EXPERIMENTAL

Material preparation

Preparation of the photo electrode

0.1 M $FeCl_3$ and 1 M $NaNO_3$ were dissolved under stirring and 20 mL precursor was added into 30 mL Teflon-lined autoclave. The FTO was put into the above solution and the hydrothermal reaction was conducted at 95 °C for 4 hours. After cleaned and dried, the film was treated at 800 ℃ for 15 min.

For coating NiOOH nano-layer, 0.1 M $NiSO_4$ was first prepared and adjusted the pH value to be 6.5~7.2. The photo-deposition process was conducted in three-electrode test system. During the light illumination, Ni^{2+} was oxidized to Ni^{3+} and then form the NiOOH. The 15 μA cm^{-2} current was also applied to accelerate this process. After photo-deposition, the electrode was carried out in the same solution by applying +1.2 V vs. Ag/AgCl (saturate KCl) for 1 min. During the illumination, the photogenerated holes will oxidize the Ni^{2+} to produce NiOOH. The valence band (VB) is as high as 2.13 V (vs. RHE), ensuring sufficient overpotential to oxidize Ni^{2+}. Subsequently, the electrodeposition process was carried out for another 1 min without light illumination.

Electrochemical Measurements

The photo-electrodes were cut into size of 1 cm * 1.5 cm and the working area is about 1 cm^2. The photoelectrochemical performance was measure in 0.5 M LiCl and 0.5 M LiOH with Pt films as counter electrode and saturated calomel electrode (SCE) as reference electrode. All the PEC water oxidation performance was recorded by Zahner electrochemical workstation. Detailly, the linear sweep voltammograms (LSV) was recorded at a scan rate of 10 mV s^{-1} and the Mott-Schottky curves were conducted at frequency 2000 HZ.

The hybrid Li-O_2 batteries were assembled in Ar-filled glovebox (H_2O<0.01ppm, O_2< 0.01ppm). The home-made H-type cells are used as test system, where two cells are separated by LAGP electrolyte. The metal lithium was put on the LAGP in the sealed environment. For the cathode side, aqueous solution containing 10 mL 0.5 M LiCl and 0.5 M LiOH is used as electrolyte. For the limited volume, the electrodes were cut into 0.5 cm * 1.5 cm with a working area of 0.25 cm^2. Before test, the cell was pumped with oxygen for more than 30 min. The light illumination was obtained with AM 1.5 G filter and infrared filter.

Microstructural and Chemical Characterization

X-ray diffraction (XRD, Bruker D8) was used to confirm the crystal structure. The existence of the NiOOH on α-Fe_2O_3 was analyzed by the Field Emission Scanning Electron Microscope (FE-SEM, S4800) and High-Resolution Transmission Electron microscope (HR-TEM, Tecnai G2 F30). The chemical valence state and valence band spectra were tested by X-ray photoelectron spectroscopy (XPS, ESCALab220i-XL spectrometer) and all the curves were calibrated using the C1s peak at 284.5 eV. The UV-Vis absorption spectrum was obtained on a UV-3600 ultraviolet-visible spectrophotometer. The photoluminescence spectra (PL) was obtained by the Fluorescence Spectrophotometer (Cary Eclipse, VARIAN).

