

C.Y. CHOI^{1,2}
Z. ZHENG³
K.W. WONG^{1,2,✉}
Z.L. DU⁴
W.M. LAU⁵
R.X. DU¹

Fabrication of cross-linked multi-walled carbon nanotube coatings with improved adhesion and intrinsic strength by a two-step synthesis: electrochemical deposition and hyperthermal proton bombardment

¹ Institute of Precision Engineering, the Chinese University of Hong Kong, Shatin, Hong Kong

² Department of Physics, the Chinese University of Hong Kong, Shatin, Hong Kong

³ Institute of Surface Micro and Nano Materials, Xuchang University, Xuchang, Henan Province 461000, P.R. China

⁴ Laboratory for Special Functional Materials, Henan University, Kaifeng 475001, P.R. China

⁵ Surface Science Western, University of Western Ontario, London, Ontario N6A 5B7, Canada

Received: 5 July 2007/Accepted: 19 February 2008
Published online: 28 March 2008 • © Springer-Verlag 2008

ABSTRACT A two-step synthesis for multi-walled carbon nanotube (MWCNT) coating was reported that includes an electrochemical deposition followed by 10 eV hyperthermal proton bombardment at a dose as low as $1 \times 10^{16} \text{ H}^+/\text{cm}^2$. Electrochemical deposition ensures an improved adhesion of MWCNT coating on metal substrates, while hyperthermal proton bombardment effectively induces inter-chain cross-linkages among MWCNTs, leading to a coating with both higher stiffness and mechanical strength. It was found experimentally that the MWCNT film made by the proposed two-step synthesis can better resist spinning and ultrasonic rinsing in both organic (hexane) and aqueous (water) media.

PACS 61.46.+w; 68.35.Np; 68.37.Ps; 81.15.Pq

that can prepare thick CNT films while foreign materials like binders and additives will be co-deposited. Recently, electrophoretic depositions (EPD) were employed to make CNT coatings for field emission purposes [12]. However, the adhesion between CNT coating and substrate is poor due to the minimal chemical interaction between CNTs and substrate. Along with the rapid development of lab-on-a-chip and microfluidics, uses of CNT-based microfluidic devices are always subjected to a strong challenge of stability towards flow stress. Only a strongly adhered CNT coating can ensure the full exploitation of CNTs for specific purposes in these areas. In this communication, we report the development of CNT coating by a two-step synthesis including an electrochemical deposition with a subsequent hyperthermal proton bombardment (HPB). The synthesis ensures formation of highly cross-linked multi-walled CNT (MWCNT) coatings strongly adhered onto metal substrates.

1 Introduction

In [1], Iijima observed multi-walled carbon nanotubes (MWCNTs) for the first time. Later on, in [2], Iijima and Ichihashi observed for the first time single-walled carbon nanotubes (SWCNTs). The first large-scale production was reported by Thess et al. in 1996 [3], in a paper published in *Science*. Although carbon nanotube (CNT) is shown to be an extraordinary material possessing unique properties for potential uses in many different areas [4–7], successful applications depend on the ways that CNTs are arranged, assembled, and combined with other molecular and chemical entities [8]. In particular, a strongly adhered CNT coating is essential for many realistic applications. Numerous coating techniques have been applied. Inherent coatings can be prepared by growing CNT directly onto substrates with metal catalysts using CVD methods [9]. However, high temperature (700 to $> 1000^\circ\text{C}$) is always involved and this greatly limits the choice of substrates. Printing and thermal spraying are two commonly used ex-situ deposition methods [10, 11]

