Supporting information

Rational Electrochemical Recycling of Spent $LiFePO_4$ and $LiCoO_2$ Batteries to Fe_2O_3/CoPi Photoanode for Water Oxidation

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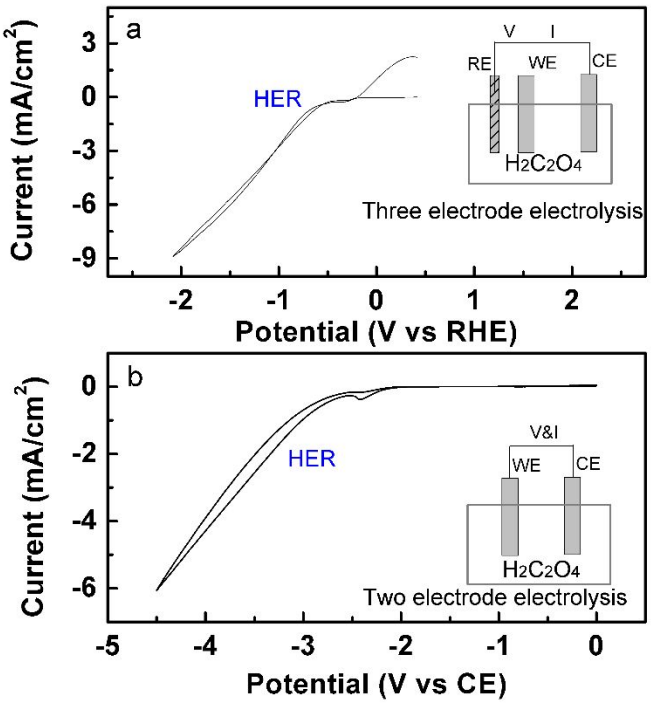

Figure S1. Cyclic voltammetry curves of the oxalic acid (6 mmol/L) measured at the room temperature, where the sweeping rate was 100 mV/s: a) three-electrode deposition with SCE as reference (RE); b) two-electrode deposition with another FTO as counter electrode (CE). The pH of the solution was adjusted to 2.8.

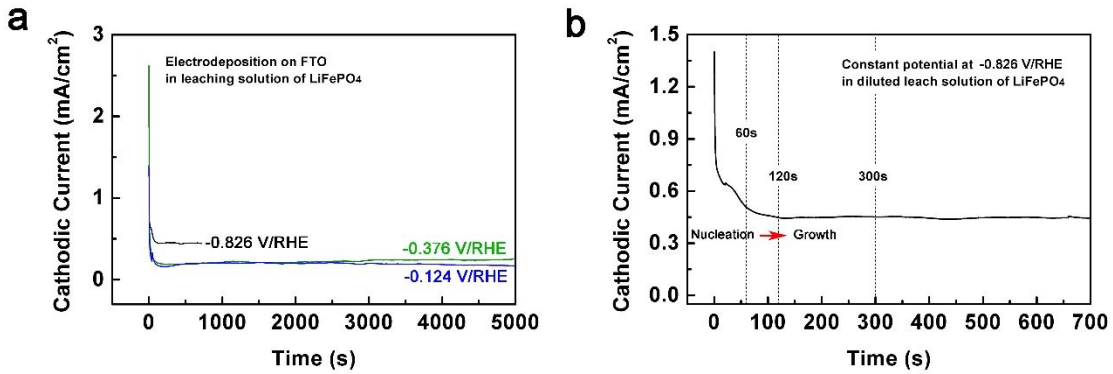

Figure S2. Electrodeposition of Fe films on FTO substrate in dilute leaching solution of $LiFePO_4$: a) J-t curves under different potential (-0.826 V, -0.376 V and -0.124V vs RHE), b) nucleation-growth in J-t curve under -0.826 V vs RHE.

