Supporting Information

Repeated Protrusion of Pyrene Nanorods on the Surface of Crosslinked Poly(allylamine hydrochloride) Microcapsules

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Experimental Section

Materials

Poly(allylamine hydrochloride) (PAH, Mn~56kDa), 1-pyrenecarboxaldehyde (Py-CHO), calcium nitrate tetrahydrate ($Ca(NO_3)_2 \cdot 4H_2O$), sodium carbonate (Na_2CO_3), ethylenediaminetetraacetatic acid (EDTA) and glutaraldehyde were purchased from Aldrich. Hydrochloride (HCl) solution (1mol/L) was purchased from Merck Company and diluted to a desired concentration. Other chemicals were used as received. The water used in all experiments was prepared *via* a Millipore Milli-Q purification system and had a resistivity higher than 18MΩ.cm.

Analytic techniques

Scanning electron microscopy (SEM) images were recorded with a Gemini Leo 1550 microscope at an acceleration voltage of 3kV. Transmission electron microscopy (TEM) images were obtained with a Zeiss EM 912 Omega microscope at an acceleration voltage of 120 kV. Confocal laser scanning (CLSM) images were taken on a LEICA TCS system (Aristoplan, Germany, 100 × oil immersion using commercial software). The samples were dropped onto copper grids with a carbon film (for

TEM), silicon wafers (for SEM), and glass slides (for CLSM), and air-dried in case needed, respectively.

Fabrication of PAH-Py-GA MCs

The PAH-doped $CaCO_3$ particles were fabricated according to literature (Z. P. Wang, H. Moehwald and C.Y. Gao, Nanotubes protruding from poly(allylamine hydrochloride)-graft-pyrene microcapsules, *ACS Nano,* 2011, 5, 3930-3936.). Briefly, PAH was dissolved in 100 mL of 0.33 M calcium nitrate solution in a beaker under magnetic agitation (~600 rpm), into which an equal volume of 0.33 M sodium carbonate solution was rapidly poured at room temperature. The final PAH concentration was adjusted to 2 mg/mL. After 20 min, the PAH doped $CaCO_3$ particles were centrifuged and washed 3 times to remove free PAH and salts. The as-prepared PAH-doped $CaCO_3$ microparticles were dispersed in ethanol and mixed with excess Py-CHO/ethanol solution. After the mixture was kept in a vessel under mild agitation for 2h, centrifugation and washing by ethanol were performed several times until the excess Py-CHO was washed away. Then the as-prepared PAH-Py-doped $CaCO_3$ microparticles were dispersed in 1% GA aqueous solution. After mild agitation for 2h, centrifugation and washing by ethanol were performed several times until the excess GA was washed away. Finally, the microparticles were incubated in 0.2 M ethylenediaminetetraacetatic acid (EDTA) solution for 15min under shaking to obtain the PAH-Py-GA MCs. The MCs were further washed with fresh EDTA solution and water, each for 3 times using centrifugation (2000g, 3 min).

Fabrication of MC-NRs composites

The as-prepared PAH-Py-GA MCs were incubated and dispersed in HCl solution with different pH under shaking. After certain time, one portion of the solution was neutralized by 1 M NaOH solution, followed by gentle centrifugation and washing for 3 times.

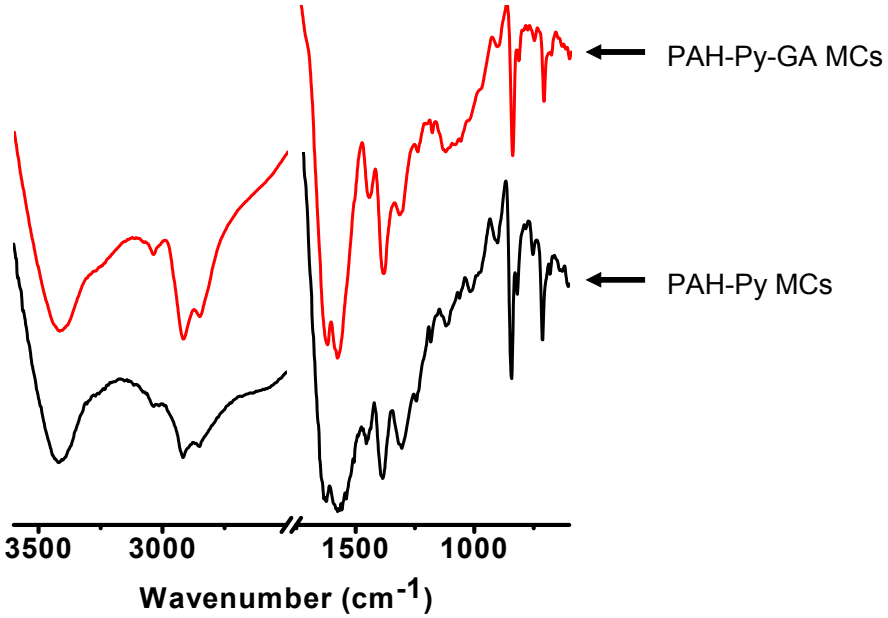

Figure S1. FTIR spectra of PAH-Py MCs and PAH-Py-GA MCs.

