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A web-based overview of semiconductor photochemistry-based current commercial applications

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Abstract

The major current commercial applications of semiconductor photochemistry promoted on the world wide web are reviewed. The basic principles behind the different applications are discussed, including the use of semiconductor photochemistry to: photo-mineralise organics, photo-sterilise and photo-demist. The range of companies, and their products, which utilise semiconductor photochemistry are examined and typical examples listed. An analysis of the geographical distribution of current commercial activity in this area is made. The results indicate that commercial activity in this area is growing world-wide, but is especially strong in Japan. The number and geographical distribution of patents in semiconductor photocatalysis are also commented on. The trends in the numbers of US and Japanese patents over the last 6 years are discussed.

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1. Introduction

Semiconductor photochemistry is a fast growing area both in terms of research and commercial activity [1,2]. A good gauge of the level of research activity in this area is provided by the level of relevant research literature produced, and this has escalated enormously during the past decade. Over the decade there have been many excellent reviews of this academic literature [1–5]. In contrast, despite an almost parallel frenzy in activity, the level and scope of commercial activity in the area of semiconductor photochemistry has received little attention and has not been reviewed. Instead, the strength and breadth of semiconductor photochemistry is usually gleaned from a steady stream of short reports in trade magazines or newspapers.

In the past it has usually proved difficult to review the number of companies and the range of products emanating from a particular research area. However, with the advent of the world wide web, much of this has changed, since most companies of consequence promote themselves and their products on their web pages. Thus, excellent search engines, like Lycos [6], Yahoo [7] and Google [8], allow most of the companies, and their products, working in a common area to be identified. As a consequence, it is

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now possible, through the world wide web, to conduct an overview of current commercial applications of semiconductor photochemistry, and the results of an attempt at this are summarised in the following pages. It should be noted that this overview is not exhaustive but does identify the major companies that are promoting products that utilise semiconductor photocatalysis. Obviously company promotional material, such as that on a company's web pages, rarely contains detailed, proprietry information concerning the product, or products. Indeed, many simply describe, in very brief terms, the function of the product(s) with little information about the role, or action, of the semiconductor active material. However, despite this dearth of detail, there is still a lot that can be learnt by browsing the web pages of the relevant commercial companies, including the size and geographical location of the company and the range and diversity of semiconductor photocatalyst products on sale. The academic literature usually provides the necessary information concerning the likely role and mode(s) of action of the light-absorbing semiconductor component in any commercial product [1-5]. In addition to this web-based overview, both the geographical distribution of companies, and original country of filing of US patents are examined, along with the variation in number of US and Japanese patents over the last 6 years. The results of this work are discussed and, where possible the key patent, or patents, associated with a commercial enterprise or product are identified.

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2. Features of semiconductor photochemistry with commercial potential

Although there are many companies currently promoting products that work via semiconductor photochemistry the functions of these semiconductor materials are usually largely based on one or more of the following three modes of action: *photomineralisation* (PCO), *photo-sterilisation* and *photoinduced super hydrophilicity* (PSH).

In order to understand the basic modes of action of semiconductor materials, it is important first to appreciate some of the features of electron energy levels in semiconductor materials. Thus, a semiconductor material comprises a manifold of electron energy levels filled with electrons called the valence band, VB, and, at a higher energy, a manifold of largely vacant electron energy levels called the conduction band, CB [1–4]. The energy difference between these two bands is called the bandgap, E_{BG} . Fig. 1 illustrates the basic electron energy features of a semiconducting material. Promotion of an electron from the valence band to the conduction band can be brought about by the absorption of a photon of ultra-bandgap light, i.e. $h\nu \geq E_{BG}$. The subsequent fate of this photogenerated electron-hole pair, e^-h^+ , is what determines largely the overall photoactivity of the semiconductor material. More often than not, the electron-hole pairs recombine to generate heat, and if this is the only process that occurs, the semiconductor will show no photoactivity. Electron-hole recombination is promoted by defects in the semiconductor material and, thus, most amorphous semiconductor materials show little if any photoactivity. If, however, the photogenerated electron and hole are able to make their separate ways to the surface of the semiconducting material then it is possible for them to interact with surface species. Under these circumstances, if an electron donor, i.e. D such as ethanol, methanol, and EDTA, is present at the surface, then the photogenerated hole can react with it to generate an oxidised product, D⁺. Similarly, if there is an electron acceptor present at the surface, i.e. A, such as oxygen or hydrogen peroxide, then the photogenerated conductance band electrons can react with it to generate a reduced product, A⁻. The overall reaction can be summarised as follows:

$$A + D \xrightarrow[h\nu \ge E_{BG}]{\text{semiconductor}} A^{-} + D^{+}$$
(1)

The above basic electron-hole generation, transport and transfer processes are also illustrated in Fig. 1.

If the change in Gibbs free energy for reaction (1) is positive, the overall process is an example of semiconductor photosynthesis ([1] and references therein). If, as is more usually the case, the change in Gibbs gives free energy is negative, then it is an example of semiconductor photocatalysis ([1] and references therein). Semiconductor photocatalysis is one of *the* major aspects of semiconductor photochemistry currently undergoing heavy commercial exploitation. Many of the current commercial systems that utilise reaction (1) employ the semiconductor photocatalyst to drive oxidation of organic pollutants by oxygen, i.e.

organic + O₂
$$\xrightarrow{\text{semiconductor}}_{h\nu \ge E_{\text{BG}}}$$
 CO₂ + H₂O + mineral acids (2)

A schematic representation of this process is illustrated in Fig. 2. Note that, in reaction (2), and Fig. 2, mineral acids

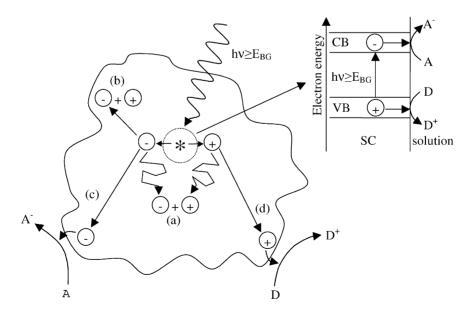


Fig. 1. Schematic illustration of the major processes that occur on a semiconductor particle upon absorption of a photon of ultra-bandgap light, i.e. $h\nu > E_{BG}$. Thus, the initial absorption process creates an electron, in the conductance band (CB), and a hole in the valence band (VB) which can then diffuse and/or migrate to the surface where they can react. The possible fates of the photogenerated electron–hole pairs include: recombination in the bulk, i.e. process (a), or at the surface, process (b), reduction of a suitable electron acceptor (A) adsorbed on the surface by the photogenerated electron, process (c), and oxidation of a suitable electron donor (D) adsorbed on the surface by the photogenerated hole, process (d).

