Chemical Communications (RSC)

Supporting Information:

Capsulation of Carbon Nanotubes on Top of Colloidally Templated and Electropolymerized Polythiophene Arrays

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1. Experimental

1.1 Materials

Polystyrene latex microbeads (0.5 μm in diameter, 2.5% solids (w/v) aqueous suspension, 3.64×10^{11} particles/ml) were purchased from polyscience co. and used without any purification. These particles contain a slight anionic charge from sulfate ester. Sodium *n*-dodecyl sulfate (SDS) was used to control the organization of the PS microbeads at the air-water interface. Millipore water (18 MΩ.cm) was used to dilute the PS suspension solution and to control the total concentration of the mixture solution. Terthiophene acetic acid (3-TAA) was synthesized as reported in literature.[1]

1.2 Preparation of Amino-functionalized MWNTs

1.2.1 Carboxylated MWNTs[2]

Multi-walled carbon nanotubes (MWNTs, 660 mg) obtained from ILJIN Co. (CVD, 95 % purity) were soaked with hydrochloric acid (HCl) for 24 hrs. The dispersed solution was transferred into 500 mL of millipore water, filtered (pore 0.1 μm filter; Whatman Nylon membrane filter) and washed with millipore water again (pH=7). The MWNTs were dried in the vacuum oven at 60°C for 20 hrs. The purified MWNTs (647 mg) was added in 80 mL of sulfuric acid (H_2SO_4)/nitric acid (HNO_3) (3:1 volume ratio) solution and sonicated for 8 hours. The dispersed solution was poured in an excess pure water, filtered (0.2 μm pore size) and then washed with water several times to be pH=7. After the filtration of the neutral solution, the filtrate was dried in the vacuum oven. The total amount of the carboxylated MWNTs (MWNT-COOH) was 632.1 mg.

1.2.2 Thionyl chlorination[3]

The MWNTs-COOH (322 mg) in a Schlenk flask tube and 20 mL of thionylchloride in the other flask were prepared. After nitrogen gas flow for 30 minutes, the thionylchloride was transferred into the tube with the MWNTs-COOH through a syringe, sonicated for 5minutes and then heated at 65°C under stirring for 24 hrs. The solution was filtered and washed with dried THF (200 mL). The thionyl

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[1] A. Yassar, C. Moustrou, H. Korri Youssoufi, A. Samat, R. Guglielmetti, and F. Garnier, *Macromolecules* 1995, **28,** 4548.
[2] B. Kim, H. Park, and W. M. Sigmund, *Langmuir* 2003, **19,** 2525.
[3] H. Kong, C. Gao, and D. Yan, *Macromolecules* 2004, **37**, 4022.

chlorinated MWNTs (MWNTs-COCl) were dried in the vacuum oven at room temperature.

1.2.3 Amidation[4]

The MWNTs-COCl (324.0 mg) and 10 mL of 1,3-diaminopropane in a Schlenk flask was sonicated for 5 minutes and reacted at room temperature for 24 hrs under nitrogen gas flow and then in 5 mL of triethylamine (TEA) and 5 piece of 4-(dimethylamino)pyridine (DMAP) at 70 ^{o}C for 24 hrs. The dispersed solution was filtered and washed with dichloromethane, and then dried at vacuum oven at room temperature.

1.3 Encapsulation of the PS-m P3-TAA array with the MWNT

The P3-TAA modified PS-m template was immersed in 3 % HCl aqueous solution containing 5.56 mg MWNT-NH_2 in 10 ml H_2O for 1 hr to allow the amine cations to electrostatically adsorb onto the anionically charged P3-TAA and PS-m surface (carboxyl and sulfate ester anions, respectively). The adsorbed MWNT-NH_2 was then chemically cross-linked in 5 ml aqueous solution with 59.5 mg glutaraldehyde to increase the array rigidity.[5]

1.4 Instrumentation

Atomic force microscopy (Agilent 5500 AFM/SPM System, Agilent Technologies) was used to investigate surface morphologies and surface analysis. The AFM measurements were carried out using a piezoscanner capable of scanning an area of ~10×10 μm^2 at room temperature. Commercially available tapping mode tips (TAP300, Silicon AFM Probes, TedPella, Inc.) were used on cantilevers with a resonance frequency in the range of 290-410 kHz. All images (AFM topography, Tapping mode) were filtered, and analyzed by using SPIP software (Scanning Probe Image Processor, Imagemet.com). The morphology of the samples were also examined by field emission scanning electron microscopy (FE-SEM) using a JSM 6330F JEOL instrument operating at 15 kV. Prior to SEM analysis, the films were thoroughly dried under vacuum for at least 24 hrs. SEM images were processed and analyzed using ImageJ software. A PHI 5700 X-ray photoelectron spectrometer was equipped with a monochromatic Al Kα X-ray source ($h\nu$=1486.7 eV) incident at 90° relative to the axis of a hemispherical energy analyzer. The spectrometer was operated both at high and low resolutions with pass energies of 23.5 eV and 187.85 eV, respectively, a photoelectron take off angle of 45° from the surface, and an analyzer spot diameter of 1.1 mm. All spectra were collected at room temperature with a base pressure of 1 x 10^{-8} torr. The peaks were analyzed first by background subtraction using the Shirley routine. All the samples were completely dried in argon gas prior to XPS measurements.

