Hierarchically Structured Inorganic-Inorganic Nanocomposites Formed in Silica Hydrogels

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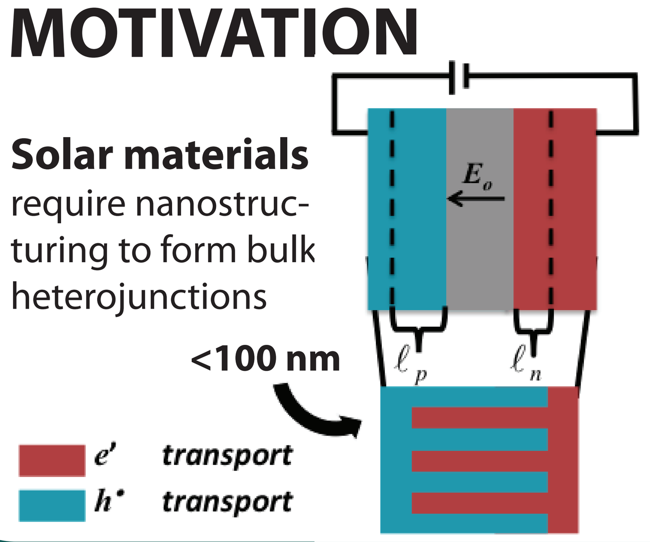
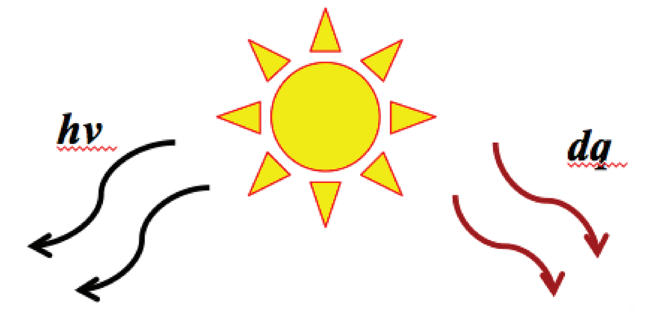
MOTIVATION

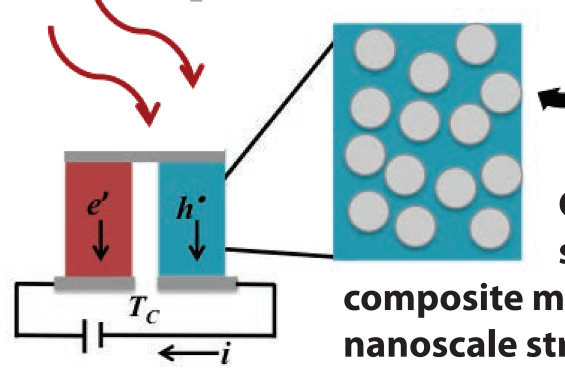
Solar materials require nanostructuring to form bulk heterojunctions





Both solar and thermoelectric materials need high conductivity --

Thermoelectric materials require nanostructuring to control thermal conductivity

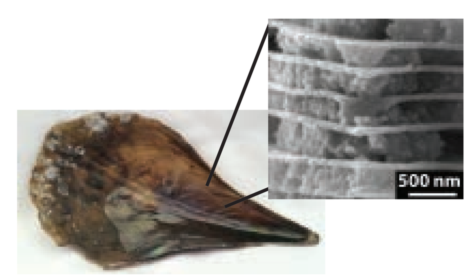


Goal: to design single crystal composite materials with nanoscale structuring

BACKGROUND

Crystal Growth in Hydrogels

Biominerals (e.g., shells) are 'single crystal' organic-inorganic nanocomposites that form in a **hydrogel**-like matrix,[1] which is used as a synthesis model.