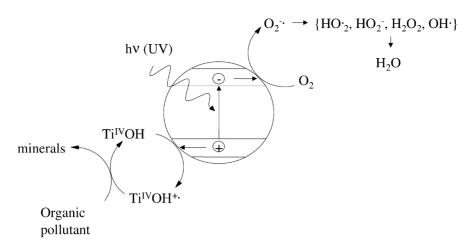


Fig. 2. Schematic illustration of the major processes associated with the photomineralisation of organics by oxygen, sensitised by a TiO₂ semiconductor particle photocatalyst, i.e. PCO. Thus, ultra-bandgap light generates electron–hole pairs. Photogenerated holes that make it to the surface can react with surface hydroxyl groups to generate adsorbed hydroxyl radicals (TiOH $^{\bullet+}$) which, in turn, can oxidise the pollutant to its mineral form. Photogenerated electrons that make it to the surface can react with adsorbed oxygen to generate superoxide, which can be subsequently reduced to hydrogen peroxide and then water. The intermediate species produced can act as a further source of hydroxyl radicals, OH $^{\bullet}$.

are only generated if there are any hetroatoms, such as sulphur, nitrogen or chlorine, present in the original organic pollutant. One reason for the rapid commercialisation of reaction (2) is that it has proved effective in the complete mineralisation of hundreds of organic materials, including many alkanes, alkenes, haloalkenes, aromatics, haloaromatics, insecticides, pesticides, detergents, and dyes [1–4]. Reaction (2) is an example of a photocatalytic oxidation reaction, which is often abbreviated as PCO; this abbreviation will be used throughout the text.

A great deal of the early work into semiconductor photocatalysis focused on the removal of organic pollutants from water. However, of probably greater interest in recent years, has been its use in the removal of organic pollutants in the gas phase. Since volatile organic carbons, i.e. VOC's, are often responsible for malodorous air, it is common for the use of semiconductor photocatalysis in the removal of VOC's, via reaction (2), to be also referred to as photodeodorisation [1,2,9].

Although there are many semiconducting materials in this world, only a few are very effective as semiconductor photocatalysts. Ideally, a semiconductor photocatalyst should be chemically and biologically inert, photocatalytically active, easy to produce and use, activated by sunlight and cheap ([1] and references therein). In fact, not surprisingly, no semiconductor fits this list of ideals, although one semiconductor, titanium dioxide, TiO₂, comes close. Thus, titanium dioxide displays all the desired features of an ideal semiconductor photocatalyst, with the exception that it does not absorb visible light. Titanium dioxide has a large bandgap, $E_{\rm BG} \approx 3.2-3.0 \, {\rm eV}$, and, therefore, is only a UV light absorber and, as a consequence, is limited to absorbing a small fraction, ca. 5%, of the solar spectrum. Despite this substantial limitation, its positive features far outweigh this one negative, and so titanium dioxide has become the semiconducting material to use in the field of semiconductor photochemistry. Its dominant position extends not only to basic research but, more importantly with respect to this overview, to commercial applications. Thus, unless stated otherwise, the semiconducting material used in all commercial devices reported in this overview is titanium dioxide. Although titanium dioxide exists in three crystalline forms, namely: anatase, rutile, and brookite, invariably the form used in semiconductor photochemistry is anatase as this appears to be the most active and easiest to produce of the three.

Most of the early work into semiconductor photocatalysis, focused mainly on the photomineralisation of organics dissolved in aqueous solution, i.e. reaction (2), and usually employed the semiconductor in the form of a powered dispersion. As a result, a number of commercial devices currently on the market utilise titanium dioxide in the form of a powder dispersion. Usually the powdered titanium dioxide used in such systems is Degussa P25, a finely divided material, $50 \text{ m}^2 \text{ g}^{-1}$, containing a 70:30 ratio of anatase to rutile ([1] and references therein). The latter material is cheap, and extremely photoactive, and as a result has become almost the "gold standard" in semiconductor photochemistry research, particularly with regard to work involving semiconductor powder dispersions. The use of slurries of TiO₂ in a commercial photoreactor is attractive because such dispersions are cheap, very effective and easy to replace. However, in any practical system, they also require a method of filtration to allow the purified product, albeit air or water, to be separated from the photocatalyst and the latter to be returned to the influent. This step is no easy task and has prompted many to try to fix the photocatalyst to an inert substrate, such as glass. However, although P25 titanium dioxide can be deposited onto glass as a film, such films are not mechanically robust and, thus, are easily removed by

rubbing by a cloth or applying the 3 M Scotch TapeTM test [10].

The optical opacity and frailty of semiconductor powder films usually render them unsuitable for many of the current commercial applications of PCO, such as a transparent photoactive coatings on glass or ceramics. As a consequence, a great deal of research has been conducted recently into the production and testing of nanocrystalline semiconductor films [2]. In most academic research such films are produced almost exclusively by the simple, cheap, and easy to effect, sol-gel process, in which a metal complex, such as titanium tetraisopropoxide is reacted in a controlled manner with water. The hydrolysed product is then usually baked, typically at 450 °C for 1 h, to produce a thin, usually 50-500 nm, nanocrystalline film of the semiconductor on the supporting substrate [2,11]. In contrast to academic research however, most PCO commercial devices that employ a semiconductor photocatalysis film, produce them using either the sol-gel process or, more often, using chemical vapour deposition, i.e. CVD, vide infra. In such systems the semiconductor photocatalyst is invariably titanium dioxide.

In the photomineralisation of organic materials sensitised by titanium dioxide, i.e. reaction (2), the photogenerated electrons reduce water to oxygen and the photogenerated holes mineralise the organic. The latter process appears to involve the initial oxidation of surface hydroxyl groups on the TiO₂ to hydroxyl radicals which then oxidise the organic and any subsequent intermediate, or intermediates [1–4]. The reduction of oxygen by the photogenerated electrons generates superoxide, O_2^- as an initial reduction product. The latter species can be further reduced to hydrogen peroxide, as an intermediate in the overall reduction of oxygen to water. Hydrogen peroxide is, of course, also a possible source of hydroxyl radicals and it appears likely that during the course of reaction (2) some of the mineralisation of the organic pollutant is brought about by oxidising species, such as hydroxyl radicals, generated via the reduction of oxygen by the photogenerated electrons [1-4]. The overall processes in the photomineralisation of organic materials by oxygen, sensitised by a semiconducting material such as titanium dioxide, are illustrated in Fig. 2.

Another possible function of a semiconductor photocatalytic material is its ability to mediate the destruction of biological materials, such as bacteria, viruses and moulds ([1] and references therein). The mode of action of the titanium dioxide appears to be very similar to that in reaction (2), i.e. the photogenerated holes generate surface hydroxyl radical species which then are able to damage or destroy the cell walls of biological materials such as bacteria, viruses and moulds. Cells with damaged, or destroyed, cell walls are not viable and quickly die. As in reaction (2), the photogenerated electrons reduce oxygen to superoxide and this can also act as a source of antimicrobial hydroxyl radicals. The photocatalytic destruction of biological material sensitised by semiconductor materials such as titanium dioxide, is generally referred to as photo-sterilisation or photo-disinfection [1,2]. The general features of the antimicrobial action exhibited by a semiconductor photocatalyst, such as TiO₂, upon exposure to ultra-bandgap light are illustrated in Fig. 3.

