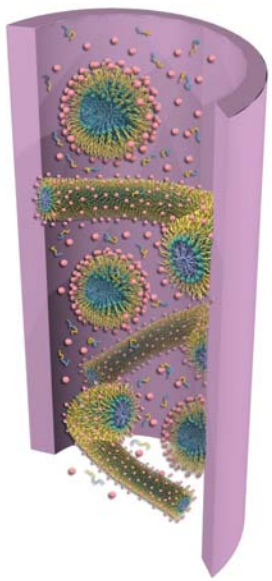
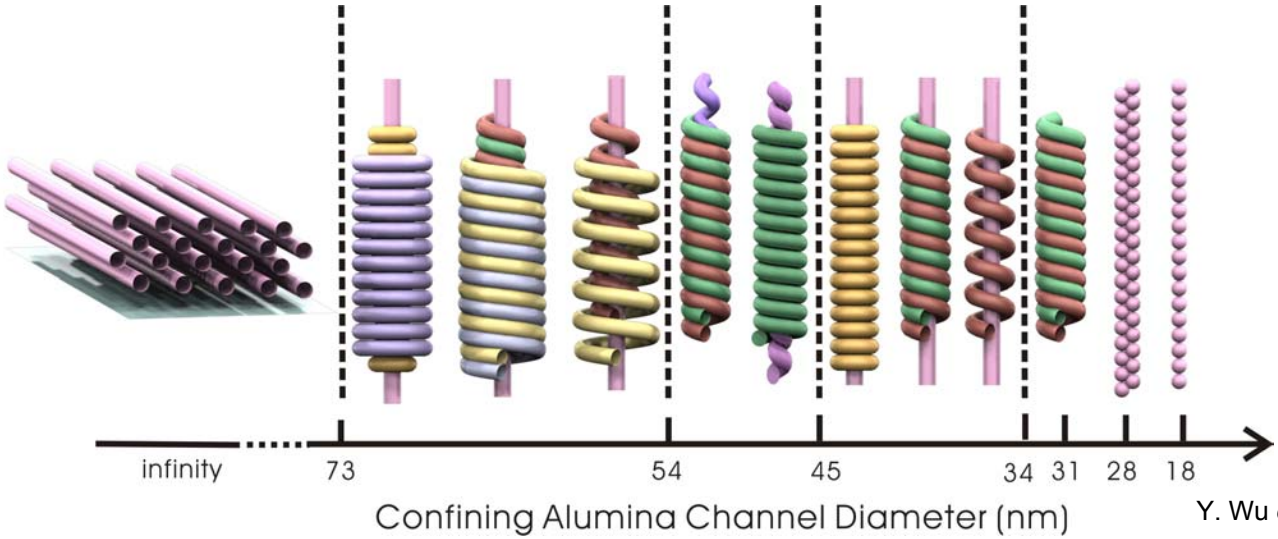
Molecular Design and 3D Assembly for Coupled Electro-Optical Functionalities

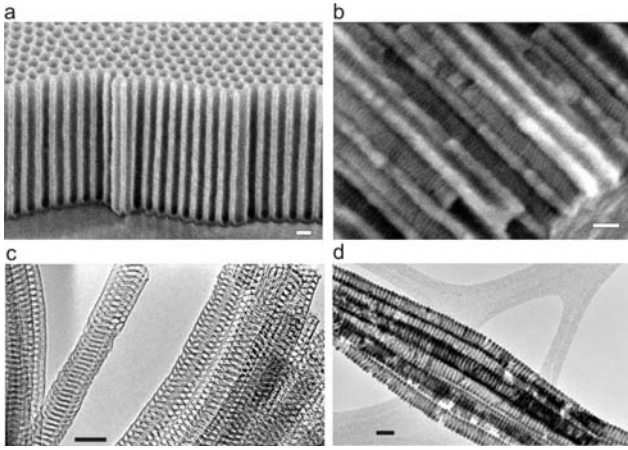
Galen D. Stucky, University of California, Santa Barbara, DMR-02-33728

Emergent Materials by Nano-Confinement



Molecular assembly is Nature's way of creating sophisticated emergent structures and functions, i.e. the properties are defined by the evolving length scale during the organization of the material system. We demonstrate for the first time how this can be done on the benchtop. The concept is generally applicable, and illustrated here by the synthesis of mesoporous silica through the cooperative assembly of a polymer surfactant and soluble silicate species in nanopore arrays of selected, varying dimensions that confine the assembly. This opens up a novel strategy for tuning and creating unprecedented mesoporous silica structures, including electro-optic nanowire arrays. This discovery can lead to important applications in biomolecule separations, environmental sensing, catalysis, bio- and nano-technology.





