

The Visible Photocatalytic Performance of Nano TiO₂ and its Application for the Photodecomposition of Methanal

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Abstract: This project was conducted to investigate how to maximise the efficiency for photodecomposition based methanal scrubbers. The project focuses on using titanium dioxide Nanoparticles (NPs) in combination with chlorophyll (Chl) to achieve photodecomposition. In order to explore different factors that can affect the decomposition rate, namely, size of photocatalyst, temperature and phase of photocatalyst. It was found that a setup with solid supported TiO₂ – Chlorophyll Nanoparticles is superior at decomposing methanal. Although inferior in terms of decomposition rate, TiO₂ – Chlorophyll Nanoparticles suspended in 6:4 DMSO/H₂O also has compelling advantages, specifically enforced contact between catalyst and methanal, and a higher water source to support the formation of free radicals.

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1 Introduction

1.1 Problem Addressed

1.1.1 Introduction to Methanal/HCHO/formaldehyde

Methanal, also named formaldehyde is a natural-occurring organic compound with the formula HCHO. Formaldehyde is an important precursor to many other materials and chemical compounds. It is mainly used in the production of industrial resins, such as for particle board and coatings. Furthermore, methanal is extensively used in construction work

and furniture.

1.1.2 Hazards of Methanal in Air

People are exposed primarily by inhaling formaldehyde gas or vapour from the air or absorbing liquids containing formaldehyde. The worker who produces formaldehyde or products that contain formaldehyde—as well as laboratory technicians, certain health care professionals, and mortuary employees—may be exposed to higher levels of formaldehyde than the general public. Formaldehyde is widely used in adhesives because of its extremely low cost and its volatility. Because of its economic benefits, the use of formaldehyde is almost unavoidable.

Moreover, methanal is a known carcinogen. Studies of workers such as industrial workers and embalmers, who were exposed to high levels of formaldehyde, have found that formaldehyde causes myeloid leukaemia and rare cancers, including cancers of the paranasal sinuses, nasal cavity, and nasopharynx.

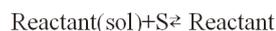
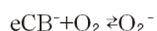
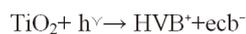
1.2 Current Methods and the Drawbacks

The current methods used are mainly of two types: Photocatalytic decomposition and adsorption.

Photocatalytic decomposition

By the absorption of UV light, the electron arrangement may show gaps for the excited electrons to leap through electronic shells. By forming electron-hole pair to react with water, hydroxide ion and dissolved oxygen which later react with methanal to form carbon dioxide and water, the harm to the human body is neutralized.

Methanal is catalytically decomposed as described below:



1.2.1 Drawbacks

TiO₂ itself has a large band gap, ca. 3.2 eV, which limits its absorption of UV light range that accounts only for ca. 5% of the solar spectrum energy. Also, without any doping or sensitising, the rate of decomposition will be very slow.

1.2.2 Absorption

The absorption of Methanal can be achieved through the following procedures^[1].

- (1) Enter the gaseous part of the two-phase stream at the bottom of the Column
- (2) The stream passes upward through two beds
- (3) Filled with modern high-performance Pall-ring like packing
- (4) The tail is partly recirculated to the reactor
- (5) Makeup water enters at the top of the column and flows downward
- (6) Taking up heat and absorbing formaldehyde and water from the gas stream
- (7) Each of the beds had an external liquid recirculation with heat exchangers
- (8) The absorber is equipped with a partial draw off tray to provide a buffer for the upper liquid recirculation pump
- (9) The liquid layer is for the lower liquid recirculation pump

The industrially important process of formaldehyde absorption in water constitutes a case of multicomponent mass transfer with multiple reactions and considerable heat effects. A stable solution algorithm is developed to simulate the performance of industrial absorbers for this process using a differential model. Good agreement with practice was achieved. Using the model, the conditions of one of the absorbers of Dynea B.V. were optimized, leading to considerable methanol savings.

1.2.3 Methanal absorption device

Drawbacks: The drawbacks of the absorption method are that it is reversible, meaning that the adsorbed methanal can escape from the system. Since the methanal is ultimately not consumed or destroyed, the methanal absorbed may still pose a health risk. The

absorption material also needs to be further processed to rid of methanal.

1.3 In Correlation with Group 6 Elements

The properties of oxygen are extensively investigated in this project. Being the 16th element in the periodic table, oxygen is an extremely electronegative atom, ranking second on the Pauling scale of electronegativity. In the world of inorganic chemistry, oxygen is most notably known for being a strong oxidising agent, hence giving the name of 'oxidation'. The role of oxygen is even greater in organic chemistry – bonding to oxygen in different ways give rise to different functional groups, each attributing to chemical characteristics of an organic molecule. From alcohols, aldehydes to ketones, the positioning of the oxygen atom is the key to understanding its chemical properties.

In our project, we focused on the carbonyl group (C=O), more specifically aldehydes in hope to investigate their toxicity and ways to eliminate this imminent health hazard. Out of the many aldehydes, methanal is the simplest molecule of its homologous series, and is also the most widely industrially used aldehyde. Due to this, we decided to primarily focus on methanal, whilst also acknowledging that the method of ridding HCHO using photodecomposition can also apply to longer chain aldehydes.

From the point of molecular geometry, methanal contains one SP² hybridised oxygen atom. As oxygen is a very electronegative element, the C=O bond is polarised, and the electron cloud in the HCHO molecule is distorted towards the oxygen atom. Along with the two paired electrons surrounding the oxygen atom, methanal molecules is able to form relatively strong hydrogen bonds, explaining its solubility in water.

