



Ligand type impact on gold nanoparticle properties



UTRGV

Leopoldo Posada¹, Zheng Zheng², Zeev Rosenzweig²

¹Department of Chemistry, University of Texas Rio Grande Valley, 1201 W. University Dr, Edinburg, TX 78539

²Department of Chemistry & Biochemistry, University of Maryland-Baltimore County, 1000 Hilltop Cir, Baltimore, MD 21250

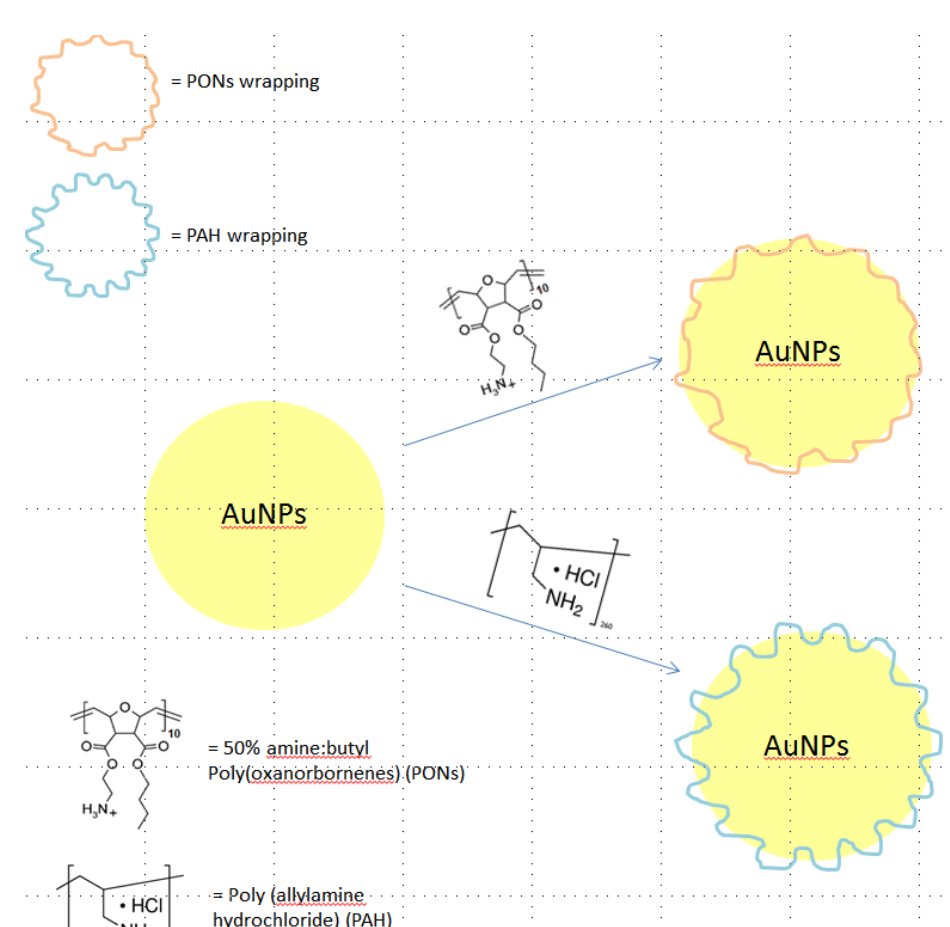
INTRODUCTION

Engineered nanoparticles (NPs) are increasingly used in wide-ranging technologies due to their unique nanoscale properties. Thus, production of these nanomaterials has increased significantly in the last decade. With the increase in production of NPs, concerns have been raised on their potential impact on human health and the environment. Having learned from history that emerging technologies, as handy as they might be, don't always come without risks; it is crucial to understand how nanomaterials interact with the environment, so that we might figure out a way to produce minimally invasive and highly sustainable nanomaterials. In this study, we used Gold Nanoparticles (GNPs) as a model. The objective of the study is to understand how different ligands attached to the GNPs affect their interactions with model membranes. Recent studies have shown that the surface chemistry of GNPs, particularly surface charge, has a significant impact on their interactions with model membranes and living organisms. For example, recent studies have shown that GNPs which are wrapped with cationic polyelectrolytes like poly (allylamine hydrochloride) (PAH) have high anti-bacterial activity. In our experiments, we used a new class of cationic polyelectrolytes, poly [oxanorbornenes] (PONs), which allows greater systematic variation of surface charge and hydrophobicity than PAH. Transmission Electron Microscopy (TEM) imaging, UV-vis spectroscopy, Dynamic Light Scattering (DLS) spectroscopy, and Zeta Potential measurements were used to characterize the newly produced PONs-coated gold nanoparticles. The results of these measurements indicate that it is possible to control the surface charge of the nanoparticles by modifying their surface with various PONs. Experiments to determine the anti-membranal activity of PONs-coated gold nanoparticles are on-going and current data indicate that surface charge is shown to have a significant impact on anti-membranal properties of gold nanoparticles.

