Exam in Surface Engineering KPO040

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Allowed material: Calculator approved by Chalmers (Chalmersgodkänd räknare). Paper, pen, eraser and ruler. Data sheet and periodic table are included with the questions. Nothing else is allowed, no formula collections or handbooks etc.

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.

Question 1 (3p)

Describe in brief one way to make a pattern, i.e. to bind a molecule to a surface, but only at certain regions on the nanoscale.

There are at least two techniques that can be used. One is nanoimprint, where a soft patterned stamp with the molecule on its surface is pushed onto the surface. The other is dip pen lithography, where an AFM tip writes the pattern with the molecule in an "ink". A less obvious option (but an acceptable answer) is to use some form of nanostructure (prepared by another method) with different materials and introduce a molecule that binds to only one of them. Similarly, electrochemistry can be used for certain types of molecules on nanoscale electrodes.

Mean: 2.3

Question 2 (8p)

You are monitoring the interaction between an antibody and its antigen by having the antibodies immobilized as a monolayer on a surface in an SPR sensor. Equilibrium is established with the protein in solution according to:

$$\frac{\Gamma}{\Gamma_{\max}} = \frac{C_0}{C_0 + K_D}$$

The antigen concentration is 10 nM and its molecular weight is 50 kg/mol. The dissociation constant is 2 nM. A quantification of the SPR response tells you have 100 ng/cm^2 of bound targets. How many antibody molecules are there per area on the surface?

Using the Langmuir equilibrium condition gives the ratio Γ/Γ_{max} = 5/6. The coverage 100 ng/cm^2 with molecular weight 50 kg/mol corresponds to 1.2×10^{12} antigen molecules per cm^2. The number of antibodies is 20% more based on the Γ/Γ_{max} ratio, i.e. around 14 000 per µm^2 (or 69 nm^2 per antibody).

Mean: 4.3

Question 3

A (3p)

You want to study the adsorption of a certain protein to titania (TiO_2) under physiological conditions. Is there any extra consideration when using SPR and QCM for this purpose (specify what)?

Regular SPR or QCM sensor chips have a gold surface, so you (or the supplier) must deposit a thin film of TiO_2 first. Further, especially for SPR the film cannot be particularly thick because of the limited probing depth of the surface plasmons (hundreds of nm).

Mean: 0.7

Note: Many people seem to overinterpret this question. That is OK but you need to show that you understand the "basic" surface in an SPR or QCM sensor is made of gold and not TiO_2.

B (3p)

You also want to know if the interaction is reversible and if so determine the dissociation rate constant (s^{-1}). How do you perform the SPR or QCM experiment?

Let the protein bind to the surface and then wash away all molecules in solution. Monitor how the signal decreases with time and try to fit an exponential decay.

Note: It does not matter how you bind the molecules to the surface with respect to flow, mass transport etc. You should also explain that the desorption should fit an exponential decay to actually determine k_{off}.

Mean: 1.4

C (3p)

If you also want to determine how much protein is on the TiO_2 surface, would you use SPR or QCM and why?

SPR is preferable because it is easier to quantify the signal (dry mass). For QCM, Sayerbrey can perhaps be used if the film is rigid, but even then you still get an (unknown) contribution from coupled water.

Mean: 0.7

Question 4 (4p)

Increasing temperature generally promotes solubility, but not for polymers such as poly(N-isopropylacrylamide) in water. Why?

Like many polymers in water, PNIPAM exhibits a lower critical solution temperature above which it collapses into the compact globule state. This is because of the entropy loss associated with the hydrogen bond configurations of the surrounding water molecules upon solvation. At a certain temperature this effect overcomes the favorable energetic interactions with the solvent (like the hydrogen bonds to the polar groups of the monomer).

Mean: 1.3

Note: Just stating that the polymer has a lower critical solution temperature is not so helpful. Stating that there is a hydrophobic effect is a bit more helpful, but you have to mention hydrogen bond configurations to show that you have really understood. (Perhaps it should have been emphasized even more that the effect occurs in water.)

Question 5 (8p)

A polymer brush has one coil for every 4 nm^2 on the surface. The monomer size is 5 Å, the Kuhn length 2 nm and excluded volume parameter 0.05 nm^3. Estimate the average volume fraction of monomers inside the brush! The height is given by:

$$H = \left[\frac{abv\Gamma}{3}\right]^{1/3} N$$

The volume of one polymer coil is best approximated as Na^3. The total volume occupied in the brush by one coil is H/Γ. Thus the volume fraction is:

$$\Phi = \frac{Na^3}{\frac{H}{\Gamma}} = \frac{\Gamma N a^3}{\left[\frac{abv\Gamma}{3}\right]^{1/3} N} = \frac{a^{8/3}\Gamma^{2/3}}{\left[\frac{bv}{3}\right]^{1/3}}$$

Inserting the values a = 0.5 nm, b = 2 nm, v = 0.05 nm^3 and Γ = 0.25 nm^{-2} gives $\Phi \approx 19\%$.

Mean: 2.3

Question 6 (6p)

TOF-SIMS and XPS can both be used for "depth profiling". How does it work in each case? Which method can go deepest?

TOF-SIMS does depth profiling by steadily "drilling" deeper into the sample, forming a hole on the surface. XPS does depth profiling by varying the angle between the surface plane and the detector, which limits from how deep inside the material emitted electrons can be detected. TOF-SIMS can go deeper (it just keeps milling) than XPS, which reaches ~10 nm at the most.

Mean: 2.4

Note: It is not quite sufficient to just say that you just tilt the sample in XPS. You should explain why this is needed and preferably what you must tilt with respect to (the detector, the source send x-rays through the sample regardless). Many people also did not understand that TOF-SIMS can continuously dig deeper into the sample.