In terms of commercial success, probably the biggest impact of semiconductor photochemistry is in the relatively new area of semiconductor photoinduced superhydrophilicity, PSH2. In this process ultra-bandgap light generates an electron–hole pair that, once again, can either recombine, or react with surface species. In the case of titanium dioxide, in the absence of any appreciable level of absorbed competing species such as an organic, the surface species available for reaction appear to be Ti(IV) and bridging O^{2-} groups. As a consequence, hydrophilic surface Ti(III) species are generated, via the reduction of the Ti(IV) surface species, by photogenerated electrons, and oxygen vacancies are

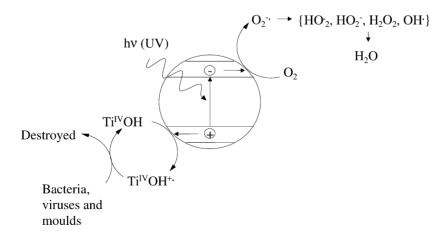


Fig. 3. Schematic illustration of the major processes associated with the photodestruction of bacteria, viruses or moulds, sensitised by a TiO_2 semiconductor particle photocatalyst. Photogenerated holes, generated by ultra-bandgap excitation by UV light, that make it to the surface can react with surface hydroxyl groups to generate adsorbed hydroxyl radicals ($TiOH^{\bullet+}$) which, in turn, can oxidise and destroy the bacteria, virus or mould. The photogenerated electrons that make it to the surface can react with adsorbed oxygen to generate superoxide, which can be subsequently reduced to hydrogen peroxide and then water. The intermediate species produced can act as a further source of hydroxyl radicals, OH^{\bullet} .

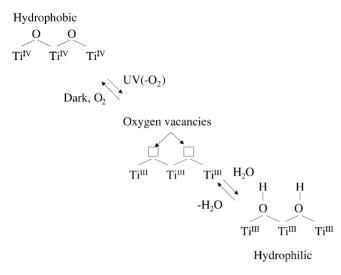


Fig. 4. Schematic illustration of the major processes associated with the photoinduced superhydrophilic property of titania, i.e. PSH. Thus, UV excitation of the semiconductor creates electron–hole pairs. The holes can oxidise bridging O^{2-} species on the surface to oxygen, thereby creating vacancies. The photogenerated electrons can reduce the Ti(IV) atoms to Ti(III). Dissociative adsorption of water onto the irradiated surface hydroxylates it and renders it considerably more hydrophilic. The process is reversed in the dark as the oxygen oxidises the Ti(III) species present and the reduced oxygen fills the bridging oxygen vacancies.

generated, via the oxidation of the bridging O^{2-} species to oxygen, by photogenerated holes. Hydroxyl ions subsequently absorb and fill the oxygen vacancies, with the result that the hydrophilic nature of the surface is increased [2]. The process is reversed, usually slowly in the dark, as the Ti(III) sites are oxidised back to Ti(IV) by ambient oxygen, and the vacancies filled by the O^{2-} ions generated as a consequence of the oxidation reaction Fig. 4 illustrates these major processes behind the phenomenon of PSH, which appears to be almost exclusive to titanium dioxide.

As a consequence of PSH, thin films of titanium dioxide are rendered much more wettable upon exposure to UV light. Interestingly, this process appears to have a high quantum yield at low light levels and thus can be effected by the low UV light levels found indoors (from fluorescent light strips) as well as outside (from the sun). Certainly, the component of UV light in sunlight is sufficient to render titanium dioxide coated glass very wettable, i.e. the water film contact angle for a TiO₂ film falls from about $60-40^{\circ}$ to ca. 0° upon its exposure to ultra-bandgap light. The phenomenon of PSH has led to the rapid commercialisation of light induced, self cleaning, non fogging titanium dioxide coated glass [2,10]. The self cleaning action arises from the fact that any dirt and grime that usually collects on a window are readily washed away on a very hydrophilic surface such as that afforded by UV-activated thin (<30 nm), transparent nanocrystalline film of TiO₂ on the glass. In addition, such thin semiconductor films can also destroy such organic deposits via PCO, which is an additional self-cleaning action since such organic deposits usually act as sites for particles of soot and

grime to collect. Thus, a thin, transparent film of titanium dioxide on glass, upon exposure to sunlight, can stay cleaner, longer than traditional glass. In addition, such a material will no longer appear to fog, since the latter is characteristic of surfaces with high (> 20°) water contact angles [2,10].

3. Commercialisation of semiconductor photocatalysis

Table 1 [12–18] lists most of the major companies that promote semiconductor photocatalysis as a method of water purification. In this table, as in all subsequent tables, the name of the company, its country of origin, associated major patents, some brief comments and its web site address are given. Encouragingly, the companies listed in Table 1 are from a number of different countries implying that the interest in this area is international. A good number of the companies listed in Table 1 appear to have 'products' that are still very much in the development stage. The latter include EcoMetal [12] and ISK [13]. ISK is interesting as it is a major manufacturer of titanium dioxide with a US patent on water purification using porous titanium dioxide containing inorganic particles [13]. However, this company does not appear to have a PCO water purification product as yet, rather, like many others, some initial research has been generated and may be developed further. Similarly, the environmental engineering company Hyosung Ebara [14], based in Korea, has an established track record in the management of waste water and, on its web site, identifies semiconductor photocatalysis as one of the advanced oxidation processes it has available. However, for Hyosung Ebara, the development of such a system appears still to be in its infancy and, as a consequence, it has no major commercial product at the present time.

Not surprising, given the substantial academic interest in the area of semiconductor photocatalysis, two companies, namely, Clearwater Industries [15], and Photox Bradford [16], have university origins, i.e. the University of Florida and University of Bradford, respectively. Clearwater Industries claim to be able to treat over 22501 per minute of contaminated water using their semiconductor photocatalyst water purification system, R2000 [15]. Although there are very few details on the web site concerning the R2000 solar oxidation system, it is clear that it is a fixed photocatalyst bed reactor and, unlike all other commercial PCO water purification systems, utilises the UV component in sunlight to drive the photocatalytic mineralisation process, rather than an artificial UV source [15].

As with Clearwater Industries, Photox Bradford appears to be a small company that is creating custom-built photoreactors for water purification. In contrast to the Clearwater Industries R2000 solar oxidation system, the PhotoxTM system utilises a slurry of titanium dioxide in which the particles are sufficiently large that a standard, off-the-shelf separator can be used to remove and return them to the photoreactor after the water has been purified. The PhotoxTM system

Table 1 Semiconductor photocatalyst systems for the purification of water

| Company | Country Patents Comments | | Comments | Reference | |
|---|--------------------------|------------------------------------|--|-----------|--|
| Eco Metal | Canada | | Small water purification company with no obvious products | [12] | |
| Ishihara Sangyo Kaisha (ISK) | Japan | US5541096 | Large TiO_2 manufacturer, Tipaque [®] , with a patent on water purification using PCO and a novel, porous catalyst | [13] | |
| Hyosung Ebara | Korea | JP2000237759 | Major water purification company with designs for a PCO water purification systems but no obvious products | [14] | |
| Clearwater Industries | USA | | Small company with Florida University origins (see Air and Water Cleaners in Table 2). Flat bed PCO reactor can treat 22501 min ⁻¹ | [15] | |
| Photox Bradford Ltd. | UK | | Small company with Bradford University origins. Its PCO uses the TiO_2 as a slurry and can treat 1681 min^{-1} | [16] | |
| Lynntech Inc. | USA | US5779912 | A small company selling a fixed bed PCO reactor | [17] | |
| Purifics Environmental Technologies Inc. | Canada | US6136203, US5589078, US5462674 | Manufacturers of the Photo-Cat [®] water and air automated treatment system and largest supplier of industrial PCO treatment systems | [18] | |

claims to be able to treat 1681 per minute of contaminated water. In Table 1, Linntech Inc. is yet another small company with a patented small scale, fixed bed, PCO reactor for water purification [16].

