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Surface wetting processing on BNNT films by selective plasma modes

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The wettability of boron nitride nanotube (BNNT) films was modified using a combination of pulsed and continuous wave (CW) mode plasma. The combined mode effectively modified the wettability of BNNT films and kept the nanostructures intact. The BNNT films changed from superhydrophobic to superhydrophilic after combined mode treatment at 600 W min. In contrast, the contact angle controllable decreased linearly in a controllable way with increasing energy input before eventually becoming superhydrophilic after 1000 W min of CW mode treatment. A high concentration of graft functional groups formed, along with point defects. More point defects formed when using combined modes and higher energy input. Mainly amine functional groups were grafted by combined mode plasma, while the CW mode plasma led to more formation of amide and imine on the BNNTs. Research into controllable wettability and selection of grafted functional groups should enable promising applications of BNNTs in composites and biology in the future.

boron nitride nanotube, wettability, plasma

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Boron nitride nanotubes (BNNTs), structurally analogous to carbon nanotubes (CNTs), have excellent mechanical and thermal properties which attract more and more research [1,2]. The group III–V atoms B and N locate alternate in BNNTs structure instead of C atoms in CNTs as a rolled hexagonal hBN layer. Different from CNTs, BNNTs are wide-band gap semiconductors (~5.5 eV) independent of nanotube chirality, but it possess much better high thermal and chemical stability which indicate many promising applications [3–7]. Recently, research into modifying BNNTs has progressively increased. The main purposes of modification are to change their wettability properties or electronic structure by doping or functionalization. BNNTs are inherently superhydrophobic because of the high density of their nanoscale structure [7–9]. However, for many applications of nanomaterials, hydrophilicity is necessary. For example,

some simulation works have been done on single BN nanotube to show superior water flow properties inside tubes compared to CNTs. Therefore the BNNTs are expected to provide a more efficient water purification device [10], as well as similar ion-selectivity application on BNNTs [11,12]. BNNT films are promising composite polymer materials with enhanced toughness, designed for working in harsh environments. Even more, biology applications, such as drug delivery carried out by nanomaterials and bio-compatible experiments, mainly ask for wettability change of BNNTs as well as functionalizations [13–18]. Wettability changes do not usually affect other properties or destroy the structures of intact BNNTs. However, application of electronic fields may change the wettability from superhydrophobic to hydrophilic. This phenomenon, known as electro-wetting was found in other nano materials, such as single carbon nanotube for nano capillary control [19,20]. Investigations of BNNT wettability have mostly been theoretical, and

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barely happened to BNNT films due to hard synthesis of high density BNNTs as well as the tender structure of nanotubes.

There are two main ways to modify the wettability of BNNT films: (1) physical structure modification to optimize the roughness and (2) chemical functionalization without destroying the structure of the surface. Room temperature plasma technique is one of the techniques employed for the surface modified [21]. Other methods like the living polymerization such as the oxidation of acids [22], nitro oxide mediated radical polymerization (NMRP) [23] are so strong and complicated processing. Different from methods above, plasma works softly and controllable to achieve surface modification while keep nanostructures well [24]. The other advantage of plasma is that this technique not only simplifies the entire manufacturing process, but also offers the flexibility of adapting its functional groups to the distinctive needs of the experiments [25]. Normally, continuous wave (CW) mode plasma is used to modify surface. However, small dose is too weak to change wettability, and strong power input may destroy the surface of BNNT film. To resolve the problem, pulsed mode is used to assist CW mode plasma. Pulsed plasma allows a high degree of control over the physical and chemical properties of the thin film deposited by providing control of the gas phase reactions and the gas-surface interactions [26]. Here, we investigated the use of continuous wave plus pulsed (CW+P) mode plasma to control wettability change as well as enhance the quantity of N-functional groups grafted onto BNNTs. The results are further compared to CW mode plasma to find out the efficiency of these two modes and aging effect [27]. N-containing gas sources were used to grafted N-containing functionalities onto the BNNTs. N-containing plasma was widely used for surface modification in both biological and chemical fields [28].

