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Magnetic-field-assisted assembly of ordered multifunctional ceramic nanocomposites for extreme environments

Kostya Kornev,
Igor Luzinov,
Fei Peng,
Department of Materials Science & Engineering, Clemson University

Jeff Owens, Tyndall AFB

Program manager Dr. Ali Sayir

Magnetic-Field-Assisted Assembly of Ordered Multifunctional Nanocomposites

PI: Konstantin G.Kornev, Co-Pis: Igor Luzinov, Fei Peng & Jeff Owens (Tyndall, FL)

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MOTIVATION

Demand of highly ordered composite materials incorporating nanofibers possessing additional non-structural functions (magnetic, electric, etc)

-Currently composite materials are made with randomly distributed nanofibers improving only mechanical properties

- No large scale ordered nanocomposites exist
- Lack of materials performing at high temperature and providing ectromagnetic radiation shielding

Nanocomposite ceramic materials

NEW PROSPECT INSIGHTS

This project aims to develop structurally ordered magnetic nanocomposites. Rigorous theoretical and experimental analysis is required to set up a viable engineering rout.

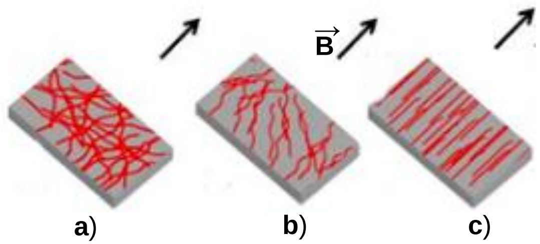


Fig.1. Alignment of the nanowebs **a)** in the absence of magnetic field, **b)** weak magnetic field, **c)** strong magnetic field

The key scientific and engineering elements to be addressed:

- A polymer-based technology of spinning of ceramic magnetic nanofibers for extreme environments;
- A polymer-based technology of formation of ceramic nanocomposites with the controlled orientation and positioning of magnetic nanofibers/nanorods and functionalization of their surfaces to achieve firm adherence to the matrix
- An analysis and understanding of structure-function relationship of magnetic ordered nanocomposites and their performance in extreme environments.

Main achievements:

✓**Experimental protocols for electrochemical template synthesis of Ni nanorods and wet chemical synthesis of nanoparticles have been successfully developed and implemented.**

-Ni nanoparticles (70-100 nm) and nanorodes (200nm x 6µm) have been synthesized

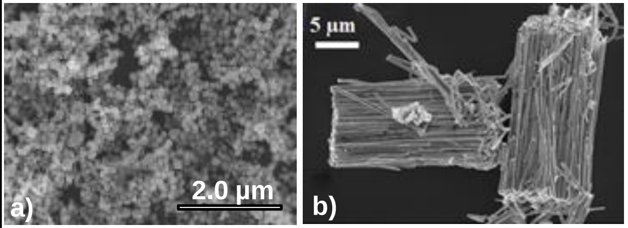


Fig.2. SEM image of synthesized **a**) Ni nanoparticle; **b**) Ni nanorods.

✓**Experimental methodology for preparation of Mullite and SiC micro/nano fibers by electospinning technique has been developed.**

-the strength of the Mullite fibers are equivalent to the commercial products

-stoichiometric SiC fiber as small as 300 nm have been fabricated.

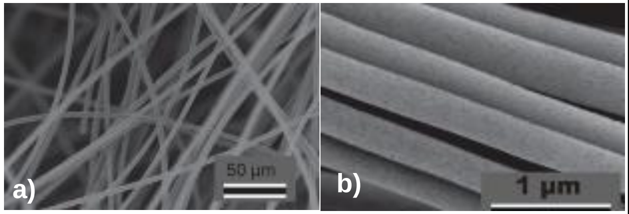


Fig. 3. SEM images of **a**) Mullite fibers sintered at 1200 ^{0}C for 2 hours; **b**) SiC nanofibers

✓**We developed an experimental methodology for evaluation of time dependent viscosity of curing Mullite droplets and films. The protocol is based on mathematical modeling and is currently used for optimization of the process of composite fabrication**

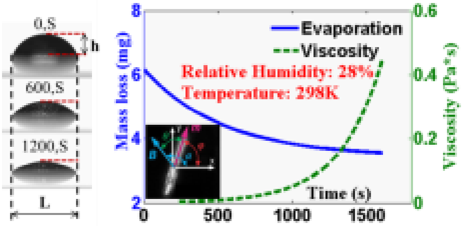


Fig.4. Evaporation of Mullite droplets with magnetic nanorods (L=const, h=f(t)); **b**) Kinetics of drop evaporation and viscosity change in time

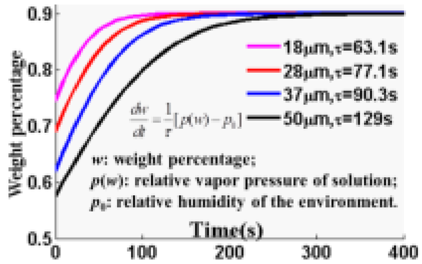
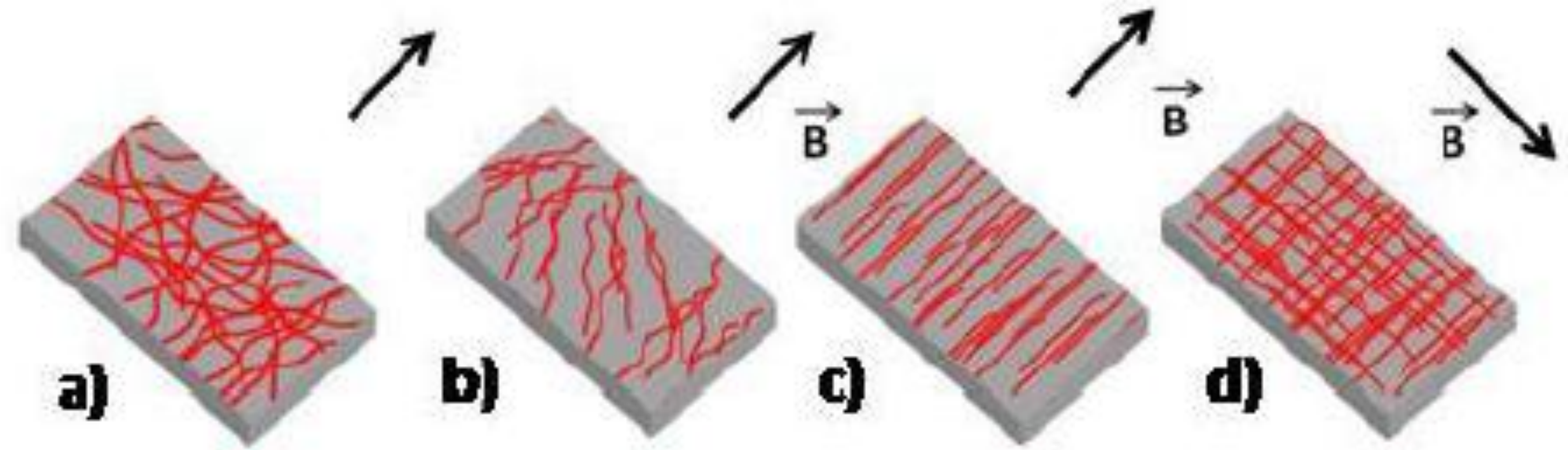


Fig.5. Evaporation of Mullite films ofdifferent thickness

Research goal

The goal of the proposed work is to develop fundamental scientific approaches to design nanocomposite ceramic materials with controlled nanostructures. Magnetically active nanofibers-nanowires form different lattices in a ceramic matrix bring new physico-chemical properties to the materials for their applications in extreme environments

Proposed structure



The key scientific and engineering elements to be addressed and delivered are:

a) a polymer-based technology of spinning of ceramic magnetic nanofibers for extreme environments;

b) a polymer-based technology of formation of ceramic nanocomposites with controlled orientation and positioning of magnetic nanofibers/nanorods

c) an analysis and understanding of the structure-function relationship of magnetic ordered nanocomposites and their performance in extreme environments.

