Eco-friendly synthesis of titanium dioxide nanoparticles for UV protection in lenses

Group 1-14

Abstract

In this study, an eco-friendly synthesis of titanium dioxide (TiO_2) nanoparticles was conducted by using *Aloe vera* (*A. vera*) extract to synthesise TiO_2 nanoparticles from titanium isopropoxide (TTIP). Thereafter, the nanoparticles were characterized using the UV-Vis spectrophotometer and the optimal ratio of volume of extract to volume of TTIP was determined. The first method of synthesis for TiO_2 nanoparticles resulted in nanoparticles with absorbances of 99.99% in the range of UV light, which is 280–400nm. This is above the 99.9% requirement for effective absorbance, but the nanoparticles also had a range of effective wavelength that overlapped with the range of visible light and as such was unsuitable for our purposes. The second method of synthesis for TiO_2 nanoparticles also resulted in nanoparticles with absorbances of 99.99% in the range of UV light, which is 280–400nm. Of the 3 nanoparticle samples synthesised, the nanoparticle sample synthesised with 75 ml of *A. vera* extract was the most suitable as it had a range of effective wavelength from 250–420 nm, and only effectively blocks out a small range of visible light. Hence, nanoparticles suitable for use in the composite layer were successfully synthesised and the optimal ratio of volume of extract to volume of TTIP was found to be 75 ml to 0.5 ml. The SEM testing and the preparation of the composite layer was unable to be performed in time. This project also opened up the possibility of using *A. vera* to synthesise TiO_2 nanoparticles which were suitable for use in a composite layer to form a coating on lenses for UV protection, hence protecting the users' eyes from UV radiation and the various ocular diseases caused by prolonged exposure of the eyes to UV radiation.

1. Introduction

Ultraviolet light can damage the eyes and cause it to develop a variety of diseases. These include cortical opacities, commonly known as cataracts. Men exposed to more UV-B light are 1.36 times more likely to develop cortical opacities (Cruickshanks et al., 1992). Other ocular diseases arising from UV light include eyelid malignancies, photokeratitis, climatic droplet keratopathy and pterygium (Yam & Kwok, 2014). It is therefore necessary to limit the intensity of UV light entering the eyes.

One way this can be achieved is through lenses that have dispersed metal nanoparticles. Lens coated with a composite layer of metal nanoparticles (preferably gold nanoparticles) dispersed in a polymer matrix on one or both sides are able to provide protection from UV radiation (Huo, 2007). The nanoparticles should have at least 99.9% absorbance in the range of 280–400 nm, which is the range of UV light, to effectively protect the user from UV radiation (American Optometric Association, n.d.).

However, the various commercial methods of production of gold nanoparticles all have toxic byproducts, or use toxic chemicals in its production, which may have environmental consequences during large-scale production (Shah et al., 2014). Hence, biological synthesis is preferred as it is non-toxic and eco-friendly.

Therefore, this project plans to biologically synthesise TiO_2 nanoparticles, which are already widely used for UV protection in commercial sunscreen and have a good absorbance for UV radiation, instead of gold nanoparticles, to avoid the environmental damages caused by commercial synthesis of gold nanoparticles. Furthermore, Khadar, A., Behara, D. K., and Kumar, M. K. (2016) synthesized TiO_2 nanoparticles using *A. vera* extract which showed a strong absorbance below 400 nm, showing that it is possible to biologically synthesise TiO_2 nanoparticles that have a good absorbance for UV radiation.

Hence, the approach of producing lenses with dispersed nanoparticles will be used, first biologically synthesising TiO_2 nanoparticles, then using polyethylenimine (PEI 600) as a dispersing agent to disperse the TiO_2 nanoparticles in a poly(methyl methacrylate) $(C_5O_2H_8)_n$ polymer to form the composite layer that is to be coated onto a lens.

