SOLAR IRRADIATION AND TiO_2 RENDER MATERIALS SELF-CLEANING

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Summary

This topic presents the state of the art on self-cleaning materials based on activation of TiO_2 - coated on or incorporated into materials – when this semiconductor is exposed to solar light. The UV-induced phenomena at the origin of the self-cleaning effect are (i) the photocatalytic oxidation of organic compounds and carbon deposited on the materials, and (ii) increased hydrophilicity which causes the spreading of water droplets on the material surface. These phenomena and the properties required for self-cleaning materials to be used in the construction area are briefly introduced. Some information is provided on the techniques employed to coat or incorporate TiO_2. The question of increasing the self-cleaning efficacy, in particular by making TiO_2 capable of being activated by solar irradiation in the visible spectral region, is briefly addressed. A discussion about the origin of the UV-induced hydrophilicity is included. Attention is called to the fact that some solid matter of biological origin and thick stains may not be satisfactorily removed. Difficulties encountered in conceiving proper and fair tests to

evaluate the self-cleaning efficacy are pointed out; it is also underlined that the mechanical and optical properties must be appropriately appraised considering the durability required. The significance of the potential impact of self-cleaning materials on outdoor air quality is discussed. Given the present concern about the growing use of nanoparticles, the potential risk associated with self-cleaning materials is debated. Finally, information on the actual commercialization of self-cleaning materials and coatings is provided.

1. Introduction

Sun light can help to clean materials that are exposed to its radiation – especially in the UV spectral region. This property is based on the photon activation of a semiconductor, a phenomenon whose chemical effects are known under the term "photocatalysis" (cf. area 6.106 presentation). The semiconductor is coated on or incorporated in the materials. Until now, TiO_2 is the only semiconductor used to that end. In the presence of oxygen and some humidity, its activation by photons creates short-live species that are capable of oxidizing organic compounds and carbon. These constituents of visually undesirable deposits on the materials are thereby gradually eliminated. Also, the adhesion of fully oxidized inorganic salts - such as carbonates, sulfates and nitrates - is supposed to be decreased as a result of the removal of the organic layer which may act as a kind of glue.

The use of photocatalytic self-cleaning materials, based on TiO_2, for building facades has thus for objective the decreasing of the periodicity of cleaning or renovating these facades, while maintaining a visual aspect as constant as possible. Accordingly, efficient self-cleaning materials present both aesthetic and economical interests**.** They are of paramount importance nowadays because, first, a higher fraction of the world population lives in city buildings, and, second, air pollution due to traffic of vehicles and industrial activities tends to increase so far, in spite of stricter regulations. Therefore, facades' soiling by solid deposits generated by combustions occurs more rapidly than ever before.

Several properties are expected from a self-cleaning – and, to some extent, air-cleaning (see Section 11) – material based on the use of TiO_2. The efficacy, that is the photocatalytic activity of TiO_2, is obviously the property that is always sought. However, it is not easy to define what activity is really needed to obtain a satisfactory material, especially for preserving an acceptable visual aspect over time under various conditions. Moreover, the durability is a necessity. For instance, materials used in buildings (windows, decorating panels, cement-based coverings, paints, etc.) must last at least ten years without loosing their characteristics. Among these characteristics, the mechanical and optical properties of the TiO_2-containing material must be as good - or almost as good – as those of the TiO_2-free material. Of course, the TiO_2-containing material must be affordable, which a priori, except for very special uses, precludes some preparations and TiO_2 precursors. Finally, as usual nowadays, environmental considerations must be taken into account regarding the potential risks during the material manufacture, transportation, use and disposal (this evaluation is called life cycle analysis or assessment). To sum up, for any type of TiO_2-containing material and any use of this material, there is a compromise between the photocatalytic activity and the other properties, the durability, the cost and the environmental considerations (advantages and disadvantages; see Section 12).

2. Preparing, Coating and Incorporating TiO_2. Thickness of the TiO_2-containing Layer

A number of techniques can be employed to prepare and to coat TiO_2 on solid, smooth supports such as glass and metals. If a coating solution is used, it can contain TiO_2 nanoparticles or a TiO_2 precursor or both. As TiO_2 precursor, titanium tetraisopropoxide is very often used. For cost reasons, titanyl sulfate may be preferred. To improve both the adhesion and the hydrophilicity of the coating, silica can be added either as a colloidal suspension or in the form of a Si derivative. All the variables of the sol-gel procedure can be adjusted to change the characteristics of the coating and its adhesion. Curiously, experimental design has not been often used to that end. A very viscous solvent and/or a substance capable of creating bonds with the TiO_2 precursor have been utilized to delay crystallization after the coating procedure and to decrease the growth rate of the particles in attempts to enhance the photocatalytic properties. Several coating techniques, e.g. dipcoating, spincoating, and spraycoating, can be used to spread the coating mixture over the support.

Techniques employed for other types of coatings in the industries using the various supports can be utilized. Chemical and physical vapor depositions are the most common. As in the case of the sol-gel method, several factors can be varied to obtain coatings that present the best compromise between the desired properties.

