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Assessment of Catalytic Function of Gold Nanorod-Bound TEMPO under NIR Irradiation

An Honors Thesis submitted in partial fulfillment of the requirements for Honors in the Department of Chemistry and Biochemistry.

By Kristi St. Clair

Under the mentorship of Dr. John Stone

ABSTRACT

Gold nanoparticles are of interest to a number of fields due to their size-dependent optical properties, high stability, and large surface area. The combination of these properties allows for a variety of uses including photothermal therapy, drug delivery and catalysis. Gold nanorods (GNR) absorb light of a given wavelength which stimulates the oscillation of electrons on the surface and is known as the surface plasmon resonance effect. The localized heating of rods via irradiation may cause enhanced effectiveness of an attached organic catalyst which allows the oxidation of alcohols to occur at room temperature. Previously, similar catalytic systems required high temperatures that reduced the lifetime of the catalyst.

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Introduction

Nanoparticles are becoming increasingly interesting in research because of their vast amount of potential uses especially in the medical field. Nanoparticles are any substance that can be reasonably measured on a nano scale (10^{-9} meters). Gold nanoparticles have sparked a lot of interest due to their compelling optical properties and uses in drug delivery and catalysis.⁶ These optical properties include varying solution colors and absorbance spectra both of which can be manipulated by the size and shape of the gold nanoparticles.⁶ Therefore, there is a relatively high degree of control over desired optical properties, size and shape of the nanorods. Gold nanorods can also be visualized on a transmission electron microscope which is useful to see if the nanorods are aggregated or to see if a coating is properly attached.

Nanoparticles are particularly useful in the medical field because their size is ideal for interacting with cells.¹ Gold nanorods are also extremely stable for long term use and have low cytotoxicity if prepared correctly.¹ Another useful characteristic of gold nanorods is their ability to be coated with a wide variety of chemicals or substances. During the preparation of gold nanorods, the rods have an outer layer of cetyltrimethylammonium bromide (CTAB) which has a positive exterior charge.² The

positively charged surface of the nanorods allows other chemicals to be linked to the surface in order to change the function of the nanorods.² For example, nanorods could be coated with a medicine which could interact with and treat cells. Polyacrylic acid (PAA) is typically the first chemical attached to the surface of nanorods because it reduces the cytotoxicity and gives the surface a negative charge.³ A Zetasizer is used to measure the Zeta Potential (surface charge) of particles in a solution. The Zetasizer shows if the coating was properly attached but can only measure particles suspended in water.

The surfaces of gold nanorods are covered in electrons that can become excited due to specific wavelengths of light.² The electrons resonate (oscillate) at the same wavelength as the light they are absorbing and can cause the nanorods to act as a catalyst and fuel other reactions.⁹ For this reason, a 785 nm laser was used to irradiate the gold nanorods which were known to absorb 785 nm light in hopes of inducing the surface plasmon resonance effect.

The overall plan for the project was to coat gold nanorods with PAA and then with (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl (TEMPO) and to use these TEMPO-coated nanorods to show that under irradiation, gold nanorods conjugated to a catalyst are more effective than the catalyst or nanorods individually. To test this, the TEMPO-coated gold nanorods were irradiated in a solution with benzyl alcohol, bromine and sodium nitrite. This was compared to all possible controls. TEMPO catalyzes the conversion benzyl alcohol into benzyl aldehyde according to the reaction scheme below.⁵

