Nanotitanium dioxide as photocatalytic degradation of pollutants

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INTRODUCTION

With all the advancement in technology and science, now it is possible to look beyond the obvious. Nanotechnology, with its focus on the nano-scale is emerging as one of the leading fields in research. This field should center on the different aspects of designing, synthesis, characterization and application of materials falls under the nano-scale definition.

The nano-science is usually classified as a sub-branch of other major fields of science, such as chemistry and physics, but involves the technology suitable for the named scale and the ways of manipulating the samples to fit the technique [1-3].

At the nano-scale, the materials often show different chemical, physical and biological behaviors. These changes are mainly attributed to the particle size which may have its structural effect.[3].

One important aspect of nano-particles is the large ratio of surface area to volume that is usually associated with the small particle size. This large ratio becomes very significant in researches dealing with surface science in general and surface chemistry in particular.[4].

Application of nano-scale materials, although has not taken its full range yet, is promising to open new horizons in improving the environment. This improvement is following suit the successful application of nano-technology in consumer products and other sectors. Both direct and indirect application of these materials are now available and proven to be useful to detect, and remove pollutants as well as to design industrial processes that are clean and environmentally friendly.

Processes such as removing contaminants from soil and ground water now are better carried out using iron nano-particle. By using zero-valent iron nano-particles, remediation of contaminated ground water is now showing potential benefits especially if the environmental concern is kept in mind.[4].

It is still, however, too early to judge on the full scale of this technology. This is true in particular when it comes to designing applications for optimal performance or to determine the potential risk to both human and environment. Awareness to activate this area of research has become vital now.

One of the main environmental applications of nanotechnology is in the water sector. Worldwide, the sources of fresh water are becoming less and less. One main reason is contamination in addition to the misuse of the resources.

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Expensive desalination of sea water is now despite its high cost being considered as an option in many areas of the world. It is a well known fact that the salted water body of the world is huge and could solve the problem of water scarcity if a technique of desalination with reasonable cost is developed.

Example of such techniques is the use of carbon nano-tube membrane with a potential ability to minimize the sea-water desalination cost. Likewise, surface water contaminated with hazardous substances or chemicals, and ground water could also be cleaned off using nanofilters. Nanosensors could also be useful in detecting waterborne contaminants.

Moving from soil and water to air, application of nanotechnologies could prove to be promising. Indoor air volumes could be purified using nano-based techniques though nano-filters. Better air quality could be attended by attaching nano-filters to automobile tailpipes (mufflers or exhaust pipes) to filter off contaminants and produce less hazardous smoke.

Another potential area of application for nanotechnology is the development of nano-sensors with the ability of detecting toxic gas leaks at extremely low concentrations.

In general, it is obvious that sky is the limit for the multitude of potential environmental applications of this emerging technology which deservedly is drawing a lot of research and attention.

What is the nanotechnology?
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The word nanotechnology has been coined of the two words: The Greek numerical prefix "nano" referring to a billionth, and the known word "technology". Therefore, Nanotechnology or Nanoscale Technology shall deal with particles of sizes 0.1 μm or 100nm.(A nonometer is one billionth of a meter; i.e., 10^{-9} m.). Nanoscale science (or nanoscience) studies the phenomena, properties, and responses of materials at atomic, molecular, and macromolecular scales, and in general at sizes between 1 and 100 nm.

As the particle size becomes very low, the properties of the matter become significantly different where quantum-scale effects start to play an important role.

To be more precise, the Nanotechnology could then be defined as "the design, the manipulation, the building, the production and application, by controlling the shape and size, the properties-responses and functionality of structures, and devices and systems of the order or less than 100 nm" [5,6].

This tiny particle size has given nanomaterials very peculiar properties such as those found in carbon tubes, fullerenes, quantum dots, quantum wires, nanofibers, and nano-composite to list few. This diversity and novelty open the door wide for new applications and techniques.

The market has responded very positively for nanomaterials, and now, it is customary to find all kind of nanoproducts sold commercially. Ceramics, metals, cosmetics, paints and varnishes, polymers, sunscreens, electronics and smart textile are just main titles for hundreds of material that could easily be found in the commercial market. However, this wide spread of these materials requires the development of new methods and instruments to cope with fast growing and increase our knowledge in nanoresearches and findings. Just like any new thing, the impact on environment and general health must also be examined and assessed. In this regard, the development of specific guidance documents at a global level for the safety evaluation of nanotechnology products is strongly recommended.