Development of polymer precursors for matrices and fibers

Nanofiber spinning/ nanorod formation

Functionalization of nanofibers/nanorods and formation of stable dispersions

Nanofiber manipulation & ordering in liquid films with time dependent rheology

Nanocomposite fabrication

First year

Mullite($3Al_2O_3$ $2SiO_2$)– Ni nanocomposites

Mullite – Mullite nanocomposites

Advantage: water soluble and e-spinnable fibers

Dispersion of Ni and Co nanowires in Mullite precursors

Ordering in magnetic field. Nematic order

(Math modeling & experiments)

E-spinning of Mullite & SiC nanofibers with Ni & Co nanoparticles

Characterization of Mullite – Ni nanocomposites

Magnetic component

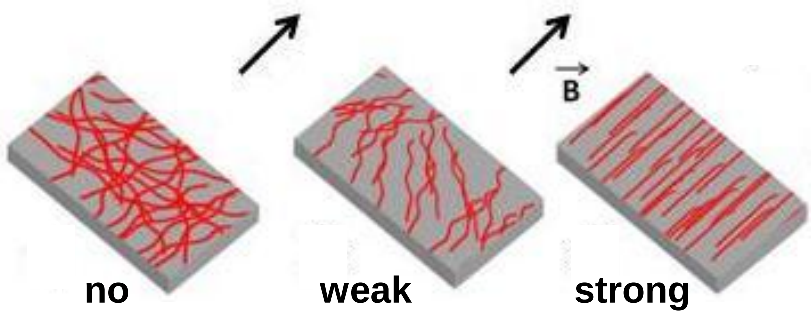
James Townsend, Ruslan Burtovyy, Igor Luzinov

Outline

- Basic requirements for the magnetic component
- Evaluation of commercial sources of Ni nanoparticles
- Synthesis of Ni nanoparticles

Magnetic component

Purpose: magnetic component ensures formation of ordered structure of ceramic nanofibers in the composite in presence of magnetic field



Requirements:

property	→	influence
magnetic	→	ordering
high density of electrons, metallic	→	radiation shielding
non-oxide	→	not incorporated in ceramics
high temperature stability	→	fabrication
dispensability of nanostructures	→	fabrication

Ni is an excellent candidate

Commercial sources (evaluation)

Benefits of commercial Ni nanoparticles: **large quantities available**

Claimed:

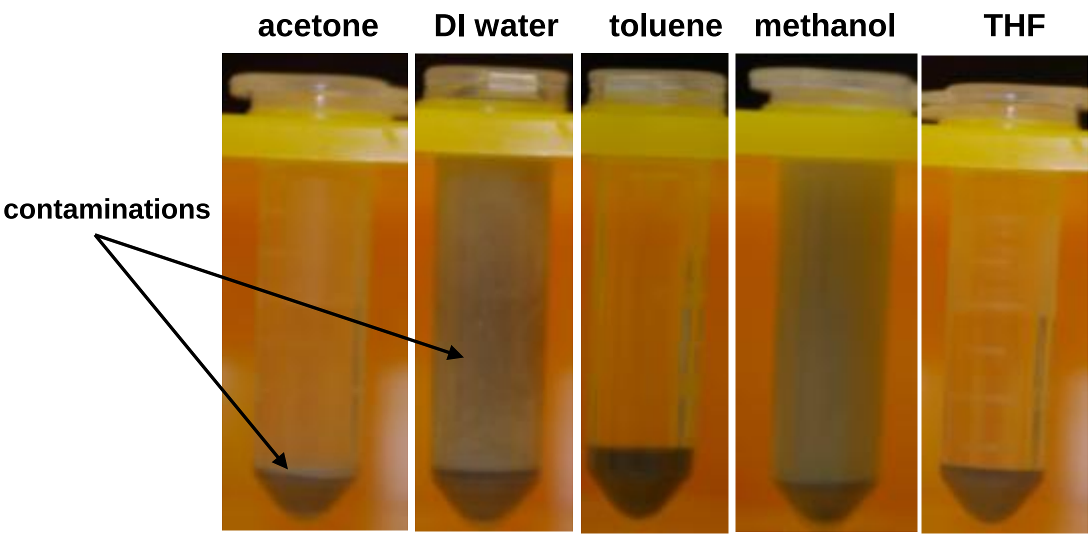
Size: <100nm
Shape: Sphere
% Ni: 99.9

Studied:

***Dispersibility*: DI water, methanol, acetone, toluene and THF**
***Purity*: TGA**
***Shape and size*: SEM**

Dispersibility

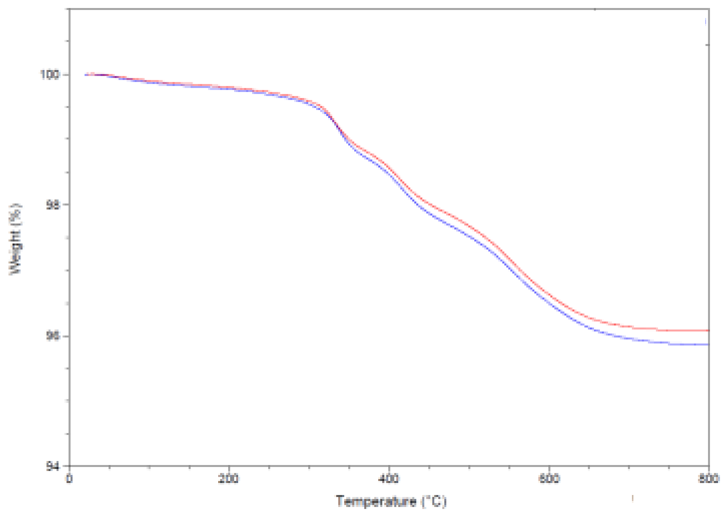
(smaller hight of the sediment-better dispersion)



- best dispersibility in acetone and THF;
- not homogeneous sediment;
- presence of contaminations.

Commercial sources (evaluation)

TGA experiment

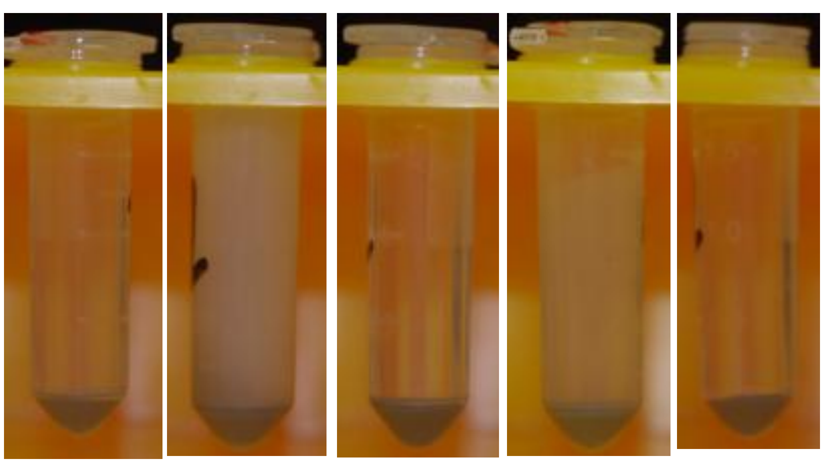


- more than 4 wt.% of unknown contaminants
- apparent possibility to clean the particles when heated above 700 ºC in inert environment

Dispersibility after heat treatment

(smaller hight of the sediment-better dispersion)

acetone DI water toluene methanol THF



- better overall dispersibility and the best dispersion in acetone and THF;
- more homogeneous sediment;
- some presence of contaminations.

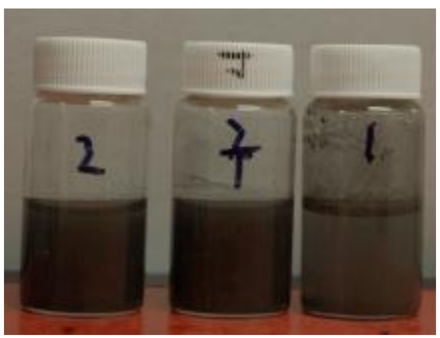
Commercial sources (evaluation)

Chemical treatment

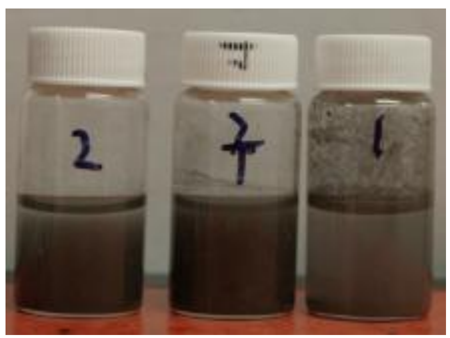
- ✓ **remove contamination by decanting water dispersion;**
- ✓ **remove contaminations by decanting THF dispersion;**
- ✓ **chemical treatment with 15 wt.% of hydrogen peroxide solution at 50 ºC for several hours**

