

Fig. 2. Maxima of averaged temperatures for different concentrations under high-grade light

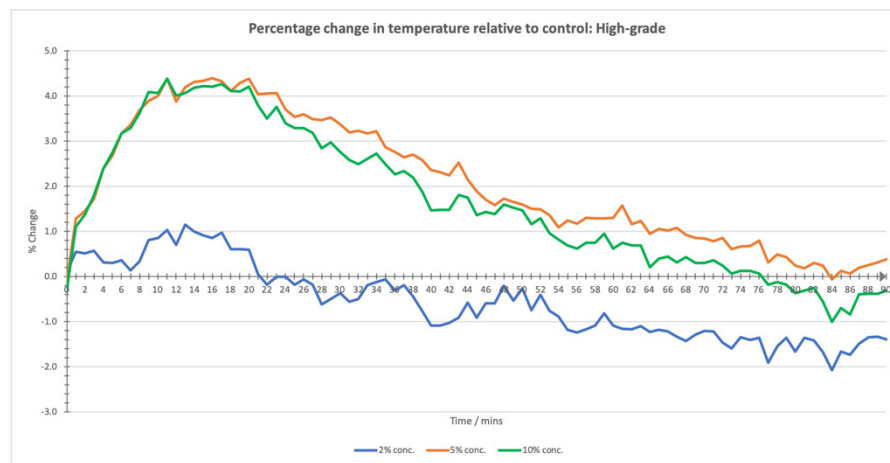


Fig. 3. Percentage change in temperature relative to control under high-grade light

As can be seen in Figure 1, when left under high-grade sunlight, all 4 concentrations undergo, at first, a steep rise in temperature. For around the first 4 minutes, the 4 concentrations each have almost a constant rate of temperature increase of 10.8 °C/sec. This rate undergoes a gradual decrease across the 4 concentrations, and around 43 °C, a distinct separation is seen between the graphs of the 0 and 2 % w.v. concentrations and the 5 and 10 % w.v. concentrations. The separation becomes gradually more pronounced, and is at its maximum when there is a difference of ~2.5°C at around 10:38, - just minutes away from the overall peak time of each of the 4 concentrations. At 10:40 (20 minutes in), all four concentrations reach their maximums. This is depicted in Figure 2 - we can see that the maximums for the 10% and 5% concentrations are nearly the same: 57.8 and 57.9 °C respectively, whereas for 2% and 0%, they are 55.8 and 55.5°C.

After the peak, this trend nearly reverses - the separation decreases till the 4 concentrations almost merge; this is also observed in Figure 3, where the % change relative to the control after 65 minutes (11:25) is <1%. Although a 'secondary peak' is reached at 11:30 in Figure 1, this can be disregarded due to the information in Figure 3, from which we can deduce that this peak is probably due to ambient temperature changes and not plasmonic heating. The

only ‘true’ peak that we can attribute to plasmonic heating is the primary one (10:40), since it is here that we observe the highest relative increases of >4%.

Moreover, we can confirm the presence of some thermoplasmonic heating in the 5% and 10% plates by studying the slopes of their graphs in Figure 3. After the peak, the slopes of all three graphs are roughly the same in magnitude, and negative - this indicates consistent loss of heat over an extended period of time, till the temperature of the control is reached. Thus, we see the presence of excess heat in these two plates, formed rapidly within the first 20 minutes and eventually lost to the surroundings, and this could be due to the gradual dissipation of localised heat from the NPs.

It is also important to note that the 2% concentration is consistently lower than the other temperatures from 10:46 to the end of the experiment. The difference is more anomalous towards the end, however, when three of the other concentrations, including the control, merge into a single temperature while the 2% concentration is about a degree lower. This could be attributed to some sort of systematic error with the insulation.