 At the nanoscale, the properties of materials/structures are different because of two factors:

1. Ratio of surface area-to-volume of structure increases (most atoms are at or near the surface, which make them more weakly bonded and more reactive)

 2. Quantum mechanical effects are important (size of structure is on same scale as the wavelengths of electrons, and quantum confinement occurs resulting in changes in electronic and optical properties [7].

Non-electrolyte-based Methods for Synthesis of Nanostructure
Hydrolysis
In some instances, precipitation from an electrolyte will cause the formation of an insoluble hydroxide that can be changed to its oxide by heat-aided dehydration. Chemical methods for fabrication of monodispersed colloidal

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microparticles have been investigated in different papers. For example, metal (hydrous) oxide particles were fabricated by hydrolysis involving adjusted deprotonation of hydrated cations. Covered colloidal particles can also be fabricated by using hydrolysis. Controlling the hydrolysis of aluminum salts, where solute complex agents were shaped instead of precipitation, materials such as hematite, chromia and titania were covered with a layer of aluminum (hydrous) oxide. Deposition of the coating occurred by surface precipitation, which was adjusted by the available surface area of the particle substrate and the concentrations of the complex agents creating the coating. The thickness of the coating was changed by the mass parameters and treatment time of the process [8, 9].

Hydrothermal
In hydrothermal methods, the reaction mixture is heated at temperatures above the boiling point of water in a closed system such as an autoclave and the sample is treated by steam at high pressure. Precipitation of zirconia under hydrothermal conditions will lead to nanopowders with a narrow size distribution and adjustable composition and nanostructure. Treating $Zr(SO_4)_2$ by this method at 250 ˚C in the presence of $MgSO_4$ or $(NH_4)_2SO_4$ caused the fabrication of acicular monoclinic zirconia. Zirconia fine particles have dimensions around 0.3–1.3 mm in length and 0.1–0.2 mm in width [10, 11].

Sol–Gel Processing
The *sol–gel* process in general is based on the transition of a system from a liquid "sol" (mostly a colloidal suspension of particles) into a gelatinous network "gel" phase. With this, it is possible to create at low temperature ceramic or glass materials in a wide variety of forms. It is a long established industrial process that is very cost-effective and versatile It has been further developed in last few years for the production of advanced nanomaterials and coatings but also in bio-MEMS application for the production of piezoelectrics, such as lead–zirconium–titanate (PZT) [12] or membranes [13]. Sol–gel processes are well adapted for oxide nanoparticles [14] and composite nanopowder synthesis as well as for access to organic-inorganic materials. A summary of all the possible interlinked combination of organic and inorganic nanocomposites that are produced by the sol–gel method is provided in Figure 1. The basic flow of the sol–gel process is described in Figure 2.
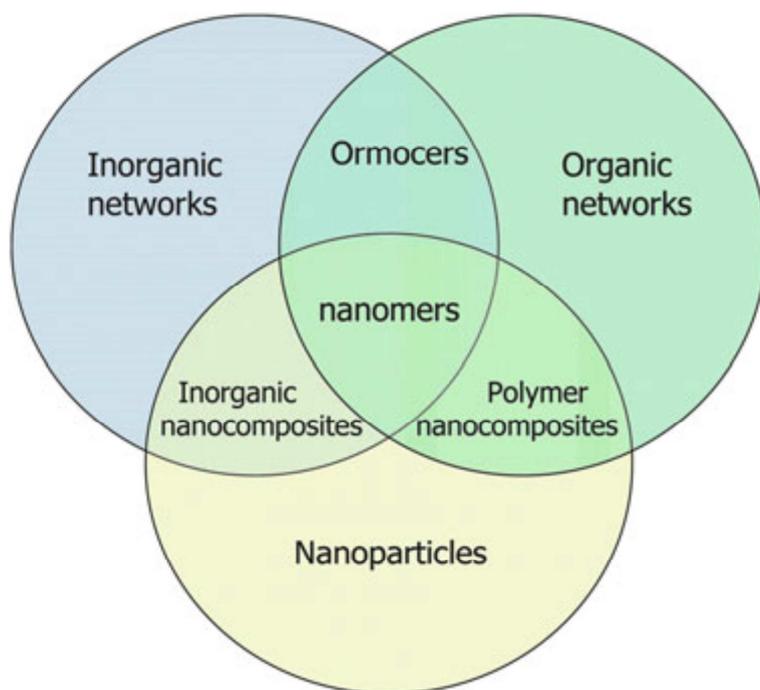

Figure 1: System model for nanocomposites produced by sol–gel [15] Precursor

Nano Crystalline Photo-catalysts
Nanocrystalline photocatalysts are ultrasmall semiconductor particles which are a few nanometres in size. During the past decade, the photochemistry of nano semiconductor particles has been one of the fastest growing research areas in physical chemistry [16]. The interest in these small semiconductor particles originates from their unique photophysical and photocatalytic properties [17].