The coating method must render TiO_2 solidly fixed on the support. This can be achieved via a thermal treatment, the addition of an anchoring substance to TiO_2, or by both methods. Thermal treatment can sinter the TiO_2 particles, and thus diminish the self-cleaning surface area. The addition of another substance can embed the TiO_2 particles and also restrict the mobility of the photoproduced charges if this substance is an insulator, such as silica. All these effects are detrimental for the efficacy.

During the coating process, which often involves a thermal treatment for increased adhesion, the support must not release into TiO_2 chemical elements that can decrease the photocatalytic activity. For instance, such detrimental migrations have been observed for sodium from glass, and for chromium and iron from stainless steel. This phenomenon leads one to first cover the support with a layer that cannot be a source of migrating chemical elements, e.g. silica for glass.

A thermal treatment obviously cannot be used in the case of polymeric materials. Accordingly, crystallization of TiO_2 at low temperature has to be sought. In addition, all polymers are photocatalytically degradable aside from those formed of C-F bonds only. Consequently, a TiO_2-containing coating cannot be applied directly on the polymer, except in the extremely rare cases where the replacement of the material before it looses its properties would be affordable. An intermediate layer can be placed between the polymer and TiO_2. This layer must have sufficient affinity with both the polymer and the photocatalytic inorganic coating while satisfying other required properties. That may bring on the use of multiple layers that progress from organic to inorganic character, but add to the complexity and expense of manufacture. Intermediate layers may be avoided by the use of a TiO_2-containing coating that includes poly(dimethylsiloxane) (PDMS), which can protect the polymeric support from photocatalytic damage. However, not surprisingly, the addition of PDMS reduces the photocatalytic activity.

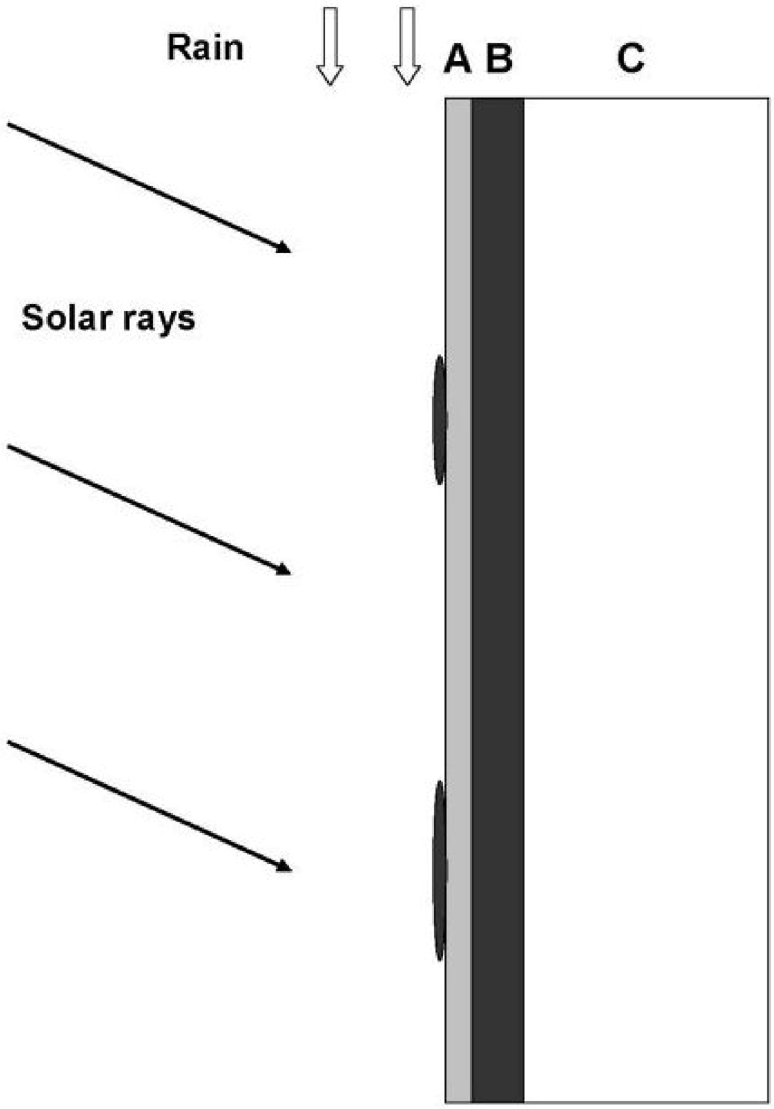

Figure 1. Scheme illustrating the self-cleaning effect under the alternate action of solar light and rain owing to the TiO_2-containing coating or layer A (dirt is symbolized as black thin ovals). B is an optional intermediate layer whose goal can be (i) to hinder the release into A of chemical elements issued from the material itself, C, during the preparation or (ii) to protect C against photocatalytic damage if C is an organic material or (iii) to provide a smoother surface if C is e.g. coarse concrete.