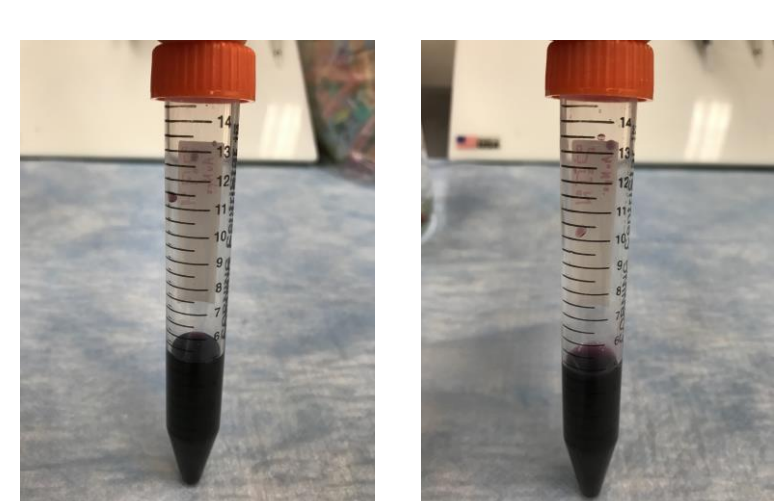
BACKGROUND

- Gold nanoparticles are nanometer scale particles that range from 1-100 nm in size.
- Due to their size, gold nanoparticles experience quantum confinement, which changes the wavelength at which they absorb light and can range depending on the gold nanoparticle size.
- Because this effect is so easily tunable, it only requires a change in size, gold nanoparticles are used in a variety of different technological applications.
- Although gold nanoparticles have nifty uses for technological purposes, they carry a major drawback, they have been shown to be toxic to organisms and detrimental to the environment.
- The purpose of this study is to compare the effects gold nanoparticles functionalized with different cationic polyelectrolytes have on liposomes, a model membrane.
- Doing so, we intend to better determine the mechanisms of gold nanoparticle toxicity, with the goal of producing less harmful and more sustainable gold nanoparticles.