1 Experimental

1.1 Synthesis of BNNT films

High density and purity BNNT films were synthesised by milling-ink accompany with annealing method on 1 cm×1 cm stainless steel substrates as shown in Figure 1(a). B powder (95%–97%, Fluka) was processed into nano-particles by ball-milling in argon (Ar) gas at 300 kPa for 150 h. The powder after ball-milling and then dispersed into ethanol solution with catalyst $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Pronalys, assay not less than 98%) by ultrasonic process for 30 min. The B ink was coated on stainless steel and annealing in furnace under 1100°C while keeping flow of nitrogen/hydrogen gas ($\text{N}_2/\text{H}_2(15\%)$) for 2 h [29–31]. The 8 samples for each treatment conditions were prepared.

1.2 Plasma modification

Plasma modifications were performed in custom built

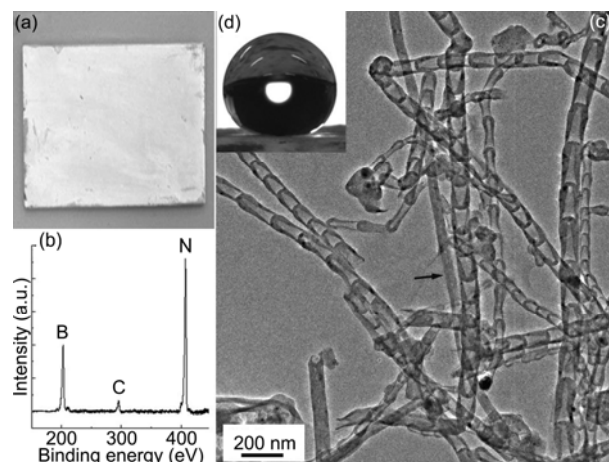


Figure 1 BNNT film produced by B milling-ink method. (a) photo of 1 cm×1 cm BNNT film, (b) XPS survey spectrum of the BNNTs, (c) TEM image, and (d) superhydrophobic droplets on BNNT film.

inductively coupled radio-frequency (RF) (13.56 MHz) plasma reactor. The reactor could be carried out continuous wave as well as pulsed mode [32]. The reaction chamber was a cylindrical glass tube, and the samples were located in the middle area of plasma source. The designed antenna with an auto RF matching network guarantee transfer 100% of the input RF power into the plasma. According to BN bond, the 100 W of RF power was used as effective modest energy [33]. The pulsed mode used frequency of 1 kHz, and a duty cycle of 10, defined as $D = T_{\text{on}}/(T_{\text{on}} + T_{\text{off}})$, where T_{on} (0.1 ms) and T_{off} (0.9 ms) are the plasma on and off times. The pressure was maintained constant at 5.5 Pa.

Ar gas plasma was used to pretreat BNNT films, for cleaning and activating the surface. Ar as an inert gas mainly no bonding were produced with materials. N rich gases plasma were then carried out to BNNT films. We chose $\text{N}_2/\text{H}_2(15\%)$ mixture gases and N_2 gas alone to perform the modification. The samples were undertaken CW+P combined mode and CW mode at the same energy input, respectively.

1.3 Characterization

The physical structure of BNNTs was investigated by supra 55VP scanning electron microscope (SEM), with coating thickness of gold 20 nm. High resolution transmission electron microscopy (HRTEM) JEOL-2010EX was used to check the nanotubes under high magnification. We also employed X-ray photoelectron spectroscopy (XPS) to show comparison results of surface chemical structure. The XPS spectra were obtained using Thermo Fischer Scientific with monochromatic X-ray focused to a 400 μm spot size. The near edge X-ray absorption fine structure (NEXAFS) measurements were performed in ultrahigh vacuum chamber at the undulator soft X-ray spectroscopy beamline of the Australian Synchrotron, Victoria and Australia. The raw

NEXAFS data were normalized to the photoelectron current of the photon beam, measured on an Au grid. An optical contact angle (CA) and surface tension instrument (KSV, model 110005) were used to measure film wettability with camera signal70x, cam200 and LB 1000-5000 software. To measure contact angle, the deionized water droplets were used, and each droplet was $(5 \pm 0.2) \mu\text{L}$.

