Seminar Speaker: Dr. Stephany Garcia McClements

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Questions from Stephany García, Rachel M. Anderson, Hugo Celio, Naween Dahal,

Andrei Dolocan, Jiping Zhou, Simon M. Humphrey. *Chemical Communications (ChemComm)*, **2013**, *49,* 4241-4243. <https://doi.org/10.1039/C3CC40387D>

Time management: this assignment should take no more than 2-3 hours outside of class.

Answers due at the beginning of class Friday Sept. 19th.

**No cut and paste allowed.**

**SA** = a word, a phrase, a sentence encompassing just one idea. **¶** = longer more cohesive answer in paragraph format, one that will provide more detail. **Cit**. means include a proper citation. If a question does not ask for a citation, that means you should be able to figure out the answer on your own based on the data or discussion provided in the article. **Chem Draw** - be sure to use the 1996 ACS template. *Don’t scale your drawings*.

1. Methods and Results

1. Outline the steps for preparation of the Au-Rh core shell nanoparticles. (**¶**)
2. What was the diameter of the AuNPs? What technique did they use to determine this? (SA)
3. Define the terms isotropic and anisotropic. Which of these structural characteristics did the Rh shell exhibit? (SA, cit)
4. Define surface energy. What is the surface energy of Au vs. Rh? What are the implications of this in terms of the thermodynamic favorability of forming Rh-Au core shell nanoparticles? (**¶,** cit)
5. What quantities of RhCl3 were used to produce “thin-Rh” vs. “thick-Rh” nanoparticles? What were the size distributions of these particles? How many Rh monolayers does this correspond to? (SA)
6. The authors used X-ray photoelectron spectroscopy (XPS) to identify the atoms on the surface of the nanoparticles. Provide a brief description of the principles behind XPS. (**¶,** cit)
7. In reporting XPS data, the measured binding energy of an electron is assigned to particular orbital, written in the form nlj, where n is the principal quantum number and l is the angular momentum quantum number (denoted by s, p, d or f). The spin angular momentum number, j, represents spin orbit coupling. Briefly describe the meaning of spin orbit coupling and the consequences observed in XPS spectra. What values can j have for a d orbital? What binding energies result for thin Rh(0) on Au from these different j states (See Figure S4 and S5(a) and Table S2)? (**¶,** cit)
8. Why was the Au signal weak or not observed in the XPS spectra of the core shell nanoparticles? (SA)
9. The authors observed a Au(0) signal in XPS spectra of the core shell nanoparticles only upon Ar sputtering. What is Ar sputtering? (SA, cit)

1. The authors observed “plasmon peaks” in their UV-Vis spectra shown in Figure 2A. What is the difference between the surface plasmon resonance observed for nanoparticles and a traditional UV-Vis absorption spectrum? (SA, cit)

1. What happens to the plasmon peak at 540 nm in the UV-Vis spectrum for the Au nanoparticles when the Rh shell is added? What happens to the Rh peak? (SA)
2. How do the powder x-ray diffraction data (Figure 2A, inset) corroborate the UV-Vis spectral data regarding the structure of the core shell nanoparticles? (SA)
3. How does time-of-flight secondary ion mass spectrometry (TOF-SIMS) yield information on the surface composition of a sample? (SA, cit)
4. Explain why the TOF-SIMS counts for Au begin to exceed the Rh counts for the thin-Rh nanoparticles after about 30 s of sputtering, but for the thick-Rh nanoparticles, Rh counts still exceed Au counts after 100 s of sputtering (Figure 2B). (SA)
5. Briefly describe the technique of energy dispersive X-ray spectroscopy (EDS) and how it provides information on the elemental composition of a sample. (**¶,** cit)
6. Why was copper observed in the EDS data the authors collected (See Figure S9)? (SA)
7. Explain how extended X-ray absorption fine structure (EXAFS) spectroscopy provides information about interactions between neighboring atoms in a sample. (**¶,** cit)
8. Compare the coordination number between Au atoms (CNAu-Au), Rh atoms (CNRh-Rh), and Au and Rh (CNAu-Rh and CNRh-Au) in Table S3. How are these consistent with a Au-Rh core shell structure? (SA)
9. Draw the cyclohexene hydrogenation reaction used as a model reaction for assessing the catalytic properties of the nanoparticles (ChemDraw, cit).
10. Which nanoparticles exhibited the highest steady-state hydrogenation activity according to Figure 3? (SA)
11. What explanation do the authors provide for the initial induction period followed by slow loss of catalytic activity observed for the nanoparticles? (SA)
12. What evidence is presented that the core shell structure is maintained during catalysis? (SA)
13. Explain why the Rh(0)/Rh(I) ratio increased during the hydrogenation reaction as evidenced by the XPS data. (SA, cit)