

Facile Fabrication of Robust Superhydrophobic Epoxy Film with Polyamine Dispersed Carbon Nanotubes

Chao-Po Hsu,[†] Ling-Yu Chang,[†] Chih-Wei Chiu,[‡] Patricia T. C. Lee,[†] and Jiang-Jen Lin^{*,†}

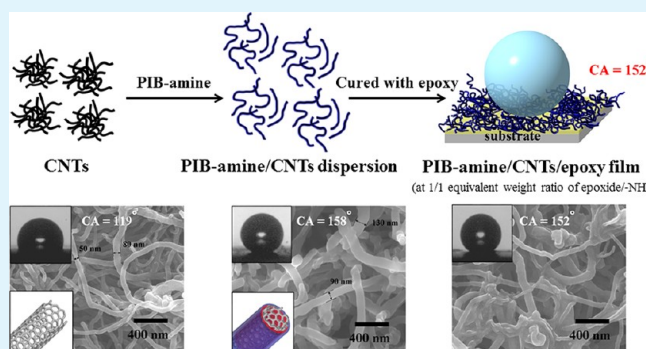
[†]Institute of Polymer Science and Engineering, National Taiwan University, Taipei 10617, Taiwan

[‡]Department of Materials Science and Engineering, National Taiwan University of Science and Technology, Taipei 10607, Taiwan

Supporting Information

ABSTRACT: Nanocomposite films of superhydrophobic surface are fabricated from the dispersion of unmodified carbon nanotubes (CNTs) and hydrophobic poly(isobutylene)–amine (PIB–amine). The PIB–amine prepared from the amidation of poly(isobutylene)-succinic anhydride and poly(oxypropylene)–amines is essential for dispersing the originally entangled CNTs into the debundled CNTs as observed by TEM. A robust CNTs/epoxy nanocomposite film with high dimensional stability is made by subsequent curing with epoxy resin. The self-standing film exhibits a superhydrophobic property, with water droplet contact angle $> 152^\circ$ due to the CNTs controlled alignment on the surface forming micrometer-size plateaus, as observed by SEM. The preparation of PIB–amine/CNTs dispersion and subsequently curing into a superhydrophobic CNTs/epoxy film is relatively simple and can potentially be applied to large surface coating.

KEYWORDS: superhydrophobic surface, carbon nanotubes, epoxy, poly(isobutylene)–amine



1. INTRODUCTION

A superhydrophobic surface with water repellent and stain free properties exists on the leaves of many plants.¹ The criteria for a superhydrophobic surface is having a water contact angle higher than 150° . Many efforts to create such a film surface have been made because of the potentials for industrial applications.² Various surface properties, for instance, snow sticking, contamination, oxidation, and electric current conduction, can be controlled by technique mimicking nature.³ The unusual wetting characteristics of a superhydrophobic surface are governed by both chemical composition and geometric microstructure of the surface.⁴ Creating local geometric roughness and tailoring its size distribution are the most important issues besides the introduction of a hydrophobic component on the material surface. The superhydrophobic surfaces can be generated by two approaches,⁵ nanomaterial self-assembling into suitable domain size and modifying an existing rough surface to reduce its surface free energy. The top-down approach encompasses the lithographic and template-based techniques,⁶ CNTs/polymer composite coatings,^{7–9} and plasma treatment of surface.¹⁰ The bottom-up technique involves mostly the unit self-assembly such as chemical bath deposition (CBD),¹¹ chemical vapor deposition (CVD),¹² and layer-by-layer deposition via electrochemical,¹³ colloidal,¹⁴ sol–gel,¹⁵ and chemical syntheses.¹⁶ However, these fabrication methods generally involve

tedious procedures, and some are energy intensive for large surface applications.

Nanomaterials, such as clay^{17,18} and CNTs,^{19,20} are utilized as a rough template for tailoring surface roughness. However, dispersing the inherently agglomerated CNTs into debundled units^{21,22} is still a challenging task and more so for the self-assembly of dispersed CNTs in the bottom-up procedure. The CNTs solvation in organic mediums is generally unsatisfactory at high concentration due to its lengthy tubular shape that tends to entangle and aggregate into lumps. Covalent bonding methods including surface oxidation into functional derivatives^{23,24} and noncovalent interaction by polymer wrapping have been well-documented.^{25,26} Noncovalent methods are preferred because of the nondestruction of CNT structure and integrity.

In this paper, we report the use of an amphiphilic polyamine to enable the dispersion of unmodified CNTs and subsequent curing with epoxy to form superhydrophobic films. The polyamine was prepared from the amidation of the available poly(isobutylene)–succinic anhydride (PIB-SA) which is the main constituent for the surface hydrophobicity.^{27,28} The CNTs wrapped by the polar tethering functionalities of the polyamine with hydrophobic PIB alkyls tend to generate a

Received: June 21, 2012

Accepted: January 21, 2013

Published: January 21, 2013

Scheme 1. Synthesis of PIB–Amine Dispersant from Amidation of PIB-SA with T403 Tri-Amine