Several review articles have been published concerning the photophysical properties of nanocrystalline semiconductors [18-22]. Such studies have demonstrated that some properties of nanocrystalline semiconductor

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particles are in fact different from those of bulk materials. Nanosized particles, with diameters ranging between 1 and 10 nm, possess properties which fall into the region of transition between the molecular and the bulk phases [17]. In the bulk material, the electron excited by light absorption finds a high density of states in the conduction band, where it can exist with different kinetic energies [16]. In the case of nanoparticles however, the particle size is the same as or smaller than the size of the first excited state. Thus, the electron and hole generated upon illumination cannot fit into such a particle unless they assume a state of higher kinetic energy [23].
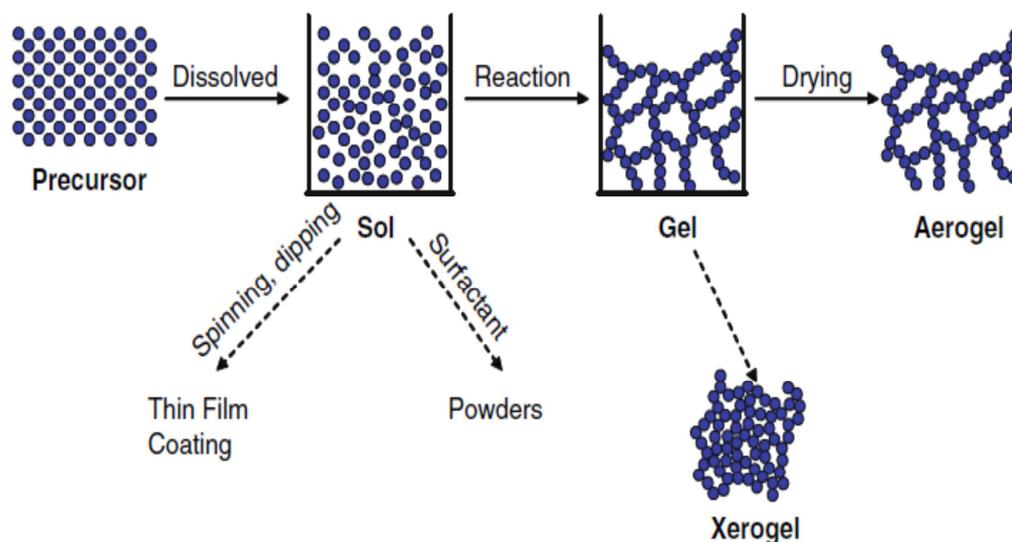

Figure 2: Basic flow of a sol–gel process [12]

Types of photocatalysts and their characteristics
Metal oxides with a wide band gap and high photocorrosion resistance are considered the most suitable photocatalysts.[24]. Table 1 shows the band gap energies at corresponding wavelength for widely used semiconductors. The most effective and consequently the most used semiconductor in water and waste water treatment studies is titanium oxide (TiO_2) with a bnd gap energy ranging between 3.0-3.2 ev. This is true because of the oxide's low cost, thermal stability, non-toxicity, chemical and biological inertness, and its' capability of promoting oxidation of organic compounds.[25]. Titanium dioxide, also known as titania, titanium white, titanic anhydride, or titanic acid anhydride, shows a photocatalytic activity that is a function of its surface and structural properties. Such properties may include photocatalytic degradation of organic pollutants in water, crystal composition, surface area, particle size distribution, porosity and band gap energy.[26].

Titanium dioxide comes in the main crystalline form of rutile. Other forms of lesser importance do occur; they are anatase, brookite and a third form known as TiO_2 (B).

To obtain the anatase, ilmenite $FeTiO_3$, is reacted with sulfuric acid to get titanium sulfate. This later compound is usually processed to produce the anatase.

The rutile form is obtained by the chlorination of raw rutile to produce titanium tetra chloride. The chloride is then oxidized in vapor phase to produce the pure rutile.[27].

When photon energy (hv) of higher than or equal to the bandgap energy of TiO2 is illuminated onto its surface, typically 3.2 eV (anatase) or 3.0 eV (rutile), the lone electron is photo-excited to the empty conduction band in femtoseconds.

The most widely used form of titanium dioxide is made by Degussa (D25) and composed of 75% anatase and 25% rutile with a specific BET (Brunauer–Emmett–Teller) surface area of 50 m^2/g.

