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Dye-Sensitized Titanium Dioxide Photocatalysis – a Novel Solution for Personal Air Filtration

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ABSTRACT

Ambient air pollution is attributed to 4.2 million deaths annually and accounts for nearly 30% of the global top 6 leading causes of death. According to the World Health Organization, 99% of the world population lives in areas with dangerously high levels of pollutants, most being in low-income countries. Although current solutions exist, none are both cheap and efficient at filtering out Particulate Matter (PM) and Volatile Organic Compounds (VOCs) outdoors. Photocatalysis, a process known to occur in photovoltaic semiconductors, has proven to degrade pollutants, but only under Ultraviolet Light, which accounts for just 3-5% of sunlight. In this experiment, the dye-sensitization method was tested to increase the filtration efficiency of a semiconductor, Titanium Dioxide (TiO_2), under visible light. The dyes tested were Flavonoids, which are natural antioxidants found in fruits that have also been previously used to improve the efficiency of photovoltaic electricity production, from Blackberry, Blueberry, Raspberry and Parsley. Each filter was coated in a solution of Dye-sensitized TiO_2. The filters' efficiencies were then evaluated by passing contaminated air through each filter into a testing chamber where the resulting quality of the air was analyzed with an air quality monitor. The Parsley-TiO_2 filter was the most efficient, removing nearly all VOCs, $PM_{2.5}$, PM_{10} and PM_1, and the estimated cost to create the filter was approximately $2. This filter could save millions of lives, due to its low cost of production, and could potentially be applied in impoverished areas of polluted cities like Beijing and New Delhi.

Introduction

Air pollution is directly attributed to causing 7 million deaths worldwide. 4.2 million of these deaths were due to ambient air pollution (AAP), most (91%) of which occurs in low and middle-income nations. This means that air pollution could ultimately be ranked as the 2nd leading cause of death globally and ambient air pollution alone would rank 3rd. Moreover, according to the World Health Organization (WHO, 2018), approximately 91% of the global population lived in areas containing levels of air pollutants beyond WHO limits in 2016. The current COVID-19 pandemic also warrants personal air filtration as one of the necessary steps to reduce the spread of the virus.

The International Agency for Research on Cancer (IARC, 2013 as cited in WHO, 2018) found that particulate matter (PM) is the most dangerous component of air pollution, the most dangerous of which is PM of 10, 2.5, and 1 micron in diameter (PM_{10}, $PM_{2.5}$, & PM_1). Volatile Organic Compounds (VOCs) are also known to be a common pollutant and are carcinogenic when inhaled.

Present Solutions

Current solutions are masks that are either expensive (Verge, 2020) or ineffective at filtering out PM from the air. 91% of deaths worldwide from AAP are in low to middle income countries in which the citizens cannot afford to buy such masks and die of diseases caused by air pollutants. Another common issue is that most filters/masks are non-reusable, so even the most sophisticated masks, such as the recently known N95 mask, would be costly to use long-term.

However, Photocatalytic Oxidation (Photocatalysis), a reaction known to occur in certain semiconductors, has been exploited in indoor and industrial air filtration (Hay et al., 2015) as well as water purification (Belver et al., 2018) (Kuvarega & Mamba, 2016) using Titanium Dioxide (TiO_2) Nano-powder. Titanium Dioxide is also widely used as an ingredient in cosmetic products such as sunscreens and lotions (Made Safe, 2018), so the material has been proven to be nontoxic for human use.

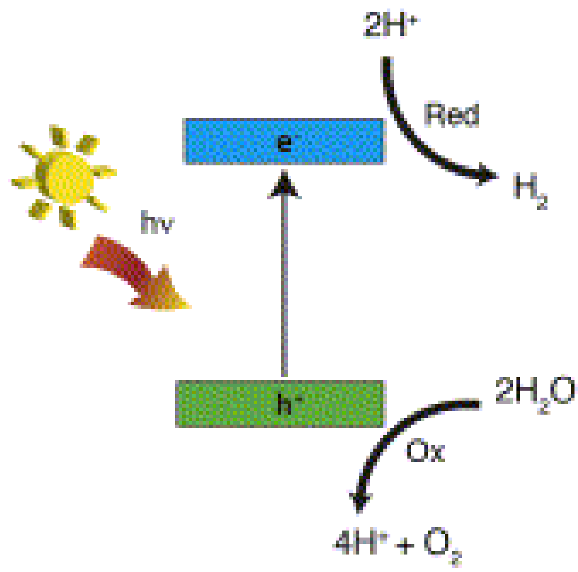

Figure 1. Schematic of Photocatalysis (Laursen & Poudyal, 2015)

