Final Technical Report:
DOE-DE-FG02-05ER46243
The Molecular Design Basis for Hydrogen Storage in Clathrate Hydrates

We have tried extensively for a year to store hydrogen in clathrate hydrates and in semi hydrates but have been unsuccessful. Rather than continue to work on the fundamentals of a project that has yet to be proven to have significant potential and impact, we changed our focus to he development of novel materials that have potential applications in CO_2 sequestration and storage, and in catalysis. These have led to peer-reviewed publications and are described. These materials continue to be studied.

I. Novel double shelled hollow particles for catalysis and gas storage.

A morphology of hollow, double-shelled submicron particles is generated through a rapid aerosol based process. The inner shell is an essentially hydrophobic carbon layer of nanoscale dimension (20 nm) while the outer shell is a hydrophilic silica layer of approximately 40 nm, with shell thickness being a function of particle size. The particles are synthesized exploiting concepts of salt bridging to lock in a surfactant (CTAB) and carbon precursors together with iron species in the interior of a droplet. This deliberate negation of surfactant templating allows a silica shell to form extremely rapid, sealing in the organic species in the particle interior. Subsequent pyrolysis results in a buildup of internal pressure forcing carbonaceous species against the silica wall to form an inner shell of carbon. The incorporation of magnetic iron oxide into the shells opens up applications in external stimuli responsive nanomaterials.

The generation of a silica shell by negating the templating effect of the surfactant is expected to be quite general allowing encapsulation of a variety of other components in the interior of the particle. In addition to the generation of a new class of hybrid materials using the aerosol technique, the fact that these systems contain iron makes them magnetically responsive. Our continuing work seeks to control and exploit particle properties through modulating layer thickness. These materials are expected to have multiple applications because they are able to incorporate the benefits of both carbon and silica and additionally include magnetic materials. Their use as catalytic materials, and in stabilizing emulsions are distinct directions of continuing research. It may also be possible to store gases in these systems at high pressures, an area of continuing research.

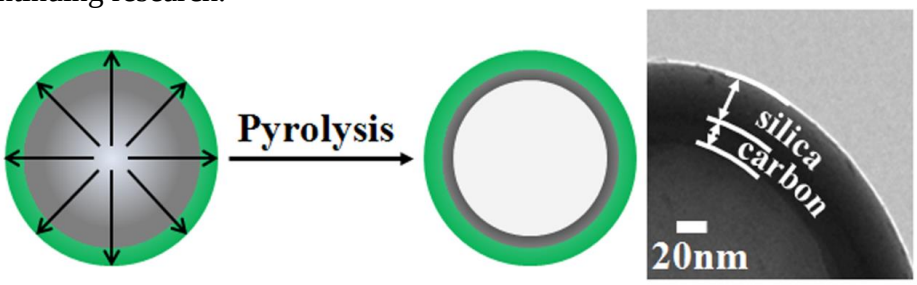
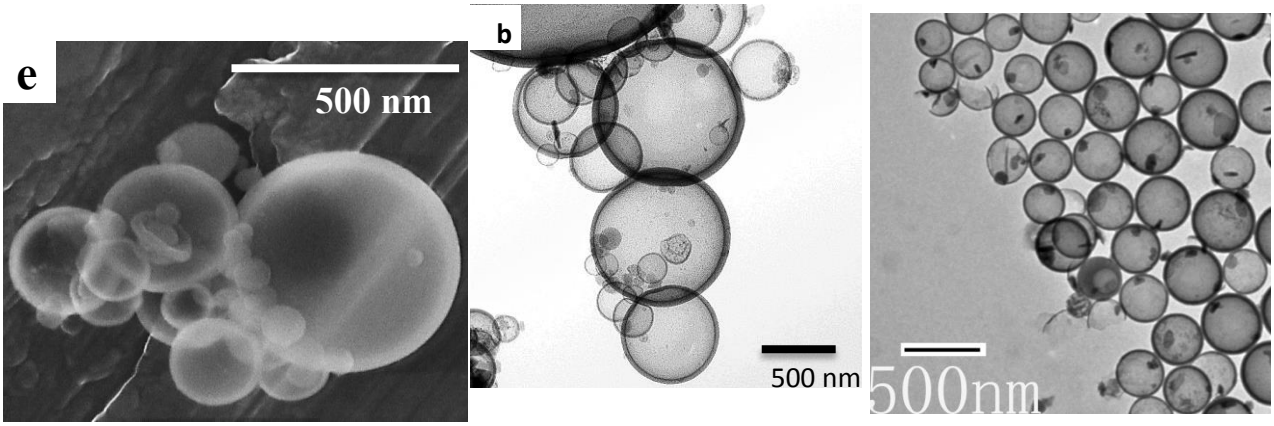


