Assessment of Silver Nanorod Synthesis

Priyanka Dilip
priyankadilip7@gmail.com

Jessica Kuleshov
jkuleshov2@gmail.com

Kian Vilhauer
vilhauer.kian@gmail.com

Christopher Yoo
jiyun1120@yahoo.com

Dr. Deirdre O'Carroll*
ocarroll@rutgers.edu

New Jersey Governor's School of Engineering and Technology

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*Corresponding Author

***Abstract*— Crucial for optical, thermal, and electrical applications, silver nanoparticles can be synthesized through various methods, most notably the strong-reducing agent (sodium borohydride-toluene) method and the polyol (ethylene glycol-tannic acid) method. The strong-reducing agent method is advantageous because of its claimed ease of reproducibility; however, the polyol method is investigated here due to its low environmental impact. A study of the reproducibility of the polyol process is presented, assessing both the exact synthesis method described in a paper reported by Javier Patarroyo and collaborators, as well as modified temperature-dependent syntheses. Additionally, a Life Cycle Assessment (LCA) of the monetary cost, energy efficiency, human health impact, and environmental impact of polyol synthesis is presented with comparisons to previous strong-reducing agent syntheses. The LCA demonstrates that the new polyol method presented here is slightly less efficient in cost-per-yield than the strong reducing agent method. Thus, Patarroyo's procedure was successfully modified to obtain reproducible, efficient, and environmentally friendly methods of silver nanorod synthesis. These silver nanorods are now being applied to phosphorescent blue organic-LEDs as well as SPASERs (nanoscale lasers) due to their excellent optical properties in the blue wavelengths.**

Introduction

As technological advances are becoming increasingly focused on producing greater output, it is imperative to increase the efficiency and enhance previously unusable sources of energy for different applications as well. A promising element that has been previously used for enhancing various devices is silver (Ag), which has the highest electrical and thermal conductivity among all metals, and whose one-dimensional structure allows extensive use on the nanoscale. So far, the nanowire form has been already used in catalysis, surface-enhanced Raman scattering (SERS), photonic crystals, microelectronics, and biological nanosensors [1]-[4].

The nanorod (AgNR) has been utilized in various fields, including photocathode, plasmonic, electronic, and antimicrobial applications. However, AgNR synthesis contains multiple chemicals that are harmful to the environment, typically using sodium borohydride in seed-mediated synthesis methods [5]. A polyol method has also been reported and is considered more environmentally friendly than conventional methods [6]. However, commercial production using polyol methods is challenging due to low yield of AgNRs. In a recent paper by Patarroyo et al., a one-pot polyol method with 80% AgNR yield is described [7]. If the polyol synthesis method is reproducible, commercial production of AgNRs using this more environmentally benign method may be possible.

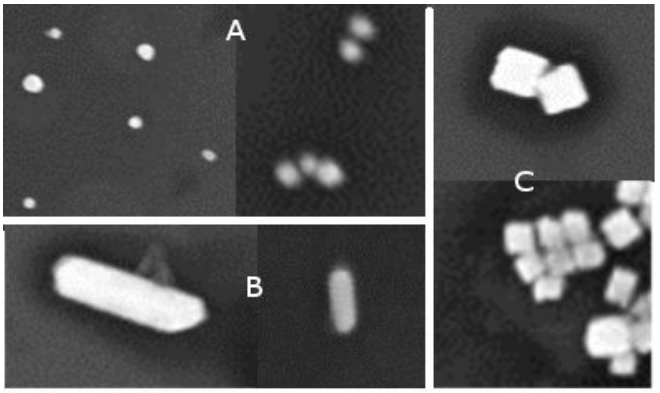

Fig. 1. SEM images of A) Silver Nanospheres, B) Silver Nanorods, C) Silver Nanocubes

The specific purpose of this research is to evaluate the reproducibility of the previously reported polyol method by Patarroyo et al. A preliminary investigation of the reproducibility was carried out by the O'Carroll research group, and only a small fraction (20%) of the product was found to be AgNRs. In this work, various synthesis parameters were identified for further investigation, such as temperature, polyvinylpyrrolidone (PVP) concentration, source of silver, and tannic acid (TA) concentration [7]. Temperature was the main focus, and was adjusted in separate experiments as a variable to observe how it affected the yield.

