BRIEFING No.10
CHEMISTRY & MATERIALS
Applications of Photocatalysis

Both the technological and economic importance of photocatalysis has increased considerably over the past decade. Improvements in performance have been strongly correlated to advances in nanotechnology; for example, the introduction of nanoparticulate photocatalysts has tremendously enhanced the catalytic efficiency of specific materials. A variety of applications ranging from anti-fogging, anti-microbial and self-cleaning surfaces, through to water and air purification and solar induced hydrogen production, have been developed and many of these have made their way into commercial products. However, extensive research continues to further optimise this technology and to widen the spectrum of potential applications. Research and application foci include anti-stick or anti-fingerprint coatings, soil repellency, and decomposition of organic matter such as microbes or fat.

When exposed to light certain semi-conducting materials such as 'photocatalysts' trigger or accelerate chemical reactions resulting, for example, in a decomposition of organic molecules. Due to their large surface area, nanosized catalyst particles show a significantly enhanced reactivity compared to larger particles or bulk material.

Numerous materials are under examination; however, none appear to match the efficiency of titanium dioxide (TiO_2)[1]. Its application requires illumination in the UV or at the extreme blue edge of the visible spectrum. Volume applications are thus mainly limited to the outdoor area. However, despite the reduced natural illumination, even indoor products such as sanitary ceramics are being increasingly applied. Moreover, research is underway to widen the exploitable spectral range towards visible light. A selection of applications is presented below:

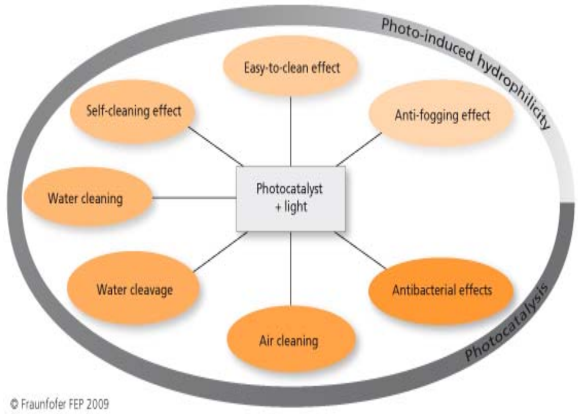

Figure 1: Spectrum of photocatalytic applications. (Source: Fraunhofer Photocatalysis Alliance)

Self Cleaning Surfaces

Cleanliness and maintenance issues are the key drivers for applications of self-cleaning surfaces[2]. Two major variants are directly related to the treatment of surfaces with photocatalysts. TiO_2 is again most commonly used:

Self Cleaning Photocatalytic Surfaces support the light induced destruction of adherent organic molecules and is of particular importance for anti-bacterial, anti-virus and fungicidal applications. Particular relevance is given to surface sterilisation in areas such as biomedical engineering and food preparation.

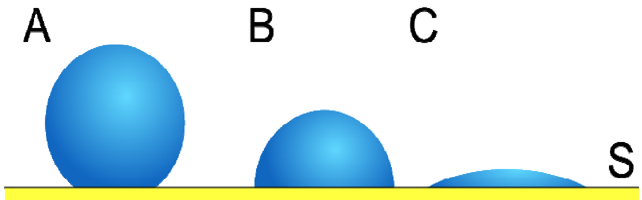

Figure 2: Illustration of surface tension. A: hydrophobic; B: normal; C: hydrophilic.

Super Hydrophilic Surfaces: "Photo-induced hydrophilicity" is generated by the exposure of a TiO_2-treated surface to intense UV light. Water is prevented from forming droplets and instead covers the surface with a homogeneous thin wetting layer, which penetrates below dirt particles.

Hydrophilic surfaces are thus easy to clean by pure water sprinkling and demonstrate considerable anti-fogging effects. Wet vehicle rear-view mirrors will therefore impact on the user´s view to a lesser extent.

A combination of both effects generates considerable self cleaning properties. Organic dirt can easily be washed off, for example by the next rain shower, surfaces remain clean, and moreover possess anti-microbial properties.

Photocatalytically active surfaces of glass, metals or ceramics are widely established. Further research is required, however, for plastic surfaces. Conventional high temperature processing is often not suitable here and the plastic surfaces themselves suffer from photocatalytic decomposition.

Air Purification

Photocatalytic surfaces have the potential to act against a variety of air pollutants and odours such as microbes, volatile organic carbons (VOC), formaldehyde, ammonia and inorganic gaseous substances such as nitrogen- or sulphur-oxides (NO_X, SO_X). Meanwhile a variety of technical products are commercially available. Applications include photocatalytic components for air filters, ventilation, and air conditioning systems via active decomposition of cigarette smoke or automotive and industrial exhaust to general air purifying effects of larger photoactive building elements.