2. Objectives and Hypotheses

Objectives

1. Synthesise and characterise TiO_2 nanoparticles from TTIP meditated with *A. vera* extract
2. Determine the optimal ratio of volume of extract to volume of TTIP for synthesis of TiO_2 nanoparticles based on size and absorbance of TiO_2 nanoparticles (smallest size and highest absorbance of at least 99.9% between 280–400 nm)
3. Incorporate the optimal nanoparticles into poly(methyl methacrylate) polymers such that the composite layer has sufficient visibility and UV absorbance (at least 99.9%) for feasible use in real life

Hypothesis

1. The optimal ratio of volume of *A. vera* extract to volume of TTIP would be 0.5 ml:75 ml.
2. Composite layer has a minimum of 99.9% absorbance of 280–400 nm radiation

3. Outline of Methods

Preparation of *A. vera* extract

A. vera plant leaves were cut and washed with distilled water. 50 g of the leaves were weighed using an electronic weighing balance and transferred into a 500 ml beaker containing 250 ml distilled water. The contents of the beaker were boiled and stirred for 2 h at 90°C using a hot plate with magnetic stirrer. The extract was filtered using filter paper and filter funnel and the filtrate obtained is the *A. vera* extract.

Preparation of TiO_2 Nanoparticles — Method 1

1 ml of TTIP was mixed with 3 ml of isopropanol in a beaker to decrease the rate of precipitation of TTIP in water. This mixture was added to 5 ml of the *A. vera* extract under constant stirring. The mixture was stirred for 4 hours at 25°C. The mixture was centrifuged and the supernatant was discarded. The pellets obtained were the TiO_2 nanoparticles. This would be sample A. This was repeated 2 more times with 10 ml and 15 ml of the *A. vera* extract. These would be samples B and C respectively.

Preparation of TiO_2 Nanoparticles — Method 2

0.5 ml of TTIP was added to 25 ml of the *A. vera* extract under constant stirring. After this, the mixture was stirred for 4 hours at 25°C. The mixture was centrifuged and the supernatant was discarded. The pellets obtained were the TiO_2 nanoparticles. This would be sample A. This was repeated 2 more times with 50 ml and 75 ml of the *A. vera* extract. These would be samples B and C respectively.

Characterization of Nanoparticles

The nanoparticles samples were each mixed 100 ml with deionised water before they were visualized under a SEM to measure its size, and analyzed with a UV-Vis spectrophotometer to measure its UV and visible light absorbance.

Absorbance is measured in absorbance units in the UV-Vis spectrophotometer. To convert it into a percentage, the formula below was used.

$$Absorbance = 2 - \log(\%T)$$

Where %T is the transmission in a percentage. The absorbance was then calculated by subtracting the transmission from 100%.

Preparation of composite layer

30 g of poly(methyl methacrylate) was heated until melted. 30 ml of nanoparticle sample A and 5 ml of PEI 600 was added and the solution was stirred until a homogenous solution was obtained. A cuvette was filled with the solution then turned upside down to empty out the excess solution and form a thin coating on the inside of the cuvette with the composite layer. The composite layer was allowed to cool and solidify. This was repeated with nanoparticle samples B and C, and repeated with deionised water as control. This process is shown in Fig 1.

