Tandem Si Micropillar Array Photocathodes with Conformal Copper Oxide and a Protection Layer by Pulsed Laser Deposition

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ABSTRACT: This work demonstrates the influence of high-quality protection layers on Si–Cu$_2$O micropillar arrays created by pulsed laser deposition (PLD), with the goal to overcome photodegradation and achieve long-term operation during photoelectrochemical (PEC) water splitting. Sequentially, we assessed planar and micropillar device designs with various design parameters and their influence on PEC hydrogen evolution reaction. On the planar device substrates, a Cu$_2$O film thickness of 600 nm and a Cu$_2$O/CuO heterojunction layer with a 5:1 thickness ratio between Cu$_2$O to CuO were found to be optimal. The planar Si/Cu$_2$O/CuO heterostructure showed a higher PV performance ($j_{sc} = 20$ mA/cm$^2$) as compared to the planar Si/Cu$_2$O device, but micropillar devices did not show this improvement. Multifunctional overlayers of ZnO (25 nm) and TiO$_2$ (100 nm) were employed by PLD on Si/Cu$_2$O planar and micropillar arrays to provide a hole-selective passivation layer that acts against photocorrosion. A micropillar Si/ITO-Au/Cu$_2$O/ZnO/TiO$_2$/Pt stack was compared to a planar device. Under optimized conditions, the Si/Cu$_2$O photocathode with Pt as a HER catalyst displayed a photocurrent of 7.5 mA cm$^{-2}$ at 0 V vs RHE and an onset potential of 0.85 V vs RHE, with a stable operation for 75 h.

KEYWORDS: Si micropillar array, tandem photocathode, copper oxide, pulse laser deposition, hydrogen evolution reaction