For further analysis of the production method, a life cycle assessment (LCA) for the synthesis of AgNRs was conducted with focus on the following points: process energy (energy required in all steps of the synthesis), carbon emissions, cost of production and disposal processes, environmental impact of utilized chemicals, and health hazards in handling synthesis components. These criteria are applied to the polyol process, and analytical results are compared to those of a seed-mediated method using sodium borohydride, which has historically produced a higher morphological yield (% nanoparticles of a particular shape) of AgNRs [6]. However, the strong reducing agent (sodium borohydride, or seed-mediated) synthesis utilizes hazardous substances, such as chloroform, phenylacetylene, and tetraoctylammonium bromide (TOAB) [7]. These chemicals may harm people interacting with them or damage the environment during production and disposal processes. Furthermore, strong reducing agent synthesis is more costly and resource-intensive than the polyol method. Thus, a comparison of the two processes is imperative to understand the necessity of optimizing the polyol process for commercial applications.

Background

AgNRs have very distinct optical properties that make them ideal for optical, electronic, and medical applications. Their anisotropic nature and adjustability of the aspect ratio during production make the AgNRs especially useful in enhancing the emission of different wavelengths on the nanoscale to increase the efficiency of light-emitting materials [8]. Specifically, blue-light emission is especially unstable because the short wavelength creates a large band gap that causes the diode emitting it to become unstable and lose its ability to phosphoresce when a voltage is applied. Several semiconducting compounds from element groups II-VI, especially those based on ZnSe, have been proven to emit blue light more efficiently than elements of other groups. However, these compounds often have structural defects that significantly reduce their lifetime [9]. Silver nanowires and nanoparticles have already been used to enhance blue, green, and red light emission by 20-50% in phosphorous-LEDs (PLEDs) [10]. Despite this advantage, they are not utilized commercially due to the inability to be mass-produced, as AgNRs are rare and crowded out by other shapes such as spheres or cubes [9].

Several methods have been attempted to determine the highest-yielding method with the lowest associated risk to produce silver nanorods on a commercial scale. One of the processes is a fungus-mediated synthesis of silver nanoparticles that did not prove to be feasible for commercial applications [11]. Another procedure is based on the partial oxidation of glucose, and is also not feasible for commercial applications [12}. The most commonly used method is the seed-mediated synthesis, or strong solvent method, typically using sodium borohydride ($NaBH_4$) as a strong reducing agent and stabilizer and sodium dodecyl sulfate (SDS) as a stabilizer as well [13]. However, the latter method is environmentally unfriendly, and though it can produce a range of structures, the strong solvent method is neither cost-efficient nor energy-efficient.

The final procedure to be considered is the polyol method, which utilizes ethylene glycol as both a reducing agent and solvent of produced silver nanoparticles. This method, first proposed by Patarroyo et al., is simpler and environmentally benign than the sodium borohydride method. However, the polyol method requires refinement to be reproduced reliably at a similarly high morphological yield of nanorods as commercially viable synthesis methods [5].

The concentrations of the ingredients in the procedure of creating Ag nanoparticles (AgNPs) are crucial in determining the size, shape, and aspect ratio of the resulting products. N. Jana and collaborators state in their research on nanowires and rods that, depending on the reducing agent, the aspect ratios of AgNPs are controllable, especially when reducing from a silver salt [14]. S. Coskun et al. detail a more in depth analysis on the polyol method and note the effects of temperature changes, injection rate, and the PVP to $AgNO_3$ molar ratio on the yield of nanowires, another form of AgNPs with a higher aspect ratio. They report that only temperature above the critical point will produce any rods or wire-like structures. The increase in injection rate of $AgNO_3$ into solution produces lower aspect ratio nanowires from multi-twin particles, and as the ratio of PVP to $AgNO_3$ increases, the diameter of the AgNPs gradually decreases and the PVP coats the Ag^+ ions instead of reacting [15]. Another study also stressed the importance of tannic acid (TA) as a reducing agent in the process of AgNP synthesis, as it helps to cap off the ends of

the growing AgNP's anisotropic growth to help reach a desirable aspect ratio [16].

An especially important study whose results are much considered is that by Patarroyo et al., who performed a synthesis of silver nanorods that found that the morphological yield was 80% Ag NRs among all Ag NPs. The supplementary information includes the procedure, with several variables, such as stirring speed and drop speed, defined [5].

For the Life Cycle Assessment (LCA) portion of this paper, the main task is to devise a method to analyze the human health impact, the environmental impact, and the overall cost efficiency of different processes. Although a paper by Pourzahedi et al. broadly analyzed various silver nanoparticle synthesis methods, including those with ethylene glycol and those with sodium borohydride, the results were mixed and were too broadly scaled to produce definitive conclusions [17]. Using a similar format of process mapping as Martins et al. and based on criteria from Papadaki et al. and Pourzahedi et al., with a flowchart of the procedure to map the energy flow, a new point system was formulated to assess the relative harm caused by the ingredients of each recipe ([18], [19], [17]).

