

Electronic Supplementary Information

Twofold pH and Temperature Stimuli-responsive Behaviour in Block Copolypeptide-Decorated Single Wall Carbon Nanotubes

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Experimental Part

Materials

Poly(*N*-isopropylacrylamide)-*block*-poly(L-glutamic acid-*co*-L-lysine) [PNiPAM-*b*-(PLG-*co*- PLLys)] was prepared according to the previous report.¹ PNiPAM-*b*-PLG-*b*-PLLys triblock was prepared by ring-opening polymerization of lysine anhydride from PNiPAM-*block*-PBLG according to the previous report.² CarboLex AP-grade SWCNTs synthesized by arc discharge were purchased from Sigma. According to the specification, they consist of 50~70 % carbon basis with the bundle size of 1.2-1.5 nm × 2-5 μm. The SWCNTs were purified by annealing at 300 °C in air for 30 min, refluxing in nitric acid (2 M) for 20 h and then filtering via 0.22 μm membrane. After being washed by distilled water to pH 7, the SWCNTs were kept in vacuum for at least 24 h before using.

SWCNT Aqueous Solutions Preparation

The block copolymer aqueous solutions (0.6 wt.-%) were prepared and adjusted to a pH of 2.5, 7 and 12.5, respectively. SWCNTs were added to the block copolymer solutions at a weight ratio of 1:10 (SWCNTs/block copolymer) and sonicated at room temperature for 40 min. Then the mixtures were centrifuged at room temperature for 1 h at a rate of 4000 rpm. The supernatant solutions were removed and used for characterization.

Characterization

Atomic force microscopy (AFM) was performed in an intermittent mode under ambient conditions at a scan rate of 2 Hz. Silicon nitride cantilevers with a typical tip radius below 10 nm were used. The AFM samples were prepared by depositing 20 μl solution onto freshly cleaved mica and incubating for 30 s. Then the sample was rinsed with millipore water and dried with air for measurements.

Dynamic and static light scattering (DLS & SLS) were performed using a 3D cross correlation Spectrometer (LS instruments) equipped with a HeNe laser ($\lambda = 632.8$ nm). The use of two detectors for the cross correlation allows extracting single-scattering information in both static and dynamic modes also for concentrated and highly scattering systems, such as SWCNT dispersions. The carbon nanotube solution was filled into a cylindrical glass tube of 10 mm inner diameter. The vial was placed in the center of a cylindrical vat filled with an index-matching fluid, cis-trans decahydronaphthalene (decalin). The temperature of the index-matching fluid was controlled between 0~40 °C (± 0.1 °C). For DLS, the time-averaged intensity correlation function was measured with the constant scattering angle ($\theta = 90^\circ$) at various temperatures. Before measurement, every temperature step was kept at least for 20 min

for equilibration. SLS measurements were performed within an angle range $20^\circ \leq \theta \leq 130^\circ$. The data were corrected with background subtraction (cell and solvent scattering)

Reference

1. J. Li, T. Wang, D. Wu, X. Zhang, J. Yan, S. Du, Y. Guo, J. Wang and A. Zhang, *Biomacromolecules*, 2008, **9**, 2670
2. X. Zhang, J. Li, W. Li and A. Zhang, *Biomacromolecules*, 2007, **8**, 3557.