Supporting Information

Near-infrared-driven water splitting for hydrogen evolution from Cu_2ZnSnS_4-based photocathode by the application of upconversion nanoparticles

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Experimental Section

Preparation of CZTS Thin Films. CZTS thin film was prepared using spray pyrolysis followed by sulfurization as our previous report. Precursor solution was prepared by dissolving copper nitrate $Cu(NO_3)_2$ (17 mM), zinc nitrate $Zn(NO_3)_2$ (11.5 mM), $Sn(CH_3SO_3)_2$ (11.5 mM) and $SC(NH_2)_2$ (50 mM) into ultrapure water and adjusted the pH 1.5 by adding a few drops of concd nitric acid. Mo-coated glass substrate (Mo/glass) that was clean by ultrasonic with alcohol. The precursor solution was sprayed onto Mo-coated glass substrate (Mo/glass) at 380℃ in air. The spray process was continued 10 min to obtain the desired thickness. After the spray process, The precursor films were then subjected to sulfurization at 600℃ for 30 min sulfur atmosphere in an evacuated Pyrex ampule to obtain CZTS thin films.

Deposition of CdS Buffer Layer CdS was deposited using a chemical bath method(CBD). CZTS thin film substrates were immersed in an aqueous solution containing 12.5 mM $CdSO_4$, 0.22 M $SC(NH2)_2$, and 11 M NH_4OH at 60℃ for 15 min.

Surface Modification with Pt. Pt particles was deposited on the prepared CdS/CZTS films by photoelectrodeposition in a solution includes 0.1 M Na_2SO_4 and 1 mM H_2PtCl_6 under a constant potential of -0.1 V with AM 1.5G solar light irradiation. CdS is the buffer layer for the formation of a pn junction between CZTS and Pt catalyst, which is efficient for the transfer and separation of photoexcited carriers from CZTS to Pt catalyst. As a buffer layer, CdS is used to solve the problem of band matching and the transport of photo-generated carriers.

Dispersion of UCNPs in Buffer Solution. 5 ml water containing 0.2 g UCNPs and 100 ml phosphate buffer solution are mixed and stirred to evenly disperse the UCNPs (2 g/L). During photoelectrochemical test and hydrogen production experiment, keep stirring to ensure the homogeneity of the solution.

PEC Measurements. All the PEC measurements including chopped and consistent linear sweep voltammetry and EIS were carried out by Solartron Modulab XM photoelectrochemical workstation with AM 1.5G solar simulator. An online gas chromatography system (Shimadazu GC-2014 gas analyzer equipped with a MS-5A column and a thermal conductivity detector) was used to detect H_2 and O_2 during the PEC water splitting. PEC measurements were operated in phosphate buffer solutions (0.2 M Na_2HPO_4/NaH_2PO_4) with different pH values by using a solar Simulator as a light source. Potentials referred to the Ag/AgCl electrode were converted to reversible hydrogen electrode using the Nernst equation:

$E_{RHE}= E_{Ag/AgCl}+ 0.059\times pH+ 0.199.$

Synthesis of $NaYF_4$:Yb20%/Er2%, $NaYF_4$, and $NaYbF_4$:Er60% seeds. The $NaYF_4$:Yb20%/Er2% seeds were synthesized by using a co-precipitation method. A total amount of 1 mmol $Ln(CH_3CO_2)_3$ (Ln=Y, Yb and Er) were added into a 100-mL three-necked flask containing the mixture of 1-octadecene (15 mL) and oleic acid (7.5 mL) under vigorous stirring at room temperature. The mixture was heated at 160 ℃ for 0.5 h, and then cooled down to room temperature. After that a methanol solution (10 mL) of NH_4F (0.148 g) and NaOH (0.1 g) was added into the flask. The temperature was then increased to 80 ℃ in order to remove the methanol from the mixture. Once the methanol was evaporated completely, the temperature was increased to 120 ℃ to remove the water in the mixture. After the water was evaporated completely, the mixture was heated to 300 ℃ for 1 h under a nitrogen environment and then cooled down to room temperature. The as-prepared nanoparticles were collected by centrifugation at 7500 rpm for 5 min, and finally dispersed in 10 mL cyclohexane.

The synthetic procedure for $NaYF_4$ and $NaYbF_4$:Er60% seeds was identical to the synthesis of $NaYF_4$:Yb20%/Er2% seeds except for the use of different lanthanide precursors and ratios.

