Supporting Information

Water-splitting artificial leaf based on a triple junction silicon solar cell: one-step fabrication through photo-induced deposition of catalysts and electrochemical operando monitoring

Duc N. Nguyen,^{a,b} Mariam Fadel,^b Pascale Chenevier,^c Vincent Artero,^{b*} Phong D. Tran^{a*}

^a University of Science and Technology of Hanoi, Vietnam Academy of Science and Technology, 18 Hoang Quoc Viet, Hanoi, 100000, Vietnam. Email: <u>tran-</u> <u>dinh.phong@usth.edu.vn</u>

^b Univ. Grenoble Alpes, CNRS, CEA, IRIG, Laboratoire de Chimie et Biologie des Métaux; 17 rue des Martyrs, Grenoble, 38000, France. Email. <u>vincent.artero@cea.fr</u>

^c Univ. Grenoble Alpes, CNRS, CEA, IRIG, SyMMES, 17 rue des Martyrs, Grenoble, 38000, France

1. Generals

Triple junction amorphous silicon solar cell (3jn-a-Si) was received from Xunlight Corporation. Fluorine-doped tin oxide coated glass was FTO TEC 10 from SOLEMS (7-10 Ω .sq). Indium-doped tin oxide coated glass was ITOSOL12 from SOLEMS (12 Ω cm). Steel paint (Hammerite) was purchased from AkzoNoBel. Thermal tape (Kapton) was purchased from Radiospares (RS Components). Other chemicals were received from Sigma Adrich and used without further purification.

2. Preparation of 3jn-a-Si samples

The 3jn-a-Si was cut with scissors to rectangular shape piece having size of 15 x 17 mm. The piece was then patterned and protected by thermal tape. The exposed areas were then etched with 1M HCl solution to remove part of the Silicon on the edges that might be damaged by the mechanical shearing of the scissors. Afterwards, epoxy or commercial Hammerite paint was used to protect the etched edges from contact with electrolyte and also to define the desired working area of the device. Prior to be used, the under-laying thermal tape that defined the working area was removed to expose the Si surface. We also applied an additional piece of thermal tape that protected the Si area where subsequent electrical contacts were made, *e.g.* for device performance assay. The step-wise preparation of these 3jn-a-Si samples is schematically illustrated in **figure S4**.

On the backside, the stainless steel substrate was scratched with store bought 600-grit sandpaper to strip away the protective layer as well as increasing the adherence of the catalyst. The same patterning method was utilized to get similar working area.

3. Monitoring the photovoltage provided by the 3jn-a-Si cell

The $1x1 \text{ cm}^2 3$ jn-a-Si cell was connected to a potentiostat in two electrodes configuration: the anode and cathode were connected to the Si front-side and the stainless steel back-side,

respectively, *via* a steel wire. The 3jn-a-Si was held in-air (without contact to any electrolyte solution) and illuminated by the simulated 1 sun light. The overall voltage provided was recorded over time at the open circuit. A chopped-light mode was also applied during the test in order to probe the stability of photovoltage generated over the operation time.

4. Determination of the actual potential provided by each side of the 3jn-a-Si

The anode and cathode of the 3jn-a-Si was connected to two different FTO electrodes which were immersed in a pH 7 phosphate buffer solution with or without 0.5 mM $[Co(WS_4)_2]^{2^-}$ added. Working area of FTO electrodes was limited to be $1x1 \text{ cm}^2$. The $1x1 \text{ cm}^2$ 3jn-a-Si cell was kept in air and illuminated by simulated 1 sun light. A potentiostat in two-electrode configuration was employed. A Ag/AgCl electrode served both as a reference and counter electrode (**figure S24a**). Whereas, the working electrode was a FTO connected either to the Si anode side or the stainless steel cathode side.

5. Preparation of a $[Co(WS_4)^2]^{2-}$ deposition bath

To 30mL of potassium phosphate buffer 0.1M at pH 7 was added 4.36 mg of $Co(NO_3)_2.6H_2O$ (0.5mM) and 10.44 mg of $[WS_4](NH_4)_2$ (1.0 mM). The yellow solution was then filtered through a hydrophilic PES membrane with 0.45 µm pore size to remove any unwanted precipitates. The $[Co(WS_4)_2]^{2-}$ solution obtained was ready for growing catalysts onto FTO, ITO or 3jn-a-Si surface.

