Solar Photocatalytic Degradation of Rhodamine B by TiO$_2$ Nanoparticle Composites

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Abstract

In this work the photocatalytic properties of titanium dioxide (TiO$_2$) in water has been studied. TiO$_2$ is a well known semiconductor with a band gap of 3.2 eV, corresponding to a wavelength of 385 nm. This means that in order to excite an electron from the valence band to the conduction band the TiO$_2$ has to be illuminated with UV-light. The photodegradation of Rhodamine B in different media has been studied with special interest in salinity and ion concentration. Also different nanocomposites has been tested to see how the photodegradation efficiency (PDE) is effected. The materials studied in combination to TiO$_2$ were Ag, Au, Si and Ge. It was found that the PDE is greatly enhanced by the addition of hydrogen ions and that the addition of hydroxyl ions did not have an effect. Of the different nanocomposites studied, it was shown that the PDE was enhanced with the combinations of TiO$_2$ and Ag, Au and Ge and that the addition of Si only decreased the PDE. The potential for this technique to clean drinking water is great, but with the drawback of needing UV-radiation limits its usage to areas around the equator. However, here the usage is the most dire and this method could prove to be a solution to the shortage of clean drinking water around the world.
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1 Introduction

Every year 2.4 million people die from illnesses caused by polluted drinking water [1]. In water, many kinds of pollutions may be present, for example viruses, bacteria and toxic chemicals. These pollutions come from agriculture, households and industry among others.

There are several methods used today to clean water and among these, mechanical filters and charcoal filters are the most common. In mechanical filters, the water passes through micropores which filtrates out particles down to 0.5 $\mu$m in size, which also includes bacteria. With charcoal filters, the water passes around the carbon and it absorbs heavy metals and some kinds of chemicals as well as odor and taste. The methods of using mechanical and charcoal filters are relatively easy but both methods have their drawbacks. The disposal cost is high, the handling of the toxic waste material is difficult and the methods are ineffective for many toxic chemicals.[2]

An alternative way of cleaning water is by using photocatalytic reactions. This method uses a combination of light and semiconductor nanoparticles as photocatalysts to degrade toxic organic pollutants, viruses, bacteria, fungi and algae. Through the process these species are degraded through several partial steps to CO$_2$, H$_2$O and inorganic anions. Because it is relatively inexpensive, chemically stable, non-toxic, non-soluble, photoactive, photostable and has well documented properties, titanium dioxide (TiO$_2$) is recognized as one of the best photocatalysts today.[3][4][5]

2 Purpose and limitations

In this report, the photodegradation of Rhodamine B using TiO$_2$ nanoparticles and sunlight is investigated. Efforts will be made to fit the experimental data to theoretical models. The main goal is to try to optimize the photodegradation process by changing the environment of the TiO$_2$ particles and adding particles of germanium, silicon, silver or gold to enhance the effect. In the future, this could become a cheap and easy way of cleaning polluted drinking water and polluted lakes or oceans.

Focus has been on the physical properties of the materials rather than the chemical properties. How the contact surfaces of the different materials interact has not been studied. The optimum loading of TiO$_2$ and Rhodamine B during the experiments has not been tested, instead results from previous studies have been used.

In this report the half life of the photodegradation of Rhodamine B is calculated from the fits of the data. However, comparison between half lives of different experiments can not be done due to the difference in sun intensities between summer and winter.
3 Theory

3.1 Titanium dioxide

TiO$_2$ is a common mineral in nature and it has many areas of application. It has three basic forms, rutile, brookite and anatase. Rutile has replaced white lead worldwide as white pigment in plastics, paints, coatings and paper because of its high light scattering efficiency and non-toxicity.[6][7] Rutile also has a high UV-light absorption, why it is used in sunscreens and cosmetics. Brookite is hard to produce in nano sized particles, why little is known about its potential applications.[8]

The anatase form of TiO$_2$ has gotten a lot of attention due to its semiconductor abilities and can be used in photodegradation processes, unlike rutile which has poor photocatalytic activity [9]. TiO$_2$ in its anatase form, can clean water and air and is in many ways an ideal photocatalyst [4]. TiO$_2$ has also been found to be of use in the cleanup process after oil spills and also in self-sterilizing surfaces. Kikuchi et al. showed that when a surface with thin film TiO$_2$ was contaminated with bacteria, all cells were killed after one hour of UV illumination. This can be compared with only using UV-light, which reduced the number of cells to 50 % in 4 hours.[10] TiO$_2$ has also been tested in cancer treatment with limited results as well as self-cleaning windows, buildings and roads [4].

One very unique aspect of TiO$_2$ is that not just one but two photoinduced processes occur when subjected to UV radiation. The first is photocatalysis and the second is that it becomes superhydrophilic. Superhydrophilicity is achieved when a TiO$_2$ film is prepared with SiO$_2$. When the film is exposed to UV radiation, oxygen is ejected from the surface. These vacancies are then occupied by water molecules which makes the surface hydrophilic.[4]

3.2 Photodegradation process

When a semiconductor particle is illuminated with wavelengths corresponding to photon energies larger than the bandgap, valence band electrons are excited to the conduction band and holes are produced in the valence band. Most of the electron-hole pairs produced recombine again after some tens of picoseconds and the energy is released as photons, phonons or both.[11][12] Coordination defects at the surface of the particle and lattice defects inside the particle trap the remaining charges [3]. The holes trapped at the surface have a highly reactive oxidation potential and the electrons have a highly reactive reduction potential. Because of this, the holes and electrons can induce catalytic reactions at the surface, which are called photocatalytic reactions.[13]

TiO$_2$ has a bandgap of 3.2 eV, which corresponds to a wavelength of 385 nm [14]. This means that electron-hole pairs are created when TiO$_2$ is radiated with UV-light with wavelengths shorter than 385 nm, see eq. 1.

\[
TiO_2 + h\nu \Rightarrow e^- + h^+
\]  

(1)
The most common reaction is that the electron-hole pair recombine and then no photocatalytic reactions take place, see eq. 2.

$$h^+ + e^- \Rightarrow TiO_2$$  \hspace{1cm} (2)

If the electron and the hole do not recombine, the created holes can migrate to the surface and react with water molecules surrounding the particles. Because the holes have a highly reactive oxidation potential, a hydroxyl radical can be created, see eq. 3.

$$h^+ + H_2O \rightarrow H^+ + OH^*$$ \hspace{1cm} (3)

The electrons can also migrate to the surface and because they have a highly reactive reduction potential, they can react with oxygen and create superoxide radicals, see eq. 4.

$$e^- + O_2 \rightarrow O_2^-$$ \hspace{1cm} (4)

The superoxide radicals can react with new electrons and create hydrogen peroxide, see eq. 5.

$$O_2^- + e^- + 2H^+ \rightarrow H_2O_2$$ \hspace{1cm} (5)

The hydrogen peroxide can also react with new electrons and create hydroxyl radicals, see eq. 6.

$$e^- + H_2O_2 \rightarrow OH^- + OH^*$$ \hspace{1cm} (6)

Hydroxyl radicals can thus be produced either by the holes or the electrons from the electron-hole pairs created.\textsuperscript{[15]} Fig. 1 is a schematic image that shows some of the pathways of electron-hole pairs described in for example eqs. 2, 3 and 4.

**Figure 1:** Schematic image showing different pathways for an electron-hole pair created at *.

(1) Recombination inside the bulk of the particle. (2) Recombination at the surface of the particle. (3) A hole migrates to the surface and reacts with a donor molecule. (4) An electron migrates to the surface and reacts with acceptor molecule.
3.3 Enhancing the photodegradation efficiency

The free radicals created are highly reactive and can attack organic molecules and degrade them. If the process continues the organic molecules are totally mineralized to CO$_2$, H$_2$O and inorganic anions. Another way for the organic molecules to be degraded is by direct reactions with the holes. However, because the two reactions give similar results, it is difficult to determine which of them that dominates.[4][5] These processes are called photodegradation processes and the photodegradation efficiency (PDE) is defined as

$$\text{PDE} = 1 - \frac{C_{\text{Final}}}{C_{\text{Initial}}}$$

where $C_{\text{Initial}}$ and $C_{\text{Final}}$ is the initial and final concentration of the pollutant respectively. From the equation it can be seen that the PDE varies between 0 and 1.

The photodegradation process can be approximated with first order kinetics when the concentration of the pollutant is lower than 1 mM [4][5]. This means that the reaction rate is linearly dependent on the concentration, $C$, of the degradable molecule, see eq. 7.

$$\frac{dC}{dt} = -kC$$  \hspace{1cm} (7)

Here $k$ is the first order rate constant which has the unit 1/time. By integrating this equation, the concentration as a function of time can be found, see eq. 8.

$$C(t) = C(0)e^{-kt}$$  \hspace{1cm} (8)

Here $C(0)$ is the initial concentration and $t$ is the time. When a reaction follows first order kinetics, the half life of the concentration is independent of the initial concentration and can be found by eq. 9.[16]

$$t_{1/2} = \frac{\ln(2)}{k}$$  \hspace{1cm} (9)

3.3 Enhancing the photodegradation efficiency

For TiO$_2$ nanoparticles, the photodegradation process only occurs for wavelengths shorter than 385 nm [14]. When light with a wavelength of 385 nm is used, only transitions between the band edges can occur and this reduces the efficiency. When light with shorter wavelengths is used, also transitions requiring higher energy can occur, see fig. 2. This increases the transition probability and the number of electron-hole pairs created. When other transitions than band edge transitions occur, the electron and hole also acquires equal and opposite momenta. This prevents the electron and the hole from annihilating and further increases the efficiency.[17]
3.3 Enhancing the photodegradation efficiency

Figure 2: Schematic image showing the formation of an electron-hole pair in TiO$_2$. For band edge transitions to occur, light with 3.2 eV is needed. When more energetic light is provided, other transitions can also occur resulting in a nonzero wavevector $k$ of the electron and hole.

Lamps emitting light with shorter wavelengths can easily be found, but using an artificial light source requires electricity and is expensive [3]. A cheaper and more ecological alternative is to use sunlight. Sunlight consists of a broad spectrum of wavelengths, including UV-light, see fig. 3.

Figure 3: Graph showing the solar spectrum at the top of the atmosphere and at sea level. Inserted is also the black body radiation curve from the surface of the sun. Image acquired from [18]
At sea level, only a very small fraction of the sunlight has wavelengths shorter than 385 nm. When sunlight is used, it is thus important to minimize the band gap as much as possible in order to get a high photodegradation efficiency.

