

Photocatalysis contributes to environmental protection and human well-being

CONTENTS It is now widely recognized that the photocatalysis industry should experience a strong growth in the years to come. Indeed, photocatalysis resulting from the use of semiconducting materials offers numerous technological applications, in the field of air or water remediation, self-cleaning surfaces, energy... This promising technology is not well known to the general public. In the area of environmental pollution, a stronger, regulatory and normative framework might have a positive impact on the applications of photocatalysts. This document aims at familiarizing readers with these technologies, showing what they already bring and how they will contribute to human health and well-being and to environmental preservation in the future.

Origins

Photocatalysis is based on the discovery, in the 1960s, of the photocatalytic properties of titanium dioxide (TiO₂). Photocatalysis has the ability to break chemical bonds leading to the elimination of chemical pollutants. Photocatalysis uses parts of radiation energy, especially UV radiation, and preferably occurs at ambient temperature and humidity. Doped and/or modified

photocatalysts also have the option to use visible light. Scientists promptly recognized the great potential of photocatalysis in various areas such as organic matter degradation, indoor and outdoor pollution control and air purification, odor control, water treatment, self-cleaning materials and surfaces, and energy concerns. Since the end of the last century, numerous applications have been

developed and among them, self-cleaning and depolluting materials (glazing, concrete, ceramics, paint, plaster) are highly advanced and have been commercially available for more than fifteen years. These and other more recent applications (air purifiers, water treatment,..) provide means of action on an increasingly polluted environment without degrading it further, and work towards improving quality of life.

What is photocatalysis?

A clean technology

Briefly, photocatalysis is a radiation-driven phenomenon through which a substance known as a “photocatalyst” is activated by natural (solar) or artificial (usually ultraviolet lamps) radiation to accelerate a chemical reaction. It may be compared to the chemical process of photosynthesis: the photocatalyst — usually titanium dioxide (TiO₂) — uses light energy, water and oxygen from the air, leading to the formation of highly reactive radicals. These radicals are able to break down specific organic or inorganic — and sometimes harmful — compounds in the atmosphere or in water, turning them into oxidized compounds (for instance carbon dioxide and water). During this chemical reaction, the photocatalyst is neither consumed nor altered, which makes the process sustainable over time.

Contrary to usual depolluting processes (filtration, flocculation,...), the products resulting from the photocatalytic reaction, namely carbon dioxide (CO₂) and water (H₂O) are harmless. Moreover numerous studies conducted on photocatalytic disinfection have demonstrated that titanium dioxide coupled with UV irradiation could be applied to eliminate micro-organisms.

Titanium dioxide is the most commonly used photocatalyst. This material can be found in a large number of everyday products.

Titanium dioxide is regarded as non dangerous to its producers or users by European regulations. It is not classified as toxic in the European Waste Catalog (EWC) and no particular security measure applies to its transportation. Independent studies conducted so far in the United States and in Europe among workers with high levels of exposure to TiO₂ have not shown any causal relationship between occupational exposure to TiO₂ and an increased risk of cancer. As a precautionary measure, TiO₂ has been classified 2B («possibly carcinogenic to humans») by the International Agency for Research on Cancer (IARC). However, if titanium dioxide proved carcinogenic, only a really massive inhalation exposure could induce pathology, if any. When designing their products, manufacturers use either liquid or agglomerated solutions to protect workers and users against inhalation exposure. This provides protection against the release of nanoparticle 

Self-cleaning and depolluting materials

Photocatalytic self-cleaning materials keep roofs, facades and glasses clean without any action other than the combined effect of sunrays and rainwater.

This is the most mature photocatalysis application today, and the glass industry played a pioneering role in this area with the introduction of self-cleaning glass, widely used since then.

Cement companies then developed concretes formulated with cements integrating TiO_2 . The Jubilee Church of Roma (by architect Richard Meier) was the first building ever erected which these materials (in 1999, completed in 2001). Since then, a large number of manufacturers producing sidings, coatings, waterproof membranes or paints have explored the possibilities of this technology and referenced photocatalytic self-cleaning systems in their catalogues. The green and blue self-cleaning facade ceramics of the Finchley Memorial Hospital in London (Murphy Philipps Architects) or the Italian Pavilion constructed from photocatalytic concrete that uses titanium dioxide to break down pollutants, such as nitrous oxides for the 2015 Milan Expo, illustrate recent applications of photocatalysis in the building sector.