6. Photo-induced assembly of OER and HER catalysts on 3jn-a-Si surfaces

The 3jn-a-Si having working area of $1x1 \text{ cm}^2$ was held upright in a fluorescence quartz cuvette from Hellma Analytics filled with 0.5 mM $[Co(WS_4)_2]^{2-}$ solution in pH 7 phosphate buffer. The system was then illuminated with a parallel beam from a Newport Xenon lamp set at 280W passing through an AM 1.5g filter and tuned to 100mW/cm^2 for the total duration of 10 minutes. The lamp's setting was decided to simulate closely the illumination

of 1 Sun. Visual inspection shows rapid deposition of the OER and HER catalysts on the Si anodic surface and steel cathodic surface indicated by the changing in color. The simultaneous evolution of O_2 and H_2 gases bubbles was also observed on the anodic and cathodic surfaces. On the Si anodic surface, the CoWO catalyst appeared to be a light yellow layer that turned the violet color of the Silicon to light blue/green. Whereas the CoWS catalyst has brown color.

When the catalyst assemblage was over, the light source was off. We collected the resultant CoWO ITO 3jn-a-Si Steel CoWS device, intensively washed it with DI water and then dried it naturally in air prior to use for catalytic assay or characterization.

7. Catalysts characterization

SEM and EDX measurements were performed with a Carl Zeiss AG - ULTRA 55 with gun voltages of 5 or 10 keV. X-ray photoelectron spectroscopy (XPS) was performed using a VG ESCALAB 220i-XL system (Thermo Scientific Theta Probe) with the X-ray source being a monochromatic Al Ka (1,486.6 eV). Calibration of the binding energy was done with adventitious carbon having 1s binding energy of 284.65 eV. ICP-OES was performed with an ICPE-9000 from Shimadzu.

8. Performance evaluation by Gas Chromatography

An S-3000 MicroGasChromatography (μ GC) from SRA Instruments was utilized in autosampling mode. The 1 cm² CoWO ITO 3jn-a-Si Steel CoWS device was put to stand upright in a typical cylindrical gas-tight glass vial containing pH 7 phosphate buffer electrolyte (0.1 M KPi). A flux of pure Argon (5mL/ minute) controlled by a mass-flow from Bronkhorst was introduced into the vial as carrier gas by a PEEK tube penetrating the rubber septum. Another PEEK tube was introduced to lead the resulting sample to the gas chromatography. Prior to measurement, a degassing phase was performed which was monitored by the μ GC. When the O₂ baseline was stable, light source was on to start the measurement. The Xenon lamp was set at 280W, with the beam passing through AM1.5g filter and tuned to 100mW/cm² to simulate 1 Sun irradiation. After 3 hours of operation, the Xenon lamp was turned off, and the μ GC would continue running for another 2 hours to collect all the O₂ and H₂ gases produced. Approximately every 92 seconds, an injection was made and a data point was created to form the real-time measurement. The aforementioned points were then added accumulatively to form the total amount of gas produced.

9. Bipotentiostat measurement

As the current CoWO|ITO|3jn-a-Si|Steel|CoWS is a compact monolithic device that works without an external bias, studying it electrochemically proved to be a challenge. Herein, we probe its behavior by splitting the anode and cathode then use bipotentiostat mode for measurement. A two-channel SP-300 potentiostat from Biologic Instrument was employed. The wiring schematic was presented in **figure 6b** (*see the main text*). By utilizing both channels, the overall voltage and current density produced from the device when it is illuminated were simultaneously monitored. As such, the channel 1 was responsible for measuring current density over time in ChronoAmperometry mode with no external bias whereas the channel 2 was responsible for measuring photopotential over time in ChronoPotentiometry with no applied current.