INTRODUCTION

Photoelectrochemical water splitting is an attractive way to produce clean hydrogen fuel by economic and convenient utilization of solar energy.1–4 The concept of photoelectrochemical (PEC) tandem device configurations that combine dual semiconducting photoabsorbers carries great potential for robust, inexpensive, and efficient unassisted solar water splitting.5–8 In such a solar-to-fuel (S2F) device, sunlight is absorbed by a pair of semiconductor photoelectrodes to split water into hydrogen and oxygen.9,10 Commonly, a bias voltage is needed from an external energy source for electron injection into the conduction band of the photoelectrode materials,11 with the goal to overcome photodegradation and achieve long-term operation during photoelectrochemical (PEC) water splitting. Sequentially, we assessed planar and micropillar device designs with various design parameters and their influence on PEC hydrogen evolution reaction. On the planar device substrates, a Cu$_2$O film thickness of 600 nm and a Cu$_2$O/CuO heterojunction layer with a 5:1 thickness ratio between Cu$_2$O to CuO were found to be optimal. The planar Si/Cu$_2$O/CuO heterostructure showed a higher PV performance ($j_{sc} = 20$ mA/cm$^2$) as compared to the planar Si/Cu$_2$O device, but micropillar devices did not show this improvement. Multifunctional overlayers of ZnO (25 nm) and TiO$_2$ (100 nm) were employed by PLD on Si/Cu$_2$O planar and micropillar arrays to provide a hole-selective passivation layer that acts against photocorrosion. A micropillar Si/ITO-Au/Cu$_2$O/ZnO/TiO$_2$/Pt stack was compared to a planar device. Under optimized conditions, the Si/Cu$_2$O photocathode with Pt as a HER catalyst displayed a photocurrent of 7.5 mA cm$^{-2}$ at 0 V vs RHE and an onset potential of 0.85 V vs RHE, with a stable operation for 75 h.
presented a simple method to prepare a Cu$_2$O/CuO heterostructure to protect the Cu$_2$O photocathode from photocorrosion in the PEC water splitting reaction. The as-prepared Cu$_2$O/CuO composite showed improved stability for the hydrogen evolution reaction by increasing the coverage of CuO on the Cu$_2$O film. However, CuO has limited stability in aqueous electrolytes as suggested by the Pourbaix diagram. Many studies have reported CuO as a photocathode for the PEC water reduction reaction, although it is uncertain how much of the photocurrent leads to H$_2$ evolution. In other studies, attempts to address this issue and to achieve long stability were focused on modifying the semiconductor surface with various n-type oxides (hole-selective layers) and cocatalyst layers like n-Ga$_2$O$_3$, AZO, CdS, NiO, TiO$_2$, ITO, Pt, NiSi, etc. Many researchers investigated semiconductor metal oxide materials, such as ZnO, WO$_3$, Cu$_2$O, SnO$_2$, and V$_2$O$_5$, either as nanoparticles or as continuous films, to create sensors (e.g., for humidity, ultraviolet, and biological analytes), and their sensing properties were found to be dependent on size, shape, defects, and dopants. Furthermore, the effect of various dopants (Mg, Al, Ga, Fe, Ni) in the electron-selective oxide layer to increase the donor density to effectively prevent any resultant charge recombination additionally improves the photovoltage. Various deposition systems and techniques (i.e., atomic layer deposition (ALD), pulse laser deposition, chemical vapor deposition, spray pyrolysis, sputtering, anodic oxidation, thermal oxidation, and electrochemical deposition) have been employed for passivating semiconductor photoabsorbers, each with their own advantages and limitation. Pulse laser deposition (PLD) is an emerging technique for industrialized use, and can achieve large-area uniform coating on 3D structures. As a result of passivation, the semiconductor can be protected from the harsh acidic/basic electrolyte environment often needed for long-term operation. Here, we demonstrate the use of pulsed laser deposition (PLD), by which ZnO and TiO$_2$ overlayers can be grown directly and homogeneously on Si/Cu$_2$O microstructures with an accurate film thickness and composition. We here...
report the fabrication of tandem Si/Cu₂O micropillar array devices with passivation layers of ZnO and TiO₂ with a precise thickness deposited by PLD. This study exhibits that the PLD approach can be effective and scalable for designing efficient and stable silicon-based tandem photocathodes for solar water splitting. In addition, we explore design aspects for these micropillar-based Si/Cu₂O PEC tandem devices. Specifically, we investigate the influence of geometrical variations to a micropillar array PEC device design on light absorption and onset potential (V_{oc}). An ITO-Au (85 nm) transparent conductive film is applied for coupling the top photoabsorber on the engineered light-trapping micropillars. In addition, we fabricated a Cu₂O/CuO heterojunction on Si planar and micropillar arrays to investigate the effect of the Cu₂O/CuO composite in PV and PEC performances. A micropillar Si/ITO-Au/Cu₂O/ZnO/TiO₂/Pt stack is compared to a planar device. Furthermore, we evaluate the roles of the n-ZnO (25 nm) and TiO₂ (100 nm) thin films as hole-selective and passivation layers.

RESULTS AND DISCUSSION

Micropillar Array Fabrication and Interlayer Deposition. The substrates with vertically ordered micropillar arrays with radial pn-junctions (p-type base and n'-type emitter) were fabricated using deep-reactive ion etching (DRIE) (Figure S1). The light absorption ability in the micropillar structure is considerably improved not only by the increased surface area of the photoelectrode but also by the manifold light scattering within the micropillar structure (Scheme 1), which is a tandem device that contains two photoabsorbers. The top cell presents a large band gap material that absorbs high energy photons, while the bottom cell has a small band gap material that harvests the low energy photons. Many device and material aspects need to be tuned carefully to achieve high efficiency, such as the bandgaps and material thicknesses, but also reflection and parasitic absorption. Furthermore, the transparent conductive oxide (TCO) layer on the substrate can achieve an effective charge separation for a relatively thick film. In general, TCO-semiconductor Schottky contacts can lead to high recombination rates and therefore usually produce low V_{oc} values. However, when a PV junction is decorated with a TCO layer, high V_{oc} values can still be obtained.

Upon following the fabrication and DRIE process of the micropillars (Figure S1), a few samples were fractured and side views were taken by scanning electron microscopy (SEM) (Figure 1). The base and tip diameters of these micropillars within the arrays are approximately identical, emphasizing the highly anisotropic nature of the DRIE process. A slight tapering occurred at about ∼20% from the top of the pillars. This effect was more pronounced for the 40 μm pillars (12 min etching), where the diameter decreased approximately 100–200 nm. In addition, the SEM images (Figure 1) show the entire side surface of the micropillars to be scalloped due to the cyclic steps in the etching process, involving gas pulses of SF₆ (etching step) and C₄F₈ (passivation step), providing scallops with an overall height of ∼340 nm, for each etching cycle.