2 Results and discussion

BNNT films prepared by the milling-ink method appeared white, which indicates high purity (Figure 1(a)). BNNT structures were characterized by EDX and TEM in Figure 1(b) and (c). EDX confirmed the expected composition of BN with C impurity arises from environmental background. The TEM image showed that the majority of the tubes were bamboo structures, while a few (arrow in Figure 1(c)) showed cylindrical tubes. The diameters of the BNNTs were around 150 nm, and their length was almost 30 μm . Contact angle tests on the BNNT film showed that it had a superhydrophobic surface with a contact angle of 156.5° , as shown in Figure 1(d), and reached to $158.1^\circ \pm 3.6^\circ$ on average.

Ar gas pretreatment with energy of 100 W min (1 min) was carried out to activate BNNT surface. From SEM images, there were no changes of physical structure, and the contact angle reduced to $152.5^\circ \pm 2.8^\circ$. The acceptable decrease due to possible polar oxygen functional groups introduced either impurity in Ar plasma process or exposed in atmospheric after activity [32,34].

Low power plasma by traditional CW mode and combined CW+P mode were performed. Pulsed mode here for the purpose of reducing total energy input to prevent possible damage and control the chemical properties by providing controllable gas phase reactions as well as gas-surface interactions [26]. N_2 alone and $\text{N}_2/\text{H}_2(15\%)$ were used as gas sources, respectively. The use of mixture was because hydrogen in the plasma has been found to enhance the selectivity of functional groups to build a stable structure in CNTs, so it is expectable to graft more useful functional groups such as amine (NH_2) groups in BNNTs by combined mode with mixture gases plasma [35,36].

The surface of BNNT films was characterized using SEM and NEXAFS before and after plasma treatments, and the data are presented in Figure 2. From the SEM, it can be seen that before plasma treatment, parts of the BNNTs were semierect but the majority were bent in one orientation. Figure 2(b) shows that the BNNT film maintained its appearance after 10 min of CW (10CW) plasma treatment. The specimen shown in Figure 2(b) had received the greatest energy input of all samples 1000 W min. In other words, the nanotubes structures were intact after plasma power up to 1000 W min by either N_2 or mixture $\text{N}_2/\text{H}_2(15\%)$. The only slight difference in the structures is that after treatment

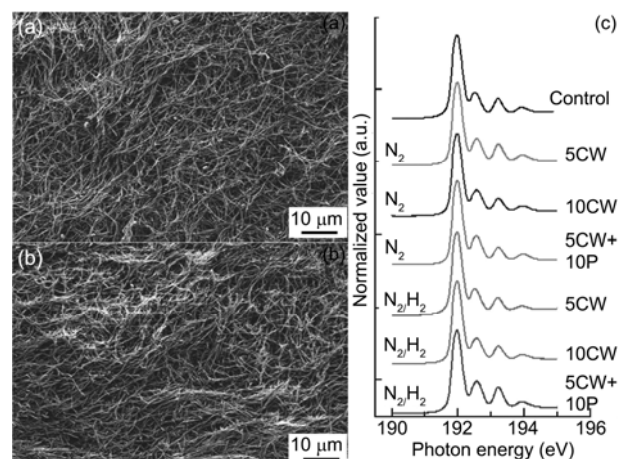


Figure 2 SEM images of BNNT films (a) before and (b) after 1000 W min plasma treatment with N_2/H_2 gas source; and (c) NEXAFS comparison of B K-edge spectra of BNNT films after different plasma treatments.

the nanotubes appeared more semierect and disordered in the high density area. This is reasonable because the ions produced by plasma energy bombard the interlaced nanoweb during plasma treatment, and can make the tips of the nanotubes disordered.