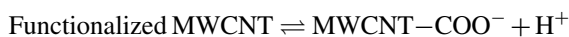
2 Experimental

For electrochemical deposition, iron substrates to be coated with MWCNTs were attached at the anode, while a graphite rod acted as a cathode. A silver/silver nitrate (Ag/AgNO_3) electrode was used as a reference electrode. MWCNTs with a nominal diameter of 10–20 nm and length of 1–2 μm (Shenzhen Nanotech Port Co. Ltd.) were used. They were functionalized intentionally by a H_2SO_4 and HNO_3 mixture (v/v 3 : 1) for at least 24 h to give MWCNTs with surface carboxylic acid groups ($-\text{COOH}$) [13]. Functionalized MWCNTs were rinsed with de-ionized (DI) water and methanol several times, and finally re-suspended into propylene carbonate. The extent of functionalization was determined by thermal gravimetric analysis (TGA) as in other work [14]. The concentration of functionalized MWCNTs was kept at 0.15 mg/ml and the pH was slightly less than 7. All electrochemical depositions were performed using a Gamry 3100 potentiostat with a voltage resolution of 0.01 mV and current sensitivity limit of 1 nA. Surfactant was added to further improve the dispersity of MWCNTs. The electrical field applied was always kept below 2 V cm^{-1} . After

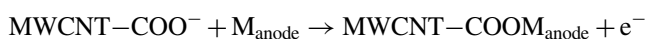
✉ Fax: +852-2603-5204, E-mail: kw Wong@cuhk.edu.hk

deposition, samples were all dried at 70 °C. All depositions performed were confirmed to be dominantly electrochemical in nature based on two observations. First, a high electro-current from several to several 10 μA could be observed at a low field of 0.33 V/cm to 2 V/cm, implying that there were vigorous electrochemical reactions occurring during deposition. It should be noted that for electrophoretic deposition, the electro-current is hardly detectable at a field as high as 10–20 V/cm [15]. Second, for higher concentration of functionalized MWCNTs, substantial amount of hydrogen evolved at the cathode and no gas evolution was found at the anode. Instead, the MWCNT coating was found to be growing at an increased deposition rate and as such, the following electrochemical half reactions were proposed:

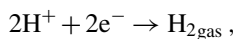
In electrolyte:



At anode:



At cathode:



where M_{anode} denotes the metal substrate at anode and should be Fe in the present study.

The electrochemically deposited MWCNT coating was then treated by HPB with a mass-resolved low-energy ion beam system [16]. Our previous works showed that HPB is capable of cross-linking adsorbed hydrocarbon, short-chain polymeric molecules, and even conducting polymers [17–20]. The same technique was applied to the electrochemically deposited MWCNT coatings to introduce substantial cross-linkages among MWCNTs in an attempt to increase the intrinsic mechanical strength of the coatings. Direct confirmation of these cross-linkages formed among the current MWCNT coating is quite difficult. The use of secondary ion mass spectroscopy (SIMS) as described by Zheng et al. [17] to compare the ratio of branched hydrocarbon to the original graphene fragments within MWCNTs before and after HPB may partly reveal the extent of cross-linking. A more systematic and detailed study is required for this, which is beyond the scope of the current work. Figure 1a shows the scanning electron micrograph of a typical electrochemically deposited MWCNTs coating after HPB, while Fig. 1b shows a large view of the same MWCNTs coating. Evidently, the tubular structure of MWCNTs remains intact after bombardment.

3 Results and discussion

The electrochemically deposited MWCNT coatings after (EC-CNT-A) and before HPB (EC-CNT-B) were firstly analyzed by a fluid flow test. For comparison, MWCNT coatings prepared by common EPD technique (EPD-CNT) were also fabricated and studied. They were prepared by immersing bare MWCNTs into the same acid mixture for a much shorter time. The acid treated MWCNTs were then deposited onto substrates under a high electric field (20 V/cm). In the