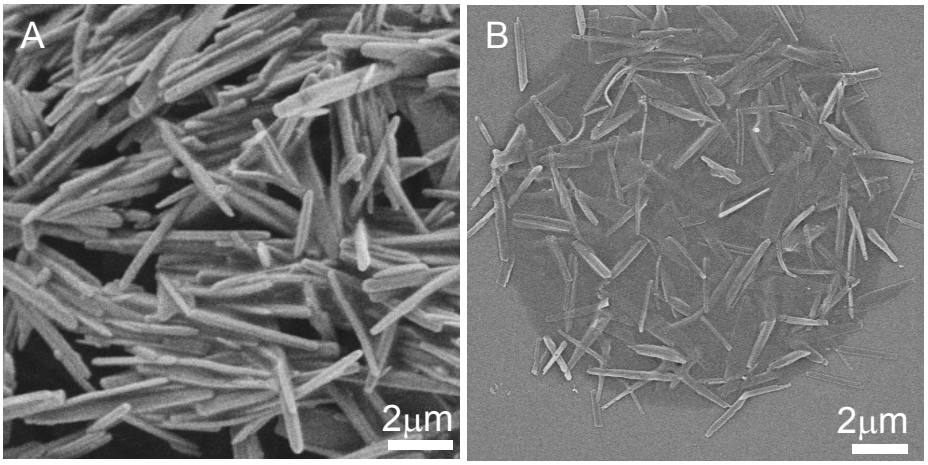

Figure S2. (A) SEM images of 1D-NRs formed by PAH-Py MCs at pH 1.5 for 4 h, and (B) a PAH-Py MC protruded with NRs after treatment at pH 1.5 for 2 h.

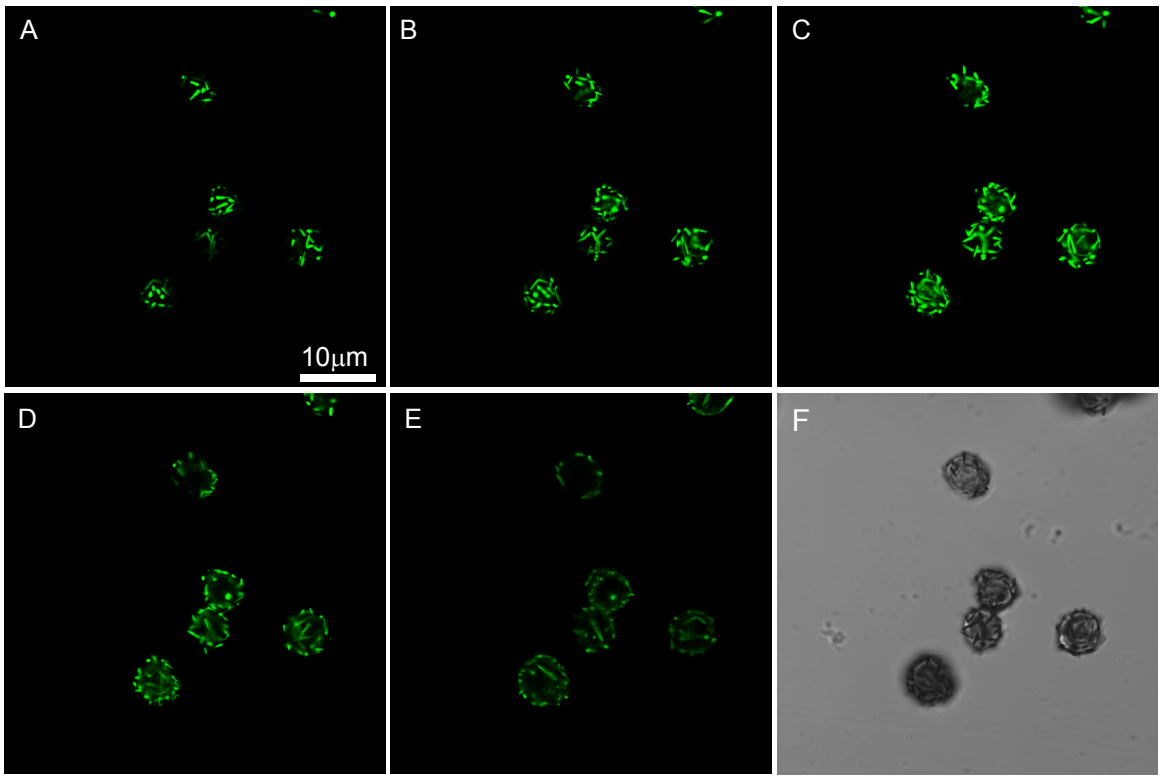

Figure S3. (A-E) Z series scanning CLSM images of PAH-Py-GA MCs protruded with Py-CHO NRs.