Y. Wu *et al. Nature Materials*, published online 17 Oct. '04

In a physically confined environment, interfacial interactions, symmetry breaking, structural frustration, and confinement-induced entropy loss can play dominant roles in determining molecular organization. The central idea of this project is to: (1) understand the spatial confinement effects on the silica/surfactant assembly behavior, and (2) explore the use of confinement effects to create novel mesostructures that are otherwise unobtainable.

The figures are:

(upright): schematic picture of the spherical and coiled cylindrical micelles in cylindrical confining environment.

(lower-left): summary of the observed confined mesostructures inside anodic alumina nanochannels with different channel diameters.

(lower-right): SEM images of porous anodic alumina (PAA) membrane and TEM images of free-standing mesoporous silica fibers and Ag mesostructured nanowires. (a) SEM image of the starting PAA membrane. (b) SEM image of the PAA membrane cross section after loading with mesoporous silica. (c) TEM image of free-standing mesoporous silica fibers. (d) TEM image of Ag nanowires with inverted mesostructures after their release from the oxide matrix. Scale bars: 100nm in (a-b) and 50 nm in (c-d).

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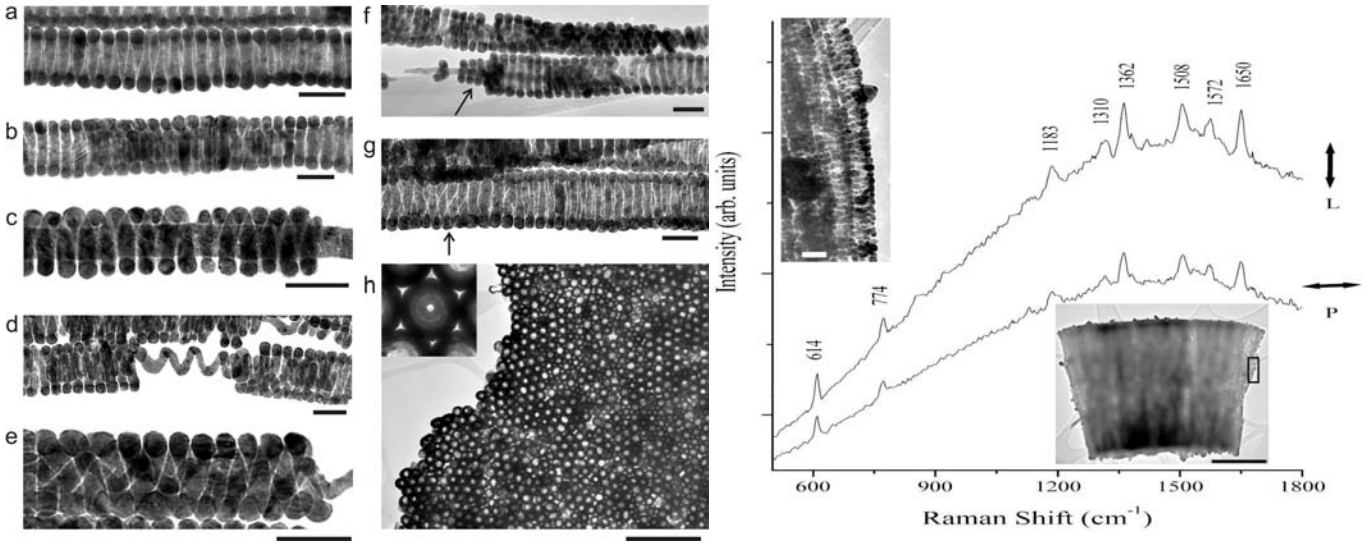
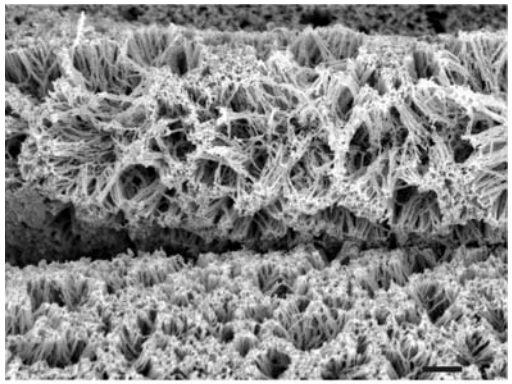
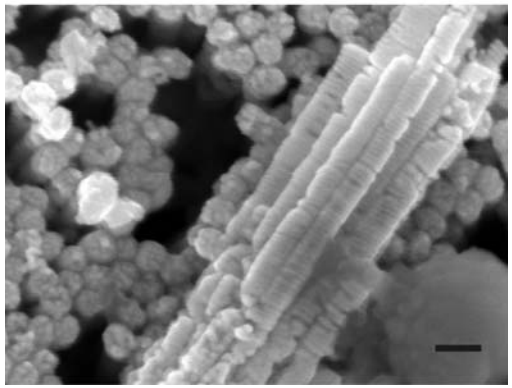
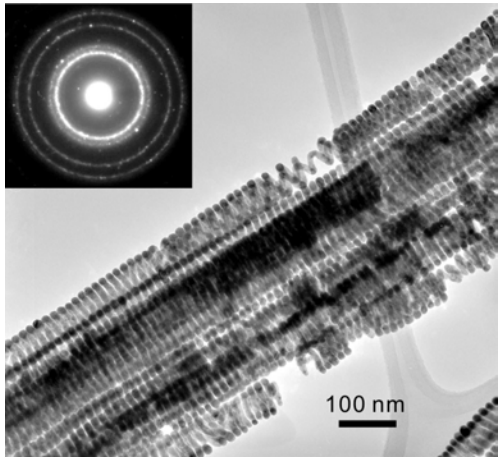
Mesostructured Nanowires and Nanowire Arrays. Inorganic nanowires are potentially important building blocks in nanoelectronic and nanophotonic devices. Using the general emergent molecular assembly methodology described above, we have fabricated mesostructured nanowire arrays with the unique features of hierarchical organization, modulated surface morphology, high surface area, and chirality. The semiconducting or metallic mesostructured nanowire arrays have promise for applications in highly sensitive sensors and high-performance thermoelectric energy conversion.