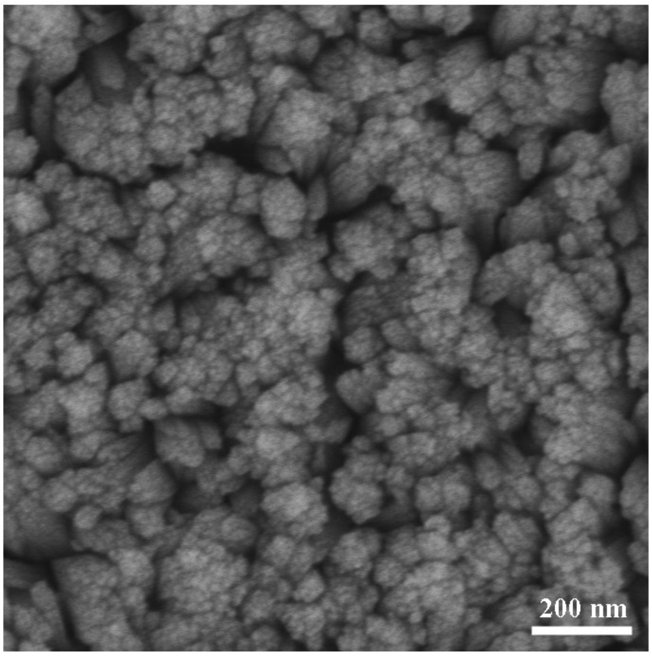

Fig. S1. the SEM image of the FeOOH after the hydrothermal method.

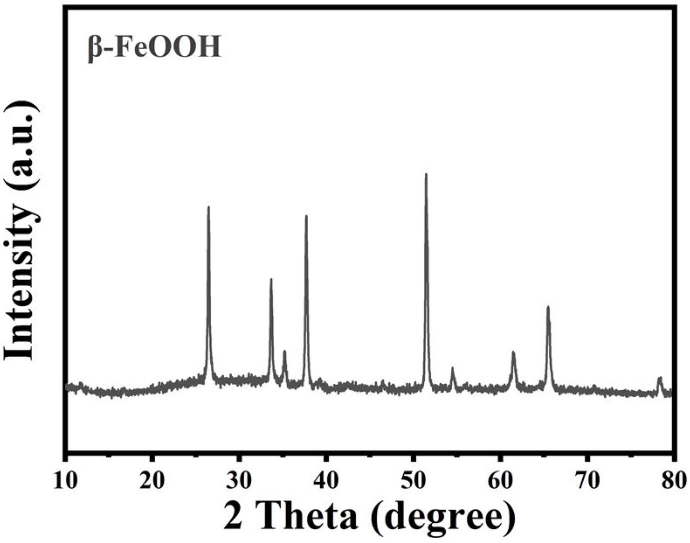

Fig. S2. XRD curve of FeOOH on the FTO.

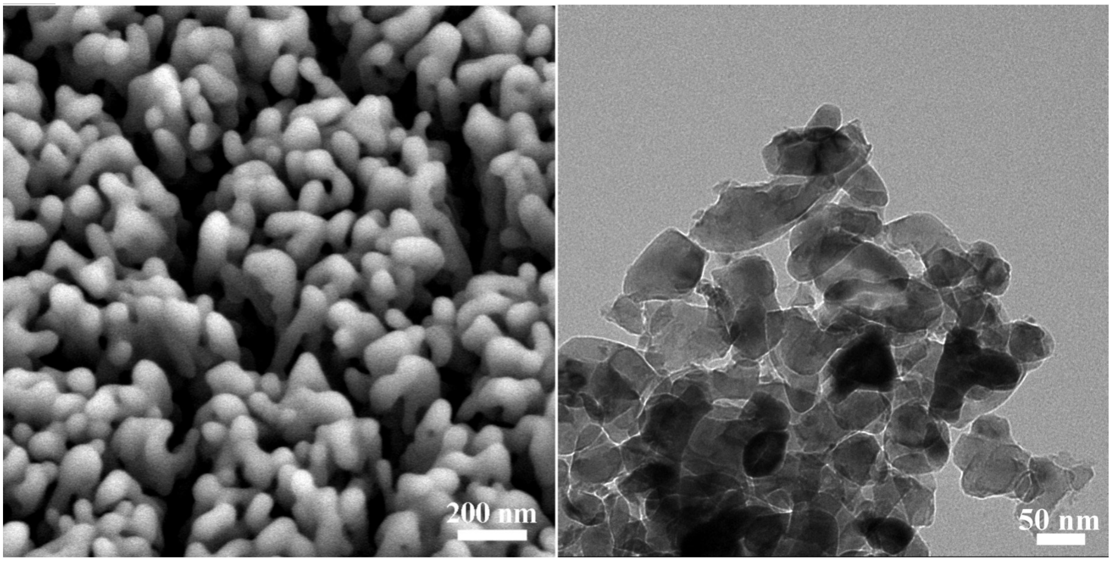

Fig. S3. the SEM and TEM image of the α-Fe_2O_3 nanorod array after heat treatment.

