FEATURE | INNOVATION

Overview Of Tio2 Photocatalysis In Water Treatment

BY HUDA ODA, EIT, MUNICIPALITY OF CHATHAM-KENT

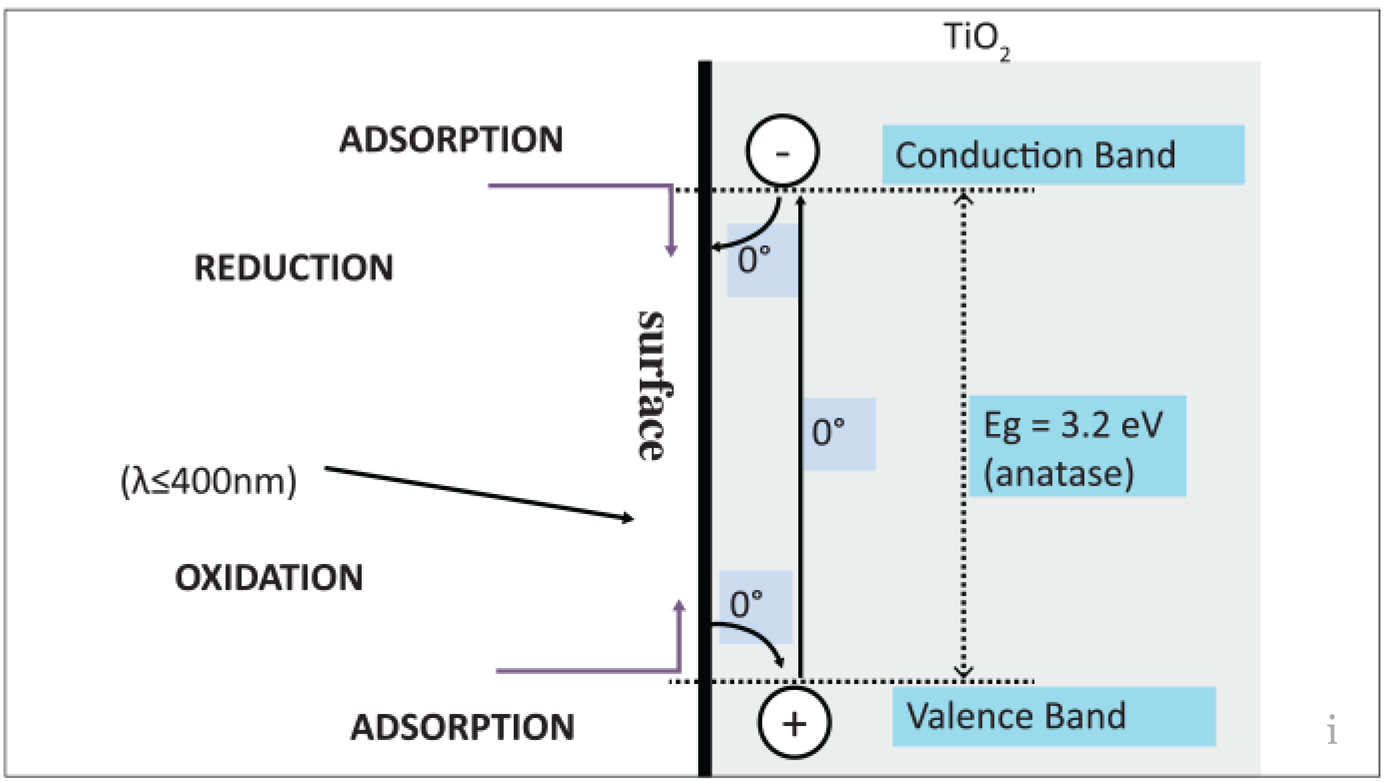
Advanced oxidization processes (AOPs), such as organic oxidation by hydrogen peroxide, ozone, and Photo-Fenton coupled with UV irradiation, have gained much popularity in the past few decades due to their effectiveness in breaking down organic matter. One AOP that has been studied for the past three decades is a type of semiconductor photocatalysis; namely, titanium dioxide photocatalysis.

Semiconductor photocatalysis, or heterogeneous photocatalysis, uses light to catalyze a metal-based substance in order to generate highly reactive, transitory species, such as hydroxyl radicals. These reactive species have the potential to degrade and mineralize recalcitrant organic matter and to inactivate waterborne pathogens. Several metal oxides and sulfides can be used as semiconductors for catalysis including TiO_2, SnO_2, Fe_2O_3, and ZnO.[1,2]

Titanium dioxide, TiO[2], can be found in many objects we use daily. Its nontoxicity, inert properties, suitability for human consumption, and catalytic properties make it a versatile compound used in objects such as toothpaste, paint, cosmetic products, food colouring, and windows. In terms of water treatment, TiO_2 has been the semiconductor of choice in most related research because it is an abundantly available, non-toxic, and photochemically and chemically stable. Moreover, TiO_2 can be reused repetitively in a treatment process as long as it is recycled effectively. Therefore, it has the potential to be a low-cost treatment option.

