Supporting information

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Experimental Section：

Fabrication of ZnO seed layer and ZnO NRs on FTO substrate: First, clean the FTO substrate. Wipe the surface of the FTO substrate with cotton, and then ultrasonically wash using detergent, deionized water, acetone, isopropanol and absolute ethanol for 10 minutes to remove residual impurities and grease, finally dry at 80 ºC in a drying oven. The sol-gel method is used to prepare ZnO seed layer. The specific implementation steps are as follows: take 0.0125 mol of zinc acetate dihydrate ($C_4H_{10}O_6Zn$) to dissolve in 25 ml of ethylene glycol methyl ether, and add 0.75 ml of ethanolamine as a stabilizer, sustained stir for 3 h at 60 ºC. A stable, transparent and clear ZnO sol solution is obtained. ZnO seed layer on the FTO substrate is prepared by the spin-coating method at 3000 rpm for 20 s and annealed at 400 ºC for 15 min. After repeated the process, ZnO seed layer is annealed at 400 ºC for 30 min. The chemical bath deposition (CBD) method is used to grow ZnO NRs on ZnO seed film. The specific steps are as follows: separately prepare 0.1 M hexamethylenetetramine ($C_6H_{12}N_4$) and 0.15 M hexahydrate nitric acid ($Zn(NO_3)_2•6H_2O$) aqueous solutions and mix them at 80 ºC, and then immerse the ZnO seed layer film vertically in the solution and grow for 3 h. The sample are taken out and washed repeatedly with deionized water, finally dried at 80 ºC.

Preparation of Cu_2O film: Dissolve 20 g of $CuSO_4·5H_2O$ in a certain amount of deionized water, magnetically stir for 30 min, add 44.82 ml of lactic acid, and then add an appropriate amount of deionized water to 200 ml. Continue magnetic stirring for 30 min, and adjust the pH to 10.5 with 5 M NaOH solution. A three-electrode electrochemical system is adopted with ZnO NRs as the working electrode, platinum-titanium mesh as the counter electrode and Ag/AgCl as the reference electrode. Cu_2O thin film is electrochemically pulse-deposited using the cathode reduction method. The deposition current sets 9 mA with the deposition time interval of 60 s and deposition temperature of 60 ºC for 6 times. Then, 0.005 mol, 0.01 mol and 0.02 mol Na_2EDTA were added into the electrolyte solution respectively and the pH value of the electrolyte keeps unchanged.