Photocatalysis

Photocatalysis or Photocatalytic Oxidation is a process in which light energy is used to accelerate a pair of chemical reactions, and it only occurs on the surface of semiconductors. When light energy is absorbed into the semiconductor molecule, the energy causes the electrons on the valence band (VB) to gain enough energy to jump to the conduction band (CB), leaving positive holes (H^+) in its place. This energy is known as band gap energy (E_{bg}) and varies between different molecules. The band gap energy between VB and CB in TiO_2 matches the energy in Ultraviolet (UV) Light. Now, the excited electron reacts with water molecules in the air to form Hydroxyl Radicals and with oxygen molecules to form Superoxide Radicals. These radicals then react with pollutants in the air to reduce them into harmless compounds. During this reaction, the activated holes simultaneously oxidize pollutants and convert them into harmless compounds as well. The electrons gained from oxidation are used to fill in the holes and thus allow the reduction-oxidation (redox) reaction to occur again. Also, since this reaction does not actually "filter" pollutants, but rather degrades them, any mask or filter which utilizes this process would almost never need to be cleaned manually. A diagram of this reaction is presented in Figure 1.

Dye-Sensitized Photocatalysis

Although photocatalytic oxidation in TiO_2 may be the best option for indoor air filtration, the photocatalyst's efficacy would be much lower during outdoor, personal usage as UV Light only accounts for 3% of the sunlight that passes through Earth's atmosphere (Lucas, 2017). However, processes such as doping and dye-sensitizing are being explored and have shown to increase the efficiency of photocatalysis in TiO_2 by possibly 200% (Archana et al., 2018) by allowing the reaction to occur in visible light. Unlike doping, which typically requires the use of other semiconductors or metals, sensitizing only requires the use of dyes and is just as efficient.

Proposed Solution

The goal of this project was to design and test novel and affordable Dye-Sensitized TiO_2 filters for combating the effects of outdoor air pollution as very few studies have been conducted on personal outdoor air filtration. The effect of four Dye-Sensitized TiO_2 filters on the amount of PM and VOCs filtered was analyzed to determine the most effective and low-cost filter. Flavonoids from Parsley and Anthocyanin from Blackberry, Raspberry, and Blueberry were tested as different sensitizers of TiO_2. Anthocyanin is a dye of the flavonoid classification and is found in most fruits and vegetables. It has recently gained attention for being an antioxidant and having anticancer properties, but it has also been tested as a potential sensitizer (Dil et al., 2019). It was hypothesized that the Parsley-TiO_2 filter would be the most efficient at removing pollutants in this study.

Materials, Methods, and Procedures

Materials

The following were the materials used to conduct this experiment.

- DM106A Air Quality Monitor – used to analyze air quality in terms of PM 2.5, PM 10, PM 1, and VOCs
- DG™ Hardware Filter Masks – base filter for coating with TiO_2 and Flavonoids
- Titanium Dioxide (99% Anatase, 100nm) from US Research Nanomaterials – photocatalyst utilized in this experiment
- Plastic Container – contains smoke to use as pollutant
- Incense Sticks – creates the smoke for this experiment
- 7 Large Ziploc Slider Zip Plastic Bags – contains the filter and air quality monitor to analyze air
- 15 Blueberries for Anthocyanin – contains anthocyanin
- 15 Blackberries for Anthocyanin – contains anthocyanin
- 15 Raspberries for Anthocyanin – contains anthocyanin
- 15 grams of Parsley for Chlorophyll/Flavonoids – contains flavonoids
- 40 ml Rubbing Alcohol – used to extract anthocyanin/flavonoids
- 4 Coffee Filters – used for filtering extracts
- 1 Roll Masking tape – used to attach filter to Ziploc Bags
- Pestle and Mortar – used to mash fruits and parsley
- 5 Plastic Containers – used to store anthocyanin/flavonoid extracts
- 4 Small Ziploc Plastic Bags – used for mashing fruits and parsley

Methods for Preparing Materials

Extracting Anthocyanin and Flavonoids

First, 12 grams (g) each of Blackberry, Blueberry, Raspberry, and Parsley were mashed into pastes in separate small Ziploc Plastic Bags with 5 milliliters (ml) of rubbing alcohol. The resulting emulsions were then strained through coffee filters to isolate the anthocyanin/flavonoid and stored in small plastic containers.