All the companies discussed so far are very much overshadowed by Purifics Environmental Technologies Inc., a Canadian-based water purification company dedicated to the application of semiconductor photocatalysis for the purification of water [18]. The Purifics system, called Photo-Cat[®]. utilises the titanium dioxide in the form of a slurry. There are no details concerning the size of the titanium dioxide particles, nor of the method of filtration, although the latter appears to be covered by a variety of US patents. Purifics is the largest supplier of industrial photocatalytic treatment systems and has found markets in the USA, Canada and Korea. Most of these systems have been used to treat contaminated ground water, however, a few have been used to treat industrial wastewater, lagoons and air. Purifics claim that their Photo-Cat[®] system is not affected by iron fouling, since by lowering the solution pH to 3 or less, the Photo-Cat[®] system keeps any iron dissolved in the aqueous phase. It is not clear, however, how practical this major adjustment in pH is in any large scale water treatment process. The Photo-Cat[®] system uses low pressure mercury lamps, i.e. λ_{max} (emission) = 254 nm, which are extremely long lasting, with lifetimes >14,000 h. The latter contrasts markedly with the lifetimes of medium and high pressure Hg lamps used in traditional advanced oxidation process systems, as these usually fall below the recommended performance ratings after only 3000 h. Since the Photo-Cat[®] system utilises a slurry of titanium dioxide it has all the advantages of photocatalyst powder dispersions, namely high surface to volume ratio, cheapness, easy to replace, and little or no mass transfer limiting effects.

Purifics appear to have overcome the problem of filtration via a proprietary filtration system, and as a result have, in the form of the Photo-Cat[®] system, a solid state device that is an efficient water and air purification system based on PCO, which can operate unattended for long periods of time [18].

The biggest commercial application of semiconductor photocatalysis is not the destruction of organics in water but rather the destruction of organics in the gas phase, and Table 2 lists the major companies that sell PCO-based air purification systems [19–29]. The VOC's that can be destroyed by PCO include: aromatics (e.g. benzene and toluene), and halocarbons (e.g. chloroform, cloromethane and carbon tetrachloride). As noted earlier, VOC's also include the organics responsible for unwanted smells, such as those found, for example, in the kitchen, the bathroom and the workplace. Consequently, a number of air conditioning systems have been developed which incorporate a photocatalyst component for purifying air via PCO. The basic principles of operation of semiconductor photocatalysis for the removal of VOC's are largely the same as in reaction (2) and so are well illustrated by the processes in Fig. 2. Much of the academic research that has been carried out in this area has been covered recently by the excellent review of Peral et al. [9].

The use of semiconductor photocatalysis for the removal of VOC's in the household and office has been commercialised by a number of different companies, including Shenzhen Sunzone Electrical Appliances Ltd. [19], Nihon Fujiair (Singapore) PTE Ltd. [21], Toyoda Gosei Corporation Ltd. [22] and Airtech International Group Inc. [20]. As you might expect, all such commercial systems require an internal UV light source to drive the photocatalyst. Usually, in such systems the UV light is provided by either a

Table 2 Semiconductor photocatalyst systems for the purification of air

| Company | Country | Patents | Comments | Reference | |
|--|-----------|------------------------------------|--|-----------|--|
| Shenzhen Sunzone Electrical Appliances Ltd. | China | | Small air cooler from a leading manufacturer of small household appliances that utilises | [19] | |
| Airtech International | USA | | PCO technology to destroy VOC's and germs Manufactures of Airsopure systems, such as model S-30 PCO sterilisation system. Can treat 70.61 min ⁻¹ | [20] | |
| Nihon Fujiair (Singapore) PTE Ltd. | Singapore | | Manufacturer of photocatalytic household air-purifiers and electronic ionisers | [21] | |
| Toyoda Gosei Co. Ltd. | Japan | JP9038190 | Tie up with Toyota to produce air cleaners for cars, using a GaN 380 nm LED as the light source | [22] | |
| Nippon Muki Co. Ltd. | Japan | JP9057112 | Small system, Freshlong [®] , for keeping agricultural produce fresh by removing ethylene (2 ml/h) | [23] | |
| KES Science & Technology Inc. | USA | | Commercialisation of NASA research, the Bio-KES system is an industrial size system designed for the removal of food spoiling ethylene and pathogens from storage environments | [24] | |
| Trojan Technologies Incorporated | Canada | US6179972, US6179971 | Trojan has signed an exclusive world wide license with KSE Inc. Has conducted large scale trials using the Air200 PCO system and can remove 99% of VOC's and operate at $20,000 1 \text{min}^{-1}$ | [25] | |
| Air and Water Cleaners | USA | | The web site for this company is 'under construction' but household PCO-based air-cleaning units from this company can be purchased for US\$ 1450. Company stems from the University of Florida | [26,27] | |
| Purifics Environmental Technologies Inc. | Canada | US6136203, US5589078, US5462674 | Manufacturers of the Photo-Cat [®] water and air automated treatment system and largest supplier of industrial PCO treatment systems | [18] | |
| Kawasaki Heavy Industries Ltd. | Japan | JP2918112, JP3122082, JP3055684 | Major manufacturer of semiconductor photocatalyst material, Folium TM , for purifying air, photo-sterilisation and self-cleaning films | [28] | |
| Mitsubishi Materials Co. | Japan | JP2988376 | Major producer of photocatalytic NO _x removing paving stones. "Noxer" paving stones can remove 0.13 mmol of NO _x m ⁻² h ⁻¹ | [29] | |

germicidal, or blacklight, bulb, since both have long operational lifetimes, typically >10,000 h, and both are excellent, cheap sources of UV light. A germicidal lamp emits almost exclusively 254 nm light and a blacklight bulb emits typically 365 nm light. The one exception to the use of UV fluorescent tubes in semiconductor photocatalyst-based air conditioning units appears to be Toyoda Gosei Corporation Ltd. [22], which has produced a 380 nm gallium nitride-based semiconductor LED to help power their photo-deodorising air conditioning units.

An interesting variation in the use of the semiconductor photocatalysis for the destruction of VOC's is the Freshlong[®] unit produced by the Nipon Muki Corporation Ltd. [23]. This unit has been designed especially for the destruction of ethylene gas in order to keep agricultural produce longer, since ethylene promotes the ripening and decay of many types of fruit and vegetables. The manufacturers of the Freshlong[®] device also note, quite rightly, that the system deodorises, as well as removes ethylene [23]. A much bigger photocatalytic system for the removal of ethylene gas has been developed by NASA and subsequently commercialised by KES Science & Technology Inc. [24]. The Bio-KES 348 system uses $48 \text{ W} \times 8 \text{ W}$ BLB's and $6 \text{ W} \times 8 \text{ W}$ germicidal lamps and a TiO₂ photocatalyst coated onto glass tubes to destroy ethylene and air bourne pathogens found in storage environments.

