Supporting Information for

A High-voltage Solar Rechargeable Device Based on a CoPi/$BiVO_4$ Faradaic Junction

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Experimental section

Preparation of $BiVO_4$ electrode

Following previous method [1], Bi layers were firstly electro-deposited on FTO substrates in 20 mM $Bi(NO_3)_3 \cdot 5H_2O$ ethylene glycol solution. The deposition was carried out by i-t method at the potential of -1.8 V vs. Ag/AgCl and the deposition charge was 300 mC/cm^2. After electrodeposition, the Bi films were washed by ethanol and dried in air. And then 150 mM $VO(acac)_2$ in DMSO was dropped on the surface of Bi electrodes, which were calcined in a muffle furnace at 450 ^oC for 2 hours in air (heating rate = 2 °C/min). In the muffle furnace, Bi and VO^{2+} were oxidized and reacted with each other to form $BiVO_4$. Finally, residual V_2O_5 in the $BiVO_4$ films was removed by soaking the samples in 1 M NaOH aqueous solution for 30 minutes.

Preparation of CoPi, CoO_xH_y, $Co(OH)_2$ and Co_3O_4

CoPi samples were electro-deposited on FTO substrates at the potential of 1.1 V vs. Ag/AgCl in 1 M potassium phosphate buffer (pH=7) solution with adding 0.5 mM $Co(NO_3)_2$ and the deposition charge was 100 mC/cm^2. CoO_xH_y samples were electro-deposited on FTO substrates at the potential of -0.8 V vs. Ag/AgCl in 0.1 M $Co(NO_3)_2$ aqueous solution and the deposition charge was 100 mC/cm^2. Then CoO_xH_y film was oxidized at the potential of 1.2 V vs. Ag/AgCl in 0.5 M Na_2SO_4 aqueous solution for 1 minute. $Co(OH)_2$ samples were grown on FTO substrates by chemical bath deposition method at 100 ^oC for 12 hours. The precursor solution was 0.1 M $Co(NO_3)_2$ and 0.5 M $CO(NH_2)_2$ aqueous solution. In order to obtain Co_3O_4, the as-grown $Co(OH)_2$ films were annealed in a muffle furnace at 500 ^oC in air for 5 minutes.

Preparation of $CoPi/BiVO_4$ and $CoO_xH_y/BiVO_4$

The CoPi and CoO_xH_y were electro-deposited on $BiVO_4$ on the same conditions as on FTO substrates as mentioned above, but the deposition charge was 20 mC/cm^2.

Assembly of solar rechargeable devices

$CoPi/BiVO_4$ or $CoO_xH_y/BiVO_4$ were used as photoelectrodes and commercial carbon cloth (Taiwan Carbon Energy Technology, W0S1002) was used as counter electrode. The electrolytes were 1 M potassium phosphate buffer solution (pH=7) and 0.5 M Na_2SO_4 aqueous solution, respectively. The two solar rechargeable devices were marked as $BiVO_4$/CoPi/$KPi_{(aq)}$/C and $BiVO_4/CoO_xH_y/Na_2SO_{4(aq)}$/C, respectively.

Characterizations of samples

The morphologies of the samples were characterized by SEM (ZEISS Gemini 300) with an accelerating voltage of 10 kV. The TEM (JEOL JEM-2100), XRD (ARL X'TRA) and Raman spectroscopy (Horiba T64000, excitation ~ 488 nm) were employed to investigate the structures of the samples. The absorbance of the samples was measured by ultraviolet-visible-near infrared spectroscopy (UV-Vis-NIR, PE Lambda 950). The chemical valence of the samples was characterized by X-ray photoelectron spectroscopy (XPS, PHI5000 Versa Probe). The binding energies were calibrated by the C1s peak at 284.6 eV. X-ray absorption spectroscopy (XAS) experiments were performed at the National Synchrotron Radiation Laboratory (NSRL, Beamlines MCD-

A and MCD-B (Soochow Beamline for Energy Materials).

Electrochemical and photoelectrochemical measurements

The electrochemical and photoelectrochemical properties of the samples were measured in a three-electrode system. A Pt electrode and Ag/AgCl were used as a counter electrode and a reference electrode, respectively. For CoPi/FTO and CoPi/$BiVO_4$ samples, 1 M potassium phosphate buffer solution (pH=7) was used as electrolyte. For CoO_xH_y/FTO, CoO_xH_y/$BiVO_4$, $Co(OH)_2$/FTO and Co_3O_4/FTO, 0.5 M Na_2SO_4 aqueous solution was used as electrolyte. The performance of solar rechargeable devices was measured by using a two-electrode system. All electrochemical and photoelectrochemical curves were recorded by the electrochemical workstation (CHI 760e, Shanghai Chenhua). An AM1.5 sunlight simulator with the intensity of 100 mW cm^{-2} was used as the light source.