In the decomposition of methanal, the metal oxide titanium dioxide is selected because of its photocatalytic capabilities. For the chemical formula, titanium dioxide can exist in three forms, namely rutile, anatase and brookite. Each form of the oxide has a unique crystalline structure, and thus each having slightly different properties. This ability of forming several stable crystalline structures is called polymorphism.

Polymorphism in inorganic salts is almost exclusive to oxides, more specifically binary metal oxides. Polymorphic oxides include CrO₂, Cr₂O₃, Fe₂O₃,

Al₂O₃, Bi₂O₃, TiO₂, SnO₂, ZrO₂, MoO₃, WO₃, In₂O₃.

- (1) Metal oxides
- (2) Phase
- (3) Conditions of pressure and temperature
- (4) Structure/Space Group
- (5) TiO₂
- (6) Rutile
- (7) Ambient conditions
- (8) Rutile-type Tetragonal
- (9) Anatase
- (10) Above 1073 K
- (11) Tetragonal (I41/amd)
- (12) Brookite
- (13) High pressure phase
- (14) Orthorhombic (Pcab)

1.4 Various crystalline structures of titanium dioxide

We have used P-25 TiO₂, which is a blend of pure anatase and rutile particles in a ratio of 3:1 since P-25 titanium dioxide is proven to be most effective serving as a photocatalyst^[2].

Oxygen compounds can also form a series known as Reactive Oxygen Species (ROS). These include peroxides, superoxide, radicals, singlet oxygen and alpha-oxygen. These species easily have a stronger oxidising power than O₂ oxygen gas. In light of its high reactivity, our project takes advantage of the reactive oxygen radicals, namely the superoxide radical (O²⁻) and the hydroxyl radical (OH). By synthesising radicals in a controlled manner, our device can rapidly oxidise methanal vapour in air into harmless carbon dioxide gas.

When TiO₂ is sensitized with a dye, and placed under radiation from light, an electron is promoted from the TiO₂'s valence band to its conduction band, leaving behind a hole in the valence that offers strong oxidizing power. After, the hole is quenched by electrons from water or methanal, generating free radicals, namely hydroxyl radicals and methanal radicals, which then can be used in other chain reactions. Types of Reactive oxygen species (<http://www.vivo.colostate.edu/hbooks/pathphys/topics/radicals.html>)

2 Project Approach

2.1 Determination of Methanal Content by Titration

Methanal content in an aqueous solution was

determined by the sodium sulphite reduction titration method. Numerous methods of titration was experimented, which is by the redox titration of methanal. The titration methods included titration with acidified potassium permanganate, bromine water, back titration using ferroin indicator, and iodometric titration.

Titration using MnO₄⁻ solution (left), Bromine water (centre), ferroin indicator (right)

2.1.1 Titration Procedure

A standardised 0.150 M Sodium Sulphite solution was prepared.

(1) 5.00 cm³ sodium sulphite solution was added to test tubes

(2) 2 drops of 1% phenolphthalein were added to the mixture.

(3) The solution was added 0.100 M sulphuric acid dropwise until the solution turns colourless.

(4) 2.00 cm³ of aqueous methanal solution 0.36% in DMSO was added to the test tube and was left to react for 15 min.

(5) 0.100 M sulphuric acid was added to the mixture dropwise via a syringe until the solution turns colourless.

2.1.2 Reaction Principle

Methanal reacts with sodium sulphite to produce OH ions, causing the solution to turn alkaline. The alkalinity can be determined via pH titration, with phenolphthalein being the pH indicator.

Methanal reacts with sodium sulphite in the following equation:



2.1.3 Relevance to the decomposition of HCHO

After researching an accurate method of determining the concentration of HCHO dissolved in water, we have successfully standardised the concentration of methanal solution. The significance of the standardisation process is to ensure, in all experiments, the amount of methanal within the system is held constant, and a drop of the peak concentration is entirely due to the decomposition effect.

Also, different concentrations of HCHO solution were placed in the DMSO/H₂O setup and allowed to equilibrate for 60 min. The [HCHO(g)] was measured using the methanal monitor, while [HCHO (aq/DMSO)] was measured using the titration method.

The two values were used to calculate the partition constant K_d in the following equation:

$$K_d = \frac{[\text{HCHO}(\text{aq/DMSO})]}{[\text{HCHO}(\text{g})]}$$

A setup determining the ratio between $\text{HCHO}(\text{g})$ and $\text{HCHO}(\text{aq/DMSO})$ have been created. In the set-up, a 30218 cm^3 rPET water bottle is used as the container 200 ml of deionized water is contained in a 354 cm^3 conical flask, set at the bottom of the rPET container, and an air pump is added to shorten time to reach the equilibrium, set at 9 $\text{cm}^3/\text{s}^{-1}$. A steel thermometer connected to the computer is used to record the temperature change every second. The temperature monitored closely to ensure there is no sudden change throughout the whole test. Then, a HCHO detector was set at the bottom of the container, as well as a fan beside the detector to ensure air circulation within the setup. After waiting 15 min for the temperature to reach a steady level, the setup is then sealed airtight by aluminum foil and plasticine right after the 2 cm^3 of formaldehyde solution (0.37% in DMSO) is added to the conical flask. After an hour, the formaldehyde detector showed no change in reading, thus the setup has reached its equilibrium. The conical flask is then taken out to titrate using the titration process previously shown in section

2.1.3 Titration Procedure

Calculations:

$$K_{\text{part}} = \frac{[\text{HCHO}(\text{aq dmsO})]}{[\text{HCHO}(\text{g})]}$$

$$[\text{HCHO}(\text{aq dmsO})] \approx [\text{HCHO}(\text{g})]$$

$$[\text{MHCHO}] = 2.9 \times 10^{-2} / 30 = 9.667 \times 10^{-4}$$

$$[\text{HCHO}(\text{g})] = 9.667 \times 10^{-4} / 10^3 = 9.667 \times 10^{-7} \text{ mol dm}^3$$

3 Result

At 60 minutes, the environmental HCHO concentration in the container is shown to be 0.29. After titrating imminently with 75 ml of the solution, we discover that the pOH is 6.89, and hydroxide ions are in 1.29×10^{-7} molarity. The equilibrium is found out as 1($\text{HCHO}(\text{aq/DMSO})$): 7.48837($\text{HCHO}(\text{g})$). The container and the whole setup.