Synthesis of $NaYF_4$:Yb20%/Er2%@$NaYF_4$, $NaYF_4$@$NaYbF_4$:Tm1%, and $NaYbF_4$:Er60%@$NaYF_4$ core-shell UCNPs. The $NaYF_4$:Yb20%/Er2%@$NaYF_4$ core-shell UCNPs were prepared by using the pre-synthesized $NaYF_4$:Yb20%/Er2% seeds. A total amount of 1 mmol Ln_2O_3 (Ln=Y) were added into a 100-mL three-necked flask. Then deionized water (5 mL) and trifluoroacetic acid (5 mL) were added into the flask and the mixture was heated at 98 ℃ with vigorous stirring. After the residual water and acid were evaporated to dryness, the solid cooled down to room temperature. Then the sodium trifluoroacetate (0.1360 g) was added to the flask with oleic acid (10 mL), 1-octadecene (10 mL) and the $NaYF_4$:Yb20%/Er2% seeds. The temperature was then increased to 80 ℃ in order to remove the cyclohexane from the mixture. Once the cyclohexane was evaporated completely, the temperature was increased to 120 ℃ to remove the water in the mixture. After the water was evaporated completely, the mixture was heated to 300 ℃ for 0.5 h under a nitrogen environment and then cooled down to room temperature. The as-prepared nanoparticles were collected by centrifugation at 7500 rpm for 5 min, and finally dispersed in 10 mL cyclohexane.

The synthetic procedure for $NaYF_4$@$NaYbF_4$:Tm1% and $NaYbF_4$:Er60%@$NaYF_4$ core-shell UCNPs was identical to the synthesis of $NaYF_4$:Yb20%/Er2%@$NaYF_4$ core-shell UCNPs except for the use of different lanthanide shell precursors and ratios.

Synthesis of $NaYF_4$@$NaYbF_4$:Tm1%@$NaYF_4$ core-shell-shell UCNPs. The $NaYF_4$@$NaYbF_4$:Tm1%@$NaYF_4$ core-shell-shell UCNPs were synthesized by using an identical procedure to the synthesis of $NaYF_4$:Yb20%/Er2%@$NaYF_4$ core-shell UCNPs except for the use of pre-synthesized $NaYF_4$@$NaYbF_4$:Tm1% core-shell UCNPs as seeds.

Preparation of Tween 20 coated UCNPs. The oleic acid ligands coated UCNPs were modified by Tween 20 using an adapted procedure from the literature. In this polymer coating process, 80 μL of Tween 20 was added into a 25-mL beaker containing 10 mL deionized water and 1 mL oleic acid coated UCNPs dispersed in cyclohexane under 3 min sonication. The milk-like dispersion was heated at 90 ℃ with vigorous stirring. After the cyclohexane was evaporated, the solution was clear and then cooled down to room temperature. Extract the supernatant into a 50-mL plastic tube, the Tween 20 coated UCNPs were collected by centrifugation at 10000 rpm for 15 min and re-dispersed in 1 mL deionized water.

