

STUDIES ON THE COMPETITIVE INTERACTION OF GLUTATHIONE WITH 3-AMINOPROPYLTRIMETHOXYSILANE-STABILIZED GOLD NANOPARTICLES

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Abstract

Gold nanoparticles (AuNps) of controlled nanogeometry have been synthesized by 3-glycidoxypropyltrimethoxysilane (3-GPTMS) mediated reduction of gold chloride in the presence of 3-aminopropyltrimethoxysilane (3-APTMS). It has been found that 3-APTMS control the size of AuNps followed by acting as potential stabilizer for the same. An increase in 3-APTMS concentration resulted into an increase in the size of AuNps. The interaction of Glutathione with 3-APTMS-stabilized AuNps has been investigated. The dynamics of GSH and AuNps has been found as a function of 3-APTMS concentration. Higher concentration of 3-APTMS results into slower kinetics AuNps-GSH interaction followed dramatic variation in the size of AuNps. A comparative study with AuNps functionalized with citrate and polyvinylpyrrolidone was performed. The results based on UV-VIS spectroscopy and impedance analysis are presented.

1. Introduction

In recent times, the nanoparticles of noble materials have been the focus of intense research due to their unique physical, chemical and optical properties^[1,2]. Nanoparticles are generally prepared by the reduction of their metal salt precursor solutions in the presence of a stabilizing agent. The size, stability and many other properties depend heavily on both the stabilizing and reducing agent^[3].

We have undertaken a comparative study on the interaction of 3-aminopropyltrimethoxysilane (3-APTMS) functionalized gold nanoparticles with glutathione. Glutathione is a tripeptide well known for its anti-oxidant properties. Glutathione prevents damage to cellular components by reactive oxygen species and is a frequently used measure of cell toxicity. The action of 3-APTMS functionalized gold nanoparticles on Glutathione is compared to that of gold nanoparticles functionalized by citrate and by polyvinylpyrrolidone (PVP).

2. Experimental

2.1 Materials and Instrumentation

3-Aminopropyltrimethoxysilane (APTMS), 3-glycidoxypropyltrimethoxysilane (GPTMS), graphite powder (particle size 1–2 mm), glutathione and Nujol oil were obtained from Aldrich Chemical Co., India. All other chemicals and reagents were of analytical grade. All experiments were performed at room temperature. Absorption spectra of samples were recorded using a

Hitachi U-2900 Spectrophotometer. All electrochemical measurements were performed in an electrochemical cell equipped with a three-electrode configuration having a working volume of 3 mL with an Electrochemical Workstation Model CHI660B, CH Instruments Inc., TX, USA.

2.2 Synthesis of Gold Nanoparticles

Three sets of gold nanoparticles were prepared functionalized with 3-APTMS, citrate and Poly N-vinyl-2-pyrrolidone (PVP). Care was taken to ensure that the precursor gold salt solutions were of the same concentration. It is worth noting that due to the size difference of the nanoparticles formed, their colloidal solutions were not of the same concentration.

2.2.1 3-APTMS functionalized AuNp

Methanolic solutions of 0.025M auric-chloride (HAuCl_4) and 0.1M 3-APTMS were stirred together vigorously. A methanolic solution of GPTMS was then added to reduce the gold salt. The mixture was stirred for an additional two minutes and then left to stand in the dark for 12 hours. For APTMS-Red gold nanoparticles, the ratio of GPTMS to Au was 800 to 1 and that of APTMS to Au was 10 to 1. This results in nanoparticles that are 6 to 10 nanometers in size^[4]. For APTMS-Purple gold nanoparticles, the ratio of GPTMS to Au was 800 to 1 and that of APTMS to Au was 400 to 1. This results in nanoparticles that are 40 to 50 nanometers in size^[4]. Below are the AFM images of thin films coated by AuNp sols.