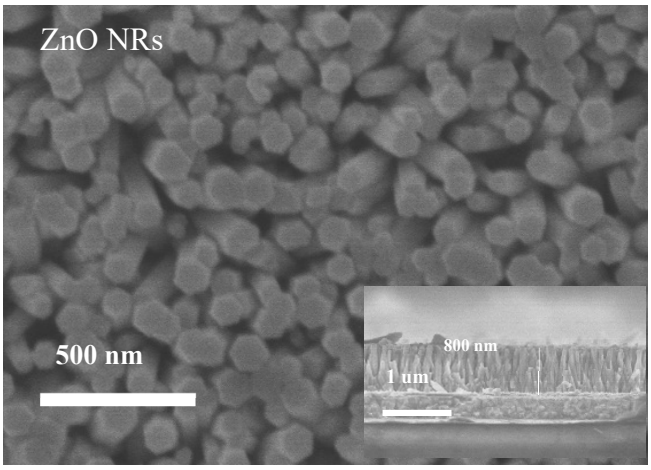

Fig.S1 The top-view and cross-sectional view of ZnO NRs

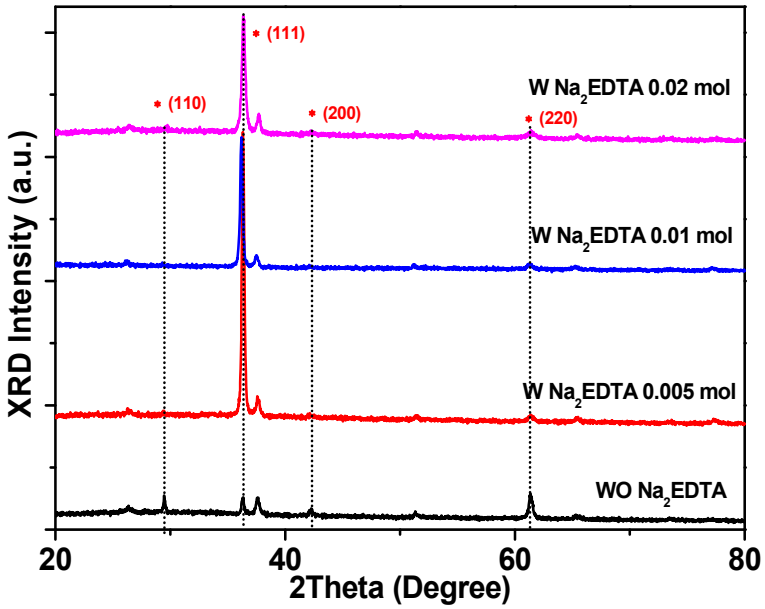

Fig.S2 XRD patterns of Cu_2O films prepared on FTO substrates with different Na_2EDTA contents

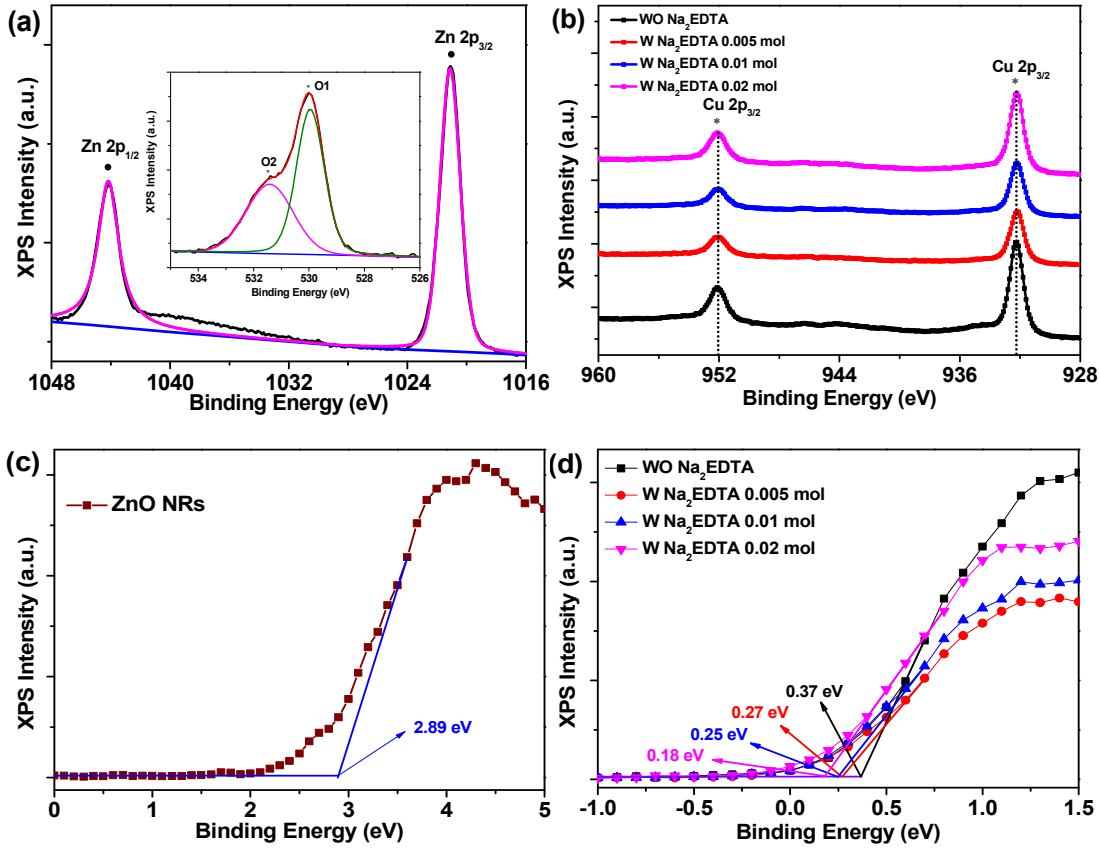

Fig.S3 (a) XPS spectra of Zn 2p and (b) Cu 2p for ZnO/Cu_2O heterostructures prepared under different Na_2EDTA additions. The inset is O1s XPS spectra for ZnO NRs. (c) Valence band spectra of ZnO NRs and (d) ZnO/Cu_2O heterostructures prepared under different Na_2EDTA additions.