Because the photodegradation reactions occur at the surface of the particles, a large surface area and a short distance to the surface is wanted. This can be achieved by making the particles very small. However, when the particle size become smaller than approximately 10 nm, the size of the particle is comparable with the de Broglie wavelength of the electrons and holes. This causes the band gap to increase due to quantum confinement. In addition to the pure excitation energy, energy is then also required to confine the created electron-hole pair inside the particle. It also increases the electrostatic attraction between the electron and the hole, causing an increased recombination rate. The optimum particle size is thus a compromise between wanting small particles for a large surface area and wanting a small band gap and a low recombination rate which sets a lower limit on the particle size.[19][5] Studies have shown that the optimum size of the particles is around 10 nm and this size will be used throughout the experiments in this study.[20]

Crystallinity is another important factor to consider in the optimization of the photodegradation efficiency. It has been shown by Ohtani et al. that amorphous TiO$_2$ has negligible photodegradation efficiency compared with TiO$_2$ of high crystallinity. The low efficiency of amorphous TiO$_2$ is caused by the high recombination rate of electrons and holes due to the large amount of defects.[21] Usually the amount of defects in the particles increases as the surface area of the powder of particles increases, which is another reason why very small particles are unwanted.[22]

The photodegradation efficiency is dependent on the concentration of TiO$_2$ particles used. When a higher concentration is used, the surface area available for reactions is increased, which increases the degradation efficiency. Above a certain concentration the degradation again decreases due to the increased light scattering of the particles and the reduced light penetration in the sample. It has been reported that the optimum concentration range is 0.15-8 mg/ml.[5] In unpublished work by K. Sattler et al., it was shown that the maximum photodegradation efficiency was reached when a concentration of 0.6 mg/ml TiO$_2$ was used. This concentration will therefore be used in all photodegradation experiments in this study.

Other parameters that effect the photodegradation process are temperature and pH value. The importance of pH will be investigated in this report and the temperature dependence has been shown to be small [5].

### 3.4 Nanocomposites

Most photoexcited electrons and holes rapidly recombine. To reduce the recombination rate and in that way increase the charges available for reactions is very important to increase the photodegradation efficiency. It has been shown in previous studies that by using nanocomposites of a semiconductor material and a material that accept electrons, the photodegradation efficiency can be dramatically increased. When electrons are removed from the semiconductor the remaining holes are less likely to recombine and the possibility
of the holes to reach the surface of the particle and participate in reactions is greatly increased.\cite{3} The transferred electrons also have a greater possibility to react with oxygen, which further increase the photodegradation efficiency \cite{23}.

When a nanoparticle is suspended in a aqueous solution it will develop an electrical double layer, which consist of the Stern layer and the diffuse layer. The Stern layer is built up of charges on the surface of the particle while the diffuse layer is built up of ions in the solution. Because of the double layer a potential barrier is created when two particles come in contact with each other.\cite{24}

When exposed to UV-light the electrons created in the TiO$_2$ can tunnel through the potential barrier between TiO$_2$ and for example silver, gold, germanium or silicon particles and thus reduce the recombination rate of the electron-hole pair, leading to an enhanced hole density on the TiO$_2$ surface. Tunneling is possible if the energy of the Fermi level of the added material is lower than the energy of the conduction band of TiO$_2$. This process is highly dependent on the height and width of the barrier, and if the photodegradation efficiency is greatly increased, it would indicate a high efficiency of the tunneling of the electrons.\cite{3} Materials with a high electron affinity and materials that bind tightly to the semiconductor should have a higher electron transfer rate and that should lead to an increase in the photodegradation efficiency.

### 3.4.1 Semiconductor-metal

When silver (Ag) is added to a solution with TiO$_2$, the two particles can interact either by collision or by binding to each other. The latter case is supported by unpublished work by K. Sattler et al., where measurements of the $\zeta$-potential showed that both pure TiO$_2$ and TiO$_2$ with Ag have the same $\zeta$-potential curve. The $\zeta$-potential is the potential difference between the layer of fluid attached to the particle and the surrounding medium and it changes with pH. When the $\zeta$-potential has a large positive or negative value, the particles in the suspension repel each other, while they tend to cluster at low values.\cite{25} The $\zeta$-potential curve differs for different materials and when the same curves are achieved for both pure TiO$_2$ and TiO$_2$ together with Ag, it indicates that the TiO$_2$ particles bind to the surface of the Ag particles.

Because the Fermi level of Ag is lower than the energy of the conduction band edge of TiO$_2$, electrons should be able to tunnel through the potential barrier when the particles are bound to each other, see fig. 4. Adding Ag should then lead to an increased photodegradation efficiency.\cite{3}

The same process can also take place for gold (Au). One difference between Au and Ag is the reflection of UV-light. Silver reflects 82 % of light around 385 nm, while gold only reflects 37 % and absorbs a larger part of the light, see fig. 5. Au particles then decrease, compared to Ag particles, the amount of light available for reactions in the TiO$_2$ particles. In order for Au to be a better candidate than Ag, it then has to be more efficient in the electron transfer. \cite{26}
The electron affinity of an atom is the energy required to remove an electron from the negatively charged ion. Au has an electron affinity of 2.31 eV and Ag has an electron affinity of 1.30 eV and this suggests that Au would give a higher electron transfer rate than Ag.\cite{27} However, in order for the electron transfer to be probable, the binding between the Au particles and the TiO$_2$ particles also needs to be good. The higher electron affinity of Au should also reduce the possibility for the transferred electrons to react with other molecules in the solution.

**Figure 4:** Schematic image of the formation of an electron-hole pair by an incoming photon. The electron can then be captured by an Ag particle and this reduces the electron-hole recombination rate.

**Figure 5:** Graphs showing the reflection at different wavelengths for (a) silver and (b) gold. It can be seen that silver reflects light at wavelengths around 385 nm strongly while gold absorbs a greater part of the light. Data obtain from \cite{26}.
3.4.2 Semiconductor-semiconductor

Another material potentially suited for enhancing the efficiency by this process is silicon (Si). Si, like TiO$_2$, is a semiconductor with an band gap of 1.11 eV [28][26]. This would indicate that Si alone would be a good candidate of cleaning water and because 1.11 eV is equivalent to approximately 1100 nm, the cleaning process would not have the disadvantage of only working in UV-light exposure. However, the band gap of 1.11 eV of Si is an indirect band gap, meaning that in order for an electron to be excited to the conduction band a three body reaction is required, with an electron, a photon and a phonon, see fig. 6. This greatly reduces the possibility for this reaction.[28]

![Graph of the band structure of silicon](image)

**Figure 6:** Schematic image of the electronic band structure of silicon. The indirect bandgap is 1117 nm and the direct bandgap is 302 nm. Image used with kind permission of Springer Science + Business Media. [29]

The direct band gap of Si crystals is in the order of 4.1 eV, meaning that higher energy photons are required to make this process possible [30]. With such a high bandgap, Si would be a poor candidate to use in sun exposure experiments. However, if the conduction band of Si lies below the conduction band of TiO$_2$ it could also potentially collect the electron generated from TiO$_2$ when exposed to UV-radiation, in the same way as with Ag, see fig. 7.

Germanium (Ge) is semiconductor that is very similar to Si. It has an indirect bandgap of 0.66 eV, but it also has a direct bandgap only 0.15 eV higher in energy and Ge can thus absorb light with wavelengths of 385 nm, see fig. 8.[28][31][30]
3.4 Nanocomposites

Figure 7: Schematic image of the formation of an electron-hole pair by an incoming photon. The electron can then be captured by the Si particle which reduces the electron-hole recombination rate.

The mobility of the electrons in the conduction band at 300 K is 1350 cm$^2$/Vs and 3600 cm$^2$/Vs for Si and Ge respectively [28]. If both Ge and Si bind to the surface of the TiO$_2$ particles, the transferred electrons would move away from the contact area faster for Ge than for Si, which might lead to a higher electron transfer rate. The electron affinity on the other hand is very similar with values of 1.24 eV and 1.20 eV for Si and Ge respectively [27].

Figure 8: Schematic image of the electronic band structure of germanium. Germanium has an indirect bandgap, but also a direct bandgap which differs very little in energy to the indirect. The direct bandgap is 1531 nm. Image used with kind permission of Springer Science + Business Media. [29]
Another consideration with semiconductors, as with metals, is the reflection of light. The reflection for Si and Ge is shown in fig. 9.

![Graphs showing the reflection at different wavelengths for (a) Si and (b) Ge.](image)

**Figure 9:** Graphs showing the reflection at different wavelengths for (a) Si and (b) Ge. It can be seen that both Si and Ge has similar reflection curves. Si reflects 53 % of the light at 385 nm and Ge reflects 48 %. Data obtain from [32]

It can be seen that there is little difference in reflection between Si and Ge. At 385 nm, the reflection is 53 % and 48 % for Si and Ge respectively and this means that the loss in photodegradation efficiency for Si and Ge due to absorption of the UV-light should roughly be the same.

### 3.5 Rhodamine B

Rhodamine B (RhoB) is a common fluorescent dye used in many different applications, from water tracer studies to cell membrane studies. It has many advantageous properties like high photostability and water solubility.[33] The solubility in water is about 50 g/l and RhoB solutions should be kept in glass vials because it get absorbed in plastics.[34]

The quantum yield of the fluorescence of RhoB is dependent on several factors, but except from concentration, the most important one is the temperature. The quantum yield increases with decreasing temperature.[33][35] This factor can easily be corrected for by letting RhoB samples adjust to for example room temperature before the fluorescence is measured. Another factor to consider is the pH value, but between pH 6.5 and pH 9.5 RhoB has a stable quantum yield.[33]

Fig. 10a and 10b shows the extinction and emission spectra of RhoB respectively.
3.5 Rhodamine B

Data obtained from [36]. In order to be able to distinguish between the excitation light and the emission light, the RhoB was excited at 365 nm in this study.

The emission has a maximum at around 564 nm and the extinction maximum is found at 543 nm. In order to be able to distinguish between the excitation light and the emission light and to filter out the excitation wavelengths, the RhoB was excited using a wavelength of 365 nm. This wavelength coincides with a smaller maximum in the extinction spectrum, as can be seen in fig. 10a.

