

Assemblies of Nanoparticles as 3D Scaffolds for New Materials: from Mechanically Strong Polymer Crosslinked Aerogels to Porous Metals and Ceramics

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Unique bulk properties such as very low thermal conductivity, low dielectric constants, high acoustic impedance, of monolithic mesoporous (>80% v/v empty space) low-density 3-D assemblies of nanoparticles known as aerogels come at a high cost: fragility. A recent breakthrough at MS&T is the development of X-aerogels where skeletal inorganic nanoparticles (e.g., silica and >30 other metal oxides) are bridged covalently by a thin conformal polymer coating that leaves the mesoporosity almost intact [1]. In essence, the inorganic framework in X-aerogels plays the role of a template for accumulation of polymer. Those 3D core-shell superstructures are true multifunctional materials with unprecedented mechanical properties that allow applications unthinkable for aerogels before (e.g., ballistic protection).

Since the mechanical properties of X-aerogels are dominated by the polymer (short elastic range, followed by plastic deformation and ultimately densification and inelastic hardening), the question is whether the inorganic framework is needed at all: purely polymer aerogels with the nanostructure of the inorganic backbone and the interparticle bonding of X-aerogels should retain the mechanical properties of X-aerogels. However, many polymers can form gels, but most polymer gels collapse upon drying. The critical factor seems to be early colloidal phase separation and a capability for interparticle covalent bonding. This model is explored with the one-step synthesis of meso- and macroporous polymer aerogels based on polyimides, polyacrylics, polyureas, polybenzoxazines and ROMP-based networks.

A second line of inquiry explores the unique 3D core-shell structure of X-aerogels for the pyrolytic synthesis of other materials such as porous ceramics through carbothermal processes taking place at the core/shell interface. Thus, a facile synthesis of monolithic SiC aerogels has already been achieved using polyacrylonitrile-coated silica aerogels made via surface-initiated polymerization of the monomer [2].

Finally, since from a carbothermal perspective core-shell superstructures may be difficult to make at will from any inorganic framework with any carbon precursor, in parallel we have been looking at interpenetrating nanoparticle networks. Thus, a general method has been developed whereas *any* gelling inorganic system can catalyze co-gelation of a resorcinol-formaldehyde (RF) network, the most common carbon-aerogel precursor. Upon pyrolysis, some interpenetrating RF-MOx systems smelt to pure metal aerogels (case of M: Fe, Co, Ni, Sn, Cu) [3,4]; some others (like with refractories Cr, Ti, Hf) yield porous carbides. Xerogels and polymer-coated (X-) RF-MOx aerogels undergo carbothermal reductions at as much as 400 °C lower temperatures than the corresponding native RF-MOx aerogels. The effect of compactness on the kinetics of reactions between nanoparticles is studied in detail for its implications in the design of energetic materials.

[1] N. Leventis "Three-Dimensional Core-Shell Superstructures: Mechanically Strong Aerogels," *Acc. Chem. Res.* **2007**, *40*, 874-884.

[2] N. Leventis *et al.* "Click Synthesis of Monolithic SiC Aerogels from Polyacrylonitrile-Coated 3D Silica Networks," *Chem. Mater.* **2010**, *22*, 2790-2803.

[3] N. Leventis *et al.* "Smelting in the Age of Nano: Iron Aerogels," *J. Mater. Chem.* **2009**, *19*, 63-65.

[4] N. Leventis *et al.* "One-Pot Synthesis of Interpenetrating Inorganic/Organic Networks of CuO/Resorcinol-Formaldehyde Aerogels: Nanostructured Energetic Materials," *J. Am. Chem. Soc.* **2009**, *131*, 4576-4577.