Table 1 Cu/O ratio of Cu_2O thin films prepared with different Na_2EDTA contents

Samples (Na_2EDTA content)	Cu/O ratio
0	0.82
0.005 mol	1.70
0.01 mol	0.87
0.02 mol	1.32

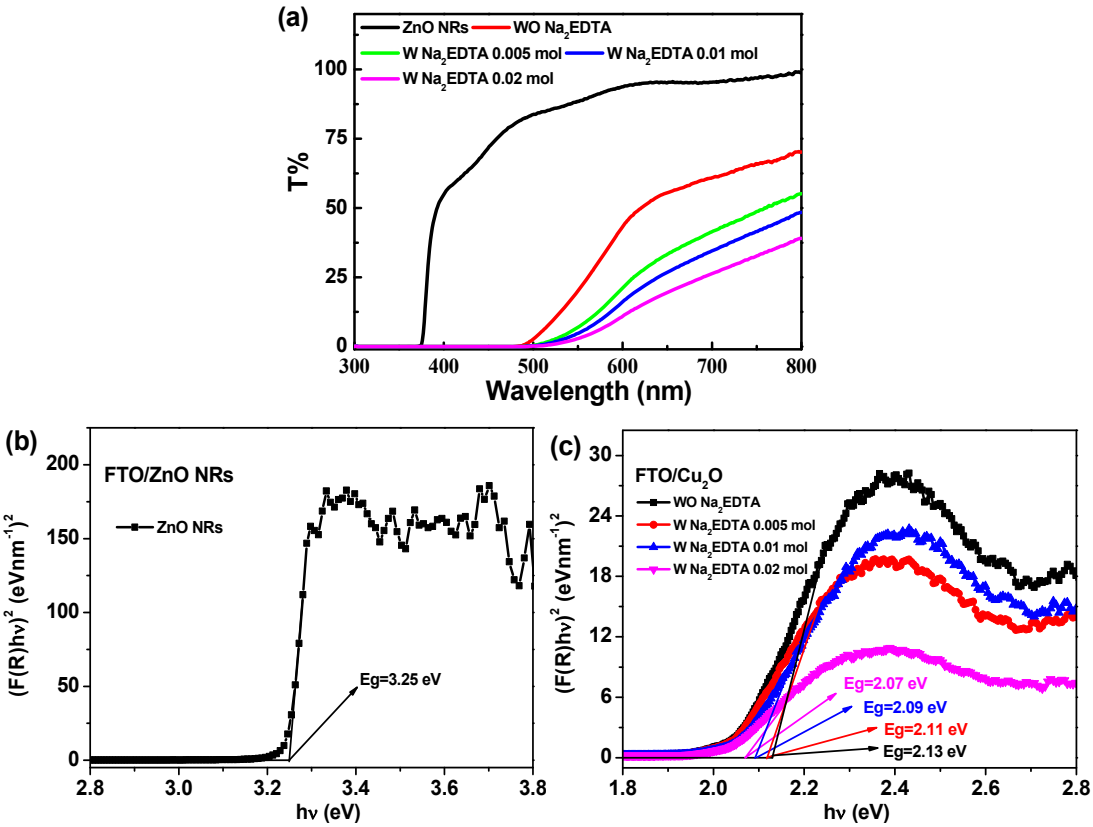

Fig.S4 (a) Transmission spectra of ZnO NRs and ZnO/Cu_2O heterojunction with different Na_2EDTA additions. Optical band-gaps of (b) ZnO NRs and (c) Cu_2O thin films deposited with different Na_2EDTA additions calculated by diffuse reflectance spectroscopy

