

## TiO<sub>2</sub>: A New Kind of Water Treatment

### 3: A new kind of water treatment – What is solar disinfection with titanium dioxide and how does it work?

The World Health Organisation (WHO) estimates that 1.1 billion people do not have access to safe drinking water. Only about half the world's population can turn a tap on in their homes to get running water. For the other half, their water supply is often not treated and can carry harmful microorganisms.

We need a new kind of water treatment that can help people to disinfect their own water supply easily so that their water becomes safe to drink. An ideal method uses easily available energy such as sunlight and does not require expensive equipment.

#### Solar Disinfection (SODIS)

When water containing microorganisms is exposed to sunlight for 24 hours it becomes safer to drink because the energy of the solar radiation destroys microorganisms. This method requires clear water, without many suspended particles; otherwise the light does not get to the microorganisms. The water should be consumed directly from the bottle to avoid re-contamination.

Recycled plastic bottles are cheap, easily on hand and are good containers for drinking water.

SODIS is a good starting point for a new kind of water treatment but it needs improvement. The main problems are that it is fairly slow and it is difficult to tell if all the contaminants have been destroyed.

Table 1: Advantages, drawbacks and dangers of using SODIS.

Advantages	Drawbacks	Dangers
<ul style="list-style-type: none"> <li>Does not require chemicals or equipment apart from plastic bottles.</li> </ul>	<ul style="list-style-type: none"> <li>Only a limited quantity of water can be processed.</li> <li>Process is slow.</li> <li>Dependent on strong sunlight.</li> <li>Fairly clear water needed.</li> <li>Constant supply of plastic bottles needed.</li> <li>Accumulation of plastic waste.</li> </ul>	<ul style="list-style-type: none"> <li>Visible light less effective than ultra-violet (UV) light.</li> <li>Not certain that all microorganisms have been destroyed.</li> <li>Variable light intensity means uncertainty.</li> <li>Does not work in the absence of bright light.</li> <li>Bottles can become contaminated.</li> </ul>

The purification process can be made faster and better using a photocatalyst, a substance which absorbs light and passes on the energy to other molecules to speed up a reaction.

#### Improved solar disinfection with a titanium dioxide photocatalyst

The most widely used photocatalyst is titanium dioxide (TiO<sub>2</sub>). If the inside of clear containers such as glass or plastic bottles are coated with a layer of very fine titanium dioxide particles the action of light is enhanced. Organic molecules and microorganisms are destroyed much faster due to the

water producing very reactive hydroxyl free radicals ( $\cdot\text{OH}$ ) which attack molecules in microorganisms. Free radicals have an unpaired electron and this makes them very reactive. Hydroxyl free radicals are very powerful oxidising agents which attack the structure of cell membranes and break down organic molecules. As a result, microorganisms are destroyed.

### Nano-structured titanium dioxide as photocatalyst

Titanium dioxide is the most frequently used photocatalyst for water and air purification. It is relatively cheap and abundant. It is non-toxic, insoluble in water and resistant to most chemicals, such as acids, bases or solvents.

Photocatalysts work best if the particles are very fine with a particle size of about 14–21 nm. This is nano-structured titanium dioxide. The particles are so small that you cannot see them when they are suspended in water. Because they are so small, the surface area to volume ratio is large.

### Why can titanium dioxide act as a photocatalyst?

The most important property of titanium dioxide that makes it a good photocatalyst is that it is a semi-conductor. Under certain conditions, electrons can become mobile in semi-conductors. For this to happen the right amount of energy needs to be supplied to the semi-conductor. For titanium dioxide, the right energy has a wavelength of about 400 nm, that is electromagnetic radiation at the boundary of visible and ultra-violet light. Titanium dioxide, as a semi-conductor can absorb portions of visible light called photons in order to mobilise its electrons.

The most important photocatalyst in nature is chlorophyll. In photosynthesis, chlorophyll captures visible light and provides the energy to build up glucose from carbon dioxide and water. Ultimately, this is the reaction which provides the energy for most forms of life on earth.

### What are semi-conductors?

In solids, the outer electrons can potentially be found in two energetic bands: the valence band,  $V_B$ , and the conduction band,  $C_B$ .

The valence band is the band which normally holds the outer electrons in a solid structure.

If electrons move into the conduction band, the electrons become delocalised (no longer belong to a particular atom anymore). This means electrons can move and transport charge.

In typical conductors, like metals, the valence band and the conduction band overlap or are very close to each other (Figure 1). Little or no energy is needed to get electrons to move from the valence band to the conduction band. A potential difference between a positive electrode and a negative electrode is sufficient to make the outer electron move and transport a charge.

In insulators, the gap between the valence band and the conduction band is large and requires a significant input of energy for an electron to move into the conduction band. The energy gap or band gap is 6–7 eV.

In semi-conductors, the energy gap between the valence band and the conduction band is in the region of 0.7–3.5 eV. With the correct energy from sunlight, electrons can move from the valence band to the conduction band.