Synthesis Procedure

The synthesis of AgNRs through this polyol method involves the addition of ethylene glycol (EG), which functions as a solvent and reducing agent, tannic acid (TA), a co-reducing agent, PVP, which functions as a capping agent, and silver trifluoroacetate (CF_3COOAg), the source of reducible silver, to a flask. The flask is then heated in a silicone oil bath and the reaction product is diluted in ethanol and acetone. Afterwards, the mixture is centrifuged and washed twice with ethanol and acetone to purify it. This method was employed in several experimental trials, each of which used different conditions to determine the optimum parameters for the synthesis method.

The first trial followed the method reported by Patarroyo et al. as closely as possible, performing the synthesis four times in parallel. Four EG solutions of specific concentrations of TA, PVP, CF_3COOAg, and HCl were prepared then heated in separate silicone oil baths for the 20 minutes described by Patarroyo et al. Afterwards, the reaction was stopped by placing each solution in an ice bath. The solutions were diluted in ethanol and acetone and then centrifuged to remove excess EG.

This method was repeated to improve consistency of results. The silicone oil baths were magnetically stirred for the duration of the reaction to ensure the solutions were heated more evenly. Two of the four solutions were heated to a lower temperature (155 °C instead of 170 °C) to investigate the impact of reaction temperature on polyol synthesis. Temperature was measured for each solution. These changes slightly improved consistency, but results were still lacking in precision. A third trial was conducted by heating all four solutions in a single silicone oil bath at a significantly higher temperature (190°C) to investigate the effect of a higher reaction temperature.

Results

A. *Nanorod Synthesis*

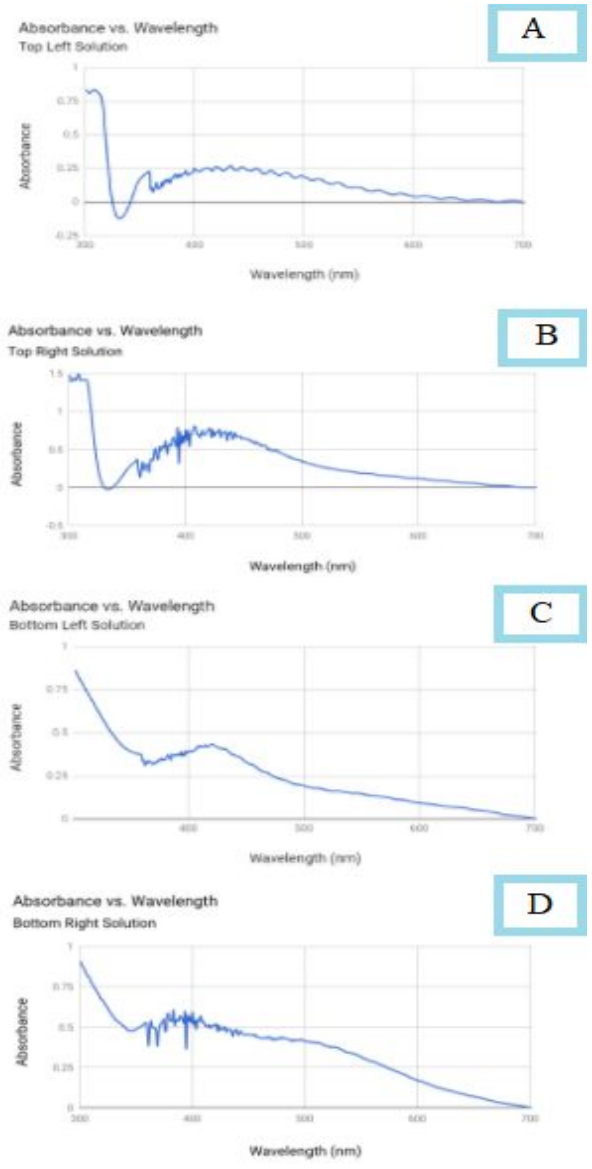

Fig 2. UV-Visible spectra of reaction products from the first trial. Each spectrum corresponds to the dark-field and SEM images from the first trial that are labeled with the same letter.

