

Solar Hydrogen Production by Amorphous Silicon Photocathodes Coated with a Magnetron Sputter Deposited Mo₂C Catalyst

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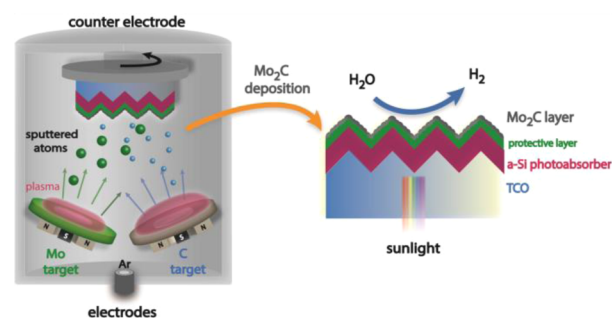
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S Supporting Information

ABSTRACT: Coupling of Earth-abundant hydrogen evolution catalysts to photoabsorbers is crucial for the production of hydrogen fuel using sunlight. In this work, we demonstrate the use of magnetron sputtering to deposit Mo₂C as an efficient hydrogen evolution reaction catalyst onto surface-protected amorphous silicon (a-Si) photoabsorbers. The a-Si/Mo₂C photocathode evolves hydrogen under simulated solar illumination in strongly acidic and alkaline electrolytes. Onsets of photocurrents are observed at potentials as positive as 0.85 V vs RHE. Under AM 1.5G (1 sun) illumination, the photocathodes reach current densities of -11.2 mA cm^{-2} at the reversible hydrogen potential in 0.1 M H₂SO₄ and 1.0 M KOH. The high photovoltage and low-cost of the Mo₂C/a-Si assembly make it a promising photocathode for solar hydrogen production.

Sunlight-driven water splitting in a photoelectrochemical (PEC) cell is a promising approach to solar energy conversion and storage.^{1–3} Similar to water electrolysis, PEC hydrogen production requires a catalyst to improve the kinetics and lower the overpotential for the hydrogen evolution reaction (HER, $2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g})$). For solar hydrogen to be cost competitive, the HER catalysts need to be efficient, inexpensive, and scalable. Recently many new classes of inorganic HER catalysts, composed of only Earth-abundant elements, have been reported.^{4–8} The integration of these catalysts into photocathodes for PEC hydrogen evolution, however, is less developed. We and others showed that molybdenum carbide (Mo₂C) is an efficient HER catalyst.^{9–11} Prior to this work, this catalyst had not been applied for PEC hydrogen evolution due to the difficulty to form a conformal catalyst layer on a photocathode using thermally prepared Mo₂C nanoparticles, which were employed in the electrochemical studies.¹² Herein, we demonstrate that confocal magnetron cosputtering from elemental sources can be used to deposit a conformal Mo₂C layer on amorphous silicon (a-Si) photocathodes (Scheme 1), which opens the doors for this catalyst to be applied in PEC hydrogen evolution.

Scheme 1. Deposition of Mo₂C Catalyst by Confocal Magnetron Cosputtering onto a-Si Photocathodes for Solar Hydrogen Production



Silicon is widely considered as an attractive photoabsorber material for solar fuel production.¹³ Although Si-based photoelectrodes are unstable in water, recent progress in surface protective layers has greatly improved their stability for water splitting.^{14–17} Until now, crystalline Si (c-Si) is the predominant form of Si used in PEC devices thanks to its availability and high efficiency. Photocurrent densities as high as -28 mA cm^{-2} at 0 V vs RHE (reversible hydrogen electrode) have been obtained using c-Si photocathodes under 1 sun illumination.¹⁴ However, the photovoltage of a single junction c-Si photoelectrode is limited by the small band gap of the material (1.1 eV).¹⁵ The most positive onset potential of photocurrents in c-Si photocathodes is +0.56 V vs RHE when Pt is used as the HER catalyst,¹⁴ and +0.4 V vs RHE when an Earth-abundant HER catalyst is used.¹⁶ The small photovoltage of c-Si implies that to achieve unassisted water splitting, a high-voltage-generating second photoabsorber component is required, which can be expensive (in the case of photovoltaic cells) or currently inaccessible (in the case of photoanodes).¹⁸ This consideration prompted us to examine a-Si as an alternative Si-based photoabsorber. a-Si has an optical band gap (Tauc bandgap) of 1.6–1.8 eV with several desirable characteristics for PEC devices: (i) high light absorption coefficient; (ii) industrial low cost

