

Supplementary Information

pH-Induced Formation of Hierarchical Structures from Preformed Amphiphilic Core-Shell Nanotubes

Cheng Hao Lee and Pei Li*

*Department of Applied Biology and Chemical Technology, The Hong Kong
Polytechnic University, Hung Hom, Kowloon, Hong Kong SAR, China*

**To whom correspondence should be addressed. E-mail: bcpeili@polyu.edu.hk*

Experimental details

Materials. Branched PEI (50% solution in water, $\langle M_n \rangle \sim 60,000$ g/mol) was purchased from Aldrich and used as-received. Methyl methacrylate (MMA, Aldrich) was purified by being washed three times with 10% (w/w) sodium hydroxide solution (MMA to NaOH (v/v) = 10 : 1), followed by repeated washing with deionized water (MMA to water (v/v) = 5 : 1) until the pH of the water dropped to 7. It was further purified by vacuum distillation prior to use. *tert*-Butyl hydroperoxide (70% w/w solution in water) was obtained from Acros and used as-received. Dichloromethane (DCM) was obtained from Lab-Scan. Freshly deionized and distilled water was used as the dispersion medium.

Determination of the grafting percentage of PEI-g-PMMA hollow particles. The prepared PMMA/PEI particles were purified by multiple cycles of centrifugation, decantation and rewetting. The purified particle dispersion was then dried with freeze-dryer (TFD 5505, Ilshin Lab. Co. Ltd.) at $-48\text{ }^{\circ}\text{C}$ with chamber pressure of 5 mTorr. The dried product was extracted with chloroform for 48 hrs using a Soxhlet extractor. The insoluble portion of PEI-g-PMMA copolymer remained in the thimble, while the PMMA homopolymer was dissolved in the chloroform. The grafting percentage is calculated as percentage of weight ratio of the grafted PMMA to the weight of charged PEI.

Synthesis of amphiphilic hollow particles and assembling to nanotubes.

Amphiphilic particles that consist of poly(methyl methacrylate) cores and branched poly(ethyleneimine) shells were synthesized according to our previously described method.^{S1,S2} The assembling process was carried out in a 20 mL jacketed flask covered with a Whatman filter paper (Whatman 2). Freeze-dried PMMA/PEI particles (0.05 g) were first mixed with 8 mL of dichloromethane. The suspension was gently stirred at 150 rpm at room temperature for 3 hrs to extract the PMMA homopolymer from the cores. Deionized water was then added dropwise (4.8 mL/min) to the DCM solution containing both the hollow particles and homopolymer, to a DCM to water volume ratios of 7:3. The resulting DCM/water mixture was subsequently stirred at

350 rpm with a magnetic stirrer. During this process, the solution temperature was thermostated by a water circulation using a temperature controlled circulator (IMT InMedtec Co.) at 25 °C. After the DCM being completely removed through evaporation, the PMMA homopolymer (white solids) became suspended in water and, was simply removed by filtration. A clear aqueous solution containing PEI-g-PMMA core-shell nanotubes was obtained.

Formation of various hierarchical structures under different solution pHs.

To study the effect of solution pH on the assembly of preformed PEI-g-PMMA nanotubes, the solution containing PEI-g-PMMA nanotubes (5mg/mL, pH = 6.5) was adjusted to various pHs (3.0, 5.0, 7.0, 9.0, 11.0 and 13.0) by a dropwise addition of either 0.01 M HCl or 0.01 M NaOH solution under gentle stirring (50 rpm). The final solution pH was measured by an Orion 555A pH meter. Each solution containing preformed nanotubes was subsequently stirred at 50 rpm for 24 hrs at 25 °C. Depending on the solution pH, the initial clear solution could turn into cloudy after several hours. The appearance of cloudiness indicated the formation of newly assembled materials.

FE-SEM characterization. Scanning electron microscopy images were obtained using a JEOL-JSM 6335F field-emission scanning electron microscopy (FE-SEM) at an accelerating voltage of 5 kV. Sample was prepared by placing a small

drop of dilute dispersion (~500 ppm) on a mica substrate, and allowed it to dry at room temperature for 24 hrs. The air-dried sample was subsequently sputtered with a thin layer of gold under vacuum to a depth of approximately 1-2 nm.

