

CPE610 / FEEG6024 Mini Project Report

An investigation into using silver nanoprisms and nanospheres for enhanced solar thermal capture

Harriet Kimpton

Abstract

A batch synthesis method was used to produce four different dilute nanofluids (silver concentration 1 ppm by volume), utilising water as the base fluid. These were silver nanospheres (SNS) with and without citrate to stabilise the nanofluid and silver nanoprisms (SNP) with and without citrate. The temperature rise of these nanofluids on exposure to simulated sunlight was measured and their performance compared to water. The change in the UV-visible spectra of the samples with time was also investigated. Results showed that three of the nanofluids exhibited a significantly greater temperature rise than the water control on exposure and hence show promise for use in direct absorption solar collectors. All of the nanofluids showed changes in their UV-visible spectra with exposure time and further work would be required to understand the relationship between the solar temperature rise and the UV-visible spectra. In addition improvements in the temperature measurement technique are required.

1 Introduction and Literature

A microfluidics manufacturing technique can be used to produce silver nanoprisms with tailored absorption in the near infrared (750-800 nm) [1, 2]. By coating the silver nanoprisms with a thin shell of SiO₂ and then imbedding the resultant particles in a poly-methyl methacrylate (PMMA) polymer matrix they can be used for energy saving glazing [3]. For this application the resultant films need to be transparent to light. For other applications production of transparent films would not be important. Another application area which shows promise is the use of nanoparticles or nanofluids in direct absorption solar collectors (DASCs) and concentrated volumetric solar systems [4-9], which have been said to have better efficiencies than selective surface plate collectors [10]. The advantages of DASCs include no hot surface and simplified construction [11]. In addition using nanofluids improves the absorption of solar energy and the transfer of thermal energy by improving the convection and thermal conductivity of the fluid [8].

A number of different reviews of nanofluid uses and applications have been carried out [12-23]. Of these some focus on heat transfer properties [19, 20, 23], whereas other are more focused on solar applications [12, 14, 15, 17, 18, 21]. One review article concentrates on the preparation and stability of nanofluids as well as giving an overview of applications [16]. Two of the articles are more general [13, 22] with [22] providing a comprehensive review article containing more than 300 references. Several of the review articles refer to the work conducted by Otonicar et al on silver, graphite and carbon nanotubes [11]. Other investigators have also looked at carbon nanotubes [24-26] and nano-horns [27, 28]. It is claimed that carbon nanotubes are one of the best nanoparticles for DASC applications due to their similarity to a black body [25], however, other researchers have found that the performance of silver nanoparticles was better [11]. Efficiency improvements reported for nanofluids compared to the base fluid alone range from 5% [11] to 29% [26]. Other nanofluids that have been investigated include CuO [29], Al₂O₃ [30], and TiO₂ [31, 32]. A good summary of the thermal properties of various nanofluids is given in [33].

Some studies have investigated silver nanofluids [11, 34-38]. Two of these studies [11, 34] utilised DASCs and showed improvements in the efficiency by using 20 nm silver nanoparticles even when compared to water on a black rather than reflective surface [11]. The concentration of nanoparticles employed was different being 0.25% in the first of these studies [11] and from 0.00016% (1.6 ppm) to 0.065% in the other with an optimum of 0.00065% or 6.5 ppm being reported [34]. A third study recommends a volume fraction of 0.03% of 10nm silver nanoparticles and states that engineering of the absorption spectrum could be carried out to further improve the performance by matching the spectrum to that of the solar spectrum [38]. It is unlikely that any of these studies has used the actual number of nanoparticles to calculate the volume percentage inclusion and have probably used the formula given

in [39]. The other three studies that have looked at silver nanofluids [35-37] used either flat plate or concentrated solar collectors so were not utilising the enhanced spectra absorbance of the nanofluids but only the improvement in thermal conductivity. These studies still showed an improvement in performance.

No evidence of commercial DASCs containing nanofluids could be found, with the largest R&D examples of collectors being by [26] at $60 \times 60 \times 1 \text{ cm}^3$, by [34] at $40 \times 40 \times 15 \text{ cm}^3$ and by [30] at $1.54 \times 0.9 \text{ m}^2$. The lack of commercial DASC is perhaps not surprising considering that nanofluids have really only been an active area of research for the last 10-15 years.

