

Amorphous Si Thin Film Based Photocathodes with High Photovoltage for Efficient Hydrogen Production

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(5) Supporting Information

ABSTRACT: An amorphous Si thin film with TiO_2 encapsulation layer is demonstrated as a highly promising and stable photocathode for solar hydrogen production. With platinum as prototypical cocatalyst, a photocurrent onset potential of 0.93 V vs RHE and saturation photocurrent of 11.6 mA/cm² are measured. Importantly, the a-Si photocathodes exhibit impressive photocurrent of ~6.1 mA/cm² at a large positive bias of 0.8 V vs RHE, which is the highest for all reported photocathodes at such positive potential. Ni–Mo alloy is demonstrated as an alternative low-cost catalyst with onset potential and saturation current similar to those



obtained with platinum. This low-cost photocathode with high photovoltage and current is a highly promising photocathode for solar hydrogen production.

KEYWORDS: Water splitting, hydrogen production, photochemistry, high photovoltage, a-Si photocathodes

S olar water splitting, a process that mimics natural photosynthesis, provides a viable solution to meet the challenge of our society's increasing energy demand.¹⁻⁵ The reduction side of solar water splitting produces hydrogen, a storable clean fuel. To be competitive with fossil fuels or hydrogen produced by other means, this process must be highly efficient and low cost.^{6–9} One promising approach is to use semiconducting photoelectrodes, within which minority carriers are generated upon solar illumination and driven to semiconductor solution interface for chemical reaction. Because it involves light absorption, charge generation and separation, and charge transfer for chemical reaction, the photoelectrodes should be carefully selected to maximize the efficiency. For example, the band gap of photoelectrodes should be suitable to allow sufficient light absorption. The conduction band or valence band of photoelectrodes should be energetically suitable for water reduction or oxidation. Additionally, the photoelectrodes should be stable under operation conditions and low cost. Those stringent requirements have limited available materials for solar water splitting and achieving practical water splitting remains challenging.

To date, a number of materials have been investigated as efficient photocathodes for hydrogen generation such as p-Si,^{10,11} p-InP,¹²⁻¹⁴ p-WSe₂,¹⁵ Cu₂O with ZnO/Al and TiO₂,¹⁶ p-GaP,¹⁷ and CdS-coated p-CuGeSe₂.¹⁸ Photocurrent densities of over 10 mA/cm² at reversible hydrogen electrode (RHE)

potential have been reported for these photocathodes.^{10–13,15} However, most of the photocathodes listed above have a photovoltage (defined as the photocurrent onset potential in respect to RHE) lower than half of 1.23 V, the minimum required voltage for overall water splitting (crystalline p-InP has photovoltage slightly higher than 0.7 V¹²). The relatively low photovoltage available from currently investigated photocathodes requires large external bias to perform water splitting and therefore limits the solar to hydrogen efficiency. Being able to develop a low-cost photocathode with high photocurrent at high voltages is therefore desirable and significant.

Inspired by the low cost and high open circuit voltage provided by amorphous Si (a-Si) solar cells,¹⁹ we herein report a photocathode with p-i-n hydrogenated amorphous Si thin film as the light absorber coated with a TiO₂ protection layer, and Pt or Ni–Mo cocatalyst for efficient water reduction, as shown in Figure 1a. Photons are absorbed in the intrinsic a-Si layer to create photogenerated carriers, which are then separated by the internal electric field created by the p-i-n junction (see Supporting Information for fabrication details). Photogenerated electrons are then conducted through the TiO₂ protection layer, as suggested by previous studies,^{12,20} to the

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Figure 1. (a) The a-Si photocathode with ZnO as conducting substrate, a-Si as light absorber, TiO_2 as a protection layer, and hydrogen evolution cocatalyst (either Pt or Ni–Mo) is schematically shown. The cathode is illuminated through the ZnO side. (b) Scanning electron microscope image shows the cross-section of an a-Si photocathode with Pt as catalyst. Scale bar is 400 nm. Yellow, ZnO; red, a-Si; green, TiO_2/Pt .

hydrogen evolution cocatalyst, where water reduction is catalyzed. The photogenerated holes on the other hand are collected by the ZnO back-contact and transported to the counter electrode. The design of our photocathode allows charge generation and chemical reaction to take place in different material layers, enabling the cathode to achieve highly efficient and stable water reduction. The tilted cross-section image of the ZnO/p-i-n a-Si/TiO₂/Pt photocathode (denoted as a-Si photocathode for simplicity hereafter) is shown in Figure 1b. The scanning electron microscopy (SEM) image is colored to help visualize different layers. The p-i-n layer is ~300 nm in thickness and was deposited by plasma-enhanced chemical vapor deposition on textured ZnO (sheet resistance 10 ohm/sq) on glass. On top of the a-Si layer, ~80 nm thick TiO2 was deposited by reactive sputtering. A 2 nm thick Pt layer was sputtered as a prototypical catalyst. Later in this manuscript we also demonstrate that electrodeposited Ni-Mo can serve as a low-cost alternative to the Pt catalyst. Details of the fabrication process can be found in the Supporting Information

