ABSTRACT

Bi-phasic photocatalytic particles have been prepared in the form of Janus-like structures (bi-phasic materials with two distinct properties on opposing sides of the particle) using a new synthetic procedure consisting of the sequential layer depositions of semiconductor oxide materials onto soluble substrates. A number of different systems have to date been investigated with an aim of photocatalytic applications. A general synthetic regime consists of utilising simple sol-gel chemistry to deposit sequential layers of photocatalytic material on top of a soluble substrate. The substrate can subsequently be removed yielding extremely fragile disks that fracture into bi-phasic powders of Janus like particles. These particles have two unique sets of properties contained in different faces of the same particle, aimed at the simultaneous reduction and oxidation of toxic species in water. This new synthetic technique is investigated for photocatalytic applications with an eye to efficient water purification, utilising the synergistic effect of the two materials to create highly effective photocatalysts. The photocatalytic activity of anatase/rutile (TiO$_2$) bi-phasic nanoparticle composites enhanced with platinum and deposited on the surface of polycarbonate filters has been successfully demonstrated. Deposition of the photocatalyst on filters overcomes expensive and time consuming recycling processes, adds porosity to the set up and reduces the scattering of nanoparticle dispersions.

I. INTRODUCTION

Photocatalytic process has been in the spotlight for many decades as a viable solution to detoxify drinking water. [1-3] Various toxic organic compounds like organochloride compounds as well as many pesticides, herbicides, surfactants and dyes can be degraded by irradiating semi-conductors and are completely oxidized into non-toxic products in aqueous solutions. However a breakthrough in photocatalyst efficiency is needed for industrial up-scaling. Many versatile approaches have been investigated and have been the subject of recent extensive reviews: [4-13] metallic and non-metallic (co-)doping, [13-20] solid-solutions, [21, 22] and the inclusion of surface plasmon resonance of precious metals, [23-27] dye-sensitizing with organic complexes, [28, 29] Z-schemes, [30-34] metallic/semi-conductors (SC) or SC/SC heterojunctions (with or without an Ohmic layer), [35, 36] UV-blue up-conversion sensitization [37] have all been considered.

All of the efficiency-boosting methods for photocatalytic materials have their own advantages, as well as constraints and many researchers now strive to combine as many of them as possible making composite solid-state hetero-structures particularly interesting. They can potentially share and synergistically benefit from the different otherwise incompatible properties observed separately. Band engineering studies have shown that the band gap and band edges position can be successfully tuned. [29, 30] Reports on new hetero-structures showed that charge carrier recombination can be efficiently prevented [38] while other works on co-catalysts (often inspired by the more mature field of electrocatalysis) demonstrated more than a tenfold increase in activity. [39, 40]

Creating intimate contact between different materials, especially semi-conductors, is however complicated. Interfaces between different crystal structures usually see the formation of defects, which then act as energy-wasteful recombination centres. Conversely, “crystal templating” occurs in some situations where the deposited layer appropriates the morphology of the base crystal. Furthermore, if the synthesis takes place sequentially, each processing conditions could adversely influence the preceding layers.
Photocatalytic materials tend to be targeted for water splitting and water purification as well as antimicrobial surfaces, which are generally tested in the laboratory scale by the degradation of standardised model dye pollutants. One of the most common dyes reported in the literature is the Rhodamine B. This molecule has multiple advantages: firstly, its maximum of absorbance of 550 nm is far away from the absorption of the widely used titanium dioxide-based photocatalysts. Secondly, its degradation mechanism is similar to that of the typical textile industry dye pollutants, and is therefore considered a valid model in water cleaning research. [41]

The method reported herein is a new approach to producing nano-composite powders with Janus-like structures and properties, effectively creating nanoscopic semiconductors heterojunctions with a synthetic method of vast flexibility. Janus was the Roman god of reflection and new opportunities, depicted by a statue of two heads. It is the ideal analogy for a single particle with two regions, faces, of differing properties, yet still able to facilitate communication between the two regions. Briefly, layered structures are prepared through various techniques via sequential layer depositions onto soluble substrates, which are subsequently removed yielding functional particles. As vertical cracking takes place within the multi-layered coating during the process, the final product is a composite nanoscale powder. The synthesis approach is aimed at providing the opportunities to combine several of the benefits previously mentioned, while circumventing the drawbacks. It is noteworthy that all the sequential layers need to show a decreasing stability with respect to the processing conditions as it is necessary to deposit one layer on top of the other without adversely altering the primary layer. Additions to the synthesis can easily be made at each step with the application of co-catalyst nano-islands [20, 42, 43] to the surface of each layer, or indeed the application of a complete layer of electron conducting material to the interlayer region. Another approach is to grow hierarchical nanostructures upon the outer layer for additional functionality. [44, 45]

