.04.021
Received 21 February 2018; Received in revised form 3 April 2018; Accepted 22 April 2018
Available online 24 April 2018
0925-9635/

amorphous carbon matrix can not only relieve the internal stress of the film, but also effectively prevent the agglomeration and oxidation of the nano-metal particles, and the cobalt particles can form a layered micro-nanostructure on the surface of diamond-like carbon film. Based on previous works, the MWCNTs was used to enhance the super-hydrophobicity of as-fabricated film with much better mechanical properties, self-cleaning and corrosion resistance.

In this study, a novel but simple path for fabricating multi-walled carbon nanotubes enhanced superhydrophobic MWCNTs-Co/a-C:H carbon-based film has been demonstrated via a safe technology, namely one-step electrochemical deposition. This process was adapted to use a MWCNTs/cobalt (II) acetylacetonate methanol solution as electrolyte without using aqueous solution to produce nanocomposite super-hydrophobic films on silicon slice. For all we know, this kind of superhydrophobic ternary MWCNTs-Co/a-C:H carbon-based film with fairly strong mechanical strength and excellent anticorrosion and self-cleaning properties haven't yet been reported. The MWCNTs and cobalt nano-particle inserts in amorphous carbon were effective to tailor the feature of nanocrystallite/amorphous microstructure as well as micro-nanoscale hierarchical surface in favor of superhydrophobicity of MWCNTs-Co/a-C:H film with the contact angle of 158.1°. and sliding angle of 2.98°. without any further chemical modification. This new outstanding robust superhydrophobic MWCNTs-Co/a-C:H carbon-based film with excellent self-cleaning and corrosion resistance could have potential applications in the industry.

2. Experimental procedure

2.1. Materials and reagents

Multi-walled carbon nanotubes (MWCNTs, purity ≥95%) were purchased from Kefu nano-materials Tech Co., Ltd., Nanjing, China, and the average diameter and average length of a MWCNT was 20–30 nm and 10–30 nm, respectively. Analytical pure methanol was provided by Zhenxing chemical plant, Shanghai, China. Cobalt (II) acetylacetonate was supplied by Alfa Aesar, China. All of the above reagents were analytical reagent grades.

2.2. Preparation of electrolyte solution

The MWCNTs with 100 mg were dispersed in 1 L methanol, then sonication was used to facilitate dispersion for 48 h. Secondly, 100 mg cobalt (II) acetylacetonate was dissolved in 500 mL methanol, likewise, sonication was used to facilitate dissolution for 10 min. Finally, the electrolyte solution was consist of 50 mL 0.2 g/L cobalt (II) acetylacetonate/methanol solution, 0.7 mL 0.1 g/L MWCNTs/methanol suspension, and 49.3 mL analytical pure methanol solution.

2.3. Substrate processing

Monocrystalline silicon wafers with dimensions of 0.7 mm × 15 mm × 30 mm was used to as a substrate. All of the Si substrates were cleaned using ultrasonic in methanol for 5 min and then immersed in aqueous solution of 10% HF for 5 min to remove the native oxide layer. Finally, the Si substrates were ultrasonic cleaning with methanol for 5 min again.

2.4. Preparation of MWCNTs-Co/a-C:H film

The MWCNTs/cobalt nanocomposite superhydrophobic film was fabricated successfully on Si substrate via a safe one-step electrochemical deposition under high voltage, atmospheric pressure and low temperature. The dimensions of 0.7 mm × 15 mm × 30 mm Si substrate was employed as the cathode and the same dimensions platinum tablets was employed as the anode, and the distance between two electrodes was 8 mm. In order to ensure the accuracy of the experimental process, this research was strict to control the following conditions: the electrolytic temperature was controlled in the water bath of the constant temperature of 55°; the time of passing the inert gas and the process of deposition were controlled in 8 h; and the voltage was set to 1200 V.

In addition, the preparation method and deposition conditions of the pure diamond-like carbon (DLC) film were consistent with that of MWCNTs/cobalt nanocomposite film, but the electrolyte was only methanol.

2.5. Characterization

The morphology of MWCNTs-Co/a-C:H film was observed by a field emission scanning electron microscope (SEM) (MLA650F, FEI, USA). The scanning probe microscope (SPM) (Veeco Dimension 3100) was used to characterize the surface roughness of as-prepared film. The microstructures of the as-prepared film were further characterized by using high-resolution transmission electron microscope (HRTEM) (FEI Tecnai G2-20). X-ray photoelectron spectroscopy (XPS) was applied to analyze the chemical composition of as-prepared film on an AXIS ULTRA apparatus (Shimadzu-Kratos, Japan). In addition, all water contact angle and sliding angle was measured at ambient temperature using a measuring apparatus. The value of water contact angle was the average measurement of 5 different positions on the same sample surface.

A corrosion monitoring instrument (CHI660E, China) was used to observe the electrochemical corrosion of the film. The saturated potassium chloride (KCl) electrode was used as a reference electrode with a platinum plate as the counter electrode. The as-prepared film was used as the working electrode and the exposed area was controlled at 1 ± 0.1 cm^2. The measurements were performed in 3.5%wt. NaCl solution at ambient temperature.

3. Results

3.1. Surface morphology

The surface morphology of pure DLC film and MWCNTs-Co/a-C:H film were determined by analysis of field emission scanning electron microscopy (SEM). SEM images of the surface of pure DLC film in different magnifications are shown in Fig. 1(a, b). It can be seen that the pure DLC film surface was very smooth, even at high magnification (Fig. 1(b)) can only see the tiny protrusions. This is because methanol was electrolyzed to produce hydrogen gas during electrochemical deposition, hydrogen has a cavitation effect on the surface of the film to form tiny protrusions. SEM images of the surface of MWCNTs-Co/a-C:H film in different magnifications are displayed in Fig. 1 (c-f). As shown in Fig. 1(c), with the incorporation of cobalt and MWCNTs, the surface roughness of MWCNTs-Co/a-C:H film sharply increases. More importantly, cobalt nano-particles and MWCNTs were embedded into the amorphous carbon films. This is more evident at higher magnification (Fig. 1(d)). The MWCNTs grow up through cobalt nano-particles and exhibit a micro-nanoscale hierarchical structure. Further amplification found the morphology of MWCNTs (Fig. 1(e)) and cobalt nano-particles (Fig. 1(f)) are protruding structure. Especially, the structure of cobalt nano-particles was a pine-cone-like hierarchical micro-nanostructure. In general, this hierarchical micro-nanostructure could prompt the film surfaces to obtain a larger contact angle and smaller sliding angle in previous research [30]. Because the hierarchical micro-nanostructure can keeps the air underneath a water droplet on the surface.

Typical data set of SPM images (10 × 10 μm^2) of pure DLC film and MWCNTs-Co/a-C:H film are shown in Fig. 2(a) and (b), respectively. The topography image of pure DLC film shows a surface formed by globular particles with, in average, diameters smaller than 200 nm. Furthermore, the average roughness (Ra) of pure DLC film was 36.6 nm with relatively smooth surface and small grains. Compared to SEM, the