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Abstract

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Keywords

hydrogen, sensitised, tandem, photo, generation, photocathode, dye, electrochemical, nio, device, sustained, solar, bivo4

Disciplines

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

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Solar hydrogen generation sustained for at least several hours is demonstrated using a dye-sensitised nickel(II) oxide photocathode and BiVO₄ photoanode connected in a tandem configuration. H₂ evolution rate is 120 nmol h^{−1} (>80% faradaic efficiency) without electrical bias or sacrificial oxidant/reductant, at pH = 7 using visible light (>420 nm).

The decomposition of water to gaseous hydrogen and oxygen requires 1.23 eV per electron transferred, which can be supplied by solar illumination.^{1,2} The conversion of solar energy into chemical energy requires efficient photocatalysts, typically semiconductors, that facilitate the important steps of light absorption, charge separation and ultimately drive the two half-reactions of water reduction and oxidation to H₂ and O₂, respectively.^{2,3} Although some oxynitride photocatalysts for overall water splitting have been reported,^{4,5} a single material which can perform all of the above tasks efficiently, using only visible photons (>420 nm), over a prolonged time and

without an applied potential or sacrificial chemical, is yet to be developed. A Z-scheme photocatalyst system, where two photocatalysts perform either the water reduction or oxidation reactions, is often used instead and offers an alternative solution to the complexity of using a single material for overall water splitting.^{6–9}

An alternative photo-electrochemical approach to water splitting is to utilize a series-connected photocathode and photoanode in a tandem configuration. A sandwich tandem configuration may have the drawback of competing light absorption of the front and back electrodes. Complementary light absorption by the photoanode and the photocathode to achieve current matching is therefore preferred. The main benefit of this configuration, similar to the Z-scheme photocatalyst approach, is the improved photovoltage of the system as well as the increased flexibility in material selection.

A number of efficient photoanodes and photocathodes have been developed,^{10–15} and water splitting using a tandem photo-electrochemical setup has been demonstrated.¹⁰ A critical issue in developing photocathodes and photoanodes for a tandem stack is high underpotentials under illumination so that both maintain high current density when no external bias is applied.

In this communication, we demonstrate sustained hydrogen generation (for at least several hours) using a tandem photo-electrochemical cell comprising a bismuth(III) vanadate photoanode and a dye-sensitised NiO photocathode. BiVO₄ has been selected due to its visible response up to $\lambda = 500$ nm, high stability in neutral pH and a relatively large underpotential for water oxidation.¹⁴ The onset of anodic photocurrent of BiVO₄ showed a sweep direction dependence with an onset of -0.7 V *versus* Ag/AgCl sweeping towards positive potential direction, while a more positive 0.3 V *vs.* Ag/AgCl when sweeping towards the negative direction. A dye-sensitised NiO photocathode, originally developed for use in p-type dye sensitised solar cells,¹⁶ where it showed near unity internal quantum efficiency, is used here.¹⁷ The donor–acceptor type dye PMI–6T–TPA (Fig. 1), is comprised of a perylenemonoimide (PMI) electron acceptor, a regioregular 3-hexyl substituted sexithiophene (6T) unit, and

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† Electronic supplementary information (ESI) available: Experimental details for preparation of dye-sensitised NiO photocathode and BiVO₄ photoanode; photo-electrochemical measurements including IPCE; schematic drawing of the water splitting photo-electrochemical cell and gas-flow system for H₂ detection; dye-sensitised NiO electrode stability in different pH aqueous solution over time. See DOI: 10.1039/c2ee22866a

Broader context

Solar hydrogen generation sustained for several hours is demonstrated using a tandem dye-sensitised NiO photocathode and a BiVO₄ photoanode photo-electrochemical device using only visible light, without electrical bias or sacrificial reactants.

