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Self- and Directed-Assembly of Hybrid, Hierarchical, Functional Materials and Synthetic Cells

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Natural materials systems evolved over billions of years to solve some of the greatest engineering challenges facing the modern world, e.g. achieving simultaneously hard, tough, and strong protection systems, perfect molecular separation, ultra-thermal insulation, and self-cleaning. The optimized property combinations found in nature often emerge as a result of hierarchical composite designs comprising disparate materials organized on multiple scales, where the feature sizes are prioritized according the relevant functional length scale (exciton, stress field, phonon, van der Waals contact, wavelength, etc.). Mimicking these evolved hierarchical designs employing the complete palette of elements and compounds available to the chemist promises the discovery of new classes of materials that derive synergistic and often emergent properties stemming from nanoscale confinement, interfacial phenomena, compartmentalization, hierarchical organization, asymmetry, catalytic activity, switchability, and collective behavior. *Developing complex structure and function within robust, scaleable, and sustainable engineering material systems is a synthesis grand challenge that served as the overarching goal of Brinker Group research over the last several decades.* To address the challenges of biomimetic materials synthesis, our group pioneered a spectrum of self- and directed-assembly methods that serve as a tool kit to fabricate synthetic structures with architectures rivaling the complexity of natural materials. These include *evaporation induced self assembly* (EISA)[1] of aerogels, obviating the need for supercritical drying and overcoming a 60 year old barrier to aerogel manufacturing[2], EISA of the first highly ordered mesoporous silica films[3], EISA of seashell-like nanocomposites[4], EISA of ordered 3D nanoparticle/silica[5] and NP/polymer[6] arrays, and aerosol-assisted EISA of the first mesoporous silica nanoparticles[7]. By combining bottom-up EISA of ordered mesoporous thin films with top-down atomic layer deposition (ALD) and plasma-directed ALD, we have fabricated a family of membranes for gas separation, CO_2 sequestration, and DNA sequencing (e.g. 8). A recent focus of our work concerns two synthetic cell-like constructs: 1) lipid-coated mesoporous silica nanoparticles (LC-MSN) wherein mesoporous silica nanoparticles are loaded with molecular, protein, or nucleic acid cargos and encapsulated within a supported lipid bilayer[9]. First demonstrated for delivery of chemotherapy drugs, the LC-MSN construct has recently been adapted to deliver plasmid DNA, mRNA, and RNA/protein complexes needed to enable nanoparticle-based CRISPR gene editing. 2) Silica cell bio-replicas that preserve and protect cellular features and functionality on the nm-µm scale and can be used to create completely synthetic red blood cells (RBCs) that circulate and deform like native RBCs but can be designed as long circulating delivery or sensing agents. This lecture will first discuss aspects of hierarchical self-assembly and then focus on designs and functions of synthetic cells.

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