Some researchers have investigated the integration of thermal storage with a solar collector [40-42]. Of these only [42] has looked at integrating a thermal store with a DASC. This paper modelled a novel DASC and showed it to be 20% more efficient than a non-integrated system. However, the working fluid did not contain nanoparticles and the volume of working fluid in the system was high, making it probably impractical for a DASC containing a nanofluid due to the nanofluid cost.

2 Aims and Objectives

A short literature review on DASCs was firstly undertaken focusing on the use of nanofluids and nanoparticles (see Section 1). A solar simulator was then used to look at the effect of sunlight on dilute solutions of silver nanospheres and prisms. The nanofluids temperature was measured and compared to water during exposure to simulated sunlight. The UV- visible spectra of the nanofluids was measured before and after exposure to see if the nanofluids were stable to simulated sunlight.

3 Experimental Method

All reagents were from Sigma Aldrich. The silver nanoprisms (SNP) and nanospheres (SNS) were manufactured by batch synthesis using a dilute silver nitrate solution, trisodium citrate, hydrogen peroxide and sodium boron hydride according to the method in [43]. Four different samples were prepared, one of SNS without citrate, one of SNS with citrate and two SNP solutions. One of the SNP solutions was then centrifuged to remove the majority of citrate and re-diluted with water to approximately the same concentration. In this way 2 samples of each type of nanoparticle was produced, one with and one without citrate. This was to investigate the effect of citrate on the stability of the nanofluids with sunlight exposure as the citrate concentration has been found to influence the stability of SNS on exposure to sunlight [44]. It is unusual to produce non stabilised SNS without citrate or polyvinylpyrrolidone (PVP) but it has been carried out by other researchers [45]. The concentration of silver in the nanofluids was $1 \times 10^{-4} \text{ mol dm}^{-3}$, which equates to 1.028 ppm (by volume) according to the formula employed by [39]. As this concentration was lower than the lowest employed by researchers previously (1.6 ppm by volume [34]), it was decided not to dilute further to produce more samples for testing.

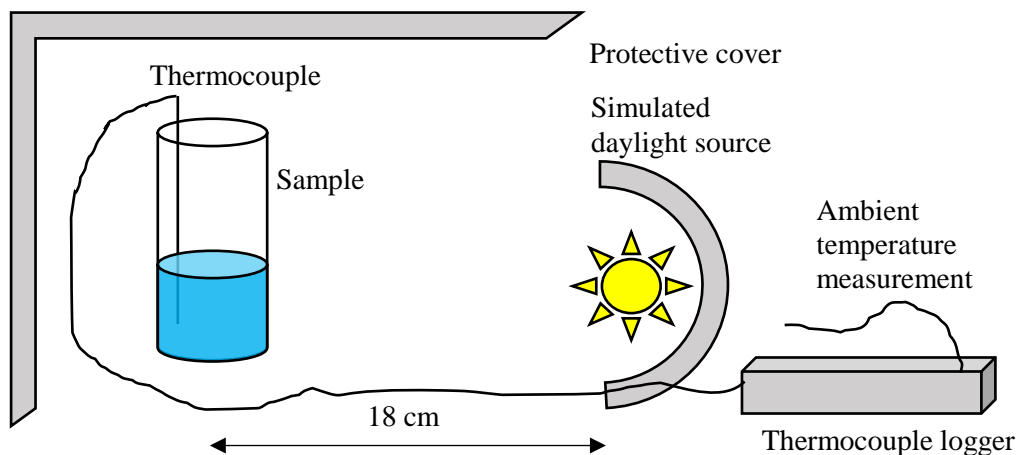


Figure 1 Schematic of Experimental Setup

UV – visible spectra was used to give an indication of the likely size and shape of the SNS and SNP as the absorption wavelength for silver nanoparticles and prisms is known to be strongly correlated to the size and shape [1, 46]. 10 cm³ of each sample was placed in a clear sample tube and a thermocouple inserted. The samples were then exposed to simulated sunlight using a Perfect Light PLS SXE300 simulator without filter and CHF-XM-500W power supply. The temperature was logged using a National Instruments NI9211 thermocouple logger, Labview software and K type thermocouples (RS components). Only one sample was exposed at once. The sample was placed 18 cm from the light source. Each sample was exposed for 1 hour at a time. The UV – visible spectra was re-measured after 2, 3, 5 and 6 hours exposure. Water was used as the control base-fluid. A schematic of the experimental setup is given in Figure 1.

