Surface Chemistry

Responsive Aligned Carbon Nanotubes**

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Aligned carbon nanotubes (ACNTs)[1] have aroused great interest because of their ability to align and their easy integration into microdevices. Surface modification of ACNTs by responsive molecules is still a challenge, but it could help to obtain better control over their properties and thus may bring about more opportunities for their application. Wettability[2] is a basic property of solid surfaces and is important in both fundamental research and industrial applications. We have reported previously superhydrophobicity on ACNT films[3] as well as control over the wettability of the films by controlling the tropism of the carbon nanotubes (CNT) and adjusting the structural parameters.[4] Herein, we report the modification of ACNT films with poly(*N*-isopropylacrylamide) (PNIPAAm),[5] a temperature-responsive polymer, through surface-initiated atom transfer radical polymerization (SI-ATRP),[6] a method which can be easily extended to modification with other responsive polymers. Both the macroscopic and the microscopic properties of the modified ACNTs exhibit remarkable responsiveness. On the macroscopic scale the ACNT film shows distinct temperature-sensitive wettability, while on the microscopic scale atomic force microscopy (AFM) studies indicate that a single CNT on this film is also temperature responsive—its diameter and rigidity can change with variation of the temperature. This responsiveness is important in applications of ACNTs, including in intelligent microdevices.[7]

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The SI-ATRP technique provides a "graft-from" approach to fabricate a polymer film on a solid surface, and has been applied in the functionalization[8] of multiwall CNT surfaces.[8c,d] In this study we used this technique to achieve PNIPAAm modification of ACNTs that had been deposited on a silicon substrate by chemical vapor deposition (CVD). The experiments involve four steps: 1) ACNTs functionalized with carboxy groups[3a,8c,8d] were obtained by immersing an ACNT film in hot (80 °C) concentrated nitric acid (63 %) for about two hours; 2) NH_2 groups were introduced onto the ACNT surface by refluxing the carboxy-functionalized ACNT film in a solution of aminopropyltrimethoxysilane in toluene; 3) initiators were anchored onto the surface by reaction of bromoisobutyryl bromide with the NH_2 groups; and 4) *N*-isopropylacrylamide was polymerized by SI-ATRP, which resulted in the PNIPAAm-modified ACNTs.

Comparison of the X-ray photoelectron spectra (see Supporting Information) of the ACNTs after the polymerization process with those of the fresh ACNTs, as well as the FTIR spectrum of the modified ACNTs (also see Supporting Information), show that PNIPAAm had been successfully coated onto the ACNT surface by the SI-ATRP process. The scanning electron microscopic (SEM) images for ACNT film with PNIPAAm modification (Figure 1 a,b) indicate that

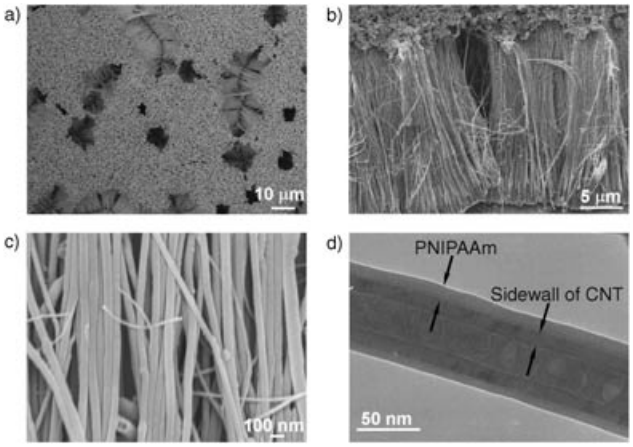

Figure 1. SEM and TEM images of PNIPAAm-modified ACNTs. SEM images viewed from the a) top and b) side. c) The magnified image of (b). d) TEM image of a single CNT taken from the ACNT film with PNIPAAm modification.

although there is some aggregation of the ACNTs (as shown by the holes in Figure 1 a), the aligned structure remains virtually intact after polymerization. The magnified image (Figure 1 c) of Figure 1 b shows a clear increase of about 15 nm in the average diameter of the CNTs relative to the fresh ACNTs, the diameter of which is about 15–50 nm (average value: ca. 39.7 nm). The transmission electron microscopy (TEM) image (Figure 1 d) of a single CNT taken from the PNIPAAm-modified ACNT film reveals a distinct layer of PNIPAAm with an average thickness of about 9.3 ± 2.0 nm compared to the TEM images (see Supporting Information) of fresh CNTs. This observation is consistent with the SEM results and further confirms the

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successful grafting of PNIPAAm. More interestingly, both the SEM and TEM images show that the modification layer is homogeneous and almost free of defects, thus indicating the good reliability of this polymerization method. Furthermore, this SI-ATRP technique can be easily extended to the modification of ACNTs with other responsive polymers; for example, we have modified the ACNTs with the electrosensitive polymer poly(2-acrylamido-2-methylpropane sulfonic acid) by a similar process, and will be reported later.

