Supplementary Materials

Up-conversion effect boosted NIR-driven photocatalytic solar fuel generation of $NaYF_4$: Yb, Er decorated $ZnIn_2S_4$ flowers with rich Zn vacancies

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1. Chemicals and Materials

Glycerol (Tianjin Fuyu Chemical Co., Ltd., AR); Deionized water (DI water); Ethanol (Tianjin Jingdongtianzheng Precision Chemical Reagent Factory, AR); Anhydrous Zinc chloride ($ZnCl_2$, Innochem, 98%); Indium chloride trihydrate ($InCl_3 \cdot 4H_2O$, Innochem, 99.99%); Thioacetamide (TAA, Innochem, ≥98%); Sodium hydroxide (NaOH, Tianjin Guangfu Fine Chemical Co., Ltd.); Ammonium Fluoride (NH_4F, Fuchen Chemical Reagent Co., Ltd.); Methyl Alcohol (Anhui Tedia High Purity Solvents Co., Ltd., AR); Erbium chloride hexahydrate ($ErCl_3 \cdot 6H_2O$, Innochem, 99.99%); Ytterbium chloride hexahydrate ($YbCl_3 \cdot 6H_2O$, Innochem, 99.99%); Yttrium chloride hexahydrate ($YCl_3 \cdot 6H_2O$, Innochem, 99.9%); Octadecene (Innochem, 90%); Oleic Acid (Aladdin, AR); Cyclohexane (Innochem, 99.7%).

2. Preparation of ZIS

Firstly, 8 mL of H_2O (PH=2.5) and 1.5 g of glycerol were mixed and sonicated for 5 minutes. Then, 81.6 mg of $ZnCl_2$, 175.8 mg of $InCl_3 \cdot 4H_2O$, and 90 mg of TAA were added to the above solution under continuous stirring. Subsequently, the solution was sonicated again and heated in an oil bath at 80 ℃. After reacting for 1 hour, the suspension was centrifuged and washed with ethanol several times until the solution was neutral. Finally, the $ZnIn_2S_4$ (ZIS) was obtained after drying the precipitate overnight.

3. Preparation of V_{Zn}-ZIS

Firstly, $ZnCl_2$ (50 mg), $InCl_3 \cdot 4H_2O$ (230 mg), TAA (240 mg), ethanol (15 mL), and DI water (15 mL) were mixed and sonicated to get a homogeneous solution. Secondly, the solution was transferred into 50 mL of stainless steel vessel followed by heating at 180 ℃ for 24 h. Finally, the $ZnIn_2S_4$ with Zn vacancy (V_{Zn}-ZIS) was obtained after washing and drying the product.

4. Preparation of UCNPs

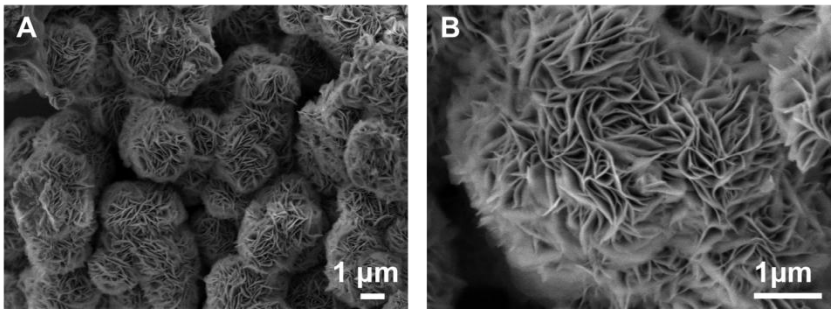
Firstly, $ErCl_3 \cdot 6H_2O$ (7.6 mg), $YbCl_3 \cdot 6H_2O$ (77.5 mg), $YCl_3 \cdot 6H_2O$, oleic acid (6 mL), and octadecene (15 mL) were mixed to obtain solution A. Secondly, NaOH (100 mg) and NH_4F (148 mg) were added to methyl alcohol (5 mL) and sonicated to obtain solution B. Subsequently, solution A was heated to 130 ℃ for 40-60 minutes under Ar

protection. Afterward, solution A was cooled naturally followed by dropping solution B under an Ar atmosphere and kept stirring for 15 minutes at room temperature. Then the mixed solution was heated to 125 ℃ to remove the methyl alcohol until no bubble could be seen on the surface of the solution. Then the above solution was heated under 300 ℃ for 1.5 hours with a condenser system. After cooling to room temperature, the above system was washed with cyclohexane and ethanol. The product ($NaYF_4$: 20%Yb, 2%Er) was denoted as UCNPs and stored in cyclohexane for further use.

