Supplementary Material (ESI) for *Soft Matter*

Honeycomb coated particles: porous doughnuts, golf balls and hollow porous pockets

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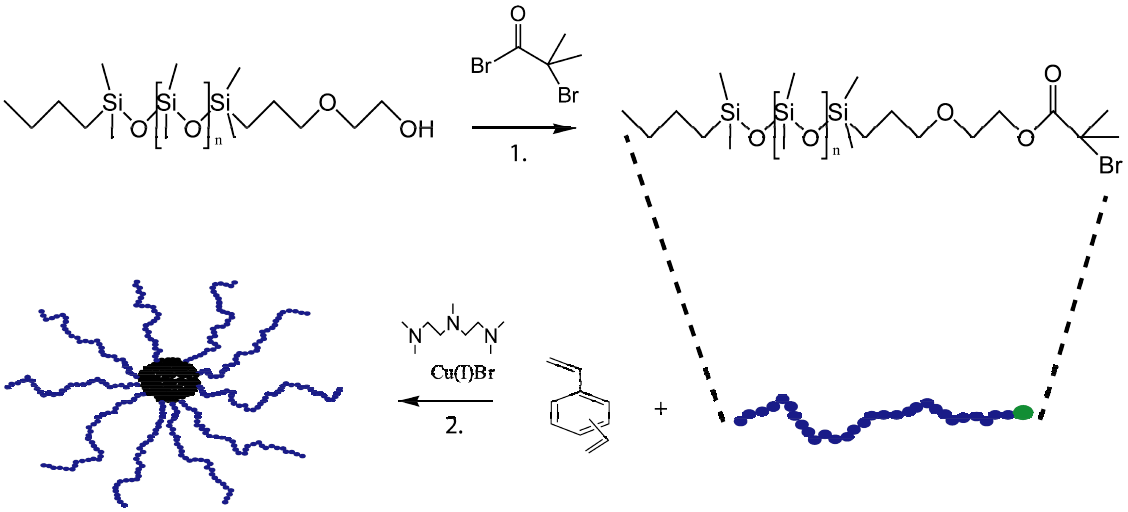
Supporting information

Materials

Methyl methacrylate (MMA), divinyl benzene (DVB) monomers were washed 3 times with 5% sodium hydroxide solution and once with distilled water. The solutions were dried over $MgSO_4$, filtered and distilled from calcium hydride. *N*, *N*, *N'*, *N'*, *N*-pentamethyldiethylenetriamine (PMDETA) was distilled from calcium hydride. THF (HPLC grade), methanol (AR grade), dichloromethane (AR grade), 2-bromoisobutyryl bromide (98%), *p*-xylene (anhydrous, 99+%), anisole (anhydrous, 99+%) , copper (I) bromide, were used without further purification. Water was purified by a Millipore system (Milli-Q-Millipore). Kaolin particles were supplied from Comalco (Rio Tinto) with the following composition: 95.7% Kaolin (3 Mole% Fe substituted for Al), 2% Mica (Illite), 1.3% Anatase (TiO_2), 0.15% Na_2O, 0.24% P_2O_5, <0.1% quartz and 0.6% moisture. Poly(dimethyl siloxane) star polymer (M_n = 255 K, PD= 1.3) was prepared as previously reported.[S1] General Scheme is summarized in Scheme S1. Poly(methyl methacrylate) star polymer (M_n = 570 K, PD= 1.23) was prepared as previously reported.[S2]

Scheme S1. Preparation of PDMS star via the arm first approach.



[1.] Dry THF and triethylamine [2.] Reaction Conditions: $[PDMS]_0 = [CuBr]_0 = [PMDETA]_0/2$ and DVB in anisole heated at 100° for 40h.

Methods

Generation of Humid Air

The humidifier involved mixing of wet and dry air with humidity control being achieved through variation of the mixing ratio.[S3] Industrial compressed air (BOC Gases) was separated into two streams. The first stream was bubbled through water which was kept at 30°C by a water bath. This 'wet' stream was then passed through a 500 mL flask to condense any excess water. The second stream bypassed the water bath and was mixed with the wet stream induced by inline mixers. The flow rates of both streams were controlled by rota-meters. Humidity was measured by a Cole Parmer resistive humidity recorder. Humidity ranges obtainable were 10-90% (± 1%) relative humidity (RH).

Typical procedure to produce porous honeycomb film

A drop (20 μL) of core cross-linked star polymer (10 g/L)/benzene solution was cast onto a glass cover slip. A humidified flow (80% R.H. @ 25°C) of air was directed onto this droplet at a rate of 3L/min. The solution formed an opaque surface within seconds and solvent was evaporated within 45 seconds. The film was then allowed to dry at 20°C

Typical procedure to produce porous honeycomb particles

A drop (20 μL) of core cross-linked star polymer (10 g/L)/particle (5% W/ V)/benzene solution was cast onto a glass cover slip. A humidified flow (80% R.H. @ 25°C) of air was directed onto this droplet at a rate of 3L/min. The solution formed an opaque surface within seconds and solvent was evaporated within 45 seconds. The film was then allowed to dry at 20°C and 30% R.H. overnight. Structures formed on the surface of Glass micro-beads see Figure S1, sodium chloride (NaCl) and Copper Sulphate ($CuSO_4$) crystals are displayed in Figure S2 (a) and (c) respectively.