Much larger air purification systems, based on semiconductor photocatalysis, have also been developed for the treatment of industrial sources of VOC's, including the off-gas emissions from soil vapour extraction, ground water air striping and process air. One of the major companies that have carried out full scale trials in this area is Trojan Technologies Inc. [25], using their Air 2000 system which has a photocatalyst that is claimed to be 5–100 times faster than traditional photocatalysts. The manufacturers of this unit guarantee the photocatalyst for 2 years; the unit is able to achieve 99% removal of VOC's and can be run at an influent feed rate of 20,000 l/min. Not surprisingly Purifics [18] also produce a large scale unit for the treatment of industrial scale VOC's and this can operate at a rate of 5.8 million litres per minute.

Kawasaki Heavy Industries Limited [28] have generated a range of semiconductor photocatalyst coating agents for use in, amongst other things, the purification of air and the removal of oxides of nitrogen such as NO₂, NO, N₂O, i.e. NO_x. The commercial use of semiconductor photocatalysts for removing NO_x usually involves the incorporation of the semiconductor photocatalysts into building materials, such as paving stones, and has been well studied in Japan. Indeed, Mitsubishi Materials [29] now manufacture "Noxer" environmentally friendly concrete paving stones that have been designed to remove NO_x from the air at roadsides, converting it into nitric acid that can then be washed away by rain. It is claimed [29] that "Noxer" paving stones can remove 0.13 mmol of NO_x m⁻² h⁻¹ and that this is 10% greater than roadside Ginko trees, which have the added disadvantage of losing their leaves during the winter. The "Noxer" paving stones for NO_x removal have been recently trialed in London [30].

Bacteria and viruses can be destroyed by a number of different methods including heat, UV light, antibiotics and chemical oxidation. One of the most popular current chemical oxidants for water disinfection is chlorine, which, with its redox potential of 1.36 V, is a substantial oxidising agent. Hydroxyl radicals, with a redox potential of 2.06 V, are even more destructive of biological material than chlorine. Thus, since the mode of action of titanium dioxide as a semiconductor photocatalyst involves the photogeneration of surface absorbed hydroxyl radicals, it follows that biological materials such as viruses and bacteria are likely to be destroyed when on the surface of a thin film of titanium dioxide exposed to ultra-bandgap light. The basic principles behind this process of photo-sterilisation, or photo-disinfection by thin semiconductor photocatalyst films are illustrated in Fig. 3.

It has been shown ([1] and references therein) that biological materials such as allergens (e.g. Der-p II antigen the common dust mite antigen), bacteria (e.g. *Pseudomonas*, *Escherichia coli*, *Streptococcus mutans* and *Mycobacterium smegmatis*), fungi (e.g. *Aspergillus niger*) and viruses (e.g. Polio Virus 1) are all destroyed very effectively by the PCO process illustrated in Fig. 3.

Table 3 [19,20,23,24,31–36] lists the companies that sell photo-disinfection/photosterilisation systems based on semiconductor photocatalysis. Not surprisingly, several of the companies that generate air conditioning units for removal of VOC's also promote their units as a method of destroying unwanted air-borne biological material, such as bacteria, viruses, allergens and fungi. Thus, the AirTech International Group [20], also trading under the name of Airsopure [31], promote a photocatalytic air sterilisation unit for the home. This unit comprises a pre-filter to removal particles of 5 μ m, a larger hospital grade HEPA filter to remove microscopic

pollutants and, finally, the photocatalytic oxidation unit to destroy any viruses and bacteria that are too small to be collected by the filters. The photocatalytic unit utilises UVC light derived from germicidal lamps. KES Science & Technology Inc. [24], a company founded on the commercialisation of NASA-sponsored research, have developed AiroCide $\operatorname{TiO_2}^{\mathbb{R}}$, a semiconductor photocatalyst-based device for the destruction of air-borne pathogens, such as bacteria viruses and fungi. AiroCide $TiO_2^{\mathbb{R}}$ is a subsequent modification of their existing Bio-KES system which was described earlier. The AiroCide[®] unit destroys bacteria, viruses, fungi, moulds and spores and is effective in killing over 93% of air-borne pathogens, including the anthrax bacillus [24]. It is promoted as an air conditioning unit for mail rooms, conference rooms, break rooms, kitchens, offices and common areas.

Several companies, such as Karpery [32] and Biocera [33], have commercialised the concept of a deposited thin film semiconductor photocatalyst on ceramics, especially plates, as an antimicrobial agent. Obviously, such films will be ineffective if the ceramics are stored in the dark. However, Sanyo [34] have produced an interesting variation on the theme of PCO-cleaned plates, namely a covered dish dryer that purifies the air, removing bad smells and microbes, by semiconductor photocatalysis as the plates dry.

The Lion Corporation [35] have a patent on the treatment of textile fabrics with a semiconductor photocatalyst so as to impart them with anti-bacterial and deodorising properties; however, no commercial product appears to have arisen from this work. Finally, the massive ceramics company, TOTO, produces a whole range of titanium dioxide coated materials, including white ceramic tiles for application in the home, work and hospital environment [36]. Their semiconductor photocatalyst thin film ceramic products exhibit both UV light induced antimicrobial agent and deodorising properties.

The basic principles behind semiconductor photoinduced superhydrophilicity, PSH, have been discussed earlier and are well illustrated in Fig. 4. All PSH coatings use semiconductor titanium dioxide, typically in its clear, nanocrystalline form. A PSH coating can function in several different ways [2]. Thus, upon ultra-bandgap irradiation the coating is rendered exceedingly hydrophilic and, as a consequence, water will not bead on its surface, but rather run off. Thus, PSH coatings have a de-fogging or de-misting action. Since water droplets will tend to run off UV-activated PSH coating, it follows that the film will dry more quickly and this is an additional attractive feature. The superhydrophilic nature of an activated TiO₂ film also prevents the formation of large water droplets, as these too will run off. Large water droplets are undesirable on car side mirrors, since they impair the view offered by the mirror, and in greenhouses, since they can spoil any produce that is being grown. Finally, it should not be forgotten that a semiconductor coating can also act as a photocatalytic oxidation catalyst, i.e. PCO, on many organics, i.e. reaction (2). Thus, through PCO, a semiconductor film is able to remove a thin layer of any organic