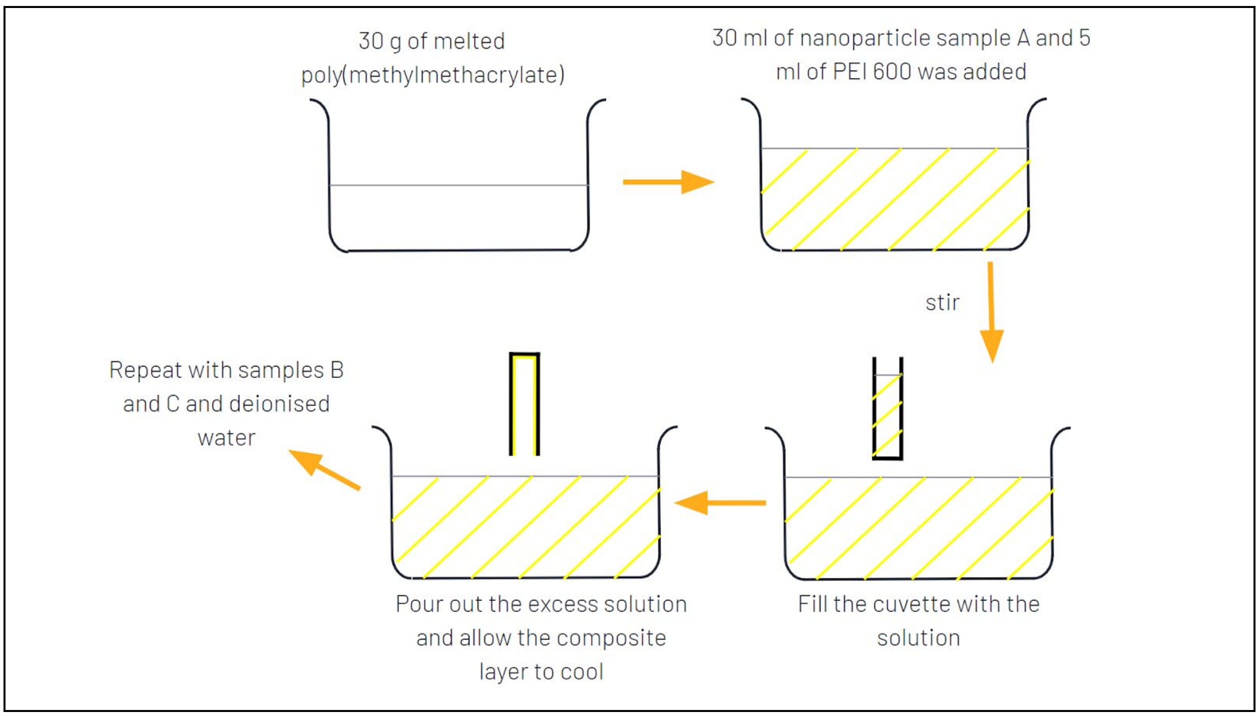

Fig 1: Process for preparation of composite layer

Testing of lens with dispersed TiO_2 nanoparticles

The cuvettes coated with the composite layer were passed through a UV-Vis spectrophotometer to check its UV and visible light absorbance.

4. Results and Discussion

Overall

1 batch of TiO_2 nanoparticles was synthesised using Method 1, and 2 batches of TiO_2 nanoparticles were synthesised using Method 2. The colour of the solution with nanoparticles synthesised using Method 1 was pale yellow, while that of Method 2 was a darker shade of yellow. The nanoparticles are shown in Fig 2, Fig 3, and Fig 4.

(a) (b) (c)

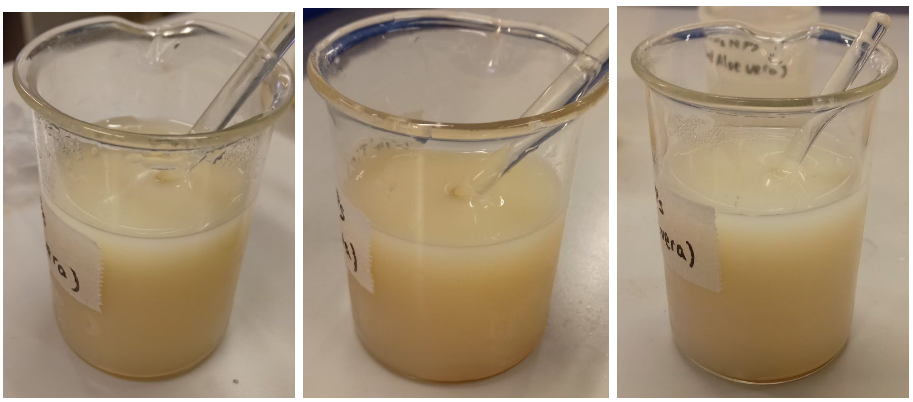

Fig 2: Nanoparticles synthesised using Method 1, (a) shows nanoparticles sample A, (b) shows nanoparticles sample B, (c) shows nanoparticles sample C

(a) (b) (c)

