

1       **Polyoxometalate complexes as precursors to vanadium doped-molybdenum or**  
2                                   **tungsten oxide thin films via aerosol-assisted CVD**

3       Sapna Ponja, Sanjayan Sathasivam<sup>a,b</sup>, Hywel O. Davies<sup>c</sup>, Ivan P. Parkin<sup>a</sup> and Claire J.  
4       Carmalt<sup>a\*</sup>

5       \*Corresponding author

6       <sup>a</sup>Materials Chemistry Centre, Department of Chemistry, University College London,  
7       20 Gordon Street, London WC1H 0AJ, UK

8       Fax: (+44) 20-7679-7463

9       E-mail: [c.j.carmalt@ucl.ac.uk](mailto:c.j.carmalt@ucl.ac.uk)

10      <sup>b</sup>Bio Nano Consulting Ltd, The Gridiron Building, One St. Pancras Square, London  
11      N1C 4AG, UK

12      Fax: (+44) 20-7396-1056

13      E-mail: [info@bio-nano-consulting.com](mailto:info@bio-nano-consulting.com)

14      <sup>c</sup>ACAL Energy Ltd, Heath Business and Technology Park, Runcorn WA7 4QX,  
15      Cheshire, England.

16      **Abstract**

17      Aerosol assisted chemical vapour deposition of substituted polyoxometalates:  
18      H<sub>4</sub>[PMo<sub>11</sub>VO<sub>40</sub>]; H<sub>7</sub>[PMo<sub>8</sub>V<sub>4</sub>O<sub>40</sub>]; [<sup>n</sup>Bu<sub>4</sub>N]<sub>4</sub>[PVW<sub>11</sub>O<sub>40</sub>] and [<sup>n</sup>Bu<sub>4</sub>N]<sub>5</sub>[PV<sub>2</sub>W<sub>10</sub>O<sub>40</sub>]  
19      resulted in the formation of vanadium-doped metal oxide thin films. Depositions were  
20      carried out at 550 °C in methanol or acetonitrile solution for the molybdenum or  
21      tungsten containing POMs, respectively. The as-deposited films were X-ray  
22      amorphous and relatively non-adherent however, on annealing in air at 600 °C  
23      decolourised translucent films which were more mechanically robust were obtained.  
24      Films deposited from H<sub>4</sub>[PMo<sub>11</sub>VO<sub>40</sub>] and H<sub>7</sub>[PMo<sub>8</sub>V<sub>4</sub>O<sub>40</sub>] consisted of V-doped  
25      MoO<sub>3</sub> in the orthorhombic phase and films from [<sup>n</sup>Bu<sub>4</sub>N]<sub>4</sub>[PVW<sub>11</sub>O<sub>40</sub>] and  
26      [<sup>n</sup>Bu<sub>4</sub>N]<sub>5</sub>[PV<sub>2</sub>W<sub>10</sub>O<sub>40</sub>] comprised of monoclinic V-doped WO<sub>3</sub>. All films were fully  
27      characterised using XPS, EDX, SEM and UV-Vis.

## 28 Introduction

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3 29 Polyoxometalates (POMs) are characterized as anionic transition metal oxygen cluster  
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5 30 compounds, diverse in structure,<sup>[1]</sup> physical and chemical properties, that lend  
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7 31 themselves to a wide range of applications, most notably as catalysts and conductive  
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9 32 materials, in the form of membranes and thin films.<sup>[2]</sup> POM clusters have a high  
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11 33 degree of solubility in a variety of inorganic and organic solvents and hence are  
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13 34 termed ‘molecular metal oxides’.<sup>[2a]</sup> In solution, POMs interact electrostatically with  
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15 35 cationic species which leads to interactions between POMs and cationic ions,  
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17 36 molecules, complexes, polymers and positively charged solid surfaces.<sup>[2a]</sup> POMs are  
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19 37 classified into two subfamilies depending on the absence (as in heteropolyanions) or  
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21 38 presence (as in isopolyanions) of a central cation or heteroatom.<sup>[1]</sup> A number of  
22  
23 39 different structural types of POM clusters exist<sup>[1, 2b]</sup> but the Keggin structure was the  
24  
25 40 first to be discovered.<sup>[1]</sup> Keggin-type POMs can be represented by the formula  
26  
27 41  $[XM_{12}O_{40}]^{n-}$  where X is the central heteroatom (e.g., P, Si, or B) with 4 oxygen atoms  
28  
29 42 bonded tetrahedrally to it, and M (usually Mo, W or V) is the addenda or peripheral  
30  
31 43 atom (the metal atoms that make up the framework). The central atom is surrounded  
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33 44 by 12 octahedrons made of  $MO_6$  and all the oxygens are shared except for the 12  
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35 45 terminal oxygens, which are attached to only one atom.

36  
37 46 Substituted POMs are a modification of the Keggin structure where an additional  
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39 47 addenda atom can be incorporated, such as vanadium to give POMs of formula,  
40  
41 48  $[PM_{12-x}V_xO_{40}]^{n-}$ .<sup>[3]</sup> The physical and chemical properties of a POM are a function of  
42  
43 49 their chemical composition, i.e. the identity of the heteroatom and addenda atom(s).  
44  
45 50 POMs with Mo or W as the addenda atoms with different heteroatoms (e.g., P, V, Nb  
46  
47 51 or W) are easy to prepare. Changing the heteroatom and/or substituting an addenda  
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49 52 atom also provides the means to add an additional element into the metal oxide films  
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51 53 which may have a significant effect on the chemical and physical properties of the  
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53 54 film and lead to doped-metal oxide films. Vanadium has been used as a dopant in the  
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55 55 production of thin films for reducing the band gap and improving photocatalytic  
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57 56 properties.<sup>[4]</sup>

58  
59 57 Thin films of Mo oxides have been made previously using dual-source precursors,  
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61 58 such as molybdenum hexacarbonyl,  $[Mo(CO)_6]$  and oxygen, and from single-source  
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63 59 precursors such as molybdenum pentacarbonyl 1-methylbutylisonitrile.<sup>[5]</sup>  
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62 Molybdenum(VI) oxide exists in two basic crystal structures with different molecular  
63 vibrational and optical properties:<sup>[5]</sup>  $\alpha$ -MoO<sub>3</sub> with orthorhombic symmetry and  
64 metastable monoclinic  $\beta$ -MoO<sub>3</sub>; MoO<sub>2</sub> also has a monoclinic structure.<sup>[6]</sup>  
65 Molybdenum trioxide (MoO<sub>3</sub>), the technologically more significant form of the oxide,  
66 exists in the orthorhombic phase and has a double layered structure.<sup>[6]</sup> MoO<sub>3</sub> is a well-  
67 known catalyst often used in the oxidative dehydrogenation of methanol to an  
68 aldehyde<sup>[7]</sup> and has also been shown to act as an excellent antimicrobial coating,  
69 forming an acidic environment that retards bacterial growth and proliferation.<sup>[8]</sup>  
70 Applications of MoO<sub>3</sub> also extend to organic electronic devices due to its low  
71 absorption in the visible spectrum and high compatibility with other materials. MoO<sub>3</sub>  
72 has also been used as a material to reduce energy barriers for charge carrier injection,  
73 extraction or transport between semiconductor and organic layers.<sup>[9]</sup>

74  
75 Like MoO<sub>3</sub>, tungsten trioxide (WO<sub>3</sub>) has many applications as an interface layer in  
76 electronic devices.<sup>[9-10]</sup> Principally, it reduces the barrier for charge injection between,  
77 for example, a tin doped indium oxide (ITO) layer and a polymer layer.<sup>[10a]</sup> WO<sub>3</sub> also  
78 has applications in gas sensing, photocatalysis and photochromism.<sup>[11]</sup> Films  
79 containing WO<sub>3</sub> have been deposited by evaporation, sputtering, electrochemical  
80 techniques and by CVD.<sup>[12]</sup> WO<sub>3</sub> undergoes a number of phase transitions during  
81 annealing and cooling:<sup>[11]</sup> monoclinic II (< -43 °C) → triclinic (-43 – 17 °C) →  
82 monoclinic I (17 – 330 °C) → orthorhombic (330-740 °C) → tetragonal (> 740 °C).  
83 The monoclinic I (hereon referred to as ‘monoclinic’) is the most stable phase at room  
84 temperature and usually remains so even after annealing.