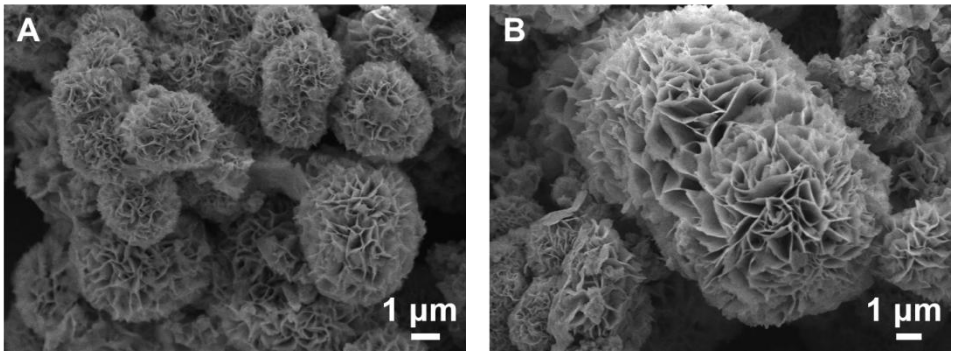
Characterizations

The scanning electron microscopy (SEM) images and energy dispersive spectroscopy (EDS) images were obtained from JSM-7800F to evaluate the morphology of samples. Transmission electron microscope (TEM) and high-resolution TEM (HRTEM) were obtained from Tecnai G2 S-Twin F20 camera. X-ray diffraction (XRD) powder diffractometer was used to analyze the crystal phase (D/MAX2550 (Cu Kα radiation, λ = 1.5418 Å). was. X-ray photoelectron spectroscopy (XPS) was obtained from ESCALAB 250 X-ray photoelectron spectrometer. UV-vis diffuse reflectance spectra (DRS) was measured on HITACHI U-4100 spectrometer to evaluate the absorbance of samples. Photoluminescence (PL) and PL decay curves were obtained from the FLUOROMAX-4 fluorescence spectrophotometer with an excitation wavelength of 350 nm. In-situ diffuse reflectance infrared Fourier-transform spectroscopy (DRIFT) spectroscopy was measured from 400 cm^{-1} to 4000 cm^{-1} on VERTEX 80v from Bruker.

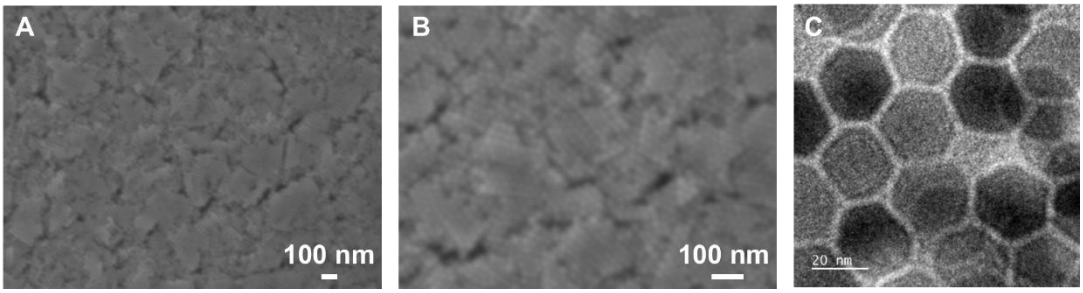
Supplementary Figures



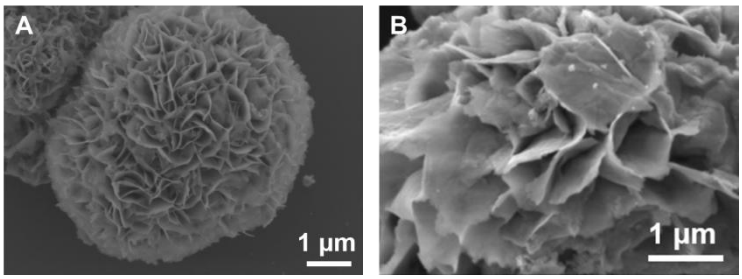
Supplementary Figure 1. (A) SEM image of ZIS; (B) is the enlargement of (A).