In this study, the photodegradation of pollutants is to be investigated and improved. If an ordinary chemical would have been used as a pollutant, advanced water analysis would have been required in order to evaluate the pollutant concentration. By choosing RhoB as pollutant, the concentration in the sample can be found by simply measuring the fluorescence from the sample. To ensure a high signal from the sample, a high initial concentration of the pollutant should be used. When too high concentrations are used, the transparency of the solution is reduced and the whole sample is not evenly illuminated. This reduces the efficiency of the photodegradation process. Because the degradation process mostly occurs at the surface of the particles, when the surface is covered with the pollution molecules, a further increase in the pollutant concentration does not give an increase in the degradation rate.[5] In unpublished work by K. Sattler et al., it has been shown that the best compromise it to use a concentration around 10 ppm. This corresponds to 21 µM and the photodegradation of RhoB should thus follow first order kinetics, see 3.2.
4 Analysis methods

The different analysis methods used in this work are described below.

4.1 Light scattering device

In order to be able to measure the concentration of TiO$_2$ particles in a sample, a measurement setup was built, using a Uniphase 155A laser and a photosensitive detector. The photosensitive detector was placed in a 90° angle to the laser beam in order to measure the light scattered by the sample, see fig. 11.

![Figure 11: Schematic representation of the light scattering device used to measure the concentration of TiO$_2$ particles in a sample. The light from the laser hits the sample and is scattered. The detector is set to detect scattered light at an angle of 90° to the laser beam.](image)

4.2 Fluorescence spectrophotometer

To measure the concentration of RhoB, a silicon solid state detector was used. The detector was a EG&G Princeton applied research model 1421, connected to a multichannel analyzer with 1000 channels. The measurement setup consisted of a UV lamp, which excited the RhoB at a wavelength of 365 nm. The light emitted from the sample went through a monochromator which filtered the light before it hit the detector, see fig. 12. The concentration was achieved by using the maximum value of the fluorescence peak at 564 nm.
4.3 Photon correlation spectroscope

To measure the size of the particles, a ZetaPlus Zeta Potential Analyzer from Brookhaven Instruments Corporation was used. It measures the hydrodynamic diameter, which is the diameter of the particle and its double layer.

In the spectroscope a laser is directed to the sample of particles and an alternating electric field is applied. Because the particle surfaces are charged, the scattered light will travel different distances as a function of time, due to the motion of the particles. An average intensity with superimposed fluctuations is detected at an angle of 90°. The decay time of the fluctuations are fitted to an autocorrelation function and from that, the diffusion coefficient is found. For spherical particles, the diffusion coefficient is inversely proportional to the diameter of the particles. Because of this, larger particles moves slower than smaller particles, which causes a slower decay time.

The intensity of the scattered light is proportional to the number of particles $N$ with diameter $d$, the square of the particle mass $M$ and the particle form factor $P$. The form factor depends on the size of the particles, the scattering angle, the wavelength and the index of refraction of the surrounding medium. To get the average diffusion coefficient $\bar{D}$ of the sample, the diffusion coefficients $D$ measured are weighted with the intensity of the scattered light according to eq. 10.

$$\bar{D} = \frac{\sum NM^2PD}{\sum NM^2P}$$  \hspace{1cm} (10)

Because the diameter is inversely proportional to the diffusion coefficient, the effective diameter is found by the software by taking the inverse of eq. 10, using the fact that the mass of the particles is proportional to the cube of the diameter. The form factor is approximated by the software.

Figure 12: Schematic representation of the fluorescence spectrophotometer used to measure the fluorescence of RhoB samples. The light from the UV-lamp excites the RhoB molecules at a wavelength of 365 nm. The emitted light is filtered in the monochromator before reaching the detector.
From the photon correlation spectroscope also the polydispersity is given. The polydispersity is a measure of the width of the size distribution of the sample and approaches zero for monodisperse samples. For narrow size distributions it has a value between 0.020 and 0.080 and larger values mean broader distributions.[37]

5 Preparations

Before all experiments, beakers, vials and other equipment were cleaned with detergent, rinsed with water, sonicated for 5 minutes in a Fisher Scientific FS3 Compact High Performance Ultrasonic Cleaning System and then rinsed with water again. When the equipment is sonicated, ultrasonic waves in the water help remove pollutions from the equipment surface. If solutions with deionized water were used, the vials and equipment were also rinsed with deionized water before usage. All chemicals were used in powder form if nothing else is written.

A standard solution is defined as a 0.6 mg/ml TiO$_2$ 10 ppm RhoB solution in deionized water. It is prepared by first adding 10.0 mg of RhoB to 1000 ml of deionized water. This solution is stirred with a magnetic stirrer for 10 minutes. Depending on the amounts needed for the experiment, TiO$_2$ nanoparticles are added to get a 0.6 mg/ml solution. This solution is stirred and sonicated for 5 minutes before usage.

When samples were extracted from a solution a glass pipette was used and solutions containing nanoparticles were stirred between every three samples to avoid sedimentation of the nanoparticles. For the same reason, during all photodegradation experiments, the vials were shaken every other minute.

In experiments where only pure RhoB was used, the samples were left a couple of hours before analysis in order for them to cool down to room temperature. When also TiO$_2$ particles were used in the samples, they were left over night to sediment.

6 Buffers

Three different buffer solutions were made during this work and the method used are described here.

**pH 4 buffer:** First, a 100 mM solution was made by adding 2042.0 mg KHP to 100 ml of deionized water. Another 100 mM solution was made by adding 400.0 g NaOH to 100 ml of deionized water. Of this solution 2.6 ml was added to the first solution to make a 100 mM pH 4.1 buffer solution.[38]

**pH 7 buffer with OH-groups:** A 100 mM pH 7 buffer solution was prepared by mixing 680.0 mg KH$_2$PO$_4$ and 116.5 mg NaOH with 79.1 ml of 10 ppm RhoB in deionized water.[38]

The KH$_2$PO$_4$ will dissociate to K$^+$ + H$^+$ + HPO$_4^{2-}$ and the NaOH will dissociate to
7 CALIBRATION

Na\(^+\) + OH\(^-\). The HPO\(_4^{2-}\) can dissociate further to H\(^+\) + PO\(_4^{3-}\). However, this effect is so small that it can be neglected.[39]

**pH 7 buffer without OH-groups:** Another 100 mM pH 7 buffer solution was made by first mixing 2220.0 mg K\(_2\)HPO\(_4\) with 113.4 ml of deionized water. To this solution, 36.6 ml 0.1 M HCl solution and 1.5 mg RhoB was added.[38]

The K\(_2\)HPO\(_4\) will dissociate to K\(^+\) + K\(^+\) + HPO\(_4^{2-}\) and the HCL will dissociate to H\(^+\) + Cl\(^-\). Also here the HPO\(_4^{2-}\) can dissociate further to H\(^+\) + PO\(_4^{3-}\), but the effect is negligible.[39][40]

All buffer solutions were stirred with a magnetic stirrer for 5 minutes after preparation. The pH value was checked with a Corning Check Mite pH-20 pH-meter, which was calibrated with a pH 7 buffer solution from Fisher Scientific before the measurements.

7 Calibration

7.1 TiO\(_2\) particle concentration

A solution was mixed by adding 20 mg TiO\(_2\) to 20 ml deionized water. The obtained solution of 1 mg/ml TiO\(_2\) was sonicated and stirred for 5 minutes. Solutions with lower concentrations were then obtained by diluting the 1 mg/ml solution with deionized water. From each of the solutions, 3 ml were extracted and inserted into square 10 mm polystyrene cuvettes. The samples were then measured in darkness using the light scattering device and the arithmetic mean of three measurements were used. The resulting data points and a fit can be seen in fig. 13.

For concentrations higher than 0.5 mg/ml, a very small increase in the voltage was seen. In order to measure higher concentrations with good accuracy, such samples need to be diluted before the measurement.

7.2 Rhodamine B concentration

The calibration of the fluorescence spectrophotometer was done by measuring known concentrations of RhoB. A 10 ppm RhoB solution was made by adding 10.0 mg RhoB to 1000 ml of deionized water. The solution was then stirred with a magnetic stirrer for 10 minutes. Lower concentrations were obtained by diluting the 10 ppm RhoB solution with deionized water.

In order to calibrate the high concentration range, solutions with concentrations of 8, 5, 4, 2.5, 2, 1.25, and 1 ppm were mixed. In the measurement, 2 ml of the different samples were inserted into 2 ml cylindrical glass vials with a diameter of 10 mm. The measurement time was 10 s and the data points and a fit can be seen in fig. 14(a).

In order to calibrate the low concentration range, solutions with concentrations of 1, 0.75, 0.5, 0.25, 0.125 and 0.1 ppm were mixed from the 10 ppm solution. In order to
increase the signal from these low concentrations, 6 ml of these samples were inserted into 45 ml cylindrical glass vials with a diameter of 25 mm. The measurement time was 30 s and the data points and a fit can be seen in fig. 14(b).

Figure 13: Graph showing the calibration curve for different concentrations of TiO$_2$ nanoparticles. Samples with concentrations higher than 0.5 mg/ml need to be diluted before measurement to avoid saturation. Each value is the arithmetic mean of three measurements and inserted is also a fit to the data points.

Figure 14: Calibration graphs for RhoB in a solution (a) in the high concentration range between 1 ppm and 10 ppm, where 2 ml glass vials were used and (b) in the low concentration range between 0 ppm and 1 ppm, where 45 ml glass vials were used.
8 Size determination

A photon correlation spectroscope was used to measure the sizes of the particles used in this work namely nanopowder of Ag and TiO$_2$ and ground powder of Ag, Au, Ge and Si.

8.1 Method

A small amount of powder of the different materials were added to vials containing 10 mM KNO$_3$. The vials were then sonicated for 5 minutes and then filtered with a 1.2 $\mu$m filter into square 10 mm polystyrene cuvettes. The cuvettes were inserted into the spectroscope and ten measurements were done for each sample with an acquisition time of one minute for each measurement.

8.2 Results

The mean values of the effective diameter and the polydispersity of the samples are shown in table 1.

Table 1: Average effective diameter and polydispersity of the particles used in the experiments.