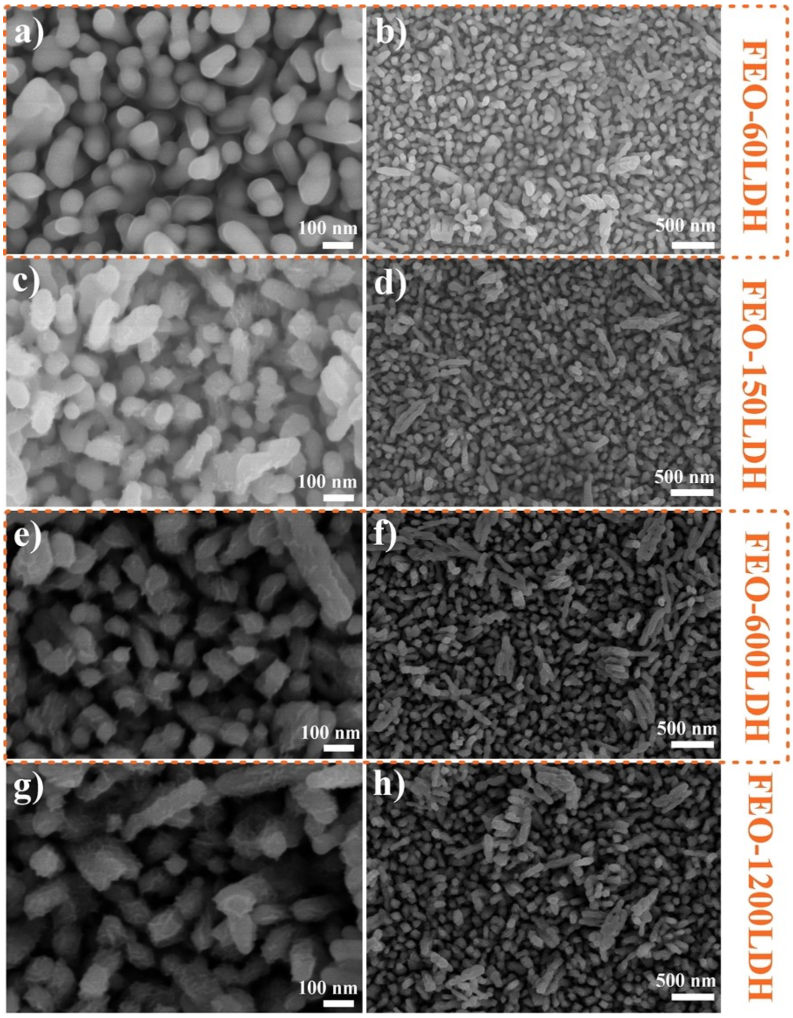

Fig. S4. SEM images for the NiOOH decorated α-Fe_2O_3: (a-b) FEO-60LDH; (c-d) FEO-150LDH; (e-f) FEO-600LDH; (g-h) FEO-1200LDH.

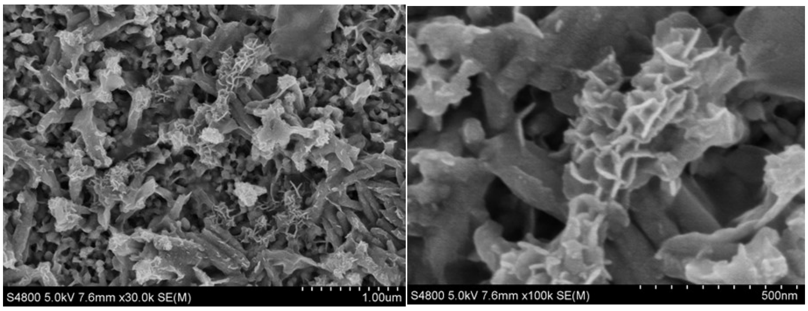

Fig. S5. the SEM images of NiOOH decorated α-Fe_2O_3 obtained from potentiostatic electrodeposition at 1.2 V for 1200s.

