Determination of the internal quantum efficiency for photoelectrochemical reaction in a semiconductor photoelectrode by photoacoustic detection

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Preparation of samples

Typically, commercial MOD solutions for bismuth oxide (Kojundo Chemical Laboratory, SYM-BIO5) and vanadium oxide (Kojundo Chemical Laboratory, V-02 DIP) were mixed at a ratio of Bi : V = 1 : 1, and butyl acetate (Wako Chemicals) and ethyl cellulose (Tokyo Chemical Industry) were added. The solution was coated on FTO glass (Geomatec,10 ohm/sq, 0.5 mmt) with a spin-coater (Mikasa, MS-B100, 1000 rpm, 15 s), and it was heat-treated using an electric furnace at 500°C for 30 min. The samples prepared without and with ethyl cellulose are denoted as wo-EC and w-EC, respectively.

Transmittance/reflectance measurement

In order to estimate LHE of the prepared transparent sample, normal incidence transmittance and 10-deg-incidence reflectance of the prepared film were measured using a homemade spectroscopic system including a laser diode module (Edmund Optics, 85-227, 405 nm, 10.2 mW) and optical power meter (Hioki, 3664) equipped with a photo-sensor (Hioki, 9742-10). A schematic image of the spectroscopic system is shown in Fig. S1. Fig. S2 shows UV-VIS spectra of FTO glass and wo-EC sample, which were measured using commercial UV-vis spectrometer (Shimadzu, UV-1800).

PA measurement

The PA signal was acquired by a digital MEMS microphone (Knowles, SPK0641HT4H-1) buried in the cell and recorded using a PC equipped with a digital I/O interface. Time-series data were acquired by analogue conversion of the PA signal followed by Fourier transform with a Hamming window function.



Fig. S1 Spectroscopic system for T/R measurement.



Fig. S2 UV-VIS spectra of FTO glass and wo-EC sample



Fig. S3 Photograph of BiVO₄/FTO samples (wo-EC and w-EC).



Fig. S4 (a) Photocurrent and (b) $E(\Delta P/\Delta P_0)$ of a BiVO₄/FTO electrode (wo-EC sample, BiVO₄-side irradiation) in aqueous Na₂SO₃+Na₂SO₄ electrolyte as a function of applied potential.