Electronic Supporting Information

Lanthanide-doped $NaYF_4$ Upconversion Nanoparticles as Bifunctional Catalysts for Overall Water Splitting

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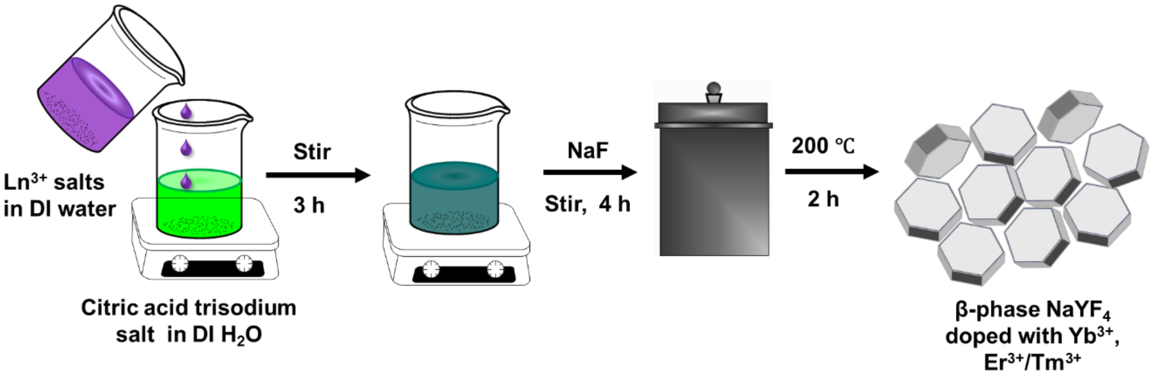
S1. Materials and Methods

S1.1. Chemicals used.

Yttrium (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), Erbium (III) nitrate pentahydrate, and Thulium (III) nitrate pentahydrate were purchased from Sigma-Aldrich. All the chemicals were used without further purification. Deionized water was used throughout the experiment.

S1.2. Synthesis of upconversion nanoparticles

To synthesize $NaYF_4:Yb^{3+}/Er^{3+}$, a mixture of Yttrium (III) nitrate hexahydrate (1.045 g), Ytterbium (III) nitrate pentahydrate (0.314 g), and Erbium (III) nitrate pentahydrate (0.031 g) was dissolved in approximately 15 mL of distilled water in a beaker. In a separate beaker, citric acid trisodium salt (27.8 g) was dissolved in 70 mL of distilled water. The lanthanide salt solution was then added dropwise to the citric acid solution under continuous stirring, and the resulting mixture was stirred for approximately 3 hours. Subsequently, sodium fluoride (NaF, 2.644 g) was introduced into the solution, followed by an additional stirring period of 4 hours. The final mixture was transferred to a Teflon-lined stainless-steel autoclave and subjected to hydrothermal treatment at 200°C for 2 hours. After cooling to room temperature, the obtained product was thoroughly washed with distilled water and ethanol, then dried overnight at 65°C. $NaYF_4:Yb^{3+}/Tm^{3+}$ was prepared by following the same procedure, only Thulium (III) nitrate pentahydrate was used instead of $Er(NO_3)_3.5H_2O$.



Scheme S1. Synthesis route of the lanthanide (Yb^{3+}, Er^{3+}/Tm^{3+}) doped β-$NaYF_4$.

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.

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 Mott-Schottky plots, 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. Then the EIS (Impedance potential mode on CH Instrument potentiostat) was measured in the voltage range of 0 to -1.5 V with the frequency of 1000 Hz.

S4. Equations used:

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

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

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

$$\eta = E_{\mathrm{RHE}} - E_{\mathrm{equilibrium}} \qquad \text{(S2)}$$

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

$$\eta = E_{\mathrm{RHE}} - 1.23 \qquad \text{(S3)}$$

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

$$\eta = b \log \mathrm{j} + \mathrm{a} \qquad \text{(S4)}$$

- 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:

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

where C_{dl} is the measured double-layer capacitance, and C_S is the specific capacitance of the catalyst (0.04 mF/cm^2 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:

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

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 Nd 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:

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

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

$$i_{ex} = \text{RT/nF}\theta\text{A} \qquad \text{(S8)}$$

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).

