**Data collection method**

X-Ray diffraction (XRD) patterns were collected in the 2 Theta range 10-80° with a Bruker AXS D8 Advance using Cu Kα (0.154 nm) radiation with a total integration time of 960 s. Raman spectroscopy was carried out on a Renishaw inVia system using a 532 nm diode-pumped solid state laser (DPSS) manufactured by Cobolt. The laser beam was focused onto the sample using a 50x long distance objective. X-Ray photoelectron spectroscopy (XPS) depth profiling was performed using a ESCALAB 250 Xi instrument manufactured by Thermo Fisher Scientific. Measurements were carried out using a monochromated Al Kα X-Ray source with an energy of 1486.68 eV. The X-Ray spot size was of 900 µm and the pass energy for the high resolution scans was of 50 eV. The depth profile for the sample was obtained by etching the surface of the sample with an Ar⁺ ion gun (2000 eV, high current) for different times (0, 60, 180 and 420 s). C 1s XPS spectra was used as an internal charge correction. Samples studied via electron paramagnetic resonance (EPR) spectroscopy were evacuated at 393 K for over 12 h to reduce the influence of physisorbed water. Samples were maintained under static vacuum (10⁻⁵ mbar) for the duration of the experiments. For EPR analysis, powder samples were prepared by drying and calcining in air at 650, 700 and 800°C in a porcelain dish a solution of 0.96 g of [Ti₄Mo₂O₈(OEt)₁₀]₂ in 20 ml of anhydrous tetrahydrofuran. High resolution transmission electron microscopy (HRTEM) images were obtained using a JEOL JEM-2100Plus microscope. Ultraviolet-visible (UV-Vis) spectra were collected in a Cary 100 diffuse reflectance UV-Vis spectrophotometer.

*(Photo)*Electrochemical measurements

*(Photo)*electrochemical performance of photoanodes was evaluated using a CompactStat, potentiostat (Ivium Technologies). Photocurrents were measured under simulated sunlight (AM 1.5G, 100 mWcm⁻²) from a filtered 300W Xenon lamp source (Lot Quantum Design) or under UV illumination (365 nm, 3.6 mWcm⁻²) from a ModuLight IM3412 LED light (Ivium Technologies). PEC cells consisted of three electrodes with Pt as the counter electrode, silver chloride (Ag/AgCl/3.5M KCl) as the reference electrode and as-prepared photoanodes as the working electrodes.

Electrochemically active surface area (ECSA) of photoanodes was investigated using cyclic voltammetry (CV), scanning from 0 to 0.17 V_{Ag/AgCl} at scan rates
between 10 and 250 mV s\(^{-1}\), in 1M KOH solution (pH=13.7). ECSA is proportional to the double layer capacitance (\(C_{dl}\)), which is estimated from the slope of the plot \(\Delta j\) vs. scan rate and dividing by two. \(\Delta j\) is equal to \((j_a-j_c)\), where \(j_a\) and \(j_c\) are the anodic and cathodic current densities, respectively, in this case taken at 0.1V\textsubscript{Ag/AgCl} in the CV scans.

Conduction and valence band (CB & VB) positions were measured from CV curves recorded in acetonitrile containing 0.1M of tetrabutylammonium hexafluorophosphate (TBAPF6) at a scan rate of 50 mV s\(^{-1}\) and using the following formula:

\[
CB \text{ (or VB)} \ (eV) = -4.8 - (E - E_{1/2})
\]

where \(E\) is the onset of the redox potential and \(E_{1/2}\) is the formal potential of \(\text{F}_2/\text{F}_2^+\) system (0.43 V\textsubscript{Ag/AgCl}).

Photoelectrochemical performances of photoanodes were carried out in a 1M KOH (pH=13.7) electrolyte solution. Illumination was directed towards the back of the FTO-ABS working electrode and a mask was placed on top of the photoelectrode to define the illuminated area. Photocurrent-time curves were performed at an applied bias of 1.23 V vs the reversible hydrogen electrode (V\textsubscript{RHE}). Photocurrent-potential curves were recorded at a scan rate of 20 mV s\(^{-1}\). The measured Ag/AgCl potentials (\(E_{Ag/AgCl}\)) were converted to RHE potentials (\(E^0_{RHE}\)) following the Nernst equation:

\[
E^0_{RHE} = E^0_{Ag/AgCl} + E_{Ag/AgCl} + 0.059pH
\]

where \(E^{0}_{Ag/AgCl}\) is 0.205 V at 25°C (3.5M KCl). Photoelectrochemical impedance spectroscopy (PEIS) was carried out under simulated sunlight (AM 1.5G, 100 mWcm\(^{-2}\)) at a direct current (DC) potential of 1.23 V\textsubscript{RHE} and an alternating current (AC) potential frequency range of 100000-0.01 Hz with an amplitude of 5 mV. Incident photon-to-current efficiency (IPCE) measurements were calculated using the same Xe light source and a triple grating Czerny-Turner monochromator. The intensity of monochromatic light was measured at the working electrode position with SEL033/U photodetector (International Light Technologies). The following equation was used to calculate the IPCE values:

\[
\text{IPCE} (\lambda) = \frac{|j (mA \ cm^{-2})| \times 1239.8 \ (V \ nm)}{P_{mono} \ (mW \ cm^{-2}) \times \lambda \ (nm)}
\]
where $j$ is the photocurrent density measured under single wavelength ($\lambda$) light illumination and $P_{\text{mono}}$ is the incident irradiation power. Oxygen ($O_2$) measurements were conducted using a Pyroscience FireStingO2 fibre-optic oxygen meter combined with a TROXROB10 oxygen probe, together with a TDIP temperature sensor to give automatic compensation for minor fluctuation in the PEC cell temperature. $O_2$ readings were recorded every 10 min for ca. 410 min. The probe was fitted into the headspace of the airtight PEC cell. The PEC cell was purged with a $N_2$ flow to ensure air $O_2$ removal before the irradiation started. The measurements were carried out under simulated sunlight (AM 1.5G, 100 mW cm$^{-2}$) with an applied bias of 1.23 V$_{\text{RHE}}$. Light was irradiated for 340 min. The Faradaic efficiency was calculated by dividing the measured amount of evolved $O_2$ by the theoretical amount of expected $O_2$ for measured photocurrents (assuming 100% Faradaic efficiency).