



TMT4320 Nanomaterials, fall 2015

## EXERCISE 10

**Guidance:** Wednesday 4<sup>th</sup> November, 18:15-20:00, H3  
**Due date:** Friday 6<sup>th</sup> November, 14:00, boxes outside R7 or on It's learning

### PROBLEM 1

- Describe the spark plasma sintering process.
- What are the advantages of spark plasma sintering compared to conventional sintering?
- Why do we want nano-sized grains in a bulk material? And is it always advantageous with very small grains, why/why not?

### PROBLEM 2

The interaction potential between nanoparticles covered by capping ligands is the sum of the van der Waals potential  $E_{\text{vdW}}$  given in equation 1 and the steric repulsion potential between carbon chains  $E_{\text{steric}}$  given in equation 2. The particles order themselves like 'soft' spheres with an effective diameter which includes the layer of organic molecules attached to them. If the particles are to self-organize, steric stabilization provided by these organic molecules must therefore be sufficiently compensated by the interparticle van der Waals attraction.

$$E_{\text{vdW}} = -\frac{A}{12} \left( \frac{4R^2}{C^2 - 4R^2} + \frac{4R^2}{C^2} + 2 \ln \frac{C^2 - 4R^2}{C^2} \right) \quad [1]$$

$$E_{\text{steric}} \approx \frac{100R\delta_{\text{SAM}}^2}{(C - 2R)\pi\sigma_{\text{thiol}}^2} kT \exp \left( -\frac{\pi(C - 2R)}{\delta_{\text{SAM}}} \right) \quad [2]$$

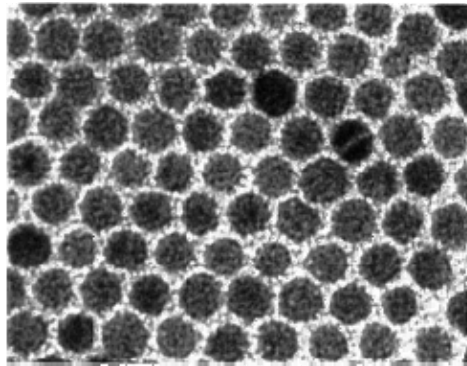
Here,  $A$  is the Hamaker constant,  $R$  is the radius of the nanoparticles,  $C$  is the centre-to-centre distance between two nanoparticles,  $\delta_{\text{SAM}}$  is the thickness of the carbon chain layer,  $\sigma_{\text{thiol}}$  is the diameter of the area occupied by the thiols on the particle surface,  $k$  is the Boltzmann constant, and  $T$  is the temperature.

- Calculate the equilibrium center-to-centre distance ( $C$ ) between two silver nanoparticles with radius  $R = 3.4$  nm covered with dodecanethiol molecules given the information below. It may be easiest to use a spreadsheet (Excel). If you are unable to calculate a reasonable value of  $C$  explain how you would proceed to calculate  $C$  and in which length range  $C$  should be.

Hamaker constant (for attraction between two silver nanoparticles):  $A = 1.9$  eV  
Thickness of the layer of carbon chains (dodecane thiol coating):  $\delta_{\text{SAM}} = 18$  Å

Diameter of the area occupied by the dodecane thiols on the particle surface:  $\sigma_{\text{thiol}} = 4.3 \text{ \AA}$   
 $T = 25 \text{ }^\circ\text{C}$   
 $1 \text{ J} = 6.242 \times 10^{18} \text{ eV}$

- b) Given the image below of dodecane thiol-covered silver nanocrystals with average radius 3.4 nm, find an average value for  $C$  for the 2D structure in the image. Compare the value of  $C$  from a) with the value from the image. (If you don't have a value from a) use  $C = 100 \text{ \AA}$ .)



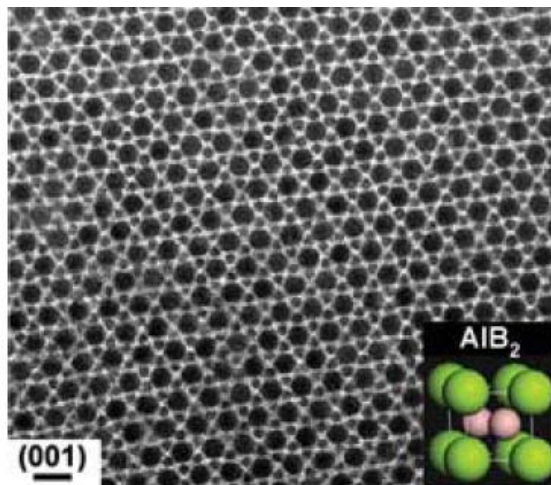
250 Å

Dodecane-capped silver nanoparticles with radius 3.4 nm deposited on a carbon substrate from a chloroform dispersion.