Most literature reports for the synthesis of heterojunctions describe products in the shape of core-shells, thin films, microscopic beads grafted with nano-particles, or related. [4, 12, 46] Heterojunctions are beneficial for water cleaning as there is a need to maximise charge separation in order to ensure the longest carrier lifetime. This will then favour the delivery of both the electrons and the holes to the catalyst surface where they will perform the target redox degradation reactions.

A synthesis route that enables the production of particles of the structure described above provides a vast array of combinations. Following a rational screening and taking the different synthesis constraints into account, one can imagine assemblies of very high efficiency. In addition, novel designs like the p-n heterojunction Ohmic structures (PNHO) are compatible and broaden the spectrum even further. [8, 12]

Many synthesis pathways are feasible but the sol-gel combined with an annealing step has been utilised initially to show bi-phasic materials of TiO₂. A simple dip-coating procedure has led to controlled thickness layers of different phases of titanium dioxide. It can then be cycled using different sols or processing conditions to induce heterojunctions, as in the case of titanium dioxide where a phase transition occurs at ~600 °C. [13, 47] The substrate and dissolving medium combination is chosen depending on the requirements of the synthesis and allow for sample versatility. The method was successfully validated by our group with the target example product being nanoscopic Janus-like particles of anatase and rutile TiO₂. The effect of nitrogen and neodymium doping of each phase was then studied, as well as the influence of the deposition of platinum nano-islands on the anatase side. [42, 48]

This paper showcases the method and examines the influence of processing parameters on a simplified final product. Anatase and rutile TiO₂ Janus-like nanoparticles with platinum nano-islands on the anatase side have been deposited on membrane filters. Time-consuming and expensive processes are usually used in order to reuse nanomaterials after their use as catalyst. Immobilization of photocatalyst on inactive supports such as glass, polymer, zeolite, silica, and ceramic has attracted wide attention. Using filters for deposition of nanoparticles introduces an advantageous porosity on the system for water cleaning. [49]

Some authors have used micro-porous track etched polycarbonate membranes to deposit nanoparticles on them. [50] Commercial polycarbonate filters have been used in this paper but different membrane filters offer endless possibilities. [51] By covering the surface of the filters with nanoparticles a recovery of the particles after photocatalysis is possible. The photocatalyst properties of the filters have been tested finding that the reduction of the scattering of the incident light during the photocatalysts test of the particles is also an added advantage to the system for water cleaning.

II. EXPERIMENTAL

Materials and methods

In a typical preparation, sequential layers of TiO₂ materials are applied to a soluble substrate consisting of a pellet like disk. Sol-gel chemistry was utilised as a simple method of building up the layers to create the functional particles (Fig. 1).
**Figure 1** Schematic of the synthetic procedure for the preparation of the bi-phasic Janus particles using the sequential layer deposition technique onto soluble substrates and their deposition on PC filters.

All substrate materials were obtained in the form of solid powders (respectively: sodium chloride, ReagentPlus® >=99.5%, purchased from Sigma-Aldrich and magnesium oxide, >=99% trace metals basis, -325 mesh, purchased from Sigma-Aldrich). They were ground and subsequently pelletized using a press (Retch PP 55) with a pressure of ca. 8 tons for ca. 15 minutes. NaCl was pressed in a 32 mm dye.

Different sols can be used to add functionality to the particles within this method. The preparation of the basic sol for titanium dioxide layer coatings is described here as an example. Titanium(IV) butoxide (reagent grade, 97%) was purchased from Sigma-Aldrich. Acetylacetone (AnalaR), acetonitrile (AnalaR), 1-butanol (98.5%), 2-propanol (technical grade) were purchased from VWR. Titanium(IV) butoxide (50 mmol, 17.0 mL) was added to a mixture of acetylacetone (25 mmol, 2.57 mL) and 1-butanol (32 mL) under vigorous stirring, giving a transparent yellow sol. After 1 hour, a mixture of 2-propanol (150 mmol, 11.5 mL) and deionised water (3.64 mL) was added before further stirring for 1 hour. Acetonitrile (40 mmol, 2.09 mL) was then added and the whole system sealed and allowed to age overnight (ca. 10 hours) before dip-coating. Sols were stable up to 6 months if stored in an air-tight container.

