Tungsten Doped TiO₂ with Enhanced Photocatalytic and Optoelectrical Properties via Aerosol Assisted Chemical Vapor Deposition

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Tungsten doped titanium dioxide films with both transparent conducting oxide (TCO) and photocatalytic properties were produced via aerosol-assisted chemical vapor deposition of titanium ethoxide and dopant concentrations of tungsten ethoxide at 500 °C from a toluene solution. The films were anatase TiO₂, with good n-type electrical conductivities as determined via Hall effect measurements. The film doped with 2.25 at.% W showed the lowest resistivity at 0.034 Ω.cm and respectable charge carrier mobility (14.9 cm²/V.s) and concentration (×10¹⁹ cm⁻³). XPS indicated the presence of both W⁶⁺ and W⁴⁺ in the TiO₂ matrix, with the substitutional doping of W⁴⁺ inducing an expansion of the anatase unit cell as determined by XRD. The films also showed good photocatalytic activity under UV-light illumination, with degradation of resazurin redox dye at a higher rate than with undoped TiO₂.

Transparent conducting oxide (TCO) films have important applications in many opto-electronic devices such as solar cells and display technologies¹⁻⁴. They combine electrical conductivity with optical transparency (>80% in the visible region)¹⁻⁵. Traditional TCO materials are based around Sn doped In₂O₃ (ITO), however due to the high costs associated with indium, research has been focused on finding alternative materials with comparable conductivity and transparency to ITO⁴.

Titanium dioxide is a widely used intrinsically n-type semiconductor with primary applications in photocatalysis⁶⁻⁷. Recently, the use of TiO₂ as a TCO material has gained widespread attention due to advantageous electronic properties and conductivity arising from d electrons unlike ITO where conductivity is due to s electrons⁸⁻¹⁰.

Furubayashi et al. has shown the possibility of achieving TiO₂ thin films with respectable conductivities and transparencies using Nb and Ta as dopants using PLD¹¹,¹². Parkin et al. were able to produce Nb and Ta doped TiO₂ films via CVD methods with sheet resistances of 6.5 Ω sq⁻¹ and 14 Ω sq⁻¹ respectively as well as resistivities of 1.1 × 10⁻³ Ω.cm and 2.7 × 10⁻³ Ω.cm⁵⁻¹³.

Using W as a dopant is another possibility as it enables the release of up to two electrons for every one dopant atom¹⁰,¹⁴. This is advantageous as it allows the use of low dopant levels that reduce defect...
concentrations and hence reduce scattering of charge carriers. W is an ideal dopant that is soluble in a TiO$_2$ matrix because it commonly occurs in the 6$^+$ oxidation state and in that state has a smaller ionic radius than Ti$^{4+}$.10,14 Hence, there is potential to obtain better conductivity and transparency compared to Nb and Ta. Xu and Chen et al. were able to obtain resistivities in the order of $10^{-2}$ Ω.cm via magnetron co-sputtering.10.

Furthermore, W doping of TiO$_2$ has multiple advantages, as it is known to enhance the photocatalytic activity by reducing charge carrier recombination and by increasing light absorption by absorbing in the visible portion of the spectrum.15.

In this paper we present the first synthesis of W doped TiO$_2$ films via a specialized solution based chemical vapor technique (CVD) known as aerosol assisted (AA) CVD. It is a simple, versatile and easily scalable technique that involves the transportation of the precursors into the deposition chamber in the form of aerosol droplets.19. The films were deposited using a toluene solution of [Ti(OEt)$_4$] and [W(OEt)$_6$] on glass substrates at 500°C and the films were transparent, photocatalytically active, coloured and conducting - enabling four functional properties in the same film.

Results and Discussion

Thin films of undoped and W doped TiO$_2$ were deposited on glass substrates via AACVD at 500°C using nitrogen as the carrier gas. An undoped TiO$_2$ film was made from a toluene (25 mL) solution of [Ti(OEt)$_4$], while for the W doped TiO$_2$ films dopant concentrations (2–20 mol.% in solution) of [W(OEt)$_6$] were used. This is to our knowledge the first example of W doped TiO$_2$ being formed by AACVD. All films were well adhered to the substrate passing the Scotch$^\text{TM}$ tape test. The undoped films were optically transparent and colourless whereas the doped films were translucent blue, with the colour intensity increasing with increasing dopant concentration. The films were air stable, showing no change in colour or conductivity after 3 months.