PNIPAAm-modified solid surfaces are reported to exhibit responsive wettability,[9] which is considered to result from the competition between intermolecular and intramolecular hydrogen bonding below and above the lower critical solution temperature of about 32–33 °C.[10] For example, we demonstrated previously[11] a reversible switching between superhydrophilicity and superhydrophobicity in a temperature range of about 10 °C on a PNIPAAm-modified rough substrate. Thus, the wettability on a PNIPAAm-modified ACNT film was also expected to be responsive to variation in temperature.

The wettability of the ACNT films with and without PNIPAAm modification was investigated by measurement of the contact angle (CA). The fresh ACNT film shows a superhydrophobicity with a contact angle of $159.5 \pm 2.2°$, while after functionalization with NH_2 groups and initiator molecules the film is much more hydrophilic, with CA values of 0 and $36.0 \pm 2.4°$, respectively; no temperature-responsive behavior was observed for any of these contact angles. Figure 2 shows the spreading behavior of a water droplet on a

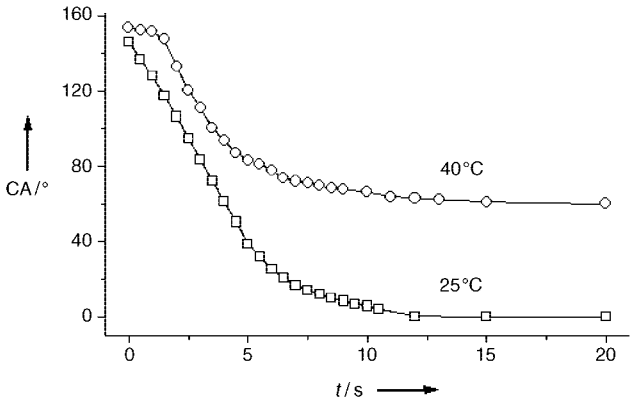

Figure 2. The spreading behavior of a water droplet on a PNIPAAm-modified ACNT film under different temperatures.

PNIPAAm-modified ACNT film under low (25 °C) and high (40 °C) temperatures. The water droplet spreads out quickly at low temperature, and superhydrophilicity with a contact angle of about 0° could be reached in about 10 seconds. At a higher temperature, however, the film remained superhydrophobic with a contact angle of about 150° for about 1.5 seconds before the water droplet started to spread to give a CA value of $63.7 \pm 1.8°$ (after about 10 seconds). This result indicates that this film is temperature-responsive and that the wettability can be controlled by variation of the temperature. More importantly, good reproducibility and reversibility of this effect was observed in experiments with repeated cycling of the temperature from 25 °C to 40 °C, and the recovery process is quick (less than 5 minutes, depending on the time needed for the water droplet to dry on the slice), thus indicating that the responsive wettability can be controlled. In contrast with the wettability switching on a PNIPAAm-modified rough silicon substrate,[11] the modified ACNT film did not show a superhydrophobic property at high temperatures, but was relatively hydrophilic. We consider this property occurs because of the looser configuration of the PNIPAAm chains as a result of the low concentration of the surface-bonded initiator (see Supporting Information) and the structural factors of the film, for example, the partial loss of roughness induced by PNIPAAm grafting.

The intermolecular and intramolecular hydrogen-bonding interactions between the PNIPAAm chains lead to an extended and a compact configuration of the PNIPAAm chains, respectively, which can result in another important property of PNIPAAm: the temperature-induced swelling and shrinkage of the volume. For example, Jones et al.[12] reported a volume change of about 30 % for a surface-modified layer of PNIPAAm when the temperature was raised from 25 to 35 °C. The microscopic properties of a single CNT form the foundation of the macroscopic properties of the ACNT film. Therefore, to confirm the temperature responsiveness of the PNIPAAm-modified ACNTs we carried out further experiments to investigate the temperature-induced contraction of the PNIPAAm layer on a single CNT by using an AFM apparatus equipped with a high-temperature facility.[13] Figure 3 a,b shows the AFM images of a single CNT taken from the PNIPAAm-modified ACNT film at temperatures of 25 and 40 °C, respectively. A clear reduction in the diameter of the nanotube, which is about 4.3 ± 0.3 nm, can be observed with an increase of temperature. The images indicate a contraction of 21–25 % in the film thickness of the PNIPAAm-modification layer compared to that of the original thickness, as determined by TEM. The corresponding phase images (Figure 3 c,d) also show a distinct change when the temperature is changed from 25 to 40 °C. The PNIPAAm-modified CNT exhibits a phase difference of about 15.4° relative to the surrounding silicon substrate at 25 °C, while this difference changes to only about 7.4° at 40 °C, thus indicating that the rigidity of the PNIPAAm layer increases with the increase in temperature. This result can be explained by the PNIPAAm chains becoming denser with the elevation of temperature. These effects further confirm the temperature responsiveness of the PNIPAAm-modified ACNTs, and are also very important for both CNTs and ACNTs in applications as intelligent microdevices, for example, as a transducer for temperature control in a microsystem.