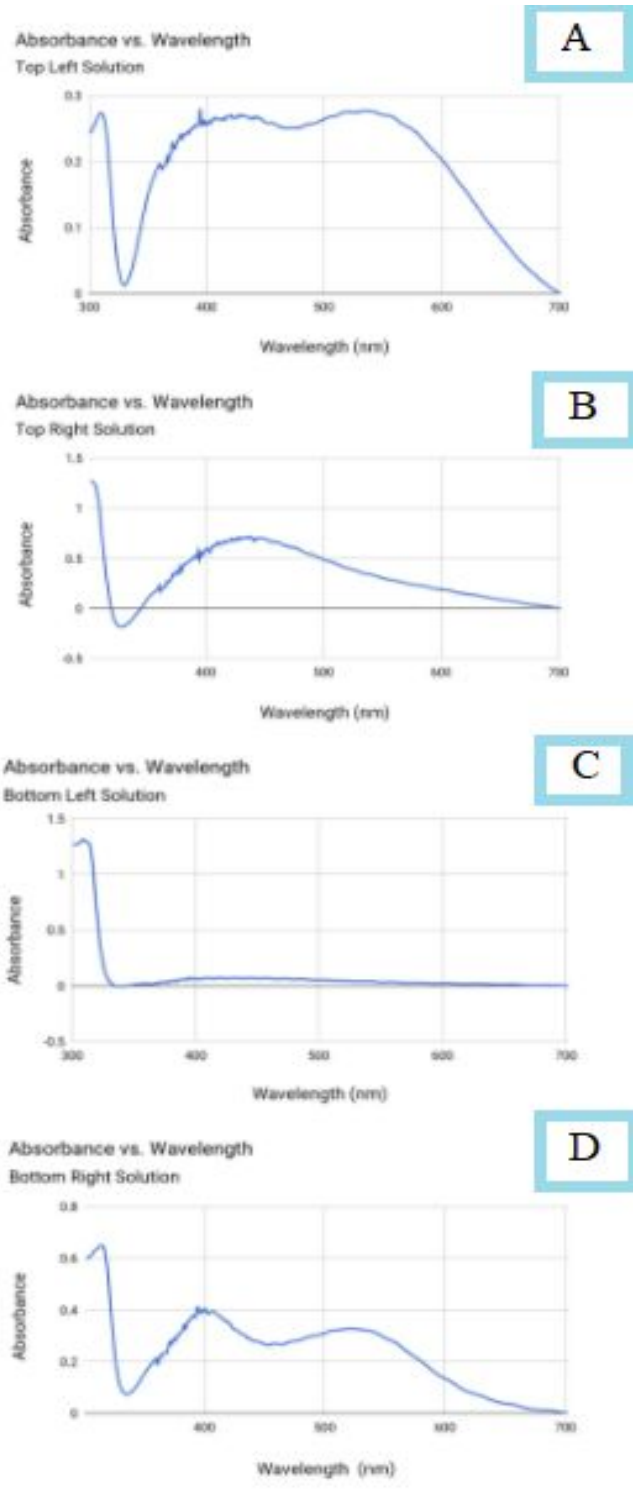

Fig. 3. UV-Vis spectra of reaction products from the second trial. Spectra correspond to SEM images from the second trial labeled with the same letter.

1) *UV-Visible Spectroscopy :*

After the reaction product was centrifuged and the excess EG was drawn off, it was redispersed in ethanol and analyzed using an Ocean Optics FHSA-TTL sample holder and SiPhotonics CCD-array UV-Visible spectrophotometer.

An absorbance spectrum from 300 to 700 nm was generated and baselined at 700 nm. Previous research has used these spectra to accurately evaluate the presence of nanorods, stating that a solution of nanorods will have two distinct spectral peaks, one around 400 nm, and another between 500 and 600 nm, and that a solution of nanospheres will only have a single spectral peak at around 400 nm [5]. The spectra of three of the four beakers of the first trial only showed one peak, indicating that the products were mostly nanospheres. One of the products showed a very slight bump around 500 nm, indicating a slight possibility of nanorods. Two of the four spectra generated from the products of the second trial, which were heated at 150°C, contained two distinct peaks in the 400 and 500 nm region. The other spectra had only one distinct peak around 400 nm. The spectra produced by the third trial also had one peak. This peak was consistently very low, indicating not only that the solutions contained exclusively spheres, but that they contained very low yields of nanoparticles.

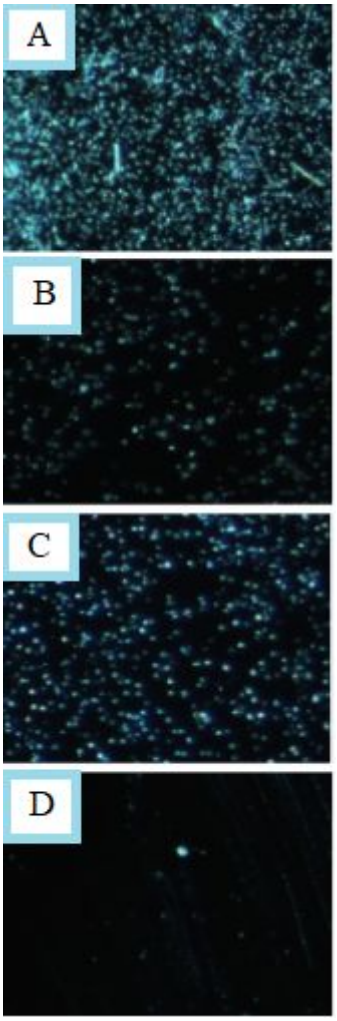

Fig. 4. Dark-field optical microscope images of reaction products from the first trial. Nanospheres appear blue-green and nanorods appear yellow or orange.