Sedimentation after chemical treatment

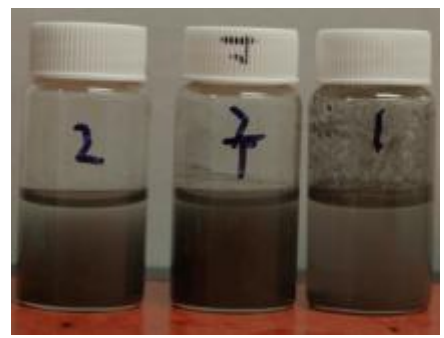
0 time



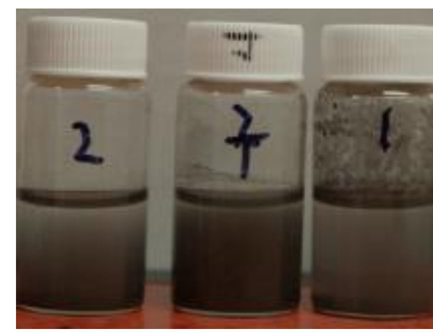
1.5 minutes



3 minutes



5 minutes

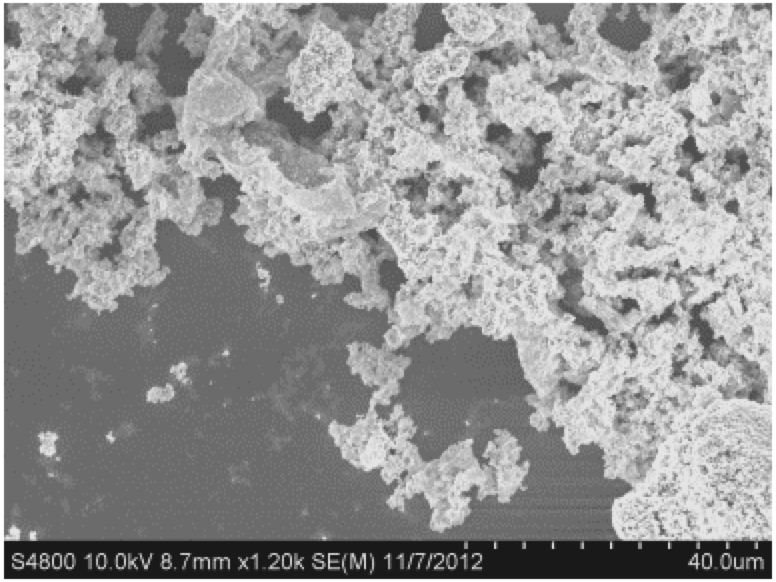


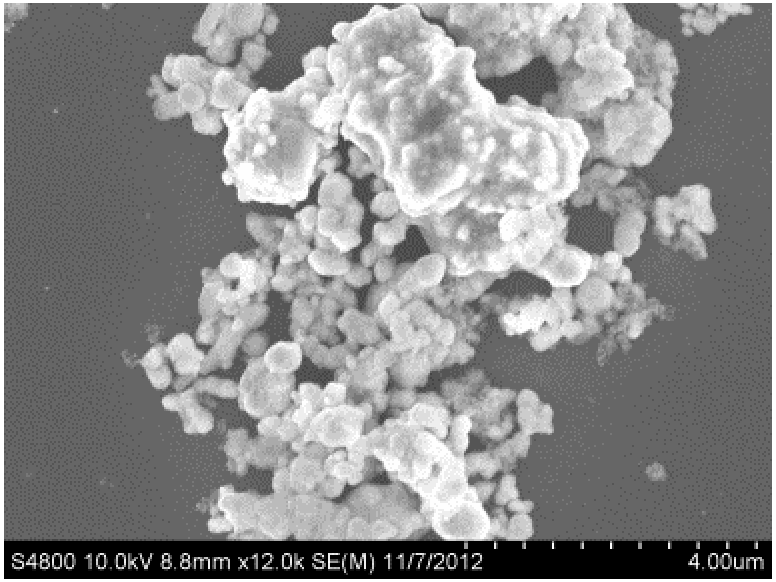
1- sample from vial 1 of original purchased nanoparticles
2- sample from vial 2 of original purchased nanoparticles
t- treated sample

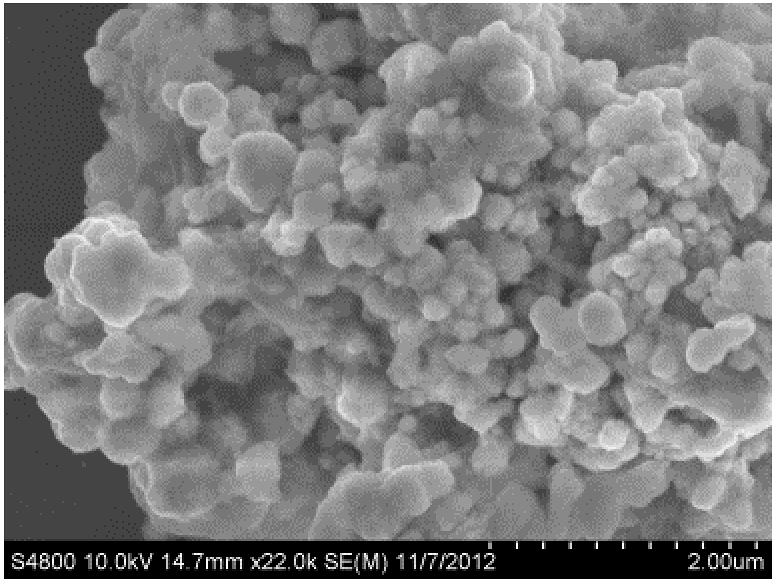
- significant improvement after chemical treatment

Commercial sources (evaluation)

SEM experiment







- presence of large quantities of non-conductive contaminations in original Ni samples;
- chemical treatment improves the quality;
- too large particles or particles fused together .

Synthesis of Ni nanoparticles

Reduction of a nickel salt by hydrazine

Zhi Gang Wu, M. Munoz, O. Montero
***Advanced Powder Technology* 21 (2010) 165–168**

Reagents:
$NiCl_2*6H_2O$
$N_2H_4*H_2O$
KOH

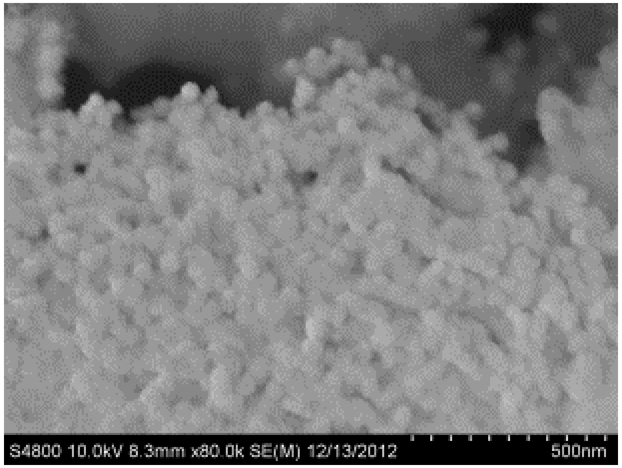
Variables:
-concentration of nickel ions;
-Ni:N_2H_4:KOH ratio.

Targeted nanoparticles' size:
-70-100 nm

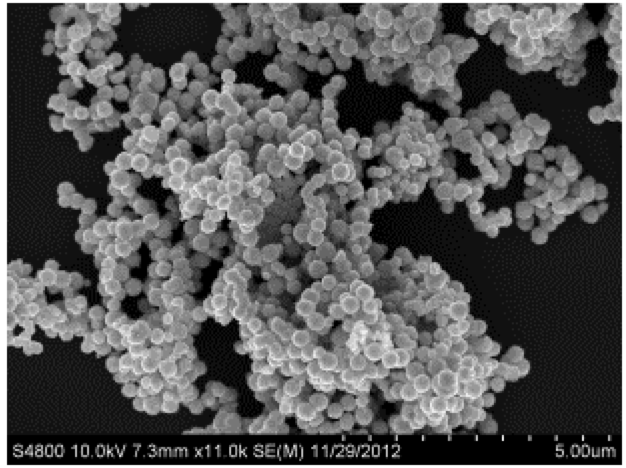
Benefits:
- straightforward procedure;
- room temperature;
- air environment.