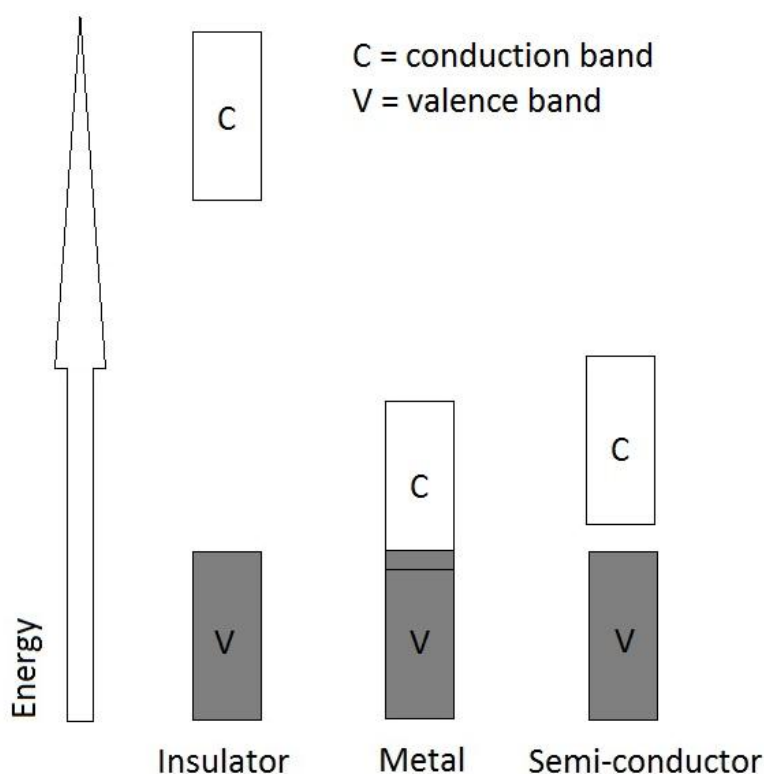


Figure 1: Valence and conduction bands in insulators, metals and semi-conductors.

In semi-conductors with band gaps of  $\leq 3$  eV, visible light can be absorbed and an electron can be raised from the valence band to the conduction band (Figure 2). We say the electron has become excited. The conduction band now has a negative charge due to the extra electron. The valence band has lost an electron, developed an electron hole and, therefore, a positive charge. If the semi-conductor is suspended in water, redox reactions can take place. Locations with excess electrons can cause reduction and electron holes can cause oxidation.

Table 2: Examples of band gaps in semi-conductors.

Semi-conductor	$E_g(\text{eV})$	Insulator	$E_g(\text{eV})$
Si	1.1	Ceramic	6-7
WO <sub>3</sub>	2.8		
TiO <sub>2</sub> (rutile)	3.0		
TiO <sub>2</sub> (anastase)	3.2		
SnO <sub>2</sub>	3.5		

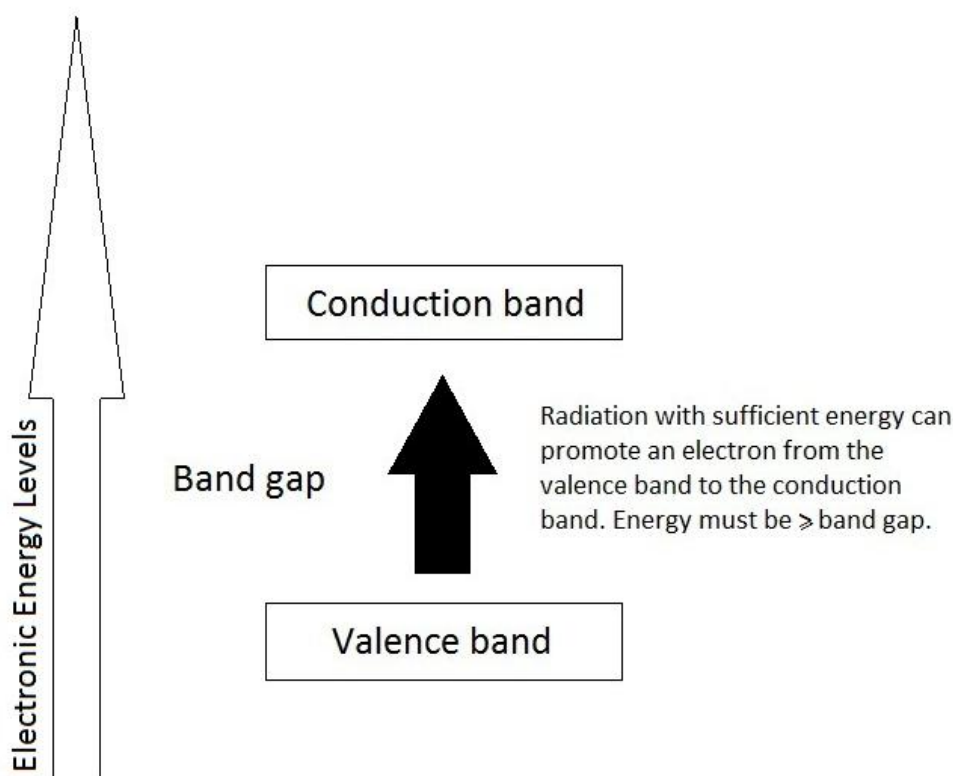


Figure 2: Semi-conductor band gap.