4 Results

An example graph for the 5-6 hour exposure for the four samples and water control is given in Figure 2. From this graph it can be seen that the nanofluids all reached a higher maximum temperature than water. In addition the nanofluid solutions all reached their maximum temperature in a shorter time. These two observations are consistent with the work of Bandarra Filho et al [34], who achieved a temperature rise to approximately 35°C for a 1.62 ppm solution of 20 nm SNS after an hour exposure to sunlight. Their water sample also heated up more slowly although the effect was more enhanced in their work. As the nanofluids in this work were more dilute (1 ppm) a lower temperature rise is expected.

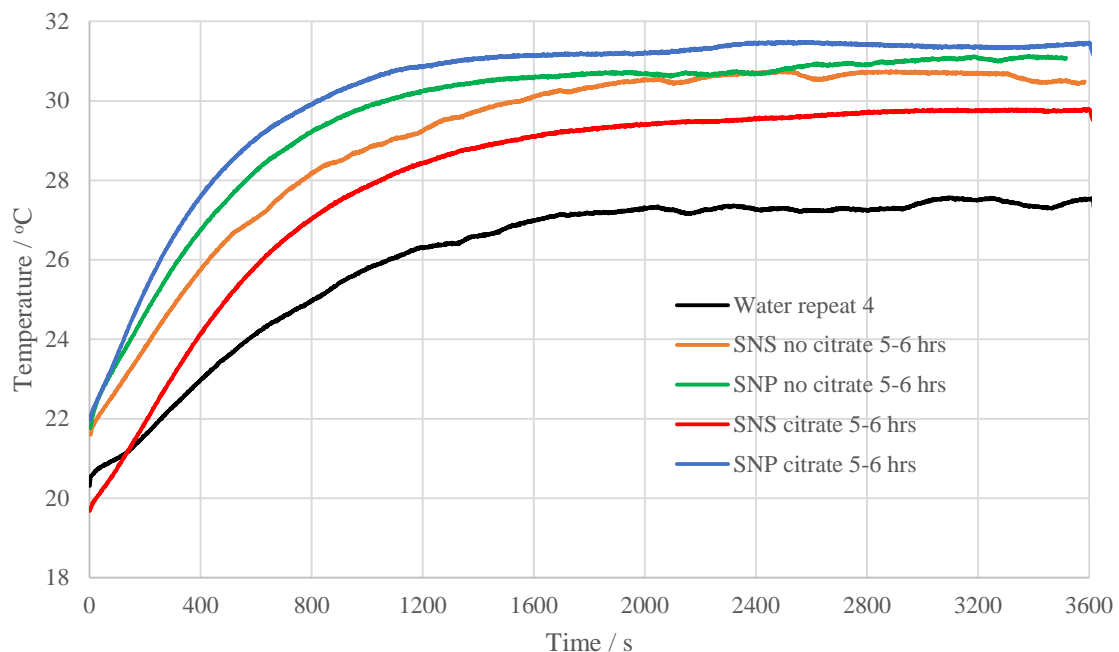


Figure 2 Example of temperature change on sunlight exposure

Box plots of the maximum temperature obtained during each hour of exposure are shown in Figure 3. On average all the nanofluids reached a higher temperature than water. However, there was a range of values obtained with the SNS citrate samples being slightly lower than the other nanofluids on average. To test the significance of the difference one way ANOVA was carried out on the maximum temperatures obtained. The resulting Tukey plot at 95% significance is shown in Figure 4. Ranges that do not pass through zero are significantly different.

Figure 4 shows that all the nanofluids except SNS citrate were significantly different to the water control. The SNS citrate sample was also just significantly different to both of the no citrate samples. More tests and perhaps an improved test method would be needed to ascertain whether the SNS citrate sample actually reached a lower temperature than the no citrate samples. There was no significant difference between the performances of the different types of nanoparticles (SNS versus SNP).

