Improvement of Superhydrophobicity of Multi-Walled Carbon Nanotubes Produced by Fluorination

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Abstract

In this work, we synthesized superhydrophobic coatings by chemical surface functionalization of multi-walled carbon nanotubes (MWCNTs). This was accomplished through the radical polymerization of 3-(trimethoxysilyl) propyl methacrylate modified MWCNTs and fluoro acrylate/methyl methacrylate. The chemical compositions and microstructures of the prepared MWCNT surface were investigated using X-ray photoelectron spectroscopy, Fourier transform infrared spectrometry, and scanning electron microscopy, respectively. The wettability of the MWCNTs surface was determined through contact angle assessments in different liquids. The resulting surface exhibited a water contact angle of 157.7°, which is clear evidence of its superhydrophobicity. The 3D MWCNT networks and the low surface energy of the -C-C- and -C-F- groups play important roles in creating the superhydrophobic surface of the MWCNTs.

Key words: superhydrophobicity, multi-walled carbon nanotubes, fluoro acrylate/methyl methacrylate

1. Introduction

Recently, superhydrophobic and conductive materials have attracted attention from researchers due to their importance in fundamental research and potential industrial applications in such areas as electronic devices, transparent films, and structural coatings [1-5]. In particular, hydrophobic and conductive films based on multi-walled carbon nanotubes (MWCNTs) have many potential applications due to their novel properties such as high aspect ratio, small radius of curvature, high mechanical strength, thermal/electrical conductivity, and good chemical stability [6-9]. However, for typical carbon nanotubes, polar substances such as water cannot wet the nanotube surface easily [10]. A large number of MWCNT applications are hampered by the hydrophobic properties of these types of CNTs. It is desirable to be able to modify the hydration properties of the surfaces of carbon nanotubes so that they become hydrophilic. The wettability of MWCNTs is one of the most important ideas in both theoretical research and practical applications [11].

Generally, superhydrophobic surfaces have a water contact angle higher than 150° and a water sliding angle of less than 10° [12]. To date, many researchers have endeavored to fabricate superhydrophobic CNTs using aligned-CNTs [11-14]. Huang et al. [13] reported a stable superhydrophobic surface composed of aligned carbon nanotubes (CNTs). However, the area of the aligned-CNT films could be limited due to the requirements of the specific preparation methods. Most recently, several studies have reported a means of preparing superhydrophobic surfaces on non-aligned CNTs [5-9,14-16]. For example, Zou et al. [6] fabricated a superhydrophobic surface (154°~160°) with conductivity using a conjugated block copolymer.

In this work, superhydrophobic coatings of multi-walled carbon nanotubes (MWCNTs) were produced by the radical polymerization of 3-(trimethoxysilyl) propyl methacrylate modified MWCNTs and fluoro acrylate/ methyl methacrylate.

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Fig. 1. Preparation procedure of fluorinated multi-walled carbon nanotubes.

Table 1. Characteristics of wetting liquids used in the present work

Wetting liquids	γ_L^d (mJ m ⁻²)	γ_L^{sp} (mJ m ⁻²)	γ_L (mJ m ⁻²)	η (MPas)	ρ (gcm ⁻³)
Water	21.8	51	72.8	1	0.998
Diiodomethane	50.42	0.38	50.8	2.76	3.325

γ_L^d : London dispersive component of surface free energy, γ_L^{sp} : specific component of surface free energy, γ_L : total surface free energy, η : viscosity, ρ : density.

2. Material and Methods

2.1. Materials and sample preparation

The MWCNTs (Nano Solution Co.) were treated with HNO₃/H₂SO₄ mixture solutions [17,18]. The oxidized MWCNTs (CNT-H) were modified with 3-(trimethoxysilyl) propyl methacrylate (TPM) in toluene at 383 K for 24 h and were then washed thoroughly with toluene several times. The obtained sample is denoted as CNT-Si. Finally, TPM-modified MWCNTs, fluoromonomer (Zonyl® TM fluoromonomer, average M_n of about 534), methyl methacrylate, and AIBN were placed in a vial and dissolved in tetrahydrofuran (THF). The mixture was degassed under a continuous stream of dry argon. A polymerization reaction was carried out at 70°C for 24 h and this was followed by washing with THF. This sample is denoted as CNT-F (Fig. 1).

