Electronic Supplementary Materials

Plasmonic-enhanced near-infrared-active material in photoelectrochemical water splitting

Chih Kai Chen,[a] Hao Ming Chen,[a] Chih-Jung Chen and Ru-Shi Liu*[a]
[a] *Department of Chemistry, National Taiwan University, Sec. 4, Roosevelt Road, Taipei 106, Taiwan.*

*Email: rsliu@ntu.edu.tw Fax:**+886-2-33668671; Tel: +886-2-33661169***

* To whom correspondence should be addressed. *Email: rsliu@ntu.edu.tw*

Experimental Section

Chemicals and substrates. Zinc acetate, absolute ethanol, zinc nitrate, yttrium(III) nitrate hexahydrate, ytterbium(III) nitrate pentahydrate, and erbium(III) nitrate were purchased from Sigma-Aldrich. Hexamethylenetetramine (HMT), oleic acid, and cyclohexane were purchased from Acros Organics. MPA and sodium fluoride were purchased from Alfa Aesar. F-SnO_2 substrates (F:SnO_2, Tec 15, 10 Ω) were purchased from Hartford Glass Company. All chemicals were used as received without further purification.

Synthesis of ZnO-seeded Substrates Zinc acetate solution in absolute ethanol (100 mL, 0.01 M) was mixed by ultrasonic agitation. The F-SnO_2 substrates were wetted with zinc acetate solution for 10 s, and then blow-dried using a stream of argon. The procedure was repeated several times. The F-SnO_2 substrates were annealed at 350 °C for 30 min to yield a layer of ZnO seeds.

Synthesis of ZnO Nanorods. The seeded substrates were suspended horizontally in a reagent solution containing 0.06 M zinc nitrate and 0.06 M HMT in a Teflon vessel, sealed in an autoclave, and heated to 110 °C for nanowire growth. The nanowire substrate was removed from the autoclave, washed with distilled water after 24 h of growth, and air-dried. The nanowire substrate was baked at 450 °C for 30 min.

Synthesis of CdTe Quantum Dots. $NaBH_4$ (0.08 g) was reacted with 0.127 g Te powder in 3.0 mL distilled water for 4 h to produce 1 M of sodium hydrogen telluride (NaHTe solution). The 1.5 mL NaHTe solution was then added to a N_2-saturated mixture (74.8 mL; pH 10.8) of 38 mM MPA and 16 mM $CdCl_2$ to give a final Cd^{2+}/MPA/HTe^- molar ratio of 1:2.4:0.5. This mixture was then heated under reflux at 90 °C for 3 h. The color of the solution changed from dark red to orange-yellow. The CdTe QDs were purified by centrifugation in absolute ethanol, which allowed the removal of free ligands, such as MPA, and unreacted precursor ions from the CdTe QDs.

Synthesis of UCNs. $Y(NO_3)_3$ 0.09 mL (0.5 M), 0.09 mL of 0.2 M $Yb(NO_3)_3$, 0.0225 mL of 0.2 M $Er(NO_3)_3$, 4 mL of 1 M NaF, 0.6 g NaOH, 2.5 mL H_2O, 3.5 mL absolute ethanol, and 10 mL oleic acid were mixed in a 20 mL Teflon vessel and sealed in an autoclave, and heated to 190 C for 8 h. The suspension was washed with ethanol several times and re-dissolved in cyclohexane to obtain UCNs. The oleic acids on the surface of UCNs were removed by adding 0.1 M HCl solution into the prepared UCNs and stirring for 3 h, then washing by the acidic ethanol. The ligand free UCNs were added to water with 0.1 M MPA solution. The prepared Au NPs were mixed together with the UCNs at the desired weight percent. Finally, the Au-UCNs were coated with a thin layer of ZnS (Fig. S5).[9]

