Improving carbon coated TiO$_2$ films with a TiCl$_4$ treatment for photocatalytic water purification

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Abstract: Using a simple thermal decomposition route, carbon-TiO$_2$ hybrid films have been synthesized from a catechol-TiO$_2$ surface complex. The coated films display enhanced visible region absorption, owing to the thin (~2 nm) layer of carbon encapsulating the TiO$_2$. While photocatalytically active under visible light alone, it is demonstrated that the activity of the carbon coated films can be improved further by a hydrolytic treatment with TiCl$_4$, leading to the introduction of small TiO$_2$ particles (5-10nm) and doping of chlorine into the structure. The combination of the carbon layer and TiCl$_4$ treatment gives increased photocatalytic performance for the photodegradation of dyes, phenolic pollutants and the reduction of toxic Cr(VI) to relatively benign Cr(III). In addition, the carbon coated films show improved bactericidal activity under UV irradiation, and hence have been successfully tested against the most common types of pollutant present in potential drinking waters.

Introduction

Removal of contamination from drinking water is quickly becoming one of the most pressing issues in the modern world\cite{1,2}. Currently, it is estimated that water scarcity affects 40% of the global population, with this number expected to rise in coming years\cite{3,4}. With a concurrent rise in the global population and increased industrialization of developing countries, contamination is becoming increasingly present in potable water sources\cite{5}. The United Nations Global Goals for Sustainable Development include a division dedicated to clean water and sanitation, with a target to provide access to clean, drinking water to all by 2030\cite{6}. To this end, it is expected that water re-use and therefore purification will become a pressing issue to be solved in coming years\cite{7}. In the removal of contamination from drinking water, there are three main targets that must be dealt with; organic molecules, inorganic metal ions and bacteria\cite{8}. Current strategies to degrade these species typically involve the use of stoichiometric reagents\cite{9,10} and/or the use of ultraviolet (UV) light\cite{11,12}. While effective, these methods are ill-suited to many of the worst affected by water contamination, due to the high cost associated with continually acquiring purification reagents or the need for energy intensive UV lamps. Semiconductor photocatalysis has been shown in recent years to be effective in water purification\cite{13–17}. Photo-oxidation of organic contamination\cite{18–20}, photodegradation of dyes, phenolic pollutants and the reduction of toxic Cr(VI) to relatively benign Cr(III). In addition, the carbon coated films show improved bactericidal activity under UV irradiation, and hence have been successfully tested against the most common types of pollutant present in potential drinking waters.

Film Preparation

It is well known that catechol binds strongly to the surface of TiO$_2$\cite{21,22}, forming a visible absorbing charge transfer complex indicating intimate contact between the resulting carbonaceous material and the TiO$_2$ surface. Subsequent hydrolysis of a solution...
of TiCl₄ in a similar manner to that which is typically used in the field of dye sensitized solar cells to deposit small (~5-10 nm) particles onto the film surface⁵⁶ was found to not significantly affect the films appearance. Upon thermal treatment under N₂ the films were found to turn from the characteristic yellow colour of the surface complex to a light brown, indicating the decomposition of the organic catechol to carbon. The general synthetic procedure is given in Figure 1, where the initial TiO₂ film is formed by a doctor blading method (see experimental) giving a film which has previously been found to be 10-12 microns thick⁵⁷. Hydrolysis of TiCl₄ to give TiO₂ is typically followed up with a thermal treatment step in air to give complete conversion to crystalline TiO₂. Here, by using relatively low temperatures and an inert atmosphere, some Cl remains in the lattice as a dopant. This represents a relatively simple method to introduce Cl as a dopant into TiO₂, which to the best of our knowledge has not been reported to date. Chlorine doped TiO₂ as a photocatalytic material is relatively unexplored, with only a few examples existing in the literature⁵⁸, where the Cl dopant is often paired with a co-dopant⁵⁹,⁶⁰. To explore the various components of the composite films, controls were prepared with only carbon coating (C-TiO₂), only TiCl₄ treatment with subsequent heating under N₂ (TiO₂-TiCl₄), and with both (C-TiCl₄-TiO₂).

**UV-vis absorption spectroscopy**

The as-prepared samples were all found to be semi-transparent, and therefore UV-vis transmission experiments were carried out to ascertain the films’ absorption characteristics (Figure 2).