EXPERIMENTAL

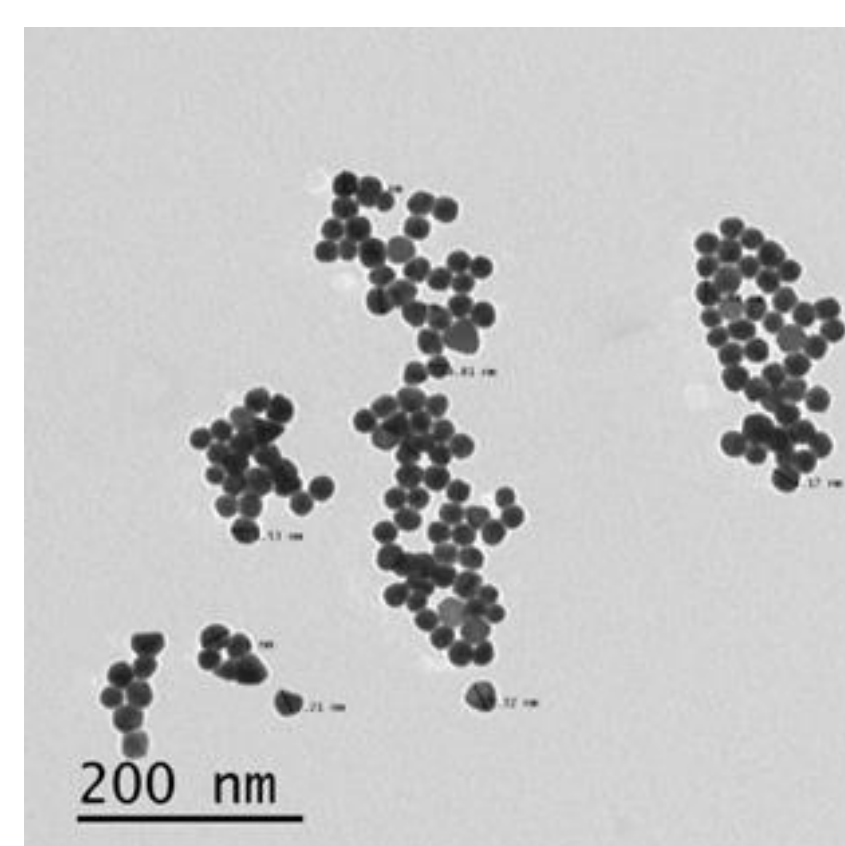


Schematic representation of gold nanoparticle wrapping functionalization with two different cationic polyelectrolytes, Poly(allylamine hydrochloride) (PAH) and Poly(oxanorbornenes) (PONs).

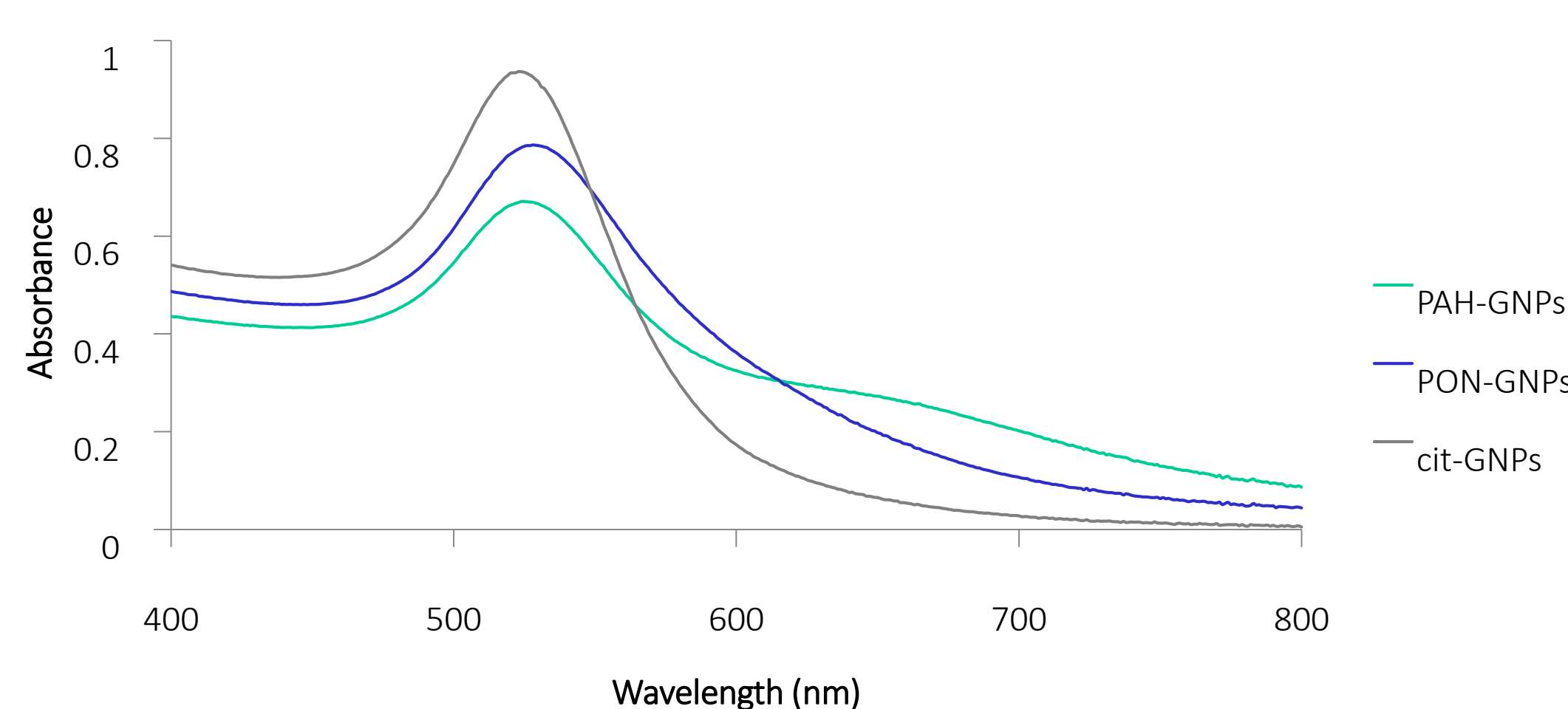


Picture of functionalized gold nanoparticles. PAH wrapped gold nanoparticles are on the right and PONs wrapped gold nanoparticles are on the left. Although visually similar, their overall properties are slightly different as can be seen through their characterizations.

