Nanoaggregates Synthesis from Low-Temperature Geopolymerization Process (for sustainability applications)

Dong-Kyun (Don) Seo, Dinesh Medpelli, Shaojiang Chen,
Joe Curcuru and Tim Boskailo

School of Molecular Sciences, Arizona State University, Tempe, USA

Geopolymer Camp, Saint-Quentin, July 10, 2018

“Tyranny” of Scale

- Energy, Water, Food, Public health, Global warming, Environmental contamination …
- 7.6 billion people in 2017; 11.8 billion by 2100
- 4 trillion cubic meters of freshwater use in 2014 (70% was for agriculture); 5.5 billion by 2020
- 575 quadrillion Btu of energy use in 2015; 736 quadrillion Btu by 2040
- 33 billion tons of energy-related CO_2 emission in 2014; 40 billion by 2040.

SCALABILITY

Prominent Applications of Geopolymer

High-strength monolithic composites (concretes, bricks, tiles, etc.); Easy and scalable production

http://www.geopolymer.org
http://www.zeobond.com/geopolymer-solution.html

“The ideal chemical process is that which a one-armed operator can perform by pouring the reactants into a bath tub and collecting pure product from the drain hole.” – ***Sir John Cornforth,*** **Nobel Laureate in Chemistry**

“Simplicity is the ultimate sophistication.”
– Leonardo da Vinci?

Geopolymer Synthesis (Geopolymerization)

1. Produce metakaolin.

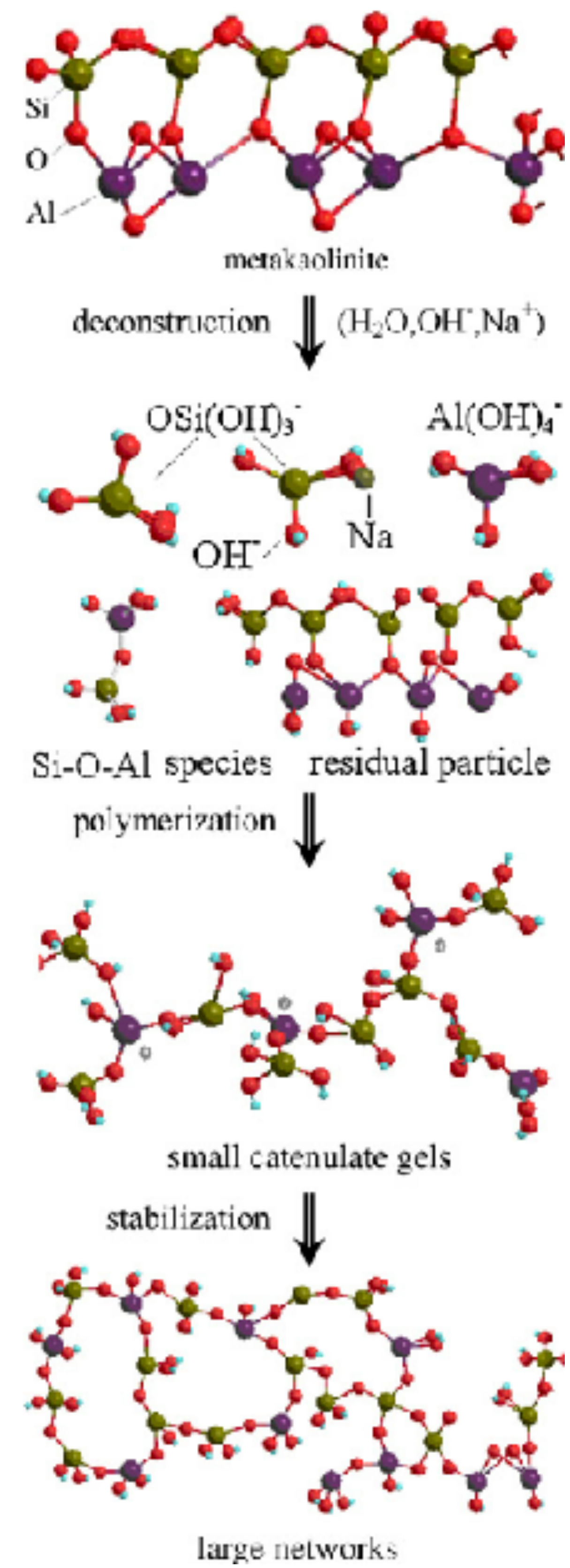
$$Al_2Si_2O_5(OH)_4 \xrightarrow{650-900°C} Al_2Si_2O_7$$

kaolinite → metakaolinite

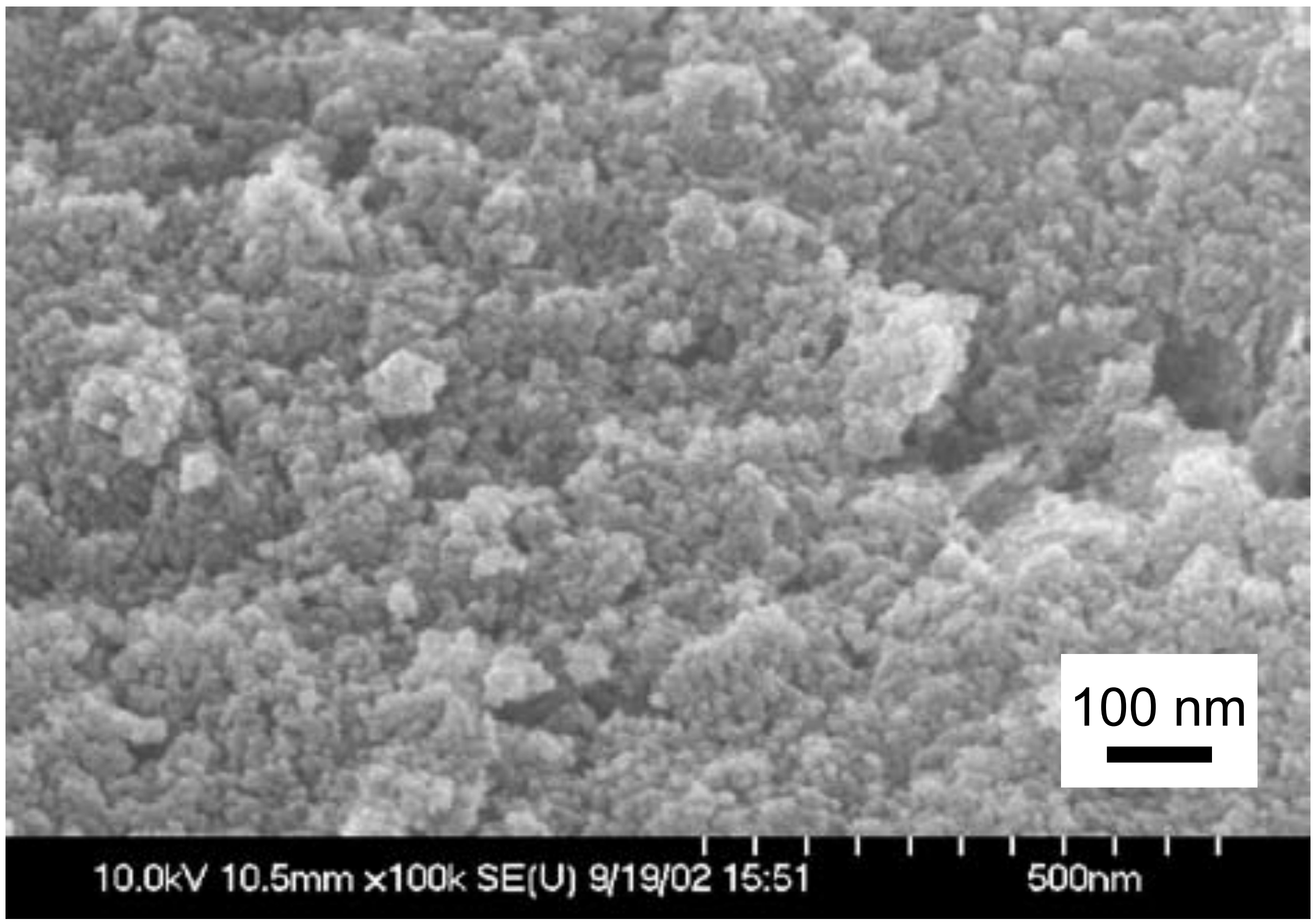
2. Produce geopolymer resin: dissolve metakaolin microparticles in a high conc. mixture solution of KOH (NaOH) + potassium silicate (sodium silicate).
3. Cure the resin at or above room temperature.

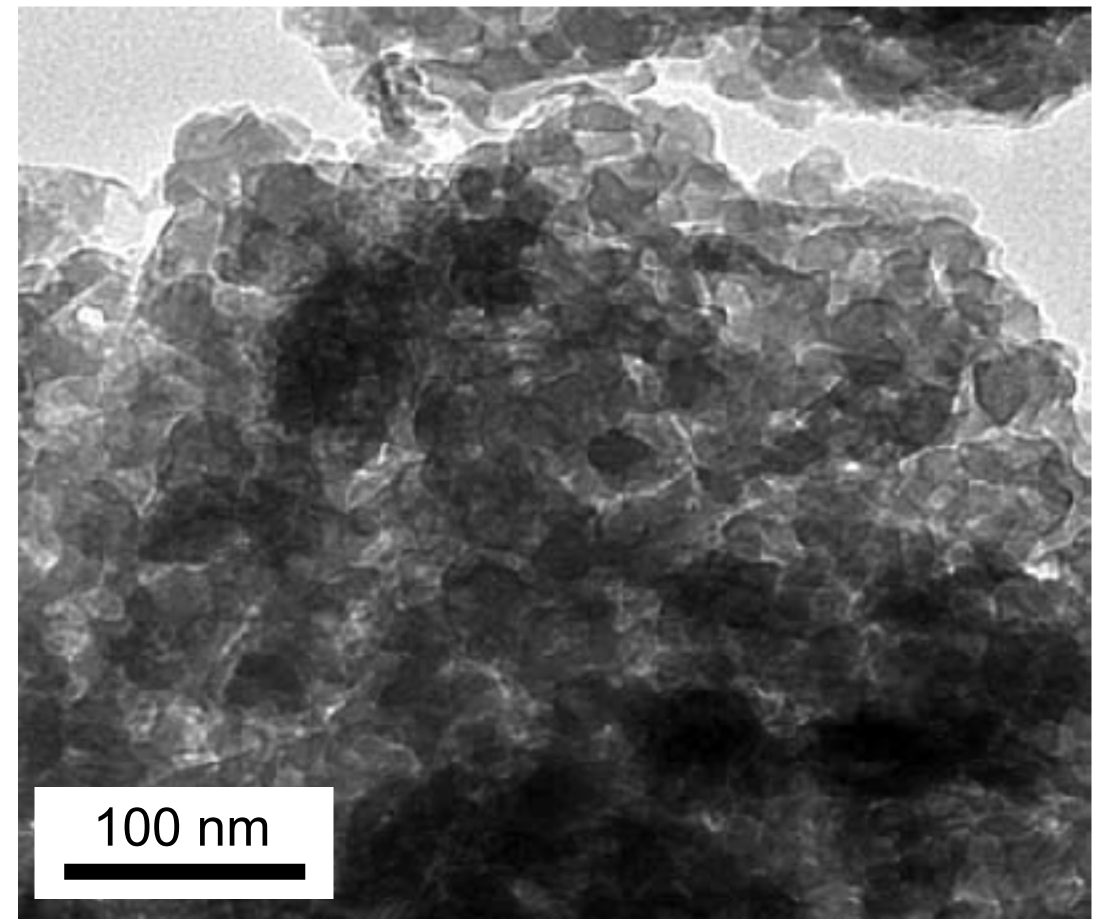
Geopolymer resin (binder)

- sticky with a viscosity of runny honey.
- moldable.
- "incomplete" dissolution of metakaolin at this stage.



Geopolymer: Innately "Nano"



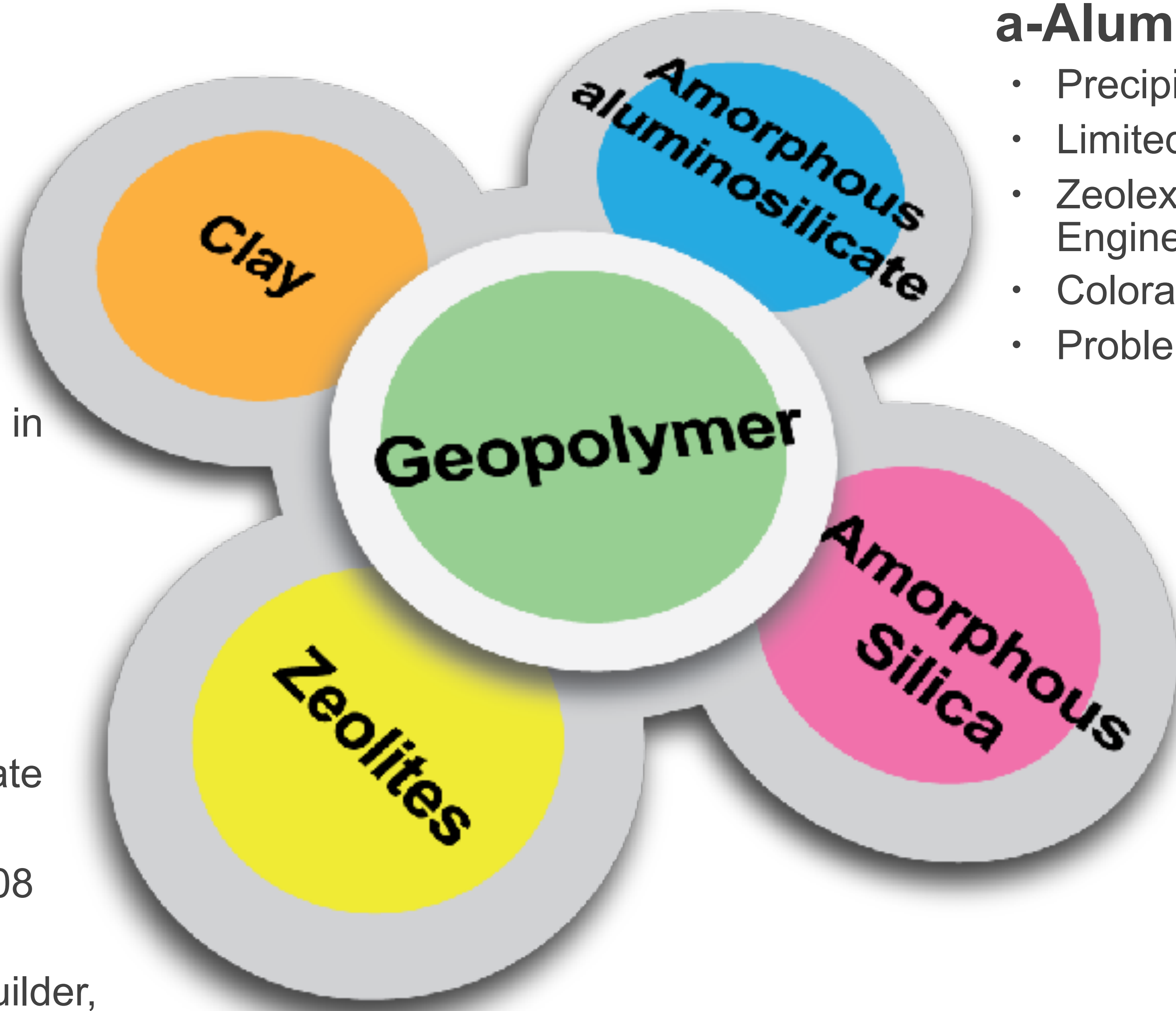


10 to 30 nm-sized nanoparticles

Similar to "Dense Dried Gel (Xerogel)"