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[4] C. Gao, Y. Z. Jin, H. Kong, R. L. D. Whitby, S. F. A. Acquah, G. Y. Chen, H. Qian, A. Hartschuh, S. R. P. Silva, S. Henley, P. Fearon, H. W. Kroto, and D. R. M. Walton, *J. Phys. Chem B* 2005, **109,** 11925.

[5] V. N. Paunov and M. in het Panhuis, *Nanotechnology*, 2005, **16**, 1522.

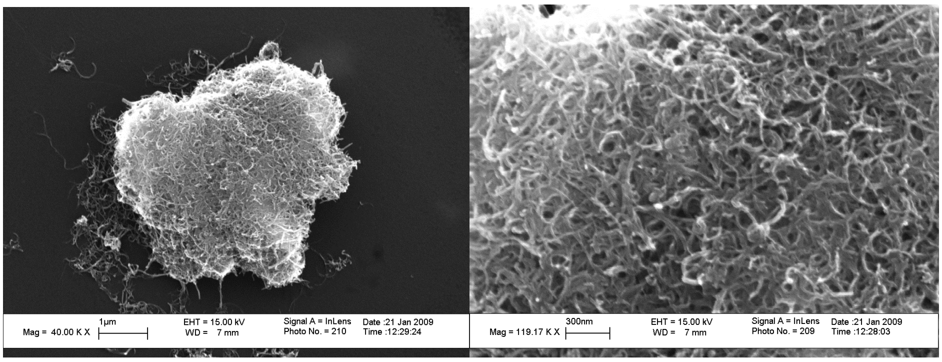

Figure S1. SEM images of the MWNTs-NH_2.

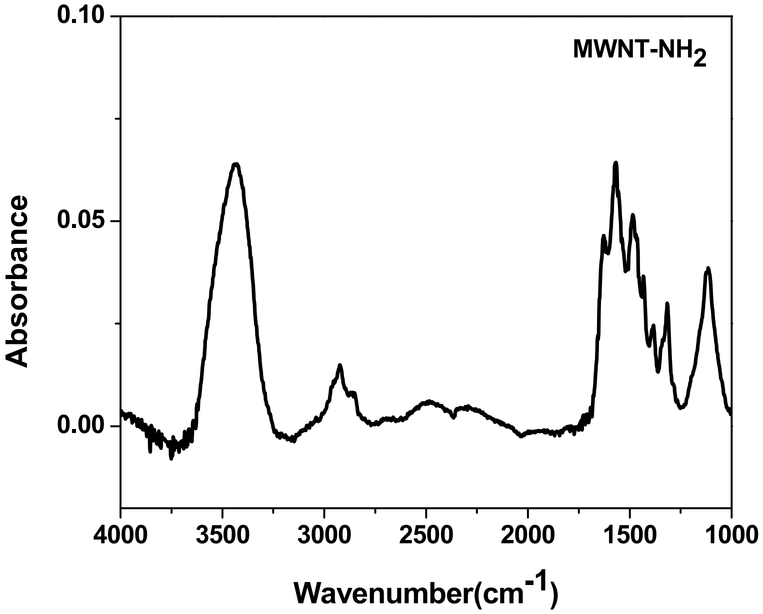

Figure S2. Fourier transform-infrared (FT-IR) spectrum of the MWNTs-NH$_2$.

Table S1. Infrared absorption bands of MWNTs-NH$_2$.

Band (cm^{-1})	**Assignment**
3433	Alkylamide N-H stretching vibration
2924	Saturated alkane C-H stretching vibration
1628	Amide C=O stretching vibration
1570	N-H deformation
1125	Alkylamide C-N stretching vibration

Figure S2 shows the IR spectrum of the MWNTs-NH$_2$. The bands at 3433, 2924 and 1125 cm^{-1} correspond to N-H, C-H and C-N stretching vibrations of the saturated alkylamide, respectively. Moreover, there are bands at 1628 cm^{-1} and 1570 cm^{-1} which are assigned to the amide C=O stretching vibration and the N-H deformation, respectively.