For cement-based materials, such as concrete and mortar, TiO_2 particles are, in principle, mixed with white cement. Obviously, the relative grain sizes of these particles and the other constituents have to be considered, the objective being to allow a maximum fraction of TiO_2 to be photo-activated and in contact with the dirt deposits and the air pollutants. Guidelines are difficult to obtain and to our knowledge, until now, only case by case studies have been performed using a series of TiO_2 powders for each cement-based mixture; in order to minimize the number of trials, experimental design was sometimes utilized. If need be, concrete made of fine aggregates can be applied on coarse concrete before spreading on the TiO_2-containing covering.

For supports having a smooth surface at the macroscopic scale - e.g. glass, metals, polymers - , coatings having a thickness comprised between 0.05 µm and a few µm can be envisaged. The thickness value essentially depends on the optical properties that are required. Given the penetration depth of UV irradiation into TiO_2, this thickness range enables a total or almost total use of the UV spectral region of solar light.

By contrast, cement-based materials, such as concrete and mortar, which have a coarser surface, require to be covered by either a cementitious layer (e.g. applied with a roller or a trowel) whose thickness is in the 1-10 mm range or several layers of paint up to a thickness of about 0.1 mm. Therefore, for cement-based coverings and paints, the main fraction of incorporated TiO_2 is not activated by solar light, unfortunately. The cost impact due to the high price of TiO_2 relative to that of the cement constituents is, however, limited insofar as about 3 wt% of TiO_2 is estimated to be sufficient to obtain satisfactory photocatalytic effects.

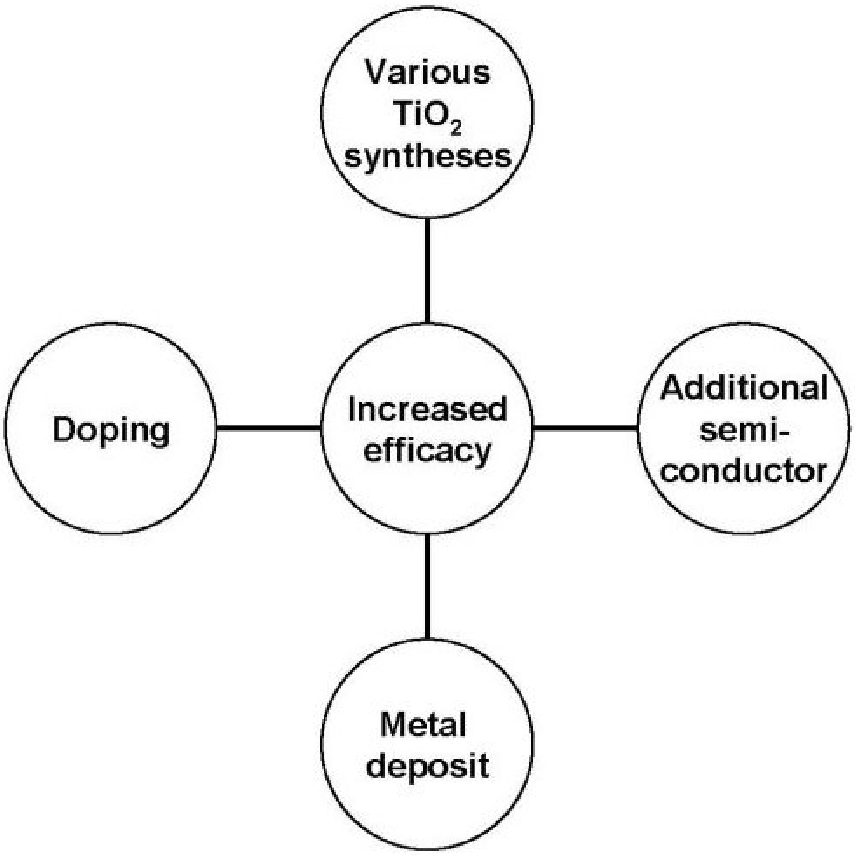

Figure 2. Scheme indicating ways of improving the self-cleaning efficacy.

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Biographical Sketch

Pierre PICHAT was "Directeur de Recherche de 1ère classe" (first-class) with the CNRS (National Centre for Scientific Research, France). He now works as an Emeritus Senior Associate. He pioneered applications of IR spectrometry to heterogeneous catalyst characterization - especially zeolites - and catalytic reactions. He has been active in heterogeneous photocatalysis for more than three decades, and founded the laboratory of "Photocatalyse, Catalyse et Environment" at the Ecole Centrale de Lyon. Basic scientific investigations into mechanisms, photocatalytic pathways and relationships between the activity and the characteristics of the materials, were carried out to improve photocatalytic efficacy. A large part of the research activity in his laboratory concerned the use of photocatalysis to develop self-cleaning materials, and for air and water purification. To a minor extent, he has also been involved in investigations of atmospheric photochemical reactions. He has published a great number of research papers and several review articles dealing with photocatalytic reactions and materials. He is a popular invited lecturer at Conferences, and a member of many International Scientific Committees in the field. At the “9th International Conference on TiO_2 photocatalysis: fundamentals and applications", held in San Diego in 2004, he received an Appreciation Award acknowledging his pioneering contributions; this award has been conferred to only three scientists in 17 years.