

## Review

Norma A. Ramos-Delgado, Miguel Á. Gracia-Pinilla<sup>a,\*</sup>, Ramalinga Viswanathan Mangalaraja, Kevin O'Shea and Dionysios D. Dionysiou

# Industrial synthesis and characterization of nanophotocatalysts materials: titania

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**Abstract:** Despite the recent synthesis and identification of a diverse set of new nanophotocatalysts that has exploded recently, titanium dioxide ( $\text{TiO}_2$ ) remains among the most promising photocatalysts because it is inexpensive, non-corrosive, environmentally friendly, and stable under a wide range of conditions.  $\text{TiO}_2$  has shown excellent promise for solar cell applications and for remediation of chemical pollutants and toxins. Over the past few decades, there has been a tremendous development of nanophotocatalysts for a variety of industrial applications (i.e. for water purification and reuse, disinfection of water matrices, air purification, deodorization, sterilization of soils). This paper details traditional and new industrial routes for the preparation of nanophotocatalysts and the characterization techniques used to understand the physical chemical properties of them, like surface area,  $\zeta$  potential, crystal size, and phase crystallographic, morphology, and optical transparency. Finally we present some applications of the industrial nanophotocatalysts.

<sup>a</sup>On sabbatical leave at FIU.

**\*Corresponding author: Miguel Á. Gracia-Pinilla**, Facultad de Ciencias Físico Matemáticas & Centro de Investigación e Innovación y Desarrollo en Ingeniería y Tecnología CIIDIT, Universidad Autónoma de Nuevo León, San Nicolás de los Garza, N.L., México, e-mail: miguelchem@gmail.com.  
<http://orcid.org/0000-0002-4716-4817>

**Norma A. Ramos-Delgado:** CONACYT Research Fellow-Instituto Tecnológico de Nuevo León, Tecnológico Nacional de México, Guadalupe, N.L., México

**Ramalinga Viswanathan Mangalaraja:** Advanced Ceramics and Nanotechnology Laboratory, Department of Materials Engineering, University of Concepcion, Concepción, Chile

**Kevin O'Shea:** Department of Chemistry and Biochemistry, Florida International University, Miami, FL, USA

**Dionysios D. Dionysiou:** Environmental Engineering and Science Program, Department of Biomedical, Chemical and Environmental Engineering, University of Cincinnati, Cincinnati, OH, USA

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## 1 Introduction

Over the past few decades, there has been tremendous development of nanophotocatalysts for a variety of industrial applications (i.e. for water purification and reuse, disinfection of water matrices, air purification, deodorization, sterilization of soils) [1–3] because it is inexpensive, non-corrosive, environmental friendly, and stable under a wide range of conditions. Titanium dioxide ( $\text{TiO}_2$ ) has shown excellent promise for solar cell applications and for remediation of chemical pollutants and toxins [4–7].

$\text{TiO}_2$  has been extensively used as the white pigment in paint because of its high refractive index, wettability, whiteness, opacity, and lacing resistance.  $\text{TiO}_2$  is also used as an additive for a wide variety of materials, from paints to toothpaste, additives for polymers employed in plastics and food packing, and in the pulp and paper industry [8]. In addition,  $\text{TiO}_2$  is included in catalysts, ceramics, coated fabrics and textiles, floor covering, printing ink, and roofing granules. The industrial demand for nano-sized  $\text{TiO}_2$  particles has resulted in the development of large-scale production processes [9].

$\text{TiO}_2$  materials have been synthesized in different shapes and sizes depending on the applications desired [10]. In general, we can define nanophotocatalysts as photoactive materials when the photoactivity can be modulated in the regime of nanometer scale; its means, they have superior efficiency due to its size [11–14]. The low cost and ready availability give  $\text{TiO}_2$  a major advantage over zinc, ceria, and/or other metals based photocatalytic materials. Titanium is the ninth most abundant element in the earth's crust, and is present in almost all rocks and sediments.

Given the high reactivity of metallic titanium, Ti is found and employed almost exclusively as titanium oxide forms; the most abundant crystalline phases are rutile and anatase [15]. Titanium exists in nature primarily as an ilmenite mineral ( $\text{FeTiO}_3$ ), rutile, anatase, and brookite (either as rock or as sand). Less common titanium oxide-bearing minerals are pseudobrookite ( $\text{Fe}_2\text{TiO}_5$ ), perovskite ( $\text{CaTiO}_3$ ), pyrophanite ( $\text{MnTiO}_3$ ), and geikielite [(Mg, Fe) $\text{TiO}_3$ ]. The properties of common minerals containing  $\text{TiO}_2$  are summarized in Table 1 [16]. Ilmenite ( $\text{FeTiO}_3$ ) represents almost 92% of the world's consumption of titanium minerals and almost 95% of the titanium mineral was employed to produce  $\text{TiO}_2$  pigment products [17].

Large quantities of  $\text{TiO}_2$  have been used in industry for many decades, and there are two production processes at the industrial scale. The annual production of  $\text{TiO}_2$  for specific photocatalysis applications is not readily available, but the U.S. Geological Survey reported that approximately 1,470,000 metric tons of  $\text{TiO}_2$  was produced in the USA, while the annual global production for 2015 was ~6,500,000 million tons, for the sulfate processes, the annual global production was ~3,400,000 million tons, and for chloride processes, the annual global production was ~3,100,000 million tons [17]. In 2015, the commercial value for titanium dioxide ( $\text{TiO}_2$  high quality) pigment is estimated to be ~US \$2300 per ton [18].