<table>
<thead>
<tr>
<th>Material</th>
<th>Effective diameter [nm]</th>
<th>Polydispersity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag nanopowder</td>
<td>113.9</td>
<td>0.307</td>
</tr>
<tr>
<td>Au</td>
<td>263.6</td>
<td>0.122</td>
</tr>
<tr>
<td>Ge</td>
<td>165.2</td>
<td>0.240</td>
</tr>
<tr>
<td>Si</td>
<td>159.4</td>
<td>0.180</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>206.8</td>
<td>0.324</td>
</tr>
</tbody>
</table>

8.3 Discussion

The use of KNO$_3$ as medium was in accordance with recommendations from the manufacturer. The amount of powder added to the vials had to be large enough so that the particles were representative for the powder, but the samples still needed to be transparent for the light.

After the vials were sonicated, a filter was used to remove particles larger than 1.2 $\mu$m. The particles used in these experiments should be smaller than that and a few such big particles could have created an error in the size determination.

The measurements showed that TiO$_2$ is 20 times larger than size indicated on the can. One explanation could be that the particles cluster in the can due to the moist air and that the clusters are not completely separated during sonication. The other materials have approximately the expected sizes. Au was harder to grind than Si and Ge and the measurement showed that the Au particles are bigger than the Si and Ge particles. The semiconductors behaves very similar in general and the sizes after grinding also were very
similar. The Ag nanopowder had an effective particle diameter of around 100 nm as promised by the company, see 15.

Also Ag ground powder was tested, but a size determination of this powder was not possible. This could be due to that the size distribution in the sample was too high which created too much fluctuations which the measurement setup was unable to handle.

The polydispersity was large for all of the samples, but slightly smaller for the ground powders. This is surprising and we expected the particles bought as nanoparticles to have a more narrow size distribution than the particles ground from a powder of larger particles.

9 Exposure vial comparison

A vial comparison experiment was made to determine which vial to use to optimize the photodegradation process with TiO$_2$. The vials analyzed were a petri dish with a plastic lid, a petri dish without lid, a petri dish covered with two different kinds of plastics and the 2 ml glass vial used during the RhoB concentration calibration analysis. The petri dishes had a diameter of 50 mm.

9.1 Method

A 50 ml standard solution with tap water instead of deionized water was prepared. From the solution, 4 ml was inserted into each of the petri dishes and 2 ml was inserted into the glass vials. Three samples of all the vials were exposed to sunlight for 0, 10, 20 and 30 minutes each, except for the petri dishes covered with different kinds of plastic, which were only exposed for 0 and 10 minutes.

The experiment took place at noon in order to maximize the UV radiation. After sunlight exposure, the samples in the petri dishes were also put into 2 ml glass vials in which the analysis took place.

9.2 Results

Each sample was measured three times and the arithmetic mean was used. The results are shown in fig. 15. The half lives was calculated to 8.1 minutes for the glass vials, 6.9 minutes for the petri dish with lid and 7.9 minutes for the petri dish without lid.
9.3 Discussion

In this experiment, tap water was used instead of deionized water. The reason for that is that the purpose of the experiment was not to give an absolute result, but a comparison between the possible vial alternatives and tap water is much easier to handle than deionized water.

The petri dish with lid showed better results than the petri dish without lid. This could be due to two things. One reason could be that some of the water in the petri dish without lid evaporates, leaving the sample with a higher concentration RhoB than it should have. Another reason could be that in order to get good results, the samples need to be shaken to avoid sedimentation of the particles. The petri dish without lid was harder to shake than the one with lid. This could have led to a lower efficiency in these samples.

When using the petri dish with plastic foil and plastic bag as lid, the samples were also very hard to shake. Still the samples showed a good efficiency. The glass vials were very convenient to handle and were easily shaken. It does not seem as though the thicker volume of the glass vial decreased the efficiency, indicating that the sample was still homogeneously illuminated.

Because all the vials showed similar results, the glass vials will for convenience be used in all future experiments if nothing else is written. Another reason for using the glass vials is that the samples do not need to be transferred from one vial to another between the experiment and the analysis.
10 UV-index dependence

The photodegradation effect of the TiO$_2$ is due to the absorption of UV-light. A trial was made to test the efficiency throughout a whole day and to compare it to the UV-index. It was also of interest to see when the efficiency is maximized and if it has a plateau during a part of the day.

10.1 Method

A 100 ml standard solution was prepared with tap water instead of deionized water. The exposure took place every half hour from 10.00 to 17.00, lasting 10 minutes each. At every measurement point, three samples were used and three samples were acting as control samples and were not exposed to sunlight.

10.2 Results

The photodegradation efficiency throughout the day can be seen in fig 16(a). In fig. 16(b) the photodegradation efficiency can be seen in comparison to the UV-index, which is normalized so that the highest points in both curves coincide.

![Figure 16](image)

**Figure 16:** (a) Photodegradation efficiency measured after 10 minutes sunlight exposure at different times during the day. (b) The photodegradation efficiency compared to the UV-index [41]. The UV-index is here scaled so that the highest points in both curves coincide. In the figure the experimentally achieved data points and the mean value of those are plotted as small and large points respectively.

10.3 Discussion

During all the measurements, the sky was clear. As can be seen in fig. 16(b), the photodegradation efficiency seems to depend on the UV-index, even though the photodegra-
dation efficiency does not decrease as much as the UV-index before 11.00 and after 14.00. It can also be seen that the efficiency is rather constant between 11.30 and 13.30. This can be useful to know if longer measurements are necessary.

The UV-index is a measure of the energy radiated per square meter and is weighted depending on the wavelength of the light and the damage the radiation can cause to the skin. Light containing shorter wavelengths get a higher UV-index than the same intensity of light with a longer wavelength. UVB radiation, which means radiation with wavelengths between 290 nm and 320 nm, is almost only present during mid day, while UVA radiation with wavelengths between 320 nm and 400 nm is more constant during the day. This means that the UV-index get a peak at mid day due to the UVB radiation, but the UVA radiation that TiO$_2$ uses is more constant. This explains why the UV-index decreases more than the PDE curve for TiO$_2$ at times before and after mid day when the highest point on both curves coincide.[42]

11 Media dependence

In order to see if the photodegradation efficiency changes when the TiO$_2$ particles are suspended in different media, several different experiments were made. The dependence on salinity, ion concentration and pH value of the solution was investigated.

11.1 pH dependences

The surface properties of TiO$_2$ particles changes with the pH value of the surrounding medium. In these experiments, the pH dependence on the sedimentation rate and the photodegradation efficiency was investigated.

11.1.1 Method

Sedimentation rate: Two solutions were made by mixing 24 mg TiO$_2$ with 60 ml tap water and deionized water respectively, to get a concentration of 0.4 mg/ml. The solutions were then sonicated and stirred for 5 minutes. To achieve different pH values in the samples, first droplets of KOH solved in deionized water were added to get a pH value above the highest measured. The pH value was then decreased by adding droplets of the pH 4 buffer. Square 10 mm polystyrene cuvettes were used in this experiment, one for each pH value. The pH value was measured with a Corning Check Mite pH-20 pH-meter, which was calibrated with a pH 7 buffer solution before the experiment.

The different samples were measured with a 2 minutes interval. Before the first measurement, each of the samples were shaken and measured directly to get an original concentration in the sample. They were then left to sediment for 50 and 80 minutes each before the concentration was measured again. The samples with tap water were only measured after 80 minutes sedimentation.
Photodegradation efficiency: One standard solution and one standard solution with tap water was prepared. The pH value in the solutions were increased by adding droplets of KOH solved in deionized water. One droplet of pH 4 buffer was added before the highest pH value samples were extracted from the solution. Samples with lower pH values were achieved by adding more droplets of pH 4 buffer. For every measurement point, two vials were prepared for each solution. One vial for each measurement point was used as a control sample an was not exposed to sunlight. The other vials were exposed to sunlight for 10 minutes at 13.00. Two hours after exposure, two droplets of pH 4 buffer was added to all vials. The samples were left to sediment over night before the analysis.

11.1.2 Results

The results for the pH dependence on the sedimentation rate for TiO\textsubscript{2} particles suspended in tap water and deionized water are shown in fig. 17(a) and fig. 17(b) respectively.

![Graphs showing the sedimentation rate at different pH values for TiO\textsubscript{2} nanoparticles](a) in tap water and (b) in deionized water. It can be seen that the sedimentation rate for particles in deionized water is clearly pH dependent and the particles sediment fast at pH values below 6. Above 7, these particles hardly sediment at all. Particles in tap water show no pH dependence on the sedimentation rate, but sediment fast for all pH values.

The pH dependence on the sedimentation rate for particles suspended in deionized water can be clearly seen. At pH values below 6 the particles sediment fast, while at pH values above 7 they hardly sediment at all. Particles in tap water show no pH dependence on the sedimentation rate, but sediment fast for all pH values.

The results of the pH dependence on the photodegradation efficiency experiment is shown in fig. 18.
Figure 18: Graph showing the photodegradation efficiency as a function of the pH value for tap water and deionized water. It can be seen that the tendency for the two media is the same. The efficiency has a plateau between pH 6 and 9 and increases dramatically for pH values above 9. A small increase can also be seen for pH values below 6. In the figure the experimentally achieved data points and the mean value of those are plotted as small and large points respectively.

It can be seen that the photodegradation efficiency is constant for pH values between 6 and 9. For pH values above 9, the efficiency increases dramatically. It also increases slightly for pH values below 6. The results for both tap water and deionized water show the same tendency.

11.1.3 Discussion

The starting concentration of 0.4 mg/ml TiO$_2$ particles was chosen because it is a high concentration that still can be measured with good accuracy, which was shown in fig. 13. A lower starting concentration would not have given such a large shift, while a higher concentration would have saturated the measurement setup.

There is a big difference between the behavior of the particles in tap water and deionized water. In tap water the particles sediment independently of the pH value, while in deionized water the pH determines the sedimentation rate. The behavior has importance in future experiments.

During the exposure, it is advantageous if the particles do not sediment. The solution is then homogeneous throughout the experiment and the effect is independent of how often the samples are shaken. However, the particles need to have sedimented before the analysis in order for it to show the correct RhoB concentration. One way of removing the particles from the analysis volume, would be to use a centrifuge. However, this is not desirable because of the need to transfer the samples between the exposure vial to the centrifuge
vial and then transfer the supernatant back to the analysis vial. Another way of dealing with solutions with particles that do not sediment is to add droplets of pH 4 buffer a couple of hours before the analysis. As seen in fig. 17(b), the particles will then sediment quite fast, making analysis possible without changing the photodegradation process. To correct for the possible change of concentration of RhoB in the samples when droplets are added, even if the added volume is small, also two droplets of pH 4 buffer is added to the control sample showing the concentration before exposure. Hereafter, the adding of pH 4 buffer to the samples will be done in all experiments after exposure.