The XRD patterns for the undoped and W doped films show reflections matching the anatase phase of TiO$_2$ (Fig. 1). The undoped film showed peaks corresponding to (101), (004), (200), (211) and (204) planes at 25.3°, 38.7°, 42.0°, 55.1° and 62.4° respectively. The doped samples showed a degree of preferred orientation in the (211) and (204) directions. This has been previously observed for metal (Nb and Ta) doped TiO$_2$ films deposited using both AACVD and PVD.13.

Due to the similarities in the ionic radii of W$^{6+}$ (0.60 Å) and Ti$^{4+}$ (0.605 Å), the substitutional doping of W$^{6+}$ with Ti$^{4+}$ should impart almost no change in the TiO$_2$ unit cell. However, XPS results (see below)
show that doped films contain W in both the 4+ and 6+ oxidation state. Therefore the observed linear shift of the XRD peaks to lower 2θ values, thus indicating an expansion in the TiO₂ unit cell, was due to the partial replacement of Ti with W⁴⁺ that has an ionic radius of 0.66 Å. This follows closely with observations made by Kafizas and Parkin for W doped TiO₂ system studied via combinatorial atmospheric pressure CVD where the majority of the W was in the 5+ oxidation state (0.62 Å)¹⁵. The lattice parameters for the undoped and doped films were calculated by fitting a La Bail model to the XRD data using GSAS and EXPGUI programs (Table 1).

Wavelength dispersive X-ray spectroscopy was used to determine the amount of W present in the films. The results show a linear increase in W content before possible saturation is reached at 15 mol.% of W in the AACVD precursor solution and 4.5 at.% in the films (Table 1).

| W content in soln/ mol.% | WTi ratio in film / at.% | a / Å  | c / Å  | Unit cell Vol. / Å³ | Vol. Expansion / % |
|--------------------------|--------------------------|-------|-------|---------------------|-------------------|
| 0                        | —                        | 3.7762(1) | 9.431(1) | 134.50(1)          | 0                 |
| 2                        | 0.63 : 29.59             | 3.785985(5) | 9.464915(5) | 135.67(2)          | 0.87              |
| 5                        | 1.65 : 28.99             | 3.78213(9)  | 9.500(2)  | 135.89(3)          | 1.04              |
| 10                       | 2.25 : 28.71             | 3.78287(6)  | 9.499(3)  | 135.93(4)          | 1.07              |
| 15                       | 4.47 : 26.52             | 3.7811(8)   | 9.51(2)   | 136.03(2)          | 1.14              |
| 20                       | 4.65 : 26.70             | 3.80095(5)  | 9.458(2)  | 136.64(3)          | 1.59              |

Table 1. The table shows the W concentration in the films as determined by WDX as well as the lattice parameter calculations for the undoped and W doped TiO₂ films grown via AACVD at 500°C.

Figure 2. The Raman spectra for the undoped TiO₂ and W doped TiO₂ films grown via AACVD. A linear blue shift in the E_g peak (from 143–158 cm⁻¹) that was observed is indicative of an expansion in the anatase unit cell.

Figure 2. The Raman spectra for the undoped TiO₂ and W doped TiO₂ films grown via AACVD.
Analysis of the film morphology using scanning electron microscopy (SEM) reveal that the surface of the AACVD grown films become more structured upon doping with W (Fig. 3). The morphology of the undoped TiO₂ film consists of compact domes roughly 100 nm in width that transform to pyramidal features perpendicular to the substrate upon W incorporation. With increasing dopant concentration the features coalesce to form larger pyramids that are roughly 500 nm in width. Furthermore, the 4.47 W at.% and 4.65 W at.% films seem to show the features coalescing even further. This has been observed previously when other transition metals such as Nb and Ta have been substituted into a TiO₂ matrix. Film thickness, obtained via side-on SEM, show that in general there is an increase in the thickness with increasing amount of dopant. This coupled with the increase in film roughness contributes to a decrease in film transparency.

X-ray photoelectron spectroscopy (XPS) was performed on the films to determine the oxidation state of the Ti and W species (Fig. 4 and Fig. 5). For the undoped film a 2p₃/₂ peak corresponding to Ti in the 4⁺ oxidation state was observed at 458.3 eV that matches to literature values. The W doped TiO₂ samples also showed this peak at 458.2 eV for Ti⁴⁺, but an additional 2p₃/₂ peak at 457.0 eV corresponding to Ti³⁺ was also observed. The intensity of the Ti³⁺ peak increased with increasing W concentration. Thus indicating that the charge compensation by electrons for the substitutional doping of W⁴⁺ and/or 6⁺ species for Ti⁴⁺ results in the reduction of the titanium to the 3⁺ oxidation state.