Supplementary data

Table S1. Previously reported silicon based monolithic artificial leaves fully immersed in electrolyte

Entry	Main structure	Electrolyte	η_{STF}	Year	Ref
1	RuO ₂ 3jn-Si Pt	$1 \text{ M H}_2 \text{SO}_4$	5%	1989	1
2	CoMo 3jn-Si NiFe _x O _y	1 M KOH	7.8%	1998	2
3	WO ₃ 2jn-Si NiMo	0.33 M	0.70%	2005	3

		H_3PO_4			
4	Co 3jn-Si NiMoZn	1 M KBi	2.5%	2011	4



Figure S1. I-V curves recorded on a FTO working electrode immersed in a pH 7 KPi electrolyte (black and green traces) and when 0.5mM $[Co(WS_4)_2]^{2-}$ was added (blue and red traces). Potential scan rate was 2 mV.s⁻¹



Figure S2. I-V curves recorded on a FTO|CoWO (blue trace), a FTO|CoWS (red trace) and a bare FTO electrode (black trace). Electrolyte was 0.1 M KPi (pH 7). Potential scan rate was 2 mV.s⁻¹





Step	Description	Schematic representation	Digital photo
1	A 15 x 17 mm piece of the 3jn- a-Si solar cell was cut with the metal shear.	3jn-a-Si Stainless-steel Ag/ZnO	
2	A 10 x 10 mm piece of thermal tape (mask 1) was put on the top surface as template for the anodic working area.	Mask 1	
3	A 12 x 15 mm piece of thermal tape (mask 2) was put on top and covered all the edges of mask 1 to determine the etching area.	Math	

2	The exposed 3jn-a-Si area was etched with a conventional cotton swab soaked in HCl 1M. Total etching time was approximately 10 minutes. The piece was washed with DI water and dried on a paper towel.		
	The stainless-steel surface was scratched with store-bought sandpaper of 600 or 1200 grit to improve the adherence of the catalyst. The surface was then wiped clean with a cotton swab and DI water to remove possible metal flakes.	As-prepared Processed	
	Mask 2 was removed. The piece was washed under a gentle stream of DI water and EtOH to remove possible contaminants then dried with compressed air. Optionally, mask 3 could be put in place to allow electrical contact for subsequent device investigations.	Mask 3	

7	Similarly, mask 4 and mask 5 with the same size as mask 3 and mask 1, respectively, were placed on the processed stainless-steel surface to limit the cathodic working area to 1 cm^2 and establish future electrical contact.	Mask 4 Mask 5	
8	Conventional acrylic paint or steel paint was used to cover the entire solar cell.		
9	Mask 1 and mask 5 were removed to reveal the final working area. The piece was then washed gently under a stream of DI water, EtOH and dried with compressed air before use. Mask 3 and mask 4 will only be removed if electrical contacts are required for future (photo)electrochemical processes.		

Figure S4. Schematic illustration for the preparation of ITO 3jn-a-Si Steel solar cell samples



Figure S5. Digital photos taken on: (**a**) the ITO front-side and (**b**) the Steel back-side of a ITO | 3jn-a-Si | Steel solar cell prior being used for any experiment



Figure S6. Evolution of H_2 gas when assaying different monolithic devices that were obtained by setting different photodeposition times to grow the CoWO and CoWS catalysts. (a) Rate of H_2 production, (b) Accumulated amount of H_2 versus time. Electrolyte was a pH 7 KPi 0.1 M buffer. Illumination was 1 sun light.



Figure S7. Evolution of H_2 gas when assaying different monolithic devices that were assembled in different deposition baths (having different Co: W molar ratio)



Figure S8. a) Evolution of H_2 and O_2 gases recorded by an online gas chromatography when assaying a monolithic device in 0.1M phosphate buffer (pH 7, STH = 1.9%) and in 0.1M borate buffer (pH 9.2); b and c) Pictures of the anodic side of the artificial leaf as prepared (left) and after 20 min exposure to electrolyte in the dark (right) in 0.5 M H_2SO_4 (b) and 1M NaOH (c)



