Experiment 3. Green synthesis of silver and gold nanoparticles - Study of their absorption spectra by UV-visible spectroscopy

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Abstract. On this paper we report the creation of Au and Ag nanoparticles in the region of 10 to 30 nms via the green method of microwave heating and using potato starch as a reducing agent. Absorbance lines were created for each of the products to compare with previous literature reports. Maximum absorbance was measured for each solution and this data was used to determine the size of those particles.

I. INTRODUCTION

In chemistry, a colloid is a mixture in which one substance of microscopically dispersed insoluble particles is suspended into a a liquid or gas. For example, colloidal gold consists of a suspension of nano sized gold particles in a liquid. These are permanently suspended and have different properties than those of bulk gold. When the gold colloid is partially coagulated or a change in their shape to a rod-like form happens, purple, violet or pale blue colors are produced and the absorption of light is accompanied by light scattering [7]. This has to do with that the size, shape and surface morphology of these nanoparticles have a great deal of effect in physical, chemical, optical and electromagnetic properties [6]. Recently, there has been a rising interest in their study.

Also, there exists the interest in the synthesizing nanoparticles in a "green process". Green synthesis is a chemical process that aims at the minimization of harmful waste and the creation of a sustainable process [6]. Key points are the utilization of nontoxic chemicals, environmentally benign solvents and renewable materials [6]. One of the aims is the eventual integration of these particles in biological systems. Recent developments such as the use of *Hibiscus rosa* has for the synthesis of gold and silver nanoparticles is worth mentioning [8].

In 1908, Mie presented the solution of Maxwell's equations for extinction spectra of spherical particles of arbitrary size. It's the only simple, exact solution of these equations that is relevant to particles. [5]

The aim of this work was first to synthesize Au and Ag nanoparticles using water as the solvent and starch as the mediator at a fixed temperature of about 90 °C. The amount of noble metal solutions was varied for each test. Some of the these included the addition of NaOH to the mix. Secondly, all these NPs were characterized via UV-vis spectroscopy. This was to study whether these variations affected positively or negatively the formation of NPs.

II. EXPERIMENTAL PROCEDURE

In this experiment potato extract was used to aid the creation of nanoparticles. It has been shown that potato extract is an efficient green reductor in the synthesis process of Au nanoparticles given its natural and abundant availability, along with its really low to none ecologic impact of its use.[10] 500g of potato product were liquified along 200 ml of water, followed by a cleaning process of filtration and decantation towards the production of starch.

A. Synthesis of Au and Ag nanoparticles

A 1% w/v starch solution was prepared with potatoes. Substances used include 25 mM Silver Nitrate solution, 8 mM Gold Chloride solution, and 0.1M Sodium Hydroxide solution. Mixing such components (also shaking, at 95C) in amounts present in Table 1 and Table 2 result in synthesis of Au and Ag nanoparticles respectively.

TABLE I: Synthesis of Au nanoparticles. The pH of each solution is to be measured before adding $HAuCl_4$.

Synthesis	Starch [mL]	Water [mL]	NaOH [mL]	pH	$HAuCl_4$ [µL]
1	1.0	3.0	0.0	X	100.0
2	1.0	3.0	0.0	X	050.0
3	1.0	3.0	0.0	X	200.0

TABLE II: Synthesis of Ag nanoparticles. For the last three reaction an unknow amount of NaOh has to be added to get the desired pH before adding $AgNO_3$.

Synthesis	Starch [mL]	Water [mL]	NaOH [mL]	pH	$AgNO_3$ [µL]
1	0.5	1.5	X	X	100.0
2	0.5	1.5	X	7	100.0
3	0.5	1.5	X	8	100.0
4	0.5	1.5	X	9	100.0

B. Characterization of NPs

UV-Vis SpectroVisR Plus spectrophotometer was used to obtain absorbance of light as a function of wavelenght. This process was repeated for each experiment reported.

III. RESULTS

From the initial part of the experiment approximately 1.062 grams of starch were obtained from the potatoes.

For each colloid body the initial starch + water mix was found to have a pH of 6. As stated in the last section, the team didn't have enough time to do the last three Ag synthesis that required tweaking the pH of the solution. Therefore, the amount of NaOH that would had been used is unknown. However, the synthesis of a pH12 AgNPs was done. All the absorbance spectra optained are shown in FIGS 1-5. The middle line is the maxima.