Once pressed, the pellets were dipped in the desired sol and withdrawn at a uniform speed. The pellets were dried in an oven for 10 minutes at 80 °C. The process was repeated once to increase the thickness of the coating and dried before the annealing step. To achieve the initial layer of rutile, the pellets were annealed in an oven at 700 °C in a muffle furnace with a ramp rate of 10 °C·min⁻¹ for either 2 or 20 hours and allowed to cool naturally. After cooling the rutile coated pellet was re-dipped in the same sol to apply a new layer of TiO₂. On the second application the pellets were annealed at 500 °C for 2 hours to ensure that the second layer was anatase whilst the first layer remained as rutile.

The coated pellets were broken in pieces and manually shaken to detach the product from the substrate in adequate dissolving medium in 50 mL centrifugation tubes: distilled water for NaCl and NaF and dilute nitric acid for MgO substrates. They were then centrifuged at 4000 RPM for 10 minutes to separate the remaining slurry of non-dissolved substrate mixed with the insoluble product and the supernatant. The process was repeated with 24 hour mild stirring intervals at room temperature to ensure complete removal of the substrate. The samples were ultimately dried at 80 °C overnight.

**Platinum coating.** One of the samples has nanoscale islands of platinum on the anatase layer to act as an electron sink. This was done using a Q150T sputter coater using a platinum target for 5 s generating a layer approximately 3 nm thick prior to dissolution of the substrate. Substrates were platinum coated on both sides. The samples are named as can be seen on Table 1.

**Table 1** Estimated band gap values for the samples.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>R/A</td>
<td>Rutile/Anatase bi-phasic Janus particles</td>
</tr>
<tr>
<td>R/A-Pt</td>
<td>Rutile/Anatase bi-phasic Janus particles with nanoscale islands of platinum on the anatase layer</td>
</tr>
</tbody>
</table>

**Polycarbonate filtration.** 8 mg of R/A, R/A-Pt and TiO₂ nanoparticles were dispersed on water and filtered on polycarbonate (PC) filters (Isopore membrane filters 25 mm, 0.2 microns pore size, Millipore). The filters were dried overnight at 70 °C.

**Characterization**

Samples were characterized by scanning electron microscopy using an Ultra-High Resolution FE-SEM S-4800 coupled with an energy dispersive X-ray analyzer (Inca X-ray analysis system, Oxford Instruments, Abingdon, UK) used for the EDS. X-Ray diffraction (XRD) patterns were recorded on a Brüker d8 DISCOVER diffractometer with a Cu kα X-Ray source (λ = 0.15418 nm and analyzed using Match 2 software. Fourier transform infrared (FTIR) measurements were carried out by a Thermoscientific i510, recording spectra in the 400- 4000 cm⁻¹ region with 32 scans. UV-vis absorption spectra were recorded using a Cary 100 UV-VIS spectrophotometer from Agilent Technologies.

**Photocatalytic dye degradation tests.** Rhodamine B was selected as a model organic pollutant. Photocatalytic measurements were taken at 365 nm (UV). A stock solution of Rhodamine B (0.005 mg/mL) in distilled
water (100 mL total) was prepared and divided into 8 mL portions in petri dishes. Nanoparticle coated PC filters (by weight, 8 mg per filter) were placed in each petri dish before irradiation and kept in darkness for 1 h before commencing. Rhodamine B degradation was measured by UV-VIS spectroscopy against a control solution of Rhodamine B at regular time intervals. Photocatalytic dye degradation studies were done using a PLUVEX 1410 UV exposure unit with a working area of 229 × 159 mm with a UV output of 2 × 8 W (2.5 mW/cm²) at a distance of 10 cm from the surface of the sample solutions.

### III. RESULTS AND DISCUSSION

#### 3.1. Janus-like particles

The versatility of the synthetic method allows for the creation of a myriad of different material combinations, with the added benefit of control over the individual layers of the Janus particles. Initial attempts at generating anatase/rutile composites of differing ratios A:R led to some interesting results regarding the band alignments and the role that each of the sides play in the photocatalytic process, allowing a better understanding of the mechanics of the mixed phase materials. [52] What is clear from the literature is that it is a highly complex assessment and that the different configurations of particles may indeed operate differently. Core shell particles for instance may not have the inner layer “core” being accessible to either sunlight or the water, forcing both oxidation and reduction to occur in the shell surface, stabilised however by the presence of the core. The physical design of the particles is therefore fundamental.