Synthesis of Ni nanoparticles

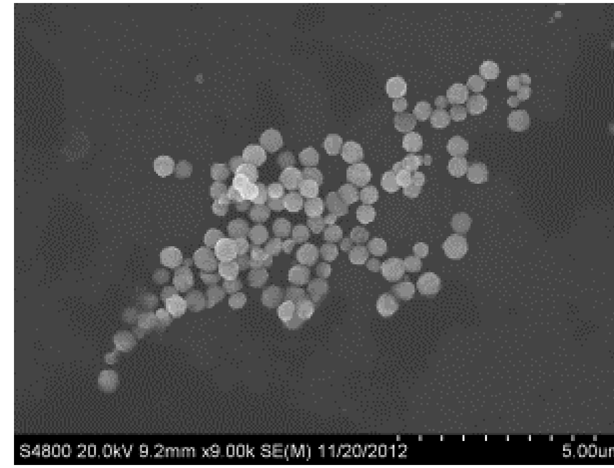
$Ni:N_2H_4:KOH$ (1:5:10)
magnetic stirring (4 hrs)



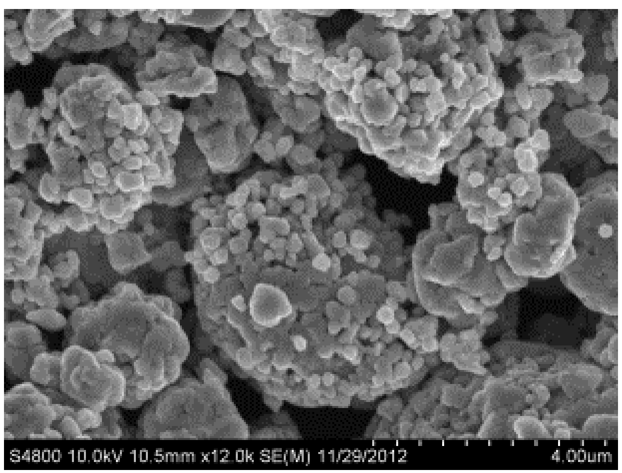
$Ni:N_2H_4:KOH$ (1:10:10)
mechanical stirring (18 hrs)



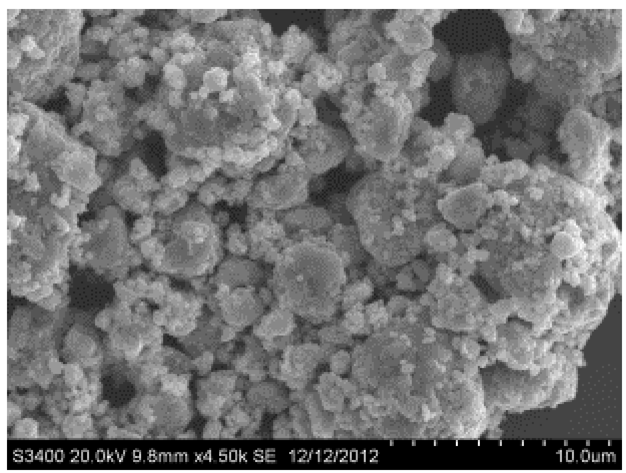
$Ni:N_2H_4:KOH$ (1:10:10)
no stirring (48 hrs)



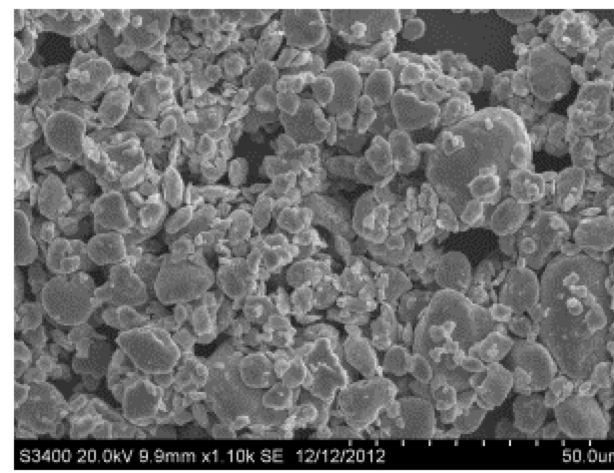
$Ni:N_2H_4:KOH$ (1:10:10)
magnetic stirring (18 hrs)



$Ni:N_2H_4:KOH$ (1:5:10)
Magnetic stirring (18 hrs)



$Ni:N_2H_4:KOH$ (1:5:10)
mechanical stirring (18 hrs)

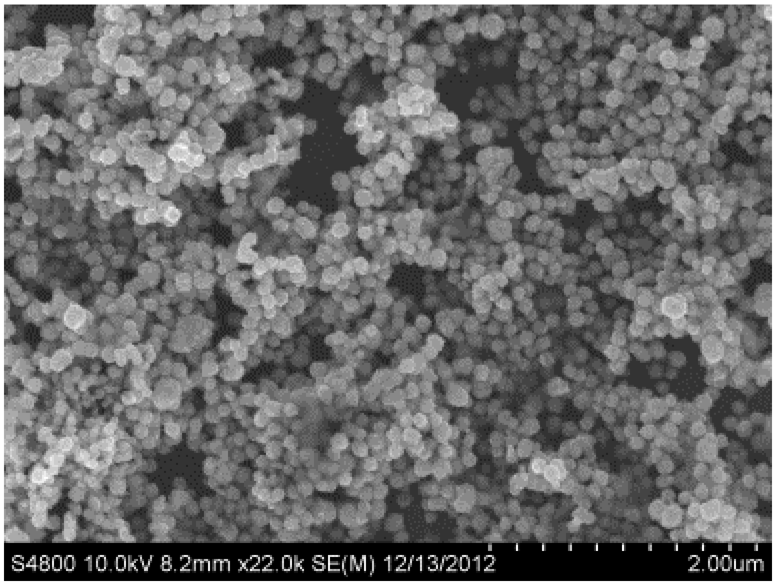


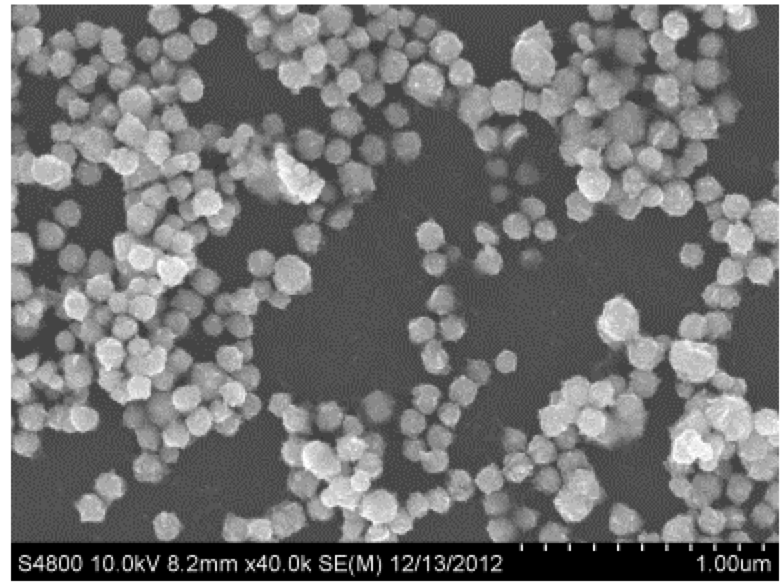
- **depending on actual experimental conditions Ni nanoparticles of various sizes and shapes can be prepared**

Synthesis of Ni nanoparticles

Targeted size

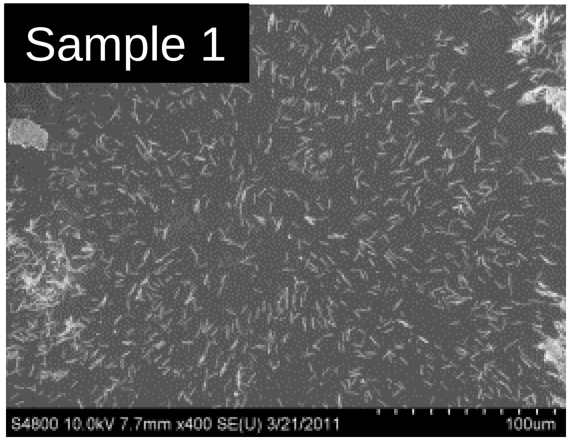
$Ni:N_2H_4:KOH$ (1:5:10)
magnetic stirring (5hrs)