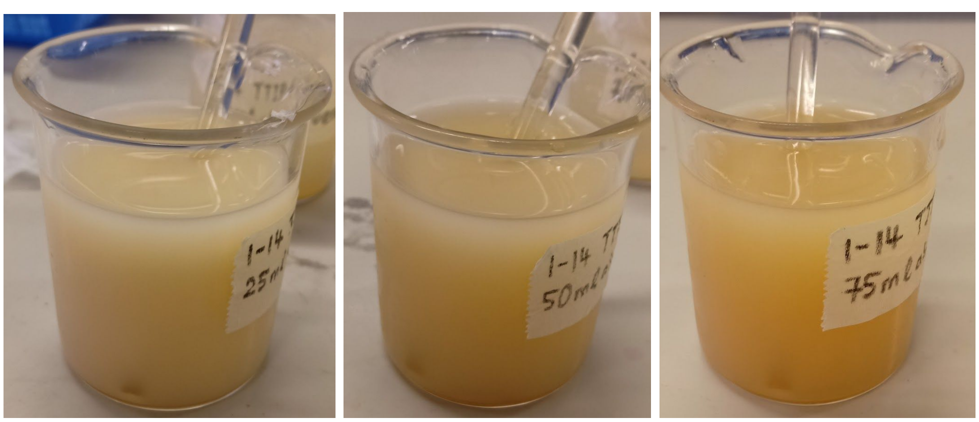

Fig 3: Nanoparticles synthesised using Method 2 (Batch 1), (a) shows nanoparticles sample A, (b) shows nanoparticles sample B, (c) shows nanoparticles sample C

(a) (b) (c)

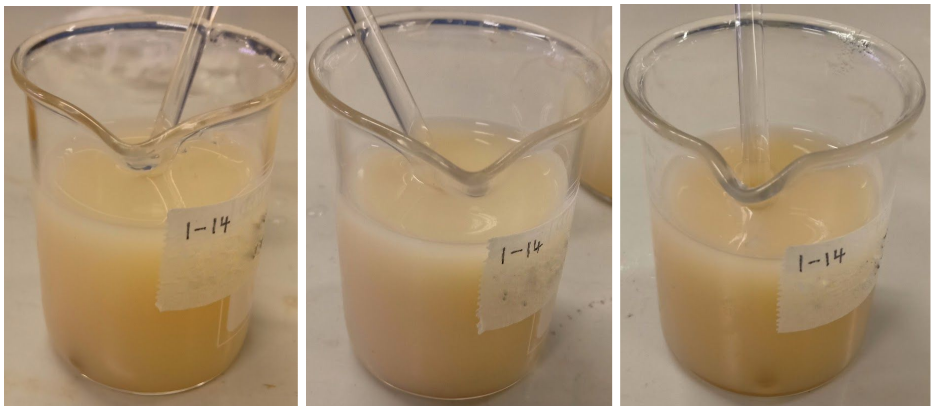

Fig 4: Nanoparticles synthesised using Method 2 (Batch 2), (a) shows nanoparticles sample A, (b) shows nanoparticles sample B, (c) shows nanoparticles sample C

The TiO_2 nanoparticles were formed by the hydrolysis of TTIP, as shown in the following equation:

$$Ti\{OCH(CH_3)_2\}_4 + 2\ H_2O \rightarrow TiO_2 + 4\ (CH_3)_2CHOH$$

However, when the TiO_2 molecules are formed, they are unstable as they have a tendency to agglomerate into larger structures to minimize surface energy. Therefore, the role of the *A. vera* extract in the reaction is to act as a capping agent, which is used to prevent agglomeration and to impart solubility, thereby ensuring that the nanoparticles do not increase in size.

Light is absorbed by the TiO_2 nanoparticles because it causes the electrons in TiO_2 to undergo electronic transition from a ground state to an excited state. TiO_2 nanoparticles absorb UV light better than visible light as TiO_2 nanoparticles are not easily excited and the more easily excited the electrons are, the longer the wavelength of light it is able to absorb. Hence TiO_2 nanoparticles absorb UV light better than visible light since visible light has a longer wavelength than UV light.