"The high effectiveness of D25 is related to the inhibition of recombination process on TiO_2 (E_{cb-}/h_{VB+}) due to the smaller band gap of rutile that absorbs photons and generates electron-hole pairs and the electron transfer from the rutile conductive band to the electron traps occurs in the anatase phase" [28].

Chemical Structure of TiO_2
TiO_2 is one of the transition metal oxides. As previously mentioned, there are four commonly known polymorphs of TiO_2 found in nature: anatase (tetragonal), brookite (orthorhombic), rutile (tetragonal), and TiO_2 (B) (monoclinic)

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[30]. Besides these polymorphs, two additional high-pressure forms have been synthesized from the rutile phase. These are TiO_2 (II) [31] with a PbO_2 structure and TiO_2 (H) [32] with a hollandite structure. In this review, only the crystal structures (Table 2) [33–35] and properties of the rutile, anatase and brookite polymorphs are considered. Rutile TiO_2 has a tetragonal structure and contains 6 atoms per unit cell (Figure 3).

Table 1: Band gap energies of various semiconductors at relevant wavelength [29]

Semiconductor	Band gap energy (eV)	Wavelength
TiO_2 (rutile)	3.0	413
TiO_2 (anatase)	3.2	388
ZnO	3.2	388
ZnS	3.6	335
CdS	2.4	516
Fe_2O_3	2.3	539

Table 2: Crystal structure data for TiO_2 [33-35]

| Properties	Rutile	Anatase	Brookite
Crystal structure	Tetragonal	Tetragonal	Orthirhombic
Lattice constant (A°)	$a= 4.5936$ $c= 2.9587$	$a= 3.784$ $c= 9.515$	$a= 9.184$ $b= 5.447$ $c= 5.154$
Space group	P4$_2$\mnm	I4$_2$\amd	pbca
Molecule (cell)	2	2	4
Volume\ molecule (A$^{°3}$)	31.2160	34.061	32.172
Density (g cm^{-3})	4.13	3.79	3.99
Ti-O bond length (A°)	1.940 (4) 1.980 (2)	1.937 (4) 1.965 (2)	1.87-2.04
O-Ti-O bond angle	81.2° 90.0°	77.7° 92.6°	77.0°-105°
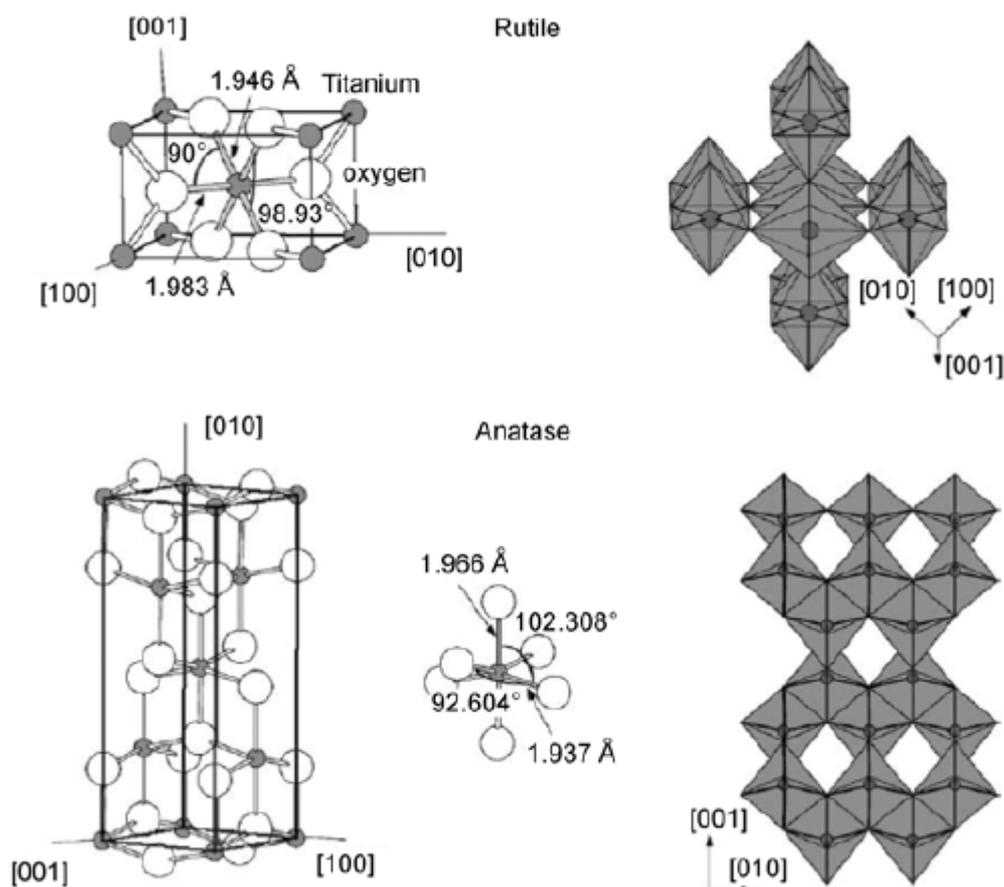
Figure 3: Crystal structures of the ruitle and anatase phases of TiO2