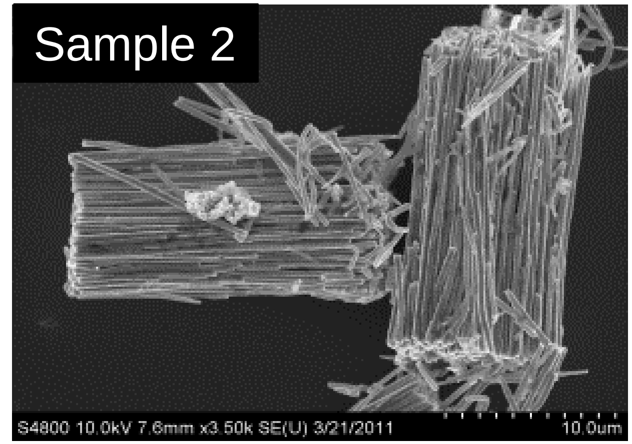




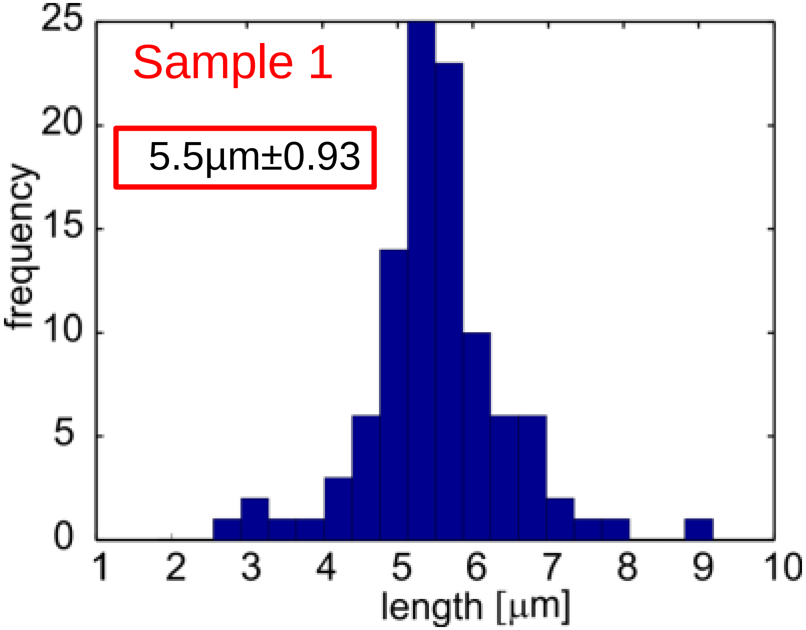
- small size (about 100 nm) spherical Ni nanoparticles were synthesizes successfully;
- the particles revealed very good dispensability in DI water

Template Synthesis of Nickel nanorods

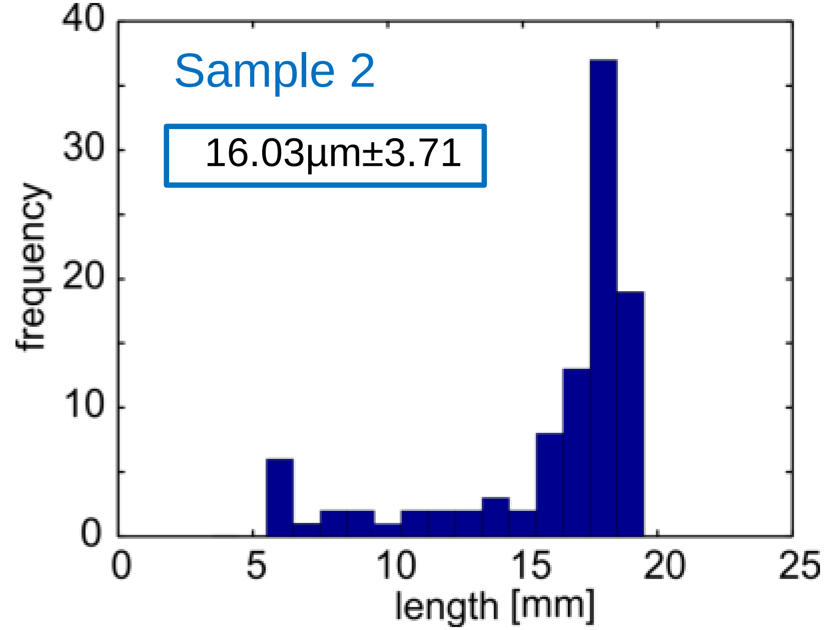




720 seconds



1450 seconds



1) Length of nanorods can be varied by changing the time of Ni electrodeposition
2) Nickel nanorods with length from 1 to 50μm were synthesized

Near future plans

- ✓ modify the surface of synthesized Ni nanoparticles with ultra-thin polymer layer ensuring their excellent dispersibility in various media;
- ✓ ensure excellent dispersibility of Ni nanorods;
- ✓ continue evaluation of other routes to incorporate magnetic components into ceramic fibers.

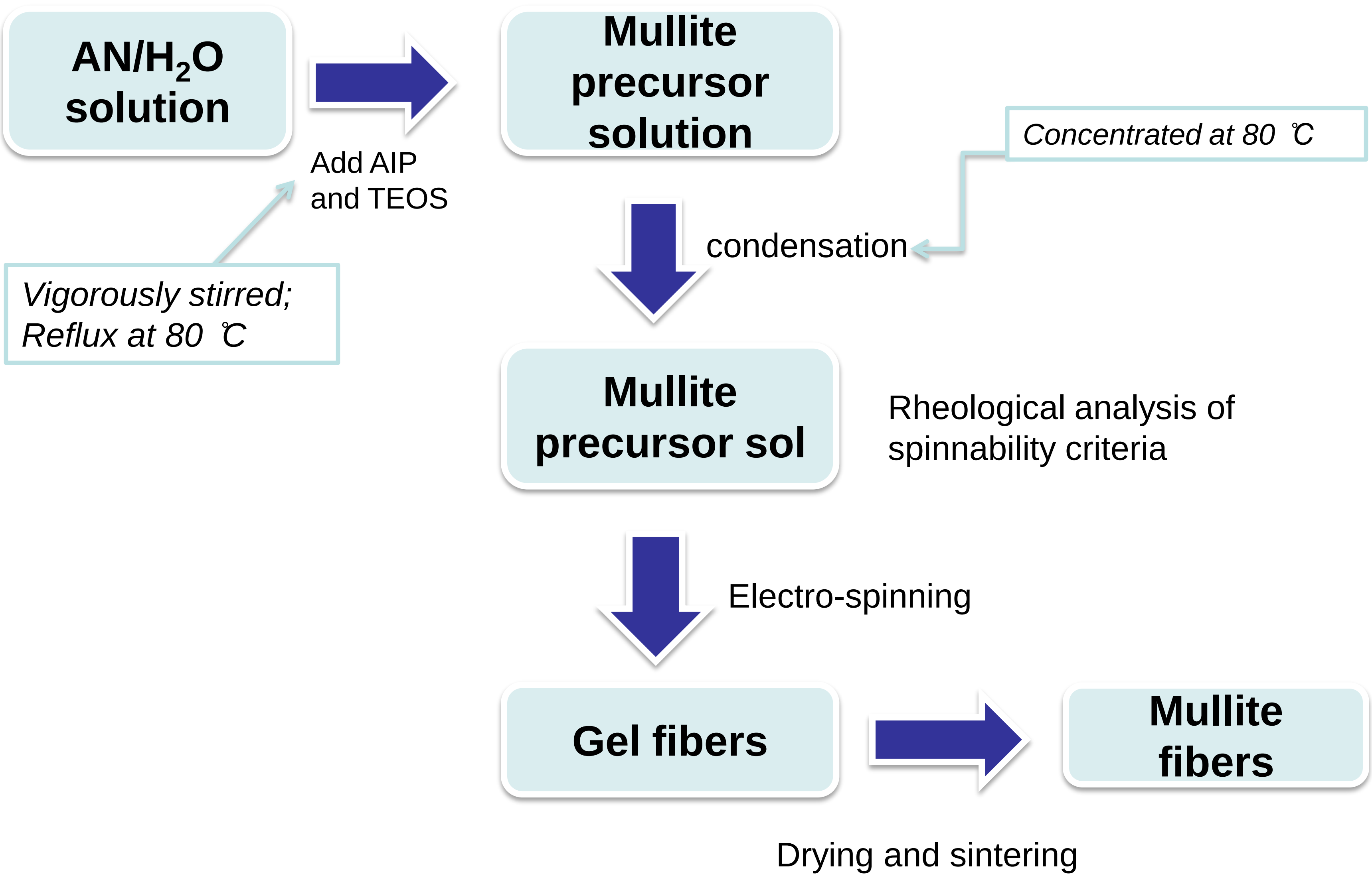
Preparation of Mullite precursors and electrospinning of Mullite fibers

