Nano Structured Materials

**Midterm Examination**

April 17th, 2020

1. **What are the main challenges that should be overcome in the fabrication of nanomaterials and nanostructure?**
2. Materials in the nanoscale exhibit a large surface area, and therefore huge surface energy. The challenge is to control the surface energy as it plays a significant role in thermal stability.
3. Achieve homogeneity in the fabrication processes. Challenge is to tailor the current fabrication techniques to ensure the product to have the desired properties with consistent size, uniform size distribution, morphology, crystallinity and chemical composition.
4. Due to the large surface energy, the system is prone to reduce the overall surface energy by agglomeration and Ostwald ripening. Challenge is to halt nanomaterials and nanostructures from coarsening.

* S. Weinberg, Introduction, in: Nanostructures Nanomater., WORLD SCIENTIFIC, 2011: pp. 1–17. https://doi.org/10.1142/9789814340571\_0001.
* Y. Tanwar, A. Sharma, Y. Tanwar, Physical Chemistry of Solid Surfaces, in: Nanostructures Nanomater., WORLD SCIENTIFIC, 2011: pp. 19–60. https://doi.org/10.1142/9789814340571\_0002.

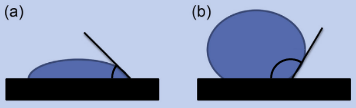
1. **What is the role of the chemical potential on the** **Ostwald ripening effect? Please justify your answer.**

Spontaneous growth is a process driven by the reduction of Gibbs free energy or chemical potential. The Ostwald ripening effect can be understood as a self-assembly process where small particles are arranged/packed together by the reduction of overall chemical potential.

Thermodynamic-wise, the chemical potential decreases when mass is transferred from a flat surface to a concave surface. Meaning that a convex surface (small particle) possesses higher chemical potential, than a concave surface (large particle). In solution, the solubility of the small particle is larger than the solubility of the large particle, as the solute is deposited onto the large particle and the small particle continues to dissolve. Dissolution of the small particles will halt when the concentration of solid in the solvent equals to the equilibrium solubility of the large particles.

* Y. Tanwar, A. Sharma, Y. Tanwar, Physical Chemistry of Solid Surfaces, in: Nanostructures Nanomater., WORLD SCIENTIFIC, 2011: pp. 19–60. https://doi.org/10.1142/9789814340571\_0002.
* G. Cao, Nanostructures and Nanomaterials, PUBLISHED BY IMPERIAL COLLEGE PRESS AND DISTRIBUTED BY WORLD SCIENTIFIC PUBLISHING CO., 2004. https://doi.org/10.1142/p305.

1. **You have a job interview and in the last round of interviews you are asked the following question: “tell me how would you measure surface tension of a solution with suspended nanoparticles”. Write down your answer(s)**
2. Ensure the nanoparticles are well dispersed
3. Measure the surface tension by contact angle. Lower contact angles (a), refer to increased wetting and therefore lower surface tension. A higher contact angle (b) indicate a higher surface tension.



1. Once the contact angle is obtained, the surface tension can be calculated with Young's equation.

* V.S. Kulkarni, C. Shaw, Surfactants, Lipids, and Surface Chemistry, in: Essent. Chem. Formul. Semisolid Liq. Dosages, Elsevier, 2016: pp. 5–19. https://doi.org/10.1016/B978-0-12-801024-2.00002-9.

1. **You want to sell an oil solution loaded with paramagnetic nanoparticles (CoFeO4), but the particles do not form a stable suspension. How could you make them stable, so you can make a profitable business?**

Stability may be achieved by the introduction of a polymer stabilizer such as PVP or PVA. The polymer stabilizer can prevent nanoparticles to agglomerate, but it can also affect the growth process of nanoparticles depending on the solid chemistry, the solvent and temperature. On the other hand, stabilization can also be obtained without a stabilizing reagent by an electrostatic stabilization mechanism.

* M. Benelmekki, M. Benelmekki, Zero-Dimensional Nanostructures: Nanoparticles, in: Nanostructures Nanomater., WORLD SCIENTIFIC, 2011: pp. 61–141. https://doi.org/10.1142/9789814340571\_0003.

1. **Prove that droplets with small radius have a higher vapor pressure than the ones with higher radius.**

This is related to question 2. Concave surfaces in a material have lower surface energy than convex surfaces, this difference influences the equilibrium vapor pressure. The relationship between particle radius and vapor pressure can be described by the Kevin equation.

Where; is the equilibrium vapor pressure of the curved solid surface,

is the equilibrium vapor pressure of flat solid surface,

is the surface energy,

is the atomic volume,

is the Boltzmann constant

is the radii of curvature

is the temperature

As depicted if the equation, if the radius increases, the overall equilibrium vapor pressure decreases.

