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Applications of Mesoporous Ordered Semiconductor Materials – Case Study of TiO₂

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Additional information is available at the end of the chapter

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1. Introduction

1.1. Titanium dioxide (TiO₂)

TiO₂ is a promising material for technological applications for its versatility [1-4], abundance, low toxicity, good chemical stability, photosensitivity and photostability [5-8]. In nature, it is found mainly in the mineral *ilmenite* [9], that can be processed industrially by two different routes [10]: The first, involves the reaction of the concentrate of *ilmenite* with hot sulphuric acid, resulting in the formation of sulphates of titanium, Fe(II) and Fe(III), being these last eliminated by centrifugation, after cooling. The final solution is then purified and hydrolyzed to produce pure TiO₂ [11]. The other usual way of obtaining consists in combining the ore with coke and gaseous chlorine under heating, resulting in CO₂ and a spongy material rich in TiCl₄. The reaction product is subjected to successive fractional distillation, with the formation of TiCl₂ and TiCl₃, due to stability of titanium in other degrees of oxidation. The different precursors of titanium are hydrolyzed, forming titanium dioxide [12].

In 1972, [13], obtained, for the first time, success in decomposition of water under irradiation with light and without application of any electric potential. They reported that, in trials where they employed n-type TiO₂ as anode and Platinum as cathode, when TiO₂ electrode illuminated under short-circuit conditions, hydrogen evolved from the Platinum electrode, while oxygen evolved from the anode. Since then, studies aimed at discovering and exploring different possibilities of technological application for TiO₂ have been given great importance [14-22].

As technological applications for TiO_2 can be cited its use in ultraviolet radiation absorbing filters [3, 23], in chemical sensors for gases [24-26], as a bactericide [27], in biomaterials for bone implants [28], in environmental photocatalysis [8, 24, 29, 30], in the photocatalytic hydrogen evolution [17, 31-36], in dye-sensitized solar cells [21, 37-44], among other.

The photocatalytic efficiency of TiO_2 depends on its structural and morphological characteristics, which are related to the method of synthesis used in the preparation of nanoparticles [18, 21, 29, 45]. To be photoactive, favoring the photocatalysis process, besides being mainly consisting of anatase crystalline phase, the TiO_2 must possess high specific surface area, good porosity, with high sized pores [35, 45, 46]. In this context, the search for TiO_2 particles that have differentiated features, with catalytic properties potentiated, constitutes a field of intense activity [19, 20, 47-50].

2. Porosity and porous materials

The porosity, related to the presence of cavities, channels or interstices is of great importance since it is related to the ability of materials to interact with atoms, ions, molecules, and nanoparticles not only at their surfaces but also throughout the bulk [51, 52]. Thus, the control of porosity is very important if the objective is the development of new materials [53, 54].

The pores are classified as closed or open, considering the ability of porous materials to interact with their neighborhoods. Figure 1 shows various types of closed (a) or opened (b, c, f) pores.

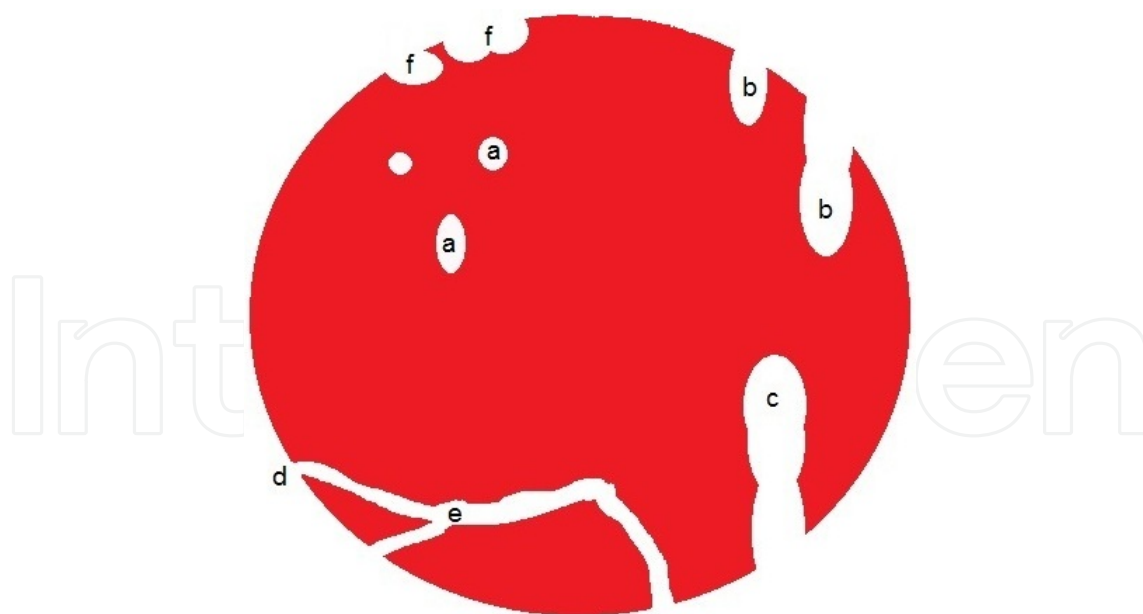


Figure 1. Schematic representation of a porous solid, presenting the most common types of pores: (a) closed; (b, c, d) opened; (e) interconnected; (f) surface roughness. Font: [55].

Open pores have continuous channels that communicate to the outer surface of the material, generating a cross-linked structure. Closed pores are inactive for the flow of liquids, gases and

other substrates, being totally isolated from their neighborhood. These pores are related to macroscopic properties such as mechanical resistance and thermal conductivity [55]. The pores can also be interconnected, (e). Otherwise used to classify the pores takes into account its format: bottleneck, (b), cylindrical, (c), and funnel type, (d). The surface roughness, represented by (f), is also a type of porosity [55].