Photoelectrode Preparation. The prepared ZnO substrates were immersed into CdTe QD suspension for 24 h. The prepared ZnO substrates were immersed into UCNs suspension for 8 h to prepare the UCN-ZnO substrate. The ZnO-CdTe substrates were immersed into the Au, UCN and Au-UCN suspension for 8 h to prepare the Au-CdTe-ZnO (Fig. S8), Au-UCNs-ZnO (Fig. S9) and Au-UCNs-CdTe-ZnO photoelectrode. The as-prepared ZnO nanorod array substrates were placed with their nanowire side up in an Au-UCNs suspesion for the desired duration. Following deposition in a chemical bath, the substrates were removed from the suspension and washed with distilled water to remove any excess Au-UCNs suspension. This Au-UCNs-CdTe-ZnO substrate was connected to a copper wire using silver paste and dried overnight. The substrate and wire were subsequently covered with insulating epoxy, exposing only the desired surface area.

Photoelectrochemical Characterization. The electrochemical characterization was carried out using three electrode-based methods. An Au-UCNs-CdTe-ZnO photoelectrode was used as the working electrode. An Ag/AgCl electrode was the reference electrode, in which the platinum plate was the counter electrode. All PECs were examined in 0.5 M Na_2SO_4 (pH = 6.8) solution, which served as the supporting electrolyte, and the photoelectrode was illuminated with a 980 nm laser at 50 mW/cm^2. Illuminating the water splitting photoelectrode with light source was low noise 980 nm Infrared DPSS Laser 1-2000 mW from the Changchun New Industries. The I–V characteristics of the PEC were recorded using a potentiostat (Eco Chemie AUTOLAB, the Netherlands) and general Purpose Electrochemical System software at 25 °C. The hydrogen and oxygen generation contucted by two electrode system with 0.5 V bias upon a 980 nm laser at 100 mW/cm^2. The chronoamperometry measurement contucted by three electrode system with 0.5 V bias upon a 980 nm laser at 100 mW/cm^2. The Au-UCNs-CdTe-ZnO photoelectrode was used as the working electrode and the Pt foil were used as counter electrode. The amount of H_2 and O_2 was accumulated in the glass system and measured through using China Chromatography 2000 gas chromatograph that was equipped with a flame ionization detector (FID).

UV-vis spectrum measurement. The UV-Vis absorption spectra of the colloidal suspension of CdTe quantum dots, gold nanoparticles, gold modified upconversion nanoparticles, Au-x-UCNs (x = 0.2, 0.4, 1.0 and 2.0 wt.%) were obtained at room temperature using a SHIMADZU UV-700 spectrophotometer with a 1 cm wide quartz cell at room temperature. The concentration of the Au-x-UCNs (x = 0.2, 0.4, 1.0 and 2.0 wt.%) colloidal suspension were controlled in 10 mg/mL of UCNs in the suspensions.

Upconversion emission spectrum measurement. The upconversion emission spectrum measurement of the colloidal suspension of upconversion nanoparticles in cyclohexane and gold modified upconversion nanoparticles in water, Au-x-UCNs (x = 0.2, 0.4, 1.0 and 2.0 wt.%) were obtained at room temperature using a HORIBA iHR-320 spectrophotometer with a 1 cm wide quartz cell at room temperature. Illuminating the water splitting photoelectrode with light source was low noise 980nm Infrared DPSS Laser 1-2000 mW from the Changchun New Industries. The light intensities were obtained at room temperature using a Gentec-Eo photo intensity meter.

Upconversion emission quantum yield measurement. The upvonversion emission quantum yield of the UCNs in cyclohexane and Au-x-UCNs (x = 0, 0.2, 0.4, 1.0 and 2.0 wt.%) were determined according to equation 1,[1-2] with rhodamine 6G (fluorescence quantum yield = 96%) in ethanol as a standard reference.

$$\Phi_{UCN} = 2\Phi_{std}\left(\frac{A_{std}}{A_{UCN}}\right)\left(\frac{I_{UCN}}{I_{std}}\right)\left(\frac{\eta_{UCN}}{\eta_{std}}\right)^2 \qquad (1)$$

The Φ_{UCN} and Φ_{std} stand for upconversion emission quantum yield of UCNs samples and fluorescence quantum yield of rhodamine 6G, respectively. A and A_{std} stand for absorbances of the UCNs samples and the rhodamine 6G, respectively. I_{UCN} and I_{std} stand for integrated upconversion emission intensity of the UCNs samples and fluorescence intensity of rhodamine 6G, respectively. η_{UCN} and η_{std} stand for the refractive index of solvent (using in the samples) and ethanol (for rhodamine 6G), respectively.