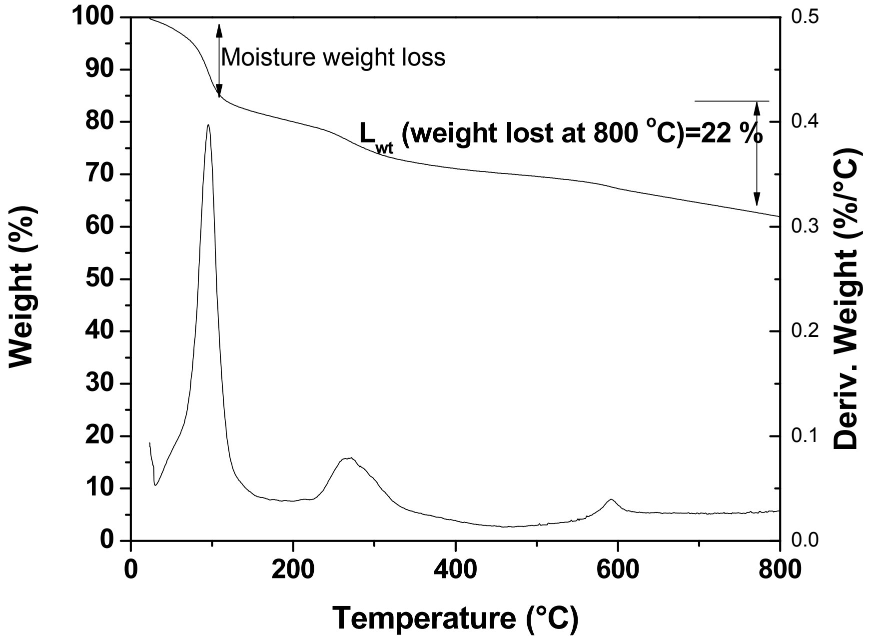

Figure S3. Thermogravimetric analysis (TGA) diagram of the MWNTs-NH_2.

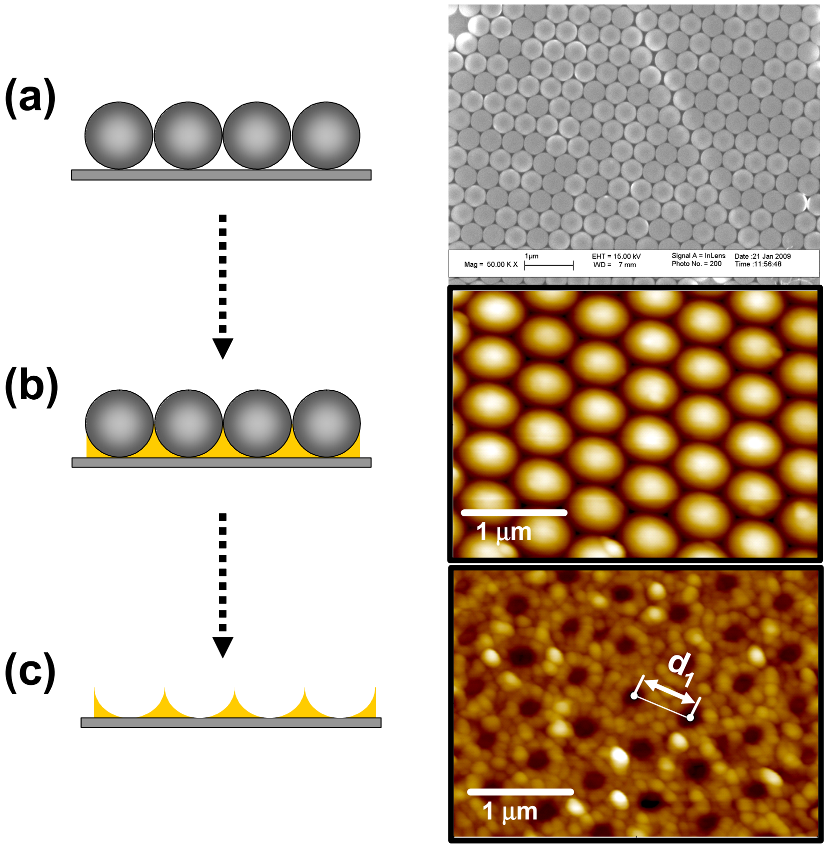

Figure S4. (a) SEM image of the 2-D PS-m array formed by LB like technique, (b) AFM image of the P3-TAA film on the PS array after the polymerization, and (c) AFM image of the highly-ordered porous P3-TAA film after the extraction of the PS particles.