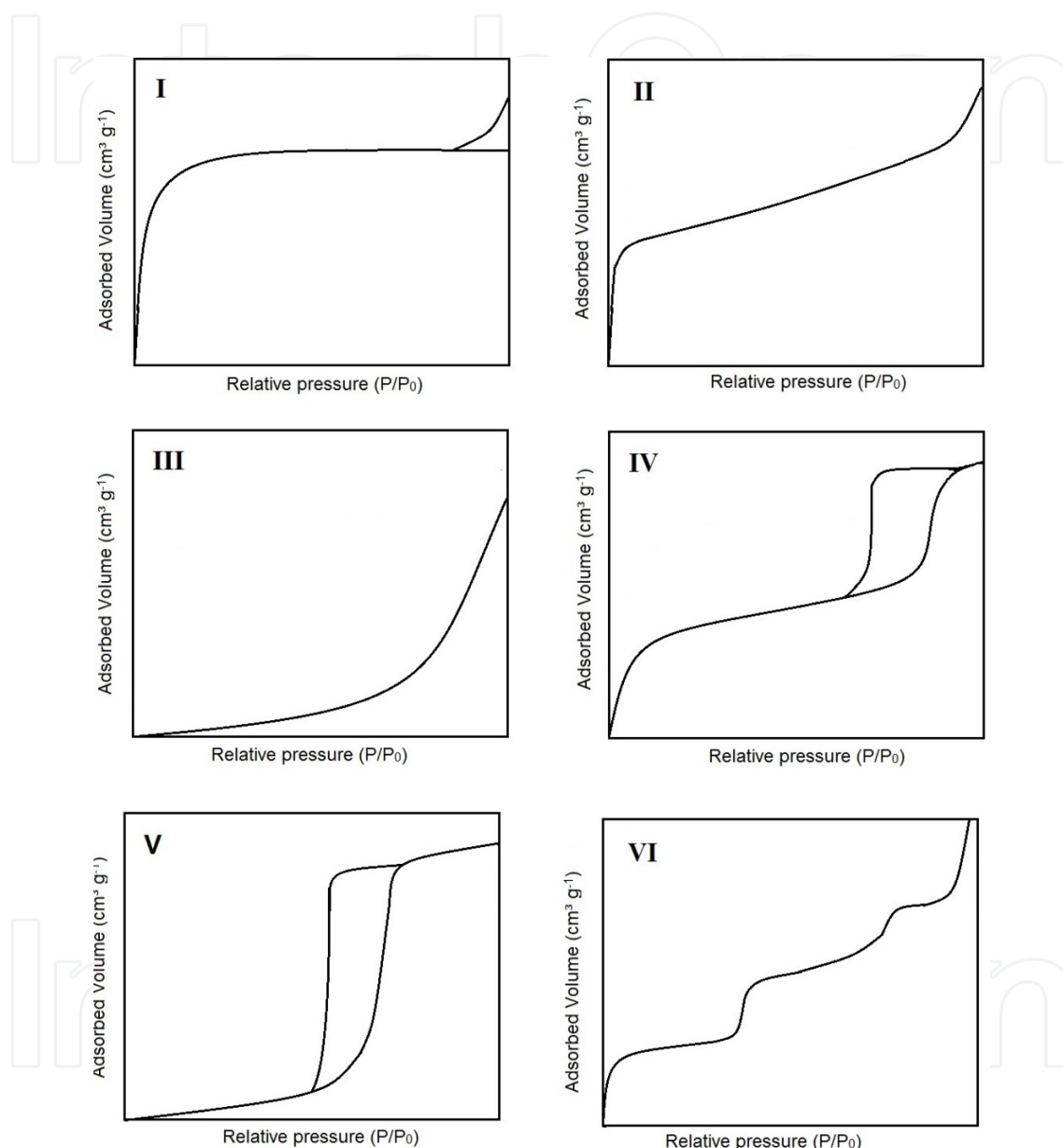


Figure 2. Representation of the six main types of isotherm: I, microporous solids; II, non-porous solids; III, macroporous solids; IV and V, mesoporous solids; VI, non-porous solids with uniform surface.

IUPAC recommends a quantitative division of the pores in three classes according to their mean diameter: micropores, lower than 2 nm; mesopores, between 2 and 50 nm; macropores, higher than 50 nm [56]. This pore size classification is based on measurements of adsorption-desorption of N₂ in boiling temperature and in the statistical width of layers of N₂ adsorbed.

The analysis of these data is usually done by using the Brunauer/Emmett/Teller method (BET), proposed by Stephen Brunauer, Paul Hugh Emmett e Edward Teller [57-59]. Applying BET, it is possible to describe the form of the adsorption and desorption isotherms for a specific solid. Knowing the format of the isotherm it is possible to define its porosity [60], Figure 2.

Microporous solids usually present a type I isotherm, whereas the isotherms II and III are related to non-porous solids finely divided or macroporous solids. Already the isotherms type IV and V present a hysteresis loop, a characteristic of mesoporous materials. The type IV hysteresis represents materials with uniform porosity, while type V hysteresis is referred to pores with non-defined forms and sizes. Finally, the type VI hysteresis is related to non-porous solids with almost uniform surface [60, 61].

3. Mesoporous nanostructured TiO₂

Organized mesoporous nanostructured titanium dioxide (TiO₂) is one of the most promising semiconductor materials, considering its current technological applications [19-21, 44, 60, 62-70]. The presence of pores in nanostructured materials tends to enhance their physical and chemical properties. Compared with bulk TiO₂, the uniform channels in mesoporous TiO₂ do not only increase the density of active sites with high accessibility but also facilitate the diffusion of reactants and products; the high surface area and large pore volume provides enhanced capability for dye loading and pollutant adsorption [60]. It is also possible to produce mesoporous TiO₂ using template-free methods. However, these materials usually present disordered mesostructures as a result of the irregular packing of building blocks [60].

4. Surfactants as drive agents in obtaining mesoporous ordered materials

Certain surfactants are capable to act as drive agents, as structural templates, in the synthesis of a semiconductor oxide, promoting its organization. This process occurs due to the spontaneous organization of the critical nuclei of the oxide formed around the structures defined by the surfactant, which control the growth of the microstructures initially formed, resulting in ordered mesoporous materials. The structural control and manipulation of the physical characteristics of a mesoporous material depends on the nature and concentration of the surfactant employed in the synthesis process [21, 71].

For a well-succeeded action of the directing agent in the synthesis, the model and the inorganic species need to interact [71]:

1. S⁺I⁻: cationic surfactants are used as structural drivers for inorganic species negatively charged;
2. S⁻I⁺: anionic surfactants are used as structural drivers for positively charged inorganic species;

3. S⁺X⁺I⁻: the surfactant and inorganic species are positively charged in the presence of species of opposite charge acting as counter ion;
4. S⁻X⁻I⁺: the surfactant and inorganic species are negatively charged in the presence of a species of opposite charge, which acts as a counter ion;
5. S⁰ I⁰: the surfactant has no load and the medium favors the neutrality of the inorganic species. In this case, the interaction between the species occurs through hydrogen bonds or dipole.

The concentration of surfactant in the reaction medium must be higher than the critical micelle concentration (CMC), which favors the auto mounting of micelles, originating bi and three-dimensional arrays responsible for empty spaces that will produce the nanoporous material [71].

5. Synthesis of mesoporous TiO₂

Among the methodologies of synthesis, the methods of sol-gel and homogeneous precipitation best favor the control of morphology [58, 72, 73]. The term sol-gel involves several synthetic methodologies based on hydrolytic processes [19, 20, 59, 74]. Hydrolysis and condensation reactions involving the precursor allows the formation of colloidal particles (sol) and subsequent formation of three-dimensional networks (gel). This process ensures a good homogeneity for the reaction product, leading, in general, to metastable phases, amorphous or not [50]. In the case of amorphous materials, a step of crystallization for oxides formed is required.

