Poly(Acrylic Acid) Coated Gold Nanoparticles for pH Sensing Applications

Cole D. BRUBAKER¹, Talitha M. FRECKER², Ian NJOROGE³, G. Kane JENNINGS³, Douglas E. ADAMS¹

¹ Dept. Civil and Environmental Engineering, Vanderbilt University
Nashville, TN USA
² Dept. Chemistry, Vanderbilt University
Nashville, TN USA
³ Dept. Chemical and Biomolecular Engineering, Vanderbilt University
Nashville, TN USA

Key words: Gold Nanoparticles, Smart polymers, pH Sensing, SHM, NDE.

Abstract

Traditionally, the use of physical sensors placed spatially throughout a structure, coupled with large-scale data collection systems and advanced computer algorithms have been used to detect, localize and communicate material damage. Though these systems have proven effective for a variety of applications, they are inherently hindered by their requirements for continuous data collection and power consumption. This research seeks to reduce, and ultimately eliminate, the need for data collection and power consumption through the development of a colorimetric ‘smart polymer’ based sensing system. Utilizing the plasmonic properties of metallic nanoparticles, this gold nanoparticle (AuNP) based system has been shown to detect changes in solution pH through distinct shifts in optical absorbance properties. For the purposes of this research, a ligand exchange between natively bound citrate capping ligands present on gold nanoparticles is performed with poly(acrylic acid) (PAA) and exposed to fluctuations in solution pH. It is hypothesized that the swelling and de-swelling of surrounding PAA polymer matrix in response to pH changes and the corresponding movement and interaction of individual AuNPs results in distinct shifts of the observed optical properties; indicative of a change in the surrounding solution properties. By monitoring shifts in optical properties, we herein evaluate the effectiveness of a PAA/AuNP system as an alternative methodology for detecting and communicating chemical fluctuations in solution pH. Furthermore, it is hypothesized that this work can be implemented and expanded towards the development of novel films capable of responding to both chemical and mechanical stimuli due to the presence of gold nanoparticles.

1 INTRODUCTION

The development of new stimuli responsive ‘smart material’ systems have the capacity to revolutionize current structural health monitoring (SHM) and nondestructive evaluation (NDE) technologies by endowing structures and materials with advanced, in situ sensing capabilities. By minimizing requirements for both power consumption and large scale data collection/processing, such systems can provide a distinct advantage over traditional SHM and NDE practices by communicating the occurrence of damage or changes in material properties through distinct shifts in optical properties alone. One recent approach towards achieving this
goal has been through the use of nanoparticles and quantum dots. Such nano-based sensing systems provide an alternative to traditional sensing approaches due to their tunable material and size dependent properties and behaviors. On the length scale of several nanometers, nanoparticles and quantum dots exhibit unique optical and electromagnetic behaviors that are not observed in the bulk state due, in part, to an increased surface area to volume ratio. By harnessing these unique material characteristics and behaviors, nanoparticles and quantum dots have been used in a number of applications to generate systems and technologies that are not feasible of achieving at the bulk scale. Within the past 15 year alone, nanoparticles and quantum dots have been implemented in a wide variety of applications ranging from medical and biological imaging [1,2,3] to solid state lighting [4,5,6], LED displays [6] and even as spectrometers [7], and are now being studied for SHM and NDE sensing applications.

Metallic nanoparticles, such as gold and silver, are ideal platforms for smart sensor development due to their unique plasmonic properties. These properties, or electromagnetic effects, including local surface plasmon resonance (LSPR), can be captured to develop a colorimetric ‘smart material’ system capable of responding to external stimuli through distinct shifts in optical properties and color. LSPR occurs when light interacts with particles much smaller than the incident wavelength, leading to an oscillation of the particle and an observed peak in the absorbance spectra [8,9]. The LSPR peak is sensitive to a number of factors including nanoparticle shape, size, inter-particle distance as well as the refractive index and dielectric of the surrounding media [8,10] where fluctuations in any of these parameters can shift the location of the observed LSPR peak. By monitoring the corresponding blue or red shift in response to changes in the surrounding environment, the plasmonic properties of metallic nanoparticles can be harnessed to develop colorimetric sensors for a variety of SHM and NDE sensing applications.

Building upon the plasmonic properties of metallic nanoparticles, this paper focuses on the response of poly(acrylic acid) (PAA) coated gold nanoparticles (AuNPs) to fluctuations in solution pH. By monitoring shifts in the recorded absorbance spectra, and observing sample solutions visually, the effectiveness of the proposed system is herein evaluated. By implementing a simple ligand exchange between natively bound citrate surface ligands and PAA, enhanced sensitivity to fluctuations in pH between 4 and 10 is obtained and confirmed through UV-Vis absorbance data.

