

## Supporting Information

### **Reliable Performance Characterization of Mediated Photocatalytic Water-Splitting Half Reactions**

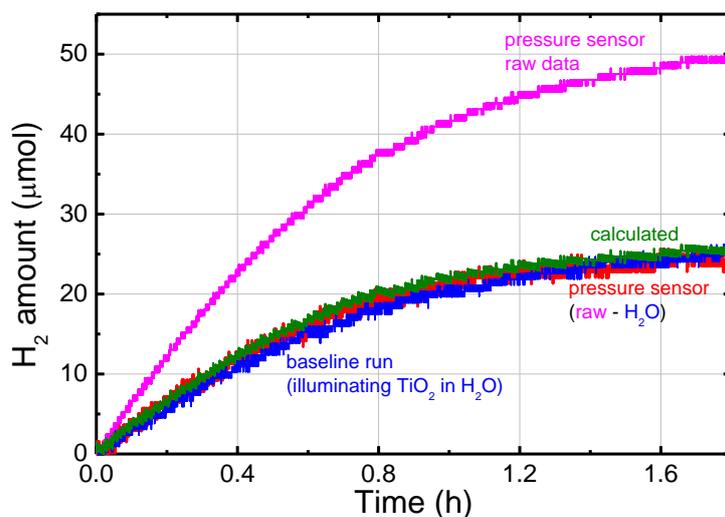
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Anatase TiO<sub>2</sub> particles were synthesized and were loaded with 10 wt% Pt by photo-depositing of H<sub>2</sub>PtCl<sub>6</sub> powders in ethanol. The same UV lamp as described in the experimental section was used to illuminate the 50 mL slurry for 4 hours in a flask in the fume hood. They were then suspended in 50 mL pH 11 NaI aqueous electrolyte containing 100 mM I<sup>-</sup> working as the HER mediator. The raw data read from the pressure sensor is plotted in purple in Fig. S1. The blue curve shows the data of the baseline run, which was conducted at the exact same conditions but without the I<sup>-</sup> mediator. The temperatures of the two runs were increasing at the same rate. By subtracting the baseline data from the raw data, the H<sub>2</sub> amount was determined (red curve). The H<sub>2</sub> evolution rate in the starting 40 minutes of illumination was estimated as ~28 μmol/h.

The calculation of the H<sub>2</sub> amount is easier than the O<sub>2</sub> amount in the aqueous electrolyte as the solubility of H<sub>2</sub> is only around ~3.7% of that of O<sub>2</sub> at 20 °C atmosphere pressure. As the amount of the evolved H<sub>2</sub> is considerably smaller than that of the evolved O<sub>2</sub> discussed in this paper, both the temperature-dependent solubility variation and the salinity variation can be neglected. The calculated curve (green in Fig. S1) is close to that of the measured curve (red in Fig. S1) when subtracting the produced water vapor amount with increasing temperature and calibrating the gas thermal expansion using the ideal gas law.

This high-resolution HER characterization experiment utilizing the pressure sensor and our correction approach confirms that the analytical pressure correction approach is universally applicable.



**Figure S1.** The generated H<sub>2</sub> molar amount recorded as a function of exposure time. The HER half reaction utilizes 100 mg anatase TiO<sub>2</sub> particles loaded with 10 wt% Pt as photoabsorber and 50 mL pH 11 aqueous electrolyte containing 100 mM I<sup>-</sup> as the mediator. The purple curve shows the raw data measured by the pressure sensor, and the blue curve is the baseline run (same conditions but no I<sup>-</sup>, i.e. exposed to the same heating conditions). By subtracting the blue curve from the raw data (purple curve), the real generated H<sub>2</sub> amount is plotted as shown by the red curve. The green curve shows the calculated result of the H<sub>2</sub> amount considering the physical effects discussed in this paper.