SOLAR PHOTOCATALYTIC DEGRADATION OF ORGANIC POLLUTANTS USING TiO$_2$ FUNCTIONAL COATINGS ON GLASS AND STEEL

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Abstract
Titanium dioxide (TiO$_2$) is a promising semiconductor photocatalyst which has led to much research into a number of applications in environmental purification, hydrogen production and next generation solar cell technologies. The development of new technologies to provide safe, clean water has become increasingly important. Industrial effluent from the textile, paper and pulp industries contain residual dyes which are introduced into the natural water courses and are a contributing factor to environmental issues. A TiO$_2$ formulation has been developed which can be coated onto glass and steel using a low cost, scalable process. The photocatalytic properties of the coating containing TiO$_2$ nanoparticles enable the degradation of organic dyes and pollutants present in wastewater. This work describes the development and optimisation of photocatalytic properties of nanoparticles present in a paste which can be used as a water treatment functional coating to facilitate removal of organic pollutants. The high photocatalytic properties of the coating are attributed to the unique formulation containing P25 TiO$_2$ along with 5-6 nm anatase particles, leading to a substantial increase in the surface area compared to formulations containing P25 nanoparticles alone.

Keywords
Water Treatment, TiO$_2$, Photocatalysis, Organic dye, Decolorisation, Nanoparticles

Introduction
The textile industry constitutes one of the largest producers of pollutants in wastewater. Highly coloured effluent is released into the ecosystem leading to environmental problems such as aesthetic pollution, an increase in BOD and COD and toxicity to living organisms either directly or through absorption or reflection of sunlight. Water pollution from organic compounds such as synthetic dyes can also be generated from paper printing, colour photography and petroleum industries, with 10-15 % of the dye production being lost during processing and released into water streams\(^1,2\). Due to the inexpensiveness, chemical stability and low toxicity, TiO$_2$ powders are commonly used as white pigments in paints, varnishes and the paper industry. Due to TiO$_2$ being active under exposure to UV light, inducing chemical reactions, the application of photocatalysis for water purification has been studied and reported extensively\(^3,4,5\). The treatment of wastewater containing dyes is a challenge due to the recalcitrant nature of the organic molecules, their resistance to aerobic digestion and their instability\(^6\). Traditional methods such as biological, chemical and physical processes are not effective in treating such waste due to high costs and disposal at such a large scale. Ozonation can be an effective technique for colour removal from wastewater additionally decreasing
Chemical oxygen demand (COD) and toxicity. The production of ozone by cold corona discharge can however be inefficient and the running costs are high. Another effective process used to treat coloured wastewater is the Fenton process, which can easily be integrated into existing treatment works. Compared to other advanced oxidation processes (AOP) this process requires a relatively short reaction time. A disadvantage of this process is flocculation which transfers impurities from the wastewater to sludge.

Photocatalytic treatment is an attractive alternative for the removal of soluble organic compounds as complete mineralisation can be achieved through photogeneration of •OH radicals originating from the water via the OH groups on the TiO₂ surface. The process does not require expensive oxidants and can also be performed at low temperature and pressure. With the immobilisation of the TiO₂ nanoparticles onto a suitable solid inert material, catalyst removal steps are also avoided. Using solar energy makes photocatalysis a clean, energy efficient and cheap alternative to other technologies. In this study a coating has been developed using a combination of commercially available TiO₂ (P25) and synthesised nanocrystalline TiO₂ anatase particles. The coating was immobilised on glass and steel panels for applications in decolourising polluted water. After the coating was annealed onto different supports the photoactivity was evaluated by monitoring the degradation of the textile dye indigo carmine under UV light using UV/Vis spectrometry. The nanoparticles were characterised by scanning electron microscopy (SEM) and BET analysis. A comparison of the photoactivity of different formulations was performed by monitoring CO₂ evolution from the photodegradation of acetone.

Experimental

Chemicals
All chemicals including Indigo carmine were purchased from Sigma-Aldrich and used without further purification.

