Enterprise in Nanotechnology

Case Study Green (G)

Self-Sanitising

Surfaces

Contents

1. Introduction - February 2002

1.1 The Players

Dr Dave Lee, a reader in biochemistry at the University of West Yorkshire (UWY), and Dr Steven Brand, a senior lecturer in materials science, have been collaborating over the last 5 years on the use of nanotechnological methods for the purification and sterilization of water. Brand, from Sunderland, and Lee, from Newcastle, agreed to bury their footballing differences for the sake of the harmony of the project. Ironically, the old shipbuilding Sunderland/Newcastle "makem/takem" relationship was preserved at UWY in that Brand makes the TiO_2-coated materials and Lee takes them for testing of their germicidal properties.

The research group has several other doctoral and postdoctoral members.

Jeanette MacDonald, a final year PhD student, essentially carries out most of Dave Lee's biological testing work. Her PhD aims have been to analyse the bactericidal properties of a range of substrate/film combinations. The project has gone well and Jeanette is just about to submit her thesis. She is looking for either a job or a postdoctoral position.

Brand employs Irishman, Pat O'Rooney, as a research fellow. Pat specialises in the fabrication of thin films on surfaces. People have to keep moving in Pat's lab: "If it stands still for a minute, Pat will coat it", the joke goes. His speciality knowledge and skills lie in using sol-gel methods to create nanofilms.

Also working for Brand is PhD student Kenneth Kinnison whose nickname is Mike. Mike has created what is known as the Weathering Lab in which the pride of place is taken by the Carbon Arc Sunshine Weathering Machine which for 500 hr subjects samples to simulated weather cycles of 120 min.

UV durability is tested similarly in a reactor which subjects the sample to 3 mW/cm^2 at 40°C and 90% relative humidity after which adhesion is measured by the Scotch-tape test.

Samples are also boiled in water for 15 minutes, dried thoroughly and then subjected to the adhesion test.

Light transmittance is also tested at 550 nm (good transparency is required on transparent substrates).

After the durability tests, samples are passed on to Dave Lee and Jeanette MacDonald for antimicrobial assessment.

(By the way: Kenneth Kinnison; weathering lab; weather; Michael Fish; Mike. Funny how some nicknames come about.)

Brand also employs a French PhD student, Anatole Deparis, who is using CAD/CAM methods to produce various designs of pump-driven UV reactors which can be used for atmosphere cleansing - a continuously circulating stream of air is brought into contact with a large surface area of self-sanitizing material which is illuminated by a UV source. Anatole, has been working for 2 years now and has produced several promising reactor designs for which the university is considering patent applications. He is currently constructing a prototype.

2. The Technology

2.1 Photocatalytic titanium dioxide

TiO_2 is an n-type semiconductor whose photocatalytic germicidal properties in the nano-particulate form have been known since 1985 following the publication of research by a Japanese group. Since then, the development of this type of technology has tended to remain mainly in the hands of the Japanese including the first examples of commercialisation (see later). There have been numerous studies of the photocatalytic action of titanium dioxide to remove organic and inorganic compounds from contaminated water and air and for the partial oxidation of organic compounds such as toluene.

Titanium dioxide has two active crystalline forms - anatase and rutile - and most research has been done using what is termed P25 titanium dioxide produced by the Degussa Chemical Company in Germany. P25 is a mixture of 75% anatase and 25% rutile with particles of mean diameter 30 nm and a BET surface area of 50 m^2/g.

The irradiation of TiO_2 with UV light produces the hydroxyl radical, hydrogen peroxide and superoxide anions. These reactive oxygen species (ROS) can damage the structure and disrupt the biochemistry of bacteria and virus-infected cells. In the presence of the hydroxyl radical and molecular oxygen, organic compounds are oxidised ultimately to carbon dioxide and water.

The rate of the germicidal action is dependent on the intensity of the UV source, but tests show that the UV light emitted from normal domestic fluorescent lights is sufficient to sanitise a surface up to 10 metres away with an exposure time of 1 hour.

