Supplementary information

Hierarchically Structured Hybrid Honeycomb Films via Micro to Nanosized Building Blocks.

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Elaboration of the silica based building blocks. The production of silica beads is provided by the Stöber bottom up synthesis [1]. Improved by the use of constant addition growth process of Nozawa *et al.*, [2] this method supplies us with monodispersed spherical amorphous beads from a few nanometers to about 2 micrometers of diameter. The Surface Initiated Polymerization (SIP) was conducted in bulk using a Nitroxide Mediated Polymerization (NMP) with a monomolecular initiator. Such process is also called Surface Initiated Nitroxide Mediated Polymerization (SINMP). Such a versatile initiator is synthesized in two steps. First an “in situ thermo-dependant trapping of carbon radicals” of the C=C monomer double bond of an alkoxysilane derivative and its consecutive grafting onto the silica surface has been developed in our previous works to elaborate initiator-grafted silica particles (SiP). The procedure is described in more details by Inoubli. [3] In a second step, a solution of 2 wt.% of SiP is mixed with a determined ratio of butyl acrylate (BuA) or Styrene (S) purchased from Aldrich and free initiator the 2-Methyl-2-[N-tertbutyl-N-(diethoxy-phosphoryl-2,2-dimethylpropyl)aminoxy]propionic acid (MAMA) provided by Arkema as BlockBuilder™. The use of free initiator in the media volume is required to form through the Fischer effect enough counter radical to displace the dissociation equilibrium to the dormant species and

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[1] Stöber, W.; Fink, A.; Bohn, E. *J. Colloid Interface Sci.* **1968**, *26*, 62-69.

[2] Nozawa, K.; Gailhanou, H.; Raison, L.; Panizza, P.; Ushiki, H.; Sellier, E.; Delville, J. P.; Delville, M. H. *Langmuir* **2005**, *21*, 4, 1516-1523.

[3] (a) Inoubli, R.; Dagreou, S.; Delville, M.H.; Lapp, A; Peyrelasse, J.; Billon, L. *Soft Matter* **2007**, *3*, 1014-1024. (b) Inoubli, R.; Dagreou, S.; Roby, F.; Khoukh, A.; Peyrelasse, J.; Billon, L. *Polymer* **2005**, *46*, 2486-2496. (c) Inoubli, R.; Dagreou, S.; Lapp, A. ; Billon L.; Peyrelasse J. *Langmuir* **2006**, *22*, 6683-89.

control the propagation of the grafted polymer chains on silica particles. No excess of counter radical is added to keep the reaction under control, the low constant temperature and the Fischer effects are sufficient. The complete volume is degassed for 15 min under nitrogen in a glass necked flask in ice bath and then heated up at 110°C. The novelty of the approach proposed here is to control both the grafting initiator density and the size of the grafted macromolecule chains in order to tailor and tune the shell thickness of the core@soft shell particles.

The non-covalently bounded polymer chains formed in the bulk are removed by several successive acetone washings and centrifugations. The number of washings is determined by a UV-2450 Shimadzu UV-Vis spectrophometer analyses which evaluates the free polymer concentration contained in the centrifugation supernatant. From 10 to 20 washings are classically required to obtain an absorbance close to zero. Analysis of the shape and the monodispersity of raw and produced core@shell particles were performed by Transmission Electron Microscopy (TEM) with a JEOL JEM-2000 FX transmission electron microscope, using an accelerating voltage of 200 kV at room temperature.

Elaboration of the ZnO based building blocks. ZnO nanorods were prepared according to a method described earlier.[4] Briefly, zinc acetate dihydrate (30 g, 0.13 mol) was dissolved in methanol (130 mL) at 70 °C. A solution of potassium hydroxide (14.8 g, 0.23 mol) in methanol (65 mL) was subsequently added under a vigorous stirring. The reaction was let under reflux for 1 week. The precipitation of the ZnO particles during the synthesis resulted in an easy separation from the mixture by centrifugation. Washings of the precipitated particles with methanol were necessary to remove the excess ions. After centrifugation (5500 rpm for 10 min) the resulting gel was redispersed in the solvent required for further modification and

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[4] C. Pacholski, A. Kornowski, H. Weller Angew. Chem. Int. Ed. 2004, 43, 4774 –4777

polymerisation. The (SIP) was conducted in bulk using a Nitroxyde Mediated Polymerization (NMP) with a monomolecular initiator covalently grafted on the ZnO surface, as described previously for Silica particles. A solution of 2 wt.% of initiator-modified ZnO is mixed with a determined ratio of butyl acrylate (BuA) or Styrene (S) with an excess of free initiator to form through the Fischer effect enough counter radical to displace the dissociation equilibrium to the dormant species and control the propagation of the grafted polymer chains. The complete volume is degassed for 15 min under nitrogen in a glass necked flask in ice bath and then heated up at 110°C.

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Honeycomb hybrid film preparation by Breath Figure process. The preparation of the HC porous structure using the breath figure approach was conducted in a Perspex glove box with relative humidity control, between 35 and 45%, at room temperature (20°C). The humid air flow was set at 2 L*min^{-1}. The core@shell building blocks were first dissolved in CS_2 or $CHCl_3$to obtain a concentration of 5 g*L^{-1} and 100 μL of the solution were directly cast on a glass substrate in the Perspex box. The porous HC films were usually obtained within 30 seconds due to the high solvent volatility.