The first step to an efficient Si−Cu₂O tandem device is to find the ideal interlayer for the Cu₂O deposition on top of the Si micropillar array. Such a layer needs to be a transparent so that sunlight can pass through it and reach the underlying Si photoabsorber. In addition, the interlayer must be conductive to provide an ohmic contact for the growth of Cu₂O film and allow charge carrier exchange between the Si and Cu₂O. Here, we investigated different interlayers such as gold (Au), copper (Cu), molybdenum (Mo), platinum (Pt), indium tin oxide (ITO), and ITO/Au deposited using a magnetron sputtering system.

The growth of the Cu₂O film on different interlayers was characterized by scanning electron microscopy (SEM) as illustrated in Figure 2. By using Cu, Au, and Pt interlayers, Cu₂O growth was compact and homogeneous on the Si substrate. Yet, due to the low conductivity of the Mo interlayer,
Cu$_2$O grew into large cuboctahedral crystals without covering the Si surface in a conformal manner. However, none of these metallic interlayers is suited for the tandem device due to their low optical transparency. Thus, a thin layer of the conducting ITO (80 nm) with a thin layer of Au (nominally 5 nm) was deposited to enhance the conductivity without compromising in transparency. The short sputtering time, which leads to small Au nanoparticles instead of a dense homogeneous film, plays an important role in the electrodeposition of Cu$_2$O, leading to specifically oriented crystal growth on the substrate. Furthermore, the combined ITO-Au nanoparticle film (i.e., the ITO/Au layer) is sufficiently transparent and conductive to deposit Cu$_2$O effectively.

**Optimization of Cu$_2$O Film Thickness.** The second step in the overall fabrication process is the deposition of Cu$_2$O on the conductive Si/ITO-Au planar and micropillar array substrates. Conformal, compact, and semitransparent Cu$_2$O films were prepared by chronoamperometric (CA) electrodeposition. To obtain a high-performance Cu$_2$O film, we deposited the material with different thicknesses (250–1300 nm) by changing the electrodeposition time (200–1300 s) at a constant cathodic potential (−0.8 V), while the temperature of the bath was maintained at 50 °C. It is important to notice that we did not elongate the deposition process for micropillar arrays with different lengths (10–40 μm) and for different pitches (8–14 μm), see Figure 3, because the highest growth rate is reached at the applied potential and temperature of the bath solution.

Because the ITO-Au interlayer is conducting, and the system is mass transport-limited during the electrodeposition, a conformal layer of Cu$_2$O is deposited on the micropillars. It was observed that Cu$_2$O forms columnar crystals in a uniform manner on Si/ITO-Au planar substrates (Figure S2) and at the bottom side of the Si/ITO-Au micropillar array substrates (Figure S3) as well as in the sidewall scalloped area. This uniformity occurred despite the fact that the ITO/Au interlayer was thinner on the scalloped sides of the micropillars when compared to the bottom side of the Si substrate, which was caused by a shadowing effect by the scallops during the interlayer deposition by the directional magnetron sputtering process.