Instrumentation and techniques
Sintering of the TiO₂ coating onto stainless steel and glass was performed in an oven in air at 450 °C for 30 mins, or the novel process of near infrared (NIR) heating which directly heats the steel or glass substrates, enabling rapid binder and water removal and sintering. The surface of the TiO₂ films were characterised using an S-4800 FEG-SEM from Hitachi (beam parameters, 1.5 KeV, 10 µA. Pore size distribution measurements were carried out by nitrogen adsorption using a Tristar II 3020 from Micrometrics. UV/Vis absorption spectra of the dye solutions were recorded using a UV/Vis spectrometer (Lambda 750S, Perkin Elmer). The photoactivity of the TiO₂ films was studied by monitoring CO₂ evolution from the photodegradation of acetone using a Perkin Elmer Spectrum 100 Fourier Transform Infrared Spectrometer (FTIR) and automation software. To study the rheological behaviour of the TiO₂ paste, a Brookfield DV-II + Pro Extra programmable rheometer was used. The NIR equipment which was used to perform rapid sintering of the TiO₂ paste was from AdPhos NIR/IR Coil lab LV2.
Preparation of TiO₂ paste

To synthesise the anatase nanoparticles titanium tetrachloride (TiCl₄) was dissolved in distilled water. The solution was heated for 30 minutes in a water bath reactor and stirred vigorously. The solution was then cooled to room temperature and ammonium hydroxide (NH₃OH) was added drop wise to the solution. P25 TiO₂ was then added along with a 10 % solution of polyethylene glycol (PEG, average Mₙ 20,000) as binder. The solution was rinsed and centrifuged three times to neutralise the medium and excess water was then removed to produce the desired paste viscosity. The TiO₂ paste was then deposited onto glass or stainless steel substrates using a doctor blade technique. The samples were sintered in an oven for 30 minutes at 450 °C or by using rapid NIR heating.

Photocatalytic experiments

To study the photocatalytic activity of the TiO₂ paste, 8 x 8 cm² glass or stainless steel coated substrates were submerged in 500 mL 10 mg/L, 2 x 10⁻⁵ mol/dm³ indigo carmine solution. UV light from a 6.8 W UV lamp array was placed 18 cm above the surface of the photocatalyst. The agitated reactive solution was illuminated and a UV/Vis spectrum was recorded throughout to monitor the decrease in the absorption maxima of the dye.

Results

Characterisation of TiO₂ paste

The texture and morphology of the TiO₂ layers can be seen in the FEG-SEM images in fig.1. The coating containing P25 nanoparticles only and TiO₂ coatings incorporating 5 or 20 wt. % anatase nanoparticles were compared. In images b and c the anatase nanoparticles are clearly visible, as well as the larger P25 nanoparticles. Image A shows the sample containing P25 TiO₂ only. Clear nanostructures can be seen having a grain size of ~30 nm. The nanoparticles have very fine sizes with large pores also visible. Images B and C show images of the TiO₂ coating containing 5 and 20 wt. % anatase nanoparticles respectively. Optimising the correct weight of anatase nanoparticles added to the paste involved increasing the surface area of the thin films, without filling the micropores and lowering the photoactivity. When observing the characteristics of the films containing varying amounts of anatase nanoparticles, along with BET analysis, it was found that using a 20 wt. % anatase nanoparticles mix; the surface area was increased significantly, without filling the porous structure enough to affect the photoactivity.
Figure 1: FEG-SEM images of TiO$_2$ paste containing P25 only and P25 + 5 and 20 wt. % anatase nanoparticles.
Specific area and porosity of nanoparticles - BET analysis

BET analysis was used to determine the surface area of the TiO$_2$ coating with varying amounts of anatase nanoparticles present. The analysis was performed on colloids of the nanoparticles, following a sintering step of 450 °C for 30 minutes. Table 1 reveals the steady increase in surface area as more anatase nanoparticles are incorporated into the paste, which should lead to a higher photoactivity. As seen in the FEM-SEM images however, it is likely that adding higher amounts of anatase nanoparticles would lead to lower photoactivities due to the decrease in porosity as the smaller nanoparticles, rather than gather around the larger P25 nanoparticles, fill the micro pores. This is confirmed when observing figure 1, which illustrates the change in particles size distribution as the percentage loading of the anatase nanoparticles is increased. When no anatase nanoparticles are incorporated into the P25, a higher a higher distribution of larger porosity is observed. However as more anatase nanoparticles are added, the pore size decreases, due a greater amount of pores being filled with anatase particles. This is again evident when observing the FEG-SEM images taken of the TiO$_2$ colloids containing different amounts of anatase nanoparticles.