TEM characterization. Transmission electron micrographs were obtained using a JEOL 100 CX II TEM at an accelerating voltage of 100 kV. Sample was prepared by wetting a carbon-coated copper grid with a small drop of dispersion (10 μ L, 300 ppm). To enhance the contrast between PEI and PMMA components, the assembled materials were stained with phosphotungstic acid (PTA) solution after drying. For the preformed nanotubes, they were stained with 0.5 wt.% PTA solution for 1 minute. In the case of hierarchical structures, they were stained with 2 wt. % (w/w) PTA solution for 3 minutes. All stained samples were then dried at room temperature before analysis.

AFM characterization. Morphologies of self-assembled nanotubes were also investigated using a Nanoscope IV Atomic Force Microscope (AFM, Digital Instruments) with a NSIV controller in a fluid tapping mode using a V-shaped silicon nitride (Si_3N_4) cantilever (NP-S, 200W, Veeco Probes, CA) at a frequency of 8 ± 0.5 kHz. Images were acquired after 5 min. of sample injection, and continued for several hours. Aqueous sample (100-200 μ L, 2 mg mL⁻¹) was thermally equilibrated to the temperature of fluid cell, and then injected into the cell at a rate of 10 μ L s⁻¹. The scan

sizes of AFM images were 0.7 and 1 μm , respectively, and the scan data were acquired at 0.5 Hz scan rate with a resolution of 512×512 lines.

***zeta*-Potential measurement.** ζ -Potential measurements were conducted on a Malvern Zetasizer 3000 HAS (Malvern, UK) with a 30 mW solid-state laser operated at a laser wavelength of 635 nm He-Ne laser. The measurements were performed at 25 $^{\circ}\text{C}$ at a concentration of ~ 0.05 mg/mL in 1mM NaCl (as dispersant medium). The pH values of the nanotube solution were adjusted from 3.0 to 13.0 by adding either 0.01 M hydrochloric acid or 0.01 M sodium hydroxide solution. Each ζ -potential value was an average of triplicate measurements.

The ζ -potential was calculated based on the measured electrophoretic mobility (μ), using Smoluchowski Approximation as defined in Eq. (1),

$$\mu = \frac{\zeta \epsilon_m V}{4\pi\eta D} \quad (1)$$

where V is the applied voltage, η is the viscosity of the solution, ϵ_m is the dielectric constant of the medium, and D is the electrode separation distance. Although this equation is valid for particles with spherical shape, *zeta*-potential measurement of higher-aspect ratio structures such as carbon nanotubes have also been reported.^{S3,S4}

It was suggested that the spherical Smoluchowski Approximation may overestimate the actual ζ -potential of the nanotubes by up to 20%.