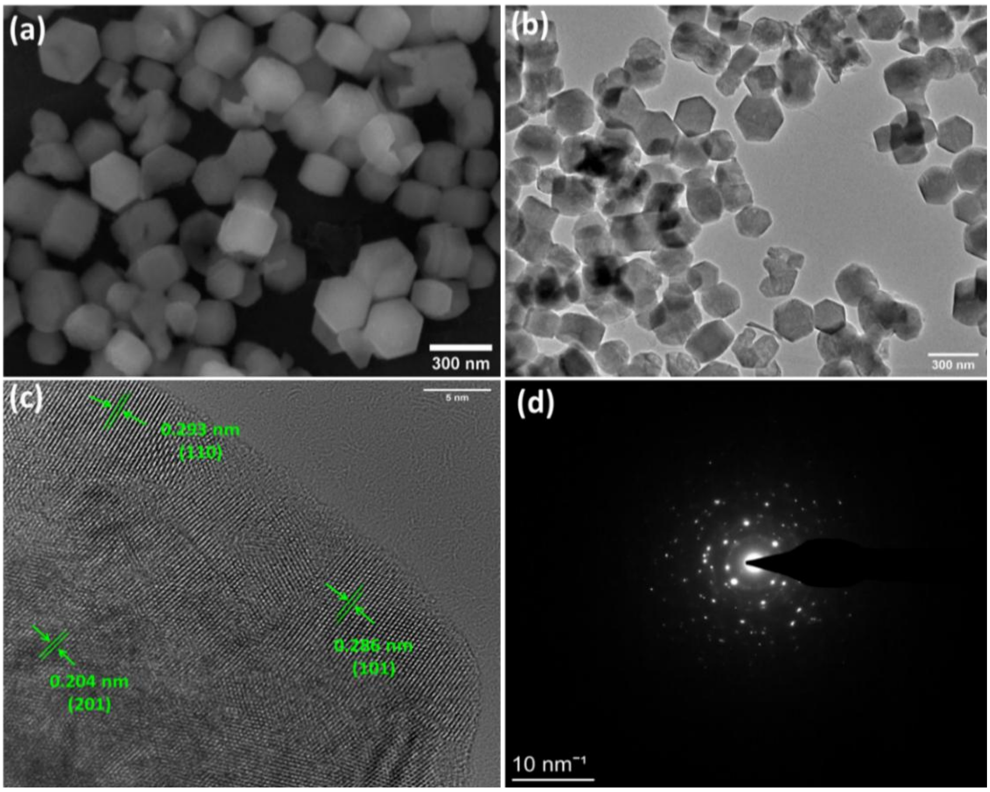


Fig. S1. (a) FESEM image, (b) TEM image, (c) HRTEM image, (d) SAED pattern of $NaYF_4$:Yb^{3+}/Tm^{3+}.

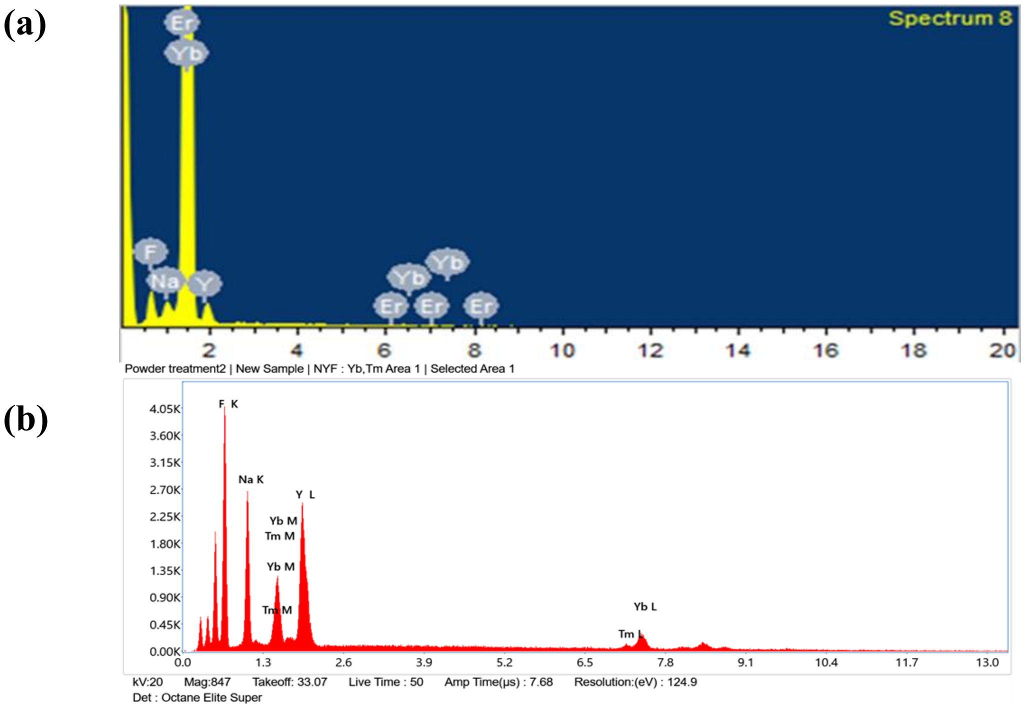


Fig. S2. EDS Spectra of (a) $NaYF_4$:Yb^{3+}/Er^{3+} and (b) $NaYF_4$:Yb^{3+}/Tm^{3+}

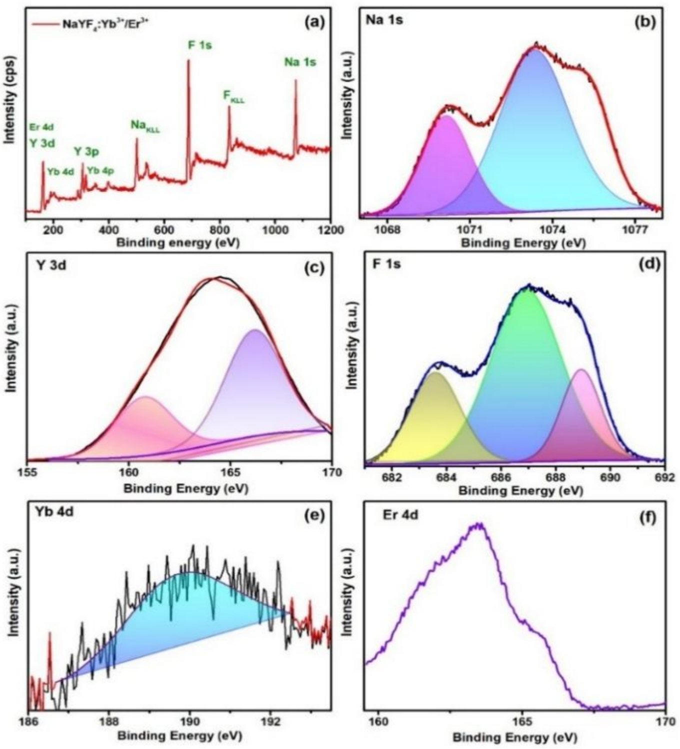


Fig. S3. (a) XPS Survey spectra, high-resolution XPS spectra for (b) Na 1s, (c) Y 3d, (d) F1s, (e) Yb 4d, and (f) Er 4d of NaYF$_4$:Yb^{3+}/Er^{3+}.