The use of solvothermal conditions is an alternative for conversion of the amorphous material to crystalline without the use of high temperatures [60, 73]. The solvothermal method consists in the dissolution of a metallic precursor in anhydrous benzyl alcohol and heating at temperatures above 423K. Under these conditions, the alcoholic hydroxyl group connects partially to the metal ion starting a polycondensation reaction. The steric hindrance, due to the greater volume of the organic group, tends to control the formation of nanoparticles which tend to stabilize in smaller sizes and narrower size dispersions than the obtained in the sol-gel process [75].

The hydrothermal method is a particularity of the solvothermal method in which the solvent is water. Under hydrothermal conditions the solubility of the amorphous particles increases significantly and the crystallization can occur concurrently with processes of re-dissolution and re-precipitation in the crystalline core [50, 76, 77]. This method has been widely used, since small variations in the main synthesis parameters (pH, concentration of precursor, among others) can cause significant changes in morphology, size, chemical constitution, between other properties of the synthesized nanostructures.

The homogeneous precipitation method has also been studied enough due to its great versatility. In this case, chlorinated precursors of titanium or even titanium tetraisopropoxide react with a base (sodium or ammonium hydroxide) forming titanium hydroxide. This compound is converted through the loss of water in amorphous TiO₂, which, under different thermal treatments, gives rise to the three known crystalline forms [78].

The combination between these strategies of synthesis and the use of molecular templates warrants a better control in obtaining ordered mesoporous materials. In this sense, two approaches can be highlighted: the soft template and hard template methods [60].

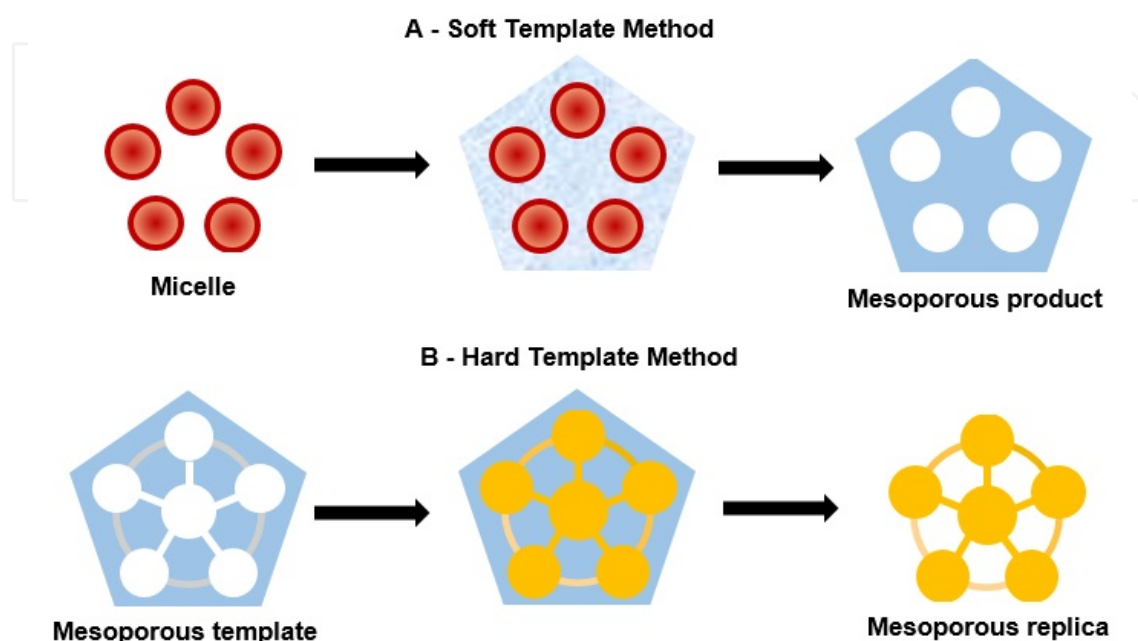


Figure 3. Representative scheme of the Soft-templating (A) and Hard-templating (B) methods, used in the synthesis of mesoporous materials.

The soft-templating method consists in the use of a template in the liquid phase, being widely used in the sol-gel processes based on titanium precursors. Due to its high chemical reactivity these precursors tend to suffer hydrolysis, giving rise to dense precipitates very quickly. The self-structuration of surfactants can produce mesostructures at the sol particle. This occurs by the spontaneous organization of molecules around autonomous micelle structures, usually in aqueous medium, giving rise to colloidal nanocrystals.

Studies have suggested that two mechanisms are related to the formation of mesoporous materials via soft-templating method [71, 79-81]. The first, known as Cooperative Self-Assembly (CSA), and the second Liquid Crystal Template (LCT). In CSA, there is a simultaneous aggregation between the inorganic precursor and the surfactant, with the formation of a liquid crystal-like phase with cubic, hexagonal or lamellar arrangement, containing both micelles and the inorganic precursor. On the other hand, in the LCT mechanism the concentration of surfactant is so high that a liquid-crystalline phase is formed without the presence of inorganic precursors. In both mechanisms, after formation of the material is necessary to remove the template for the obtaining of porosity. For this, the procedure most commonly used is the calcination [71].

Chiola, Ritsko and coworkers, reported in 1971 the obtaining of mesoporous silica [82]. However, the special characteristics of the produced materials did not were at first explained

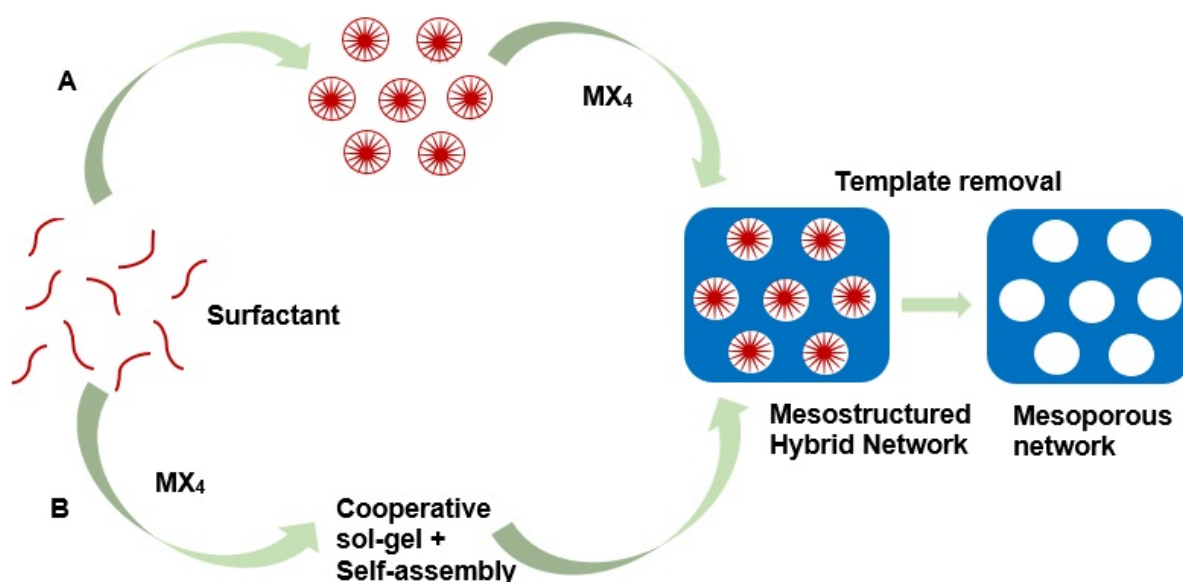


Figure 4. Formation of mesoporous structures: (A) Cooperative self-assembly process (CSA), and (B) Liquid-crystal templating process (LCT).

