Supplementary Information

Effects of size on the photocatalytic property of high-index faceted pseudocubic and rhombohedral $\alpha$-Fe$_2$O$_3$ nanocrystals

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Quantum yield calculation

$$\Phi = 4 \times \frac{\text{initial rate of O}_2 \text{ production (mol s}^{-1})}{\text{photo flux (mol s}^{-1})}$$

(4 photons absorbed per O$_2$).

Taking the Fe$_2$O$_3$-6.0 as an example

Using a wavelength of 420 nm, the intensity of light measured at 100 mW/cm$^2$, impinging on 7 cm$^2$ surface area. O$_2$ released at the 2 min reaction time was used for determining.

Energy of a single photon at 420 nm = $h.c/\lambda = 6.626 \times 10^{-34} \times 2.998 \times 10^8 / (420 \times 10^{-9}) = 4.730 \times 10^{-19}$ J
Total power absorbed = $7 \text{ cm}^2 \times 100 \text{ mW/cm}^2 \times 2 \times 60 \text{ s} = 84 \text{ J}$

Number of $O_2$ molecules produced = $7.32 \mu\text{mol} \times 6.022 \times 10^{23} = 4.41 \times 10^{18}$

Quantum Yield $O_2 = \frac{4.41 \times 10^{18}/(84 \text{ J}/4.73 \times 10^{-19} \text{ J})}{400} = 9.93 \%$

**Turn over Frequency calculation**

Taking the $Fe_2O_3$-6.0 as an example

Moles of Fe = $2 \times 5 \text{ mg}/159.6882 \text{ g mol}^{-1} = 6.26 \times 10^{-5}$ mol

The production of $O_2 = 7.32 \mu\text{mol} (2 \text{ min})$

$\text{TOF} = \frac{7.32 \mu\text{mol}}{6.26 \times 10^{-5} \text{ mol}/120 \text{ s}}$

$\text{TOF} = 0.97 \times 10^{-3} \text{ mol} (O_2)/\text{mol (Fe)} \text{ s}$

TOF for other catalysts were determined similarly.

The computational process of the valence band and conduction band of $\alpha$-$Fe_2O_3$:

\[ E_{CB} = X - E_C - \frac{1}{2} E_g \]

\[ X = \sqrt[3]{X_{Fe}^x \times X_O^y} \]

\[ = \sqrt[3]{4.06^2 \times 7.54^3} \]

\[ = 5.886 \text{ eV} \]

Taking the $Fe_2O_3$-6.0 as an example

$E_g = 1.964 \text{ eV}$

$E_{CB} = 5.886 - 4.5 - 0.5 \times 1.964$

\[ = 0.404 \text{ eV} \]

$E_{VB} = E_{CB} + E_g$

\[ = 0.404 + 1.964 \]

\[ = 2.368 \text{ eV} \]