2) Dark-Field Imaging :

UV-Vis spectroscopy is not entirely accurate in its representation of shapes due to possible contamination, and does not show percentages of different shapes of nanoparticles. In order to have a more accurate visual representation of the nanoparticles and their dispersion and possible characterization, a Nikon optical microscope (Optiphot 66) with Carl Zeiss Inc. Xe lamp and Pixelink camera was utilized. The solutions were drop-cast onto a piece of silicon and imaged at different magnifications.

In images obtained from the dark-field microscope, AgNRs are supposed to scatter yellow light, as opposed to the blue/green light scattered by nanospheres and other AgNPs. The first trial was imaged zooming in at 20x, 40x, and 100x, and nanorods were only spotted on few of the samples. The second trial and third trial were not imaged with the dark-field microscope, due to relative difficulty of using the microscope and because of the inconclusive data that it provided.

3) SEM Imaging :

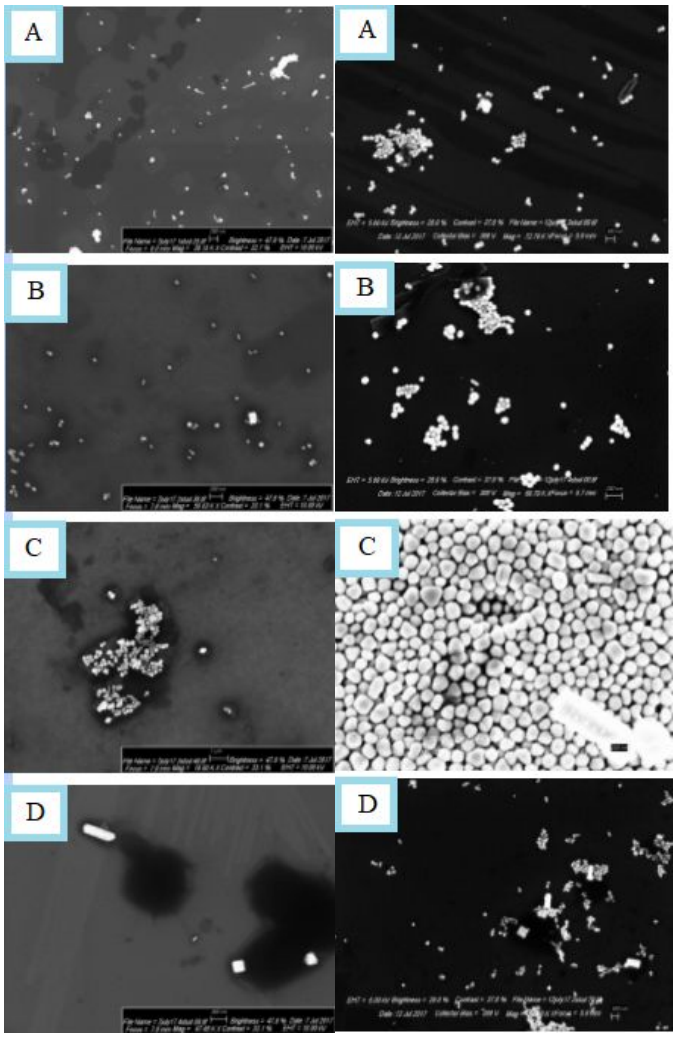

Fig. 5. SEM images from the first and second trials.

The method of imaging that produced the most accurate representation of AgNPs was the Zeiss Sigma Field Emission SEM. Samples were prepared by drop-casting solutions onto silicon wafers. These samples were imaged from 40,000-100,000x magnification, with 1000 ms exposure rate and 20 gain, and showed the distinct shapes of each nanoparticle. In the samples with the highest AgNR concentration, the morphological yield of AgNRs was determined to be about 21%. There were many variations across samples in terms of shape and dispersion, which is due to slight variations in several factors, especially temperature due to the uneven heating on the hot plate that was used. Some samples appeared more clumped and were composed entirely of nanospheres, and one of the samples was entirely nanocubes, a result that had not been previously seen by Dr. O'Carroll's research group. Images of solutions from the second trial that had reacted at lower temperatures showed very low yields of AgNRs, despite the fact that their UV-visible spectra contained the two distinct peaks that generally indicate the presence of AgNRs. The results suggest that UV-visible spectra are not as accurate of a metric as previous research claims.