because the absence of adequate methods of analysis. In 1990, scientists from Mobil Oil Corporation [83], reported obtaining of mesoporous silicate molecular sieves, denoted by M41s, synthesized using a supramolecule-templating process, giving rise to a new and fascinating research field. Subsequently, efforts have been concentrated in studies related to synthesis and applications of mesoporous materials [9, 72, 84-91].

In 1995, the preparation of mesoporous TiO₂ using sol-gel method associated with a surfactant as structural template were at first reported [92]. Since then, efforts have been spent on the proposition of methods of synthesis of ordered mesoporous TiO₂, aiming to contribute to the improvement of the photocatalytic activity of this material, aiming its different applications [93-96].

Nanometric structures of mesoporous TiO₂ were produced using the sol-gel methodology, under acidic (pH 3 to 4) and alkaline (pH 7 to 9) media, using cetyl trimethyl ammonium bromide (CTAB), sodium dodecyl benzenesulphonate (DBS) and nonylphenol ethoxylate as surfactants (NPE) [72]. The effect of the surfactant and pH on morphology, particle size, surface area, and pore size distribution was studied being the synthesized oxides evaluated considering the degradation of naphthalene. Using CTAB under acidic pH the nanometric material is 100% anatase, while under alkaline pH the material was produced in two crystalline phases, anatase (84.7%) and brookite (15.3%). In the presence of DBS, under acidic pH, 83% of the crystalline phase was anatase and 17% rutile, while under alkaline pH, 100% was anatase. However, using NPE a mixture 94.7% anatase and 5.3% rutile was produced under acidic pH, while under alkaline pH the phases are anatase and brookite (8.28%). The authors suggested that the good result obtained for the degradation of naphthalene (97% up to 4 h under irradiation in the visible - $\lambda > 400$ nm) using the mesoporous material obtained in the presence

of CTAB in acidic medium is due to the surface area ($86.7 \text{ cm}^3 \text{ g}^{-1}$) and to the mean pore volume ($0.0569 \text{ cm}^3 \text{ g}^{-1}$).

A variant of the Soft Templating method is the Evaporation Induced Self Assembly (EISA) [97, 98]. It was originally designed for the preparation of fine films of mesostructured silica [79], and has been successful in obtaining different mesoporous materials (TiO_2 , ZrO_2 , Al_2O_3 , Nb_2O_5 , Ta_2O_5 , WO_3 , HfO_2 , SnO_2 , etc) [79, 80]. In this method, organic solvents such as ethanol, propanol, etc, are used as reaction medium. By virtue of the use of non-aqueous medium and block copolymer surfactants, the rate of hydrolysis well as redox reactions and phase transformation are minimized. EISA presents advantages when compared to aqueous sol-gel reaction, such as more control and homogeneity in the formation of particles, high crystallinity in reaction temperatures between 373 and 573K.

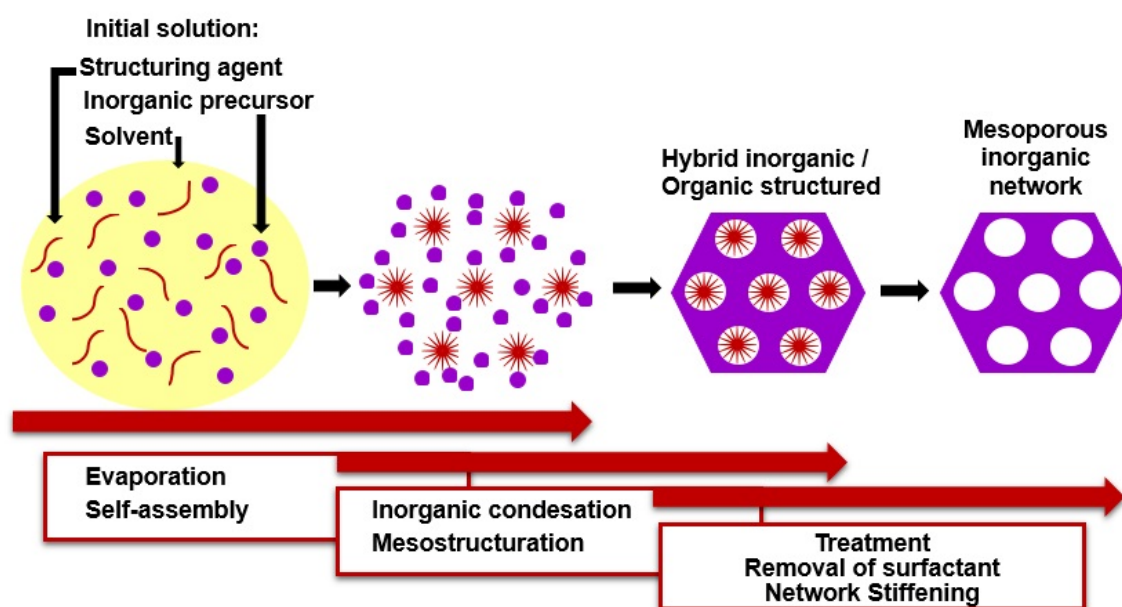


Figure 5. Scheme presenting the most representative steps of Evaporation Induced Self-Assembly (EISA).

A methodology capable of producing monodisperse spheres of TiO_2 at room temperature, using titanium (IV) butoxide (TBT) mixed to ethylene glycol, used as template, was proposed in [99]. The mixture was subsequently subjected to a conventional hydrothermal treatment. Thus, it was possible to obtain nanoparticles with surface area up to $233.2 \text{ m}^2 \text{ g}^{-1}$ and mean pore volume of $0.27 \text{ cm}^3 \text{ g}^{-1}$. The photocatalytic activity of the synthesized material was evaluated by degradation of methylene blue, Red MX-5B and phenolphthalein under UV irradiation, when were obtained kinetic constants of degradation of 6.7, 13.2, and $14.7 \text{ w}\% \text{ min}^{-1}$, respectively, attributed to the greater surface area of the catalyst. The synthesis of

TiO₂ spheres based on EISA, using titanium (IV) tetra isopropoxide and Triton X-100 has been also reported, aiming their application in DSSCs [100]. The particle size could be controlled changing the Ti/H₂O molar ratio and adjusted between 500 and 1100 nm, with a surface area of 56-151 cm² g⁻¹.