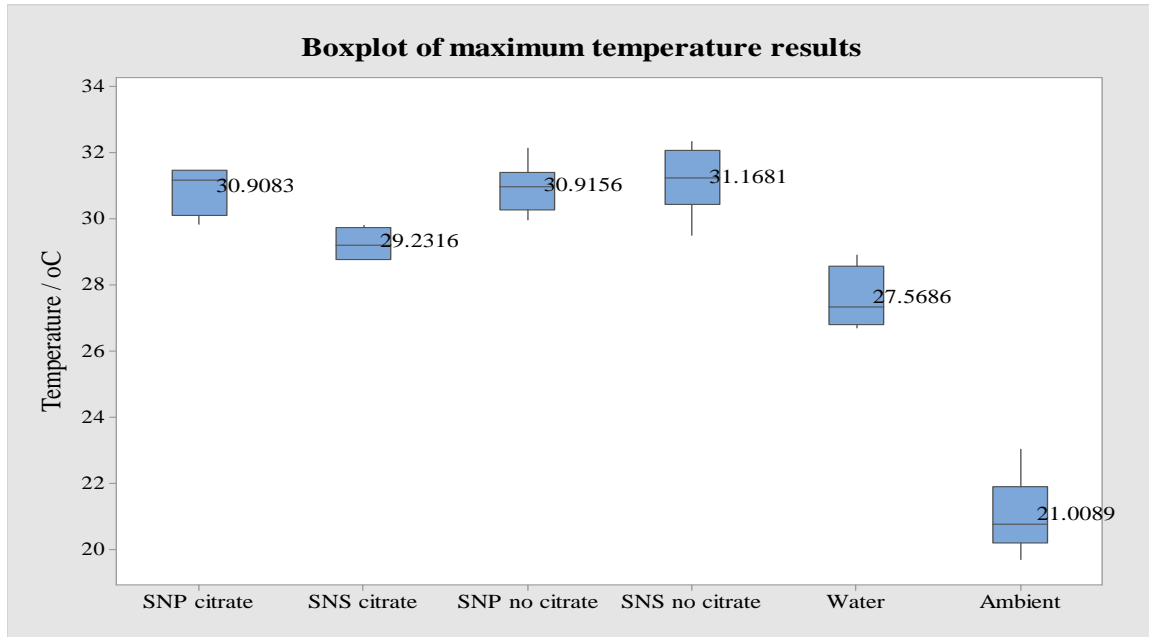


Figure 3 Boxplot of maximum temperature achieved during 1 hour exposure to simulated sunlight. The values averaged over the tests is also given