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Creating 5% Dye-Sensitized TiO_2 Solutions

The 5% Dye-Sensitized TiO_2 solutions were prepared by combining 10ml of each Anthocyanin/Flavonoid extract and 0.5g of Titanium Dioxide Nanopowder. A control TiO_2 solution was prepared by mixing 0.5g of Titanium Dioxide Nanopowder and 10ml rubbing alcohol. 10ml of rubbing alcohol was used as a blank control.

Coating and Preparing the Filters

Six base filters were labeled with one of the four Dye-Sensitized filter names along with one control (TiO_2 only) and one blank (rubbing alcohol only). The filters were then dipped in a bowl containing the corresponding solution to ensure an even coating as well as consistency between the filters. The coated filters were air dried for 5-10 minutes before being dried in an oven for one hour at 150° Fahrenheit for the nano-sized pores to open (Figure 2).

Figure 2. Air-dried Dye-Sensitized TiO_2 filters

Preparing the Testing Chambers

The testing chambers were created by cutting off a corner from each of the large Ziploc Bags and taping one of the filters to the inside of the open corner of each bag with the masking tape. The testing chambers were made airtight by sealing with a masking tape to avoid air from leaking in during the experiment.

Experimental Procedure

Two types of chambers were created – six testing chambers, mentioned above, and one smoke chamber which was a plastic container with smoke from a burning incense stick. The filters' efficiency was tested by covering the opening of the smoke chamber with the filter-covered corner of one of the testing chambers. All rising smoke had to pass through the filter and into the bag, where an air quality monitor was placed to analyze the resulting air quality (Figure 3). This process was repeated with each filter including the control and blank filters. Three trials were completed. The air quality was measured in VOCs (μg/m^3) as well as PM 1, PM 2.5, and PM 10 (μg/m^3). The initial concentration of pollutants inside the container was recorded before each filter was tested to determine the quantity of pollutants that were removed.

Figure 3. Horizontal view of experimental setup with smoke chamber and testing chamber

Results

The raw data collected from the experiment was in the form of the concentrations of pollutants in the unfiltered and filtered air, and thus the following formula was used to calculate the percentage of each type of pollutant that was removed. **Equation 1:** Formula to determine the filtration efficiency of each filter

$$100 - \left(\left[\frac{Concentration\ of\ Pollutant\ in\ Filtered\ Air}{Concentration\ of\ Pollutant\ in\ Unfiltered\ Air}\right] * 100\right)$$

The formula above divides the concentration of pollutants in the testing chamber by the concentration of pollutants in the smoke chamber to return a decimal. That decimal is then multiplied by 100 to attain the percentage of pollutants that were not removed by the filter. Finally, the resulting percentage is subtracted from 100 to reveal the percentage of contaminants removed. This formula was applied to all the raw data to find the degradation efficiencies of each filter during each trial. The results were put into tables and then averaged to find the mean degradation efficiency of each filter for each pollutant. The results from the PM 2.5 trials and the VOC trials can be seen in Tables 1 and 2, respectively.

Table 1. Filtration efficiencies of each filter for PM 2.5 during each trial

Filters Tested	Trial 1 Removal Efficiency (%)	Trial 2 Removal Efficiency (%)	Trial 3 Removal Efficiency (%)	Mean (SD) Removal Efficiency (%)
Io filter (Negative Control)	0.0	0.0	0.0	0.0 (0.0)
lank filter (Control 1)	16.1	9.4	31.6	19.1 (11.4)
iO2 only filter (Control 2)	23.5	15.3	52.0	30.3 (19.2)
aspberry + TiO2 filter	34.8	43.4	57.9	45.3 (11.6)
lackberry + TiO2 filter	55.2	31.7	56.5	47.8 (13.9)
lueberry + TiO2 filter	34.2	20.1	55.9	36.7 (18.0)
arsley + TiO2 filter	68.8	66.2	68.9	67.9 (1.5)

The tabled results from the PM 10 and PM 1 trials are not displayed here. As seen in the tables, the average PM 2.5 and VOC removal efficiencies of the filters coated in a Dye-Sensitized TiO_2 solution were significantly higher than the controls. Specifically, the filter coated in Parsley Flavonoids and TiO_2 was the most efficient at removing pollutants. This pattern was also apparent in the results from the PM 10 and PM 1 trials.