## 2 Industrial synthesis process

Owing to the low natural availability of pure  $\text{TiO}_2$  for commercial use, the mineral ilmenite, containing nearly 52.6% of  $\text{TiO}_2$  and 47.4% of iron oxide, is used as a raw material for the industrial production of  $\text{TiO}_2$ . In general, the ilmenite is an abundant mineral in primary and secondary deposits. The secondary deposits are the favored source of  $\text{TiO}_2$  because they are sandy and easily converted to the finely ground raw material required for industrial processing, unlike primary deposits where minerals can be found in the rocks. In general, two chemical processes are employed to obtain the  $\text{TiO}_2$  pigment, sulfate process (batch-closed) and chloride process (continuous-open), which employs advanced technology and has a lower cost than the sulfate process. The sulfate process is more labor intensive and has greater waste and higher environmental liability costs. A comparison of the primary advantages and disadvantages of the two processes for the manufacture of  $\text{TiO}_2$  is provided in Table 2. In general, the sulfate process is considered an old process that produces  $\text{TiO}_2$  on anatase and rutile crystalline phases; however, it generates a great volume of waste and some by-products that must be managed. On the other hand, the chloride process is a new technology that uses chlorine gas to produce the rutile  $\text{TiO}_2$  crystalline phase and less waste than the sulfate process. This technology can be scalable for implementation for bigger industrial plants.

**Table 1:** Properties of some mineral of titanium.

Name (formulae)	$\text{TiO}_2$ (%w)	Color	Hardness (Mohs scale)	Density (g/cm <sup>3</sup> )	Crystallographic system	Transparency
Ilmenite ( $\text{FeTiO}_3$ )	52.6	Black	5–6	4.5–5	Hexagonal	Opaque
Perovskite ( $\text{CaTiO}_3$ )	58	Black, brown, yellow	5.5	4.48	Monoclinic	
Rutile, anatase, brookite ( $\text{TiO}_2$ )	95	Reddish-brown, red, yellowish or black	6–6.5 (rutile) and 5.5–6 (anatase and brookite)	4.2–5.5 (rutile) and 3.8–3.9 (anatase) and 4–4.1 (brookite)	Tetragonal (rutile, anatase) orthorhombic (brookite)	Opaque or semitransparent

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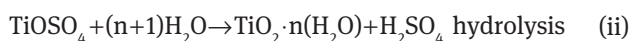
**Table 2:** Comparison of the sulfate and chloride processes.

Sulfate process	Chloride process
Long established and simple technology	New and advanced technology
Uses lower-grade, cheaper ores	Needs high-grade ore
Batch process	Continuous process
Large amount of waste materials formed	Small amount of waste formed, with toxicity problems: $\text{Cl}_2$ and $\text{TiCl}_4$
Pollution control expensive	Recovery and recycling of chlorine is possible
Produces anatase and rutile crystalline phases	Produces only rutile crystalline phase

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## 2.1 The sulfate process

The sulfate process requires a number of separate unit operations: acid digestion, hydrolysis, and calcination, as represented below (Figure 1). Acid digestion converts the raw mineral form to a Ti-sulfate form, which is hydrolyzed to a hydrated titanium oxide form and heated to dry and calcination of the material. Details for the separate operation are provided below and the overall chemistry of the process represented as:



**Acid digestion:** The raw mineral, ilmenite, is digested in concentrated sulfuric acid in 60% excess relative to the  $\text{TiO}_2$  content. The excess acid plays a fundamental role to ensure 94–96% digestion and determines the particle size of the pigments. Subsequent hydrolysis, via an exothermic reaction, produces titanium sulfate (cake-like material). The undigested ore is filtered off, scrap iron is added to reduce the remaining  $\text{Fe}^{3+}$ , the temperature is reduced to  $15^\circ\text{C}$  to crystallize large quantities of iron (II) as sulfate heptahydrate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ), which is separated.

**Hydrolysis:** The titanium sulfate is heated to  $109^\circ\text{C}$  leading to hydrolysis, yielding a gel (precipitate) and a high quantity sulfuric acid (residual). The gel is subsequently washed to remove the remaining acid. Seed crystals are added to initiate crystallization leading predominantly to  $\text{TiO}_2$  in the anatase and rutile phases. The crystalline phase of the final product can be controlled through the use of different seed crystals.

**Calcination (drying):** The final operation involves heating of the hydrolysis material in rotatory kilns ( $200\text{--}300^\circ\text{C}$ ) to remove the water. For yielding, specific crystalline phases of the final product (rutile, anatase, or mix phases) should control the drying temperature, between  $800^\circ\text{C}$  and  $850^\circ\text{C}$  for the anatase phase or  $900\text{--}930^\circ\text{C}$  for producing the rutile phase. In addition, control of the heating profiles (ramps) can be used to tailor physic/chemical properties.

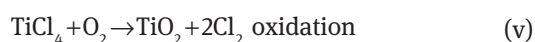
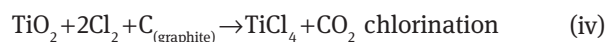
**Post-treatment:** The  $\text{TiO}_2$  product (anatase, rutile, or mix phases) are ground and functionalized or undergo surface modification for specific applications.

The sulfate process generates residual sulfuric acid, which can be recycled and employed for the first step of the process (acid digestion). A large quantity of iron sulfate

heptahydrate is also produced, which can be decomposed to sulfuric acid and iron oxide, which is highly desirable for use in the steel industry.