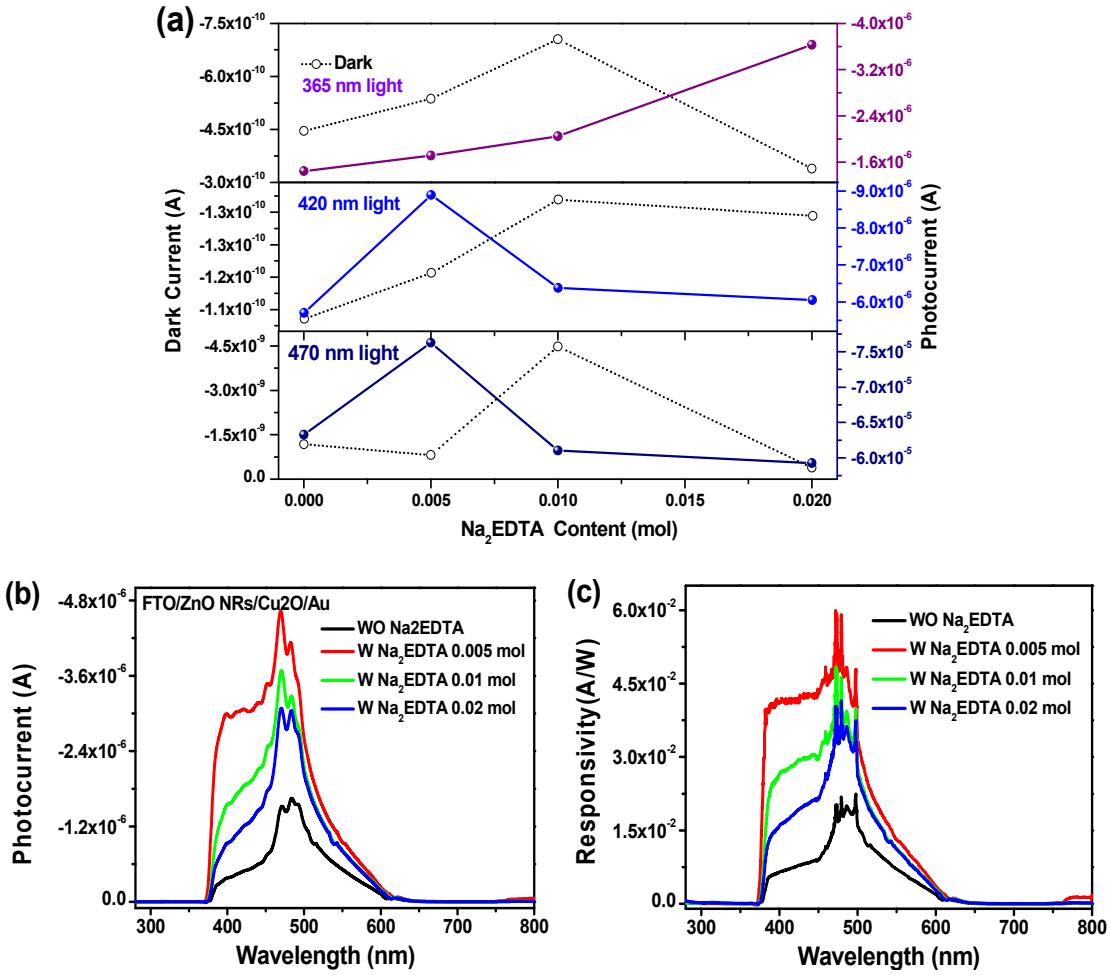

Fig.S5 (a) Photocurrent and dark state current curves of ZnO NRs/Cu_2O heterostructure devices with different Na_2EDTA contents under UV and visible light irradiation. (b) Photocurrent and (c) responsivity under different light wavelengths for the devices with different Na_2EDTA content

Table 2 The information of energy level of ZnO NRs and Cu_2O films with different Na_2EDTA additions.