2 EXPERIMENTAL SECTION

2.1 Materials

All polymers and reagents including tetrachloroauric (III) acid (≥99%, Sigma Aldrich), trisodium citrate dehydrate (Sigma Aldrich) and poly(acrylic acid) (PAA) (Mw ~100,000 35 wt. % in H₂O, Sigma Aldrich) were used as received with no further modification or purification. 18.2 MΩ-cm Mili-Q water was used for all experiments and also to wash glassware prior to use. pH buffer solutions were obtained by mixing appropriate amounts of citric acid (Fisher), sodium hydroxide (Fisher), sodium bicarbonate (Fisher) and sodium phosphate dibasic heptahydrate (Fisher) and Mili-Q water [11,12].
2.2 Synthesis of Gold Nanoparticles

The gold nanoparticles used in this report were synthesized according to a modified Turkevich method [13,14]. In short, the synthesis procedure was performed as follows. On a stir plate, 50mL of 0.25mM gold(III) chloride trihydrate (HAuCl₄•3H₂O) in a flat bottom flask was brought to a boil under reflux conditions to ensure a constant reaction volume. Once boiling, 1mL of sodium citrate (194mM) was quickly injected into the flask under vigorous stirring and heating. After addition of the sodium citrate reducing agent, the solution quickly changed color from clear to bright red, indicating the formation of gold nanoparticles. The solution was then heated for an additional 15 minutes and stirred under reflux conditions for 2 hours. The resulting solution was transferred to a brown bottle and stored in a refrigerator until use. As synthesized nanoparticles had an average diameter of approximately 26nm, as confirmed by UV-Vis absorption data and corresponding calculations [15], as well as with dynamic light scattering (DLS) measurements (Figure 1).

![Figure 1: DLS Size Distribution of as Synthesized AuNPs](image)

2.3 Synthesis of PAA Coated Gold Nanoparticles

PAA capped gold nanoparticles were obtained through a ligand exchange process previously reported in the literature [16]. 1mL of stock AuNP solution was transferred into centrifuge tubes, and the pH of the solution was raised through the addition of 40µL NaOH (0.5M) to facilitate the ligand exchange. This change in pH can be visually observed, as the color of the gold nanoparticle solution shifted from bright red to purple/blue (Figure 2), indicating AuNPs have some inherent pH sensitivity capabilities from the natively bound citrate ligands. Next, 10µL of PAA solution was added to the AuNP solution and sonicated for 1 hour to perform the ligand exchange. Following sonication, the PAA coated AuNP solution was centrifuged at 15,000 RPM for 15 minutes, and the supernatant was carefully removed. PAA coated AuNPs were then dried to remove any excess supernatant and resultant pellets of PAA coated AuNPs were re-suspended in 1mL of the desired pH buffer solution or water and again sonicated for an additional 60 minutes to thoroughly disperse in the aqueous media. A solution of PAA coated AuNPs re-suspended in water is shown in Figure 2, where a darker blue/gray color can be visually observed following the ligand exchange process.

2.3 Characterization Techniques

To study the response of PAA coated AuNPs in response to fluctuations in solution pH, absorbance data was collected at various levels of pH and in 18.2 MΩ-cm Mili-Q water.
Absorbance data was collected using a Cary 60-UV-Vis spectrophotometer and accompanying software in the spectral range from 400 – 800nm. A background for each buffer solution was recorded prior to obtaining absorbance data to ensure the recorded data was representative of the response of PAA coated AuNPs only. DLS measurements used to determine the size of the as synthesized AuNPs were performed on a DLS Malvern Nano ZS. It should be noted that DLS measurements record hydrodynamic radius, which includes the surrounding capping ligands or polymer shell.

![Figure 2: Stock AuNP Solution (Left), Stock AuNP Solution at Elevated pH (Middle) and PAA Coated AuNPs in Water (Right)](image)

3 RESULTS AND DISCUSSION

The results for PAA coated AuNPs tested at various levels of pH are included below. Ligand exchange between citrate capped AuNPs and PAA were confirmed through UV-Vis absorption data, shown in Figure 3. Here, a red shift in the extinction and LSPR peak was observed between as synthesized AuNPs and PAA coated AuNPs, where the maximum peak position shifted from 519nm to 527nm following polymer encapsulation. These results align with those previously reported and confirmed through IR measurements [16], where the exchange of PAA onto the surface of AuNPs corresponded with a red shift in the recorded absorbance data. The size of PAA coated AuNPs increased from 26nm to 126nm following polymer encapsulation (Table 1).