Kriven, W.M.;Bell, J. L.; Gordon, M. "Microstructure and Microchemistry of Fully-Reacted Geopolymers and Geopolymer Matrix Composites" *Ceramic Transaction*. **2003**, 153, 227

Geopolymer as Inorganic Nanomaterial



Nanoclay

- Crystalline aluminosilicate
- 2D (layered) nanomaterial
- 9 Kt in 2007
- $200M in 2009
- Reinforcing fillers in polymer nanocomposites

Synthetic zeolites

- Crystalline aluminosilicate
- Micropores
- 1.3 Mt in 2008
- $9B in 2008
- Detergent builder, catalysis, adsorbents, purifications, ion exchange, etc.

a-Aluminosilicate

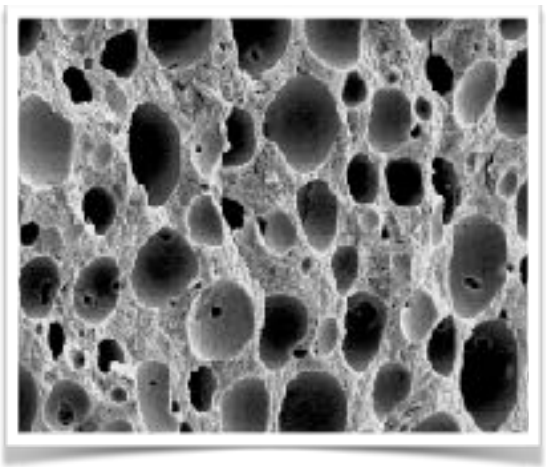
- Precipitated aluminosilicate
- Limited uses
- Zeolex® series from Huber Engineered Materials
- Colorant, filler, etc.
- Problem of instability in water

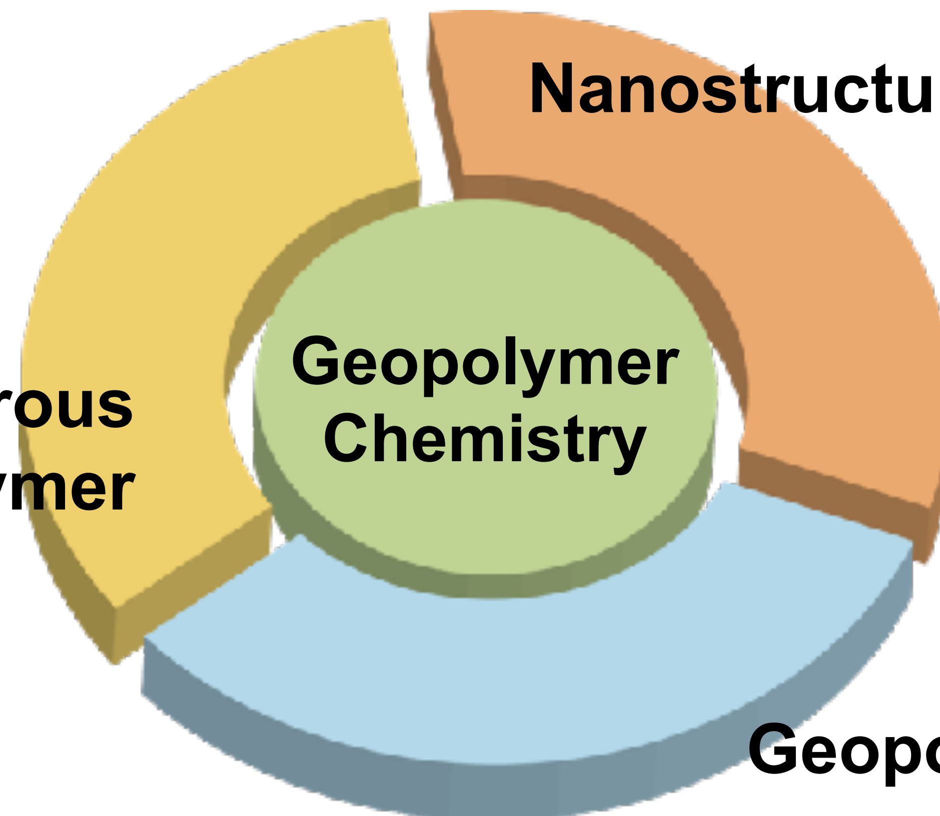
a-Silica

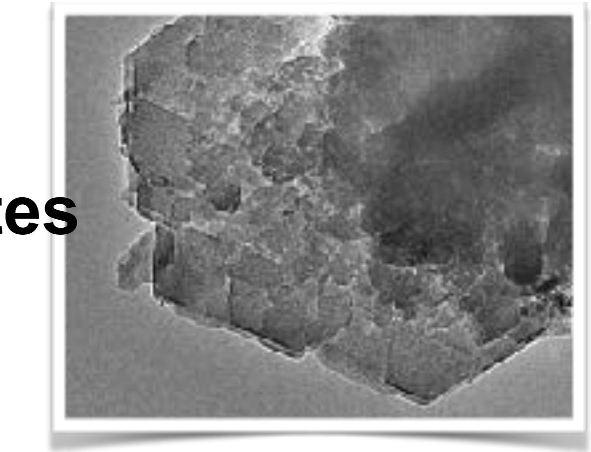
- Gel, sol and **precipitated silica**
- 3 Mt by 2018
- $7B by 2018
- Dehydration, purification, rheology modification, filler/ reinforcing filler, etc.

Inexpensive; Scalable Production; Platform Technology

New Nanostructured Aluminosilicates







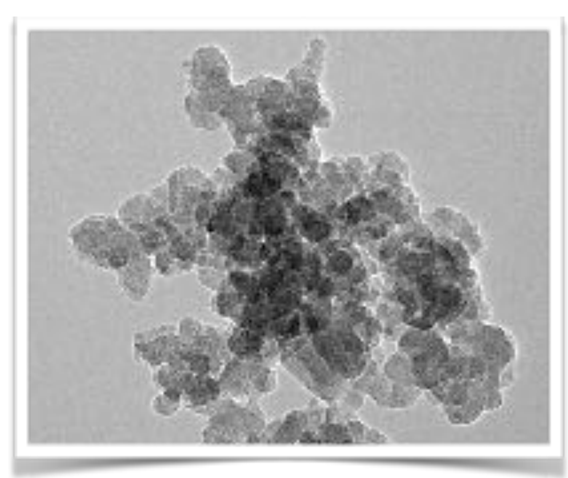
Meso-/macroporous geopolymer

- Porous geopolymer with co-existing macropores and mesopores
- Environmental remediations and catalysis

Nanostructured zeolites

- Structurally engineered highly-crystalline zeolites with textural mesoporosity.
  - CO_2 separation, gas purification, catalysts, ion exchangers, thermal energy storage, water purification, antibacterial agents, etc.

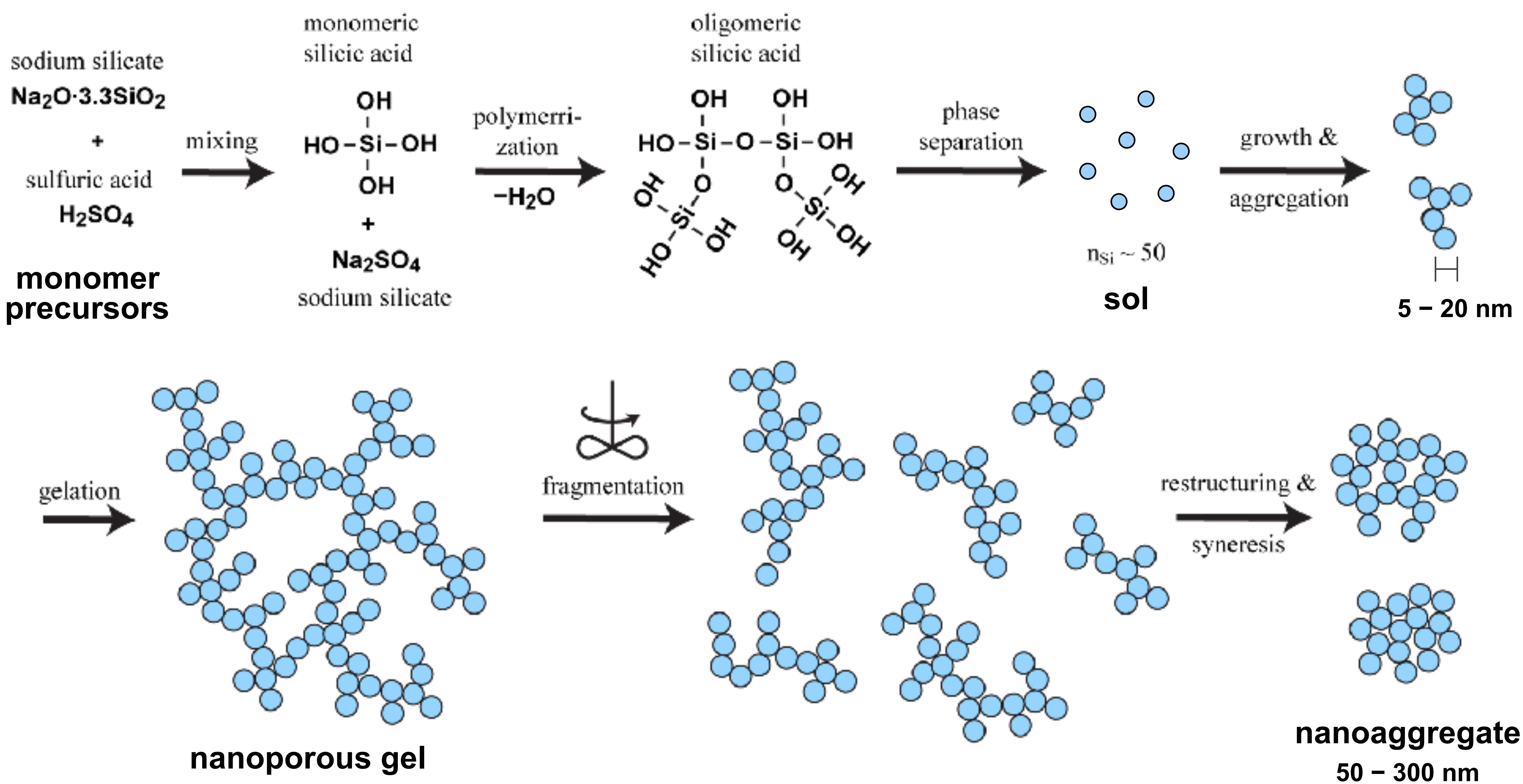
Geopolymer nanoaggregates



- Grape-shape aggregates (200 – 800 nm) of fused primary nanoparticles (10 – 30 nm); Well-defined mesoporosity; Surface area: 100 – 300 m^2/g
- Amorphous or partially zeolitic
- Reinforcing fillers, dye/drug carriers, acid scavenger, antibacterial fillers, etc.

"New Functional Materials" from Geopolymer Chemistry

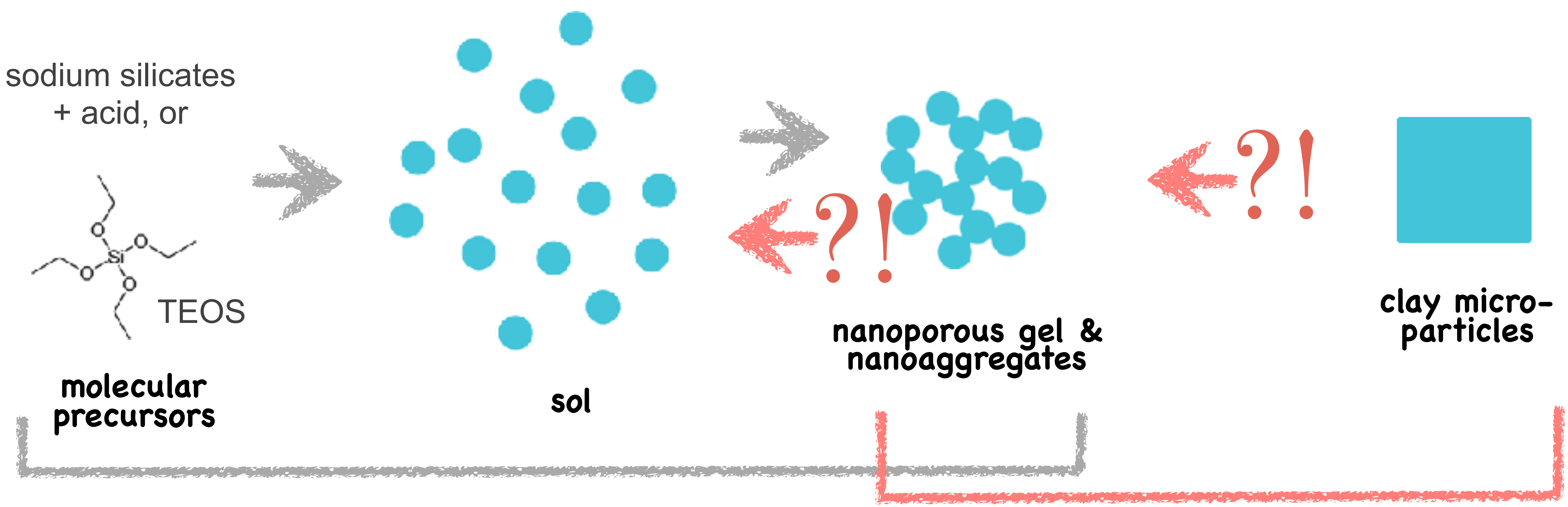
Production of Precipitated Silica



Adapted from Sebastian Wilhelm and Matthias Kind, "On the Relation between Natural and Enforced Syneresis of Acidic Precipitated Silica", *Polymers* **2014,** *6,* 2896-2911.

Ralph K. Iler, "The Chemistry of Silica: Solubility, Polymerization, Colloid and Surface Properties and Biochemistry of Silica" **1979**.