Characterization of Nanoparticles Synthesised Using Method 1

With reference to Fig 5 and Table 1, the nanoparticles samples A, B, and C, all had absorbances of 99.99% which is greater than the 99.9% requirement for effective absorbance, for the range of of 280–400 nm, implying that these nanoparticles would be effective in blocking UV light when used in the composite layer.

However, all the synthesised nanoparticles also effectively absorbed light of wavelengths between 400 nm and 520 nm. This wavelength range overlaps with that of visible light (400–700nm). This means that if these nanoparticles were to be used in the composite layer, visible light, particularly purple and blue light, may be blocked and visibility may be limited. This would have made all of them unsuitable for use in our composite layer which is to be coated onto lenses.

Hence, it was necessary to experiment and find an alternative synthesis method to address the shortcomings of the nanoparticles formed using this method.

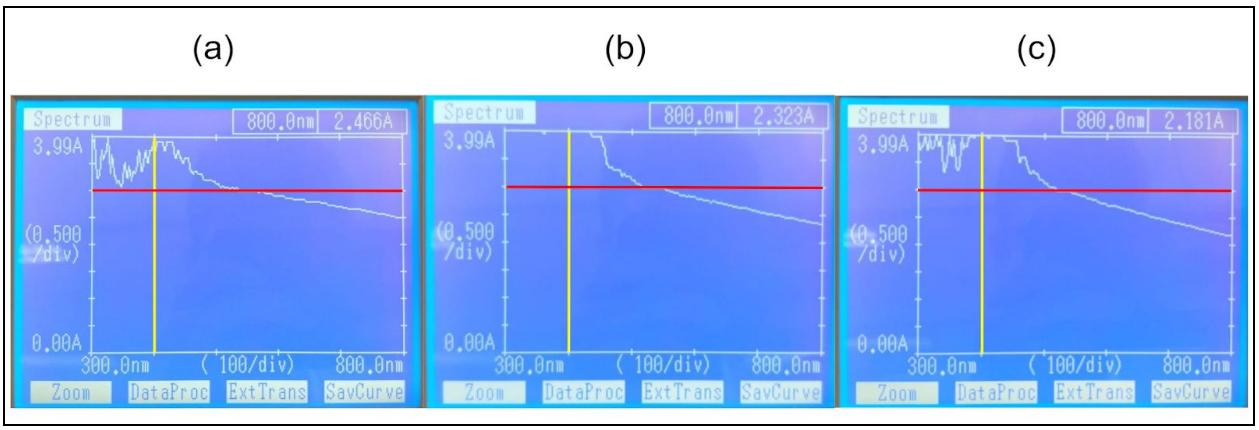

Fig 5: Batch 1 UV-Vis spectroscopy results, (a) shows nanoparticles sample A, (b) shows nanoparticles sample B, (c) shows nanoparticles sample C

Volume of extract used / ml	Range of Effective Wavelength
5	300nm–550nm
10	300nm–520nm
15	300nm–520nm

Table 1: Table of Batch 1 UV-Vis spectroscopy results

We were unable to obtain an SEM scanning of our TiO_2 nanoparticles in time as the NUS lab was closed due to Covid-19.

Characterization of Nanoparticles Synthesised Using Method 2

With reference to Fig 6 and Table 2, the nanoparticles samples A, B, and C, all had absorbances of 99.99% which is greater than the 99.9% requirement for effective absorbance, for the range of of 280–400 nm, implying that these nanoparticles would be effective in blocking UV light when used in the composite layer.

However, with reference to Fig 6 (a), Fig 6 (b) and Table 2, the nanoparticles samples A, and B, also effectively absorbed light of wavelengths between 400 nm and 480 nm, making them unsuitable for use in our composite layer which is to be coated onto lenses.

With reference to Fig 6 (c) and Table 2, the nanoparticle sample C effectively absorbed significantly less light of wavelengths between 400 nm and 420 nm, making them the most suitable for use in our composite layer which is to be coated onto lenses. Since it only effectively blocks out a small range of visible light, only some purple light will be blocked, and visibility will be largely unaffected, making nanoparticle sample C suitable for use in our composite layer which is to be coated onto lenses.