The SEM images and X-ray diffraction (XRD) characterization revealed that the prepared films have columnar triangular cubes or truncated cubic crystal growth with (111) orientation for shorter and longer deposition times, respectively (Figure 4). Paracchino et al. reported that the columnar film with cubes exposing the triangular (111) faces parallel to the substrate showed a higher photocurrent. The crystal structure of the deposited layers was confirmed by X-ray diffraction (XRD). Figure 4 shows the XRD pattern of Cu$_2$O showing (110), (111), and (200) peaks at 30°, 36.9°, and 42.7°, respectively, on p-Si/ITO/Au micropillar array. For the ITO/Au interlayer, an ITO peak was found at 31° and for the Au (200) peak was found at 38.6°. For the silicon substrate, two peaks were observed, (200) and (400) at 33.3° and 61.3°, respectively. The intensity of the ITO peak diminished with increasing Cu$_2$O film thickness, as well as the Au peak, which was completely covered in a broad peak of the Cu$_2$O with higher intensity. Finally, a Cu$_2$O (220) peak was found in close proximity with the p-Si (400) peak at 61.3°, upon thicker Cu$_2$O deposition, which occurs from the difference in the surface energy of the cubic crystal facets.
Preparation of Cu$_2$O/CuO Heterojunction. After the electrodeposition, the Cu$_2$O film was subsequently converted into a Cu$_2$O/CuO heterojunction film by a thermal annealing process at 350 °C in air. To optimize the film thickness ratio between Cu$_2$O and CuO, we followed two different strategies. First, electrodeposited Cu$_2$O samples were prepared with different film thicknesses by variation of the deposition time on the Si/ITO-Au substrate, followed by annealing all samples at a constant annealing time of 1 h at 400 °C. Second, samples were prepared with the same initial Cu$_2$O thickness, followed by annealing the samples at different annealing times (0.5–3 h) at 400 °C.

SEM images were taken to provide the thicknesses of both copper oxides on the Si/ITO-Au substrates (Figure 5). The morphology of the sample changed after thermal oxidation in air, from a continuous film before thermal oxidation to a...
bilayer-structured film after thermal oxidation. This observation implies that the outer layer of the Cu₂O film was transformed into CuO, and a Cu₂O/CuO heterojunction was formed. When samples with different initial thicknesses of Cu₂O were oxidized in air using the same annealing time (Figure 5a−c), the thickness of the newly formed CuO film on top of Cu₂O layer was the same. In the second case, when the thermal oxidation process time was increased from 0.5 to 3 h (Figure 5d−f), the thickness of the outer CuO layer increased. By consuming the Cu₂O layer underneath the CuO, the thickness of the inner Cu₂O layer was reduced. This trend is clearly indicated in Figure 6a. Diao et al. reported that the whole Cu₂O layer can be oxidized to CuO, leading to a continuous porous film. These results confirm that the Cu₂O to CuO thickness ratio can be controlled accurately by varying the deposition time of the initial Cu₂O film thickness and the subsequent thermal oxidation time.

The XRD patterns of the Cu₂O/CuO heterostructure film on Si/ITO-Au substrates, in which the diffraction peaks of both cubic Cu₂O and monoclinic CuO appear (Figure 6b,c), provide direct evidence for the formation of the Cu₂O/CuO bilayer heterostructure. The emerging XRD diffraction peaks at 31.1°, 36.5°, and 39.2° could be indexed to the (110), (002), and (200) planes of CuO, respectively. In addition, from the XRD plots at increasing annealing times (Figure 6b), the intensity of the CuO [002] peaks increases, while the Cu₂O [111] peak intensities decrease. In contrast, when the initial CuO film thickness increased by the subsequent oxidation time is kept constant (Figure 6c), the spectrum hardly changes.

**Photovoltaic (JV) Measurements on Si Micropillar Arrays with a Radial pn-Junction.** Micropillar array dimensions (height and pitch) have an influence on important functional parameters such as surface area, light absorption, and charge separation, which finally regulate the device efficiency. In addition, the relationships between the fabrication process and the characteristics of device performance are tough to predict. For instance, it is known that with increasing micropillar height, the total junction area in the solar cell increases, and the reflectivity of sunlight probably decreases. The effect of micropillar dimensions (i.e., height and pitch) with integrating radial pn-junction was here
investigated by examining the resulting photoelectrical performance.

Figure 7a–d shows the JVs characteristics of samples with different pillar heights and pitch from 10 to 40 μm and 8 to 14 μm, respectively. Samples with pillars performed better in both current density (JSC) and open circuit voltage (VOC) as compared to a flat sample, which indicates that the pillar structures significantly improve the properties such as local surface area and light absorption properties in solar cells. The values of the fill factor (FF) and efficiency (η), along with their respective JSC and VOC are shown in Table S1. A minor increase of VOC is observed, from 450 mV for the flat sample to ≥550 mV for micropillars.