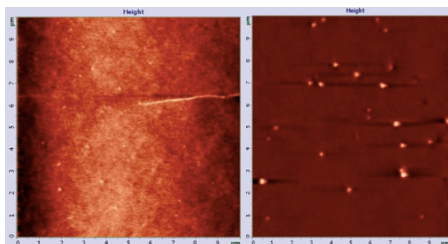


Figure 1. AFM images of thin films with AuNp_{red} and $\text{AuNp}_{\text{purple}}$

2.2.2 Citrate functionalized AuNp

To a boiling rapidly stirred solution of 1mM HAuCl_4 , a 1% solution of trisodium citrate dehydrate was added. Stirring and heating were continued for about 10 minutes until a ruby red color appeared. The solutions were taken in a ratio of 10:1. Citrate acts both as a reducing agent and a stabilizing agent in these nanoparticles. The nanoparticles formed are in the 10-20 nanometer range^[5].

2.2.3 PVP functionalized AuNp

An aqueous auric chloride solution was added to an aqueous PVP solution in a 1:15 ratio under vigorous stirring. Then, a designated amount of NaOH dissolved previously in water, which

serves as initiator ^[6] for the chemical reduction, was added to the mixture.

2.2 UV-Vis Spectra

Each set of AuNps first had their absorption spectra recorded. A certain concentration of GSH was then added. The UV-Vis spectrum was then taken in five-minute intervals after addition. To record the spectra, 200 microliters of AuNp-GSH solution were taken at the time stops and added to 2mL of cold double distilled water in a cuvette.

3. Results

3.1 Impedance Measurements

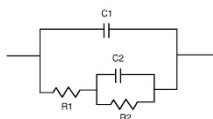


Table 1. Elements of the equivalent circuit

	C1 (F)	R1 (ohm)	C2 (F)	R2 (ohm)
Blank	1.955E-9	385.1	1.882E-6	1.921E4
APTMS	2.82E-9	542	1.636E-6	8.2E4
Citrate	6.08E-9	163	7.086E-7	2.54E4
PVP	3.208E-9	423.8	1.531E-6	8.601E4

C1, representative of the double layer capacitance is significantly lower for APTMS_{red} functionalized AuNp graphite paste electrode. This suggests more responsive electrochemical characteristics, which is advantageous to electrochemical sensing.

3.2 UV-Vis spectra

3.2.1 APTMS_{red} functionalized AuNp

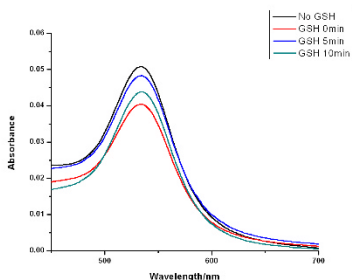


Figure 3. The interaction of APTMS_{red} functionalized AuNp with 0.1mM GSH After initial addition, there is peak suppression but no peak shifting. With the passage of time,

the amount of peak suppression reduces. The interactions were only recorded with 0.1mM GSH, as lower concentrations had very little effect. APTMS acts as powerful stabilizer and prevents aggregation of AuNp, therefore allowing the exploitation of nanogeometry in the electrochemical sensing of GSH. This introduces selectivity.

3.2.2 APTMS_{purple} functionalized AuNp

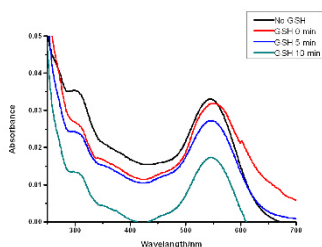


Figure 4. The interaction of APTMS_{purple} functionalized AuNp with 0.1mM GSH. Again, after initial addition, there is peak suppression but no peak shifting. With the passage of time, the amount of peak suppression increases unlike what is found with APTMS_{red}. The interactions were only recorded with 0.1mM GSH, as lower concentrations had very little effect.

