

Electronic Supporting Information

Mo-doped TiO₂ photoanodes using [Ti₄Mo₂O₈(OEt)₁₀]₂ bimetallic oxo cages as a single source precursor

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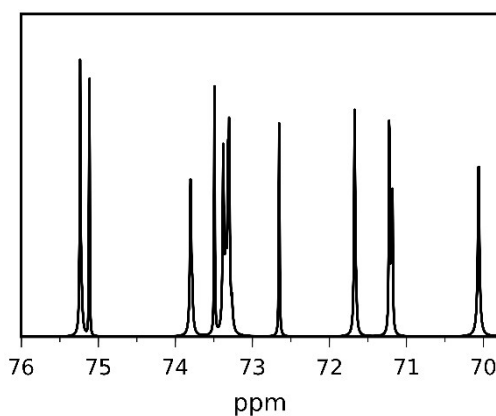


Fig. S1 ¹³C NMR spectra of the -OCH₂- resonance region of [Ti₄Mo₂O₈(OEt)₁₀]₂, in agreement with literature [1]

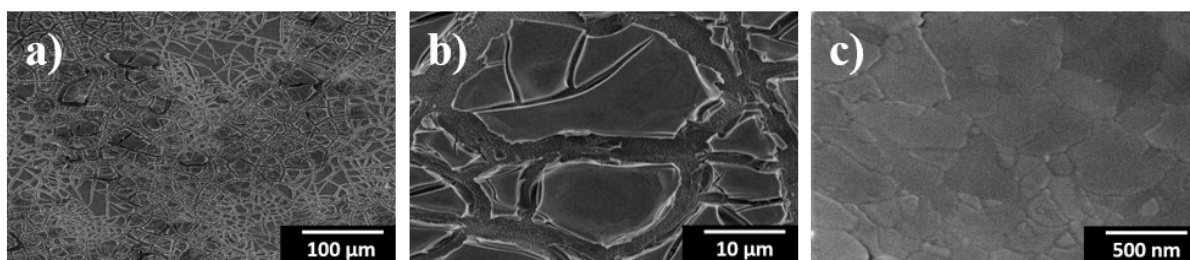


Fig. S2 SEM images of TiO₂-650 photoanode.