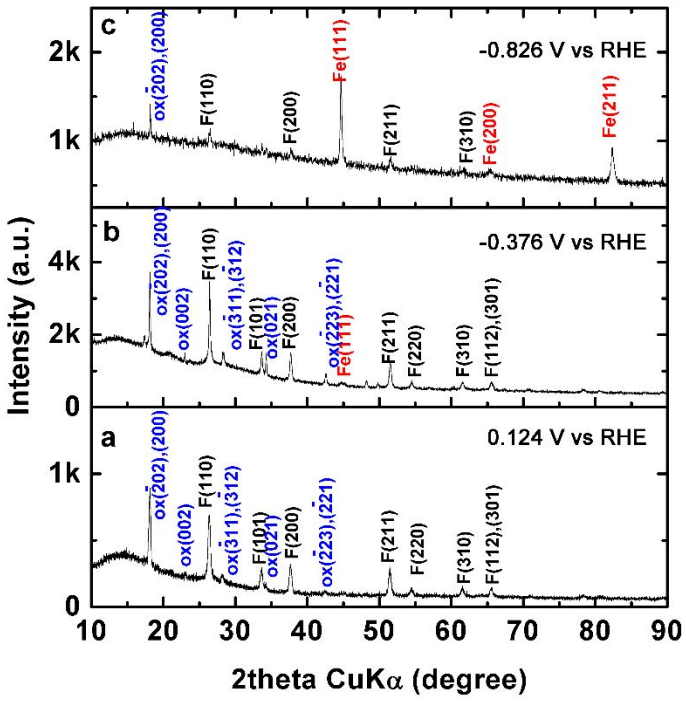

Figure S3. XRD patterns of different films deposited from a leaching solution (8.3 mM) for 30 mins at various potentials: a) 0.124 V; b) -0.376 V; c) -0.826 V. The oxalate $FeC_2O_4 \cdot 2H_2O$ was marked as "ox" in blue.

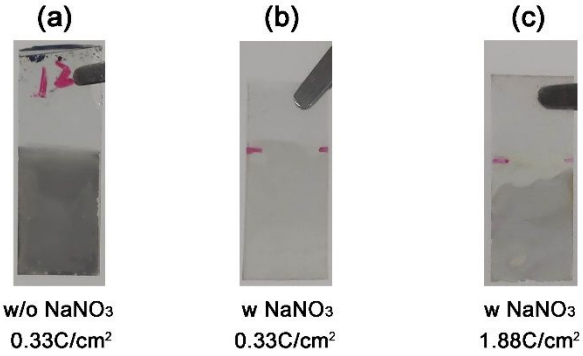

Figure S4. Optical images of films deposited from leached solution of $LiFePO_4$: a) without $NaNO_3$ supporting salts; b) and c) with 0.1 M $NaNO_3$ supporting salts. a) and b) were deposited with accumulated charge of 0.33 C/cm^2. c) was deposited with accumulated charge of 1.88 C/cm^2.

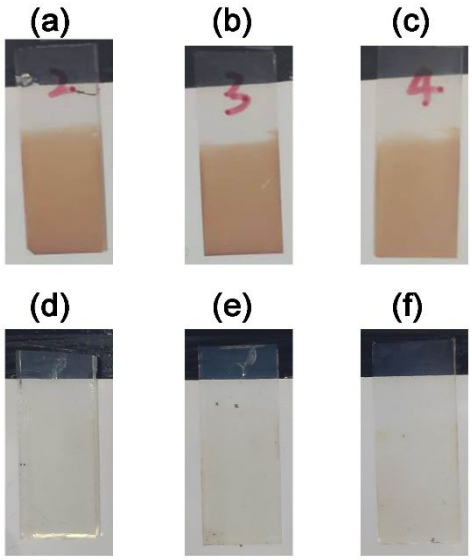

Figure S5. Optical images of annealed Fe films deposited from leached solution of $LiFePO_4$: a-c) without $NaNO_3$; d-f) with 0.1 M $NaNO_3$. The accumulated charge was kept at 0.33 C/cm^2.