85  
86 CVD has increasingly become the preferred method for producing metal oxide films  
87 mainly because of the higher deposition rates,<sup>[13]</sup> uniform coverage, good  
88 reproducibility, and highly dense and pure films.<sup>[14]</sup> Aerosol-assisted CVD is a variant  
89 that has additional advantages over conventional CVD which includes that the  
90 precursors do not have to be highly volatile or thermally stable.<sup>[15]</sup> This opens up the  
91 possibility of using precursors that would not have been suitable for conventional  
92 CVD such as POMs.

93  
94 Keggin-type POMs have been deposited *via* AACVD<sup>[6, 16]</sup> however, this paper, to our  
95 knowledge, is the first study on the deposition of binary metal oxide thin films:  
96 vanadium doped MoO<sub>x</sub> ( $x = 2-3$ ) and WO<sub>3</sub> using single-source precursors called

97 substituted Keggin-type POMs *via* AACVD. All POMs and films were characterized  
98 spectroscopically.

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## 101 **Experimental**

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103 The reagents were purchased from Sigma Aldrich (99.9% purity unless stated  
104 otherwise) and used without further refinement. The identity of the POMs was  
105 confirmed by <sup>31</sup>P NMR and FT-IR which were consistent with XPS and EDX. POMs  
106 (1- 4) were prepared by literature procedures.<sup>[3, 17]</sup>

### 107 108 Preparation of H<sub>4</sub>[PMo<sub>11</sub>VO<sub>40</sub>] (1)

109  
110 POM (1) was synthesised following a method given by ACAL Energy Ltd which was  
111 scaled down to suit to the quantities required in the present study.<sup>[17]</sup> V<sub>2</sub>O<sub>5</sub> (0.45 g,  
112 2.47 mmol) and MoO<sub>3</sub> (7.92 g, 55.02 mmol) were suspended in distilled water (50  
113 mL) with moderate stirring. 85% H<sub>3</sub>PO<sub>4</sub> (0.57 g, 5.82 mmol) was added to the  
114 mixture followed by additional distilled water (45 mL). The pale yellow mixture was  
115 heated at reflux (120 °C). After two days, a drop of H<sub>2</sub>O<sub>2</sub> was added and the mixture  
116 was left at reflux for a further five days, resulting in a clear orange/red solution. The  
117 solution was cooled to room temperature and clarified by vacuum filtration producing  
118 an orange solution. The solvent evaporated overnight in a fume hood leaving behind  
119 an orange solid.

### 120 121 Preparation of H<sub>7</sub>[PMo<sub>8</sub>V<sub>4</sub>O<sub>40</sub>] (2)

122  
123 POM (2) was supplied in aqueous solution which was evaporated in a fume hood to  
124 leave behind an orange solid.<sup>[17]</sup>

### 125 126 Preparation of [<sup>n</sup>Bu<sub>4</sub>N]<sub>4</sub>[PVW<sub>11</sub>O<sub>40</sub>] (3) and [<sup>n</sup>Bu<sub>4</sub>N]<sub>5</sub>[PV<sub>2</sub>W<sub>10</sub>O<sub>40</sub>] (4)<sup>[3]</sup>

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128 A stock solution of V(V) was prepared by dissolving NH<sub>4</sub>VO<sub>3</sub> (5.85 g, 50.01 mmol)  
129 and NaOH (4.00 g, 100 mmol) in distilled water (100 mL). NaH<sub>2</sub>PO<sub>4</sub>·2H<sub>2</sub>O (0.08 g,  
130 1.43 mmol) was added to a solution of Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O (1.65 g, 6.32 mmol) in distilled  
131 water (80 mL) followed by the addition of conc. HCl (4.34 mL) and stirred. After  
132 stirring, the stock solution (1 mL) was added to the solution (4 mL was added when  
133 [<sup>n</sup>Bu<sub>4</sub>N]<sub>5</sub>[PV<sub>2</sub>W<sub>10</sub>O<sub>40</sub>] was prepared). The solution turned from clear to yellow or  
134 orange, respectively. Further distilled water (20 mL) was added to the solution and  
135 heated under reflux (120 °C) for three days. *n*-Bu<sub>4</sub>NBr was added to the solution and  
136 the precipitates were filtered off and washed with distilled water and ethanol.

137 [ $n\text{Bu}_4\text{N}$ ] $_4$ [PVW $_{11}$ O $_{40}$ ] and [ $n\text{Bu}_4\text{N}$ ] $_5$ [PV $_2$ W $_{10}$ O $_{40}$ ] were collected as pale yellow and  
138 yellow solids, respectively.

139

#### 140 AACVD Procedure

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142 The depositions were carried out in an in-house built CVD rig at 550 °C.<sup>[18]</sup> The glass  
143 substrate consisted of 50 nm SiO $_2$  barrier coated float-glass of size 90 × 45 × 4 mm  
144 (Pilkington NSG Ltd). The coating prevents the ions from within the glass diffusing to  
145 the surface preventing contamination of the film with metals such as sodium and  
146 calcium. The glass substrate was first cleaned with detergent and water, followed by  
147 propan-2-ol, propanone, and then air dried. The Mo films were deposited from a  
148 methanol based precursor solution ([H $_4$ [PMo $_{11}$ VO $_{40}$ ] (**1**) (7.5 × 10 $^{-3}$  M) and  
149 [H $_7$ [PMo $_8$ V $_4$ O $_{40}$ ] (**2**) (7.5 × 10 $^{-3}$  M)) and W films used acetonitrile as the solvent  
150 ([ $n\text{Bu}_4\text{N}$ ] $_4$ [PVW $_{11}$ O $_{40}$ ] (**3**) (2.7 × 10 $^{-3}$  M) and [ $n\text{Bu}_4\text{N}$ ] $_5$ [PV $_2$ W $_{10}$ O $_{40}$ ] (**4**) (1.7 × 10 $^{-3}$   
151 M)). Deposition time for the methanol solution and acetonitrile solutions were 30 and  
152 45 minutes respectively. Different solvent systems were used as AACVD requires the  
153 precursor to be soluble in the solvent. Although all the POMs have a substituted  
154 keggin structure, the bulkier counter ion of the W POMs requires a less polar solvent  
155 to be soluble. The precursor solution was kept at room temperature. The aerosol of the  
156 precursor solution was generated by emersing the bubbler into a Vicks ultrasonic  
157 humidifier (at room temperature). The ultrasonic vibrations travel through the water  
158 and the flask to create the precursor aerosol mist. Nitrogen gas (99.9%; supplied by  
159 BOC) at a rate of 0.5 L/min was used to push the aerosol into the CVD chamber.  
160 Films were annealed at 600 °C in air for 30 minutes.