Bottom-Up or Top-Down



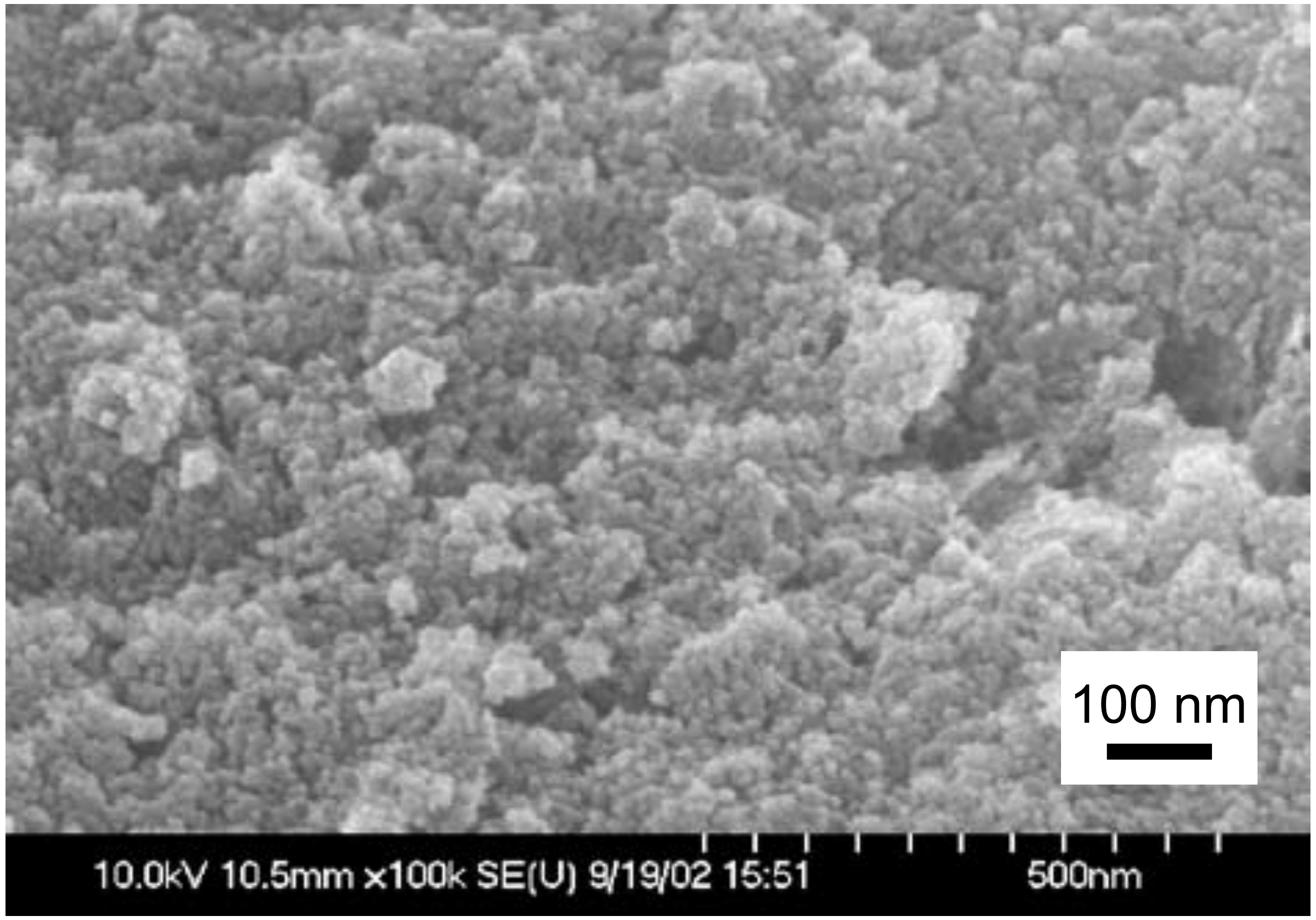
Bottom-up synthesis

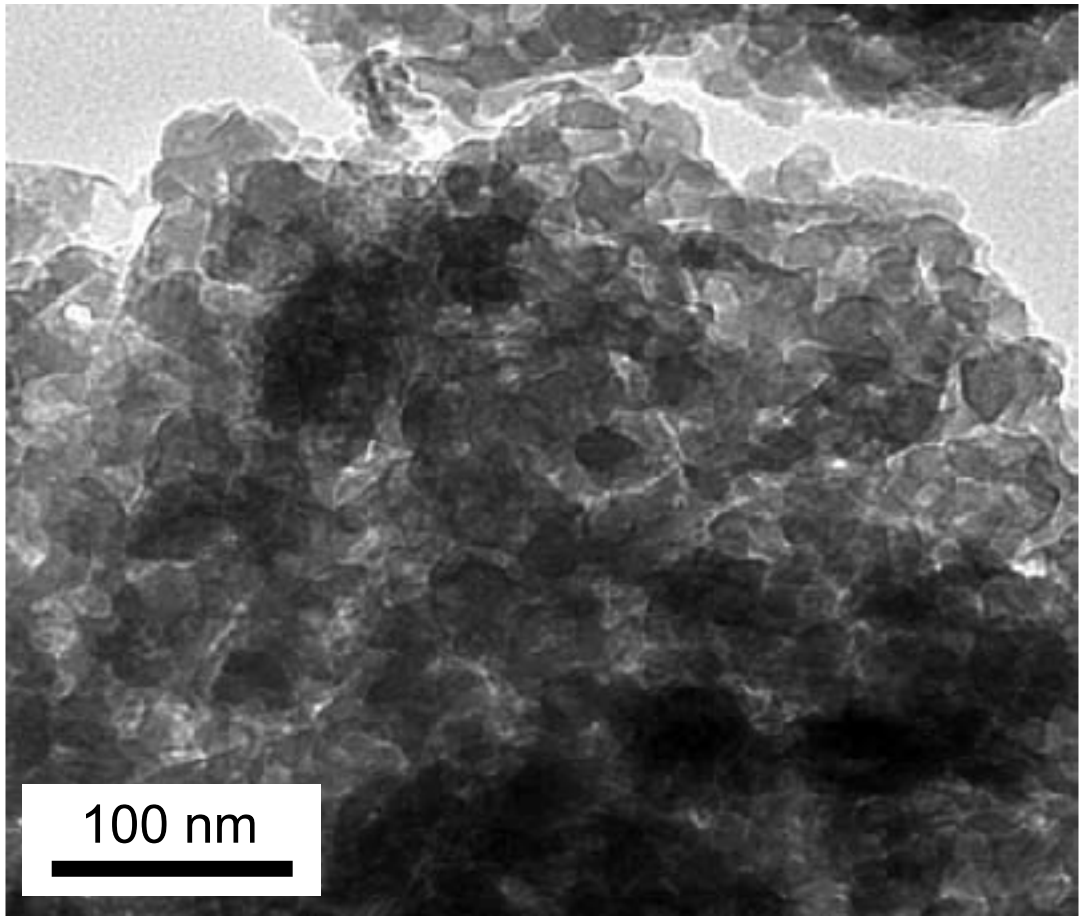
- Good control of structure and composition
- Inefficient use of materials
- Guiding principle: self-assembly of sol particles
- Nanoporous monoliths and particles, nanoparticles, etc.

Top-down synthesis

- Lack of general synth. principles/ methods for nanostructured materials
- Nanoporous geopolymer?!!
- Geopolymer nanoaggregates?!!
- Efficient use of materials
- High production yield (10 to 1000 times more by volume)

Geopolymer: Innately "Nano"





10 to 30 nm-sized nanoparticles

Similar to "Dense Dried Gel (Xerogel)"

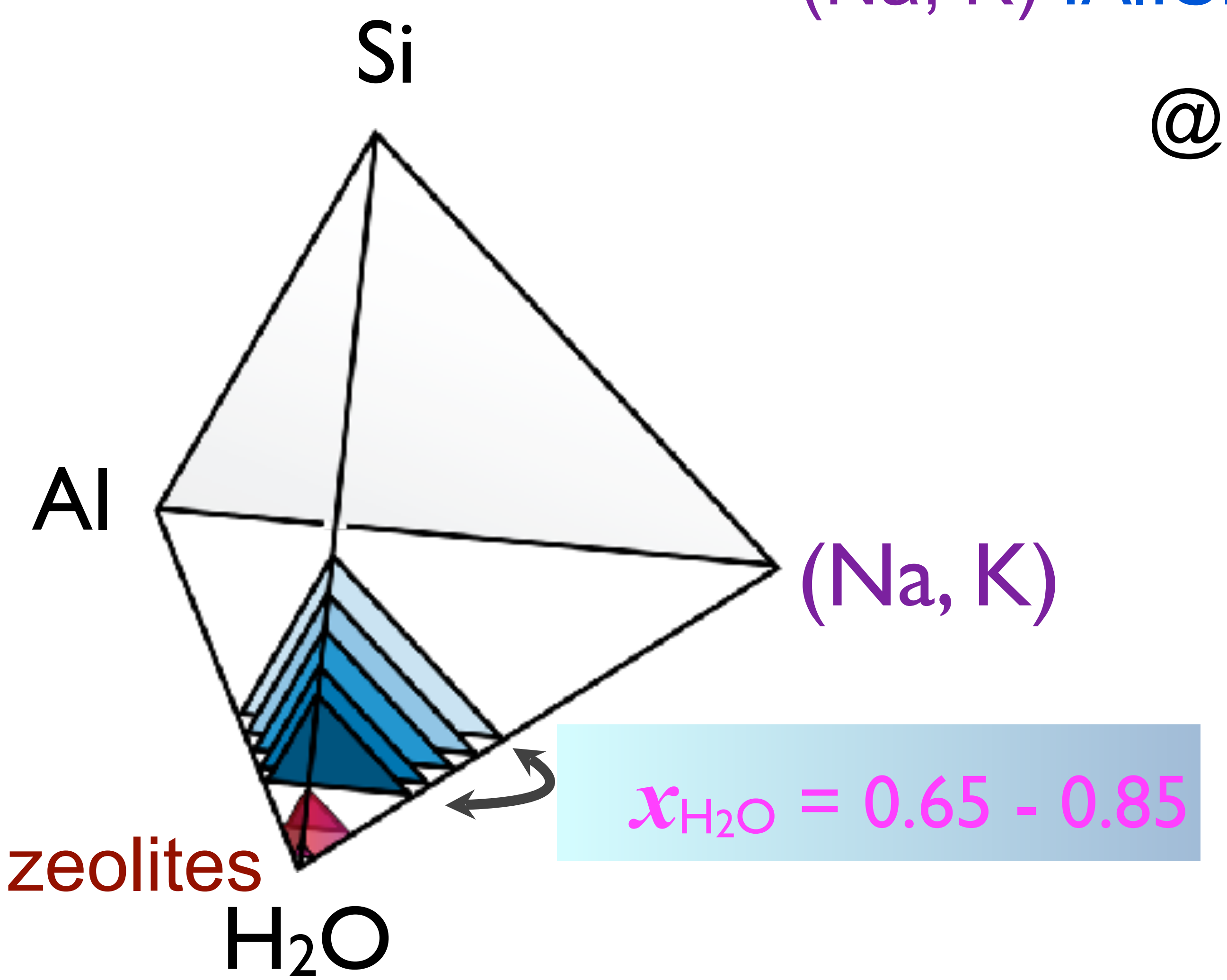
Kriven, W.M.;Bell, J. L.; Gordon, M. "Microstructure and Microchemistry of Fully-Reacted Geopolymers and Geopolymer Matrix Composites" *Ceramic Transaction*. **2003**, 153, 227