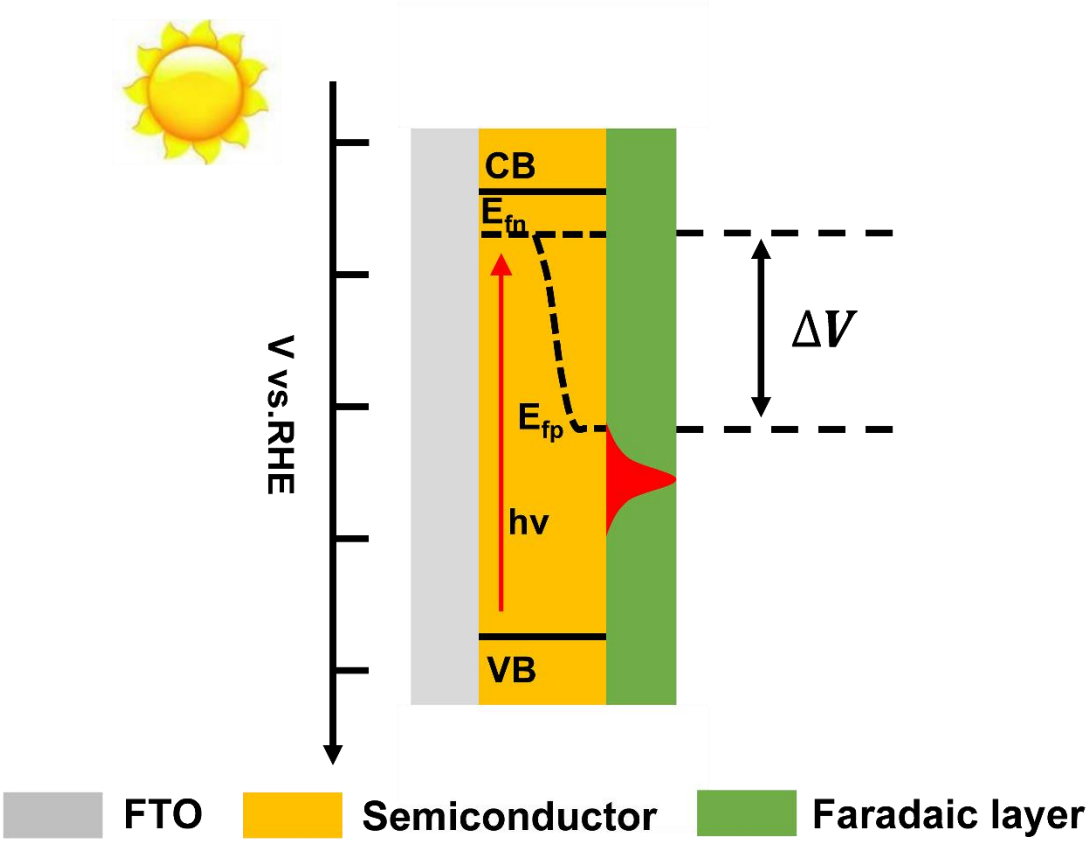

Figure S1. Schematic diagram of photovoltage in a Faradaic junction.

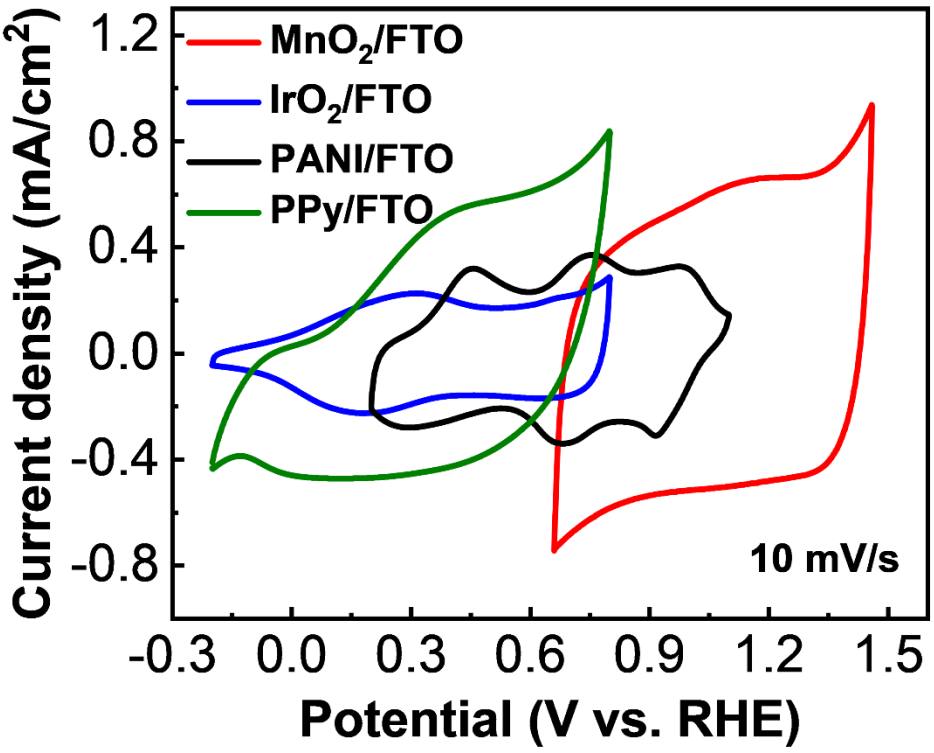

Figure S2. Potential windows of some conventional Faradaic materials.

