

CHEM 588 Physical Methods in Materials Chemistry
Spring, 2008

Problem Set #1

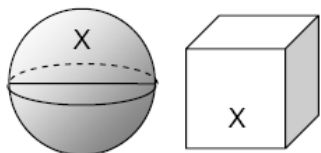
Due 02.07.08

Questions e-mail: xu8@uiuc.edu

1. Consider adsorption of the following molecules on a surface. How many molecules would that correspond to for the first monolayer on to a 100 cm^2 surface in each of the following cases? You must show your work. Surface area of the molecule is given in parenthesis.

(a) N_2 (77 K, 16.2 \AA^2) (b) benzene (273 K, 43.0 \AA^2) (c) Kr (77 K, 20.2 \AA^2)

2. If there are 1, 3, and 100 nm spherical nanoparticles what would their corresponding surface areas (m^2/g) be, assuming the density is 6 g/cc ? Compare the results with cubic nanoparticles with the same widths.



3. (a) Calculate the surface area of an atom with a radius of 0.15 nm and a mass of 100 amu 's. (b) In a recent article*, MOFs (metal-organic framework) have been synthesized with surface areas up to $4,500 \text{ m}^2/\text{g}$. Discuss your calculation from (a) with the results from this article. (c) What type of an isotherm did MOF-177 in the article show? Explain the phenomena.

* Yaghi, O. M. et al., *Nature* **2004**, 427, 523-527

4. Describe the differences between a single point BET and a multi point BET.

Problem set #1 Answer:

1. You should use the cross sectional area not surface area (assume the molecules are spherical).

- a. 2.47×10^{17}
- b. 9.30×10^{16}
- c. 1.98×10^{17}

2. Both the spherical and cubic nanoparticles yield the same surface areas.

1 nm: $1000 \text{ m}^2/\text{g}$

3 nm: $333 \text{ m}^2/\text{g}$

100 nm: $10 \text{ m}^2/\text{g}$

3. a. Surface area: $1700 \text{ m}^2/\text{g}$

b. Discuss about several factors: monolayer or multilayer, interactions between gas molecules, etc

c. Type I isotherm-Langmuir isotherm

4. Single point BET assumes C_B is large. It simplifies the calculations but can only give good approximation. There is a little error compared to a multipoint analysis.

Multipoint BET assumes that C_B is any value, large or small, allowing for an intercept that is non-zero. It can give more accurate results.

The error associated with single point BET can be eliminated or greatly reduced if an initial multipoint BET is performed to get correct C_B value.

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Problem Set #2

Due 02.19.08

Questions e-mail: xu8@uiuc.edu

1. Please describe the difference between TGA and DSC. (Compare them side by side.)

2. What would be the best technique to analyze the contents of **recycled plastic** among so many thermal analysis techniques? Explain why.

3. Thermal analysis and light scattering technique are both used in this paper. Please briefly describe how the authors use them to support their ideas.

Jian Xu, Shizhong Luo, Wenfang Shi, and Shiyong Liu **Langmuir** 2006, 22, 989-997.*

4. Please briefly introduce how the authors use light scattering to investigate the size changes of nanobubbles.

Fan Jin, Xiaodong Ye, and Chi Wu **J. Phy. Chem. B** 2007, 111, 13143-13146.*

Problem set #2 Answer:

1. Describe the difference between TGA and DSC in the following aspects: principle, application, equipment, information we can get, data, sample requirement etc.
2. We should choose DSC. Different polymers have different peaks.
3. The authors mainly use the changes of radius of polymer micelles to confirm that their structure has two-stage collapse character under different temperature ranges. From light scattering results, they were also able to determine the transition temperature of different polymers. Different light scattering physical parameters were used to confirm their conclusion.
4. In this letter, the authors were able to investigate the kinetic and structural scaling during slow coalescence of nanobubbles under aqueous solution. The whole process has two main stages: the aggregation and the coalescence. At the lower C_{NaCl} , the process essentially stops in the aggregation stage with some limited coalescence. At higher C_{NaCl} , coalescence occurs after the aggregation and results in large bubbles.

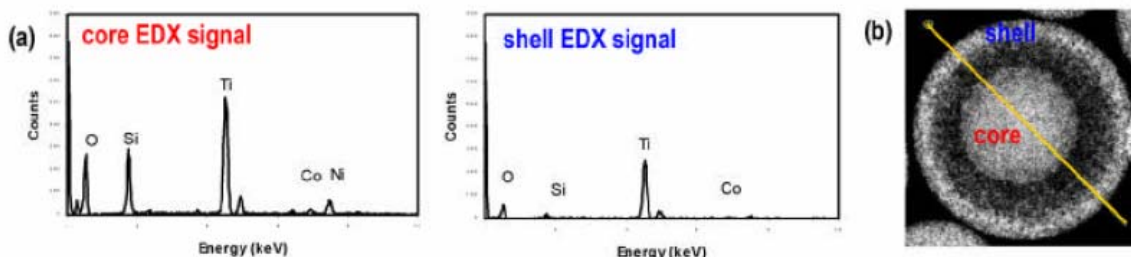
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Problem Set #3

Due 03.06.08

Questions e-mail: xu8@uiuc.edu

1. EDX spectra of ball-in-ball type structure is shown in a. Please predict the EDX line scan analysis signals represented in b.