The FF determines the maximum power point of a solar cell and can be calculated from the FF, short-circuit current density (JSC), and open-circuit voltage (VOC), the efficiency can be calculated using eqs.

\[ FF = \frac{J_{mp} \cdot V_{mp}}{J_{SC} \cdot V_{OC}} \]  

\[ \eta = \frac{V_{OC} \cdot J_{SC}}{P_{in}} \cdot FF \]

where Jmp is the current density, Vmp is the voltage at the maximum power point, and Pin is the input power, which is 100 mW/cm² (AM 1.5).

When viewing the dependence on pillar height (Figure 7e), JSC values increase from the flat substrate up to 20 μm height, but drop again for >30 μm pillar heights. The latter decrease is due to charge carrier recombination by an increasing number of defect states with increasing micropillar height.85 Most likely, these defects have been introduced by the DRIE method used to make the pillars. The working principle of the applied Bosch process, which is an alternating process of etching (SF6) and passivation (C4F8) steps, has led to the scallp structures,86 which further increases the number of defect states. We conclude that for these pillar arrays, optimal performance is achieved with a 4 μm diameter, 12 μm pitch, and pillar height of 20 μm.

PV Performance of Copper Oxide-Covered Micropillar Arrays. In a tandem device, the overall photovoltage is generated by the absorption of two photons instead of one. Each of these photons creates a pair of charge carriers (e⁻ and h⁺) in the total photoabsorber stack. First, it is important to find the proper thickness of the top photoabsorber so that part of the sunlight can pass through it and illuminate the bottom photoabsorber to get the total photovoltage. Second, we fabricated Si micropillar substrates with varying heights, pitches, and copper oxide thicknesses to find the maximum current density output resulting from these aspects. A Cu2O film thickness of ~650 nm appears most favorable with respect to the resulting short circuit current density (Jsc), measured in an aqueous PEC setup (Figure S6b), as shown in Figure 8a. It is well-known that a thicker layer limits the charge separation efficiency and a thinner layer does not absorb all incoming light. Si micropillars covered with optimized Cu2O film thickness of ~650 nm were fabricated with varying pillar heights, from a planar substrate to 40 μm height, and the highest Jsc was produced at 20 μm height (Figure 8b). Finally, the micropillar pitches were varied between 8 and 14 μm, and 12 μm pitch gave the highest Jsc; see Figure 8c.

In case of Si/Cu2O/CuO heterostructure fabrication, we deposited 650 nm thick Cu2O on a planar substrate followed by thermal oxidation process at 400 °C while varying the annealing time as shown in Figure 6a. As a result, Cu2O/CuO heterojunction layer with a different thickness ratio between

Figure 8. Plots of the current density as a function of different parameters of the Si/ITO-Au/Cu2O heterostructure film as top photoabsorbers: (a–d) varying the Cu2O film and Cu2O/CuO film thickness on planar substrates, (b–e) varying the microcell height, for micropillar samples covered with a Cu2O film (650 nm) or Cu2O (630 nm)/CuO (120 nm) heterostructure film (with 5:1 thickness ratio between Cu2O/CuO) at a pitch of 12 μm, and (f) varying the micropillar pitch, for micropillar samples covered with a Cu2O film (650 nm) or Cu2O (630 nm)/CuO (120 nm) heterostructure film (with 5:1 thickness ratio between Cu2O/CuO) at a pillar height of 20 μm.
Cu₂O and CuO film was formed on planar Si substrates. The highest J\textsubscript{sc} output was observed for the Cu₂O (630 nm)/CuO (120 nm) heterostructure film with thickness ratio of 5:1 on planar Si substrate, respectively (Figure 8d). This is considered as an optimum Cu₂O/CuO heterostructure film for flat samples, and this was applied on Si micropillar substrates with varying micropillars height and pitch. When the optimized layer thickness of the Cu₂O/CuO heterostructure was placed on Si micropillars with varying heights and pitches, surprisingly no clear trends in the output current density were observed with respect to these parameters (Figure 8e and f). The observed behavior could possibly be due to parasitic resistances and optical losses, where the former occurs presumably between the copper oxides and between Cu₂O and silicon. In a comparison between the Cu₂O and Cu₂O/CuO heterojunction systems, the former all perform better at the optimized pillar parameters (Figure 8), while only at the low-performance sides of these parameters are comparable performances observed. Therefore, we conclude that Si micropillar arrays with a pitch of 12 μm, a height of 20 μm, and a (nonoxidized) Cu₂O layer thickness of 650 nm are optimal, and we fixed these for further study.