1. Q. Liu, T. Yang, W. Feng and F. Li, *J Am Chem Soc*, 2012, **134**, 5390.
2. W. Q. Zou, C. Visser, J. A. Maduro, M. S. Pshenichnikov and J. C. Hummelen, *Nat Photonics*, 2012, **6**, 560.

Characterization of Materials. TEM and HRTEM images, electron diffraction patterns, and elemental maps were obtained under a JEOL JEM-2100F electron microscopy. The morphology of the nanowires was determined with a JEOL JSM-6700F field-emission scanning electron microscope.

The band position measurement. The flat band potential were determined from the relationship between monochromatic photocurrent density j^2 and applied voltage E using the relation derived for small band bending :[1-2]

$$E - E_F = Bj^2$$

Straight lines were applied for each sample to obtain the position of flat band potentials. It is generally known that E_{CB} (conduction band) of many n-type semiconductors is 0.1~0.3 eV more negative than E_F (flat band).[3] On the basis of this, the difference is assumed to be -0.3 eV for the determination of the band positions for each samples by electrochemical measurements. Figure S7 illustrates the comparison of band positions determined by electrochemical measurements, which indicates that the conduction bands (CB) of the CdTe are higher than that of ZnO. The hydrogen and oxygen redox potential were also illustrated in the Figure S7. According to the Nernst equation (E_{RHE} = E-Ag/AgCl +0.059pH + 0.196), the measured potentials vs the RHE scale can be obtained from the potentials vs Ag/AgCl. This indicates that the CB of the CdTe quantum dots is more negative potential than the ZnO, allowing the excited electrons transfer to the CB of the ZnO. This result also provides the evidence that oxygen evolution from water oxidation can be done by the valence band holes photoproduced in CdTe.

1. J. Akikusa, S. U. M. Khan, *Int. J. Hydro. Eng.* 1997, **22**, 875.

2. K.-W. Cheng, C.-M. Huang, G.-T. Pan, W.-S. Chang, T.-C. Lee, T. C. K. Yang, *J. Photochem. Photobiol. A.* 2007, **190**, 77.

3. Y. Matsumoto, *J. Solid State Chem.* 1996, **126**, 227.

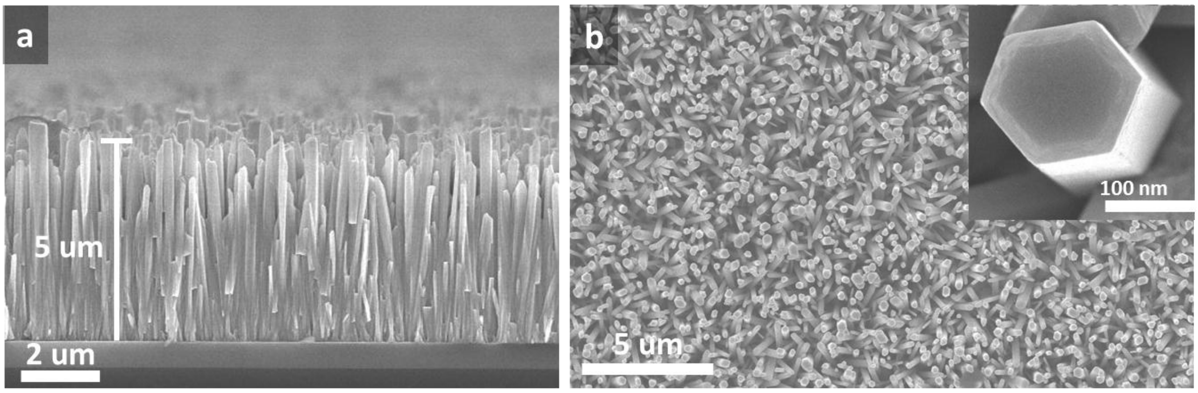

Figure S1. Scanning electron microscopy images of the ZnO nanorods array. a) Cross-section view b) top view of the ZnO nanorods array. (Inset: ZnO nanorods top view)

