Supporting information:

The evolved gas volume was measured using an inverted burette to collect the gases during photoelectrochemical water splitting at a current density of 7 mA/cm^2 in 0.1 M KOH. As a photocathode, an a-Si:H/a-Si:H/µc-Si:H triple junction solar cell with a ZnO/Ag/Pt rear contact was used (A = 0.5 cm^2). Prior to the measurement, the aqueous solution, which was used as a barrier, was saturated with oxygen by bubbling molecular oxygen through the solution. No membrane was integrated between the anode and the cathode. Thus, recombination of hydrogen and oxygen or reduction of oxygen on the photocathode could be an issue in particular under prolonged operation. The theoretically expected total gas volume was calculated by combining Faraday's law of electrolysis with the ideal gas law:

$$V_{\text{theo}} = \frac{R\,T}{F\,p\,z} Q$$

Here, R is the ideal gas constant, T is the absolute temperature, F is Faraday's constant, p is the pressure, z = 4/3 is the number of electrons involved, and Q is the charge (integrated photo current). The measurement error was estimated to be $V_{\text{meas}} = \pm 0.2\ \text{ml}$.

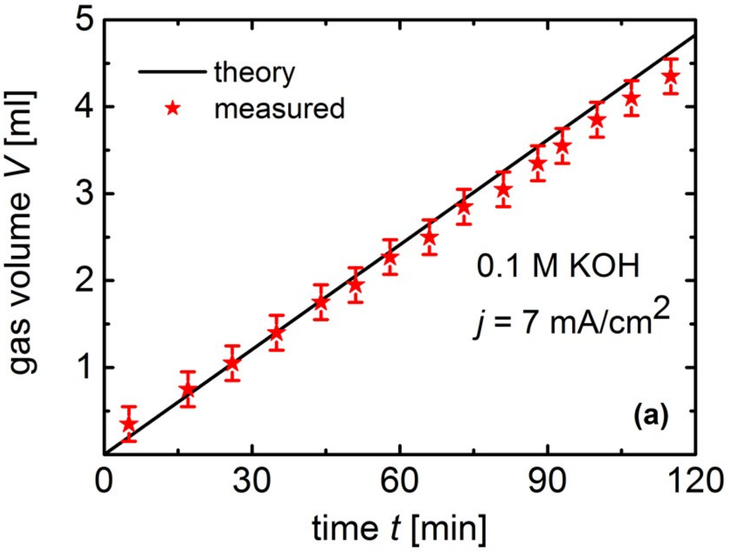

Fig S1: Volume of gas produced by an a-Si:H/a-Si:H/µc-Si:H triple junction based photocathode under AM 1.5 solar illumination for two hours of operation in 0.1 M KOH.

The faradaic efficiency η_F of the water splitting process was computed as the ratio between measured and theoretically expected total gas volume:

$$\eta_F = \frac{V_{meas}}{V_{theo}}$$

According to first order propagation of error, the uncertainty of the faradaic efficiency was

$$\Delta\eta_F = \frac{\Delta V_{meas}}{V_{theo}}$$

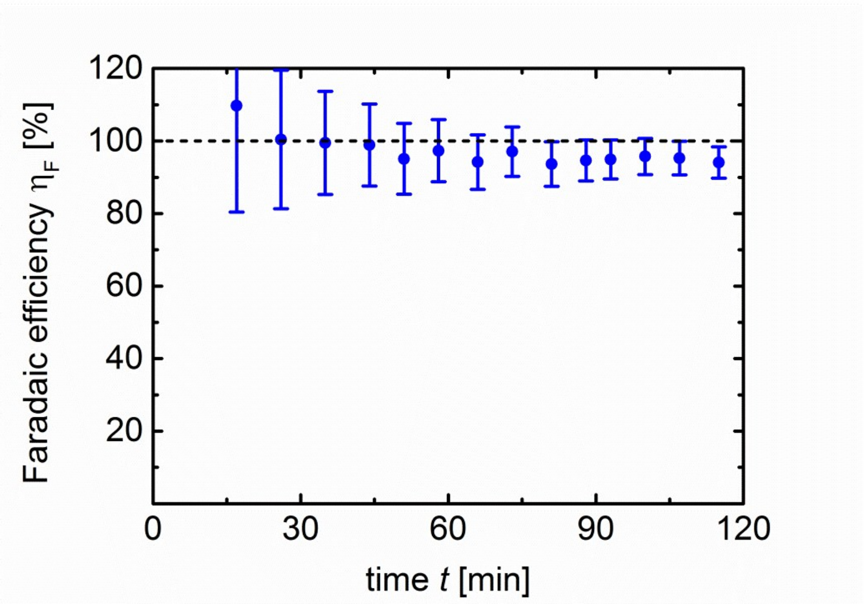

Fig S2: Evaluated faradaic efficiency over time calculated from Fig. S1.