Table 3 Semiconductor photocatalyst systems for sterilisation/disinfection

| Company | Country Patents Comments | | Comments | Reference |
|-------------------------------|--------------------------|-----------------------|---|-----------|
| Shenzhen Sunzone Electrical | China | | Small air cooler from a leading manufacturer | [19] |
| Appliances Ltd. | | | of small household appliances that utilises | |
| | | | PCO technology to destroy VOC's and germs | |
| Airtech International | USA | | Manufactures of the Airsopure Sterliser and | [20,31] |
| | | | the Airsopure TM model S-30 PCO sterilisation | |
| | | | system which can treat 70.61 min^{-1} | |
| Nippon Muki Co. Ltd. | Japan | | Small system, Freshlong [®] , for keeping | [23] |
| | | | agricultural produce fresh by removing fungi | |
| | 110.4 | | as well as ethylene | 10.41 |
| KES Science & Technology Inc. | USA | | Commercialisation of NASA research, the | [24] |
| | | | Bio-KES system is an industrial size system designed for the removal of food spoiling | |
| | | | ethylene and pathogens from storage | |
| | | | environments. This company also produces the | |
| | | | AiroCide TiO ₂ system that kills over 93% of | |
| | | | airborne pathogens including anthrax | |
| Karpery Industrial Co. Ltd. | China | | Manufacturer of a PCO-based germ killer | [32] |
| Rupping maastrui ee. Da. | China | | household ceramic producer | [52] |
| Biocera Co. Ltd. | Korea | | Manufacturer of an antimicrobial | [33] |
| | | | semiconductor photocatalyst (Bio Cera) for | [] |
| | | | coating chopping boards, tableware and enamel | |
| Sanyo | Japan | | PCO-based covered dish drier | [34] |
| Lion Corporation | Japan | JP9296364 | Patented TiO ₂ antimicrobial coating for fabrics | [35] |
| ТОТО | Japan | JP10071666, US5874701 | A giant in the white ceramics industry. This, | [36] |
| | | | company is a pioneer of PCO-coated materials | |
| | | | and has carried out extensive trails on the use of | |
| | | | TiO ₂ -coated tiles and white ware for the home, | |
| | | | work and hospitals. However, there do not | |
| | | | appear to be any PCO products for sterilisation | |

material that may deposit on it. The above combination of attractive features of semiconductor photocatalyst films has led to a great deal of commercial interest and the rapid development of a number of major commercial products in which the key feature is the PSH action of the semiconductor film; a list of the major companies associated with the latter commercialisation process are contained in Table 4 [36–42].

Top of the list in Table 4 is the major ceramics company, TOTO, which has been one of the pioneers of research into PSH coated materials [36]. On its web pages it claims to have over 350 patents in this area. TOTO appears to be the world's first company to succeed in developing and applying superhydrophilic photocatalyst technology, which they have named 'HydrotechTM'. The latter is the combination of superhydrophilicity and photocatalytic decomposition of organic substances. As yet the only products that appear to have arisen from TOTO's work in this area is the HydrotechTM side mirror film, in which the semiconductor photocatalyst is deposited on a thin plastic film which, in turn, can be applied to car side mirrors [36]. Interestingly, in order to develop such a plastic film, TOTO have had to create an optically clear, nanocrystalline film of titanium dioxide that exhibits PSH, but very little PCO activity, which can then be deposited onto the plastic film substrate. TOTO are not the only manufacturers of PCO films for car side mirrors

[37]. Thus, the Murakami Corporation [37] have one of their products, the Hydrophilic Clear Mirror, HCM, which works via PCO, rather than PSH, technology. Unlike the TOTO system, which utilises a plastic film coated with the photocatalyst, the Murakami HCM system is a permanent, hard overcoating on the glass car mirror. The coating comprises a thick titania film, typically 100-1000 nm, onto which is coated a porous, silica film, 10-50 nm thick. The latter film is highly hydrophilic but has a tendency to lose this property over time as stains are deposited. Thus, the function of the titania underlayer in the HCM is to remove, via PCO, any organic material that may deposit onto the surface of the film and so preserve the overall hydrophilic nature of the coating. Deals struck between Murakami and various car companies means that the latest models of many popular makes of car are typically equipped with HCMs [37]. These car manufacturers include: Toyota, Nissan, Honda, Mitsubishi, Daihatsu and Suzuki,

The commercialisation of PSH recently underwent a quantum leap with the announcement by Pilkington Glass of their product ActivTM, as the world's first self-cleaning glass [38]. This glass is now available in the following countries: United States, Germany, Austria, Switzerland, France, Ireland, and Benelux. From Summer 2002 it will be available in: UK, Denmark, Sweden, Italy, and Poland. Pilkington ActivTM glass is a CVD coated float glass for

| Table 4 | | | | |
|---------------|---------------|---------|-----|---------------------|
| Semiconductor | photocatalyst | systems | for | superhydrophilicity |

| Company | Country | Patents | Comments | Reference |
|-------------------------------------|---------|-------------|--|-----------|
| тото | Japan | US6165256 | A giant in the white ceramics industry. This company is a pioneer of PSH-coated materials and has developed their 'Hydrotech' technology for car side mirrors | [36] |
| Murakami Corporation | Japan | EP0978494 | Another giant in PSH technology, this company has developed the hydrophilic clear mirror, HCM, based on PSH technology | [37] |
| Pilkington Glass plc | UK | WO 00/75087 | First major glass company to launch a self-cleaning glass based on PCO and PSH. After successful trials, Activ TM glass is now on sale in many European countries and is set for the UK in 2002. | [38] |
| Pittsburgh Plate Glass Co. (PPG) | USA | | Following rapidly on the heels of Pilkington Glass, PPG have recently launched SunClean TM , a self-cleaning glass based on PCO and PSH | [39] |
| AFG | USA | | AFG have announced the introduction of Radiance-Ti TM , a self-cleaning glass based on PCO and PSH | [40] |
| Nippon Sheet Glass | Japan | EP1066878 | This major glass manufacturer has a patent on a self-cleaning glass based on PCO and PSH, but no apparent product yet | [41] |
| Taylor Made Systems | USA | | Producer of self cleaning marine glass | [42] |

use in almost all exterior glass applications. It possesses the three main features of semiconductor photocatalyst films, namely, it is able to break down, loosen and destroy dirt and other organic material that may deposit on the surface through PCO, where the source of UV light is provided by the sun. In addition, through the process of PSH, the film is able to prevent large water droplets forming on its surface, and as a consequence, the water sheets off the glass, making it more transparent and much quicker to dry without spots and streaks. Not surprisingly, other major glass manufacturers have quickly followed the example of Pilkington Glass and launched their own versions of self-cleaning glass based on PCO and PSH. Thus, the Pittsburgh Plate Company, PPG, have launched their SuncleanTM self-cleaning glass, which they estimate will cost between 10 and 20% more than windows with ordinary glass [39]. The method of manufacture of the titanium dioxide coating which forms the basis of SuncleanTM glass is also by CVD method. PPG recommend that SuncleanTM glass is not exposed repeatedly to any hard water sources, since the inorganic deposits will not be destroyed by the titanium dioxide photoactive coating. In addition, it would be inappropriate to apply some other common brand of materials used for treating glass, especially those that are used to aid water run-off, such as Clear-ShieldTM or PPG AquapelTM glass treatments. The latter products are hydrophobic and therefore act counter to the action of the titanium dioxide PSH coating. Other chemicals that should not be used include: hydrofluoric acid, silicone sealants, sodium hydroxide, high boiling siloxanes and fluorine-containing chemicals. Obviously, abrasive cleaners should also be avoided as they will damage the photocatalytically active coating. The above concerns raised by PPG are very likely to apply to all PSH and/or PCO titanium dioxide coatings. The major glass manufacturer AFG Industries [40] has also introduced their own version of self-cleaning glass, called Radiance TiTM. The Nippon Sheet Glass Company [41] has a major patent on self-cleaning glass based on photocatalysis and semiconductor photoinduced superhydrophilicity but, as yet, does not appear to have a product, although, given the activity in this area, the generation of one appears inevitable. Finally, the major manufacturer of marine glass, Taylor Made Systems [42], has recently announced a self-cleaning glass for the boat industry based on semiconductor photocatalysis. It appears very likely that over the next few years there will be a proliferation of both small and large companies releasing products based on semiconductor photocatalysis, especially ones based on thin, clear titanium dioxide films on glass, i.e. light induced self-cleaning glass.