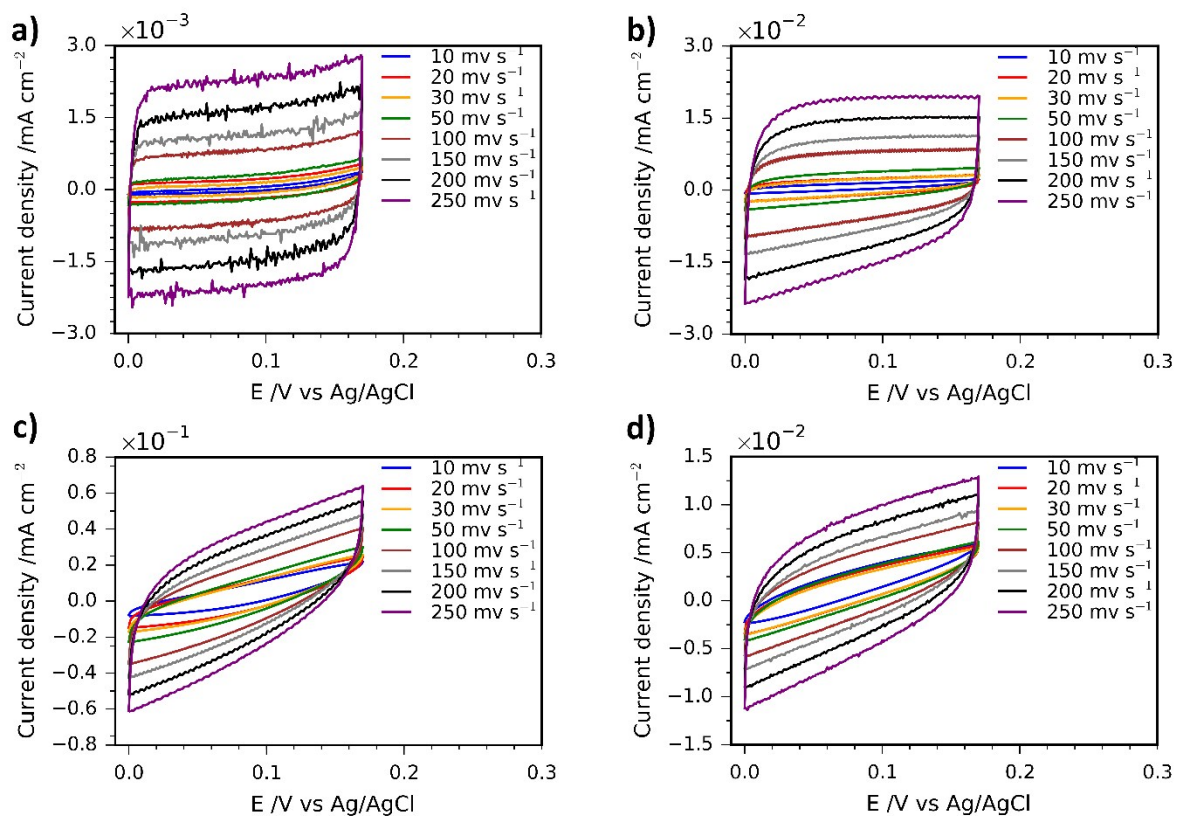


Fig. S3 Cyclic voltammetry curves for (a) TiO_2 -650, (b) Mo:TiO_2 -650, (c) Mo:TiO_2 -700 and (d) Mo:TiO_2 -800.

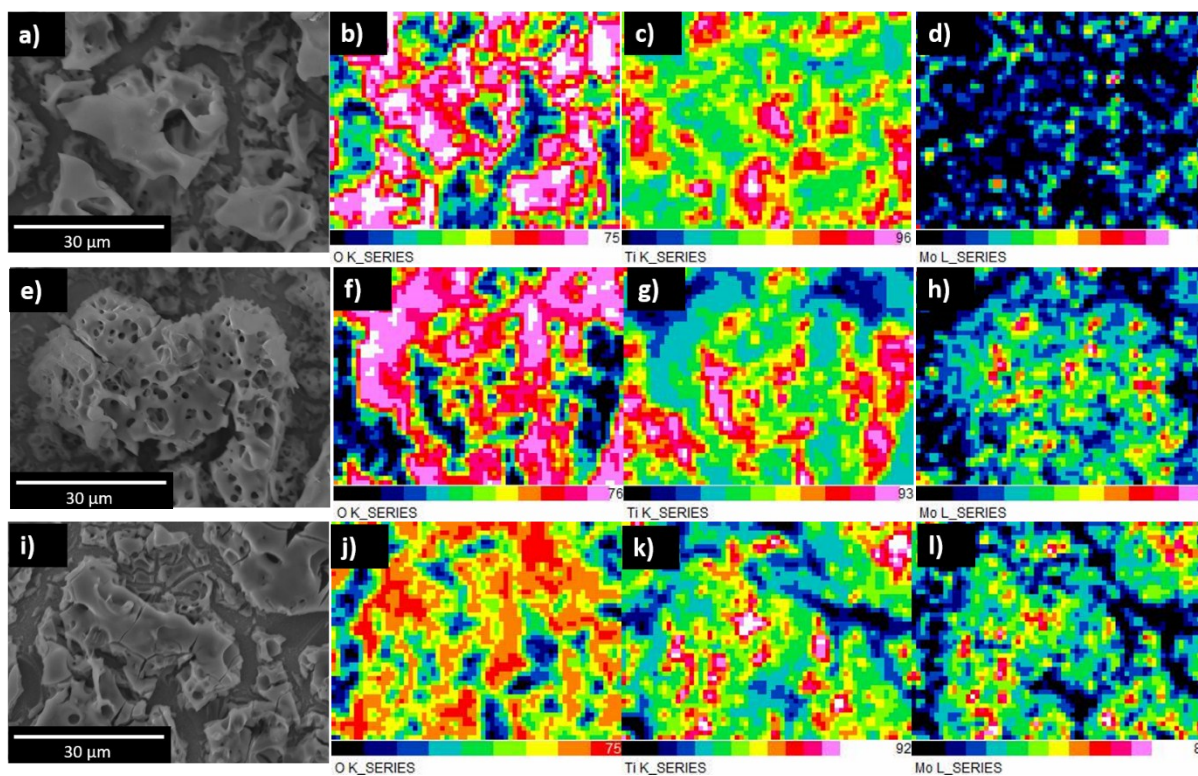


Fig. S4 SEM-EDXS images of Mo:TiO_2 photoanodes. (a-d) Mo:TiO_2 -800, (e-h) Mo:TiO_2 -700 and (i-l) Mo:TiO_2 -650.

