Advances (and limits) in photocatalytic building materials

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ABSTRACT

Titanium dioxide has often been indicated as emerging technique for environment depollution, specially in urban environments. It can be easily added to building materials, such as concrete or mortar elements, or as coating to any other façade. This paper tries to summarize the advances in this technology field and the limits it still shows.

Keywords: titanium dioxide, photocatalysis, self-cleaning

1 ABOUT PHOTOCATALYSTS

Some substances are able to promote, and specifically accelerate, some chemical reactions that take place in proximity to their surface: if this catalytic effect is shown when the substance is activated by an energy source, generally light with proper wavelength, it is called photocatalysis. This is the case of wide band gap semiconductors, such as transition metal oxides, which can be activated by sunlight and produce an acceleration of chemical reactions, including the degradation of the most diffuse polluting compounds in liquid or gas phase. Among these materials, titanium dioxide in its crystal structures (anatase, rutile and brookite) is undoubtedly the most relevant and studied.

1.1 TiO_2 in photocatalysis

The photocatalytic reactions induced by TiO_2 can be exploited to solve purification issues arising not only from the industrial harmful byproducts, but also from heating and transportations. It has good efficiency in degrading inorganic compounds, such as nitrogen oxides, in gas and liquid phase. The degradatin of organic compounds can also be accelerated by its photoactivation, and this is of great interest, given the intense production of volatile organic compounds (VOCs) in our everyday life: exhausts, combustion gases, cigarette smoke, cooking are activities that generate VOCs, but also furniture and cleaning products are indoor sources of these contaminants. Extensive studies have been carried out on the removal of organic and inorganig outdoor and indoor pollutants by TiO_2 nanoparticles under UV illumination: these particles are often integrated in air purification devices, which are commercially available from several companies. A long list of experimental studies is available in scientific literature on this topic.

Photocatalysts are not only used for breaking down large volumes of soilage: they are also capable of destroying it as it accumulates, e.g., to prevent cigarette smoke residue stains, or unpleasant odours due to the presence of VOCs. Bright UV lamps are sometimes used in city and highway tunnels to reduce pollution released by traffic, degrading both VOCs and nitrogen oxides, NOx [1,2].

1.2 Superhydrophilicity and self-cleaning

Besides photocatalytic applications of TiO_2, another phenomenon arises from UV irradiation, that is, the alteration of TiO_2 wettability and formation of a highly hydrophilic surface state: this behaviour is defined as photoinduced superhydrophilicity [3].

With this complex surface modification mechanism, water reaches contact angles close to zero on the surface of irradiated TiO_2. Moreover, this surface is not solely hydrophilic: on the contrary, it presents an amphiphilic nature, with hydrophobic and hydrophilic domains of nanometre size alternating across the surface [4].

The double photoinduced phenomenon of photocatalysis and superhydrophilicity results in the self-cleaning effect (Figure 1): grossly, surface contaminants will be first partially photomineralized, and subsequently washed away by water, which spreads below them in tight contact with the TiO_2 surface. Moreover, drops formation on superhydrophilic surfaces is avoided, which precludes stain formation due to slow water evaporation from the surface.

More precisely, self-cleaning should be referred to as "easy cleaning", as dirt and particles can adhere on the surface of titanium dioxide, even when irradiated; it is then extremely easy to remove them, since the action of UV light (available in natural sunlight) and water (for isntance that provided by rain) can help removing stains and dirt.

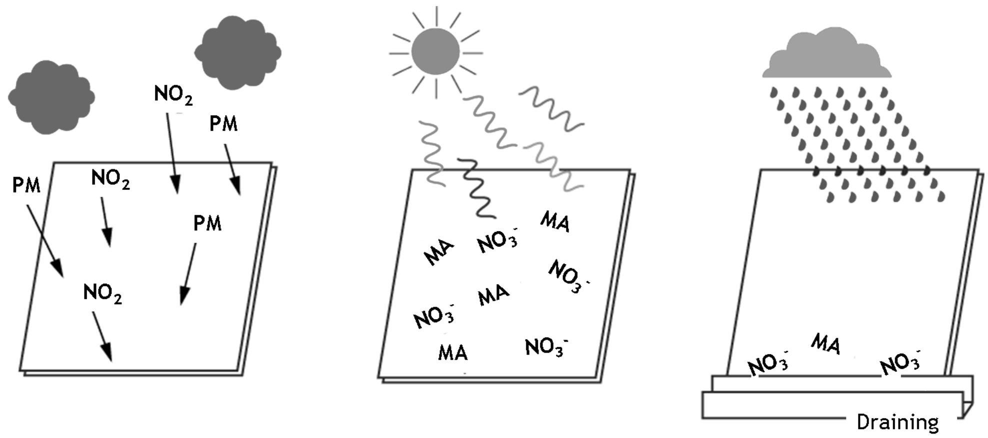

Figure 1: Self-cleaning mechanism on building facades (PM = particulate matter, MA = mineral acids).

This has become popular in several fields, even clothing: some companies are applying self-cleaning functionalities to fabrics for an easier cleaning and deodorizing of clothes. Anyway, the chief success of self cleaning is the built environment: self-cleaning glass, tiles, paints, mortars and many other materials and components.

The soiling of facades is due to the adhesion of particulate matter on the surface of materials, which are often porous (and therefore more prone to adsorbing such compounds). Particulate usually attaches to the surface through organic bonds, such as fatty acid chains and carboxylic groups. The twofold role of TiO_2 is then the photocatalytic degradation of such groups and the onset of superhydrophilicity, which drives rainwater in direct contact with the surface, removing particles which are at that point loosely adherent, thus reducing the need for maintenance.