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manufacturing processes; (iii) optimal conduction band alignment for solar hydrogen production.¹⁹ Lin et al. previously reported PEC hydrogen evolution by a-Si photocathodes coated with Pt or Ni–Mo as HER catalysts. At a pH 4 buffer solution, these photoelectrodes gave a maximum photovoltage of 0.93 V vs RHE and a saturated photocurrent density of -11.6 mA cm^{-2} .¹⁹ However, until now a-Si-based photocathodes have not been applied for PEC hydrogen evolution in strongly alkaline solutions, and only few examples of a-Si tandem junction photocathodes have been reported to work in acidic solutions.^{20,21} At these extreme pHs, ion conductivity and mobility are optimized, which leads to lower resistance losses in water splitting devices. Taking advantage of the fact that Mo₂C is an active and stable catalyst in both acidic and basic media, we show here that a-Si photocathodes coated by Mo₂C are able to evolve hydrogen at pH = 1 and 14.

Magnetron sputtering is an industrial-scale method to deposit thin film coatings for a large variety of different materials and applications.²² It has been employed since the 1970s to deposit thin films, among them also metal carbide films such as TiC,²³ TiC-based nanocomposites,²⁴ and other transition metal carbides.^{25,26} A thorough understanding of the involved processes nowadays enables tuning of film properties such as composition, density, thickness, and crystallinity. Therefore, magnetron sputtering was used for the deposition of molybdenum carbides as catalyst layers. Initially both Mo₂C and MoC were deposited on fluorine-doped thin oxide (FTO) electrodes. The compositions of the films were confirmed by XPS (Figure S1). The electrocatalytic activity of these films in 0.1 M H₂SO₄ and 1 M KOH was examined by linear sweep voltammetry (Figure 1a,b).²⁷ The activity in acid is slightly higher than the activity in base, consistent with earlier reports.

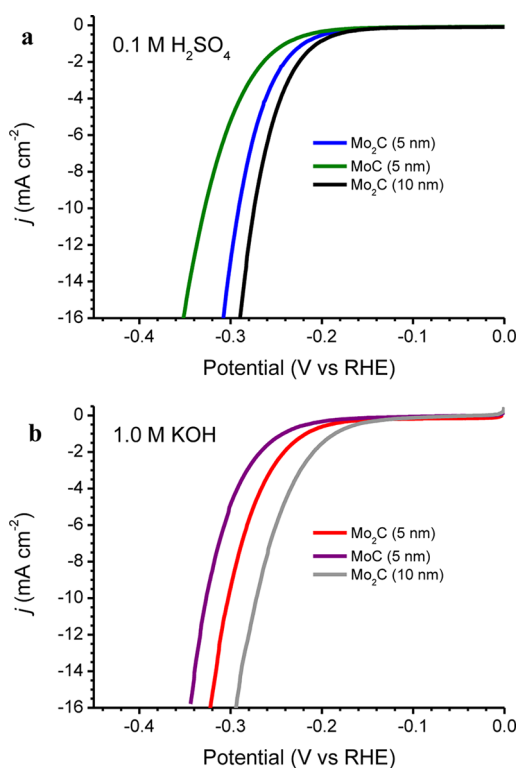


Figure 1. Linear sweep voltammetric (LSV) data for Mo₂C and MoC catalyst films sputtered onto FTO in (a) 0.1 M H₂SO₄ and (b) 1 M KOH at a scan rate of 5 mV s⁻¹.