3.2.3 Citrate functionalized AuNp

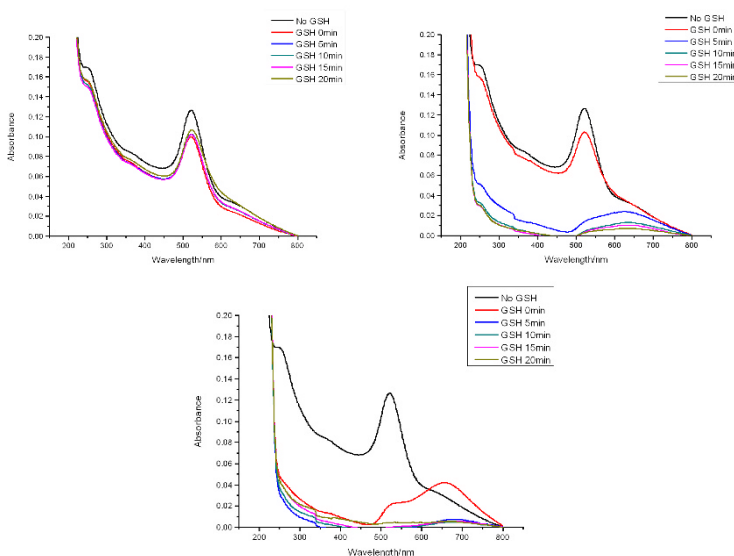


Figure 5. The interaction of citrate functionalized AuNp with 0.01, 0.05 and 0.1mM GSH

At lower concentrations, GSH initially causes peak suppression that reduces with time. At higher concentrations, the peak is shifted and then suppressed, indicating the agglomeration of the nanoparticles.

3.2.4 PVP functionalized AuNp

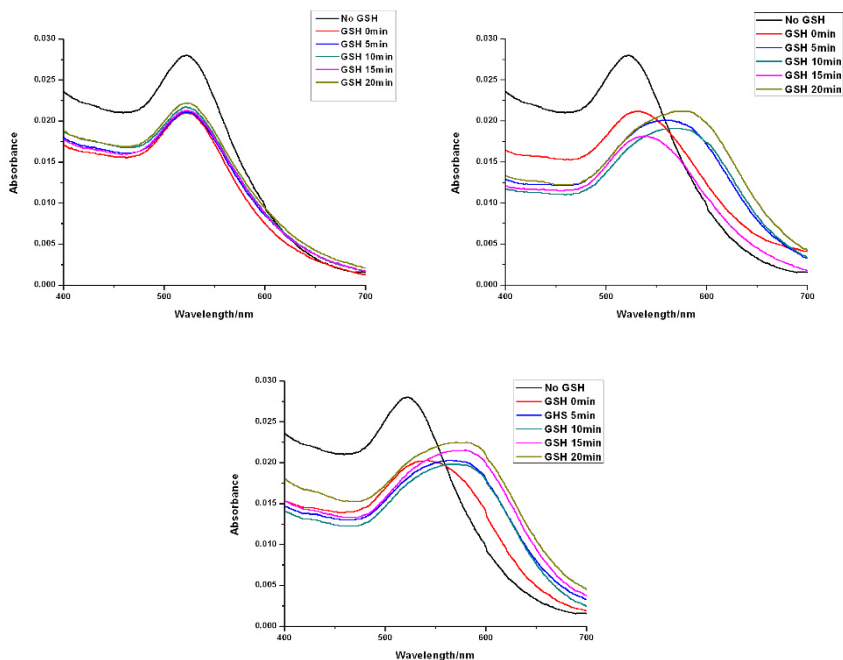


Figure 6. The interaction of PVP functionalized AuNp with 0.01, 0.05 and 0.1mM GSH

At low GSH concentrations, there is peak suppression. At higher concentrations, the peak shifts indicating agglomeration of the nanoparticles.

4. Conclusion

APTMS functionalized gold nanoparticles were found to be very resistant to agglomeration in the presence of glutathione. This tendency to preserve their nanogeometry and their responsive electrochemical characteristics make them a strong candidate for glutathione sensing applications. Further work is in progress to better investigate these interactions.

5. References

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