The types of organisms against which TiO_2 has been shown to be active are given below:

Bacteria

Escherichia coli
Pseudomonas stutzeri
Seratia marcescens
Staphylococcus aureus
Clostridium perfringens spores
Salmonella typhimurium
Streptococcus mutans
Lactobacillus acidophilus
Streptococcus cricetus
Streptococcus rattus
Actinomyces viscosus
Bascillas pumilus
Streptococcus sobrinus
Bacillis subtilis

Yeast, Fungi

Saccharomyces cerevisiae
Candida albicans
Hyphomonas polymorpha

Viruses

Phage Q β
Phage MS-2
Poliovirus 1
Lactobacillus phage PL-1

Some studies have shown that TiO_2 is also active against cancerous cells.

2.2 Types of photocatalytic technology

To create disinfection or purification systems based on nanoparticulate TiO_2 one has the possibility of directly attaching nanoparticles to a surface or to use the sol-gel process, for example, to apply a thin layer of particles on a substrate.

Possible substrates are metal, alloys, glass, glass fibre, cellulose, plastics, ceramics and wood.

There are two important systems for photocatalytic reactors: *liquid-solid* for water purification and *gas-solid* for air purification.

3. The Problem

Many of the obvious candidates for use as substrates for carrying photocatalytic layers such as cellulose nitrate, plastics, nylon are organic materials hence will be subject to the same degradative action as the target materials. Also, many adhesives which might be used to fix the photocatalytic layer to the substrate are organic polymer resins which will also be subject to degradation.

As a consequence, there have been major durability problems when attempts have been made to create commercial coated products.

Methods have been developed to overcome this problem. A spattering process; a coat and bake method; a spray and bake process: these have all been used to produce organic-free coatings where the substrate is a heat-resistant inorganic material.

However, the high-temperature baking process makes the cost of these solutions prohibitive.

4. The Innovation

The combined research groups of Brand and Lee devised one solution to the durability problem for which they own intellectual property rights.

The first statement of the patent description reads as follows.

The present invention is related to a structure carrying a photocatalyst which is useful for antifouling, cleaning water, deodorization, pasteurisation, a treatment of waste water, decomposition of water, a control of algae growth, and various chemical reactions.

The solution was to first lay down on a surface an adhesive layer formed from a silica sol which is not affected by the photocatalysis. Then a layer of photocatalytic particles is deposited ~100 nm thick using a sol containing nanoparticulate TiO_2 and a silica additive which increases adhesion.

5. UWY Enterprise Structure

Establishment of an enterprise and spinout culture at the University of West Yorkshire is not well-advanced. UWY does not have a lot of experience in creating spin-outs and was not successful in obtaining any funds from the government's University Challenge scheme for seedcorn purposes. However, there is a newly established not-for-profit company, UWY Innovations Ltd., which is staffed by personnel whose job it is to identify university products and services which are potential candidates for commercialisation and to provide help to the academics involved in the fields of intellectual property rights (IPR), business plans, marketing and finance.

UWY Innovations (UWYI) has a team of advisers assigned to particular subject areas. The UWYI adviser whose remit includes nanotechnology is Vikki Gunton, 42, who has a degree and PhD in pharmaceutical chemistry. After university, Gunton spent 5 years as an R&D scientist with a major pharmaceutical company before joining with four friends from university to start up Paisley Pharmaceuticals Ltd which synthesised speciality chemicals to order. With Gunton as Managing Director, this company traded with reasonable success for 8 years before being bought over yielding modest sums for the four founding members and the other shareholders.

In the past 6 months, Gunton has had several meetings with Dave Lee, Steve Brand and their fellow scientists at which she explained the university's policy on spin-out companies. At the first of these meetings, a spin-out company team was formed which was comprised of the five academics involved. Pat O'Rooney agreed to be team leader.

As stated in the university's policy on intellectual property, all rights to innovations made in the course of research by university employees belong to the university (unless under special circumstances where other agreements have been made).

The UWY will not relinquish the IPR in favour of a spinout company but will expect licensing fees and royalties where applicable. The governing body of the university must give permission for the incorporation of every spinout company and this will only occur if an IPR agreement has been agreed with the prospective management of the new company. The university, of course, has every wish that the company will succeed and, accordingly, the licensing tariffs are normally set at much more favourable levels than would normally be the case with business-to-business licensing agreements.

