Supplementary Information (SI) for RSC Applied Interfaces.
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Supporting Information for

Bifunctional $NaGdF_4:Yb^{3+}/Er^{3+}$ Upconversion Nanoparticles for Efficient Overall Water Splitting

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S1. Chemicals used.

Gadolinium (III) Nitrate hexahydrate was purchased from Alfa Aesar. Ytterbium (III) nitrate hexahydrate was purchased from Sisco Research Laboratories (SRL), Citric acid was purchased from Acros Organics. Sodium Fluoride and Potassium Hydroxide (KOH) were purchased from Fisher Scientific. Polyvinylidene difluoride (PVDF), carbon black, N-methyl-2-pyrrolidinone (NMP), and Erbium (III) nitrate pentahydrate were purchased from Sigma-Aldrich. All the chemicals were used without further purification. Deionized water was used throughout the experiment.

S2. Characterization of the synthesized materials and instrument details

In this present work, the in-depth characterization of the synthesized materials were carried out by using the following characterization techniques: (i) X-ray diffraction (XRD, PANalytical EMPYREAN with Cu Kα (λ = 0.15405 nm) radiation at a scanning speed of 3° min^{-1}), (ii) Raman spectra (Bay Spec., Nomadic Raman microscope with a 532 nm laser excitation), (iii) Field emission scanning electron microscopy (FESEM, Thermo-Scientific, APREO 2S), (iv) High-resolution transmission electron microscopy (HR-TEM, Cs-corrected STEM, JEOL ARM 200 CF), (v) Energy dispersive X-ray spectra (EDX, Oxford Instruments attached to a Carl Zeiss SEM), (vi) X-ray Photoelectron Spectroscopy (XPS, Thermo-Scientific, Theta Probe spectrometer) (vii) A CHI660E-CH instruments electrochemical workstation was used to perform all the electrochemical studies. (viii) A Photo Emission Tech., Inc. make Xenon

lamp (#SS50AAA) was used as a light source. Type of the lamp: Xenon short arc, Lamp Power: 150 W, Illumination area mm (in): 50 x 50 (1.97 x 1.97), Light source: Steady State (shutter controlled), Air Mass: AM1.5G, Intensity Adjustment: 100 mW/cm^2 ± 15%, Simulator class: Class AAA, voltage: 110-220 V AC Sigle Phase. No Filter was used as we are mimicking the natural solar radiation.

S3. Electrode preparation:

Nickel foam (5 mm × 5 mm) was used as the conductive substrate for the UCNP-based catalysts in this study. Prior to use, the NF was cleaned by dipping it in 0.5 M HCl and sonicated for 30 minutes to remove surface oxide layers. It was then thoroughly rinsed with deionized water and ethanol, followed by drying in an oven for 5 hours. To prepare the catalyst ink, 500 µL of N-methyl-2-pyrrolidone (NMP) and 5 mg of polyvinylidene fluoride (PVDF) were mixed and stirred until a clear solution was obtained. Separately, 5 mg of carbon black was uniformly blended with 40 mg of the catalyst. These two mixtures were then combined and stirred continuously at ~400 rpm for ~12 hours. The resulting slurry (catalyst ink) was applied onto the NF via drop-casting and subsequently dried in an oven.

For the measurement of Transient photocurrent plot, the working electrode was prepared by uniformly dropping the suspension (10 mg sample, 10 µl Nafion, 250 µl ethanol, sonicated for 30 min) on FTO glass (0.5 cm ×0.5 cm) and dried at 80˚C overnight.

S4. Equations used:

- To convert all measured potentials versus Ag/AgCl to potentials versus RHE, we used the following equation:

$$E_{RHE} = E_{Ag/AgCl} + 0.059\ pH + 0.197 \quad (S1)$$

- The overpotentials (η) for hydrogen evolution reaction (HER) were calculated using equation:

$$\eta = E_{RHE} - E_{equilibrium} \quad (S2)$$

- The overpotentials (η) for oxygen evolution reaction (OER) were then calculated using equation:

$$\eta = E_{RHE} - 1.23 \quad (S3)$$

- These overpotentials were subsequently employed in the Tafel equation to derive the Tafel slope (in mV/dec):

$$\eta = b \log j + a \quad (S4)$$

- Electrochemical impedance spectroscopy (EIS) was conducted within a frequency range of 0.01 Hz to 100 kHz (with an amplitude of 5 mV) at −0.28 V versus RHE (for HER) and at 1.55 V vs. RHE (for OER).
- The ECSA of the catalysts was calculated using the following equation:

$$\text{ECSA} = C_{dl}/C_S \quad \text{(S5)}$$

where C_{dl} is the measured double-layer capacitance, and C_S is the specific capacitance of the catalyst (0.04 mF/cm² in 1 M KOH). The double-layer capacitance (C_{dl}) was measured by cyclic voltammetry within the non-Faradaic region at various scan rates, using 1 M KOH as the electrolyte. The slope of the plot Δj versus scan rate provides the value of C_{dl}.