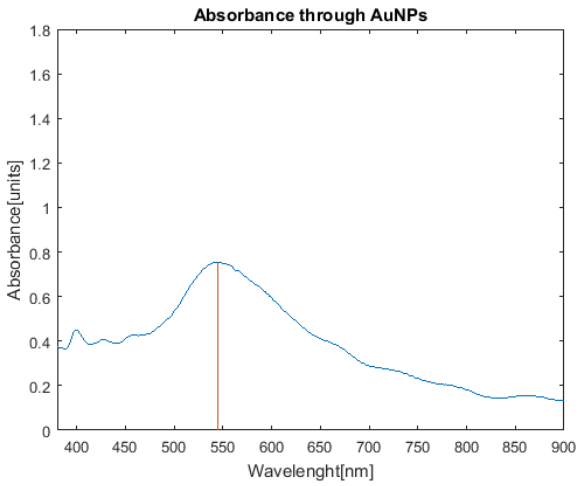

FIG. 1: UV–visible absorbance spectra for AuNPs. Synthesis 1 done with 50 µL of $HAuCl_4$.

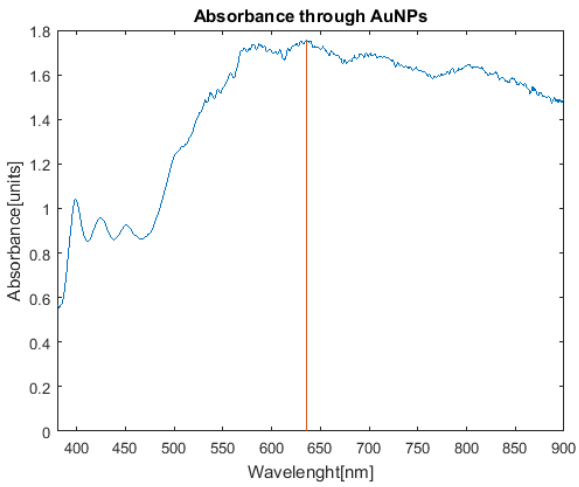

FIG. 2: UV–visible absorbance spectra for AuNPs. Synthesis 2 done with 100 µL of $HAuCl_4$.

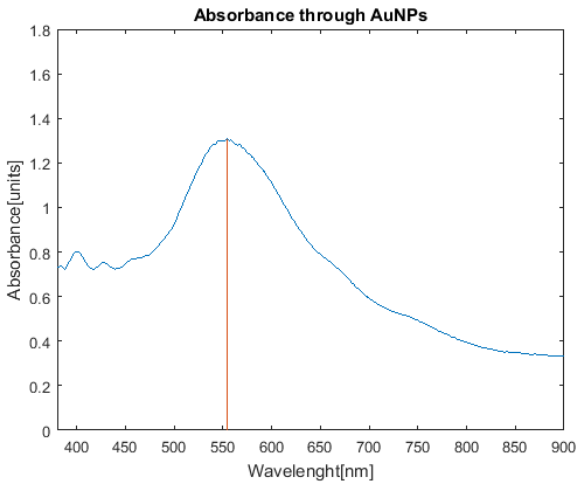

FIG. 3: UV–visible absorbance spectra for AuNPs. Synthesis 3 done with 200 µL of $HAuCl_4$.

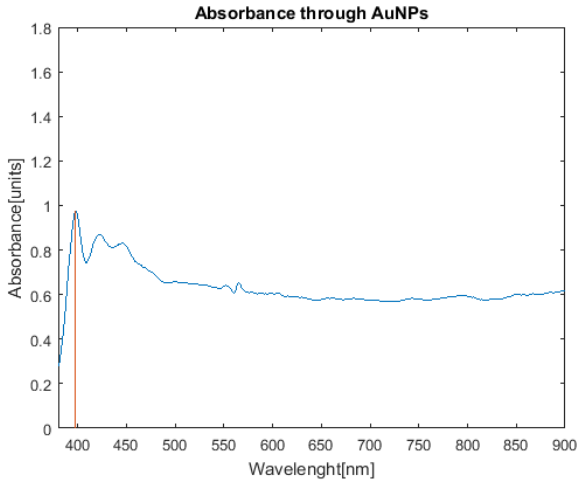

FIG. 4: UV–visible absorbance spectra for AuNPs. Synthesis 4 done with 100 µL of $AgNO_3$.

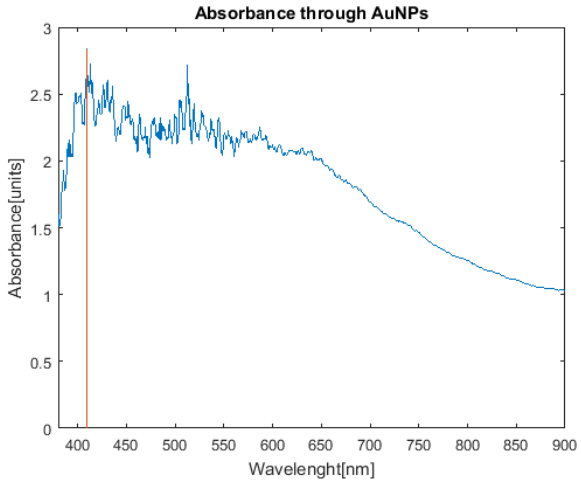

FIG. 5: UV–visible absorbance spectra for AuNPs. An extra synthesis done as synthesis 4 with 100 µL of $AgNO_3$ but addind enough NaOH to get a pH of 12.