3.1 Methanal Oxidation by Dye-sensitised TiO_2

3.1.1 Photocatalysis

Photocatalysts catalyse photoreactions. Photocatalysts are semi-conductors in which the valence band and conduction band are close to each other. The energy gap between the bands is called the band gap. Upon

radiation by light with energy corresponding to the band gap, an electron will be promoted from the valence band to conduction band. The electron is said to be excited and will either escape the photocatalyst or fall back to the valence band. A hole in the valence band is left behind and has strong oxidizing power.

3.1.2 Dye-sensitisation And the Properties of Dyes

As mentioned above in 2.3, TiO_2 alone is not efficient in decomposing methanal since only UV light is used for the decomposition reaction. Therefore, in order to increase the efficiency of a photodecomposition-based methanal decomposition device, the TiO_2 must be sensitized to utilise the visible light region as well. The principle of dye-sensitising is as follows:

- (1) A dye adsorbed on the TiO_2 absorbs photons with energy corresponding to the band gap.
- (2) The dye is excited from ground state to excited state. The excited electron is injected to the conduction band of TiO_2 and the dye is oxidized.
- (3) The hole is quenched by electrons from water or methanal.
- (4) Free radicals are generated.

3.2 Use of Photocatalysts

The effectiveness of the Chlorophyll- TiO_2 with solid support or in colloidal suspension is compared to determine which method can decompose methanal at a higher rate. In a colloidal suspension; Chlorophyll. Chlorophyll was extracted through the following process:

- (1) Fresh water-spinach leaves were rinsed and washed.
- (2) The leaves were dehydrated in an oven set at 200°C for 20 min.
- (3) The dehydrated leaves were crushed and rinsed using a glass mortar and pestle.
- (4) 4.000 g dehydrated leaves were put in a Soxhlet extractor.
- (5) 250.00 cm^3 hexane was poured into the Soxhlet extractor apparatus.
- (6) An electronic heater is turned on at 100°C and the mixture is refluxed for 3 h.

3.3 Soxhlet Extractor in Operation

Chlorophyll sensitised TiO_2

- (1) To a beaker, 2.000 g P25 TiO_2 was added.
- (2) 15 cm^3 chlorophyll solution was transferred into the beaker.
- (3) The beaker was sonicated for 5 min and was

left to stand afterwards.

(4) The upper hexane layer was decanted.

(5) The remaining hexane was boiled away under an electronic heat plate set at 80°C.

(6) The remaining solid was collected.

3.4 Complete Decolourisation of Chlorophyll Solution

3.4.1 Haem as Photocatalyst Dye

The possibility of using haem was also explored. Having a dark red colour complimentary to the green colour of chlorophyll, we suspect that haem can further expand the spectrum of light viable for photodecomposition. Haem is one of the many naturally occurring porphyrins, which are known to be photosensitive. Haem has a molecule structure very similar to chlorophyll and is relatively easy to be extract. It is mostly found in animal blood, muscle and tissue cell. In animals, the dye binds to globin molecules to form dark red haemoglobin in blood, giving blood its dark crimson colour. Furthermore, haem also binds with other proteins to form various proteins, including myoglobin, found in muscle cells. As a porphyrin molecule, haem is known to have photolytic abilities. Though its effect is not as significant as chlorophyll, haem is able to absorb wavelengths of light (green, blue light). When both are used in conjunction, a higher proportion of the solar spectrum can be utilised for photodecomposition, increasing the efficiency.

3.4.1 Comparing naturally occurring porphyrins. Chlorophyll (left), haem (middle), porphyrin (right).

Comparison of the absorption spectrums of Chlorophyll (left) and Haem (right).

Extraction of haemoglobin from fish blood^[3]

A haemolysate sample (0-2 cm³) is added to 1.8 cm³ of a solution containing 0-35 cm³ of 0.003 M zinc acetate and 1-45 cm³ of TRIS (trimethamine) buffer 0.1 M, pH 7.4. After mixing, the tubes are incubated for 30 min at 37°C. With haemoglobins an immediate flocculation is seen which has settled as a precipitate by the end of the incubation period.

3.4.2 Extracting haem from freshwater fish blood

Haemoglobin denaturation (<http://chemistry.elmhurst.edu/vchembook/568denaturation.html>).

Denaturation of proteins involves the disruption and possible destruction of both the secondary and

tertiary structures. Since denaturation reactions are not strong enough to break the peptide bonds, the primary structure (sequence of amino acids) remains the same after a denaturation process. Denaturation disrupts the normal alpha-helix and beta sheets in a protein and uncoils it into a random shape.

Denaturation occurs because the bonding interactions responsible for the secondary structure (hydrogen bonds to amides) and tertiary structure are disrupted. In tertiary structure there are four types of bonding interactions between "side chains" including: hydrogen bonding, salt bridges, disulfide bonds, and non-polar hydrophobic interactions. which may be disrupted. Therefore, a variety of reagents and conditions can cause denaturation. In our experiments, we used heavy metal salts and acetone.