Using the EISA strategy excellent catalysts based on CeO₂, capable to oxidize harmful gases, as CO, NO_x and hydrocarbons, in non-toxic gases, were synthesized [81]. The tribloc copolymer P123 and polyvinyl pyrrolidone (PVP) were used as templates. In this way, were obtained catalysts with different pore sizes (about 40 μm, 2 μm and < 0.3 μm) and specific surface area of 32.5 m² g⁻¹.

Damages to the mesoporous structure can occur due to the presence of residual templates, as for example the blocking of pores or even poisoning of catalytic sites on the surface of the mesoporous material. Calcination has been pointed as a way to promote the elimination of some surfactants [101]. Non-ionic surfactants, as Triton X-100, can be easily removed by washing of the oxide formed [102].

In the hard-templating method the solid is formed around a template, usually zeolites and meso and macroporous silica, via interactions between the template and the precursor [60]. This methodology is more complex when compared to the soft-templating method. However, it is highly effective in obtaining mesoporous structures [103]. By applying this methodology nanostructures are formed on surface of the templates [104].

The obtaining of uniform nanospheres of TiO₂ based on hard-templating methodology, using silica as template and (NH₄)₂TiF₆ as precursor, has been proposed [105]. This material presented surface area of 54.2 m² g⁻¹ and pore volume of 0.15 cm³ g⁻¹. The photocatalytic activity of this material was evaluated regarding the degradation of the dyes methylene blue, rhodamine B and methyl-orange. The levels of degradation were respectively 95%, 95% and 90%. This result was attributed to the high surface area and charge separation in these monodisperse materials.

In reference [106] the obtaining of mesoporous TiO₂ is proposed using the combination of hard-and soft-templating methods. Using mesoporous silica in the first step (hard-templating) and Pluronic P123 as driver agent in the soft-templating stage, to control of morphology of the particles, was possible the production of three-dimensionally ordered mesopores with surface area of 145 m² g⁻¹ and pore volume of 0.246 cm³ g⁻¹. Due to the porous of the material obtained and the three-dimensional periodicity of the spheres, the authors highlight the possible applications that these materials can have, as in environmental photocatalysis, solar cells and in lithium rechargeable batteries. Finally, the authors highlight the ease with which this methodology can be extended for the synthesis of other mesoporous metal oxides.

Figure 6 presents the main differences between the hard and soft template methods, while Table 1 presents the structure of the main surfactants suggested as driver agents for the synthesis of mesoporous materials.

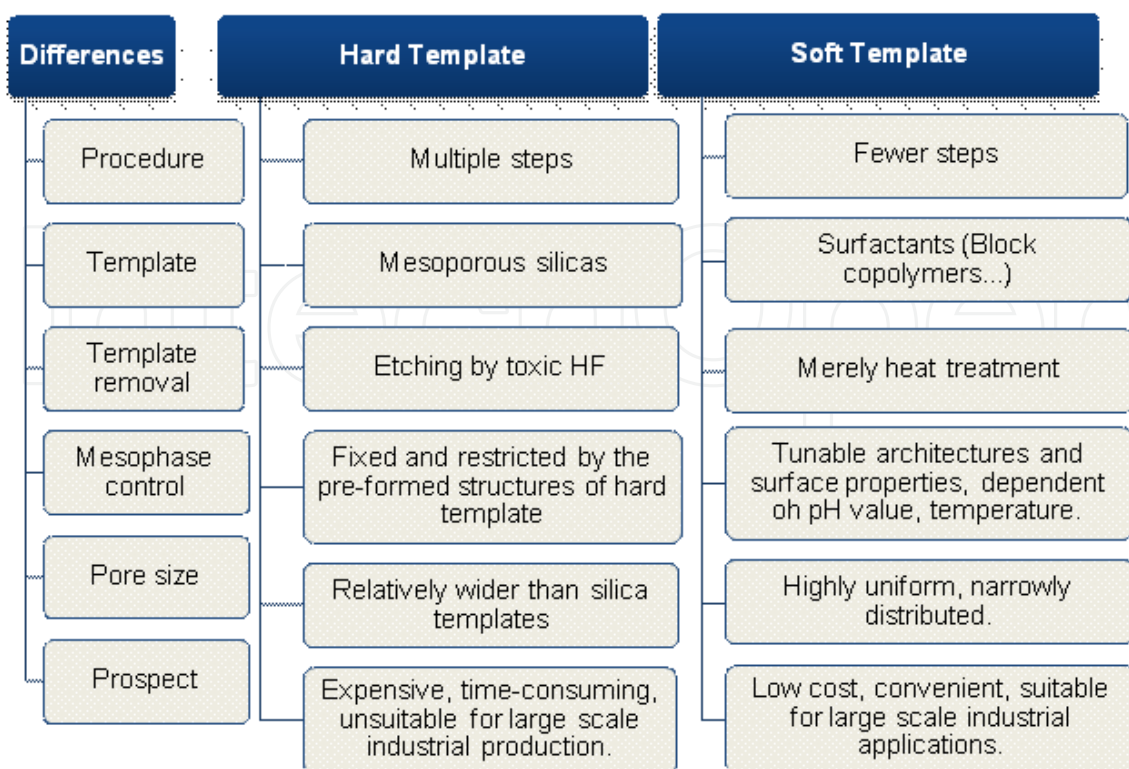
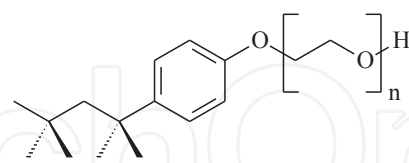
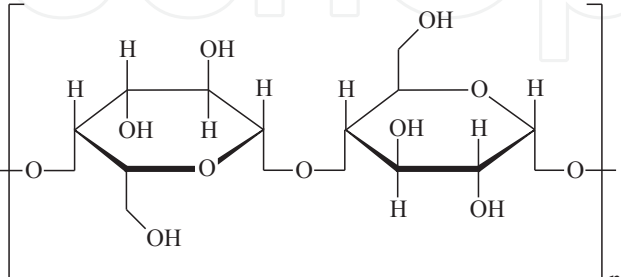


Figure 6. Comparison between hard and soft templating [107].