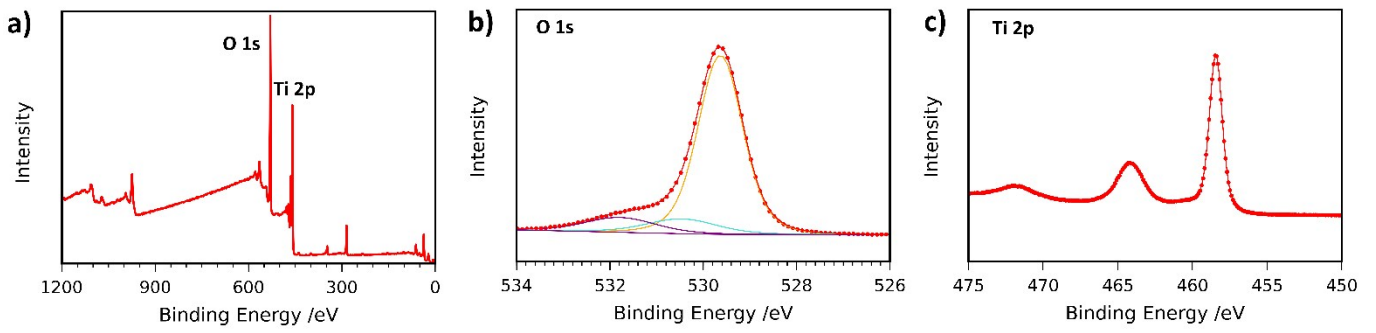


Fig. S5 XPS spectra of TiO₂-650. (a) Survey, (b) O 1s and (c) Ti 2p.

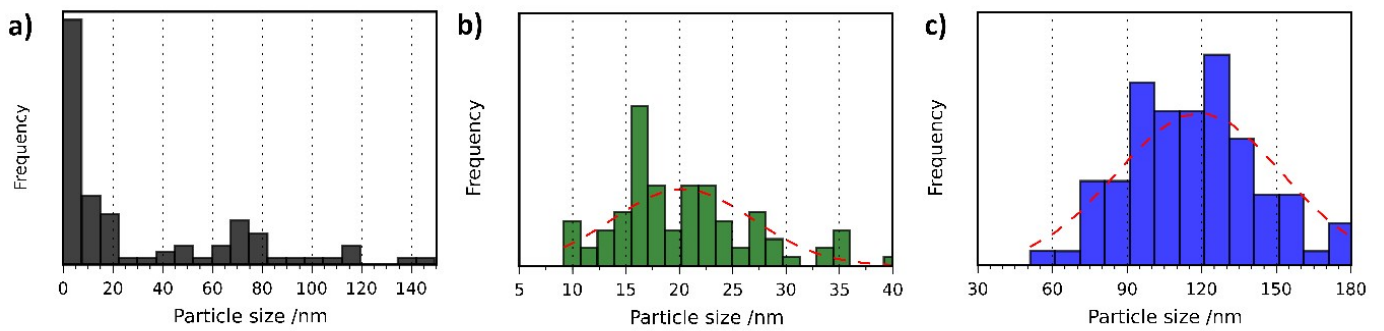


Fig. S6 Particle size distributions. (a) Mo:TiO₂-650, (b) Mo:TiO₂-700 and (c) Mo:TiO₂-800.

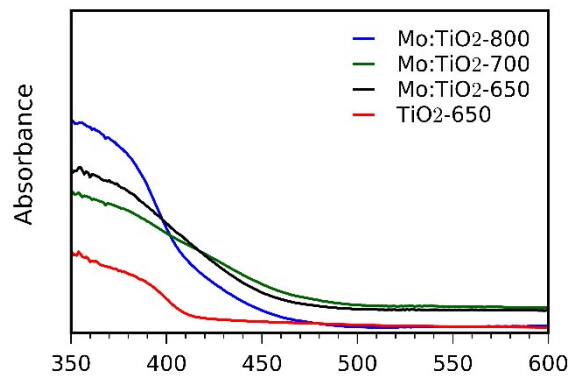


Fig. S7 Diffuse reflectance UV-Vis absorption spectra of Mo:TiO₂-650, Mo:TiO₂-700, Mo:TiO₂-800 and pure TiO₂-650 photoanodes.