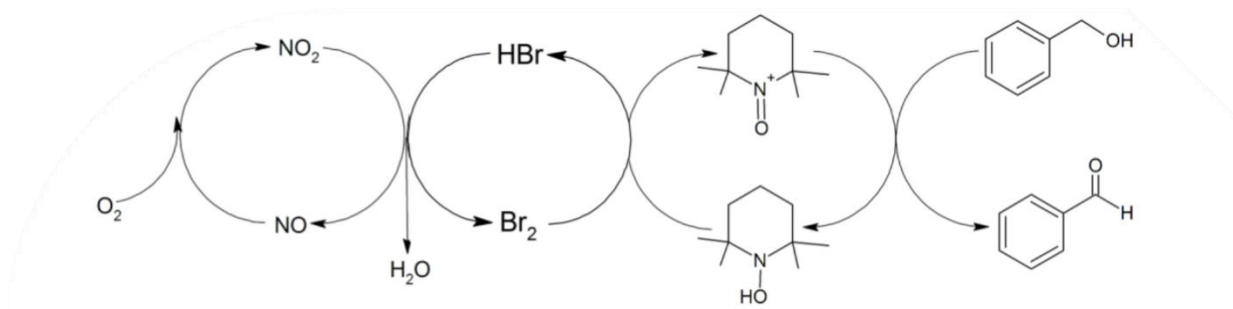


Figure 1. Reaction scheme of the conversion of benzyl alcohol to benzyl aldehyde with the catalyst TEMPO and the use of bromine, sodium nitrite and oxygen to regenerate the catalyst.

TEMPO is a small organic catalyst that oxidizes alcohols.⁸ Oxidation of alcohols has a wide variety of applications in many fields including medicine design and preparation.⁷ Catalysts increase the rates of many reactions especially in the human body. Increasing the rates of some reactions could have large implications for medicine by increasing rate of producing medicine, slowing a disease or increasing a bodily function that may be deficient.

There is a significant amount of research into using gold nanoparticles as catalysts because of their size and low cytotoxicity.⁴ One study found that gold nanospheres can be coated in TEMPO and this combination does increase catalytic function but that study did not test the effect of the surface electron oscillation on the reaction.⁷ That study found that the increased function of TEMPO is only due to the physical arrangement and increased surface area of the TEMPO on the surface of the nanoparticles.⁷ No research has found evidence of the surface electrons of gold nanorods increasing the effects of catalysts. Therefore, this research could be highly significant because this could imply that gold nanorods could increase the function of many other catalysts, providing many other functions with the utilization of the surface electron oscillation.

Methods

To make gold nanorods, we use a seed mediated growth approach.⁶ We use CTAB as a surfactant, AgNO₃ for silver ions, HAuCl₄ for gold ions, Ascorbic Acid (Vitamin C) as a reducing agent and gold spheres as seeds that will be 'grown'. To change the approximate aspect ratio (length:width) of the nanorods, the amount of silver ions can be varied.¹ To make gold nanorods at about 790 nm, combine 9.5 mL of CTAB, 0.08 mL of AgNO₃, and 0.250 mL of HAuCl₄ in a 15 mL conical tube. Invert the tube to mix. Add 0.055 mL of ascorbic acid and invert the tube. The solution should shift from a gold color to clear. Finally add 0.012 mL of prepared seed particles and invert the tube to the horizontal position. The tube is left in a 30°C chamber for 12 hours. After 12 hours, the tube is placed in the centrifuge at 10,000 rpm for 30 minutes to pull the nanorods out of solution. The supernatant (liquid on top of the nanorods) is removed to dispose of any excess reactants and water is added to resuspend the nanorods.

To coat the nanorods with PAA, add 1 mL of nanorods to a small eppendorf tube. Add 0.100 mL of 0.1 M NaCl and 0.200 mL of PAA at the same time. Place the eppendorf tube on a rocker where it is mixed for 30 minutes. After mixing, the eppendorf tube is placed in a centrifuge at 13,000 rpm for 10 minutes and the supernatant is removed. The nanorods are resuspended in 1.0 mL of 1 mM MES buffer at 5.4 pH. The nanorods could be resuspended in water instead if a zeta potential needs to be performed.

To coat the nanorods with TEMPO, 0.100 mL of 0.001 mg TEMPO/mL ethanol is added to the 1 mL of nanorods coated with PAA. In a glass scintillation vial, 1.2 mg of 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC) is weighed out. After EDC is

weighed out, the TEMPO/nanorod solution is poured into the glass scintillation vial with the EDC. The final vial is placed on the counter to sit for about 15 hours. EDC is needed to attach the TEMPO to the end of the PAA on the surface of the nanorods. After sitting for 15 hours, the TEMPO should be successfully bound to the PAA on the surface of the nanorods which can be confirmed with zeta potential and UV-Vis spectra.