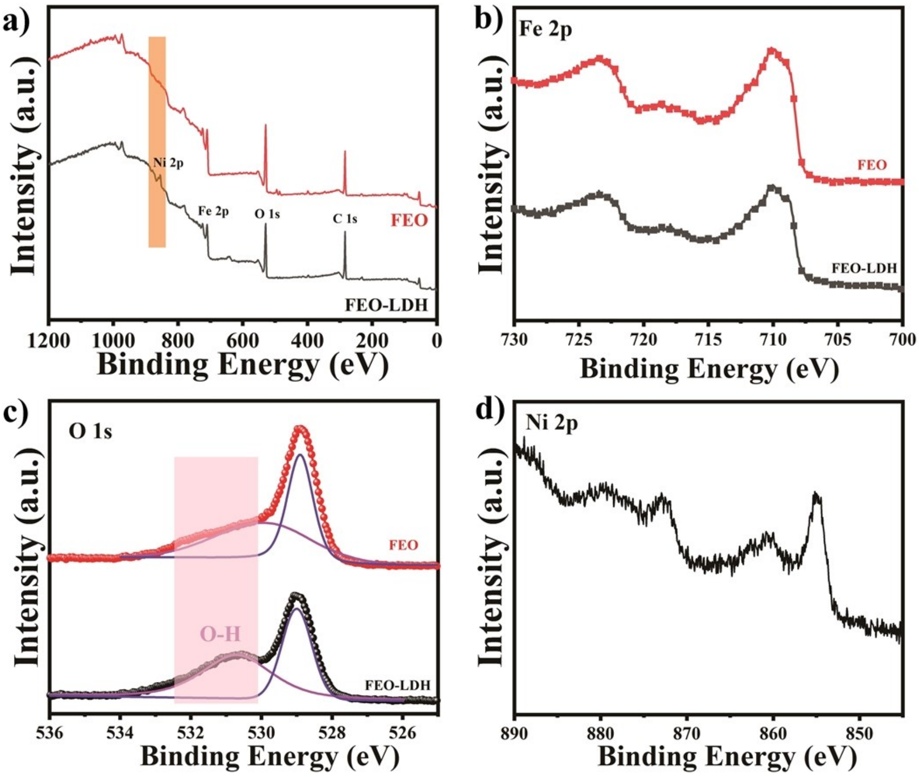

Fig. S6. the XPS spectrum of FEO-300LDH.