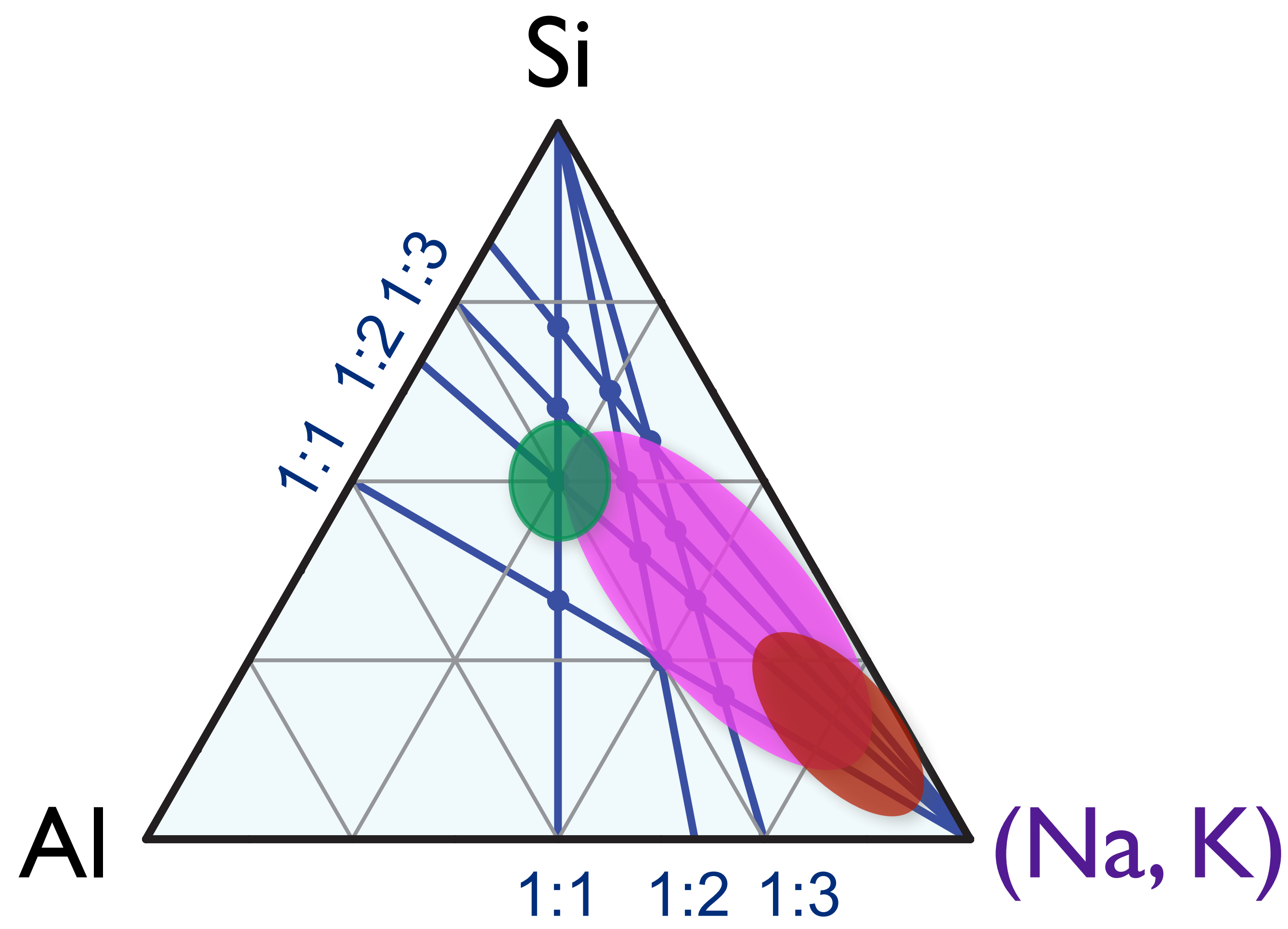
Synthetic Exploration

Homogeneous Gel Formation Region with Excess Alkali and Water

(Na, K) :Al:Si = (2−6):1:(1-3); x_{H2O} = 0.65−0.85

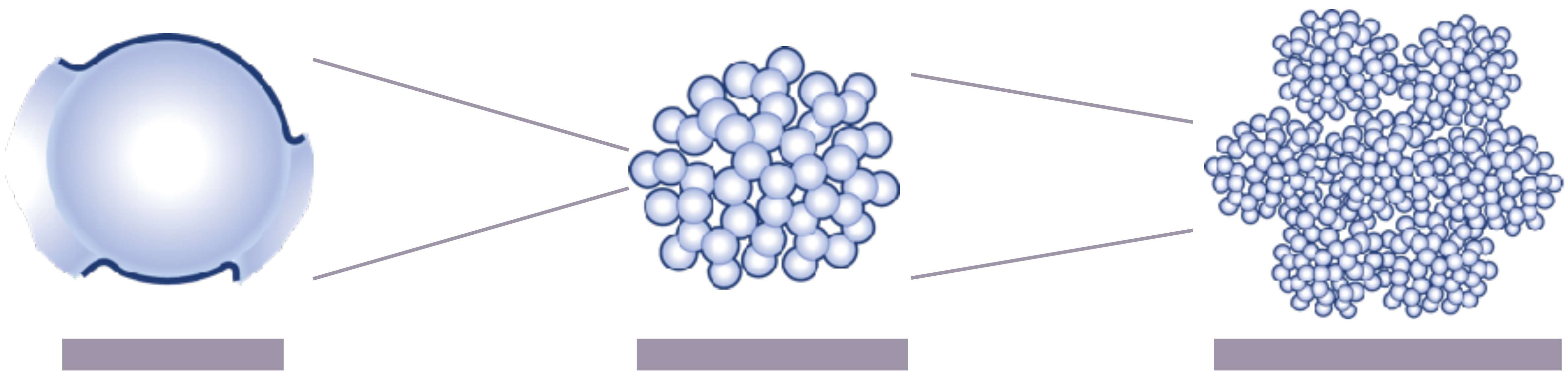
@ 60−120°C; 0.5−72 hrs; sealed



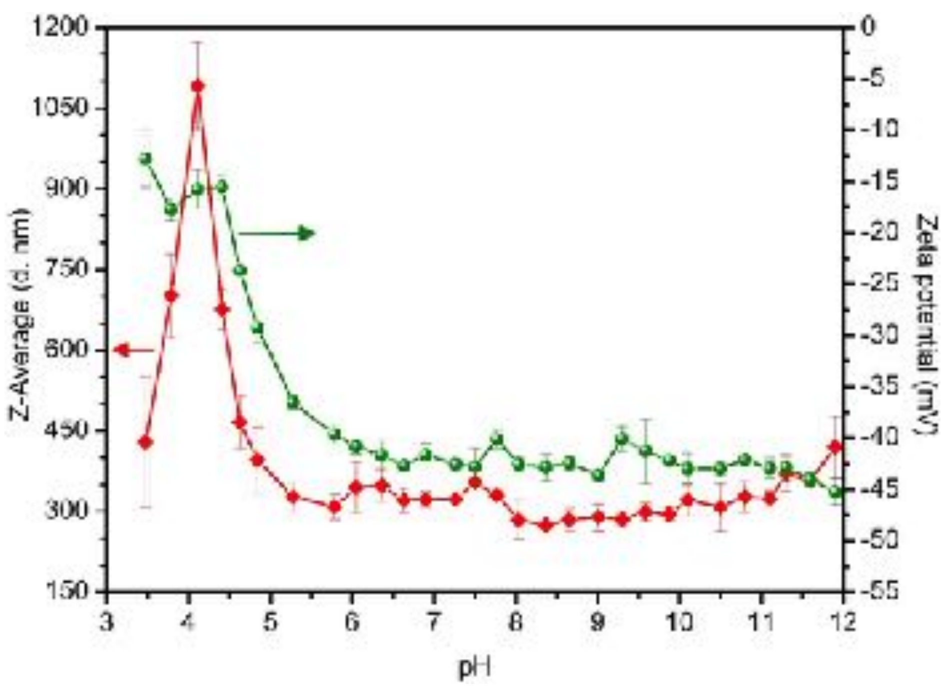


K-Geopolymer Nanoaggregates

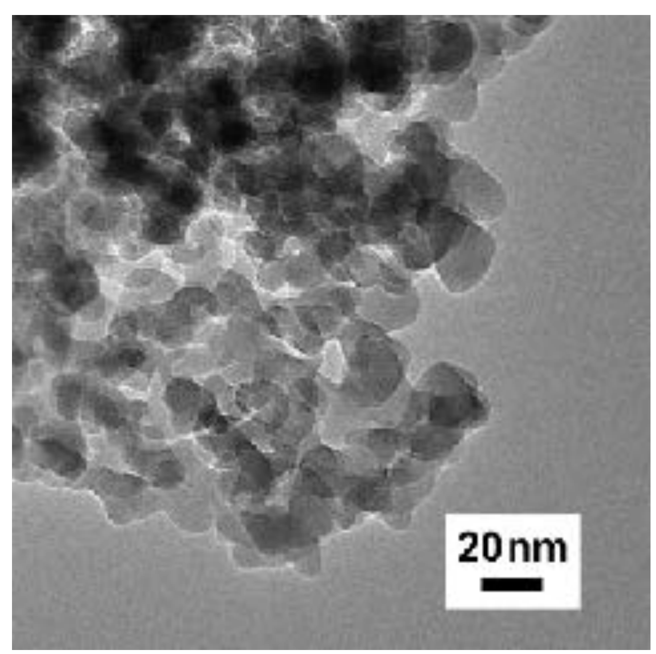
primary particle | nanoaggregate | agglomerate



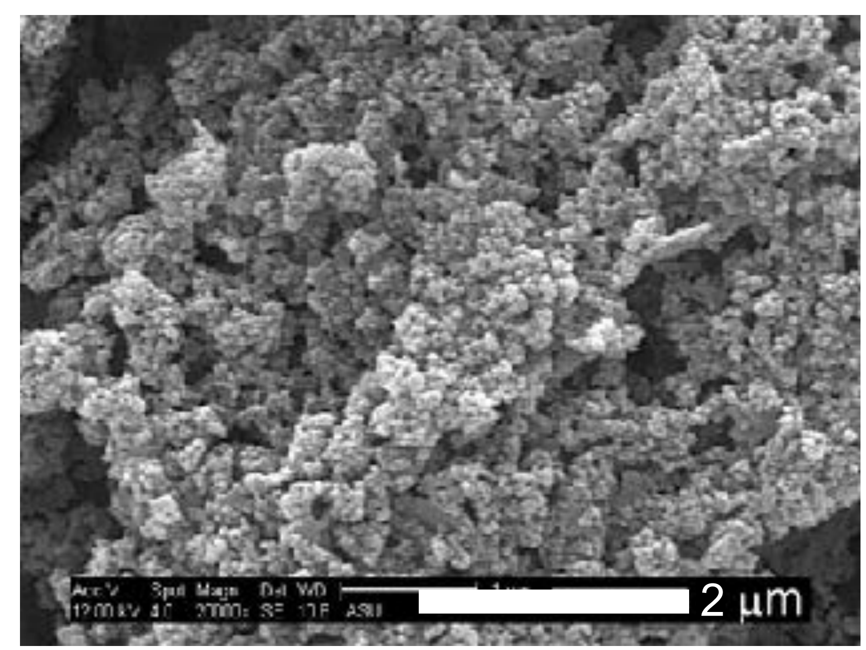
10 − 30 nm | **100 − 500 nm** | **>1 µm**



