Exam in Surface Engineering KPO041

Date: 2020-03-21

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Allowed material: Everything (including computer with internet connection).

Grading: Maximum 60 points. Guidelines for grades 3, 4 and 5 are 24p, 36p and 48p.

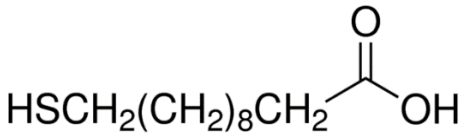
Hints: Motivate all answers carefully but avoid lengthy and irrelevant text to save time. All answers should be in English.

Due to the current COVID-19 pandemic, this exam is done at home. The rules for such exams state that all material and help tools are allowed. (The questions have been constructed with this in mind.) No contact between students is allowed during the exam. Answers are submitted as a document online. Examiner is available only over phone.

By uploading your exam solutions you certify that you have solved the problems on your own without receiving any help from another person.

Question 1

In a surface modification project, you are forming self-assembled monolayers on gold with mercapto-undecanoic acid (MUA):



A (8p)

Describe one experimental technique that can determine the amount of MUA on the surface after monolayer formation and how you would implement it to obtain this information. Explain if you think there is any source of error in the measurement.

Best choice is SPR. It gives the "dry mass" directly so you can use data from the real-time binding in solution. The quantification is quite accurate if a model based on the evanescent field extension and the sensitivity to the bulk refractive index is used. The values of these parameters depend on wavelength but are generally known. (Alternatively, Fresnel models can be used.) One needs to assume a thickness of the film to get its refractive index, but this is relatively easy based on the length of the molecule. Next, a refractometric parameter that relates concentration to refractive index is used to get the surface coverage. (This can be obtained from measuring the refractive index of solutions with different concentration.)

Alternatively, QCM can be used because the monolayer will be sufficiently thin and rigid for the Sauerbrey approximation to work. This gives the mass coverage directly from the frequency response, which is convenient, but it should be noted that with this method there will be a small error due to some coupled water.

Other methods or other versions of these two methods should not be excluded and may give you points as well if they are motivated well.

Mean: 3.8

Note: Just stating that "I would use SPR" and explain how it works in general does not give many points. You should explain how you use it in this particular case to get the MUA coverage (see for instance the exercises in the lecture slides).

B (6p)

Explain how you would determine the reaction rate constant (k_{on}) of MUA binding to Au. Describe both how to conduct the experiment and how to analyze the data.

You need to do a real-time measurement. Introduce the MUA at a known concentration to a clean gold surface, either SPR or QCM. Fit the resulting curve to the Langmuir model with k_{off} = 0 (the binding is irreversible):

$$\frac{\Gamma(t)}{\Gamma_{\max}} = 1 - \exp(-k_{\text{on}} C_0 t)$$

Your sensor response will be proportional to surface coverage, so the only unknown parameter in the fitting is k_{on}. If the fit is bad, it could be due to diffusion influencing the kinetics, in which case the flow rate should be increased.

Mean: 2.6

C (3p)

Do you expect avidin (isoelectric point ~11) to stick to the MUA-modified Au in a physiological buffer?

Yes because it will be positively charged and the MUA layer will be negatively charged.

Mean: 1.8

D (3p)

Do you expect XPS data to show the presence of Au on the MUA-modified surface?

Yes because the MUA layer is very thin (~2 nm). XPS probes at least 5 nm deep. (We have seen this effect in data generated in the projects.)

Mean: 2.0

Question 2

A (6p)

You are binding proteins with a hydrodynamic diameter of 10 nm to a surface by simply placing it into an aqueous solution with a concentration of 1 µg/mL. Assuming diffusion determines the rate, estimate how long time you will have to wait to reach a coverage of 100 ng/cm^2.