The NEXAFS results showed that besides B-N bonding, three further peaks at the π^* onset of B K-edge were investigated in Figure 2(c) at 192.50, 193.22 and 193.93 eV, respectively. These satellite peaks are commonly observed in various BN materials [37–40]. Electron negative elements had been introduced around excited B atoms to form point defects in the represent of $\text{B}-\text{N}_x-\text{O}_y$ bonds in hexagonal ring [41,42]. Relative to the control sample, the satellite peaks were wider after plasma treatment, which mean that the structure has become less ordered. For CW mode plasma, the peaks at 193.22 eV ($\text{B}-\text{N}-\text{O}_2$) and 193.93 eV ($\text{B}-\text{O}_3$) decreased while there was a slight increase in the peak at 192.5 eV ($\text{B}-\text{N}_2-\text{O}$) as a result of increased N grafting. In contrast, the CW+P mode results in increased intensity of all three satellite peaks. In addition, the BNNT film after CW+P mode $\text{N}_2/\text{H}_2(15\%)$ gas plasma with most energy input of 600 W min presented strongest satellite peaks, i.e. with increasing of energy input, more defects happened on BNNTs. The low power (100 W) plasma appears to have minimized the damage to the BNNTs, while keeping the energy input under 1000 W min via CW mode with N_2 gas plasma results in fewer impurities contaminating the surface of the BNNTs films. On the other hand, the combined mode with an energy input of 600 W min via N_2/H_2 mixture gas plasma produces more point defects.

Contact angle tests were carried out to investigate the wettability changes. Contact angle measurements in Figures 3 and 4 showed the superhydrophobic BNNT films change to hydrophilic by N_2 and N_2/H_2 plasma, respectively. Two gases got the similar results, and the CW mode plasma decreased CA gradually with increased power input. The CA

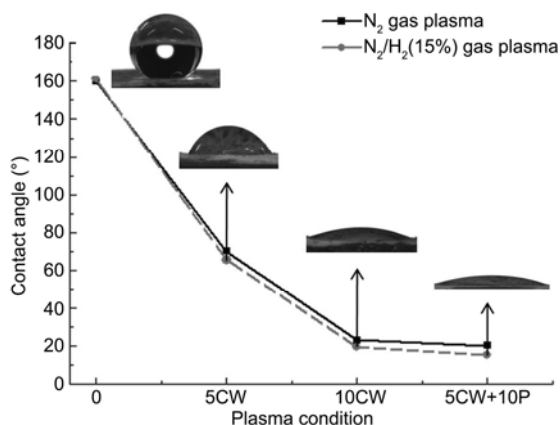


Figure 3 Contact angle tests and images of different gas sources plasma.

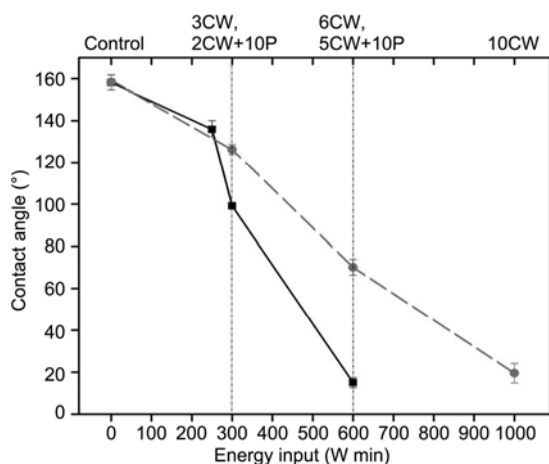


Figure 4 Comparison of contact angle changes with energy input by CW mode (dashed line) and CW+P mode (solid line).

changed from superhydrophobic before treatment with 5CW mode to 70° (with N_2 plasma) and 65.2° (with N_2/H_2 plasma) afterwards, and go on decreased to 17.9° and 14.5° by N_2 and N_2/H_2 after 10CW plasma with 1000 W min, respectively. In contrast, the combined mode plasma directly changed the wettability of the BNNT films to superhydrophobic (less than 10°) after mixture gas plasma treatment for 5 min CW plus 10 min pulsed (5CW+10P) at a lower energy input of 600 W min. Figure 4 made a further comparison between energy input of two modes plasma. Our results show a linear decrease in CA with increasing energy input for the CW mode treatment and superhydrophilic was obtained at the energy input of 1000 W min. However, with the addition of pulsed plasma mode, the combined mode treatment, an even stronger change was achieved at the same energy input as CW mode. The superhydrophilic of BNNT films was obtained at lower energy input of 600W.min using combined mode 5CW+10P, compared to 77.8° at the same energy input via 6CW mode treatment. Figure 5 presented the controllable plasma treatments on one piece of BNNT film by mask plasma treatment.