Heavy metal salts disrupt the salt bridges in proteins, denaturing them. Salt bridges result from the neutralization of an acid and amine on side chains in the proteins. Heavy metal salts usually contain Hg⁺², Pb⁺², Ag⁺¹ Tl⁺¹, Cd⁺² and other metals with high atomic weights. Since the metal salts are ionic they disrupt salt bridges in proteins through a type of double replacement reaction where the positive and negative ions in the salt bridge change partners with the positive and negative ions in the heavy metal salt added. The reaction of a heavy metal salt with a protein leads to an insoluble metal protein salt.

Heavy metals may also disrupt disulfide bonds, which are formed by oxidation of the sulfhydryl groups on cysteine, holding different protein chains and loops within a single chain, because of their high affinity and attraction for sulfur, also leading to the denaturation of proteins.

When acetone is added to protein solution, the electronegative oxygen present in the ketone group (C=O) of acetone interrupts the intra H₂ bonds that stabilises the tertiary structure of any protein, breaking the structure of the protein and denaturing it.

Considering the numerous possible methods to denature the protein present in haemoglobin, 3 different solutions were tested, which were acetone, butan-2-ol, and zinc ions respectively, after which the mixture was then centrifuged to theoretically precipitate the exposed haem. In testing, it is found that zinc ions proved to be the most effective, consistently resulting in a high amount of haem precipitate, whilst acetone and butan-2-ol mixtures, under the same testing parameters and conditions,

returned inconclusive results, proving to be unreliable at best.

After further testing, it is found that zinc ions solution at a concentration of 0.1M returned the most precipitate, hence concluding that such a concentration is the most efficient at denaturing the protein in haemoglobin.

From the above graph, after 3 min in the centrifuge, the blood samples have been sedimented, the tubing is now named as A, B and C respectively from left to right.

Tubing A solution give out a dim pink colour, maintain a semi-gel like form and texture, the tubing B sedimented grey-blue solid particles in small amount which is believe as haemoglobin percipitation that have been denatured by copper ion, tubing C is containing a larger of amount of percipitation which give out while-grey when observe, also very pale pink solution, the solution have been identify as free haem(aq,acetone) and the residue is globin(s).

3.5 Phthalocyanines

Phthalocyanines only have a localised positive metal ion located in the centre of the molecule, and the rest of the molecule is mostly non-polar. As the phthalocyanines are aromatic molecules, the species exhibits strong pi-stacking, offering it strong thermal and photodegradative resistance. However, this property also makes phthalocyanines soluble in only a handful of solvents. To use it as a dye, we aim to bind the metal phthalocyanine to Titanium dioxide by polyaniline, a conductive polymer which is also known to have photocatalytic properties. Using the conductive nature of PANI, we hope to effectuate efficient electron hole transfer from the phthalocyanine dye to the TiO_2 .

The phthalocyanines are synthesized with phthalic anhydride as a starting material. The ring formation is catalyzed by ammonium heptamolybdate and chloride ions. The desired metal ion complex is formed by adding various metal chlorides i.e. zinc chloride, copper chloride, manganese chloride. The chelated phthalocyanine is created by not adding metal salts to the solid mixture. To test the purity of the compounds created, thin layer chromatography and UV-visible spectrum tests as well as quantitative solubility tests were conducted.

3.6 Absorption spectrums

3.6.1 Cu

To make the metal complex, anhydrous CuCl_2 , phthalic anhydride, urea, and ammonium molybdate are ground in a clean, dry mortar until it becomes homogeneous, then transferred to a 50 mL beaker and placed in a laboratory microwave oven (1000 W model) for 6 min. After each interval of 1 min, the microwave is stopped for 5 s (without opening its door) to allow for the removal of the generated ammonia fumes. The complex formed was washed with diluted hydrochloric acid followed by dilute sodium hydroxide and lastly acetone to remove all unreacted impurities. The remaining solid was purified by dissolving it in concentrated sulphuric acid and precipitating it out in water to obtain a pure compound. The isolated yield was calculated at 12%.

3.6.2 pTSA - PANI

para-toluene sulfonic acid (pTSA) is a common dopant to increase the conductivity of polyaniline (PANI).

pTSA is synthesised with toluene as starting material. Toluene is sulfonated with concentrated sulphuric acid heated under reflux for 6 hours.

50ml 2 M ammonium persulphate solution, acidified with 25ml 2M hydrochloric acid. Into the solution was added 2 g TiO_2 p25 NPs, sonicated and strongly stirred. With vigorous stirring under ice bath, 5 ml 2.1475 M Aniline hydrochloride was added with a syringe, drop-wise. Once all Aniline hydrochloride was added, the mixture was coated on metal sieves. The PANI- TiO_2 was made sure to be applied before complete polymerisation (solution is dark green in colour).

Preparation of polyaniline base (PANI base) The PANI salt prepared using the above procedure was dedoped using large excess of 0.5 M NH_4OH to obtain the corresponding base. The ammonia solution containing polyaniline-HCl salt was kept overnight under vigorous stirring and then filtered. The residue was washed with 500 mL of 0.5M NH_3 . The deep blue polyaniline emeraldine base was dried and collected.

Preparation of polyaniline salt doped with p-toluene sulfonic acid (PANI-pTSA).

Obtained PANI base was protonated with p-toluene

sulfonic acid 1.5 M solution in water. The protonation was achieved by extended mixing of PANI base and the acid solution for 24 hrs. The solution was filtered and a dark green emeraldine salt was obtained.

3.7 Solid supported catalysts

Preparation of TiO₂ suspension

(1) 2.000 g TiO₂ was weighed and transferred to a mortar.

(2) 25.0 cm³ ethane-1,2-diol was added to the mortar using a pipette.