(F) transmission channel image.

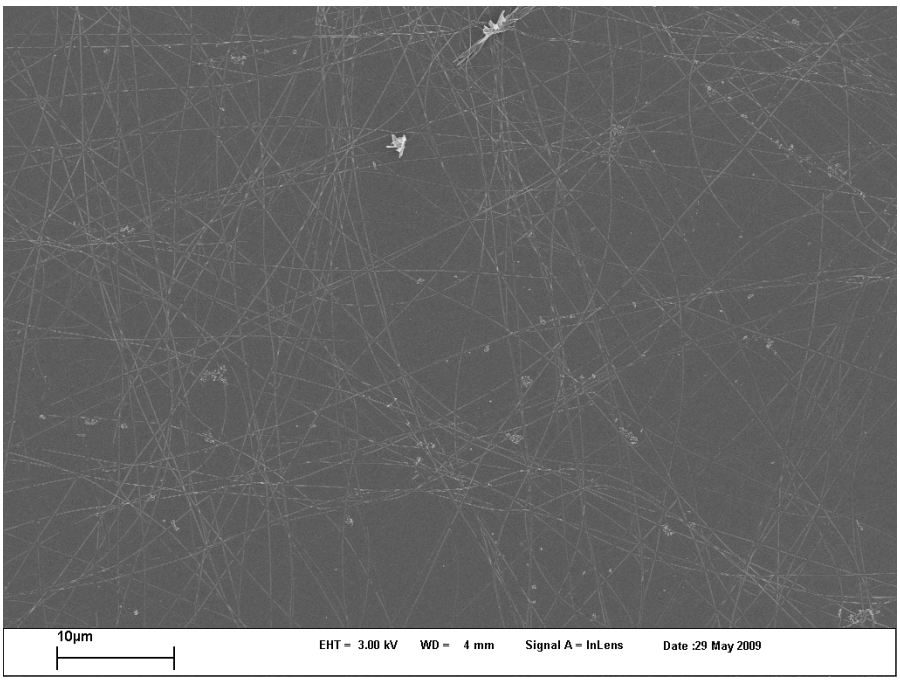

Figure S4. SEM image of nanotubes grown from uncrosslinked PAH-Py MCs.