It was observed that each of the samples displayed superior visible light absorption when compared with pristine TiO₂. Of note is the absorption characteristics of TiO₂-TiCl₄, the visible light absorption of which is in keeping with the presence of Cl-doped TiO₂ being present. As reported by Wang et al.⁵⁸, the extension of the absorption of TiO₂ into the visible by Cl doping typically leads to a broad absorption up to ~ 700 nm, accounting for the shift in absorption into the visible for TiO₂-TiCl₄.

**X-ray diffraction**

X-ray diffraction traces of the prepared materials are given in Figure 3.

Several peaks were found which match well with the reported 2θ values for anatase TiO₂ (JCPDS card #21-1272). The remaining peaks are identified as being due to the FTO glass substrate. Upon modification of the film, no new peaks were found, suggesting either amorphous materials and/or their presence being in too low a concentration to be detectable by XRD analysis. The crystallinity of the underlying TiO₂ film is found to be largely unaffected by the modifications made, keeping high crystallinity after modification. This is advantageous as good crystallinity has been noted to be important in ensuring rapid charge migration through the structure, resulting in improved photocatalytic efficiencies⁶¹.

**Electron microscopy**

Scanning electron microscope (SEM) images of the pristine TiO₂ film surface revealed an interconnected porous network of...
particles of approximately 20 nm in size (Figure S1). However, no discernible differences were noted when the films were subjected to the carbon and/or the TiCl₄ treatments (Figure S2-4). To study the surface at greater magnification transmission electron microscope images were gathered (Figure 4). The unmodified TiO₂ particles were found to be well-defined particles of around 20 nm in size. Clear lattice fringes of 0.35 nm were measured (Figure S5), which can be indexed to the [100] plane of anatase TiO₂. By contrast, images of the carbon coated sample (C-TiO₂) revealed that the lattice fringes were entirely obscured with amorphous material, with a layer of this material observed around the edges of the particles of around ~2 nm. This material we assign as a carbonaceous layer, formed by the pyrolytic decomposition of catechol. Images of C-TiCl₄-TiO₂ revealed smaller particles (5-10 nm) deposited across the surface, which originate from the hydrolysis of TiCl₄. It is noteworthy that, upon treatment with TiCl₄, the lattice fringes that were previously entirely obscured were now found to be at least partially visible (Figure S6), and the carbon layer was in places much thinner than in the C-TiO₂ sample. To prove the presence of Cl dopants in the particles originating from the hydrolysis of TiCl₄, TEM elemental mapping experiments were carried out upon C-TiCl₄-TiO₂ (Figure 5). The presence of Cl was clearly confirmed by the EDS mapping, showing the Cl present across the film. No distinct areas of high Cl concentration were noted, indicating that the doping of chlorine into the structure is applied equally across the entire structure, and is not confined to any particular area. Additional TEM images are given in the supporting information (Figure S7-9).

**X-ray photoelectron spectroscopy**

High resolution X-ray photoelectron spectroscopy (XPS) scans of the carbon and chlorine regions are given in Figure 6. Carbon is often found in XPS studies due to adventitious carbon introduced in the handling of samples. However, it was found that samples containing pyrolysed catechol had significantly higher peak intensities in the carbon region. Typically, carbon XPS peaks are split into the various chemical states of carbon. Fits of these various chemical states are given in Figure 6B. The lowest energy peak (~284 eV) has been previously assigned to sp₂ hybridised carbon in other carbon nanomaterials[43], which sees the greatest increase in intensity over the adventitious carbon in the unmodified sample. This is in keeping with the pyrolytic decomposition of catechol leaving the aromatic features of the catechol intact. The shoulder peak (~285 eV), typically assigned to sp³ hybridised carbon, sees only a very small increase in intensity when compared to the pristine TiO₂ sample, indicating that the majority of the added carbon exists as planar sp₂ type carbon. The small peak at higher binding energy (~288 eV) is typical of carbon attached to oxygen[44], and sees little difference between C-TiO₂ and pristine TiO₂. High resolution XPS of the chlorine region (Figure 6C) revealed the presence of chlorine in the TiO₂-TiCl₄ and C-TiCl₄-TiO₂ samples, but not the pristine or C-TiO₂ samples. This confirms that the TiCl₄ hydrolysis and subsequent heat treatment under N₂ is not converting the deposited material entirely into TiO₂, and that some Cl is retained within the structure as a dopant. The two peaks for chlorine can be assigned to the 2p₁/₂ and 2p₃/₂ states of chlorine, which appear in positions in accordance with previously reported values for...
chlorine doped materials. No evidence for the introduction of nitrogen into the sample by the heating step under N₂ was found in the nitrogen region of the XPS (Figure S10), which discounts the presence of N-doped TiO₂, a common strategy for improving photocatalytic activity of TiO₂, in the samples which could have caused similar changes in the films' properties. Survey scans with peak assignments, as well as high resolution scans of the Ti and O regions are given in the supporting information (Figure S11-12).