* Y. Tanwar, A. Sharma, Y. Tanwar, Physical Chemistry of Solid Surfaces, in: Nanostructures Nanomater., WORLD SCIENTIFIC, 2011: pp. 19–60. https://doi.org/10.1142/9789814340571\_0002.

1. **You are in charge of a nanoparticles production line and there is a problem with the size distribution that is too widespread and the client is asking you to narrow it down or She will look for another provider. Your boss asks you to make recommendations on how to make the distribution narrower. What would you recommend? (Justify your answer and list any assumptions you make).**

The problem can be tackled from two approaches: Ostwald ripening and diffusion-limited growth.

First, Ostwald ripening can be implemented to narrow the size distribution of nanoparticles by removing small particles as large particles grow at the expense of the smaller particles. With this approach, will narrow the size distribution, but will also increase the final size of the nanoparticles.

On the other hand, diffusion-limited growth would reduce the size distribution of the nanoparticles. Diffusion-limited growth can be achieved by:

1. Increasing the solution viscosity,
2. Introducing of a diffusion barrier (polymer layer) to limit the nanoparticles to further growth,
3. Keeping the concentration of growth species at low levels, and/or
4. Controlling the supply of growth species as the rate of reaction can be manipulated through the control of the concentration of the reactants.

However, some considerations are to be considered. Solutions a) and b) could introduce new reagents to the process which may increase the cost and/or composition of the final product, though the viscosity can me amended by temperature changes. Solutions c) and d) may not require additional reagents but may slow down the production.

* S. Weinberg, Introduction, in: Nanostructures Nanomater., WORLD SCIENTIFIC, 2011: pp. 1–17. https://doi.org/10.1142/9789814340571\_0001.
* M. Benelmekki, M. Benelmekki, Zero-Dimensional Nanostructures: Nanoparticles, in: Nanostructures Nanomater., WORLD SCIENTIFIC, 2011: pp. 61–141. https://doi.org/10.1142/9789814340571\_0003.

1. **You want to produce a nanoporous silica glass, please explain how would you prepare such glass.**

Surfactants will be used in the synthesis of mesoporous silica nanoparticles (MSNs) due to their tendency to form micelles. Silica sources tend to aggregate and form silica networks around these micelles. Ionic surfactants will define the MSN templating through electrostatic interactions between the surfactant micelles and the silicate source. For instance, a typical cationic surfactant hexadecyltrimethylammonium chloride (CTAC) and an anionic silicate source tetraethylorthosilicate (TEOS) would be used as reactants. The pore size control is limited to the used template, however varying chain lengths in CTAC can impact the final pore size of the MSN.

The synthesis of MSNs will follow the process bellow:

1. Dissolve the CTAC in DI water to form a clear micelle solution
2. After stirring the solution quickly add the TEOS to the solution
3. Separate the products by centrifugation or filtration
4. Wash with DI water and ethanol to remove the surfactant on the surface of MSNs
5. Dry the MSNs in an oven

* María Pérez-Page, Erick Yu, Jun Li, Masoud Rahman, Daniel M. Dryden, Ruxandra Vidu, and  
  Pieter Stroeve. Template-based syntheses for shape controlled nanostructures. *Advances in*  
  *Colloid and Interface Science*, 234:51–79, aug 2016. 10.1016/j.cis.2016.04.001
* M. Kruk, M. Jaroniec, and A. Sayari. Application of Large Pore MCM-41 Molecular  
  Sieves To Improve Pore Size Analysis Using Nitrogen Adsorption Measurements. *Langmuir*,  
  13(23):6267–6273, nov 1997. 10.1021/la970776m

1. **Explain how come Pluronics can act as a surfactant.**

Pluronics are triblock co-polymers (PEO-PPO-PEO). The hydrophilic PEO and the hydrophobic PPO segments within Pluronics, provide the “amphiphilic” properties of surfactants (as they contain both hydrophilic and hydrophobic portions on the same molecule). Pluronics with a longer PPO segment and shorter PEO segments will be hydrophobic and those with the reverse composition will be hydrophilic.

* A. Sundblom, A.E.C. Palmqvist, K. Holmberg, Study of the Pluronic−Silica Interaction in Synthesis of Mesoporous Silica under Mild Acidic Conditions, Langmuir. 26 (2010) 1983–1990. https://doi.org/10.1021/la902144h.
* V.S. Kulkarni, C. Shaw, Surfactants, Lipids, and Surface Chemistry, in: Essent. Chem. Formul. Semisolid Liq. Dosages, Elsevier, 2016: pp. 5–19. https://doi.org/10.1016/B978-0-12-801024-2.00002-9.