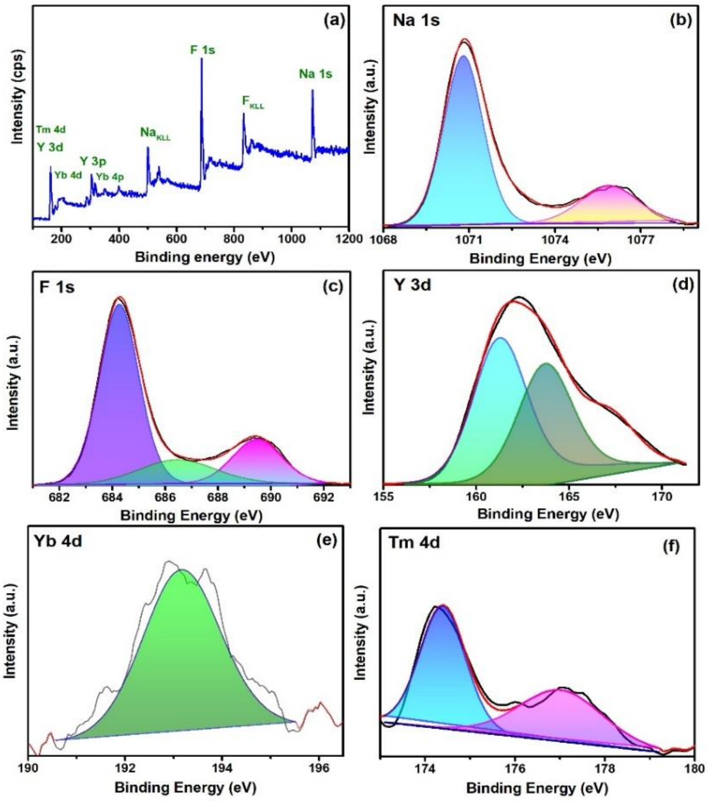


Fig. S4. (a) XPS Survey spectra, high-resolution XPS spectra for (b) Na 1s, (c) Y 3d, (d) F 1s, (e) Yb 4d, and (f) Tm 4d of NaYF$_4$:Yb^{3+}/Tm^{3+}.

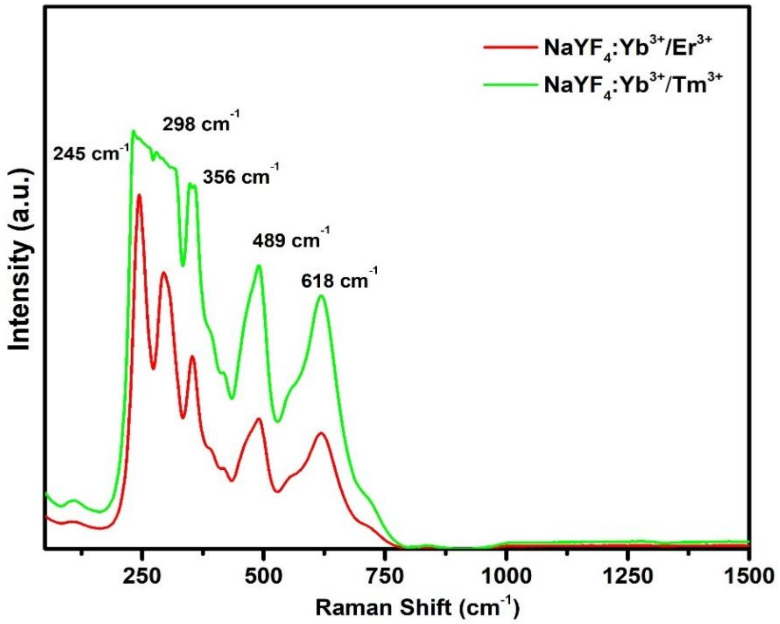


Fig. S5. Raman spectra of the UCNPs.