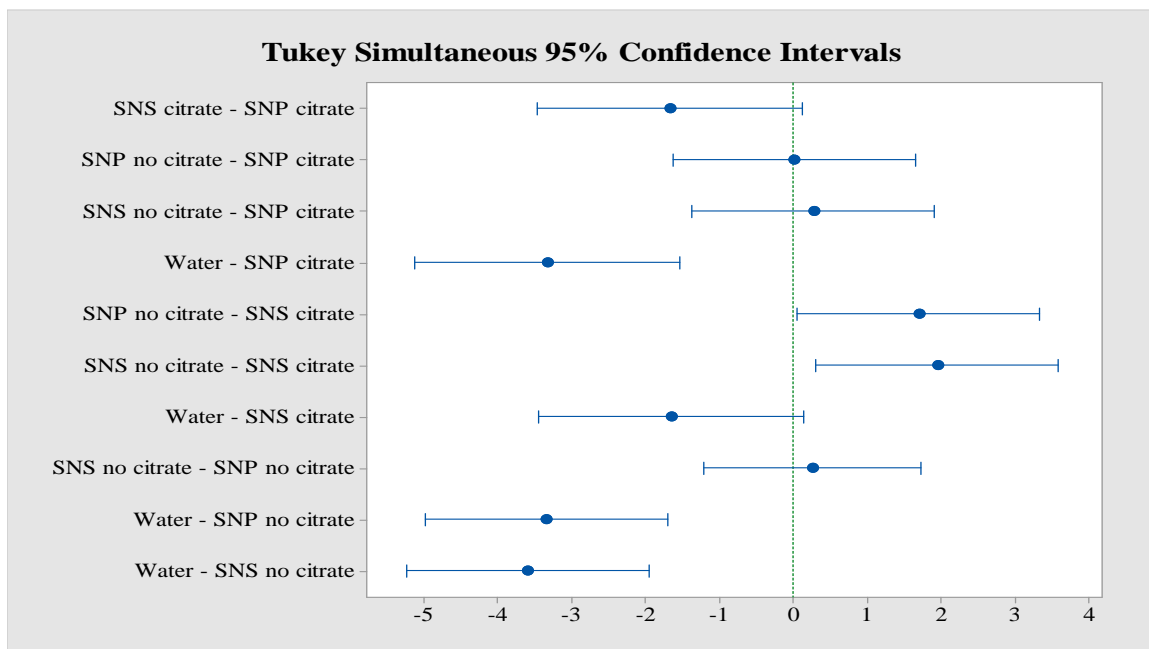


Figure 4 Significance test on maximum temperatures achieved for each sample

The UV-visible spectra for the four nanofluid samples are shown in Figure 5, Figure 6, Figure 7 and Figure 8. The SNS citrate sample (Figure 5) showed a small shift in maximum absorption and a reduction in peak height on exposure to simulated sunlight. The position of the maxima is consistent with SNS with a particle size of about 20nm [44, 47, 48].

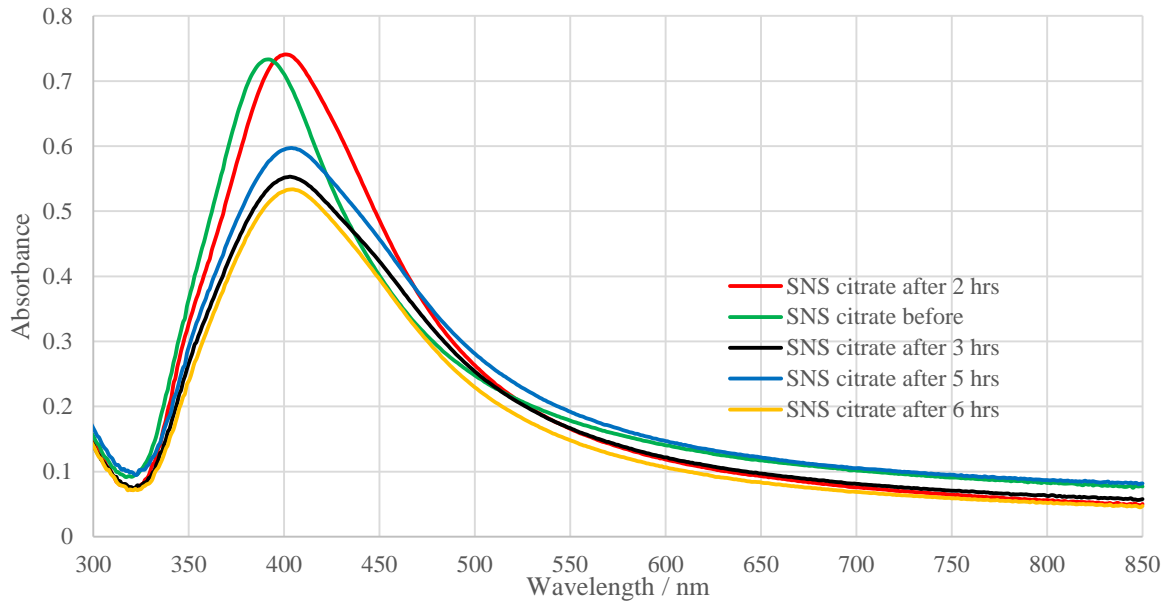


Figure 5 UV-visible spectra for SNS citrate

The UV-visible spectra for the SNS no citrate sample (Figure 6) changed considerably after the first 2 hours of exposure. Initially a well-defined maxima at 391 nm was observed suggesting an initial particle size of <20nm. The maxima then reduced considerably and the peak broadened after exposure. There was only a small difference in the spectra obtained after 2, 3, 5 and 6 hours, perhaps due to the solution stabilising. Further testing after longer exposure would be needed to confirm this.