2. Give the resolution of the following methods: Light microscopy, TEM, SEM, STEM
Which methods are capable of depth profiling?

3. Discuss the results of the analysis techniques utilized in the following article.
Emphasize what information is derived from the following techniques: SEM, TEM, STEM,
and EDS. (keep your answer in 2 pages)

Xu, J., Dozier, A., Bhattacharyya, D., *Journal of Nanoparticle Research* 2005 7, 449-467.

4. Describe how the authors use TEM techniques (all the techniques used in this
paper) to investigate their materials and draw their conclusion from the TEM
results.

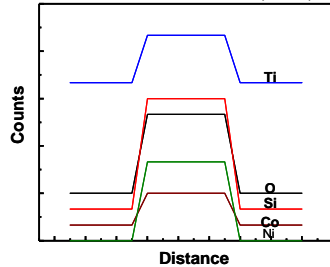
Bang, J. H.; Suslick, K. S. *J. Am. Chem. Soc.* 2007, 129, 2242-2243.

Problem set #3 Answer:

1. I have corrected your answers of this question in your homework.

Core elements: O, Si, Ti, Ni, Co

Shell elements: O, Si, Ti, Co



2. Light microscopy: ~200 nm

TEM: ~0.2 nm, capable of depth profiling

STEM: might be better than 0.2 nm, capable of depth profiling

SEM: ~1 nm, capable of depth profiling

3. This is a long paper about using all kinds of TEM techniques including: TEM, SEM, STEM, and EDX, to investigate the structure of metal nanoparticles. You can write up your answers based on each figure. Or you can prepare your answer based on each technique which is a better way to organize your points.

4. The authors used TEM techniques to confirm that the nanoparticles they prepared were hollow structured. Bright-field and dark-field TEM were used to directly observe the nanostructures. HRTEM images were able to provide better resolution and confirmed that the structure was hollow. EDX spectra together with line scan were able to confirm the elements of the shell.

Problem set #4 Answer:

1. Describe the difference between XPS and AES in the following aspects:

Mechanism/Principles (how the photons ejected from XPS and AES?)

Methodology

Applications

Data (different energies)

Advantages and Disadvantages of each technique (limitations)

2. (short answers)

STEM and XPS were used in this paper to investigate the structure of LiCoO_2

with and without AlPO_4 coating.

STEM together with EDX was able to investigate the structure of LiCoO_2 particles.

Figure 2, 3, 5, 6 give us straightforward images of LiCoO_2 particles with and without AlPO_4 coating.

Figure 7, 8, 9, 10, 11 tell us the different energy states of different elements in the LiCoO_2 particles with and without AlPO_4 coating.

3. This is a very good example of how XPS can be used to investigate the surface oxidation states of catalysts which then can be used to maximize the catalytic efficiency. The interconversion of different oxygen/palladium phases altered the catalytic activity. The reaction rate exhibited a strong increase with temperature in the stability region of PdO seeds growing within the Pd_5O_4 surface oxide. The above conclusion can be drawn from the Figure 2, 3, 4. Not exclusively the number and size of the PdO seeds, but rather the temperature is the most important parameter controlling the reaction rate also in the PdO seed stability range. (You should discuss the results with direct XPS data.)

4. EELS: In (EELS) a material is exposed to a beam of electrons with a known, narrow range of kinetic energies. Some of the electrons will undergo inelastic scattering, which means that they lose energy and have their paths slightly and randomly deflected. The amount of energy loss can be measured via an electron spectrometer and interpreted in terms of what caused the energy loss. Thus we can detect the chemical information in the sample.

Mössbauer spectroscopy is a spectroscopic technique based on the Mössbauer effect. In Mössbauer Absorption Spectroscopy, a solid sample is exposed to a beam of gamma radiation, and a detector measures the intensity of the beam that is transmitted through the sample, which will change depending on how many gamma rays are absorbed by the sample. The atoms in the source emitting the gamma rays are the same as the atoms in the sample absorbing them. The number, positions, and intensities of the dips (also called peaks) provide information about the chemical environment of the absorbing nuclei and can be used to characterize the sample.

The authors can draw their conclusion of having core-shell structure nanoparticles based on different results from EELS and Mossbauer Spectroscopy. EELS data taken over the entire particle yielded an O:Cr:Fe ratio

of 10:1.1:9.3 which different dramatically from a scan or the shell where the ratio was 10:0.3:6.3 which indicated the formula of Fe_xO_y . This proved that the elements in the shell were primary Fe and O and the core was Cr. Mossbauer spectra showed the evidence of Fe_2O_3 . From Mossbauer spectra they can also confirm that there was no Fe^0 in the particles. So it was likely that it's Cr. Figure 2 together with supporting information were able to conclude that the nanoparticle is core-shell type.

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Problem Set #5

Due 04.01.08

Questions e-mail: xu8@uiuc.edu

1. Define Bremsstrahlung in one (or two) paragraph(s).

2. Describe different AFM modes in your own words.

3. Explain how X-ray diffraction can be used to determine the absolute configuration (chirality) of molecules.

4. Explain how time-resolved XRD was utilized in the following paper:
Nature 2000, 406, 970-974.

Why is this system so amenable to XRD?

5. Discuss how the authors use TEM and XRD to support their conclusions.
Angew. Chem. Int. Ed. **2006**, 45, 407-411.

Please type your homework!!!