- The turnover frequency (TOF) of the catalysts was calculated with the equation:

$$\text{TOF} = j \times N_A/n \times F \times N_d \quad \text{(S6)}$$

where j is the measured current density, N_A is Avogadro's number (6.0232×10^{23} mol^{-1}), n represents the number of electron transfers (for HER, n=2 and for OER, n =1), F is the Faraday constant (96,485 C/mol), and N_d is the number of active sites involved in the reaction. The value of N_d was estimated by measuring the voltammetric charge (Q) in the non-Faradaic region and using the following equation:

$$N_d = Q/\text{Scan rate} \times 1.602 \times 10^{-19} \quad \text{(S7)}$$

- Exchange current density (i_{ex}) was calculated using the following equation:

$$i_{ex} = \frac{RT}{nF\theta A} \quad \text{(S8)}$$

Where R is the universal gas constant (8.314 J K^{-1} mol^{-1}), T is the reaction temperature (298 K), n is the number of electrons, F is the Faraday constant (96485 C mol^{-1}), θ is the charge transfer resistance calculated from EIS (R_{CT}), and A is the area of the loaded catalyst on nickel foam (0.25 cm^2).

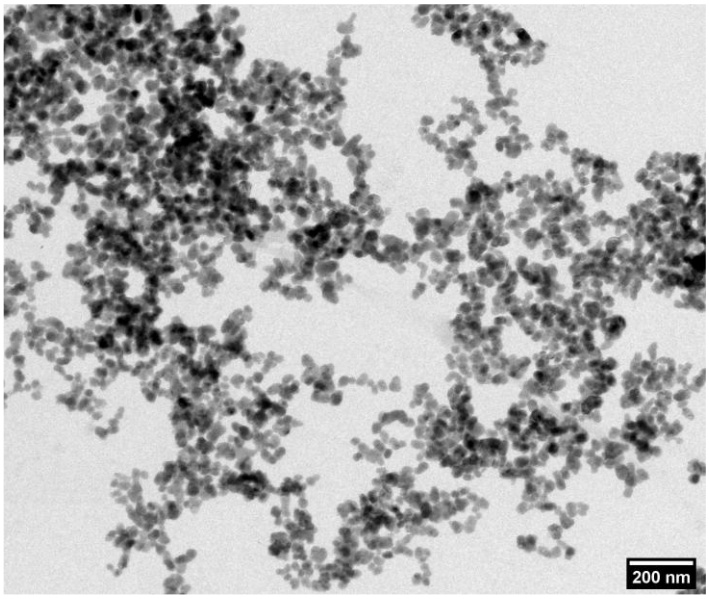

Fig. S1. TEM image of the $NaGdF_4:Yb^{3+}/Er^{3+}$ nanoparticles.

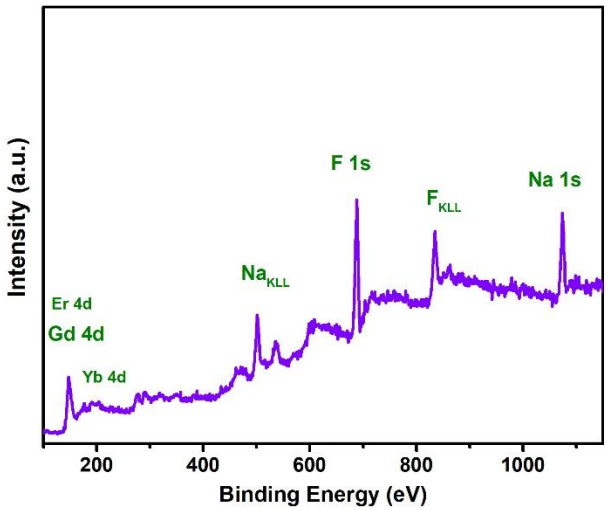

Fig. S2. XPS Survey spectra of $NaGdF_4:Yb^{3+}/Er^{3+}$ nanoparticles.