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#### 163 Analysis of the POM precursors

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165  $^{31}\text{P}$  NMR was performed on a Bruker AMX300 (Mo POMs) and Bruker AV400 (W  
166 POMs) at 121.4 and 162.0 MHz, respectively. The probe temperature was  
167 thermostated at 300 K and 292.4 K, respectively. The Mo POMs (**1**) and (**2**) were in a  
168 D $_2$ O solvent system and the W POMs (**3**) and (**4**) were dissolved in CD $_3$ CN. FT-IR  
169 analysis was carried out using a Bruker alpha platinum-ATR. Energy dispersive X-  
170 ray analysis (EDX) was carried out using a JEOL JSM-6301F Field Emission  
171 instrument with an acceleration voltage of 20 kV. Samples were placed onto  
172 conductive carbon tape that was attached to stainless steel holders. The samples were

173 then coated with a fine layer of carbon to stop charging. X-ray photoelectron  
174 spectroscopy (XPS) was carried out using a Thermo Scientific K-Alpha instrument  
175 with monochromatic Al-K<sub>α</sub> source to identify the oxidation state and chemical  
176 constituents. The peaks modelled using CasaXPS software with binding energies  
177 adjusted to carbon (284.5 eV) in order to compensate for the effects of charging.

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#### 179 Analysis of the films

180

181 EDX and XPS analysis were performed using the same instruments as above.  
182 Scanning electron microscopy (SEM) was carried out using a JEOL JSM-6301F Field  
183 Emission instrument with acceleration voltage of 5 kV. For EDX and SEM  
184 measurements sample preparation involved cutting the films down to coupons of 10  
185 mm x 10 mm or less and attaching them on stainless steel holders using conductive  
186 carbon tape. Contacts from the top of the film to the carbon tape were made using a  
187 solution of silver paint. The samples were then coated with a fine layer of carbon or  
188 gold, respectively, to stop charging. X-ray diffraction (XRD) was done using a  
189 microfocus Bruker D8 GAADS powder X-ray diffractometer with monochromated  
190 Cu K<sub>α1</sub> (1.54056 Å) and Cu K<sub>α2</sub> (1.54439 Å) radiation with an intensity ratio of 2:1, a  
191 voltage of 40 kV and current of 40 mA. The X-ray incident angle was 5° and the  
192 detector angle was 22°. The sample height was adjusted to focus the X-ray beam.  
193 Peak positions were compared to patterns from the Inorganic Crystal Structure  
194 Database (ICDS). The lattice parameters were calculated from powder X-ray  
195 diffraction data using the software GSAS and EXPGUI *via* the Le Bail method.  
196 UV/Vis/Near IR transmittance and reflectance spectra were produced using the Perkin  
197 Elmer Precisely Lambda 950 spectrometer using an air background and recorded  
198 between 320-2500 nm. The data obtained from this was used to calculate the band gap  
199 *via* a Tauc plot. Water droplet (5 μL) contact angles were carried out using an FTA-  
200 1000 drop shape instrument.

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## 204 **Results and discussion**

205  
206 Single source polyoxometalate precursors were synthesised for use in AACVD to  
207 deposit V-doped Mo and W oxide thin films. In general POM  $H_4[PMo_{11}VO_{40}]$  (**1**) was  
208 synthesised *via* a reflux of  $V_2O_5$  and  $MoO_3$  in the presence of  $Na_2CO_3$  and a drop of  
209  $H_2O_2$ . POMs  $[^nBu_4N]_4[PVW_{11}O_{40}]$  (**3**) and  $[^nBu_4N]_5[PV_2W_{10}O_{40}]$  (**4**) were  
210 synthesised by refluxing together a solution consisting of  $NaH_2PO_4 \cdot 2H_2O$ ,  
211  $Na_2WO_4 \cdot 2H_2O$ , concentrated HCl, and a stock solution made of  $NH_4VO_3$  and NaOH.  
212 These POMs, like others reported in the literature, are easy to synthesise resulting in a  
213 good yield.

214  
215 The FTIR spectra of the POMs (**1**, **2**, **3** and **4**) show the characteristic bands for the  
216 Keggin structure: 780-800, 860-880  $cm^{-1}$  (M-O-M; bridging), 960-990  $cm^{-1}$  (M=O;  
217 terminal) and 1060-1080  $cm^{-1}$  (P-O) where M corresponds to Mo or W.<sup>[19]</sup> However  
218 for POMs (**1**) and (**2**) these bands appear at reduced wavenumbers which is likely a  
219 feature of the substituted Keggin structure. The FTIR spectra of the W POMs (**3**) and  
220 (**4**) show an additional peak at  $\sim 1480\text{ cm}^{-1}$  most likely due to a C-N or a C-H stretch  
221 originating from the counter ion. It is noteworthy that bands were also seen in the  
222 3600, 3300 and 1600  $cm^{-1}$  region for all of the POMs, which correspond to the  
223 symmetric stretching, asymmetric stretching and bending vibrations in water,  
224 respectively.<sup>[20]</sup>

225  
226 P  $^{31}P$  NMR was also carried out on the powders. The  $^{31}P$  NMR spectra of (**1**) had a  
227 single major peak with a chemical shift of -3.0 ppm but the spectra of (**2**) contained a  
228 number of peaks including one in the region of -3 ppm. Other studies have also found  
229 multiple peaks in the NMR spectra when more than one V atom is present which is  
230 the case for (**2**).<sup>[21]</sup> The additional peaks represent different resonances due to the  
231 presence of different isomers.<sup>[21a]</sup> It has been reported in the literature that the peaks in  
232 the  $^{31}P$  NMR for  $[PV_xM_{12-x}O_{40}]$  POMs depended on the value of  $x$ .<sup>[21b]</sup> POM (**3**)  
233 containing a single vanadium atom also produced a single peak in the  $^{31}P$  NMR  
234 spectra at -15.1 ppm<sup>[21b]</sup> and the spectra of (**4**) which has two V atoms showed a peak  
235 at -15.1 ppm and -14.1 ppm. Again, the presence of a second peak may also be  
236 explained by the different V-P resonances that arise because of the presence of  
237 different isomers.

