

Supporting Information

Sustained solar hydrogen generation using a dye-sensitised NiO photocathode / BiVO₄ tandem photo-electrochemical device

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Experimental

NiO nanoparticle powders were purchased from Inframat. A slurry was used for doctor blading and was produced by grinding 2 g of NiO powder with 10 μ L acetylacetone, 25 μ L Triton (X100) and 12 mL of water (added in small aliquots whilst grinding). The slurry was then sonicated for 30 minutes, and centrifuged for 20 seconds at 4000 rpm to remove any remaining large agglomerates. Using the Magic tape (3M) control film thickness, NiO films of \sim 1.8 μ m were produced, with an active area of 3 cm² on FTO glass. Electrodes were sintered at 823 K for 10 min, before being cooled and sensitized in a 0.2 mM PMI-6T-TPA dye solution (in dimethylformamide, Aldrich) for 4 hours.

Photo-electrochemical measurements were conducted with a potentiostat (Zahner) and an H-type cell (Makuhari Rikagaku Garasu Inc.) composed of working and counter electrodes components divided by a Nafion 117 membrane (DuPont). An Ag/AgCl electrode and platinum mesh were used as reference and counter electrodes respectively. The reference and working electrodes were placed into the same compartments of H-cell, with a 0.1 M aqueous (DI water) solution of Na₂SO₄ as the electrolyte, bubbled with Ar before measurements. The light sources were two Xe lamps with plano-convex lens to produce a collimated light beam. For IPCE measurements, the wavelength of the incident light was controlled by monochromator (Newport). The amount of evolved H₂ was determined using an online gas chromatograph (Shimadzu, GC-8A, Ar carrier).

BiVO₄ powders preparation followed the same route published by Iwase et al.¹ from a liquid-solid state reaction utilizing 2.3 g of Bi₂O₃ (Fluka; 98.0%) and 0.9 g of V₂O₅ (Aldrich; 99.6%). The mixture was vigorously stirred in 50 mL of 1.0 M acetic acid (aq.) at room temperature for 11 days. The obtained BiVO₄ powder was washed with DI water to remove residual acetic acid. The particle size of the BiVO₄ was determined to be around 100-200nm. A BiVO₄ doctor blading pastes was produced and applied to an FTO substrate in a manner similar to the

aforementioned NiO paste and electrode. The BiVO₄ electrode on FTO glass was sintered at 673 K for 5 hours.

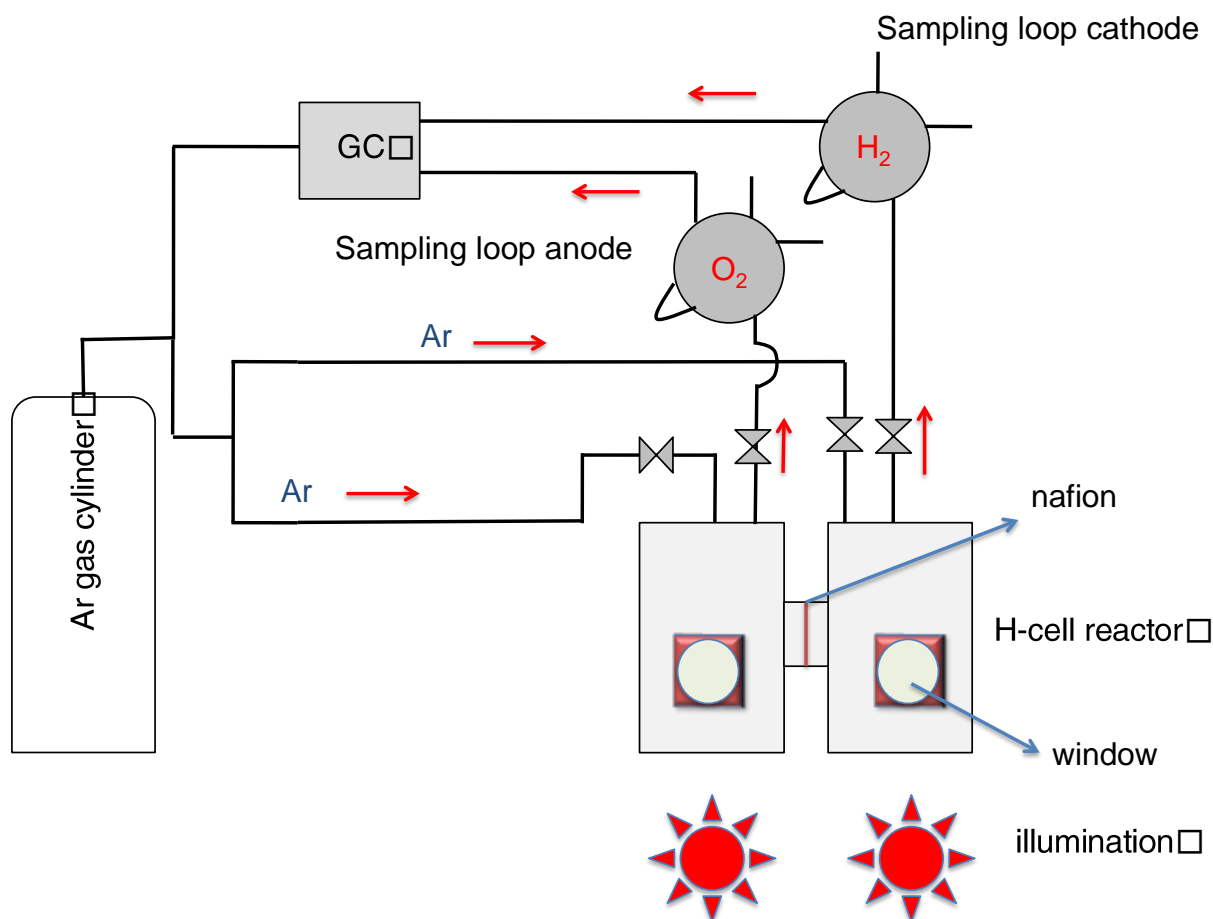
The Incident Photon to Charge carrier conversion Efficiency (IPCE) was measured in H-cell using a 300W Xe lamp, monochromator and potentiostat. The working electrode was held at 0V vs Ag/AgCl, and revealed photocurrent up to 650nm, which is in good agreement with the absorption profile of the dye on NiO in aqueous solution (optical band gap ~1.9 eV).