You need to use the Ilkovic equation and solve for t:

$$t = \left[\frac{\Gamma}{2C_0}\right]^2 \times \frac{\pi}{D}$$

Note that you can use mass concentrations for both Γ and C_0. Estimate D from Einstein-Stokes as $k_B T/[6\pi\eta R] \approx 4.3\times10^{-7}$ cm^2/s (R = 5 nm). You should get $t \approx 5$ h.

Mean: 4.6

B (3p)

How can you easily reduce this time without using up more protein?

Easiest way is to stir the solution to get convection, thereby supplying new molecules to the surface faster.

Mean: 1.6

C (3p)

You switch to using a patterned surface where the materials that binds the protein is arranged in wires. The regions in between are inert. Is the surface coverage on the wires higher or lower after the same time has passed? (In comparison with the surface exposing only the protein binding material.)

Any patterned surface will give a higher flux to the binding regions. The infinite planar geometry gives the lowest flux. Therefore the surface coverage will become higher.

Mean: 1.5

Question 3 (6p)

You run a plasma treatment of a polystyrene cup with normal air as process gas. Give a brief explanation of the surface chemistry and the change in surface properties.

Polystyrene, like most plastics, is hydrophobic. If you run a plasma treatment with air, your primary reactive gas will be O_2. (Nitrogen can have similar effects, but the species generated in an O_2 plasma are much more reactive.) The process will etch the polystyrene chemically, but the top layer will always have more polar groups during the process. So if you leave the cup in the plasma forever, it will disappear, but that takes a very long time. What you will see in practice is that the surface becomes hydrophilic. You might also get better barrier properties by cross-linking chains on the surface.

Mean: 2.9

Question 4 (8p)

Give an explanation why polyacidic brushes have higher pK_a in comparison with the same polymer when it is free in solution. It is recommended that you skim through the appended papers to find clues to the answer.

The key point to realize is that the brush is a denser environment than the same polymer in solution, i.e. the volume fraction of monomers is higher. This means that there is stronger electrostatic repulsion when monomers deprotonate and become charged. Hence, it becomes more energetically favorable to keep the monomers protonated instead, which shifts the pK_a.

The explanation above is sufficient, but one can also discuss counterions. At least at high ionic strength they can go into the charged brush and screen the charges, but this leads to an entropic penalty because of their confinement. Thus, in the end there is still a free energy cost for charging the monomers which becomes higher for a brush because more monomers are closer to each other.

An alternative explanation, which is acceptable, is favorable interactions between monomers. These naturally become more frequent in the dense brush environment. However, you need to state something more than just the fact that the brush is dense with monomers.

Mean: 4.9

Note: This was intended to be a relatively difficult question since some other are relatively easy. A lot of people gave good answers though!

Question 5 (6p)

Cellulose can be made positively charged. Explain how and why the process works, i.e. the physics and chemistry behind it.

Cellulose can be modified with chitosan, a polysaccharide of biological origin with amines that gives it positive charges. Cellulose has no negative charges in its pristine form, but in practice there are some carboxylic acid groups which makes it negative. Therefore polyelectrolyte complexation can occur with chitosan spontaneously. The main driving force for the complexation is the entropy gain from released counterions.

Mean: 2.9

Question 6 (8p)

Explain how some method we have talked about in the course might be useful (or could have been useful at an earlier stage) for reducing damage from the coronavirus outbreak. This can involve diagnosing the disease, understanding how the virus in infecting us, evaluating treatments etc. Use your imagination! (There is no correct answer, your should come up with your own idea and your answer will be evaluated based on how reasonable it is.)

Suggestion: Use SPR or QCM to create a sensor that detects the virus by a specific receptor on the surface that recognizes the virus. Take samples from patients and test if have the coronavirus or not. This can limit the spread of the disease by isolating the right people. The most challenging part is probably to prevent other things binding to the surface.

This question may seem difficult but actually it is relatively easy since I give points to almost any answer as long as it shows you know what you are talking about. (You do not have to prove beyond reasonable doubt that your idea will save the world from the virus.)

Mean: 5.5