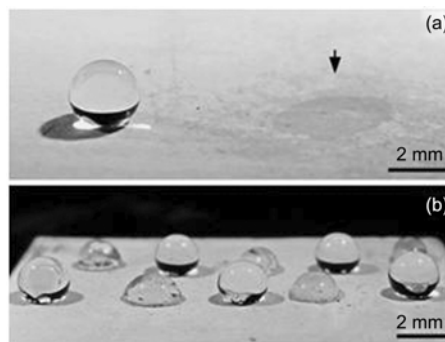


Figure 5 Photos of (super)hydrophilic patterns on superhydrophobic BNNT films created by masked plasma treatments 5CW+10P (a) and 5CW (b).

(Super)hydrophilic patterns were achieved on superhydrophobic BNNT films created by masked plasma treatments 5CW+10P (Figure 5 (a)) and 5CW (Figure 5 (b)).

The functional groups grafted using both plasma modes (CW and combined CW+P) were examined using XPS, as shown in Figure 6. The investigation aims to discuss the affection of different gases source as well as different modes. Before plasma treatment, B 1s core-level photoemission spectra of the films showed a typical B–N peak at binding energies (BEs) of 190.1 eV (Figure 6(a)). The C1s binding energies of the BNNTs were corrected the lowest binding energy peak to 284.6 eV (Figure 6(e)). After CW mode plasma treatments with N_2 and N_2/H_2 , a shoulder at 191.3 eV appears in the B 1s spectrum, which corresponds to B bonded in a ternary BN_xO_y species, in agreement with the NEXAFS results [43]. This is also supported by the increase in the oxygen: boron ratio from 0.18 before plasma treatment to 0.22 after 10CW plasma treatment with N_2/H_2 and 0.26 after treatment with N_2 plasma. On the other hand, the 5CW+10P plasma also creates BN_xO_y species, with O/B ratio increased to 0.24 by N_2/H_2 plasma treatment. The C 1s spectra of the films treated with both plasma modes show peaks consistent with amide (288.1 eV) and amine (285.8 eV), but also indicate the presence of imine (nitrile) (286.7 eV) [44,45]. While the N_2 alone plasma treated films in figure 6(f) presented more imine grafted. The C 1s spectra showed that the CW+P mode resulted in more amine groups grafted onto the BNNTs, while the CW mode formed more amide when N_2/H_2 was used and more imine when N_2 was used. This difference arises because the CW mode plasma with continuous and higher energy inputs supports the dissociation and further reaction of freshly formed amine to form amide and imine in the presence of O and C impurities. While the P mode, with its off-time and lower energy input, can retain more amine [46,47]. Though the energy input of 10CW (1000 W min) is much higher than that of 5CW+10P (600 W min), the total amount of functional groups introduced by 10CW is only slightly higher than that by 5CW+10P (Figure 6). The investigation confirmed that the wettability changes of BNNT films are

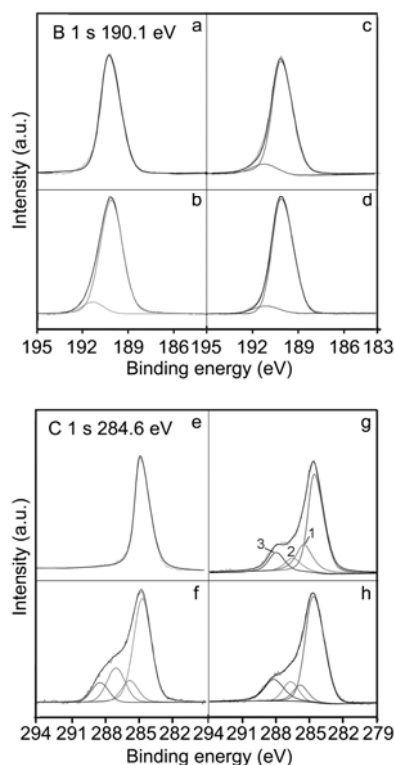


Figure 6 B 1s and C 1s regions of the XPS spectra, respectively. The plasma conditions of BNNT films ((a), (e)) before plasma treatment, ((b), (f)) after 10CW with N_2 , ((c), (g)) after 5CW+10P with N_2/H_2 , and ((d), (h)) after 10CW with N_2/H_2 plasma treatments. In the C 1s, fitting peaks represent amine (1), imine (2) and amide (3).

mainly caused by surface chemical modification induced by plasma.

