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Aerosol assisted chemical vapour deposition of tungsten oxide films from polyoxotungstate precursors: active photocatalysts

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Aerosol assisted chemical vapour deposition of polyoxotungstate precursors $[n\text{-}Bu_4N]_2[W_6O_{19}]$ and $[n\text{-}Bu_4N]_4H_3[PW_{11}O_{39}]$ produces films of WO_{3-x} and WO_3 on glass sunbstrates; the WO_3 films show significant photocatalytic decomposition of a test organic pollutant – stearic acid – when irradiated with either 254 or 365 nm radiation.

Chemical Vapour Deposition (CVD) is an industrially applicable technique for depositing thin solid films onto substrates. For example, Pilkington Glass have commercialised the worlds first self-cleaning, photoactive coating from the CVD of titania on glass; Pilkington Activ^{tm}.[1] The CVD process involves the vaporisation, transportation and decomposition of molecular precursors to promote film growth. The precursors are vaporised thermally and hence the key requirement for CVD film growth is precursor volatility. Tungsten oxide thin films have been deposited from the dual-source CVD reaction of tungsten hexafluoride or hexacarbonyl and oxygen,[2,3] and from single source precursors such as tungsten(VI) oxo-alkoxides,[4] $[WO(OR)_4]$, or tungsten(VI) and tungsten(VI) ethoxides.[5] Aerosol assisted chemical vapour deposition (AACVD) negates the volatility requirement and employs a solution of the precursor, from which an aerosol mist is generated by an ultrasonic humidifier. This precursor-solvent mist is transported to the CVD reactor containing the substrate by a carrier gas. On reaching the reactor the solvent mist evaporates at the elevated temperatures employed, producing the precursor in the gaseous state. In AACVD a single-source precursor does not have to be volatile, solubility is now the important criterion for precursor design. This allows growth of films from precursors whose application in CVD would traditionally be unthinkable due to their low volatility. Despite this the AACVD approach has been generally applied to single source precursor molecules that fail the volatility requirements, rather than being designed in their own right. We report here the application of the readily synthesised family of polyoxotungstate anions as single source precursors for the CVD of tungsten oxide thin films. The polyoxotungstates can be readily made with incorporated P and Si so doped tungsten oxide films are potentially accessible. Thus this procedure employs large, charged, cluster molecules in the CVD process where it is the convention to use small, neutral monomers. Unexpectedly the yellow tungsten oxide films grown in this study turned out to be effective photocatalysts. This latter point is important as thin film tungsten oxide has been classified as an ineffective photocatalyst[6] – this may be due to the fact that the reduced blue form has been used to test for photocatalytic activity.

Two polyoxotungstate anions $[n\text{-}Bu_4N]_2[W_6O_{19}]$, **1**,[7] and $[n\text{-}Bu_4N]_4H_3[PW_{11}O_{39}]$, **2**,[8] were synthesised by literature procedures. The precursors (0.25 g) were dissolved in acetone (50 cm^3), an aerosol generated by a PIFCO ultrasonic humidifier and nitrogen carrier gas used (1.0 dm^3 min^{-1}) to promote flow of the aerosol to the reaction chamber. Reaction run times were for thirty minutes. Coatings were obtained on glass substrates pre-coated with SiO_2 at a minimum deposition temperature of 410 °C for **1** and 480 °C for **2**.

The as-formed films obtained from both **1** and **2** were blue and hazy. The coatings showed good adherence in the centre of the substrate. All of the films could be scratched with a scalpel. Heating the films in air at 550 °C for thirty minutes changed the colour of the films from blue to pale yellow. Blue tungsten oxide films are indicative of partially reduced WO_{3-x}, whereas yellow tungsten oxide films are indicative of stoichiometric WO_3.

Raman spectra of the films deposited are shown in Figure 1. The blue as-formed films deposited from **1** can be identified as monoclinic γ-WO_{3-x}. In particular, the weak band at 192 cm^{-1} is characteristic of partially reduced WO_{3-x} and W^V–W^{VI} ion pairs.[9] Spectra of the yellow annealed films show sharper peaks and correspond to monoclinic γ-WO_3. The films deposited from **2** showed very similar Raman spectra to those deposited from **1**, except for some extra bands observed at 520 and 912 cm^{-1} for the as-formed blue film. X-ray diffraction patterns for the blue as-formed films from **1** showed crystalline films with reflections corresponding to monoclinic γ-WO_3.[10] The (0 2 0) reflection appears to be enhanced indicating preferred orientation. The yellow annealed film deposited from **1** gives a pattern indicative of a more randomly orientated monoclinic γ-WO_3