The behavior of the particles in fig. 17 is interesting due to the fact that the isoelectric point (IEP) of TiO$_2$ lies around pH 6 [43]. The IEP is defined as when particles in a solution have no net electrical charge on the surface in comparison to the surrounding medium. The net charge on the surface is changed by changing the pH-value of the solution. At the IEP the particles should then sediment faster than particles with a net charge on the surface, due to coulomb repulsion.[44] However, even though an increase in the sedimentation rate can be seen when the pH goes below seven, a decrease can not be seen when the pH is lowered further. One reason for this could be that when the pH value passes the IEP of the particles they cluster. When they have clustered, they might stay clustered also when the pH value changes from the IEP.

In the pH dependence on the photodegradation efficiency, the samples in tap water and deionized water were exposed on different days, why direct comparisons between the photodegradation efficiencies can not be made. However, it can be seen that the samples with tap water and deionized water show the same tendency and this indicates that the effect is media independent. Due to the higher ion concentration in tap water than in deionized water, more buffer solution was required to change the pH value. In order to avoid changing the concentrations in the samples too much, a narrower pH range was used for tap water than for deionized water. The addition of one droplet of pH 4 buffer before the highest pH value samples were extracted was to ensure that all samples had the same types of ions in them, however at different amounts.

The results in fig. 18 show a plateau in the graph between pH 6 and 9, where the efficiency is low. This is important to know for future experiments with different medias, where the pH value may differ slightly. Both at pH values above 9 and below 6, the efficiency increases. The efficiency for pH values below 6 could possibly be even higher, but may have been lowered due to the small dilution of the solution when the buffer was added. This result can be compared with the results from a similar experiment with zink oxide [2]. In that experiment the same tendency was seen but the plateau was only seen between pH value 6 and 7.

Because the sedimentation rate is pH dependent for deionized water, see fig. 17(b), it could have been argued that the pH dependence on the efficiency is due to the different sedimentation rates in the samples. However, tap water show no pH dependence on the sedimentation rate, but still show the same pH dependence on the efficiency as deionized water. The conclusion is thus that the pH dependence on the efficiency is not due to the difference in sedimentation rate between the samples.

Even if the efficiency clearly is pH dependent, the effect of having different amounts of
ions in the medium when the pH value is kept constant needs to be investigated further. Conclusions of that can not be made from this experiment.

11.2 Ion concentration dependence

In this experiment, the photodegradation efficiency dependence on the ion concentration was investigated. Also an analysis of the dependence of certain ions was performed.

11.2.1 Method

First, 280 ml of the standard solution was prepared. After that, 50 ml of the pH 7 buffer solution with OH-groups was mixed with 30 mg TiO$_2$ to make a 0.6 mg/ml TiO$_2$ 10 ppm RhoB solution. By adding different amounts of the two solutions, samples with ion concentrations 0, 2, 4, 6, 8, 10, 15, 20, 25, 30, 35, 38, 40, 42, 45 and 50 mM were made. Three small glass vials were filled for each concentration and two of the three vials were exposed at noon, the third working as a control sample.

A third solution was made by adding 24 mg TiO$_2$ to 40 ml of the pH 7 buffer solution without OH-groups. Samples with ion concentrations 0, 2, 4, 6, 8, 10, 15, 20, 25, 30, 35, 40, 45 and 50 mM were made by adding different amounts of this solution and the standard solution. The same procedure as before was then followed except that these samples were exposed at 13.00.

To make a comparison between the two buffer solutions, two 25 mM solutions were made by adding 7.5 ml of the buffer solutions to 22.5 ml of 10 ppm RhoB solution in deionized water and 18 mg TiO$_2$. 14 vials were filled for each solution and the samples were exposed for different times at noon.

11.2.2 Results

The results of the ion concentration dependence experiments are shown in fig. 19. It can be seen that the photodegradation increases dramatically when ions are added. Adding more ions does not increase the efficiency further, but the efficiency reaches a plateau at an ion concentration of 2 mM. The same effect is seen for the two buffer solutions.
11.2 Ion concentration dependence

Figure 19: Graphs showing the photodegradation efficiency as a function of ion concentration when pH 7 buffer solutions containing (a) KH$_2$PO$_4$ and NaOH and (b) K$_2$HPO$_4$ and HCl was used. It can be seen that the efficiency dramatically increases when ions are added, but also that a further increase in ion concentration does not increase the efficiency further. The effect seems to be independent of whether the buffer contains OH-groups or not. In the figure the experimentally achieved data points and the mean value of those are plotted as small and large points respectively.

The results of the comparison measurement between the two buffer solutions can be seen in fig. 20. The photodegradation efficiency is approximately the same for both of the buffer solutions.

The concentration of H$^+$ in the pH 7 buffer without OH-groups was calculated to 24.4 mM if all K$_2$HPO$_4$ is dissociated. In the same way, the concentration of H$^+$ and OH$^-$ in the pH 7 buffer with OH-groups was calculated to 63.2 mM and 36.8 mM respectively, see A.

The half lives were calculated to 5.2 minutes for the buffer with OH groups and 5.5 minutes for the buffer without OH groups.
11.2 Ion concentration dependence

Figure 20: Graphs showing the photodegradation efficiency as a function of ion concentration when pH 7 buffer solutions containing (a) KH₂PO₄ and NaOH and (b) K₂HPO₄ and HCl was used. It can be seen that the efficiency dramatically increases when ions are added, but also that a further increase in ion concentration does not increase the efficiency further. The effect seems to be independent of whether the buffer contains OH-groups or not. In the figure the experimentally achieved data points and the mean value of those are plotted as small and large points respectively. The lines represent fits to exponential functions.

11.2.3 Discussion

pH 7 buffer solution was used in order to keep the pH value in the solutions constant near the original value of the standard solution and to avoid changing the pH value when larger amounts of buffer solution was used.

In the results it can be seen that the photodegradation efficiency increases dramatically already when the lowest concentration of the two buffers are used. When higher concentrations of ions are used, the efficiency stays constant. In the comparison measurement between the two buffer solution it can be seen that the photodegradation efficiency is approximately the same.

In both of the buffer solutions used, H⁺ ions was achieved when the molecules dissociated. The concentrations of H⁺ ions in the buffers were 24.4 mM and 63.2 mM for the buffer without OH-groups and with OH-groups respectively. The concentration of OH-groups in the buffer solution with OH-groups was calculated to 36.8 mM. Because the increase in the photodegradation efficiency seem to be independent of which of the two buffer solutions that are used, it is not likely that it is caused by the OH-groups. Because the increase is as big in the two cases it is reasonable to believe that it is caused by ions.
that both of the solutions contain. The concentration of $H^+$ ions in the buffer solution with OH-groups is higher than the concentration of OH$^-$. If all of the OH$^-$ ions would bind to H$^+$ ions and form water, the remaining concentration of H$^+$ ions would be 26.4 mM. That concentration is very similar to the concentration of H$^+$ ions in the buffer solution without OH-groups.

As can be seen in eq. 5, H$^+$ ions can react with electrons and O$_2^*$ and form H$_2$O$_2$, which according to eq. 6, can form OH$^*$. If the amount of O$_2^*$ available for reactions is rather small, the addition of H$^+$ ions might saturate the reaction. That would lead to an increase of the photodegradation efficiency when the lowest concentration of ions is used and a plateau when even higher concentrations are added. Another reason for this reaction would also be that more electrons participate in reactions, which leads to a lower recombination rate of electrons and holes.

11.3 Tap water, ocean water and salinity dependence

The purpose of these experiments was to investigate the photodegradation efficiency of TiO$_2$ particles in different media and to see if tap water and ocean water could be substituted with deionized water. The dependence of the salinity on the photodegradation efficiency was also investigated.

11.3.1 Method

**Tap water:** In order to compare the photodegradation efficiency of tap water and deionized water, 20 ml of the standard solution and 20 ml of the standard solution with tap water instead of deionized water were prepared. From each of the solutions, nine small glass vials were filled. One vial of each solution was exposed for 0, 10 and 20 minutes. Three vials of each solution were exposed for 30 and 40 minutes to ensure the ability to analyze the samples in large glass vials. The exposure took place at noon.

**Salinity dependence:** In this experiment, the salinity dependence on the photodegradation efficiency was investigated. 100 ml of the standard solution was prepared. To 50 ml of the standard solution 1546.4 mg table salt, see 15, was added to make a 3 wt % salinity solution. This solution was stirred for 5 minutes with a magnetic stirrer. To make a 1 wt % solution, 7 ml of the standard solution was added to 14 ml of the 3 wt % salinity solution and to make a 2 wt % solution 14 ml of the standard solution was added to 7 ml of the 3 wt % salinity solution. For each of the concentration eight vials were filled and the samples were exposed at 11.30.

**Ocean water:** To compare the photodegradation efficiency of TiO$_2$ in ocean water and in deionized water with corresponding salinity, 20 ml of the standard solution and 20 ml of the standard solution with ocean water instead of deionized water were prepared. To 19.3 ml of the pure standard solution, 0.7 g of table salt was added to make a 3.5 wt% salinity solution. Seven vials were filled for each solution and they were exposed at noon.
11.3 Tap water, ocean water and salinity dependence

11.3.2 Results

The results from the comparison between tap water and deionized water are shown in fig. 21.

Figure 21: Graph showing the normalized concentration of RhoB for samples with tap water and deionized water as a function of exposure time. The samples were exposed at noon. It can be seen that the efficiencies in the two cases are very similar. The lines represent fits to exponential functions.

It can be seen that the efficiency is very similar in both cases but that tap water is slightly better. The 40 minutes measurement point for tap water is here excluded because the concentration of RhoB was too low to be measured also in the large glass vials. The half lives were calculated to 6.4 minutes for tap water and 7.9 minutes for deionized water.

The results of the salinity dependence experiment is shown in fig. 22. It can be seen in the graph that the photodegradation efficiency decreases with increasing salinity. The half lives were calculated to 18.5 minutes for 0 % salinity, 30.7 minutes for 1 % salinity, 35.2 minutes for 2 % salinity and 40.5 minutes for 3 % salinity.
11.3 Tap water, ocean water and salinity dependence

**Figure 22:** Graph showing the normalized concentration of RhoB for samples containing different concentrations of salt as a function of exposure time. It can be seen that the efficiency decreases with increasing salinity. In the figure the experimentally achieved data points and the mean value of those are plotted as small and large points respectively. The lines represent fits to exponential functions.