We found that lower energy input 5CW+10P treatment could modify the wettability of BNNT films in a similar way to 10CW treatment with high energy input. However, the aging results further proved that the functional groups introduced by CW+P mode could attached stronger to BNNT than those by CW mode. The CA of the 5CW+10P treated BNNT films increased to 42.8° after 100 h aging in air, while the CA of the 10CW treated films jumped back to 81.5° . This is because the CW mode plasma treatment creates a strong cross-linking on BNNTs and this structure serves as a base for the further P mode treatment, which gives rise to better bonding of functional groups during P mode treatment [48,49].

3 Conclusion

High density of BNNT films was modified by two different types of plasma treatments to achieve controllable wettability: CW+P combined mode and CW mode. CW+P treatment under lower energy input (600 W min) effectively changed the BNNT films from superhydrophobic to superhydrophilic. In contrast, the contact angle after CW mode

plasma treatment decreased in a controllable way with increasing energy input, and superhydrophilicity was achieved at 1000 W min. Point defects (BN_xO_y species) were investigated by NEXAFS after treatment. The combined mode and the use of hydrogen in the gas mixture resulted in more defects, which are helpful for wettability change. The grafted group resulting from CW+P plasma treatment was mostly amine, while CW mode with higher energy led to preferential formation of amide and imine on BNNTs after treatment with N_2/H_2 and N_2 , respectively. We have shown that the combination of continuous plus pulsed mode plasma effectively changes the wettability of BNNT films at lower energies. Being able to selectively graft functional groups onto BNNT films by using different modes of plasma will be beneficial for applications of BNNTs as biological materials as well as high strength composites at next step [50,51].

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- 1 Zhao T L, Liu L H, Li G M, et al. Preparation and electrochemical property of CMC/MWCNT composite using ionic liquid as solvent. *Chin Sci Bull*, 2012, 57: 1620–1625
- 2 Zeng F G, Li X, Liu W H, et al. Synthesis of CNT film on the surface of micro-pyramid array and its intense pulsed emission characteristics. *Chin Sci Bull*, 2012, 57: 1739–1742
- 3 Golberg D, Bando Y, Kurashima K, et al. Synthesis and characterization of ropes made of BN multiwalled nanotubes. *Scr Mater*, 2001, 44: 1561–1565
- 4 Chen Y, Zou J, Campbell S J, et al. Boron nitride nanotubes: Pronounced resistance to oxidation. *Appl Phys Lett*, 2004, 84: 2430–2432
- 5 Chopra N G, Luyken R J, Cherrey K, et al. Boron nitride nanotubes. *Science*, 1995, 269: 966–967
- 6 Zhang H, Yu J, Chen Y, et al. Conical boron nitride nanorods synthesized via the ball-milling and annealing method. *J Amer Ceram Soc*, 2006, 89: 675–679
- 7 Li L H, Chen Y. Superhydrophobic properties of nonaligned boron nitride nanotube films. *Langmuir*, 2009, 26: 5135–5140
- 8 Yum K, Yu M F. Measurement of wetting properties of individual boron nitride nanotubes with the wilhelmy method using a nanotube-based force sensor. *Nano Lett*, 2006, 6: 329–333
- 9 Lee C H, Drelich J, Yap Y K. Superhydrophobicity of boron nitride nanotubes grown on silicon substrates. *Langmuir*, 2009, 25: 4853–4860
- 10 Hilder T A, Gordon D, Chung S H. Salt rejection and water transport through boron nitride nanotubes. *Small*, 2009, 5: 2183
- 11 Yuan Q, Zhao Y P. Transport properties and induced voltage in the structure of water-filled single-walled boron-nitrogen nanotubes. *Biomicrofluidics*, 2009, 3: 022411
- 12 Won C Y, Aluru N R. A chloride ion-selective boron nitride nanotube. *Chem Phys Lett*, 2009, 478: 185–190
- 13 Sun T L, Feng L, Gao X F, et al. Bioinspired surfaces with special wettability. *Accounts Chem Res*, 2005, 38: 644–652
- 14 Liu, K, Yao X, Jiang L. Recent developments in bio-inspired special wettability. *Chem Soc Rev*, 2010, 39: 3240–3255
- 15 Shahzad Y, Shah S N H, Ansari M T, et al. Effects of drug-polymer dispersions on solubility and in vitro diffusion of artemisinin across a polydimethylsiloxane membrane. *Chin Sci Bull*, 2012, 57: 1685–1692