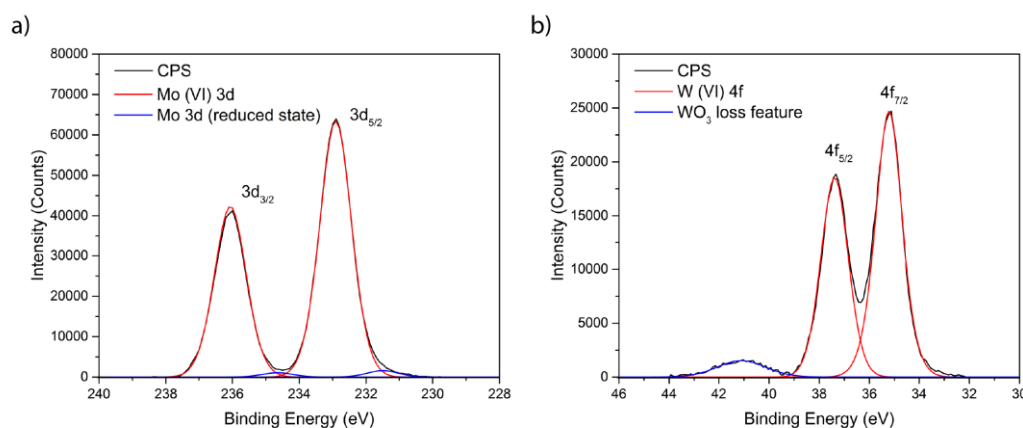


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238 X-ray photoelectron spectroscopy (XPS) was carried out on the four POM powders to  
239 determine their oxidation state. Sample XPS spectra for the Mo 3d and W 4f  
240 transitions of POM (1) and (3) is shown in Figure 1. The Mo based POMs (1) and (2)  
241 showed Mo 3d<sub>5/2</sub> peaks at 232.9 and 232.7 eV respectively corresponding to Mo in  
242 the +6 oxidation state.<sup>[6, 22]</sup> Peaks at lower binding energies corresponding to reduced  
243 states in the Mo 3d XPS spectra were also observed. This is common occurrence for  
244 Mo<sup>6+</sup> species during XPS analysis.<sup>[23]</sup> XPS of POMs (3) and (4) showed W in the +6  
245 oxidation state with both W 4f<sub>7/2</sub> binding energies at 35.3 eV. <sup>[16, 24]</sup> All four POMs  
246 contained P and V in the +5 oxidation state as indicated by binding energies of 133.5  
247 ( $\pm 0.2$ ) and 517 ( $\pm 0.5$ ) eV respectively.<sup>[25] [26]</sup>

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249 The binding energy range for the O was between 530.5-533.6 eV matching ranges  
250 found in literature.<sup>[6, 27]</sup> There are four O environments in the substituted Keggin  
251 POMs in comparison with the three for a standard Keggin POM structure (the extra  
252 M-O environment; where M = Vanadium).

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Figure 1: Example XPS spectra of the Mo 3d and W 4f transitions for POM (1) and (3) respectively. The Mo 3d<sub>5/2</sub> peak in POM appears at 232.9 eV corresponding to Mo<sup>6+</sup> and the W 4f<sub>7/2</sub> peak is centred at 35.3 eV matching W<sup>6+</sup>.

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259 Energy dispersive X-ray spectroscopy (EDX) was used to determine atomic ratios of  
260 the POM powders (Table 1). The POMs are in close agreement with the stated  
261 formula of the anions. The discrepancies could be explained by the presence of other  
262 POMs that may have been synthesised, such as [PM<sub>0</sub><sub>12</sub>O<sub>40</sub>]<sup>n-</sup>, since the methods of  
263 synthesis are similar.

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Table 1: The approximate ratio of atoms relative vanadium in the POMs. An average of the atomic ratios was by analysis three different areas per sample.

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**Approximate ratio of atoms relative to vanadium**

POM	P	Mo/W	V	O
H <sub>4</sub> [PMo <sub>11</sub> VO <sub>40</sub> ] ( <b>1</b> )	1	12	1	37
H <sub>7</sub> [PMo <sub>8</sub> V <sub>4</sub> O <sub>40</sub> ] ( <b>2</b> )	1	9	4	38
[ <sup>n</sup> Bu <sub>4</sub> N] <sub>4</sub> [PVW <sub>11</sub> O <sub>40</sub> ] ( <b>3</b> )	2	10	1	42
[ <sup>n</sup> Bu <sub>4</sub> N] <sub>5</sub> [PV <sub>2</sub> W <sub>10</sub> O <sub>40</sub> ] ( <b>4</b> )	2	11	2	49

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269 The POM powders - H<sub>4</sub>[PMo<sub>11</sub>VO<sub>40</sub>] (**1**), H<sub>7</sub>[PMo<sub>8</sub>V<sub>4</sub>O<sub>40</sub>] (**2**), [<sup>n</sup>Bu<sub>4</sub>N]<sub>4</sub>[PVW<sub>11</sub>O<sub>40</sub>]

270 (**3**) and [<sup>n</sup>Bu<sub>4</sub>N]<sub>5</sub>[PV<sub>2</sub>W<sub>10</sub>O<sub>40</sub>] (**4**) – were then used as precursors in the deposition of

271 V doped  $\alpha$ -MoO<sub>3</sub> and WO<sub>3</sub> thin films. AACVD was carried out at 550 °C using

272 nitrogen as a carrier gas at a flow rate of 0.5 L/min. Methanol and acetonitrile were

273 used as the solvents in the deposition of Mo and W films respectively.

274

275 V doped  $\alpha$ -MoO<sub>3</sub> from H<sub>4</sub>[PMo<sub>11</sub>VO<sub>40</sub>] (**1**) and H<sub>7</sub>[PMo<sub>8</sub>V<sub>4</sub>O<sub>40</sub>] (**2**)

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277 Methanol solutions of H<sub>4</sub>[PMo<sub>11</sub>VO<sub>40</sub>] (**1**) and H<sub>7</sub>[PMo<sub>8</sub>V<sub>4</sub>O<sub>40</sub>] (**2**) were used as

278 precursors to deposit V-doped  $\alpha$ -MoO<sub>3</sub> thin films. The as deposited black, non-

279 adherant and X-ray amorphous films were annealed under air at 600 °C for 30 minutes.

280 The annealed films were translucent yellow in appearance and well adhered to the

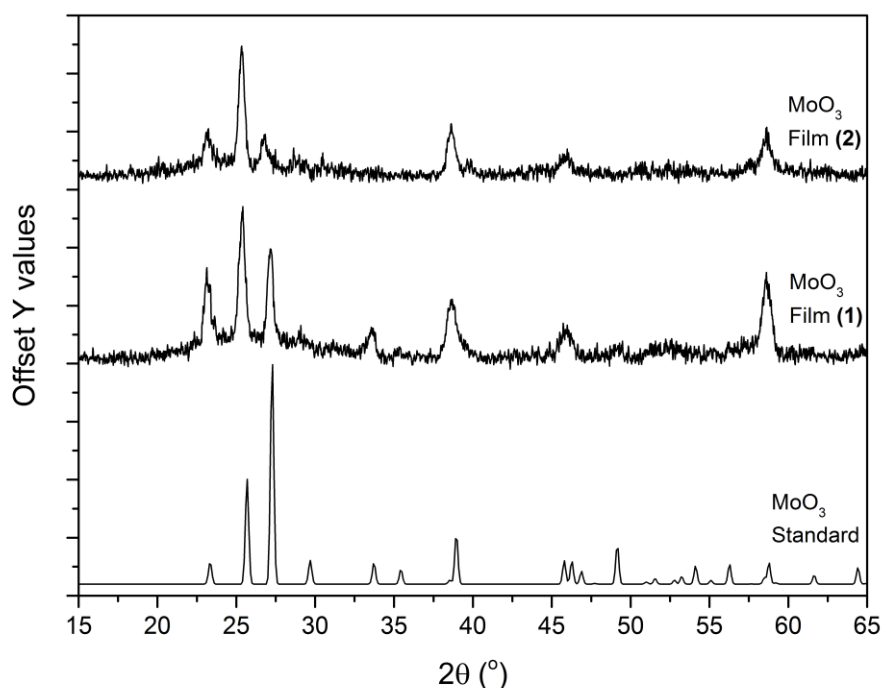
281 substrate, passing the Scotch<sup>TM</sup> tape test.

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283 X-ray diffraction studies showed that the annealed films were crystalline and

284 consisted of orthorhombic  $\alpha$ -MoO<sub>3</sub> with preferential orientation (Figure 2).