Figure 1a: Double-shelled hollow particles

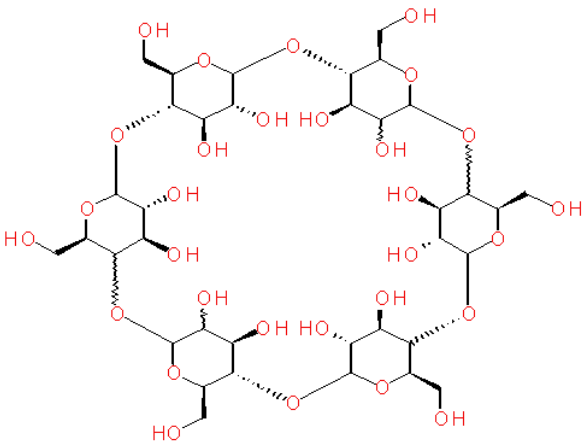


Currently we are developing ultra thin shelled hollow particles for a number of encapsulation technologies. Figure 1b illustrates these particles.

Figure 1b: Ultra thin hollow particles of silica for encapsulation.

II Rod-like carbon nanostructures produced by the direct pyrolysis of α-cyclodextrin

Carbon nanostructures were produced by the direct pyrolysis of a cyclic glucose oligosaccharide (α-cyclodextrin) without the use of a metal catalyst. The nanorods evolve from surfaces of structureless carbon when the precursor is carbonized at 1000 °C. The conversion of initially-obtained featureless carbon to the nanostructures can be controlled by the pyrolysis time. The nanorods are of diameters 14 - 40 nm and consist of multiple disordered curved graphite layers with relatively short persistence lengths. These materials have the potential to be used in gas storage technologies, in catalysis and in electrode development.



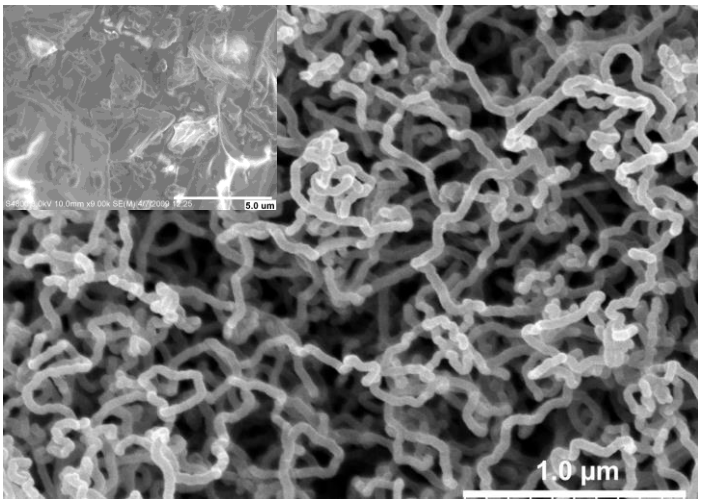


Figure 2: Chemical structure of α-cyclodextrin (a), SEM image of α-cyclodextrin after 24 hours of pyrolysis (b). The inset is morphologically indistinctive α-cyclodextrin prior to pyrolysis.