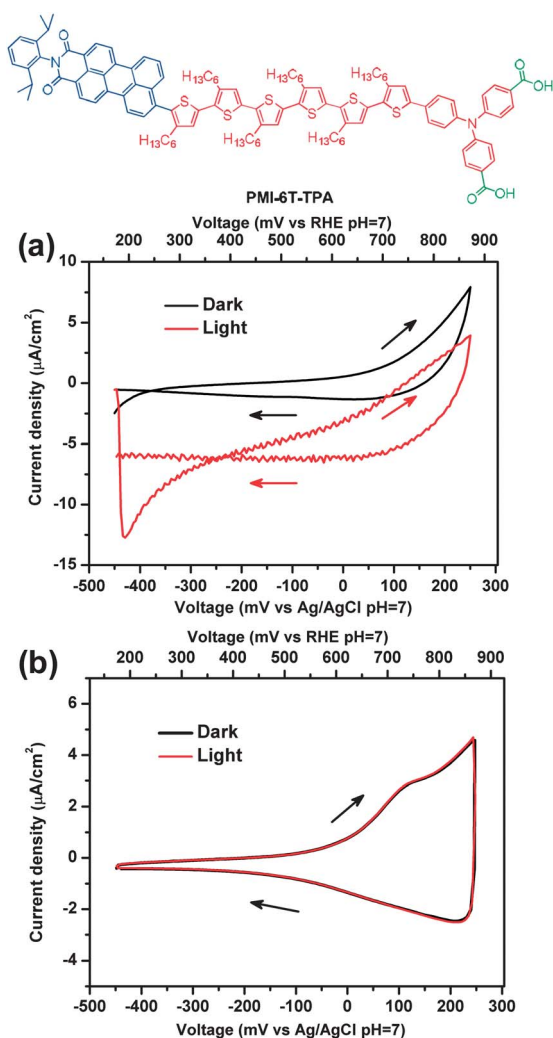


Fig. 1 Cyclic voltammograms (vs. Ag/AgCl reference electrode) in 0.1 M Na_2SO_4 aqueous solution (pH = 7), measured with a scan rate of 4 mV s^{-1} . (Red) under illumination $\lambda > 420 \text{ nm}$, and (black) in the dark for (a) dye-sensitized NiO photocathode and (b) NiO.

triphenylamine (TPA) as electron donor. Initial tests showed that a monolayer of this dye on NiO electrodes is very stable against degradation for several months when kept in the dark in 1.0 M HCl, 1.0 M NaOH or deionised water. The coloration of the electrode gradually disappeared over ~ 12 days under illumination in the acidic solution, however, remained largely unchanged for the same time in an alkaline or deionised aqueous solutions (ESI, Table S1†). These observations indicated not only that the dye is chemically stable, but also firmly attached to the NiO for a prolonged time. This is in contrast to most dye-sensitized photoanodes, which show significant dye desorption under water oxidation conditions, limiting long term stability.^{18,19}

Fig. 1(a) compares the first cycle (dark) and second cycle (light) of cyclic voltammograms (CV) of a dye-sensitized NiO photocathode recorded in a three-electrode setup using 0.1 M Na_2SO_4 in deionized water at pH = 7. The photocathode was prepared as described in the ESI.† The Ag/AgCl reference electrode and the photocathode were placed in one of the compartments of an H-cell, while the Pt mesh counter electrode was placed in the second compartment, separated by a Nafion 117 membrane (DuPont). A 300 W Xe lamp

(Perkin-Elmer, CERMAX PE-300BF) with a $\lambda > 420 \text{ nm}$ long pass filter was used to illuminate the sample with an illuminated area of 3 cm^2 .

Upon illumination, the current shifted cathodically by $\sim 6 \mu\text{A cm}^{-2}$, a value which was nearly independent of the applied voltage within the measured range. The onset of cathodic current shifted positively under illumination in the reverse scan (towards negative potentials), which represents an increase of underpotential for H^+ reduction $\eta = -(E - E_{\text{RHE}})$, where E is the applied potential and E_{RHE} is calculated to be -0.413 V at pH = 7 versus NHE. Hysteresis was observed between the forward and reverse scans despite the rather slow scan rate, which may be related to transient pH shifts within the pores of the dye-coated NiO pores or the slow back-reaction of H_2 oxidation on the photocathode. The CVs measured for undyed NiO under the same conditions (Fig. 1(b)) did not show any noticeable shift under illumination within the measured voltage range. The peak around 100 mV vs. Ag/AgCl is attributed to partial oxidation of NiO as previously reported by Boschloo and Hagfeldt.²⁰ This first peak is shifted to slightly higher positive potentials when the NiO is coated with the dye, suggesting that either the dye effectively blocks the NiO surface, or the chemical attachment of the dye through the carboxylate binding ligand shifts the oxidation potential of the first peak. The long-term stability of dye-coated NiO films in aqueous solutions support the hypothesis that the dye effectively insulates the NiO surface.