The photoelectrochemical performance of the a-Si photocathode was characterized in a three-electrode setup with Ag/ AgCl as the reference electrode, Pt as the counter electrode and the a-Si cathode as the working electrode. The 0.5 M potassium hydrogen phthalate (KHP) aqueous solution with pH of 4 was used for the measurements. The cells were illuminated through the glass substrate (Figure 1a), and illumination was provided by a solar simulator (Solar Light, model 16S-300-005) with AM 1.5 filter. Upon 100 mW/cm² solar illumination, a photocurrent density of 11.6 mA/cm² was measured at 0 V vs RHE. The saturation photocurrent density also linearly scales with light intensity, as shown in Figure 2a and Supporting Information Figure S1. More importantly, the onset potential of photocurrent, where water reduction begins, was measured to be 0.93 V vs RHE (Figure 2a), which is 930 mV more positive than the reversible potential for hydrogen generation. The photocurrent



Figure 2. Photoelectrochemical characterization of a-Si photocathodes with Pt cocatalyst. (a) J-V plots of a representative a-Si photocathode under different simulated solar illumination intensities in 0.5 M aqueous potassium hydrogen phthalate solution. (b) Comparison of the photocurrent at 1 sun for various photocathodes reported in the literature and the work presented here at applied biases of 0.6, 0.7, and 0.8 V vs RHE. The data for n⁺p Si substrate, p-WSe₂, p-InP nanopillar (NPL) are taken from literature reports. The a-Si photocathodes presented in this work show significantly higher photocurrent at large positive bias as compared to other photocathodes.

onset potential by our a-Si photocathode for water reduction is one of the highest reported to date. It is relevant to compare the present result to prior work with crystalline Si. While AM1.5 current densities can exceed 20 mA/cm² for planar and nanowire configurations, the reported onset potentials of crystalline Si are at most 400 mV vs RHE for p-Si/Pt^{11,21} and 540 mV for n⁺p Si microwires,¹⁰ which is significantly lower than our a-Si photocathode. Also, the onset potential measured in our a-Si photocathode is 200 mV more positive than state-of-the-art p-type InP nanopillars.¹² The performance advantage arises from the bandgap of a-Si (~1.7 eV) and an optimized solid junction for charge separation. The maximum efficiency of the photocathode was calculated as

$$\eta = \frac{-j_{\max}\left(E_{\max} - E\left(\frac{H^+}{H_2}\right)\right)}{I_0} \times 100\%$$

where j_{max} and E_{max} are the current density and electrode potential at maximum power point, $E(\text{H}^+/\text{H}_2)$ is the Nernst potential of hydrogen generation, and I_0 is the power density of illumination. The maximum efficiency for hydrogen generation is 6.0% for the a-Si photocathode under 1 sun illumination. It is worth mentioning that the efficiency reported here does not take into account the overpotential loss at the counter electrode.²² Given the high photovoltage and low cost of a-Si photocathodes, the 6.0% efficiency, comparable with crystalline n⁺p Si microwire arrays, is significant. We note that the saturation current density of 11.6 mA/cm² obtained here is lower than the 15–17 mA/cm² measured in the-state-of-the-art a-Si solar cells due to relatively low incident photon-to-electron conversion efficiency (IPCE) in wavelength near band edge.¹⁹ In fact, the current density and thus the efficiency of our a-Si photocathode can be further improved through the design of surface texture to improve absorption of low energy photons. Although triple-junction a-Si solar cells have been coupled with catalysts for water splitting,^{8,23,24} our work aims at developing an a-Si based photocathode, which can be used in the future to couple with photoanodes to develop a low cost two junction water splitting cell.

The performance at high photovoltage of the a-Si photocathode is highlighted in Figure 2b, where the photocurrents of several promising photocathodes at large positive voltages in respect to RHE are compared. The data for planar n⁺p Si, p-WSe₂, and p-InP nanopillars are taken from previous reports.^{10,12,15} For our a-Si photocathode, the measured photocurrents are ~6.1 and 9.4 mA/cm² at 0.8 and 0.7 V vs RHE, respectively. By contrast, drastically lower photocurrents (<0.5 mA/cm²) are obtained at similar biases for other photocathodes (Figure 2b). Being able to achieve high photocurrent density at more positive voltage for a photocathode would alleviate the voltage requirement from the photoanodes and significantly improve the water splitting efficiencies.