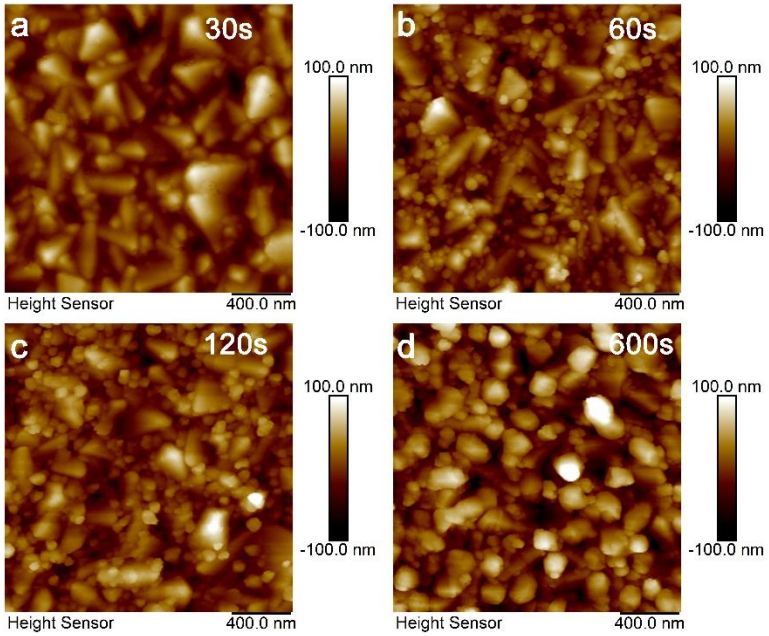

Figure S6. AFM height topographic images of the Fe films through two-electrode configuration at 4.0 V under various deposition time: a) 30 s; b) 60 s; c) 120 s and d) 600 s. This also showed the nucleation is instantaneous, the growth is not epaxial.

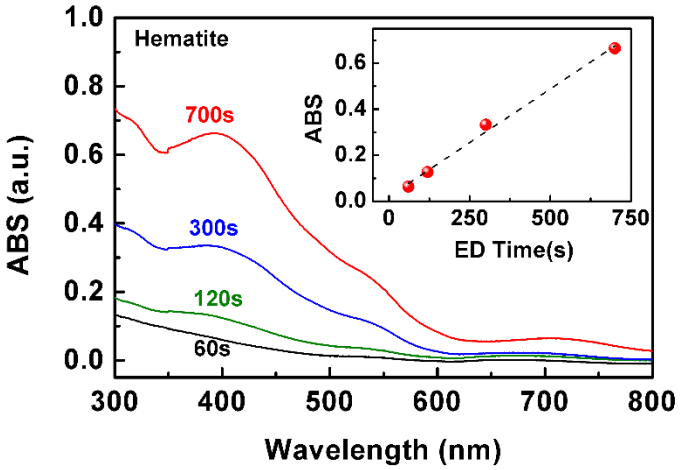

Figure S7. UV-Vis spectra of hematite prepared from iron films, which was deposited for various time (in Figure S2b).

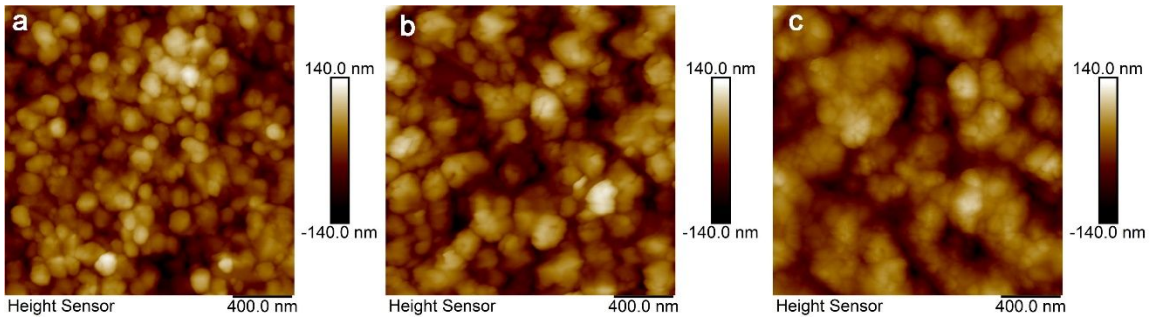

Figure S8. AFM height topographic images of the hematite films annealed at 770 °C for various deposition time: a) 3min; b) 5 min; c) 7 min. Images showed the particle fusion and size increased with the annealing time.

