Photocatalyst Sheet Performance Under IntenseUV Irradiation and Increased TemperaturesSupplementary Information

Talib M. Rahman^a, D. J. Osborn III^a, Anthony E. Pellicone^a, Patrick C. Tapping^a, Tsuyoshi Takata^b, Takashi Hisatomi^b, Hiroshi Nishiyama^c, Kazunari Domen^c, Gunther G. Andersson^d, Gregory F. Metha^a*

^a Department of Chemistry, School of Physics, Chemistry and Earth Sciences, University of Adelaide, Australia

^b Research Initiative for Supra-Materials (RISM), Shinshu University, Japan

^c Office of University Professors, The University of Tokyo, Japan

^d Flinders Institute for NanoScale Science and Technology, Flinders University, Australia

SI SECTION I: ADDITIONAL FIGURES



Figure SI-1: H₂ production of the photocatalyst sheet with time for increasing illumination. Legend is in units of $\times 10^{19}$ photons cm⁻²·hr⁻¹.



Figure SI-2: a) Arrhenius fitting of four increasing light intensities for temperatures ranging from 23–120 °C. Light intensities are in units of $\times 10^{19}$ photons·cm⁻²·hr⁻¹. Inset includes standard errors for 1.75×10^{19} photons·cm⁻²·hr⁻¹ b) Apparent activation energies calculated for each light intensity depicted in a).



Figure SI-3: Plot of $-\log K_w$ vs temperature for saturated water. For temperatures above 100 °C pressure equal to the saturated pressure of water is applied to maintain liquid water. Reproduced using: Bandura, A. V. & Lvov, S. N. The Ionization Constant of Water over Wide Ranges of Temperature and Density. J. Phys. Chem. Ref. Data 35, 15-30, doi:10.1063/1.1928231 (2006).

Table SI-1: Ion concentrations at temperatures for saturated water and the ratio of the increase in ion concentration relative to ambient.

Temperature °C	[H ⁺]/[OH ⁻]	Ratio increase in ion concentration
23	9.260E-08	1
35	1.416E-07	1.529
50	2.344E-07	2.532
75	4.467E-07	4.824
90	6.095E-07	6.583
120	9.931E-07	10.73

SI SECTION II: ONE SUN EQUIVALENTS

Equating concentrated solar equivalents for photocatalyst performance under any light source requires three key data sets:

- 1) The absorbance of the photocatalyst as a function of wavelength (absorbance profile)
- 2) The spectral power density of the source of light used in the investigation
- 3) The spectral power density of the standard solar reference (Figure SI-4).

UV-visible DRS measurements of $CoO_y/RhCrO_x/Al:SrTiO_3$ nanoparticles were interpreted to give the Kubelka-Munk absorbance of the photocatalyst as a function of photon energy (Figure SI-5).



Figure SI-4: Standard reference spectra of ASTM G-173-03. Black line represents AM 1.5 G, global total spectral irradiance at 1000 W·m-2, and the red line represents AM 1.5 D, direct normal spectral irradiance at 900 W·m-2. Reproduced using: ASTM, A., 2008. G173: Standard Tables for Reference Solar Spectral Irradiance at Air Mass 1.5: Direct Normal and Hemispherical for a 37 Degree Tilted Surface



Figure SI-5: Normalised Kubelka-Munk function of UV-Vis DRS measurements of $CoO_{v}/RhCrO_{x}/Al$:SrTiO₃ nanoparticles (blue) and absorption fitting (black).

This KM-function shows an absorption tail, where absorption decreases as the photon energy decreases below the bandgap. This KM-function has been normalized and a fit function

applied. Assuming that the material absorbs all photons with energy above the bandgap, and that the absorption tail is due to the decreasing density of electron states as the photon energy falls below the bandgap, the KM-function has been approximated as the integral of a Gaussian function, or a cumulative normal distribution function, Eq. 1.

$$KM(x;\mu,\sigma) = \frac{1}{\sigma\sqrt{2\pi}} \int_{-\infty}^{x} exp\left(\frac{-(t-\mu)^2}{2\sigma^2}\right) dt$$
 Eq. 1

Where μ represents the photon energy, *x*, at which the material's absorption is at half-maximum (the band gap edge), and σ is the standard deviation of the normal distribution, representing homogeneous and inhomogeneous line broadening, or the slope of the absorption tail. The fitting of the KM function in Figure SI-3 was performed using a least squares method. The fitted KM function provides a well-defined, analytical expression of the absorption profile which can then be applied to the spectra of the light source used in the investigation, as well as the reference solar spectra. Note that for convenience, the KM function can be transformed from a photon energy to a wavelength axis to match the reference spectral data.

In order to count the number of absorbable photons in the reference spectrum, the vertical axis is transformed from spectral power density $(W \cdot m^{-2} \cdot nm^{-1})$ to spectral photon density (photons.hr⁻¹·cm⁻²·nm⁻¹) by dividing through by the photon energy. The KM function is then applied to determine the number of photons, Eq. 2

$$sparc = \int_0^\infty KM(\lambda; \mu, \sigma) \times P_{ref}(\lambda) \, d\lambda$$
 Eq. 2

Where $P_{ref}(\lambda)$ is the photon flux of the reference solar spectra as a function of wavelength.