The a-Si photocathodes were further characterized by measuring the incident photon to charge conversion efficiency (IPCE) at an applied bias of 0.4 V (Figure 3). Ultraviolet light



Figure 3. Incident photon to charge conversion efficiency (IPCE) of a representative a-Si photocathode measured at 0.4 V vs RHE. The orange trace is the integrated photocurrent obtained by multiplication of IPCE with the standard AM 1.5 G solar spectrum.

with wavelength below 370 nm exceeds the band gap of the ZnO back contact and is absorbed without contributing to the photocurrent. IPCE rises quickly and reaches over 60% in the visible light region between 400 to 580 nm with the highest value of 75% measured at 500 nm. Such high IPCE indicates efficient charge separation within the p-i-n layer and efficient electron transport through the TiO₂ layer. Convoluting the IPCE spectrum with photon flux from AM 1.5 G solar irradiation yields photocurrent of 10.8 mA/cm², which is in good agreement with the value measured from J-V with the solar simulator (Figure 2a).

The stability of the a-Si photocathode was also evaluated during 12 h of operation. The photocurrent measured at 0 V vs RHE was recorded and is plotted in Figure 4. The a-Si photocathode exhibits good stability in aqueous solution, with



Figure 4. Photocurrent at 0 V vs RHE as a function of time. The protected a-Si photocathode is highly stable for water reduction.

less than 5% decay over the measured period. By contrast, the a-Si photocathode without TiO_2 protection showed poor stability, with the photocurrent decaying to 10% of its original value after 12 h of measurement (Supporting Information Figure S2). The result clearly suggests that the stability is due to the TiO_2 coating, which has also been shown to be an effective protection layer in previous studies for other material systems, including crystalline Si and InP.^{12,20}

The low-temperature processing (about 200 °C) and the use of ultrathin light absorber material (<300 nm in thickness) makes the presented device structure low-cost and economically scalable. An important step toward its large-scale application is to replace the Pt catalyst with other nonprecious metals or molecular catalysts.²⁵⁻²⁷ Here we demonstrate the use of a Ni-Mo alloy by electrodeposition as an alternative hydrogen evolving catalyst. Ni-Mo was photoelectrodeposited on the a-Si photocathode from a solution containing Ni-(SO₃NH₂)₂, H₃BO₃, and Na₂MoO₄, as previously reported.²⁵ A bias of -1 V vs Ag/AgCl reference electrode was applied to yield $\sim 16 \text{ mA/cm}^2$ deposition current under illumination. The deposition time is about 30 s with 500 mC/cm² of charge passed. After catalyst deposition, the sample was rinsed with DI water and then measured in KHP buffer solution with pH of 4.5. Figure 5a compares the photoelectrochemical performance of a-Si cells with Ni-Mo (blue trace) and Pt (orange dash trace) cocatalysts. Compared with the a-Si cell with Pt catalyst, a-Si with Ni-Mo shows slightly lower onset potential of ~0.87 V versus RHE and similar current densities of ~11 mA/cm² at 0 V. The maximum efficiency of a-Si cells with Ni-Mo catalyst is 5.5%, slightly lower than that with Pt as catalyst. Notably, high photocurrents of \sim 1.2, 3.8, and 6.4 mA/cm² are measured at large biases of 0.8, 0.7, and 0.6 V versus RHE, respectively. This result demonstrates the use of low-cost absorber materials in combination with earth-abundant catalysts for highly efficient solar water reduction.

In conclusion, we have demonstrated a low-cost a-Si based thin film photocathode for highly efficient water reduction. In particular, the photocurrents obtained at large positive bias in respect to RHE are the highest reported to date for any photocathode. The a-Si photocathode has achieved over 6.0% efficiency and stable operation. The work here presents an important advance toward designing efficient photocathode with high photovoltage for water splitting.



Figure 5. Photoelectrochemical characterization of a-Si photocathodes with Ni–Mo catalyst. (a) J-V plot measured in KHP buffer solution for a-Si cathode with Ni–Mo catalyst (blue trace) and Pt catalyst (orange dash trace). (b) Chronoamperometry measurement of a-Si with Ni–Mo at bias from 0.8 to 0.6 V vs RHE under chopped light illumination.