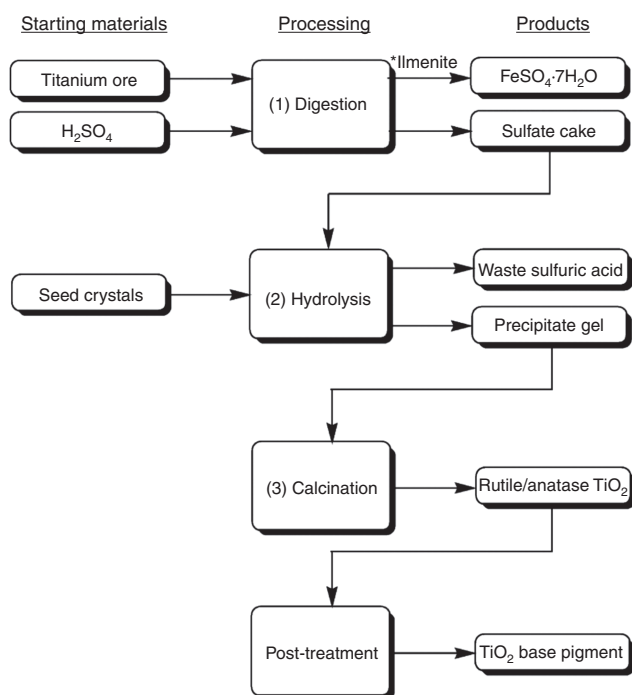
## 2.2 The chloride process

The chloride process is a continuous process (Figure 2). In this, natural and synthetic rutile or titanium slags are used as starting materials for the generation of  $\text{TiO}_2$ , transformations involved in the process and the overall chemistry of the process can be represented as:

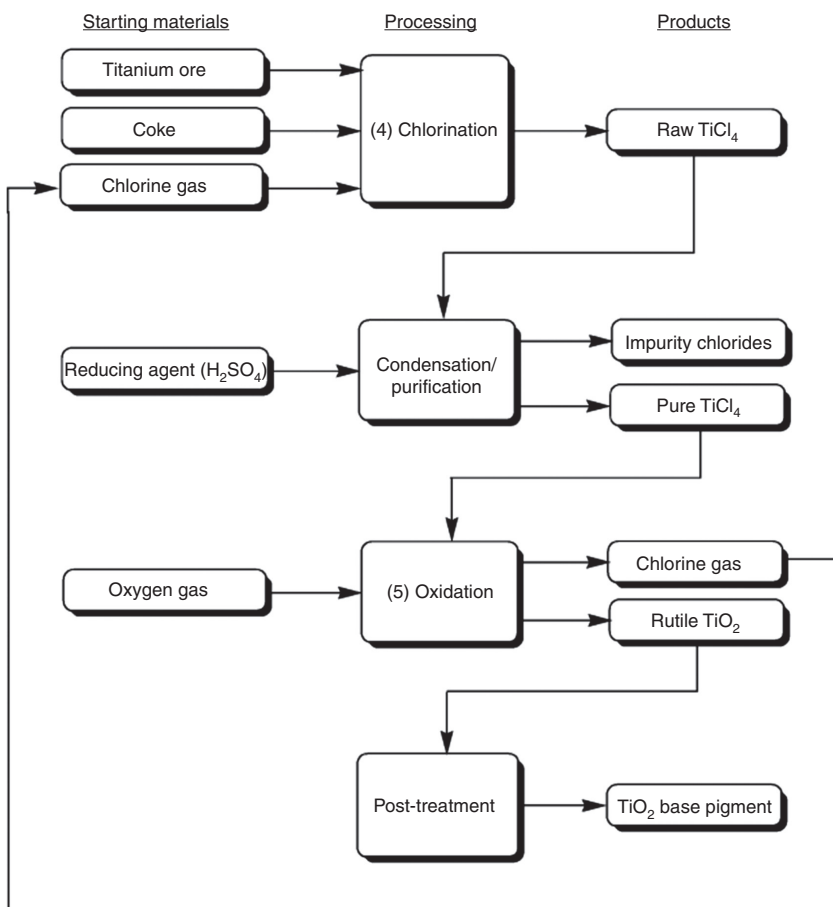


The chloride process can be applied to a variety of raw materials, but is often applied to titanium slag, prepared from the mineral, ilmenite, which is composed of 52.6%  $\text{TiO}_2$ .

**Chlorination:** Dry titanium ore material is heated in the presence of chlorine vapor, and a coke-assisted exothermic reaction is carried out at a temperature of  $\sim 950^\circ\text{C}$  with the addition of molecular oxygen to the reaction.



**Figure 1:** Representation the various stages of the sulfate process used for the manufacture of  $\text{TiO}_2$ . Reprinted with permission from Ref. [15]. Copyright 2004 Royal Society of Chemistry.



**Figure 2:** Industrial flow diagram representing the different stages of the chloride process used for the manufacture of rutile TiO<sub>2</sub> base pigments. Reprinted with permission from Ref. [15]. Copyright 2004 Royal Society of Chemistry.

The principal products of the reaction are gaseous titanium (TiCl<sub>4</sub>) and carbon dioxide (CO<sub>2</sub>) and other impurities; these impurities must be removed by distillation.

**Oxidation:** TiCl<sub>4</sub> (purified) is burned with oxygen at a reaction temperature of ~1000°C, producing the TiO<sub>2</sub> rutile phase, and the chlorine gas liberated as a by-product can be reused for chlorination, the first step of the process.

