



Analysis of a technique for synthesis of size-controlled colloidal bismuth nanoparticles

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Abstract

Research was performed to analyze and attempt to modify a pre-existing bismuth nanoparticle formulation. This method involved a metal salt precursor, a carbonyl-containing polymer for size control, a solvent suitable to all solutes, and a reducing agent. Initially, the research sought to modify the polymer used previously in the literature, though solubility issues prevented this exploration. Thus, analysis of the efficacy of the previously investigated technique in yielding a nanoparticle product and analysis of the size-control relationship between polymer and metal salt ions in solution was performed. IR Spectra confirmed the interaction between the carbonyls of the polyvinylpyrrolidone and Bi^{3+} ions. UV-Visible spectra were used to confirm that light-scattering characteristics of the product were consistent with that of a nanoparticle product. A size-controlled nanoparticle product was confirmed to have been synthesized.

Introduction

The importance of metal nanoparticle (NP) research to various areas of chemistry makes continued efforts to find and optimize methods for their synthesis a worthwhile pursuit. With an understanding of the different aspects of their synthesis, exploring alternatives for one aspect is an effective way to improve upon a pre-existing formulation. I sought to explore the effect of altering a pre-existing, analyzed procedure to use a different polymer matrix, and to test the efficacy of this new formulation in improving antibiotic efficacy³, as it has a distinct effect on size control of NPs during synthesis. A polymer matrix is one aspect of the synthesis, and a particularly important one at that. While changing which polymer was used was not successful, the results gathered instead replicated spectroscopy results of an article by Wang, et. al. and corroborated the results¹.

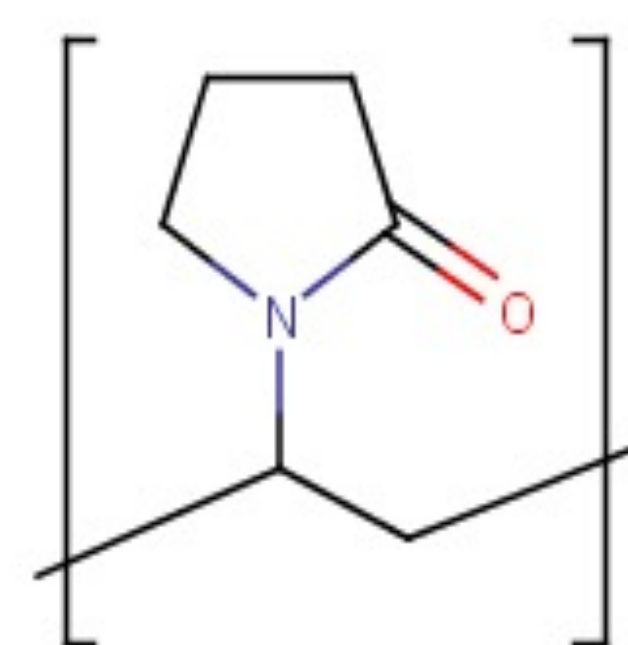


Figure 4. Vinyl pyrrolidone monomer, a carbonyl-containing monomer.

The article by Wang, et al. proposes that polar interactions between the carbonyl oxygen of PVP and the bismuth(III) ions stabilize the structure during NP formation and prevent or restrict aggregation¹. This mechanism is explored in the research I performed, and an attempt to replicate the results of the researchers is made. Having discussed the importance of the matrix component of nanoparticle formulation, the other components must be discussed. Bismuth (III) chloride salt was the supplier of bismuth, and the Bi^{3+} cations were attracted to the electronegative carbonyl groups in the matrix. Sodium borohydride was used as the reducing agent because it is particularly strong and effective. The solvent used is particularly important, as the matrix, reducing agent, and salt must all be able to dissolve into solution for the reaction to occur. Dimethyl formamide proved an effective solvent for this combination of solutes. Once the reducing agent is added, and time is taken for the reaction to occur, then the nanoparticle product must be eluted from solution. One method for this is mechanical, with a tabletop centrifuge. The other uses a competing solvent to disrupt solubility, in this case, acetone.