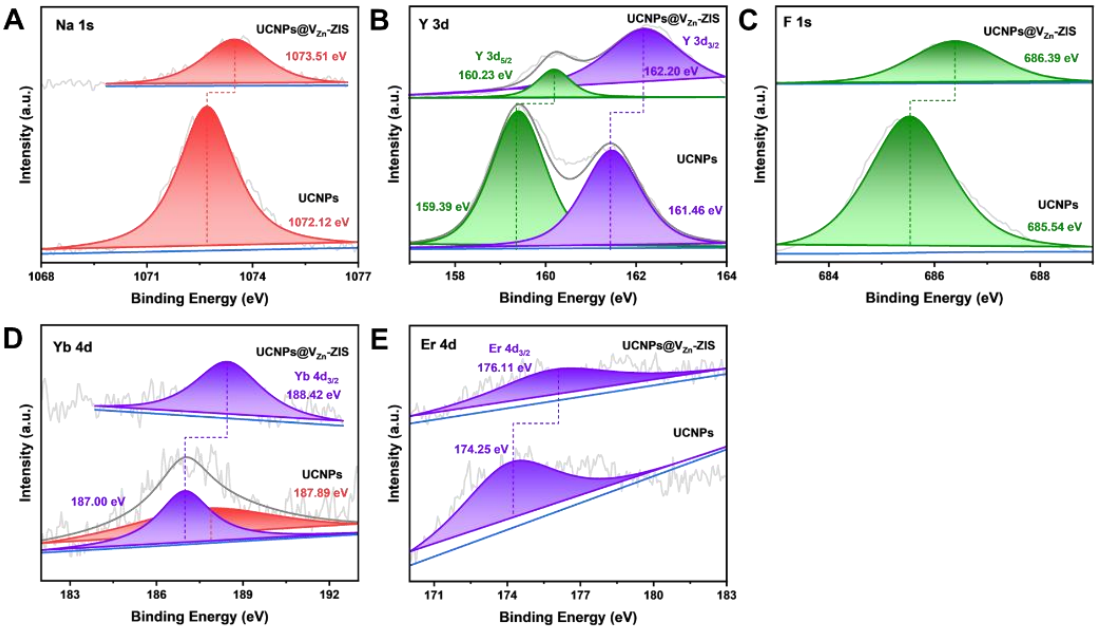
Supplementary Figure 2. (A) SEM image of V_{Zn}-ZIS; (B) is the enlargement of (A).



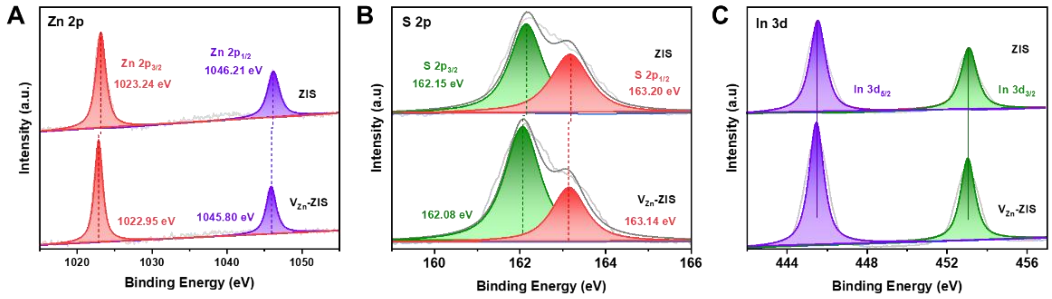
Supplementary Figure 3. SEM images (A and B) and TEM image (C) of UCNPs.



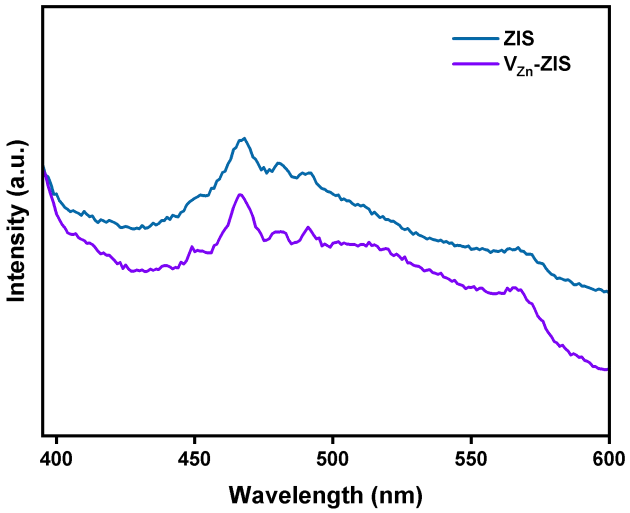
Supplementary Figure 4. (A) SEM image of UCNPs@V_{Zn}-ZIS; (B) is the enlargement of (A).