### Electrochemical Impedance Measurements

Electrochemical impedance has been proven to be an effective tool in probing the electronic structure of semiconducting films. Impedance data for the prepared films was analysed according to the Mott-Schottky equation:

\[
\frac{1}{C^2} = \frac{2}{\varepsilon \varepsilon_0 N_d} \left( E - E_{fb} - \frac{k_B T}{e} \right)
\]

Where \( \varepsilon \) is the dielectric constant of the material, \( \varepsilon_0 \) is the permittivity of a vacuum, \( N_d \) describes the charge carrier density, \( E \) describes the applied potential, \( E_{fb} \) is the flat band potential and \( k_B / T \) describes thermal energy, which is considered to be small enough to be safely ignored. Plotting the inverse square of the capacitance against the applied potential therefore allows the flat band for the material to be easily read from the x-axis intercept, while the slope gives information about the charge carrier density and p- or n-type character of the material. The Mott-Schottky plots of the prepared films are given in Figure 7. All the films exhibit the positive slope associated with n-type materials, meaning that the dominant charge carriers in the films are electrons. Interestingly there appears to be little difference in the slopes of the plots, indicating that the charge carrier density in each film is approximately constant. Flat bands were determined using the fits shown in Figure 7, and are given in Table 1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Flat Band Potential (V vs Ag/AgCl)</th>
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<tbody>
<tr>
<td>TiO₂</td>
<td>-0.555</td>
</tr>
<tr>
<td>TiO₂-TiCl₄</td>
<td>-0.330</td>
</tr>
<tr>
<td>C-TiO₂</td>
<td>-0.451</td>
</tr>
<tr>
<td>C-TiCl₄-TiO₂</td>
<td>-0.358</td>
</tr>
</tbody>
</table>

A clear shift is observed in the flat band potential upon going from pristine TiO₂ to C-TiO₂. This is to be expected, as carbon is well known to be a good electron accepting material, drawing electrons from electron rich TiO₂ and therefore shifting the flat band to more anodic potentials. The flat band potential of TiO₂-TiCl₄ is also found to have shifted anodically. Doping is often found to have pronounced effects upon the flat band of semiconducting materials, and a large anodic shift of the flat band is in keeping with dopant states being introduced just above the valence band maximum in a similar fashion to what has been observed in N-doped TiO₂ films. This supports the presence of Cl doped TiO₂ being present upon TiCl₄ treatment. It is expected that if some lattice O ions are replaced with less electronegative Cl ions that dopant states would appear above the valence band maximum, and therefore the Fermi level of the semiconductor (and therefore the flat band) would be shifted anodically.

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**Figure 6.** A) XPS scans of the carbon 1s region, B) peak fitting of the carbon peak for C-TiO₂ and C) XPS scans of the chlorine region.

**Figure 7.** Mott-Schottky analysis of the prepared films showing the linear regions used for fitting in green.
Photocatalytic Tests

The set up used for photocatalytic testing against methyl orange (MO), 4-chlorophenol (4-CP) and Cr(VI) is shown in Figure 8.

Prior to photocatalytic tests, each pollutant was stirred in this set up until no change in the absorption was observed (Figure S13-15). It is well known that photocatalytic degradation of pollutants in water follows pseudo 1st order rate kinetics[69], and therefore the rate constant can be obtained according to the following equation:

\[-\ln\left(\frac{C}{C_0}\right) = k_{app}t\]

Where \(C/C_0\) is the fractional remaining concentration at a particular time, \(k_{app}\) is the pseudo 1st order rate constant in min\(^{-1}\) and \(t\) is time in minutes. The pseudo 1st order rate constant can therefore be obtained simply by reading the slope of a plot of \(-\ln(C/C_0)\) against time. The rate plot for the prepared films for degradation of MO is shown in Figure 9.