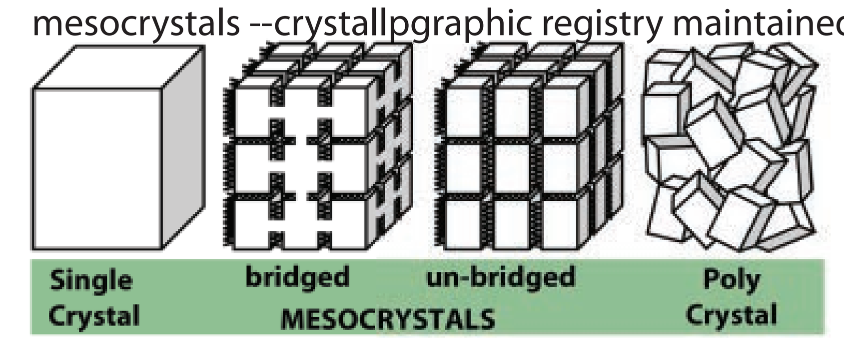


These composite structures have unique properties and length scales that meet the dimensions needed in solar and thermoelectric materials

1. L. Addadi, D. Joester, F. Nudelman, S. Weiner, *Chem. A. Eur. J* **2006**, *12*, 981.

Mesocrystals

'Single crystal' nature of seashells results from the cooperative alignment of crystalline subunits also called mesocrystals --crystallpgraphic registry maintained.



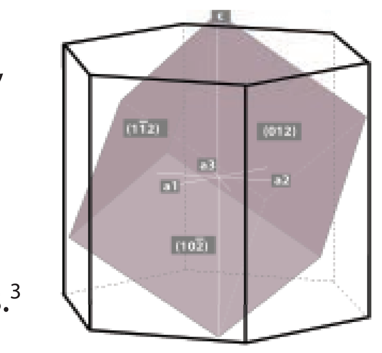
2. H. Imai, Y. Oaki, *Mater. Res. Bull.*, **2010**, *35*, 138.

Hematite, α-Fe_2O_3

Hematite has a hexagonal lattice (*R-3c*), but forms hierarchically structured, pseudocubic crystals.

Formation of hematite in pseudocubic shapes has been related to {012} planes.[3]

Hematite has a net magnetic moment along c-axis, visible range band gap, applications to photocatalysis.



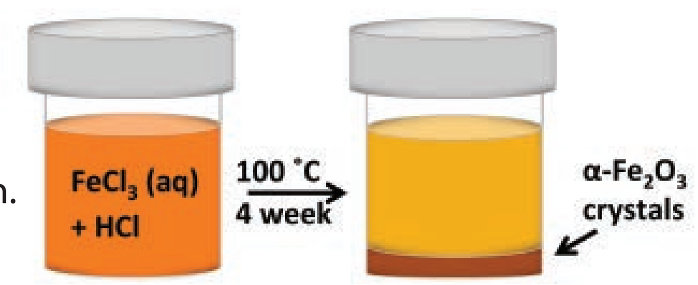
3. T. Sugimoto, A. Muramatsu, K. Sakata, D. Shindo, *J. Coll. Int. Sci.* **1993**, *158*, 420.

Solution (Hydrothermal) Growth Method

Hydrolysis of iron (III) chloride under acidic conditions is known to form hematite.[4]

$$2FeCl_3 \xrightarrow{H_2O} Fe_2O_3 + 3HCl$$

pH decreases during the course of reaction due to further acid generation.



4. M. Ohmori, E. Matejevic, *J. Coll. Int. Sci.* **1993**, *160*, 288.

Silica Hydrogel Preparation

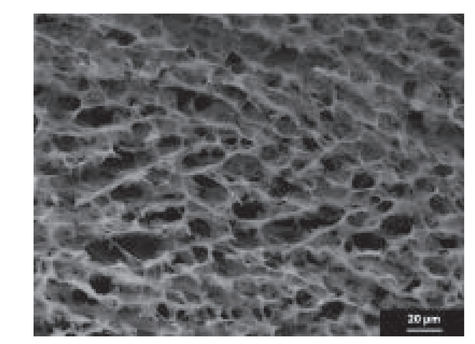
Sodium metasilicate nonahydrate solutions will gel upon addition of acid

$$Na_2SiO_3 + 2HCl \xrightarrow{H_2O} SiO_2 + 2NaCl + H_2O$$

Gel times are strongly dependent on pH (amount of acid used) and weakly dependent on the concentration of sodium metasilicate in solution