4) Temperature Change :

Various experiments state that temperature stimulates the production of nanorods when increased [15]. This hypothesis was separately tested, and the results were not factored into the analyses discussed above. These solutions were heated to 190°-200°C, instead of 170°C. The solutions quickly turned a dark green and then grey. Almost no precipitate appeared to be in the samples after centrifugation, and when imaged with the UV-Vis, two of the samples did not have any peaks, and the other two samples had one peak, indicating only nanospheres. In future trials, the temperature will be lowered below 170°C to determine its effect on nanorod production as well.

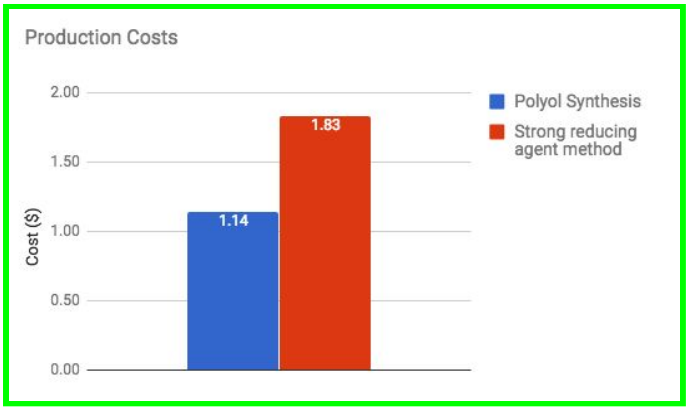

Fig. 6. Comparison of the cost per gram of silver processed in each synthesis method.

B. Life Cycle Assessment

Monetary costs of the strong reducing agent method are 1.6 times higher (thus nearly twice as much) than those of the modified polyol method described in this paper. Additionally, process energy requirements of the former are also greater by

an approximate factor of 3. When considering commercial applications, this disparity in production cost and energy usage is of considerable importance because organic LEDs are manufactured in substantial quantities.

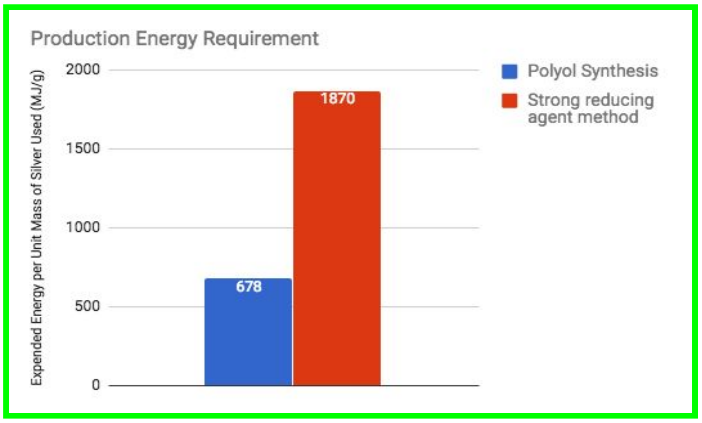

Fig. 7. Comparison of the energy required to process one gram of silver in each synthesis method.

In terms of human impact, the total of the NFPA values for the strong reducing agent method is over 6 times the total for the polyol synthesis, while the average (accounting for number of chemicals used) suggests the first method is approximately 3 times more harmful. This evaluation was made with respect to all 4 factors - flammability, reactivity, health impacts, and special warnings (carcinogenicity etc.) - and one can conclude that the procedure utilizing sodium borohydride is far more dangerous to humans than the polyol method. Since the AgNRs will be produced in the lab for nanoscale and OLED research using methods that require long periods of exposure, the human impact reduction by the altered polyol method is an excellent advance, even when considering relative yields.

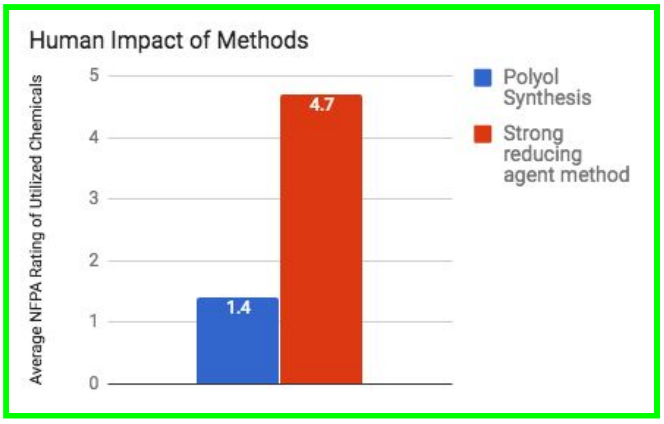

Fig. 8. Comparison of human impact of each synthesis method, compared based on the NFPA ratings of the chemicals used in each process.