No degradation was observed for plain TiO\(_2\), while TiO\(_2\)-TiCl\(_4\), C-TiO\(_2\) and C-TiCl\(_4\)-TiO\(_2\) displayed increasingly rapid decolourisation of MO. As such it can be noted that the introduction of Cl doped TiO\(_2\) improved the photocatalytic rate somewhat, as does the introduction of a carbon layer, while together they produce a highly effective photocatalyst. A summary of the photocatalytic activities of the samples is given in Table 2.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pseudo 1st order rate constant (x10(^{-3}) min(^{-1}))</th>
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</thead>
<tbody>
<tr>
<td>TiO(_2)</td>
<td>0.03</td>
</tr>
<tr>
<td>TiO(_2)-TiCl(_4)</td>
<td>3.14</td>
</tr>
<tr>
<td>C-TiO(_2)</td>
<td>4.87</td>
</tr>
<tr>
<td>C-TiCl(_4)-TiO(_2)</td>
<td>10.11</td>
</tr>
</tbody>
</table>

While dye decolourisation is widely applied as a preliminary measure of photocatalytic activity[70,71], we have previously found that it is not always a good metric for determining the effectiveness of a photocatalyst due to photosensitization of the semiconductor by the dye[72]. Excitation of an analyte dye in addition to the photocatalyst can increase rates significantly[73], and can make even plain TiO\(_2\) appear to be active under visible only irradiation[74,75]. While not necessarily a problem if the end goal of a material is to degrade that specific dye, it leads to a photocatalyst which at best has activity which is specific to that particular dye, and could have vastly different activity against a different pollutant. Therefore, while an easy way of screening materials, the rates obtained using visible dyes should not be taken as being final. With this thought, further studies upon 4-CP, a colourless, UV absorbing phenolic pollutant, were carried out (Figure 10).

The 1st order rate constants for 4-CP photodegradation are summarized in Table 3.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pseudo 1st order rate constant (x10(^{-3}) min(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO(_2)</td>
<td>0.27 ± 0.17</td>
</tr>
<tr>
<td>TiO(_2)-TiCl(_4)</td>
<td>0.85 ± 0.13</td>
</tr>
<tr>
<td>C-TiO(_2)</td>
<td>1.00 ± 0.13</td>
</tr>
<tr>
<td>C-TiCl(_4)-TiO(_2)</td>
<td>3.86 ± 0.36</td>
</tr>
</tbody>
</table>

Immediately, a significant loss of activity is noted when comparing the degradation of 4-CP to MO. This can be ascribed to the loss of photosensitization that occurred using the visible dye MO. Otherwise a similar trend was seen in the photocatalytic activities,
although the TiO$_2$-TiCl$_4$ and C-TiO$_2$ films appeared to be within experimental error of one another, both had superior activity to pristine TiO$_2$. The C-TiCl$_4$-TiO$_2$ film produced significantly improved activity over all other samples, confirming that the combination of Cl-doping and a carbon layer is effective as a photocatalytic material. An advantage of the immobilization of the photocatalytic material as a film is the simplification of re-use. With a view to testing this, repeated runs of 3 hours each were carried out upon the photocatalytic degradation of 4-CP (Figure 11). Degradation efficiency is determined as $1-C/C_0$, the fractional quantity of 4-CP destroyed in 3 hours. Initially, no losses of activity were noted, however towards 30 hours of irradiation (10 runs) the activity began to decrease. However, it was found that the photocatalyst could be regenerated by simply heating once again under nitrogen using the same method that was used in the synthesis (dotted lines in Figure 11). Using this method, the photocatalyst could be tested for 90 hours with no losses in activity. After 90 hours of testing, TEM studies revealed that the material in the film appeared to be largely unaffected by the irradiation/regeneration steps that had been applied, with the same ~10 nm particles and carbon layer upon larger ~20 nm particles being observed (Figure 12, SX).

In this study, tert-butyl alcohol (TBA) was used as a scavenger of hydroxyl radicals, disodium EDTA was used to scavenge photogenerated holes and continuous degassing using N$_2$ was used to exclude O$_2$ from the solution, hindering the reduction of O$_2$ to the superoxide ion$^{[78,79]}$. It was found that hydroxyl radicals play a minor role in the degradation of 4-CP, with a small decrease in the degradation caused by addition of TBA. The main oxidizing species however appears to be photogenerated holes, with addition of disodium EDTA causing almost complete loss of activity. The removal of O$_2$ from the 4-CP solution causes a partial drop in activity, indicating that electron transfer to O$_2$ to form superoxide is indeed important, which supports the formation of hydroxyl radicals which may be accessed via the superoxide ion$^{[18]}$. 