Y. Wu *et al. Nano Letters*, published online Oct. '04







Figures:

(right): SEM and TEM images of released Ag mesostructured nanowire arrays. (top) Large-area image. Scale bar: 1 μm; (middle) high-magnification side-view image showing the ordered mesoscale fine textures on the nanowires. Underneath is vertically aligned nanowire array. Scale bar: 100nm. (down) TEM image of the released nanowire bundle. Inset is the selected-area electron diffraction pattern.

(down-left): TEM images showing different architectures of the prepared Ag mesostructured nanowires. (a) single-helix; (b) stacked-donuts; (c) core-shell with a single-helix shell and a solide nanowire core; (d) core-shell with S-helix core; (e) core-shell with double-helix shell and single-helix core; (f) coaxial three-layered structure (indicated by the arrow); (g) longitudinally heterostructured nanowire with a double-helix segment (indicated by the arrow) sandwiched between two single-helix segments; (h) end view of the closely packed mesostructured nanowire bundle showing the circular cross-sections of individual nanowires. Inset of (h) shows a 103 nm diameter cross-section with three concentric Ag layers and an inner hollow core. The scale bars: 40 nm in (a-g) and 700 nm in (h).

(down-middle): Surface-enhanced Raman spectra (SERS) of R6G molecules adsorbed on a bundle of aligned Ag mesostructured nanowires with excitation polarized parallel (indicated as L) and perpendicular (indicated as P) to the nanowire longitudinal axis. The sample was prepared by dropping a drop of 10^{-5} M R6G methanol solution onto the Ag nanowires bundle and let the solution dry naturally. The Ag nanowires bundle was on a TEM grid, which helped to check the structure and oriention of the nanowires under TEM. The lower right inset shows the TEM image of the nanowire bundle (scale bar: 1 μm) with the area inside the rectangle magnified in the upper left inset (scale bar: 60nm).