Method

Nanoparticle synthesis used a 5 PVP to BiCl_3 ratio¹, as done by Wang et. al. NP synthesis and solution prep began when 0.2779 g of PVP polymer was added to 50 mL of distilled dimethyl formamide (DMF) solvent. Then, 0.1577g of bismuth chloride salt (Bi(III)Cl) was measured in a non-oxygenated atmosphere. The polymer matrix solution was degassed using nitrogen for five minutes before salt was added, and a small aliquot was taken for analysis before 50 mL of 3 M sodium borohydride solution was added to reduce the salt. The solution was separated into 25 mL test tubes, acetone was added, and the tubes were sealed to prevent exposure to oxygen. The tubes were placed in a tabletop centrifuge and spun to cause elution of the nanoparticle product. The solvent was extracted from the eluted particles, which were resuspended in DMF and diluted with water to create a 30 parts water to 1 part NP solution ratio.

UV-Vis

Spectroscopy measurements were taken using a Vernier spectrophotometer and a quartz cuvette. All measurements were taken using an air blank. Measurements were taken of the polymer matrix solution, the polymer and salt solution, and the final nanoparticle solution. After Analysis of the UV-Vis results, further measurements of the polymer and salt solution were taken using cuvettes of lesser path lengths, so that the spectra could be better compared to the spectra from the synthesis steps. The cuvette path lengths used were 5 mm and 0.5 mm.

IR

Spectroscopy measurements were taken using JASCO with a sodium chloride lens. An air blank was used.

Results

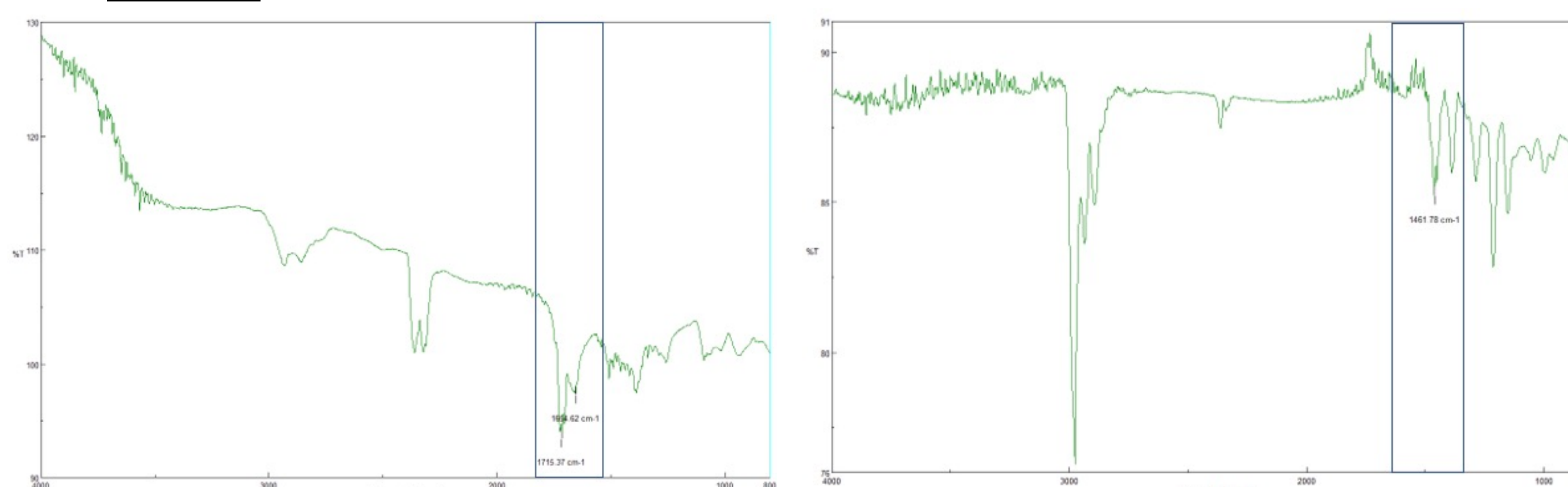


Figure 1. This figure depicts the IR spectrum of PVP polymer in DMF solvent. The boxed region is the area of interest in the spectrum, in the fingerprint region, from 1500 to about 1800 cm^{-1} . There is a singular, clear peak in this region, representing the carbonyl in the repeating unit of PVP.

Figure 2. This figure depicts the IR spectrum of PVP polymer in DMF solvent after the BiCl_3 salt is added. The boxed region is the area of interest in the spectrum, in the fingerprint region.