However, photocatalysis is associated with a certain amount of ozone (O_3) development, which may cause harm at higher concentrations. Although small, this effect should be taken into account.

Water Treatment

This application is described in detail in a separate ObservatoryNANO Briefing.[1]

Destruction of Warfare Agents

Photocatalysts have the potential to decompose various hazardous substances at least in mild conditions. Researchers have examined the photocatalytic degradation of chemical warfare agents (CWAs). Results indicate that photocatalysts may support the detoxification of hazardous compounds. However, they must be applied as an additional component within larger decontamination measures and are not sufficiently suitable as stand-alone approaches[3, 4].

Hydrogen Production by Water Cleavage

The idea of photocatalytic water splitting is based on a photocatalyst powder in solution plus sunlight for clean hydrogen/energy production.

Research is underway to examine various types of photocatalysts for their suitability. Researchers successfully enhanced the reactive spectrum of TiO_2 towards visible light by doping with small amounts of nitrogen[5]. Further attempts are based on the utilisation of other bi-elementary photocatalysts (for example Titanium disilicide ($TiSi_2$)[6]) An informative overview may be found in [7].

Impacts

Economic/Industry

In 2009 the global market for photocatalytic products was $848 million. The expected compound annual growth rate (CAGR) will be 14.3% for the next five years and the global volume is expected to reach $1.7 billion in 2014[8].

The sales volume of construction materials representing the largest sector is forecast to increase from $740.3 million in 2009 to approximately $1.5 billion by 2014.

The CAGR for consumer products is predicted to rise by 13.2% over the next five years with the appropriate market volume increasing from $85.1 million in 2009 to $158.4 million in 2014.

Other products contributed with smaller sales volumes of a total of $22.1 million in 2009. The market is projected to reach $33.6 million in 2014 at a five year CAGR of 8.7%.

The given market figures refer to the overall photocatalysis sector. Nanoscale photocatalysts are included within these values but are not emphasized in detail. However, the fraction of nano-enabled products has been increasing during recent years, and this trend is likely to continue in future.

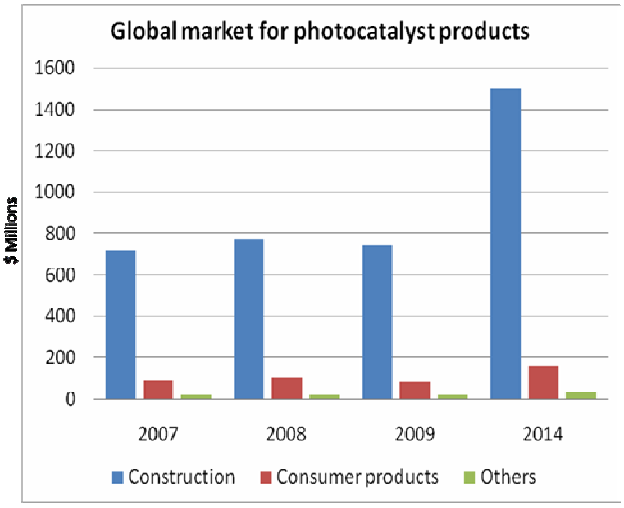

Figure 3: *Market volumes of photocatalytic applications. (Data-source: BCC Research).*

European product examples (selection)

In addition to water treatment it is self-cleaning surfaces, air purification and sterilisation that are currently the three major applications of photocatalysis. Meanwhile photocatalytic cement and glass are well established.

"TX Active®" of the Italcementi Group is a photocatalytic cement, able to reduce organic and inorganic pollutions in the air or on surfaces. It is particularly efficient in the decomposition of NOx-based substances from industry, transport and residential heating systems[9]. Application examples exist in Italy, France, Belgium, Morocco and the US. In Italy alone at least 400,000 m^2 of surfaces have been coated already in 2007[10]. A number of indoor surfaces particularly in sports halls and on tunnel walls have also been treated.

"Pilkington Activ™" is a self-cleaning glass by Pilkington Ltd. A photocatalytic coating on the outside surface cleaves organic pollutants upon UV-illumination; dirt is thus easily washed off by rain[11].

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"Hydrotect" flags, tiles and sanitary ceramics of Deutsche Steinzeug AG possess antibacterial, odour absorbing and self-cleaning properties based on surface refinement. The hydrophilic surface forms a thin coating and causes water to widely spread instead of forming droplets. The flag can then be easily cleaned by sprinkling[12].