The results from the comparison of ocean water and deionized water with a 3.5 wt% salinity can be seen in fig. 23.

**Figure 23:** Graph showing the normalized concentration for different exposure times for samples with ocean water and deionized water with 3.5 wt% salinity. It can be seen that the efficiency for the two are roughly the same. The lines represent fits to exponential functions.

It can be seen that the photodegradation efficiency for both solutions are roughly the same. The half lives were calculated to 23 minutes and 20.7 minutes for deionized water with w
3.5% salinity and ocean water respectively.

### 11.3.3 Discussion

The photodegradation efficiency of TiO$_2$ in tap water is very similar to that of TiO$_2$ in deionized water. The reason that deionized water is preferred to be used in experiments is that it is well defined and that the experiments can be reproduced. It is important to check though that the photodegradation process also works well in an environment that is more similar to that of future application areas. The result shows that the efficiency is as high, or even slightly higher for tap water than for deionized water. The reason for this might be that some of the ions in the tap water enhances the efficiency. This has to be investigated further.

When the salinity solutions were mixed, it was assumed that the standard solution had the same density as water at room temperature. It can be seen in fig. 22 that the efficiency decreases with increasing salinity. One explanation could be that the positively charged sodium ions from the salt adhere to the TiO$_2$ particle surface and hinders the charge carriers from reacting. Another reason could be that the TiO$_2$ particles cluster when salt is added. This is indicated by the increased sedimentation rate that was observed in the samples containing salt. If the particles cluster, the surface area is decreased and the faster sedimentation rate leads to inhomogeneous solutions in the samples, which would decrease the efficiency. It should be noted that the photodegradation still occurs even for salinity concentrations around 3 wt%, only at a slower rate.

The photodegradation efficiency curve of TiO$_2$ in ocean water and in deionized water with corresponding salinity show great resemblance. The data point for TiO$_2$ in ocean water at 40 minutes differs but this is probably due to a larger error and not a real deviation from the exponential behavior. The largest difference between the two media is that ocean water contains many different ions and substances in addition to salt. However, due to the similarity between the two curves, the photodegradation efficiency seems to depend only on the salinity. That the efficiency is salinity dependent was shown in fig. 22. Because ocean water might be a future area of interest, it is important to investigate the photodegradation efficiency in ocean water. However, in order to make reproducible experiments it is preferred if deionized water with added salt can be used instead of ocean water, as discussed above.

According to these experiments the substitution of tap water or ocean water with deionized water seems to be valid.

### 12 Nanocomposites

In an effort to increase the photodegradation efficiency different nanocomposites were tested. Composites with TiO$_2$ together with different wt% of Ag, Au, Si and Ge were investigated to see if the combination gives a higher photodegradation efficiency as well as at which concentration the efficiency is maximized. The adsorption effect of Ag, Au, Si
and Ge was also investigated.

When an increase in PDE was seen, the load where the maximum was seen was then used to do a time measurement. This was conducted to see a quantitative difference between the different mixtures and to be able to calculate the half life of RhoB in the samples.

In all experiment the vials were changed after exposure to reduce the amount of particles adhered on the inside surface of the glass vial. Those particles would otherwise give a reduced signal during the analysis, which could lead to misinterpreted results. For each concentration, three vials were prepared were one of these worked as a control sample and was not exposed to sunlight.

12.1 Concentration optimization for metals

12.1.1 Method

Gold: A 200 ml standard solution was prepared. To 80 ml of this solution, 96 mg of Au, see 15, was added to make a solution with 200 wt % Au of the TiO$_2$ concentration. Before adding the Au powder, it was grinded in a mortar to reduce the size of the particles in the powder. Different amounts of the two solutions were then mixed to get different wt % Au in the samples. The samples were exposed at noon.

Silver, nanopowder: A 130 ml standard solution was prepared. To 60 ml of this solution, 36 mg Ag nanopowder, see 15, was added to make a solution with 100 wt % Ag of the TiO$_2$ concentration. Different amounts of the two solutions were mixed to get different wt % Ag in the samples, which were exposed at noon.

A 70 ml standard solution and a 60 ml standard solution with a 100 wt % Ag nanopowder was also prepared separately. The 60 ml solution was prepared by adding 36 mg TiO$_2$ and 36 mg Ag nanopowder to 30 ml of deionized water. This solution was sonicated for 5 minutes and then stirred with a magnetic stirrer for 1 hour to give the Ag and TiO$_2$ more time to adhere to each other. After this, 30 ml of a 20 ppm RhoB solution was added to make a 0.6 mg/ml TiO$_2$ 10 ppm RhoB solution with a 100 wt % Ag. Different amounts of the two solutions were then mixed to get different wt % Ag in the samples, which were exposed at noon.

Silver, ground powder: In this experiment Ag powder was used, see 15. The powder was ground in a mortar before use to reduce the size of the particles in the powder. A 120 ml standard solution was prepared. Then 48 mg TiO$_2$ and 96 mg Ag ground powder was added to 40 ml of deionized water. This solution was sonicated for 5 minutes and then stirred with a magnetic stirrer for 1 hour to give the Ag and TiO$_2$ more time to adhere to each other. After this, 40 ml of a 20 ppm RhoB solution was added to make a 0.6 mg/ml TiO$_2$ 10 ppm RhoB solution with a 200 wt % Ag grinded powder. Different amounts of the two solutions were then mixed to get different wt % Ag in the samples, which were exposed at noon.
12.1 Concentration optimization for metals

12.1.2 Results

The results for TiO$_2$/Au is seen in fig. 24

![Graph showing (a) the photodegradation efficiency for different wt% of Au powder and (b) the adsorption effect of RhoB of the Au powder. The efficiency decreases when up to 10 wt % Au is added. Adding more Au leads to an increase in the efficiency until a maximum is reached when around 60 wt % Au is used. Adding more Au then again gives a decrease in the efficiency. It can also be seen that there is a small adsorption of RhoB by the Au powder, which does not increase with increasing load of Au. In the figure the experimentally achieved data points and the mean value of those are plotted as small and large points respectively.](image)

**Figure 24:** Graph showing (a) the photodegradation efficiency for different wt% of Au powder and (b) the adsorption effect of RhoB of the Au powder. The efficiency decreases when up to 10 wt % Au is added. Adding more Au leads to an increase in the efficiency until a maximum is reached when around 60 wt % Au is used. Adding more Au then again gives a decrease in the efficiency. It can also be seen that there is a small adsorption of RhoB by the Au powder, which does not increase with increasing load of Au. In the figure the experimentally achieved data points and the mean value of those are plotted as small and large points respectively.

It can be seen that the efficiency decreases when up to 10 wt % of Au is added and then increases for wt % > 10. A maximum is reached at around 60 wt % followed by a decrease in efficiency. A small adsorption of the RhoB was found when using Au, which did not increase for increasing loads.

The results for the TiO$_2$/Ag nanopowder is shown in fig. 25. It can be seen that the photodegradation efficiency decreases with increasing wt % of Ag nanopowder. The decrease is strong up to 40 wt % Ag and then reaches a plateau. The adsorption of RhoB by the Ag nanopowder is strong and at 100 wt % the original concentration has decreased to below 80 %.
12.1 Concentration optimization for metals

Figure 25: Graph showing (a) the photodegradation efficiency for different wt% of Ag nanopowder and (b) the adsorption of RhoB by the Ag nanopowder. It can be seen that the photodegradation efficiency decreases for increasing wt % of Ag. It can also be seen that the adsorption of RhoB increases with increasing wt % of Ag. In the figure the experimentally achieved data points and the mean value of those are plotted as small and large points respectively.

The results for the TiO$_2$/Ag nanopowder, where the particles have more time to adhere to each other, is shown in fig. 26.

Figure 26: Graph showing (a) the photodegradation efficiency for different wt% of Ag nanopowder and (b) the adsorption of RhoB by the Ag nanopowder. In these samples the Ag and the TiO$_2$ was stirred with a magnetic stirrer for 1 h in deionized water to give more time for the particles to adhere to each other. It can be seen that the photodegradation efficiency decreases for increasing wt % of Ag but has a small maximum at around 80 wt %. It can also be seen that the adsorption of RhoB increases with increasing wt % of Ag. In the figure the experimentally achieved data points and the mean value of those are plotted as small and large points respectively.
12.1 Concentration optimization for metals

It can be seen that the photodegradation efficiency decreases with increasing wt % of Ag nanopowder. As in fig. 25 the decrease is strongest in the lower range of added Ag. However, it can be seen that there is a small maximum at around 80 wt %. It can also be seen that the adsorption of RhoB increases with increasing wt % Ag.

The results for the TiO$_2$/Ag, where ground Ag powder was used and the particles have had time to adhere to each other, is shown in fig. 27.

![Graph showing the photodegradation efficiency and adsorption of RhoB](a) (b)

**Figure 27:** Graph showing (a) the photodegradation efficiency for different wt % of Ag ground powder and (b) the adsorption of RhoB by the Ag ground powder. In these samples the Ag and the TiO$_2$ was stirred with a magnetic stirrer for 1 hour in deionized water to give more time for the particles to adhere to each other. It can be seen that by adding Ag ground powder the photodegradation efficiency increases and the highest efficiency is reached at 200 wt % of Ag. It can also be seen that there is no adsorption of RhoB by the Ag ground powder. In the figure the experimentally achieved data points and the mean value of those are plotted as small and large points respectively.

It can be seen that the photodegradation efficiency is increased with increasing amounts of Ag ground powder added. The highest photodegradation efficiency is observed at 200 wt % Ag. It can also be seen that there is no adsorption of RhoB by the Ag ground powder.

### Discussion

The ground powders of Ag and Au used above was ground from a high purity powder form of the metals, see 15. The powder was ground in a mortar to reduce the size of the particles. It can be argued that the size of the particles after such a simplistic grinding method would vary a lot. However, as seen in table 1 the polydispersity, which is a measure of the width of the size distribution of the sample, for Au was the lowest of all powders.
12.1 Concentration optimization for metals

This could be compared to Ag nanopowder, a factory made nanopowder, which had the highest polydispersity of all powders tested, TiO$_2$ excluded.