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Rutile:
The TiO$_6$ octahedron.is slightly distorted [36–38]. At pressure above 60kbar, the TiO$_2$(II) form becomes the thermodynamically favorable phase, while the rutile form is most stable form at ordinary temperatures and pressure. Zhang *et.al.* reported that anatase and brookite transformed to the rutile phase when they reach a certain particle size. When the particle size is above 14nm, the rutile form predominates. [40]. Once the rutile phases is formed, it grows much faster than anatase. The poor photocatalytic activity of rutile could be improved by following certain preparation routes, Sclafani *et.al.* concluded. [41].

Anatase:
This phase exists in a tetragonal structure with a more distorted octahedron than the distortion found in rutile. Figure 1. [42,43].

At temperatures as low as 0K, anatase is more stable than rutile. However, the nergy difference between the two phases is small (~2 to 10 kJ/mol), as reported by Muscat *et. al.*[44].

The high electron mobility, low dielectric constant and lower density are all factors made anatase to be preferred over other polymorphs for solar cell application.[30].

This increased photoreactivity is because of the slightly higher Fermi level, lower capacity to adsorb oxygen and higher degree of hydroxylation in the anatase phase [45].

Selloni [46] reported that the reactivity of (001) facets is greater than that of (101) facets in an anatase crystal, while Yang et al. [47] were able to synthesize uniform anatase crystals containing 47% (001) facets using hydrofluoric acid as a morphology controlling agent.

Brookite: Brookite TiO$_2$ belongs to the orthorhombic crystal system. Its unit cell is composed of 8 formula units of TiO$_2$ and is formed by edge-sharing TiO$_6$ octahedra (Figure 2). Because of its complicated structure with a large cell volume combined with its low density, this phase was the least explored phase and its use in experimental investigations was limited.

TiO$_2$ is a large-band semiconductor, with band gaps of 3.2, 3.02, and 2.96 eV for the anatase, rutile and brookite phases, respectively [48]. The valence band of TiO$_2$ is composed of the 2p orbitals of oxygen hybridized with the 3d orbitals of titanium, while the conduction band is only the 3d orbitals of titanium [49].
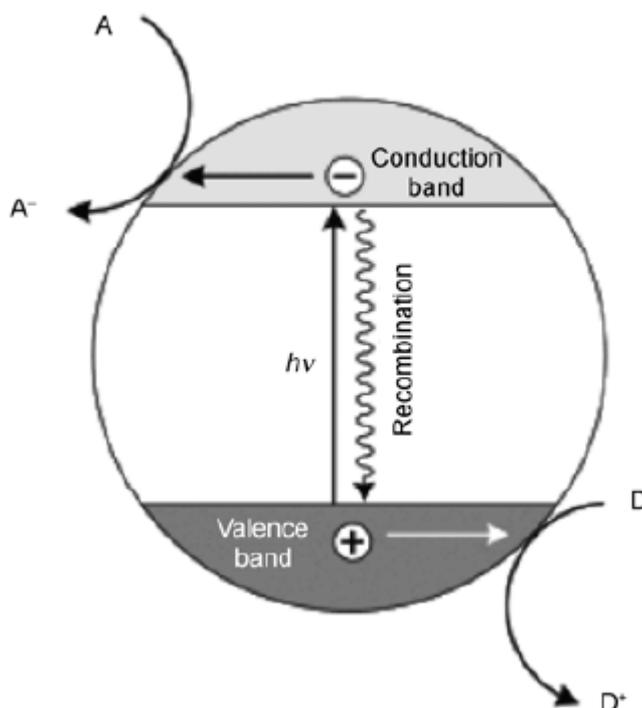

Figure 4: Illustration of the principles of photocatalysis showing the energy band gap diagram of a TiO$_2$ spherical particle