In conclusion, we successfully grafted PNIPAAm onto ACNTs by using an SI-ATRP method and observed the temperature responsiveness of the resulting surface. A water droplet exhibits different spreading behaviors on the film surface, which shows different wettability under low and high temperatures. The good reproducibility of this effect shows a high degree of control over the responsive wettability of the ACNT film. Correspondingly, a distinct reduction in the diameter of the modified CNT, as well as a clear increase in the rigidity of its surface can be observed with an increase of

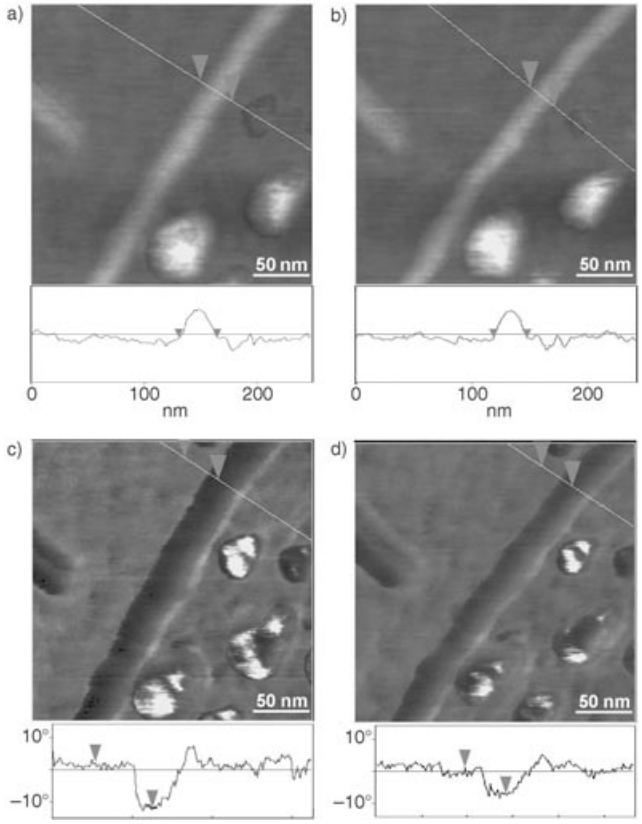

Figure 3. AFM images of a single CNT taken from the PNIPAAm-modified ACNT film under different temperature. a, b) Morphological images; c, d) corresponding phase images; a), c) 25 °C; b), d) 40 °C.

temperature, which is the result of the temperature-induced contraction of the PIPAAm modification layer. This responsiveness of ACNTs may help to obtain better control over their properties, and thus extend their range of applications.

Experimental Section

Preparation of an ACNT film on a silicon substrate: These were prepared by pyrolysis of iron phthalocyanines (FePc) containing both the metal catalyst and carbon source required for the growth of the nanotube. The pyrolysis of FePc was performed under an Ar/H_2 (1:2 v:v) flow of 50–60 $cm^3 min^{-1}$ at 600–900 °C on a 1×1 cm^2 cleaned silicon template in a flow reactor consisting of a quartz glass tube and a furnace fitted with an independent temperature controller. The pyrolysis time was 1 h.

Modification of PNIPAAm on ACNTs: The ACNT film was firstly left to stand for at least one week and then put in a high-vacuum chamber (for example, the high-vacuum chamber of a SEM apparatus) for about 3 h before further treatment to gain better stability of the aligned structures of the ACNTs in the subsequent experiments. The ACNT film was immersed in hot (80 °C) concentrated nitric acid (63 %) for at least 2 h to generate hydrophilic groups, such as carboxy or hydroxy, on the ACNT surface. After washing the film with copious amounts of double-distilled water, it was dried in a vacuum oven at room temperature. It was then refluxed in a solution of aminopropyltrimethoxysilane in toluene at a concentration of about 5 wt % for about 6 h to obtain a NH_2-functionalized ACNT film. The subsequent polymerization of PNIPAAm was carried out for 3 h by using the method previously reported.[11]

Water contact angle, SEM, and TEM measurements: The water contact angle was measured on a SCA20 system (Dataphysics) with a super-thermostat. The measurement was conducted under saturated humidity. The SEM images were obtained on a field emission SEM apparatus (JSM-6700F, JEOL). The CNTs were scratched from the ACNT film and then dispersed in water by super-sonication, after which a droplet of water containing CNTs was dropped onto a copper mesh containing 400 grids. The TEM images were obtained on a JEM-100CXII (JEOL).

AFM studies: The CNTs were scratched from the ACNT film and then dispersed in water by super-sonication, after which a droplet of water containing CNTs was dropped onto a hydrophilic silicon wafer. The AFM images and the corresponding phase images of a single CNT were obtained in the tapping mode on a NanoScope IIIA MultiMode AFM (Digital Instrument) with a hot stage, at temperatures in the range of 20–50 °C.

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