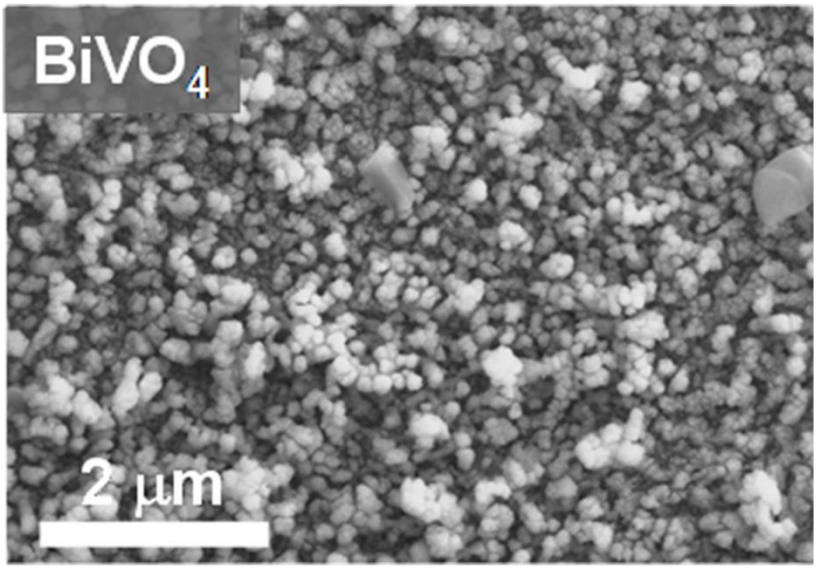

Figure S3. SEM image of bare $BiVO_4$ on a FTO substrate.

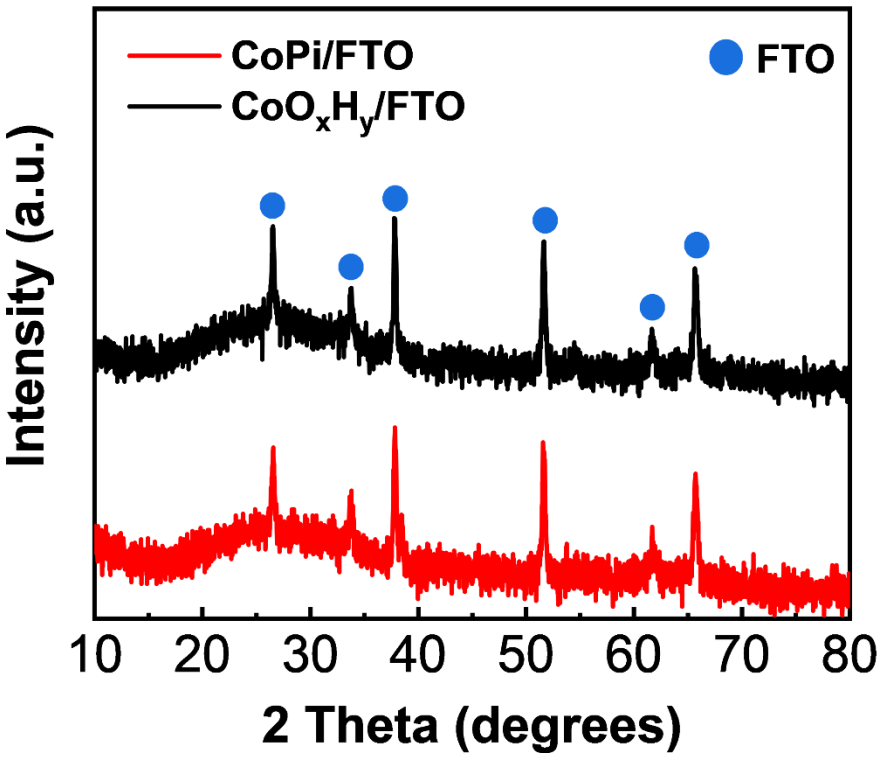

Figure S4. XRD patterns of CoPi/FTO and CoO_xH_y/FTO.