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Photocatalytic degradation mechanisms using TiO$_2$
1. Photocatalytic oxidation
The detailed mechanism of the process has been detailed previously in literature [50] and will be only briefly summarized here. It is well established that conduction band electrons (e$^-$) and valence band holes (h$^+$) are generated when aqueous TiO$_2$ suspension is irradiated with light energy greater than its band gap energy (*E*g, 3.2 eV). The photogenerated electrons could reduce the dye or react with electron acceptors such as O$_2$ adsorbed on the Ti(III)-surface or dissolved in water, reducing it to superoxide radical anion O$_2$ $^{\bullet-}$. The photogenerated holes can oxidize the organic molecule to form R$^+$, or react with OH$^-$ or H$_2$O oxidizing them into OH$^\bullet$ radicals. Together with other highly oxidant species (peroxide radicals) they are reported to be responsible for the heterogeneous TiO$_2$ photodecomposition of organic substrates as dyes. According to this, the relevant reactions at the semiconductor surface causing the degradation of dyes can be expressed as follows:

$$TiO_2 + h\nu(UV) \rightarrow TiO_2(e_{CB}{}^- + h_{VB}{}_+) \tag{1}$$

$$TiO_2(h\nu_{B+}) + H_2O \rightarrow TiO_2 + H^+ + OH^\bullet \tag{2}$$

$$TiO_2(h\nu_{B+}) + OH- \rightarrow TiO_2 + OH^\bullet \tag{3}$$

$$TiO_2(e_{CB-}) + O_2 \rightarrow TiO_2 + O_2{}^{\bullet-} \tag{4}$$

$$O_2{}^{\bullet-} + H+ \rightarrow HO_2{}^\bullet \tag{5}$$

$$Dye + OH^\bullet \rightarrow degradation\ products \tag{6}$$

$$Dye + h\nu_{B+} \rightarrow oxidation\ products \tag{7}$$

$$Dye + e_{CB-} \rightarrow reduction\ products \tag{8}$$
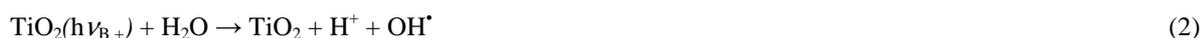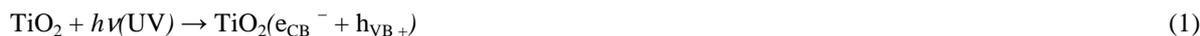
The resulting •OH radical, being a very strong oxidizing agent (standard redox potential +2.8 V) can oxidize most of azo dyes to the mineral end-products. Substrates not reactive toward hydroxyl radicals are degraded employing **TiO$_2$** photocatalysis with rates of decay highly influenced by the semiconductor valence band edge position [51]. The role of reductive pathways (Eq. (8)) in heterogeneous photocatalysis has been envisaged also in the degradation of several dyes but in a minor extent than oxidation [52].

2. Photosensitized oxidation
The mechanism of photosensitized oxidation (called also photo-assisted degradation) by visible radiation ($\lambda > 420$ nm) is different from the pathway implicated under UV light radiation. In the former case the mechanism suggests that excitation of the adsorbed dye takes place by visible light to appropriate singlet or triplet states, subsequently followed by electron injection from the excited dye molecule onto the conduction band of the TiO$_2$ particles, whereas the dye is converted to the cationic dye radicals (Dye$^{\bullet+}$) that undergoes degradation to yield products as follows [53]:

$$Dye + hv(VIS) \rightarrow 1Dye* \text{ or } 3Dye* \tag{9}$$

$$1Dye* \text{ or } 3Dye* + TiO_2 \rightarrow Dye^{\bullet+} + TiO_2(e_{CB-}) \tag{10}$$

$$TiO_2(e_{CB-}) + O_2 \rightarrow O_2{}^{\bullet-} + TiO_2 \tag{11}$$

$$Dye^{\bullet+} \rightarrow degradation\ products \tag{12}$$
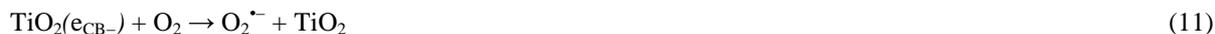
The cationic dye radicals readily reacts with hydroxyl ions undergoing oxidation via reactions 13 and 14 or interacts effectively with O$_2{}^{\bullet-}$, HO$_2{}^\bullet$ or HO$^{\bullet-}$ species to generate intermediates that ultimately lead to CO$_2$ (Eqs. (15)–(19)).