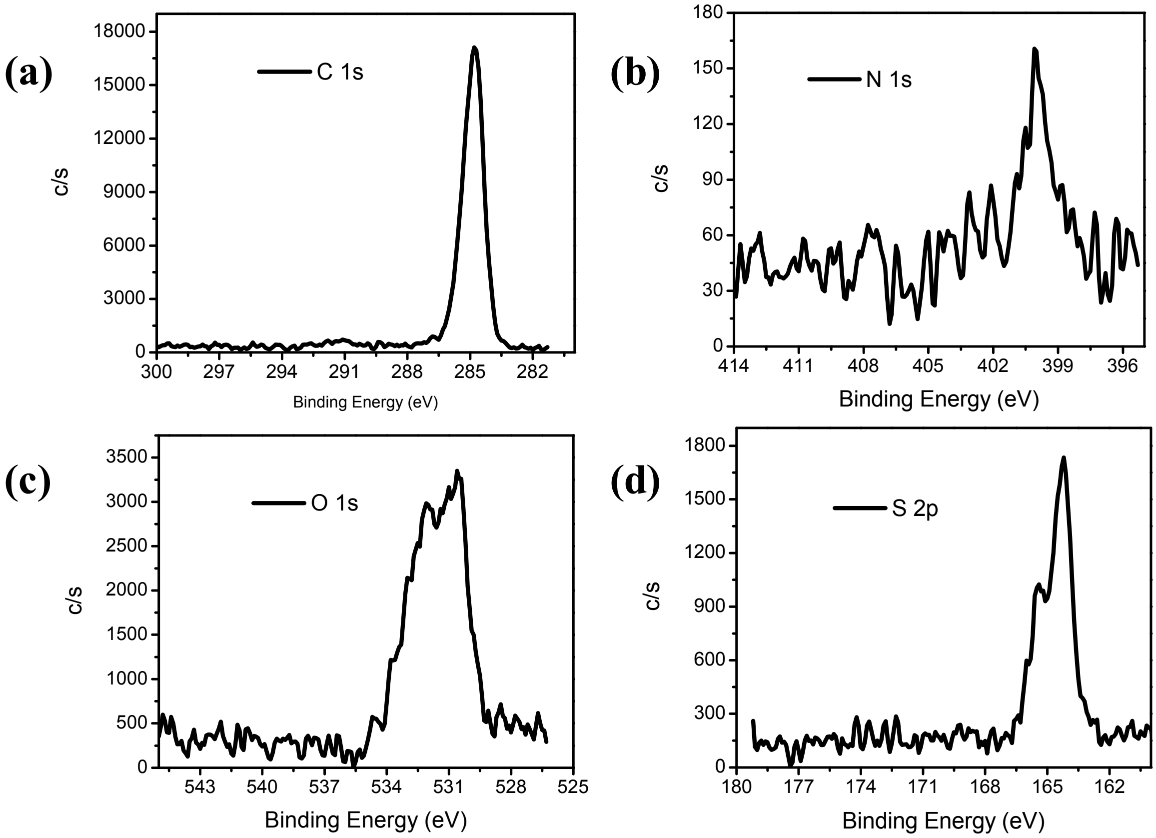

Figure S5. XPS high resolution scans of MWNT-NH$_2$ P3-TAA hollow capsule: (a) C1s, (b) N 1s, (c) O 1s, and (d) S 2p.

Table S2. Summary of atomic concentrations determined from XPS.

Film on ITO	C1s (%)	N1s (%)	O1s (%)	S2p (%)
1. P3-TAA 2D array (inverse colloidal array of P3-TAA)	78.75	0	11.29	9.96
2. MWNT-NH2 P3-TAA array (Janus hollow microcapsule)	85.27	0.48	9.73	4.51

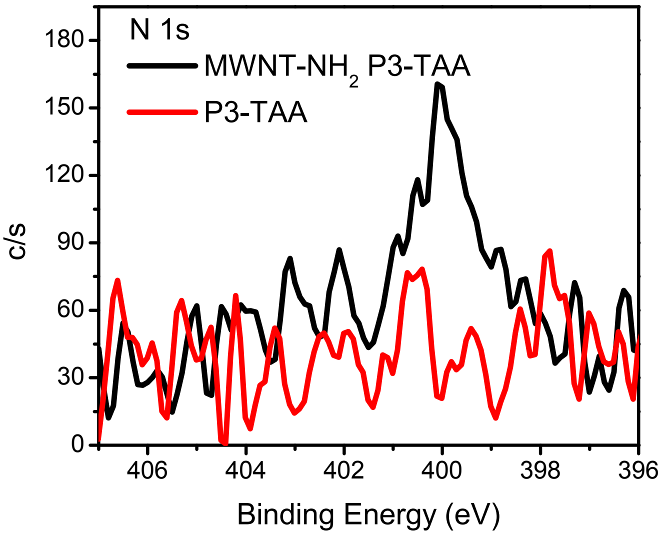

Figure S6. N 1s high resolution XPS scan of P3-TAA inverse colloidal 2D array and Janus hollow microcapsule array of MWNT-NH$_2$ P3-TAA