With the same thickness of 5 nm, Mo₂C is more active than MoC; the overpotential (η) at the same current density is about 40 mV less for the former. Similar trends in activity have been previously observed in other forms of Mo₂C and MoC, suggesting that Mo₂C is intrinsically more active than MoC for the HER.^{28,29} Increasing the thickness from 5 to 10 nm only slightly increased the catalytic activity. Tafel plots are shown in Figure S2. The long-term stability of the Mo₂C thin film catalyst was examined by potentiostatic electrolysis. At $\eta = 310 \text{ mV}$, a Mo₂C film (5 nm) exhibited a constant activity in 1 M KOH during 10 h; a similar film retained more than 80% of the initial current density after 10 h of continuous electrolysis in 0.1 M H₂SO₄ at the same potential (Figure S3). Table 1 summarizes the HER performance of magnetron-sputtered Mo₂C and MoC thin films. The activity of Mo₂C is noteworthy considering the very low loading of the catalyst. For example, the loading of 5 nm Mo₂C film is only $4 \mu\text{g cm}^{-2}$. By comparison, previously reported Mo₂C catalysts have loadings in the order of mg cm^{-2} . Thus, the lower geometrically averaged activity of these thin films compared to the most active Mo₂C nanoparticles is largely due to lower loading. Nevertheless, the electrochemical data confirms the catalytic activity of magnetron-sputtered Mo₂C thin films. As shown below, because PEC water splitting devices have a lower requirement on the current density than electrolyzers, the activity of Mo₂C thin films is sufficient to drive high PEC performance on a-Si.

A 5 nm film of Mo₂C was then deposited on a-Si photocathodes for PEC hydrogen evolution. Each a-Si photocathode is a p-i-n stack with an intrinsic layer of $\sim 230 \text{ nm}$ in thickness and was deposited by plasma-enhanced chemical vapor deposition on textured ZnO (sheet resistance $10 \Omega \text{ cm}^{-2}$) on glass. A 100 nm layer of TiO₂ was used to protect the a-Si layers from photocorrosion. To enhance the surface affinity of TiO₂, a 20 nm layer of aluminum-doped zinc oxide was deposited by ALD in between the a-Si and TiO₂ layers.^{30,31} Scanning electron microscopy (SEM) images of the complete photocathode are shown in Figure 2. While different layers are already visible in the conventional image, they are more clearly distinguished in the image acquired using an Energy selective Backscattered (EsB) detector, which shows the elemental Z contrast of the different layers (Figure 2, right). The Mo₂C layer is dense and conformal on top of the TiO₂ layer.

The a-Si/Mo₂C photocathodes were tested for PEC hydrogen evolution in strongly acidic and alkaline solutions under simulated 1 sun AM 1.5G illumination. Figure 3 displays the current–potential curves in the dark and under illumination. The PEC activity is similar in 0.1 M H₂SO₄ and 1 M KOH. The fill factor in 0.1 M H₂SO₄ is slightly higher than in 1 M KOH, likely because the electrocatalytic activity of Mo₂C is slightly higher in 0.1 M H₂SO₄ (Figure S4). The onset of photocurrent is about 0.85 V vs RHE, which is also confirmed by PEC response under chopped illumination (Figure S5). The photovoltage of a-Si is 0.93 V (SI);¹⁹ thus, the 5 nm Mo₂C film has an onset potential of only 80 mV for PEC HER. Photocurrent densities of about -11.2 mA cm^{-2} are obtained at 0 V vs RHE. The transient behavior of photocurrents disappeared at potentials negative of 0.7 V vs RHE, indicating fast electron extraction by the catalyst film at these potentials (Figure S5). The high photovoltage of a-Si/Mo₂C photocathodes results in significant photocurrent densities at positive potentials. Photocurrent densities of -1.8 and -2.6 mA cm^{-2} are already obtained at 0.6 V vs RHE in acidic and alkaline solutions, respectively. Photocurrent densities of -6.0 to -7.0 mA cm^{-2} are obtained at 0.4 V vs RHE, which is the