One of the key benefits to this synthetic procedure is the control that can be gained over the individual phases within the system. There is the potential for anatase/rutile junctions with differing thickness, ratios of each phase as well as co-catalysts on each side of the particles or indeed an Ohmic layer which is a definite advantage over other systems (e.g. core-shells). On this diagram, the interface and the surface reaction areas on top and bottom of the powder are indeed of the same order of magnitude (depending on their respective surface roughness and size), conversely to the previous systems where nanoparticles are preferentially deposited onto microscopic ordered substrates. [53]

Fig. 2 shows SEM micrographs of two titanium dioxide layers deposited on a NaCl substrate before dissolution. A uniform coverage by the titanium dioxide layers and large surface fissures, created during the annealing step, are observed. On removal from the substrate, these fissures propagate all the way down revealing the Janus-like particles. EDS analysis show signals related to the presence of titanium and oxygen in the sample as well as sodium and chlorine from the substrate.

Titanium dioxide Janus particles can be used as photocatalysts for dye degradation. However, the ability to selectively dope the anatase or the rutile layer with any combination of anion or cation, leads to a vast number of different materials that can be synthesised using this method. By way of example we have previously prepared anatase and rutile materials co-doped with nitrogen and neodymium selectively into the different layers. [48] Layers deposited on a soluble substrate benefit from further modifications. Rutile-anatase crystalline layers on a sodium chloride substrate were sputtered with platinum to form Pt nanoscale islands. [42] Platinum was found to be beneficial on the surface of the anatase as it acts as an electron sink for the reduction reactions, further preventing recombination and enhancing the lifetimes of the excited state. After dissolution of NaCl substrate, the modified powders showed an expected enhanced performance [54] in the photo-induced degradation (under UV and visible light) of Rhodamine B dye.

XRD diffraction patterns of TiO₂ samples deposited on both substrates are shown in Fig. 3. The obtained powders from NaCl substrates (annealed for 2h at 700 °C) (Figure 3, R/A and R/A-Pt samples) showed diffraction peaks of anatase (COD 9009086) and of rutile (COD 904143) as well as a peak at 24.4°.
26 corresponding to the presence of sodium titanate Na$_2$Ti$_6$O$_{13}$ (COD 4000748) can be observed. [55] The presence of sodium titanate is due to ionic mobility within the “solid” matrix of the sodium chloride with sodium ions infiltrating the rutile/anatase titania crystal lattices at the high temperatures required for rutile and anatase crystallization. To avoid this issue, other soluble substrates can be used as MgO. [40] In addition, Fig. 3 also shows the diffractogram of commercial titanium dioxide with diffraction peaks corresponding to anatase (COD 9009086).

Table 2

<table>
<thead>
<tr>
<th>Sample name</th>
<th>$E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R/A</td>
<td>2.8</td>
</tr>
<tr>
<td>R/A-Pt</td>
<td>2.7</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>3.0</td>
</tr>
</tbody>
</table>

The major advantage of this novel way of producing nano-composite powders with Janus structures is the range of materials available via sol-gel processes and the composite materials that can be produced. Titanium dioxide bi-phasic nanoparticles have been already produced using this methodology [42, 48] but many other oxide semiconductor combinations are possible. It is noteworthy that the substrate and dissolving medium combination needs to be adapted to the annealing temperature and solubility requirements of the desired semiconductors. In addition, the use of sol-gel enable doping with elements of different nature to improve the absorption efficiency of the semiconductors used. Several elements as nitrogen, [20] sulphur [19, 56] or even different lanthanides [41, 49, 57] have been used to improve the properties of titanium dioxide. This methodology has been proved robust enough to support different doping of the layers as our previous work on nitrogen and neodymium doped particles has showed. Extra steps can be also added to the synthesis to create co-catalyst nano-islands that enhance the material performance [20, 42] or even to create a new layer of electron conducting material in the interlayer region.

3.2. Polycarbonate filters coated with nanoparticles

TiO$_2$, R/A and R/A-Pt nanoparticles have been deposited by filtration on the surface of polycarbonate filters. The main advantages of the deposition of nanoparticles on the filters is the improved recovery of the particles after their use as photocatalysts and the reduction of the scattering of the nanoparticles in the dispersion during the photocatalytic measurements. Fig. 7 shows the UV-vis spectra of the different nanoparticles deposited on PC filters. As expected all the samples absorbed on the UV range and a shift to higher wavelength is observed in the R/A-Pt sample. Band gaps estimated from the UV-vis spectra (Fig. 7, inset) of the samples are 2.8, 2.7 and 3.0 eV for TiO$_2$, R/A and R/A-Pt respectively [58].