Technology readiness levels

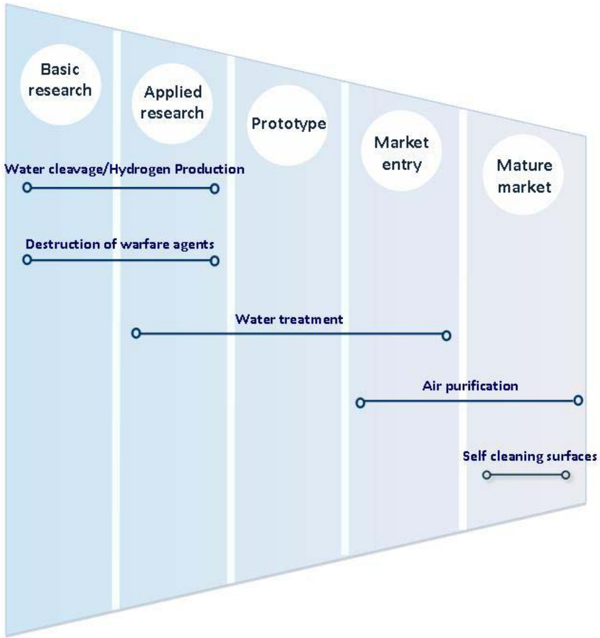

Figure 4: *Technology Readiness Levels for selected applications of Photocatalysis.*

Societal impacts

Photocatalysis is not within the specific focus of the wider public; however, there are tangible impacts from the numerous applications as outlined previously. In addition to an increased utilisation of nano-particulate photocatalysts some of these applications are becoming increasingly widespread and established in day-to-day consumer products. Photocatalysis is most widely used for environmental, cleaning, and aesthetic applications. Energy applications are at an earlier stage of research, and thus of less relevance with respect to current impacts. General impacts may be summarised as follows,

- reduction of pollutants
- minimised utilisation of chemicals
- enhanced acquisition expenditure

Relevant societal concerns include occupational health and safety, life cycle assessment (degradation and waste processing: risks of nanoparticles in environment/food chain), labeling/registration/supply-chain communication, and balancing environmental benefits/safety[13, 14, 15].

Health and risk

Environment, Health & Safety aspects of photocatalysts have been considered by ObservatoryNANO within the EHS review of the Chemistry and materials sector[16]. TiO_2 in its bulk form is successfully used as an additive in widely distributed consumer products such as cosmetics, sun screens, toothpastes etc. A review of literature pertaining to nano TiO_2 has illustrated that in relation to inhalation, this material demonstrates increased toxicity as particle size decreases due to the increasing surface area. However, the ability of particles to exert toxicity within the body depends on the level of exposure, and the subsequent behaviour after it enters the body. Dermal exposure studies to date have not yet demonstrated any penetration or toxicity via this route.

In relation to environmental exposure, the fate and behaviour of TiO_2 following release into the environment also remains uncertain to date[17] .

Based upon the evidence relating to potential hazard to date, it is advisable that procedures for manufacturing, use and waste management should avoid uncontrolled or accidental release of TiO_2 nanoparticles and subsequent exposure to humans or the environment.

Challenges

Photocatalytic applications are the focus of numerous research activities. Particular effort is spent on;

- new materials and coating concepts for photocatalysts and their application to different surfaces such as glass, ceramics, metals, plastics / prevention of the damage by self-oxidising
- optimized durability of the photocatalytic effect
- increased photocatalysis efficiency
- development of appropriate quantitative measurement methods for the photocatalytic effect
- environmental sustainability & biocompatibility.

Numerous research activities focus on shifting the photocatalytic effect towards visible light. Appropriate realisations are based on chemical dopants. Most prominent representatives are silver-, gold-, iron- or nitrogen doped TiO_2, hematite Fe_2O_3 or tungsten oxide (WO_3)[18, 19].

EU Competitive Position

Japan is the global leader in photocatalytic applications with respect to both production and consumption of photocatalytic products. Patent applications underline this with patent applications growing consistently and Japan contributing more than 40 % of the total volume. However, the EU is quite well positioned, taking second position ahead of the US.