Low-grade light

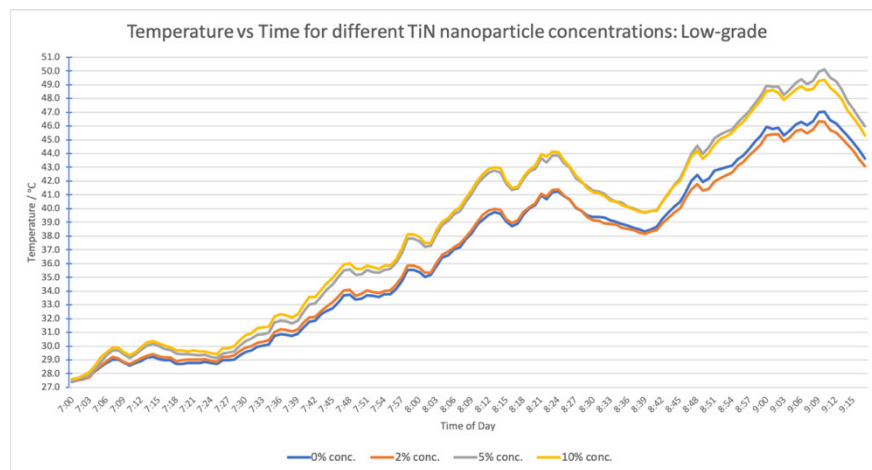


Fig. 4. Temperature vs time for different concentrations of Titanium Nitride nanoparticles under low-grade light

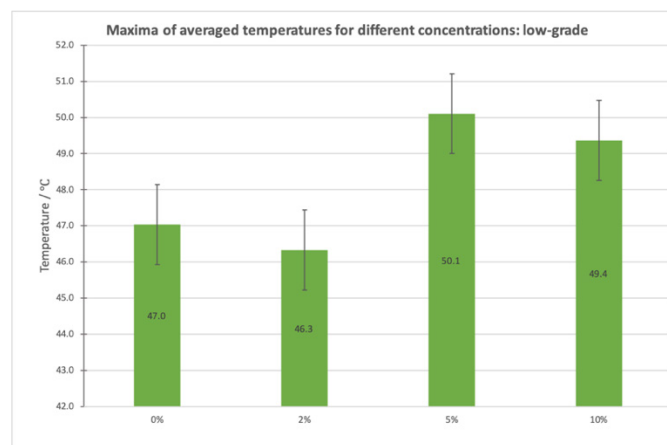


Fig. 5. Maxima of averaged temperatures for different concentrations under low-grade light

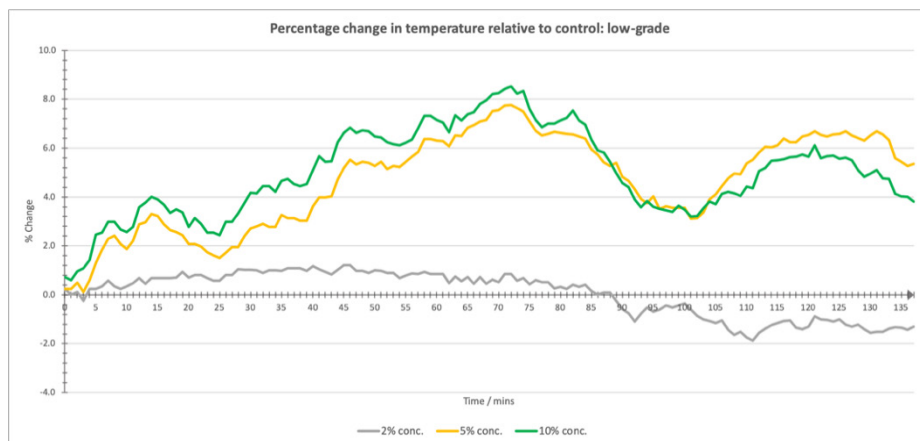


Fig. 6. Percentage change in temperature relative to control under low-grade light

Investigating the same concentrations of paint under low-grade light yields both similarities and differences in observations.

Like in high-grade light, a distinct separation is seen between the graphs of the 0 and 2 % w.v. concentrations and the 5 and 10 % w.v. concentrations in Figure 4. However, this separation begins just 3 minutes in, becomes gradually more pronounced, and is consistent till the end. The separation is at its maximum when there is a difference of ~3.5°C at 9:09. Additionally, the slope of each graph in Figure 4 - and hence the rate of temperature increase - is lower than the initial slopes in Figure 1, which is expected from low-grade light.

We can observe a primary peak at 9:10/130 minutes, a secondary peak at 8:24/84 minutes, and many more sub-peaks. Once again, the 2% concentration is partially anomalous, because as seen in Figure 6, there is a negative change relative to the control - yet, this does not affect the distinct difference between the maxima of 0%, 2% and 5%, 10%, which are well outside the limits of experimental error in Figure 5.