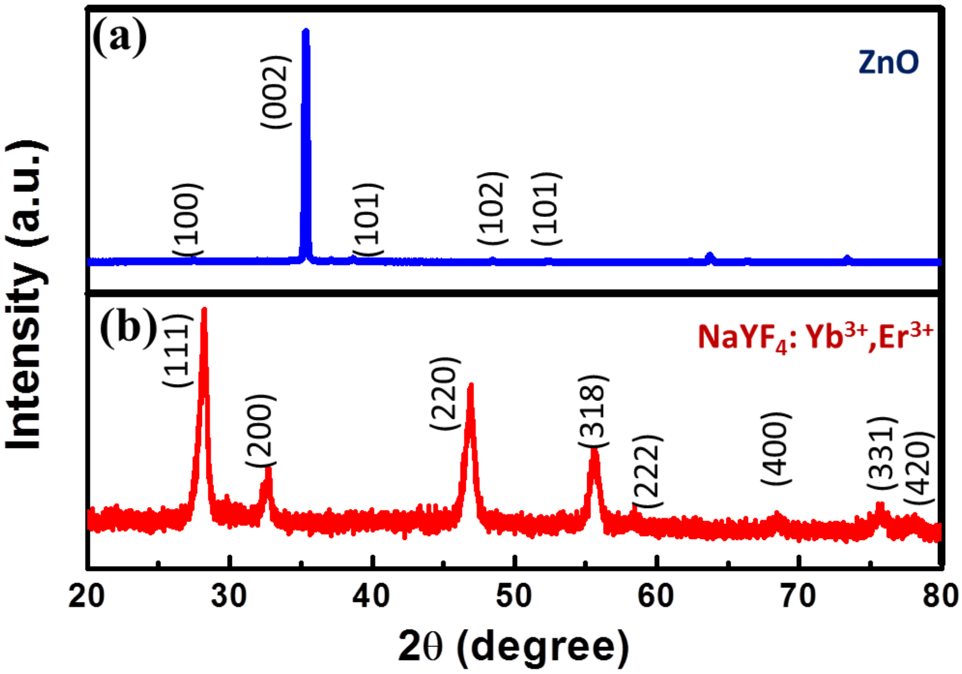

Figure S2. X-ray diffraction (XRD) patterns of a) ZnO nanorod and b) Er^{3+}/Yb^{3+} co-doped $NaYF_4$.