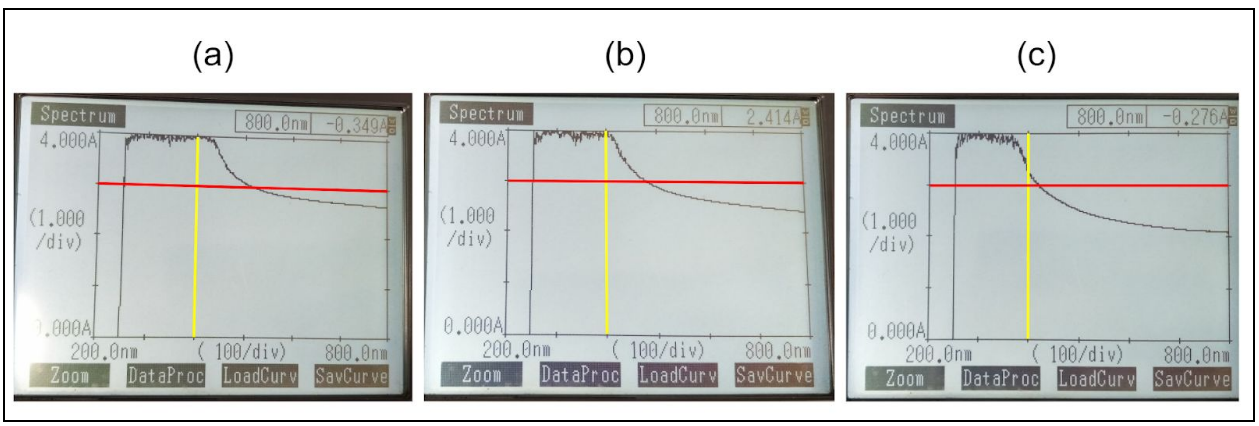

Fig 6: Batch 1 UV-Vis spectroscopy results, (a) shows nanoparticles sample A, (b) shows nanoparticles sample B, (c) shows nanoparticles sample C

Volume of extract used / ml	Range of Effective Wavelength
25	250nm–520nm
50	250nm–480nm
75	250nm–420nm

Table 2: Table of Batch 1 UV-Vis spectroscopy results

With reference to Fig 7 and Table 3, the results of the UV-Vis spectroscopy for Batch 2 nanoparticles were similar to that of Batch 1, with the exception of nanoparticles sample B, where the range of effective wavelength decreased slightly in range.

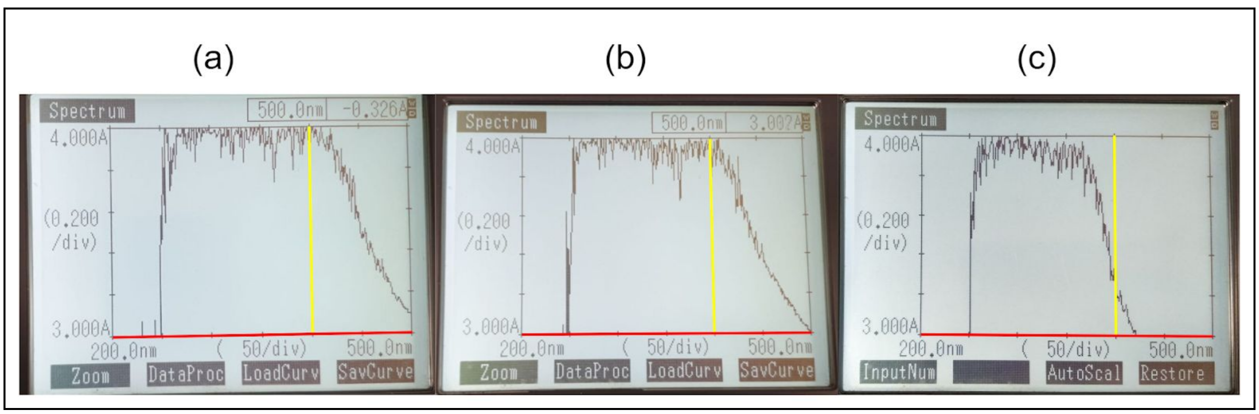

Fig 7: Batch 2 UV-Vis spectroscopy results, (a) shows nanoparticles sample A, (b) shows nanoparticles sample B, (c) shows nanoparticles sample C