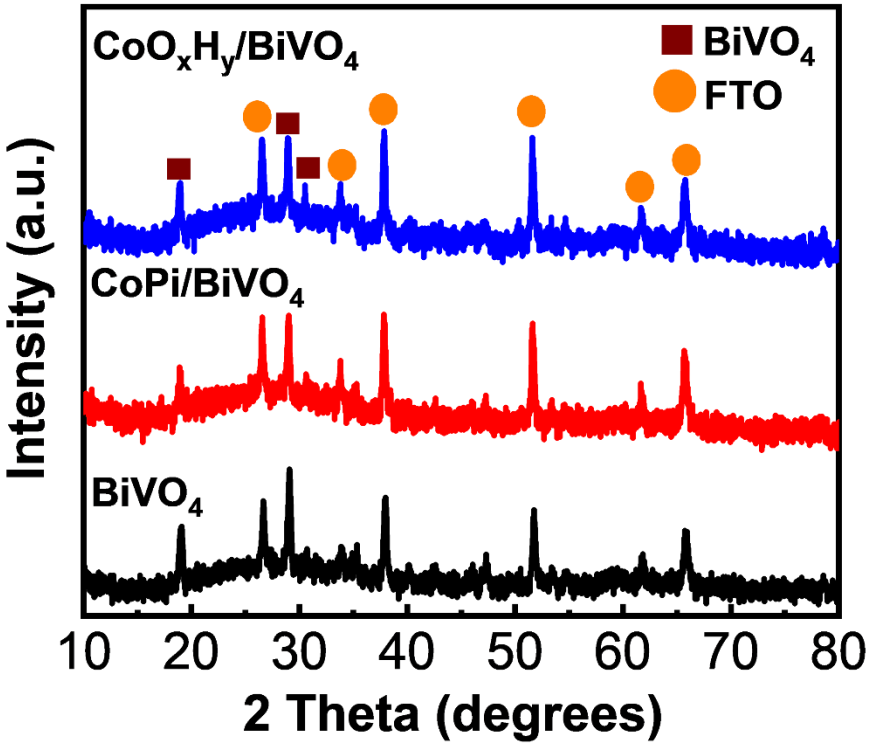

Figure S5. XRD patterns bare $BiVO_4$, CoPi/$BiVO_4$, CoO_xH_y/$BiVO_4$.

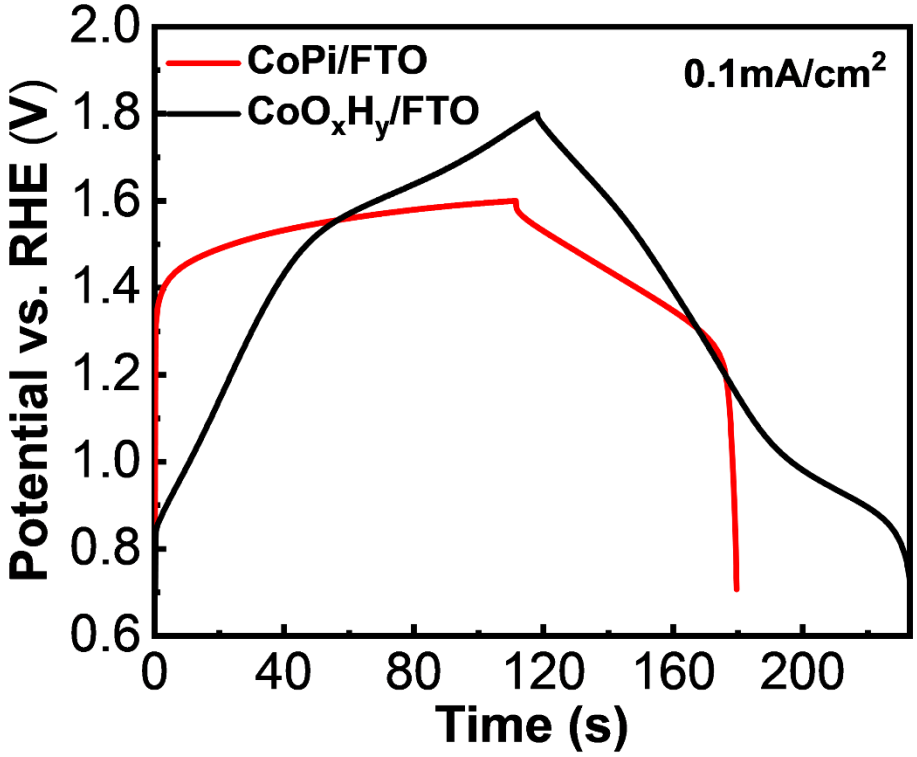

Figure S6. GCD curves of CoPi/FTO in 1M potassium phosphate buffer solution (pH=7) and CoO_xH_y/FTO in 0.5 M Na_2SO_4 aqueous solution, respectively.

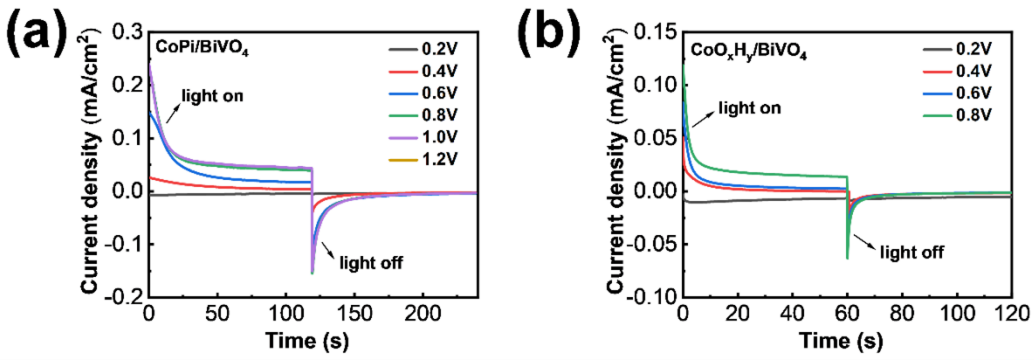

Figure S7. Current-time curves of $CoPi/BiVO_4$ in 1M potassium phosphate buffer solution (pH=7) and $CoO_xH_y/BiVO_4$ in 0.5 M Na_2SO_4 aqueous solution, respectively.