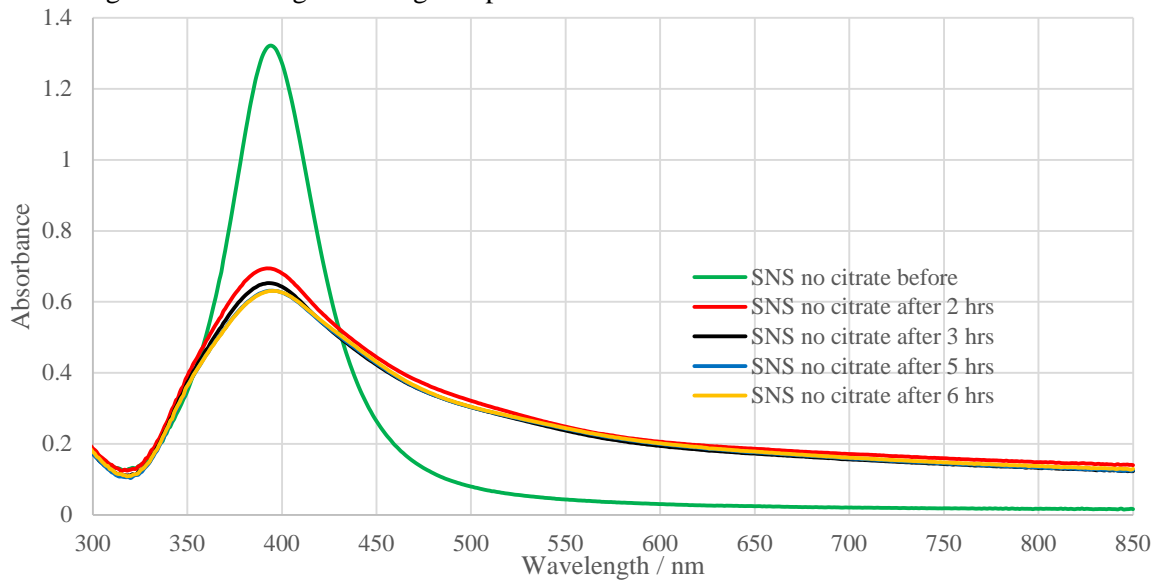


Figure 6 UV-visible spectra for SNS no citrate

The peak of the UV-visible spectra for SNP with citrate was initially greater than 850 nm (Figure 7). This is greater than the peak obtained by [49] but similar to that obtained by [1] in a microfluidic reactor with high flow rate for SNPs confirming that nanoprisms had been produced. The height of the peak then dropped after exposure with the possibility of another peak forming in the 550-700 nm region. This could indicate the formation of nanodisks or nanodecahedrons [44, 50]. The SNP citrate nanofluid was therefore not stable when exposed to simulated sunlight.