Many of the companies discussed so far require supporting materials, such as specialist photocatalytic materials and lamps, for their semiconductor photocatalyst products. Although most of these companies do not identify the suppliers of their source materials, this has not stopped the suppliers themselves from promoting their semiconductor photocatalyst wares on their websites. Thus, Table 5 lists a number of companies turned up by the search engines that appear to provide the supporting products for semiconductor photocatalysis. The list in Table 5 begins with Kawasaki Heavy Industries Ltd. [28], which appears to be one of the major manufacturers of semiconductor photocatalyst material.

 Table 5

 Supporting products for semiconductor photocatalysis

| Company | Country | Patents | Comments | Reference |
|---|-------------|------------------------------------|---|-----------|
| Kawasaki Heavy Industries Ltd. | Japan | JP2918112, JP3122082, JP3055684 | | |
| Applied Inorganic Chemicals | New Zealand | | Company developing new types of photocatalyst—especially low temperature cured films | [43] |
| LG Electronics | Korea | | Has developed a 5 nm TiO ₂ catalyst coating solution and its method of production to be used in home appliances such as air conditioning units | [44] |
| Nippon Soda Corporation | Japan | | Has developed the 'Bistrater' TiO ₂ photocatalyst for a wide range of applications including self-cleaning glass | [45] |
| Tekenaka Corporation | Japan | EP0590477 | A large building materials company with patents on PCO. Has recently launched Sparkt ^(®) , a UV light activated antibacterial form of titanium that can be used also to prevent odours and reduce NO_x | [46] |
| Altair Technologies Inc. | USA | | Producer of TiNano TM an anatase TiO ₂ PCO powder, particle size 30–50 nm, with a high surface area (60 m2 g^{-1}) which exhibits a high UV absorption, high photocatalytic activity and excellent thermal stability. | [47] |
| Shenzhen Chengyin High-tech Co. Ltd. | China | | A high tech product manufacturer with a PCO titania photocatalyst product | [48] |
| Nanopac Co. Ltd. | Korea | KR185287, KR185561 | Manufacturer of titania powders and sols for semiconductor photocatalysis applications | [49] |
| Nihon Parkerizing Co. Ltd. | Japan | | Manufactures PALTITAN TM a neutral, stable aqueous-based titania photocatalyst coating material for antifouling, anti-bacterium, NO _x removal and deodorization | [50] |
| Marusyo Sangyo Co. Ltd. | Japan | | Another titania coating material producer | [51] |
| Sukgyung A T Co. Ltd. | Korea | | Producer of a titania sol for PCO applications | [52] |
| Kemira Pigments | Finland | | A titania producer particularly associated with the cosmetics industry. Products for PCO include RutileX and AnataseX200 which have been recently successfully trailed by customers | [53] |
| Mitsubishi Paper Mills Ltd. | Japan | JP10156141 | Manufactures a light catalyst sheet comprising a semiconductor photocatalyst in a non-woven sheet. This material is used in air-purifiers and deodourisers | [54] |
| Molza | Japan | | Large manufacturer of paper and now a producer of a TiO_2 light catalytic paper for antibacterial and deodourising | [55] |
| NEC | Japan | EP1067166A2 | International manufacturer of light sources has produced a cold cathode fluorescent lamp for PCO work which emits at 368 nm (model: MCPD-2000). The patent describes a TiO ₂ -coated fluorescent lamp for photocatalysis applications | [56] |

Their product, FoliumTM, is promoted as an ideal material for coating building materials, glass and plastics. Kawasaki Heavy Industries Ltd. have conducted extensive trials with their FoliumTM photocatalyst which have confirmed its photocatalyst credentials. The New Zealand-based company, Applied Inorganic Chemicals [43], carry out large research projects within New Zealand and overseas. Their chief area of expertise in semiconductor photocatalysis appears to be within the development of a number of photocatalyst types, including a low temperature cured photocatalytic film for plastics, metals, glass and low temperature building materials. This product appears to be less abrasive-resistant than traditional films of titanium dioxide, which are cured at much higher temperatures, but more photoactive. The electronics giant, LG Electronics, have recently developed a titanium dioxide catalyst coating, which they plan to use in household appliances such as air-conditioning units and deodorisers [44]. LG Electronics have spent over US\$ 2.5 billion researching into this area of nanotechnology, and have 14 patents based on the products of their research in and out of Korea. Their novel coating solution appears to be highly active and contains titanium dioxide particles as small as 5 nm [44]. The Nippon Soda Corporation has developed the BistrataTM titanium dioxide photocatalysts for a wide range of applications, including self-cleaning glass, although it is not clear if this company produces such self-cleaning glass or just the coating for it [45]. The Tekenaka Corporation is one of the largest building materials companies in Japan and has a number of patents on the use of semiconductor photocatalysts in building materials [46]. This company has recently developed Sparkt[®], which is a titanium dioxide coating on titanium metal. Such a coating is found to be photocatalytically active and is able to reduce odours and destroy bacteria upon ultra-bandgap illumination [46]. It is not clear from the company's website how near to commercialisation this and their other products are. Altair Technologies Inc. [47], Shenzhen Chengyin High-tech Co. Ltd. [48] and Nanopac Co. Ltd. [49] are all manufactuers of PCO titania powders, although the latter company also makes titania sols [49]. Titania sols as a PCO coating solution are the main products of Nihon Parkerizing Co. Ltd. [50], Marusyo Sangyo Co. Ltd. [51] and Sukgyung A T Co. Ltd. [52]. Kemira pigments is an intriguing addition to the list of titania PCO manufacturers since it is usually associated with the production of pigments for the cosmetic industry [53]. However, customer trails have been successfully completed in their new range of titania PCO materials, which have the general name 'ANX'.

Mitsubishi Paper Mills Ltd. [54] have incorporated an inorganic absorbant, which allows a titanium dioxide photocatalyst to be fixed into non-woven fabrics. Such materials can be used to create honeycomb and corrugated paper, which can then be used in air purifiers and deodorisers. Mitsubishi Paper have developed a room air purifier that uses this light catalyst sheet and have plans to develop similar products for automobiles, toilets and wall-mounted air purifiers [54]. It may well be that Mitsubishi Paper provide the photocatalyst sheets that are used in many of the semiconductor-based photocatalyst air purifiers currently on sale in Japan. A titanium dioxide light catalyst paper is also produced by the Molza company in Japan [55]. Finally, the Japanese-based, international light manufacturer, NEC [56], has just produced a cold cathode fluorescent lamp specifically for the excitation of semiconductor photocatalysis. The lamp emits light with a main wavelength at 368 nm and, thus, is ideally suited for most semiconductor photocatalyst applications. As noted previously, such lamps usually have extremely long lifetimes and are commonly found in most commercial manifestations of semiconductor photocatalysis. NEC have also taken out a European patent on a UV lamp coated with titanium dioxide, possibly as a simple system for air purification.