Introduction of a variety of different scavengers in high concentration has been used previously to effectively remove certain key species from the test, and the corresponding change in the degradation efficiency can be used to shed light upon the mechanism. Usually, scavenging experiments are carried out upon dye solutions$^{[76,77]}$. However, as discussed previously, we believe this to be unreliable, as photosensitization can lead to the production of reactive species which would not occur in the photocatalytic degradation of different analytes, once again making the test an unreliable method to determine the important reactive species generated. Therefore, scavenging tests upon C-TiCl$_4$-TiO$_2$ were carried out using the photocatalytic degradation of 4-CP (Figure 13).

Figure 11. Recyclability test of C-TiCl$_4$-TiO$_2$ upon 4-chlorophenol. Each run is three hours. Dotted lines denote regeneration of the photocatalyst by heating under N2.

Figure 12. TEM images of C-TiCl$_4$-TiO$_2$ after 90 hours of use, showing the intact carbon layer and mix of large (20nm) and small (5-10nm) particles.

Figure 13. Scavenging tests upon the photocatalytic degradation of 4-chlorophenol.
In addition to organic pollution, heavy metal contamination is becoming increasingly common in urban industrialised water sources. Soluble chromium (VI) is a typical toxic metal contaminant resulting from a variety of industrial processes, which can be remediated by reduction to less toxic Cr(III). The photocatalytic reduction of Cr(VI) using C-TiCl₄-TiO₂ with phenol as a sacrificial electron donor is shown in Figure 15.

Table 4 Cr(VI) photocatalytic reduction

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pseudo 1st order rate constant (min⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No catalyst</td>
<td>0.00(5) ± 0.06</td>
</tr>
<tr>
<td>TiO₂</td>
<td>4.03 ± 0.08</td>
</tr>
<tr>
<td>C-TiCl₄-TiO₂</td>
<td>10.35 ± 1.15</td>
</tr>
</tbody>
</table>

Interestingly, TiO₂ alone gave some activity, most likely owing to photosensitization of the film by the chromium(VI) source, which has a pale yellow colour in aqueous solution. Solutions used in Cr(VI) photoreduction tests are typically acidified, which has been suggest to be due to the consumption of H⁺ during the reduction as follows:

\[
\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}
\]

The low pHs used in this type of test are often too low to be used with many visible light active semiconductors such as sulfides, which are unstable in highly acidic solutions. Here, the highly stable carbonaceous material allows use of low pH and visible light irradiation, proving the applicability of this type of system for Cr(VI) photoreduction.

On this basis of the photocatalytic action for Cr(VI) and the scavenger tests described previously, the mechanism of action can be determined, and is represented in Figure 14.

Bactericidal activity

*Escherichia coli* (E. coli) are commonly used as a marker for bacterial content in contaminated water. Of the UV radiation reaching the earth surface, more than 95% consists of longer wavelength UV-A component. Thus, in the present study the bactericidal activity of the TiO₂ and C-TiCl₄-TiO₂ samples were studied using the standard *E. coli* strain under UV-A exposure. To determine the relationship between UV-A light intensity and efficiency of photocatalytic inactivation, the disinfection kinetic constants were calculated using the classic disinfection model of Chick-Watson equation, shown as follows:

\[
\log \frac{N}{N_0} = -kt
\]

where \( N/N_0 \) is the fraction remaining bacterial concentration at a particular time, \( k \) is the disinfection kinetic constant, and \( t \) is the contact time. Due to the simplicity of this log-linear equation corresponding pseudo-first order kinetics, this model has been widely used to compare the efficiency of photocatalytic inactivation through the values of disinfection rate constant, \( k \), where higher \( k \) means better disinfection effectiveness. Figure 16 shows the linear fitted plots of the photocatalytic disinfection kinetics as per Chick-Watson model. Inset shows the digital photograph of the TiO₂ and C-TiCl₄-TiO₂ samples (3.5 × 3.5 cm²) analysed for this study. The *E. coli* disinfection rate constant for C-TiCl₄-TiO₂ sample \( (k = 4.31 \times 10^2 \pm 0.36 \times 10^2 \text{ min}^{-1}) \) was observed to be nearly twice that of the pristine TiO₂ \( (k = 2.65 \times 10^2 \pm 0.24 \times 10^2 \text{ min}^{-1}) \). Figure 17 shows the digital photographs of the Agar plates cultured with water samples spiked with *E. coli* with the photocatalyst (TiO₂ and C-TiCl₄-TiO₂ samples) after (a) 120 minutes (b) 150 minutes and (c) 180 minutes of UV exposure. Clearly, the C-TiCl₄-TiO₂ samples show an enhanced bactericidal activity with total inactivation of *E. coli* observed after 3 hours of UV-A illumination as compared to the pristine TiO₂ sample. TiO₂ and carbon modified TiO₂ including nanocarbon/TiO₂ composite, multi-walled carbon nanotubes coated by TiO₂, TiO₂/carbon nanotubes composites etc have been widely tested for photocatalytic bactericidal activity. The prevalent mechanism...
for the photocatalytic bactericidal activity of *E. coli* consists of oxidative damage of the cell wall and cell membrane and alterations of the internal DNA molecules.

