Supporting Information (SI)

Multi-Electron Reduction of Wells-Dawson Polyoxometalate Films onto Metallic, Semiconducting and Dielectric Substrates

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**Figure S1.** FT-IR spectra of (NH$_4$)$_6$P$_2$Mo$_{18}$O$_{62}$ and (NH$_4$)$_6$P$_2$W$_{18}$O$_{62}$ (1% in KBr pellets).

FT-IR peaks of (NH$_4$)$_6$P$_2$Mo$_{18}$O$_{62}$ (Fig. S1a): 3484 and 3150 cm$^{-1}$, strong, broad bands attributed to N–H stretching vibrations (non-bonded, antisymmetric and symmetric; $v_{as}$ and $v_s$ respectively) of NH$_4^+$ cations; 1616 and 1400 cm$^{-1}$, strong, broad bands ascribed to N–H bending vibrations (antisymmetric and symmetric; $\delta_{as}$ and $\delta_s$ respectively) of NH$_4^+$ cations; 1077 cm$^{-1}$, $v_{as}$ of P–O$_a$ bonds; 1003 and 938 cm$^{-1}$, $v_s$ and $v_{as}$ of Mo=O$_d$ bonds respectively; 905 cm$^{-1}$, $v_{as}$ of Mo–O$_b$–Mo bridges; 772 cm$^{-1}$, $v_{as}$ of Mo–O$_c$–Mo bridges.$^{36-41,44}$

FT-IR peaks of (NH$_4$)$_6$P$_2$W$_{18}$O$_{62}$ (Fig. S1b): 3567 and 3149 cm$^{-1}$, strong, broad bands attributed to $v_{as}$ and $v_s$ of N–H bonds of NH$_4^+$ cations respectively; 1616 and 1400 cm$^{-1}$, strong, broad bands ascribed to $\delta_{as}$ and $\delta_s$ of N–H bonds of NH$_4^+$ cations respectively; 1090 cm$^{-1}$, $v_{as}$ of P–O$_a$ bonds; 961 cm$^{-1}$, $v_{as}$ of W=O$_d$ bonds; 915 cm$^{-1}$, $v_{as}$ of W–O$_b$–W bridges; 781 cm$^{-1}$, $v_{as}$ of W–O$_c$–W bridges.$^{38,40,44-46}$
Figure S2. $^{31}$P NMR spectra of (NH$_4$)$_6$P$_2$Mo$_{18}$O$_{62}$ and (NH$_4$)$_6$P$_2$W$_{18}$O$_{62}$ (in D$_2$O).

$^{31}$P NMR peaks of (NH$_4$)$_6$P$_2$Mo$_{18}$O$_{62}$ (Fig. S2a): a single peak with high intensity at -2.5743 ppm attributed to [P$_2$Mo$_{18}$O$_{62}$]$^{6-}$ anion, indicating only one component.$^{[41-43]}$

$^{31}$P NMR peaks of (NH$_4$)$_6$P$_2$W$_{18}$O$_{62}$ (Fig. S2b): a peak with high intensity peak at -12.4856 ppm attributed to α-[P$_2$W$_{18}$O$_{62}$]$^{6-}$ isomer (~95% of total amount);$^{[42,47]}$ two small peaks at -10.9884 and -11.7999 ppm attributed to β-[P$_2$W$_{18}$O$_{62}$]$^{6-}$ isomer (<5%).$^{[42,48]}$
Figure S3. XPS spectra of thick POM films: (a) H₃PW₁₂O₄₀, (b) H₃PMo₁₂O₄₀, (c) (NH₄)₆P₂W₁₈O₆₂, and (d) (NH₄)₆P₂Mo₁₈O₆₂, onto Al-coated Si wafers. (POM concentration, 5 mg ml⁻¹ in MeOH; drop casting at RT; 10-nm-thick Al film; 5-nm-thick SiO₂ film.)
Figure S4. UPS spectra of thick POM films: (a) H₃PW₁₂O₄₀, (b) H₃PMo₁₂O₄₀, (c) (NH₄)₆P₂W₁₈O₆₂, and (d) (NH₄)₆P₂Mo₁₈O₆₂, onto Al-coated Si wafers. The work function ($W_F$) and the HOMO energy level ($E_{HOMO}$) values of POMs are depicted in the spectra (left and right values respectively). The ionization energy ($I_E$) value of POMs results from the sum: $W_F + E_{HOMO}$. (POM concentration, 5 mg ml⁻¹ in MeOH; drop casting at RT; 10-nm-thick Al film; 5-nm-thick SiO₂ film.)
Figure S5. UV-Vis monitoring of POM films: (a) (NH₄)₆P₂Mo₁₈O₆₂ and (b) (NH₄)₆P₂W₁₈O₆₂, onto Al-coated quartz slides, upon increase of POM film thickness. In all cases the change of IVCT band of POMs is shown. The increase of POM film thickness was realized as follows: (A, D) spin-coating of a 5 mg ml⁻¹ POM solution, (B, E) spin-coating of a 10 mg ml⁻¹ POM solution, and (C, F) solvent-evaporation of a 5 mg ml⁻¹ POM solution. (c) UV-Vis spectrum of an Al–coated quartz slide. (POM concentration, 5–10 mg ml⁻¹ in MeOH; spin-coating, 600–700 rpm, 30–40 s; drop casting at RT; no thermal treatment applied; 5–10 nm thick Al film.)