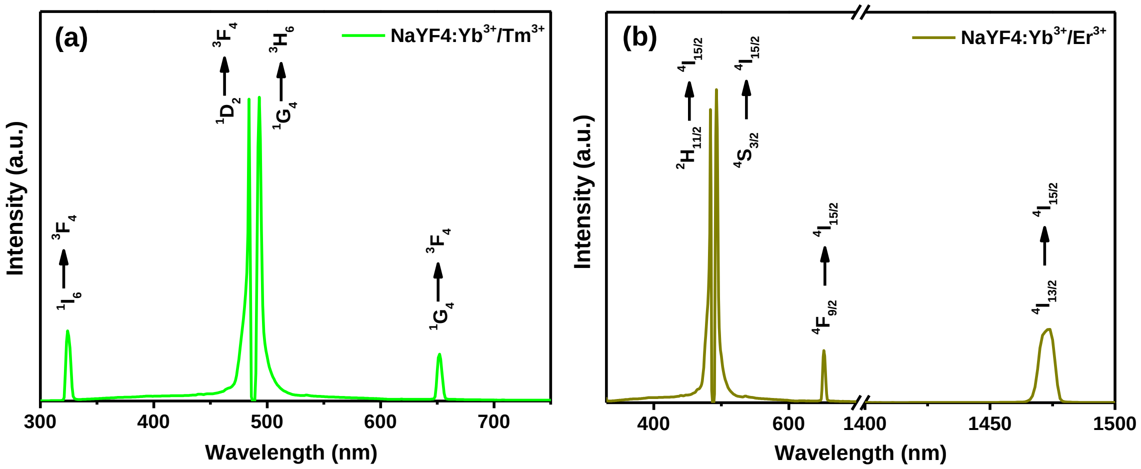


Fig. S6. (a) Upconversion photoluminescence spectra of (a) NaYF$_4$:Yb^{3+}/Tm^{3+} and (b) NaYF$_4$:Yb^{3+}/Er^{3+} under 980 nm excitation.

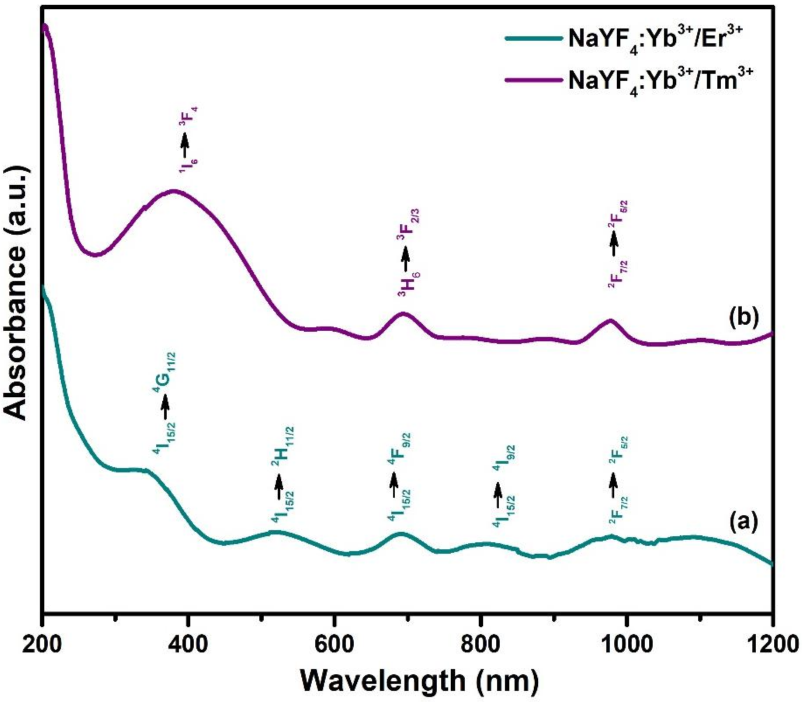


Fig. S7. UV-Vis-NIR spectra of NaYF$_4$:Yb^{3+}/Er^{3+} (a) and NaYF$_4$:Yb^{3+}/Tm^{3+} (b).

The Yb^{3+}, Er^{3+}/Tm^{3+}-doped NaYF$_4$ UCNPs exhibit characteristic 4f-4f absorption bands. NaYF$_4$:Yb^{3+}/Er^{3+} showed characteristics Er^{3+} bands at 347, 523, 682, and 807 nm, corresponding to transitions from the $^4I_{15/2}$ ground state to $^4G_{11/2}$, $^2H_{11/2}$, $^4F_{9/2}$, and $^4I_{9/2}$, respectively. The absorption band at ~982 nm, in the spectra of both the UCNPs, originate from Yb^{3+} ($^2F_{7/2} \rightarrow {}^2F_{5/2}$) and serves as the primary sensitization channel for NIR-to-visible upconversion. The NaYF$_4$:Yb^{3+}/Tm^{3+} showed characteristics Tm^{3+} bands at ~388 and ~690 nm corresponding to $^1I_6 \rightarrow {}^3F_4$, $^3H_6 \rightarrow {}^3F_{2/3}$ transitions, respectively. These features confirm the presence of Yb^{3+}, Er^{3+}/Tm^{3+} dopants in the β-NaYF$_4$.