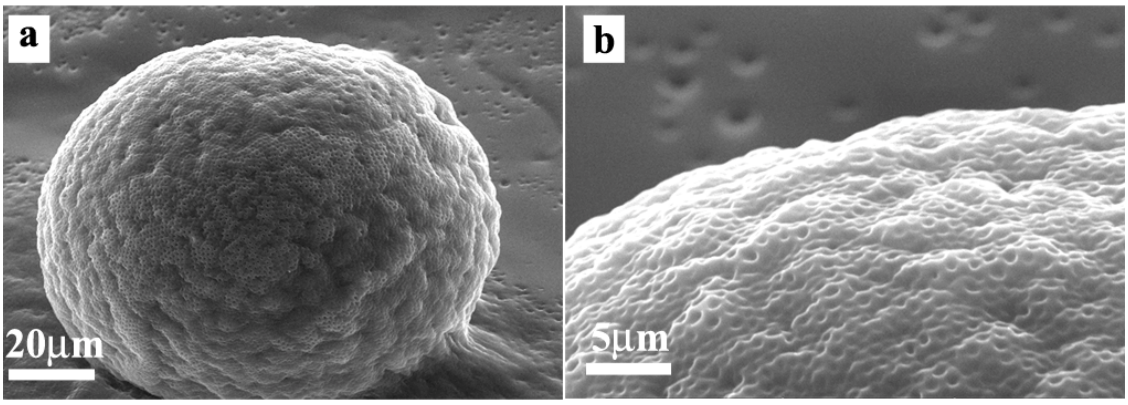


Figure S1. Scanning electron micrograph of honeycomb coated glass mico-beads

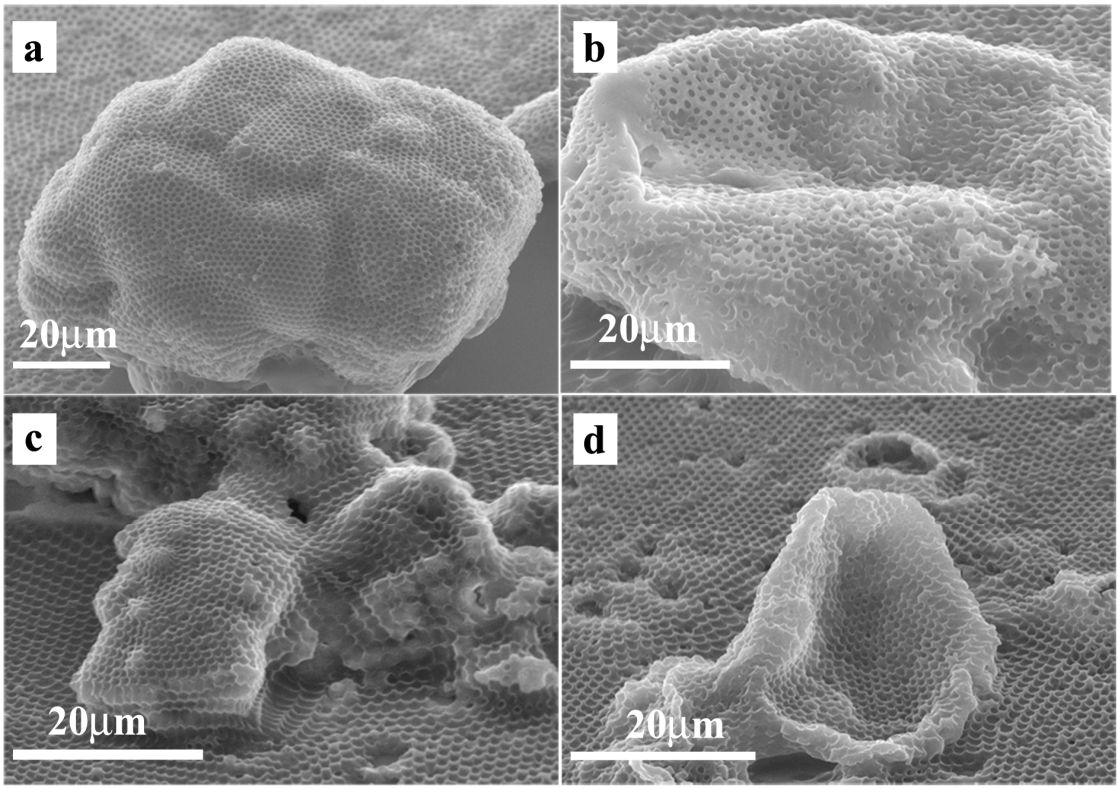


Figure S2. Scanning Electron micrographs of (a) Honeycomb coated NaCl crystals before and (b) after dissolution of NaCl particles, note possible incomplete dissolution of NaCl crystals. (c) Honeycomb coated $CuSO_4$ crystals before and (d) after dissolution of $CuSO_4$ particles.