The chloride and sulfate processes are both extensively used in the large-scale production of TiO<sub>2</sub>. The process employed depends on the specific application and desired properties. The older sulfate process produces anatase and rutile TiO<sub>2</sub> phases, generally desired for photocatalysts and quality paper and ceramics [20], and the rutile phase predominantly produced by the chloride process is employed for normal quality paper, paper laminates, plastics, paints, fibers, food, cosmetics, and most inks [21]. As economic and environmental terms, for industrial production, the continuous chloride process is favorable compared to the batch sulfate process.

In fact, large volume industrial processes operate with continuous feed, while batch processes are synonymous to low-volume production (such as, a pharmaceutical factory).

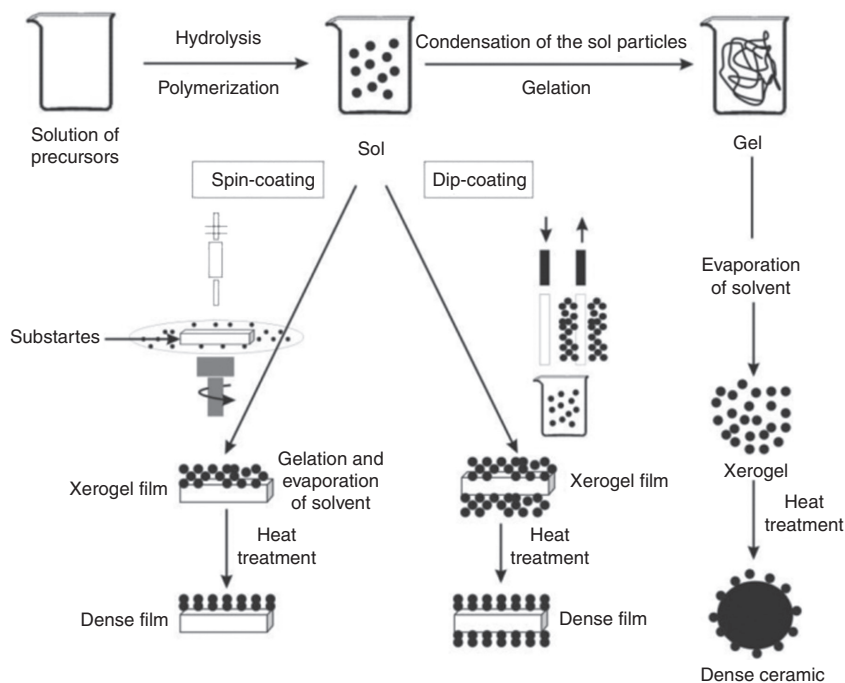
### 2.3 Advanced technique: sol-gel and aerosol

The development of TiO<sub>2</sub>-based materials and industrial processes has been driven by the paint and coating applications where the TiO<sub>2</sub> pigments have been used for decades. With the advancement of material science and the evolution of synthetic methodologies allowing strict control of phase, size, and dispersion [22], now, it is possible to control the photocatalytic properties [23, 24]. TiO<sub>2</sub>-coated windows and tiles are examples of self-cleaning materials; such materials have been used inside and outside to help the urban control of air pollutants. The Chubu International Airport (Japan) has glass windows, which are coated with a photocatalytic film [area of 20,000 m<sup>2</sup>

(2005)]. With the applications of nanophotocatalytic films on glass surface or concrete walls, self-cleaning has received tremendous attention [25]. In the future palazzo Milan-Italia with “The Tree of Life building”, the building was covered with thousands of panels made from photocatalytic impregnated cement. Upon solar excitation, the nanophotocatalysts in the cement are excited to generate reactive species, which in turn can convert a number of air pollutants ( $\text{NO}_x$  and others) in salts. This application was dubbed as the depolluting effect [26, 27]. Specific structures with self-cleaning  $\text{TiO}_2$ -based materials are i) Cowboy Stadium (Dallas, TX, USA), ii) Tokyo University (Japan), iii) Kaigaya Station (Japan), and iv) Yas Marina Circuit (UAE) [28]. The most common cement-based materials (with photocatalytic properties) involve flat applications (roadways, roofing panels, roofing tiles), paint applications (interior and exterior paints, street furniture, masonry blocks), and tunnels (paints, concrete panels, concrete pavements, ultra-thin white-topping) [29].

The sol-gel process used to prepare  $\text{TiO}_2$ -based nanophotocatalysts, employs chemical solutions to synthesize advanced inorganic materials (like semiconductors) at relatively low temperatures. The sol-gel process involves several steps: hydrolysis, condensation, polymerization, gelation, aging, drying, and finally, densification. Usually, alkoxide precursors are used; the hydrolysis and condensation reactions usually occur simultaneously. These

reactions are very sensitive to variables such as pH of the reaction, reflux temperature, water concentration, reaction time, and nature of the solvent. After obtaining the gel, following the aging, these then were dried and given heat treatment to obtain the desired nanophotocatalysts [23, 24]. This technique presents several advantages like versatility (to produce thin films and coatings, monoliths, composites, porous membranes, powders, and fibers), extended composition ranges, high homogeneity, high purity, and less energy consumption. However, the sol-gel method also has disadvantages: cost of precursors, poor processing reproducibility, shrinkage by drying (leading to cracking due to capillary stresses), preferential precipitation, and eliminating residual porosity and -OH groups and the difficulty to obtain a large amount of nanophotocatalysts. Figure 3 shows a schematic representation of the summary of the sol-gel process, techniques, and products [30]. This technique is a powerful tool to produce coatings and thin films of nanophotocatalysts. A number of methods are available to produce thin films: i) dip coating, ii) spin coating, iii) spray coating, iv) roller coating, and v) electro-phoretic deposition. Recently, Ferrari and his group [31] have reported new results in order to optimize the sol-gel synthesis of  $\text{TiO}_2$  at the industrial scale; their results showed that  $\text{TiO}_2$ , produced by the sol-gel using titanium tetraisopropoxide as the precursor, presented a high environmental impact and cost due to the energy



**Figure 3:** General scheme of possible routes to obtain thin films and powders by sol-gel technique. Reprinted with permission from Ref. [30]. Copyright 2014 Multidisciplinary Digital Publishing Institute.