ASSOCIATED CONTENT

Supporting Information

Deposition of the amorphous Si photocathode, structural, and photoelectrochemical characterization detail. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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SUPPORTING INFORMATION

1. Fabrication of a-Si photocathodes

The fabrication procedure for a-Si photocathodes is similar to that used to make single junction a-Si:H solar cells with stabilized efficiencies greater than 10%.¹ It starts with the deposition of a 1.8 µm thick pyramidally textured ZnO transparent front electrode on a glass substrate by low-pressure chemical vapor deposition using diethylzinc and H₂O as precursor gases. Next, the structure was transferred into a plasma-enhanced CVD reactor to deposit amorphous silicon layers at 200°C. The growth sequence of the p-i-n structure was (1) 5 nm p-type nanocrystalline silicon (2) 10 nm of

p-type amorphous silicon carbide (3) 250 nm of intrinsic amorphous silicon as the active light absorber material (4) two 5 nm nanocrystalline n-type silicon layers with a 20 nm n-type silicon oxide layer sandwiched between these two. Finally, another layer of ZnO was deposited on top to protect the a-Si from exposure to air and moisture. The detail of doping process can be found in previous publication.² In general, phosphine was used as n-type doping and trimethyl boron was used as p-type doping. Immediately before the sputtering of the protection layer, the top ZnO layer was etched in 0.2M HCl solution for 60 seconds. Sputter deposition was carried out in an AJA Orion-5. A 8 nm Ti layer was sputtered in 5 mTorr Argon gas, followed by 80 nm of TiO₂ using reactive sputtering in a gas mixture of 4 mTorr Argon and 1 mTorr O₂. We found the Ti layer is important to prevent damage of a-Si during reactive sputtering process. According to previous studies, the thin Ti layer is likely to be partially oxidized to TiO₂.³ For the hydrogen evolution catalyst either a 2 nm Pt layer made by sputtering or a Ni-Mo alloy layer made by electrodeposition (see below) was deposited on top of the TiO₂.

2. Structural Characterization

A Scanning Electron Microscope (SEM, Zeiss Gemini Ultra-55) was employed to examine the structure of the a-Si photocathode. Images were taken at working voltage of 3 KV to avoid charging. The tilted cross-section image shown in Fig. 1 was colorized to help visualize different layers of the photocathode.

3. Photoelectrochemical Measurement

Once prepared, the a-Si photocathode was characterized using a CHI 6091d potentiostat in a three-electrode configuration, with a-Si photocathode as working electrode, a Ag/AgCl reference electrode (BASi RE5B) and Pt wire as counter electrode. The electrolyte used was 0.5 M potassium hydrogen phthalate solution. Other electrolytes such as 0.5 M potassium dihydrogen phosphate solution with pH adjusted to 4 were also used and yielded similar results. The electrolyte was purged with forming gas (95% Ar and 5% H₂) to exclude O_2 in the solution and maintain constant Nernst potential of H⁺/H₂. Typically, voltage was linearly scanned from 1 V to -0.3 V vs RHE at a scan rate of 10 mV/s. Other scan rates and voltage range were also tested. Cathodic current (current flows out of working electrode) was defined as negative in our potentialstat. The I-V curves presented were as-measured, without correction. The electrode was illuminated with a solar simulator (solar light, model 16S-300-005), the intensity of which was adjusted to 100 mW/cm², calibrated using a radiometer (Solar light, PMA-2100) and a pyranometer (PMA-2144). Because of its high electron mobility, the electrode was illuminated through the backside of the sample (glass side). For light intensity dependence measurements (Fig. S1), a series of neutral density filters were placed in front of solar simulator to adjust the light intensity. For chronoamperometry measurement, the potential of working electrode was held at 0.7 V or 0.8 V vs RHE and the current density under chopped light illumination was recorded.

Incident photon to charge conversion efficiency (IPCE) was measured in a homebuild setup, using a 150 W Xenon lamp (Newport) coupled with a 1/8m Monochromator (Oriel) as the light source. The intensity of monochromatic light was calibrated with a Si photodiode (Thorlabs FDS100-CAL). The working electrode was biased at 0.4 V vs RHE with a Gamry Reference 600 potentialstat.

4. Electrodeposition of Ni-Mo catalyst

Ni-Mo catalyst was photoelectrodeposited on an a-Si photocathode using the previously described three-electrode configuration. The electrolyte contained 1.3 M Ni(SO₃NH₂)₂, 0.5 M H₃BO₃ and 0.02 M Na₂MoO₄.⁴ All the chemicals were used without further purification. The pH of solution was adjusted to 4.5 with KOH solution. During the deposition, the potential was applied at -1 V vs Ag/AgCl until 500 mC/cm⁻² of charge passed. The working electrode was illuminated with intense simulated solar light (~300 mW/cm²). The electrode was rinsed with DI water before photoelectrochemical characterization in KHP buffer solution for hydrogen generation.



Figure S1: photocurrent at 0 V vs RHE as a function of light intensity. The photocurrent is linear in the light intensity.



Figure S2. Photocurrent density as a function of time at 0V vs RHE for the a-Si photocathode without TiO₂ protection.



Figure S3. Morphology of electrodeposited Ni-Mo film.

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