Peaks corresponding to W 4f overlap with Ti 3s peaks in XPS, therefore W was only detectable for the 2.25 at.% and above doped films (Fig. 5). In these films, 4f₇/₂ peaks corresponding to W⁶⁺ was seen at 35.2 eV as well as 4f₅/₂ peaks for W⁴⁺ at 33.8 eV. There was consistently six times greater W⁶⁺ compared to W⁴⁺ in all the films. In a previous study where Kafizas and Parkin studied W doping of TiO₂ via a combinatorial APCVD method, XPS studies showed the presence of mainly W⁵⁺ and some W⁴⁺, lacking the desired 6⁺ oxidation that enables enhanced electrical properties.

The electrical properties of the doped films were determined though Hall effect measurements with all films displaying n-type conductivity (Table 2). The undoped sample was too resistive to measure on the Hall effect instrument but two-point probe measurements showed conductivity in the MΩ range. With a dopant concentration of 0.63 at.% and 1.65 at.% sheet resistance drops to 4.9 kΩ sq⁻¹ and 3.4 kΩ respectively. For the 0.63 at.% doped sample the resistivity was 0.63 Ω cm and the charge carrier concentration was to the order of 10¹⁷ cm⁻³ enabling a carrier mobility of 13 cm²/V s. The resistivity (0.29 Ω cm), charge carrier concentration (10¹⁸ cm⁻³) and mobility (13 cm²/V s) were also similar for the 1.65 at.% W doped film. A further increase in dopant concentration to 2.25 at.% resulted in the film with the best electrical properties for this study. There was a decrease in sheet resistance and resistivity to 212 Ω sq⁻¹ and 0.034 Ω cm respectively. This is comparable to the results obtained by Xu and Jin et al. for W doped TiO₂ films grown by rf sputtering. The carrier mobility, at 14.9 cm²/V s, was slightly better than the 0.63 at.% and 1.65 at.% films while the carrier concentration was an order of magnitude higher. At
4.47 at.% doping of W in TiO₂, the sheet resistance was reduced to 78 Ω·sq⁻¹ with a resistivity of 0.042 Ω·cm and an increased carrier concentration in the order of 10²⁰ cm⁻³. However, the carrier mobility was diminished to 0.32 cm²/V·s (Fig. 3), this is likely to be due to the increased dopant amounts, specifically W in the 4⁺ oxidation, that behave as scattering sites for the charge carriers. In general, the lower than expected electrical performance of the W doped films synthesized via AACVD is primarily due to the W⁴⁺ center reducing carrier mobility.

UV-Vis spectroscopy was used to show the optical transmission of the undoped and doped TiO₂ films (Fig. 6). The undoped film was transparent in the visible region with 55% transmission, this was similar to the 0.63 at.% doped film that also showed transmission close to 55%. With increasing dopant concentration, the films become less transparent - transmission at a wavelength of 500 nm was roughly 50%, 30%, 7% and 3% for the 1.65 at.%, 2.25 at.%, 4.47 at.% and 4.67 at.%. The decrease in transmission has been observed previously for other transition metal doped TiO₂ films and is attributed to the increase in absorption in the infrared region (see supporting information for reflectance and absorption curves).
Furthermore, the transmission of the films decreases from 600 nm most likely due to Ti$^{3+}$ states induced by the W doping that give rise to absorption from d-d transitions.

The UV light induced photocatalytic properties of the undoped and W doped TiO$_2$ films were determined using resazurin dye based 'intelligent ink'. The ink contained resazurin dye, hydroxyl-ethyl cellulose, glycerol and distilled water. The degradation of the dye on the surface of the films was induced by a UVA (365 nm) light source with a photon flux of $1.09 \times 10^{15}$ photons/cm$^2$/s. The reduction in the concentration of the dye with time was monitored using UV-Vis spectroscopy. The formal quantum efficiency (FQE) and formal quantum yield (FQY) were calculated to enable easy comparison with literature.