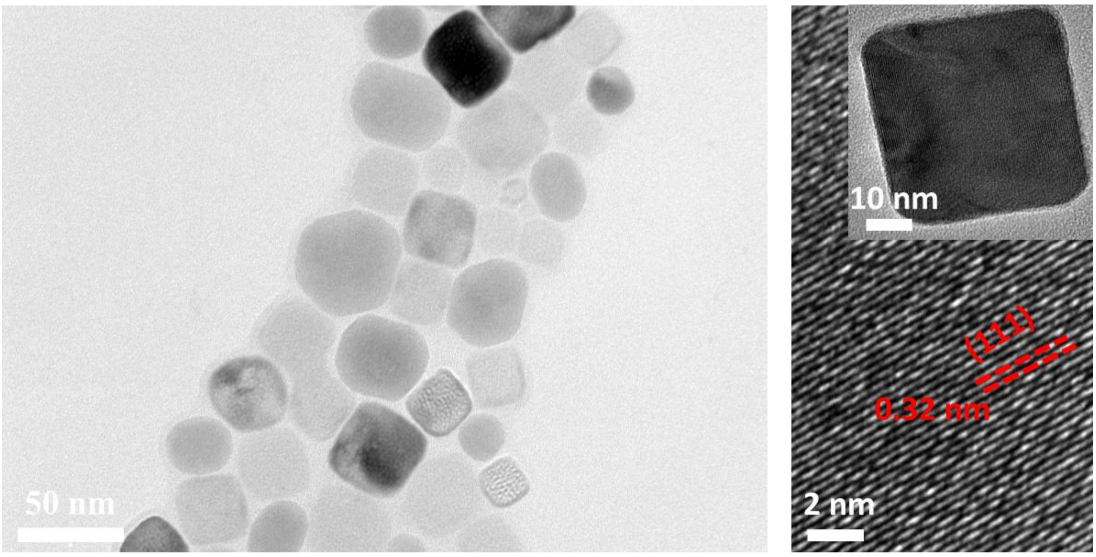

Figure S3. TEM (left) and HRTEM (right) images of the as-synthesized Er^{3+}/Yb^{3+} co-doped $NaYF_4$ nanoparticles.

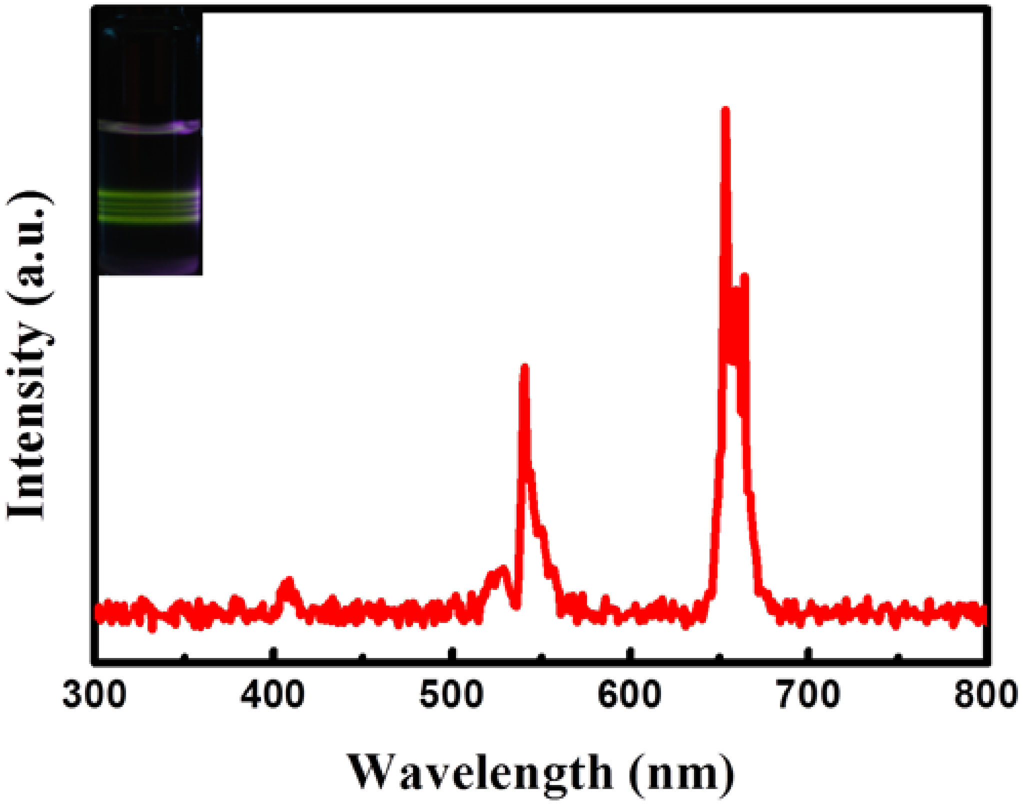

Figure S4. Upconversion emission spectrum of the Er^{3+}/Yb^{3+} co-doped $NaYF_4$ suspending in the cyclohexane.