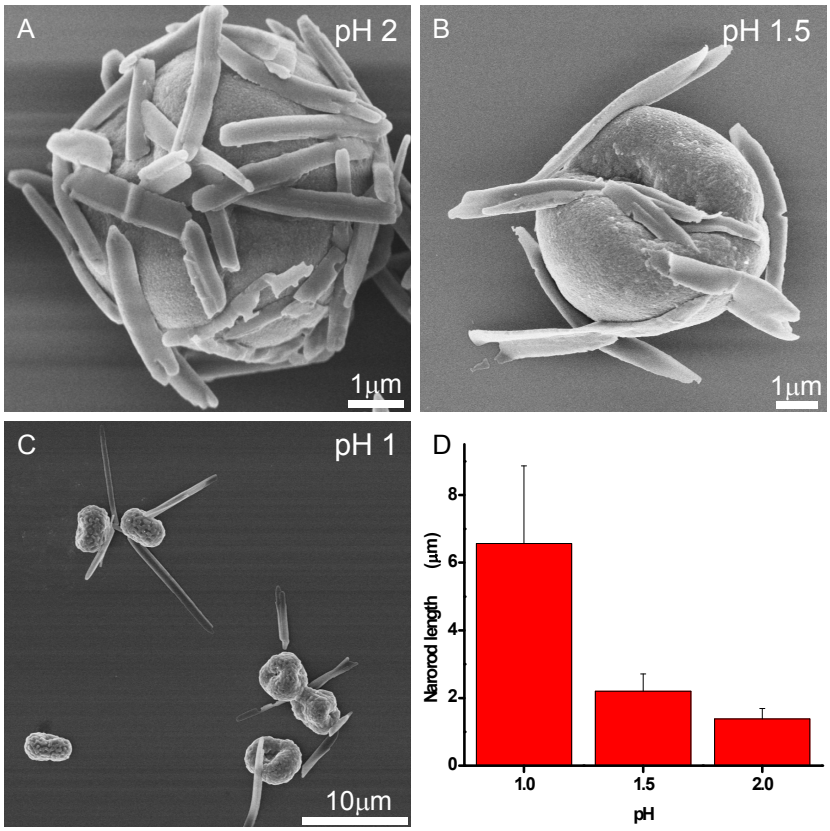

Figure S5. SEM images of PAH-Py-GA MCs protruded with Py-CHO NRs at (A) pH 2, (B) pH 1.5, and (C) pH 1, respectively. (D) The NRs length at different pH.

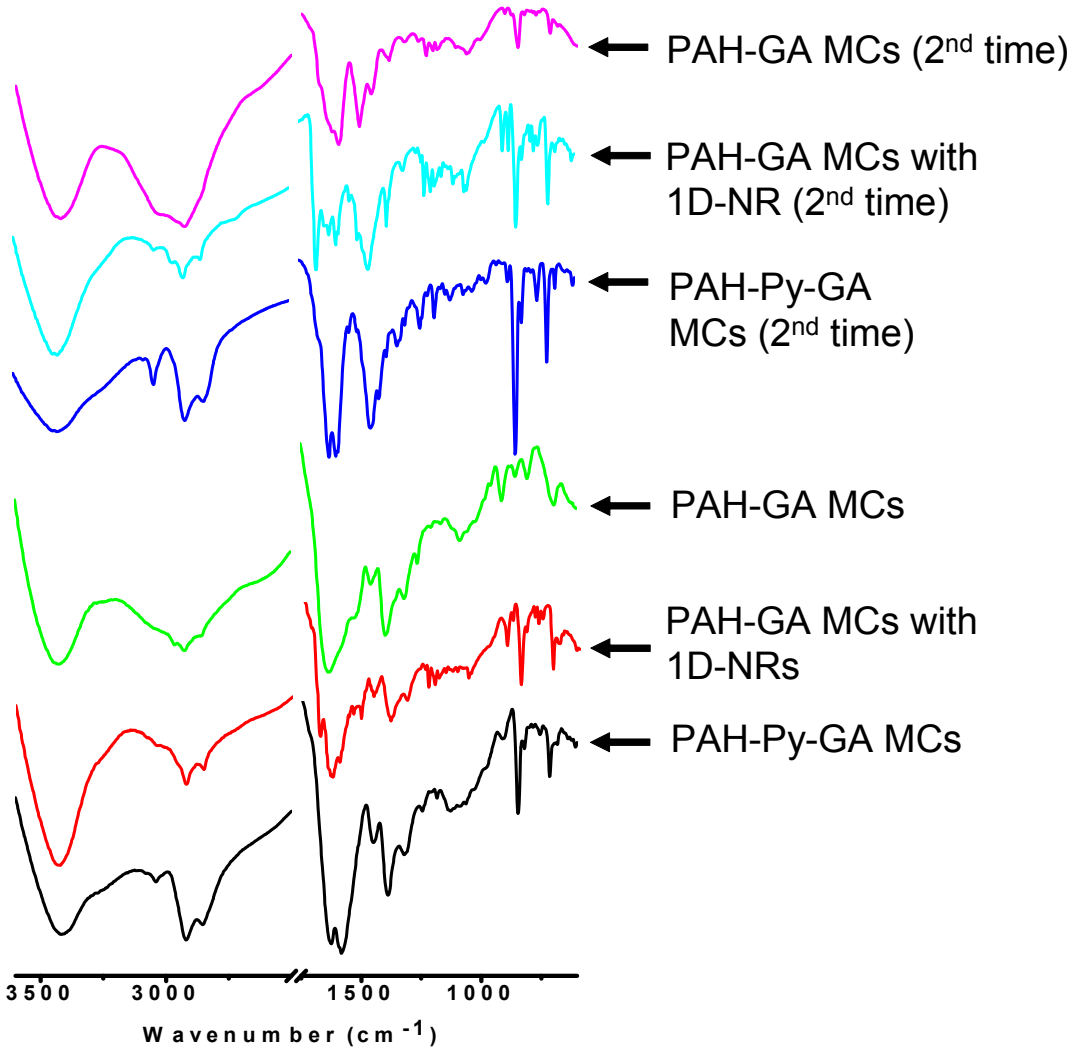

Figure S6. Confirmation of the chemical structure variation by FTIR spectroscopy during the twice 1D-NR formation from the PAH-Py-GA MCs.