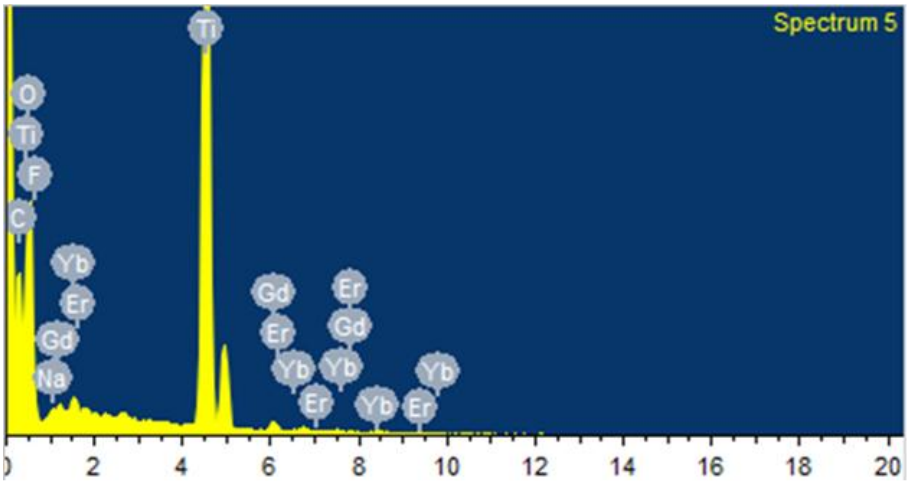

Fig. S3. EDS spectra of $NaGdF_4:Yb^{3+}/Er^{3+}$.

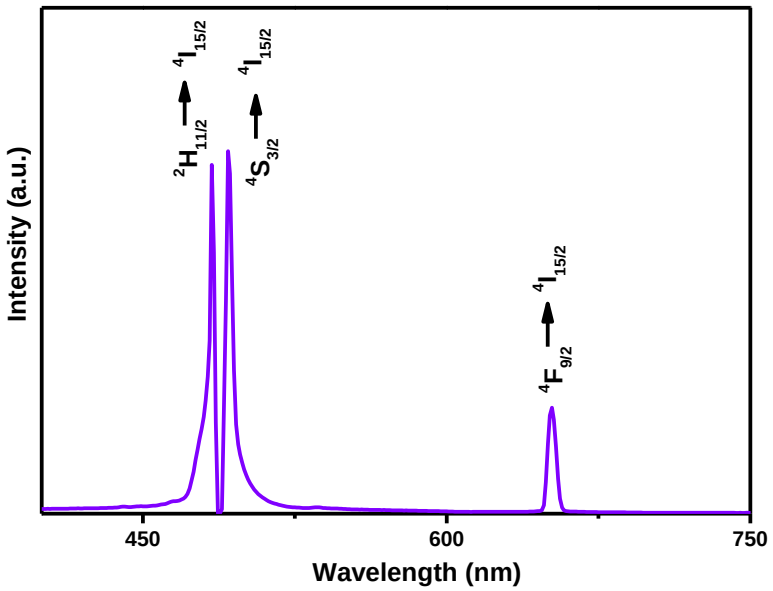

Fig. S4. Upconversion photoluminescence spectra of $NaGdF_4:Yb^{3+}/Er^{3+}$ under 980 nm excitation.

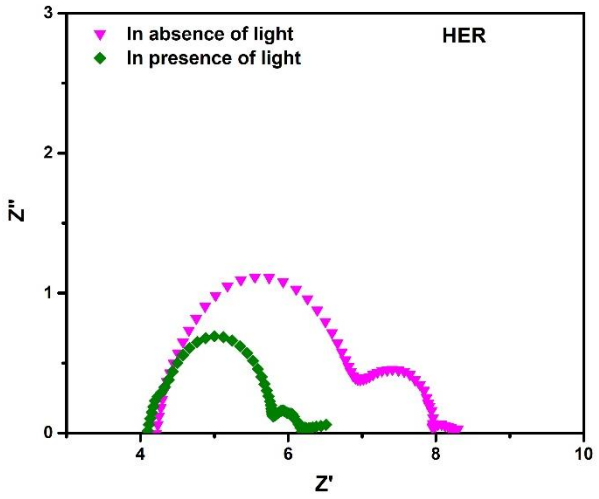

Fig. S5. EIS plots for the HER at a potential of 0.28 V of the $NaGdF_4:Yb^{3+}/Er^{3+}$ (with and without illumination).

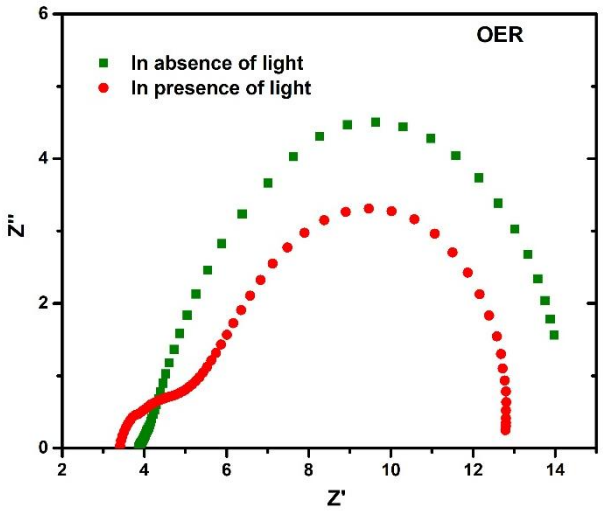

Fig. S6. EIS plots for the OER at a potential of 1.55 V of the $NaGdF_4:Yb^{3+}/Er^{3+}$ (with and without illumination).