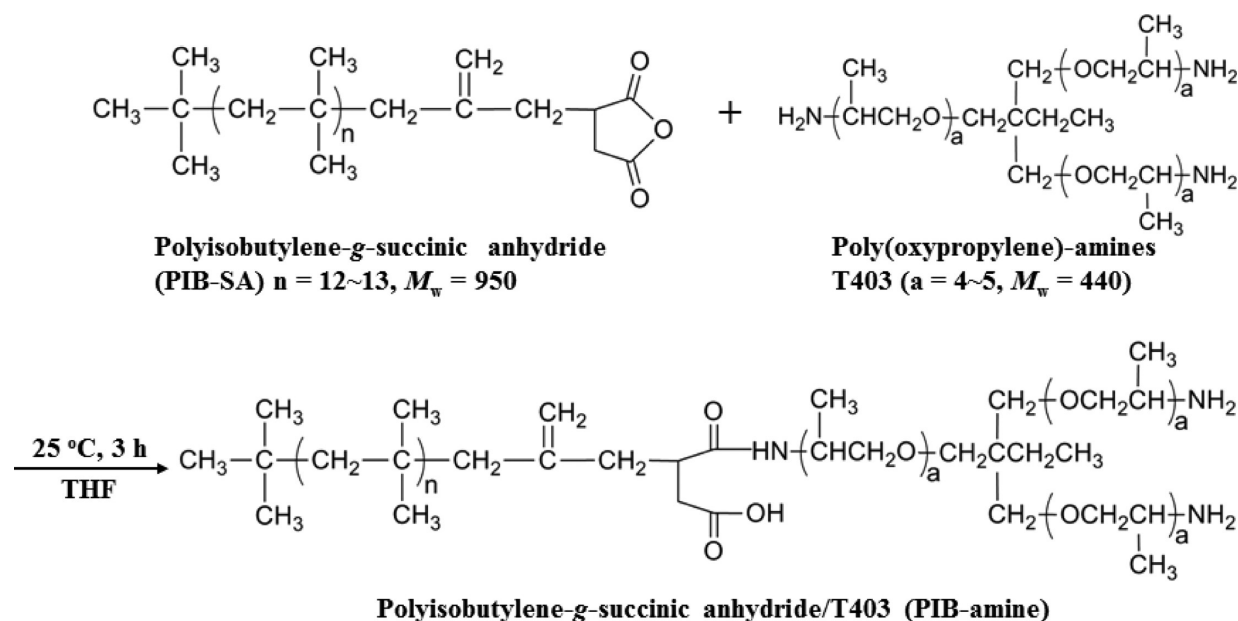


Table 1. Water-Droplet Contact Angles and Physical Properties of the Films with and without CNTs Films

| | weight fraction (w/w) | contact angle ($\pm 1^\circ$) | contact angle hysteresis ($\pm 1^\circ$) ^a | sheet resistance (Ω/sq) ^b | hardness ^c | temperature ($^\circ\text{C}$) ^d | | |
|-----------------------------------|-----------------------|---------------------------------|---|--|-----------------------|---|-------------------|-------------------|
| | | | | | | 75 wt % retention | 50 wt % retention | 25 wt % retention |
| PIB-amine/CNTs | 1/4 | 152° | | 55 | <2 B | | | |
| | 1/2 | 158° | 7.3° | 78 | <2 B | 352 | 396 | 422 |
| | 2/1 | 144° | | 87 | <2 B | | | |
| | 4/1 | 118° | | 241 | <2 B | | | |
| PIB-amine | 1/0 | 109° | 7.3° | | <2 B | 308 | 366 | 401 |
| pristine CNTs | 0/1 | 119° | 1.2° | 17 | <2 B | 681 | 710 | 734 |
| PIB-amine/epoxy ^e | | 100° | 7.2° | | 2 H | 348 | 380 | 406 |
| PIB-amine/CNTs epoxy ^e | | 152° | 7.2° | | 3 H | 347 | 381 | 410 |

^aInclined angle = 20°. ^bMeasured by using a four-point probe for electric surface resistance. ^cPencil hardness. ^dMeasured by TGA from 100 to 800 °C heating profile at 10 °C/min in N₂. ^e1:1 equivalent ratio of epoxide/NH.

controlled size and shape of roughness.^{29,30} The presence of PIB alkyls is essential for providing a steric hindrance when dispersing CNTs in solvent and forming ultimate hydrophobic surface after curing with epoxy resin. Therefore, the superhydrophobicity of the films relied on the combination of roughness and chemical composition which were provided by CNTs aggregation and hydrophobic PIB copolymer. The formation of a large and facile process is unprecedented for not involving the functionalized CNTs or fluorinated alkyl hydrophobes.

2. EXPERIMENTAL SECTION

2.1. Materials. Carbon nanotubes (CNTs) were supplied by Seedchem Company Pty., Ltd., and prepared from chemical vapor deposition. The CNTs are 95% pure and contain 5% catalyst (Fe, Co, and Ni). The dimension of CNTs is 40–60 nm in diameter and 0.5–10 μm in length. Polyisobutylene-g-succinic anhydride (PIB-SA) with molecular weight (M_w) of 950 was obtained from Chevron Corp. Poly(oxypropylene)-amines (POP-amines), triamines of $M_w = 440$ (abbreviated as T403), were purchased from Huntsman Chemical Co. Diglycidyl ether of bisphenol A (DGEBA, trade name as BE-188) with an epoxy equivalent weight (EEW) of 188 was obtained from Chang Chun Chemical Co., Taiwan.

2.2. Synthesis of PIB–Amine Copolymer. Synthesis of PIB-amine copolymer is described as follows: to a three-necked and round-bottomed flask, equipped with a mechanical stirrer, T403 (0.44 g, 1 mmol) was charged, followed by the dropwise addition of PIB-SA (0.95 g, 1 mmol) in THF (50 mL). Under constant stirring, the mixture was maintained at 25 °C for 3 h. The product of NH₂/MA at 3:1 molar ratio was prepared and abbreviated as PIB-amine. The PIB-amine copolymer was analyzed by Fourier transform infrared (FT-IR) spectra. The characteristic absorptions at 1552 cm^{-1} and 1647 cm^{-1} were obtained for amidoacid functionalities. The molecular weight was measured by using gel permeation chromatography (GPC) and showed the average molecular weight of 3338 M_w , and polydispersity of 1.40.