Data

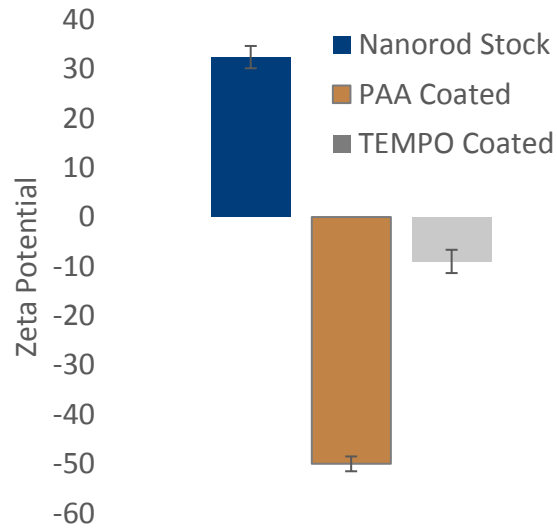


Figure 2. Mean zeta potential (n=5) of each step of the nanorod coating process.

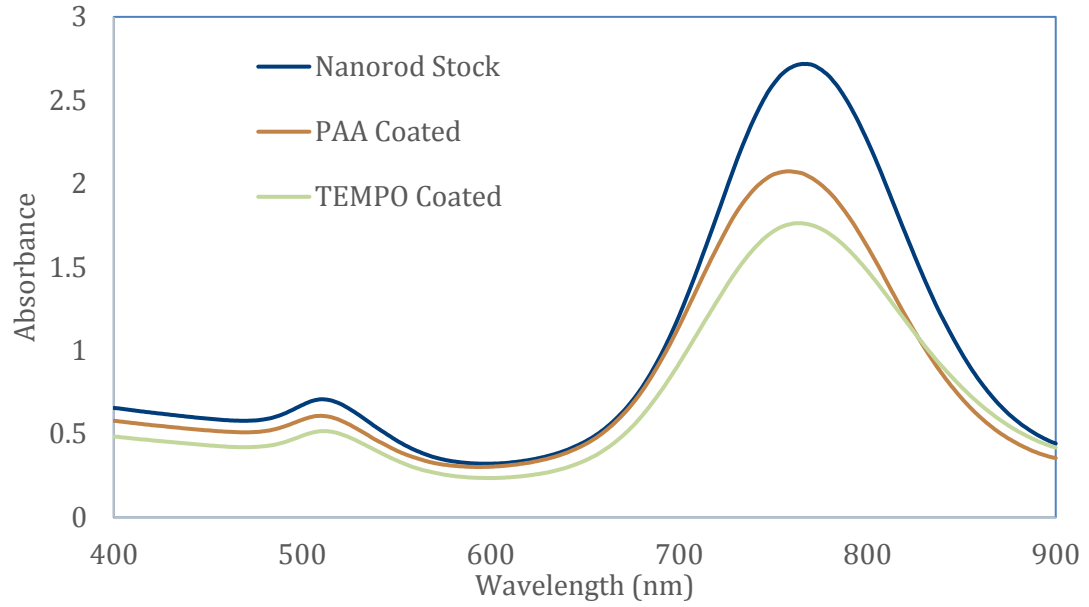


Figure 3. UV-Vis spectra of GNR. All coatings show Gaussian symmetry, indicating that they are stable and mono-dispersed. Slight red shift of the transverse peak from the stock solution to the final coating suggests functionality of the surface.