Volume of extract used / ml	Range of Effective Wavelength
25	250nm–550nm
50	250nm–500nm
75	250nm–420nm

Table 3: Table of Batch 2 UV-Vis spectroscopy results

Therefore, it can be concluded that method 2 resulted in nanoparticles sample A, and B, which were not suitable, and nanoparticle sample C, which were suitable, for use in our composite layer which is to be coated onto lenses.

We were unable to obtain an SEM scanning of our TiO_2 nanoparticles in time as the NUS lab was closed due to Covid-19.

Testing of lens with dispersed TiO_2 nanoparticles

We were unable to prepare and test the composite layer for lenses due to time constraints.

5. Conclusions and recommendations for future work

In conclusion, TiO_2 nanoparticles suitable for possible use in the composite layer for lenses were successfully synthesized using method 2. The optimal ratio for volume of TTIP to volume of extract was 0.5 ml:75 ml, which resulted in nanoparticles which had a peak wavelength from 250nm–400nm and a peak absorbance of 99.99%.

For future work, the nanoparticles samples can be visualised under the SEM to measure its size. The nanoparticles can also be used to prepare the composite layer which can then be checked for its feasibility and effectiveness for use as UV protection in lenses via the UV-Vis spectrophotometer. The composite layer can also be tested for its durability and stability over time to ensure a durable and long lasting coating on the lenses. If feasible and effective for use as UV protection in lenses, the nanoparticles and composite layer can then be produced on a large scale to produce a coating for lenses suitable for commercial applications. This helps provide users with UV protection for their eyes, while at the same time remaining eco-friendly, since a biological synthesis is used to synthesize the nanoparticles instead of the various toxic commercial methods. All experiments can also be repeated for reproducibility. Due to time constraints, all experiments were performed less than 3 times. To ensure reliable results, the experiments can be repeated for a total of 3 times.

References

American Optometric Association. (n.d.). UV protection. Retrieved August 11, 2020, from https://www.aoa.org/patients-and-public/caring-for-your-vision/uv-protection

Cruickshanks, K. J., Klein, B. E., & Klein, R. (1992). Ultraviolet Light Exposure and Lens Opacities: The Beaver Dam Eye Study [Abstract]. American Journal of Public Health, 82(12), 1658-1662. doi:10.2105/ajph.82.12.1658

Grześkowiak, M., Wróbel, R. J., Grzechulska, J., & Przepiórski, J. (2014). Preparation and characterization of titania powders obtained via hydrolysis of titanium tetraisopropoxide. Materials Science-Poland, 32, 71-79. doi:10.2478/s13536-013-0163-z

Huo, Q. (2007, December 27). Lenses Having Dispersed Metal Nanoparticles For Optical Filtering Including Sunglasses. Retrieved from https://patentimages.storage.googleapis.com/a3/c4/99/6b6e34f5ab139d/US20070298242A1.pdf

Khadar, A., Behara, D. K., & Kumar, M. K. (2016). Synthesis and Characterization of Controlled Size TiO_2 Nanoparticles via Green Route using Aloe vera Extract. International Journal of Science and Research, 5(11), 1913–1916. Retrieved from https://pdfs.semanticscholar.org/14e5/3dec8f9fb1c50d06c066ea63fc2ac7dfadac.pdf?_ga=2.200214510.192445207.1591882288-890111514.1591882288

Shah, M., Badwaik, V., Kherde, Y., Waghwani, H. K., Modi, T., Aguilar, Z. P., . . . Dakshinamurthy, R. (2014). Gold nanoparticles: Various methods of synthesis and antibacterial applications. Frontiers in Bioscience, 19(8), 1320-1344. doi:10.2741/4284

Yam, J. C., & Kwok, A. K. (2013). Ultraviolet light and ocular diseases. International Ophthalmology, 34(2), 383-400. doi:10.1007/s10792-013-9791-x