4. Distribution of companies and patents in PCO and PSH

The geographical distribution of the companies currently promoting goods based on semiconductor photocatalysis is illustrated in Fig. 5. From Fig. 5 the dominance of Japan in this subject area is apparent, although it is interesting to note that interest in America is also strong. An inspection of the distribution of patents, European, US and Japanese, in this area is very similar to that of patents illustrated in Fig. 5, as might be expected. Two key patent generators are Japan and America. It is possible to examine the numerical distribution of US and Japanese patents in the area of semiconductor photocatalysis over the last 6 years and the results of such an exercise are illustrated in Fig. 6. The results in Fig. 6 show that, as many of those in the area know already, interest in semiconductor photocatalysis has always been strong in Japan and has increased markedly over the last 6 years. Interestingly, however, the number of Japanese patents in 2001 was slightly less than that in 2000, although the number is still many hundreds. It is possible, therefore, that much of the basic research and patenting in this area is nearing completion in Japan. If this is the case, we can expect to see an increasing influx into the European and US markets of photocatalyst products from Japan over the next few years. From the data illustrated in Figs. 5 and 6 it is apparent that industrial interest into semiconductor photocatalysis is increasing. The recent announcement by the major glass manufacturers in the UK, Europe and the US of self-cleaning glass based on semiconductor photocatalysis for the household represents a major leap forward in non-Japanese industrial activity in this area. Given this recent impetus, it is hard to imagine industrial and research activity in this area doing anything but increasing.

For the future, the major objective must be to find an alternative to titanium dioxide. The benefits that a visible light activated semiconductor photocatalyst film would accrue are manifest and obvious. The usual suggested alternative to titanium dioxide is tungsten oxide, which has a bandgap of about 2.6 eV and therefore absorbs in the visible. However, this oxide is generally considered to be mechanically soft and difficult to lay down in the form of nanocrystalline thin, hard, robust films. In addition, tungsten oxide can be dissolved by a strong alkalies. Thus, tungsten oxide does not have the chemically inert credentials of titanium dioxide, and it remains to be seen if it can be generated in a form that is commercially viable for semiconductor photocatalysis.

5. Home of the future?

Fig. 7 illustrates the possible impact of semiconductor photocatalysis on a typical home of the future. Thus, the family car may well be fitted with PSH/PCO defogging side mirrors and a PCO deodouriser. The house and the car may have a PSH/PCO titania coating to maintain its good

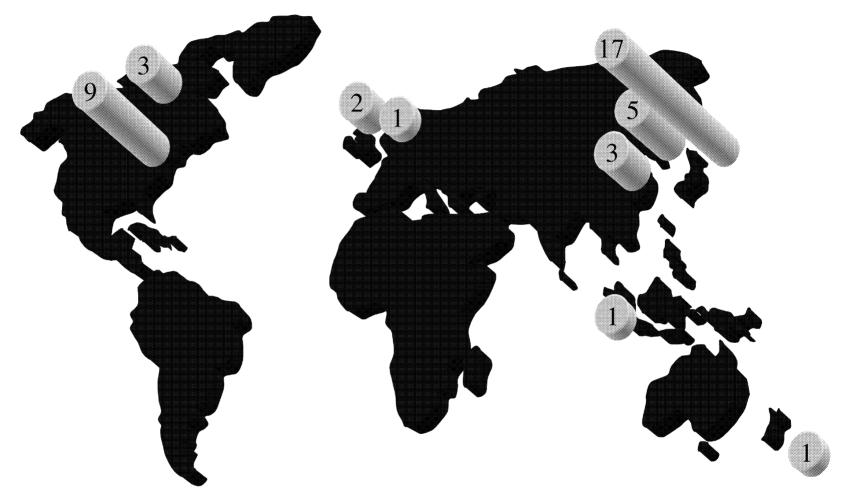


Fig. 5. Geographical distribution of the number of companies that promote PCO and PSH products on the world wide web.

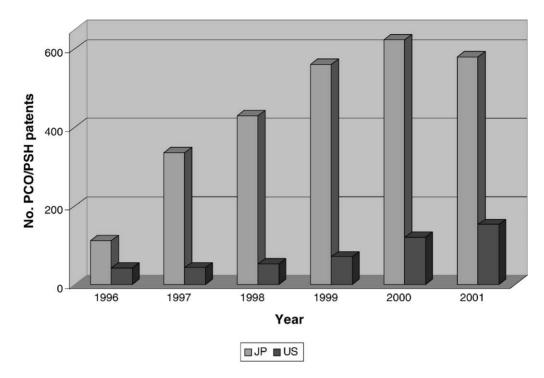


Fig. 6. Histogram of the numbers of Japanese (grey) and US (black) PCO and PSH patents published over the last 6 years.

appearance. The street light may be fitted with titania coated glass to ensure transmission of the light is high for long periods. The paving stones will be light induced, PCO-based self-cleaning with the ability to remove noxious fumes, such as NO_x . The house may be fitted with PCO deodourising tiles and materials, such as curtains. All the windows will be self-cleaning PCO/PSH glass and all the table surfaces will be covered with an antimicrobial light-activated PCO thin film. The house may well also contain one or more

air-conditioning units that have a central PCO unit and be supplied with water that has been purified by PCO. The unwanted fumes from the central heating unit and stench pipe may be treated by PCO before being vented to the environment. Intriguingly, all the semiconductor photochemistry items suggested above for this 'home of the future' are commercially available now. Thus, the realisation of the 'home of the future', illustrated in Fig. 7 may not be so far away!

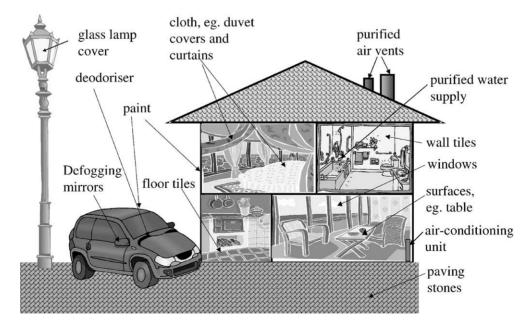


Fig. 7. Illustration of the possible impact of PCO and PSH on the 'home of the future'.

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6. Conclusion

The different commercial applications of semiconductor photochemistry include the photomineralisation of organics, photo-sterilisation and photo-demisting. The major current commercial activities in these different areas are reviewed. Although this commercial activity is global, there is little doubt that it is dominated by Japan. However, this position is likely to change over the next few years with the recent announcement of the major glass manufacturing companies in the US, UK and Europe of a self-cleaning household glass based on semiconductor photocatalysis. Commercial and research activity in semiconductor photocatalysis appears to be strong and increasing. A major objective for future work is the development of a semiconductor photocatalyst film which is able to utilise visible as well as UV light. If this objective is achieved, it would be expected to produce a substantial leap in commercial activity.

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