The major players with respect to R&D, according

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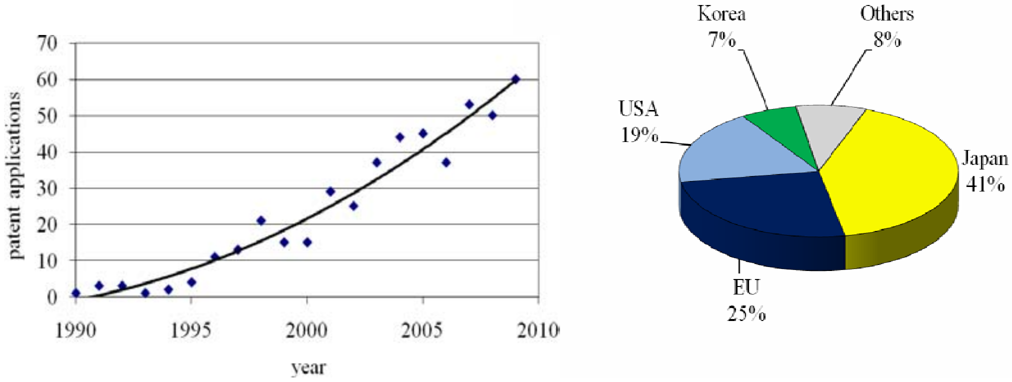

***Figure 5:** Patent applications at the World Intellectual Property Organisation (WIPO) based on a keyword search in the conceptual context of the term "photocatalysis". (Data-source: WIPO).*

to statistical patent analysis, are the Japanese Toto Ltd. and the US based Carrier Corp.. However, the French Saint-Gobain Glass and the Italian Italcementi are following. Further European companies include Kronos International, BASF, Reckitt Benckisers, Kemira Pigments and Evonik Degussa.

Europe is well positioned in terms of publicly funded research; according to expert statements, the quality of European research is competitive and world leading together with Japan and the US.

Summary

- Photocatalysts boost chemical reactions under irradiation with light. This is particularly true for the decomposition of organic substances such as fats, oils or even microbes.
- The catalytic efficiency is considerably enhanced by the utilization of nano-scale photocatalysts.
- TiO_2 is the most commonly used photocatalyst.
- Much R&D-effort is spent on the optimisation of existing as well as the development of new photocatalytic materials.
- Applications make use of the self-cleaning, anti-fogging, anti-microbial or water cleaving properties.
- Industries impacted are the construction sector, automotive and aerospace industries, the medical sector, food production and packaging, and sustainable energies in the longer term.
- Numerous applications have already achieved commercial maturity but have not yet widely penetrated the mass markets.
- The global market volume is expected to increase by double-digit rates.
- European industry and research is quite active and well positioned; however, Japan is currently in a world leading position.

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References

[1] "Photocatalysis for Water Treatment"; ObservatoryNANO, Briefing No. 2, August 2010
[2] Bräuer, G. et al.; *Surface and coating technologies*; Technology Guide, H.-J. Bullinger (Ed.), Springer, 2009
[3] Stengl, V. et al.; The Open Process Chemistry Journal, 2008, 1, 1-7.
[4] Zasshi, Y., Seko, Y.; PubMed 19122437, 129(1):53-69, 2009.
[5] Rumaiz, A.K.; Appl. Phys. Lett., 95, 262111 (2009).
[6] Ritterskamp, P. et al.; Angew. Chemie Int. Ed. Vol 46, 41, pp. 7770 (2007)
[7] Kudo, A., Miseki, Y.; Chem. Soc. Rev., 38, 253-278 (2009).
[8] Margareth Gagliardi, M.; "Photocatalysts: Technologies and Global Market" BCC Research Report (AVM069A), March 2010.
[9] http://www.italcementigroup.com/NR/rdonlyres/1F30E487-C0A2-4D6F-AB6D-C14555FD866F/0/Scientificresults.pdf)
[10] http://www.italcementigroup.com/NR/rdonlyres/96036B14-4C6D-4E07-9854-1B1CE1AD6593/0/TXactivetechnicalreport2009.pdf)
[11] http://www.pilkington.com/europe/uk+and+ireland/english/products/bp/bybenefit/selfcleaning/activblue/default.htm)
[12] http://www.deutsche-steinzeug.de/en/hydrotect_new/grafik/Hydrotect_GB.pdf))
[13] http://hesa.etui-rehs.org/uk/newsevents/newsfiche.asp?pk=1477).
[14] http://www.eeb.org/index.cfm/activities/industry-health/nanotechnology).
[15] http://www.cefic.org/Policy-Centre/Environment--health/Nanomaterial).
[16] http://www.observatorynano.eu/project/filesystem/files/EHSanalysis_ChemMatsOct10.pdf)
[17] Stone, V.*et al*. 2009, "ENRHES – Engineered nanoparticles: review of health and environmental safety", EC contract number 218433.
[18] Akarsu, M. „Herstellung undotierter und dotierter TiO_2-Partikel und Untersuchung Ihrer photokatalytischen Aktivität", Dissertation 2006.
[19] "New Visible Light Photocatalyst Kills Bacteria, Even After Light Turned Off"; Science Daily, News release, Jan 20th, 2010. Materials Research Society, "Photocatalysis for energy and environmental sustainability"; 2010.