Hence for low-grade light, we note more gradual, sustained heating over a larger period of time (135 minutes). This is confirmed in Figure 6, which depicts the 5% and 10% concentrations as consistently higher than the control, and amongst themselves some crossing and variance that can be attributed, with certainty, to fluctuations in ambient temperature and/or lighting, since the trend is followed by each graph. When considering the slope of graphs in Figure 6, we see that low-grade light produces temperatures that gradually increase, but rarely dissipate, unlike for high-grade light in which the peak was followed by a steady emission of radiation. This could be because low-grade light enables the NPs to release localised heat incrementally.

Discussion and Conclusion

From the quantitative analysis, it is evident that the thermoplasmonic effect exists under both high-grade and low-grade light: for low-grade light, sustained periods of time result in gradual heating. Additionally, the 2% concentration paint displayed almost no heating relative to the control - this could be because the quantity of TiN nanopowder, 0.2g, was not sufficient enough to be even partially exposed to the surface of the metal substrate. This could be eliminated with not only higher concentrations of the nanopowder in paint, but also methods such as laboratory spin-coating to cover the substrate (albeit unsuitable for practical, large-scale applications of paint), or the sonication of the colloidal NPs to ensure an even spread of them on the substrate, in order to maximise their surface area.

Nevertheless, the formulation of a ‘thermoplasmonic paint’ with significant photo-thermal properties has been shown. This type of paint exhibits a heating time of approximately 2 hours to reach a maximum; thus, its applications may be especially seen in the usage of low-grade thermal energy by conductive surfaces (since the present investigation uses a coated metal substrate as a transducer of heat).

A thermoplasmonic paint-enabled solar cell could be used in spacecraft and space exploration vehicles. This energy source seems to be a suitable substitute for radioisotope thermoelectric generators (RTGs), which were used in the NASA Voyager probes [10], and have also been included in realistic proposals for interstellar probes by NASA [11]. These are nuclear batteries used in low-maintenance, low-power situations for durations too long and impractical for traditional fuel cells or solar cells. The stability over time, as well as resistance to photo-decay of TiN is an added benefit to such an energy source. Thermoplasmonic paint will also eliminate the safety hazards associated with the radioactive materials in RTGs, and hence is a lucrative alternative [12].

Terrestrially, too, thermoplasmonic paint is a possible substitute for some solar applications. As the experiment has shown, especially in the case of low-grade light, due to the continuously high relative temperature and its incremental release to the surroundings, TiN NPs may be useful in the immediate storage and release of thermal energy to the surroundings, which is a feature that photovoltaics falls short in, as there is an inevitable loss of thermal energy when energy is converted from one form to another and back (solar energy converts light energy to electric and subsequently chemical energy, and reverts this when energy is required to be drawn from batteries). Thermoplasmonic paint eliminates this and offers a direct photo-thermal effect, bypassing peripheral losses of energy. However, one shortcoming (in the paint as well as in the general domain of thermoplasmonics) is that the energy cannot be drawn and utilized in a controlled, deliberate manner yet.

With the above-mentioned characteristics of the thermoplasmonic paint in mind, another realistic application may be in the process of pasteurisation and water disinfection. Pasteurisation of water occurs when its temperature is raised to 65 °C for 3 minutes [13]. As evidenced by the experiment, the thermoplasmonic paint can sustain heating for periods much larger than 3 minutes, and is capable of reaching temperatures ~60 °C with a 5-10% concentration; thus, it is hypothesised that at slightly higher concentrations, solar disinfection (SODIS) would be possible. Also, one process of pasteurising fluids such as water involves the passing of water through ‘plate heat-exchangers’, which are essentially thin metal plates with temperatures of low magnitudes [14]. This is almost exactly replicable by the current experimental setup, wherein thin metal plates have been used, and this could result in a significant carbon reduction from existing energy-intensive heat-exchanger systems.

Thus, theoretically, clean water can be produced at a near-continuous rate after prior heating of the plates to the optimum temperature, which would be extremely beneficial to rural areas and villages with lack of access to safe potable water and who receive sufficient sunlight, because while pasteurisation does not sterilise water, it reduces the number of pathogens by many orders of magnitude and hence can reduce the incidence of water-borne diseases by 35-40% [15]. Since this method works in low-grade light, water disinfection could be available to the people from ~07:00 to evening-time. The low maintenance associated with thermoplasmonic paint, in addition to the other advantages, makes this a seemingly sustainable and long-term solution.