![Figure 3: UV-Vis Absorbance Spectra of AuNP and PAA Coated AuNP in Water](image)
In the results presented here, though, a new phenomenon is observed with the emergence of a secondary peak in the absorption data beginning near 600nm. It is hypothesized that this new peak is a result of the generation of the lossy mode resonance (LMR) phenomenon due to the presence of PAA surrounding individual AuNPs. LMR is a second type of electromagnetic resonance phenomenon in addition to LSPR that is typically associated with the absorption or addition of thin films and corresponding changes in the surrounding dielectric constant around a material [17]. In fact, a pH responsive system utilizing fiber optic cables and a PAA/AuNP smart polymer system has been demonstrated to be effective at monitoring changes in solution pH through shifts in LMR peak position alone [18]. Typically, LMR is associated with layer-by-layer polymer deposition and can be used to track the number of layers deposited on a substrate through the emergence and magnitude of the LMR peak [17,18], but is here useful for observing shifts in solution pH due to PAA coated AuNPs. UV-Vis absorbance data for samples suspended in water and pH 4 and pH 10 buffer solutions are shown in Figure 4.

For all three solutions shown in Figure 4, LSPR and LMR peaks can be distinguished after AuNPs have been coated with PAA; indicating that PAA coated AuNPs are stable in all solutions tested and showed little signs of aggregation. It should be noted that the absorbance data for Samples 2 and 3 suspended in pH 4 buffer are negative due to errors in correctly zeroing the software prior to recording absorbance data, and does not represent negative absorbance values. Furthermore, the noise in the observed data and relatively low absorbance in the plots is due to low concentration of AuNPs in solution used to obtain UV-Vis data. As only 1mL of AuNP solution was used to prepare test solutions, increasing the overall...
concentration of AuNP present would likely lead to smoother data with better defined maximum peaks and shape than the plots shown here. Figure 5 shows a comparison of the response of PAA coated AuNPs in pH 4 buffer, water and pH 10 buffer, where LSPR peak positions have been labeled accordingly. Again, the units of absorbance between samples is arbitrary and dependent on the concentration of gold nanoparticles in solution, and the overall shape of the absorbance curve and relative peak heights are the main points of study.

Figure 5: Comparison of UV-Vis Absorbance Spectra of PAA Coated AuNP at Various Levels of pH

The pH sensitivity of PAA coated AuNPs displayed in Figure 5 comes from the ionizable nature of the PAA polymer matrix, and its ability to undergo a transition from a coiled to a stretched conformation in response to fluctuations in pH [16,19]. At low values of pH (pH 4), PAA becomes partially protonated and adopts a stretched conformation due to electrostatic interactions with an increased number of sites available for hydrogen bonding with the surrounding aqueous media, resulting in particles with large hydrodynamic radii [16]. At higher values of pH (water and pH 10), PAA tends to adopt a more coiled and collapsed state due to the reduced number of sites for hydrogen bonding and a lack of electrostatic repulsion, leading to smaller AuNP polymer composites [16]. DLS measurements of PAA capped AuNPs suspended in pH 4, water and pH 10 solutions are included in Table 1 confirming this behavior, where the largest size PAA coated AuNP is obtained when particles are suspended in pH 4 solution. Again, DLS measurements report the hydrodynamic radius of a particle, including the surrounding ligands or polymer shell.

<table>
<thead>
<tr>
<th></th>
<th>pH 4</th>
<th>Water</th>
<th>pH 10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Size (d.nm)</td>
<td>178.2 ± 1.55</td>
<td>126.0 ± 1.25</td>
<td>110.3 ± 1.87</td>
</tr>
</tbody>
</table>

Table 1: Size of PAA Coated AuNPs at Various Levels of pH

The results presented in Table 1 for DLS measurements are used to confirm the trends observed with the UV-Vis data in Figures 4 and 5 and associated LMR peak intensities. As discussed earlier, LMR is a phenomenon generated by the addition of a coating to a material,
and can be used to measure relative coating thickness through shifts LMR peak intensity alone [18]. To evaluate the effectiveness of this phenomenon for detecting fluctuations in pH in our system, we compare the ratio of relative peak intensities between the LMR and LSPR peaks in pH 4, water and pH 10 solutions. It is expected that the samples with the largest hydrodynamic radii, and corresponding thickest surrounding polymer shell, should have the highest peak intensity ratios as determined from UV-Vis data. LMR/LSPR peak intensity ratios for all three solutions based on the UV-Vis data presented in Figure 5 are included below in Table 2. LSPR and LMR values used to calculate peak intensity ratios were obtained by taking the maximum value in the spectral range 500 – 575nm and 600 – 800nm, respectively, for each sample.