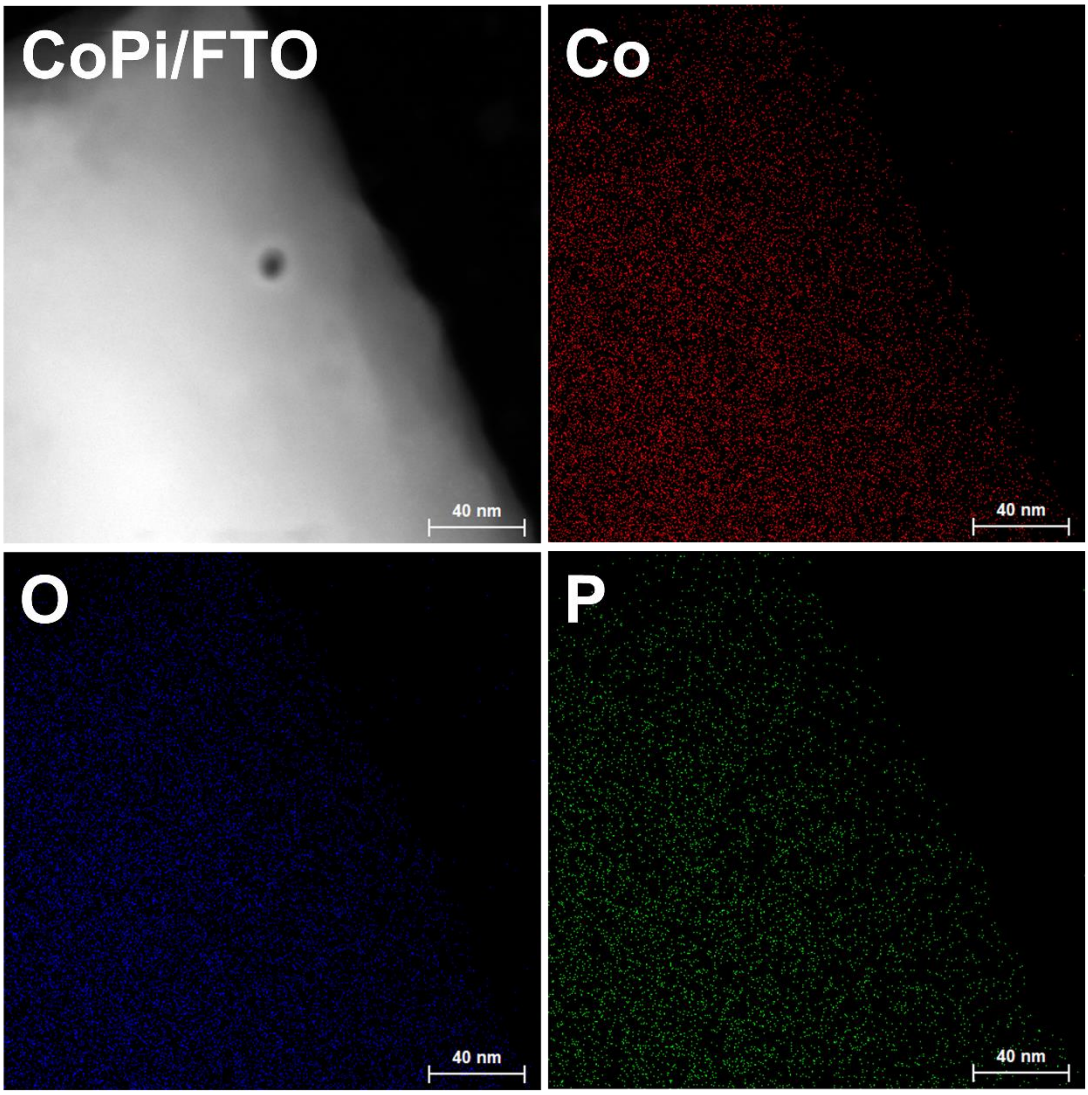

Figure S8. Elemental mappings in a dark-field TEM image of CoPi/FTO.