2.3. CNTs Dispersion by PIB–Amine Copolymer and Epoxy Cured Films. An example of CNTs dispersion by copolymer is described below; CNTs (0.1 g) were dispersed in THF (10 g) with PIB-amine copolymer (0.05 g, 0.036 mmol) as dispersant, under an ultrasonic vibrator (LEO-1502) that was operated at 150 W and 40 kHz for CNTs dispersion. After ultrasonic vibration, the PIB-amine/CNTs was prepared by drop-casting PIB-amine/CNTs solution on glass substrate (20 × 70 mm) and then drying in a vacuum oven at 80 °C for 1 h. Another example of preparing PIB-amine/CNTs epoxy film is described below; the PIB-amine/CNTs (0.1 g/0.05 g) in THF solution were dispersed in DGEBA (0.025 g,

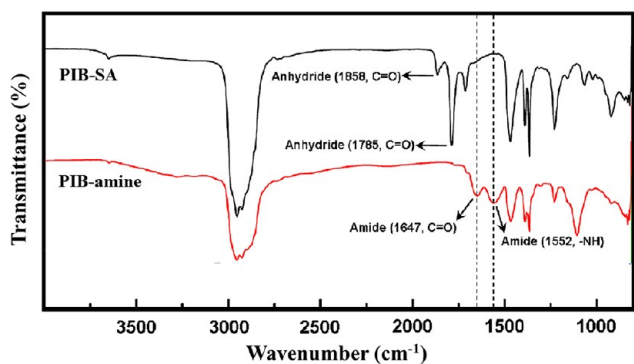


Figure 1. FT-IR spectrum of PIB-amine copolymer.

0.071 mmol), at a 1/1 equivalent weight ratio of epoxide/N-H. The mixtures were drop-cast on glass substrate and programmed at 80, 120, and 150 °C each for 1 h.

2.4. Characterization and Instruments. Fourier transform infrared spectroscopy (FT-IR) was recorded on a Perkin-Elmer Spectrum One FT-IR Spectrometer in the range of 4000–400 cm^{-1} . Samples were prepared by dissolving in THF and evaporating into a thin film on a KBr plate. Transmission electron microscopy (TEM) was performed on a Zeiss EM 902A, operated at 120 kV. The dispersions of copolymer/CNTs in THF at 0.001 wt % was dropped onto a carbon-coated copper grid and dried at ambient temperature. Scanning electronic microscopy (SEM) was performed on a Zeiss EM 902A, operated at 80 kV. The samples were prepared by dropping a small amount of the PIB-amine/CNTs dispersions on a clean glass surface, followed by a dehydration oven step at 60 °C for 2 h. The samples were then fixed on a SEM holder

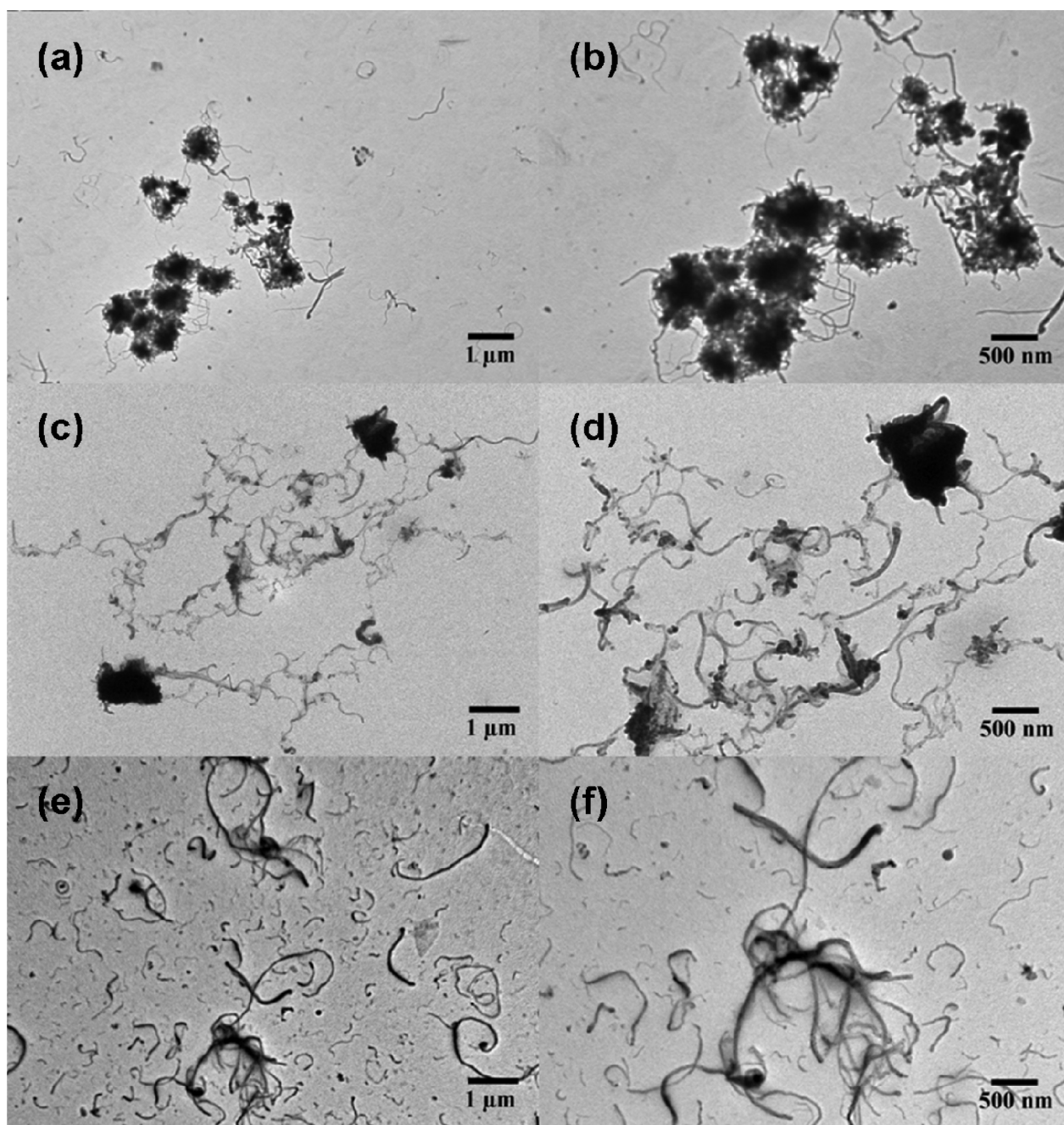


Figure 2. TEM micrographs of CNTs aggregation or fine dispersion (a and b) pristine CNTs, (c and d) PIB-SA/CNTs at 1:1 weight ratio, and (e and f) PIB-amine/CNTs at 1:1 weight ratio.