Statistical Analysis

A single factor ANOVA test revealed that the PM 2.5 filtration efficiency was significantly different between filters ($p = 0.002$). The PM 2.5 filtration efficiency of each of the Dye-sensitized filters were compared with the TiO_2 filter using a two-sample t-test and the Parsley-TiO_2 filter was the most efficient filter ($p = 0.07$). A single factor ANOVA test revealed that the VOC filtration efficiency was significantly different between filters ($p < 0.01$). The VOC filtration efficiency of each of the Dye-sensitized filters were compared with the TiO_2 filter using a two-sample t-test and the Parsley-TiO_2 filter was the most efficient filter ($p = 0.27$).

Table 2. Filtration efficiencies of each filter for VOCs during each trial

Filters Tested	Trial 1 Removal Efficiency (%)	Trial 2 Removal Efficiency (%)	Trial 3 Removal Efficiency (%)	Mean (SD) Removal Efficiency (%)
No filter (Negative Control)	0.0	0.0	0.0	0.0 (0.0)
Blank filter (Control 1)	10.0	42.9	89.8	47.6 (40.1)
TiO2 only filter (Control 2)	89.5	70.5	91.9	84.0 (11.7)
Raspberry + TiO2 filter	93.4	91.1	94.9	93.1 (1.9)
Blackberry + TiO2 filter	94.9	90.3	94.8	93.4 (2.7)
Blueberry + TiO2 filter	94.9	88.9	94.8	92.9 (3.4)
Parsley + TiO2 filter	96.0	92.1	94.9	94.3 (2.0)

Two types of graphs were used to visualize the data from the experiment, Bar Graphs and Box Plots. The data from the tables was used to create a bar graph to illustrate the variances between the average pollutant removal efficiencies of each filter. The Bar Graphs from the PM 2.5 and VOC trials are shown in Figures 4 and 5, respectively.

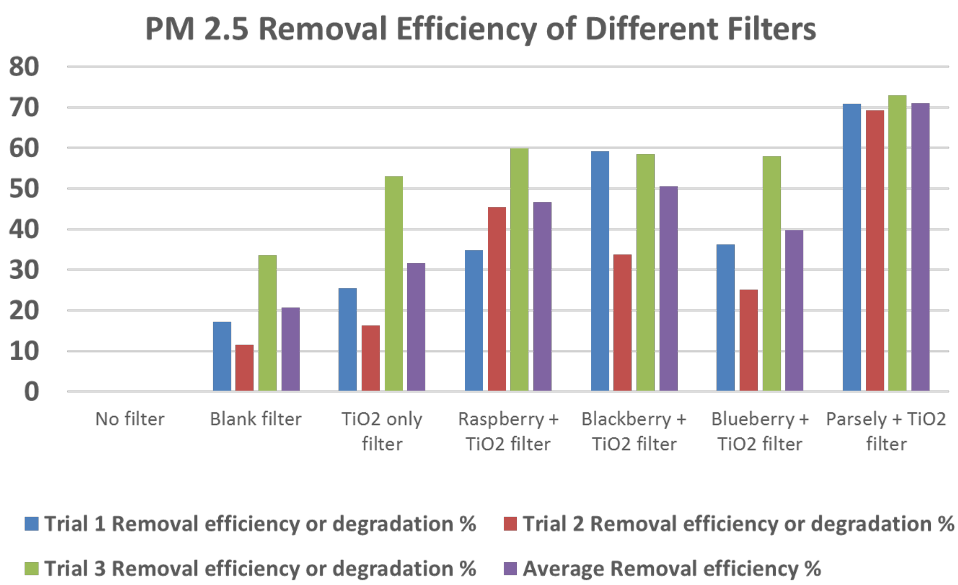

Figure 4. Graph comparing the PM 2.5 removal efficiencies of each filter

The graph above provides a comparison of each filter and helped determine that the filter coated in Parsley Flavonoids and TiO_2 was the most efficient at removing pollutants. The graphed results of the PM 10 and PM 1 trials are not displayed here, but the Parsley-TiO_2 filter was the most efficient in those trials as well.