The J\textsubscript{V} curves of planar and micropillar Si substrates were measured without and with different overlayers on top (Figure 9; J\textsubscript{V}-measurement setup shown in Figure S6a), by measuring dry and contacting only the Si cell on top and bottom. After the ITO layer (~80 nm) was deposited, the current density increased for both the planar and the micropillar Si solar cells due to its antireflection property. After a Cu₂O film of ~650 nm thickness was electrodeposited over the Si/ITO-Au substrates, both the V\textsubscript{OC} as well as the J\textsubscript{SC} values dropped significantly, due to the parasitic light absorption by Cu₂O and the consequently reduced light intensity on the Si. For a planar solar cell, the J\textsubscript{SC} decreased by 7 mA/cm\textsuperscript{2} due to the Cu₂O layer, while for a Si micropillar solar cell the J\textsubscript{SC} decreased with 22 mA/cm\textsuperscript{2}, making the output practically comparable. This indicates that the Cu₂O layer absorbs more sunlight when fabricated over the micropillar array.

Interestingly, when a Cu₂O (630 nm)/CuO (120 nm) heterojunction layer was deposited on the planar and micropillar substrates, the drop of the V\textsubscript{OC} and J\textsubscript{SC} values was nearly similar as compared to the Cu₂O overlayer, but the fill factor (FF) decreased considerably (Figure 9). The low slope close to V\textsubscript{OC} in the J\textsubscript{V} curves shows that the device behavior is dominated by a series resistance, which is attributed to a poor conductance between the top (Cu₂O/CuO) and bottom (Si) photoabsorbers. We found voids formed between the Si surface and the Cu₂O/CuO layer after thermal oxidation.
of the preceding Si/Cu$_2$O device. Interestingly, this void formation was more extensive in case of the micropillar arrays (Figure S4b), potentially because of the larger surface area and/or the presence of different curvatures in the micropillar samples. Apparently these voids explain the increased series resistance observed in Figure 9. Possibly, the thermal annealing process, which was carried out to prepare the Cu$_2$O/CuO heterojunction, led to cracks at the Cu$_2$O−Si interface (see Figure S4).

Pulsed Laser Deposition of Protection Layers. For a high-performance Cu$_2$O-based PEC electrode, the quality of the buried p−n junction, the protection layer, and the cocatalyst are the most important parameters. The p−n junction must be connecting and uniform, the protection layer must be conformal and pinhole-free, and the catalyst nanoparticle islands must be robust and adhered strongly on the electrode surface. A protection layer is needed to prevent direct contact of the Cu$_2$O film with the electrolyte to avoid photocorrosion, and thus to maximize the performance of the device. Here, we explored the use of pulsed laser deposition (PLD) as a method to apply a conformal and high-quality protection overlayer on micropillar array structures. Previously, Luo et al. reported a high photocurrent density by fabricating a Cu$_2$O nanowire-structured photoelectrode. Yet, the challenging part is to increase the photocurrent for unassisted water-splitting devices. The photocurrent is dependent on the difference between the quasi-Fermi level of the electrons in the n-type oxide layer and the holes in Cu$_2$O under illumination in a heterojunction device. Therefore, choosing a suitable n-type oxide layer is important for producing a high photocurrent. We explored the use of zinc oxide (n-ZnO), an n-type material, combined with titanium oxide (TiO$_2$) as a protective layer to improve the stability and performance of a Cu$_2$O-based photocathode. HR-SEM images of the electrodes after protection layer deposition of 20 nm of ZnO and 100 nm of TiO$_2$ are shown in Figure 10a,b on both planar and micropillar samples. These images clearly show the homogeneous coating of the complete stack of layers on both substrates. The difference in contrast of each layer in images shows the quality and conformity of deposition achieved by the PLD technique. The band energy-level alignment diagrams of p-Cu$_2$O with n-ZnO and n-TiO$_2$ are shown in Figure S5. A conduction band offset between the Cu$_2$O and ZnO layer is about ∼1 eV, which improves the separation of the quasi-Fermi levels in the two oxides under illumination to 0.45 eV in agreement with the 0.45 V positive shift of the onset potential, and hence the buildup of an extra photovoltage for hydrogen generation.