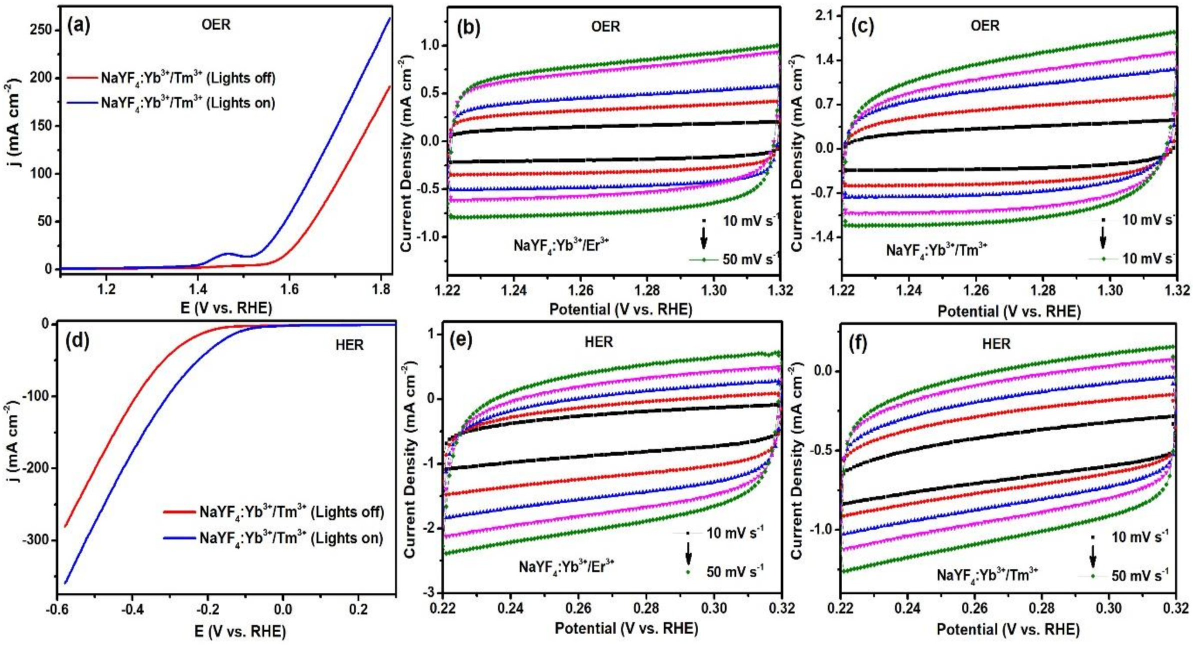


Fig. S8. (a) LSV (5mV/s) for OER NaYF$_4$:Yb^{3+}/Tm^{3+} with light on and light off, cyclic voltammetry obtained in a non-faradaic region at various scan rates for OER (b) NaYF$_4$:Yb^{3+}/Er^{3+}, (c) NaYF$_4$:Yb^{3+}/Tm^{3+}, (d) LSV (5mV/s) for HER NaYF$_4$:Yb^{3+}/Tm^{3+}, cyclic voltammetry obtained in a non-faradaic region at various scan rates for HER (e) NaYF$_4$:Yb^{3+}/Er^{3+}, (f) NaYF$_4$:Yb^{3+}/Tm^{3+}.

Table S1. Current density, Overpotential, and Tafel slope values of all samples for electrocatalytic OER conducted under dark conditions (lights off).

Materials	At Onset Potential	Overpotential at 25 mA cm^{-2}	Overpotential at 50 mA cm^{-2}	Tafel Slope (mV dec^{-1})
NaYF$_4$:Yb^{3+}/Er^{3+}	350 mV	440 mV	500 mV	124
NaYF$_4$:Yb^{3+}/Tm^{3+}	310 mV	370 mV	420 mV	113

Table S2. The obtained values of C_{dl}, ECSA, RF, exchange current density (i_{ex}), and turnover frequency (TOF) of the synthesized electrocatalysts by OER under dark conditions (Light off).

Materials	**C_{dl} (mF)**	**ECSA (cm^2)**	**RF**	**R_{CT} (Ω)**	**R_S (Ω)**	**i_{ex}**	**TOF (s^{-1})**
$NaYF_4:Yb^{3+}/Er^{3+}$	0.15	3.75	15	9.2	5.4	10.4	3.3
$NaYF_4:Yb^{3+}/Tm^{3+}$	0.21	5.25	21	8.78	3.4	11.7	6.5

Table S3. Current density, Overpotential, and Tafel slope values of all samples for electrocatalytic HER conducted under dark conditions (lights off).

Materials	**At Onset Potential**	**Overpotential at 25 mA cm^{-2}**	**Overpotential at 50 mA cm^{-2}**	**Tafel Slope (mV dec^{-1})**
$NaYF_4:Yb^{3+}/Er^{3+}$	95 mV	194 mV	275 mV	143
$NaYF_4:Yb^{3+}/Tm^{3+}$	133 mV	252 mV	310 mV	136

Table S4. The obtained values of C_{dl}, ECSA, RF, exchange current density (i_{ex}), and turnover frequency (TOF) of the synthesized electrocatalysts by HER under dark conditions (Light off)

Materials	**C_{dl} (mF)**	**ECSA (cm^2)**	**RF**	**R_{CT} (Ω)**	**R_S (Ω)**	**i_{ex} (mA cm^{-2})**	**TOF (s^{-1})**
$NaYF_4:Yb^{3+}/Er^{3+}$	0.22	5.5	22	2.79	4.51	18.4	2.1
$NaYF_4:Yb^{3+}/Tm^{3+}$	0.09	2.25	9	4.32	3.87	11.9	3.4

