Comment on "Efficient Photochemical Water Splitting by a Chemically Modified n-TiO $_2$" (III)

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TECHNICAL COMMENT

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Khan *et al.* (*1*) presented a device for photoproduction of hydrogen that, at a claimed efficiency of 8.35%, would approach the photoconversion efficiency of amorphous silicon photovoltaic cells. Even allowing for the fact that the cell still requires additional energy input from an electric power supply, this would be a remarkable achievement. Unfortunately, the claim is based on an incorrect calculation that underestimates the energy contribution from the external electric power supply. Based on the information provided, one cannot calculate the actual efficiency of the cell. However, the information presented allows for the possibility that the external power supply alone provides more energy than would be required to electrolyze water even in the absence of light.

Missing is a direct measurement of the voltage E_{app} generated by the power supply. The calculation of E_{app} from other data is at best misleading.

Given the actual voltage difference generated by the power supply and the current through the device, the power P_{elec} that is contributed by the external electric power supply is given by

$$P_{elec} = E_{app} J_p. \qquad (1)$$

Here, J_p is the current flowing through the circuit and E_{app} is simply the potential difference between the two terminals of the power supply. If one adjusts the voltage on the power supply such that the current approaches zero, E_{app} will not drop to zero, but approach a finite value. Looking at the other half of the circuit, E_{app} can also be interpreted as the potential difference across the hydrogen-producing cell, including its photovoltaic component. In the limit of zero current, E_{app} would thus be the open-circuit potential difference across the cell.

Figure 3 in (*1*) suggests [in agreement with note 22 of (*1*)] that $E_{app} = 0$ at $J_p = 0$. The definition of E_{app} used by Khan *et al.* therefore differs from the physically relevant definition given above by a constant term—the open-circuit voltage. Khan *et al.* [note 22 of (*1*)] define the photoconversion efficiency, $\varepsilon(photo)$, as

$$\varepsilon(photo) = \frac{J_p(E_{rev} - E_{app})}{I_0} \qquad (2)$$

where E_{rev} is the standard-state reversible potential and I_0 is the intensity or power density of the incident light. With the correct choice of E_{app}, this equation has a ready interpretation: The rate of chemical energy output of the cell (J_pE_{rev}) (*2*) is reduced by the electrical input (J_pE_{app}) to the cell. What remains is that part of the minimum theoretical power demand that is not covered by the external power supply, and it is attributed to the photon input. This unambiguous energy contribution to the electric output by the light is compared with the total light power flux (I_0) that hits the surface of the cell.

It could easily happen that overcoming internal losses in the cell—for example, overpotentials or ohmic losses—would require an amount of external electric power that exceeds J_pE_{rev}. In that case, $\varepsilon(photo)$ would be negative and if one were to replace the solar hydrogen cell with a more efficient electrolytic device, the electric power input alone would be sufficient to produce the same amount of hydrogen from water. Contrary to the view expressed by Khan and Akikusa (*3*), negative efficiencies are not "unrealistic"; such a situation can occur easily even if the light demonstrably contributes to the voltage maintaining the hydrogen-producing current. A negative sign only indicates that the electric power supplied already exceeds the theoretical minimum required for breaking up water into hydrogen and oxygen. However, a negative efficiency is also compatible with a cell in which the light fails to contribute power to the photocurrent. In an extreme, hypothetical case, light might only act as an on/off switch that either opens or closes an electric circuit that is completely driven by the external power supply. However, even for such a cell, after subtracting the open-circuit voltage from E_{app} and with J_p>0, Eq. 2 would still result in a positive photoconversion efficiency.

What is the actual efficiency of the hydrogen-generating cell presented in (*1*)? To answer that question, one would need to know the full voltage supplied by the external power supply at zero current. One possible interpretation of note 22 in (*1*) is that the applied voltage is shifted by 1 V, which suggests that the electric power supply under optimal conditions provides 1.3 V. If that were the case, the device described would have a negative efficiency at its optimal operating point and might as well be replaced by a nonsolar electrolyzer consuming no more electric power.

In any event, the bias voltage $E_{app}(J_p = 0)$, which has been ignored by the authors, will lower the calculated efficiency. Since the cell seems not to generate hydrogen without the assistance of a power supply, the power supply will have to overcome a bias voltage which will add to the voltage drop shown by Khan *et al.* [figure 3 of (*1*)]. If perchance this bias voltage were actually zero, the experimenters should have noticed. The cell would be on the verge of spontaneously generating hydrogen. Any additional driving force—for example, from increased light flux—should turn spontaneous hydrogen production on. Another indication that this is not the case is that cells of different materials considered in both (*1*) and (*3*) all share the feature that $E_{app} = 0$ at $J_p = 0$, which suggests that it is built into the definition of E_{app} just as in note 22 of (*1*). Without including the zero-current voltage supplied by the power supply, the photoconversion efficiency presented in figure 3 of (*1*) fails to include the most important energy contribution of the electric power supply.

The total conversion efficiency, which is also given by Khan *et al.* (*1*), is a meaningless number. It is always possible to compare a light flux to the power demand of a given rate of hydrogen production, even if the light flux does not contribute in any way to the production of hydrogen.

What is missing in the study of Khan *et al.* is the potential difference between the two terminals of the voltage supply as function of the current flow. However, the most straightforward reading of the data presented suggests that the externally applied electric power alone might be sufficient to drive the electrolysis.

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References and Notes

1. S. U. M. Khan, M. Al-Shahry, W. B. Ingler, *Science* **297**, 2243 (2002).
2. I assume, as did Khan *et al.* (*1*), that 100% of the the current J_p contributes to the electrolysis of water.
3. S. U. M. Khan, J. Akikusa, *J. Phys. Chem. B* **103**, 7184 (1999).

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