### Supplementary Information for Semiconductor/Mixed Ion & Electron Conductor

### Heterojunction for Elevated-Temperature Water Splitting

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## S1. Justification of the assumption of fast electronic and ionic transport

In order to highlight the influence of the absorber/MIEC and the MIEC/gas interfaces on the efficiency, and to use a 1-D approximation in our model, we assumed that the electronic and ionic transport are fast in the MIEC. As we show below, the fast transport assumption is valid, especially at elevated temperature. Figure S1 shows typical dimensions of our proposed device, and Figure S2 shows the ionic and electronic transport overpotentials (at 2 A cm<sup>-2</sup>, a typical current density under 200 suns) as a function of temperature for 15% Sm-doped CeO<sub>2- $\delta$ </sub>,<sup>1</sup> a promising MIEC for photocathodes. As a result of the aspect ratio, the ionic transport overpotential dominates at elevated temperature. With the chosen dimensions, the voltage loss for oxygen ion transport would be 10 mV at current density of 2 A cm<sup>-2</sup> at 873 K. At temperatures above 700 K, the total transport overpotential is negligible as compared to the total photovoltage generated in the absorber (~1 V).



Figure S1: Schematic of the device geometry with typical dimensions.



**Figure S2:** Overpotentials for  $Sm_{0.15}Ce_{0.85}O_{1.9-\delta}$  electronic and ionic transport based on the above device geometry. H<sub>2</sub>-to-H<sub>2</sub>O partial pressure ratio is 1.

### S2. Dark and open circuit condition

As we show below, the conventional open-circuit condition (no net current, no illumination) cannot be achieved as long as there is a chemical potential gradient between the anode and cathode chamber. Even without illumination, there is a small driving force for oxygen to diffuse across the cell from the air side to the steam side, due to a slight difference in the oxygen partial

pressure. Because the light absorber is electronically shorted to the cathode, a small electronic and ionic current flows through the cell. Essentially, in the dark, the cell operates as an oxygen permeation membrane between the air and the steam side such that the Fermi level is not flat as shown in Figure S3a. This was accounted in for our simulation. Under illumination, a small portion of the photovoltage (0.06-0.15 V) goes towards offsetting the current in the "wrong" direction.



**Figure S3:** Schematic band diagram at a) dark condition and b) quasi-open-circuit condition. CB and VB are conduction and valence band, respectively.

Because open-circuit condition can never be achieved in our cell, we define a quasi-open-circuit condition in which the small Nernst voltage is balanced by the photovoltage. Under this condition, we relate the forward thermionic emission velocity  $S_{forward}$  to the reverse emission velocity  $S_{reverse}$ :

$$0 = J / q = n_{abs}^0 S_{forward} - n_{MIEC}^0 S_{reverse}$$
(S1)

where  $n_{MIEC}^0$  is the electron concentration in the MIEC in equilibrium with the gas phase, and  $n_{abs}^0$  is the electron concentration in the light absorber. Note that  $n_{abs}^0$  is not the equilibrium

electron concentration, but rather the concentration under the quasi-open-circuit condition. In other word, to achieve zero net current condition, illumination is needed to raise the quasi-Fermi level  $E_{f,n}$  by the same amount as the Nernst potential ( $E_{Nernst}$ ). This is illustrated schematically in Figure S3b.

# S3. Effect of density of states in the absorber



**Figure S4:** The influence of the effective density of states on solar-to-hydrogen efficiency. Simulation conditions same as in Table 1 except that 400 suns concentration was used to accentuate the difference between these materials.

In the present model, the temperature-dependent effective density of states in the light absorber was taken from values for Si. While the effective density of states is strongly dependent on the material, the contribution to the temperature-dependent carrier concentration is much weaker than that of the band-gap. Figure S4 shows the influence of effective density of states on the PEC solar-to-hydrogen efficiency. Between GaN,<sup>2</sup>  $Al_{0.4}Ga_{0.6}As^3$  and Si,<sup>4</sup> the difference in the effective density of state has only a small effect on the efficiency, especially at lower temperature. In fact, using the effective density of states of GaN or  $Al_{0.4}Ga_{0.6}As$  gives better solar-to-hydrogen efficiencies than Si at high temperatures.

### S4. Auger recombination

Auger recombination was not included in the present model because the rate is proportional to the absorber thickness. Here, we calculated the Auger recombination rate, and compared it to the surface recombination rate under illumination. The Auger recombination rate is given as:

$$\Gamma_{Auger} = \left( C_n (n^2 p - n_{eq}^2 p_{eq}) - C_p (n p^2 - n_{eq} p_{eq}^2) \right) \cdot d$$
(S2)

where  $C_n$  and  $C_p$  are the recombination coefficients, *n* and *p* are the electron and hole concentrations, respectively, and the subscript *eq* denotes values at equilibrium. Since Auger recombination is a bulk process, the rate is normalized by thickness *d* so that we could compare with the surface recombination rate. As an example, we took the recombination coefficients for Si:  $C_n = 2.8 \times 10^{-31} cm^6 s^{-1}$  and  $C_p = 1.2 \times 10^{-31} cm^6 s^{-1}$ .<sup>5</sup> They are assumed to be temperature independent. As shown in Figure S5, with absorber thickness of 1 µm, the Auger recombination rate is much less than surface recombination rate we obtained for all temperatures.



**Figure S5:** Comparison of Auger and surface recombination rates under illumination using parameters in Table 1. The absorber thickness is  $1\mu m$ .

#### S5. Energy balance

Eq. 11, shown again below, requires some comments:

$$P_{sun} = \left[\sigma T^4 + (e^{\Delta \mu_{abs}/k_B T} - 1)P_{BB}\right] + \frac{J \cdot \Delta \mu_{abs}}{q} + \left[\frac{qJ_{H_2O}^{in}}{F} \cdot \Delta H_{H_2O}^0(T) + \frac{J \cdot T\Delta S_{rxn}}{2q}\right]$$

The first combined term represents blackbody radiation for both equilibrium ( $\sigma T^4$ ) and excess carriers ( $(e^{\Delta\mu_{abs}/k_BT} - 1)P_{BB}$ ). Emissivity is assumed to be unity.  $P_{BB}$  can be expressed as,

$$P_{BB} = \frac{2\pi}{h^3 c^2} \int_{E_g}^{\infty} \frac{(h\nu)^3 d(h\nu)}{e^{h\nu/k_B T} - 1}$$
(S3)

where h is Planck constant and c is the speed of light. The last combined term in Eq. 11

represents the thermal energy consumed. There are two contributions:  $\frac{qJ_{H_2O}^{in}}{F} \cdot \Delta H_{H_2O}^0(T)$ accounts for the energy used to heat/boil the water supplied at flux  $J_{H_2O}^{in}$ , and  $\frac{J \cdot T \Delta S_{rxn}}{2q}$ 

accounts for the entropy change of the steam that is dissociated to hydrogen and oxygen. The latter is the reaction entropy of the water-splitting conditions under illumination, *i.e.*, it is not the standard reaction entropy. Such reaction entropy is evaluated as follows:

$$\Delta S_{rxn}(T) = \Delta H^0_{rxn}(T) - \Delta G_{rxn}(T)$$
(S4)

where  $\Delta H_{rxn}^0(T)$  is the standard reaction enthalpy for water splitting and  $\Delta G_{rxn}(T)$  is the Gibbs free energy (*i.e.* the electrical energy) for water splitting under steady state condition.

### References

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