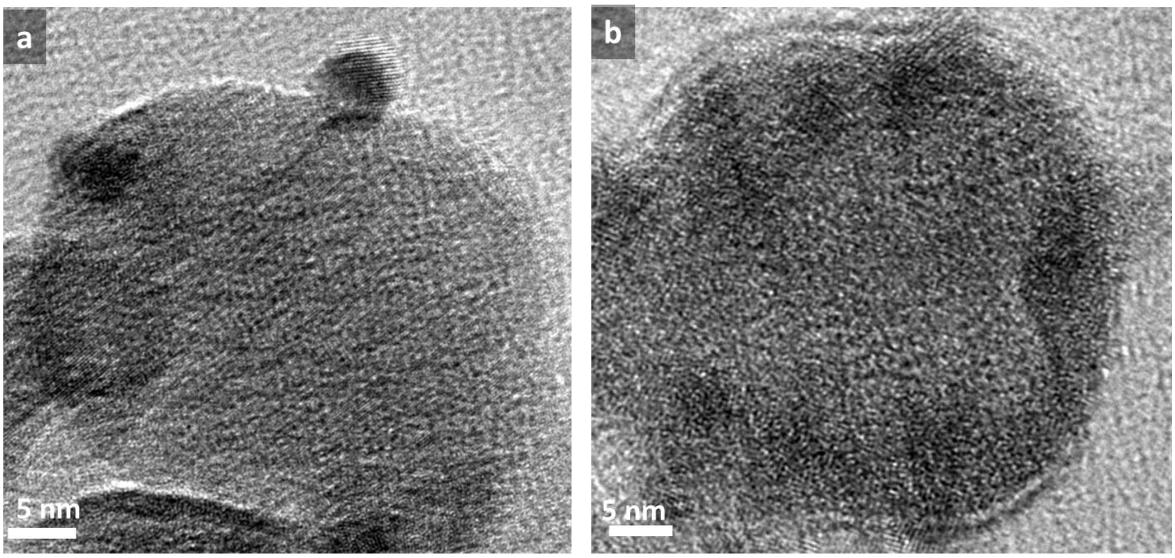

Figure S5. (a) TEM image of the Au 1.0% wt.-UCNs nanoparticles. (b) TEM image of the Au 1.0% wt.-UCNs nanoparticles after coated with ZnS.

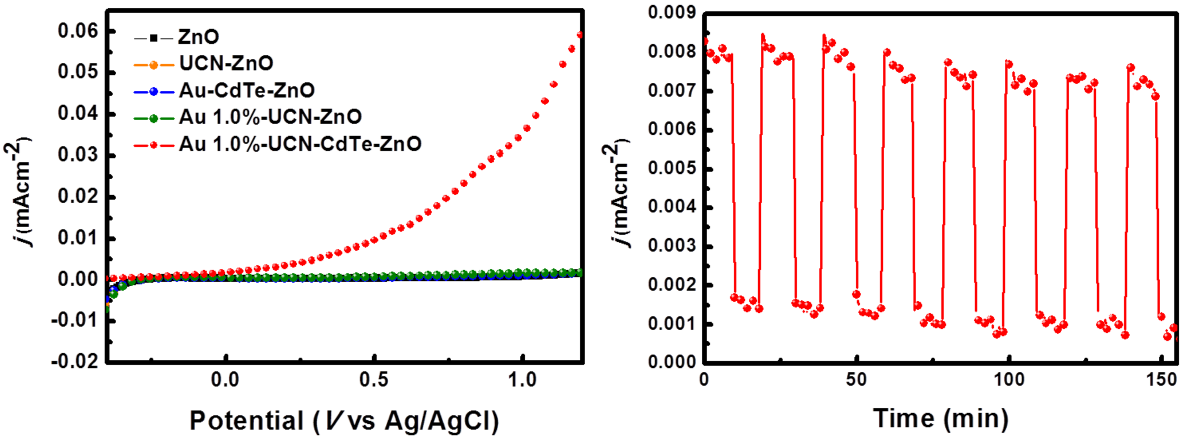

Figure S6. (a) Linear-sweep voltammograms of the Au-CdTe-ZnO, Au 1.0% wt.-UCN-ZnO and UCN-ZnO photoelectrode. (b) The chronoamperometry measurement of the Au 1.0% wt.-UCNs-CdTe-ZnO.