In terms of environmental impact, the strong reducing agent methods contain substances that are significantly less soluble than chemical components of the polyol method. To process a similar amount of silver, approximately 11 times more water would be required to dissolve the components of the strong reducing agent method as compared to dissolving those of the polyol method. This result has both disadvantages and benefits. If a company has an effective filtration process strategy prior to waste release, then the sodium borohydride method may be more convenient in terms of disposal. On the other hand, more precipitate would collect in the ground or water body where the waste is released, which would be more problematic than the dissolved chemicals (which would get neutralized by natural marine processes) for microorganisms in the soil or marine life than the dissolved chemicals. Thus, industries must determine which production method is better suited for their disposal program and environment, or whether other factors presented in this paper, such as aforementioned monetary costs, are more essential in comparing the two methods. However, to aid in this selection, an analysis of carbon emission values, derived from production energy requirement, leads to the evaluation that the strong reducing agent method produces 27 times more carbon than the polyol method. These results strongly suggest polyol synthesis is more environmentally benign than its alternative.

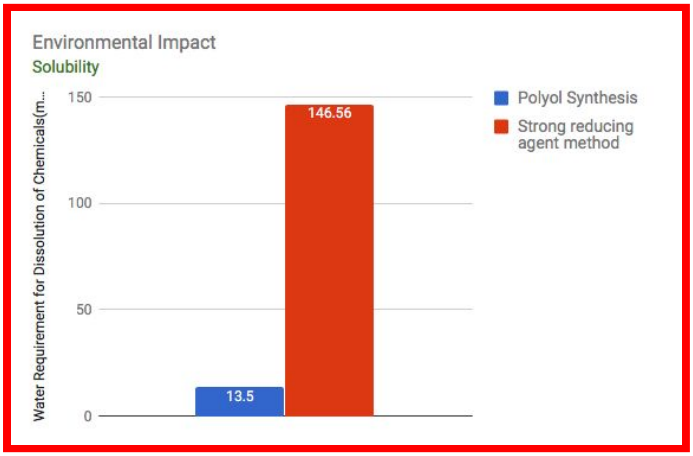

Fig. 9. Amount of water required to dissolve all the chemicals used in one trial of each synthesis method.

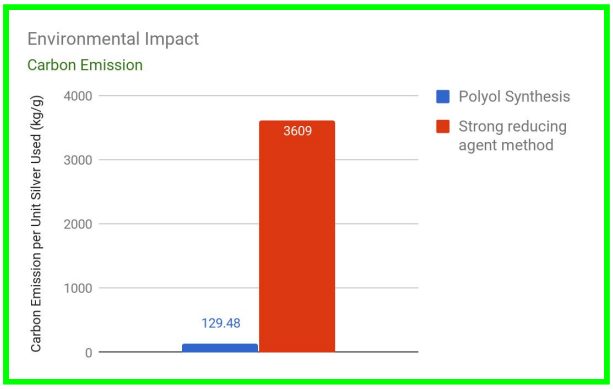

Fig. 10. CO_2 emissions per gram of Ag processed in each synthesis method.

Conclusions

Overall, it has been concluded that the polyol method reported in a previous paper does not produce the reported yield of silver nanorods, after extensive testing. As opposed to the estimated 80% morphological yield of AgNRs, the final count only turned out to be 21%. Although there are many broader applications, such as nanoscale lasers and other plasmonic devices, that these structures can be used for, it is imperative to further improve on this process because of its promise as a greener method and its promise in future innovations. For future studies, more variables, such as stirring rate, dropping rate, PVP concentration, and silver concentration, should be tested in order to see their effect on the overall yield of silver nanorods.

The LCA strongly suggests that the modified polyol method is more effective than the strong reducing agent method in terms of the human impact, environmental hazards, monetary costs, as well as energy efficiency, even when scaled according to relative yields. From an industry perspective, the ramifications are enormous due to the excellent potential of silver nanorods to act as blue-light emitting phosphorescent material stabilizers, such as in SPASERs, or surface plasmon lasers, and in organic LEDs.

