

Evaporation-Induced Self-Assembly: Nanostructures made easy

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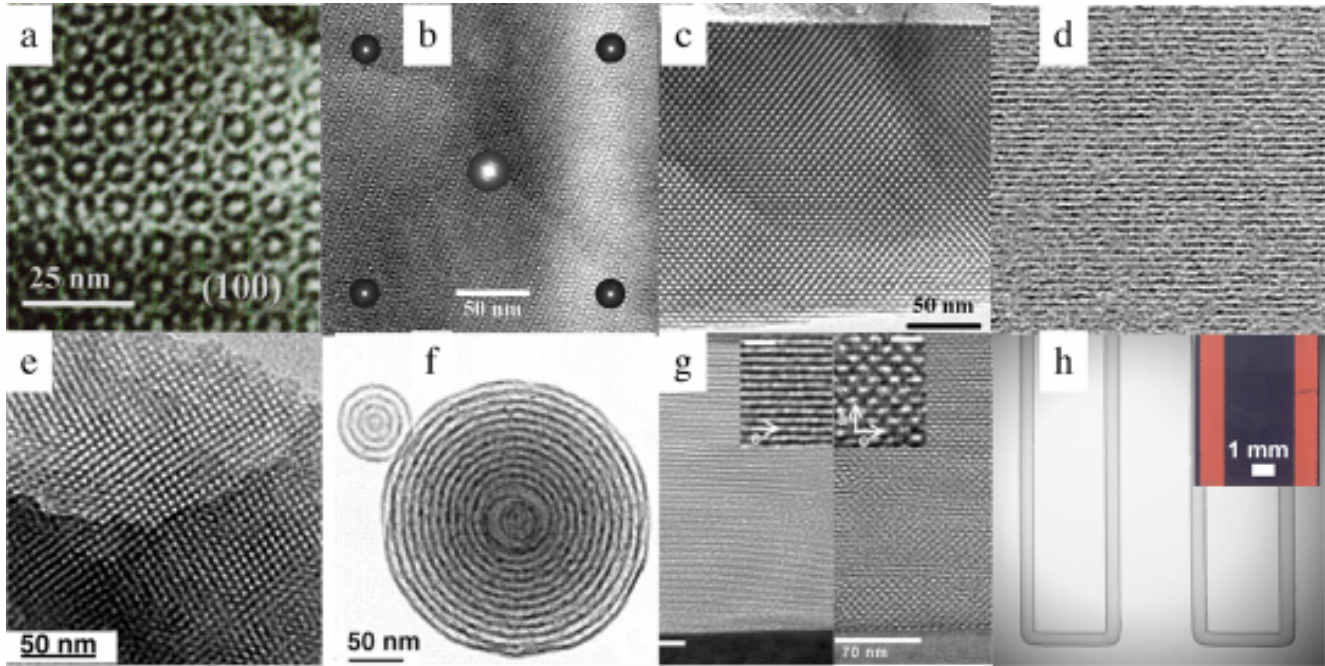


Figure -TEM micrographs of porous and composite nanostructured films and particles formed by evaporation-induced self-assembly. **a, b**: Plain-view of cubic thin film mesophases (Lu, et. al., Nature 1997), **c**: cross-sectional TEM of hydrophobic, fluoroalkylated silica mesophase (Brinker, et. al, Adv. Matls., 1999), **d**: polyalkylmethacrylate/silica nanocomposite (Sellinger, et. al., Nature 1998), **e**: conjugated polymer/silica nanocomposite (Lu, et. al., Nature 2001), **f**: nanostructured particles formed by aerosol-assisted EISA (Lu, et. al., Nature 1999), **g**: optically induced phase transformation (hexagonal to cubic) developed in photosensitive mesophase (Doshi, et. al., Science 2000).