The effect of POM film thickness on the reduction degree of (NH₄)₆P₂Mo₁₈O₆₂ film onto Al substrate was investigated with UV-Vis spectroscopy (Fig. S5a). As shown in this figure, a ~2nm-thick (NH₄)₆P₂Mo₁₈O₆₂ film formed by spin coating of a 5 mg ml⁻¹ POM solution, exhibits an IVCT band at 684 nm indicating a reduction degree of ~4e⁻. Gradual
increase of film thickness (slightly higher than 2 nm and formed by spin-coating of a 10 mg ml\(^{-1}\) POM solution) results in red-shift of IVCT band (684→692 nm) indicating decrease in the reduction degree (2\(\rightarrow\)4e\(^{-}\)).\(^{36,50}\) A much higher increase of film thickness (e.g. by drop casting of a 5 mg ml\(^{-1}\) POM solution) induces further red-shift of IVCT band (692→697 nm) showing additional decrease in reduction degree (2\(\rightarrow\)4e\(^{-}\)). Similar results were also obtained with the increase of \((\text{NH}_4)_6\text{P}_2\text{W}_{18}\text{O}_{62}\) film thickness (Fig. S5b), although in that case larger red-shifts of IVCT band and therefore higher decrease in the reduction degree was observed. Thus, it seems that the following general rule is valid: the lower the POM film thickness the higher the reduction degree of Wells-Dawson POMs onto Al substrates.
Figure S6. UV-Vis monitoring of POM films: (a) a thick (NH₄)₆P₂Mo₁₈O₆₂ film, (b) a thick (NH₄)₆P₂W₁₈O₆₂ film, and (c) a thin H₄SiW₁₂O₄₀ film, onto Al-coated quartz slides, upon increase of thermal treatment temperature. In (a, c) the change of IVCT band of POMs is shown, whereas in (b) the change of both IVCT and OMCT bands of POM is presented. ((a, b) POM concentration, 5 mg ml⁻¹ in MeOH; solvent evaporation at RT; thermal treatment in air, at a temperature range of RT-190 °C, for 5 min; stay in air at RT, 60 min. (c) POM concentration, 10 mg ml⁻¹ in MeOH; spin coating, 700 rpm, 30 s; thermal treatment in air, at a temperature range of RT-190 °C, for 5 min; 10-nm-thick Al film.)

The effect of thermal treatment temperature on the reduction of thick (NH₄)₆P₂Mo₁₈O₆₂ film onto Al substrate, was studied with UV-Vis spectroscopy (Fig. S6a). Initially the thick (NH₄)₆P₂Mo₁₈O₆₂ film is less reduced (~4e⁻) than the thin respective film, based on the IVCT band position (697 vs. 692 nm respectively; Figs. S6a vs. 2a).[7,36,50] Upon increase of thermal treatment temperature, the IVCT band of the thick (NH₄)₆P₂Mo₁₈O₆₂ film
decreases in intensity and red-shifts until complete elimination indicating thermal reoxidation of the film (by dioxygen) in a way similar to the thin respective film. Similar IVCT results were also obtained for the thermal reoxidation of a thick (NH₄)₆P₂W₁₈O₆₂ film onto Al substrate (Fig. S6b right). Furthermore, upon increase of thermal treatment temperature of a thick (NH₄)₆P₂W₁₈O₆₂ film onto Al substrate, a large increase in intensity of the OMCT band at ~318 nm attributed to O_b,c→W CT is observed (Fig. S6b left) indicating reformation of W–O_b,c–W bridges and thermal reoxidation of that film. Similar IVCT band observations were also made for the thermal reoxidation of thin H₄SiW₁₂O₄₀ film onto Al substrate (Fig. S6c).[19,45,50]
Figure S7. UV-Vis spectra of thin POM films: (a) H$_3$PW$_{12}$O$_{40}$, (b) H$_3$PMo$_{12}$O$_{40}$, (c) (NH$_4$)$_6$P$_2$W$_{18}$O$_{62}$, and (d) (NH$_4$)$_6$P$_2$Mo$_{18}$O$_{62}$, onto bare quartz slides. The energy gap ($E_g$) value of each POM is calculated from the corresponding spectrum as the ratio of 1240/threshold absorption (nm) of the OMCT band in the near-visible area.$^{[63]}$ POM concentration, 10 mg ml$^{-1}$ in MeOH; spin-coating, 600-700 rpm, 40-120 s; no thermal treatment applied.)
Table S1. Energy levels’ values of POMs deduced from the UPS spectra of POM films on Al substrates (Figure S4) and the UV-Vis spectra of POM films on SiO₂ substrates (Figure S7). The LUMO values ($E_{LUMO}$) of POMs result from the subtraction: $I_E - E_g$. The energy levels’ values in parenthesis are the corresponding values, which were resulted also from experimental measurements (UPS, UV-Vis) and published in a previous publication of our group.$^{[28]}$