$$Dye^{\bullet+} + OH- \rightarrow Dye + HO^\bullet \tag{13}$$

$$Dye + 2HO^\bullet \rightarrow H_2O + oxidation\ products \tag{14}$$

$$O_2{}^{\bullet-} + H+ \rightarrow HO_2{}^\bullet \tag{15}$$

$$HO_2{}^\bullet + H^+ + TiO_2(e_{CB-}) \rightarrow H_2O_2 + TiO_2 \tag{16}$$

$$H_2O_2 + TiO_2(e_{CB-}) \rightarrow HO^{\bullet} + HO^- + TiO_2 \tag{17}$$

$$Dye^{\bullet+} + O_2^{\bullet-} \rightarrow DO_2 \rightarrow \text{degradation products} \tag{18}$$

$$Dye^{\bullet+} + HO_2^{\bullet}(\text{or } HO^{\bullet}) \rightarrow \text{degradation products} \tag{19}$$
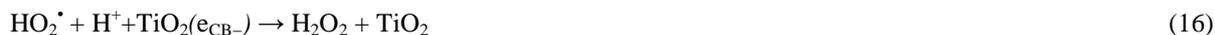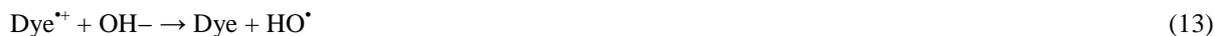
In experiments that are carried out using sunlight or simulated sunlight (laboratory experiments) it is thought that both photooxidation and photosensitizing mechanism occurred during the irradiation and both TiO_2 and the light source are necessary for the reaction to occur. In the photocatalytic oxidation, TiO_2 has to be irradiated and excited in near-UV energy to induce charge separation. On the other hand, dyes rather TiO_2 are excited by visible light followed by electron injection onto TiO_2 conduction band, which leads to photosensitized oxidation. It is difficult to conclude whether the photocatalytic oxidation is superior to the photosensitizing oxidation mechanism, but the photosensitizing mechanism will help to improve the overall efficiency and make the photobleaching of dyes using solar light more feasible [54].

CONCLUSION

The future may go nano! This may seem like an overstatement, but with the fast growing application of the nanotechnology, especially in the fields of research-both for purely scientific purpose or for developments of new applications, information and communication technology, electronics, energy, medical and biological applications, and much more, the above statement may prove to be accurate sooner than one imagines.

At the nano level, new nano-biomaterials and nano devices are being introduced every day. These devices started to tune the properties, responses and functions of living and non-living matters, at the nano world with particle sizes below 100 nm.

As outlined in this paper, the nanoparticles of semiconductors, such as TiO_2, could be used as a photoctalyst for the degradation of pollutants. Titanium dioxide could be very close of being the ideal photocatalytic semiconductor because it is cost effective, solution photo-stability, non-toxicity, redox selectivity and strong oxidizing power of holes.

REFERENCES

[1] G Mansoori; and T Soelaiman, J. *ASTM International* 2, **2005**, 21.
[2] G Mansoori, *Annual Review of Nano Research*, **2008**, 2, Chap.2.
[3] G Mansoori ; T Rohani.Bastami; A Ahmadpour; Eshaghi, *Annual Review of Nano Research*, **2008**, 2, Chap.2.
[4] W Zhang; T Masciangioli, *Environ. Sci. Technol.*, **2003**, 37, 102A.
[5] K Sattler, **2010**, New York.
[6] B Bhushan, *Springer*, **2004**, Berlin.
[7] Z Hussain; E Yousif; R Noman, *lambert academic publishing,* **2015**.
[8] M Ozawa; S Suzuki; C Loong; P Thiyagarajan, *John Wiley & Sons, Inc., Hoboken ,NJ*, **2008,** 18, 105–110.
[9] S Novak; T Kosma_c, in Ceramics –Processing, Reliability, Tribology andWear (ed. G. M€uller),Wiley VCH, Weinheim, **2000**, 150–155.
[10] C Bozo; F Gaillard; N Guilhaume, *Applied Catalysis A: General*, **2001**, 220, 69–77.
[11] G Kanade; O Baeg; K Apte; L Prakash; B Kale, *Materials Research Bulletin,* **2008**, 43, 723–729.
[12] A Shanaghi; A Sabour; T Shahrabi; M Aliofkhazraee, *Protection of Metals and Physical Chemistry of Surfaces*, **2009,** 45, 305–311.
[13] C Guizard; A Julbe; A Larbot; L Cot, *Journal of Alloys and Compounds*, **1992,** 188, 8–13.
[14] B Lakshmi; K Dorhout; R Martin, *Chemistry of Materials 9*, **1997**, 3, 857–862.
[15] W Luther, *Technologiezentrum GmbH, Dusseldorf*, **2004**, Germany.
[16] A Henglein, *Berichte der Bunsen- Gesellschaft-Physical Chemistry*, **1997**, 101, 1562–1572.
[17] W Bahnemann; D Bockelemann; R Goslich; M Hilgendorff; D Weichgrebe, *In: Photocatalytic purification and treatment of water and air, Elsevier Science Publishers*, **1993**, 301–319.
[18] A Henglein, T*opics in Current Chemistry*, **1988**, 143, 113–180.
[19] A Henglein, Chemical Reviews, **1989**, 89, 1861–1873.
[20] Y Wang; N Herron, *The Journal of Physical Chemistry*, **1991**, 95, 525–532.
[21] A Zeltner; M Anderson, *Kluwer Academic Publishers*, **1996**, 643–656.
[22] B Levy, *Journal of Electroceramics*, **1997**, 1, 239–272.