2.2. Characterization

X-ray photoelectron spectroscopy (XPS) measurements were done on an ESCALAB220i-XL (VG Scientific, UK) spectrometer with monochromatized Al K α X-ray radiation as the X-ray source for excitation to confirm the surface functional groups of the treated MWCNTs. Fourier transform infrared (FT-IR) spectroscopy on KBr pellets was performed with a Bio-Rad Co. Digilab FTS-165. Corresponding images of the resulting films were obtained by scanning electron microscopy (SEM, HITACHI S4200).

The contact angle (CA) of the film was determined to be $20 \pm 1^\circ$ using the sessile drop method (Phoenix Series Contact Angle Analyzer, Phoenix 150/300). Distilled water and diiodomethane were selected for measurement of the contact angle of the films. For each sample, each calculated contact angle was an average of 10 measurements with a standard deviation below 1° [19]. The surface free energy and other characteristics of the three wetting liquids are listed in Table 1.

3. Results and Discussion

XPS was used to investigate the introduction of elements on the MWCNT surfaces, as shown in Fig. 2. In the figure, the XPS spectrum of the samples shows carbon peaks (285.08 eV), oxygen peaks (532.08 eV), silicon peaks (835.07 eV), and fluorine peaks (690.08 eV). The XPS spectrum of CNTs-H shows oxygen peaks (533.4) that are attributable to an increase in the number of surface oxygen groups (C-O, O=C-O), which are the result of chemical oxidation [17]. The silicon peak (835.07 eV) and the fluorine peak (690.08 eV) are attributable to silanol groups and fluorine groups (-CF-), respectively [20]. This suggests that the fluoromonomer is grafted onto the surfaces of the CNT-Si via chemical modification.

Figs. 3a and b shows schematic diagrams illustrating the changes of the contact angle and the surface properties. As shown in Fig. 3a, the water droplet retains an ellipsoidal shape on the MWCNTs; the droplet has a contact angle of 115.5° , sug-

Fig. 2. Wide-scan X-ray photoelectron spectroscopy spectra of pristine MWCNTs, oxidized MWCNTs (CNT-H), silanol group coated MWCNTs (CNT-Si), and fluorinated MWCNTs (CNT-F). MWCNTs: multi-walled carbon nanotubes.

Fig. 3. Scanning electron microscope image illustrating the changes of water contact angle of multi-walled carbon nanotubes (MWCNTs): (a, c) pristine MWCNTs; (b, d) fluorinated MWCNTs.

gesting that the pristine MWCNTs are hydrophobic [16]. The CA of CNT-F increases to 157.7° after it is polymerized with fluoromonomer because the surface of CNT-Si is grafted with $-CF_2-$ groups (Fig. 3b). This indicates that the wettability of MWCNTs can become superhydrophobic by varying the chemical composition of the MWCNTs [5]. According to Liu et al. [10], the wettability of CNTs is controlled by the surface energy and surface roughness. The surface roughness of the MWCNTs and CNT-F were examined by SEM, with resulting images shown in Figs. 3c and d. The pristine MWCNT films showed an assembled bundle structure (Fig. 3c). After polymerization, the images revealed that the surface roughness of the MWCNTs contained porous MWCNT networks. The porous CNT-F networks became deeper and larger than those of the pristine MWCNTs, leading to the formation of a hierarchical 3D interpenetrating network. The surface roughness allowed air to become trapped between the solid surface and the water droplet, which decreased the contact

Fig. 4. Dispersive (γ_s^L), polar (γ_s^{SP}), and Surface free energy (γ_s) components of pristine multi-walled carbon nanotubes (MWCNTs), oxidized MWCNTs (CNT-H), silanol group coated MWCNTs (CNT-Si), and fluorinated MWCNTs (CNT-F). unit: mJ m^{-2} .

area with water. According to previous research, trapped air is thought to be an important factor that affects the degree of superhydrophobicity [5,14-16]. Therefore, these results show that the hydrophobic surfaces of films are affected by the $-CF_2-$ groups and by the surface roughness.