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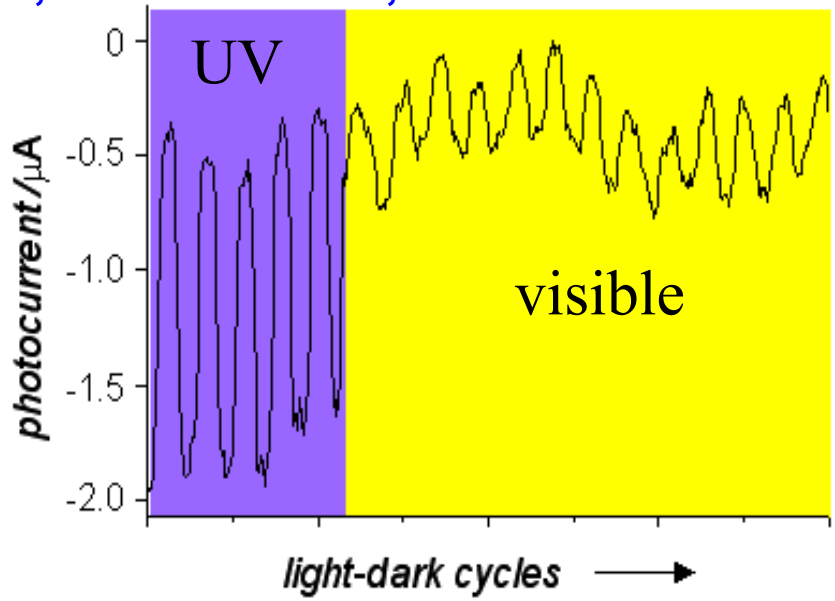
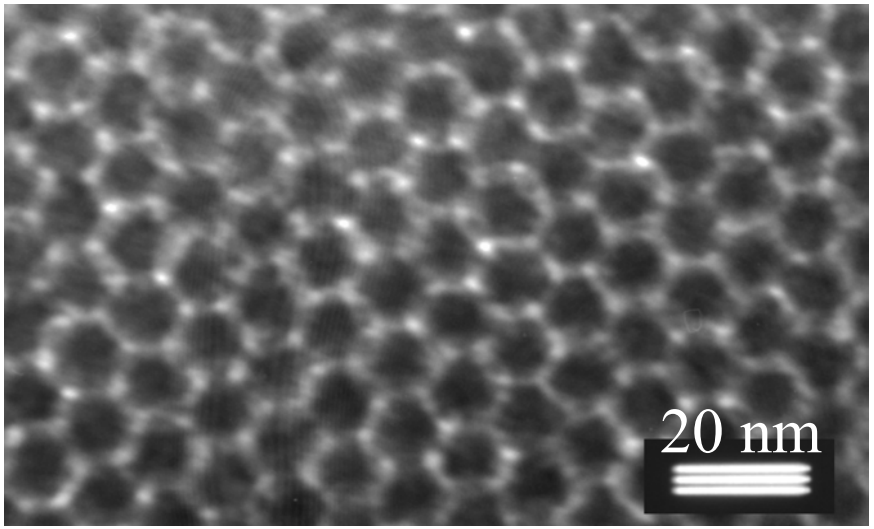
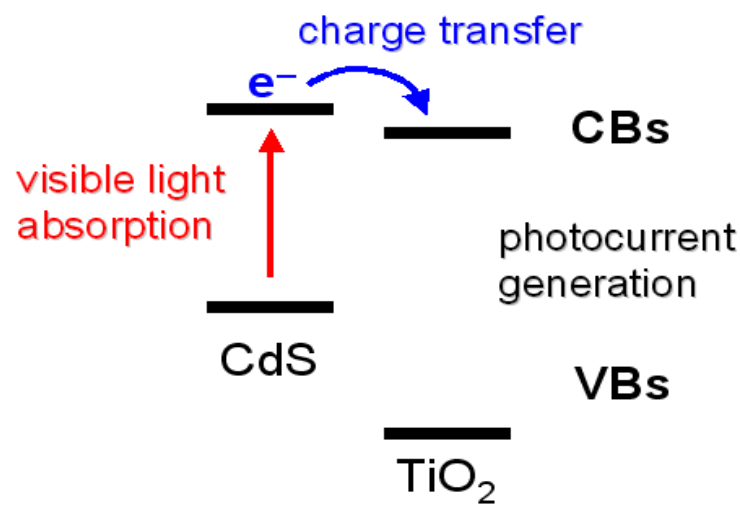
3-D Mesoporous Frameworks with Nanocrystalline Multi-Compositional Walls.

We have developed a fast and inexpensive fabrication route for functional materials composed of light-harvesting PbS or CdS nanocrystals embedded in a high-surface-area nanoporous, mesostructured TiO_2 semiconductor matrix. These novel thin film composites have the ability to efficiently convert solar energy into electricity and therefore are promising candidates for next-generation low-cost, alternative energy sources.







Bartl *et al.*, *Angew. Chem. Int. Ed.* **2004**, *43*, 3037.