The results for the photodegradation efficiency for Au was found to be complex. When Au is added the photodegradation efficiency decreases drastically but after 10 wt % the photodegradation efficiency increases drastically again to reach a maximum at about 60 wt %. After this maximum the photodegradation efficiency decreases once more. The behavior is hard to explain but in part it can be explained by the reflection of UV-light and the electron transfer. The reflection of Au is around 40 % in the UV range, see fig. 5, which could explain why the PDE decreases when Au is added. However, above 10 wt % it seems as though the electron transfer from TiO$_2$ to Au begins to be effective and the gain in efficiency due to the electron transfer becomes larger than the loss of efficiency due to the absorption of UV-light by the Au particles. For increasing load above 60 wt % the absorption of UV-light is again the dominant reaction and the PDE decreases once again. Also, for increasing load of Au, not all Au particles would be completely surrounded by TiO$_2$, limiting further increase in PDE.

For the above explanation to be true an very effective electron transfer needs to occur to cancel out the very high reduction in PDE seen for the lower loads of Au. An effective electron transfer occurs when the width of the potential barrier between the Au and the TiO$_2$ is reduced. This would occur if the TiO$_2$ and the Au would make a close contact to each other.

With the use of Ag nanopowder the PDE decreased. In both experiments the PDE decreases for low loads of Ag but in the experiment where the Ag nanopowder have had more time to adhere to the TiO$_2$, an small increase is seen after 40 wt % and a maximum is reached at 80 wt %. This behavior is the same as seen in Au, but not as strong, which shows that the electron transfer between the TiO$_2$ and the Ag nanopowder is poor. This could be due to weak or no bonding between the semiconductor and the metal which enhances the width of the potential barrier. Even at the peak the efficiency is not as strong as then when using pure TiO$_2$, which makes the Ag nanopowder a poor candidate to use if an increase in PDE is wanted.

The adsorption of RhoB by the Ag nanopowder decreases when the samples have been given more time to adhere to each other. This would indicate an enhancement of the binding between the TiO$_2$ and the Ag nanopowder. Despite this the PDE did not increase above the one achieved for pure TiO$_2$, which again indicates a poor electron transfer.

When Ag ground powder was used the technique of adhesion was used because of the increase in binding seen with Ag nanopowder. The PDE for Ag ground powder was found to, opposite to Ag nanopowder, increase the PDE of TiO$_2$. A reason for the different properties of Ag nanopowder and Ag ground powder could be its surface properties. The production of the two differ, and although the production process of Ag nanopowder is not known, the production process of nanopowder often leaves the particles with different surface properties compared to bulk material. The Ag ground powder, as well as Au ground powder, is more like the bulk material in its optical properties and then it is also likely that the rest of the surface properties are also the very much alike. This indicates that, combined with the results for Ag ground powder, that there is a close bonding by the Ag
and the TiO$_2$ and that the electron transfer is effective. It also confirms that the reflection of Ag, seen in fig. 5, is high in the UV-range.

The wt % Ag grinded powder in the samples shown in fig. 27 is the amount that was weighted. The true wt % in the samples is not as high. When the Ag grinded powder was mixed with the TiO$_2$ in the aqueous solution, a large amount sedimented to the bottom immediately and some floated on the top. This amount was never added to the exposure vials, but instead when filling the exposure vials, the solution between the bottom and the surface was extracted. The reason for this was to only get Ag particles in the solution that was close to the size of TiO$_2$, and that would participate in the reaction. For this reason the true wt % Ag in the samples was much less then that presented in the graph. A way to measure how much Ag that was really used was not found, but this is an important knowledge to have and a mehtod to do this has to be found.

12.2 Time measurement metals

12.2.1 Method

A 60 ml standard solution was prepared. To 30 ml of this solution, 10.8 mg Au was added to make a solution with 0.6 mg/ml TiO$_2$ with 60 wt % Au. A third solution was also prepared with 30 ml 10 ppm RhoB together with 10.8 mg Au. 12 vials were filled from each of the solutions and these were then exposed for different times at noon.

The same process was then redone with Ag ground powder instead of Au, but here the Ag and TiO$_2$ were allowed to adhere for one hour before the addition of RhoB. The exposure took place at the same time to be able to see which of the two metals would be the most effective to use when an increase in PDE is wanted.

12.2.2 Results

The results from the comparison between TiO$_2$, TiO$_2$/Au and pure Au as well as the comparison between TiO$_2$, TiO$_2$/Ag ground powder and pure Ag ground powder are shown in fig. 28. It can be seen in fig 28a that the combination of TiO$_2$/Au increases the PDE compared to pure TiO$_2$ and that there is no cleaning power if only Au is used. The same apply for Ag ground powder.
The result for the comparison between TiO$_2$, TiO$_2$/Au and TiO$_2$/Ag ground powder is shown in fig. 29. It can be seen that both Au and Ag ground powder enhances the PDE approximately as much. The half lives were calculated to 20.2 minutes for pure TiO$_2$, 12.7 minutes for TiO$_2$/Au and 13.6 minutes for TiO$_2$/Ag ground powder.
12.3 Concentration optimization for semiconductors

12.3.1 Method

Silicon: A 160 ml standard solution was prepared. To 50 ml of this solution 30 mg of Si powder was added, see 15, which had been ground in a mortar to reduce the size of the particles, to make a solution with 100 wt % Si of the TiO₂ concentration. Different amounts of the two solutions were mixed to get different wt % of Si in the samples, which were exposed at noon.

A 110 ml standard solution and a 50 ml standard solution with a 100 wt % Si grinded powder was also prepared separately. The 50 ml solution was prepared by adding 30 mg TiO₂ and 30 mg Si grinded powder to 25 ml deionized water. This solution was sonicated for 5 minutes and then stirred with a magnetic stirrer for 1 hour to give the Si and TiO₂ more time to adhere to each other. After this, 25 ml of a 20 ppm RhoB solution was added.

Figure 29: Graph showing the comparison of the cleaning process for TiO₂, TiO₂/Au and TiO₂/Ag ground powder. It can be seen that the cleaning process when adding Ag ground powder or Au increases the PDE by an equal amount. In the figure the experimentally achieved data points and the mean value of those are plotted as small and large points respectively. The lines represent fits to exponential functions.

12.2.3 Discussion

The concentrations of Ag ground powder and Au used in these experiments where the same as was found in 12.1 to increase the PDE most. These were 60 wt % and 200 wt % for Au and Ag ground powder respectively. Both the materials enhance the PDE by an equal amount which indicates that Au would have a more efficient electron transfer then Ag grinded powder due to the lower reflection of Au in the UV-range, see fig. 5.
to make a 0.6 mg/ml TiO$_2$ 10 ppm RhoB solution with a 100 wt % Si. Different amounts of the two solutions were then mixed to get different wt % Si in the samples, which were then exposed at noon.

**Germanium:** A 200 ml standard solution was prepared. To 80 ml of this solution 96 mg Ge was added, see 15 , which had been ground in a mortar to reduce the size of the particles, to make a solution with 200 wt % of the TiO$_2$ concentration. Different amounts of the two solutions were mixed to get different wt % of Ge in the samples, which were exposed at 11.30.

### 12.3.2 Results

The results for TiO$_2$/Si is shown in fig. 30.

![Graphs showing (a) the photodegradation efficiency for different wt% of Si powder and (b) the absorption effect of the Si powder.](image)

**Figure 30:** Graphs showing (a) the photodegradation efficiency for different wt% of Si powder and (b) the absorption effect of the Si powder. It can be seen that the photodegradation efficiency decreases with increasing amounts of Si in the samples. The adsorption of RhoB by the Si powder is strong and at 90 wt % the original concentration has decreased to little over 80 %. In the figure the experimentally achieved data points and the mean value of those are plotted as small and large points respectively.

It can be seen that the photodegradation decreases with increasing amounts of Si in the samples. Also the adsorption of RhoB by the Si powder reaches about 80 % of the original when 90 wt % Si is used.

The results for TiO$_2$/Si, where the TiO$_2$ and the Si have had more time to adhere to each other, is shown in fig. 31. It can be seen that the photodegradation efficiency decreases with increasing amounts of Si in the samples. An adsorption of RhoB by the Si powder can also be seen which reaches 90 % of the original concentration at 90 wt % Si.
12.3 Concentration optimization for semiconductors

Figure 31: Graphs showing (a) the photodegradation efficiency for different wt% of Si powder and (b) the adsorption effect of the Si powder. It can be seen that the photodegradation efficiency decreases with increasing amounts of Si in the samples and that there is an adsorption of RhoB by the Si powder. In the figure the experimentally achieved data points and the mean value of those are plotted as small and large points respectively.

The results for the TiO$_2$/Ge is shown in fig. 32.

Figure 32: Graph showing (a) the photodegradation efficiency for different wt% of Ge powder and (b) the adsorption effect of RhoB of the Ge powder. It can be seen that the Ge powder enhances the photodegradation efficiency and that the efficiency reaches a maximum when around 130 wt% Ge is used. It can also be seen that there is no adsorption of RhoB by the Ge powder. In the figure the experimentally achieved data points and the mean value of those are plotted as small and large points respectively.

It can be seen that the photodegradation efficiency is enhanced when Ge is added and that
the enhancing effect reaches a plateau at around 130 wt % Ge. No adsorption effect of RhoB by the Ge powder was found.

### 12.3.3 Discussion

In both the Si and the Ge experiments, ground powder of the two semiconductors were used, see 15. The discussion applied for Ag ground powder can also be adapted here, that ground powder more follows the bulk materials properties. If so the reflection of the two materials are basically the same, see fig. 9 and the difference between the two materials would then be its electron transfer efficiency.

For Si it can be seen that the PDE decreases both when the Si is allowed to adhere to the TiO₂ before the RhoB is added and when RhoB is added at the same time as Si and TiO₂. The decrease in efficiency seems to be linear in both experiments and this indicates that there is no electron transfer between Si and TiO₂. This could be due to weak bonding between the materials which would give a wide potential barrier. That the decrease is linear is thus explained by the increasing absorption of the UV-light by the Si particles when higher loads are used.

The difference between the results for Si with and without adhesion is that when adhesion is applied, the decline in PDE is less then without adhesion. This is explained by the lower adsorption of RhoB in these samples. When adhesion is applied the Si and the TiO₂ have more time to adhere to each other and this leaves fewer sites for the RhoB to bind to the Si. If more Si is surrounded by TiO₂, the Si would in turn block less UV-light from the TiO₂, which would decrease the PDE less then if no binding was present.