Pore structure depends on pH/gel time and concentration of socium metasilicate in solution

As an inorganic hydrogel, silica has thermal stability for hydrothermal conditions

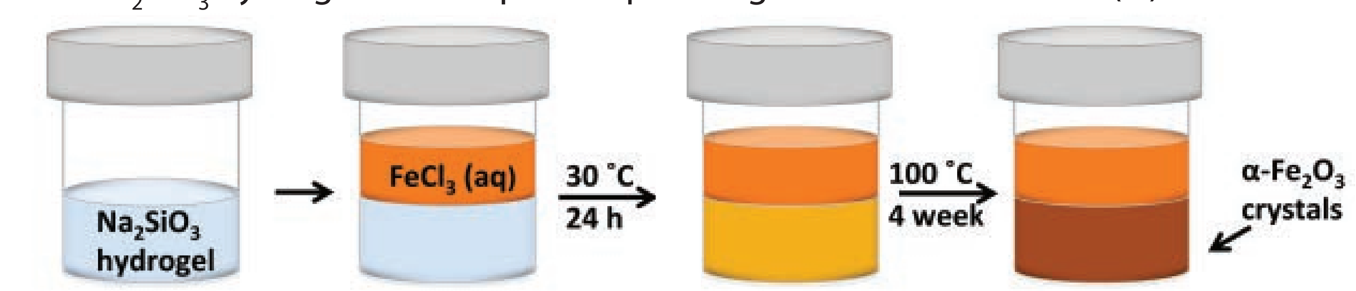


Porous, cellular microstructure of (freeze-dried) silica hydrogel (0.25 M Na_2SiO_3 and 0.5 M HCl)

Hematite Growth in Silica Hydrogel

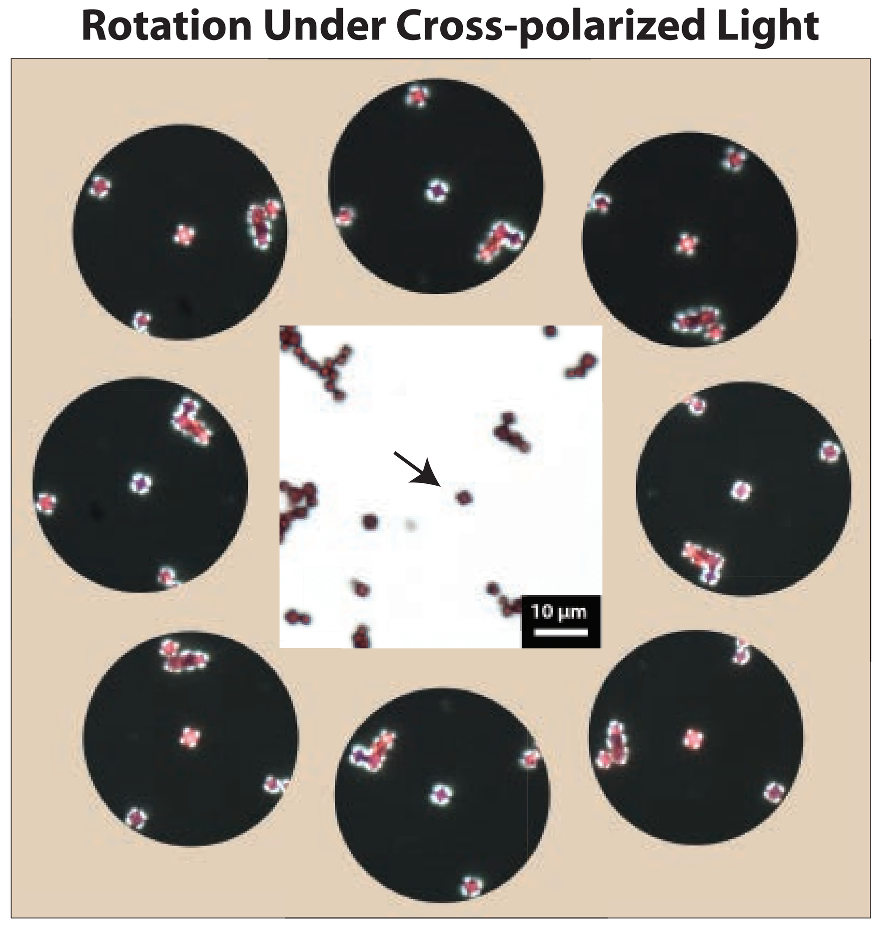
Iron (III) oxides have a wide pH range of stability in aqueous synthesis at elevatedtemperature