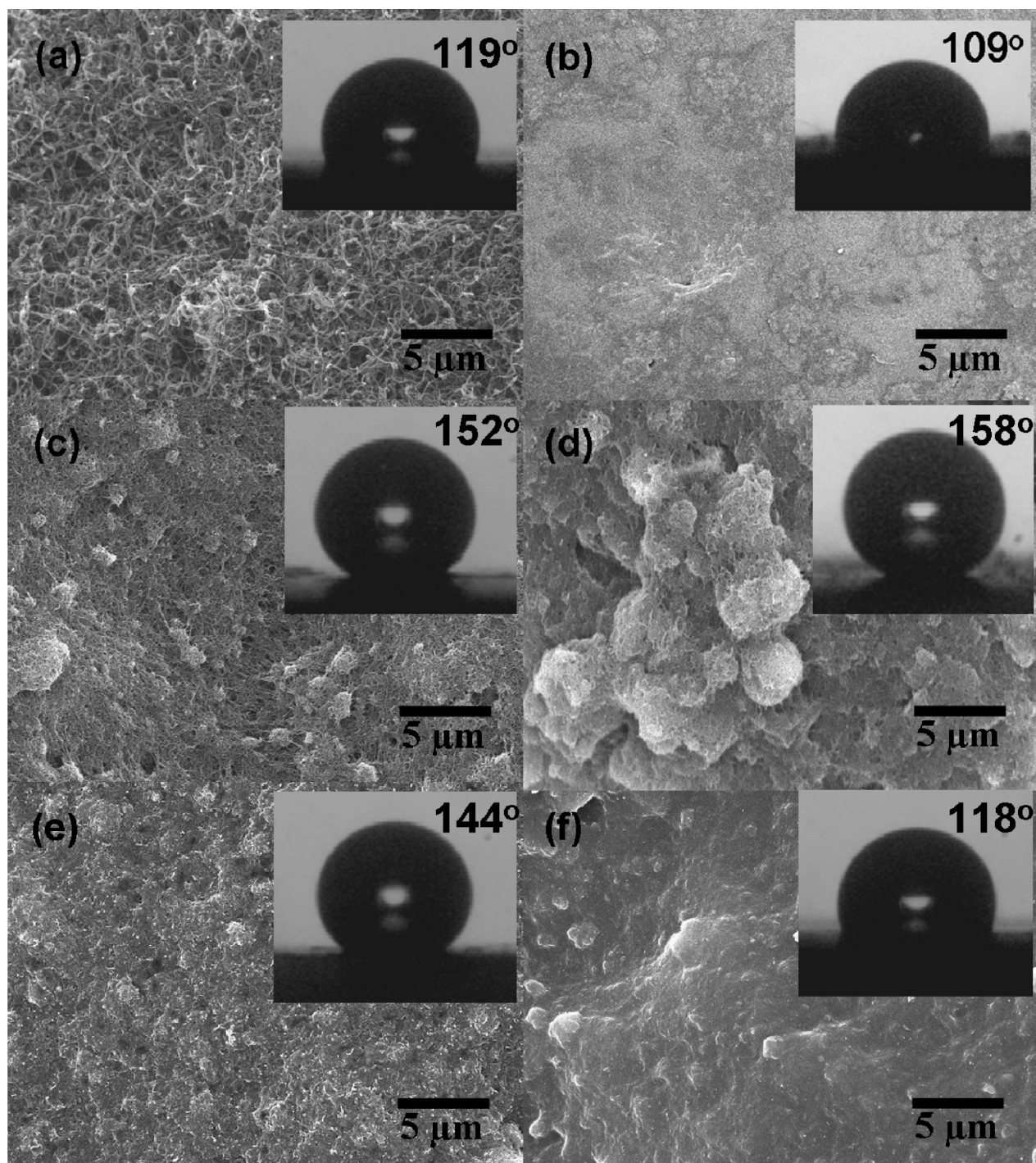


Figure 3. SEM micrographs of roughness and contact angle image (inset): (a) pristine CNTs, (b) as-synthesized PIB-amine, and PIB-amine/CNTs with weight ratios of (c) 1/4, (d) 1/2, (e) 2/1, and (f) 4/1.

with conductive carbon paste and coated with a thin layer of Au prior to measuring. Static contact angle measurements for water drops on films were performed using a Kruss G10/DSA10 apparatus using the sessile drop method. Measurements made at five different points on each sample surface were averaged. AFM measurements were performed on a Seiko SPI3800N, series SPA-400HV (Seiko Instruments) instrument. The thermal analyses were analyzed by using thermal gravimetric analysis (TGA), on a Perkin-Elmer Pyris 1 model, at a heating rate of 20 °C/min from 100 to 800 °C under a nitrogen flow. Pencil hardness was measured according to the method of ASTM D 3363-74. The pH environment effect of contact angle values was measured in the pH range from 3 to 11. The background pH buffer solution from 3 to 4 was

adjusted by H_3PO_4 and KH_2PO_4 , from 5 to 8 by KH_2PO_4 and Na_2HPO_4 , and from 9 to 11 by Na_2HPO_4 and Na_3PO_4 , in each case at a concentration of 0.1–0.2 M.