(3) The contents are mixed thoroughly using a pestle.

(4) The contents are sonicated for 5 min.

Coating

(1) Stainless steel kitchen sieves are washed with ethanol to remove any oils present on the surface.

(2) Using a cotton bulb, the TiO₂ suspension was dabbed gently onto the wire gauze part of the sieve.

(3) The sieve was heated to remove all ethane-1,2-diol at 250°C.

(4) The TiO₂-coated sieve was left to cool and immersed into chlorophyll solution prepared.

(5) The sieve was left to stand until all the hexane evaporated away.

The same process was repeated on stainless steel wool scrubs to investigate how increasing the surface area of the catalyst will affect the decomposition rate. For the stainless-steel wool scrubs, airbrushes was used to apply both the TiO₂ and chlorophyll solutions.

Comparison between chlorophyll-sensitized TiO₂-coated sieve (left) and uncoated sieve (right)

TiO₂ coated steel wool (left) vs uncoated steel wool (right)

Coating the steel wool scrubs with chlorophyll

Steel Wool supported catalysts

Experimental setup for solid supported photocatalysts

3.7 Experimental Setup

The following apparatus is used for the experimental runs.

- Lights
 - o 12.5 W O-ring LED lights (White, red, blue, green)
 - o 60 W 395 nm UV-A lamp
- Uni-t A25f Air Quality Monitor
- Air pump set at 9 cm³ s⁻¹
- Reaction flask scaffolding

- Air delivery tubes and air stone
- Chlorophyll-sensitized TiO₂ coated sieves

Labelled diagram of the anatomy of a methanal decomposition device

Displaying the experimental setup

The experimental setup consists of air-tight plastic box with 4 ring light emitting diodes (LEDs) mounted on a plastic frame structure encasing a 100 cm³ conical flask which acts as the reaction flask. An electrical air pump feeds air into the reaction flask through an air stone.

Air pump in action.

3.8 Measurement of Methanal content in the air

3.8.1 Procedures

The procedures to conduct one complete run to determine the rate of decomposition of methanal are specified below

Preparation of experimental device:

1. 100 cm³ deionised water was added into a conical flask.

2. a) The conical flask was secured into the scaffolding and the temperature of the water is recorded.

b) the coated sieves were secured onto the scaffolding and the temperature of the air was recorded

3. The air pump set at a flow rate of 9.0 cm³ s⁻¹ and the LEDs lights were switched on and the box is sealed shut.

4. The device is left for 30 min to be warmed up until the steady temperature was achieved.

5. After the 30 min, the temperature of the water / is recorded once again.

Preparation of Methanal sample

6. 4 cm by 4 cm tissue squares are cut out and placed on a watch glass.

7. Dilute methanal solution was created by diluting formalin solution to c.a. 0.036% v/v.

8. 0.050 cm³ methanal solution was transferred to the tissue paper using a micropipette.

Conducting the run

9. The watch glass along with the soaked tissue paper is placed into the setup immediately.

10. The box is sealed airtight.

11. Paper boxes were put over the devices to block ambient light.

12. The methanal concentration was recorded at 1 min intervals.

4 Results

4.1 Experiment 1: Effect of various colours of light on the photocatalyzed decomposition of HCHO

Graph 1 Effect of red light on the TiO₂ photocatalyzed decomposition of HCHO

Graph 2 Effect of blue light on the TiO₂ photocatalyzed decomposition of HCHO

Graph 3 Effect of green light on the TiO₂ photocatalyzed decomposition of HCHO

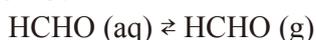
Graph 4 Effect of white light on the TiO₂ photocatalyzed decomposition of HCHO

Graph 5 Effect of UV light on the TiO₂ photocatalyzed decomposition of HCHO

Graph 6 Effect of various colours of light on the TiO₂ photocatalyzed decomposition of HCHO

According to the graphs above, the concentrations of the HCHO that were placed under red, blue, green and white LED lights increased gradually from around 0.6 mg dm⁻³ to around 0.7 mg dm⁻³. However, the situation for the HCHO that was placed under UV light differs from that of the others. With the pump and UV light turned on, the concentration of HCHO remained at around 0.7 mg dm⁻³. To conclude, the concentration of HCHO increased as red, blue, green and white LED lights are turned on, while the concentration of HCHO that was placed under UV light remained the same.

There is an equilibrium between HCHO (aq) in the conical flask and HCHO (g) in the chamber of HCHO.



It was found that pumping the HCHO(g) into the conical flask facilitates the solvation of HCHO into water

The concentration of HCHO increased under the effect of all (i.e. red, blue, green and white LED) lights irradiation except UV.

We reason that the heating effect of the LED lights decreases the solubility of HCHO in TiO₂ suspension and this contributes to a higher concentration of HCHO (g) in the chamber. However, since UV can decompose HCHO in TiO₂ suspension, its HCHO concentration did not increase as the other four LED lights did while the UV light is on.

4.2 Experiment 2: Effect of various colours of light on the chlorophyll-sensitized TiO₂ photocatalyzed decomposition of HCHO

Graph 7: The effect of various colours of light on the chlorophyll doped TiO₂ photocatalyzed decomposition of HCHO.

The chlorophyll-sensitized non-NPs TiO₂ exhibit different chemical properties compared with the non-NPs TiO₂ solution. Red LED light showed a moderate photocatalytic decomposition rate.

We propose that the chlorophyll have a better absorption at longer wavelength in visible light region, that is red light. The electron at valence band of the chlorophyll was promoted to the conduction band under red light irradiation. The excited electron was then injected into the conduction band of TiO₂ for further reduction of dissolved oxygen. The hole of the oxidized chlorophyll acted as a potent oxidizing agent to decompose HCHO and/or oxidize water to form hydroxyl radicals.