III. Carbon Microspheres as Network Nodes in a Novel Biocompatible Gel

The gelation of hydrophobically modified chitosan solutions can be accomplished through the incorporation of uniform carbon microspheres. The carbon particles act as nodes in the gel network where hydrophobic alkyl groups, attached to the polysaccharide backbone, interact with multiple carbon microspheres to form a three-dimensional matrix. Rheological characterizations show significant increases in elastic moduli upon incorporation of the carbon microspheres. We therefore report a new system to gel a biocompatible polymer solution with monodisperse carbon microspheres that can be easily synthesized from inexpensive precursors. The potential applications of these gels are significant due to the biocompatibility of hm-chitosan, the strong adsorption capacity of the carbon microspheres and their relatively monodisperse size distribution. Such uniform carbon microspheres have found use in electrode fabrication, tissue engineering and in environmental remediation. Incorporation of these materials into biocompatible gel structures may enhance application potential in drug delivery and tissue engineering platforms, and facilitate processing.

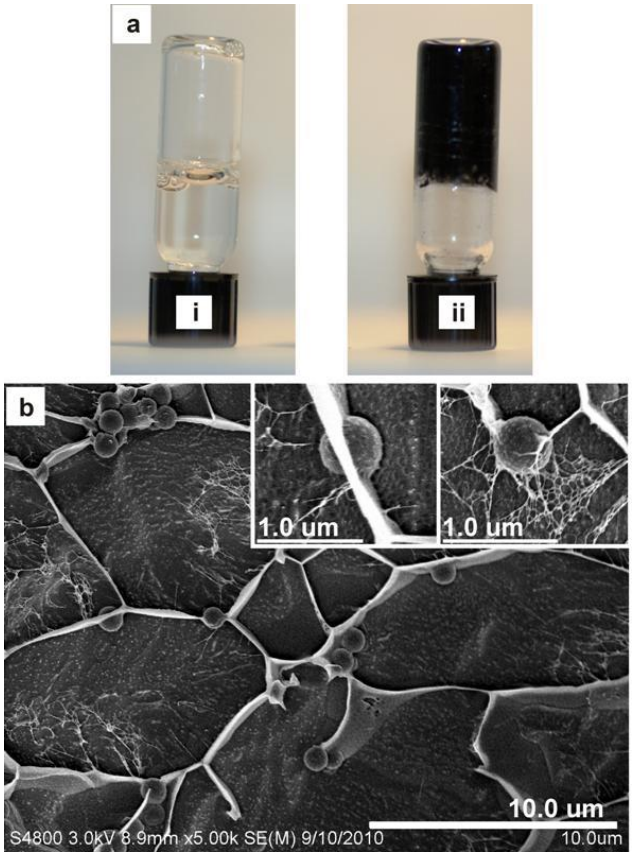


Figure 3: (a) Photograph of samples: i) 1.1wt% hm-chitosan and ii) 1.1wt% hm-chitosan and 4wt% carbon microspheres. (b) Cryo-SEM of 1.1wt% hm-chitosan and 4wt% carbon microspheres show the microspheres located primarily at junctions.

Publications

1. Wang, Y.; Sunkara, B.; Zhan, J.; He, J.; Miao, L.; McPherson, G.; Spinu, L.; John, V. “Facile Synthesis of Submicron Hollow Particles with a Nanoscale Double Layer Shell Structure”, *Langmuir*, 2012, 28(39), 13783.
2. St. Dennis, J.; Zheng, R.; Pesika, N.; Ashbaugh, H.; Raghavan, S.; McPherson, G.; He, J.; John, V.T. "Carbon Microspheres as Network Nodes in a Novel Biocompatible Gel", *Soft Matter*, 2011, 7(9), 4170..
3. St. Dennis, J.; Venkataraman, P.; He, J.; Jones, C.; Obrey, S.; Currier, R.; John, V.; Lebron-Colon, M; Sola-Lopez, F.; Meador, M. "Rodlike Carbon Nanostructures from α-cyclodextrin - Morphology and Microstructure", *Carbon*, 2011, 49, 718.