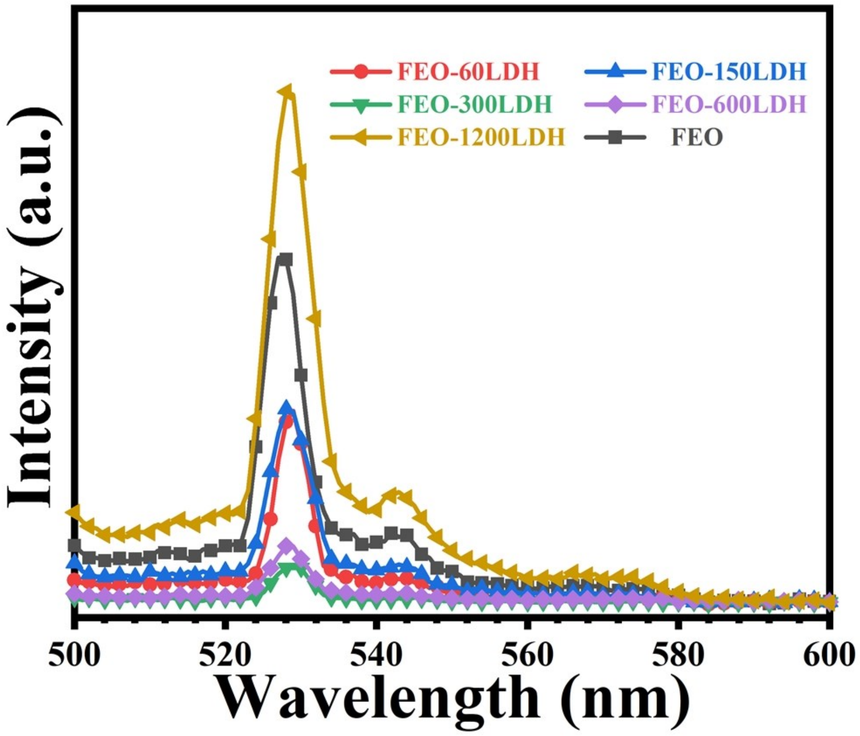

Fig. S7. Photoluminescence spectroscopy (PL) of the different samples with the excitation wavelength of 386 nm.

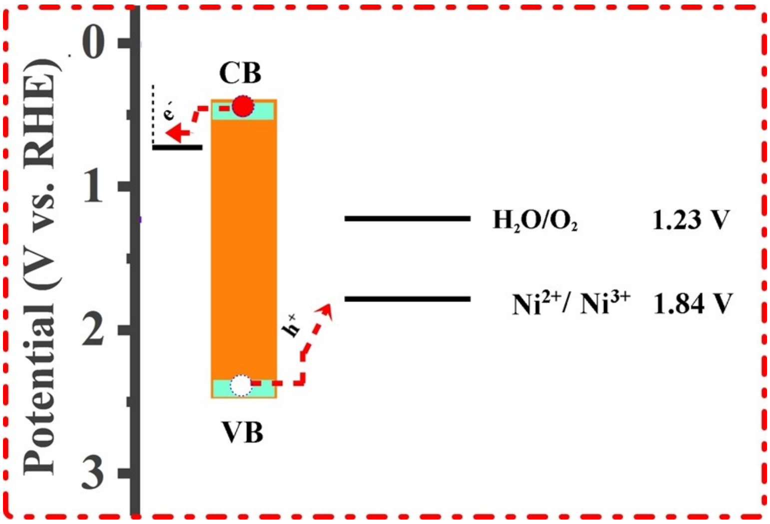

Fig. S8. The schematic of photo-induced electron transfer route.

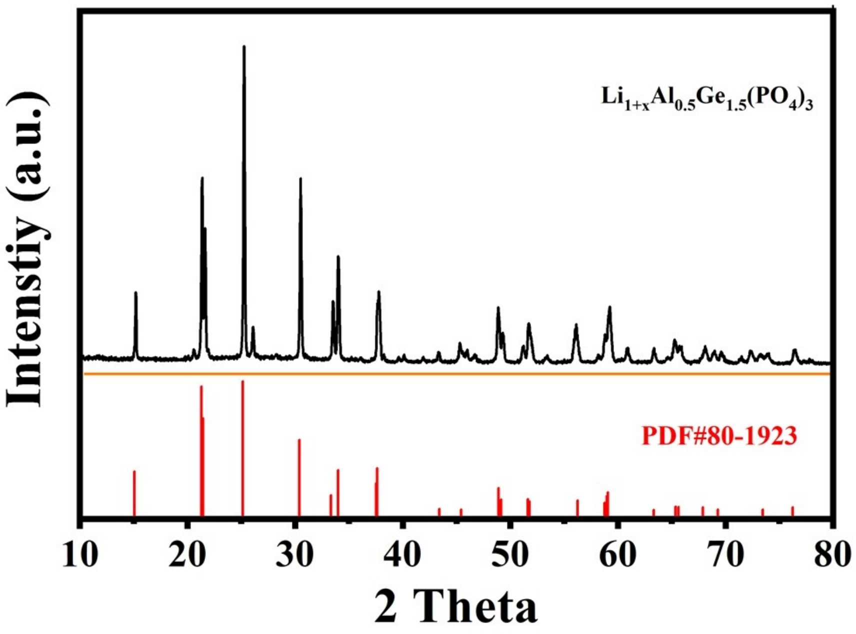

Fig. S9. the XRD pattern of the solid-state LAGP electrolytes and standard PDF card for $LiGe_2(PO_4)_3$ (JCPDS#80-1923).