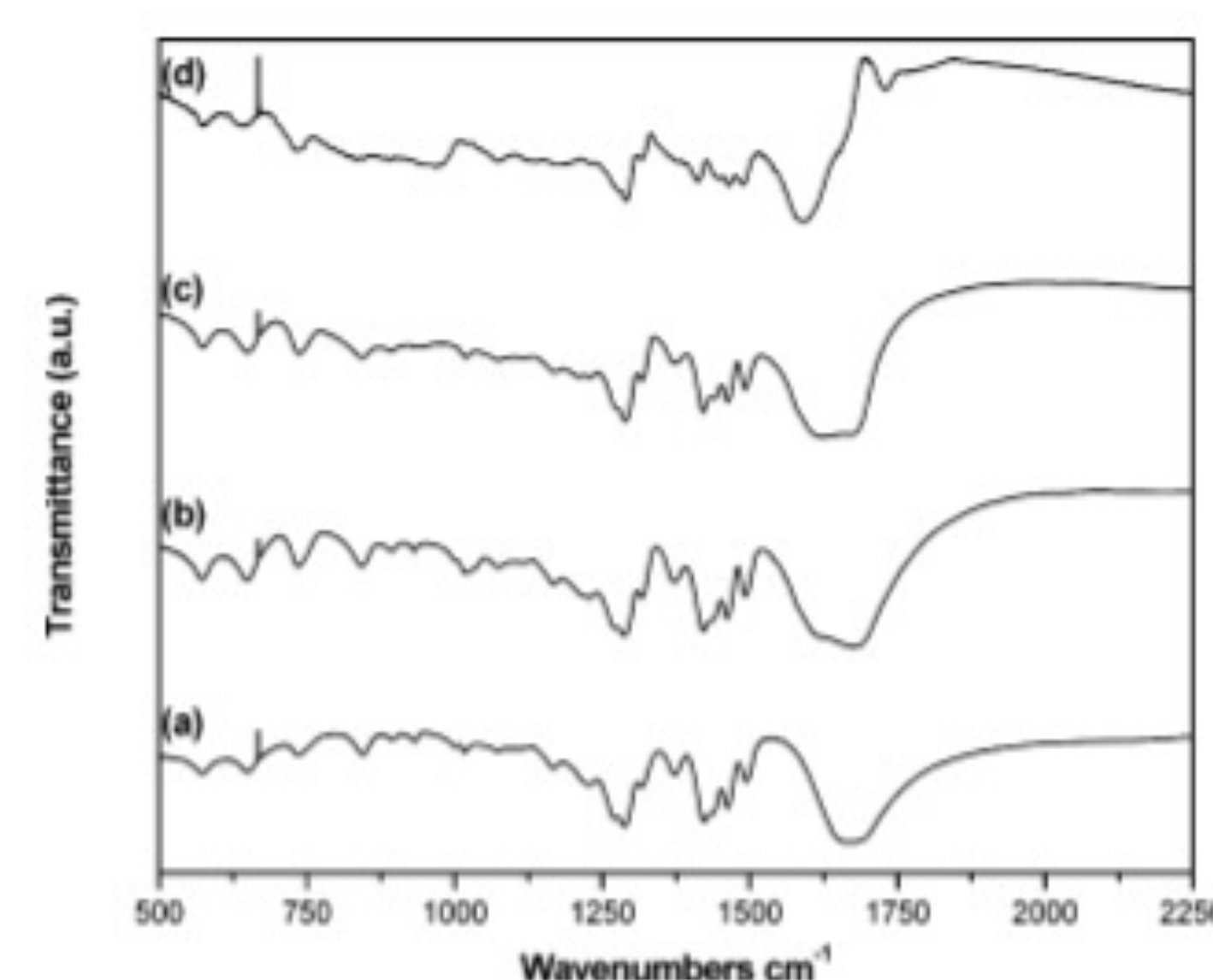


Figure 3. From the results of Wang et. al.¹, "IR spectra of (a) pure PVP; the complexes with different molar ratios of PVP to BiCl : (b) 10, (c) 5, and (d) 1. In all cases, the concentration of BiCl is 10 mM." Appearance of peak around 1750cm^{-1} and decrease of peak around 1550cm^{-1} indicates a shift caused by the interaction between the polymer and the Bi^{3+} ions in solution.