For the purposes of this investigation, the standard solar equivalent used is ASTM G-173, AM 1.5D (Figure SI-4). AM 1.5D is the reference spectra most similar to that of concentrated sunlight, as this reference includes only direct normal spectral irradiance. Applying the absorption profile to the AM 1.5D reference spectra gives the number of absorbable photons for the Al:SrTiO₃ catalyst under one standard concentrated solar equivalent as 8.32×10^{18} photons $hr^{-1} \cdot cm^{-2}$, as shown in Figure SI-6. The authors refer to this as a Solar Equivalent.



Figure SI-6 Spectral photon density of reference spectra ASTM G-173-03, AM 1.5D (red), with usable photons based on the absorption function overlayed (green).

The Solar Equivalent can then be used to standardize the concentrated solar equivalent of the light source used, Eq. 3

Simulated Concentration Equivalent =
$$\frac{\int_{0}^{\infty} KM(\lambda;\mu,\sigma) \times P_{s}(\lambda) d\lambda}{\int_{0}^{\infty} KM(\lambda;\mu,\sigma) \times P_{ref}(\lambda) d\lambda} \qquad \text{Eq. 3}$$

Where $P_s(\lambda)$ is the photon flux of the light source used as a function of wavelength. For a monochromatic light source, such as that used in this investigation, Eq. 2 simplifies to

Monochromatic Sun Equivalent =
$$\frac{P_{\rm s}}{\int_0^\infty KM(\lambda;\mu,\sigma) \times P_{\rm ref}(\lambda) \, d\lambda}$$
 Eq. 4

Where $P_{\rm s}$ is the photon flux from the monochromatic source.

SI SECTION III: GIBBS FREE ENERGY OF WATER SPLITTING

Determining Gibbs free energy for water splitting at arbitrary temperatures and pressures has been explored extensively in literature, including by Wang and colleagues in their article "Efficiency Accreditation and Testing Protocols for Particulate Photocatalysts toward Solar Fuel Production".¹ A limitation of the body of work, and aforementioned article, is that it only considers pressure ranges between 0.05 and 1 bar. Using the same methodology expressed in literature, the Gibbs free energy for water splitting can be represented as a function of elevated temperature and pressures. To determine the Gibbs free energy of water splitting at elevated temperatures and pressures, $\Delta G_{H_2O \rightarrow H_2 + \frac{1}{2}O_2}(T, P)$ the equation is given by Eq. 5.^{1.1,5}

$$\Delta G_{H_2O \to H_2 + \frac{1}{2}O_2}(T, P) = G_{H_2}(T, P) + \frac{1}{2}G_{O_2}(T, P) - G_{H_2O}(T, P)$$
 Eq. 5

Here, $G_i(T, P)$ is the absolute molar Gibbs of species *i* at an arbitrary temperature *T* and total pressure *P*. Note that since the system is a mixture of chemicals, the total pressure *P* is the sum the partial pressures each species in the reaction for this case p_{H_2} , p_{O_2} and p_{H_2O} .⁶

The overall 3-dimensional plot over a wide range of pressures and temperatures is shown in Figure SI-5. For example, the $\Delta G_{H_2O \rightarrow H_2 + \frac{1}{2}O_2}(T, P)$ at 90 °C and 1.000 bar is 218.45 kJ·mol⁻¹ while at 120 °C and 1.985 bar the Gibbs free energy reduces to 193.40 kJ·mol⁻¹. The corresponding Gibbs free energy for the temperatures investigated within this paper can be found below in Table SI-1.



Figure SI-7: 3-dimensional plot of the calculated Gibbs free energy of water splitting in terms of total system pressure between 0.006–10 bar and temperatures between 273.15–450 K.

Temperature (°C and K)	Total Pressure (bar)	$\Delta G_{H_2 O \to H_2 + \frac{1}{2}O_2}$ (kJ.mol ⁻¹)
23 (296.15)	1.000	235.1
35 (308.15)	1.000	232.9
50 (323.15)	1.000	230.1
90 (363.15)	1.000	218.5
120 (393.15)	1.985	193.4

Table SI-2: Gibbs free energy values calculated at the temperatures and pressures investigated

ADDITIONAL REFERENCES

1 Wang, Z. et al. Efficiency accreditation and testing protocols for particulate photocatalysts toward solar fuel production. Joule 5, 344-359 (2021). https://doi.org:10.1016/j.joule.2021.01.001

2 Atkins, P. W., De Paula, J. & Atkins, P. W. Atkins' Physical Chemistry. 8th ed. edn, (Oxford University Press, 2017).

Stone, R. Introduction to Internal Combustion Engines Solutions Manual. 3rd ed. 1999.
 edn, (Macmillan Education UK, 1999).