In all cases, the colloid of the gold and silver nanoparticles had a purple-greenish and yellow coloration, respectively. The adding of NaOh made the Ag colloids get a darker yellow tone.

Apart from FIG 2, all the other graphs appear to be consistent with the theory. This will be talked upon in the next section.

IV. DISCUSSION OF RESULTS

For the AuNPs graphs (FIG 1-3) the expectation was to get a shift of the peak to higher wavelengths for increasing amount of $HAuCl_4$. In the AgNPs graphs (Fig 4-5) it was expected for the peak to stay at the same place but for it's height to increase, given that NaOH promotes an increasing reaction rate of AgNPs synthesis [3]. This is mostly followed. Valencia (2013) predicts that for AgNPs generated from starch 1% w/v, $AgNO_3$ and NaOH (same substances as ours, albeit different concentrations) and a cooking time of 12 hours the peak of maximum absorbance was in between 411-414 nm. Pretty similar to our result of 409 nm (FIG 5). The average size of these NPs was 10-30 nm in diameter, which may be an educated guess for our own. Raveendran (2003) got Ag nanoparticles with a max wavelength of 419 nm for 100 micro. A mean partice diameter of 5.3 nm [6]

The influence of reaction temperature during nanoparticle synthesis is briefly treated in Dankesreiter (2011) and should be taken into consideration [9].

The biggest offender of the obtained results is without doubt seen in FIG 2. The team has not been able to generate an explanation for the unexpected result. A simple guess would be sample contamination.

Regarding AuNPs, Philip (2010) used a 5 mL hibiscus extract with 30 mL aqueous solution of HAuCl4, getting a colloid of violet color (g1). For colloids g2, g3 and g4, the addition of the extract is varied as 10, 20 and 30 mL, respectively [8]. His results can be seen in FIG 6. Here the absorption peaks range between 548 and 573 nm. Our peaks range in between 542 and 552 nm, showing at least some similarities; but given that the process was diverse the comparision may no be valid.

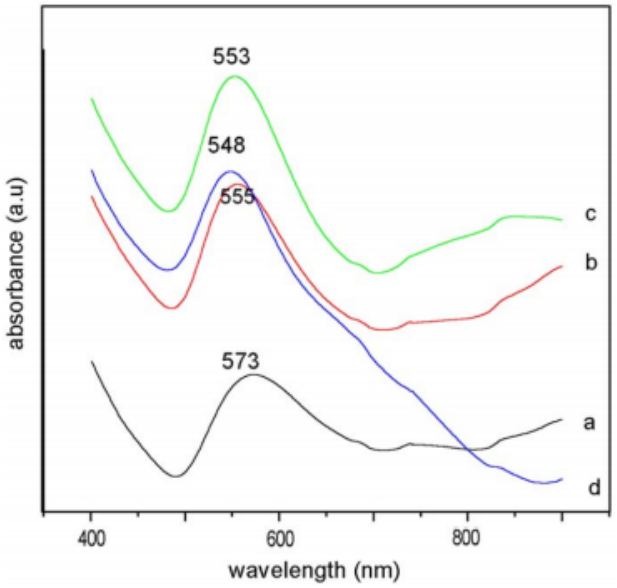

FIG. 6: UV–visible spectra of gold colloids: (a) g1, (b) g2, (c) g3 and (d) g4. Taken from reference 8.

Lastly, It should be expected to get different results than those given in the literature given the presence of a different supporting substrate and solvent layer on top of the nanoparticles. To solve this, different spectroscopy techniques should be used [5]

V. CONCLUSION

By the means of UV-vis spectroscopy it was possible to determine the length and size of gold and silver nanoparticles. These were apparentely about 30nm in length according to the literature.

Optical spectroscopy (which includes UV-vis) is the simplest method to test the optical properties of metal nanoparticles caused by LSPR phenomena [4]. However, when measuring absorbance at different pHs, it was proven that the solvent and substrate into which the particles are suspended has a great deal of effect in disturbing the measurements. This could be solved using different spectroscopy techniques like SERS or SHG in the future [5].

Raveendran (2003) mentions that the quality of the silver nanoparticles produced via the "green" process are comparable to those prepared using typical methods. Their non-toxicity makes them ready to use in biological systems.

Today, the use of noble metal nanoparticles solves real-world problems. Color-change urine dipstick tests wouldn't be possible without them.

VI. REFERENCES

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