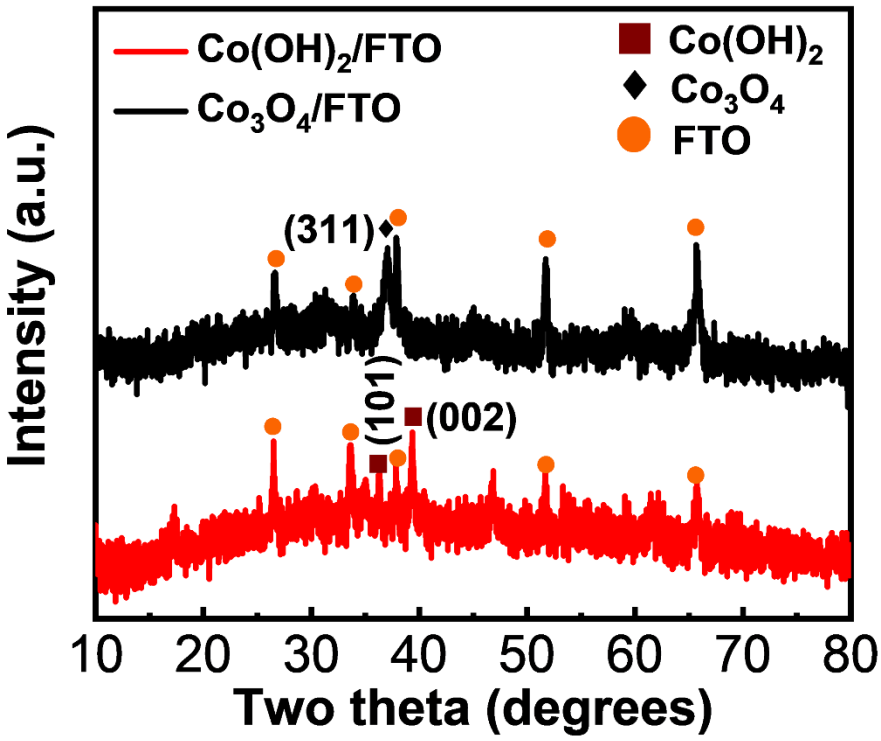

Figure S9. XRD patterns of $Co(OH)_2$/FTO and Co_3O_4/FTO.

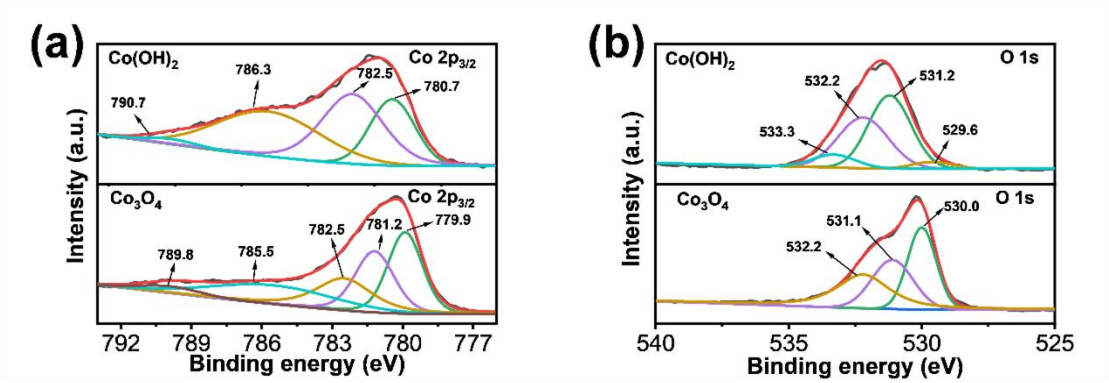

Figure S10. XPS of $Co(OH)_2$/FTO and Co_3O_4/FTO.

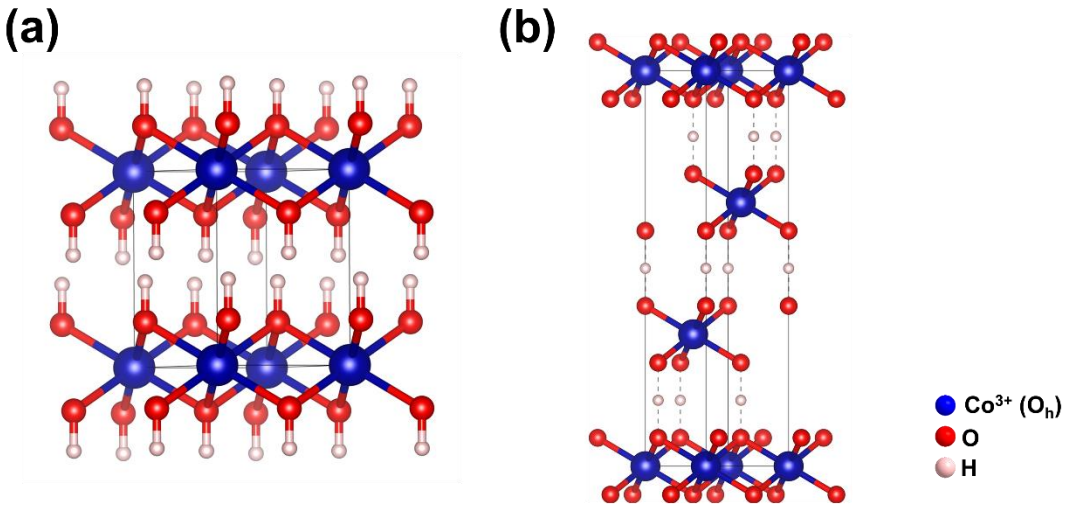

Figure S11. Crystal structures of $Co(OH)_2$ (a) and CoOOH (b).