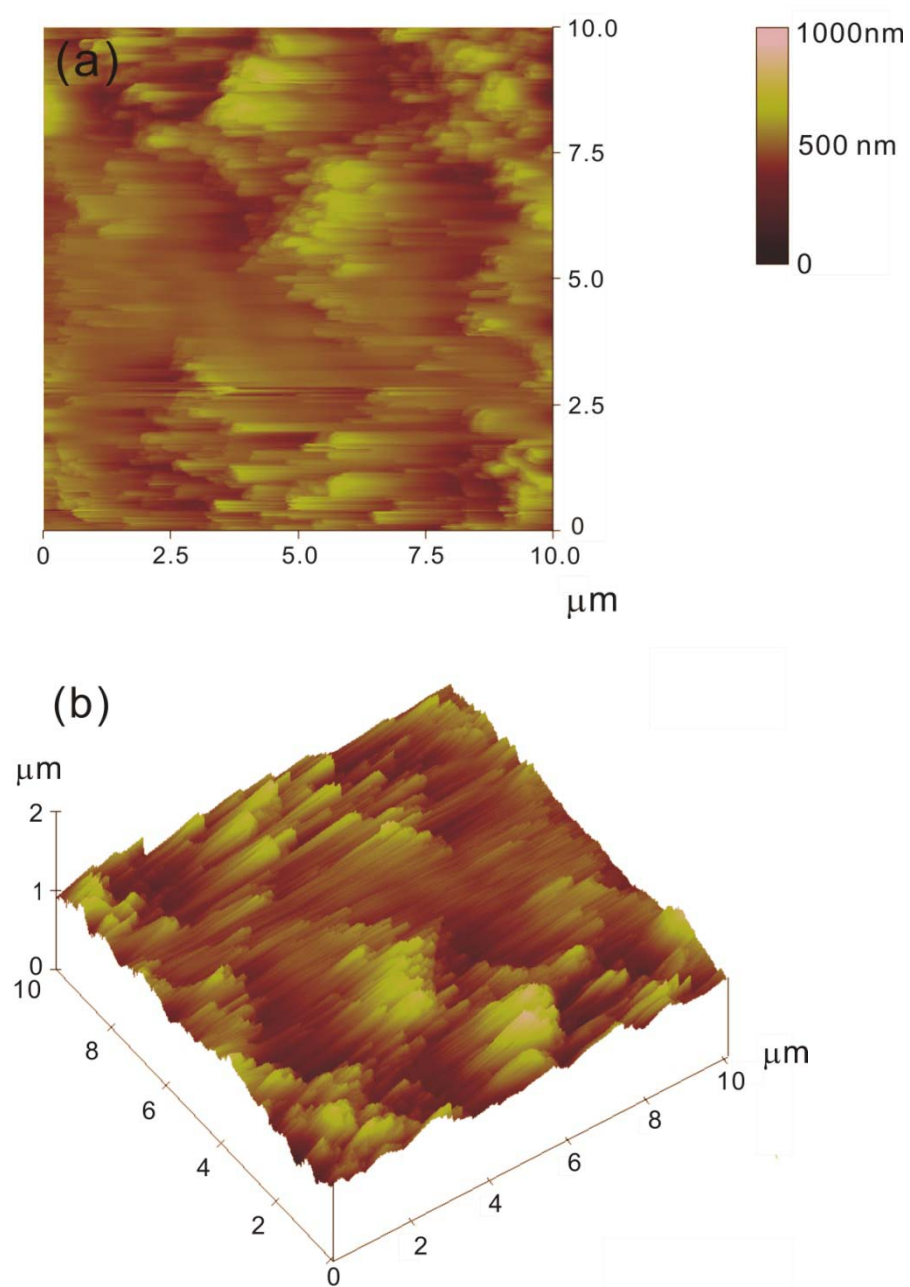


Fig. S1 AFM image of columnar structures in (a) 2D and (b) 3D profiles. The hierarchical structure was assembled from preformed nanotubes in aqueous solution of pH 9.

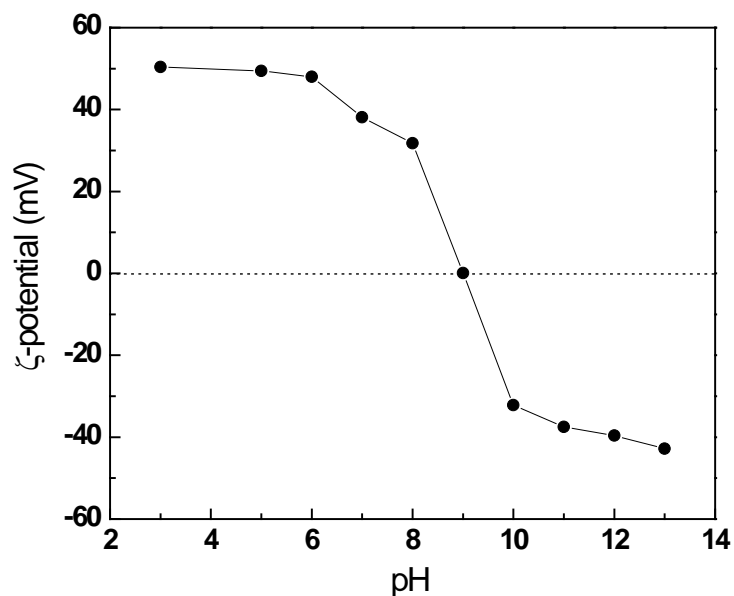


Fig. S2 ζ -potential of PEI-g-PMMA nanotubes as a function of solution pH. The preformed nanotubes were dispersed in 1 mM NaCl solution at 25 °C at a concentration of ~ 0.05 mg/mL .

References

- S1. P. Li, J. Zhu, P. Sunintaboon and F. W. Harris, *Langmuir*, 2002, **18**, 8641-8646.
- S2. C. H. Lee, K. M. Ho, S. Z. D. Cheng, F. W. Harris, P. Li, *Soft Matter*, 2009, **5**, 4914-4921.
- S3. B. White, S. Banerjee, S. O'Brien, N. J. Turro, I. P. Herman, *J. Phys. Chem. C*, 2007, **111**, 13684-13690.
- S4. H. Hu, A. Yu, E. Kim, B. Zhao, M. E. Itkis, E. Bekyarova, R. C. Haddon, *J. Phys. Chem. B*, 2005, **109**, 11520-11524.