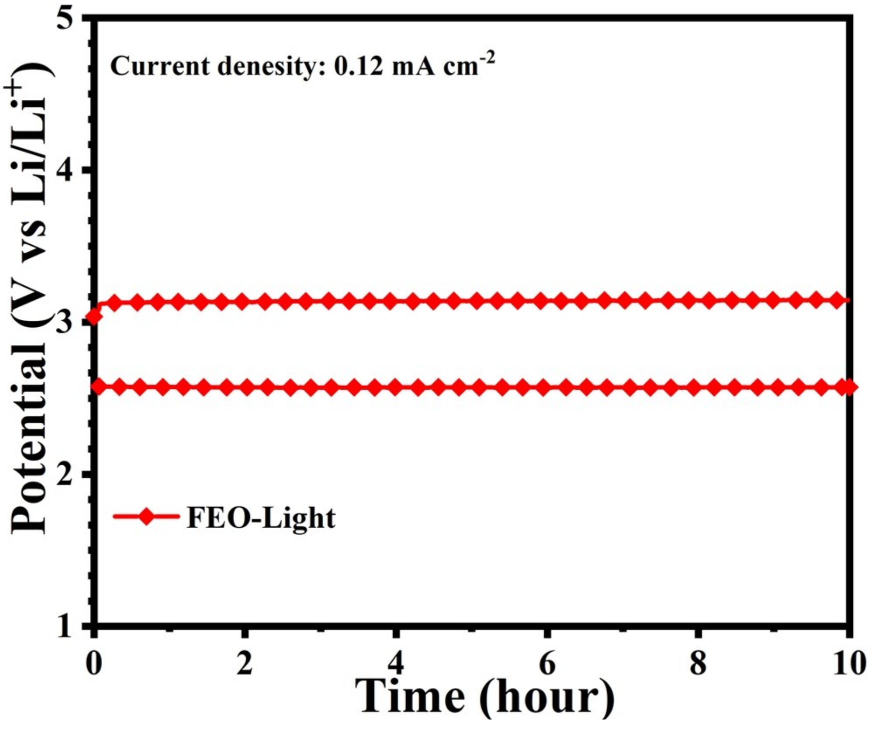

Fig. S10. Galvanostatic discharge/charge curves at 0.12 mA cm^{-2} for 10 hours with α-Fe_2O_3 as cathode.

Table S1 Electrochemical performance of the solar-enhanced hybrid lithium-oxygen batteries in this study, compared with some other reported batteries in previous literatures.

Type of electrolyte	Cathode	Discharge Product	Over-potential	Ref.
Aqueous Solution	FEO-300LDH	LiOH	0.36 V	This Work
Aqueous Solution	CNT	LiOH	0.88V	*RSC Adv.*, **2014**, 4, 13119
Aqueous Solution	$LaMn_{0.7}Co_{0.3}O_{3-x}$ nanotubes	LiOH	0.81 V	*J. Mater. Chem. A*, **2018**, 6, 16943–16949
Aqueous Solution	$LaMn_{0.7}Co_{0.3}O_3$	LiOH	0.85 V	*Chem. Asian J.*, **2018**, 13(5): 528-535.
Aqueous Solution	$NiCo_2O_4$	LiOH	0.92 V	*Energy Environ. Sci.*, **2014**, 7, 2630–2636.
Aprotic Solution	Ag/NiO-Fe_2O_3/Ag	Li_2O_2	1.71 V	*Energy Storage Mater.*, **2019** 16: 155–162.
Aprotic Solution	Cobalt Nitride	Li_2O_2	1.23 V	*ACS Nano*, **2018**, 12(1): 128-139.