Table 1. Summary of HER Performance and Tafel Slopes

catalyst (loading/mg cm ⁻²)	electrolyte	Tafel slope (mV dec ⁻¹)	j_0 (mA cm ⁻²)	η @ 10 mA cm ⁻² (mV)
Mo ₂ C 5 nm (~0.004)	0.1 M H ₂ SO ₄	69	0.7×10^{-3}	290
	1.0 M KOH	80	2.0×10^{-3}	300
MoC 5 nm (~0.004)	0.1 M H ₂ SO ₄	83	1.3×10^{-3}	327
	1.0 M KOH	83	1.2×10^{-3}	328
Mo ₂ C 10 nm (~0.009)	0.1 M H ₂ SO ₄	67	0.9×10^{-3}	270
	1.0 M KOH	78	4.4×10^{-3}	270
Mo ₂ C ^a (~1–3)	1.0 M H ₂ SO ₄	56	1.3×10^{-3}	200
	1.0 M KOH	54	3.8×10^{-3}	210
Mo ₂ C/CNT ^b (2)	0.1 M HClO ₄	55.2	1.4×10^{-2}	152
Np-Mo ₂ C NWS ^c (0.21)	0.5 M H ₂ SO ₄	54		~130

^aMo₂C microparticles from ref 9. ^bMo₂C nanoparticles dispersed on carbon nanotubes, from ref 10. ^cMo₂C nanowires from ref 11.

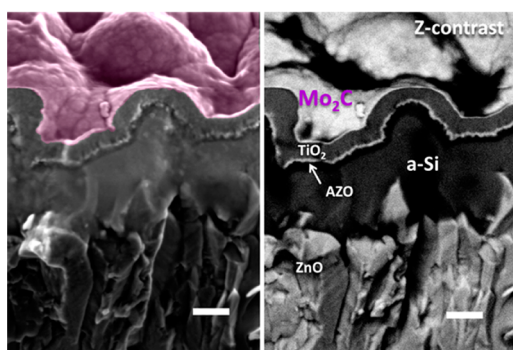


Figure 2. Scanning electron microscopy images of a complete a-Si photocathode. The image on the left is a conventional SEM image where the Mo₂C layer has been colored for ease of visualization. The image on the right is an image acquired using an Energy selective Backscattered (EsB) detector. Heavier elements appear brighter in the right image, following the order of Z contrast $Z_{\text{Mo}} > Z_{\text{Zn}} > Z_{\text{Ti}} > Z_{\text{Si}}$. Layers from top to bottom are Mo₂C (5 nm), TiO₂ (100 nm), AZO (20 nm), a-Si (300 nm), and ZnO (2 μm). Scale bars corresponds to 200 nm. The angle of view is 45°.

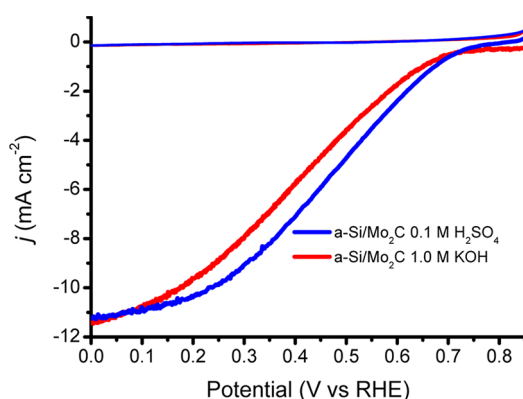


Figure 3. Linear sweep voltammetry (LSV) curves for a-Si/Mo₂C photocathode in 1.0 M KOH and 0.1 M H₂SO₄ under simulated AM 1.5 (1 sun) illumination. The sweep rate is 5 mV s⁻¹.

onset potential of state-of-the-art crystalline silicon photocathodes. It is noted that the PEC performance of a-Si/Mo₂C at extreme pHs is comparable to a-Si/Pt and a-Si/Ni–Mo at pH 4.¹⁹ This suggests that the thin Mo₂C film is as good a catalyst as Pt and Ni–Mo for PEC hydrogen evolution, and the performance of the device is mostly limited by the a-Si layer.