A box plot was used to show variances in the PM 2.5 trial results for each filter, this can bee seen in Figure 6. The shaded regions depict the range of the results and the black lines in the middle of the box display the median filtration efficiency for the filter.

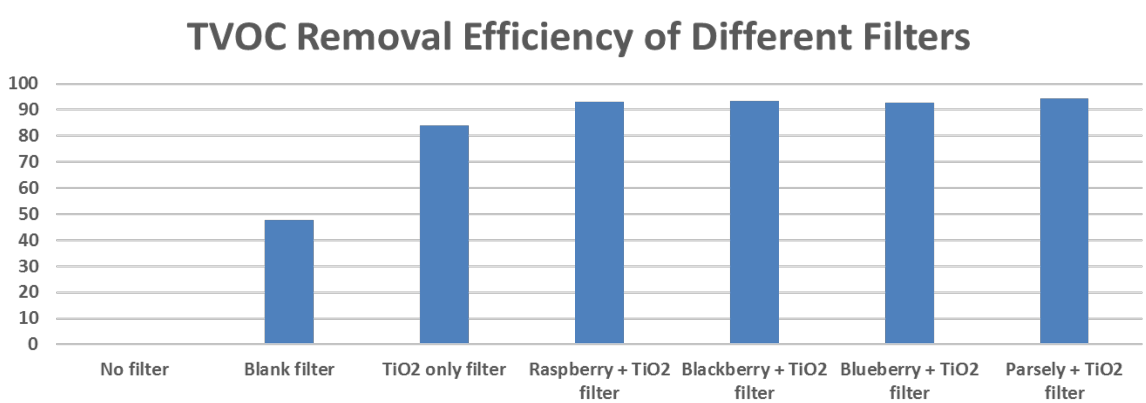

Figure 5. Graph comparing the VOC removal efficiencies of each filter

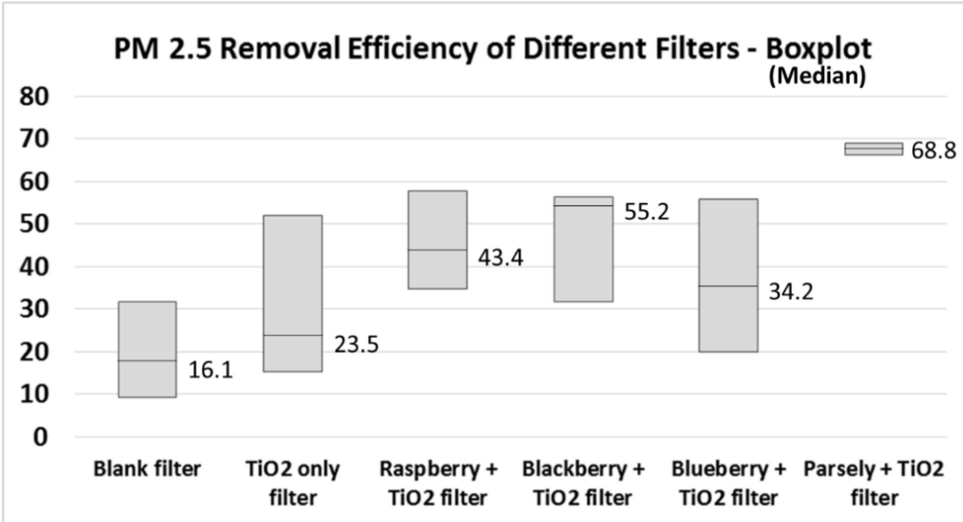

Figure 6. Box plot displaying variances in the PM 2.5 trial results for each filter.

The compact shaded region of the results for the Parsley-TiO_2 filter show not only that the filter was the most effective at removing PM 2.5, but also that this result was consistent across all three PM 2.5 trials.