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[23] H Weller; A Eychmuller, *In: Douglas C. Neckers, David H.Volman and Gunther von Bunau, eds. Advances in Photochemistry*, **1995**, 20, John Wiley and Sons. Inc.

[24] A Fox; T Dulay, *Heterogeneous Photocatalysis. Chemical Reviews*, **1993**, 93, 341–357.

[25] P Mandelbaum; A Regazzoni; M Belsa; S Bilme, *Journal of Physics and Chemistry B.*, **1999**, 103, 5505-5511.

[26] S Ahmed; G Rasul; R Brown; A Hashib, *Journal of Environmental Management*, **2011**, 92, 311-330.

[27] G Hawley, *Litton Educational Publishing Incorporation*, **1971**.

[28] C Hurun; G Agrios; A Gray; T Rajh; C Thurnaur, *The Journal Physics and Chemistry B,* **2003**, 107,4545-4549.

[29] K Rajeshwar; J Ibanez; *Acadmic Press, San Diego*, **1997**.

[30] O Carp; L Huisman; A Reller, *Prog in Solid State Chem*, **2004**, 32, 33–117.

[31] K Mor; K Varghese; M Paulose *et al*, *Solar Energ Mater Solar Cell*, **2006**, 90, 2011–2075.

[32] X Chen; S Mao, *Chem Rev.*, **2007**, 107, 2891–2959.

[33] L Thompson ; T Yates Jr, Chem Rev., **2006**, 106, 4428–4453.

[34] U Diebold, *Sur Sci Rep*, **2003**, 48, 53–229.

[35] L Linsebigler; G Lu; T Yates, Chem Rev., **1995**, 95, 735–758.

[36] Y Simons; F Dachille, *Acta Cryst*, **1967**, 23, 334–336.

[37] M Latroche; L Brohan; R Marchand *et al*, *J Solid State Chem*, **1989**, 81, 78–82.

[38] T Cromer; K Herrington, *J Am Chem Soc*, **1955**, 77, 4708–4709.

[39] H Baur, *Acta Crystallogr*, **1961**, 14, 214–216.

[40] S Mo; W Ching, *Phys Rev B*, **1995**, 51, 13023–13032.

[41] A Norotsky; C Jamieson; J Kleppa, *Science*, **1967**, 158, 338–389.

[42] Q Zhang; L Gao; J Guo, *Appl Catal B Environ*, **2000**, 26, 207–215.

[43] A Sclafani; L Palmisano; M Schiavello, *J Phys Chem*, **1990**, 94, 829–832.

[44] J Muscat; V Swamy; M Harrison, *Phy Rev B*, **2002**, 65, 1–15.

[45] K Tanaka; V Capule; T Hisanaga, *Chem Phys Lett*, **1991**, 187, 73–76.

[46] A Selloni, *Nature Mater,* **2008**, 7, 613–615.

[47] G Yang; H Sun; Z Qiao *et al*, *Nature*, **2008**, 453, 638– 641.

[48] W Wunderlich; T Oekermann; L Miao et al, *J Ceram Process Res*, **2004**, 5, 343–354.

[49] T Paxton, *Phys Rev B*, **1998**, 57, 1579–1584.

[50] A Houas; H Lachheb; M. Ksibi E; Elaloui; C Guillard, *J. M. Hermann, Appl. Catal. B: Environ.*, **2001**, 31, 145.

[51] V Maurino; C Minero; E Pelizzetti; M Vincenti, Coll. Surf. A 151, **1999**, 329.

[52] K Vinodgopal; I Bedja; S Hotchandani; P Kamat, *Langmuir 1*, **1994**, 1767.

[53] C Galindo; P Jacques; A Kalt, *J. Photochem. Photobiol. A: Chem*, 2001, 141, 47.

[54] G Epling, C Lin, *Chemospher*e, **2002**, 46, 561.