A chronoamperogram (Fig. 2(a)) of the illuminated dye-sensitized photocathode, biased at 0 V versus Ag/AgCl using a Pt counter electrode, reveals that after an initial spike the photocurrent reaches $1.7 \mu\text{A cm}^{-2}$ within ten minutes and then increases to plateau at around $3.9 \mu\text{A cm}^{-2}$ over a four-hour period. The sample showed no sign of degradation even after this period and the photo-electrochemical tests were highly repeatable with multiple experiments completed on the same photoelectrode. During the testing, the lamp was shuttered twice causing the photocurrent to drop to approximately 100 nA cm^{-2} within seconds (inset of Fig. 2(a)) confirming that the observed current under illumination is indeed a photocurrent.

The H_2 generation rate was measured throughout the course of the test, and is shown in Fig. 2(a). H_2 detection was done using a gas-flow system as described below and shown in ESI, Fig. S1.† 5 mL of the “overhead” gas was injected into a molecular sieve column of a gas chromatograph (Shimadzu, GC-8A, Ar carrier, 4.2 mL min^{-1}). From the carrier gas flow rate and the integrated signal intensity, the H_2 generation efficiency was calculated. There was a small amount of H_2 detected after the first hour, however we could not reliably calculate the faradaic efficiency due to the rather small H_2 peak in the gas chromatogram. After 2 hours of illumination a sample was collected (72 second collection time). This yielded 2.6 nmol H_2 , corresponding to a faradaic efficiency for hydrogen generation of $97 \pm 7\%$ (Table 1). The error arises from the fluctuations in photocurrent, which corresponds to a cathodic charge in the range of 0.029 to 0.033 C within the sampling time. Other sources of measurement error, such as the error in measuring the gas flow rate or the error in gas quantity measurement by the GC are not calculated here. We think these additional sources of error are likely to be responsible for faradaic efficiency values slightly above 100% after the 3rd and 4th hours.

Fig. 2(b) shows the spectral response of the photocurrent of the photocathode under monochromatic light in the range of 350–800 nm (Incident Photon to Current Efficiency – IPCE) of both sensitized

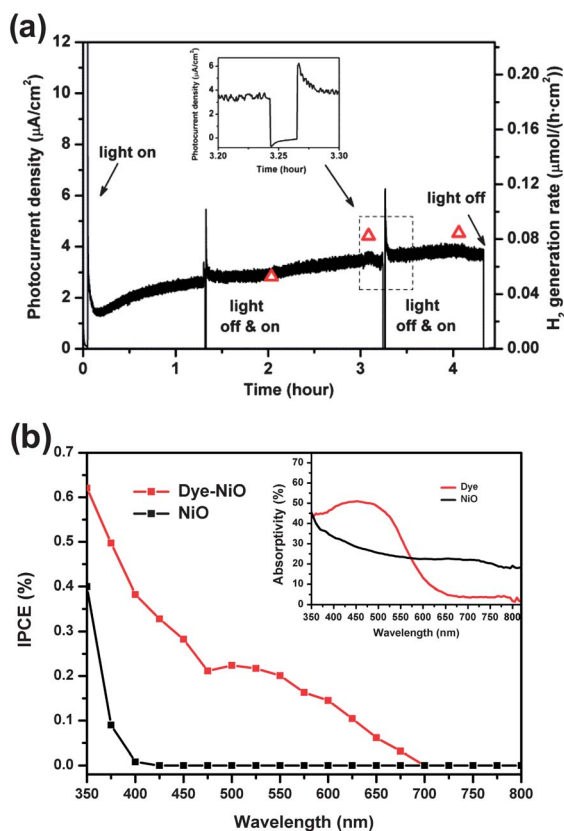


Fig. 2 (a) Chronoamperogram (left axis) and hydrogen generation rate (right axis, red triangles) measured by illuminating a dye-sensitized NiO photocathode (0 V vs. Ag/AgCl) with a Pt counter electrode; (b) IPCE spectrum of dye sensitized NiO electrode (red) and NiO electrode (black), in conditions the same as above. The step between each point is 25 nm. The inset shows the absorptivity of the NiO film and the dye attached to NiO (dyed film minus undyed film).