Discussion and Conclusions

It was first hypothesized that the filter coated in the Parsley-TiO_2 solution would be the most effective at removing pollutants. This hypothesis was proven to be true based on the results from the PM 2.5, PM 10, PM 1, and VOC trials. The Parsley-TiO_2 filter had an average PM 2.5 removal efficiency of 67.9% and an average VOC removal rate of 94.3%. Broadly, the Dye-Sensitized TiO_2 filters were much more effective than the blank (control) filter and only cost 1-2$ to make each filter. This answers the research question and fulfills the goal of this experiment, creating and testing an efficient and low-cost personal outdoor air filter. However, as this experiment was conducted indoors with little exposure to sunlight, and therefore UV Light, the potential maximum efficiency of the filters was not exhibited fully. If this innovative solution were used in the real world, the filters' efficiency would have been greatly increased as natural sunlight has also shown to be nearly 100 times as intense as indoor light (Lanca et al., 2019).

For the dye-sensitization to work, dye molecule usually requires less band gap energy between its HOMO (Highest Occupied Molecular Orbital) and its LUMO (Lowest Unoccupied Molecular Orbital) than there is between the VB and CB of TiO_2. It is due to this that the electrons in the dye molecule can get excited and jump to the LUMO in the presence of visible light even though photons contain less energy than UV Radiation. From there, the activated electrons are transferred to the TiO_2 molecule to complete the reduction reaction of pollutants. While the electrons on the HOMO jump to the LUMO and reduce pollutants, they leave holes in their place, which are then able to oxidize pollutants. Visible light accounts for approximately 44% of sunlight (Dastrup), so Dye-Sensitizing can greatly increase the efficiency of photocatalysis by converting TiO_2 into a heterogeneous photocatalyst, which has been explored for water filtration (Youssef et al., 2018). A diagram of Dye-Sensitized Photocatalysis can be seen in Figure 7.

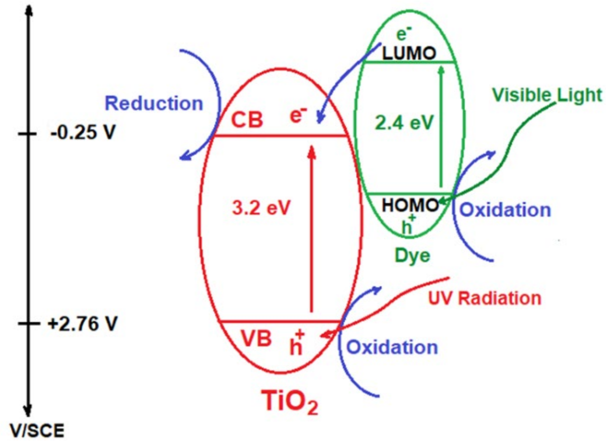

Figure 7. Schematic of Dye-Sensitized Photocatalysis in TiO_2 (Zyoud et al., 2018)

In conclusion, this project has shown the novel, affordable, and effective use of Dye-Sensitized TiO_2 filters in outdoor personal air filtration. Although the filters used in this experiment were not 100% effective, the efficiency of such filters could near such levels in real-world application. Further studies could be done to explore the activation of Photocatalysis in Infrared Light (Chatti et al., 2016), which would greatly increase the efficiency of the reaction. Also, TiO_2 air purification has shown potential uses for removing COVID-19 (Mathur, 2020) and the photocatalyst also has disinfectant properties (Talebian et al., 2020), which would allow the filters explored in this experiment to possibly be used as PPE for Medical Workers and Citizens in the battle against COVID-19.

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References

Archana, J., Harish, S., Kavirajan, S., Navaneethan, M., Ponnusamy, S., Shimomura, M., … Hayakawa, Y. (2018, February 6). *Ultra-fast photocatalytic and dye-sensitized solar cell performances of mesoporous TiO2 nanospheres*. Applied Surface Science. https://doi.org/10.1016/j.apsusc.2018.01.105.

Belver, C., Bedia, J., Gómez-Avilés, A., Peñas-Garzón, M., & Rodriguez, J. J. (2018, November 23). *Semiconductor Photocatalysis for Water Purification*. Nanoscale Materials in Water Purification. https://doi.org/10.1016/B978-0-12-813926-4.00028-8.