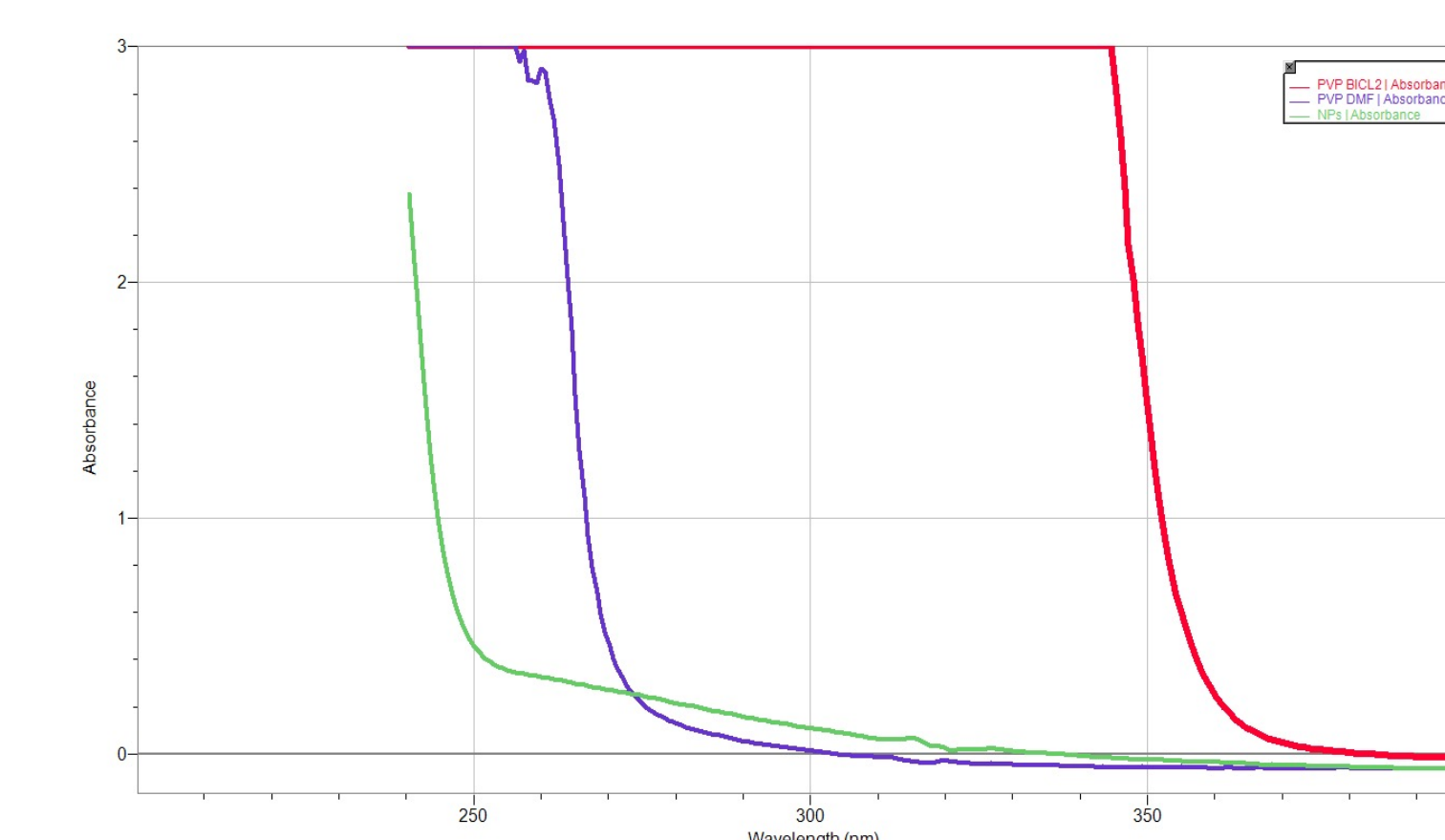


Figure 5: The graph above depicts the results of three samples run using UV-Vis spectroscopy, namely, a solution of PVP polymer in DMF solvent (blue), this solution to which salt has been added (red), and the final nanoparticle solution (blue), diluted 30-fold with water as described in the Wang et. al. paper.