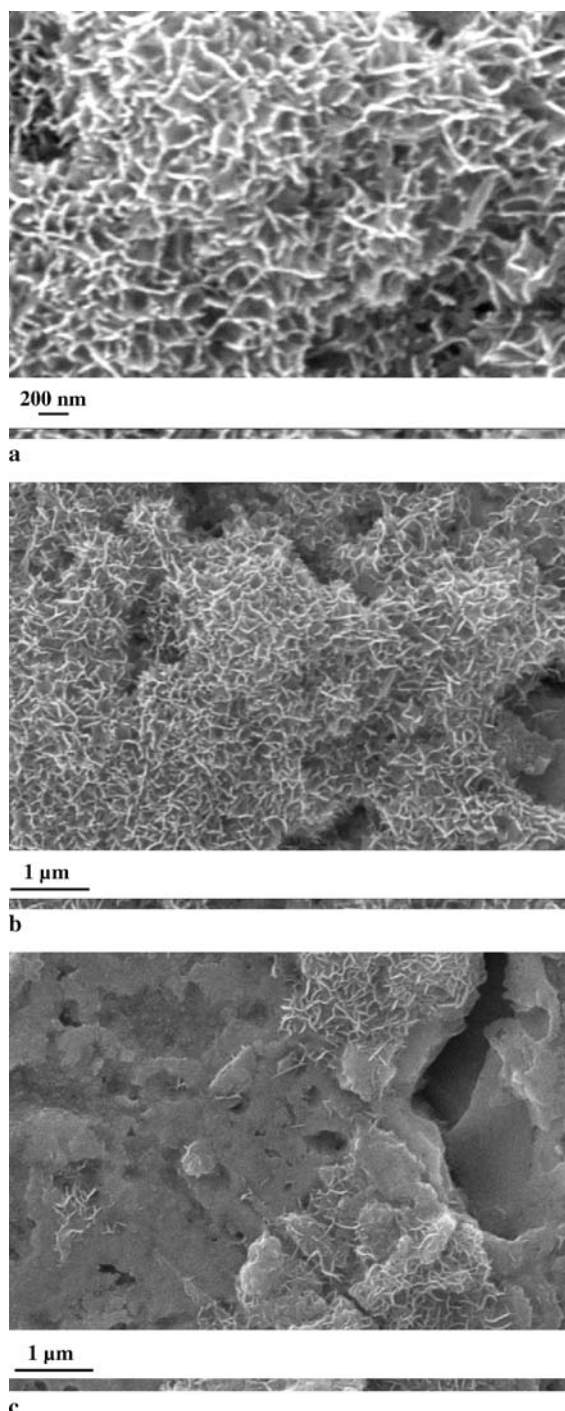


FIGURE 1 Scanning electron micrographs of (a) electrochemically deposited MWCNT film with HPB (EC-CNT-A) after water rinsing for 15 min, (b) a wider view of the same sample in (a), and (c) electrochemically deposited MWCNT film without HPB (EC-CNT-B) after water rinsing for 15 min

fluid flow test, samples were rinsed with spinning in hexane for 5 min at 120 rpm, then in deionized (DI) water for another 5 min at the same spinning rate. This fluid flow test simulates a fluid flowing environment to the coating. The thicknesses of coatings before and after rinsing were measured using a profilometer with a load of 24 mg. Table 1 summarizes the test results. As the coating on EPD-CNT could not adhere tightly onto the substrate, it was easily scratched away by the

Sample	Hexane rinsing			Water rinsing		
	Before	After	% change	Before	After	% change
ECD-CNT-A	3.0 μm	3.0 μm	No change	3.6 μm	1.8 μm	-33%
ECD-CNT-B	3.6 μm	3.6 μm	No change	3.6 μm	all removed	-100%
EPD-CNT	Thickness cannot be measured as the adhesion of the coating is too weak. It was scratched away by the probe tip of the profilometer during measurement					