To obtain more detailed information pertaining to the surface energetics of the CNT-F films, the surface free energy was analyzed based on the method of Fowkes [21]. The total surface free energy can be divided into the London dispersive and specific (or polar) components.

$$\gamma_s = \gamma_s^L + \gamma_s^{SP} \quad (1)$$

where γ_s is the total surface free energy, the subscript S represents a solid state, and γ_s^L and γ_s^{SP} are the London dispersive and specific (Debye, Keesom or van der Waals, H-bonding, π -bonding, and other small polar effects) components of the surface free energy of the constitutive elements. The London dispersive and specific components were determined by measuring the contact angles of two testing liquids with known London dispersive and specific components. The surface free energy of a solid can be determined on the basis of contact angle measurements using the geometric mean, according to Fowkes' proposition [21] based on a solid (subscript S)–liquid (L) droplet–air system, which can be described by the following equation:

$$\gamma_L(1 + \cos\theta) = 2\sqrt{\gamma_L^L \gamma_s^L} + 2\sqrt{\gamma_L^{SP} \gamma_s^{SP}} \quad (2)$$

where θ is the contact angle of a liquid droplet in the solid state. The surface free energy components of the samples are shown in Fig. 4. As reported in our previous work, the specific component, γ_s^{SP} , is highly dependent on the surface functional groups, and the dispersive component, γ_s^L , is largely dependent on the total electron density in the carbon [19].

As shown in Fig. 4, the total surface energy and γ_s^{SP} value of the MWCNTs increase when the MWCNTs are given an acid treatment. This increase arises due to an increase in the number of hydrophilic functional groups ($-OH$, $C=O$, and $O=C-O$) during the acid oxidation process [22]. After grafting fluoromono-

mer onto the CNT-Si surface, a decrease in the surface free energy was observed. Related to the superhydrophobicity, it was reported that the surface free energy decreased in the order $-\text{CH}_2 > -\text{CH}_3 > -\text{CF}_2 > -\text{CF}_3 > -\text{CF}_3\text{H} > -\text{CF}_3$ [10,16]. Therefore, the decrease in the values of both γ_s^f and γ_s^{sp} stems from the substitution of the lower energy -C-F- groups by the grafted -C-F- groups on the MWCNT surfaces [23].

4. Summary

In conclusion, we successfully prepared superhydrophobic films based on fluoromonomer-grafted MWCNTs. The surface of the films exhibited a high contact angle of 157.7° . The 3D MWCNT networks and the low surface energy of the -CF- groups play important roles in creating the superhydrophobic surface of the MWCNT films. The stable superhydrophobic MWCNT films proposed in this study can be used in many industries and can be extended to control the adhesion properties of a wide variety of superhydrophobic functional materials.

