

NDnano Summer Undergraduate Research 2018 Project Summary

1. Student name & home university: Yuko Inoue – University of Notre Dame

2. ND faculty name & department: Prof. Svetlana Neretina – Aerospace and Mechanical Engineering

3. Summer project title: Quantitative assessment of the role of dissolved oxygen in the catalytic reduction of 4-nitrophenol by metal nanoparticles

4. Briefly describe new skills you acquired during your summer research:

Throughout the ten weeks working in the lab, I learned how to use scientific equipment, such as a dissolved oxygen sensor and a spectrophotometer, and its associated software programs. In addition, I learned how to handle chemicals, prepare gold nanoparticles and clean equipment with Aqua Regia.

5. Briefly share a practical application/end use of your research:

The reduction of 4-nitrophenol into 4-aminophenol, a chemical used in the preparation of Tylenol, is one of the most widely studied model catalytic reactions. While this reaction has been well-characterized, there is still much debate over the cause of the induction time, an initial time period where no reaction seemingly occurs. We propose that induction time is related to dissolved oxygen content in the aqueous solution. A mechanistic explanation for the cause of the induction time would allow for control over the induction time, or even eliminating it. Control over the induction time increases the efficacy of the catalytic reduction.

6. 50- to 75-word abstract of your project:

The reduction of 4-nitrophenol to 4-aminophenol by borohydride is a commonly used model reaction for characterizing the efficacy of catalysts. Although this reaction has been intensely studied, the cause of induction time, an initial period where no reaction seemingly occurs, has only recently been imputed to dissolved oxygen. The performed study characterizes the effect of catalyst on induction time. There is a weak correlation between induction time and borohydride concentration and a strong correlation between induction time and amount of catalyst.

7. References for papers, posters, or presentations of your research:

- (1) Menumerov, E., Hughes, R., Neretina, R. Catalytic Reduction of 4-Nitrophenol: A Quantitative Assessment of the Role of Dissolved Oxygen in Determining the Induction Time. *Nano Lett.* **16**, 7791-7797. (2016).
- (2) Roa, R., Angioletti-Uberti, S., Lu, Y., Dzubilla, J., Piazza, F., Ballauff, M. Catalysis by Metallic Nanoparticles in Solution: Thermosensitive Microgels as Nanoreactors. *Zeitschrift Für Physikalische Chemie*, **232(5)**, 773-803. (2018).
- (3) Wunder, S., Polzer, F., Lu, Y., Mei, Y., Ballauff, M. Kinetic Analysis of Catalytic Reduction of 4-Nitrophenol by Metallic Nanoparticles Immobilized in Spherical Polyelectrolyte Brushes. *J. Phys. Chem. C*. **114(19)**, 8814-8820. (2010).
- (4) Wunder, S., Lu, Y., Albrecht, M., Ballauff, M. Catalytic Activity of Faceted Gold Nanoparticles Studied by a Model Reaction: Evidence for Substrate-Induced Surface Restructuring. *ACS Catalysis*. **1(8)**, 908-916. (2011).

Project Summary

As ever-increasing strains are put on the world's finite natural resources, there is an intensifying need for efficient energy consumption techniques. Improving or finding new catalysis techniques is salient in reducing energy consumption, as many processes for the industrial production of fertilizer, chemicals, and food are catalytically driven. Nanoparticles are especially well-suited for catalysis because catalysis is a surface-driven process and nanoparticles have a high surface-to-volume ratio.

The reduction of 4-nitrophenol (4-NP) into 4-aminophenol (4-AP) by borohydride is a widely used model catalytic reaction because this reaction allows for an uncomplicated assessment of catalysts using the kinetic data obtained from real-time spectroscopic monitoring of the aqueous solution. Although this reaction has been intensely studied in recent years, there is still much debate about the cause of induction time, an initial time period where no reaction seemingly occurs. Theories in literature about the cause of induction time range from an oxide layer coating the catalyst to borohydride and 4-NP reconstructing the surface of the catalyst substrate. The existing theories are discordant and there is no major consensus on which theory is correct. We propose that there is a much simpler explanation and that the cause of induction time is related to dissolved oxygen in the aqueous solution.

The proposed theory is that there are two main reactions at play. The first reaction is a forward reaction in which the oxygen molecules on 4-NP are replaced with hydrogen, thus converting 4-NP into 4-AP. The second reaction is a rapid side reaction in which the dissolved oxygen in solution replaces the hydrogen on the 4-AP, thus transforming 4-AP back into 4-NP. Until the borohydride consumes all the oxygen in solution, the side reaction of 4-AP being transformed back into 4-NP is faster than the forward reaction, making it appear as if no reaction is occurring. When the dissolved oxygen in solution falls below a critical level, the side reaction stops and the induction time ends.