The undoped TiO$_2$ film was able to degrade resazurin at a rate of $1.4 \times 10^{11}$ dye molecules/s/cm$^2$, this was inferior to the 0.63 at.%, 1.65 at.% and 2.25 at.% W doped TiO$_2$ films that had a degradation rate of $3.2 \times 10^{11}$, $3.5 \times 10^{11}$ and $2.4 \times 10^{11}$ dye molecules/s/cm$^2$ respectively. However at 4.47 at.% and

![Figure 5. The Ti 2p and W 4f XPS peaks for the W doped TiO$_2$ grown via AACVD. The intensity of the W 4f peak that coincides at the same region as Ti 2p increases with increasing dopant concentration. Both W 6+ and 4+ is observed.](image-url)
4.65 at.% doping levels the rates of degradation ($7.9 \times 10^{10}$ dye molecules/s/cm² for both) was inferior to the undoped TiO₂ film. Furthermore, compared to SGG Bioclean™ self-cleaning glass, that was able to degrade resazurin dye at $1.2 \times 10^{11}$ dye molecules/s/cm² all the films excluding the 4.47 at.% and 4.65 at.% doped films were superior. This shows that the presence of W in the TiO₂ films does indeed enhance the photocatalytic properties but excess dopants can also be detrimental. The initial increase in the photocatalytic properties of the films with doping was most likely due to the increase in surface microstructure (and also due to the decrease in grain boundaries that are charge carrier recombination sites) due to larger, better shaped particles as observed from the SEM images. This facilitates a high surface area and more photoactive sites for the dye to be degraded during UV A illumination. With excess dopant concentrations (4.47 at% and 4.65 at.%), an increase in the surface area is offset by the presence of more photoinduced charge carrier recombination sites that in total reduce the photoactivity.

The formal quantum efficiency (FQE) and yield (FQY) for the films were calculated using the dye degradation rates, the UV A photon flux and UV A photon absorption for each of the films (Fig. 7). The 0.63 at.% and 1.65 at.% doped films showed the best results, with a FQE of $2.98 \times 10^{-4}$ dye molecules per incident photon and FQY of $3.26 \times 10^{-4}$ dye molecules per absorbed photon for the 0.63 at.% doped film and

| W content in mol/mol% | W/Ti ratio in film/at.% | Film thickness/μm | Sheet resistance/Ω sq⁻¹ | ρ/Ω.cm | μ/μm²/Vs | N/cm⁻³ |
|-----------------------|-------------------------|-------------------|--------------------------|---------|----------|--------|
| 0                     | —                       | —                 | —                        | —       | —        | —      |
| 2                     | 0.63 : 29.59            | 1.3               | 4861                     | 0.63    | 13.0     | $7.63 \times 10^{17}$ |
| 5                     | 1.65 : 28.99            | 0.8               | 3433                     | 0.29    | 13.4     | $1.64 \times 10^{18}$ |
| 10                    | 2.25 : 28.71            | 2.8               | 212                      | 0.034   | 14.9     | $1.23 \times 10^{19}$ |
| 15                    | 4.47 : 26.52            | 5.4               | 78                       | 0.042   | 0.32     | $4.70 \times 10^{20}$ |
| 20                    | 4.65 : 26.70            | 4.1               | 154                      | 0.063   | 0.049    | $2.02 \times 10^{21}$ |

Table 2. The electrical properties of the undoped and doped TiO₂ films grown via the AACVD reaction of Ti(OEt)₄ and W(OEt)₆ in toluene at 500°C as determined by Hall effect measurements.
2.99 \times 10^{-4} \text{ dye molecules per incident photon (FQE)} \text{ and } 3.14 \times 10^{-4} \text{ dye molecules per absorbed photon (FQY) for the 1.65 at.\% doped film. This was more than double what was observed for the undoped TiO}_2 \text{ film grown under the same conditions. The principle reason for this was the more structured surface morphology observed for the doped films compared to the undoped. Furthermore, the FQEs of the 0.63 at.\% and 1.65 at.\% W doped films were also both more than double what was observed (1.2 \times 10^{-4} \text{ dye molecules per incident photon) for SGG Bioclean}^{13}. \text{ The FQY of SGG Bioclean}^{13} \text{ was however far superior with results an order of magnitude higher than the best preforming W doped TiO}_2 \text{ film.}