Surfactant	Structure	References
Polyethylene glycol	$\text{H} \left[\text{O} - \text{CH}_2 - \text{CH}_2 \right]_n - \text{H}$	[108, 109]
Triton X-100		[109-112]
Ethyl cellulose		[77, 113, 114]

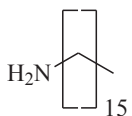
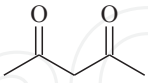

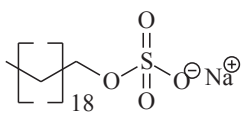
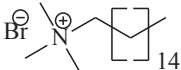
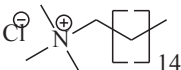
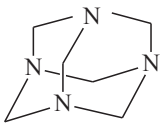
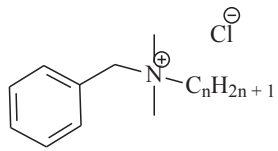
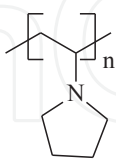
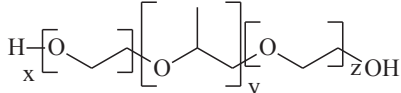
Surfactant	Structure	References
1-hexadecyl		[115]
Acetylacetone		[115]
Isopropanol		[115]
Sodium dodecyl sulfate		[116]
Cetyltrimethyl ammonium bromide		[5, 110, 117, 118]
Cetyltrimethyl ammonium chloride		[5]
Hexamethylene tetramine		[118]
Benzalkonium chloride	 n = 8, 10, 12, 14, 16, 18	[5]
Polyvinyl pyrrolidone		[118]
Pluronic P123		[62]

Table 1. Main surfactants suggested as driver agents for the synthesis of mesoporous materials and their chemical structures.

6. Technological applications of mesoporous TiO₂

6.1. Environmental photocatalysis

One of the potential applications of heterogeneous photocatalysis is the environmental remediation [8, 20, 74, 119-122]. Different semiconductor oxides have shown to be capable of triggering photocatalytic, highlighting the TiO₂ [19, 20, 123]. In this context, nanostructured materials tend to favor the photocatalytic applications of these materials [60].

Kim and Kwak reported studies where the photocatalytic activity of a mesoporous TiO₂ prepared using di-block copolymers via sol-gel synthesis was evaluated, using methylene blue as oxidizable substrate [50]. The materials with small crystallite size (about 5.1 nm), high surface area (about 210 m² g⁻¹) and small pore size distribution were the ones who exhibited the best photocatalytic activities, using ultraviolet radiation, with apparent constants of degradation around 0.093 min⁻¹. The particles synthesized presented spherical morphology with surface areas dependent on the type of di-block copolymer used.

In [58] is related a sol-gel synthesis of a TiO₂ with intermediate porosity, under hydrothermal conditions using a water-soluble cationic surfactant, obtaining a mesoporous TiO₂ with maximum pore size of 6.9 nm and maximum surface area of 284 m² g⁻¹. The synthesized material had its photocatalytic activity evaluated on degradation of methylene blue. The synthesized product showed to be superior (95%) to TiO₂ P25 (24%), using irradiation with UV radiation under the same reaction conditions. The greater photocatalytic efficiency was attributed to the higher surface area, when compared to this parameter measured to TiO₂ P25 (50 m² g⁻¹), and the ordination of the synthesized material, attributed to the use of the surfactant.

The synthesis of a TiO₂ supported on SBA-15 mesoporous silica, reported in [124], resulted in materials efficient to degrade photocatalytic phenols. SBA-15 silica presents hexagonal arrangement and bi-dimensional pores with diameter up to 30 nm. The materials obtained have surface area of 361.4 m² g⁻¹ and pore volume of 1.217 cm³ g⁻¹.

6.2. Hydrogen production

Hydrogen production via heterogeneous photocatalysis based in the electronic excitation of a semiconductor material using UV-Visible radiation is promising for the production of clean and sustainable energy [19, 54, 125]. Generally speaking, this process is based on the electronic excitation of the photocatalyst. From there, the photo-generated hole at the valence band reacts readily with a sacrificial reagent, while in conduction band electrons are trapped by a co-catalyst, being used in the reduction of H⁺ ions, with the production of hydrogen [126].

Mesoporous TiO₂ of intermediate porosity have generally high surface area and high density of active sites, which tends to facilitate the diffusion of reagents, favoring the conversion of solar energy in photocatalytic reactions [41, 93, 127].

A porous composite based on TiO₂ incorporated to silica MCM-48 (Mobil Crystalline Materials n° 48) was proposed as photocatalyst for hydrogen production [128]. The authors reported that the tetrahedrally coordinated TiO₂ act as active sites on photocatalysis of water reducing

the potential, facilitating the formation of gaseous hydrogen, even in the absence of a co-catalyst.

Microspheres of TiO₂ doped with carbonates has also been proposed for hydrogen production under visible ($\lambda > 400$ nm) irradiation [129]. A rate of H₂ production of 0.2 mmol h⁻¹ g⁻¹ was achieved using the photocatalyst charged with 1 wt% Pt. The photocatalytic performance was attributed to the characteristics of the mesoporous structure such as the diameter of the microspheres, between 0.5 and 4 μ m, pore size in the range between 3 and 11 nm and high surface area (500 m² g⁻¹).

A mesoporous TiO₂-SiO₂ mixed oxide with molar ratio of 97:3, calcined at 773 K was also proposed for hydrogen production [66]. It produced hydrogen at a rate of 0.27 cm³ h⁻¹ g⁻¹, an expressive value when compared to the rate achieved using TiO₂ P25 (0.17 cm³ h⁻¹ g⁻¹). This mixed oxide has characteristics that favored its photocatalytic activity, such as a surface area of 162 m² g⁻¹, pore diameter of 4.3 nm and pore volume of 0.24 cm³ g⁻¹.

6.3. Electrodes in Lithium ion batteries

Mesoporous materials have been used in the production of electrodes for Lithium ion batteries. Physical properties such as particle size, porosity and pore size determine the performance of this class of batteries [127]. The mesoporous structure favors the transport of electrolyte, facilitating the contact between the surface of the electrode and the electrolyte and shortening the path of diffusion of the Li⁺ ions.

These batteries have a long life cycle, rapid loading and unloading capacity, being capable to store high energy densities in a compact and lightweight container. Because of this, it has been used as power sources for portable electronic devices [127, 130, 131].

Mesoporous TiO₂ is a promising material in this kind of battery by offering numerous advantages, such as high potential of ions insertion, low cost, low toxicity, easy synthesis and stability to pH variation [60]. Anatase is generally regarded as the most suitable polymorph of TiO₂ for Li⁺ insertion, superior to rutile and with more stable structure than brookite. However, anatase with large particle sizes present poor performance due to its low capabilities to promote ionic diffusion and electronic conductivity [132, 133]. Thus, the control of particle size and porosity during its synthesis is imperative for obtaining materials with desirable characteristics.

The particle size influence on the dynamic process of storage of Li⁺ ions, ensuring a significant increase on battery performance when the particle size is reduced. For example, the discharge capacity of TiO₂ rutile with particles of 300 nm is 110 mAh g⁻¹, while this same parameter for particle sizes of 30 and 15 nm is, respectively, 338 and 378 mAh g⁻¹ [134].

