Analysis of the Catalytic Effects of Multi-branched Gold Nanostructures (MGNs) on the Kinetics of the Degradation of P-nitrophenol (PNP)

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Introduction

What are MGNs?

Multi-branched gold nanostructures (MGNs) are star-shaped gold nanoparticles. These metallic nanoparticles have recently been a point of interest within the nanoscience community, because unlike most other metallic nanoparticles, MGNs have a tunable morphology and density with minimum modifications to the overall dimensions.

By modulating the concentration of 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES) buffer added to the growth solution, the concentration of $HAuCl_4$ added and the pH of the growth solution, researchers can effectively determine what "type" of MGN they want. MGNs can be used for a wide variety of applications including biomedical uses, use in sensors that utilize localized surface plasmon resonance, thermoplasmonics, and in this case, catalysis.

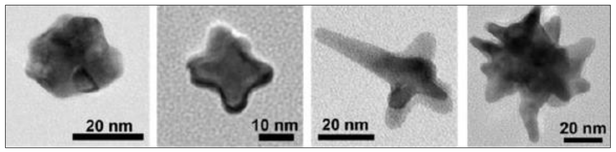

Figure 1. Various sizes of MGNs with protrusion lengths varying from 0 nm (spherical) to 20 nm protruding from the central core (star-shaped). Imaging was done using a Transmission Electron Microscope (TEM)[2].

Why Catalysis?

In order to have a better understanding of how the morphology of MGNs affects their catalytic ability, we used MGNs to catalyze the degradation of p-nitrophenol (PNP) to p-aminophenol (PAP) in the presence of sodium borohydride ($NaBH_4$). This is a model reaction in which there is only one possible product. Previous work has shown that this reaction can be described by the Langmuir-Hinshelwood model.

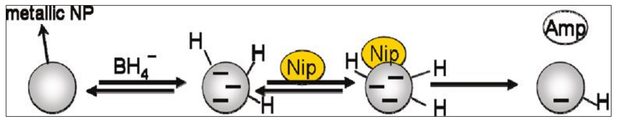

Figure 2. Illustration of the Langmuir-Hinshelwood mechanism that determines how molecules interact with metallic nanoparticles. P-nitrophenol (Nip) adsorbs to the surface of the metallic nanoparticle and P-aminophenol (Amp) desorbs from it[3].

Methods

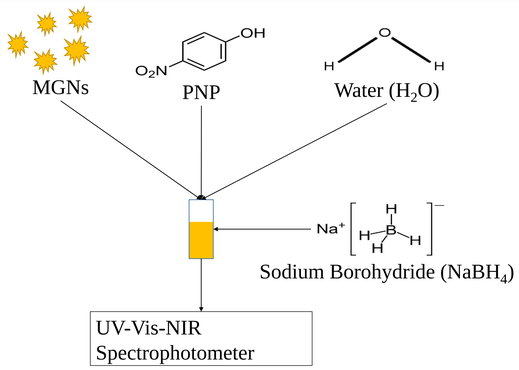

Figure 3. Catalysis Protocol. Materials are mixed in a 2.5 mL cuvette and analyzed using kinetics software through the UV-Vis-NIR Spectrophotometer at the 400 nm wavelength.

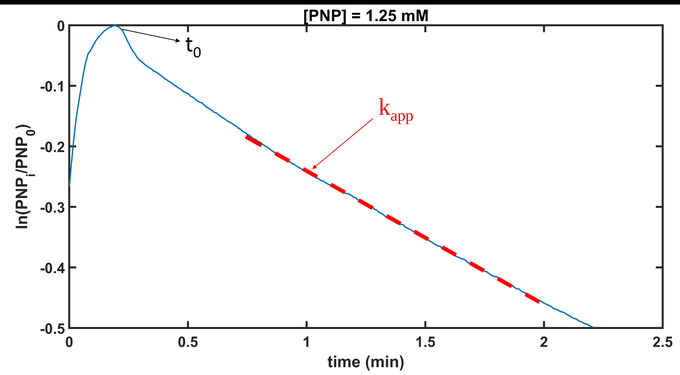

Figure 4. Calculating the apparent kinetic rate constant (k_{app}). In areas of the plot for which the slope is constant, the reaction can be modeled using pseudo-first order kinetics. The rate constant (k_{app}) is considered apparent, because it is a function of the concentration of the reagents.

We observed the values of k_{app} at various concentrations of PNP for each isotherm. The Langmuir-Hinshelwood model expresses k_{app} as

$$k_{app} = \frac{k \cdot S \cdot K_{Nip}^{n} \cdot c_{Nip}^{n-1} \cdot \left(K_{BH_4^-} \cdot c_{BH_4^-}\right)^{m}}{\left(1 + \left(K_{Nip} \cdot c_{Nip}\right)^{n} + \left(K_{BH_4^-} \cdot c_{BH_4^-}\right)^{m}\right)^{2}}$$

According to this expression, the apparent rate constant (k_{app}) decreases as the concentration of PNP increases.