3. RESULTS AND DISCUSSION

3.1. Synthesis of PIB-Amine Copolymer. The synthesis of copolymer involves the reaction of cyclic anhydride and amine ($-\text{NH}_2$) to generate an amide in the linking site (in Scheme 1). The anhydride ring-opening reaction is selective at ambient temperature. The compounds have characteristic chemical moieties including a hydrophobic

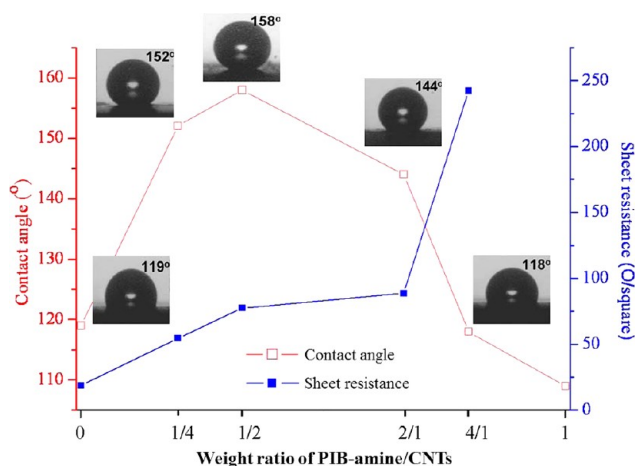


Figure 4. Contact angle and sheet resistance as a function of different weights of PIB-amine/CNTs.

poly(oxypropylene) block, amine, carboxylic acid, and amide functionalities. The polyamine reactions stated above were confirmed by FT-IR analyses of PIB-amine (Figure 1). The characteristic peaks of the anhydride at 1785 and 1858 cm^{-1} , while preserved on the spectrum of PIB-SA, disappear on that of the PIB-amine series and the peaks of the amide at 1552 and 1647 cm^{-1} preserved, suggesting a complete anhydride ring-opening reaction between anhydride and amine.

3.2. Observation of CNTs Dispersion by TEM. The PIB-amine was applied for disperse CNTs in THF by ultrasonic vibrator, and the dispersion was analyzed by TEM (Figure 2). The TEM images revealed the pristine CNTs rendered large aggregation and CNT bundles in a range of 1–5 μm . Compared to the copolymers dispersion, the TEM images revealed partial aggregation and fine dispersion for PIB-SA/CNTs and PIB-amine/CNTs, respectively. Due to the PIB-amine having one side with strong hydrophobic interaction and another side with stacking attraction between lone pair of amine group to CNTs surface, CNTs can be dispersed homogeneously by PIB-amine through copolymer wrapping.

3.3. Morphologies and Water Contact Angles of the Polymer/CNTs Surfaces. To mimic nature's lotus effect, the weight ratio of PIB-amine/CNTs in the dispersion solution used for drop-coating on glass substrate was reduced and the corresponding contact angles measured with a contact angle meter (Table 1). Figure 3 shows the SEM morphology and the water contact angle (CA). As shown in Figure 3a, the

pristine CNTs have CA of 119° with individual CNTs randomly entangled on the surface. On the other hand, Figure 3b shows the as-synthesized PIB-amine has a smooth surface without any roughness and it has a CA of 109°. In comparison, the combination of PIB-amine/CNTs shows CA of 152°, 158°, 144°, and 118° at PIB-amine/CNTs weight ratios of 1/4, 1/2, 2/1, and 4/1, respectively. This is attributed to the fact that the CNTs surface when coated with PIB-amine caused changes in CNTs diameter, and at weight ratio of 1/2 resulted in an uneven surface with microscale roughness (Figure 3d). These morphological features of the dispersion coating are similar to that of the lotus surface microstructures,³¹ having a superhydrophobic property like that of the lotus leaf self-cleaning property (see Supporting Information Movie S1). The PIB-amine/CNTs surface makes the water droplets move freely on the surface at a very low slide angle.

The effects of the copolymer content on CA and sheet resistance are further shown in Figure 4. The CA increased to a maximum of 158° at PIB-amine/CNTs weight ratio of 1/2, and after this optimal ratio, the CA decreased with increasing PIB-amine content. Furthermore, there is more copolymer coverage on the CNTs surface and the CNTs diameter increased with increasing copolymer content. Due to the surrounding copolymer, the sheet resistance increased with increasing copolymer content. This result further confirmed that the wettability of the CNTs surfaces can be controlled by changing the weight ratio, leading to different structure morphologies.

3.4. Film Robustness with Epoxy Resin Modification. For long-term durability application, antiscratching is important. The copolymer/CNTs show weak mechanical property and can easily be damaged by external force. The robustness of the CNTs superhydrophobic surface improved significantly upon incorporation of the epoxy resin as shown in Figures 5 and 6. In Figure 7, the rough surface is shown for the epoxy cured PIB-amine/CNTs at weight ratio of 1/2. The roughness at averaged root-mean-square (RMS) of 56.9 nm is consistent to the SEM observation in Figure 6. Specifically, the PIB-amine not only can act as dispersants for CNTs to form a stable CNTs/polymer suspension but is also a curing agent for epoxy resin. The PIB-amine contains amine groups, which can react with the epoxy group during the curing process. While the amine termini interacting with CNTs surface generate an aligned structure that consequently reacts with added epoxy, the robust surface was tailored. The PIB-amine/CNTs epoxy films have water CA of 152° and CAH of ca. 7°. Furthermore, the prepared surfaces, when exposed to