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286 **Figure 2: XRD pattern of the films deposited from POMs,  $H_4[PMo_{11}VO_{40}]$  (1) and**  
287  **$H_7[PMo_8V_4O_{40}]$  (2).**

288 The diffraction patterns of films (1) and (2) were fitted to a Le Bail refined model  
289 which an approximately 4% expansion in the  $\alpha$ - $MoO_3$  unit cell compared to standard  
290 values (Table 2) - this is consistent with the observed shift to lower  $2\theta$  values in the  
291 XRD patterns.<sup>[28]</sup> The expansion also suggested that substitutional doping of  $\alpha$ - $MoO_3$   
292 with  $V^{5+}$  had not occurred as the ionic radii of  $V^{5+}$  is smaller than that of  $Mo^{6+}$ .  
293 However, due to the layered nature  $\alpha$ - $MoO_3$  it is possible that  $V^{5+}$  is intercalated  
294 leading to the observed expansion in the unit cell of the  $\alpha$ - $MoO_3$ . This has previously  
295 been reported with Li ions forming  $Li_xMoO_3$  precipitates between layers of  $MoO_3$ .<sup>[29]</sup>

296  
297 **Table 2: Lattice parameters of films from POMs  $H_4[PMo_{11}VO_{40}]$  (1) and  $H_7[PMo_8V_4O_{40}]$  (2)**  
298 **calculated from XRD data *via* the Le Bail method.**

Film	a / Å	b / Å	c / Å	Unit Cell Volume / Å <sup>3</sup>	Volume expansion / %
$H_4[PMo_{11}VO_{40}]$ (1)	4.0135(7)	14.308(4)	3.6772(4)	211.16(8)	4.05(9)
$H_7[PMo_8V_4O_{40}]$ (2)	3.996(1)	14.044(4)	3.759(3)	211.0(2)	3.99(3)

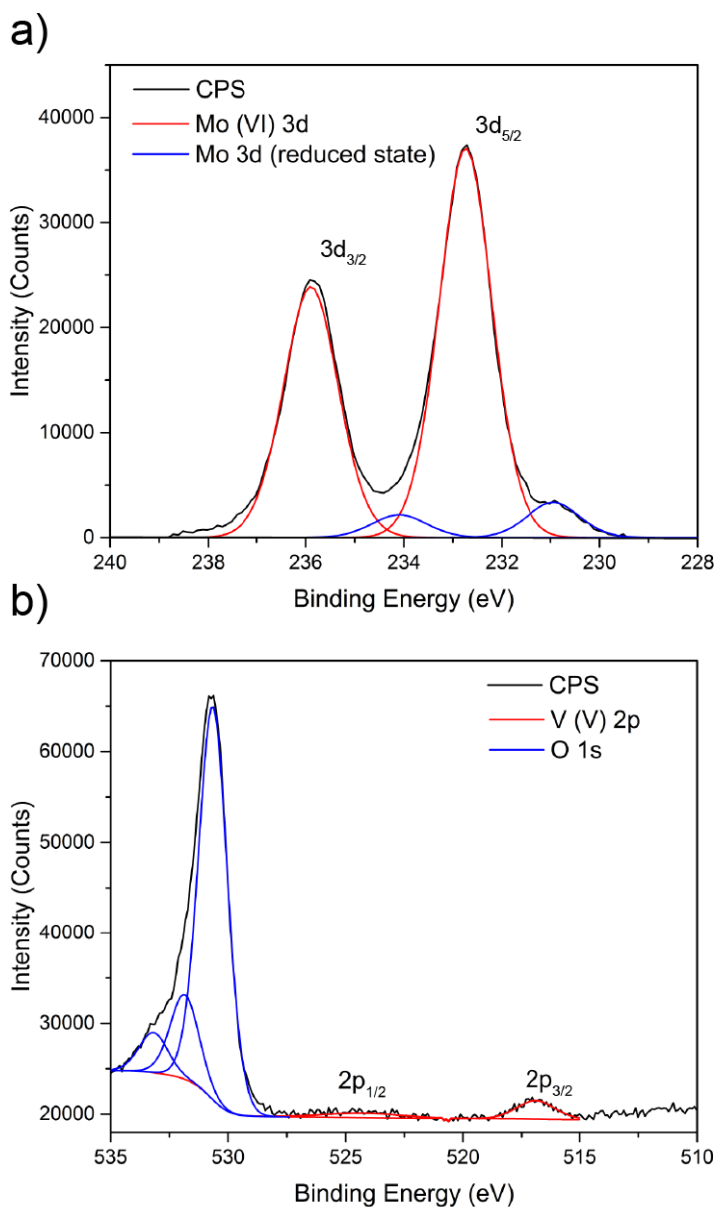
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301 Furthermore, the 4% expansion in the  $\alpha$ -MoO<sub>3</sub> framework of both films is in spite of  
302 film (2) having a higher V content compared to film (1) as determined by EDX  
303 analysis. This suggests that the excess V in film (2) may exist in the amorphous  
304 oxide form.

305

306 Mo in the annealed films (1) and (2) was in the +6 oxidation state as shown by a  
307 3d<sub>5/2</sub> peaks for both films at 232.7 eV (Figure 3a). As with the XPS spectra of the  
308 POM powders, peaks at lower binding energies (230.9 eV) corresponding to reduced  
309 surface states were observed.<sup>[23]</sup> XPS also showed the dopant V species to be in the  
310 +5 oxidation state with 2p<sub>3/2</sub> peaks for the two  $\alpha$ -MoO<sub>3</sub> films centered at 517.1 eV  
311 (Figure 3b).<sup>[30]</sup>

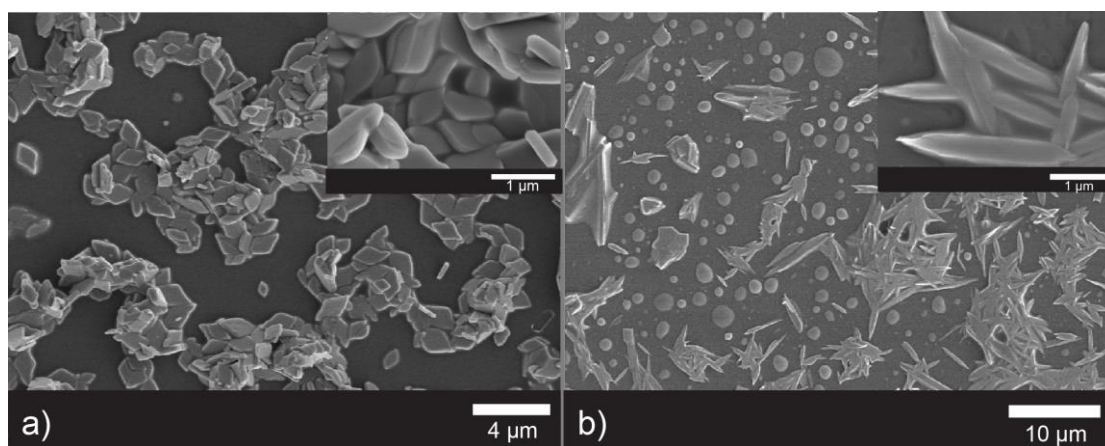


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313 **Figure 3: a) Sample XPS spectrum of Mo 3d taken from  $\alpha$ -MoO<sub>3</sub> film 1. The 3d5/2 peak was seen**  
314 **at 232.7 eV corresponding to Mo<sup>3+</sup>, a peak at 230.9 eV corresponds to 3d5/2 peak for Mo in a**  
315 **reduced state. b) Sample XPS spectrum of the V 3d and O 1s peaks. V2p3/2 at 517.1 eV matches**  
316 **well with literature reports for V<sup>5+</sup>.**

317 Figure 4 shows the surface morphology of the  $\alpha$ -MoO<sub>3</sub> films as probed with a  
318 scanning electron microscope. Film (1) was dominated by clusters of irregularly  
319 stacked diamond shaped flat discs. The diamond shaped discs were almost regular in  
320 shape (0.5 x 0.3  $\mu$ m) with a thickness of 0.1  $\mu$ m. Film (2) consisted of a mixture of  
321 tapered long needles and spherical particles. The long needles appeared to be roughly  
322 the same size (1.5 x 0.2  $\mu$ m) and the majority of the spherical particles had a diameter  
323 of 0.5-2  $\mu$ m. In both films the space between the particles is assumed to be bare glass.