<table>
<thead>
<tr>
<th></th>
<th>pH 4</th>
<th>Water</th>
<th>pH 10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ratio</td>
<td>1.14</td>
<td>.851</td>
<td>.686</td>
</tr>
</tbody>
</table>

Table 2: Peak Intensity Ratios (LMR/LSPR)

The results shown in Table 2 align with those presented in Table 1, where the highest LMR/LSPR peak intensity ratio occurs at pH 4, followed by water and pH 10 solution. These results are in agreement with prior work [16], and demonstrate the effectiveness of a PAA coated AuNP system as an alternative methodology for detecting and communicating changes in pH through shifts in optical properties alone. By evaluating LMR/LSPR peak intensities ratios, the relative degree of polymer swelling and corresponding level of pH can easily be determined due to the presence of AuNPs and their unique electromagnetic and optical properties. The slight shift in LSPR peak position for samples suspended in pH 4 should also be noted. This data follows a similar trend for as synthesized citrate AuNPs vs PAA coated AuNPs (Figure 3), where a thicker polymer layer causes a red shift in absorbance compared to those suspended in water or pH 10. The corresponding red shift is likely caused by a change in the dielectric of the surrounding media due to polymer swelling, but further analysis will be required to confirm this optical shift. Samples of pure PAA dispersed in solution were also tested to confirm that the observed shifts in absorbance were due to PAA coated AuNPs and not excess PAA in solution. When dispersed in water and pH buffer solutions, PAA did not display any absorbance (UV-Vis data not shown here), indicating that the resulting changes recorded in Figures 4 and 5 are a direct result of PAA coated AuNPs and their optical properties.

Finally, films of pure PAA and PAA/PAA coated AuNPs were cast to evaluate the effectiveness of this proposed system as a possible thin surface coating. To prepare films, 0.5g of PAA was added to 1 mL water or PAA coated AuNP solution and sonicated for 60 minutes. Samples were then drop cast onto a PDMS coated glass slide and left to dry overnight. The corresponding films are shown in Figure 6. Similar to the PAA solutions tested, films of pure PAA did not display any absorbance in the visible range. PAA/PAA coated AuNP films, though, exhibited characteristic absorbance nearly identical in shape to that obtained for PAA coated AuNPs in solution, as both the LSPR and LMR peaks were present after casting. The purple/red coloration was also maintained. As PAA is hydrophilic in nature, the response of PAA coated AuNP films were not tested in pH buffer solution due to the fact that they readily dissolve in water. Future work will evaluate the effectiveness of cross-linked PAA films in response to fluctuations in solution pH to study their optical behaviors. Due to the presence of AuNPs, it is hypothesized that such a film may also be capable of detecting and communicating the occurrence of mechanical loads in addition to fluctuations in pH. Utilizing
the principles of plasmon coupling and monitoring shifts in the LSPR peak due to the movement of individual AuNPs in response to film deformation, mechanical loadings can be communicated through distinct shifts in optical properties. Colorimetric, mechano-responsive systems have been previously developed [20], but lack the dual responsiveness of the system proposed using PAA coated AuNPs. Future work will focus on the multi-stimuli responsive nature of a PAA/AuNP thin film system.

Figure 6: PAA (L) and PAA/PAA Coated AuNP (R) Films (Left) and Absorbance Spectras (Right)

4 CONCLUSIONS

In this work, the effectiveness of poly(acrylic acid) (PAA) coated gold nanoparticles (AuNPs) for detecting and communicating changes in solution pH was evaluated. By monitoring shifts in the recorded absorbance spectra and changes in optical properties, PAA coated AuNPs were able to distinguish between solutions of pH 4, water and pH 10. Relying on the electromagnetic properties associated with AuNPs and the pH responsive nature of PAA, the peak intensity ratio between lossy mode resonance (LMR) and localized surface plasmon resonance (LSPR) offers an effective methodology for determining solution pH. At low levels of pH (pH 4), PAA adopts a stretched conformation, leading to an increased LMR peak intensity and higher LMR/LSPR peak ratio compared to solutions with higher pH (water and pH 10) where PAA exhibits a coiled state. These trends, and the overall pH sensitivity of the PAA coated AuNP system was also confirmed through dynamic light scattering (DLS) measurements. Furthermore, thin films of PAA containing AuNPs were cast to evaluate the possibility of using the proposed system as a surface coating. By creating thin films containing AuNPs and a pH responsive polymer agent, it is hypothesized that a multi-stimuli responsive system can be designed to be capable of responding to both chemical and mechanical stimuli through distinct shifts in optical properties alone. Reducing requirements for physical sensors, and instead relying on this in situ material state sensing, AuNPs provide a promising direction for the future of nano-based ‘smart material’ systems for a variety of SHM and NDE sensing applications.
5 ACKNOWLEDGMENTS

This project was supported by the U.S. Office of Naval Research under the Multidisciplinary University Research Initiative on “Sound and Electromagnetic Interacting Waves” (through Grant No. N00014-10-1-0958).

REFERENCES