



EULANETCERMAT
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TASK 1.1: Synthesis of ceramic materials with applications in environment (water and soils)



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R E V I E W I N G

- ✓ Synthesis of Nanoparticles with homogeneous composition and controlled crystal size (Sub-task 1.1.1).
- ✓ Nanoparticle arrangement with uniform particle size, integration, and dispersion control (Sub-task 1.1.2).



Nanotechnology*:

- **Application** of science and technology to **characterize, understand, design, engineering, and manipulate** materials at **nanoscale level**
- To achieve **novel bulk properties** associated with its unique structure

**Rahmat Saptono. Procedia Engineering 50, 369 – 380, (2012).*



Nanoceramics and nanocomposites* put under one category:

Novel bulk or coating materials with **microstructure architecture**, characterized by **at least one** of the ceramic phases **having length scale between 1 and 100nm**.

nanoceramics playing an increasingly important role in many fields**

Properties of ceramics, such as:

Hardness, stiffness, toughness, temperature and corrosion resistance,

other properties and combinations of properties:

electronic, biological, optical, dielectric/piezoelectric, insulation, etc.

understanding relationships between nanostructured ceramics and these properties.

* *Basu, B. Current Science; 95[5]:570-571 (2008).*

** *M. J. Hampton, et al. Adv. Mater., 20 2667 –2668 (2008).*



Synthesis of Nanoparticles with homogeneous composition and controlled crystal size (Sub-task 1.1.1).

Nanoparticles including inorganic compounds produced with a **precision shape** and **uniform size** by different methods such as the templating method
Risk: particles not tightly attached \longrightarrow environmental and health hazard.

controlled crystal size* :

Example: dense **nanstructured Ytria Stabilized Zirconia** (3YTZP) with a grain size $< 100\text{nm}$ is **resistant to hydrothermal aging** against commercial submicrometer 3YTZP due to the **lack of yttrium segregation** in the nano-TZP. A key process to **industrial production**** by traditional pressing and sintering is the formation of **soft agglomerates** of the nanosized powder using **spray freeze drying**.

* A. Paul, B. Vaidhyanathan and J.G.P. Binner, J. Am. Ceram. Soc., 94[7]2146(2011).

** B. P. C. Raghupathy and J. G. P. Binner. J. Nanopart. Res., 14 [7], article 921 (2012).



Synthesis of Nanoparticles with homogeneous composition and controlled crystal size (Sub-task 1.1.1). (CONT)

Nanoceramic types (Nitrides & Silicon nitride, Carbides, Borites, Sialon, Oxides, Mullites, etc.)

non-oxide ceramics*: combining the **synthesis technology for fine-grained starting powders** and the **rapid sintering** technology for **spark plasma sintering (SPS)** → ceramics of **improved heat, corrosion resistance and mechanical properties**.

Silicon nitride (Si_3N_4) for structural applications at high temperatures **(to densify use of low sintering additives)****.

* M. Hotta. Journal of the Ceramic Society of Japan, 120 [4] 123-130 (2012).

** Y. Ukyo. J. Mater. Sci., 32, 54835489 (1997).



Synthesis of Nanoparticles with homogeneous composition and controlled crystal size (Sub-task 1.1.1). (CONT)

Carbides:

Carbon nanotubes (CNTs)*: major challenge: the large-quantity production (annealing the ball milled graphite powder in the milling chamber by exothermic reaction).

Silicon carbide (SiC) ceramics of low density, high hardness, excellent mechanical strength at high temperatures, and good thermal stability. **Complicated to densify** (similar to Si_3N_4): **solid-phase sintering with B-C additives**, or **liquid-phase sintering with metal oxide additives****.

*Karimi, E. Z.; Zebarjad, S. M.; Khaki, J. Vahdati; Izadi, H. J. of Alloys and Compounds (2010), 505(1), 37-42

**M. Keppeler, H.-G. Reichert, J. M. Broadley, G. Thurn, I. Wiedmann and F. Aldinger, J. Eur. Ceram. Soc., 18, 521-526 (1998).



Synthesis of Nanoparticles with homogeneous composition and controlled crystal size (Sub-task 1.1.1). (CONT)

Borites

Cubic boron nitride (cBN) highest hardness and thermal conductivity next to diamond, and more thermally stable and less reactive with iron than diamond (cutting tools for machining hardened steel and cast iron). Difficult to densify .

Drawbacks: cBN transforms into low-hardness hexagonal BN (hBN) at high T => high-density cBN bodies produced by **sintering under an ultrahigh pressure (greater than 5GPa)**. A combination of ceramics and cBN would be a promising material for cutting tools with high hardness and fracture toughness.