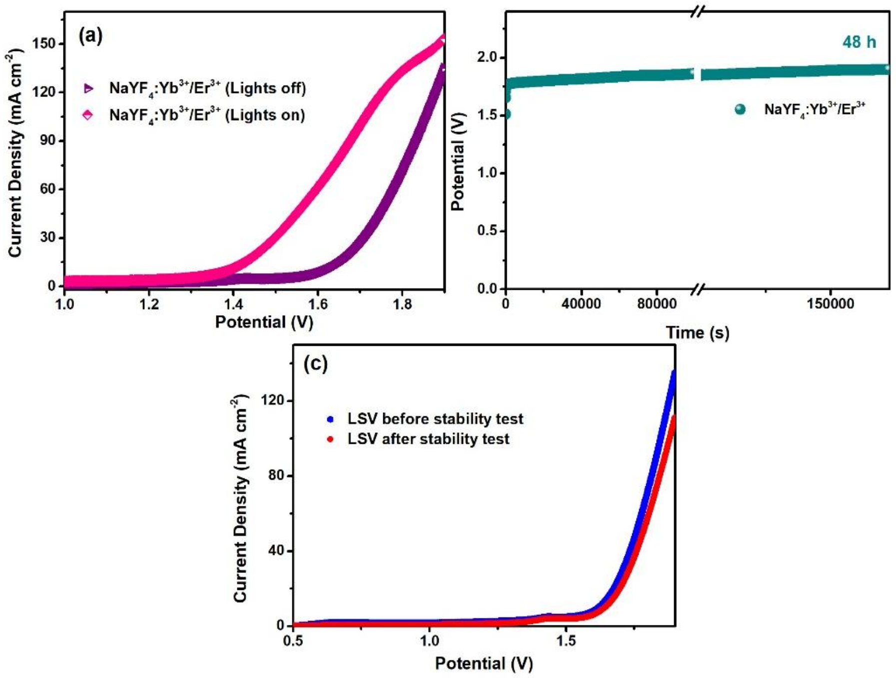


Fig. S9. (a) LSV curves of $NaYF_4{:}Yb^{3+}/Er^{3+} \| NaYF_4{:}Yb^{3+}/Er^{3+}$ water electrolysis cell in 1.0 M KOH, (b) Overall water splitting chronopotentiometric curve for 48 h, (c) LSV curves before and after 48 h stability test of $NaYF_4{:}Yb^{3+}/Er^{3+}$.

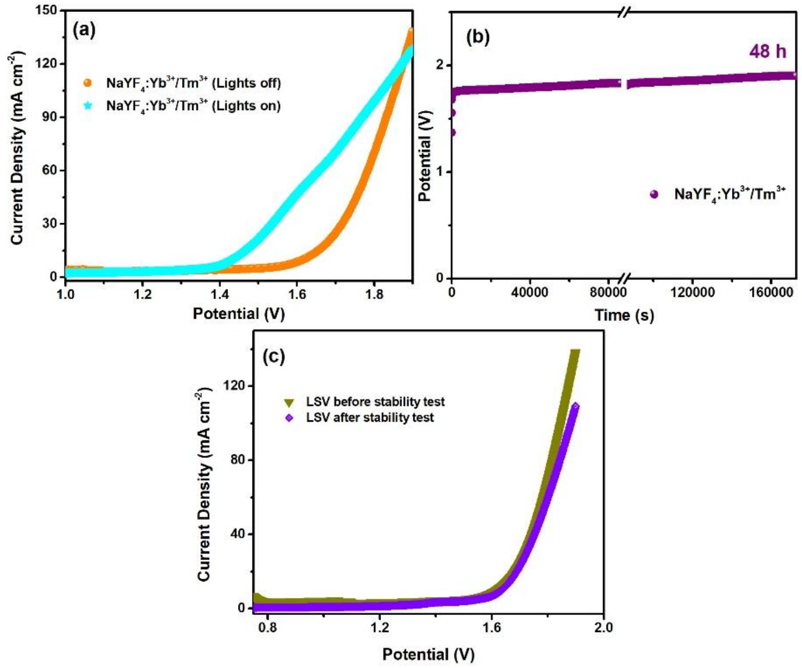


Fig. S10. (a) LSV curves of $NaYF_4{:}Yb^{3+}/Tm^{3+} \| NaYF_4{:}Yb^{3+}/Tm^{3+}$ water electrolysis cell in 1.0 M KOH, (b) Overall water splitting chronopotentiometric curve for 48 h, (c) LSV curves before and after 48 h stability test of $NaYF_4{:}Yb^{3+}/Tm^{3+}$.

Table S5. Current density, Overpotential, and Tafel slope values of all samples for PEC-OER conducted under light irradiation (lights on).

Materials	**At Onset Potential**	**Overpotential at 25 mA cm^{-2}**	**Overpotential at 50 mA cm^{-2}**	**Tafel Slope (mV dec^{-1})**
$NaYF_4:Yb^{3+}/Er^{3+}$	250 mV	330 mV	370 mV	102
$NaYF_4:Yb^{3+}/Tm^{3+}$	240 mV	310 mV	350 mV	108

Table S6. The obtained values of C_{dl}, ECSA, RF, exchange current density (i_{ex}), and turnover frequency (TOF) of the synthesized electrocatalysts by PEC-OER (Light on).