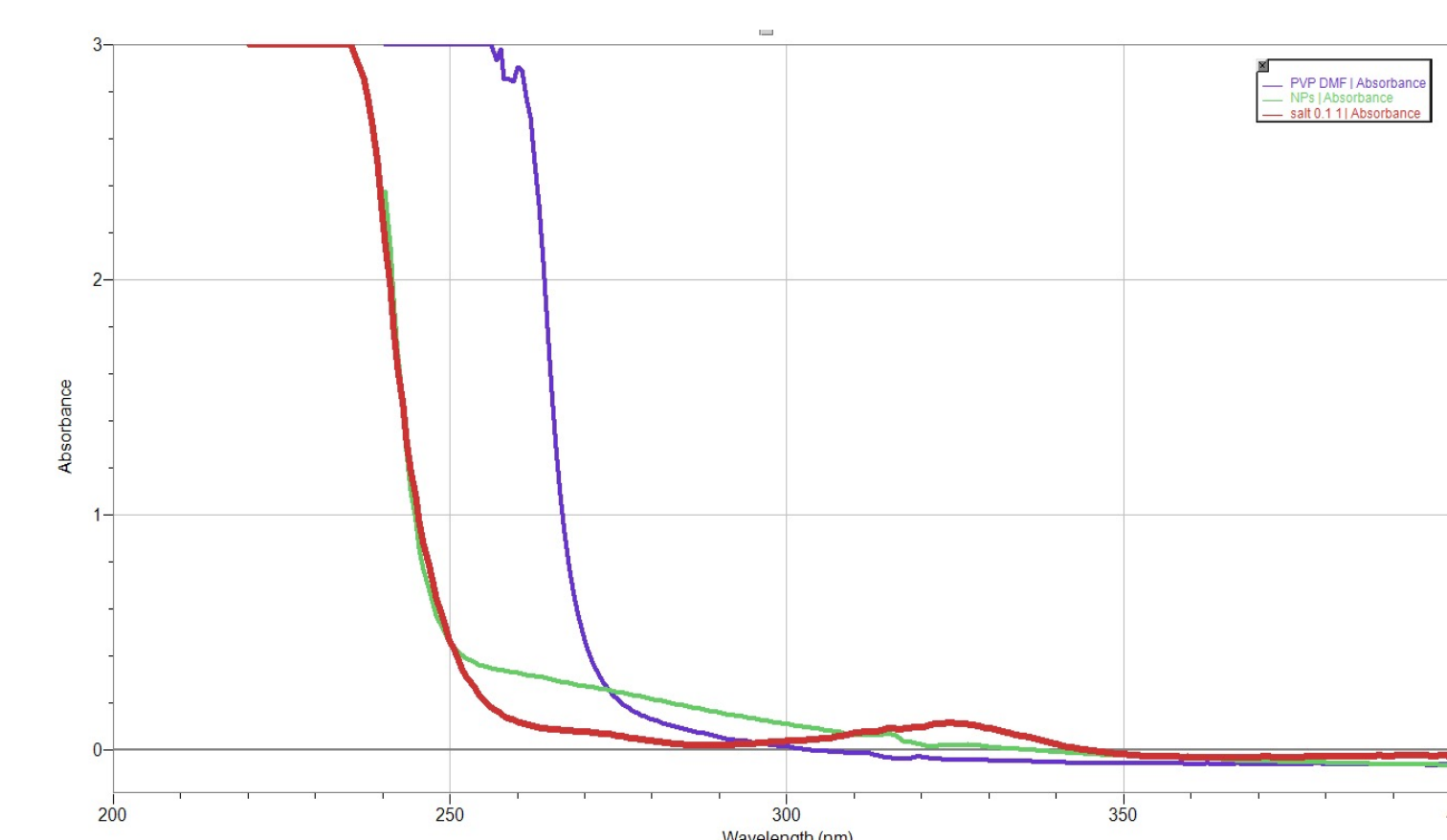


Figure 6: The graph above depicts the results of three samples run using UV-Vis spectroscopy, namely, a solution of PVP polymer in DMF solvent (blue), this solution to which salt has been added (red), and the final nanoparticle solution (blue), diluted 30-fold with water as described in the Wang et. al. paper.