pH versus zeta potential and particle size

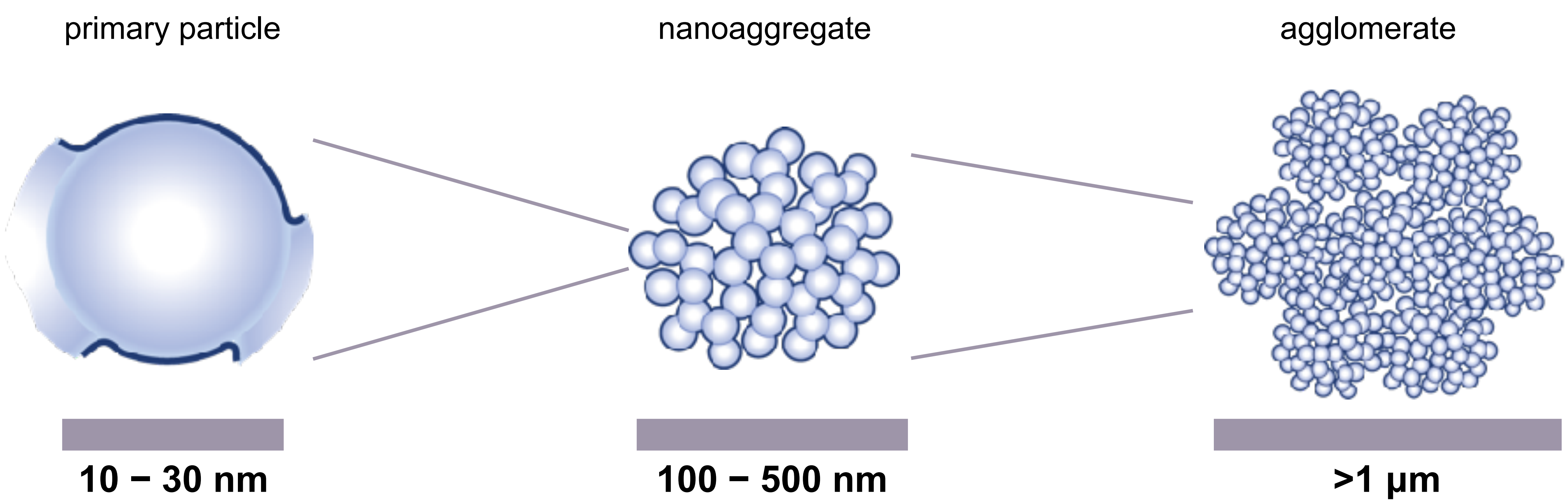


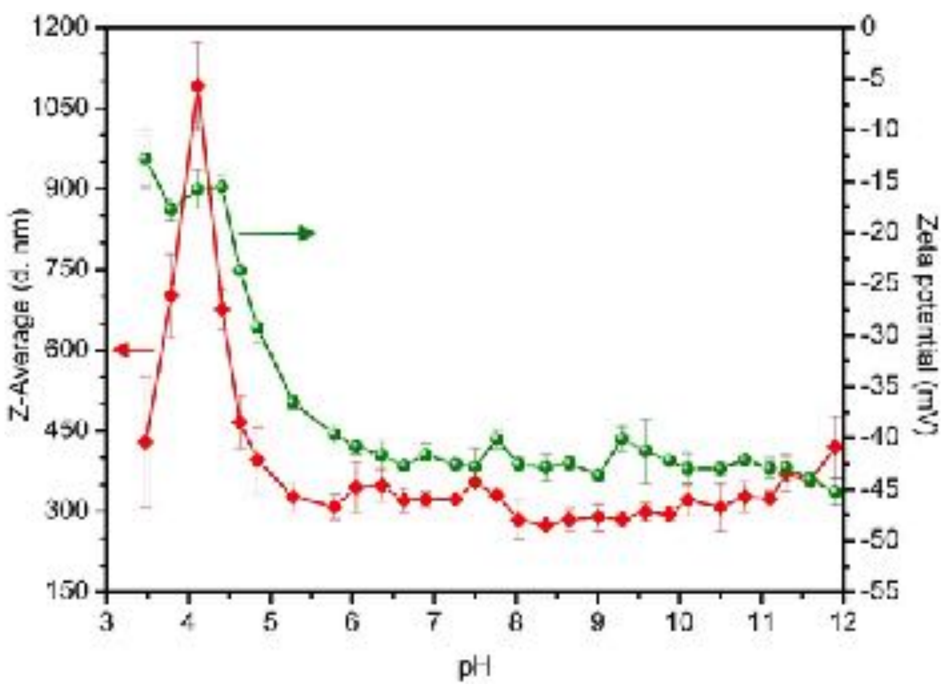
TEM micrograph



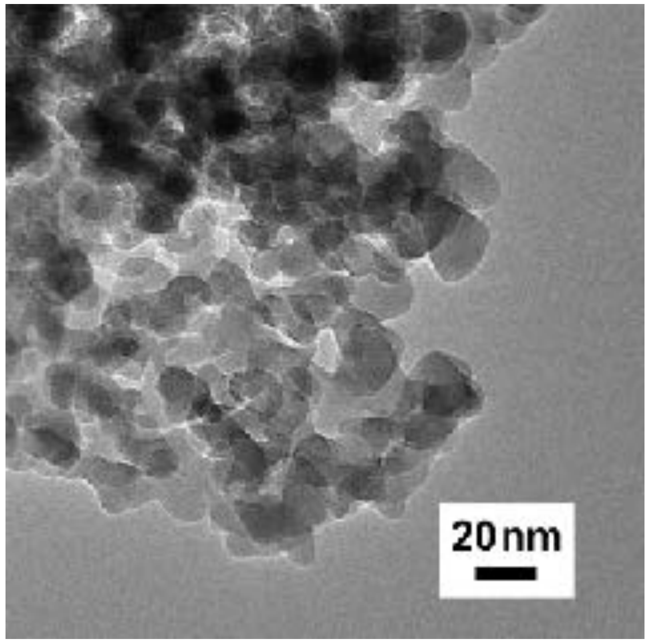
SEM micrograph

K-Geopolymer Nanoaggregates

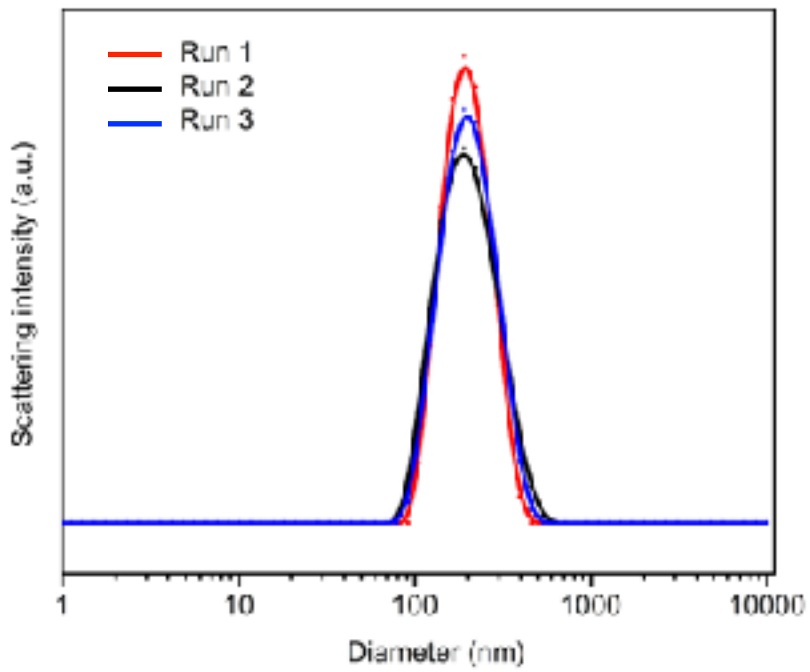




pH versus zeta potential and particle size



TEM micrograph

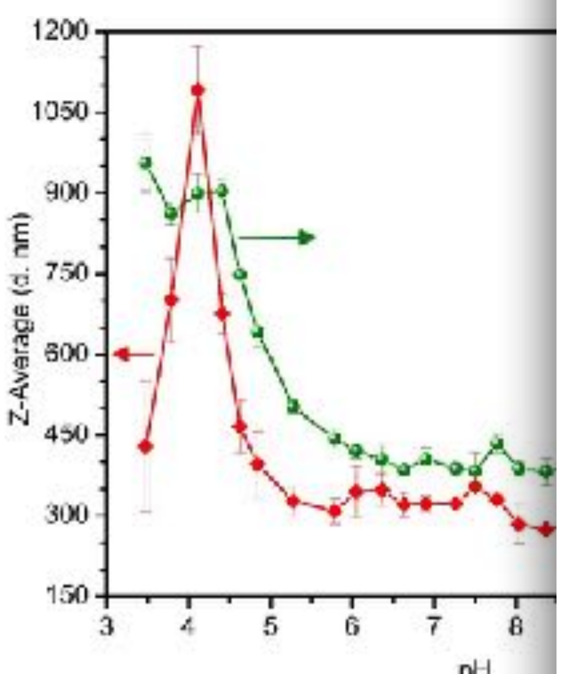


Hydrodynamic diameter distribution from DLS

K-Geopolymer Nanoaggregates

primary particle

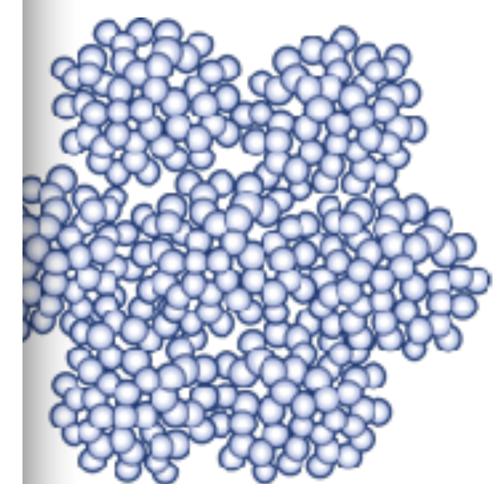
10 – 30 nm



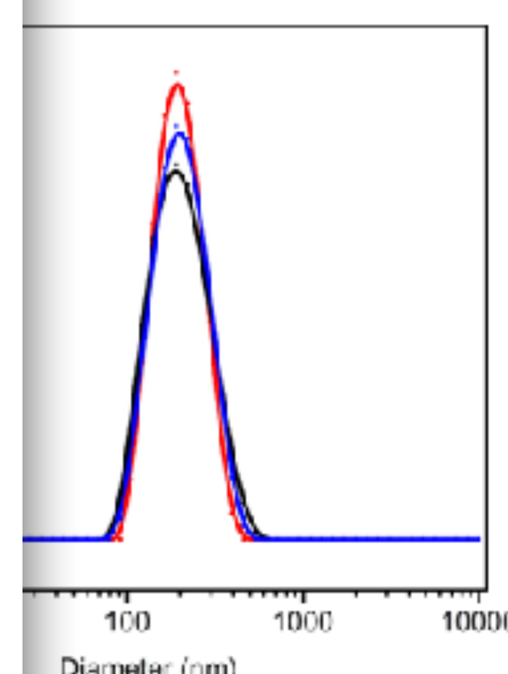
pH versus zeta potential and particle size

- Obtained as a thick paste
- Kg-quantity production per batch
- High production yield ~ 1 kg/L after washing

agglomerate



>1 µm



namic diameter distribution from DLS

Morphology after K-Geopolymer Gelation

Homogenization of precursors for 40 min at room temperature

↓

Heat the geopolymer resin at 60 °C for 30 min for gelation

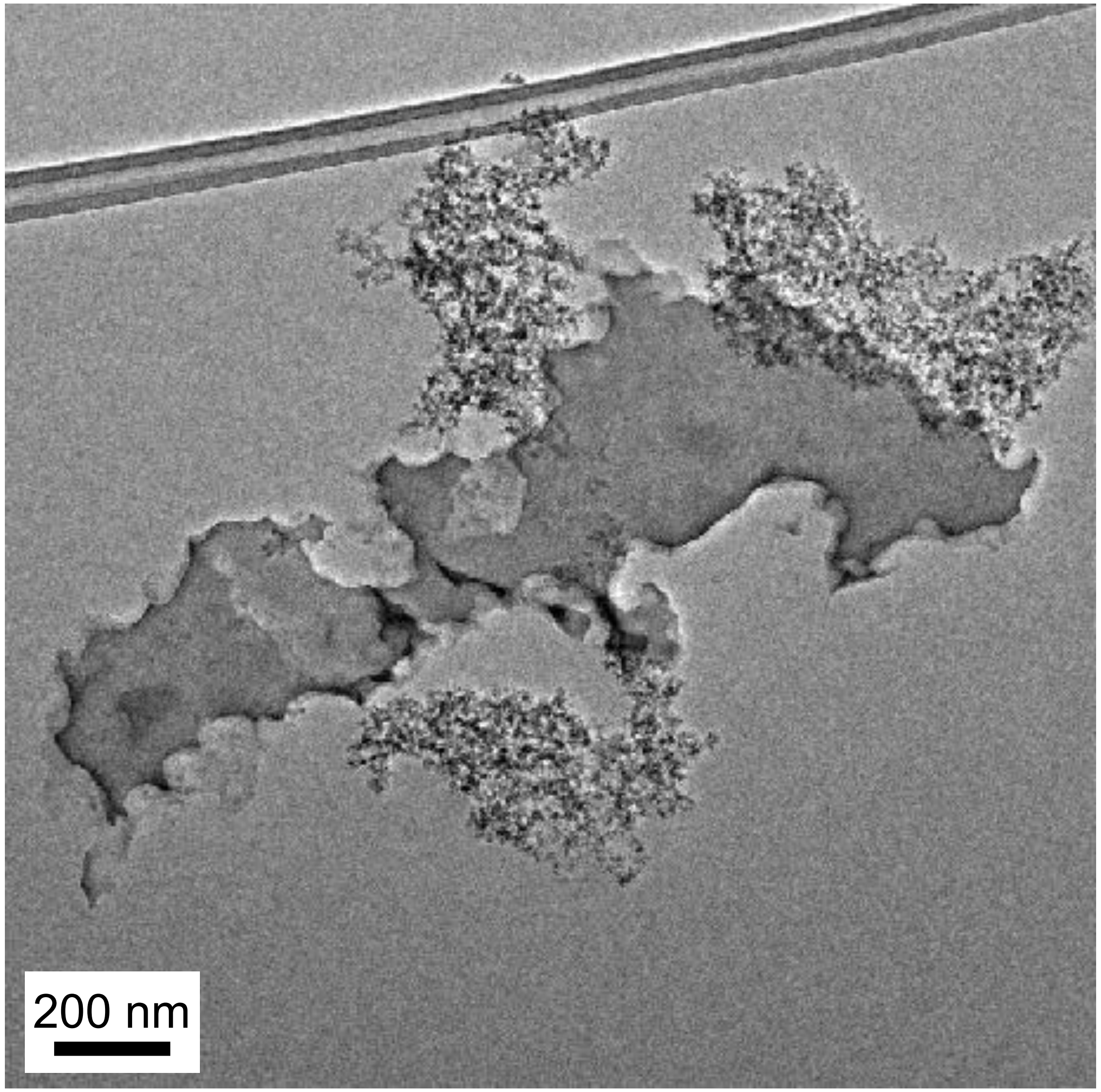
↓

Remove heat and add 8× water to quench the reaction

↓

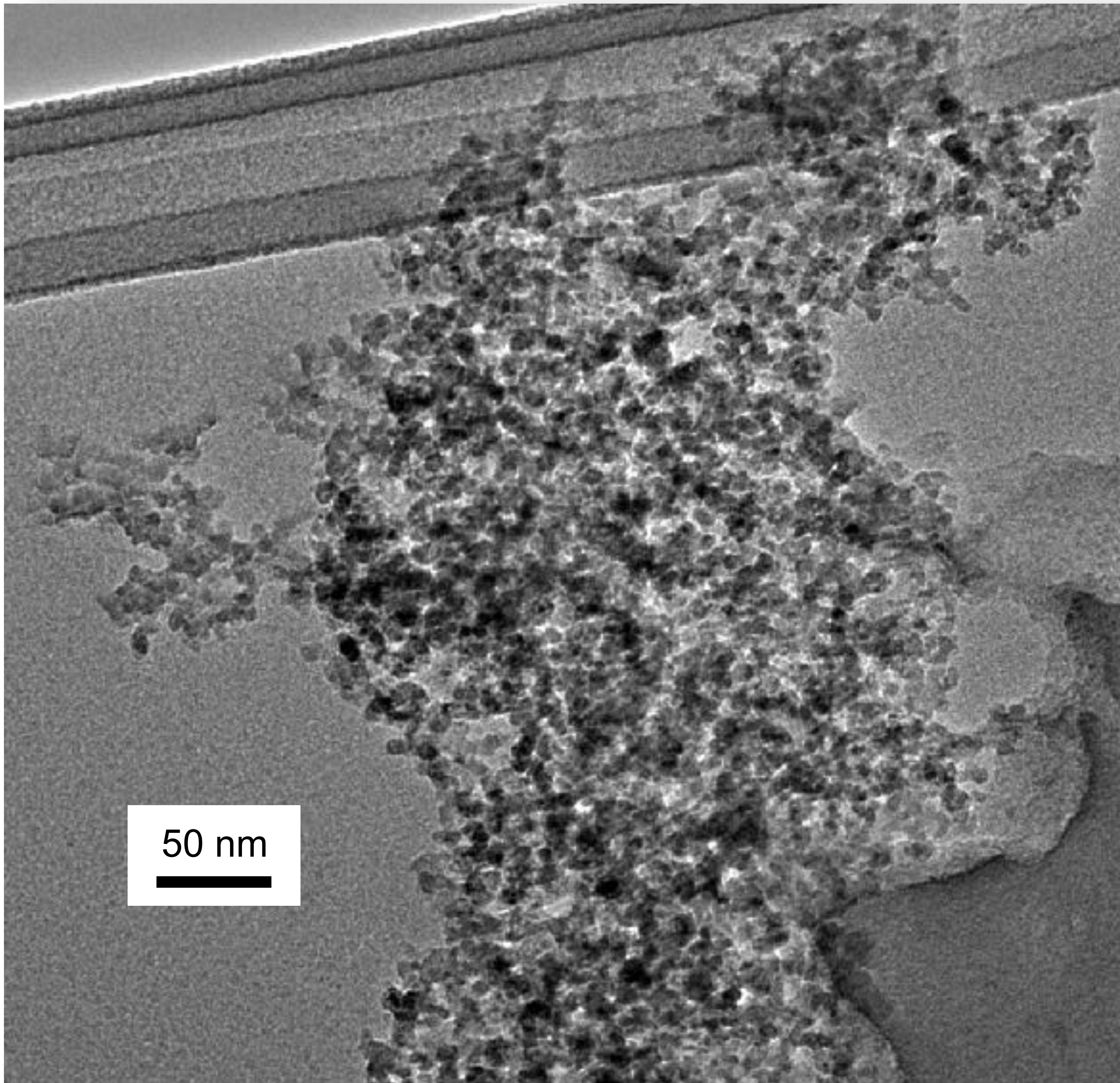
Collect particles from the cloudy supernatant.

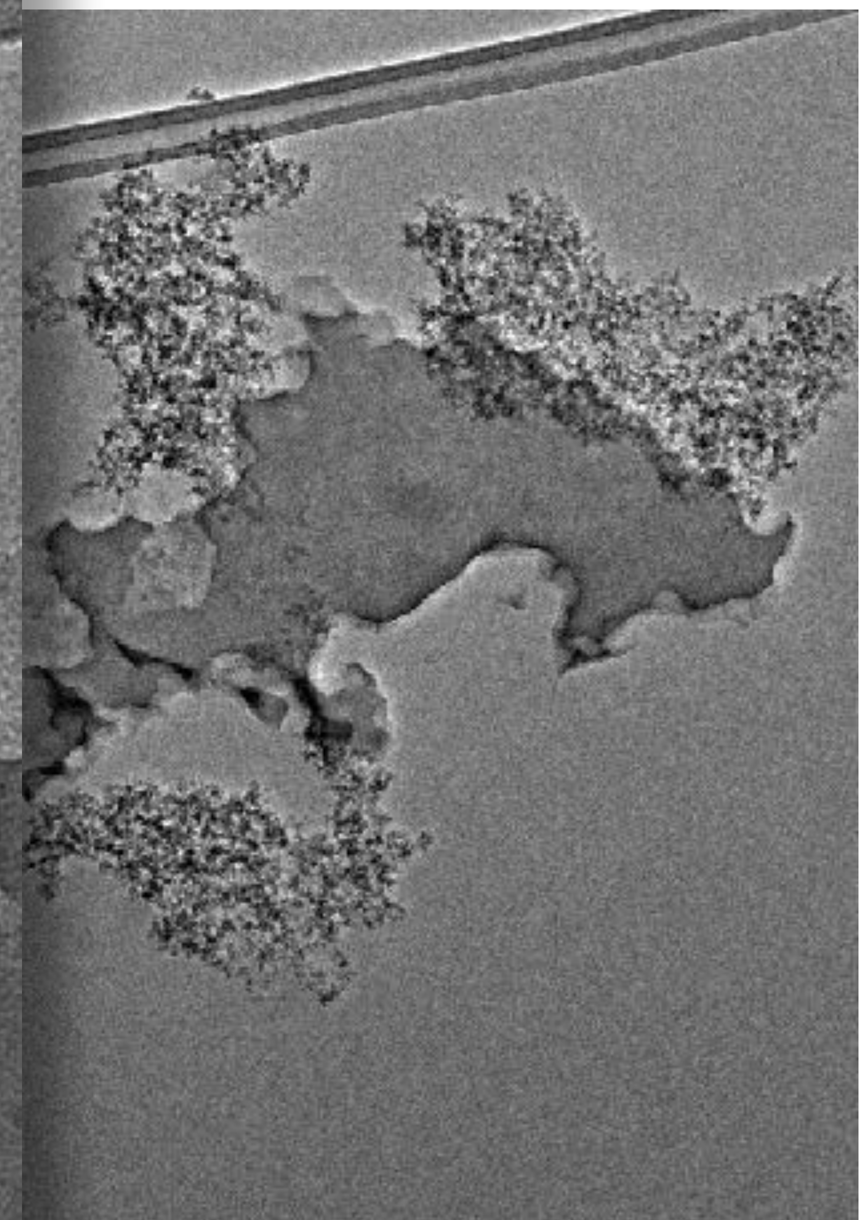
Quenching Geopolymerization in its Early Stage



Mixture of unreacted dense metakaolinite particles and fine gel structures.