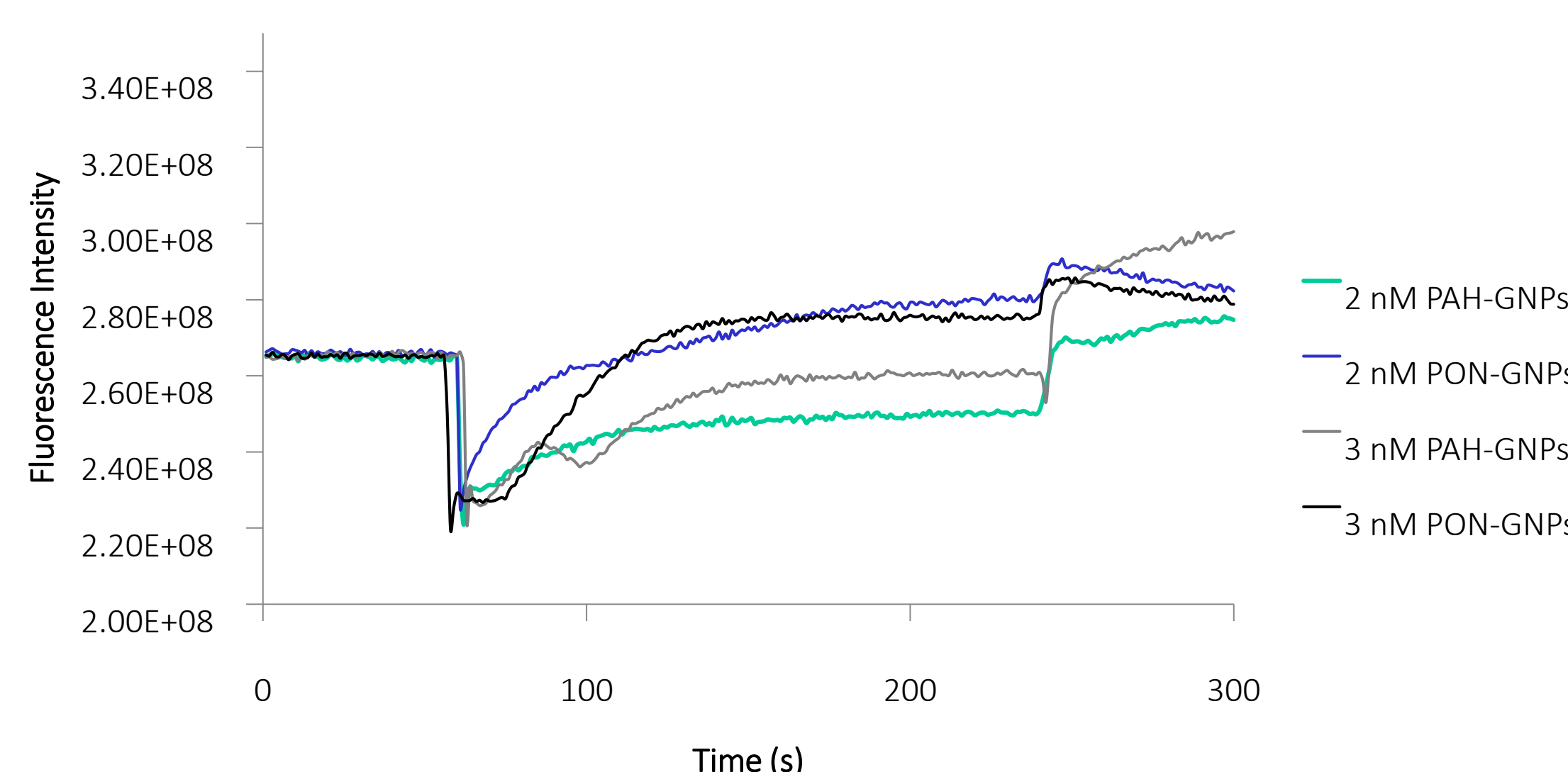
RESULTS



Transmission Electron Microscopy (TEM) image of 20 nm diameter gold nanoparticles. TEM imaging was used to correlate with the data from Dynamic Light Scattering (DLS) spectroscopy to confirm the size of the gold nanoparticles.



Absorbance spectrum of the three types of gold nanoparticles used in the study. The slight shift in the λ_{max} , as well as the decrease in peak absorbance of the different gold nanoparticles indicates an increase in size and a decrease in concentration.