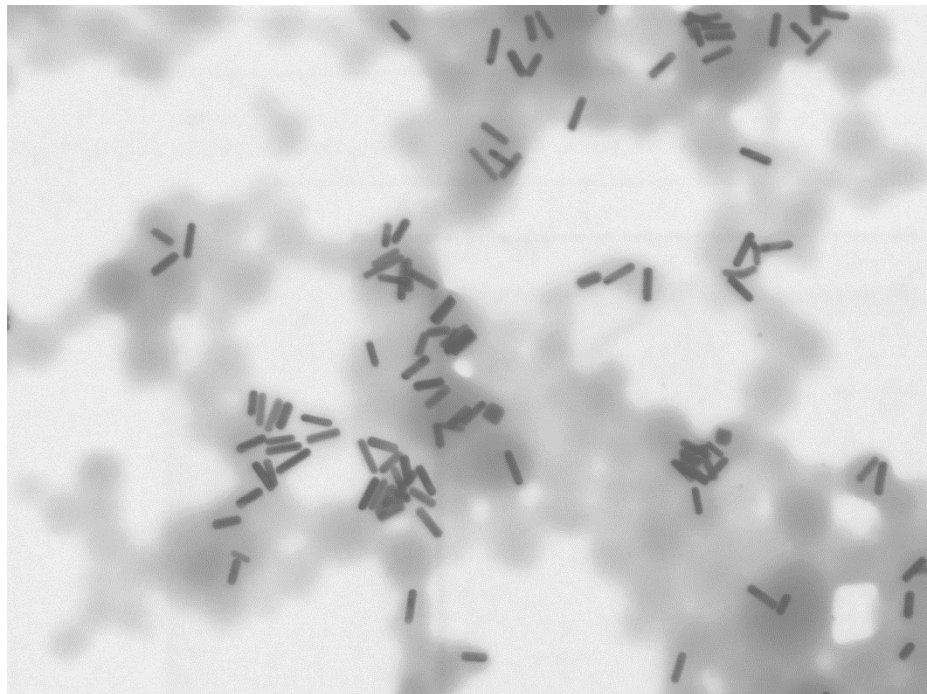


Figure 4. TEM image of TEMPO coated GNR (length \sim 50 nm).

Table 1. Conversion of benzyl alcohol to benzaldehyde based on energy source and TEMPO/Nanorod conjugation.

Nanorods	TEMPO Location	TEMPO Conc. (mg/mL)	Energy Source	% Conversion	Turnover
Conjugated	on Rods	0.000033	Laser	0.09%	665.8
Plain	in Solution	1.33	Laser	0.33%	0.22
None	in Solution	1.33	Laser	0.25%	0.16
Plain	in Solution	1.33	Hot Plate	1.70%	1.40
None	in Solution	1.33	Hot Plate	1.60%	1.32
Conjugated	on Rods	0.000033	Hot Plate	0.39%	10652.8

Table 2. GNR concentration as calculated from the absorbance values in Figure 3.

	Concentration of Nanorods (nmol/L)
Nanorod Stock	0.613
PAA Coated	0.478
TEMPO Coated	0.400

Data Analysis

The zeta potentials show the average surface charge of the nanorods in solution.⁷ Nanorods coated with just CTAB show a high positive reading because of the positive ends of CTAB that protrude from the nanorods. Nanorods coated in PAA would give a very negative value (about -30mV) because of the negatively charged carboxylic acid.³ It was hypothesized that TEMPO coated nanorods would give a neutral reading for the zeta potential because it would cover the negatively charged PAA and the ends of TEMPO are not charged. This is supported by our current data because the zeta potential of TEMPO coated nanorods is much closer to 0 than PAA coated or CTAB coated rods (Figure 2).

This suggests that the TEMPO is in fact being coated successfully on the surface of the nanorods.

A normal nanorod absorption spectra, as seen in Figure 3, has two peaks. One peak (around 510 nm) is the absorption measured across the width of the nanorod which rarely shifts. The other peak is the absorption measured along the length of the nanorod and can change greatly for each batch of gold nanorods prepared. A 'good' spectra has a peak around 785 nm that is narrow and has a high absorption. The narrow peak suggests that the rods are not aggregated. Aggregation can be presumed when the peak at ~785 nm is broad or has tailing (far right side is significantly above 0).

While the nanorod stock shows no aggregation, each successive coating shows an increase in the broadness of the peak, suggesting an increase in aggregation with each coating (Figure 3). This was anticipated due to the required centrifugation step between each coating which is known to cause some aggregation which can sometimes be reversed with sonication.¹ Although the solution becomes slightly more aggregated with each coating, the final coated rods are mono-dispersed, as can be seen in Figure 4, suggesting the rods are highly functional.

The irradiated, conjugated nanorods showed a significantly higher turnover number (products per catalyst) than all other controls that were irradiated (Table 1). The conjugated nanorods also had a much higher turnover number when heated on a hot plate than its comparative controls (Table 1). This suggests that the conjugated nanorods do in fact supply energy to an attached catalyst when irradiated via the surface plasmon resonance effect. The increase in turnover number, when the gold nanorod-conjugated system was heated, is not fully understood and could be the source of future research.

Conclusion

Gold nanorods were synthesized with a seed-mediated approach and coated in a layer of PAA.⁶ TEMPO was covalently bound to the surface of the PAA-coated gold nanorods which was verified by the UV-Vis spectroscopy and Zeta Potential analysis. A baseline oxidation study was conducted and confirmed the minimal conversion of benzyl alcohol under all conditions except with TEMPO-coated gold nanorods. TEMPO-coated gold nanorods produced a significant increase in the turnover number of benzyl alcohol which is likely due to the surface plasmon resonance effect.