324



325

326 **Figure 4: SEM of films produced using POMs H<sub>4</sub>[PMo<sub>11</sub>VO<sub>40</sub>] (1) and H<sub>7</sub>[PMo<sub>8</sub>V<sub>4</sub>O<sub>40</sub>] (2).**

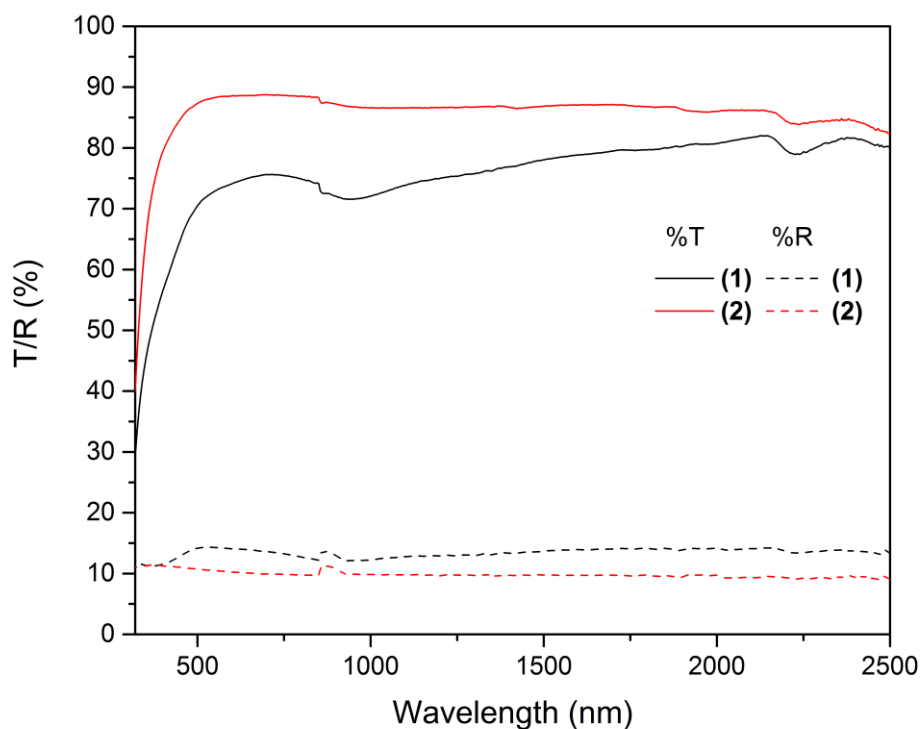
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328 As expected films (1) and (2) showed high transmittance with the latter having a  
329 much greater transparency of ~90% at 550 nm (Figure 5). The observed variation  
330 between the two films is most likely an outcome of the composition of the POM used  
331 for depositing the MoO<sub>3</sub> films.

332

333 The indirect band gaps were calculated using data collected from UV-vis *via* the Tauc  
334 plot.<sup>[31]</sup> The band gaps for the V-doped MoO<sub>3</sub> films (1) and (2) were 2.85 eV and 2.98  
335 eV, respectively. The band gaps of these are in close agreement with literature values  
336 for the polycrystalline structure (2.8 eV).<sup>[23]</sup>

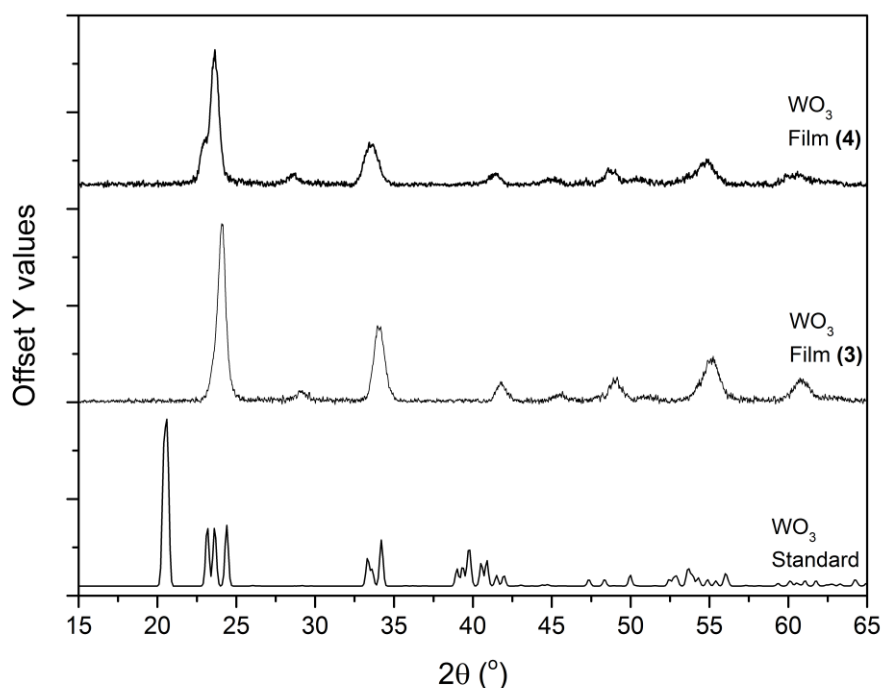
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338 **Figure 5: The transmission (black) and reflectance (red) spectra for the films using the POMs**  
339 **H<sub>4</sub>[PMo<sub>11</sub>VO<sub>40</sub>] (1) (solid line) and H<sub>7</sub>[PMo<sub>8</sub>V<sub>4</sub>O<sub>40</sub>] (2) (dashed line).**

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342 V doped WO<sub>3</sub> from [nBu<sub>4</sub>N]<sub>4</sub>[PVW<sub>11</sub>O<sub>40</sub>] (3) and [nBu<sub>4</sub>N]<sub>5</sub>[PV<sub>2</sub>W<sub>10</sub>O<sub>40</sub>] (4)

343  
344 The W POMs - [nBu<sub>4</sub>N]<sub>4</sub>[PVW<sub>11</sub>O<sub>40</sub>] (3) and [nBu<sub>4</sub>N]<sub>5</sub>[PV<sub>2</sub>W<sub>10</sub>O<sub>40</sub>] (4) - were used as  
345 precursors to deposit V doped WO<sub>3</sub> in an acetonitrile solution at 550 °C and a  
346 nitrogen flow rate of 0.5 L/min. Brown poorly adherent films were deposited on the  
347 top plate and XRD showed that they were amorphous. Upon annealing at 600 °C for  
348 30 minutes the films became adherent and translucent. XRD showed that the  
349 annealed films were crystalline monoclinic WO<sub>3</sub> (Fig. 5). The annealed films were  
350 studied using a variety of analytical techniques.