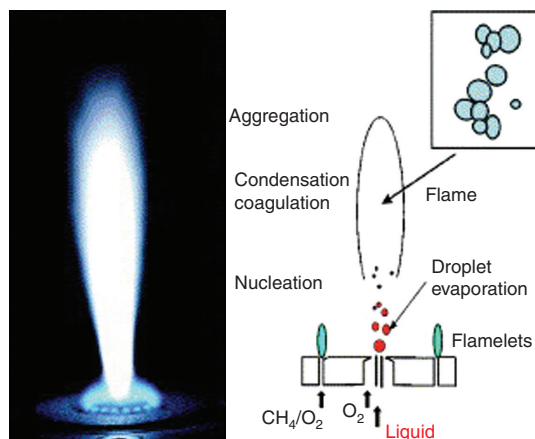


used to prepare this precursor. This problem can be resolved by reducing the non-renewable energy consumption, using microwave technique to heating the reaction mixture due to the more efficient heat transfer mechanism, using renewable energy, as solar cells or substituting titanium tetraisopropoxide by other  $\text{TiO}_2$  precursors.

The new industrial process to produce nanophotocatalysts is the aerosol process, where the manufacturing of  $\text{TiO}_2$  is the largest product after carbon black, producing almost 5 million of tons by the year 2011 [32].  $\text{TiO}_2$ -like photocatalysts or anti-fogging films can be produced in scalable flame and plasma reactors with rates approximately 2 g/min [32, 33]. This process uses aerosol reactors for the synthesis of particles at high temperature assisted by flames, plasma, and spray. The principal advantage of this process is the control over the size and morphology of the particles, also allowing the obtaining of a single or multiple component (e.g. structure-kind core/shell or Janus particles) [34]. The size and morphology can be optimized by the understanding of the different kinds of mechanisms involved in the synthesis like the use of laminar or turbulent flow to control the coalescence of nanoparticles, and the principal disadvantage are i) the low quantity of production for scalable industrial application, ii) the presence of agglomerates and aggregates, iii) the use of high temperature 1000–1500°C, and iv) this process is limited to be used only by a liquid precursor-solvent mixture into the flame reactor [33]. The nanophotocatalyst formation involves several processes such as nucleation, coalescence (coagulation), and agglomeration. At nucleation, the liquid precursors are mixed with gases into the flame reactor generating droplets at different sizes, due to the high temperature of the pyrolysis by the combustion of  $\text{CH}_4/\text{O}_2$ . These droplets are evaporated and produce small particles with a high concentration or supersaturation. On the flame, these primary particles can increase the size by coalescence processes, and finally, on the last part of the flame, these large particles can increase the size by agglomeration processes. The strict control on these processes allows the production of new nanophotocatalysts with specific properties. Figure 4 shows a schematic representation of the flame spray process.

### 3 Industrial characterization techniques

The photocatalytic properties of  $\text{TiO}_2$ -based nano-materials are highly dependent on the structural features, and thus, the characterization is critical in the development,



**Figure 4:** Flame spray pyrolysis and schematic of nanophotocatalyst formation. Reprinted with permission from Ref. [33]. Copyright 2002 Elsevier.

design, and application of  $\text{TiO}_2$ . In general, the  $\text{TiO}_2$  market has grown in the last century. In the last decade, this growth has been accelerated by nanoscience and nanotechnology; due to this reason, the  $\text{TiO}_2$ -based nano-materials are used on different kinds of applications such as i) coatings (architectural, industrial, and automotive), ii) plastics (outdoors furniture, appliances, plastic bags, and boxes), iii) paper (quality magazines, catalogs, and laminates), and iv) specialties (ink, rubber, leather, and elastomers). Therefore, any application needs specific physicochemical properties of titania, and the industry needs to have control making adjustment on the processes of synthesis for supplying the current demand of titania. The industrial characterization techniques play a determinant role to control the different physicochemical properties of titania.

Characterization of the specific surface area [Brunauer, Emmett, and Teller (BET) and Barrett-Joyner-Halenda method (BH)], X-ray diffraction (XRD), density ( $\text{g}/\text{cm}^3$ ), crystallite size [by nanoparticle tracking analysis (NTA), dynamic light scattering (DLS), scanning electron microscopy (SEM), and transmission electron microscopy (TEM)],  $\zeta$  potential (surface charge), transparency (influence by the particle size), and contact angle (CA) are important to establish structure-reactivity relationships.