Acknowledgements

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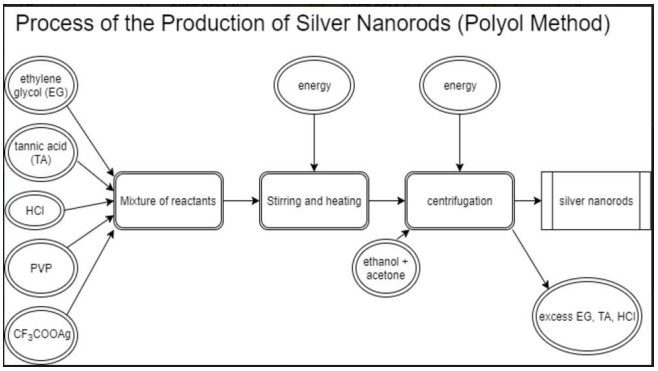
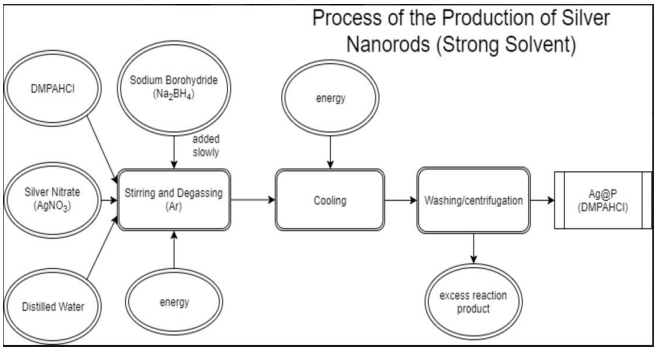
Appendix I

1. **Ag**: silver
2. **AgNPs**: silver nanoparticles
3. **AgNR**: silver nanorods
4. **CF_3COOAg**: silver trifluoroacetate
5. **EG**: ethylene glycol
6. **LCA**: Life Cycle Assessment
7. **$NaBH_4$**: sodium borohydride
8. **OLED**: organic light emitting diode
9. **PVP**: polyvinylpyrrolidone
10. **SDS**: sodium dodecyl sulfate
11. **SERS**: Surface-Enhanced Raman Spectroscopy
12. **TA**: tannic acid
13. **TOAB**: tetraoctylammonium bromide

Appendix II

Additional Raw Data from Life Cycle Assessment





	Polyol (Ethylene Glycol / Tannic Acid)						Strong Solvent (Sodium Borohydride / Toluene)				
	Solubility (g/100mL) in 25 degC Water	Solubility on Logarithmic Scale of 5	Unit (direct reciprocal)	Quantity per synthesis	Minimum Water Required to Dissolve (mL)		Solubility (g/100mL) in 25 degC Water	Solubility on Logarithmic Scale of 5	Unit (direct reciprocal)	Quantity per synthesis	Minimum Water Required to Dissolve (mL)
Ethylene Glycol		5.0		0.00671 L	6.71	Sodium borohydride (powder, ≥98%)	38	2.6	2.63 ml/g	0.02 g	0.0526
Silver Trifluoroacetate	170	4.2	0.59 ml/g	0.025 g	0.01475	TOAB	60	3.8	1.67 ml/g	0.000035 g	5.85E-05
HCl (ACS reagent, 37%)	67.3	3.8	1.49 ml/g	1000 scaled to 1	0.000125	DMPA (97%)	12.7	3.1	7.87 ml/g	2g	15.74
PVP (avg mol weight 40,000)	100	4.0	1 ml / g	0.025 g	0.025	Phenylacetylene (98%)	0.0456	0.7	2192.98 ml/g	0.93 g	100
Tannic Acid (ACS reagent)	280	4.5	0.36 ml/g	0.00306 g	0.0011016	Toluene (anhydrous, 99.8%)	52	3.7	1.92 ml/g	0.014 L	26.88
						Allyl mercaptan (90%)*	6.7	2.8	14.93 ml/g	0.185 g	2.76205
						Potassium Persulfate	4.49	3.7	22.27 ml/g	0.05 g	1.1135
						[Rh(cod)Cl]2				0.823 g	
						buthanol				0.02 L	
						Silver Nitrate (ACS reagent, >99.9)	257	4.4	0.389105 ml/g	0.02 g	0.007782
TOTAL	617.3	21.5			13.50196320		173.9356	24.7			146.5559988
											factor of 10.85442886

DISPOSAL

PRODUCTION			
MSDS Lab Safety Ratings (Add all 4 quadrants from NFPA diamond)			
Polyol (Ethylene Glycol / Tannic Acid)		Strong Solvent (Sodium Borohydride / Toluene)	
Ethylene Glycol	2	Sodium borohydride (powder, ≥98%)	7
Silver Trifluoroacetate	1	TOAB (98%)	4
HCl (ACS reagent, 37%)	3	DMPA (97%)	6
PVP (avg mol weight 40,000)	0	Phenylacetylene (98%)	5
Tannic Acid (ACS reagent)	1	Toluene (anhydrous, 99.8%)	5
		Allyl mercaptan (90%)*	3
		Potassium persulphate (99%)	4
		Silver Nitrate (ACS reagent, >99.9)	6
		[Rh(cod)Cl]2	2
		Buthanol	5
TOTAL	7		47
AVERAGE	1.4		4.7
			factor of 3.36

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