Zhaoxi Chen, Fengjiao Liu, Yuan Yue, and Fei Peng

Outline

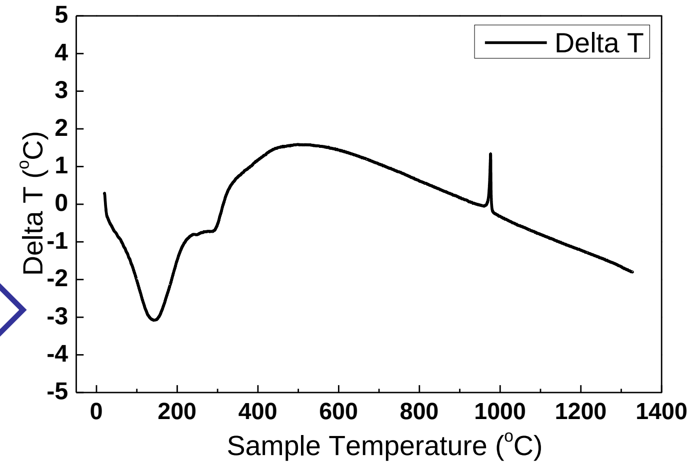
- Objective
  - providing the group with ceramic nanofibers and formation of nanocomposites
  - incorporating magnetic nanoparticles into ceramic nanofibers
  - Conversion of ordered preforms into ceramic composites
- Mullite fibers
- Silicon Carbide fibers

Making Mullite fibers



Results: thermal analysis

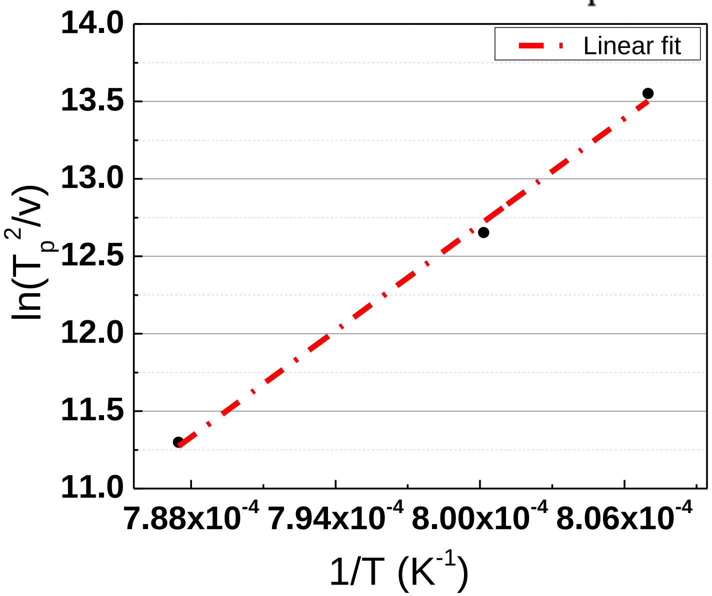
The sharp peak at about 980^0C indicates good homogeneity of precursor and high mixing level.



DTA curve of sample 3-3. Heating rate: 5 ^0C/min

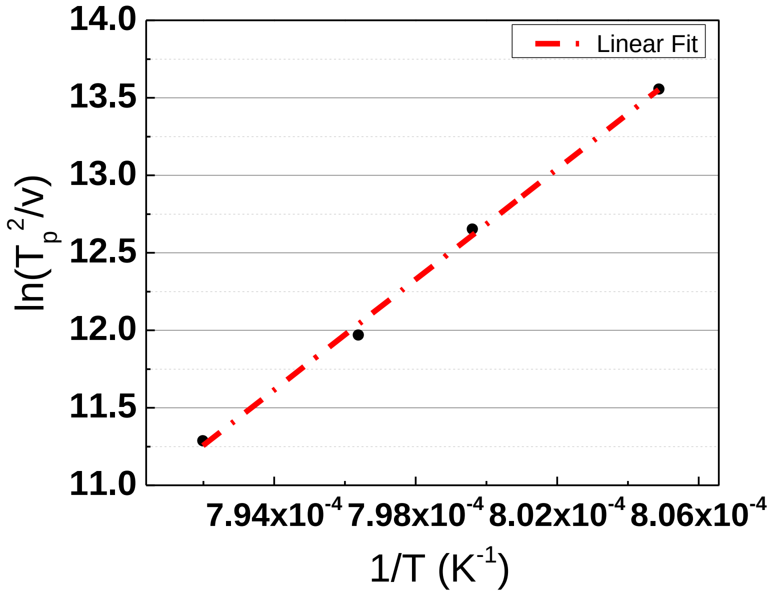
The Kissinger equation was most commonly used:

$$\ln\left(\frac{T_P^2}{v}\right) = \ln\left(\frac{E_a}{R}\right) + \frac{E_a}{RT_p} - \text{Const}$$