Future Work

While this project has produced interesting and useful results, there are still several concepts that need to be investigated and improved. For example, table 1 shows the percent conversion rates of all of the oxidation trials are relatively low which means that a small amount of error could have large impacts on this data. Bromine is known to be responsible for a small amount of conversion without the presence of a catalyst and this was accounted for in the calculations of the turnover number.⁵ Ideally, the percent conversion of the trails should be much larger than the percent conversion of the bromine that is subtracted out in order to minimize the effects of the calculational and experimental errors.

Another aspect that needs to be investigated is the mechanisms involved in the high turnover number of the catalyst conjugated gold nanorod system when heated. If better understood, this mechanism could be very useful for increasing the efficiency of several polymerization reactions that TEMPO also catalyzes. Polymerization reactions

were previously limited due to the sensitivity of the reactants to the high temperatures needed to make TEMPO produce a significant amount of product.⁵ It is now possible that high temperatures will not be necessary due to a mechanism that is not yet fully understood.

Other future work includes quantifying the exact amount of TEMPO that is bound to the surface of the nanorod and increasing the concentration of the nanorod stock solutions (Table 2). Knowing the exact amount of TEMPO on the surface of the nanorods would increase the accuracy of the turnover number calculations. Increasing the concentration of the nanorod stock solutions before coating with TEMPO could increase the percent conversion of the oxidation reactions which would also decrease the errors of the turnover number.

References

1. Burrows, N. D., Harvey, S., Idesis, F. A., & Murphy, C. J. (2016). Understanding the Seed-Mediated Growth of Gold Nanorods through a Fractional Factorial Design of Experiments. *Langmuir*, 33(8), 1891-1907. doi:10.1021/acs.langmuir.6b03606
2. Burrows, N. D., Lin, W., Hinman, J., Dennison, J., Vartanian, A., Abadeer, N., . . . Murphy, C. (2016). Surface Chemistry of Gold Nanorods. *Langmuir*, 32, 9905-9921. doi:10.1021/acs.langmuir.6b02706
3. Gole, A.; Murphy, C. J. (2005) Polyelectrolyte-Coated Gold Nanorods: Synthesis, Characterization and Immobilization. *Journal of Chemistry of Materials*, 17 (6), 1325-1330.
4. Imada, Y., Ohsaki, M., Noguchi, M., Maeda, T., Fujiki, M., Kawamorita, S., . . . Naota, T. (2015). Flavin-Functionalized Gold Nanoparticles as an Efficient Catalyst for Aerobic Organic Transformations. *ChemCatChem*, 7(1), 3-3. doi:10.1002/cctc.201402931
5. Liu, R.; Liang, X.; Dong, C.; Hu, X. (2004) Transition-Metal-Free: A Highly Efficient Catalytic Aerobic Alcohol Oxidation Process. *J. Am. Chem. Soc.*, 126 (13), 4112-4113.

6. Murphy, C. J.; Sau, T. K.; Gole, A. M.; Orendorff, C. J.; Gao, J.; Gao, L.; Hunyadi, S. E.; Li, T. (2005) Anisotropic Metal Nanoparticles: Synthesis, Assembly, and Optical Applications. *J. Phys. Chem. B*, 109 (29), 13857-13870.

7. Swiech, O., Bilewicz, R., & Megiel, E. (2013). TEMPO coated Au nanoparticles: synthesis and tethering to gold surfaces. *RSC Advances*, 3(17), 5979-5986.
doi:10.1039/c3ra23106b

8. Tebben, L., & Studer, A. (2011). Nitroxides: Applications in Synthesis and in Polymer Chemistry. *Angewandte Chemie International Edition*, 50(22), 5034-5068.
doi:10.1002/anie.201002547

9. Wu, X., Ni, Y., Zhu, J., Burrows, N. D., Murphy, C. J., Dumitrica, T., & Wang, X. (2016). Thermal Transport across Surfactant Layers on Gold Nanorods in Aqueous Solution. *ACS Applied Materials & Interfaces*, 8(16), 10581-10589.
doi:10.1021/acsami.5b12163