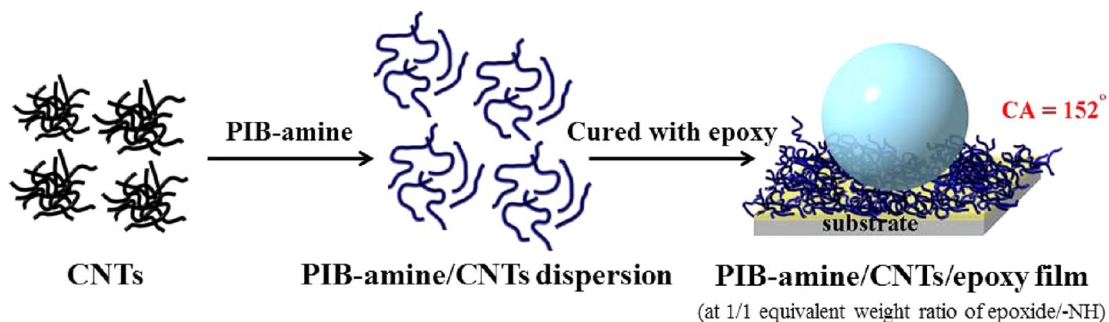


Figure 5. Conceptual illustration of PIB-amine dispersed CNTs and cured with epoxy.

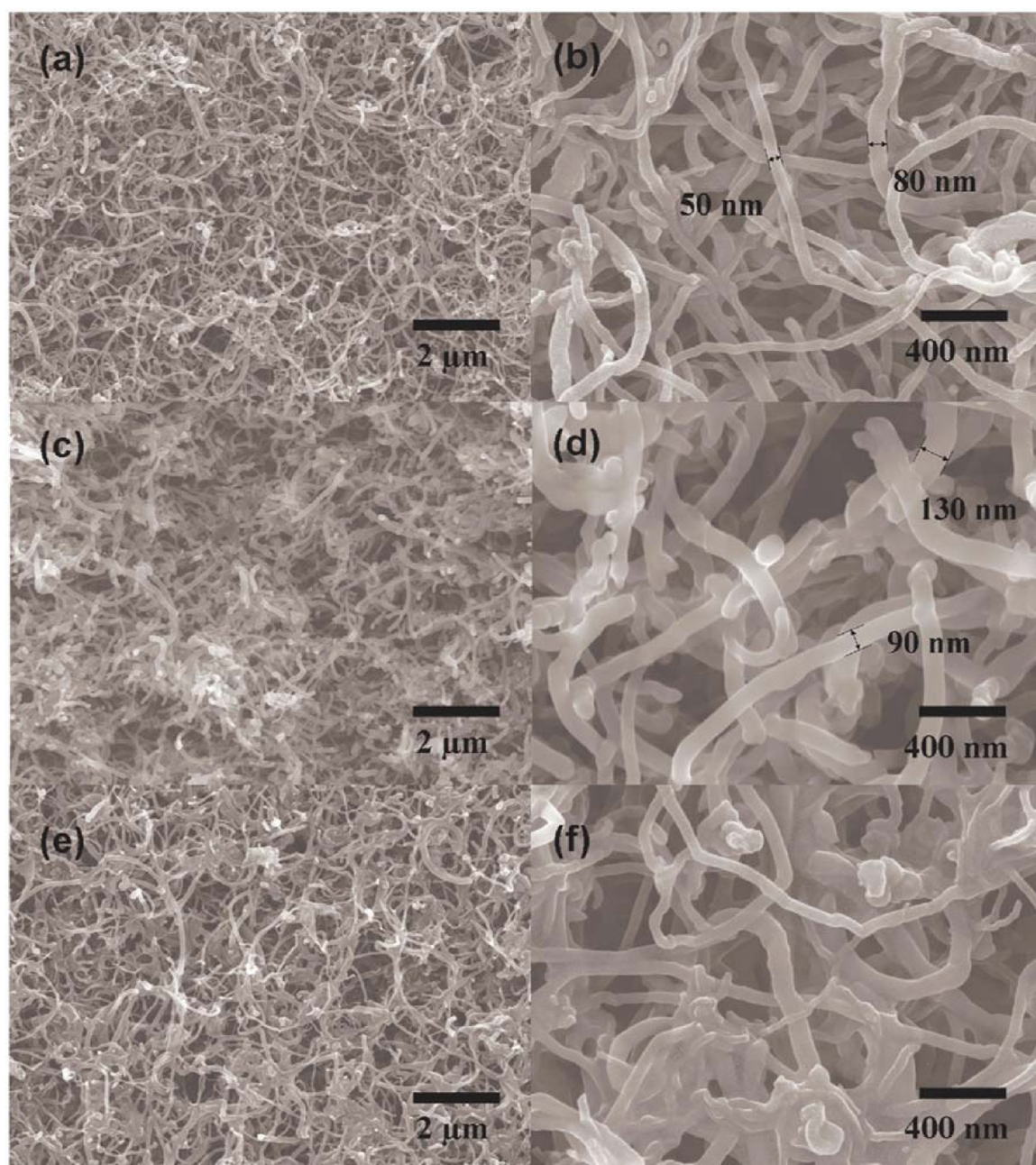


Figure 6. SEM micrographs of CNTs appearance on film surface: (a and b) pristine CNTs, (c and d) PIB-amine/CNTs at 1/2 weight ratio, and (e and f) PIB-amine/CNTs/epoxy.

air for several months or even immersed in a water bath, remained essentially unchanged with the same water CA and looked the same as the original pristine film (see Supporting Information Movie S1).

In addition, the properties of thermal decompositions of the films were analyzed by TGA (Table 1 and Supporting Information Figure S1), showing the following trend of stability: CNTs > PIB-amine/CNTs > PIB-amine/CNTs/epoxy > PIB-amine/epoxy > PIB-amine. It is noted that the addition of CNTs actually stabilized the polymer matrix. Further, the film hardness increased with the CNTs addition from 2 to 3 H. The enhancement is attributed to the CNTs homogeneous interaction with the epoxy polymer matrix.