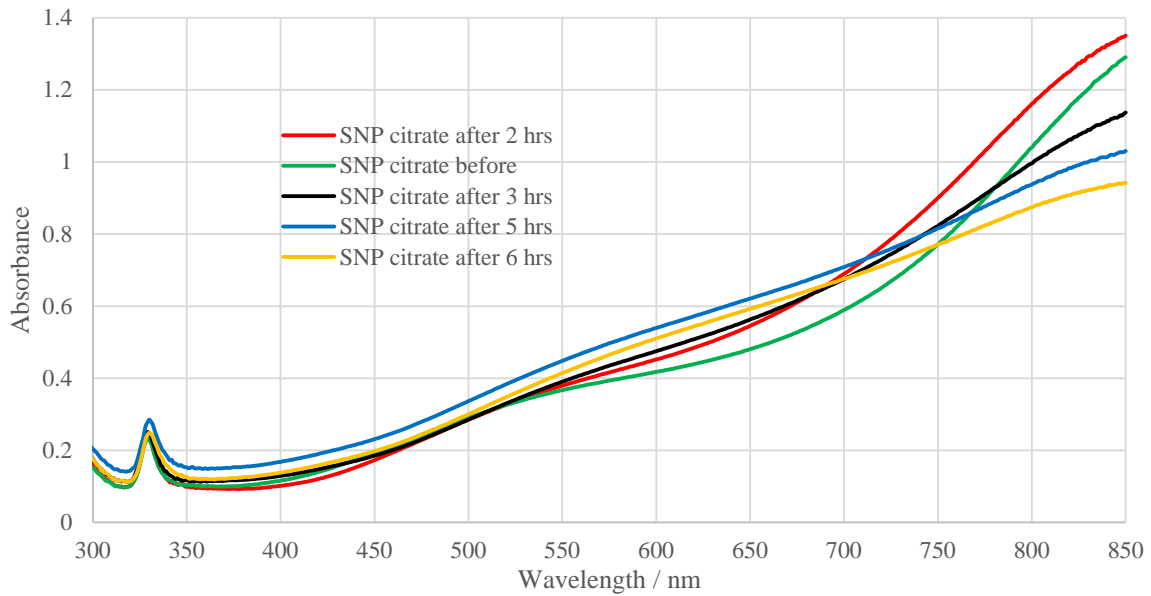


Figure 7 UV-visible spectra for SNP citrate

The SNP no citrate sample initially started with an absorption maxima of about 845 nm (Figure 8). On exposure the intensity of the peak dropped and the wavelength of the maxima decreased to about 780 nm. Like the SNS no citrate sample the SNP no citrate sample appeared to stabilise after about 3 hours exposure.

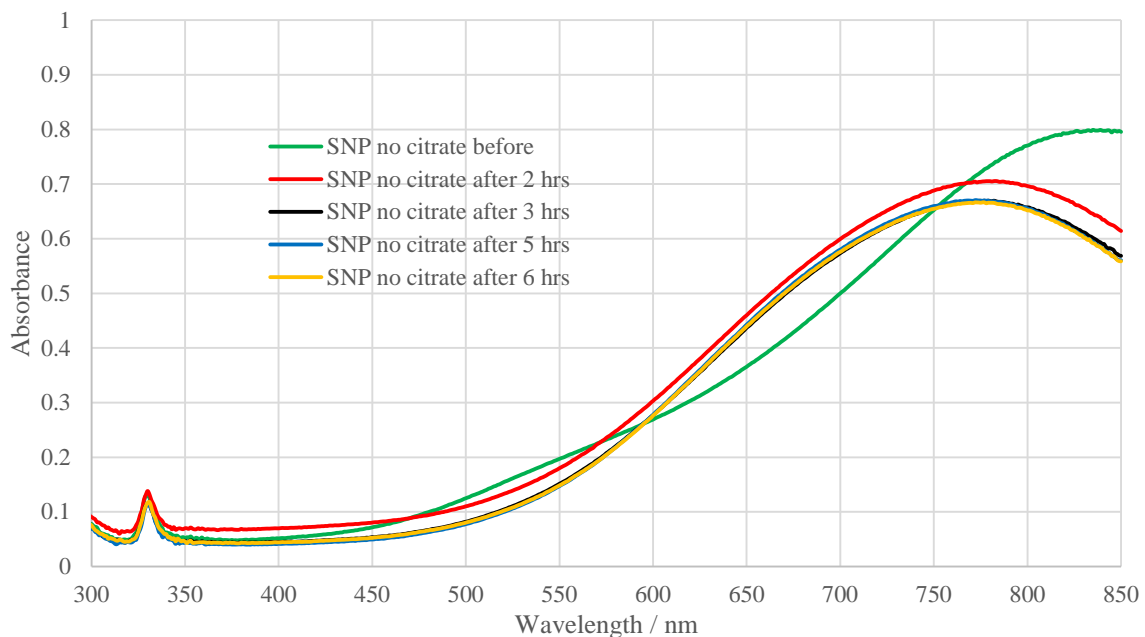


Figure 8 UV-visible spectra for SNP no citrate

Although the SNS citrate nanofluid tended to give slightly lower maximum temperatures than the other samples when exposed it is not possible to ascertain from these results whether there is a link between the maximum temperature of the nanofluid and the shape of the nanoparticles. In fact both the SNS samples had similar UV-visible spectra after exposure but had significantly different maximum temperatures (Figure 4). Further work would be required to understand the effect of the particle shape on the efficiency of solar energy capture.