Chatti, M., Adusumalli, V. N. K. B., Ganguli, S., & Mahalingam, V. (2016, July 4). *Near-infrared light triggered superior photocatalytic activity from MoS2–NaYF4:Yb3+/Er3+ nanocomposites*. Dalton Transactions. https://pubs.rsc.org/en/content/articlelanding/2016/dt/c6dt02548j.

Dastrup, A. *Physical Geography*. Lumen. https://courses.lumenlearning.com/geophysical/chapter/energy-from-the-sun/.

Dil, M. A., Haghighatzadeh, A., & Mazinani, B. (2019, July 29). *Photosensitization effect on visible-light-induced photocatalytic performance of TiO2 /chlorophyll and flavonoid nanostructures: kinetic and isotherm studies*. ResearchGate. https://www.researchgate.net/publication/334747403_Photosensitization_effect_on_visible-light-induced_photocatalytic_performance_of_TiO2_chlorophyll_and_flavonoid_nanostructures_kinetic_and_isotherm_studies.

Hay, S. O., Obee, T., Luo, Z., Jiang, T., Meng, Y., He, J., … Suib, S. (2015, January 14). *The viability of photocatalysis for air purification*. Molecules (Basel, Switzerland). https://dx.doi.org/10.3390/molecules20011319.

Kuvarega, A. T., & Mamba, B. B. (2016, August 24). *Photocatalytic Membranes for Efficient Water Treatment*. IntechOpen. http://dx.doi.org/10.5772/62584.

Lanca, C., Teo, A., Vivagandan, A., Htoon, H. M., Najjar, R. P., Spiegel, D. P., … Saw, S.-M. (2019, July 18). *The Effects of Different Outdoor Environments, Sunglasses and Hats on Light Levels: Implications for Myopia Prevention*. Translational vision science & technology. https://www.ncbi.nlm.nih.gov/pmc/articles/PMC6656201/.

Laursen, S., & Poudyal, S. (2015, June 5). *Photo- and Electro-Catalysis: CO2 Mitigation Technologies*. Novel Materials for Carbon Dioxide Mitigation Technology. https://doi.org/10.1016/B978-0-444-63259-3.00008-2.

Lucas, J. (2017, September 15). *What Is Ultraviolet Light?* LiveScience. https://www.livescience.com/50326-what-is-ultraviolet-light.html.

Mathur, G. (2020, November 9). *Ultraviolet and Titanium Dioxide Based Photocatalysis HVAC System to Eliminate COVID-19 for Occupant's Safety & Health in Automobiles - SAE Video*. SAE International. https://www.sae.org/news/video/content/12867/.

The Scoop on Titanium Dioxide in Cosmetics. MADE SAFE. (2018, April 13). https://www.madesafe.org/the-scoop-on-titanium-dioxide-in-cosmetics/.

Talebian, S., Wallace, G. G., Schroeder, A., Stellacci, F., & Conde, J. (2020, July 29). *Nanotechnology-based disinfectants and sensors for SARS-CoV-2*. Nature News. https://www.nature.com/articles/s41565-020-0751-0.

Wetsman, N. (2020, January 7). *Atmos Faceware makes clean air an expensive accessory*. The Verge. https://www.theverge.com/2020/1/7/21050763/atmos-faceware-climate-change-technology-disaster-capitalism-price.

World Health Organization. (2018, May 2). Ambient (outdoor) air pollution. https://www.who.int/news-room/fact-sheets/detail/ambient-(outdoor)-air-quality-and-health.

Youssef, Z., Colombeau, L., Yesmurzayeva, N., Baros, F., Vanderesse, R., Hamieh, T., … Acherar, S. (2018, June 6). *Dye-sensitized nanoparticles for heterogeneous photocatalysis: Cases studies with TiO2, ZnO, fullerene and graphene for water purification*. Dyes and Pigments. https://doi.org/10.1016/j.dyepig.2018.06.002.

Zyoud, A. H., Saleh, F., Helal, M. H., Shawahna, R., & Hilal, H. S. (2018, May 30). *Anthocyanin-Sensitized TiO2 Nanoparticles for Phenazopyridine Photodegradation under Solar Simulated Light*. Journal of Nanomaterials. https://www.hindawi.com/journals/jnm/2018/2789616/.