- 16 Sun T L, Qing G Y, Su B L, et al. Functional biointerface materials inspired from nature. *Chem Soc Rev*, 2011, 40: 2909–2921
- 17 Sun T L, Qing G Y. Biomimetic smart interface materials for biological applications. *Adv Mater*, 2011, 23: 57–77
- 18 Qing G Y, Wang X, Fuchs H, et al. Nucleotide-responsive wettability on a smart polymer surface. *J Am Chem Soc*, 2009, 131: 8370–8371
- 19 Mugele F, Baret J C. Electrowetting: From basics to applications. *J Phys-Condens Matter*, 2005, 17: R705
- 20 Mattia D, Rossi M P, Kim B M, et al. Effect of graphitization on the wettability and electrical conductivity of CVD-carbon nanotubes and films. *J Phys Chem B*, 2006, 110: 9850–9855
- 21 Felten A, Bittencourt C, Pireaux J J, et al. Radio-frequency plasma functionalization of carbon nanotubes surface O₂, NH₃, and CF₄ treatments. *J Appl Phys*, 2005, 98: 074308
- 22 Yu H, Jin Y, Peng F, et al. Kinetically controlled side-wall functionalization of carbon nanotubes by nitric acid oxidation. *J Phys Chem C*, 2008, 112: 6758–6763
- 23 Lu C H, Wang J H, Chang F C, et al. Star block copolymers through nitroxide-mediated radical polymerization from polyhedral oligomeric silsesquioxane (POSS) core. *Macromol Chem Phys*, 2012, 211: 1339–1347
- 24 Dai X J, Chen Y, Chen Z Q, et al. Controlled surface modification of boron nitride nanotubes. *Nanotechnology*, 2011, 22: 245301
- 25 Chen I H, Wang C C, Chen C Y. Preparation of carbon nanotube (CNT) composites by polymer functionalized CNT under plasma treatment. *Plasma Process Polym*, 2010, 7: 59–63
- 26 Harsch A, Calderon J, Timmons R B, et al. Pulsed plasma deposition of allylamine on polysiloxane: A stable surface for neuronal cell adhesion. *J Neurosci Methods*, 2000, 98: 135–144
- 27 Meyer-Plath A A, Finke B, Schröder K, et al. Pulsed and CW microwave plasma excitation for surface functionalization in nitrogen-containing gases. *Surf Coat Technol*, 2003, 174–175: 877–881
- 28 Favia P, Stendardo M, d'Agostino R. Selective grafting of amine groups on polyethylene by means of NH₃-H₂ RF glow discharges. *Plasma Polym*, 1996, 1: 91–112
- 29 Meyer-Plath A A, Schröder K, Finke B, et al. Current trends in biomaterial surface functionalization-nitrogen-containing plasma assisted processes with enhanced selectivity. *Vacuum*, 2003, 71: 391–406
- 30 Chen Y, Fitz-Gerald J, Williams J S, et al. Synthesis of boron nitride nanotubes at low temperatures using reactive ball milling. *Chem Phys Lett*, 1999, 299: 260–264
- 31 Li L H, Chen Y, Glushenkov A M. Synthesis of boron nitride nanotubes by boron ink annealing. *Nanotechnology*, 2012, 21: 105601
- 32 Dai X J, Plessis J D, Kyratzis I L, et al. Controlled amine functionalization and hydrophilicity of a poly (lactic acid) fabric. *Plasma Process Polym*, 2009, 6: 490–497
- 33 Dai X J, Church J S, Huson M G. Pulsed plasma polymerization of hexamethyldisiloxane onto wool: Control of moisture vapor transmission rate and surface adhesion. *Plasma Process Polym*, 2009, 6: 139–147
- 34 Inagaki N, Tasaka S, Narushima K, et al. Surface modification of PET films by pulsed argon plasma. *J Appl Polym Sci*, 2002, 85: 2845–2852