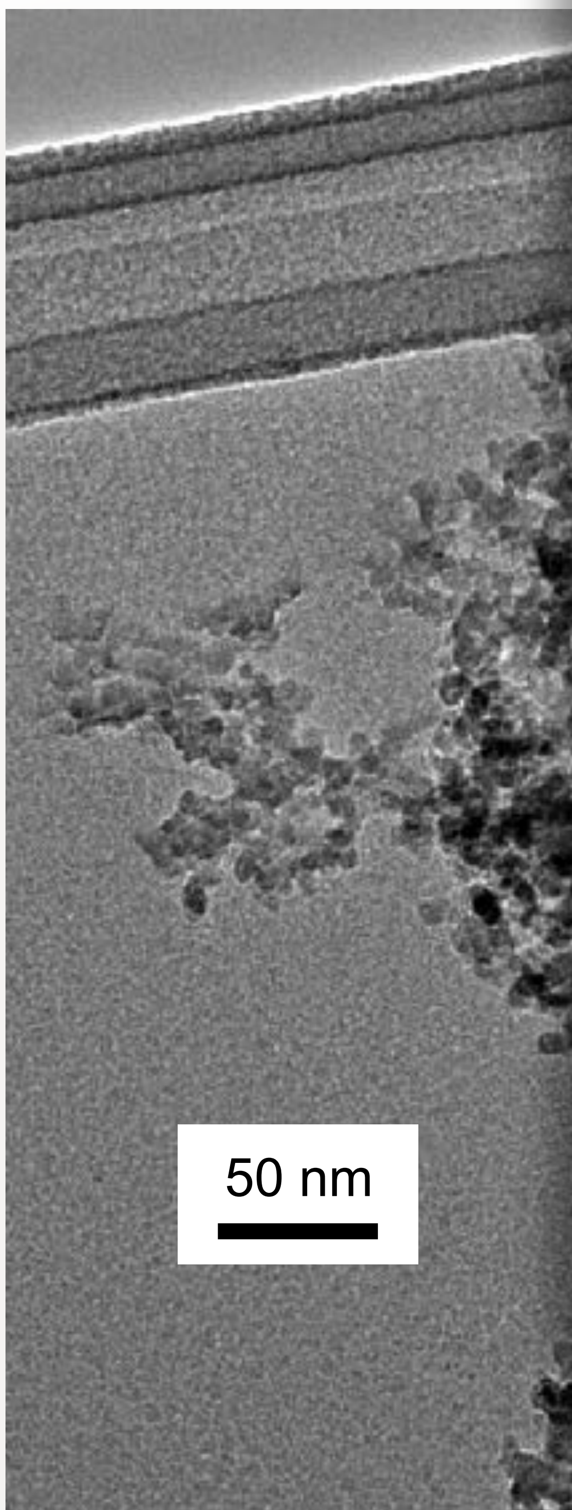
Morphology after K-Geopolymer Gelation

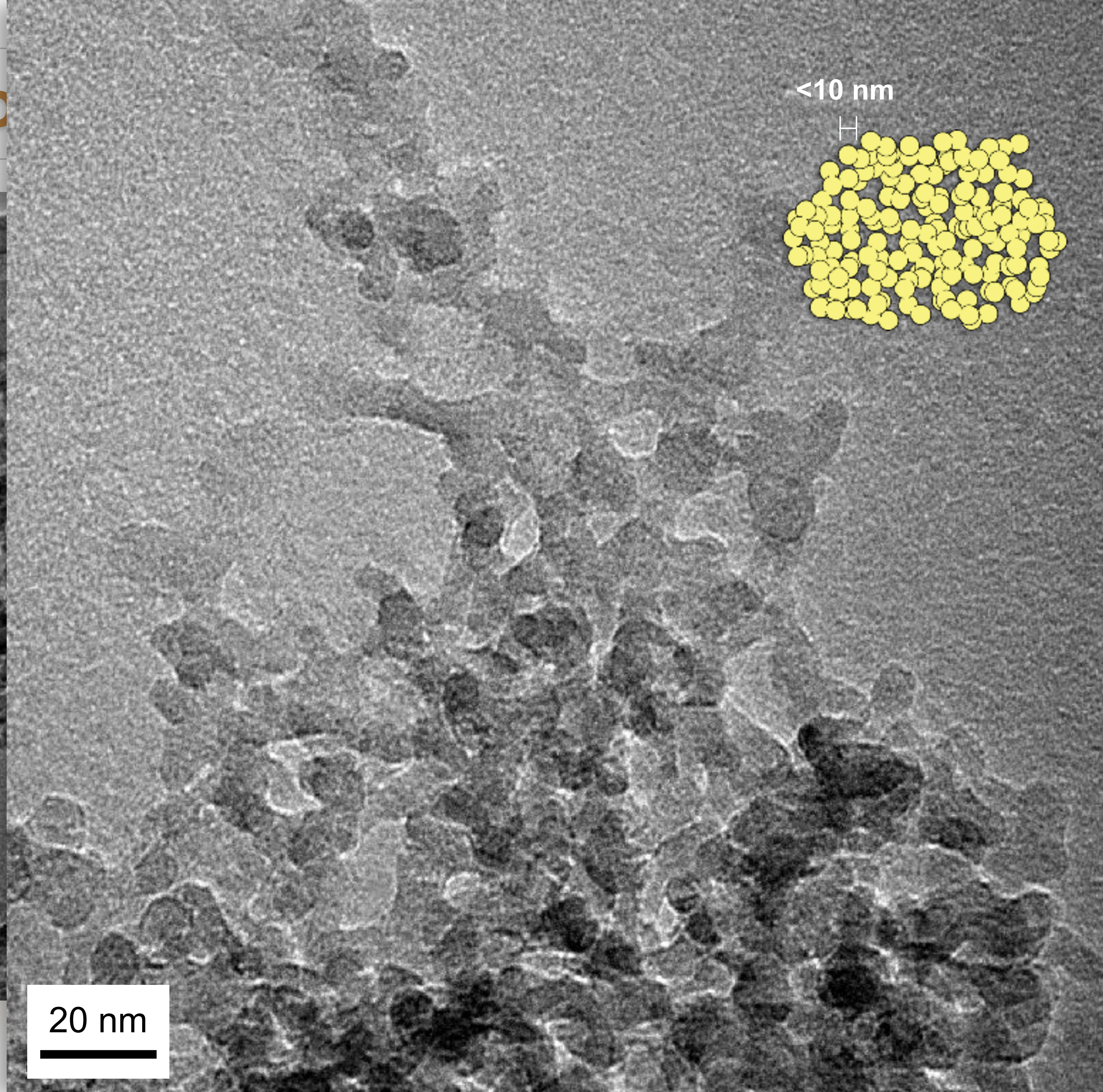




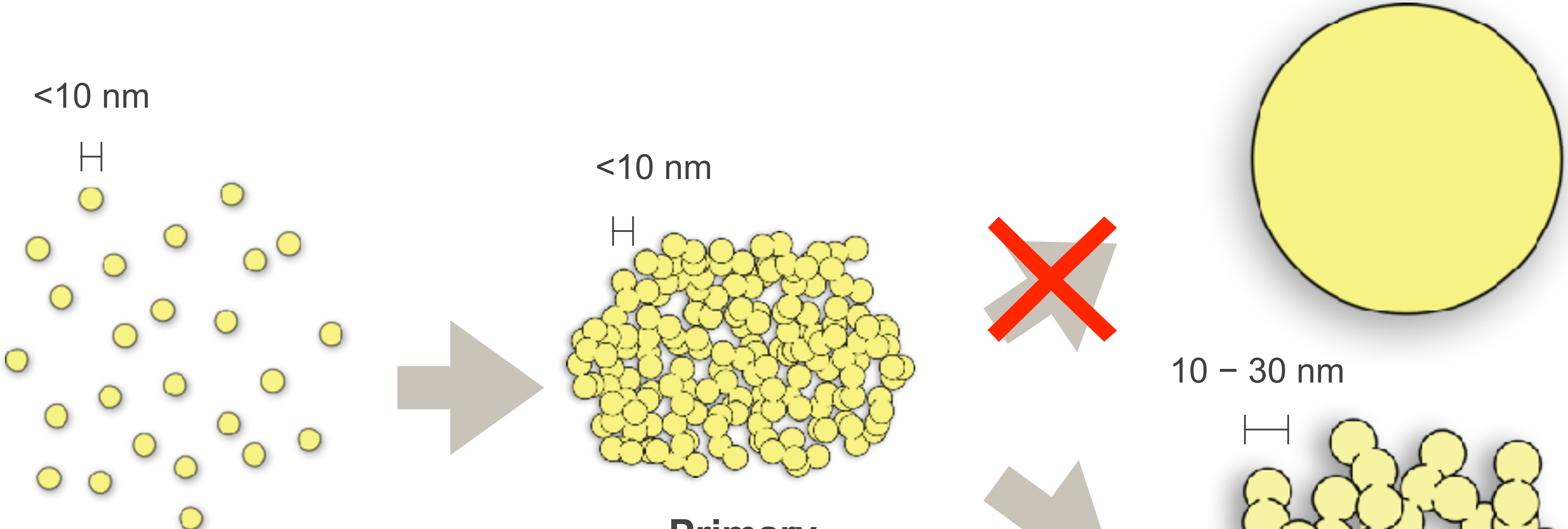
nreacted dense metakaolinite
d fine gel structures.

Morpholo



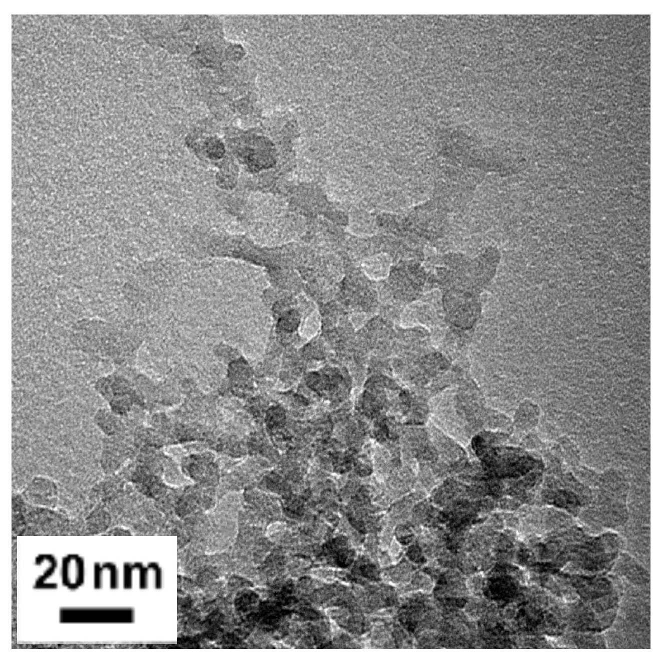


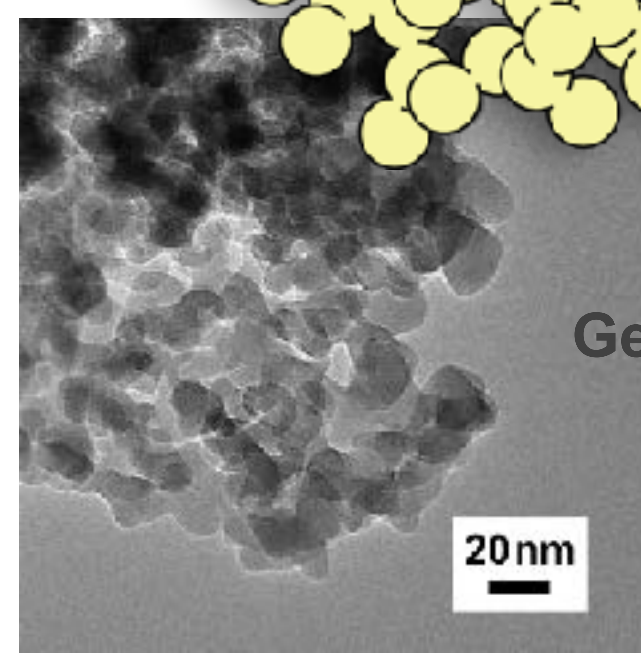
Aggregative Growth of Geopolymer



Prenucleation clusters

Primary geopolymer gel





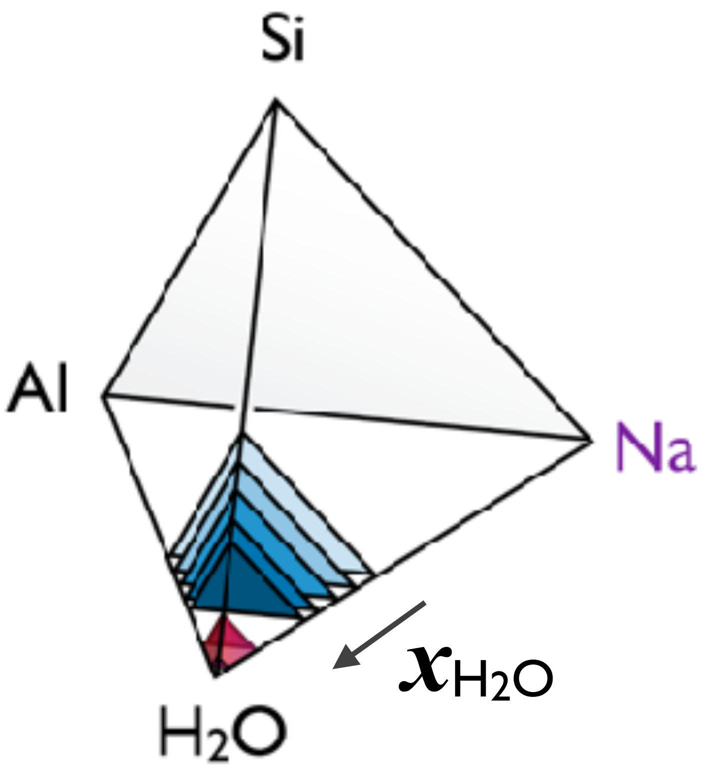
Geopolymer

Cf. ~4 nm-sized geopolymer clusters were observed in SAXS studies

Steins, P. *et al.* "Structural Evolution during Geopolymerization from an Early Age to Consolidated Material" Langmuir **2012**, *28*, 8502−8510