Question 7 (6p)

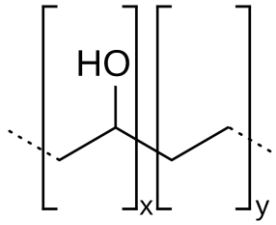
Describe oxidative modification of the surface of cellulose. Draw the chemical structure before and after. What is the most important property change in the cellulose and why is it useful?

There are two methods (one is sufficient to describe). TEMPO oxidation makes the 6th carbon (the one that sticks out) from alcohol to carboxylic acid. Periodate oxidation makes the diol (neighboring alcohol groups) into two separated aldehydes. Then these are oxidized further into carboxylic acid groups. The most important property change is that the cellulose becomes negatively charged, at least at high pH. This makes it possible to do further modifications based on electrostatic interactions among other things.

Mean: 3.4

Question 8 (4p)

The O_2 barrier performance of poly(ethylene-co-vinyl alcohol) can be increased. How? The increased performance is obtained at the expense of what?



The O_2 barrier is improved by a higher fraction of alcohol monomers because they form hydrogen bonds with neighboring chains. This makes the barrier worse with respect to moisture, however, because the material has a higher affinity for water.

Mean: 2.5

Note: The idea is that you should know what a copolymer is (more than one monomer type), at least with the given structure.

Question 9 (6p)

Describe at least two common applications of plasma treatments and what the plasma does to the surface in each case.

As examples, there are some coating technologies used in industry: Making surfaces hydrophobic by depositing Teflon ($-CF_2-$). Improve O_2 barrier properties of PET bottles by depositing amorphous carbon or silica (SiO_x). Other examples can be activation, i.e. formation of reactive groups like radicals for bonding plastics together, or etching of different materials (many examples, either chemical or ablation).

Mean: 3.7

Notes: You must describe actual applications, not just state broad terms like “activation” of the surface. To show that you understand the process should also preferably say something about, for instance, what happens to the surface chemistry or what kind of gases that are used in the plasma.

Question 10 (6p)

Hydrophobic surfaces are often less biocompatible than hydrophilic surfaces and more likely to initiate a foreign body reaction. Why?

When an implant is put into the body, the surface becomes filled with proteins within a minute. The proteins will change their structure to a higher extent on the hydrophobic surface because contact points are formed between the surface and what is normally the “hidden” protein interior. The altered structure exposes groups that are normally not accessible and make the surface look

more “foreign”, which initiates the response from the immune system (you do not have to be more specific).

Mean: 2.8

Helpful constants and data

Boltzmann's constant: 1.381×10^{-23} JK^{-1}

Avogadro's number: 6.022×10^{23} mol^{-1}

Permittivity of free space: 8.854×10^{-12} $m^{-3}kg^{-1}s^{4}A^{2}$

Planck's constant: 6.626×10^{-34} $m^{2}kgs^{-1}$

Speed of light in vacuum: 2.998×10^{8} ms^{-1}

Kelvin temperature scale: 0 °C = 273.15 K

Elementary charge: 1.602×10^{-19} C

Properties of water at room temperature

Density: 1.0×10^{3} kgm^{-3}

Dynamic viscosity: 1.0×10^{-3} Pas

Relative permittivity (static field): 80

Refractive index (at 589 nm): 1.333

Surface tension: 7.2×10^{-2} Jm^{-2}

B = Solids Hg = Liquids Kr = Gases Pm = Not found in nature

1																	18
1 H 1.00794	2											13	14	15	16	17	2 He 4.002602
3 Li 6.941	4 Be 9.012182											5 B 10.811	C 12.0107	7 N 14.00674	8 O 15.9994	9 F 18.9984032	10 Ne 20.1797
11 Na 22.989770	12 Mg 24.3050	3	4	5	6	7	8	9	10	11	12	13 Al 26.581538	14 Si 28.0855	15 P 30.973761	16 S 32.066	17 Cl 35.4527	18 Ar 39.948
19 K 39.0983	20 Ca 40.078	21 Sc 44.955910	22 Ti 47.867	23 V 50.9415	24 Cr 51.9961	25 Mn 54.938049	26 Fe 55.845	27 Co 58.933200	28 Ni 58.6534	29 Cu 63.545	30 Zn 65.39	31 Ga 69.723	32 Ge 72.61	33 As 74.92160	34 Se 78.96	35 Br 79.504	36 Kr 83.80
37 Rb 85.4678	38 Sr 87.62	39 Y 88.90585	40 Zr 91.224	41 Nb 92.90638	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.90550	46 Pd 106.42	47 Ag 196.56655	48 Cd 112.411	49 In 114.818	50 Sn 118.710	51 Sb 121.760	52 Te 127.60	53 I 126.90447	54 Xe 131.29
55 Cs 132.90545	56 Ba 137.327	71 Lu 174.967	72 Hf 178.49	73 Ta 180.94.79	74 W 183.84	75 Re 186.207	76 Os 190.23	77 Ir 192.217	78 Pt 195.078	79 Au 196.56655	80 Hg 200.59	81 Tl 204.3833	82 Pb 207.2	83 Bi 208.58038	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	103 Lr (262)	104 Rf (261)	105 Db (262)	106 Sg (263)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110 Ds (269)	111 Rg (272)	112 Cn (277)	113 Uut (277)	114 Uuq (277)	115 Uup (277)	116 Uuh (277)		118 Uuo (277)

57 La 138.9055	58 Ce 140.116	59 Pr 140.50765	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.964	64 Gd 157.25	65 Tb 158.92534	66 Dy 162.50	67 Ho 164.93032	68 Er 167.26	69 Tm 168.93421	70 Yb 173.04
89 Ac 232.0381	90 Th 232.0381	91 Pa 231.035888	92 U 238.0289	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)