Formation of hollow honeycomb film

The cast film on the particle surface was allowed to float on the surface of distilled water for 8 hours. The samples were then allowed to dry at 20°C and 30% R.H. overnight. The film was then prepared for SEM analysis. For NaCl and $CuSO_4$ film treated as above, See Figure S1 (b) and (d) respectively.

Film formation on particles with PMMA based star polymer

Film formation from PMMA/EGDMA microgels was also carried out with the normal procedure described above and the formed film is shown in Figure S3.

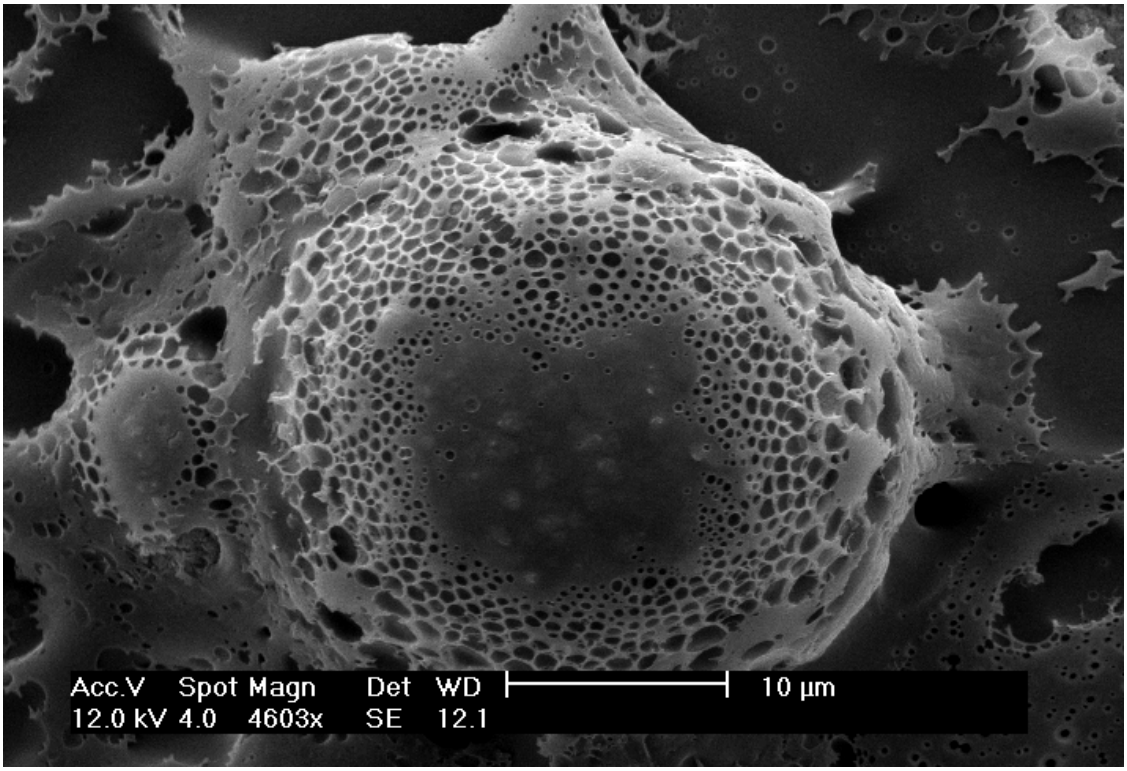


Figure S3. Scanning electron micrograph of Kaolin particle coated with poly(methyl methacrylate) honeycomb film.

CHARACTERIZATION

Polymer characterization by SEC

Size Exclusion Chromatography was performed on a Shimadzu system with a Wyatt DAWN DSP multi-angle laser light scattering (MALLS) detector (683 nm) and a Wyatt OPTILAB EOS interferometric refractometer. THF was used as the eluent with three Phenomenex phenogel columns (500, 10^4 and 10^6 Å) operated at 1mL/min with column temperature set at 30 °C.

Film Analysis by microscopy

Films were analysed by optical microscopy (Nikon Microflex AFX II) and scanning electron microscopy (SEM) (XL 30 Philips Head SEM). Sample was tilted to maximum 70° to image cross-sections.

References for supporting information

S1 Connal, L. A.; Qiao, G. G. *Adv. Mat*. 2006, **18**, 3024.

S2 Connal, L. A.; Gurr, P. A.; Qiao, G. G.; Solomon, D. H. *J. Mater. Chem.* 2005**,** **15**, 1286.

S3 Thomas, C. *Analytica Chimia Acta*, 1993, **272**, 179.