#### 3.1 Specific surface area (SSA)

The SSA of a material is determined by the amount of molecular nitrogen physically adsorbed at equilibrium at its normal boiling point ( $-196^\circ\text{C}$ ) in a range of pressure less than an atmosphere. The records obtained are the volumes

of gas adsorbed at a series of pressures in the adsorption chamber, whose graph is named isotherms; the SSA, pore size, and pore area are determined therefrom. The International Union of Pure and Applied Chemistry (IUPAC) defines porosity as macroporous ( $>50$  nm), mesoporous (2–50 nm), and microporous ( $\leq 2$  nm). A number of methods exist to measure the specific surface area, the most common are BET and BJH [35, 36].

### 3.2 X ray diffraction (XRD)

XRD analysis has been used to determine the crystalline structure. Each crystalline solid has a unique characteristic X-ray pattern (fingerprint), which can be used for identification. XRD may also be used to determine the structure in the crystalline state, including the size and the shape of the unit cell. In the case of nanophotocatalysts with several crystallographic phases [30], some reports have been using this technique to determine the composition of the different phases; the detection limit is around 1–3% [37–39].

### 3.3 Particle size

Particle size is a critical property of the nanophotocatalysts because it directly affects the physical and chemical properties, band gap, reactivity, photo-reactivity, and others that can be modulated by nanoparticles. While a variety of techniques have been used to measure the average particle size at the industrial scale, the principal methods are:

#### 3.3.1 Nanoparticle tracking analysis (NTA)

This unique method involves visualizing and analyzing particles (from 10–2000 nm) in liquids and relates the Brownian motion rate with the particle size. The movement rate is related to the viscosity of the liquid, temperature, and the particle size. The size of the particle can be determined by the scatter of the laser light (illumination source) [40].

#### 3.3.2 Dynamic light scattering (DLS)

A simple convenient method, DLS, is one of the most popular light-scattering techniques. DLS allows for the measurement of the particle size from micron to

nanometer diameter by changes in the intensity of the light scattered from a suspension or solution. DLS measurements at a fixed angle can determine the mean particle size in a limited size range based on the analysis of the Brownian motion [41, 42].

#### 3.3.3 Scanning electron microscopy (SEM) and transmission electron microscopy (TEM)

These techniques are used to characterize individual particles (measure of particle size and disseminate particles of aggregates). Modern electron microscopes have software to examine the size distribution and particle shape. High-resolution transmission electron microscopy (HRTEM) has the capacity to determine crystallographic information of the nanoparticles. The principal disadvantages are high cost and the time required for sample preparation. To conduct SEM measurements of nanophotocatalysts often requires preparation of the material as a film structure on a thin conductive layer (carbon or metallic). For TEM analysis, the thickness samples must be less of 100 nm. The practical resolutions for SEM and TEM are 1 and 0.1 nm [38, 43–45].

### 3.4 $\zeta$ Potential (surface charge)

Particles have a specific charge on the surface, which influences the properties of the materials. Adsorption of substrates at the surface of the nanoparticles and aggregation are dramatically affected by surface charge and are often controlled by electrostatic interactions. The surface charge is very important to consider in preparing suspensions or emulsions [46]. The surface charge, a powerful tool to understand the physical-chemical properties of the nanophotocatalysts, can be measured on powders or thin films of the nanophotocatalysts. The  $\zeta$  potential is measured and used to determine the surface charge and the particle size. The  $\zeta$  potential depends on the atomic arrangement of the material surface and is crucial in controlling the adsorption surface properties. The nanophotocatalysts can possess a different surface charge in an aqueous media depending on the chemical process used in the preparation and the solution pH [47, 48].

### 3.5 Optical transparency

The optical transparency is critical for self-cleaning coatings on glass or plastic materials. Such transparent coatings need to exhibit high transmittance (close to 85%) of

visible light. The transmittance can be modulated by the concentration  $\text{TiO}_2$  in the material. The surface roughness (SR) also plays an important role in the transmittance as increasing SR leads to a fractional loss in optical transmission [49, 50].

### 3.6 Contact angle (CA)

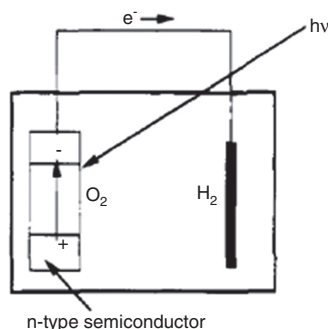
The coatings or thin films of the nanophotocatalysts have received considerable attention for their unique property to undergo hydrophilic surface changes upon illumination. The UV light-initiated self-cleaning thin photocatalysts films [40] are valuable for a wide range of applications on the design of new materials for building materials (thin films over glass and new additives in concrete). In general, a  $\text{TiO}_2$  thin film presents a contact angle of  $10^\circ$  (depending on roughness surface or pattern surface) (present a hydrophobic behavior), after the surface was exposed to UV light. The initial contact angle start to exhibit diminishing, which tends to be near the value of  $0^\circ$ , and at this stage (hydrophilic behavior), the surface becomes completely non-water repellent, called “highly hydrophilic”. This property can remain for a couple of days depending on the ambient conditions. This property is very relevant for self-cleaning functions or anti-fogging functions [51, 52].

## 4 Some applications

The production at the large scale of commercial nanophotocatalysts provides innumerable applications due to the easy accessibility to nanomaterial at low cost [15]. Therefore, we showed several applications of nano-titania [53], starting with the photocatalytic applications like artificial photosynthesis, photo-degradation of pollutants and hazardous compounds, smart materials (self-cleaning), among others.