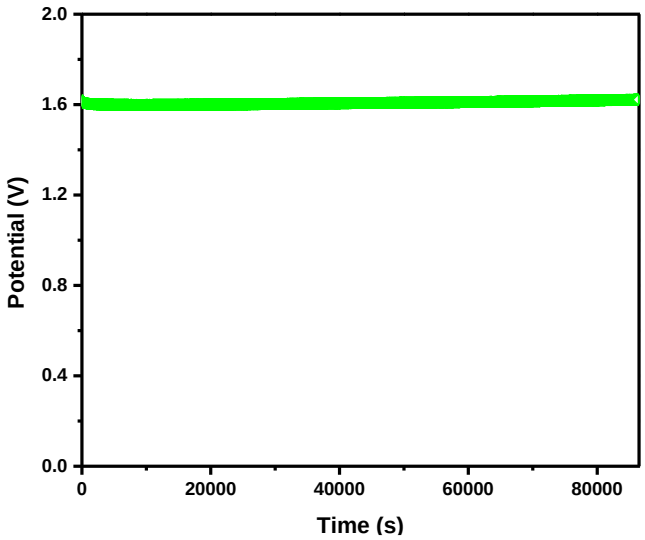

Fig. S7. Chronopotentiometry stability test for 24 h of $NaGdF_4:Yb^{3+}/Er^{3+}$ at 20 mA cm^{-2}.

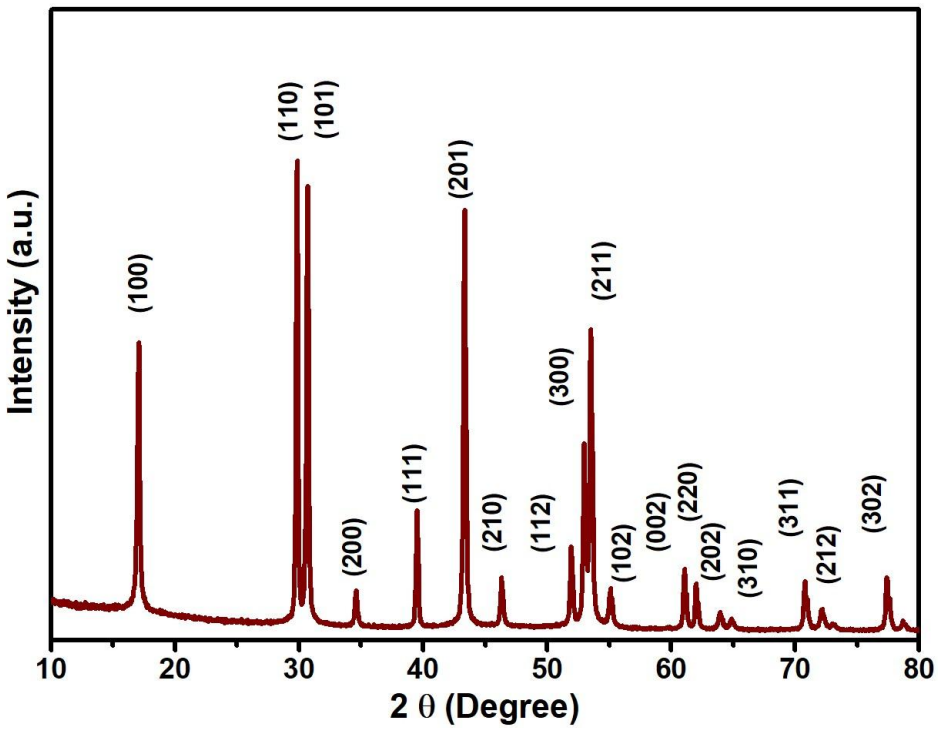

Fig. S8. XRD pattern of $NaGdF_4:Yb^{3+}/Er^{3+}$ after stability test.