### Disinfectant free radicals created from water itself

Organic molecules and microorganisms in water are destroyed by oxidation. Oxidation of water by an electron hole forms hydroxyl radicals,  $\bullet\text{OH}$ . They are more powerful oxidising agents than chlorine or ozone ( $\text{O}_3^+$ ), both used in water disinfection. Hydroxyl radicals can convert organic molecules to carbon dioxide and water and destroy the cell structure of bacteria. This is called mineralisation.

As shown in Figure 3, a water molecule loses an electron to the positively charged electron hole in the valence band and forms a hydroxyl free radical. An oxygen molecule gains an electron from the negatively charged conduction band and forms a superoxide anion. They are medium strength oxidising agents.

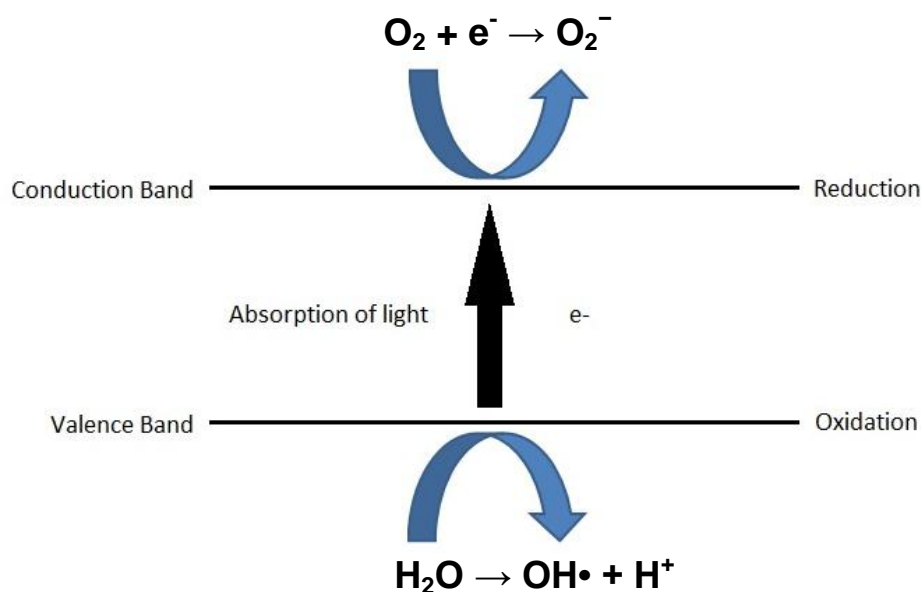


Figure 3: Semiconductor acting as photocatalyst.

### Using a nano-structured anatase / rutile mixture

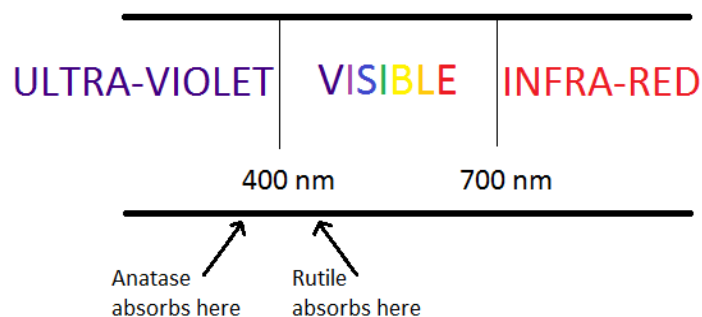


Figure 4: Section of electromagnetic spectrum around visible light.

Titanium dioxide absorbs violet visible light and near-UV light. The two forms, rutile and anatase, absorb at different sections of the spectrum (Figure 4). Rutile is able to absorb violet light with a wavelength of 415 nm. This is just within the visible region. Anatase only absorbs at the edge of visible light and near-UV light, at 385 nm. This is in the near-UV region, UVA.

The  $\text{TiO}_2$  photocatalyst is a mixture and consists of 80% anatase and 20% rutile; so there is a higher proportion of anatase, the form of  $\text{TiO}_2$  which absorbs UV light.

It is not completely understood why the mixture of anatase and rutile works better as a visible light photocatalyst than rutile on its own.

It is known, however, that the role of the rutile is to move the catalytic activity of the titanium dioxide powder into the visible region whereas anatase is needed because it is a better photocatalyst.

**Some facts about visible  
and UV light:**

- Humans cannot see wavelengths below 400 nm.
- The shorter the wavelength of electro-magnetic radiation, the higher the energy.
- Visible light starts at 400 nm.
- UV light has higher energy than visible light.
- UVC is the highest energy UV light. It has a wavelength around 250 nm and is very damaging to cells.
- UVC does not normally reach the Earth's surface because it is absorbed by the ozone layer.
- Mercury vapour lamps, used in UV water treatment, produce UVC radiation of 254 nm.