P. Klimczyk, E. Benko, K. Lawniczak-Jablonska, E. Piskorska, M. Heinonen, A. Ormaniec, W. Gorczyńska-Zawisła and V. S. Urbanovich. J. Alloys Compd., 382, 195205 (2004).



Synthesis of Nanoparticles with homogeneous composition and controlled crystal size (Sub-task 1.1.1). (CONT)

SiAlON ceramics: high hardness and excellent corrosion and oxidation resistance at high temperatures. SiAlON is of Si_3N_4 crystal structure **in which some Si and N atoms are replaced by Al and O atoms** (some metal cations M, such as those of Li, Mg, Ca, Y or most rare-earth elements, are incorporated as a stabilizer)*

Drawbacks: difficult to achieve uniform composition and form homogeneous and fine-grained microstructure from the powder mixtures.

*S. Hampshire, H. K. Park, D. P. Thompson and K. H. Jack, Nature, 274, 880-882 (1978).



Synthesis of Nanoparticles with homogeneous composition and controlled crystal size (Sub-task 1.1.1). (CONT)

Mullites ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) ceramics: polycrystalline mullite **retains >90% of its room-temperature strength to 1500°C** and displays very high creep resistance. Mullite (low dielectric constant) => substrate material in high-performance packaging applications. Optical applications mainly as a window material within the mid-infrared range.

Synthesis: colloidal processing. Controlling size and relative charges on the starting sol particles => modify microstructures (uniform and consistent grain sizes)

Miao, X.; Ponton, C. B.; Marquis, P. M. British Ceramic Proceedings, 51(Nanoceramics), 157-64 (1993).



Synthesis of Nanoparticles with homogeneous composition and controlled crystal size (Sub-task 1.1.1). (CONT)

Oxides: TiO₂, and FeO nanoparticles produced at room temperature with no post-annealing process. For size-controlled nanoparticles, a **liquid-phase infiltration** (LPI) method to the reverse micelle (RM) reaction. The average sizes of the nanoparticles were 4.6 and 2.0nm for TiO₂ and FeO, respectively. Also TiO₂/Au films with a highly ordered periodic structure by the LPI method using colloidal crystals as a template.

The **LPI process is conducive to the preparation of advanced nanoceramics with highly ordered structures.**

Iizuka, Sachihiko; Ooka, Sachiyo; Nakata, Akiyoshi; Mizuhata, Minoru; Deki, Shigehito. *Electrochimica Acta*, 51(5), 802-808 (2005).



Synthesis of Nanoparticles with homogeneous composition and controlled crystal size (Sub-task 1.1.1). (CONT)

New methods for powder production to overcome size limitations of milling processes

Sol-Gel and Precipitation Technologies valuable tool for producing and processing ceramic materials for advanced applications (currently nanoceramics).

Combustion Chemical Vapor Condensation (CCVC) production of nanopowders, **the NanoSpray Combustion Processing** to convert a liquid solution containing chemical precursors into an ultra-fine aerosol to produce nanopowders. **Gas phase synthesis of nanocrystal particles of ceramics (oxides, nitrides, carbides and composites)**. Use of metalorganic precursors and the **Chemical Vapor Condensation (CVC)** => tremendous progress

Polymer-mediated Synthesis Functionalized nanoparticles and their assembly. Polymers are excellent stabilizing agents which can be used in nanoparticles synthesis.

Hahn, Horst. Book of Abstracts, 216th ACS National Meeting, Boston, August 23-27 (1998), MACR-011.



Synthesis of Nanoparticles with homogeneous composition and controlled crystal size (Sub-task 1.1.1). (CONT)

Reverse micelle Synthesis Typically, the ratio of surfactant to precursor is a major contributor to the size of the nanoparticles. The micelle size is tunable and dependent on the water to surfactant ratio.

Protein Microtube-mediated synthesis Nature's ability to form self-assembled structures for nanotechnological applications (alternative to conventional fabrication methods). Biomolecules and three main templating principles have been outlined: (1) **crystal surface layers of bacterial cells** with a normal distribution of physicochemical affinity sites at the protein surface for the **production of highly oriented semiconductor and metal nanocluster arrays**; (2) **nanometer-sized ferritin and ferritin-like protein cages** as the size-constrained reaction environments for **encapsulation of inorganic materials**; (3) various biomolecules of linear morphology such as **viruses, microtubules and lipid nanotubes for creation of one-dimensional array of nanoparticles, and tubular and wire-like nanostructures**.



Synthesis of Nanoparticles with homogeneous composition and controlled crystal size (Sub-task 1.1.1). (CONT)

Supercritical fluid (SCF): The greatest advantage is the nanomaterials size and morphology control, which determine the application potential of the nanoparticles, as their properties vary significantly with size.