3.5. Effect of pH Value on Surface Contact Angles. To evaluate the stability and durability of the superhydrophobic film,

the time-dependence and pH effect on the CA values were further studied. As shown in Figure 8a, the time-dependence of the CA values was evaluated and the results showed that the CA of PIB-amine/CNTs and PIB-amine/CNTs epoxy films remained essentially unchanged at $>150^\circ$. This shows that the superhydrophobic surfaces have long-term stability. In contrast, the CA of the pristine CNTs film revealed a dramatic decrease from an initial value of 119° to 75° within 1 h. In Figure 8b, the CA results were maintained close to CA of 150° and revealed only a slight change of CA on variation of pH. This indicates that pH values of the aqueous solution have little effect, implied that such superhydrophobic surface can be used for not only pure water but also corrosive liquids, and thus will greatly extend the industrial applications in all pH environments.

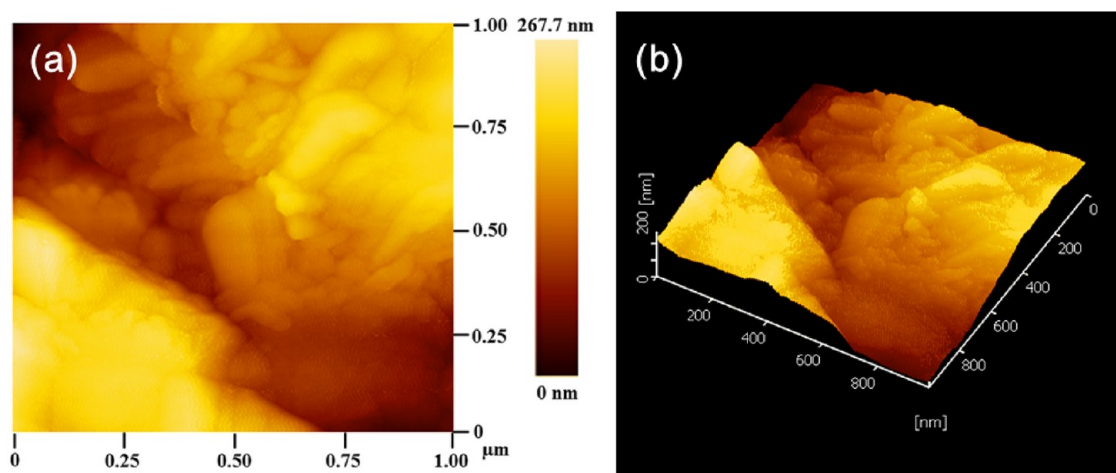


Figure 7. AFM micrographs of PIB-amine/CNTs/epoxy (a) topographical and (b) 3D images.

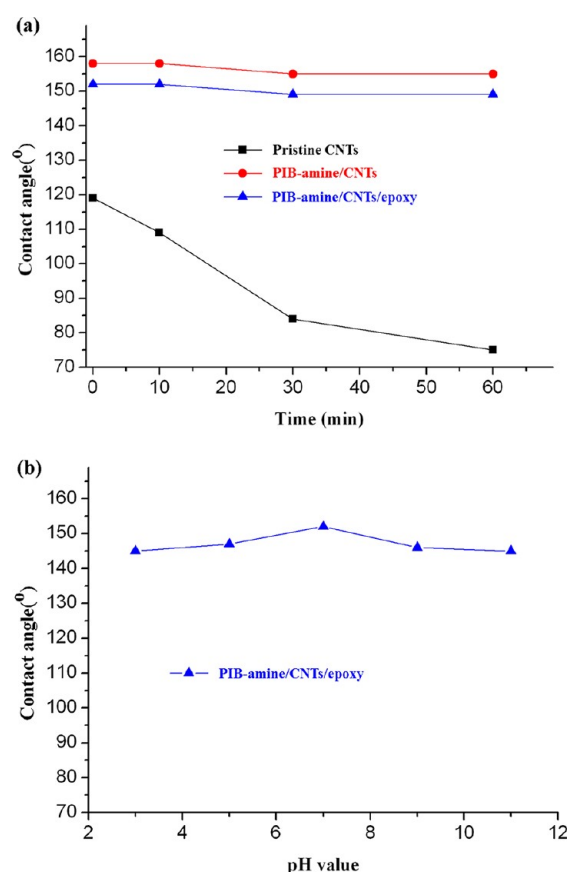


Figure 8. Surface stability of contact angle against various (a) time dependences and (b) pH values.

4. CONCLUSION

PIB-amine copolymer, consisting of hydrophobic alkyls and multiple amine termini, was synthesized and used to disperse CNTs in an organic medium. The amine associated CNTs enabled the formation of a tailored roughness of epoxy surface on glass substrate. The superhydrophobic surface can be fabricated by varying the copolymer/CNTs weight ratio, and the measurement of water contact angle up to 158° correlated well to the SEM observed surface roughness of micrometer scale in fiber-knitted lumps. The generated epoxy film was shown to be stable against a harsh pH environment and long-term immersion

in water. The dual functionality of PIB-SA/POP-amines as a dispersant for CNTs and reacting with epoxy is essential for creating this robust surface. The uses of PIB-SA/POP-amines in affecting CNTs dispersion in organic medium and reacting with epoxy with tailored roughness provides a new avenue to form a surface with self-cleaning and controlled functions, potentially applicable for conductor and other optoelectronic devices.

ASSOCIATED CONTENT

Supporting Information

Thermal gravimetric analyses of PIB-amine/CNTs and a movie showing the free rolling of water droplets and wetting test. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

*Tel: +886-2-3366-5312. Fax: +886-2-2363-8076. E-mail: jianglin@ntu.edu.tw.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We acknowledge financial support from the National Science Council (NSC) and the Ministry of Economic Affairs, Taiwan.