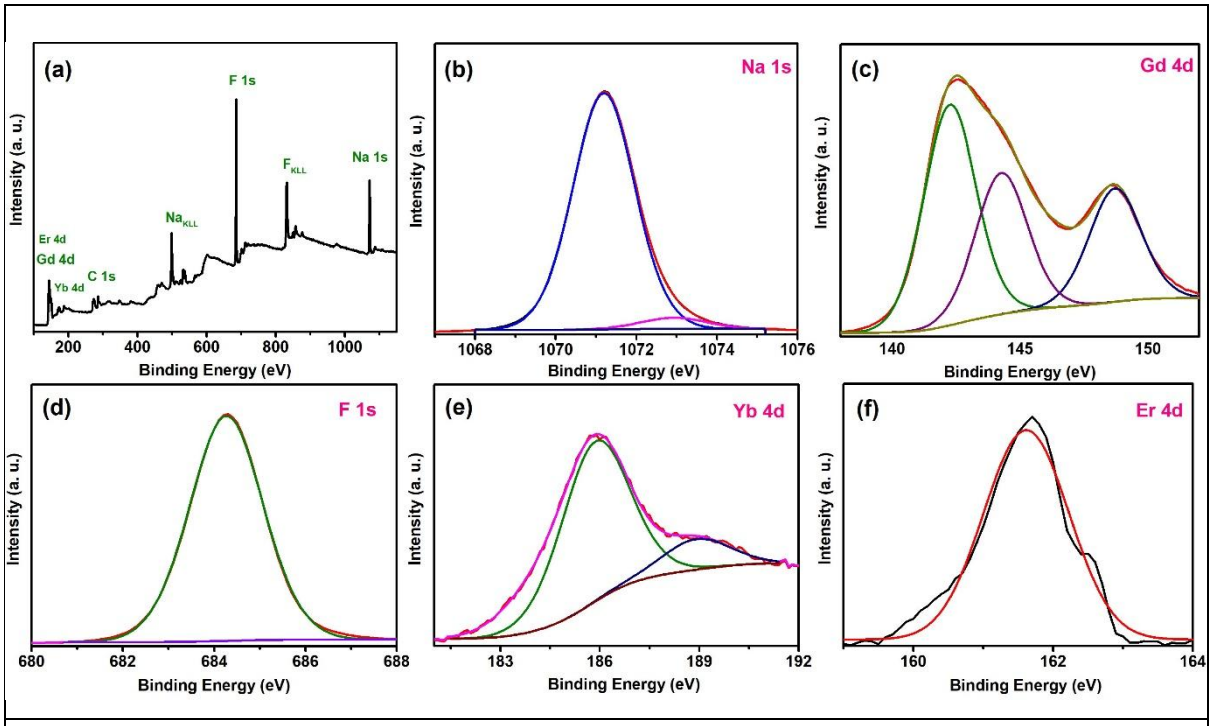

Fig. S9. (a) survey spectrum, high-resolution XPS spectra of (b) Na 1s, (c) Gd 4d, (d) F 1s, (e) Yb 4d and (f) Er 4d of NaGdF4:Yb^{3+}/Er^{3+} after stability test

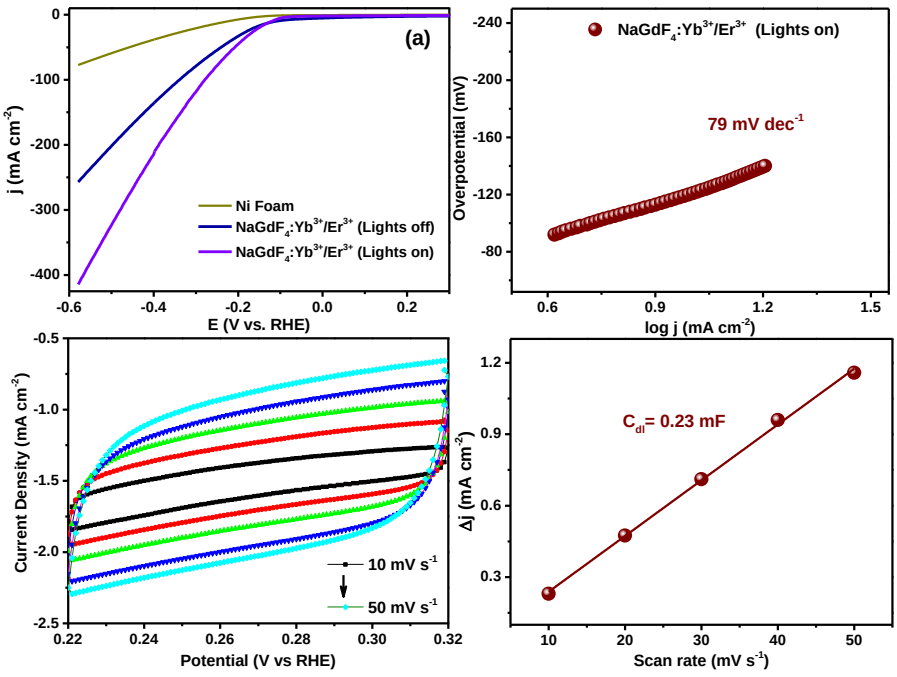

Fig. S10. (a) LSV curve (5 mV s^{-1}) for HER with and without illumination, (b) associated Tafel slope plot, (c) CV profiles recorded at different current densities within the non-Faradaic region, and (d) plot of current density versus scan rate (ν) for $NaGF_4$:Yb^{3+}/Er^{3+} under light irradiation.