Studies involving the application of mesoporous microspheres of anatase with regular porosity showed that pore structure significantly influences on specific capacity, speed capability and performance cycle of the batteries [60]. The materials with higher surface area had the best performance. It was also observed that when the pore size was very small, the transport of Li⁺ in the electrolyte was heavily restricted.

6.4. Solar cells

Solar cells have a great advantage when compared to conventional power generation systems, since in these solar energy can be directly converted into electric. The traditional solar cells are basically constituted by two layers of semiconductor materials, an n-p type pair. When photons with appropriate energy reach the semiconductor pair, electrons are excited producing electricity [135].

The first solar cells were based on crystalline silicon. Actually, studies are being conducted with the goal of developing efficient photovoltaic cells and low cost, since the crystalline silicon-based cells are of very high cost.

The solar cells can be classified as:

- a. First generation solar cells, where are the silicon solar cells used commercially, which today correspond to about 86% of the solar cells market [136];
- b. Second generation solar cells. More profitable than the first generation solar cells, but still less efficient;
- c. Third generation solar cells, where are the dye-sensitized organic cells;
- d. Hybrid solar cells [137].

In the organic solar cells are used semiconductor organic polymers or small and medium organic molecules, such as phthalocyanines, fullerenes, poly-(p-phenylenevinylene) (PPV). These cells can be produced on flexible substrates, and are promising in terms of production costs. On the other hand, they still have low efficiency, as well as some limitations, such as the possibility of degradation of the organic component.

In 2009, Park and co-workers developed an organic solar cell based on a polymer-fullerene composite, with a reasonable energetic efficiency (6.5%) [138].

Dye-sensitized solar cells, DSCs, Figure 7, are devices constituted by a semiconductor material, a sensitizer (dye), a conductive glass, an electrolyte and a platinum counter-electrode. Unlike conventional systems, where semiconductor assumes both the task of absorbing light as the charge carriage, in DSCs such functions are separated: the light is absorbed by a dye anchored to the surface of a semiconductor, and the charge separation occurs at the semiconductor-electrolyte interface [139].

A great leap in this area was given by [140] by using mesoporous nanocrystalline TiO_2 films in place of single crystals of oxide semiconductor as substrates for the adsorption of the sensitizer dye. The use of mesoporous films resulted in a significant increase in the conversion efficiency of incident light in current, I_{PCE} , which went from 0.13 to 88% [141]. The principal reason for this was the increase in the amount of dye adsorbed due to the greater surface area in general available in the mesoporous films. Using mesoporous films, the overall efficiency of conversion of solar cells sensitized by dye reached 7% in the decade of 90 [140]. Actually, the best cells exceed the 13% [142, 143], confirming the feasibility of commercial applications of these devices.

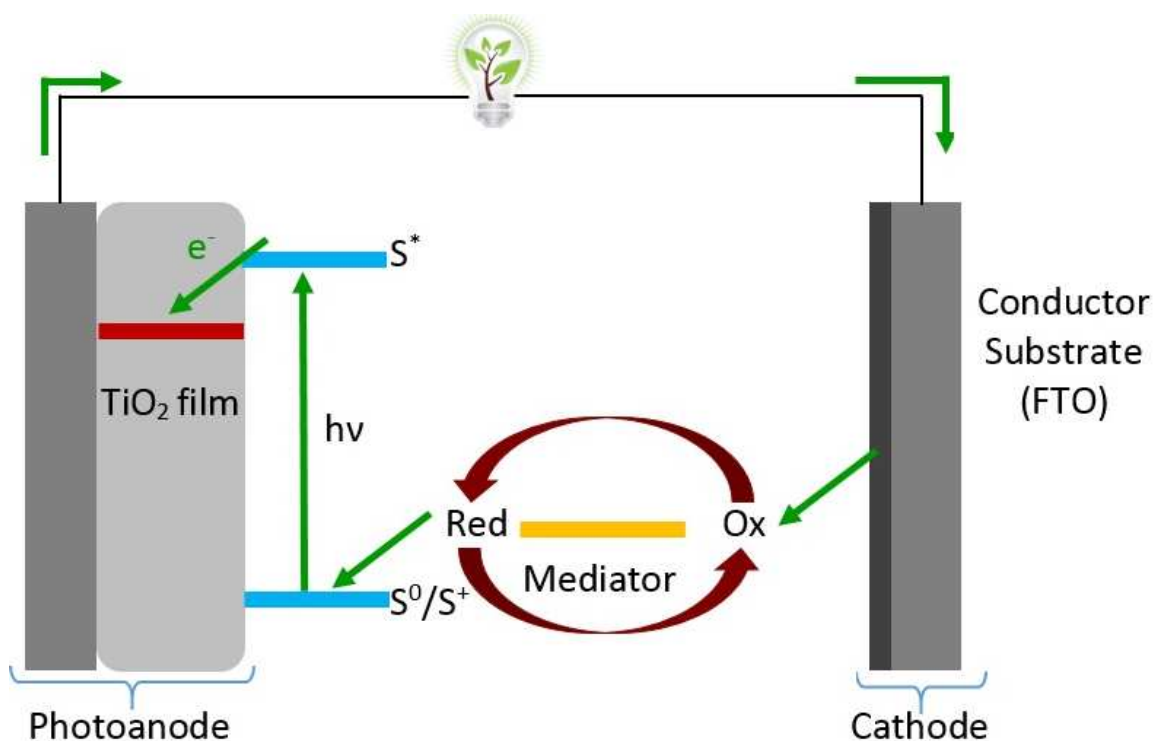


Figure 7. Simplified diagram showing the functioning of DSCs.

The I⁻/I₃⁻ redox pair dissolved in nitriles is thermodynamically capable to reduce the photo oxidized dye on the surface of TiO₂. The difference between the energy of the semiconductor conduction band and the redox potential of the electrolyte determines the maximum open-circuit potential than a DSC can achieve. Additionally, the kinetics of reduction is one or two orders of magnitude faster than the process of recombination between the electron in the conduction band of the oxide and the photo oxidized dye [144]. This difference makes the charge separation process in the TiO₂-sensitizer-electrolyte interface to be very efficient. The disadvantages of using liquid electrolytes based on I⁻/I₃⁻ redox pair include the toxicity of species of iodine and the inner filter effect caused by the strong absorption of light in the visible region by I₃⁻, which makes DSCs efficiency dependent on the exposed face.

The system TiO₂/Ru(II) complex/(I⁻/I₃⁻) is relatively simple and efficient, allowing a considerable advance in the understanding of the charge separation process from absorption of sunlight in sensitized semiconductors. However, this system presents challenges to be overcome, to its large-scale implementation. There stands out the high cost of the Ru(II) complexes, the high toxicity of the electrolyte and the need for an efficient sealing of the device in order to prevent the leakage of the electrolyte and the consequent loss of activity. Even so, modules up to 6000 cm² have been produced [145].