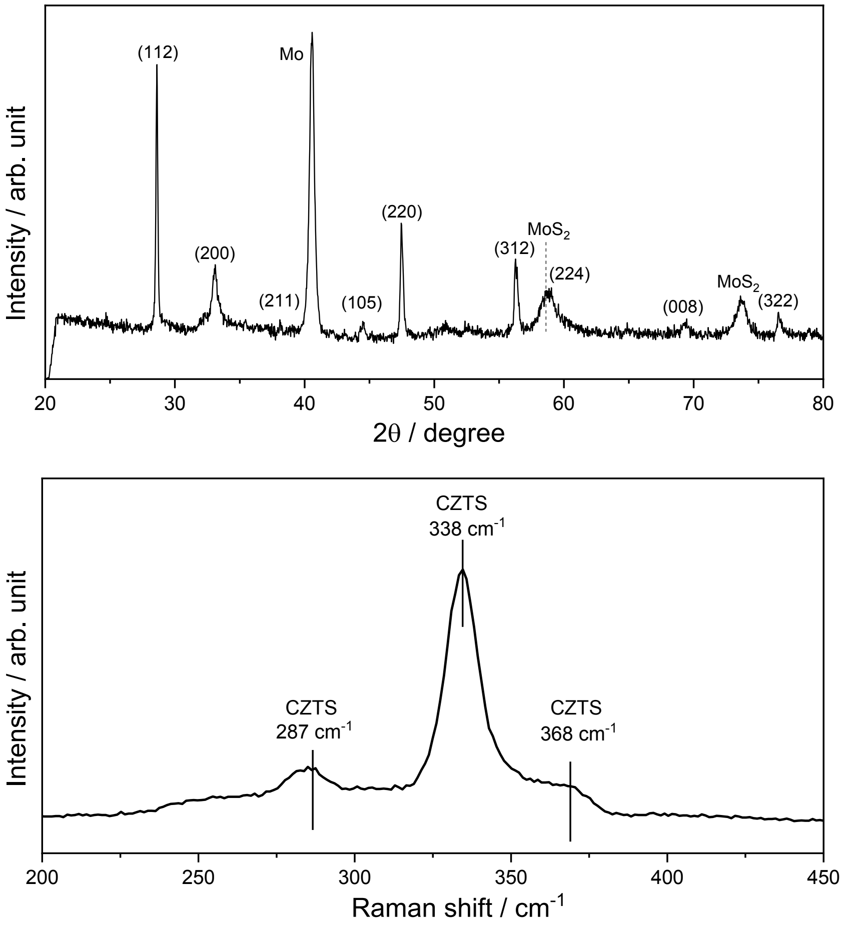

Fig. S1 the XRD and Raman spectrum of the CZTS film

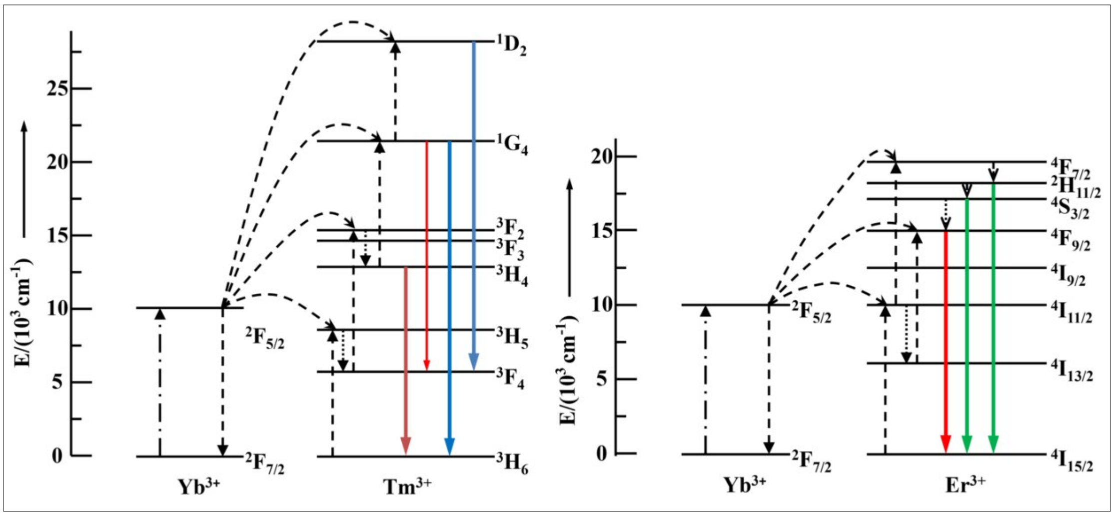

Fig. S2 Schematic illustration of the upconversion mechanism for Yb^{3+}/Tm^{3+} and Yb^{3+}/Er^{3+} codoped UCNPs under 980 nm excitation. Generally, the dopant Yb^{3+} is the sensitizer, which is capable of efficiently absorbing the wavelength of 980 nm and then transfers the energy to Tm^{3+} and Er^{3+}. The dopants Tm^{3+} and Er^{3+} are the emitters. Tm^{3+} can emit blue light at around 450 and 475 nm, while Er^{3+} can emit both green light at 543 nm and red light at 660 nm. Briefly, the red to green ratio (R/G) for Er^{3+} emissions can be tuned by varying the doping concentrations of Yb^{3+} and Er^{3+}.