Compared to literature, the W doped films display the same order of photocatalytic activity (FQE and FQY) relative to W doped TiO}_2 \text{ films studied by combinatorial APCVD}^{15}. Resazurin based redox dye test preformed on Pilkington Activ}^{17} \text{ self-cleaning glass by Mills et al. shows a FQE of } 2.5 \times 10^{-4} \text{ dye molecules/incident photon}^{26}. \text{ This is in the same order of magnitude as what was observed for the W doped TiO}_2 \text{ samples in this study, indicating the films are on par with industry standards.}

**Conclusion**

Transparent, electrically conductive and photocatalytically active thin films of W doped TiO}_2 \text{ films were synthesised via a solution based CVD technique (AACVD). The structured morphology of the doped films combined with the good conductivities (optimum of 0.034Ω. cm) and optical transparency in the visible region make them suitable candidates for electrodes in photovoltaic devices. Furthermore, the doped films displayed enhanced photocatalytic activity compared to the undoped TiO}_2 \text{ sample in the destruction of resazurin redox dye when illuminated by UVA radiation. In conclusion, this paper presents the single step formation of W doped TiO}_2 \text{ films with four desirable functional properties:}

1. Transparent in the visible region
2. Photocatalytically active
3. Coloured
4. Electrically conducting

**Methods**

**General Procedure.** Depositions were carried out under nitrogen (99.99\% from BOC). Precursors were placed in a glass bubbler and an aerosol mist was created using a piezoelectric device. All chemicals were procured from Aldrich and were utilised as received.
[Ti(OEt)₄] (2 g, 8.8 mmol) was dissolved in toluene (25 ml) and [W(OEt)₅] was added in dopant amounts (0 mol.% – 20 mol.%). The resulting solution was stirred for 30 minutes and then atomised. The precursor flow was kept at 1 L.min⁻¹. The substrate temperature was kept at 500 °C. Deposition time was 45 minutes. After the deposition the bubblers were closed and the substrates were cooled under a flow of nitrogen.

At the end of the deposition the nitrogen flow through the aerosol was diverted and only nitrogen passed over the substrate. The glass substrate was allowed to cool with the graphite block to less than 100 °C before it was removed. Coated substrates were handled and stored in air. The coated glass substrate was cut into 1 cm × 1 cm squares for subsequent analysis.

**Film Analysis.** Powder X-ray diffraction (PXRD) was used to analyse the samples in a modified Bruker-Axs D8 diffractometer with parallel beam optics equipped with a PSD LynxEye silicon strip detector to collect diffracted X-ray photons. This instrument uses a Cu source for X-ray generation with CuKα₁ and CuKα₂ radiation of wavelengths 1.54056 Å and 1.54439 Å respectively, emitted with an intensity ratio of 2:1, a voltage of 40 kV and current of 30 mA. The incident beam angle was kept at 1° and the angular range of the patterns collected was 20° < 2θ < 66° with a step size of 0.05° counted at 0.5 s/sep.

Scanning Electron Microscopy (SEM) was performed to determine surface morphology and film thickness using a JEOL JSM-6301F Field Emission SEM at an accelerating voltage of 5 kV.

The W:Ti at.% composition was investigated via wavelength dispersive X-ray (WDX) analysis on a Philips instrument. The average W:Ti % over four area scans (200 mm²) of each position analysed was taken.

X-ray photoelectron spectroscopy (XPS) was performed using a Thermo Scientific K-alpha photoelectron spectrometer using monochromatic Al-Kα₁ radiation. Survey scans were collected in the range 0–1100 eV (binding energy) at a pass energy of 160 eV. Higher resolution scans were recorded for the principal peaks of Ti (2p), W (4f), O (1s), C (1s) and Si (2p) at a pass energy of 50 eV. Peak positions were calibrated to carbon (284.5 eV) and plotted using the CasaXPS software.

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Author Contributions
S.S. and D.S.B. designed/carried out the experiments, preformed the sample characterization measurements and analyzed all the results. S.S. wrote the manuscript. S.S. and Y.L. made the figures for the manuscript. N.C. preformed some of the XPS measurements. C.J.C. and I.P. supervised S.S, D.S.B, Y.L. and N.C. and were involved in the design of experiments, editing of the manuscript and discussions through out the work. S.A.A. was involved in a number of scientific discussions and analysis of results. A.O.A. generated ideas and spearheaded the initial collaboration between the institutions. S.N.B. was involved with a number of scientific discussions and analysis of results and has provided valuable insights, which have in turn, directed the research.

Additional Information
Supplementary information accompanies this paper at http://www.nature.com/srep

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