4.3 Experiment 3: Effect of various colours of light on the chlorophyll-sensitized TiO₂ NPs photocatalyzed decomposition of HCHO

According to the above graph, it can be concluded that the chlorophyll-sensitized TiO₂ NPs have similar effects to those that are not chlorophyll-sensitized.

As shown in the above graph, only red light has a significant drop in methanal content. At t = 140 min, the red-light setup was able to fully decompose 4.89×10^{-7} mol HCHO in the box. Although a drop in HCHO concentration was also observed for UV (395 nm) and white light, the decrease is not at all significant. The concentration of white light dropped only by 0.01 mg cm⁻³ while that of UV dropped by 0.02 mg cm⁻³ from 70 min to 130 min. Green light and blue light showed that the rate of decomposition was not able to counter the rate of which HCHO was vaporised.

4.4 Experiment 4: Effect of Solid supported Chlorophyll-sensitized TiO₂ NPs photocatalyzed decomposition of HCHO

The effectiveness of solid supported photocatalyst is also determined. The tests conducted for the solid supported photocatalyst is only irradiated under red light since only significant decomposition was observed for red light irradiation from the previous

two experiments.

Graph 9: Concentration of HCHO under different conditions

Graph 10: Decrease in concentration of HCHO plotted against time

[HCHO] decomposed (graph 10) was calculated by subtracting the vaporisation rate by the tests with catalyst. The purpose of this is to show the actual working efficiency of the test which is not dependant on the temperature effect.

In the first test, before $t = 30$ min, [HCHO] was increasing at a gradual diminishing rate. After peaking at $t = 30$ min, [HCHO] experiences an exponential drop, and reaches 0.00 at $t = 30$ min. Accounting for the rise of HCHO concentration during the first half of the experiment, the decomposition rate counteracts the rate of vaporisation of HCHO, thus the graph shows a concave-down shape. At $t = 30$ min, all methanal has been vaporised, so the [HCHO] in air stops increasing. Without the increase of [HCHO (g)] to balance off the rate of decomposition, the concentration drops rapidly.

In test 2, where the humidity was lowered by the use of CaCl_2 , there is a lower rate of decomposition rate. Because the free radical formation depends on the concentration of H_2O molecules in contact with the TiO_2 catalyst, the lower the humidity, the lower the decomposition rate. This proves that free radical oxidation is the staple of the methanal decomposition. This implies that the device should be humidified to maintain a high decomposition rate.

Comparing the efficiency between Chlorophyll-sensitised TiO_2 NPs in a suspension mixture and that with solid support, it is obvious that the solid support method yields a higher efficiency. In order to completely decompose 0.05 cm^3 0.036% HCHO solution, 140 min were required for the chlorophyll-sensitized TiO_2 NPs in suspension, while only 70 min was needed for the solid supported catalysts.

The efficiency of the solid supported Chlorophyll-sensitised TiO_2 NPs device is around 2 times that of Chlorophyll-sensitised TiO_2 NPs in colloidal dispersion.

Below are calculations for the efficiency of the 3 experimental devices

Number of moles of HCHO molecules in each sample:

$$0.05 \times 0.036\% \times 0.815 \div 30 \\ = 4.89 \times 10^{-7} \text{ mol}$$

Average rate of decomposition of HCHO with Chlorophyll-sensitised TiO_2 NPs in colloidal dispersion

$$4.89 \times 10^{-7} \div 140 = 3.49 \times 10^{-9} \text{ mol min}^{-1}$$

Average rate of decomposition of HCHO with solid supported $\text{TiO}_2 - \text{Chl}$ NPs

$$4.89 \times 10^{-7} \div 62 = 7.89 \times 10^{-9} \text{ mol min}^{-1}$$

Comparison on all setups experimented

4.5 Experiment 5: Effect of all methods of methanal removal

Graph 11: Comparing the effects of different setups on the concentration of HCHO

Graph 11 shows that the sieve supported device has decomposed all methanal vapour in air at $t=62$ min, while the DMSO/ H_2O suspension device has decomposed all methanal vapour at $t=140$ min.

Above shows the effect of different setups on the concentration of HCHO in air. We have compared the effect of our device (i.e. Sieve Supported, Stainless Steel Wool Supported, and DMSO – H_2O Suspension) against a commercially available methanal removing product, Bio-formaldehyde.

Commercially bought formaldehyde removal agent

According to the package description, the removal agent contains a probiotic that will consume formaldehyde. It is described that the removal agent should be sprayed onto the suspected origin of methanal vapour. To recreate the ideal conditions, two pumps of Bio-Formaldehyde solution is sprayed on a household white tile, with a piece of printer paper placed on top to retain the liquid. The setup is shown below:

Aside from the commercially bought formaldehyde removal agent, we also sought to verify colloquial myths that certain plants could reduce the odour of methanal. To do this, an *Epipremnum aureum* (Devil's Ivy) plant was placed into a conical flask sealed with parafilm. Before sealing the flask, an air stone was placed into the water to maintain a high oxygen concentration. The setup environment has a controlled CO_2 supply which maintains a steady CO_2 concentration.

Preparation of the plant

Setup with plant as absorption agent

Graph 11 shows that, at 20 min, the sieve supported device has already reached maximum for methanal concentration, while the other two were still slowly increasing. Furthermore, after the division point of 22

min, setup C had already started its reducing trend of formaldehyde concentration. In about 160 min, setup C have successfully decomposed the formaldehyde in a meter-detectable area into zero.