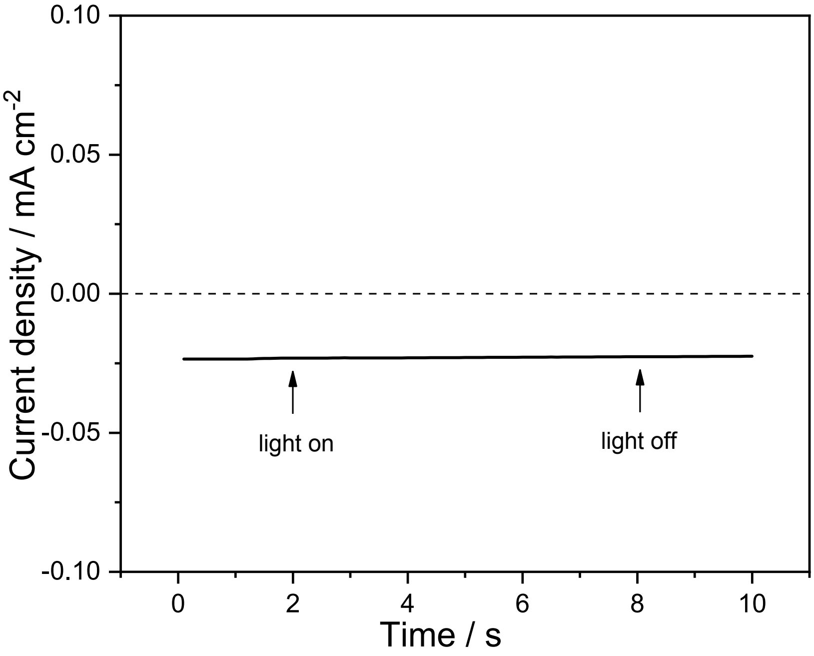

Fig. S3 CZTS/CdS/Pt photoelectrode under the same laser illumination in buffer solution without the involvement of UCNPs.

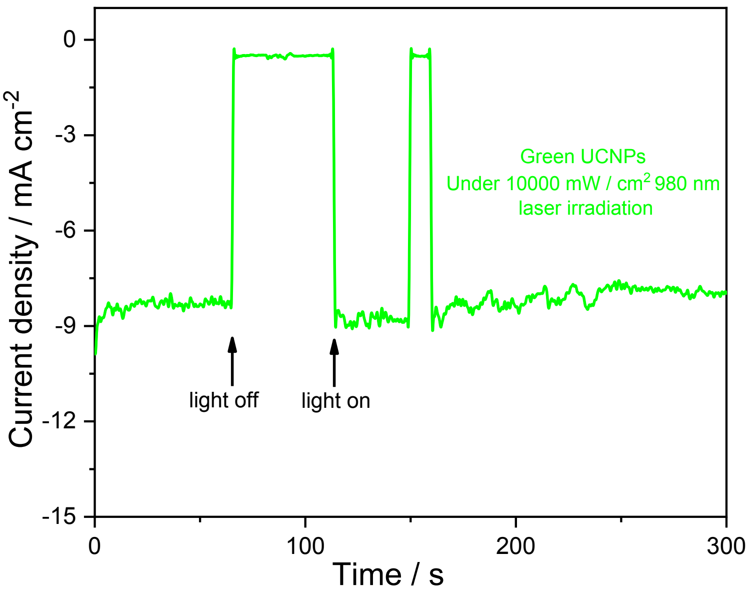

Fig. S4 Current density of the CZTS/CdS/Pt photoelectrode in buffer solution (pH 6.5) containing UCNPs was measured under 10000 mW/cm^2 980 nm laser irradiation.

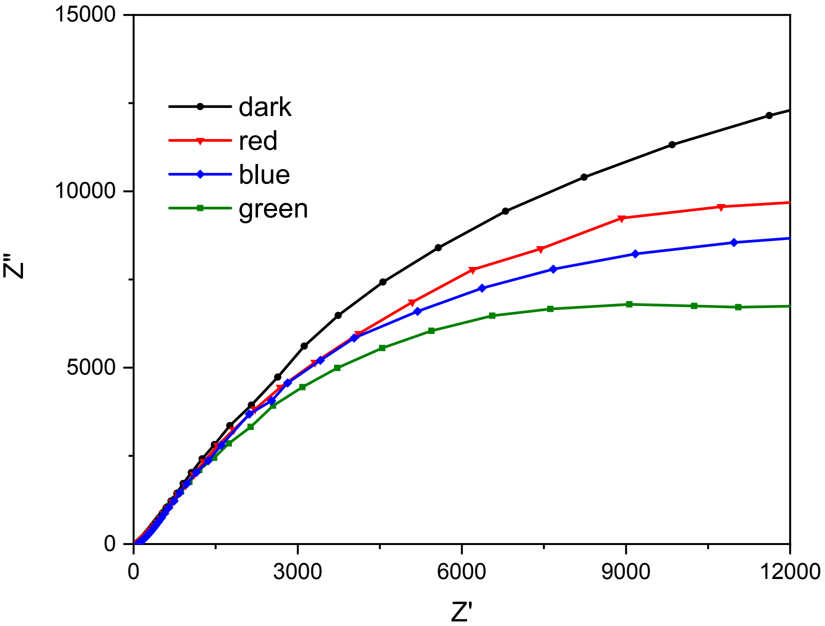

Fig. S5 EIS curve of CZTS/CdS/Pt photocathode in buffer solutions with different up-conversion materials