REFERENCES

- (1) Nakajima, A.; Hashimoto, K.; Watanabe, T.; Takai, K.; Yamauchi, G.; Fujishima, A. *Langmuir* **2000**, *16*, 7044–7047.
- (2) Erbil, H. Y.; Demirel, A. L.; Avci, Y.; Mert, O. *Science* **2003**, *299*, 1377–1380.
- (3) Zhai, L.; Cebeci, F. C.; Cohen, R. E.; Rubner, M. F. *Nano Lett.* **2004**, *4*, 1349–1353.
- (4) Cassie, A. B. D.; Baxter, S. *Trans. Faraday Soc.* **1944**, *40*, 546–551.
- (5) Wenzel, R. N. *Ind. Eng. Chem.* **1936**, *28*, 988–994.
- (6) Li, J.; Fu, J.; Wu, Y.; Xue, L. J.; Han, Y. C. *Appl. Surf. Sci.* **2006**, *252*, 2229–2234.
- (7) Luo, C.; Zuo, X. L.; Wang, L.; Wang, E. G.; Song, S. P.; Wang, J.; Wang, J.; Fan, C. H.; Cao, Y. *Nano Lett.* **2008**, *8*, 4454–4458.
- (8) Wang, C. F.; Chen, W. Y.; Cheng, H. Z.; Fu, S. L. *J. Phys. Chem. C* **2010**, *114*, 15607–15611.
- (9) Peng, M.; Liao, Z.; Qi, J.; Zhou, Z. *Langmuir* **2010**, *26*, 13572–13578.

- (10) Teare, D. O. H.; Spanos, C. G.; Ridley, P.; Kinmond, E. J.; Roucoules, V.; Badyal, J. P. S.; Brewer, S. A.; Coulson, S.; Willis, C. *Chem. Mater.* **2002**, *14*, 4566–4571.
- (11) Honoso, E.; Fujihara, S.; Honma, I.; Zhou, H. *J. Am. Chem. Soc.* **2005**, *127*, 13458–13459.
- (12) Ma, M. L.; Mao, Y.; Gupta, M.; Gleason, K. K.; Rutledge, G. C. *Macromolecules* **2005**, *38*, 9742–9748.
- (13) Soeno, T.; Inokuchi, K.; Shiratori, S. *Appl. Surf. Sci.* **2004**, *237*, 543–547.
- (14) Nakajima, A.; Saiki, C.; Hashimoto, K.; Watanabe, T. *J. Mater. Sci. Lett.* **2001**, *20*, 1975–1977.
- (15) Daoud, W. A.; Xin, J. H.; Tao, X. M. *J. Am. Ceram. Soc.* **2004**, *87*, 1782–1784.
- (16) Ming, W.; Wu, D.; van Benthem, R.; de With, G. *Nano Lett.* **2005**, *5*, 2298–2301.
- (17) Lin, J. J.; Chu, C. C.; Chiang, M. L.; Tsai, W. C. *Adv. Mater.* **2006**, *18*, 3248–3252.
- (18) Chiu, C. W.; Lin, J. J. *Prog. Polym. Sci.* **2012**, *37*, 406–444.
- (19) Chang, L. Y.; Lee, C. P.; Huang, K. C.; Wang, Y. C.; Yeh, M. H.; Lin, J. J.; Ho, K. C. *J. Mater. Chem.* **2012**, *22*, 3185–3191.
- (20) Chen, X.; Hong, L.; Xu, Y.; Ong, Z. W. *ACS Appl. Mater. Interfaces* **2012**, *4*, 1909–1918.
- (21) Dujardin, E.; Ebbesen, T. W.; Hiura, H.; Tanigaki, K. *Science* **1994**, *265*, 1850–1852.
- (22) Dong, R. X.; Liu, C. T.; Huang, K. C.; Chiu, W. Y.; Ho, K. C.; Lin, J. J. *ACS Appl. Mater. Interfaces* **2012**, *4*, 1449–1455.
- (23) Liu, J.; Rinzler, A. G.; Dai, H.; Hafner, J. H.; Bradley, R. K.; Boul, P. J.; Lu, A.; Iverson, T.; Shelimov, K.; Huffman, C. B.; Fernando, R. M.; Shon, Y. S.; Lee, T. R.; Colbert, D. T.; Smalley, R. E. *Science* **1998**, *280*, 1253–1256.
- (24) Peng, H.; Alemany, L. B.; Margrave, J. L.; Khabashesku, V. N. *J. Am. Chem. Soc.* **2003**, *125*, 15174–15182.
- (25) Li, C. Y.; Li, L.; Cai, W.; Kodjie, S. L.; Tenneti, K. K. *Adv. Mater.* **2005**, *17*, 1198–1202.
- (26) Sinani, V. A.; Gheith, M. K.; Yaroslavov, A. A.; Rakhnyanskaya, A. A.; Sun, K.; Mamedov, A. A.; Wicksted, J. P.; Kotov, N. A. *J. Am. Chem. Soc.* **2005**, *127*, 3463–3472.
- (27) Lu, X.; Zhang, W.; Wang, C.; Wen, T. C.; Wei, Y. *Prog. Polym. Sci.* **2011**, *36*, 671–712.
- (28) Gabriel, S.; Jérôme, R.; Jérôme, C. *Prog. Polym. Sci.* **2010**, *35*, 113–140.
- (29) Yao, X.; Song, Y.; Jiang, L. *Adv. Mater.* **2011**, *23*, 719–734.
- (30) Verho, T.; Bower, C.; Andrew, P.; Franssila, S.; Ikkala, O.; Ras, R. H. A. *Adv. Mater.* **2011**, *23*, 673–678.
- (31) Cheng, Y. T.; Rodak, D. E.; Angelopoulos, A.; Gacek, T. *Appl. Phys. Lett.* **2005**, *87*, 194112.