Photoelectrochemical Performance of the Photocathodes. To assess the PEC performance of the devices, J–E measurements of Cu$_2$O/ZnO/TiO$_2$/Pt on the Si/ITO-Au planar and micropillar array photocathodes were performed with the same Cu$_2$O film thickness of ∼650 nm (see Figure S11). As a proof of concept, Pt was used as the HER catalyst, and it was deposited electrochemically under dark condition using an aqueous solution of 1 mM H$_2$PtCl$_6$ for 15 min (for planar) and 19 min (for micropillars) with a thickness of nominally 3 nm using a procedure reported previously. Pt is used as a catalyst because (i) it has been well studied, and (ii) it is purely as a reference case for testing the activity of the PEC cell without having to worry about the catalytic performance. PEC measurements were performed under
illumination in 0.5 M Na₂SO₄ with 0.1 M sodium phosphate buffer solution (pH 5) as electrolyte.

The Cu₂O film on the planar substrate only delivered a photocurrent density of 5 mA cm⁻² at 0 V vs RHE, which is lower than that on the micropillar substrate (7.5 mA cm⁻²) (see Figure 11a). In addition, as compared to the planar device, the electrode with the micropillar array showed a slightly higher anodic shift of the onset potential of +0.85 V versus RHE. It suggests that a large proportion of photogenerated carriers effectively separate in the micropillar arrays. A stability test for planar and micropillar devices was performed for 75 h (Figure 11b). The devices showed an excellent stability without degradation over time, indicating that the PLD method is effective for conformal and pit-free layer deposition of ZnO and TiO₂.

To better understand the PEC performance of these photocathodes, we measured the incident-photon-to-current efficiency (IPCE) of both devices and used it to calculate the integrated photocurrent under AM 1.5 G (100 mW cm⁻²) solar irradiation (Figure 11c). The overall current densities correspond well with the values of the photocurrent plotted in Figure 11a. The IPCE clearly shows a broad plateau response through a wider spectral range for the micropillar array compared to the planar device. The production of H₂ gas was confirmed by the formation of bubbles evolving, and measurements by gas chromatography for a micropillar photocathode biased at 0 V vs RHE with a near-ideal faradaic efficiency (Figure 11d; small deviations attributed to measurement inaccuracies, gas dissolution, and possible parasitic processes).

# CONCLUSIONS

In summary, we have developed a highly photostable tandem Si/Cu₂O micropillar photocathode with passivating ZnO and TiO₂ overlayers directly on the micropillar array devices by using the pulsed laser deposition method. These conformal protection films grown with precise thickness formed on both planar and microstructure devices. The Cu₂O photocathode with a thickness of ~650 nm combined with Si micropillar arrays (20 μm height and 12 μm pitch) delivered an optimal photocurrent of 7.5 mA/cm² at 0 V vs RHE, a photovoltage of 0.85 V, and stability beyond 75 h using an n-ZnO hole-selective layer, a TiO₂ protection layer, and a Pt HER catalyst. In case of Cu₂O/CuO heterostructure, an improved performance was gained for planar samples but not for micropillared samples. The high onset potential achieved in Si/Cu₂O micropillar sample is attributed to the radial buried pn-junction PV cell as the bottom photoabsorber. The ZnO layer forms a promising heterojunction with Cu₂O for a good separation of the photogenerated charge carriers in the film. As a result, high photostability is achieved by the protective layers that prevent photocorrosion of the PV−PEC tandem device. Our study presents a successful case for the use of PLD to achieve conformal coating of protective layers on high-aspect ratio micropillar arrays, which offers a new path to stable PEC water splitting devices as well as to high-efficiency solar cells.

# ASSOCIATED CONTENT

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Notes

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# REFERENCES