DUAL ACTION

These materials act according to a two-step principle: degradation and washing. First, TiO_2 laid across the surface of materials or blended with them degrades soiling (organic degradation) through the dual effect of natural light and ambient humidity. And second, rainwater washes loosened dirt away.

BENEFITS

Photocatalysis offers various benefits: lasting aesthetics of buildings, reduction of maintenance services and maintenance costs, environmental benefit (water savings, limited use of cleaning products)... For glass surfaces, for instance, tests reveal that cleaning frequency has been divided by a factor of three. As a result, the overall cost of office building cleaning can be halved and bigger savings are possible, provided facade exposure is optimal.



Italian Pavilion in Expo Milano 2015, Michele Molè et Susanna Tradati, studio Nemesi & Partners

Feedback

The Cité des arts et de la musique of Chambéry (France), designed by architect Yann Keromes, opened its doors in 2003. It is one of the first French buildings erected with self-cleaning cement containing TiO_2 . Its designers made this choice so that the facade would keep its original aspect without requiring any maintenance. The colorimetric monitoring in progress is meant to validate the relevance

of such a choice. Since 2003, ten measurement campaigns involving 191 color measurement points on the building have been conducted,

showing that the original color of the facades is totally preserved, with minor colorimetric variances invisible to the naked eye.



Depolluting performance

Besides their self-cleaning properties, these products have a positive impact on air pollution, mainly on volatile organic compounds (VOCs) and nitrogen oxides (NO_x). These pollutants are produced either by building materials indoor or by combustion engines outdoor contributing to ozone pollution. Hence the obvious interest of this technology.

Photocatalysis does work provided UV radiation exposure and humidity are appropriate. Laboratory experimentations conducted with concrete show reductions of NO_x and VOCs. Simulations of real situation applications, for example sound proofing walls near motorways, show the potential of NO_x abatement under the alarm level with respect to the guidelines of the European Commission.

Feedback

The «Canyon street» experimentation was carried out under the PICADA (Photocatalytic Innovative Coverings Applications for Depollution Assessment) European research program. It aimed at reproducing the environmental conditions of a street (on a 1:5 scale) whose walls were covered with two types of coating, (namely) one based on a depolluting cement and the other one on a regular cement. The protocol implied producing exhaust gas on a continuous basis

for seven hours during the day. The results measured through sensors embedded in the coatings were striking. It was shown that the efficiency of depolluting action increases with a longer contact time of gases with the wall surface. On the contrary, action is reduced if the wind blows pollutants away from the street. These data are critical, considering that winds are virtually nonexistent during pollution peaks. The Life+ European project PhotoPAQ (Demonstration

of Photocatalytic remediation Processes on Air Quality) was launched in 2011 to demonstrate the usefulness of photocatalytic construction materials for air pollution reduction in the urban environment, under real atmospheric conditions. The PhotoPAQ organized two extensive field campaigns in Europe, including a large-scale test in Brussels (Belgium), where photocatalytic cement-based materials were applied on the walls of the Leopold II tunnel.

Improving indoor air quality

Energy efficiency requiring a proper insulation of buildings, indoor air quality has become a major concern and a public health issue. Photocatalytic air cleaners and passive photocatalytic products such as paints and ceramics with depolluting properties are solutions that may be considered to address this challenge. A photocatalytic air cleaner consists of a fan (the airflow rate depends on the fan power and does not exceed 1000 m³/h on mainstream models), a particulate filter, and a horizontal or pass-through photocatalytic medium using one or several lamps (generally UVA or UVC lamps). It may feature complementary equipment such as an ionizer or an activated carbon filter.



CERTIFICATION AND EXPERIMENTATIONS

Standardization programs and studies are underway for these air-purifying devices. Their goal is twofold: to withdraw non-compliant products from the market and to provide information on the operation of products, but also on their uses and limitations. In all cases, implementing such products requires a real scientific and technical expertise and a good knowledge of the pollutants present in the atmosphere to be treated.

Preliminary experiments on several commercial air purifiers according to the European standard under inquiry at the CEN level obviously demonstrated the need for a product certification. By-products formation and influence of aging were carefully checked. These preliminary studies however could conclude that there was no TiO₂ nanoparticles release in the atmosphere for all the studied commercial devices.

The testing of photocatalytic passive materials (tiles, paint) will also be possible using other specifically designed standards, in order to assess surface reactions and their effective contribution to indoor air pollution control. (See Annex 1)

Water treatment

Numerous research studies are focusing on photocatalytic applications for water treatment intended to remove industrial, organic, pharmaceutical and medical, sometimes persistent residues.