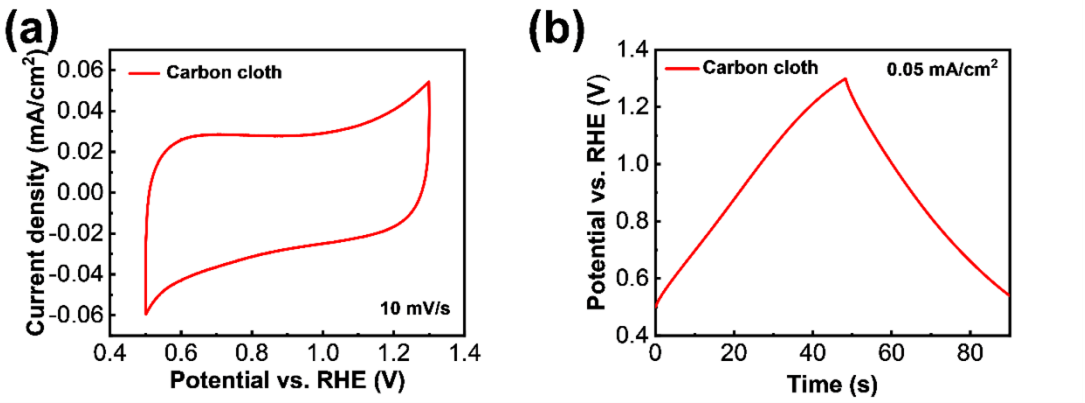

Figure S12. CV curve and GCD curve of a carbon cloth counter electrode in the dark, electrolyte: 1 M potassium phosphate buffer solution (pH=7).

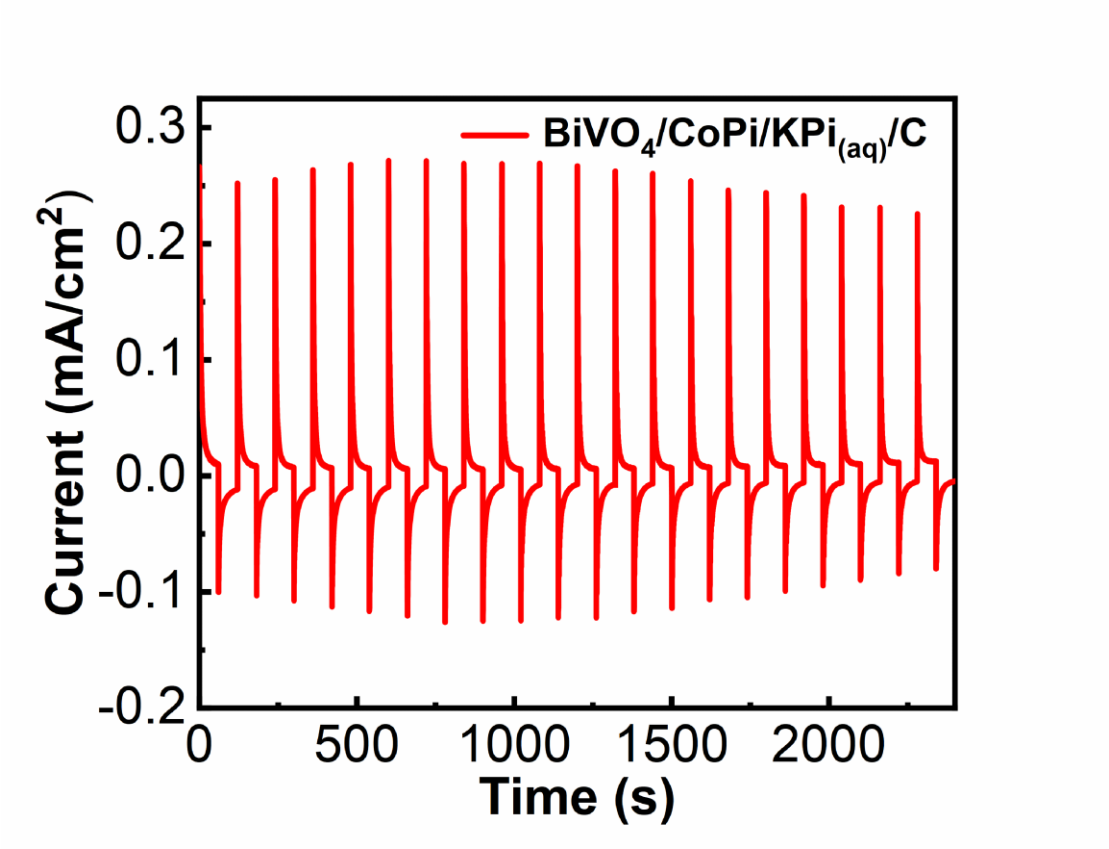

Figure S13. Cyclic stability of the $BiVO_4$/ $CoPi/KPi_{(aq)}$/C full-cell during photo charge and dark discharge under zero bias.