Acidified Na_2SiO_3 hydrogels form a pH compatible growth matrix for iron (III) oxides



RESULTS: MORPHOLOGY

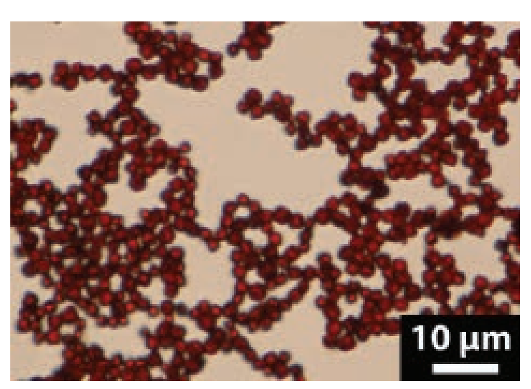
Rotation Under Cross-polarized Light

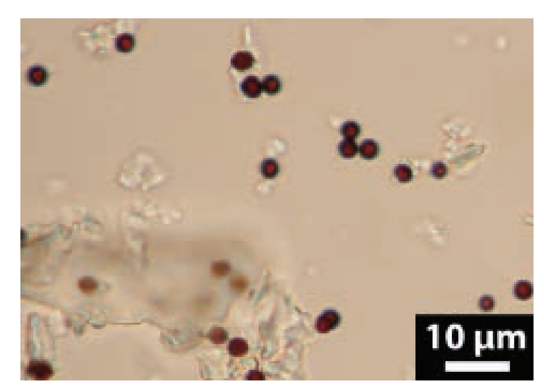


Rotation of both solution (shown above) and hydrogel grown particles under cross polarized light shows both poly and single crystal signatures:

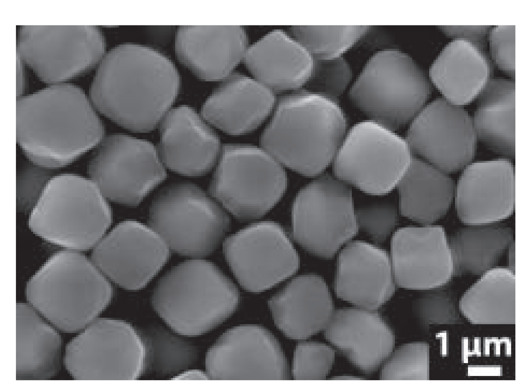
A maltese cross surrounds the brightly light red cores, which blink upon rotation under cross-polarized light.