**Conclusions**

C-TiCl₄-TiO₂ has been demonstrated as a versatile photocatalyst for environmental water remediation. It has been shown that using simple processing techniques both chlorine doping and thin carbonaceous layers may be deposited upon TiO₂ films. Together these two modifications are found to produce a very effective photocatalyst for the degradation of dyes, colourless pollutants, the photoreduction of chromium(VI) and the killing of bacteria. Such a comprehensive study of a single material against all of these pollutant types is rarely found in the literature, but is important if photocatalytic materials are to be applied beyond the laboratory. The films also display good re-useability, being able to be regenerated and continually used for 90 hours without significant losses of activity. We believe that this combination of high activity, good re-useability and versatility of activity towards an example of each type of pollutant present in water sources demonstrates that this material is a prominent candidate for real world water purification.

**Experimental Section**

**Film preparation:**

FTO glass substrates were cut into 2cm x 2cm squares before being ultrasonically cleaned in a solution of detergent (Decon 90, -5% in tap water) for 15 minutes. The substrates were then rinsed with tap water, deionised water and finally ethanol. Titania paste (Dyesol 18-NRT) was then doctor bladed in 1 cm x 2 cm strips onto the surface of the FTO using scotch tape (3M) as a spacer before heating to 510 °C in stages on a controlled hotplate to remove the organic templates, leaving a highly porous TiO₂ film. The temperature profile of the heating regime was as follows: 325 °C for 5 minutes, 375 °C for 5 minutes, 425 °C for 5 minutes, 475 °C for 10 minutes, 510 °C for 10 minutes. The heating ramp rate between each stage was 10 °C min⁻¹ apart from the final stage where it slowed to 5 °C min⁻¹. The sintered TiO₂ films were then allowed to cool gradually on the hotplate to room temperature. Narrower (0.9 cm x 2 cm) and wider films (3.5 cm x 3.5 cm) were also fabricated in the same way for the bactericidal testing studies.

**Sensitisation:**

Films were dipped into catechol (5 mg/ml) for 30 minutes during which time the films became yellow in colour. The films were then rinsed thoroughly with de-ionised water before submerging in a solution of titanium tetrachloride (40 mM) and heating at 65 °C for 30 minutes. Films were washed thoroughly once again with deionised water and allowed to air dry before heating under N₂ (10 minutes at 200 °C, 30 minutes at 300 °C), during which time the films turned from yellow to brown, indicating the thermal decomposition of the catechol-TiO₂ surface complex.

**Characterisation:**

Films were digitally photographed of the Agar plates cultured with water samples spiked with *E. coli* with the photocatalyst (left hand side TiO₂ and right hand side C-TiCl₄-TiO₂ samples) after (a) 120 minutes (b) 150 minutes and (c) 180 minutes of UV-A exposure.
X-ray diffraction data were acquired on a Bruker D2 phaser model diffractometer using monochromated CuKα radiation. UV-visible absorption of the films was measured using a JASCO V-670 spectrophotometer. XPS scans were carried out using a Kratos Analytical AXIS Nova instrument with monochromated 1486.6 eV Al Kα irradiation. Transmission electron microscope (TEM) images were obtained using a Jeol JEM-2011 TEM operated with an accelerating voltage of 200 kV. TEM elemental mapping was acquired on a FEI Titan Themis electron microscope using a Super-X high sensitivity windowless EDX detector. SEM images were collected using a Carl Zeiss SIGMA HD VP Field Emission SEM, operated in InLens mode with a 10 kV accelerating voltage. Mott-Schottky analyses were performed using an Autolab PGST3AT30 with FRA software to control a standard three electrode setup. Ag/AgCl reference electrode and Pt wire counter electrode were used, with the film constituting the working electrode. The electrolyte used was 0.1 M Na2SO4 and the frequency used was 100 Hz. In all cases where a result is accompanied by an error range, the error has been calculated by three measurements on three separately prepared samples.