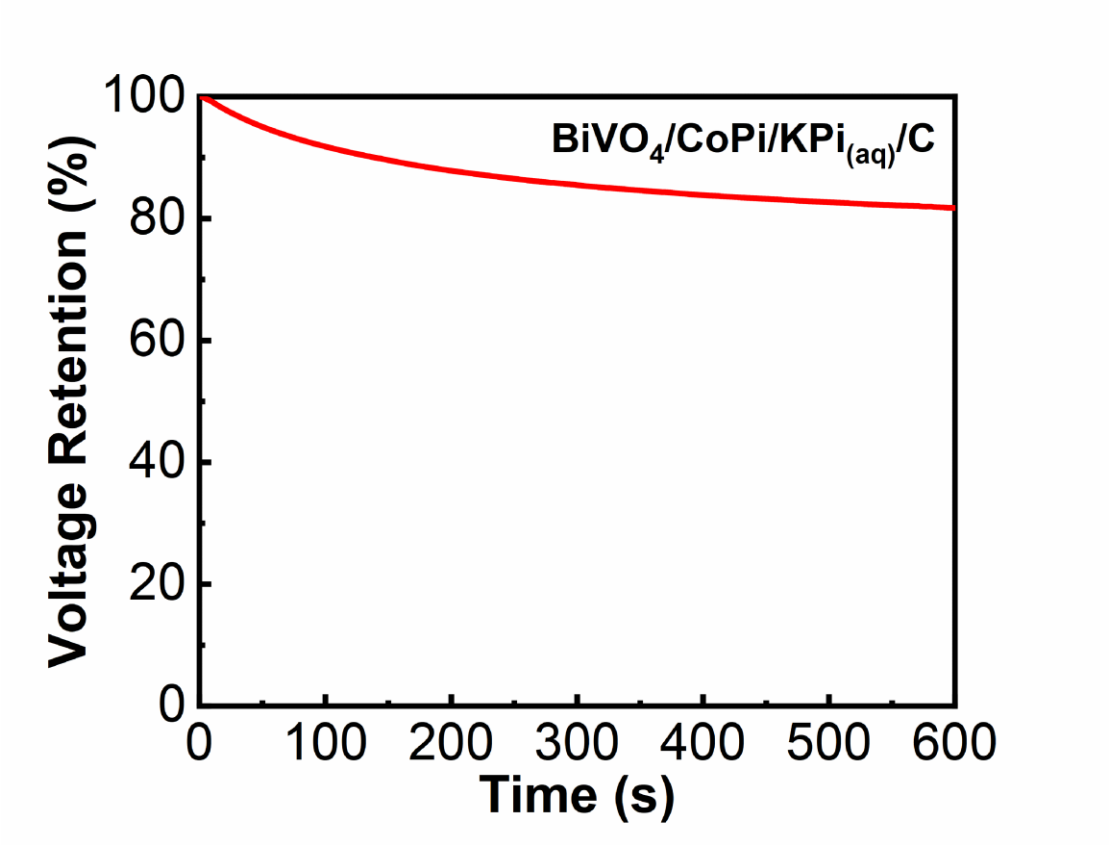

Figure S14. OCP stability of the $BiVO_4$/CoPi/$KPi_{(aq)}$/C device in the dark.

Table S1 The output voltage of two-electrode solar rechargeable devices in this study and previous literatures.

	Different configurations of two-electrode devices	Dark output voltage (V)	Ref.
1	TiO_2-dye-LiI/AC/ Polymer electrolyte/AC/Pt	0.45	[2]
2	TiO_2/NiO/Na_2SO_4(aq)/Pt/Si	0.45	[3]
3	Si/Porous Si/Polymer electrolyte/Porous Si	0.55	[4]
4	$BiVO_4$/PbO_x/NaPi(aq)/Pt	0.65	[5]
5	Si/WO_3/H_2SO_4(aq)/C	0.50	[6]
6	$BiVO_4$/CoPi/$KPi_{(aq)}$/C	0.88	this work

References

[1] D. Kang, Y. Park, J. C. Hill and K. S. Choi, *J. Phys. Chem. Lett.*, 2014, **5**, 2994-2999.

[2] T. Miyasaka and T. N. Murakami, *Appl. Phys. Lett.*, 2004, **85**, 3932-3934.

[3] Y. Wang, J. Tang, Z. Peng, Y. Wang, D. Jia, B. Kong, A. A. Elzatahry, D. Zhao and G. Zheng, *Nano Lett*, 2014, **14**, 3668-3673.

[4] A. S. Westover, K. Share, R. Carter, A. P. Cohn, L. Oakes and C. L. Pint, *Appl. Phys. Lett.*, 2014, **104**, 213905.

[5] S. Safshekan, I. Herraiz-Cardona, D. Cardenas-Morcoso, R. Ojani, M. Haro and S. Gimenez, *ACS Energy Lett.*, 2017, **2**, 469-475.

[6] P. Wang, X. Chen, G. Sun, C. Wang, J. Luo, L. Yang, J. Lv, Y. Yao, W. Luo and Z. Zou, *Angew. Chem. Int. Ed.*, 2021, **60**, 1390-1395.