Diphasic Gel

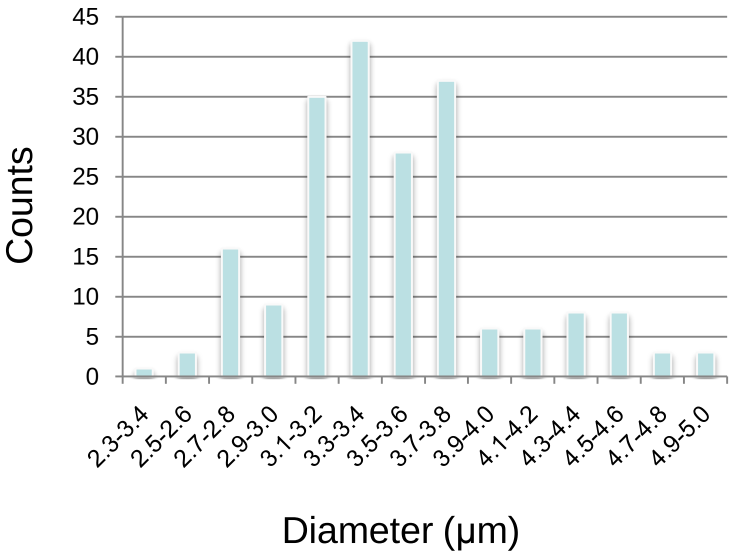
Ea = 905 ± 51 KJ/mol



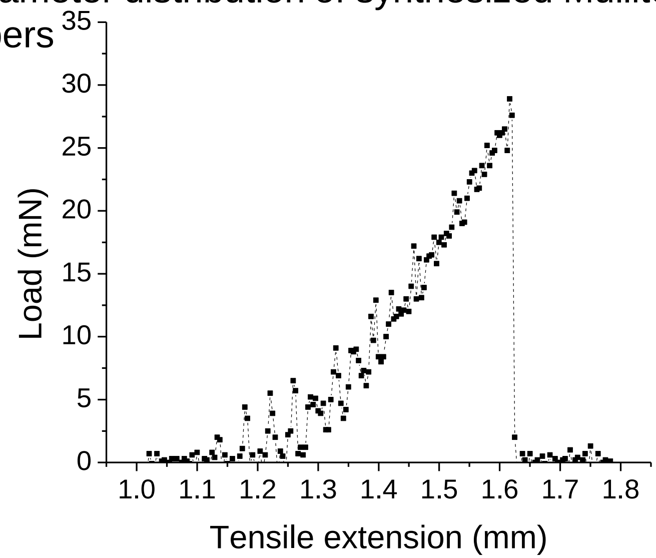
Monophasic Gel

Ea = 1411 ± 52 KJ/mol

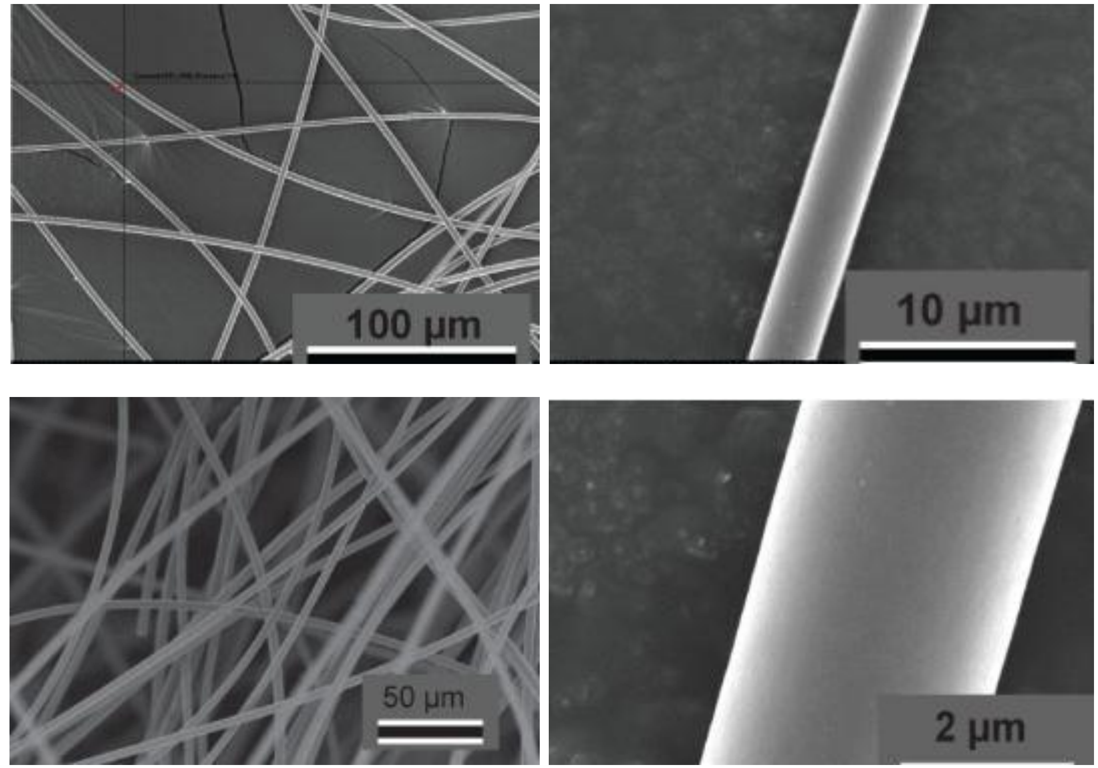
Single filament tensile test on Mullite fibers



Diameter distribution of synthesized Mullite fibers



A typical load-elongation curve of mullite fibers in single filament tensile test



SEM images of Mullite fibers sintered at 1200 ^{0}C for 2 hours.

Average diameter:

$$\overline{D} = 3.535 \pm 0.542\mu m$$

Mean tensile strength:

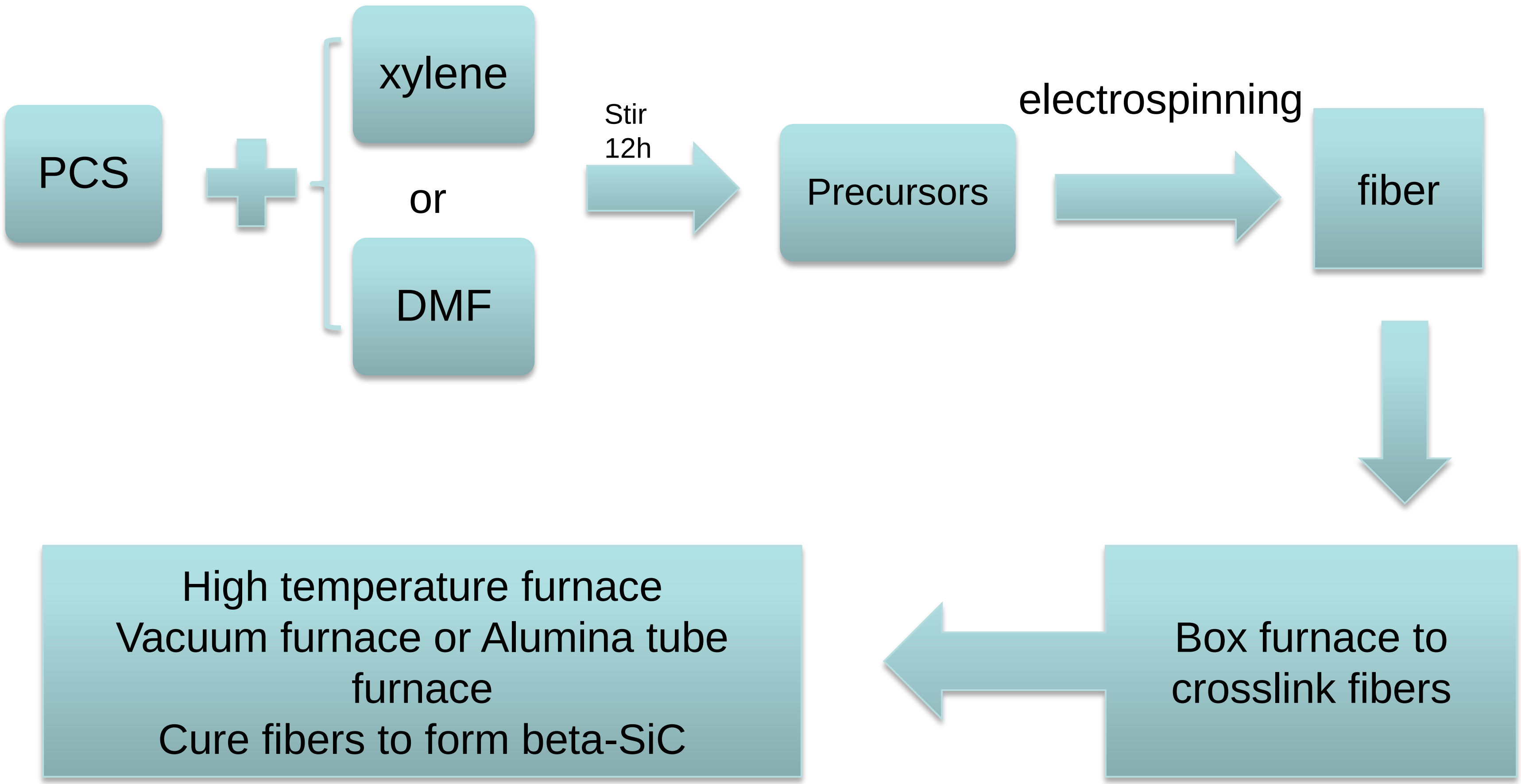
$$\overline{\sigma} = 1.935 \pm 0.601 GPa$$

Gauge length:

$$L = 5mm$$

Strain rate: 5mm/min

SiC Fibers from E-Spin of PCS



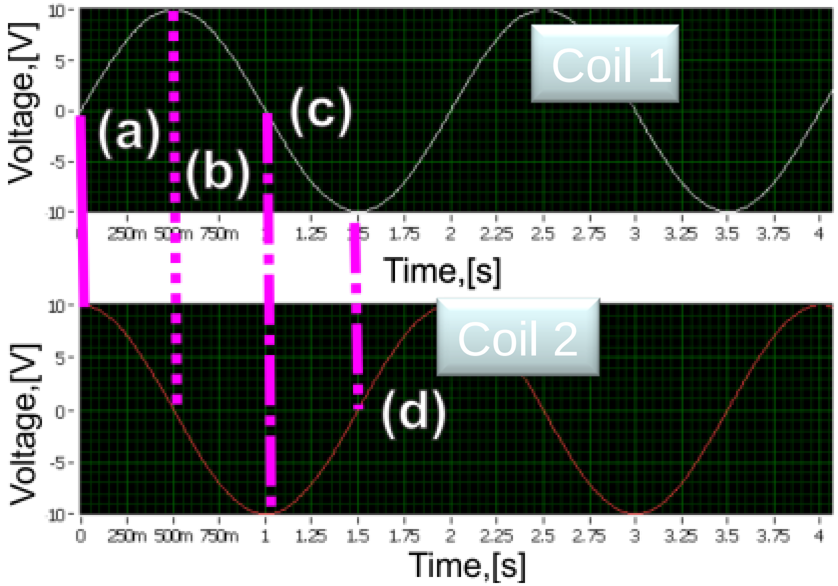
Near future plans

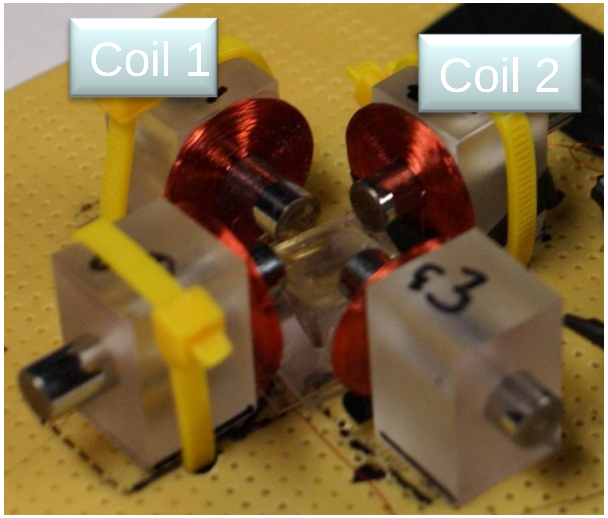
- ✓ **Reduce Mullite fiber diameters to the nanometer range**
- ✓ **Characterize SiC fibers**
- ✓ **Study Mullite and SiC gelation kinetics**
- ✓ **Electrospin magnetic Mullite and SiC fibers**
- ✓ **Convert ordered preforms to ceramic composites**
- ✓ **Study a possibility of microwave convertion of Mullite & SiC preforms into ceramic composites**
  (together with Tyndall AFB)