Kinetic Phase Diagram for Na-Geopolymer

@ 90 °C for 6 hrs; sealed

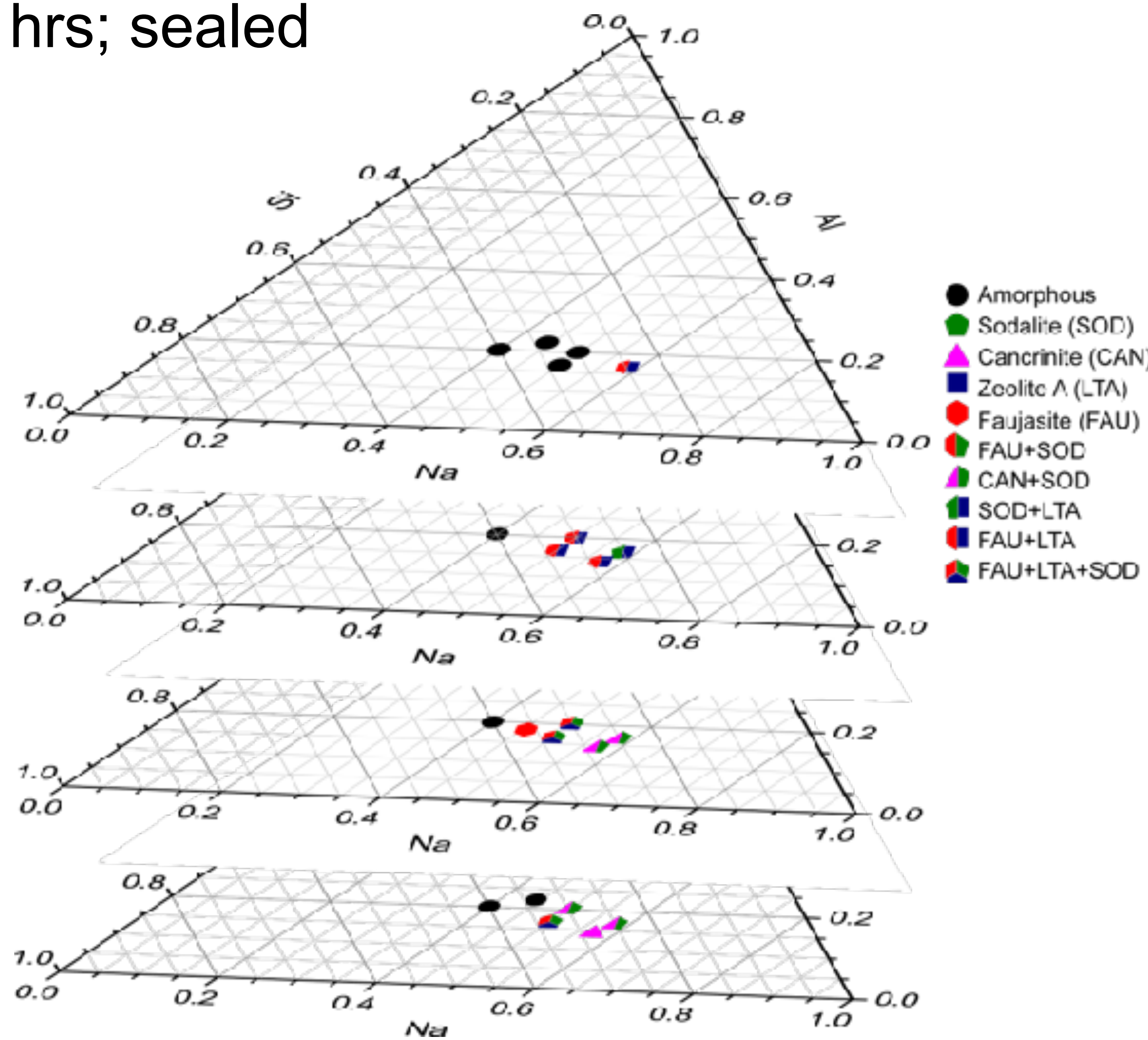


0.85

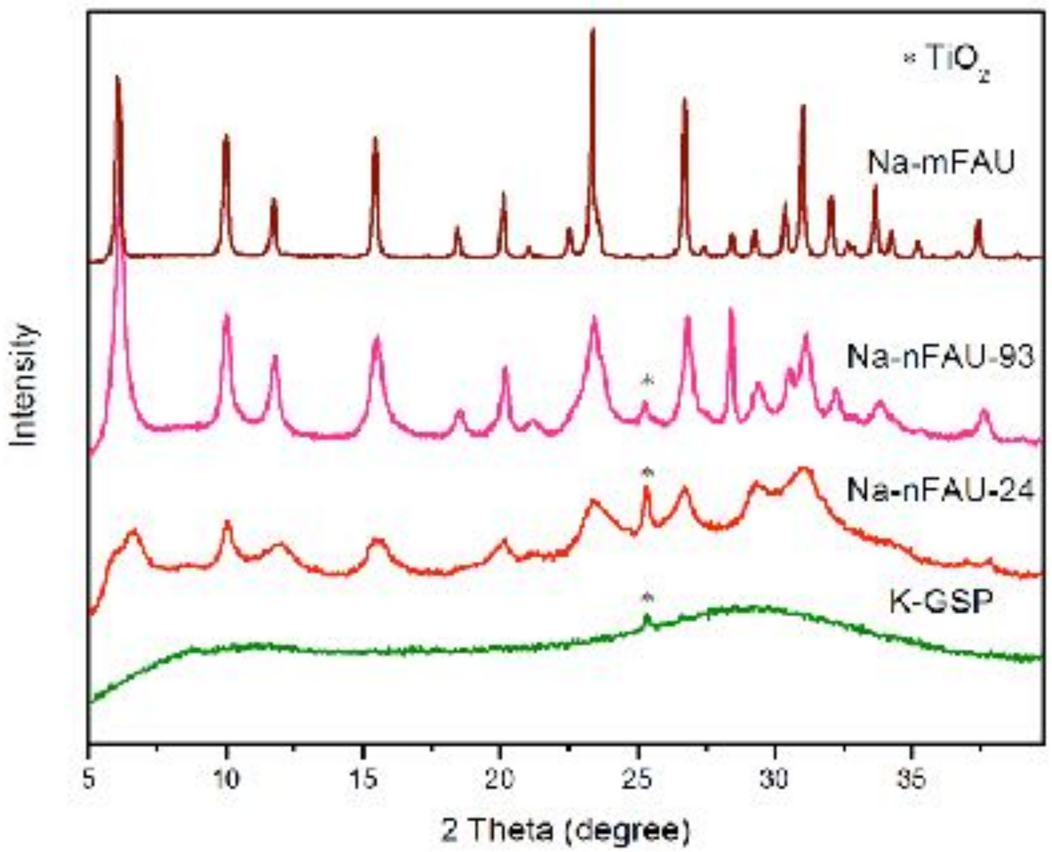
0.80

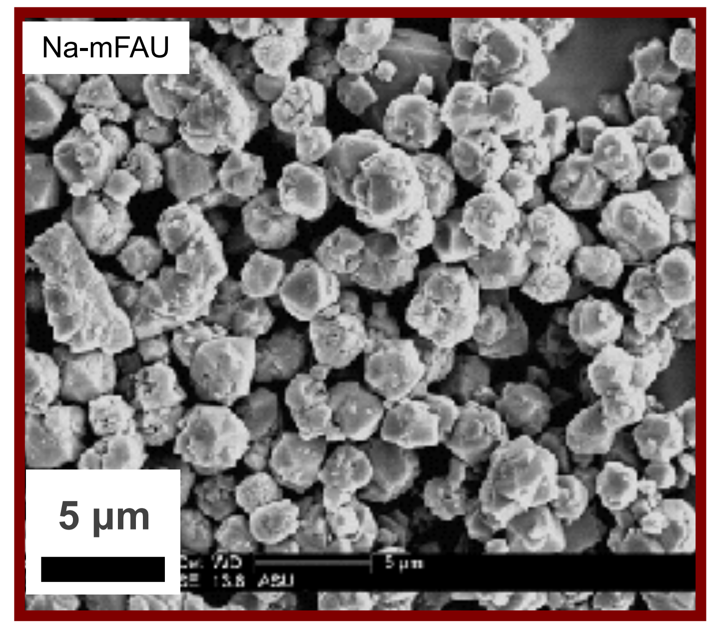
0.75

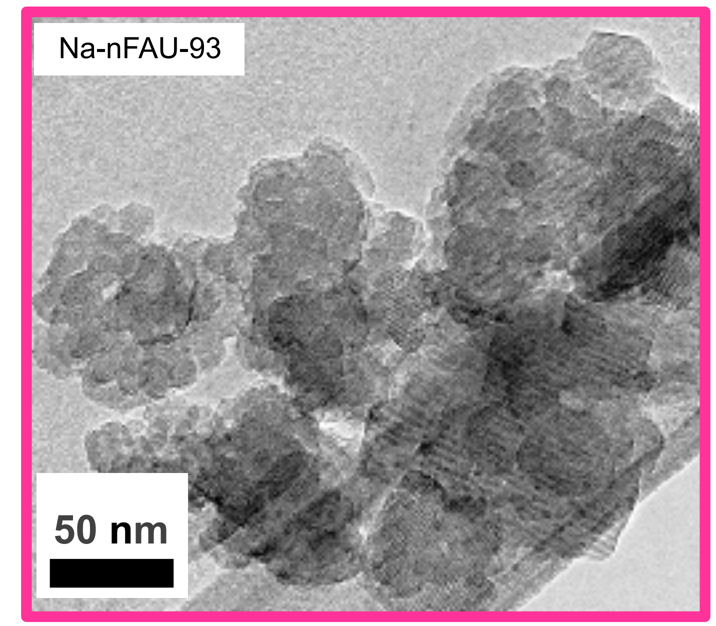
x_{H_2O} = 0.70

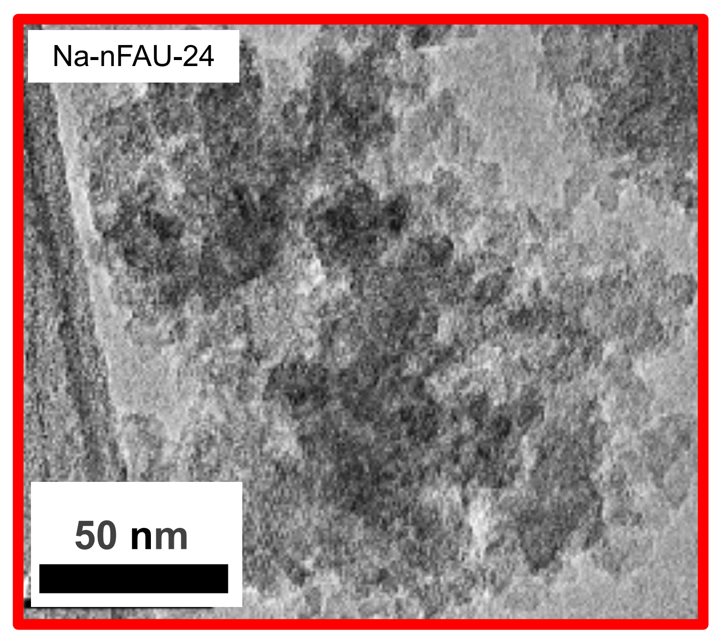


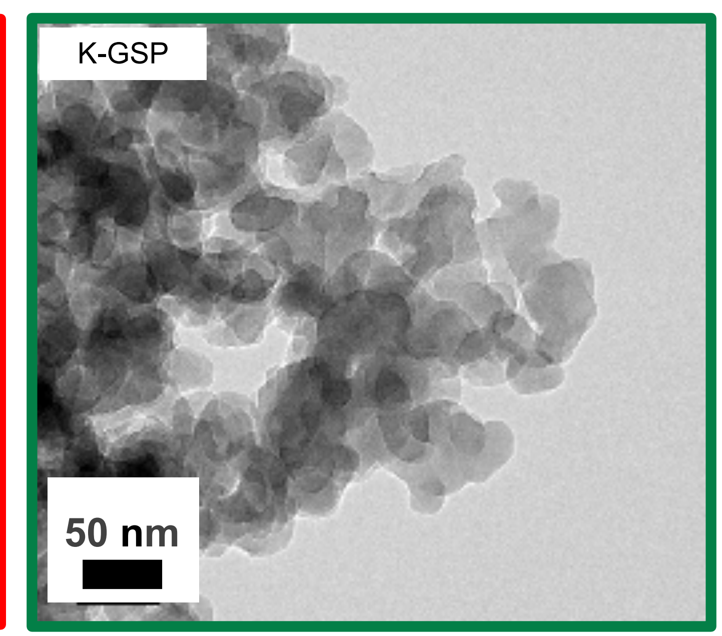
Faujasite (FAU) Zeolite Nanoaggregates





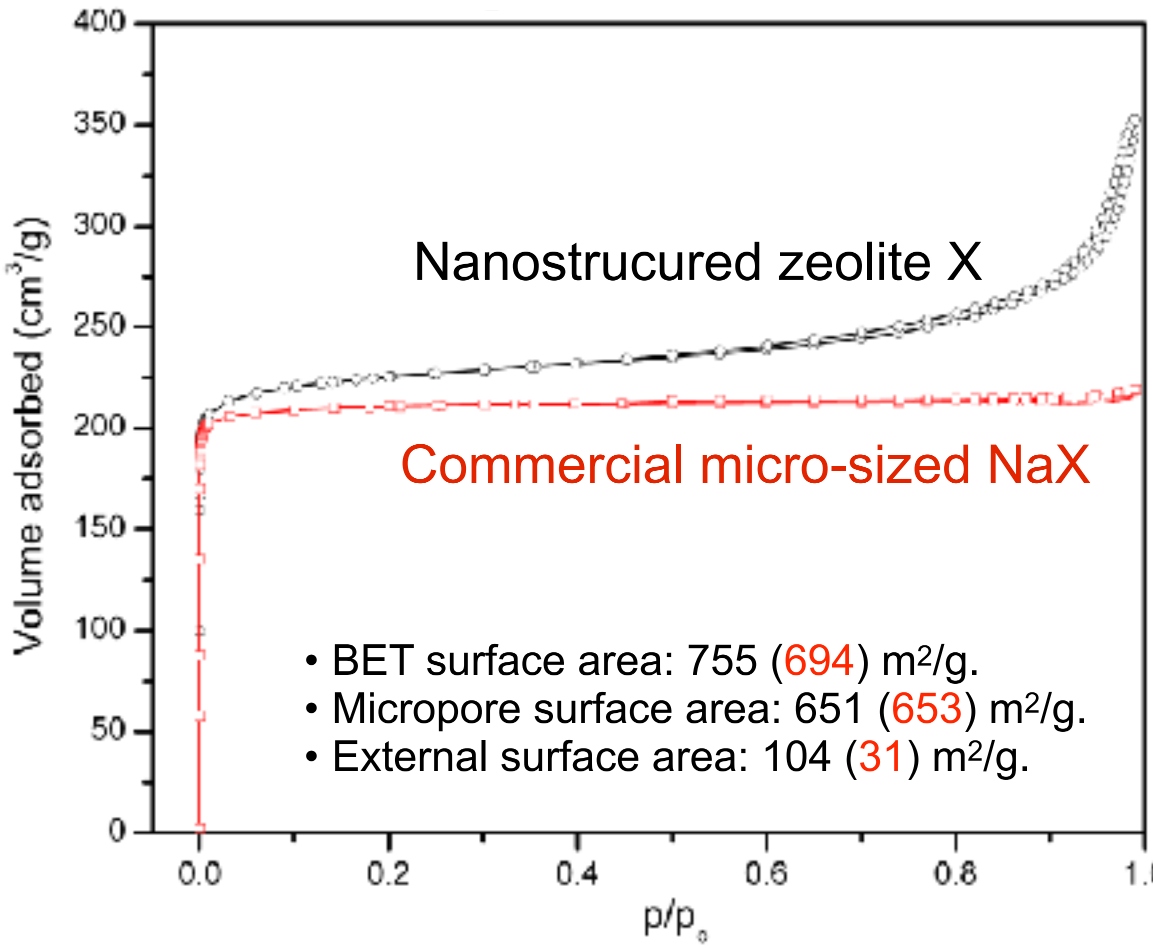


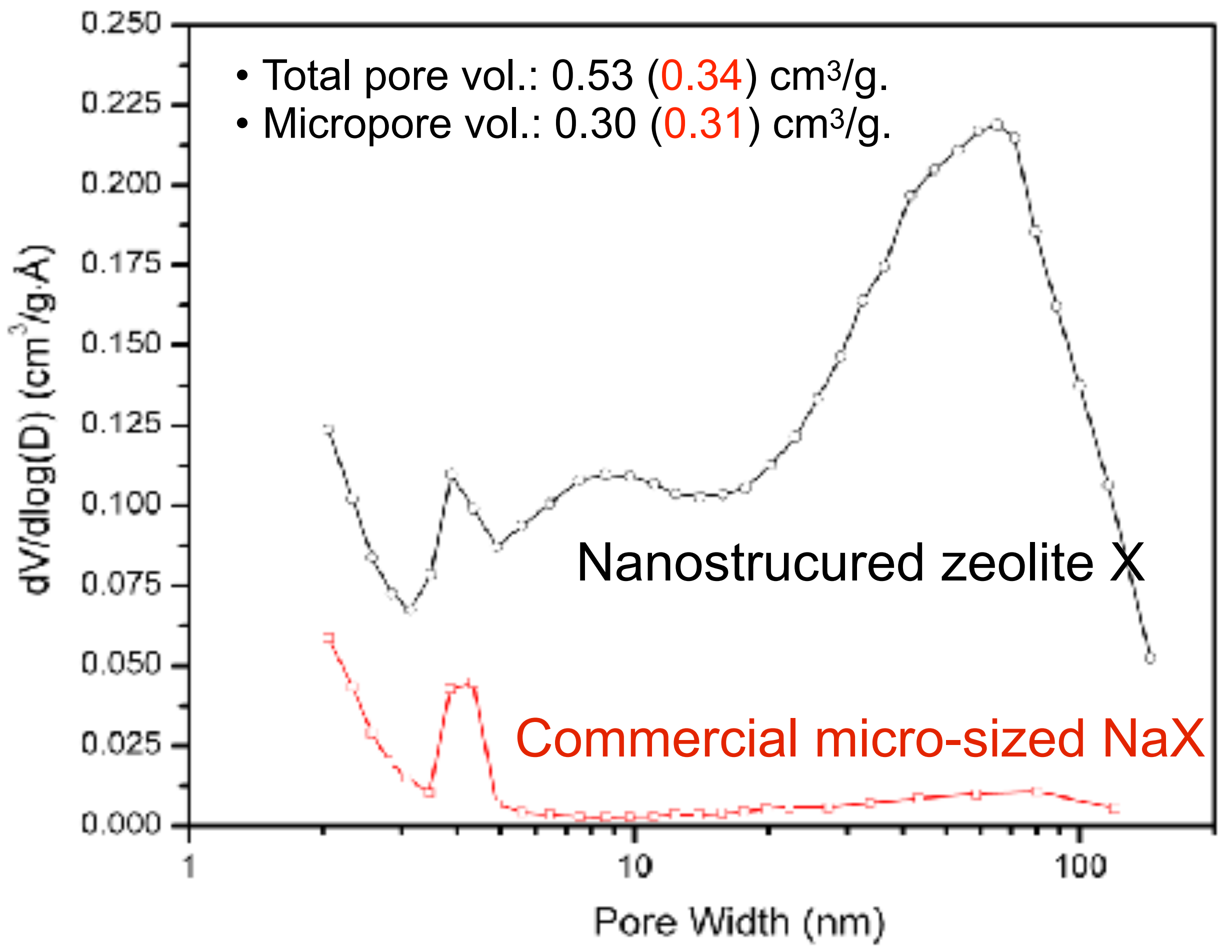




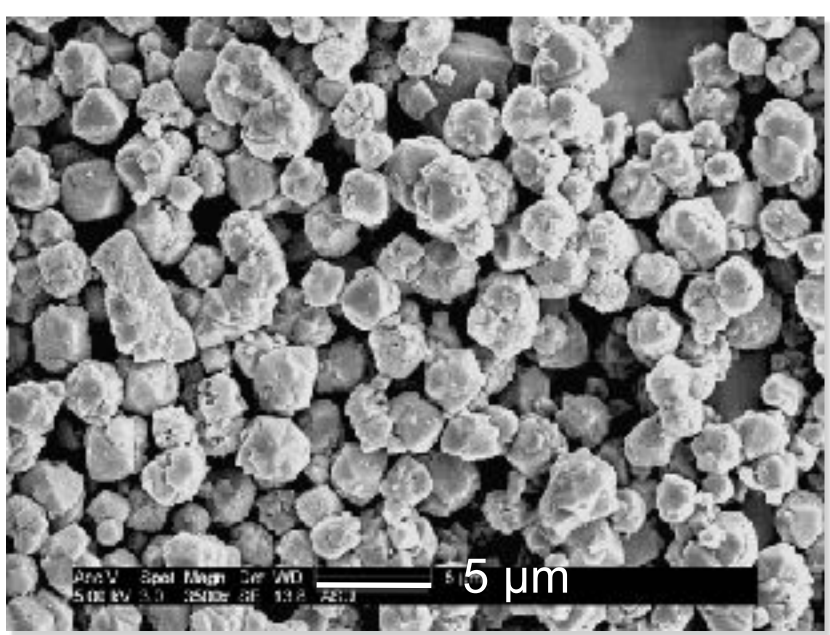
- Na-mFAU: Commercial microsized faujasite zeolite (as the reference).
- Na-nFAU-93: Highly crystalline nanostructured FAU type zeolite with 93% crystallinity (Scherrer size ~24 nm).
- Na-nFAU-24: Poorly crystalline faujasite (FAU) type zeolite with 24% crystallinity (10~30 nm).
- K-GSP: Amorphous K-based geopolymer small particle (DLS size ~ 500 nm).