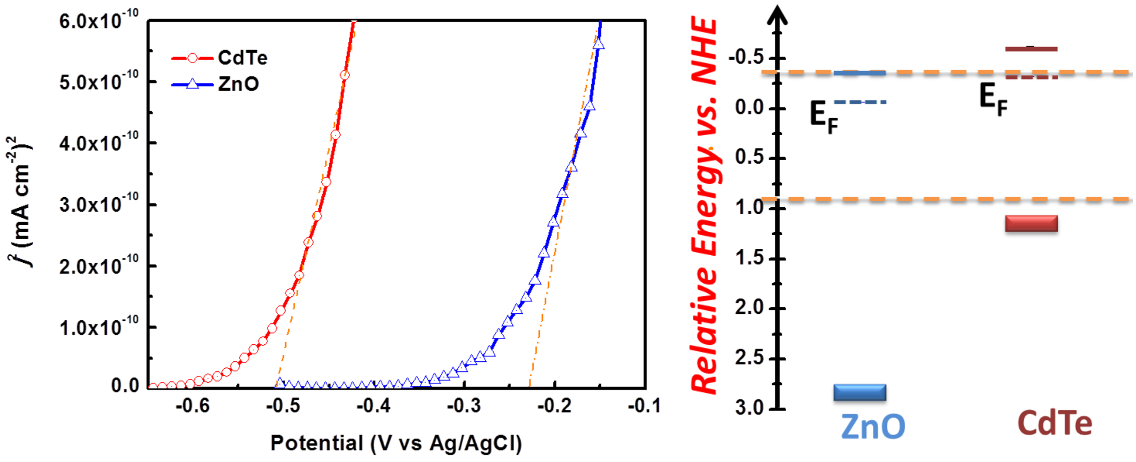

Figure S7. (Left) A polt of j^2 measured at incident light wavelength kept at 395 nm versus applied voltage for ZnO rods and CdTe. (Right) Band position of ZnO rods and CdTe. (electrolyte : 0.5 M Na_2SO_4, pH = 6.8)

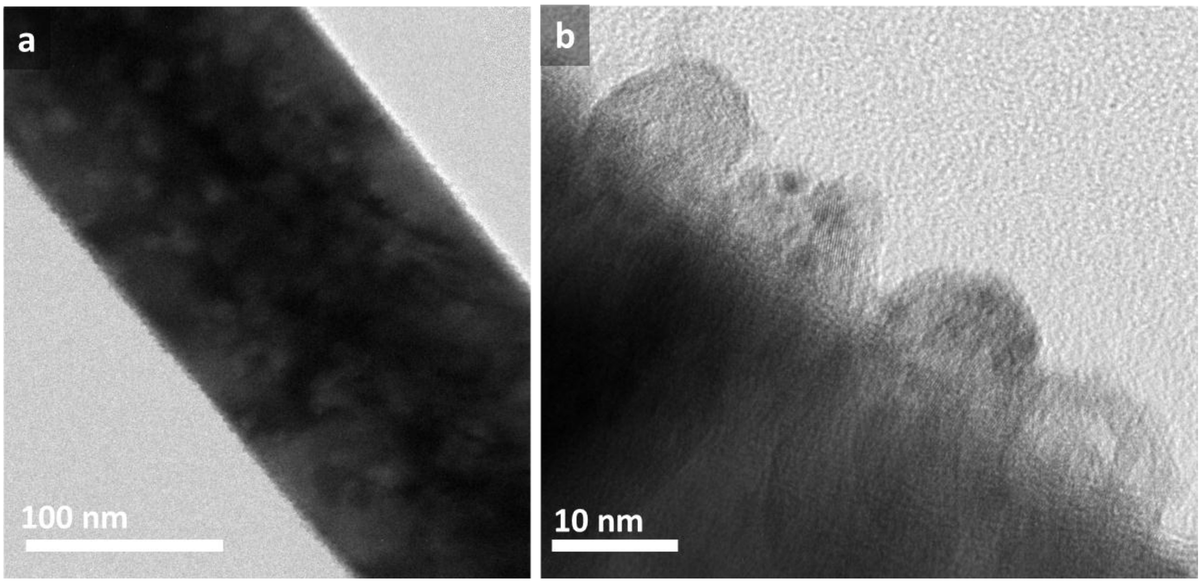

Figure S8. (a) TEM image of the Au-CdTe-ZnO. (b) HRTEM image of the Au-CdTe-ZnO.