1.3 Antivegetative effect

TiO_2 is also able to mediate the destruction of bacteria, viruses and other biological materials. This is often referred to as photosterilization, and it is of great interest for applications connected to air purification, specially in medical-related environments such as operating theatres, due to the chance to induce the death of bacteria, viruses, as well as allergens and fungi [5].

Antibacterial activity can be a method of controlling biological growth on concrete surfaces and avoid unsightly stains: biofilm growth causes the triggering of undesired chemical and aesthetical changes of concrete and mortar surfaces. The presence of TiO_2 doesn't explicate a bactericidal activity in this frame, that is, existing cells that compose the biofilm are not killed. The correcct definition is anti-vegetative: titanium dioxide can counteract biofilm microorganisms growth, and photokill planktonic cells, but cell inactivation on young biofilms is much more complex and rarely observed [6]. The inhibition of algae adhesion on cement substrates and on roofing membranes modified with TiO_2 (and WO_3) was also proved [7]. Therefore, applications of TiO_2 technology should focus on a preventative technique rather than on restoration ones.

2 APPLICATIONS

The use of TiO_2 modified materials in the built environment finds its roots in Japan at the end of last century, and it has been constantly diffusing, spreading also in European countries. Figure 2 reports an example of this: the Marunouchi Building, built in 2002 in Tokyo, whose windows consist of a self-cleaning glass (glass coated with a nanometric, transparent TiO_2 layer).

Figure 2: Marunouchi Building, Tokyo.

This is correlated with the increase in the generation of pollution and depletion of natural resources caused by intense and rapid industrial expansion, which pushes

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towards the development of sustainable materials, technologies and energy sources. A growing number of scientific studies and patents has been released in the last few decades on titanium dioxide nanopowders production and characterization, including their integration in construction materials.

Examples of functionalized materials are photoactive paints for interior or exterior, glass, tiles, self-cleaning fabrics; complete devices, like TiO_2-containing air purifiers, are also in commerce. These examples, which list just some of the available photocatalytic materials, make clear the interest in active principles capable of solving the cited air quality issues, or at least mitigate them.

Construction materials represent the most easily available medium to distribute photoactive substances over the widest surface area possible, gaining the maximum efficiency thanks to a versatile support for the photocatalyst and to a limited increase in materials costs. The introduction of heterogeneous photocatalysis principles in building materials also allows to exploit self-cleaning, which is mostly exploited in glass windows and in white concrete buildings, both in public buildings and in private housings: among the most representative examples of self-cleaning concrete we can list the church Dives in Misericordia in Rome, Italy (2003), designed by architect Richard Meyer, represented in Figure 3.

Figure 3: Dives in Misericordia, Rome, Italy

Several experimental works investigate the behaviour of TiO_2-modified construction materials. On the other hand, few information is available on the actual behaviour of the photocatalyst integrated in the material, and particularly on its evolution in time. This is actually a critical issue, as the photoinduced performances rely on the integrity of the material itself.

Two main cases can be identified, that is, cement-based materials containing TiO_2 nanoparticles (concrete, mortars), and TiO_2 coatings deposited on other materials (window glass, plastic).

Concretes and mortars naturally undergo chemical modifications which are due to the exposure to the environment. This involves mainly a carbonation phenomenon, with CO_2 entering the material, reacting with its high content of calcium hydroxide and producing the precipitation of calcium carbonates, which may shield the TiO_2 nanoparticles leading to a partial deactivation and a loss of efficiency of photoinduced properties [8]. A study carried out in the laboratories of the Department of Chemistry, Materials and Chemical Engineering at Politecnico di Milano focused on this issue, and data collected in this experimental work will be taken as example of the photoactivity decrease due to concrete carbonation (Figure 4).

On the other hand, coatings can be divided into thin films (e.g. sol-gel deposition on glass) or thick films (e.g. TiO_2 containing paints). The former can be eroded by atmospheric agents, removing the photoactive component from the surface. Paints are thicker, therefore it is more difficult to erode them completely, but they are usually composed of an orgainc binder which may be degraded by TiO_2 itself in time, leading to paint flocculation and fading.

Figure 4: Carbonation chamber (left) and experimental setup for photocatalysis tests (right) on concrete specimens containing TiO_2 (model reactant: Rhodamine B dye)

In all cases, the possible degradation of the supporting material can cause the loss of the photoactive principle: scientific research still needs to walk a long way before assuming that self-cleaning and depolluting effects will last for the whole lifetime of structures.

3 FINAL REMARKS

The huge mass of data available on photocatalytic and self-cleaning materials surely states the usefulness of TiO_2 in adding functionalities to materials where it is contained and helping decreasing environmental pollution. Yet, it is difficult to understand the actual behaviour in time of photocatalytic materials and in classifying them on the basis of their efficiencies.

These aspects can be investigated through large scale experimental setups and pilot projects, which are fundamental to define the behaviour of materials modified with titanium dioxide in real practice.

Although the attention of a large part of scientific community has been devoted to titanium dioxide for decades, practical applications are more recent, and have found a worldwide diffusion only in the last few years. An idea of the maturity of a product that still attracts so much basic and applied research is given by market volumes, but also the growing number of patent applications and standards promulgated is indicative of a massive passage from laboratory to real applications. The market for photocatalytic construction materials is expected to grow from a volume of 800 million dollars to 1.5 billion dollars by 2014, as proposed in the 2010 market report "Photocatalysts: Technologies and Global Markets" by BCC Research, which makes this technology a key advancement in building materials.

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