Table 1 Faradaic efficiency of H₂ generation by the photocathode and the tandem photo-electrochemical cell

Time (hours)	Faradaic efficiency (%)	
	Photocathode	Tandem
1	— ^a	—
2	97 ± 7	—
2.3	—	88 ± 2
3	121 ± 8	82 ± 2
4	117 ± 6	79 ± 3

^a Value in first hour could not be calculated due to small H₂ peak.

and non-sensitized NiO, at 0 V versus Ag/AgCl. The bandwidth of the monochromator was set to around 5 nm. IPCE values in the range of 0.1% up to 0.6% at the peak have been measured. The shape of the spectral response closely followed the absorptivity of the dye attached to the NiO photocathode, further suggesting that photon absorption by the dye is primarily responsible for photocurrent generation. We note that the light intensity for these monochromatic measurements was much lower than the white light illumination in Fig. 1 and 2.

We suggest that the mechanism for visible light-driven H₂ generation using the photocathode is dye-sensitized hole injection from the

photo-excited dye into the valance band of NiO leading to a dye anion as shown in Fig. 3. Transient absorption measurement in our previous report of the same photocathode in inert glutaronitrile solvent showed the characteristic spectroscopic signatures of a reduced anion as the photoactive intermediate.¹⁷ The first reduction potential of the dye measured by cyclic voltammetry is −0.9 V versus NHE, which is −1.3 V versus RHE at pH = 7. We propose that the photo-induced dye anion can reduce water producing H₂, in a mechanism similar to that reported by Li *et al.*²¹

Fig. 4(a) shows the CVs of BiVO₄ and dye-sensitized photocathode measured independently under the same conditions in the H-cell using a three-electrode configuration. The light was periodically blocked while the potential was scanned at a rate of 4 mV s^{−1}. The onset of anodic current for BiVO₄ sweeping towards the positive potential direction was −0.1 V versus Ag/AgCl, which is within the range reported in the literature.¹⁴ As indicated in the figure, there is a relatively wide potential window, where both photocathode and photoanode generate photocurrent. When the two electrodes are connected in a series tandem configuration without any external bias, a steady photocurrent was sustained over 4 hours, as shown in Fig. 4(b). The photocurrent initially reaches 1.8 μA cm^{−2} (after an initial spike) and further increases throughout the duration of the test, appearing to plateau around 2.7 μA cm^{−2}. During this extended testing the H-cell did not appear to be especially warm suggesting increased diffusion is not responsible for this. No degradation in the performance has been observed over the longest test of 12 hours (not shown). H₂ gas was detected using the same procedure as above, with the faradaic efficiency for H₂ generation calculated to be ~80% (Table 1). Unfortunately, O₂ evolution could not be detected. The calibration of our setup indicates that we need at least 2 orders of magnitude larger photocurrent to detect oxygen due to the low sensitivity of our GC detector to oxygen. Several authors, however, have previously reported IPCE and O₂ evolution using BiVO₄ photoanode in a three-electrode system.^{14,22,23} Furthermore, BiVO₄ powder is a well-established O₂ evolving photocatalyst in Z-scheme systems for water splitting.^{7,8} Although we could not detect O₂ due to

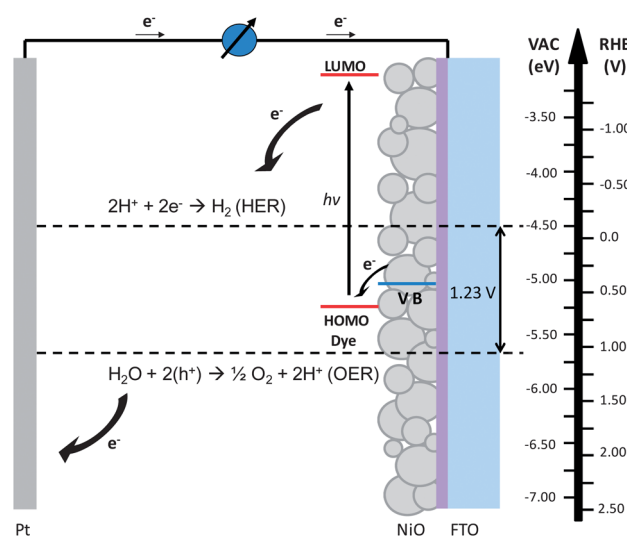


Fig. 3 Scheme for the electron-transfer processes occurring from the dye-sensitized NiO photocathode in 0.1 M Na₂SO₄ pH 7 aqueous solution. (HER: Hydrogen Generation Reaction; OER: Oxygen Generation Reaction.)