Photocatalytic testing:

Narrow films (0.9 cm x 2 cm) were submerged into a solution of methyl orange (2 ml, 4.6x10⁻⁶ molar) in a quartz cuvette. The films were stirred in the dark for up to 30 minutes to establish an adsorption equilibrium, determined as the point at which no further change to the absorbance of the solution occurred, and then irradiated with a white LED (30 W applied power) fitted with a UV filter (>400 nm, Thorlabs). The decolourisation of methyl orange was followed by measuring the absorption at 483 nm at regular time intervals using a JASCO V-670 spectrophotometer. The degradation of 4-chlorophenol was measured in the same way, using 4-chlorophenol of 156 μmol concentration followed up with the peak at 280 nm. In the assessment of the recyclability of the films, a single measurement after 3 hours irradiation was taken to calculate the degradation efficiency, between runs the film was washed with deionised water overnight and dried under a stream of N2. Where severe losses in activity were observed, the films were regenerated by heating under N2 (10 minutes at 200 °C, 30 minutes at 300 °C). Scavenging experiments were carried out on the same 4-chlorophenol solution used in the regular studies, but with the addition of the molecular scavengers (50 mM) tert-butyl alcohol, disodium EDTA, or with constant bubbling of N2 gas during irradiation. Note: due to interferences between disodium EDTA and 4-chlorophenol in the UV-vis trace, the 4-chlorophenol peak at 280 nm was used to determine the degradation efficiency. Chromium(VI) reduction was carried out in a similar fashion to the degradation of organic pollutants. 2ml of a solution containing Potassium dichromate (4x10⁻⁴ M) and phenol (6x10⁻⁵ M) adjusted to pH 1 using H2SO4 (4M) was added to a quartz cuvette. A film was then added to the solution and irradiated using the same white LED and filter as was used in the organic photodegradation tests.

Bacterial Strain

The standard E. coli ATCC 23716 (American Type Culture Collection, Rockville, MD, USA) were used in this study. The freeze-dried cultures were rehydrated and reactivated according to the manufacturer’s instructions. The reactivated E. coli were cultured on petri dishes with Brillance E. coli/colliform Agar (Oxoid) selective media using the ‘spread plate’ technique. The E. coli colonies with purple colour appeared on the petri dishes after incubation at 37 °C for 20-24 h. The freshly cultured E. coli colonies were used to spike the deionised water (DI) which was sterilised at 121 °C for 15 mints prior to use.

Bacteriacidal Testing

Substrates coated with TiO2 and C-TiCl6-TiO2 layers (3.5 x 3.5 cm²) were each immersed in 50 ml of sterilised DI water spiked with E.coli (with initial concentration of 1.2 x 10⁶ CFU/ml, where CFU is colonies forming unit) and illuminated with UV-A lamp. The lamp was placed on top of the water sample at about 8 cm from its surface. An 11W low-pressure blacklight fluorescent lamp (PLS G23, Casell Lighting) emitting predominantly at 365 nm provided UV irradiation. The photon flux emission of the lamp was determined by potassium ferrioxalate actinometer, as described by Murov et al.[9], and found to be 4.90 x 10⁶ Einstein/s. At specific time intervals, 2 ml of the water sample were pipetted out and immediately analysed with respect to viable E. Coli cells by the serial dilution culture method. For each dilution, 200 μl of the sample were spread on petri dishes with Brillance E. coli/colliform Agar (Oxoid) selective media. The petri dishes were incubated at 37 °C for 20-24 h before viable counts were determined.

References


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Acknowledgements

The authors would like to thank the CRITICAT Centre for Doctoral Training (Ph.D. studentship to O.G.; grant code: EP/L016419/1) and EPSRC GCRF (grand code: EP/P510944/1) for financial support. X-ray photoelectron spectra were obtained at the National EPSRC XPS Users’ Service (NEXUS) at Newcastle University, an EPSRC Mid-Range Facility. Open data: http://dx.doi.org/10.7488/ds/2070

Keywords: Photocatalysis • Water Purification • Carbon layer • Cl-doping • Bacteria

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