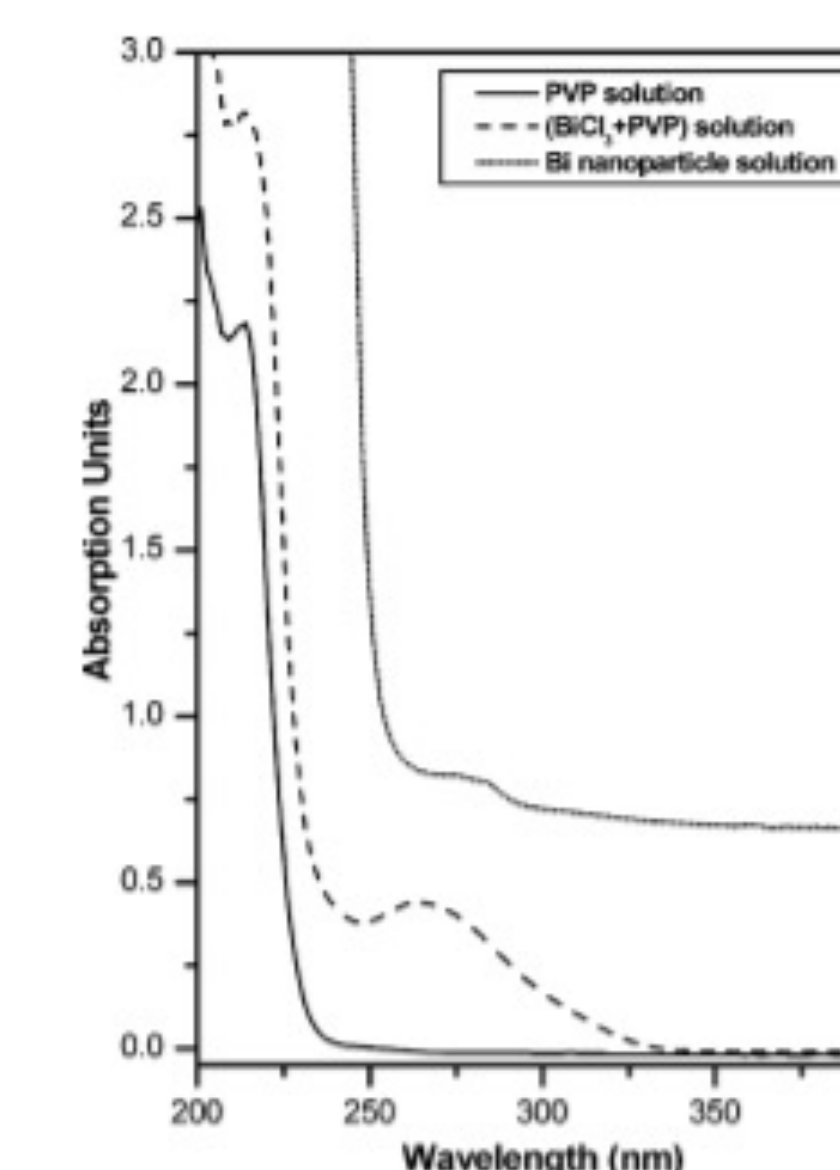


Figure 7. The UV-vis results from Wang et. al.¹: "UV-visible spectra of BiCl_3 aqueous solution, PVP + BiCl_3 aqueous solution and PVP-Bi nanoparticle DMF solution formed with $\eta_{\text{PVP}}/\eta_{\text{BiCl}_3} = 0.075$ and 10 mM BiCl_3 ." The spectra show an increase in the peaks through the synthesis steps from matrix to addition of salt to reduction.

Discussion

The results regarding successful synthesis of colloidal BiNPs as reported above attest to the efficacy of the method designated by Wang et. al.¹, and to the replicability of the reported results:

- IR spectra show the shift of the Carbonyl peak from 1715 to 1461 cm^{-1} . This shift is indicative of effectiveness of the PVP at facilitating the even dissolution of bismuth ions throughout the solution, which directly controls the size of the particles formed, as discussed by Oberdisse². This was similarly true of the results presented in the article by Wang et al.
- Qualitative analysis of the UV-Vis absorption spectra collected reveals evidence that the NPs were formed, as the slope of the NP spectra has specific characteristics indicative of light scattering, a unique characteristic of NPs.
- The change from figure 6 to figure 7 shows that the use of a smaller cuvette size was an effective technique to shift the absorbance downward and allow qualitative analysis in this range.

The results confirm the efficacy of the method presented by Wang et. al., with PVP as a polymer useful in promoting size control of synthesized BiNPs. The efficacy of this polymer stems from its electronegative carbonyl. Future research into the optimization of the size control function of the polymer matrix in BiNP synthesis should involve additional polymers that contain electronegative functional groups. The effectiveness of such polymers at size control can be examined as a function of the ratio of polymer to salt, as in Wang et. al. Further investigations into the effect of size consistency and average size on improving antibiotic efficacy against β -lactam resistant bacteria would also be beneficial³.

Citations

- Wang, Y. W.; Hong, B.H.; and Kim, K.S. "Size Control of Semimetal Bismuth Nanoparticles and the UV-Visible and IR Absorption Spectra", *J. Phys. Chem. B.* **2005**, *109*, pp 7067-7072.
- Oberdisse, J. "Aggregation of colloidal nanoparticles in polymer matrices", *Soft Matter* **2006**, *2*, pp 29-36.
- Li, H.; Wang, R.; and Sun, H. "Systems Approaches for Unveiling the Mechanism of Action of Bismuth Drugs: New Medicinal Applications beyond Helicobacter Pylori Infection", *Acc. Chem. Res.* **2019**, *52*, pp 216-227.