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References

- [1] Robotjazi, H., Bao, J. L., Zhang, M., Zhou, L., Christopher, P., Carter, E. A., . . . Halas, N. J. (2020). Plasmon-driven carbon–fluorine (C(sp³)-F) bond activation with mechanistic insights into hot-carrier-mediated pathways. *Nature Catalysis*, 3(7), 564-573. doi:10.1038/s41929-020-0466-5
- [2] Baffou, G., Cichos, F., & Quidant, R. (2020). Applications and challenges of thermoplasmonics. *Nature Materials*, 19(9), 946-958. doi:10.1038/s41563-020-0740-6
- [3] Maier, S. A. (2017). *World Scientific Handbook of Metamaterials and Plasmonics*. World Scientific Handbook of Metamaterials and Plasmonics. doi:10.1142/10642-vol1
- [4] Tune, D. D., & Shapter, J. G. (2013). The potential sunlight harvesting efficiency of carbon nanotube solar cells. *Energy & Environmental Science*, 6(9), 2572. doi:10.1039/c3ee41731j
- [5] Neumann, O., Urban, A. S., Day, J., Lal, S., Nordlander, P., & Halas, N. J. (2012). Solar Vapor Generation Enabled by Nanoparticles. *ACS Nano*, 7(1), 42-49. doi:10.1021/nn304948h
- [6] Zhang, C., Wang, S., Chen, Z., Fan, J., Zhong, Z., & Zhang, X. (2019). A tungsten nitride-based degradable nanoplatform for dual-modal image-guided combinatorial chemo-photothermal therapy of tumors. *Nanoscale*, 11(4), 2027-2036. doi:10.1039/c8nr09064e
- [7] Ishii, S., Sugavaneshwar, R. P., & Nagao, T. (2016). Titanium Nitride Nanoparticles as Plasmonic Solar Heat Transducers. *The Journal of Physical Chemistry C*, 120(4), 2343-2348. doi:10.1021/acs.jpcc.5b09604
- [8] Guler, U., Suslov, S., Kildishev, A. V., Boltasseva, A., & ShalaeV, V. M. (2015). Colloidal Plasmonic Titanium Nitride Nanoparticles: Properties and Applications. *Nanophotonics*, 4(3), 269-276. doi:10.1515/nanoph-2015-0017
- [9] Ishii, S., Sugavaneshwar, R. P., Chen, K., Dao, T. D., & Nagao, T. (2015). Sunlight absorbing titanium nitride nanoparticles. 2015 17th International Conference on Transparent Optical Networks (ICTON). doi:10.1109/icton.2015.7193490
- [10] Voyager - Spacecraft - Radioisotope Thermoelectric Generators (RTG). (n.d.). Retrieved from <https://voyager.jpl.nasa.gov/mission/spacecraft/instruments/rtg/>
- [11] Innovative Interstellar Probe. (n.d.). Retrieved from <http://interstellarexplorer.jhuapl.edu/index.php>
- [12] Jaziri, N., Boughamoura, A., Müller, J., Mezghani, B., Tounsi, F., & Ismail, M. (2020). A comprehensive review of Thermoelectric Generators: Technologies and common applications. *Energy Reports*, 6, 264-287. doi:10.1016/j.egy.2019.12.011
- [13] Islam, M. F., & Johnston, R. B. (2006). Household pasteurization of drinking-water: the chulli water-treatment system. *Journal of health, population, and nutrition*, 24(3), 356–362.
- [14] Vieira, M., Pereira, J., & Lucher, C. (2008). Pasteurization with a Plate Heat Exchanger. *Experiments in Unit Operations and Processing of Foods*, 113-123. doi:10.1007/978-0-387-68642-4_15

[15] Fewtrell, L., Kaufmann, R. B., Kay, D., Enanoria, W., Haller, L., & Colford, J. M. (2005). Water, sanitation, and hygiene interventions to reduce diarrhoea in less developed countries: A systematic review and meta-analysis. *The Lancet Infectious Diseases*, 5(1), 42-52. doi:10.1016/s1473-3099(04)01253-8