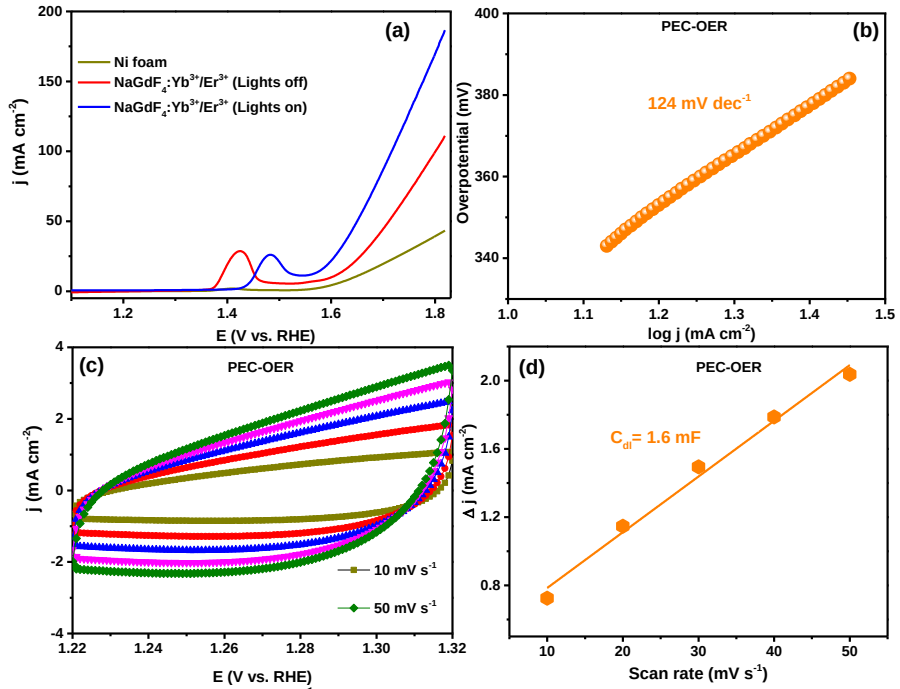

Fig. S11. (a) LSV curve (5 mV s^{-1}) for OER with and without illumination, (b) associated Tafel slope plot, (c) CV profiles recorded at different current densities within the non-Faradaic region, and (d) plot of current density versus scan rate (ν) for $NaGF_4:Yb^{3+}/Er^{3+}$ under light irradiation.

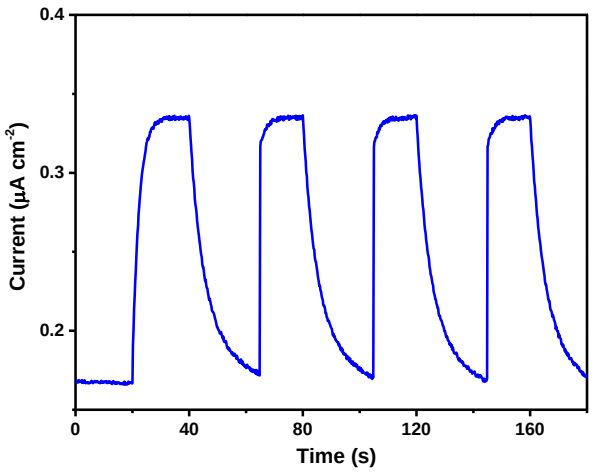

Fig. S12. Transient photocurrent response plots of (a) $NaGdF_4:Yb^{3+}/Er^{3+}$.

Table S1. The obtained values of onset potential, overpotentials (at 10 and 25 mA cm^{-2}), Tafel slope, C_{dl}, ECSA, RF, exchange current density (i_{ex}), and turnover frequency (TOF) of $NaGdF_4:Yb^{3+}/Er^{3+}$ catalysts towards HER with and without illumination.

Performance evaluation parameters	**Under illumination**	**Without illumination**
Onset Potential	80 mV	98 mV
η_{10}	115 mV	119 mV
η_{25}	159 mV	178 mV
Tafel slope	79 mV dec^{-1}	165 mV dec^{-1}
R_{ct}	2.12 Ω	3.8 Ω
C_{dl}	0.23 mF cm^{-2}	0.16 mF cm^{-2}
ECSA	5.75 cm^2	4 cm^2
RF	23	16
i_{ex}	24.2 mA cm^{-2}	13.5 mA cm^{-2}
TOF	24.6 s^{-1}	12.7 s^{-1}

Table S2. The obtained values of onset potential, overpotentials (at 10 and 25 mA cm^{-2}), Tafel slope, C_{dl}, ECSA, RF, exchange current density (i_{ex}), and turnover frequency (TOF) of $NaGdF_4:Yb^{3+}/Er^{3+}$ catalysts towards OER with and without illumination.