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References

- [1] Darmanin T, Guittard F, Amigoni S, Taffin de Givenchy E, Noblin X, Kofman R, Celestini F. Superoleophobic behavior of fluorinated conductive polymer films combining electropolymerization and lithography. *Soft Matter*, **7**, 1053 (2011). <http://dx.doi.org/10.1039/C0SM00837K>.
- [2] Song W, Zhang J, Xie Y, Cong Q, Zhao B. Large-area unmodified superhydrophobic copper substrate can be prepared by an electrodeless replacement deposition. *J Colloid Interface Sci*, **329**, 208 (2009). <http://dx.doi.org/10.1016/j.jcis.2008.09.059>.
- [3] Zhu Y, Zhang JC, Zhai J, Zheng YM, Feng L, Jiang L. Multifunctional carbon nanofibers with conductive, magnetic and superhydrophobic properties. *ChemPhysChem*, **7**, 336 (2006). <http://dx.doi.org/10.1002/cphc.200500407>.
- [4] Li M, Zhai J, Liu H, Song Y, Jiang L, Zhu D. Electrochemical deposition of conductive superhydrophobic zinc oxide thin films. *J Phys Chem B*, **107**, 9954 (2003). <http://dx.doi.org/10.1021/jp035562u>.
- [5] Han JT, Kim SY, Woo JS, Lee GW. Transparent, conductive, and superhydrophobic films from stabilized carbon nanotube/silane sol mixture solution. *Adv Mater*, **20**, 3724 (2008). <http://dx.doi.org/10.1002/adma.200800239>.
- [6] Zou J, Chen H, Chunder A, Yu Y, Huo Q, Zhai L. Preparation of a superhydrophobic and conductive nanocomposite coating from a carbon-nanotube-conjugated block copolymer dispersion. *Adv Mater*, **20**, 3337 (2008). <http://dx.doi.org/10.1002/adma.200703094>.
- [7] Sethi S, Dhinojwala A. Superhydrophobic conductive carbon nanotube coatings for steel. *Langmuir*, **25**, 4311 (2009). <http://dx.doi.org/10.1021/la9001187>.
- [8] Luo C, Zuo X, Wang L, Wang E, Song S, Wang J, Wang J, Fan C, Cao Y. Flexible carbon nanotube-polymer composite films with high conductivity and superhydrophobicity made by solution process. *Nano Lett*, **8**, 4454 (2008). <http://dx.doi.org/10.1021/nl802411d>.
- [9] Tzeng Y, Chen Y, Sathitsuksanoh N, Liu C. Electrochemical behaviors and hydration properties of multi-wall carbon nanotube coated electrodes in water. *Diamond Relat Mater*, **13**, 1281 (2004). <http://dx.doi.org/10.1016/j.diamond.2003.11.048>.
- [10] Liu H, Zhai J, Jiang L. Wetting and anti-wetting on aligned carbon nanotube films. *Soft Matter*, **2**, 811 (2006). <http://dx.doi.org/10.1039/B606654B>.
- [11] Liu H, Feng L, Zhai J, Jiang L, Zhu D. Reversible wettability of a chemical vapor deposition prepared ZnO film between superhydrophobicity and superhydrophilicity. *Langmuir*, **20**, 5659 (2004). <http://dx.doi.org/10.1021/la036280o>.
- [12] Zhu L, Xiu Y, Xu J, Tamirisa PA, Hess DW, Wong C-P. Superhydrophobicity on two-tier rough surfaces fabricated by controlled growth of aligned carbon nanotube arrays coated with fluorocarbon. *Langmuir*, **21**, 11208 (2005). <http://dx.doi.org/10.1021/la051410+>.
- [13] Huang L, Lau SP, Yang HY, Leong ESP, Yu SF, Praver S. Stable superhydrophobic surface via carbon nanotubes coated with a ZnO thin film. *J Phys Chem B*, **109**, 7746 (2005). <http://dx.doi.org/10.1021/jp046549s>.
- [14] Men XH, Zhang ZZ, Song HJ, Wang K, Jiang W. Fabrication of superhydrophobic surfaces with poly(furfuryl alcohol)/multi-walled carbon nanotubes composites. *Appl Surf Sci*, **254**, 2563 (2008). <http://dx.doi.org/10.1016/j.apsusc.2007.08.084>.
- [15] Shakerzadeh M, Teo HE, Tan C, Tay BK. Superhydrophobic carbon nanotube/amorphous carbon nanosphere hybrid film. *Diamond Relat Mater*, **18**, 1235 (2009). <http://dx.doi.org/10.1016/j.diamond.2009.04.010>.
- [16] Meng LY, Park SJ. Effect of fluorination of carbon nanotubes on superhydrophobic properties of fluoro-based films. *J Colloid Interface Sci*, **342**, 559 (2010). <http://dx.doi.org/10.1016/j.jcis.2009.10.022>.
- [17] Ham H, Koo C, Kim S, Choi Y, Chung I. Chemical modification of carbon nanotubes and preparation of polystyrene/carbon nanotubes composites. *Macromolecular Res*, **12**, 384 (2004). <http://dx.doi.org/10.1007/bf03218416>.
- [18] Kim MS, Lim S, Song MY, Cho H, Choi Y, Yu JS. Acid treatments of carbon nanotubes and their application as Pt-Ru/CNT anode catalysts for proton exchange membrane fuel cell. *Carbon Lett*, **11**, 336 (2010).
- [19] Park SJ. In: Hsu JP, ed. *Interfacial Forces and Fields: Theory and Applications*, Marcel Dekker, New York, 385 (1999).
- [20] Jung MJ, Kim JW, Im JS, Park SJ, Lee YS. Nitrogen and hydrogen adsorption of activated carbon fibers modified by fluorination. *J Ind Eng Chem*, **15**, 410 (2009). <http://dx.doi.org/10.1016/j.jiec.2008.11.001>.
- [21] Fowkes FM. Attractive forces at interfaces. *Ind Eng Chem*, **56**, 40 (1964). <http://dx.doi.org/10.1021/ie50660a008>.
- [22] Nuriel S, Liu L, Barber AH, Wagner HD. Direct measurement of multiwall nanotube surface tension. *Chem Phys Lett*, **404**, 263 (2005). <http://dx.doi.org/10.1016/j.cplett.2005.01.072>.
- [23] Hsieh CT, Chen WY, Wu FL, Hung WM. Superhydrophobicity of a three-tier roughened texture of microscale carbon fabrics decorated with silica spheres and carbon nanotubes. *Diamond Relat Mater*, **19**, 26 (2010). <http://dx.doi.org/10.1016/j.diamond.2009.10.017>.