For the steel wool supported catalyst device, the decomposition rate was slower but the methanal level was kept at a low level. The total time to for [HCHO (g)] to drop to zero is 278 min with a 12V LED light supporting its decomposition. The maximum [HCHO] was attained at 38 min. A much smaller reading is shown comparing to setup with the plant as absorption agent. The formaldehyde concentration than stay in a slowly and insignificant change increase during the next 2 h 40 min. After the division point, the concentration started to show a slight decrease till zero at 4 hour and 38 min.

Combining the data above, all of our setups have proven to have a higher efficiency compared to the other two. Also, there was seen a higher initial increase of methanal, but the proportion was shorter than that other methods.

4.5 Contrasting and justifying the differences in experiments 1, 2 & 3

4.5.1 Size of Catalyst and the relationship to the light absorption

The rate of decomposition in experiment 1 is negligible and incomparable to that in experiments 2 & 3. Since the rate of decomposition is low, any fluctuation in [HCHO(g)] could be due to the temperature effect observed. However, the total drop in [HCHO(g)] is substantial in experiments 2 & 3, suggesting that there is a negative relationship between size of particles and photodecomposition rate.

Nano-sized particles have an extremely large surface area to volume ratio, allowing the particle to be react more readily, and increasing the rate of reaction (decomposition). This is shown by experiments 2 & 3 as the rate of decomposition is large enough to exceed the rate of vaporisation, whereas the rate of decomposition is always kept under the rate of vaporisation, rendering it unable to scrub methanal in a reasonable time period.

By comparing the data of the UV irradiation from experiments 1 & 2, it was seen that the size of particles affects the absorption of light to undergo photocatalysis. In experiment 1, it was observed that the UV caused a significant drop in [HCHO].

However, in experiment 2, UV showed little to no response to the UV irradiation. We reasoned that this is because in the non-Nano grade photocatalyst, the relative size of the chlorophyll molecules is small compared to the TiO₂ crystals. However, in the Nanoscale TiO₂, the chlorophyll molecule is relatively larger. Moreover, more chlorophyll molecules were able to adhere to the lattice structure of the nanoscale TiO₂ nanoparticles due to the large surface area of the nanoparticles.

This is supported by our data of chlorophyll capacitance per gram of TiO₂.

Size of TiO₂

Chlorophyll capacity

(Mass of Chl / 1 g of TiO₂)

Nano

1.50×10^{-3} g

Non-Nano

3.33×10^{-4} g

We also deduced that the low efficiency of Chlorophyll-sensitised TiO₂ NPs under UV irradiation is because the chlorophyll molecules has obstructed the absorption of UV. The main absorption peak of TiO₂ is around 320 nm, close to the wavelength of UV-A of 395 nm. At the same wavelength, chlorophyll has little absorption, and undergoes transmittance. Therefore, the increased surface area of TiO₂ nanoparticles has led to an increase of chlorophyll, hindering the absorption of UV light in TiO₂.

Absorption spectra of chlorophyll (left) and titanium dioxide (right)

4.5.2 Heating effect

The effect of temperature on the concentration of methanal in air is investigated by comparing the data from the first experiment and the two latter ones. In experiment 1, even though decomposition takes place, there is seen little drop in [HCHO(g)]. We previously justified this phenomenon by suggesting that low decomposition rate of non-Nano grade photocatalysts was the reason. However, by comparing the data from the control setup I.e. green light, from both Nano and non-Nano setups, both experiments showed that a small increase of temperature reflected a large increase of [HCHO (g)].

3a. Catalyst in suspension vs on solid support

There is a major difference in the rate of decomposition when the photocatalyst was switched

to a solid support. From the data above, using the catalyst with a solid support showed a double in efficiency. In experiments 1 & 2, the surface area of which decomposition reactions can occur is fully determined by the size of the bubbles & the surface area of HCHO in conical flask because TiO₂ blocked the photons. Even after using an air stone to diffuse the methanal containing air into the reaction flask, there is nonetheless low contact surface area between bubbles and the TiO₂ suspension, and only the methanal close to the air bubble can be decomposed. Furthermore, the green colour of the reaction flask was gradually decreasing in intensity, which is an alarming sign that the chlorophyll was being oxidised. The decrease of available chlorophyll lowers the efficiency of the photocatalyst, hence lowering the overall efficiency of the device. Since the efficiency drops over time, more time is needed to fully decompose the vaporised methanal.

3b. Advantages and Disadvantages of the two methods

Solid Support	
In suspension	
Advantages	
Disadvantages	
Advantages	
Disadvantages	
Long exposure time with HCHO	
Amount of catalyst used is unknown	
Exact amount of catalyst is known	
Small contact area with HCHO due to higher screening effect	
Chlorophyll is not readily consumed	
Water vapour in air is only water source	
Has high water source	
Short lifespan of chlorophyll	
Easy to replenish photocatalyst	
Contact with HCHO gas is dependant on placement of air delivery tube	
Enforced contact with HCHO gas	
Hard to replenish photocatalyst	
Not dependant on radicals for oxidising agents	
Greatly dependant on the formation of free radicals	
High efficiency	
Comparatively lower efficiency	

As discussed above, both methods have benefits and shortcomings. A major benefit of the solid support approach is that the catalyst can be easily replenished. For a liquid suspension, when the

photocatalyst requires replacement, the whole mixture must be discarded and refilled. However, for the solid support approach, the chlorophyll layer can simply be replenished by smearing chlorophyll solution onto the wire gauze. Therefore, this method requires less maintenance and is more user-friendly.

The primary benefit of the liquid suspension approach is that the concentration of photocatalyst in the reaction mixture is variable. When encountering a higher concentration of methanal, in order to increase the efficiency in the solid support system, more metal wire gauze must be used. This will take up more space and there will be an uneven spreading of methanal onto the catalyst. However, for the liquid suspended catalysts, the efficiency can be increased by adding more chlorophyll sensitised TiO₂ into the reaction flask. The set up does not take up any extra space or require reconfiguration.