Finally, it was decided to form a company in order to prepare for business in respect of contacting potential suppliers, creating a web site and preparing for a pilot project (see next section).

Dave Lee, Steve Brand, Jeanette MacDonald, Anatole Deparis, Pat O'Rooney and Victoria Gunton all became directors. According to university regulations, Lee and Brand, as permanent members of academic staff, had to assume non-executive roles. Lee, Brand and Gunton each personally contributed £10K, which was to be convertible to equity (ordinary shares) at a future date.

Providing she is paid at least the **normal stipend for a first postdoc**, Jeanette MacDonald said that she would agree to sign **a one year contract** to administer the Phase 1 pilot project (see below) under the guidance of Brand and Lee and to take charge of the bacterial testing. Also, the appointment of a **laboratory technician** would be sought to assist in the process of taking samples and growing the cultures.

6. Phase 1

6.1 The Deal

After several approaches to the West Yorkshire National Health Trust, meetings were arranged with the general managers and Chief Surgical Registrars in St James Hospital and the General Infirmary in Leeds. Both hospitals agreed to provide one operating theatre which could be set up to test the self-sanitizing tiles. The theatres would be stripped of their old tiles and new tiles with the self-sanitizing layer put in their place. For six months, swabs and air samples would be taken at regular intervals during the day in the converted operating theatres and also from a control theatre in each hospital. Cultures would be grown and bacterial populations estimated.

The Health Authority were willing, as a gesture of goodwill, to contribute £20K to the project with no strings. The hospitals would also make available laboratory space at St. James for the growth and analysis of the cultures. All other costs would be the responsibility of the spin-out company.

Each lab had a total of approximately 200 m^2 of tile space and it was estimated that it would take a three man team about 5 days to strip the theatre and put up the new tiles.

6.2 Raw Materials

Consulting the website of the UK's National Tile Association reveals that there are no major tile manufacturers in the UK. Most of the major ceramic tile suppliers are importers from Spain, Portugal and Italy. If major demand developed for the tiles then it might be advantageous to negotiate directly with the tile manufacturers, but for the pilot project, a Leeds-based supplier was used - Tilly Tyler's Tiles Ltd. White ceramic tiles 25x25 cm were supplied at a cost of £3 each.

The coatings were applied in Brand's lab. One man using a semi-automated dipping process could produce about 100 tiles during an 8-hour day.

(Degussa P25 nano TiO_2 was used at a cost of £210 per kilogram. This would coat around 500 tiles.

The silica and siloxane resin required for the adhesive can be obtained from many suppliers and cost around 10p per tile at bulk prices. The drying process is estimated to add another 20p to the cost of each tile.

For faster production, an industrial dipping machine would cost around £100K and produce up to 900 tiles over a 24 hour period and which would automatically process batches of 100 tiles from its loading palette.

7. Competitors

7.1 UK

There are presently no UK-based companies dealing with self-sanitising materials in the UK.

7.2 Japan

There are currently trials of self-sanitizing TiO_2 layers taking place in **90 hospitals in Japan**.

7.3 Competing Technologies

There are several technologies which might compete with nano TiO_2. The biggest current industry for water purification is based on activated charcoal.

Using high-intensity UV light on its own is another possibility.

Another nanotechnology is whispered to be on the verge of commercialisation: the sol-gel process can be used to produce long nanofibres of alumina. The interstices in the fibres can be made to be of the same order as the dimensions of viruses and bacteria which can then be filtered from air or water. The alumina only traps the germs and opens the possibility that the filter itself becomes a health hazard. This is also a problem with activated charcoal: in many domestic water filters using activated charcoal the filter, if not changed regularly can act as a source of pathogens.

The ultimate technology here might be using the sol-gel process to create nano alumina fibres containing nano-titania particles. This composite material would trap and kill bacteria.

With the publication of this idea, its patentability disappears.

There may be a lucrative joint venture between the owners of the alumina fibre patent and the experts in nano titanium dioxide germicide.

References to original work and reviews in the field of photocatalytic disinfection can be found in the following review.

Blake, D.M. et al, *Application of the Photocatalytic Chemistry of Titanium Dioxide to Disinfection and the Killing of Cancer Cells,* Separation and Purification Methods, **28**, 1 (1999).