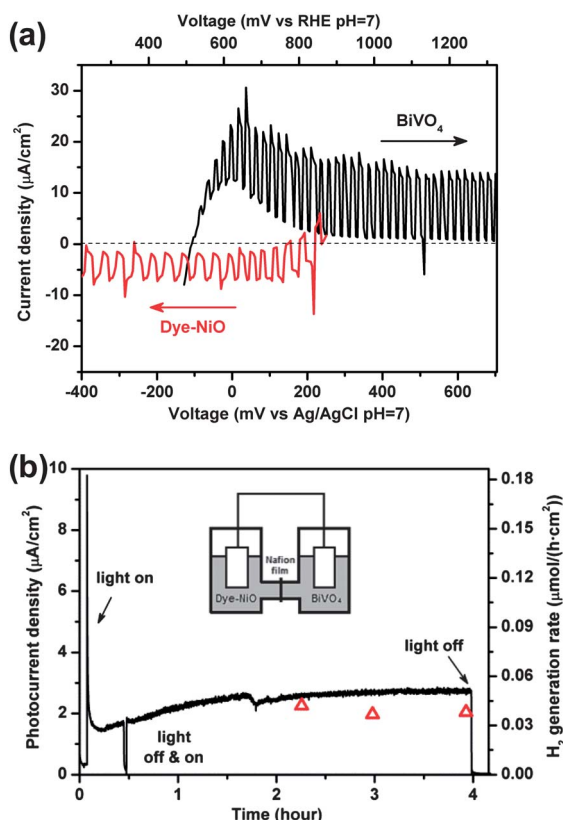


Fig. 4 (a) Cyclic voltammogram of BiVO_4 photoanode (black) and dye-sensitised NiO photocathode (red). (b) Chronoamperogram of individually illuminated dye-sensitised NiO and BiVO_4 connected in series as illustrated in the inset. Hydrogen generation rates are shown by red triangles.

low sensitivity, the observed long-term, stable photocurrent, the lack of any significant change in the pH of the water electrolyte and previous reports of O_2 evolution using BiVO_4 all indicate that O_2 is generated in our tandem photo-electrochemical cell, in other words, water is split to H_2 and O_2 . We need to significantly improve the performance of the tandem cell to be able to confirm this.

The sustained solar-hydrogen generation using a dye-sensitised photocathode using a rather simple metal-free organic dye is a significant result and among the first demonstrations using a tandem photo-electrochemical cell using the dye-sensitised approach. Due to the limitations of the optical arrangement of the H-cell, the electrodes for these tests were connected in series side by side, both of them illuminated independently using two lamps. By changing the light intensity on either side and monitoring the photocurrent, it was determined that both of the electrodes were limiting the photocurrent. At the operating potential of 0.3 V vs. Ag/AgCl, both photocathode and photoanode generated approximately the same photocurrent. In real-world applications a stacked sandwich tandem arrangement may mean that the photocathode and photoanode compete for photon absorption. An advantage of using the concept of dye-sensitised photoelectrodes is the ability to tune the dye absorption to achieve complimentary absorption, using established dye-design principles.²⁴ Dyes that absorb the near-infrared part of the solar spectrum have been intensively investigated for dye-sensitised solar cells. Developing dye-sensitised photocathodes with absorption complimentary to the photoanode, whilst maintaining high hole injection efficiency, is an

important goal. Furthermore, the recombination reactions mechanisms in aqueous solutions should be further studied to improve the internal quantum efficiency. Further work should focus on establishing the reaction mechanism between photogenerated dye anion and water, and developing catalytically active sensitisers to increase the IPCE.

In summary, we demonstrated sustained solar-driven hydrogen generation utilising a tandem photo-electrochemical cell illuminated by visible light. The photocurrent response of the tandem cell comprising of a dye-sensitised NiO photocathode and BiVO_4 photoanode was stable over several hours and corresponded to a faradaic efficiency of hydrogen generation of 80%. The dye-sensitised NiO photocathode was characterized in a three-electrode setup, and shows generation of H_2 due to dye-sensitised hole injection into the valance band of NiO, followed by reduction of water by the photogenerated dye anions.

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