- 35 Choukourov A, Biederman H, Slavinska D, et al. The influence of pulse parameters on film composition during pulsed plasma polymerization of diaminocyclohexane. *Surf Coat Technol*, 2003, 174–175: 863–866
- 36 Maiyalagan T, Viswanathan B. Template synthesis and characterization of well-aligned nitrogen containing carbon nanotubes. *Mater Chem Phys*, 2005, 93: 291–295
- 37 Franke R, Bender S, Hormes J, et al. A quasi-atomic treatment of chemical and structural effects on K-shell excitations in hexagonal and cubic BN crystals. *Chem Phys*, 1997, 216: 243–257
- 38 Jimenez I, Gago R, Albella J M, et al. Identification of ternary boron-carbon-nitrogen hexagonal phases by X-ray absorption spectroscopy. *Appl Phys Lett*, 2001, 78: 3430–3432
- 39 Wong S S, Hemraj-Benny T, Banerjee S, et al. Investigating the structure of boron nitride nanotubes by near-edge X-ray absorption fine structure (NEXAFS) spectroscopy. *Phys Chem Chem Phys*, 2005, 7: 1103–1106
- 40 Niibe M, Miyamoto K, Mitamura T, et al. Identification of B-K near edge X-ray absorption fine structure peaks of boron nitride thin films prepared by sputtering deposition. *J Vac Sci Technol A*, 2010, 28: 1157–1160
- 41 Petravic M, Peter R, Kavre I, et al. Decoration of nitrogen vacancies by oxygen atoms in boron nitride nanotubes. *Phys Chem Chem Phys*, 2010, 12: 15349–15353
- 42 Caretti I, Jimenez I. Point defects in hexagonal BN, BC(3) and BC(x)N compounds studied by X-ray absorption near-edge structure. *J Appl Phys*, 2011, 110: 023511
- 43 Vincent H, Chassagneux F, Vincent C, et al. Microtexture and structure of boron nitride fibres by transmission electron microscopy, X-ray diffraction, photoelectron spectroscopy and Raman scattering. *Mater Sci Eng A*, 2003, 340: 181–192
- 44 Poncin-Epaillard F, Chevet B, Brosse J C. Modification of isotactic polypropylene by a cold plasma or an electron beam and grafting of the acrylic acid onto these activated polymers. *J Appl Polym Sci*, 1994, 53: 1291–1306
- 45 Dai X J, Chen Y, Chen Z Q, et al. Controlled surface modification of boron nitride nanotubes. *Nanotechnology*, 2011, 22: 245301
- 46 Gengenbach T R, Chatelier R C, Griesser H J. Characterization of the ageing of plasma-deposited polymer films: Global analysis of X-ray photoelectron spectroscopy data. *Surf Interface Anal*, 1996, 24: 271–281
- 47 Kemnitz C R, Loewen M J. “Amide resonance” correlates with a breadth of C–N rotation barriers. *J Am Chem Soc*, 2007, 129: 2521–2528
- 48 Li L H, Dai X J, Xu H S, et al. Combined continuous wave and pulsed plasma modes: For more stable interfaces with higher functionality on metal and semiconductor surfaces. *Plasma Process Polym*, 2009, 6: 615–619
- 49 Dai X J, Zhao J H, Michalski W P, et al. Controlling cell growth on titanium by surface functionalization of heptylamine using a novel combined plasma polymerization mode. *J Biomed Mater Res A*, 2011, 97A: 127–134
- 50 Zhang M X, Qing G Y, Sun T L. Chiral biointerface materials. *Chem Soc Rev*, 2012, 41: 1972–1984
- 51 Qing G Y, Sun T L. The transformation of chiral signals into macroscopic properties of materials using chirality-responsive polymers. *NPG Asia Mater*, 2012, 4: e4