### 4.1 Artificial photosynthesis

The high consumption of energy added to the contamination of megacities has increased the effort to find new materials that offer to reduce this global problem. From the middle of the 1990s, the artificial photosynthesis [54] has increased interest and is considered a new way to decrease the gas pollutants and simultaneously obtain organic compounds with high value in terms of commercial and environmental. The photocatalysts has been the most studied



**Figure 5:** Representation illustration of liquid junction of  $\text{TiO}_2$  electrode cell for solar water splitting. Reprinted with permission from Ref. [53]. Copyright 2002 American Chemical Society.

materials to be applied. In general, in this new research area, we can find two complementary schemes, first to study the water splitting for  $\text{H}_2$  production [55] and second for the production of organic compounds from  $\text{CO}_2$  [56].

Until now, hydrogen has just recently started to be considered as an alternative fuel on a large scale, presenting some advantages as renewable energy, clean, renewable, production of water (as a product of combustion). The principal disadvantage is the cost of generation and storage.

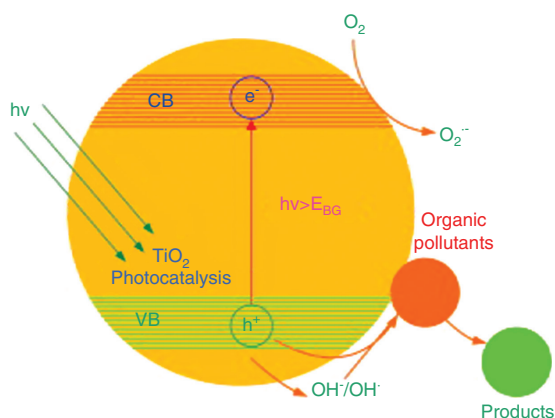
The photocatalytic hydrogen production offers a new alternative due to its low cost and being environmentally friendly. Hydrogen can be generated using solar energy and commercial  $\text{TiO}_2$ , which has gained importance due to the strong catalytic activity and chemical stability [57, 58]. It is important to note that a co-catalyst has frequently been introduced to accelerate the water-splitting reaction. Owing to the fact that  $\text{TiO}_2$  is activated by UV light, a small fraction of solar energy, dye molecules, or visible light-absorbing semiconductors can be good options to use as excitation sites over  $\text{TiO}_2$ . On the other hand, photoelectrochemical systems for water splitting could be easily achieved using an external electric field, generally exhibiting a relatively high efficiency (Figure 5). However, these systems are expensive for practical applications [55, 59].

In the case of  $\text{CO}_2$  reduction, the products are generally CO, formic acid, elemental C, formaldehyde, methanol, and methane. In all cases, the selectivity and efficiencies can be controlled by kinetic limitations and thermodynamic stability [60].

### 4.2 Photo-degradation of pollutants and hazardous compounds

Advanced oxidation processes (AOPs) have been used for the last decades for water purification and treatment or elimination of pollutants and hazardous compounds





**Figure 6:** Schematic illustration of the processes by illumination on TiO<sub>2</sub>, photo-generating of hole-electron pair, and resumption of the mechanism for the photo-degradation of pollutants and hazardous compounds. Reprinted with permission from Ref. [61]. Copyright 2012 Elsevier.

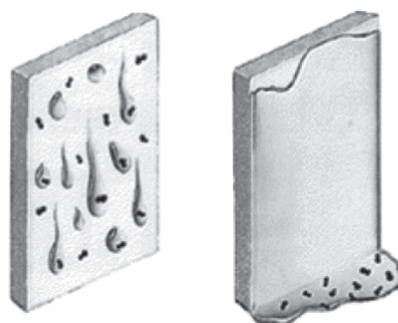
like pesticides, natural toxins, and other contaminants, through the generation of hole/electron pair (Figure 6). The tremendous promise of AOPs has resulted in a major demand of nanophotocatalysts because photocatalysis is among the most popular AOPs [61–64].

Owing to the availability to access solar energy for the photo activity of the nanophotocatalysts or the use of light-emitting diodes (LEDs) with low-energy consumption (for a continuous use system of 24 h), therefore, the energetic cost is low for the photo-degradation of pollutants, and hazardous compounds could be cheap and profitable [63].

The main industrial applications of TiO<sub>2</sub>-based photocatalysts is for the degradation of dyes used in the textile industry [64], expired pharmaceutical compounds (drugs) [65], spills of toxic compounds like pesticides [66], natural toxins like cyanobacterial toxin microcystin-LR [61], and personal care products (such as a series of parabens) [67]. Such nanophotocatalysts have also been used for the treatment of winery wastewater using a photocatalytic reactor [68]. Today, the use of photoreactors of pilot plants has grown quickly in the development and use of different kinds of photocatalytic reactors, especially to be used with solar radiation [69–71].

### 4.3 Smart materials (self-cleaning)

The development and exploration of photocatalytic materials over the past two decades have been tremendous. In the capacity of self-cleaning and air cleaning simultaneously, these new kinds of applications, has focused on TiO<sub>2</sub> and ZnO because they show a high stability, low cost, and strong capacity of photo-decomposition of organic pollutants



Ordinary uncoated tile    Hydrophilic tile coated with TiO<sub>2</sub>

**Figure 7:** Illustration of uncoated and coated tile with a hydrophilic TiO<sub>2</sub> layer. Reprinted with permission from Ref. [75]. Copyright 2012 Multidisciplinary Digital Publishing Institute.

[72, 73]. In general, the nanophotocatalysts can be integrated on the surface to treat the glass of windows, walls of structures, or flat surfaces [74–77] or in the bulk of the structure (concrete) (Figure 7) [78–80]. Recently, TiO<sub>2</sub> has been used for prepared self-decontamination textiles [81–84] and showed a high performance to UV shielding and antibacterial activity.