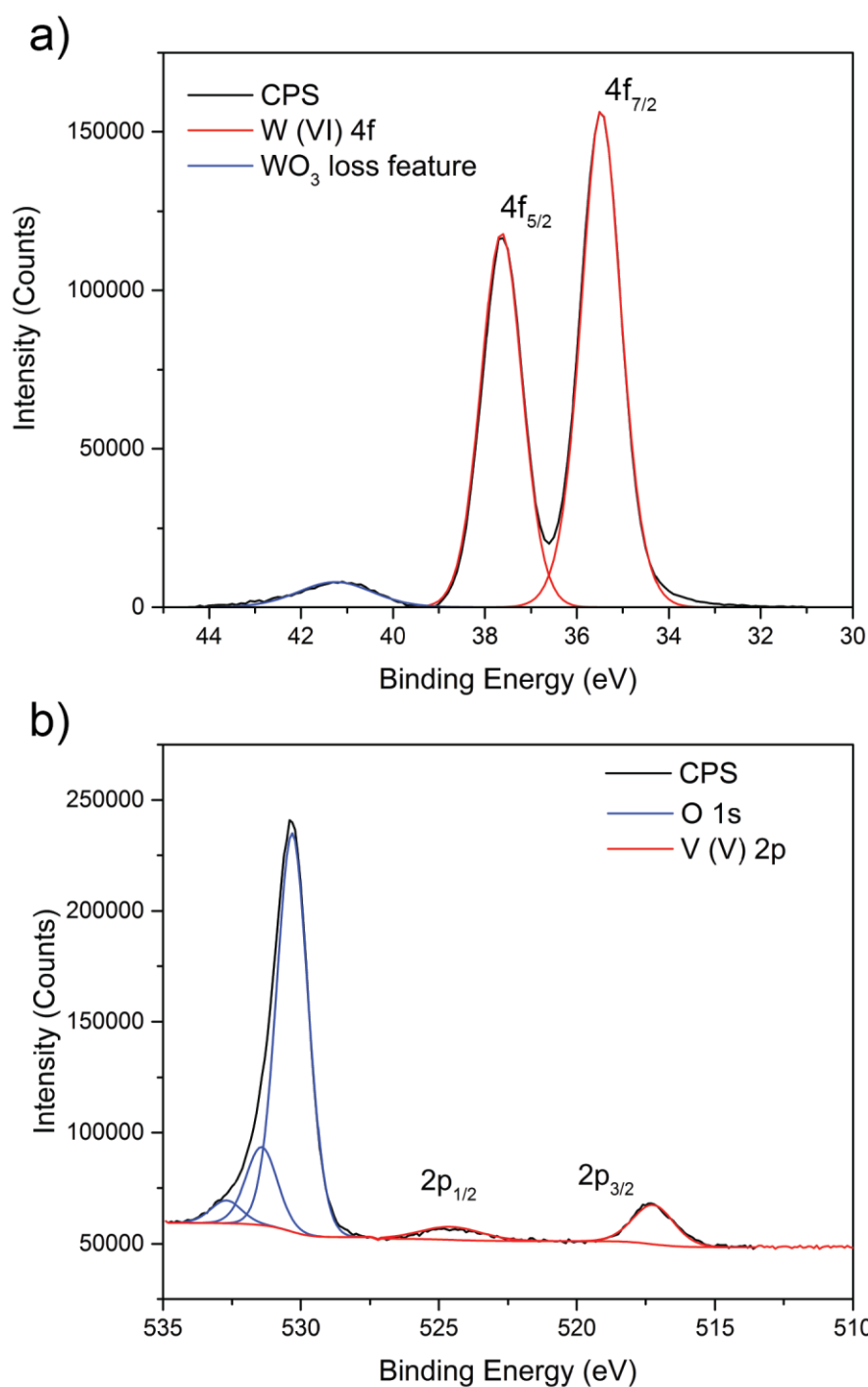
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352 **Figure 6: The XRD pattern of the tungsten films deposited using the POMs  $[\text{Bu}_4\text{N}]_4[\text{PVW}_{11}\text{O}_{40}]$**   
353 **(3) and  $[\text{Bu}_4\text{N}]_5[\text{PV}_2\text{W}_{10}\text{O}_{40}]$  (4).**

354  
355 A minor shift in the XRD pattern was observed when compared to a standard  $\text{WO}_3$   
356 pattern.<sup>[32]</sup> Films from (3) and (4) were fitted to a Le Bail refined model which  
357 indicated that the unit cell of (3) shows a minor contraction of 0.23%, however this is  
358 within error hence the unit cell size volume remains similar (Table 5). The unit cell of  
359 (4) had expanded by ~3%, indicating possible interstitial doping of V into the  $\text{WO}_3$   
360 unit cell as  $\text{V}^{5+}$  has a smaller ionic and crystal radii than  $\text{W}^{6+}$  (Table 5).

361  
362 **Table 3: Lattice parameters of films deposited from POMs  $[\text{Bu}_4\text{N}]_4[\text{PVW}_{11}\text{O}_{40}]$  (3) and**  
363  **$[\text{Bu}_4\text{N}]_5[\text{PV}_2\text{W}_{10}\text{O}_{40}]$  (4) calculated from XRD data *via* the Le Bail method.**

Film	a / Å	b / Å	c / Å	Unit Cell Volume / Å <sup>3</sup>	Volume Change / %
$[\text{Bu}_4\text{N}]_4[\text{PVW}_{11}\text{O}_{40}]$ (3)	7.281(1)	7.5429(3)	7.6975(7)	422.77(7)	0.23(3)
$[\text{Bu}_4\text{N}]_5[\text{PV}_2\text{W}_{10}\text{O}_{40}]$ (4)	7.400(1)	7.5932(9)	7.755(1)	435.72(11)	2.83(1)

364  
365 XPS analysis showed the presence of W and V in the AACVD grown  $\text{WO}_3$  films (3)  
366 and (4) (Figure 7). The W 4f7/2 peak was at 35.5 eV and 35.3 eV respectively, thus  
367 confirming the presence of  $\text{W}^{+6}$ .<sup>[33]</sup> The peak for V2p3/2 appears at 517.2 eV  
368 matching to  $\text{V}^{+5}$ .<sup>[34]</sup>



369

370 **Figure 7: a) The XPS spectrum for W 4f (film (3)) showing the 4f<sub>7/2</sub> peak positioned at 35.5 eV -**  
 371 **matching W<sup>+6</sup>. b) The V in films from (3) and (4) was in the +5 oxidation state as evident from the**  
 372 **V 2p<sub>3/2</sub> peak being centered at 517.2 eV.**