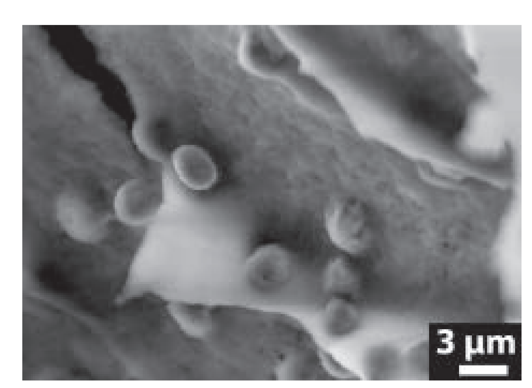
SOLUTION / HYDROGEL





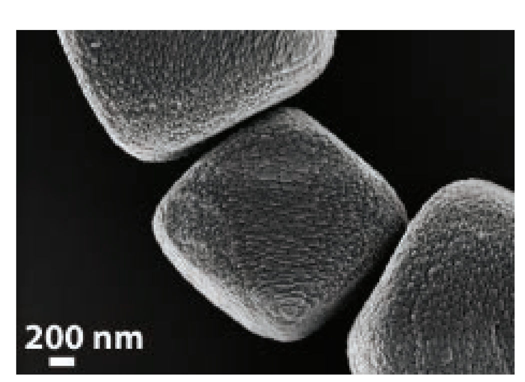
Optical microscope imaging

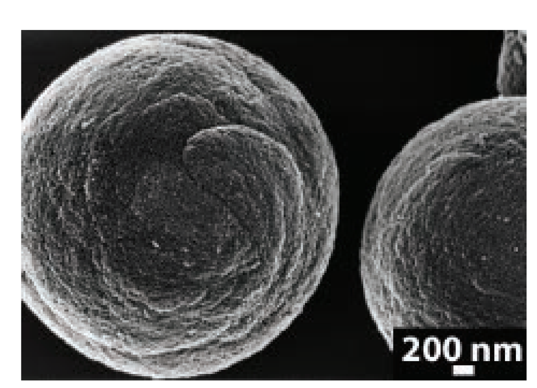




Hematite pseudo-cubes formed in solution

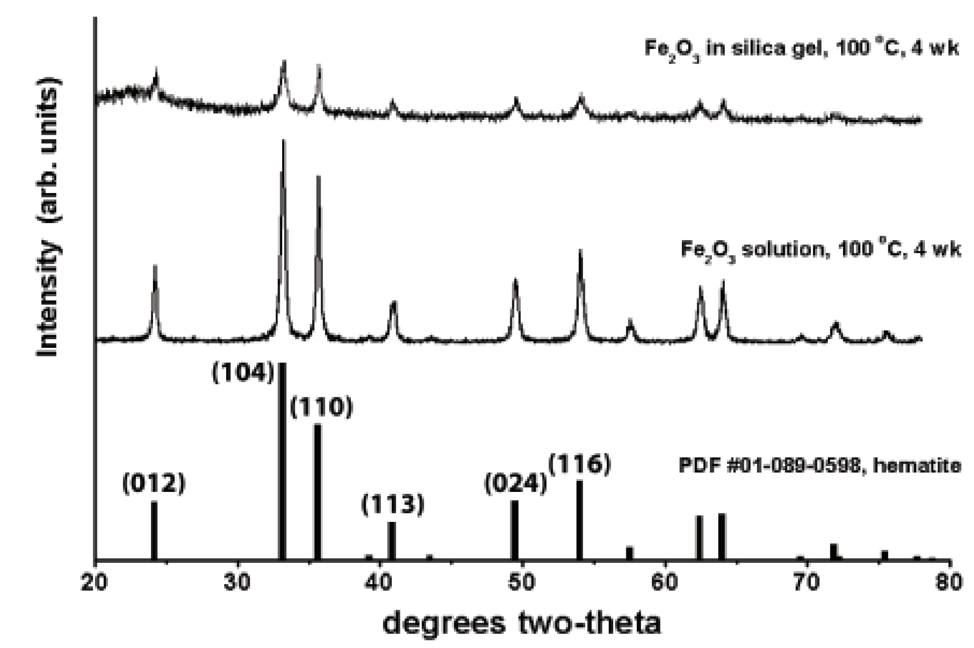
Hematite spheres formed within the gel network





Both solution and gel-grown hematite show rough surface textures characteristic of aggregate growth models

HIERARCHICAL STRUCTURE OF COMPOSITES



Sherrer analysis of X-ray patterns (shown left) shows both solution and hydrogel grown particles are composed of subunits.