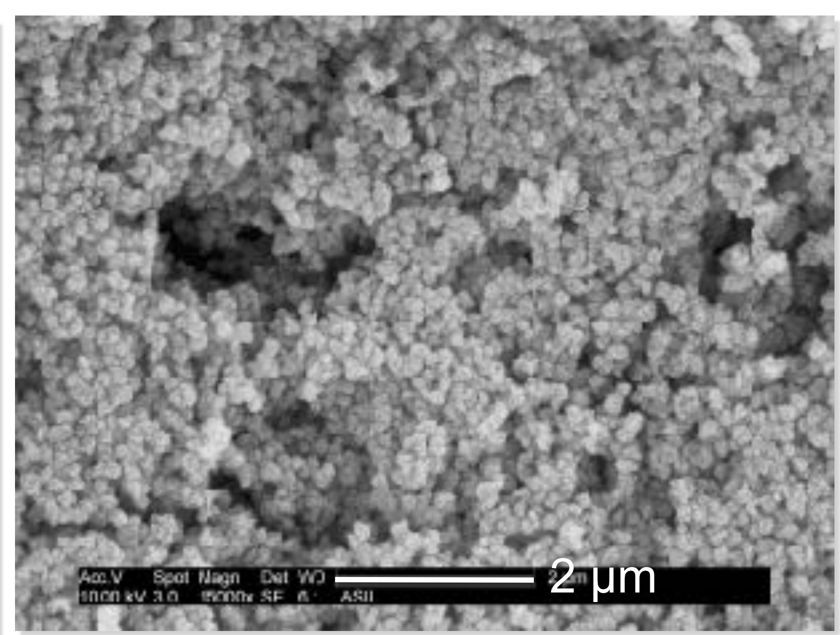
Nanostructured vs. Mico-sized





Commercial NaX (~2 µm)

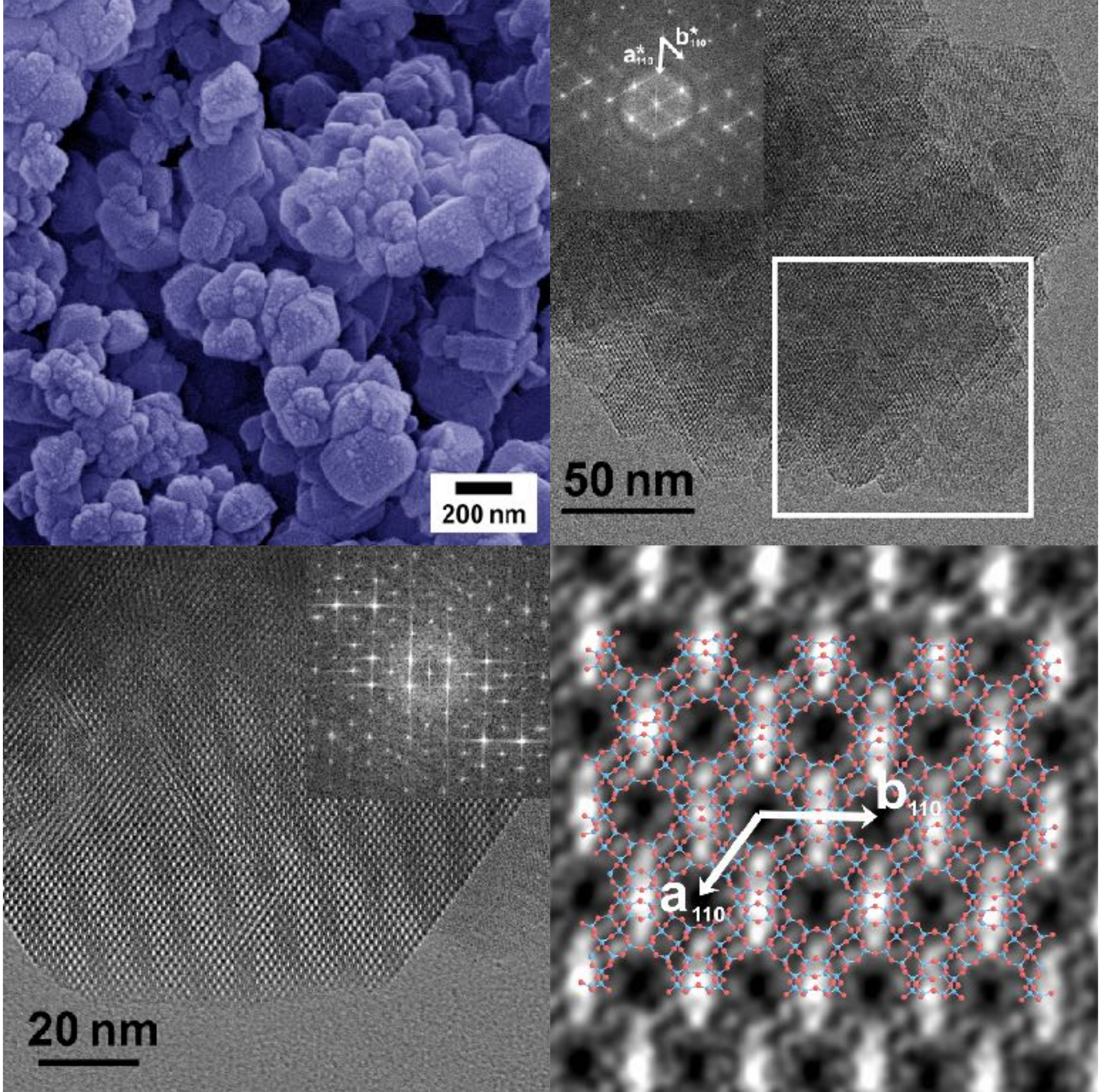


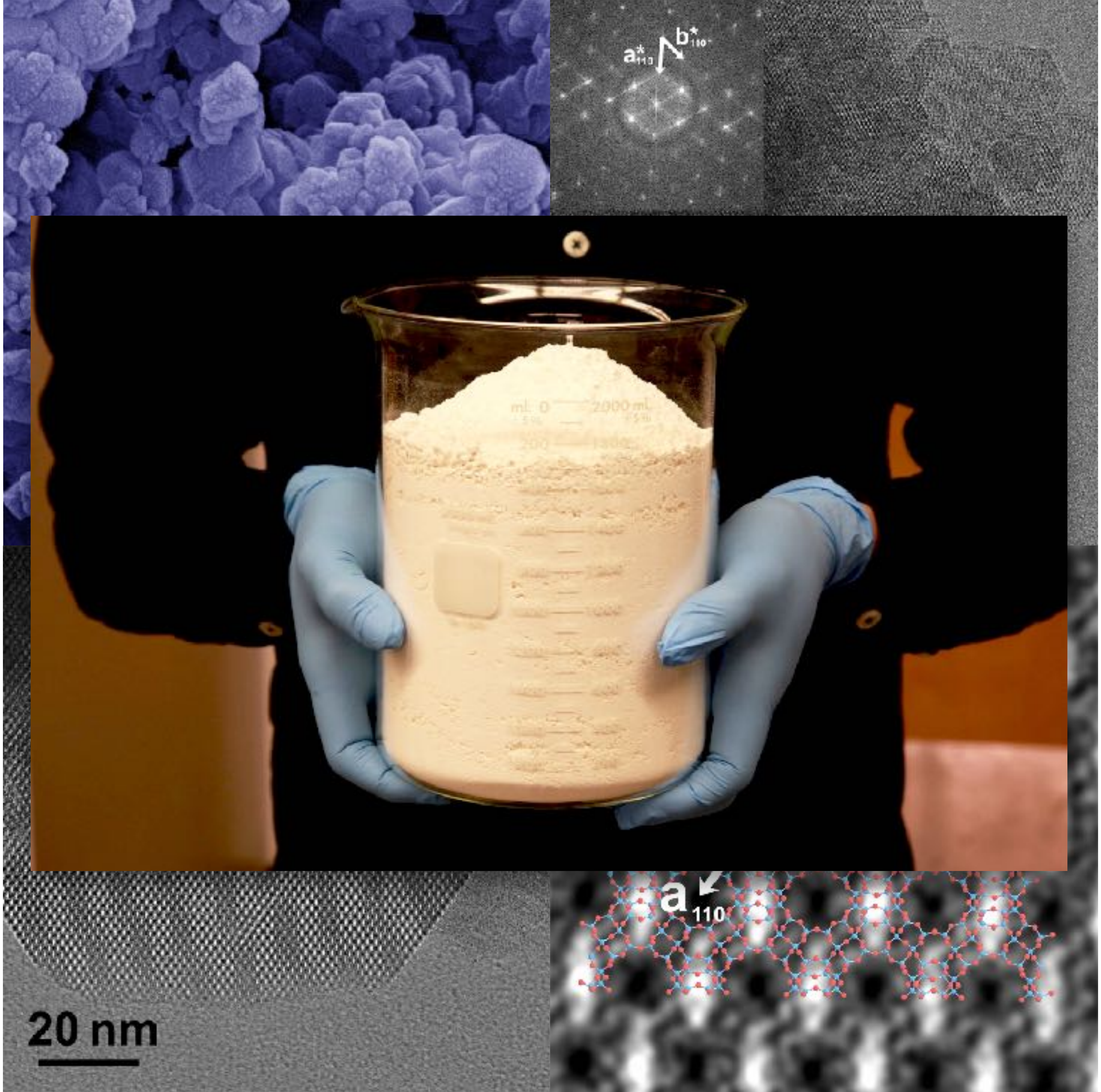


Our zeolite X (nanostructured)

Seo, D.-K., Medpelli, D., Ladd, D. & Mesgar, M. "Geopolymer resin materials, geopolymer materials, and materials produced thereby." WO2013044016A2 (2013); US9296654B2; US9862644B2; EP2758355A4; CN103946181A; KR20140069200A.

⊥(110)





⊥(110)

Take-Home Message

- Geopolymer process can produce aluminosilicate nanomaterials including nanoaggretes easily and inexpensively in a scalable manner.
- Geopolymeric nanomaterials can perform well in sustainability applications.
- Geopolymer technology can be a platform materials technology for various chemical industries.

National Science Foundation
NIH National Institutes of Health
LECCEL