The measured potentials vs. the Ag/AgCl were converted to the reversible hydrogen electrode (RHE) scale via the Nernst equation:^{2,3}

$$V_{\text{RHE}} = V_{\text{Ag/AgCl}} + V_{\text{Ag/AgCl vs NHE}}^0 + 0.059 \times \text{pH}$$




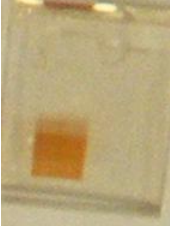


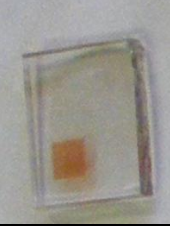
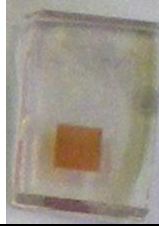











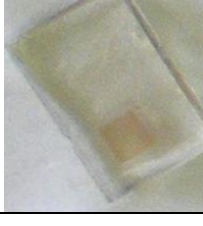
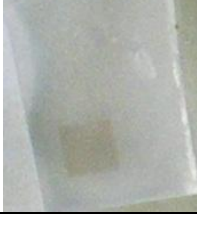
$$\text{With pH} = 7: V_{\text{RHE}} = V_{\text{Ag/AgCl}} + 209 \text{ mV} + 413 \text{ mV} = V_{\text{Ag/AgCl}} + 622 \text{ mV}$$

where V_{RHE} is the converted potential vs. RHE, $V_{\text{Ag/AgCl}}$ is the experimental potential measured against Ag/AgCl reference electrode, $V_{\text{Ag/AgCl vs NHE}}^0$ is 209 mV (3M NaCl) at 25° C.



SI Figure 1. Schematic drawing of the water splitting photo-electrochemical cell and gas-flow system for H₂ detection.

SI Table 1. Dye-sensitized NiO electrode stability in different pH aqueous solution over time

		1M HCl	DI water	1M NaOH
Films kept in dark between inspections	0 hrs			
	188 hrs			
	5110 hrs (213 days)			
Films (with 5110 hrs exposure time) subsequently illuminated under direct sunlight	5110 + 25hrs			
	5110 + 120 hrs			
	5110 + 290 hrs			
	5110 + 2951 hrs (213 + 123 days)			

References

1. A. Iwase, A. J. Kudo, *J. Mater. Chem.*, 2010, **20**, 7536.
2. F. F. Abdi and R. V. D. Krol, *J. Phys. Chem. C*, 2012, **116**, 9398
3. S. Hoang, S. Guo, N. T. Hahn, A. J. Bard, and C. B. Mullins, *Nano Lett.*, 2012, **12**, 26