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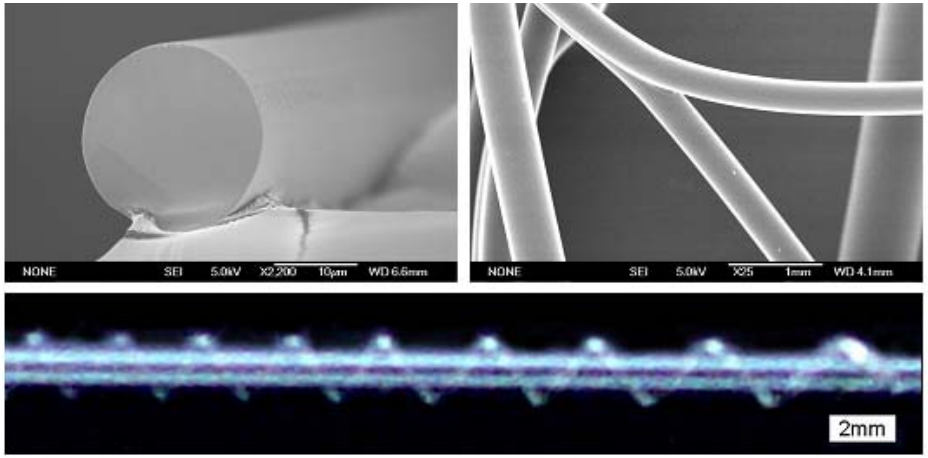
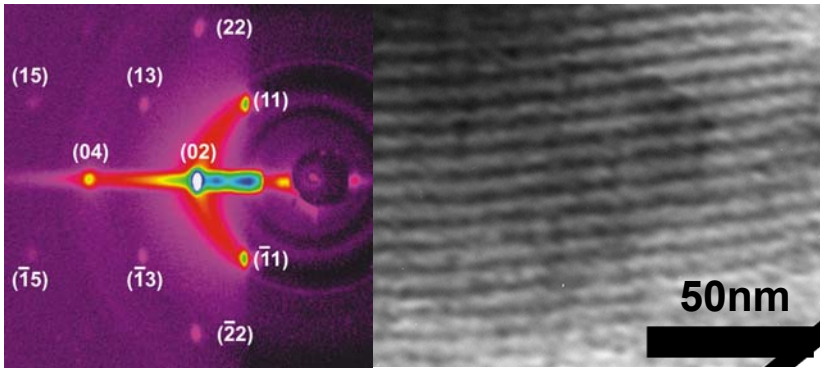
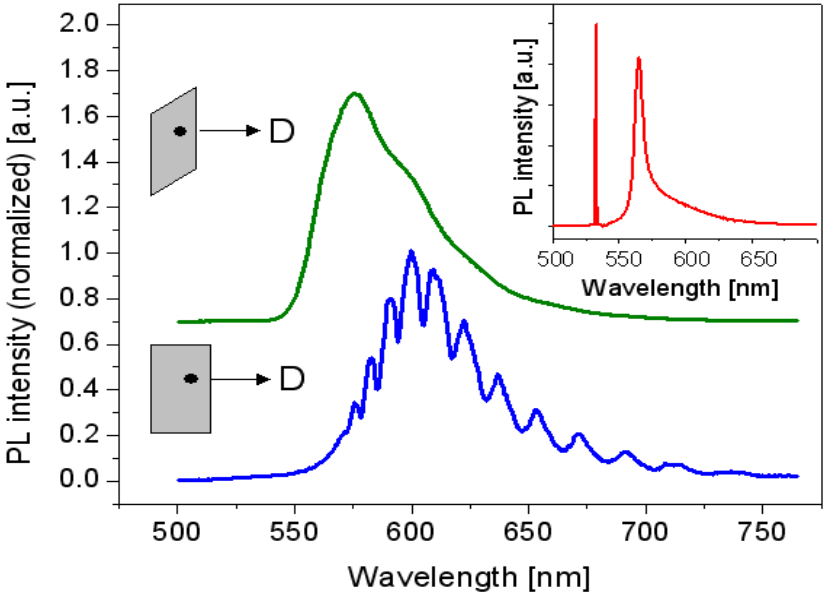
Dye-Activated Hybrid Mesostructured Titania Waveguides. Guiding and amplifying light has been demonstrated using a mesostructured titania composite synthesized by molecular assembly of a titania precursor and a structure-defining polymer. The relative high refractive index of the titania composite results in the efficient trapping of light. Modifying the titanium precursor with a fluorocarbon improves the stability and allows easy processing into fibers and thick (50 μm) films. Organic dyes that very efficiently absorb and emit light are readily incorporated in the material during processing, giving films that can act as mirrorless lasers. Such materials may be of broad use in optical information-processing devices.





2D SAXS pattern (top left), TEM image (top right) and waveguiding/lasing spectra (bottom) of dye-doped mesostructured titania films.



Bartl *et al.*, *J. Am. Chem. Soc.* **2004**, *126*, 10826.

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OUTREACH: weekly radio show broadcast live on campus FM station (KCSB 91.9). Streamed from the KCSB website at www.kcsb.org/webcast. Archived shows at www.scienceguys.com

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Graduate students Jerry Macala and Arnold Forman