The spectroscopic peak of 4-NP and the dissolved oxygen content in solution were measured concomitantly. Large custom-made cuvettes were used to accommodate the dissolved oxygen sensor (Figure 1). The induction time was extracted from the spectroscopic data (Figure 2). The end of the induction time corresponded to an exceedingly low level of oxygen. Increasing the borohydride concentration increased the rate of oxygen consumption and shortened the induction time. The dissolved oxygen content for varying borohydride concentrations was then characterized. Borohydride consumed the oxygen in solution, and the rate of consumption increased roughly by a factor of 10 when there was a catalyst present. Without the catalyst, the rate of oxygen removal was primarily dependent on the borohydride concentration (Figure 3, left). With the catalyst, there was a weak correlation between borohydride and the rate of oxygen consumption and a strong correlation between the rate of oxygen removal and the amount of catalyst (Figure 3, right).

These experiments have shown that there is a correlation between the amount of borohydride in solution and the rate of oxygen removal. Consequently, there is a correlation between the induction time and borohydride. This borohydride dependence on induction time is consistent with our hypothesis and, as a result, this work has advanced the understanding of an important model reaction.

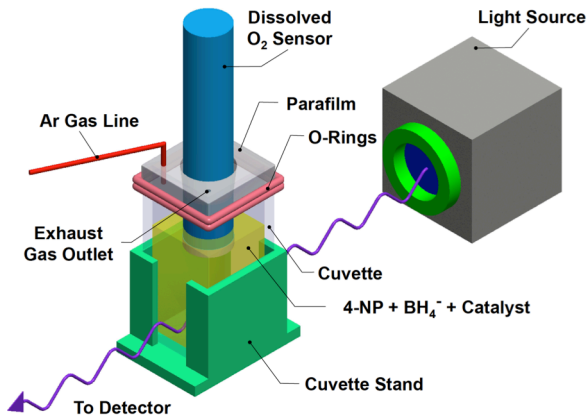


Figure 1. Experimental setup for simultaneously monitoring the spectroscopic peak of 4-NP and the dissolved oxygen content within the aqueous solution.

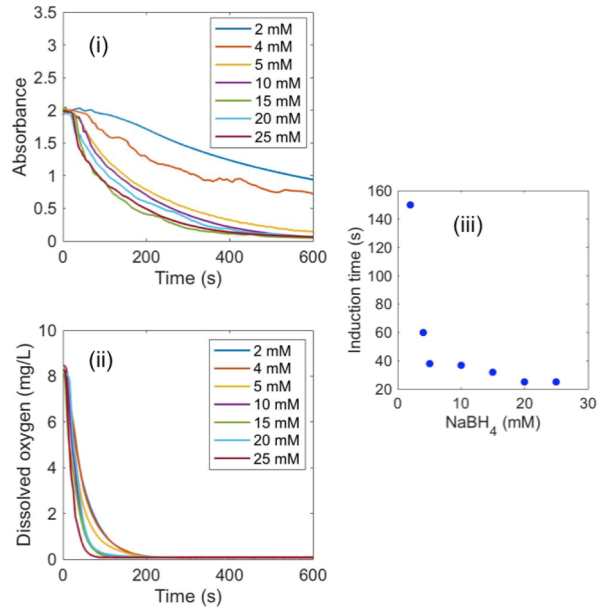


Figure 2. The time-dependent (i) absorbance and (ii) dissolved oxygen content of the 4-NP aqueous solution for varying concentrations of NaBH_4 . Extracted from the absorbance data for each concentration of NaBH_4 is the (iii) induction time.

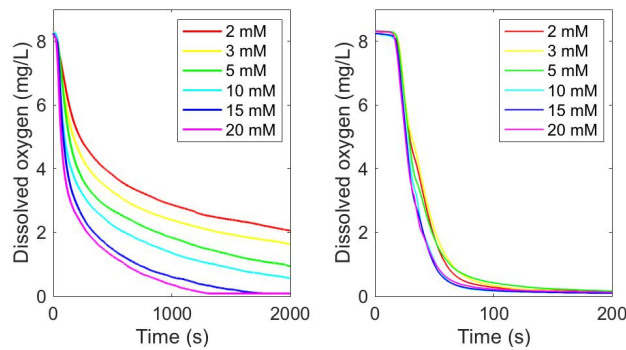


Figure 3. The time dependence of the dissolved oxygen content with (right) and without (left) a catalyst present.