Alternatively, several other materials have been proposed to build DSCs. Organic compounds, such as indole and anthocyanins derivatives also have been proposed as sensitizers [146-150]. Recently, [151] described DSCs possessing efficiencies higher than 12% using a Zn(II) porphyrine as sensitizer and Co(II)/(III) complexes as redox pair. Another approach that has

attracted much attention involves the use of solid systems that, at first, dispense step of sealing and increase solar cell stability in real conditions of operation [152-155].

A major breakthrough in the development of solid DSCs has been achieved with the use of perovskites, as the $\text{CH}_3\text{NH}_3\text{PbI}_3$, as sensitizers [156-158]. These compounds are chemically very stable and can be produced *in situ* from precursors solutions and have a wide range of absorption, from visible to near infrared. When adsorbed on surface of TiO_2 films, $\text{CH}_3\text{NH}_3\text{PbI}_3$ is capable of injecting electrons efficiently and be regenerated by hole transporter materials (HTM) as spiro-MeOTAD (2,2',7,7'-tetraquinoxaline[N,N-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene). DSCs with efficiencies higher than 14% have been described using this approach [156]. It is interesting that the use of this same material in DSCs with Ru(II) complexes results in conversion efficiencies between 2 and 3% [159, 160]. This makes clear that it is not enough to simply replace one or another component in the DSCs to achieve greater efficiencies. It is necessary a good understanding of the characteristics of each part of the interfaces of the device and of the different processes of electron transfer that occur between the components.

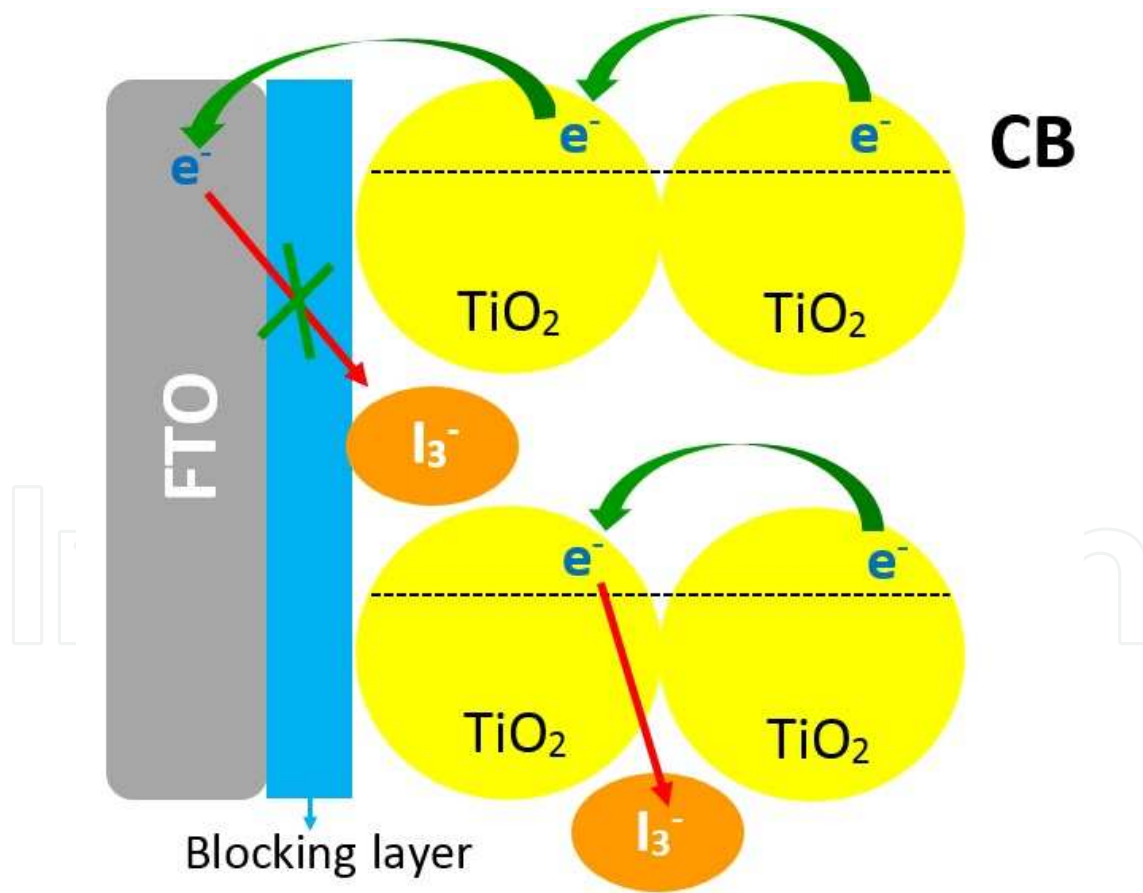


Figure 8. Decrease of electronic recombination on the FTO/electrolyte interface due to the application of the blocking layer.

In all approaches described above, it is common the need to deposit multiple layers of semiconductor oxides with different functions. Besides the nanoporous layer, responsible for dye adsorption and transport of electrons, there is the blocking layer deposited on the surface of the substrate which is responsible for reduction of the electronic recombination on the substrate-electrolyte interface, Figure 8.

Additionally, scattering layers, composed of particles with size between 400 and 700 nm can be deposited, which contributes to a greater use of the incident light. Several proposals can be found in the literature in relation to different layers of metal oxides in DSCs. In these are included the use of different techniques of deposition and also various materials. The research groups working in this area agree that the deposition of different semiconductor oxide layers with different morphologies is indispensable for production of high efficiency DSCs [143, 161]. However, there is still no consensus on the best deposition technique to be employed and what better composition to be used for the different electrolytes.

Recently, we reported the production of contact-blocking layers using the *layer-by-layer* (LbL) technique, which showed excellent performance in DSCs based on liquid electrolytes [162-164]. This technique stands out for its low cost, possibility of control of composition, thickness and morphology of films and the possibility to be employed on a large scale. It was noted, for example, that the use of a mixture between TiO₂ and more insulating oxides as Nb₂O₅ results in an increase of all the photoelectrochemical parameters of the DSCs [165].

7. Conclusion

In this chapter, aspects related to obtaining and application of mesoporous nanostructured materials in photocatalytic processes had been addressed, emphasizing its application in advanced oxidative processes, increasing the overall efficiency of conversion in dye sensitized solar cells, manufacturing of electrodes for lithium-ion batteries and hydrogen production, with focus on TiO₂. Although many advances have occurred, some challenges still needed to be overcome so that these materials become more efficient and economically viable. On the other hand, the potential that mesoporous materials demonstrated and the improvements already achieved promote the study and development of what is a promising source of technological applications.

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