Results

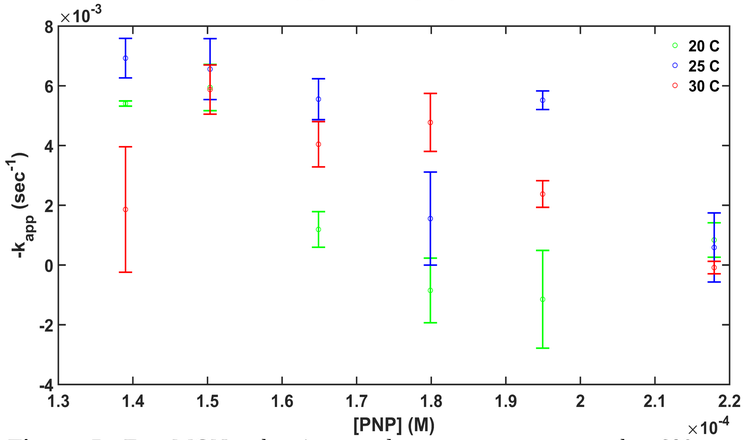

Figure 5. For MGNs showing a plasmon resonance at the 689 nm wavelength, a correlation between the increase in PNP and decrease in k_{app} can be seen. Three temperatures were measured and in all trials the general trend followed the Langmuir-Hinshelwood model.

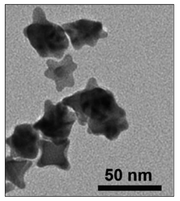

Figure 6. ~660 nm MGNs[2].

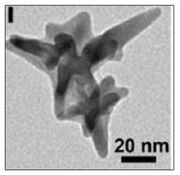

Figure 7. ~800 nm MGNs[2].

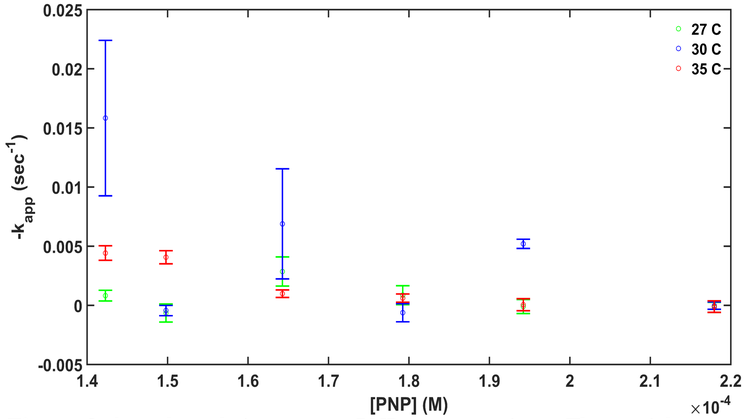

Figure 8. k_{app} degradation versus PNP concentrations. These trials were done with MGNs with a plasmon resonance at 800 nm. This shows a similar trend to that of the 689 nm MGNs.

Conclusion

The Langmuir-Hinshelwood model loosely approximates the apparent rate constants as a function of the concentration of PNP for the MGNs that showed plasmon resonances at the 689 nm wavelength and the 800 nm wavelength. Current curve fitting efforts have suggested that a relation with the Langmuir-Hinshelwood model exists, however further analysis must be done in order to ascertain an adequate explanation for the trends that have been recorded.

Future Work

Future work includes accurately determining the morphology of the MGNs and how the PNP interacts with their surfaces. Also, curve fitting the k_{app} versus PNP figures to the Langmuir-Hinshelwood model will help in understanding future metallic nanoparticles with MGN-like morphologies.

References

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(3) Wunder, S., Lu, Y., Albrecht, M., & Ballauff, M. (2011). Catalytic Activity of Faceted Gold Nanoparticles Studied by a Model Reaction: Evidence for Substrate-Induced Surface Restructuring. ACS Catalysis ACS Catal., 908-916.

Acknowledgements

I would like to thank Naiya Soetan for her excellent mentorship and Dr. Rizia Bardhan for allowing me to participate in her lab during this research experience. The Vanderbilt Institute for Nanoscale Science and Engineering (VINSE) Research Experience for Undergraduates (REU) program was funded by the National Science Foundation (NSF) grant number: NSF DMR-1263182. UV-Vis Spectroscopy was done in the Bardhan Lab at Vanderbilt University by a Cary 5000 UV-Vis-NIR Spectrophotometer.