The lack of stability to sunlight of the no citrate samples is in contrast to the work of [44] and suggests that some citrate is required to stabilise the nanofluid. It would have been advantageous to measure the

UV-visible spectrum of samples of the nanofluids following heating to the same temperature to ascertain whether the lack of stability was due to time / temperature or as a direct result of sunlight exposure. The lack of stability of the citrate containing samples is also in contrast to the work by [44], which suggested that stable nanofluids were obtained with concentrations of $\leq 5.0 \times 10^{-4} \text{ mol dm}^{-3}$. The concentration of citrate in the nanofluids investigated in this study were less than this but the ratio of silver to citrate was different suggesting that the stability may be related to the ratio of silver to citrate ions rather than the absolute citrate concentration. Further work would be needed to confirm this.

There was a weak correlation between exposure time and maximum temperature for the two citrate samples, with the maximum temperature increasing slightly with exposure time, but no correlation between exposure time and maximum temperature for the no citrate and water samples. The temperature rise seen with time was within the variance observed for the water sample so is unlikely to be related to the changes in the UV-spectra observed.

5 Challenges

Ideally it would have been useful to be able to expose more than one sample at a time to the simulated sunlight. This would have allowed a control sample to always be tested at the same time as a test sample. However, even if a larger simulator was available care would still be needed to prevent the test sample from indirectly heating the control sample and hence influencing the result. Consistent placement of the thermocouple was also a significant challenge. Inconsistencies in the thermocouple placement may have contributed to the spread of results obtained. Designing a better test cell with a specific place for a thermocouple would help this.

It would also have been beneficial to test a range of concentrations of nanofluids. This would have required changing the nanofluid preparation method, which was not practical in this short project. It would also be useful in the future to produce SNS with larger diameters, so that the effect of shape on the resultant temperature rise can be studied. If the concentration of the nanofluids was increased it would no longer be possible to directly measure the UV-visible spectra without sample dilution. This would necessitate a change in the experiment design. Using the method of determining the concentration of nanoparticles from [39] does not give an indication of the number of silver nanoparticles in the solution. It is likely that the SNP samples contained significantly less nanoparticles than the spheres but at present there is no simple method of determining nanoparticle size and amount for non-spherical samples. It may be possible in the future to develop an accurate method of determining the nanoparticle concentration utilising transmission electron microscopy (TEM) and Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) [51] but this may still be difficult for non-spherical particles [52].

With no insulation surrounding the samples the temperature rise measured was small. Again a redesigned test cell with insulation would help to overcome this issue, giving larger differences in temperatures and hence magnifying any differences between samples. Continuation of the testing would also help to determine if the UV-visible spectra would continue to change or if some of the nanofluids had stabilised.

6 Conclusions

Three of the nanofluids tested, namely SNS no citrate, SNP citrate and SNP no citrate, showed a significant improvement in maximum temperature achieved on exposure to simulated sunlight when compared to water. The fourth sample tested was not shown to be significantly different to the water control, however, it still reached a higher maximum temperature in some of the tests when compared to water. The nanofluids therefore show potential to enhance the capture of solar energy for DASC applications. All of the UV-visible spectra for the nanoparticles changed with exposure to sunlight. The effect of these changes on the temperature rise would require further investigation.

7 Recommendations and Future Work

A better designed test cell is needed to ensure consistent placement of the thermocouple and provide some insulation to increase the maximum temperature obtained, facilitating differentiation between samples. The cell design needs to be flexible enough to investigate different geometries.

More concentrated nanofluids need to be tested as well as mixed solutions containing both SNS and SNP. The testing needs to be carried out over longer periods to assess the longer term stability of the nanofluids and if any relationship exists between the UV-visible spectra and the maximum temperature rise. It would also be useful to compare the silver-nanofluids with other nanofluids such as Al_2O_3 nanofluid to see if the enhanced performance is directly related to the absorption spectra or if it due to other changes within the nanofluid such as enhanced surface area. Ideally it would be beneficial to the understanding if SNSs could be manufactured with similar sizes to SNPs to investigate the effect of shape of particles.

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