- c) Calculate the parameter  $\chi = 2L/D_{\text{core}} = \delta_{\text{SAM}}/R$  for the dodecanethiol-coated silver nanoparticles. Is the 2D structure in the image consistent with the  $\chi$  value? Explain.

### PROBLEM 3

Nanoparticles with bimodal size distribution can self-assemble into superlattices as shown below.



TEM image of a binary superlattice self-assembled from 6.7 nm PbS and 3.0 nm Pd. Inset: Modeled unit cell of the corresponding three-dimensional structure.

The image is taken from an article by E. V. Shevchenko *et al.* (*Nature*, 2006, 439, 55-59), in which they describe superlattices formed by mixing two types of nanoparticles and depositing the mixture on substrates. In the experimental section of the article, the synthesis of the various nanoparticles was described as follows:

### METHODS

Nanoparticle synthesis: Au, Ag and Pd nanoparticles were prepared by modifying the method of ref. 27. Metal salts were dissolved in 10 ml of toluene with ultrasonication in the presence of dodecyldimethylammonium bromide (DDAB). For synthesis of 5.0 nm Au and 4.2 nm Ag nanoparticles, we used 0.034 g  $\text{AuCl}_3$  and 0.025 g  $\text{AgNO}_3$ , respectively, and 0.0925 g DDAB. 3.0 nm Pd nanocrystals were synthesized from 0.0237 g  $\text{PdCl}_2$  with 0.157 g DDAB. Forty microlitres of a 9.4 M aqueous solution of  $\text{NaBH}_4$  were added drop-wise to the solution of metal salt with vigorous stirring. After 20 min, 0.8 ml 1-dodecanethiol was added and the stirring was continued for five more minutes. The nanoparticles were precipitated by adding ethanol, and the solid redispersed in 10 ml toluene in the presence of 0.8 ml 1-dodecanethiol and refluxed for 30 min under nitrogen.  $\text{Fe}_2\text{O}_3$  nanocrystals were synthesized by methods adapted from ref. 28. Briefly, 11 nm and 13.4 nm  $\text{Fe}_2\text{O}_3$  nanocrystals were synthesized by injecting 0.2 ml iron pentacarbonyl into 10 ml trioctylamine in the presence of 0.65 g oleic acid at 270 °C and 250 °C, respectively. After heating of the reaction mixtures at 320 °C for 1 h, the reaction mixture was cooled to room temperature. 0.17 g trimethylamine N-oxide was added to oxidize the iron nanoparticles to  $\gamma\text{-Fe}_2\text{O}_3$ , and the reaction mixture was heated to 130 °C for 1.5 h and 320 °C for 1 h. Details of the synthesis of PbSe, PbS and  $\text{LaF}_3$  nanocrystals can be found in refs 7, 29 and 30, respectively.

- What are the functions of the chemical compounds used to synthesize the Au, Ag, Pd and  $\text{Fe}_2\text{O}_3$  nanoparticles in the article cited above? (Cation precursor, surface-adsorbing species, etc.)
- What is in general the maximum deviation in size distribution for obtaining self-assembled superlattices?
- What are the governing factors behind the assembly of binary nanoparticle superlattices as shown in the image above?
- Why can the superlattice structure change when a carboxylic acid or tri-*n*-octylphosphine oxide (TOPO) is added to the binary nanoparticle mixture?

### PROBLEM 4

In many synthesis processes it can be difficult to obtain a highly homogeneous product with respect to crystallographic structure, morphology, or particle size.

- If you are given a mixture of carbon nanostructures containing carbon nanotubes, fullerenes and carbon black (amorphous carbon), how would you separate these three from each other? Assume that your final product should be a separate batch of nanotubes and one of fullerenes. The carbon black is a byproduct that you don't need to keep.
- If you have a dispersion of gold nanoparticles with a wide size distribution, how would you separate these into for example 3 different size groups?