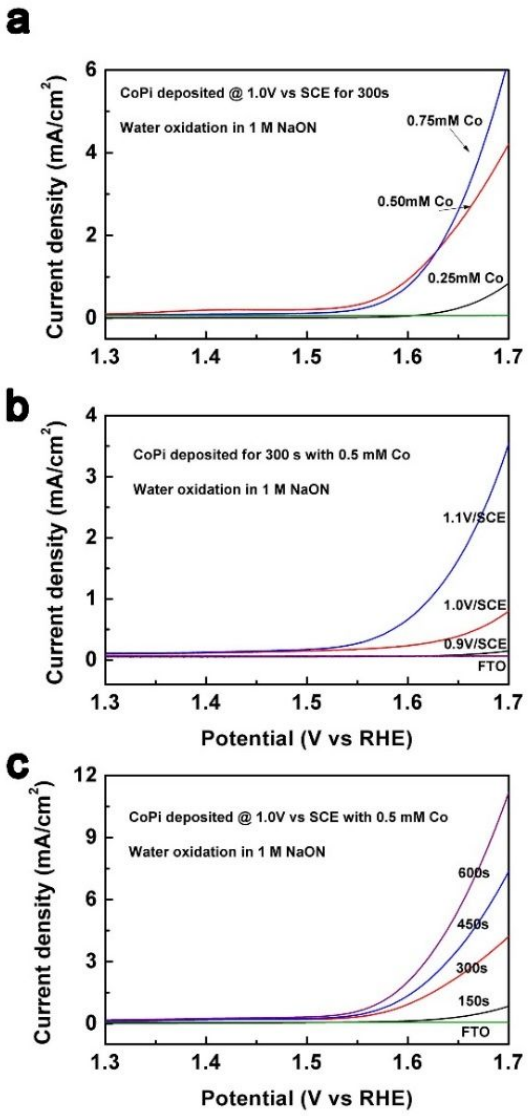

Figure S9. OER of CoPi prepared with leaching Co solution in various conditions: a) influence of Co concentrations; b) electrodeposition potentials; c) electrodeposition time.

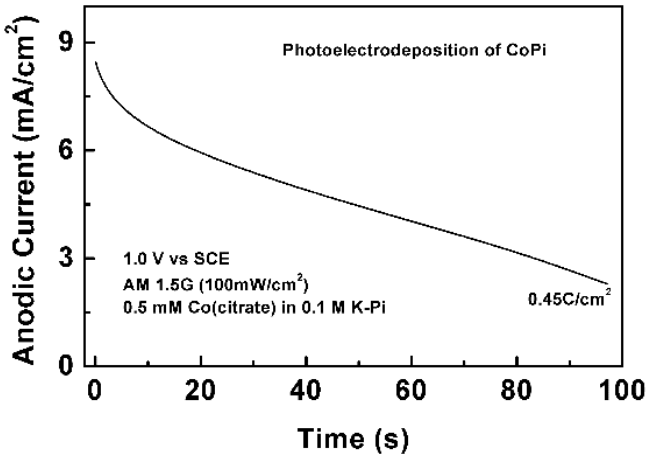

Figure S10. *J-t* curve of the photoelectrodeposition of CoPi on hematite photoanode.

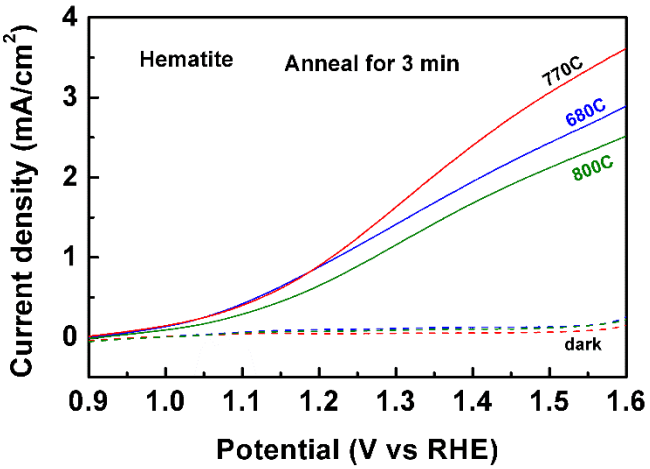

Figure S11. *J-V* curves of hematite photoanodes, which were annealed for 3 min at various temperature: 680 °C, 770 °C and 800 °C.