Figure 7 UV-vis spectra of the nanoparticles deposited on PC filters.

Fig 8 shows the characteristic FTIR spectra of the polycarbonate filters. The carbonyl group presents an infrared absorption band near 1770 cm$^{-1}$. The stretching band of the C–O bond can be observed around 1150 to 1250 cm$^{-1}$. In the 2850 to 3000 cm$^{-1}$ region there are some bands related to the methyl groups and around 1500 cm$^{-1}$ the stretching band of the benzene ring can be found.

Figure 8 FTIR spectra of the nanoparticles deposited on PC filters.
When nanoparticles are deposited on the filters, a reduction in the previous bands can be observed as well as the appearance of a wide band below 500 cm\(^{-1}\) related to the stretching vibration of Ti–O.

The titanium dioxide nanoparticles have been deposited on the PC filters by filtration. The porous surface (dp 200 nm) of a polycarbonate filter can be observed on Fig. 9a. While a homogeneous mass distribution of the particles throughout the filters can be observed on Fig. 9, the particles are forming agglomerates when filtered. This is especially significant in the case of the commercial sample of titanium dioxide (Fig. 9b).

![Figure 9](image)

**Figure 9** SEM micrographs of a PC filter (a), and TiO\(_2\) NP (b), R/A (c), R/A-Pt (d) particles deposited on the PC filters.

To assess the photocatalytic activity of the samples deposited on the polycarbonate filters, a model organic pollutant, Rhodamine B was degraded under UV, results of which are shown in Fig. 10 and Fig. 11. Some differences can be observed when comparing the photocatalysts behaviour of the particles in dispersion [33] and deposited on polycarbonate filters. While TiO\(_2\) commercial nanoparticles used as the titania standard (anatase powder, 99% trace metals basis) performed the best under dispersion conditions. [33] The best results when the particles are deposited on the surface of a PC filter are obtained by the R/A-Pt particles. This different behaviour can be explained by the higher aggregation state of TiO\(_2\) particles on the filter reducing the surface area available for the reaction. As can be observed on Fig. 11 the presence of Pt on the nanoparticles improves the activity of R/A-Pt nanoparticles versus R/A ones due to the reinforcing electron sink effect of the platinum in the first sample.

![Figure 10](image)

**Figure 10** Photocatalytic dye degradation results under UV light irradiation (365 nm) at 25 °C of Rhodamine B in water (a) using titanium dioxide (a) rutile/anatase (c) and rutile/anatase-platinum (d) powders deposited on PC filters as photocatalysts. All samples were stirred in the dark for 30 minutes prior to exposure to light and time T=0.

![Figure 11](image)

**Figure 11** Photocatalytic dye degradation under UV light irradiation (365 nm) at 25 °C of Rhodamine B in water versus time water (a) using titanium dioxide (b) rutile/anatase (c) and rutile/anatase-platinum (d) powders deposited on PC filters as photocatalysts.

**IV. CONCLUSION**

A new way of producing “Janus-like” particles has been described. Two substrates have been envisaged and tested. The advantages and drawbacks of the method were studied and discussed.

It is possible to have several sequential layers, being only limited by processing constraints. These structures are all favourably influenced by the good contact between each layer ensured by the layering method. Also, there is an intrinsic nanoscopic separation of each catalysts for the two half reactions of water splitting which decreases the reverse back-electron transfer reaction of H\(_2\) and O\(_2\) into H\(_2\)O. Finally, many soluble substrates are possible, therefore offering a high versatility in the procedure, and adaptability to the processing constraints. A huge number of potential combinations of materials are
possible given the experimental constraints imposed by the substrates.

The photocatalytic activity of R/A and R/A-Pt bi-phasic nanoparticles deposited on the surface of PC filters has been successfully tested. We note that the rutile and anatase both co-stabilise each other working synergistically to separate the electrons from the holes and then the platinum further enhances the system by acting as an electron sink on the anatase surface. The immobilisation of the photocatalyst in order to reuse them overcomes expensive and time consuming recycling processes. In addition the use of filters brings porosity to the setup and reduces the scattering of the suspension.

We believe that the future of this novel design strategy for functional materials could be a really significant development in the field, yielding unprecedented control over the synthesis of new combinations of materials married together for photocatalytic applications such as solar energy harvesting.

V. ACKNOWLEDGEMENTS

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VI. REFERENCES


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