A stability test was conducted for the a-Si/Mo₂C photocathode in 1 M KOH. The photocurrent density is stable under

continuous illumination during 1 h (Figure 4a). The Faradaic efficiency of PEC HER in 1 M KOH was determined, showing a

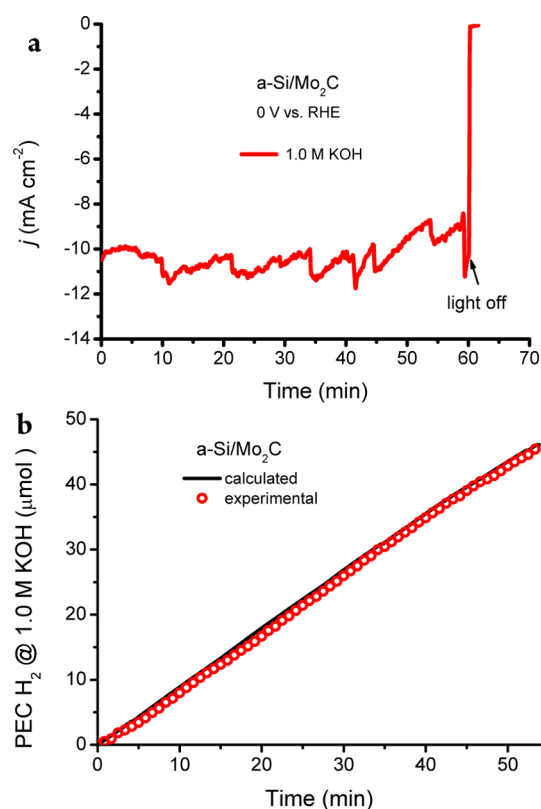


Figure 4. (a) Long-term stability test for a-Si/Mo₂C photocathode during PEC hydrogen evolution at 0 V vs RHE in 1 M KOH. Fluctuations in the photocurrent are due to bubble formations at the surface of the photoelectrode. (b) Faradaic efficiency during photoelectrochemical hydrogen evolution in 1 M KOH for an a-Si/Mo₂C photocathode. Conditions: 0 V vs RHE, AM 1.5 (1 sun) illumination.

quantitative efficiency (Figure 4b). At a longer time scale, the photocurrent density slowly decays (Figure S6). As the Mo₂C catalyst is stable in 1 M KOH during electrolysis for 10 h (see above), the deactivation is likely due to the instability of the TiO₂-protected a-Si photocathode. There was only one prior report of PEC hydrogen evolution in alkaline solution using a Si-based photocathode.³² The reported Ni/Ti/p-Si photocathode degraded over the course of several hours in 1 M KOH as well. Moreover, TiO₂-protected Cu₂O photocathode had similar stability in base.³¹ To further probe the origin of deactivation, the

a-Si/Mo₂C photocathodes after 1, 2, and 5 h of operation were analyzed by XPS. Mo₂C was still found on the photocathodes, but its amount decreased with time. Moreover, signals due to Si were observed, suggesting that corrosion of the TiO₂ protective layer and the AZO and a-Si layers underneath occurred during long-term operation. Thus, the stability of TiO₂ protective layer is limited to several hours under reductive conditions in base. Annealing of the TiO₂ layers¹⁵ and sputtering of metallic molybdenum interlayers³³ have been shown to improve the stability of crystalline silicon photocathodes in acidic electrolytes. In future work, similar approaches will be attempted to improve the stability of the a-Si/Mo₂C photocathodes in alkaline solutions.

In summary, the activity and stability of Mo₂C in strongly acidic and basic solutions enable us to prepare efficient a-Si/Mo₂C photocathodes that operate in these solutions. High photocurrent densities and photovoltages are obtained with these photoelectrodes. This is the first report of PEC hydrogen evolution in strongly alkaline solutions by a-Si-based photocathodes. It is also the first application of Mo₂C as a HER catalyst in PEC water splitting. W₂C was previously deposited on c-Si photocathodes;³⁴ however, the role of W₂C was to support the Pt catalyst, as W₂C had low activity for HER. Magnetron sputtering is the key technology for the deposition of conformal Mo₂C films. The work is also the first application of magnetron sputtering for the deposition of a catalyst layer onto a photoabsorber. The promising results reported here should motivate the further utilization of this industrially viable and up-scalable technique for the integration of Earth-abundant water splitting catalysts into PEC devices.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details and supporting data. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b03417.

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Notes

The authors declare no competing financial interest.

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