TABLE 1 Summary of change in thickness of MWCNT coatings in the fluid flow test

probe tip of the profilometer. For EC-CNT-B, the adhesion of coating was much stronger through the chemical anchorage between the $-\text{COOH}$ on MWCNTs and the metal substrate due to the above-mentioned electrochemical reactions. This coating can resist hexane spinning. However, it was removed by spinning in DI water. It is because the chemical anchorage is basically $-\text{COO-Fe-}$, which is readily soluble in water [21]. However, after bombardment by hyperthermal protons at 10 eV of a dose of $1 \times 10^{16} \text{ H}^+/\text{cm}^2$ (EC-CNT-A), $\sim 70\%$ of the MWCNT coating remained intact even after water rinsing. It has been shown that HPB (10 eV) on a sample system that contains H atoms can efficiently transfer energy to the H atoms and increase their reactivity [17]. As such, chemical bonds involving H atoms will be easily broken, leaving reactive radicals for cross-linkage formation. In our case, the $-\text{O-H}$ bonds of the $-\text{COOH}$ functional groups on the surface functionalized MWCNTs can therefore be effectively attacked by the 10 eV protons. It leads to formation of reactive radicals for adjacent bond formation. On the other hand, as the π -bonds of the $\text{C}=\text{C}$ double bonds on the graphene plane of MWCNT are relatively weak ($\sim 2.8 \text{ eV}$), they can also be easily broken by 10 eV HPB, leaving carbon radicals which can move along the graphene plane. In this case, when a carbon radical meets another within the same graphene plane, $\text{C}=\text{C}$ double bond is recovered. However, when it meets another radical on an adjacent MWCNT, C-C cross-linkage will be formed and this links the two MWCNTs together. As such, a massive cross-linked MWCNT film that resists spinning in both hexane and water is formed. Formation of intertube cross-linkages observed here is consistent with the theoretical study of Åström et al. who found that ion irradiation can induce intertube covalent bonding [22]. In our case, protons were preferred to atomic hydrogen here because protons are proved to have more effective interactions with planar structures like MWCNTs as stated by Ruffieux et al. [23]. Although high energy ion and electron irradiation have also been demonstrated to create intertube bridging among SWCNTs [24, 25], the present study shows that use of low dose HPB ($\sim 10 \text{ eV}$ at $10^{16} \text{ H}^+/\text{cm}^2$) is already capable of creating covalent linkages between MWCNTs and this technique can better avoid amorphization of MWCNTs that can be easily induced by energetic electron and heavy ion irradiations. Furthermore, it is expected that under such a mild bombarding condition (low dose, low energy and low mass), cross-linkages are limited to the outmost shells of MWCNTs. As the inner tubes should remain intact, the basic properties of MWCNT can be preserved.

To further investigate the adhesion characteristics of the MWCNT coatings, they were immersed in an ultrasonic bath of DI water for a solubility test. The coatings were checked at regular time intervals until all MWCNTs were removed. It was observed that EPD-CNT coating was easily removed by

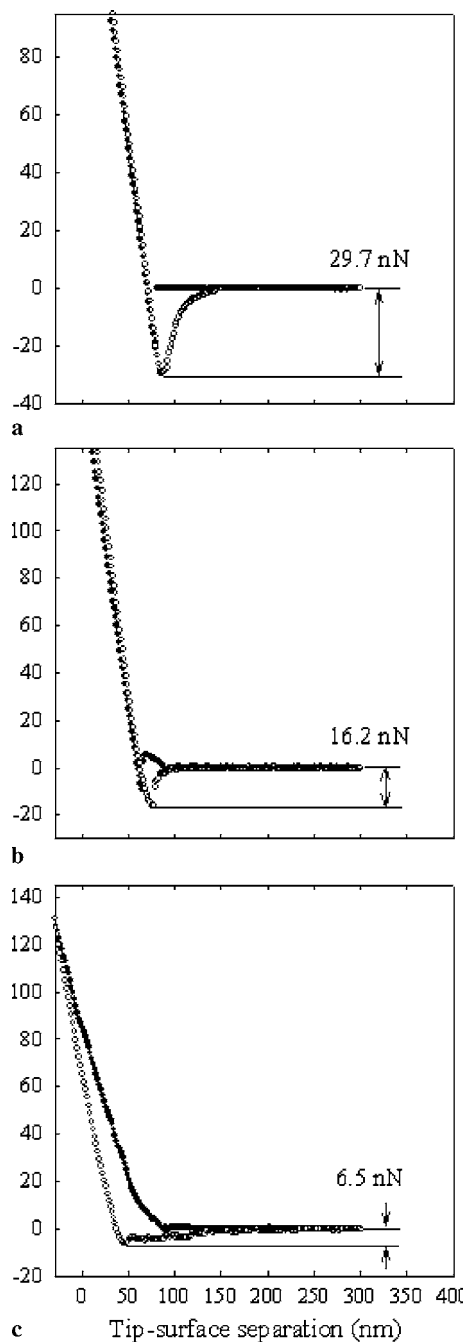


FIGURE 2 Force curves on (a) Fe substrate, (b) electrochemically deposited MWCNT film before HPB (EC-CNT-B) and (c) electrochemically deposited MWCNT film after HPB (EC-CNT-A). (Solid dots denote the approaching curve; open dots denote the retracting curve)