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<th>POMs</th>
<th>$W_F$</th>
<th>$E_{HOMO}$</th>
<th>$I_E$</th>
<th>$E_g$</th>
<th>$E_{LUMO}$</th>
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<td>$\text{H}<em>3\text{PW}</em>{12}\text{O}_{40}$</td>
<td>6.1 (5.7)</td>
<td>2.7 (2.3)</td>
<td>8.8 (8.0)</td>
<td>3.9 (3.4)</td>
<td>4.9 (4.6)</td>
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<tr>
<td>$\text{H}<em>3\text{PMo}</em>{12}\text{O}_{40}$</td>
<td>5.4 (5.8)</td>
<td>2.8 (2.2)</td>
<td>8.2 (8.0)</td>
<td>3.1 (2.9)</td>
<td>5.1 (5.1)</td>
</tr>
<tr>
<td>($\text{NH}_4$)$<em>6\text{P}<em>2\text{W}</em>{18}\text{O}</em>{62}$</td>
<td>6.2 (5.8)</td>
<td>2.5 (2.5)</td>
<td>8.7 (8.3)</td>
<td>3.4 (3.1)</td>
<td>5.3 (5.2)</td>
</tr>
<tr>
<td>($\text{NH}_4$)$<em>6\text{P}<em>2\text{Mo}</em>{18}\text{O}</em>{62}$</td>
<td>5.9 (5.8)</td>
<td>3.0 (2.3)</td>
<td>8.9 (8.1)</td>
<td>3.0 (2.6)</td>
<td>5.9 (5.5)</td>
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From the above Table it is observed that almost all the energy levels’ values of POMs obtained in the present work are slightly higher than the corresponding values reported in our previous publication.$^{[28]}$ This result was attributed to the higher film thickness and lower homogeneity of POM films in the present case, due to the use of drop casting (instead of spin-coating)$^{[28]}$ as a film coating method of POMs. Anyway, in both cases the trend of the energy levels’ values of POMs is the same.
Figure S8. XPS spectrum of a thick (NH$_4$)$_6$P$_2$Mo$_{18}$O$_{62}$ film onto SiO$_2$-coated Si wafer. (POM concentration, 5 mg ml$^{-1}$ in MeOH; solvent evaporation at RT; no thermal treatment applied; 5-nm-thick SiO$_2$ film.)

The most reducible Wells-Dawson POM film, (NH$_4$)$_6$P$_2$Mo$_{18}$O$_{62}$, was found to be in oxidized state onto SiO$_2$, as shown in its XPS spectrum (Fig. S8).
**Figure S9.** UV-Vis monitoring of POM films: (a) a thin (NH₄)₆P₂W₁₈O₆₂ film, (b) a thin H₄SiW₁₂O₴₀ film, and (c) a thick (NH₄)₆P₂Mo₁₈O₆₂ film, onto bare quartz slides, upon increase of thermal treatment temperature. In (a, b) the whole spectra are presented, whereas in (c) only the IVCT band is shown. ((a, b) POM concentration, 10 mg ml⁻¹ in MeOH; spin coating, 700 rpm, 30 s; thermal treatment in air, at a temperature range of RT-190 °C, for 5 min. (c) POM concentration, 5 mg ml⁻¹ in MeOH; solvent evaporation at RT; thermal treatment in air, at a temperature range of RT-190 °C, for 5 min; stay at RT, 60 min.)

Upon increase of thermal treatment temperature in thin POM films, (NH₄)₆P₂W₁₈O₆₂ and H₄SiW₁₂O₴₀, onto SiO₂ substrates, no IVCT band appears indicating that those films are not reduced (Fig. S9a, b). In contrast, the thick (NH₄)₆P₂Mo₁₈O₆₂ film is reduced onto SiO₂ substrate upon increase of thermal treatment temperature; though it is reduced to a lower degree (<2e⁻, based on the IVCT position) than the thin respective film (Figs. S9c vs. 6a).