Table 1: Surface area of TiO$_2$ colloids following sintering at 450 °C, 30 mins

<table>
<thead>
<tr>
<th>P25 + anatase nanoparticles (%)</th>
<th>Surface area (m$^2$/g)</th>
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<tbody>
<tr>
<td>0</td>
<td>52</td>
</tr>
<tr>
<td>10</td>
<td>67</td>
</tr>
<tr>
<td>25</td>
<td>86</td>
</tr>
<tr>
<td>40</td>
<td>109</td>
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Figure 2: Pore size distribution of TiO$_2$ colloids at different anatase nanoparticle loadings
Figure 3: FEG-SEM of TiO$_2$ nanoparticles following sintering, with varying amounts of anatase nanoparticles present

Photocatalytic experiments
The photocatalytic activity of the TiO$_2$ coating in degrading acetone in the gas phase was investigated using UV light. The photocatalyst was coated onto glass and steel panels using the same thickness and area. Figure 4 shows the photoactivities of different formulations of paste sintered using different heating methods. Monitoring the evolution of CO$_2$ was found to be a successful method to compare the photoactivity. The P25 paste coated on stainless steel substrates using a thicker layer showed the highest photoactivity. In contrast the substrate coated and rapidly sintered using a large scale
NIR oven showed the lowest photoactivity. The low photoactivity of the coating was attributed to the high temperatures achieved during sintering leading to an increase in the particle size and loss of surface area. A comparison of the particle sizes from coatings sintered using different NIR settings are shown in figure 5. The second image shows clearly the larger, fused nanoparticles formed when the coating is over sintered.

![Figure 4: Photocatalytic degradation of acetone as a function of irradiation time using different TiO$_2$ paste formulations and substrates](image)

![Figure 5: FEG-SEM of TiO$_2$ nanoparticles following NIR sintering, with the second image showing the effect of over sintering](image)
A number of experiments were performed using UV/Vis spectroscopy to monitor the degradation of the textile dye indigo carmine. Absorption spectra of indigo carmine are shown in figure 6. Spectra was recorded every 20 minutes and revealed the steady loss of absorption at 610 nm. Using this technique it was possible to study the degradation rates of coatings prepared on varying substrates as well as sintering techniques. The effect of sintering techniques on the photoactivity was studied by using different substrates, and revealed that using a lower power NIR heating setting yielded higher photoactivities compared to conventional oven sintering. The low photoactivity of the high powered NIR treated samples is attributed to the higher temperatures resulting in a transition from the anatase to rutile crystalline structure which has a lower surface area and has a much lower photoactivity. Figure 7 reveals that at high NIR heating temperatures almost no photoactivity is observed, however at lower temperature rapid NIR heating it is possible the substrate is not at a high temperature for long enough to allow for changes in the structure of the TiO$_2$ so no loss of photoactivity occurs.

Figure 6: Absorption spectrum of indigo carmine dye solution during photodegradation process with TiO$_2$ photocatalyst
Figure 7: Effect of sintering method on the degradation of indigo carmine

Conclusions
The results of this study have shown that the degradation of organic dyes is possible using steel and glass coated with a novel TiO\textsubscript{2} photocatalyst. The experimental results show that the addition of anatase nanoparticles to commercially available P25 TiO\textsubscript{2} nanoparticles results in an increase in surface area and higher photoactivity. The use of TiO\textsubscript{2} immobilised on glass and steel substrates is a promising method as it avoids any filtration steps to remove the catalyst from slurry and combined with the use of solar irradiation, can be used as a low energy water treatment of coloured effluent.

References