a 2-min ultra-sonication in DI water. While for EC-CNT-B and EC-CNT-A, it took 15 min and more than 25 min for all coatings to be removed. Figure 1b and c show the scanning

Sonication time	Results
EC-CNT-A: > 25 min	A thin MWCNT coating still remained on the surface.
EC-CNT-B: 15 min	MWCNT coating was completely removed.
EPD-CNT: 2 min	MWCNT coating was completely removed.

TABLE 2 Results of solubility test using water ultra-sonication

electron micrographs of EC-CNT-A and EC-CNT-B after 15 min of water rinsing. It is evident that most of the MWCNTs remained on EC-CNT-A, while only a minute amount of MWCNTs were left on EC-CNT-B after rinsing with water. These results imply that a much-improved film adhesion can be achieved for the MWCNT coating prepared by electrochemical deposition, and further improvement can be made by HPB. As discussed, the improved adhesive strength and intrinsic strength exhibited by EC-CNT-B and EC-CNT-A should be attributed to the chemical anchorages formed during electrochemical deposition and the cross-linkages induced during HPB. MWCNT coatings were also analyzed by local force spectroscopy using atomic force microscopy. Figure 2a–c shows the corresponding force curves on Fe substrate, EC-CNT-B and EC-CNT-A. EPD-CNT coating was excluded because the EPD-CNT coating was scratched away by the AFM cantilever. Evidently, the adhesive force (curve minimum) decreases from that on bare Fe surface at 29.7 nN, to that on EC-CNT-B at 16.2 nN, and finally to 6.5 nN on EC-CNT-A. The decrease in adhesive force is up to 78% from that of bare Fe surface to EC-CNT-A surface. Carbon-derived materials are well known to be good solid lubricants due to their low coefficients of friction (COFs) [26]. It is, therefore, not surprising that EC-CNT-B displays a much lower adhesive force than Fe surface. Here, EC-CNT-A shows an even lower adhesion force. It is proposed that as the MWCNTs were effectively cross-linked by HPB, the tougher cross-linked film can better resist the penetration of cantilever. As a result, the interaction between cantilever and MWCNTs was kept at minimal, leading to a lower adhesion force.

4 Summary and conclusion

In summary, cross-linked MWCNT coatings with improved adhesion and intrinsic strength were fabricated using a two-step synthesis. An electrochemical deposition is used to improve the adhesion of coating. Then, HPB is employed to induce cross-linkages among MWCNTs, leading to a coating of higher stiffness and mechanical strength. As HPB can be practically scaled up by employing an electron cyclotron resonance microwave plasma to generate hyperther-

mal protons with a high flux over a large area, this treatment bears a technology impact in CNT-based device production. In addition, the coating with such improvement in adhesion and intrinsic strength should be able to sustain the flow stress encountered in most microfluidic cells and biological sensing lab-on-a-chips.

ACKNOWLEDGEMENTS This work was supported by the Institute of Precision Engineering of the Chinese University of Hong Kong, Department of Physics of the Chinese University of Hong Kong, the RGC Direct Grant (CUHK No. 2060280), the National Natural Science Foundation of China (Grant No. 20574058), and the Program for Science & Technology Innovation Talents in Universities of Henan Province (HASTIT-16, 2008).