The TiO_2 photocatalysis process involves the simultaneous occurrence of oxidation and reduction reactions caused by the photogeneration of electron-hole pairs. Specifically, the process starts when electrons at the outer shell of a TiO_2 particle absorb UV light in the valence band, absorb energy, and move up to a higher energy level, the conduction band. When electrons are promoted in that way, they leave behind positively charged electron holes in the valence band. The result is the formation of electron-hole pairs (see Figure 1). Since the excited electrons are unstable and the holes are transient, many times, electron-hole pairs recombine to return to their original state. On the other hand, some pairs make it to the particle surface and ultimately produce reactive oxygen species, including hydroxyl radicals (OH∗), in the presence of dissolved oxygen and water molecules. These species, OH∗ in particular, have high oxidation potential enabling them to degrade difficult organic matter and inactivate numerous pathogenic microorganisms.

Titanium dioxide naturally occurs as very small solid particles whose diameters are measured in the nano-meter scale. When mixed with water, the particles distribute themselves so well, the water becomes a murky solution similar to that of diluted milk. This makes it very difficult to separate the particles from the water after usage. Considering that TiO_2 is reusable, this is a major drawback to using it in its particle form. Hence, many studies investigated the use of TiO_2 in photocatalysis in alternative suspended forms such as nanotubes, nanowires, and nanofibers.[3,4] TiO_2 has also been studied in immobilized particle form[5] onto various surfaces for ease of recovery.



Researchers have also studied modifications of TiO_2 photocatalysis by doping the TiO_2 nanomaterials or by using electric potential, photoelectrocatalysis, to enhance the process's capacity and performance. TiO_2 nanomaterials may be doped with iodine/nitrogen, silver, or ruthenium-based complexes.[6] Photoelectrocatalysis utilizes TiO_2 that has been fixed onto an electrode and an electrical potential is added to drive excited electrons to a cathode. This process enhances quantum efficiency of TiO_2. Dunlop *et al.*[7] studied the disinfection of *E. coli* by open circuit and positive potential TiO_2 photocatalysis and suggested that yield was enhanced by the added positive potential.

Commercially, TiO_2 photocatalysis has made limited advancements over the years. Recently Panasonic has invested in engineering a small-scale, commercial water purification system based on TiO_2 photocatalysis. The purification system utilizes simulated sunlight to catalyze TiO_2 bound to zeolite, a commercial adsorbent and catalyst. The TiO_2 particles are electrostatically bound to the zeolite particles.[8] When the solution is stirred, TiO_2 particles separate from the zeolite making them available for the photocatalysis process, and when the solution stills, the TiO_2 particles become bound again to zeolite. The process does not require a binder chemical, and the ability of the TiO_2 to separate and bind again to the zeolite alleviates concerns regarding active site surface area and photocatalyst recovery. This UV/TiO_2 technology has been tested in a number of institutions in India, targeting applications in groundwater treatment.

Microsphere Technology Inc. of Ireland produces PHOTOSPHERES®, hollow glass microspheres coated with TiO_2 by covalent bonds (see Figure 2). The process of photocatalysis occurs on the surface of the spheres, and the PHOTOSPHERES® can be recovered by floatation or simple filtration for reuse.[9] The University of Waterloo has developed a similar technology where TiO_2 particles are immobilized onto colloidal superparamagnetic substrate microspheres.[10] The immobilized TiO_2 onto microspheres allow for maximum surface area for photocatalysis, and the superparamagnetic feature of the microspheres allows for catalyst recovery using simple magnetic recycling.

The versatility of TiO_2 photocatalysis makes it an attractive option to consider in a number of industries where water treatment is required. TiO_2 photocatalysis has been studied to remove recalcitrant organic matter such as lignin in the pulp and paper industry, organic dyes in the textile industry, perfluoroalkyl substances in the chemical industry, and pesticides in the pharmaceutical industry[1]. However, despite the availability of the basic science behind this technology, TiO_2 photocatalysis has not yet succeeded in significantly transferring technologically to the industry, partly due to the wider acceptance of other AOPs such as UV/H_2O_2. The latter is considered a technology that is easier to engineer, and it does not involve the same concerns regarding surface area, mass transfer, and catalyst surface fouling as UV/TiO_2.[11] TiO_2 photocatalysis retains unique benefits that can be pragmatic in niche applications such as using it as a polishing or preparatory step in conjunction with another water treatment process or in applications where cost and time are less restrictive such as in space-station water treatment.[11] The full potential of this technology remains to be discovered.

Resources

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4. Zhang *et al.*, 2009. High-performance multifunctional TiO_2 nanowire ultrafiltration membrane with a hierarchical layer structure for water treatment.
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6. Sokolowski *et al.*, 2014. Effects of nanotechnologies on disinfection by-production formation.
7. Dunlop *et al.*, 2002. The photocatalytic removal of bacterial pollutants from drinking water.

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9. Microsphere Technology Ltd. **http://microspheretechnology.com/microsphere/applications/water-treatment/**

10. University of Waterloo. **https://uwaterloo.ca/research/waterloo-commercialization-office-watco/business-opportunities-industry/reusable-superparamagnetic-titanium-dioxide-TiO** $_2$

11. Loeb *et al.* The Technology Horizon for Photocatalytic Water Treatment: Sunrise or Sunset?