Figure S9: Digital photo taken on (**a**) the front-side and (**b**) back-side of a CoWO | ITO | 3jna-Si | Steel | CoWS after completing the assemblage of CoWO and CoWS catalysts



Figure S10. SEM images taken on the front-side of an as-prepared ITO | 3jn-a-Si | Steel solar cell and after different catalyst photodeposition time



Figure S11. EDX patterns taken on the front-side of the 1.9% CoWO | ITO | 3jn-a-Si | Steel | CoWS monolithic device



Figure S12. EDX elemental mapping taken on the front-side of the 1.9% CoWO | ITO | 3jn-a-Si | Steel | CoWS monolithic device



Figure S13. XPS analysis recorded on the front-side (CoWO) and the back-side (CoWS) of the 1.9% CoWO | ITO | 3jn-a-Si | Steel | CoWS monolithic device



Figure S14. I-t curve recorded at +1.8 V vs. RHE for CoWO as OER catalyst grown on ITO in 0.1 M phosphate buffer (pH = 7). The current density was normalized to the geometrical surface area of the electrode.



Figure S15. Correlation of corrected absorbance (red dots) and thickness (blue squares) with deposition time for CoWO films electrodeposited on FTO at a current density of 2 mA.cm⁻². The absorbance was measured at 380 nm and corrected from light scattering by substraction of the absorbance measured at 550 nm where CoWO does not absorb. Film thickness was

measured from SEM cross section images. This measurement was difficult because breaking the glass slide disrupts the film near the breaking line. Two samples deposited for 30 and 60 min could be measured reliably (Figure S25). The dotted black line is the best linear fit for both sets of data.



Figure S16. SEM images taken on the stainless-steel back-side of an as-prepared ITO 3jn-a-

Si Steel solar cell and after different catalyst photodeposition time



Figure S17. EDX patterns taken on the stainless-steel back-side of the 1.9% CoWO | ITO | 3jn-a-Si | Steel | CoWS monolithic device



Figure S18. EDX elemental mapping taken on the stainless-steel back-side of the 1.9% CoWO | ITO | 3jn-a-Si | Steel | CoWS monolithic device



Figure S19. I-t curve recorded at -0.23 V vs. RHE for CoWS as HER catalyst grown on stainless steel in 0.1 M phosphate buffer (pH = 7). The current density was normalized to the geometrical surface area of the electrode.



Figure S20. H_2 evolution curves when repeating the solar-driven overall water splitting assayed using the best CoWO ITO 3jn-a-Si Steel CoWS monolithic device immersed in a 0.1M KPi (pH 7) electrolyte solution. Illumination was 1 sun light. Device was kept 3 days in the solution in dark between two assays



Figure S21. SEM images taken on the CoWO catalyst layer (front-side) of the CoWO | ITO | 3jn-a-Si | Steel | CoWS device: (a) after the preparation, and (b) after 3h of solar-driven water splitting experiment



Figure S22. SEM images taken on the CoWS catalyst layer (back-side) of the CoWO | ITO | 3jn-a-Si | Steel | CoWS device: (**a**) after the preparation, and (**b**) after 3h of solar-driven water splitting experiment



Figure S23.Evolution of Co, W mass concentration dissolved in the phosphate electrolyte solution over the operation time of the best CoWO | ITO | 3jn-a-Si | Steel | CoWS monolithic device



Figure S24. (a) A two-electrode configuration employed to probe the actual anodic and cathodic potential generated at the anode and cathode sides of a ITO |3jn-a-Si| Steel solar cell when the latter is illuminated by 1 sun light, and (b) Anodic and cathodic potential generated by an illuminated ITO |3jn-a-Si| Steel solar cell being wired with two FTO electrodes which were immersed in a pH 7 phosphate buffer without (dash traces) and with

0.5 mM $[Co(WS_4)_2]^{2-}$ catalyst precursor (bulk traces). Light illumination was of simulated 1 sun light



Figure S25. Scanning electron microscopy side-view images (left: scattered electron detector, right: secondary electron detector) of an FTO-glass slide with an electrodeposited layer of CoWO (30 min deposition).

References.

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