Performance evaluation parameters	**Under illumination**	**Without illumination**
Onset Potential	290 mV	320 mV
η_{10}	310 mV	370 mV
η_{25}	370 mV	410 mV
Tafel slope	124 mV dec^{-1}	142 mV dec^{-1}

R_{ct}	9.2 Ω	10.01 Ω
C_{dl}	1.6 mF cm^{-2}	0.7 mF cm^{-2}
ECSA	40 cm^2	17.5 cm^2
RF	160	70
i_{ex}	11.1 mA cm^{-2}	10.2 mA cm^{-2}
TOF	3.8 s^{-1}	3.5 s^{-1}

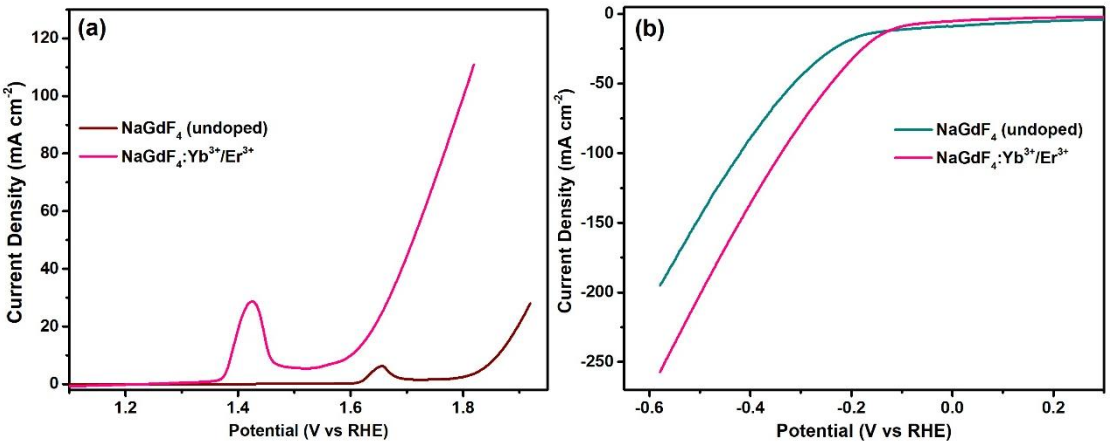

Fig. S13. Comparison of performance of undoped-$NaGF_4$ with lanthanides (Yb^{3+}/Er^{3+})-doped $NaGdF_4$ towards (a) OER, (b) HER.

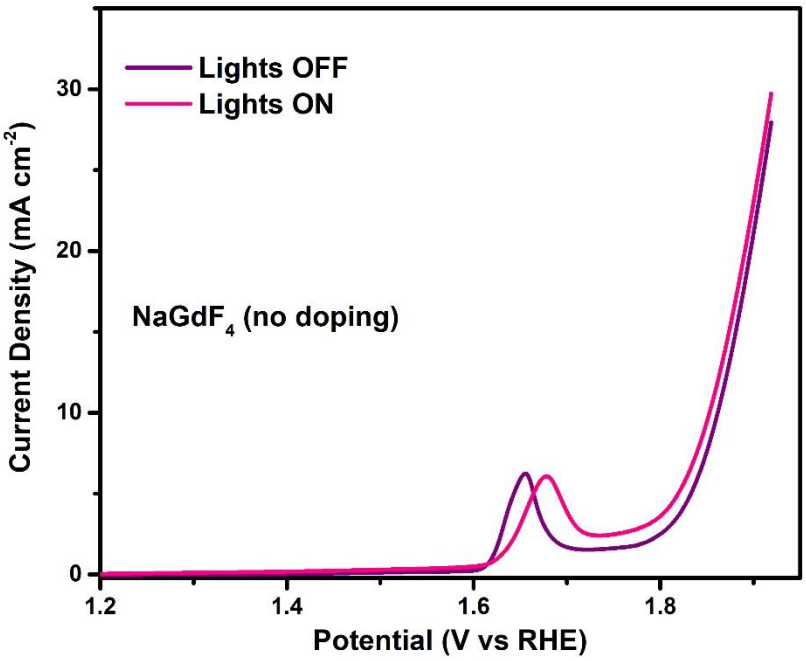

Fig. S14. OER by undoped-$NaGdF_4$ in Lights Off/On conditions (No significant increase in the current response or decrease in overpotential, unlike the doped sample, i.e., $NaGdF_4:Yb^{3+}/Er^{3+}$ (Fig. S11a).