ACTION ON ORGANIC POLLUTANTS

Effluent treatment usually involves aerobic biological processes. These biological treatments prove ineffective or insufficient due to the poor biodegradability of some kinds of pollutants. One option is to combine them with other chemical oxidation processes like photocatalysis with photoreactors. It is also referred to as Advanced Oxidation Process (AOP). The efficiency of these treatments has been studied for the past two decades and demonstrated on most organic products, specifically on synthetic chemicals such as solvents, pesticides, dyes, more recently pharmaceutical compounds (antibiotics, analgesics, steroids or cyanotoxins)... Most of these organic substances are fully mineralized by photocatalysis. This promising technology is still underused in Europe but widely applied in North America. Like air treatment, it needs further characterization and numerous studies are underway. (Some examples Annex 2)



Standardization work and research

Various standardization initiatives aiming at providing users with the necessary guarantees regarding the reliability and harmlessness of systems are underway. These works are mainly supported by the National Standardization bodies, European Photocatalysis Federation, national associations, EU institutions, European manufacturers and industrial companies. It should be stressed that standards can actually demonstrate the efficiency of devices/materials under laboratory-controlled conditions.

A lot of work on standardization for the whole range of photocatalysis applications, from air purification and water treatment to self-cleaning surfaces led to the definition of national, European (CEN/TC 386) or international (ISO/TC 206/WG 9) standards (Annex 1). See the list in Annex 1. In order to guarantee the efficiency and safety of the products on the market to the consumer, the next step is the certification of the products based on the available standards.

ANNEX 1

European Standards (CEN/TC 386)

CEN/TS 16599-2014 (on light sources)
EN 16546-1 (efficiency of photocatalytic devices)
EN 16845-1 (anti-soiling activity under solid/solid conditions for porous surfaces)
CEN/TS 00386023: degradation of nitric oxide (NO) in air by photocatalytic materials.

French standards

XP B44-011 (NO_x abatement, continuous gas flow)
XP B44-013 (COV batch in closed chamber)
XP B44-200 (COV in continuous one-pass flow, particules).

Italian UNI standards

UNI 11247-2010 (NO_x abatement, continuous gas flow)
UNI 11484-2013 (NO_x abatement, continuous gas flow - CSTR reactor)
UNI 11238-2007 (BTEX abatement)
UNI 11259-2008 (Rhodamine-B

test for hydraulic binders - discoloration test)

German standard

DIN 52980: Photocatalytic activity of surfaces - Determination of photocatalytic activity by degradation of methylene blue

Other national standards

ISO 22197-1 standard was adopted as national standard in UK, Germany and Spain

ANNEX 2

The significant research and development activities in the field are illustrated by the 85 CORDIS research projects using the keyword photocatalytic (From www.cordis.europa.eu). See for instance:
- PhotoPAQ (2010-2014): Demonstration of Photocatalytic remediation processes on Air Quality
- Light2CAT (2012-2015): Visible LIGHT Active PhotoCATalytic Concretes for Air pollution Treatment

- Life MINO_x-street (2013-2018): Monitoring and modelling NO_x removal efficiency of photocatalytic materials: A strategy for urban air quality management
- PHOTOAIR (2014): Exploring the potential for photocatalytic air purification
- INTEC (2013-2014) Smart INks as a standard TEsting tool for self Cleaning surfaces
- PHOTOMEM (2010-2012): Photocatalytic and Membrane Technology Process for Olive Oil Wastewater Treatment"
- LIMPID (2012-2015): Nanocomposite materials for photocatalytic degradation of pollutants
- FOPS-WATER (2014-2019): Fundamentals of Photocatalytic Splitting of Water
- CO2SF (2014-2016): Solar Fuel Chemistry: Design and Development of Novel Earth-abundant Metal complexes for the Photocatalytic Reduction of Carbon Dioxide.



EUROPEAN PHOTOCATALYSIS FEDERATION

The European Photocatalysis Federation (EPF) brings together more than 100 manufacturers and research bodies (universities, laboratories, research centers...) from most European countries, with the purpose of promoting and disseminating this new technology. EPF strongly supports and funds the standardization and certification actions. Every two years, the Federation holds the European Symposium on Photocatalysis (Journées Européennes de la Photocatalyse, JEP). This meeting offers the opportunity to share information on the latest developments and innovations and facilitates exchanges between industry and academia.