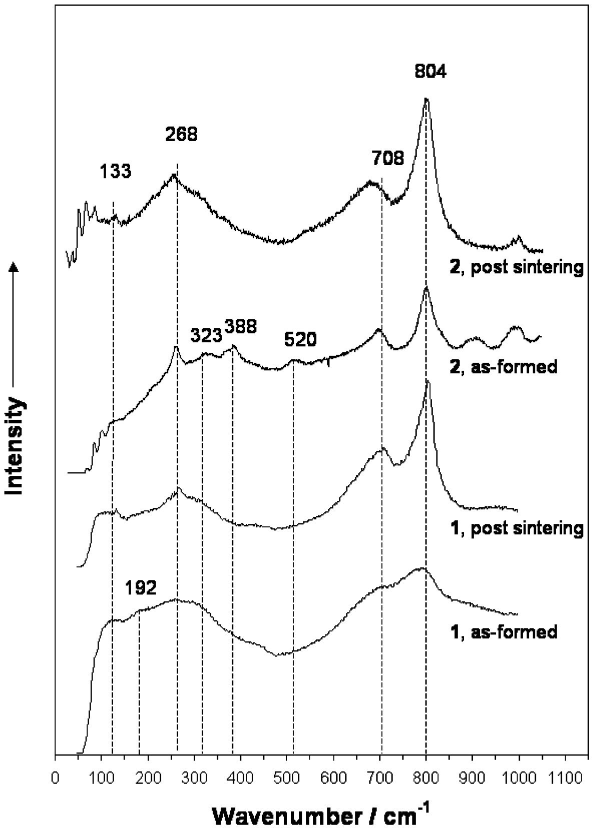

Fig. 1 Raman spectra of tungsten oxide films deposited from $[n\text{-}Bu_4N]_2[W_6O_{19}]$, **1**, and $[n\text{-}Bu_4N]_2[PW_{11}O_{39}]$, **2**.

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material.[10] X-ray patterns from **2** showed γ-WO_3 reflections in the sintered material. Film thicknesses were *ca* 500 nm as determined from reflection interference fringes and SEM measurements. X-ray photoelectron analysis of the films showed the presence of tungsten and oxygen in the expected ratios. For **2** some 0.6 atom% P was also detected. Binding energy shifts of 531.2 eV for O1s and 36.0 eV for $W4f_{5/2}$ exactly matched literature values for WO_3.[11]

The photocatalytic activity of the films towards the destruction of a test organic material – stearic acid – was investigated. It was applied by spin coating 7.5 µl of 0.4 M stearic acid (in methanol) onto the glass surface at 3000 revolutions min^{-1}. Recording the IR spectrum of the stearic acid over the range 3000–2800 cm^{-1} allowed the amount of stearic acid over-layer to be determined. The films were then irradiated with UV light (254 or 365 nm, 8W) and the amount of stearic acid on the glass was recorded every 30 minutes up to a total time of two hours. The yellow annealed films deposited from **1** and **2** destroyed 50 and 70% respectively of the stearic acid after 2 h irradiation at 254 nm. The blue films showed no photocatalytic activity (probably as W^V centres are present that act as e–h^+ recombination centres). The yellow coatings have excellent photocatalytic activity, comparable with that for TiO_2, the most thoroughly researched photocatalyst in the literature. Titania has a band-gap of 3.2 eV and can only make use of roughly 1% of solar energy,[12] whereas WO_3 has a band gap of 2.8 eV[13] and so is able to utilise more solar radiation. The experiment was performed again using 365 nm light of the same intensity. After 2 hours irradiation at 365 nm *ca.* 10% of the stearic acid had been destroyed by the yellow films from **1** and **2**. After 24 hours between 30–45% of the organic film had been removed, notably a control of blank glass showed no loss of stearic acid under the same illumination conditions. Thus, tungsten oxide can make use of the longer wavelengths to photocatalyse the destruction of a test organic substance.

Both the yellow and blue tungsten oxide films show low contact angles for water droplets (typically 10–15°) and marked photoinduced superhydrophilicity (decreases to *ca* 1–2° on irradiation with 254 nm).

To conclude, we have used large polyoxotungstate anions to prepare tungsten oxide thin films on glass by aerosol assisted CVD. We have shown that large, charged precursors can be employed in AACVD. Our choice of precursors, as well as being unconventional, is particularly interesting since these polyoxotungstates can be easily prepared with the exchange of one or more of the tungsten atoms for a range of other metal atoms. In addition, we have demonstrated that the yellow fully stoichiometric tungsten oxide films are effective photocatalysts for the destruction of stearic acid over-layers. Thus, these films have potential application as self-cleaning coatings.

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