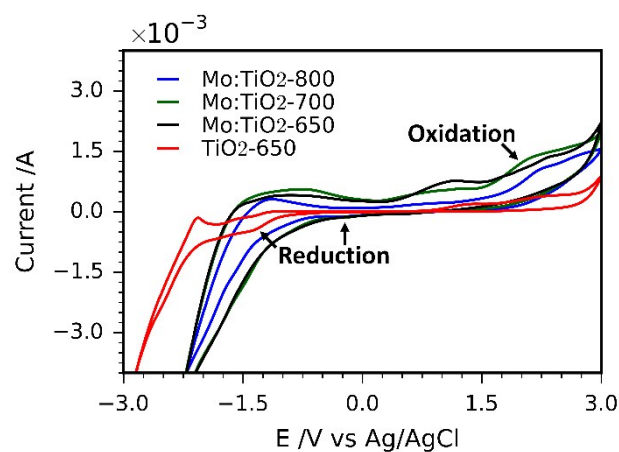


Fig. S8 Cyclic Voltammetry curves of TiO₂-650 and Mo:TiO₂ photoanodes in acetonitrile containing 0.1M of TBAPF₆ at a scan rate of 50 mv s⁻¹.

Table S1 Electrochemical characteristics of the bare TiO₂ and Mo:TiO₂ photoanodes.

Sample	E ^{ox} _{peak} (V)/ VB (eV)	E ^{red} _{peak} (V)/ CB (eV)	E _g (eV)
Mo:TiO ₂ -650	2.32 / -6.69	-0.19 / -4.18	2.51
Mo:TiO ₂ -700	2.08 / -6.45	-0.22 / -4.15	2.30
Mo:TiO ₂ -800	2.23 / -6.60	-0.23 / -4.14	2.46
TiO ₂ -650	2.22 / -6.59	-1.36 / -3.01	3.58

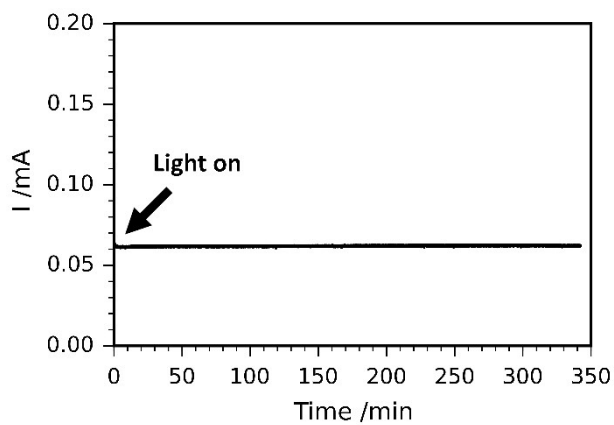


Fig. S9 Photocurrent-time curve of Mo:TiO₂-700 obtained during the O₂ measurement experiment at 1.23V_{RHE}.

Faradaic efficiency calculation

To calculate the Faradaic efficiency, first the amount of O₂ evolved in the headspace of the PEC cell was calculated using the ideal gas law and the %O₂ measurements. Next, the theoretical amount of O₂ expected for a water oxidation reaction with 100% Faradaic efficiency was calculated. The following equation was used:

$$Q = n(e^-) * F$$

where Q is the charge in C, obtained from the photocurrent-time curve (Fig. S12); $n(e^-)$ is the number of electrons in mol; and F is the Faraday constant (96485.3329 C mol⁻¹). The theoretical amount of O₂ generated was calculated by dividing $n(e^-)$ by four, which is the number of electrons involved in the oxidation of water. Finally, the Faradaic efficiency was calculated by dividing the amount of O₂ evolved in the headspace by the theoretical amount of O₂ expected for 100% Faradaic efficiency ($\mu\text{mol}/\mu\text{mol} \times 100$).²

- 1 S. Eslava, B. P. R. Goodwill, M. McPartlin and D. S. Wright, *Inorg. Chem.*, 2011, **50**, 5655–5662.
- 2 J. A. Seabold and K.-S. Choi, *Chem. Mater.*, 2011, **23**, 1105–1112.