5 Discussion

5.1 Limitations and the Future outlook

Dependence on free radicals for oxidation of methanal implies that the concentration of methanal around photocatalyst must be high for the method to be effective. Furthermore, the lifespan of hydroxyl radicals and superoxide radicals are very short lived, as most of them. The concentration may not be as high as in the experimental setups since the photocatalyst is not immersed in water where methanal gas is constantly pumped in.

Without high concentration of methanal or other reducing agents around the photocatalyst, the dye may be oxidized easily thus the effectiveness may drop rapidly over time in real life application.

Effect of different dyes and photocatalysts on photocatalytic decomposition of methanal would be investigated. A prototype would be built after optimizing the combination of dye with photocatalyst.

Furthermore, the green colour of the reaction flask was gradually decreasing in intensity, which is a sign that the chlorophyll was being oxidised. The decrease of available chlorophyll lowers the efficiency of the photocatalyst, hence lowering the overall efficiency of the device. This can be solved by adding chlorophyll-hexane solution to the reaction mixture to extend the lifetime of the setup.

As briefly mentioned above, the possibility of integrating haem as a natural dye is also being

explored. More time is needed to refine the extraction process of haem such that the haem extracted is of a decent purity for effective photocatalysis.

Apart from haem, other photosensitive dyes like phthalocyanine and porphyrins can also be explored.

6 Conclusions

Effect of various wavelength of light, catalyst size and chlorophyll dye on photodecomposition of methanal by TiO₂ was investigated and Nano TiO₂ coupled with red light and chlorophyll dye with a stainless-steel sieve solid support was found to be the most effective method of decomposing methanal. The most effective method shows a decomposition rate of methanal

7.89×10^{-9} mol min⁻¹, under the condition of solid supported chlorophyll-sensitised TiO₂ NPs under red light irradiation of (graph 11).

7 Implications

Through this miniaturised setup, it is proved that methanal decomposition is achievable and feasible by photocatalysis. Through the data show in section 4, the device is very effective at removing high concentrations of methanal in the air, while being relatively compact and easy to operate. This methanal decomposition device can be widely employed in sites suspected of having high methanal concentration, for example, construction sites, new homes, wood processing factories and so on.

In practice, the device can operate under two settings: with sunlight, and without sunlight. This enables the device to run under any condition.

With sunlight, LEDs are not required to undergo photocatalysis. From the transparent top part of the device, the reaction flask receives sunlight, which more than enough, includes all wavelengths of light used in the photodecomposition. The device will also charge under sunlight to run the LEDs at night time or low-light situations.

Without sunlight, the LEDs will use the dry cells or the solar charged batteries (if adequately charged) to operate. The device will emit red light specifically to maximise the efficiency of decomposition.

In short, the prominent feature of the created methanal decomposition setup is that it is potentially more effective than any out in the market and cheap to use, with the ability to operate with or without

sunlight.

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References

- [1] Ogilvie, J. F.; Horne, D. G. *The Journal of Chemical Physics* 1968, 48 (5), 2248-2256.
- [2] Ohtani, B.; Prieto-Mahaney, O.; Li, D.; Abe, R. *Journal of Photochemistry and Photobiology A: Chemistry* 2010, 216(2-3), 179-182.
- [3] Carrell, R. W.; Lehmann, H. *Journal of Clinical Pathology* 1981, 34(7), 796-799.
- [4] Methanal. <https://en.wikipedia.org/wiki/Methanal> (accessed Feb 13, 2019).
- [5] Methanal vs Methanol - Whats the difference? | WikiDiff. <https://wikidiff.com/methanol/methanal> (accessed Feb 13, 2019).
- [6] Facts About Formaldehyde. <https://www.epa.gov/formaldehyde/facts-about-formaldehyde> (accessed Feb 13, 2019).
- [7] Formaldehyde. <https://pubchem.ncbi.nlm.nih.gov/compound/formaldehyde> (accessed Feb 13, 2019).
- [8] Lazonyby, J. Methanal (Formaldehyde). <http://essentialchemicalindustry.org/chemicals/methanal.html> (accessed Feb 13, 2019).
- [9] Titanium dioxide. https://en.wikipedia.org/wiki/Titanium_dioxide (accessed Feb 13, 2019).
- [10] Understanding TiO₂ Photocatalysis: Mechanisms and. <http://pubs.acs.org/doi/abs/10.1021/cr5001892> (accessed Feb 13, 2019).
- [11] Cristal Corporate Website. <http://www.cristal.com/> (accessed Feb 13, 2019).
- [12] Ruichem - TiO₂, Titanium, Pigment | Manufacturer & Suppliers. <http://www.ruitio2.com/> (accessed Feb 13, 2019).
- [13] Titanium Dioxide (Anatase and Rutile): Surface Chemistry, Liquid-Solid Interface Chemistry, and Scientific Synthesis of Supported Catalysts. <http://pubs.acs.org/doi/abs/10.1021/>

- cr300230q (accessed Feb 13, 2019).
- [14] Products: Titanium Dioxide (TiO₂). <https://www.tronox.com/products/titanium-dioxide/> (accessed Feb 13, 2019).
- [15] What Is Titanium Dioxide - TiO₂? - Go Clean Label. <https://gocleanlabel.com/titanium-dioxide-tio2/> (accessed Feb 13, 2019).
- [16] Titanium dioxide. https://pubchem.ncbi.nlm.nih.gov/compound/titanium_dioxide (accessed Feb 13, 2019).