## 5 Conclusion

The traditional industrial processes for the production of TiO<sub>2</sub>, such as sulfate and chloride routes, have allowed for the production of nanophotocatalysts with well-defined properties such as anatase and rutile crystalline phases in the sulfate process and only rutile crystalline phase in the chloride process. On the other hand, emergent industrial processes for the production of nanophotocatalysts as sol-gel and aerosol have attracted tremendous attention because of its versatility in the production of films, powders, and composites due to smart materials can be designed at specific synthesis conditions. The use of techniques of material characterization plays an important role to understand and control the most important parameters in nanophotocatalysts, such as SSA, XRD, crystallite size, optical transparency, and contact angle. Finally, we showed some applications of industrial nanophotocatalysts and provide the excellent and practical applicability.

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## Bionotes



**Norma A. Ramos-Delgado**  
CONACYT Research Fellow-Instituto Tecnológico de Nuevo León, Tecnológico Nacional de México, Guadalupe, N.L., México

Norma A. Ramos-Delgado completed her BSc and MSc at the Autonomous University of Baja California, México. She obtained her PhD degree from the Universidad Autónoma de Nuevo León (2014), México. She joined the Nuevo Leon technology Institute in 2014, actually CONACYT Research Fellow-New Leon technology Institute, where her research involved developing titania-based photocatalysis and Environmental Analytical-Chemistry. [https://www.researchgate.net/profile/Norma\\_Ramos-Delgado](https://www.researchgate.net/profile/Norma_Ramos-Delgado).



**Miguel Á. Gracia-Pinilla**  
Facultad de Ciencias Físico Matemáticas & Centro de Investigación e Innovación y Desarrollo en Ingeniería y Tecnología CIIDIT, Universidad Autónoma de Nuevo León, San Nicolás de los Garza, N.L., México, [miguelchem@gmail.com](mailto:miguelchem@gmail.com)

Miguel Á. Gracia-Pinilla obtained his BS degree with honors from the National University of Colombia and his PhD from the Autonomous University of New Leon (2008), México, and then performed a sabbatical year at the Florida International University (FIU) USA (2015). He has worked at the Autonomous University of New Leon as an Associate Professor from 2008. He works on nanotechnology and its application to solar energy conversion and photocatalytic materials. [https://www.researchgate.net/profile/Miguel\\_Angel\\_Pinilla](https://www.researchgate.net/profile/Miguel_Angel_Pinilla).



**Ramalinga Viswanathan Mangalaraja**  
Advanced Ceramics and Nanotechnology Laboratory, Department of Materials Engineering, University of Concepción, Concepción, Chile

Ramalinga Viswanathan Mangalaraja is a Professor Titular and Director at the Department of Materials Engineering, University of Concepción, Chile. He is the President of the Chilean Metallurgy and Materials Society. He studied Physics at the Maduri Kamaraj University and received his MSc in Materials Science in 1995 and MTech in Ceramic Technology and PhD in Technology in 2003 from the Anna University, India. He works on nanotechnology-driven energy ceramics (functional ceramics for energy applications) and micro-nano-structure-property relationship. [http://www.materiales.udec.cl/docentes\\_mangalaraja.html](http://www.materiales.udec.cl/docentes_mangalaraja.html).



**Kevin O'Shea**

Department of Chemistry and Biochemistry,  
Florida International University, Miami,  
FL, USA

Kevin O'Shea earned his BS degree with honors from CSU, Sacramento, and his PhD from UCLA in Chemistry. He is currently a Professor of Chemistry and Senior Associate Dean of the Graduate School at the Florida International University. His primary research interests are focused in the areas of the reactions of reactive oxygen species (ROS) with organic compounds of biological importance resulting in diseases and disorders and environmental applications of ROS related to water purification. He is the author or coauthor of over 123 refereed journal publications, and his work has received over 3217 citations with an H factor of 32. <http://www2.fiu.edu/~osheak/index.html>.

**Dionysios D. Dionysiou**

Environmental Engineering and Science  
Program, Department of Biomedical,  
Chemical and Environmental Engineering,  
University of Cincinnati, Cincinnati, OH, USA

Dionysios D. Dionysiou is currently a Professor of Environmental Engineering and Science Program at the University of Cincinnati. He teaches courses and performs research in the areas of water quality, treatment, and monitoring. He is the author or coauthor of over 307 refereed journal publications, and his work has received over 9890 citations with an H factor of 53. [http://ceas.uc.edu/bcee/Dr\\_Dionysios\\_Dionysiou.html](http://ceas.uc.edu/bcee/Dr_Dionysios_Dionysiou.html).



## Graphical abstract

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Norma A. Ramos-Delgado, Miguel Á. Gracia-Pinilla, Ramalinga Viswanathan Mangalaraja, Kevin O'Shea and Dionysios D. Dionysiou  
**Industrial synthesis and characterization of nanophotocatalysts materials: titania**

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**Review:** This review examines the importance and versatility of  $\text{TiO}_2$  as a photocatalyst, solar cell component, mediator of chemical pollutants and toxins, and other industrial uses. Traditional and new industrial synthesis routes as well as nanoscale characterization techniques are presented, complete with application examples such as photocatalysis, water/air purification, or disinfection.

**Keywords:** industrial synthesis; nanomaterials; nanophotocatalysts; photocatalysis; titania.