Time-based fluorescence intensity graph depicting cationic polyelectrolyte functionalized gold nanoparticle interactions with liposomes. GNPs were added one minute after start and a detergent was added at the four minute mark to completely lyse the membrane.

	Dh (nm)	ζ -potential (mV)
cit-GNPs	24.8 \pm 0.11	-43.7 \pm 1.02
PAH-GNPs	61.2 \pm 0.34	47.9 \pm 0.60
PON-GNPs	46.5 \pm 0.72	45.5 \pm 0.65

Characterization of gold nanoparticles initially and after functionalization with the different cationic polyelectrolytes using Dynamic Light Scattering (DLS) spectroscopy and ζ -potential analysis.

INSTRUMENTATION



Images of instrumentation used to characterize and gather data from the gold nanoparticles used in the study. From left to right: (1) UV-vis spectrophotometer (2) Nanozetasizer (3) Fluorescence spectrophotometer (4) Transmission Electron Microscope. UV-vis spectrophotometer was utilized to determine concentrations of gold nanoparticle solutions. Nanozetasizer was used to measure gold nanoparticle diameter size, and to determine the surface charge of gold nanoparticles through zeta potential analysis. Fluorescence spectrophotometer was used to determine the percent lysis of liposomes due to gold nanoparticle interactions. TEM was utilized to image the gold nanoparticles to give a more accurate depiction of diameter size.

DISCUSSION

Characterization of gold nanoparticles before and after being functionalized shows significant differences in the overall properties of the gold nanoparticles, most notably their size and surface charge. The initial results from the time based fluorescence intensity study showed very similar results for both of the different gold nanoparticles. The 2 nM PAH-GNPs showed a percent lysis higher than 100%, which can be attributed to the manner in which percent lysis is calculated. All other concentrations of gold nanoparticles showed lysis range of around 60-80%, with PAH functionalized gold nanoparticles having consistently higher percent lysis than did the PONs functionalized gold nanoparticles. Characterization of the functionalized gold nanoparticles shows that PAH functionalized gold nanoparticles have a much higher increase in size than do the PONs functionalized gold nanoparticles. This difference in size between the functionalized gold nanoparticles can be explained by the much bigger size of the PAH relative to the PONs, which results in a higher degree of wrapping. Finally, even with a much bigger size in diameter of the PAH functionalized gold nanoparticles to the PONs functionalized gold nanoparticles, they both have very similar surface charges, which can be attributed to the PONs packing more efficiently to the surface of the gold nanoparticles.

CONCLUSION

By functionalizing gold nanoparticles with different kinds of cationic polyelectrolytes, such as poly(allylamine hydrochloride) and poly(oxanorbornenes), our studies have found that certain gold nanoparticle properties can be modified, most importantly diameter size and surface charge. Further experimentation with liposomes, as model membranes, showed initial results that suggest that shifting properties of gold nanoparticles can have substantial effects on such membranes.

FUTURE WORK

- Further liposome/gold nanoparticle interaction studies will be conducted using a larger range of concentrations to more accurately determine the effects gold nanoparticles with different functionalizations have on model membranes.
- We will take advantage of the tunable properties of poly(oxanorbornenes) to create a more complex library of functionalized gold nanoparticles to test their effects on various systems.
- Collaboration with other laboratories from the Center for Sustainable Nanotechnology to test the effects of gold nanoparticles on living organisms will be conducted.

REFERENCES

1. N.R., Jana; L., Gearheart; C. J., Murphy. Seeding Growth for Size Control of 5-40 nm Diameter Gold Nanoparticles. *J. Am. Chem. Soc.* **2001**, *122*, 6782-6786.
2. D., Bartzak; A. G., Kanaras. Preparation of Peptide-Functionalized Gold Nanoparticles Using One Pot EDS/Sulfo-NHS Coupling. *Langmuir.* **2011**, *27*, 10119-10123.
3. J. S., Bosich; S. E., Lohse; M. D., Torelli; C. J., Murphy; R. J., Hamers; R. D., Klaper. Surface chemistry, charge, and ligand type impact the toxicity of gold nanoparticles to *Daphnia magna*. *Environ. Sci.:Nano.* **2014**, *1*, 260-270.

ACKNOWLEDGEMENTS

This research project is supported by a National Science Foundation Center for Chemical Innovation on Sustainable Nanotechnology (CSN) Award No.CHE-150 3408.