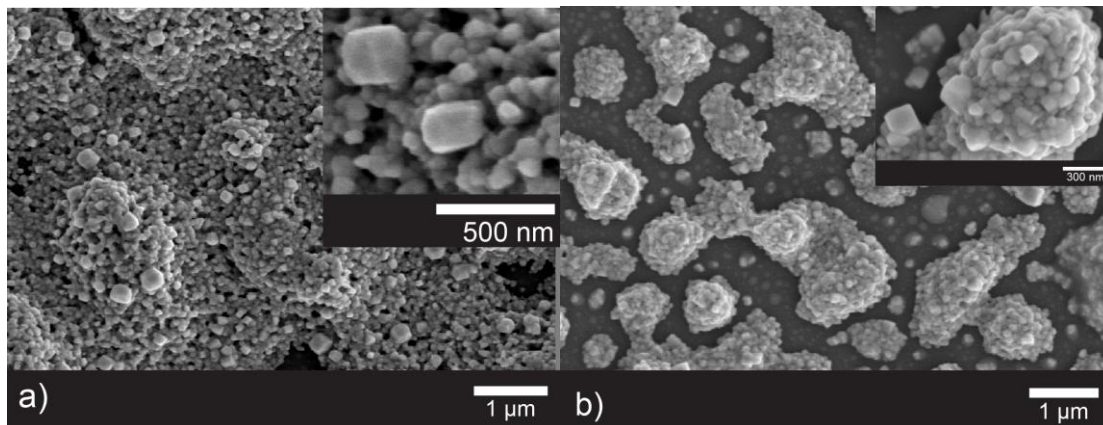
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374 **The morphology of films (3) and (4) is shown in Figure 8. Film (3) consists of a**  
 375 **porous network of particles that are 250 nm or smaller which cover the whole area**  
 376 **analysed. Film (4) is however composed of clusters of WO<sub>3</sub> which are made up of**

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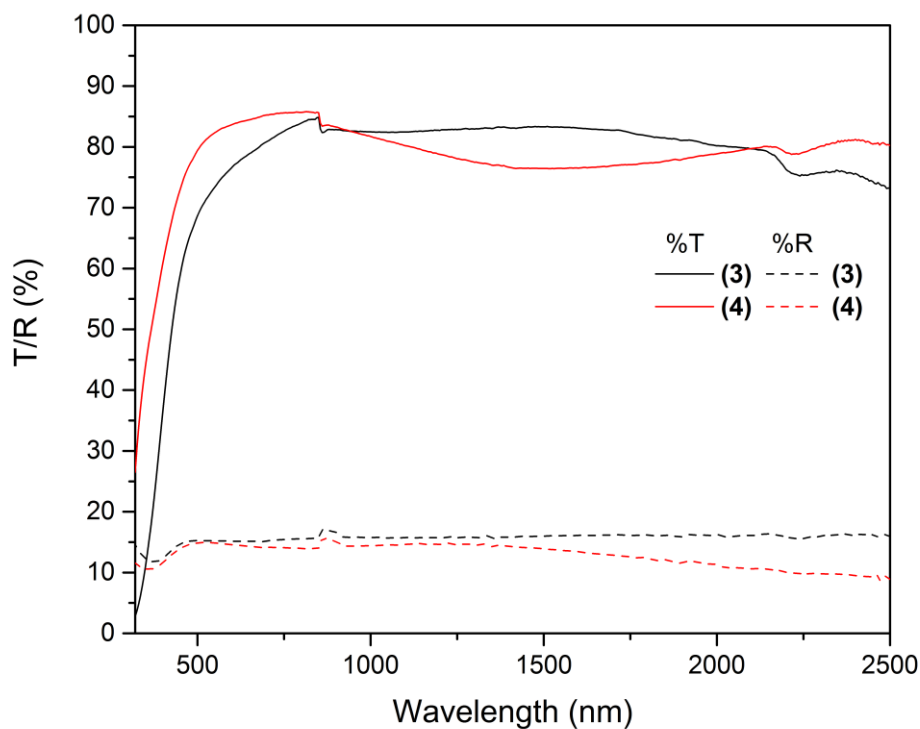


377 particles that up to 250 nm in width. Both films have varying morphologies even  
 378 though they consist of  $\text{WO}_3$  which, as with films (1) and (2), is due to the nature of  
 379 the POM used to deposit the films.



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 384 **Figure 8: SEM of the tungsten films, deposited using the POMs,  $[\text{Bu}_4\text{N}]_4[\text{PVW}_{11}\text{O}_{40}]$  (3) and**  
 385  **$[\text{Bu}_4\text{N}]_5[\text{PV}_2\text{W}_{10}\text{O}_{40}]$  (4).**

386  
 387 The maximum transmittance at 550 nm was observed to be  $\sim 85\%$  for the film  
 388 deposited from POM (4) whereas film (3) reached similar maxima but at a higher  
 389 wavelength (Fig. 7). In general, all films were found be poorly reflective ( $< 18\%$ ).



390

391 **Figure 9: The transmission (black) and reflectance (Red) spectra of the tungsten films deposited**  
392 **using the POMs, [<sup>n</sup>Bu<sub>4</sub>N]<sub>4</sub>[PVW<sub>11</sub>O<sub>40</sub>] (3) (solid line) and [<sup>n</sup>Bu<sub>4</sub>N]<sub>5</sub>[PV<sub>2</sub>W<sub>10</sub>O<sub>40</sub>] (4) (dashed line).**

393  
394 The band gaps of these films were calculated using the same method described for  
395 films **1** and **2** (see above). The band gaps were found to be 2.6 eV and 2.7 eV for  
396 films from POMs **(3)** and **(4)**, respectively, lower than the value (3.2 eV) for un-doped  
397 tungsten oxide films.<sup>[35]</sup> Although doping generally increases the band gap due to the  
398 Moss-Burstein effect,<sup>[18]</sup> there have been reports suggesting that doping vanadium  
399 into WO<sub>3</sub> can reduce the bandgap.<sup>[4a]</sup>

400

### 401 **Water contact angles**

402

403 Water contact angles were calculated for the films. Film from POM **(1)** had a water  
404 contact angle of 98.5° indicative of a hydrophobic nature whereas **(2)** had an angle of  
405 41.6° suggesting it is hydrophilic. The films differed in V atom content and  
406 morphology. Therefore, it would seem reasonable to suggest that the hydrophobicity  
407 of the film was reduced with greater V doping and/or film morphology (Fig. 3).  
408 Ashraf *et al.*<sup>[6]</sup> found MoO<sub>2</sub> films to have a water contact angle between 75-125° and a  
409 needle-like morphology. However, in the present study, it was the film from **(2)** that  
410 had a needle-like morphology (Fig. 3). The water contact angles for the W films **(3)**  
411 and **(4)** were much lower, with angles of 22.7° and 13.4°, respectively, suggesting that  
412 the films were hydrophilic in nature. These are in good agreement with literature  
413 values for WO<sub>3</sub> films annealed at 500 °C.<sup>[36]</sup>

414

415

### 416 **Conclusion**

417

418 The present study has showed the use of polyoxometalates, with general formula  
419 [PM<sub>12-x</sub>V<sub>x</sub>O<sub>40</sub>]<sup>n-</sup> (M=Mo or W), as single-source precursors to form vanadium doped  
420 metal-oxide films *via* aerosol assisted chemical vapour deposition. This technique was  
421 an advantageous method as the precursor only needed to be soluble in a suitable  
422 solvent and volatility was not a requirement. Depositions were carried out at 550 °C  
423 with methanol or acetonitrile as the solvent for Mo and W, respectively. The POMs  
424 **(1)** and **(2)** deposited films were amorphous and non-adherent. However, on annealing  
425 the films consisted of vanadium-doped MoO<sub>3</sub>. The films deposited using the tungsten  
426 POMs, **(3)** and **(4)**, also followed a similar trend with the as-deposited films being  
427 amorphous and after annealing they were characterised as vanadium-doped WO<sub>3</sub>. The

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2 428 range of film morphologies obtained had important implications on the water contact  
3 429 angles of the film.

4 430  
5 431 It can be concluded that POMs provide a single-source route to the formation of  
6 432 doped metal oxide films; furthermore controlled amounts of dopants could be  
7 433 incorporated, to some extent, into the film, which have implications on the functional  
8 434 properties.

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10 435  
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15 440 assistance in SEM and NMR, respectively.

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