REFERENCES

- 1 S. Iijima, *Nature (London)* **354**, 56 (1991)
- 2 S. Iijima, T. Ichihashi, *Nature (London)* **363**, 603 (1993)
- 3 A. Thess, R. Lee, P. Nikolaev, H. Dai, P. Petit, J. Robert, C. Xu, Y.H. Lee, S.G. Kim, A.G. Rinzler, D.T. Colbert, G.E. Scuseria, D. Tomanek, J.E. Fischer, R.E. Smalley, *Science* **273**, 483 (1996)
- 4 M.F. Yu, *Phys. Rev. Lett.* **84**, 5552 (2000)
- 5 R. Saito, M.S. Dresselhaus, G. Dresselhaus, *Physical Properties of Carbon Nanotubes* (Imperial College Press, London, 1998)
- 6 S.J. Tans, M.H. Devoret, H. Dai, A. Thess, R.E. Smalley, L.J. Geerligs, C. Dekker, *Nature (London)* **386**, 474 (1997)
- 7 T.W. Odom, J.L. Huang, P. Kim, C.M. Lieber, *Nature (London)* **391**, 62 (1998)
- 8 O. Zhou, H. Shimoda, B. Gao, S. Oh, L. Fleming, G.Z. Yue, *Acc. Chem. Res.* **35**, 1045 (2002)
- 9 H.M. Cheng, F. Li, G. Su, H.Y. Pan, L.L. He, X. Sun, M.S. Dresselhaus, *Appl. Phys. Lett.* **72**, 3282 (1998)
- 10 Y. Zhou, L. Hu, G. Grüner, *Appl. Phys. Lett.* **88**, 123 109 (2006)
- 11 C. Bower, O. Zhou, W. Zhu, A.G. Ramirez, G.P. Kochanski, S. Jin, *Mater. Res. Soc. Symp. Proc.* **593**, 215 (2000)
- 12 B. Gao, G.Z. Yue, Q. Qiu, Y. Cheng, H. Shimoda, L. Fleming, O. Zhou, *Adv. Mater.* **13**, 1770 (2001)
- 13 S. Banerjee, T. Hemraj-Benny, S.S. Wong, *Adv. Mater.* **17**, 17 (2005)
- 14 Y.J. Qin, J.H. Shi, W. Wu, X.L. Li, Z.X. Guo, D.B. Zhu, *J. Phys. Chem.* **107**, 12 899 (2003)
- 15 Y. Abe, R. Tomuro, M. Sano, *Adv. Mater.* **17**, 2192 (2005)
- 16 W.M. Lau, X. Feng, I. Bello, S. Sant, K.K. Foo, R.P.W. Lawson, *Nucl. Instrum. Methods Phys. Res. B* **59/60**, 316 (1992)
- 17 Z. Zheng, X.D. Xu, X.L. Fan, W.M. Lau, R.W.M. Kwok, *J. Am. Chem. Soc.* **126**, 12 336 (2004)
- 18 Z. Zheng, K.W. Wong, W.C. Lau, R.W.M. Kwok, W.M. Lau, *Chem. Eur. J.* **13**, 3187 (2007)
- 19 Z. Zheng, W.M. Kwok, W.M. Lau, *Chem. Commun.* **29**, 3122 (2006)
- 20 W.M. Lau, Y.H. Wang, Y. Luo, Z. Zheng, K.W. Wong, K.Y. Wong, *Can. J. Chem.* **85**, 857 (2007)
- 21 D.R. Lide, *CRC Handbook of Chemistry and Physics*, 80th edn. (CRC, Florida, 2000)
- 22 J.A. Åström, A.V. Krasheninnikov, K. Nordlund, *Phys. Rev. Lett.* **93**, 215 503 (2004)
- 23 P. Ruffieux, O. Gröning, M. Biemann, P. Gröning, *Appl. Phys. A* **78**, 975 (2004)
- 24 A. Kis, G. Csányi, J.-P. Salvetat, T.-N. Lee, E. Couteau, A.J. Kulik, W. Benoit, J. Brugger, L. Forro, *Nature Mater.* **3**, 153 (2004)
- 25 H. Stahl, J. Appenzeller, R. Martel, P. Avouris, B. Lengeler, *Phys. Rev. Lett.* **84**, 5186 (2000)
- 26 K. Miyoshi, K.W. Street Jr., R.L. Vander Wal, R. Andrews, A. Sayir, *Tribol. Lett.* **19**, 191 (2005)