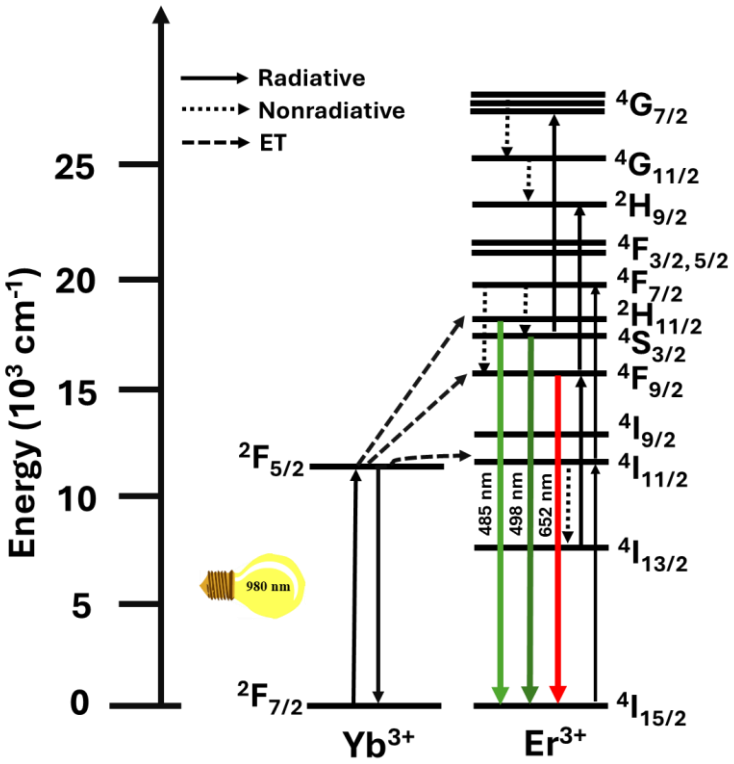

Fig. S15. Plausible energy transfer diagram.

Table S3. Comparison of reported upconversion-assisted HER/OER electrocatalysts and photoelectrodes

S.N.	Catalyst	Reaction type	Electrolyte	Reported Performance	Ref.
1.	UCNPs-$ZnFe_2O_4/TiO_2$	PEC-OER	1 M KOH	UCNPs-ZFO/TiO_2 exhibited a higher photocurrent density of 0.795 mA cm^{-2} at 1.23 V *vs. RHE* than the pristine TiO_2, UCNPs/TiO_2 and ZFO/TiO_2 samples.	[1]
2.	Mo-doped BVO integrated with UCNC containing SiO_2-capsulated PtOEP/DPA chromophores was used as the upconversion probe	PEC-HER	aqueous Na_2SO_4	A current Density of 2.3 mA cm^{-2} at 1.23 V vs RHE was achieved.	[2]
3.	$NaYF_4$:Yb,Er/Cu_2ZnSnS_4 photocathode	PEC-HER	Na_2HPO_4/NaH_2PO_4 solution (pH 6.5)	The photocathode generated an appreciable photocurrent density of -4 mA cm^{-2} and an onset potential of 0.6 V_{RHE} under 5000 mW cm^{-2} light irradiation.	[3]

4.	NGF/$BiVO_4$ embedded Cu_2O 980 nm Laser Diode	PEC-HER	0.1 M Na_2SO_4	Photocurrent produced by 980 nm light was enhanced by a factor of 40 to about 1 mA cm^{-2}	[4]
5.	$NaYF_4$:Yb/Tm@Ag_3PO_4/Ag@g-C_3N_4	PEC-HER	0.5 M Na_2SO_4	NIR-active $NaYF_4$:Yb/Tm@Ag_3PO_4/ Ag@g-C_3N_4 showed H_2 evolution rate of 23.56 mmol/g/h.	[5]
6.	$NaYF_4$:Yb^{3+}/Er^{3+}	PEC-HER/OER	1 M KOH	Overall water splitting was achieved at 1.62 V, which further decreased to 1.38 V under illumination.	[6]
7.	$NaYF_4$:Yb^{3+}/Tm^{3+}	PEC-HER/OER	1 M KOH	Overall water splitting was achieved at 1.63 V, which further decreased to 1.42 V under illumination.	[6]
8.	$NaGdF_4$:Yb^{3+}/Er^{3+}	PEC-HER/OER	1 M KOH	The fabricated cell only required ~1.52 V to deliver a current density of 10 mA cm^{-2}, in the presence of light, which is lower than that in the absence of light.	This work

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