Materials	**C_{dl} (mF)**	**ECSA (cm^2)**	**RF**	**R_{CT} (Ω)**	**R_S (Ω)**	**i_{ex}**	**TOF (s^{-1})**
$NaYF_4:Yb^{3+}/Er^{3+}$	0.31	7.75	31	6.3	2.9	16.3	5.7
$NaYF_4:Yb^{3+}/Tm^{3+}$	0.27	6.75	27	3.7	3.3	27.8	16.7

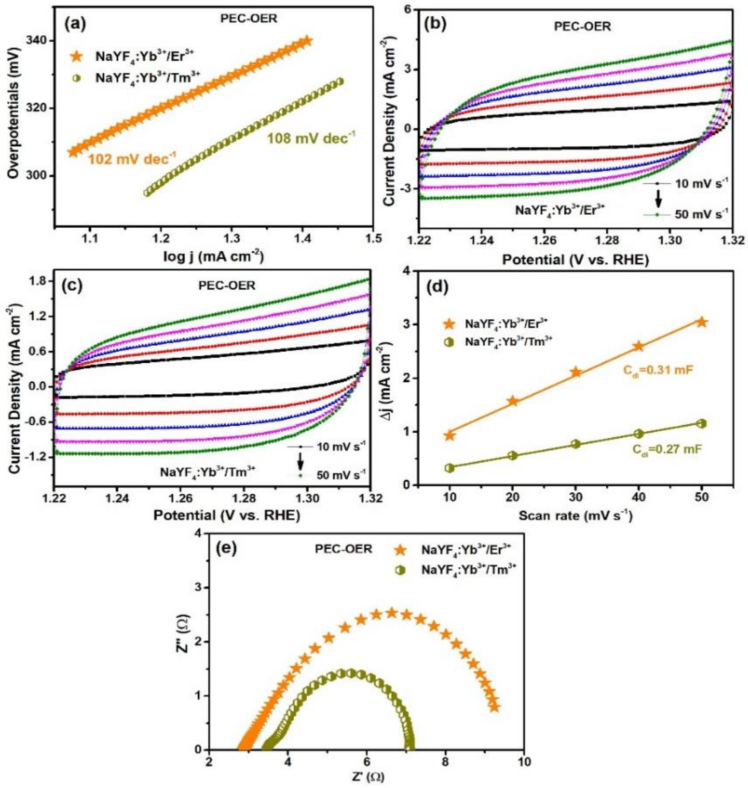


Fig. S11. (a) Tafel slopes, (b) and (c) CV curves at various scan rates, (d) Δj vs. scan rate plot for C_{dl} calculation, and (e) EIS plots of the UCNPs ($NaYF_4:Yb^{3+}/Er^{3+}$, $NaYF_4:Yb^{3+}/Tm^{3+}$) as catalysts for PEC-OER (under the light exposure).

Table S7. Overpotential and Tafel slope values of all samples for PEC-HER conducted under light irradiation (lights on).

Materials	**At Onset Potential**	**Overpotential at 25 mA cm^{-2}**	**Overpotential at 50 mA cm^{-2}**	**Tafel Slope (mV dec^{-1})**
$NaYF_4$:Yb^{3+}/Er^{3+}	88 mV	185 mV	240 mV	128
$NaYF_4$:Yb^{3+}/Tm^{3+}	60 mV	165 mV	223 mV	126

Table S8. The obtained values of C_{dl}, ECSA, RF, exchange current density (i_{ex}), and turnover frequency (TOF) of the synthesized electrocatalysts by PEC-HER.

Materials	**C_{dl} (mF)**	**ECSA (cm^2)**	**RF**	**R_{CT} (Ω)**	**R_S (Ω)**	**i_{ex}**	**TOF (s^{-1})**
$NaYF_4$:Yb^{3+}/Er^{3+}	0.41	10.25	41	2.43	3.73	21.1	5.1
$NaYF_4$:Yb^{3+}/Tm^{3+}	0.15	3.75	15	2.88	3.23	17.8	8.9

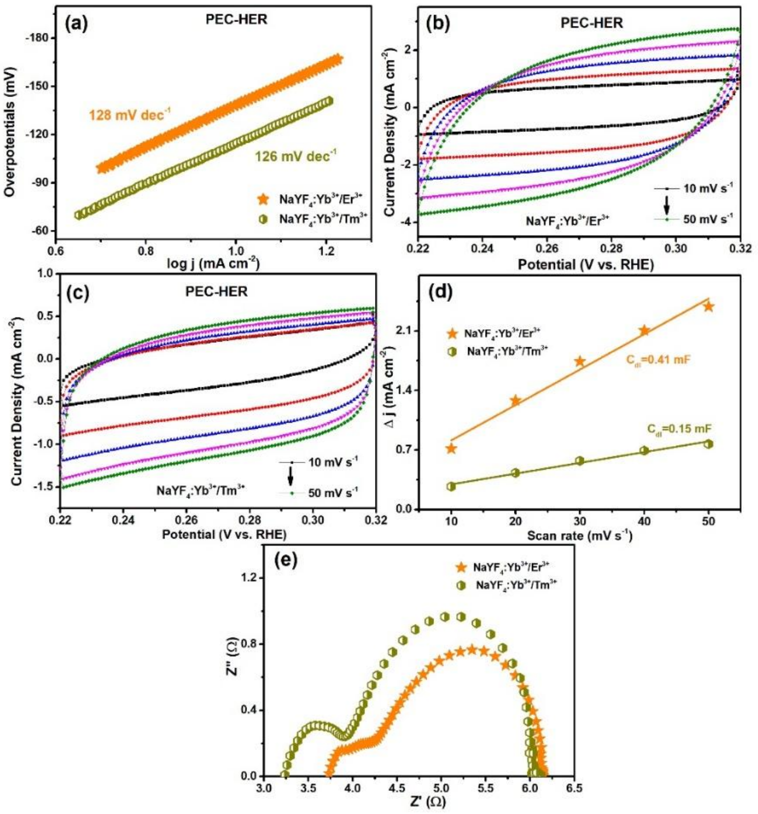


Fig. S12. (a) Tafel slopes, (b) and (c) CV curves at various scan rates, (d) Δj vs. scan rate plot for C_{dl} calculation, and (e) EIS plots of the UCNPs ($NaYF_4$:Yb^{3+}/Er^{3+}, $NaYF_4$:Yb^{3+}/Tm^{3+}) as catalysts for PEC-HER (under the light exposure).