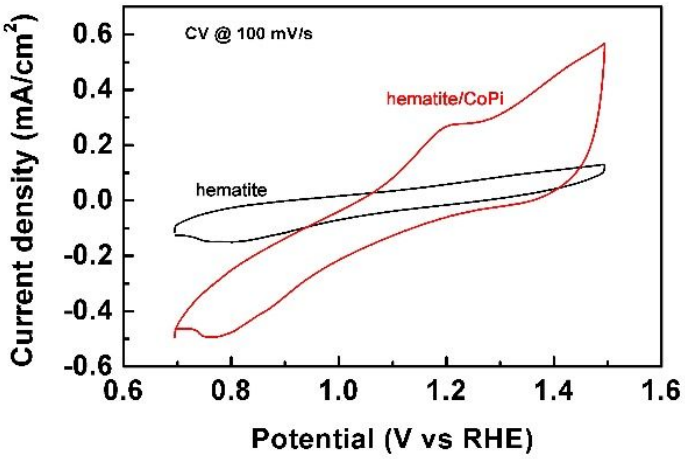

Figure S12. CV curves in dark condition showed the charge storage of hematite and hematite/CoPi. The sweeping rate was 100 mV/s.

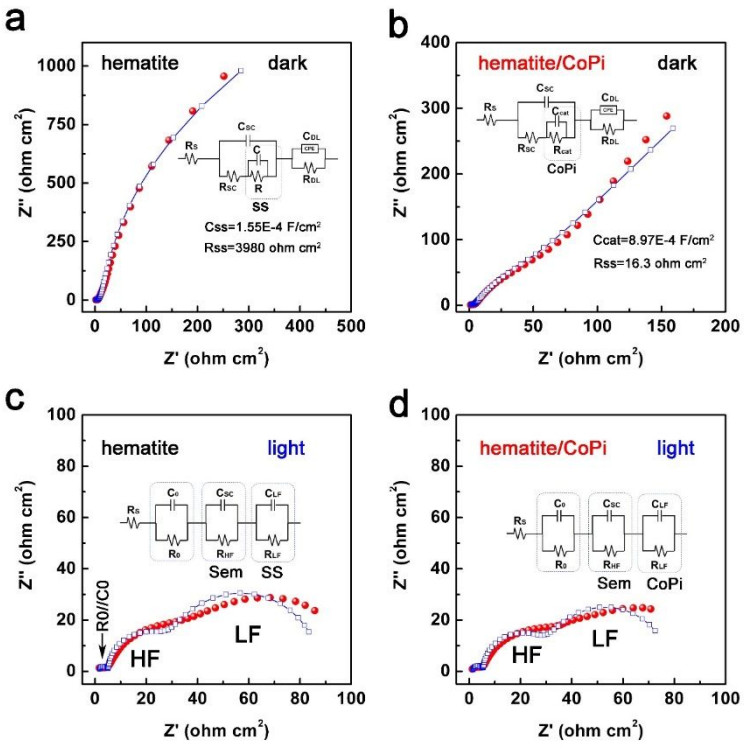

Figure S13. (Photo)electrochemical impedance spectra of the hematite and hematite/CoPi photoanodes: a) and b) Nyquist plots (EIS) of the hematite and hematite/CoPi under dark condition, respectively; c) and d) Nyquist plots (PEIS) of the hematite and hematite/CoPi

under illuminate condition (AM 1.5G 100 mW/cm^2), respectively. The potential at 1.23 V vs. RHE was used for all the measurements. The electrochemical equivalent circuits for EIS (a and b)[1] and for PEIS (c and d).[2] For the latter two, the R_0//C_0 at very high frequency was introduced, which may be related to the external circuit existing only under light condition.

References:

1. Klahr, B.; Gimenez, S.; Fabregat-Santiago, F.; Bisquert, J.; Hamann, T. W., Photoelectrochemical and Impedance Spectroscopic Investigation of Water Oxidation with "Co-Pi"-Coated Hematite Electrodes. *J. Am. Chem. Soc.* **2012,** *134*, 16693-16700.
2. Peter, L., Kinetics and Mechanisms of Light-Driven Reactions at Semiconductor Electrodes: Principles and Techniques. In *Photoelectrochemical Water Splitting: Materials, Processes and Architectures*, The Royal Society of Chemistry: 2013; pp 19-51.