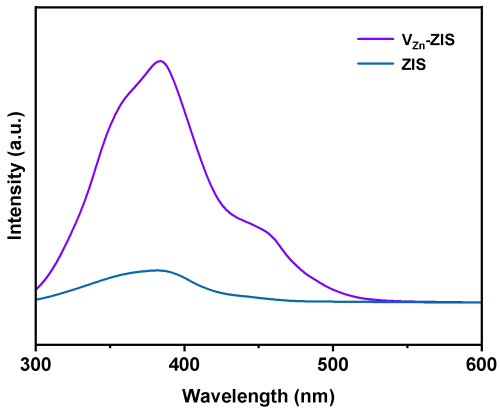
Supplementary Figure 5. XPS spectra of (A) Na 1s; (B) Y 3d; (C) F1s; (D) Yb 4d and (E) Er 4d of UCNPs@V_{Zn}-ZIS.



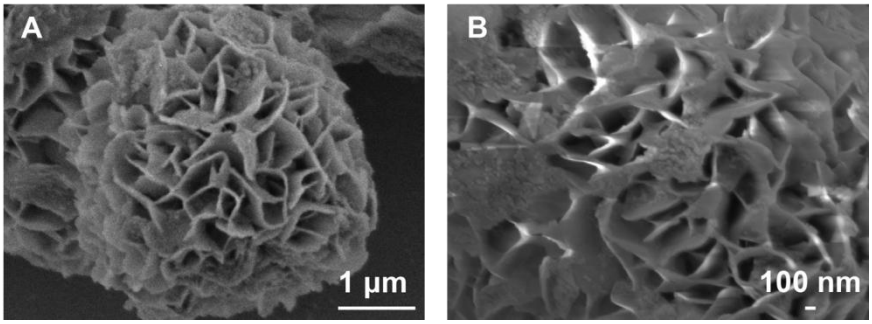
Supplementary Figure 6. XPS spectra of (A) Zn 2p; (B) S 2p and (C) In 3d of ZIS and V_{Zn}-ZIS.



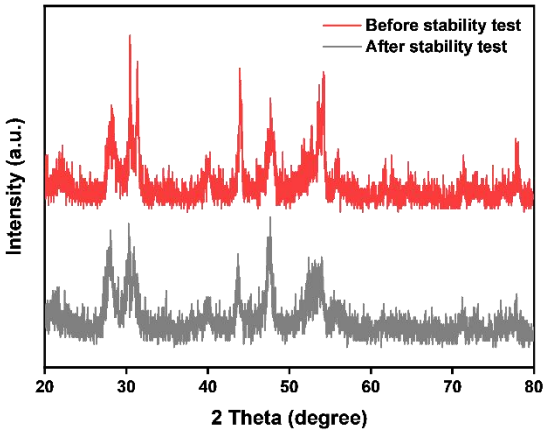
Supplementary Figure 7. PL curves of ZIS and V_{Zn}-ZIS.



Supplementary Figure 8. SPV spectra of ZIS and V_{Zn}-ZIS.



Supplementary Figure 9. (A) SEM image of UCNPs@V_{Zn}-ZIS after stability test; (B) is the enlargement of (A).



Supplementary Figure 10. XRD patterns of UCNPs@V_{Zn}-ZIS before and after stability test.

Supplementary Table 1. XPS fitting data of Zn 2p and In 3d of ZIS and V_{Zn}-ZIS, and the calculated concentration of Zn vacancies

Samples	Elements	Area	Area/RSF*	Zn/In#	V_{Zn} concentrations&
ZIS	Zn 2p	50631.00	9059.04	0.56	0
	In 3d	117387.20	16157.91		
V_{Zn}-ZIS	Zn 2p	50826.54	9094.03	0.47	16%
	In 3d	141193.20	19434.72		

*The RSF (relative sensitivity factor) of Zn 2p and In 3d are 5.589 and 7.265, respectively [1].

#$Zn/In = (Area/RSF)_{Zn}/(Area/RSF)_{In}$

&V_{Zn} concentrations = $(Zn/In_{(ZIS)}-Zn/In_{(VZn-ZIS)})/Zn/In_{(ZIS)}$

The concentration of Zn vacancies in $m_{(UCNPs)}$:$m_{(VZn-ZIS)}$ of 1:6, 1:4, 1:1, 4:1, and 6:1 are about 14%, 13%, 8%, 3%, and 2%, accordingly, when utilizing V_{Zn}-ZIS with the Zn vacancies of 16%.

Reference

1. Zhang, S., Zhang, Z., Si, Y. et al. Gradient Hydrogen Migration Modulated with Self-Adapting S Vacancy in Copper-Doped $ZnIn_2S_4$ Nanosheet for Photocatalytic Hydrogen Evolution. *ACS Nano,* **2021**, 15, 15238-15248. DOI : 10.1021/acsnano.1c05834.