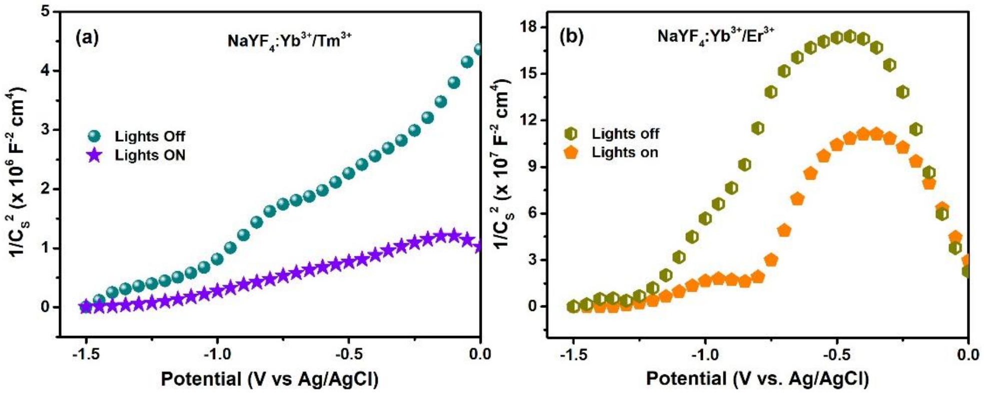


Fig. S13. Mott-Schottky plots of (a) $NaYF_4:Yb^{3+}/Tm^{3+}$, (b) $NaYF_4:Yb^{3+}/Er^{3+}$ in the presence and absence of light.

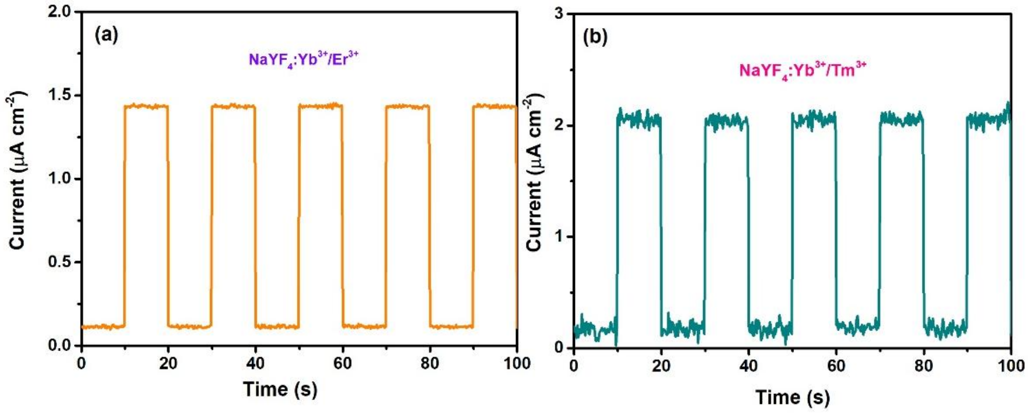


Fig. S14. Transient photocurrent response plots of (a) $NaYF_4:Yb^{3+}/Er^{3+}$, (b) $NaYF_4:Yb^{3+}/Tm^{3+}$.

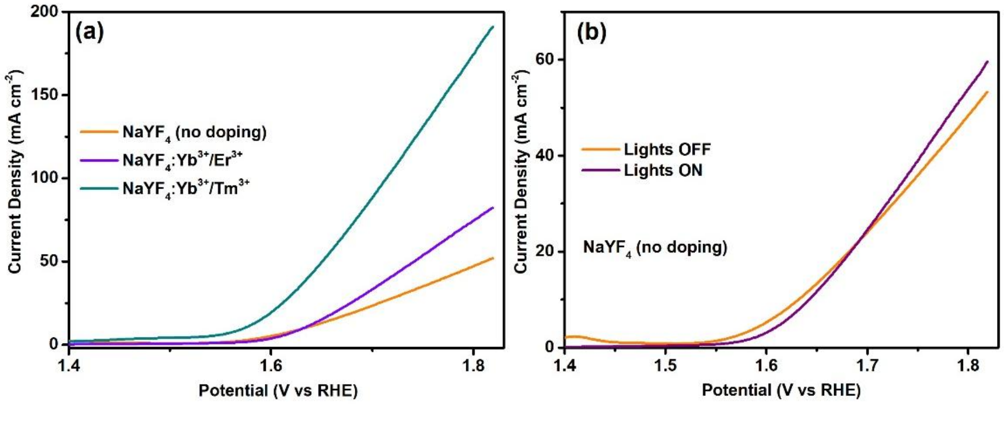


Fig. S15. (a) Comparison of OER performance of undoped-$NaYF_4$ with lanthanides (Yb^{3+}, Er^{3+}/Tm^{3+})-doped β-$NaYF_4$, (b) OER by undoped-$NaYF_4$ in Lights Off/On conditions (No significant increase in the current response or decrease in overpotential, unlike the doped samples (Fig. 2a, S8a)).