Magnetic ordering and kinetics of solidification of Mullite precursors

Yu Gu & Konstantin G. Kornev

Experimental setup for nanorod ordering. Two sinusoidal signals are used for generation of rotating magnetic field

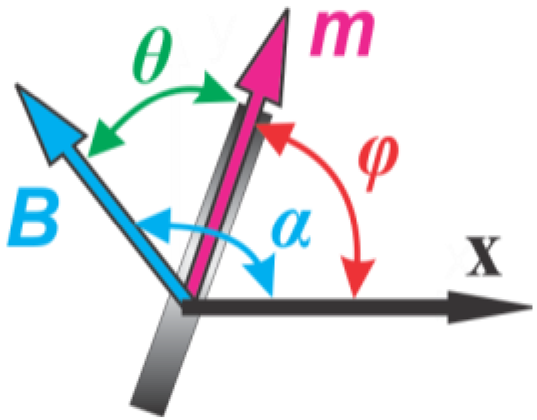




Rotation of a single nanorod at 0.5Hz

Designed system can produce rotating magnetic fields up to 50mT at frequencies from 0.1Hz to 1 kHz

Nanotube rotation: critical frequency



B – magnetic field vector
m – magnetization of nanorod
e - unit vector directed perpendicularly to the plane of the nanorod rotation
γ - drag coefficient
φ - angle nanorod axis makes with the X-axis

The torque balance equation:

$$\left(\gamma d\varphi/dt\right)\mathbf{e} = \mathbf{m}\times\mathbf{B}$$

$$\varphi(t) = \alpha(t) - \theta(t)$$

$\alpha = \omega t$

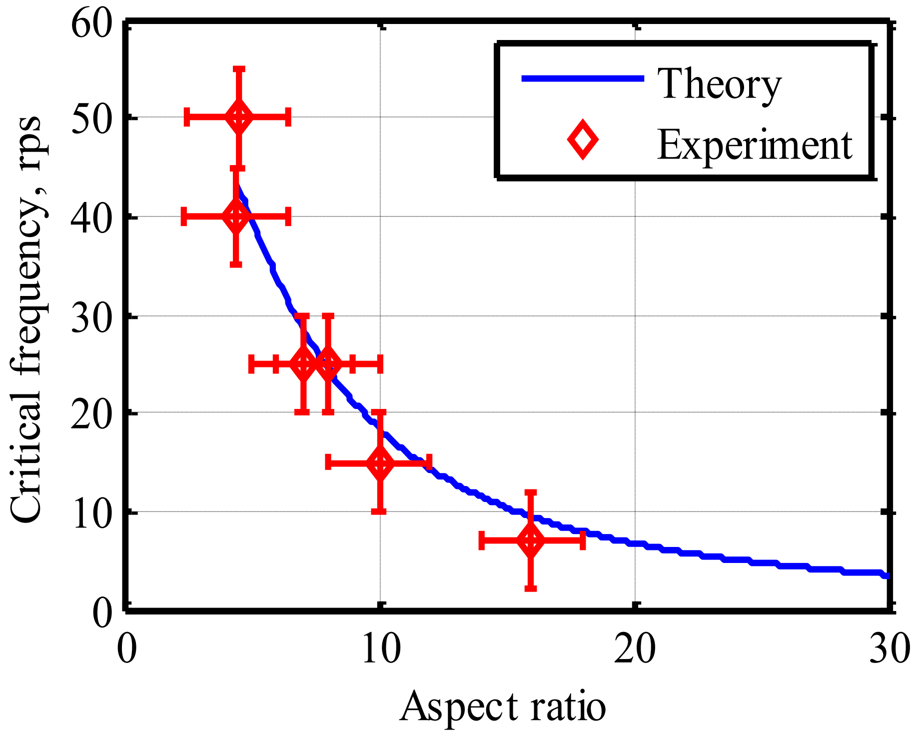
$\omega_{cr} = mB/\gamma$

maximum frequency beyond which the nanorods do not rotate in unison with magnetic field

Toward microsecond time response

Critical frequency

$$f_c = \frac{\chi B^2}{8\pi\eta\mu_0}\left(\frac{l}{d}\right)^{-2}\left(3\ln\left(\frac{l}{d}\right)-2.4\right)$$



fc **– critical frequency at which the nanorod stops rotating synchronously with the field**

fc **DOES NOT DEPEND ON THE NANOROD SIZE, ONLY ON THE ASPECT RATIO!**

l **– length of the rod,** ***d*** **– diameter of the rod**
χ – magnetic constant of the material
μ_0 - magnetic permeability of vacuum

Ni nanorods show a time response which is at least comparable with the best existing liquid crystals!

Diffusion limited evaporation of mullite droplets with Ni nanorods

$$\frac{\partial P}{\partial t} = D\Delta P$$

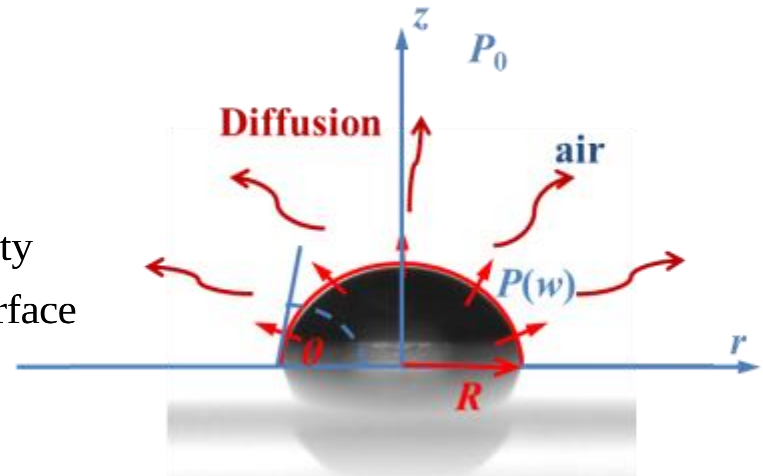
P: vapor pressure, *D*: diffusion coefficient

Dimensionless:

$$\frac{R_0^2}{DT_0}\frac{\partial P}{\partial \tilde{t}} = \tilde{\Delta} P \qquad \frac{R_0^2}{DT_0} << 1 \qquad R_0 \sim 10^{-3} m, T_0 \sim 10^{3} s, D \sim 10^{-5} m^2/s$$

⇩

Quasi-static approximation: $\Delta P = 0$

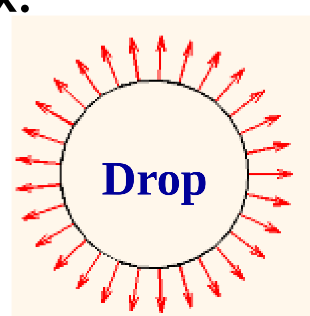


Boundary condition:

$$\begin{cases} p(r=\infty, z=\infty) = p_0 & \text{Infinity} \\ p(r=R, z=h(r)) = p_v & \text{Drop surface} \end{cases}$$

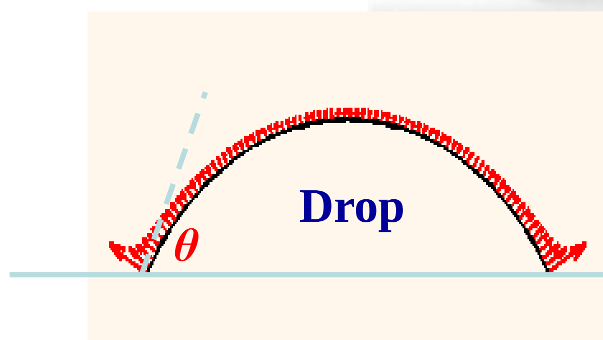
Evaporation flux:

$$J = D(\vec{n}\cdot\nabla P)$$



Entire sphere

Uniform flux



θ=60°

Non-uniform flux

Film: drop at 0 contact angle is expected to evaporate faster near the edge

Near future plans

✓ Characterization of Mullite films and correlation structure with kinetics of its evaporation;

✓Analysis of ordering kinetics of an assemble of Ni nanorods

✓ Incorporation of Co nanorods into Mullite matrix and study their ordering kinetics.