When Ge is used the PDE increases for increasing loads and reaches a plateau at about 130 wt %. The increase in PDE is quite large and the efficiency is doubled in the time these samples were exposed. This indicates a very effective electron transfer between Ge and TiO₂, despite the drawback of the low reflection of Ge of about 50 - 60 % in the UV-range. The PDE is expected to reduce once again for even higher loads than whats tested here due to increase absorption of UV-light by the Ge particles and the saturation of electron transfer due to that all TiO₂ has bound to the Ge particles.

### 12.4 Time measurement semiconductor

#### 12.4.1 Method

A 60 ml standard solution was prepared. To 30 ml of this solution, 23.4 mg Ge was added to make a solution with 0.6 mg/ml TiO₂ with 130 wt % Ge. A third solution was also prepared with 30 ml 10 ppm RhoB together with 23.4 mg Ge. 12 vials were filled from each of the solutions and these were then exposed for different times at noon.

#### 12.4.2 Results

The results from the comparison between TiO₂, TiO₂/Ge and pure Ge can be seen in fig. 33.
13 Summary and conclusions

In this report the photodegradation of RhoB using TiO$_2$ nanoparticles in different media and nanocomposites of TiO$_2$ was investigated.

The effective diameters of the different particles used were measured and the results showed that the ground powders contained smaller particles than the manufactured nanopowders. The TiO$_2$ particles were 20 times as big as indicated on the can. The polydispersity was large in all the samples.

Figure 33: Graph showing the comparison of the cleaning process for TiO$_2$, TiO$_2$/Ge and pure Ge powder. It can be seen that the cleaning process when adding Ge is greatly increased compared to using pure TiO$_2$. It can also be seen that just using Ge powder does not have an effect on the cleaning process. In the figure the experimentally achieved data points and the mean value of those are plotted as small and large points respectively. The lines represent fits to exponential functions.

It can be seen that the combination of TiO$_2$/Ge greatly increase the PDE compared to pure TiO$_2$ and that there is no cleaning power if only Ge is used. The half life for pure TiO$_2$ and for TiO$_2$/Ge was calculated to 28.0 minutes and 11.0 minutes respectively.

12.4.3 Discussion

The concentration of Ge used in this experiment was the same as the maximum value found in fig. 32, with lay at a value of 130 wt %. It can be seen that the PDE is greatly increased with the combination TiO$_2$/Ge and the half life of pure TiO$_2$ was 2.5 times longer than the half live of TiO$_2$/Ge. This can be compared to when using TiO$_2$/Ag grinded powder which raised the PDE by 50 % compared to using pure TiO$_2$, see fig. 29. This shows that the combination TiO$_2$/Ge is the nanocomposite to be used to enhance the PDE.
By measuring the PDE at different times during a day, it was found that a plateau in the PDE existed between 11.30 and 13.30. Exposures done earlier or later gave a lower PDE. When time measurements were performed, the time was chosen so that the entire exposure was in the interval when the PDE was constant.

The sedimentation rate of the particles at different pH levels was constant and high when tap water was used, but decreased at pH values above 6 when deionized water was used. This means that TiO$_2$ particles in pure deionized water sediment very slowly but that the sedimentation rate can be greatly increased by adding droplets of pH 4 buffer. For TiO$_2$ particles in tap water the shaking of the samples during exposure is more important due to their fast sedimentation. On the other hand, no buffer was needed in order to be able to analyze those samples.

The pH dependence on the PDE was the same when both tap water and deionized water was used. The experiments showed that the efficiency was low at neutral pH values, but increased for pH values below 6 and above 9. This behavior is important to know about if the method is to be used in medias with different pH values.

When ions were added to the solution, the PDE greatly increased. The reason for this is probably the addition of hydrogen ions that can participate in the formation of hydroxyl radicals. Because the PDE reached a plateau already when the lowest concentration of ions was used, the reaction seems to be saturated by the hydrogen ions. The experiments also showed that the PDE did not seem to depend on the added hydroxyl ion concentrations.

It was found that the PDE was approximately the same when tap water and deionized water was used or when ocean water and deionized water with 3.5 wt % salinity was used. The latter result suggests that the PDE in ocean water only is dependent on the salinity and not on the other molecules and ions in the ocean water. Deionized water can thus be used instead of tap water or ocean water to make reproducible experiments. The PDE was also shown to decrease with increasing salinity. This might be due to that the ions in the salt bind to the surface of the TiO$_2$ particles and hinders the photocatalytic reactions.

Nanocomposites of TiO$_2$ together with ground powders of Au, Ag and Ge enhanced the PDE in comparison to when pure TiO$_2$ was used. When Si ground powder and Ag nanopowder were used the PDE instead decreased. The best alternative results were achieved with Ge and the half life was 2.5 times longer for pure TiO$_2$ than with the TiO$_2$/Ge composite. The optimum loading of Ge was around 130 wt % of the TiO$_2$ concentration and such a high concentration can be explained by the fact that the TiO$_2$ particles were larger than expected and that all particles do not bind to each other.

14 Future

In the future photocatalysis of TiO$_2$ can become an important way to clean water. In order to help people with polluted drinking water, the process need to be cheap and effective. It is important to try to enhance the efficiency, but the method must also be cost effective. The sedimentation rate of the particles determine how often the samples with polluted water need to be stirred during the cleaning process. The biological aspects are of course
also vital. The effect of TiO$_2$ nanoparticles and potential enhancing materials in biological systems need to be thoroughly investigated before the technique can be used.

Another possible application is to use the method to clean contaminated lakes. One example is lake Taihu in China, which suffered from blooms of toxic blue green algae. Four million persons are depending on the lake for their drinking water and to clean it with other toxins is therefore not a good option.[45] To spread out a layer of TiO$_2$ on the lake on a sunny day would have been a simple way to deal with the problem. For this cleaning process to be effective, it must be fast. Because it is dependent on the UV-light from the sun, the process only can occur when the particles are close to the surface. It is thus important to know the sedimentation rate, which determines for how long the particles stay at the surface. If the particles sediment too fast, the time available for reactions is too short for the lake to be cleaned.

Because the method can be used in ocean water, a possible future application is to clean the ocean from oil spill. Because the oil floats on the surface of the ocean, the TiO$_2$ particles can be spread out on top of the oil layer in order to degrade it. Some studies have already been done in this area, but in order for this application to become a reality, the efficiency of the particles in oil need to be investigated further [46].

Also when the method is to be used for cleaning lakes or oceans, it is important to study what happens to the particles when the cleaning process is finished and the particles sediment to the bottom. Eventually a part of the particles will be flushed up on the shore and it must then not be dangerous for the environment. Another scenario is if the method is used in a shallow lake. The particles might then be reactive also when they have sedimented to the bottom and it is important that they do not harm the ecosystem.

Because most of the produced electron-hole pairs recombine before they reach the surface, it is important to have a short distance for them to travel before they can react. One way to achieve this without reducing the surface area available for reactions would be to use nanorods instead of nanospheres. If studies would show that the efficiency increases when nanorods are used, the increased cost of buying or producing nanorods must also be considered.

A lot of research has already been done about the photodegradation process using TiO$_2$ nanoparticles. Even if there still are problems to solve, this method is in the future likely to become a good alternative for cleaning of water.
15 Chemical list

Ag nanopowder  Silver, 99.5 % silver nanopowder, <100 nm, Aldrich Chemistry

Ag powder  Silver, 99.999 % silver powder, Apache Chemicals

Au  Gold, 99.9995 % gold powder, Strem Chemicals

Ge  Germanium, 99.999 % germanium powder, Aesar

HCl  Hydrochloric acid

KHP  Potassium hydrogen phtalate

K₂HPO₄  Dipotassium hydrogen phosphate

KH₂PO₄  Potassium dihydrogen phosphate

KOH  Potassium hydroxide, Aesar

NaOH  Sodium hydroxide

Ocean water  Water collected from the Pacific ocean, 5 m from the coast at Waikiki Beach, Honolulu, Hawaii

Rhodamine B  C₂₈H₃₁ClN₂O₃, BDH Chemicals Ltd, a common fluorescent dye

Si  Silicon, 99.999 % silicon powder, Aesar

Standard solution  10 ppm Rhodamine B and 0.6 mg/ml TiO₂ nanoparticles in deionized water, solution most commonly used in the experiments

Table salt  Sodium Chloride, Sodium Silicoaluminate, Sodium Thiosulfate, Potassium Iodide

TiO₂  Titanium dioxide, 10 nm particles, anatase, 99%, Nanostructured & Amorphous Materials Inc
References


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A Appendix

Calculation of hydrogen ion and hydroxyl ion concentrations

**pH 7 buffer with OH-groups**
Dissociation of HPO$_4^{2-}$ → H$^+$ + PO$_4^{3-}$ has been neglected.
KH$_2$PO$_4$ + NaOH → K$^+$ + H$^+$ + HPO$_4^{2-}$ + Na$^+$ + OH$^-$

0.1 M KH$_2$PO$_4$
0.1 M NaOH

\[
\begin{align*}
V_{KH_2PO_4} &= 100 \text{ ml} \\
V_{NaOH} &= 58.2 \text{ ml}
\end{align*}
\]

Molar KH$_2$PO$_4$ = 0.1 \cdot \frac{100}{100} = 63.2 mM
Molar NaOH = 0.1 \cdot \frac{58.2}{100} = 36.8 mM

⇒ 63.2 mM H$^+$, 36.8 mM OH$^-$

**pH 7 buffer without OH-groups**
Dissociation of HPO$_4^{2-}$ → H$^+$ + PO$_4^{3-}$ has been neglected.
K$_2$HPO$_4$ + HCL → K$^+$ + K$^+$ + HPO$_4^{2-}$ + H$^+$ + Cl$^-$

0.1 M K$_2$HPO$_4$
0.1 M HCl

\[
\begin{align*}
V_{K_2HPO_4} &= 756 \text{ ml} \\
V_{HCl} &= 244 \text{ ml}
\end{align*}
\]

Molar K$_2$HPO$_4$ = 0.1 \cdot \frac{756}{1000} = 75.6 mM
Molar HCl = 0.1 \cdot \frac{244}{1000} = 24.4 mM

⇒ 24.4 mM H$^+$