[Byrappa K](#), [Ohara S](#), [Adschiri T](#). [Adv Drug Deliv Rev](#). Feb 14;60(3), 299-327 (2008).



Nanoparticle arrangement with uniform particle size, integration, and dispersion control (Sub-task 1.1.2).

Several studies consider the nanoparticle arrangement with uniform particle size to control the dispersion of the nanopowders and determining different properties. Quite a few sintering methods to progress in nanopowders properties have been also regarded.

As an example:

New synthesis method for size-controlled polymer nanoparticles using soap-free emulsion polymerization involves sequential ultrasonic irradiation for acoustic emulsification of a water-insoluble monomer such as Me methacrylate (MMA) in an aqueous medium, followed by emulsion polymerization in the obtained solution without surfactants. Polymerization in this solution yielded size-controlled polymer nanoparticles. Moreover, colloidal crystal films could be easily prepared using the fluidic-cell method.

Nakabayashi, Koji; Kojima, Maya; Inagi, Shinsuke; Hirai, Yuki; Atobe, Mahito. ACS Macro Letters 2(6), 482-484 (2013).



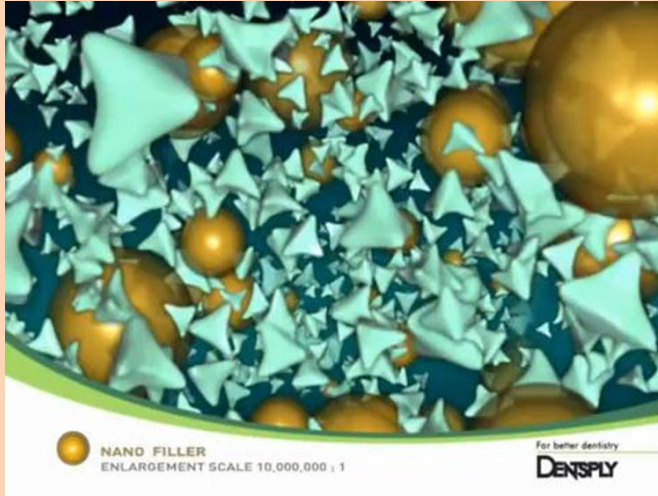
Nanoparticle arrangement with uniform particle size, integration, and dispersion control (Sub-task 1.1.2).(CONT)

Nanostructured materials have unusual physical and mechanical properties (superplasticity in ceramics and transparency for usually opaque materials).

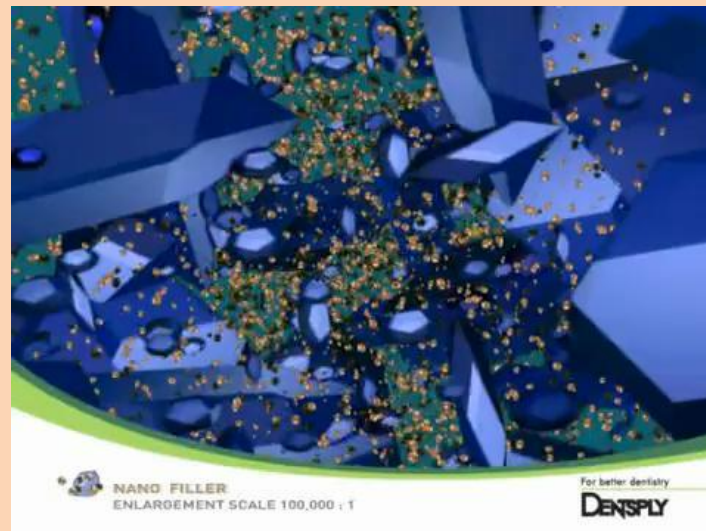
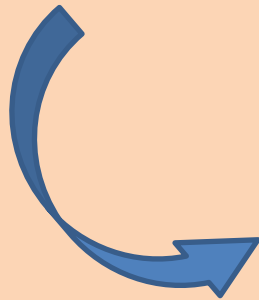
The single **biggest challenge** when preparing nanostructured materials is the fact that, due to their ultrafine size, **nanopowders have a tremendous tendency to agglomerate**, and generally the smaller the particles, the larger the size the agglomerates.

One should **create very weak agglomerates** that crush readily to yield the fundamental particles. Methods for obtaining powders from suspensions and controlling the strength, size and chemistry of the resulting agglomerates can be achieved. Work focused on examining **the task of a range of diverse surfactants on the rheology of nanoceramic suspensions**. The natural pH of nanoceramic suspensions is quite different to that for submicron particles (different synthesis routes used).

Binner, Jon; Vaidhyanathan, Bala; Liang, Yunchen. Materials World, 12(4), 30-32 (2004).



Nanoceramics in Dental Materials



WITH EULANETCERMAMAT



before



after

THANKS FOR YOUR ATTENTION