Scherrer Analysis of Subunit Size

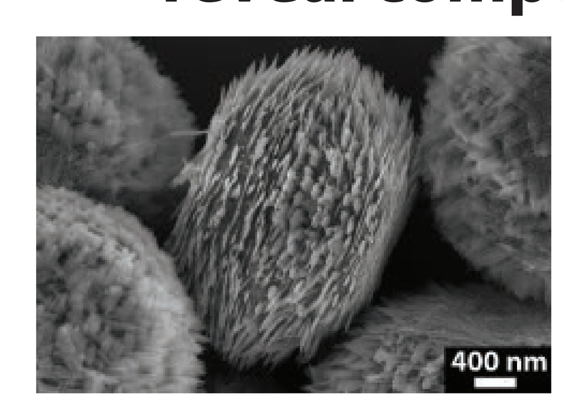
Degrees two-theta	(*hkl*)	Sol'n grown crystallite size (Å)	Gel grown crystallite size (Å)	Δ crystallite size (%)
24.1	012	347	280	-19
33.1	104	360	159	-56
35.6	110	480	395	-18
40.8	221	217	221	~0
49.4	024	269	203	-25
53.9	116	317	196	-38

Main reduction in subunit size upon growth in gel is related to the {104} (which is the related to plate-like structures[2]), and may imply that the subunits change to more needle-like upon growth in the gel.

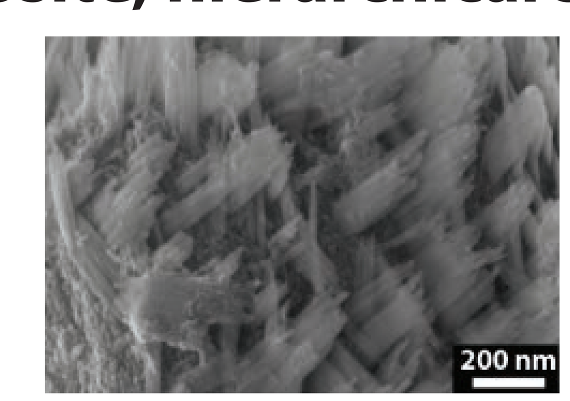
ETCHING STUDIES reveal composite, hierarchical structure

Etching studies conducted with 1 M NaOH to selectively dissolve silica gel.

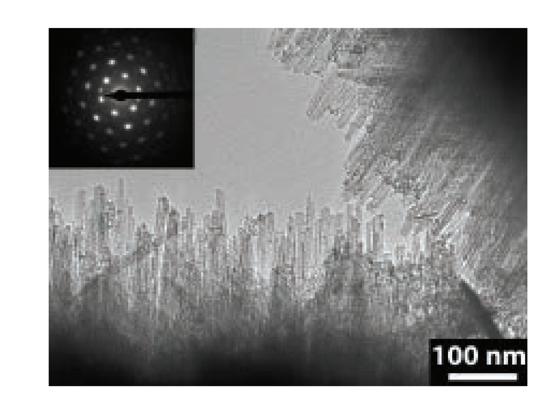
The etching has no effect on solution grown particles, but reveals the ordered internal structure of hematite grown in silica hydrogel.



FESEM of gel-grown hematite spheresafter 5 d exposure to NaOH



FESEM of etched particle surface shows bundled rods within a matrix



TEM of exposed rods and electron diffraction (inset) w/ hexagonal symmetry

CONCLUSIONS

Hierarchically structured (mesocrystals) of hematite with single crystal characteristics can be formed by a hydrothermal synthesis in silica hydrogel.

As a growth matrix, silica hydrogel can be used to modify the morphology and hierarchical structure of the subunits that compose the hematite mesocrystals.

The hematite-silica nanocomposites both have length scales <100 nm and crystallographic registry, satisfying the structural goals set forth in this work.

FUTURE DIRECTIONS

Characterize internal structure: obtain both chemical information on composite structure and crystallographic information on subunit assembly within the hematite-silica nanocomposites.

Use the experimental variables of hydrogel density and growth rate to manipulate size, aspect ratio and assembly of subunits in hierarchical hematite/silica nanocomposites. Use additives and chemical functionality in the hydrogel matrix to control iron oxidation state and thereby phases of iron oxides.

Grow iron oxide-silica nanocomposites on a substrate to allow thermal and electric property measurement.

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