Supporting Information

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I. X-ray Electron Spectroscopy (XPS) Result for ACNT film with PNIPAAm modification

XPS data were collected on an ESCA Lab 220i-XL (VG Sci., UK), using a monochromatic Al K X-ray source. The photoemission angle was 30°. The elemental compositions were determined from the peak area of the XPS spectra. The compositions of the elements C, O, N, and Si at untreated ACNTs surface are respectively 77.2, 11.2, 10.7, 0.8, percents, respectively. The surface showed a distinct content of N atom, while the XPS result for the fresh ACNT film showed only a very small N atom content. Furthermore, the surface composition ratio for C, N, O atoms is approximately 7.7:1:1. Comparing with that of the theoretical atom composition ratio of 6:1:1, the compositions for N and O atom show good consistency, while the C atom composition is relatively a little higher, which is considered to be the influence of the CNT. These results indicate that PNIPAAm has been coated on to the surface of ACNTs.

II The FT-IR Investigation of PNIPAAm Modified ACNT Film

The IR spectroscopy of the PNIPAAm modified ACNTs (Figure S1) was measured by the instrument
of EQINOX55 (Bruker). 20 scans were collected between 4000 and 370 cm\(^{-1}\), and the resolution is 1 cm\(^{-1}\). The PNIPAAm modified ACNTs were scratched from the silicon substrate, and then the IR experiment was done by the transmission mode with the KBr powder.

In Figure S1, the sharp absorption peak at 3425 cm\(^{-1}\) is considered to be the stretch for the \(\text{─OH}\) group of water that bonded to the polymer chain through intermolecular hydrogen bonding, while the boulder peak at 3286 can be attributed to the stretch for the hydrogenbonded \(\text{─NH}\) group. The antisymmetric stretching vibration of the \(\text{─CH}_3\) and/or \(\text{─CH}_2\) groups can be formed at 2923 cm\(^{-1}\).

The C=O groups give rise to a strong band at 1644 cm\(^{-1}\). The mixed vibration of C─N and N─H appears at 1386 cm\(^{-1}\), and the antisymmetric deformation of \(\text{─CH}_3\) is at 1457 cm\(^{-1}\). Since the major absorption peaks of the ACNTs grafted by the uncross-linked PNIPAAm layer are the same as those of commercial linear PNIPAAm (see Figure S2), it is reasonable to conclude that the surface of the ACNTs has been coated by PNIPAAm.

![Figure S1. FT-IR result for PNIPAAm modified ACNTs](image_url)
Figure S2. FT-IR spectrum for commercial linear PNIPAAm.

III SEM Images of Fresh ACNTs

Figure S3. SEM images of fresh ACNTs from top view (A) and side view (magnified image) (B)

III TEM Image of A Single CNT before PNIPAAm Polymerization
IV. Responsive Wettability on the PNIPAAm Film from A Low Concentration of Initiator.

The surface concentration of initiator was lowered by forming mixed self-assembled layer of \((\text{CH}_3\text{O})_3\text{CH}_2\text{CH}_2\text{NH}_2\) and \(\text{CF}_3(\text{CF}_2)_8\text{CH}_2\text{Si}(\text{OCH}_3)_3\), which is inert. The solution concentration ratio of \((\text{CH}_3\text{O})_3\text{CH}_2\text{CH}_2\text{NH}_2\) and \(\text{CF}_3(\text{CF}_2)_8\text{CH}_2\text{Si}(\text{OCH}_3)_3\) was 1:7 and 1:19. The XPS data indicated that the surface concentration of \text{NH}_2 group was much lower than that of the homogeneous film of \((\text{CH}_3\text{O})_3\text{CH}_2\text{CH}_2\text{NH}_2\), and a relatively large surface concentration of \text{F} atom existed. Because the initiator molecules can only react with \text{NH}_2 group, it can be inferred that the initiator concentration is diluted by \(\text{CF}_3(\text{CF}_2)_8\text{CH}_2\text{Si}(\text{OCH}_3)_3\). However, the AFM images (Figure S5) for the PNIPAAm film grown from this diluted initiator surface is homogeneous, therefore, it can be inferred that the PNIPAAm chain did not grow upwardly, but spread all around, and it may take a much looser configuration.

The surface concentration of initiator on ACNT is determined by that of defects on their surface, because the generation of hydrophilic \(-\text{COOH}\) or \(-\text{OH}\) groups can only occur at these places. Therefore, it can be inferred that the surface concentration of initiator molecules is low and thus the PNIPAAm chains can be looser than the densely packed state.
Figure S5. Typical AFM image for PNIPAAm film fabricated from the mixed layer of initiator and CF₃(CF₂)₈CH₂CH₂Si(OCH₃)₃ (solution concentration ratio for (CH₃O)₃CH₂CH₂NH₂ and CF₃(CF₂)₈CH₂CH₂Si(OCH₃)₃ is 1:19). (a) morphological image; (b) phase image

Figure S6 shows the temperature dependences of water CA on PNIPAAm film grown from the pure initiator layer and the mixed layer of initiator and CF₃(CF₂)₈CH₂CH₂Si(OCH₃)₃. It shows from the figure that although the hydrophobic material—CF₃(CF₂)₈CH₂CH₂Si(OCH₃)₃ was used to dilute the surface concentration of initiator, the wettability of two PNIPAAm films grown from the diluted initiator surface at both low and high temperatures exhibited more hydrophilic properties. This effect is considered to be due to that the PNIPAAm chains became much looser because of the dilution of the surface-bonded initiators, which made the hydrophilic groups, such as −C=O and −NH₂.
Figure S6. Temperature dependences of water CA on PNIPAAm film grown from the pure initiator layer (○) and the mixed layer of initiator and CF₃(CF₂)₈CH₂CH₂Si(OCH₃)₃ (△ and □). The ratio for solution concentration of (CH₃O)₃CH₂CH₂NH₂ and CF₃(CF₂)₈CH₂CH₂Si(OCH₃)₃ were 1:7 (□) and 1:19 (△), respectively.