Self-Assembly - Living systems provide us many examples of intricately organized composite architectures preserved in silica or calcium carbonate. Most natural composites are formed by complex biomineralization processes; however, recently, self-assembly strategies have emerged as a more efficient means to organize inorganic and organic precursors into precise 2 or 3-D architectures. Self-assembly typically employs asymmetric molecules that are pre-programmed to organize into well-defined supramolecular assemblies. Most common are *amphiphilic surfactant* molecules or *block copolymers* composed of hydrophobic and hydrophilic parts. In aqueous solution above the *critical micelle concentration (cmc)*, surfactants assemble into *micelles*, spherical or cylindrical structures that maintain the hydrophilic parts of the surfactant in contact with water while shielding the hydrophobic parts within the micellar interior. Further increases in surfactant concentration result in the self-organization of micelles into thermodynamically-defined, periodic, hexagonal, cubic, or lamellar *mesophases*. In addition to surfactant concentration, surfactant shape is also influential in controlling the resultant mesophase due to packing considerations. Surfactant shape may be described by a dimensionless *critical packing parameter* $g = V/a_0l$, where V is the total volume of the surfactant chains plus any co-solvent, a_0 is the effective head group area at the micelle surface, and l is the

kinetic surfactant tail length. Decreasing values of g favor mesophases with progressively increasing curvature: lamellar→cubic ($Ia3d$)→hexagonal.

Evaporation-Induced Self-Assembly EISA of silica – Two decades ago Mobil researchers demonstrated that surfactant self-assembly conducted in the presence of hydrophilic silicate precursors resulted in the spontaneous formation of surfactant/silica mesophases that upon heating were converted to so-called mesoporous silicas characterized by a precise periodic arrangement of mono-sized pores. However these procedures resulted exclusively in the precipitation of ill-defined, irregular micropowders. In order to form mesoporous silicas as uniform films (or well-defined spherical particles) our laboratory pioneered the development of an evaporation-induced surfactant self-assembly *EISA* procedure. Beginning with a homogeneous solution of soluble silica and surfactant prepared in ethanol/water solvent with initial surfactant concentration $c_o \ll cmc$, preferential evaporation of ethanol concentrates the depositing film in water and non-volatile surfactant and silica species. The progressively increasing surfactant concentration drives self-assembly of silica-surfactant micelles and their further organization into lyotropic liquid crystalline mesophases. Surfactant removal by washing or pyrolysis creates supported, highly ordered mesoporous films (Figures a-c) of interest for sensors, membranes, catalyst supports, and low dielectric constant films.

EISA is not limited to the construction of inorganic structures – it can be extended readily to form hybrid organic-inorganic composites. Using the surfactant-water-oil detergent phase diagram as a conceptual guide, we can consider as *oil* a wide variety of hydrophobic, organic precursors and reagents (monomers, crosslinkers, oligomers, functionalized polymers, initiators, etc.). In a process akin to washing dishes, we use micelle formation to spatially separate and organize organic precursors (sequestered within the hydrophobic micellar interiors) and inorganic precursors (organized around the hydrophilic micellar exteriors). Further self-organization of micelles into periodic hexagonal, cubic, or lamellar mesophases simultaneously positions both the organic and inorganic precursors into precise three-dimensional arrangements. Combined organic/inorganic polymerization “locks-in” the nanocomposite architecture and covalently bonds the organic/inorganic interface. The beauty of this approach is its simplicity and efficiency: if we seek to prepare laminated organic/inorganic composites, many hundreds of alternating organic/inorganic layers can be assembled in seconds using a single processing step (Figure d shows a portion of a nanocomposite coating that contained over 150 layers formed in a single dip-coating step).

Starting with an *aerosol* dispersion of the same precursor solutions used to create mesoporous or nanocomposite films, *EISA* is also a route to ordered porous and composite powders. Within an aerosolized droplet, solvent evaporation creates a radial gradient of surfactant concentration within each droplet that steepens in time. This surfactant enrichment induces silica-surfactant self-assembly into micelles and further organization into liquid crystalline mesophases. The radial concentration gradient and presence of the liquid-vapor interface (that serves as a nucleating surface) causes ordered silica-surfactant liquid crystal domains to grow radially inward. A TEM micrograph of a representative porous particle is shown in Figure f. This class of particles is being used widely as a high surface area support for nanocrystalline catalysts; recently mesoporous silica particles have emerged as promising *nanocarriers* for delivery of drugs, therapeutics, and imaging and diagnostic agents to cells.