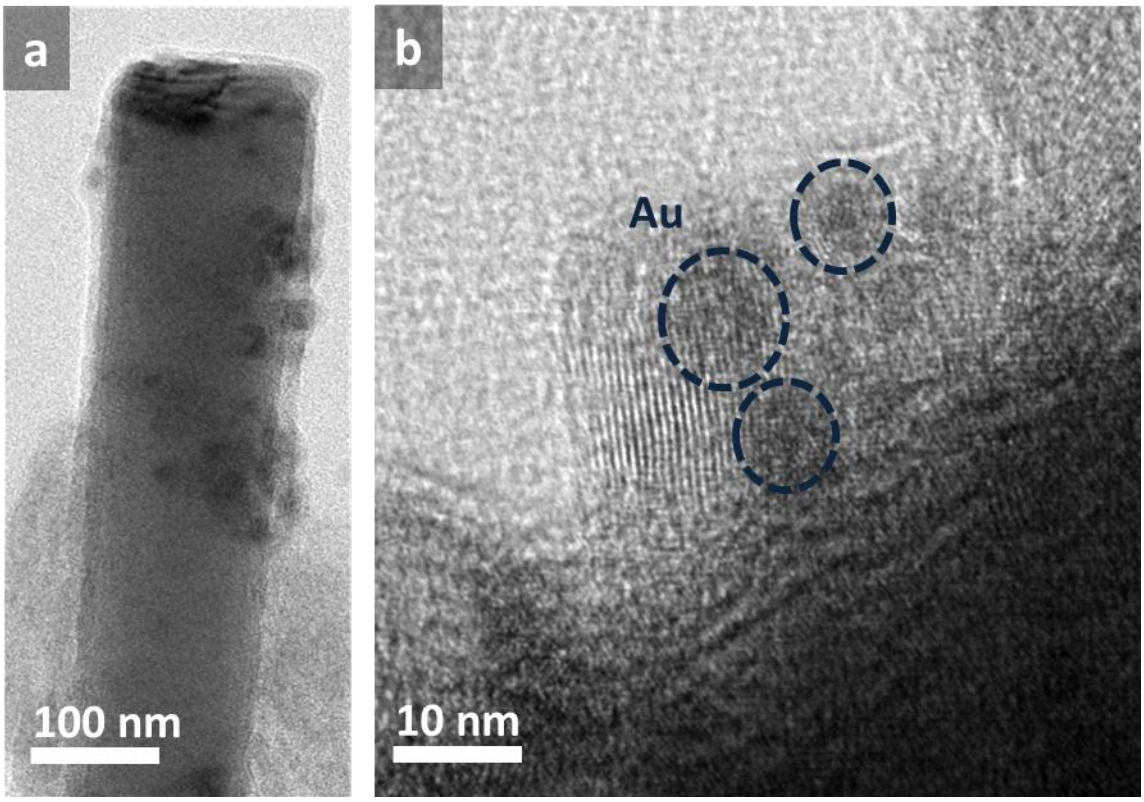

Figure S9. (a) TEM image of the Au-1.0%-UCNs-ZnO. (b) HRTEM image of the Au-1.0%-UCNs-ZnO.

Table S1. Upconversion emission quantum yields of the Er^{3+}/Yb^{3+} co-doped $NaYF_4$ suspending in the cyclohexane and water soluble colloid suspension of the Au-x-UCNs (x = 0, 0.2, 0.4, 1.0 and 2.0 wt.%).

Samples	**quantum yield, %**
UCNs (cyclohexane)	0.43±0.02
UCNs (water)	0.15±0.01
Au 0.2 wt%-UCNs (water)	0.14±0.01
Au 0.4 wt%-UCNs (water)	0.22±0.04
Au 1.0 wt%-UCNs (water)	0.40±0.04
Au 2.0 wt%-UCNs (water)	0.00