Samples (Na_2EDTA content)	E_C (eV)	E_V (eV)	E_g (eV)	E_F (eV)	$\triangle E_C$ (eV)	$\triangle E_V$ (eV)
0	-3.43	-5.56	2.13	-5.19	1.01	2.13
0.005 mol	-3.39	-5.50	2.11	-5.23	1.05	2.19
0.01 mol	-3.38	-5.47	2.09	-5.22	1.06	2.22
0.02 mol	-3.32	-5.39	2.07	-5.21	1.12	2.3
ZnO NRs	-4.44	-7.69	3.25	-4.80	-	-

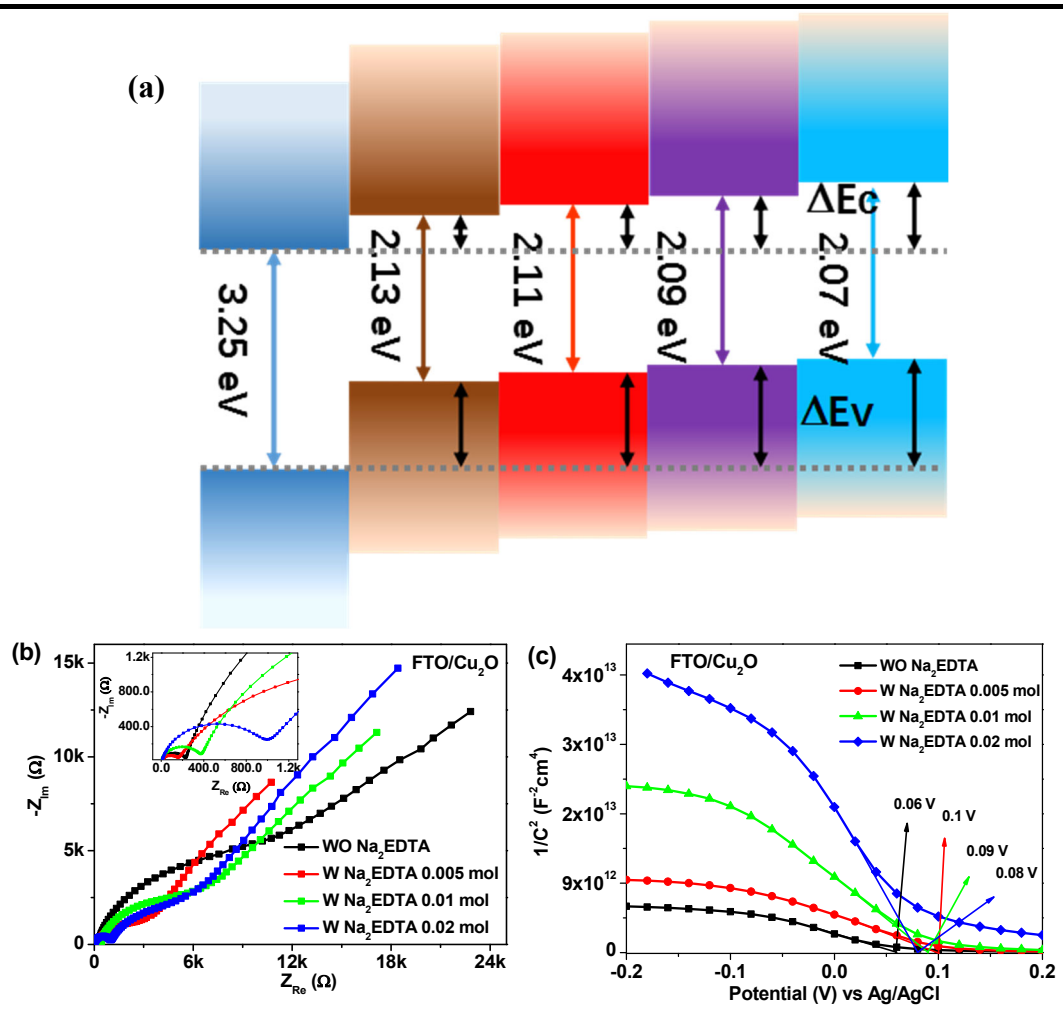

Fig.S6 (a) Schematic diagram of type-II band alignment of ZnO/Cu_2O heterojunction films. (b) EIS spectra and (c) M-S curves of Cu_2O thin films with different Na_2EDTA additions

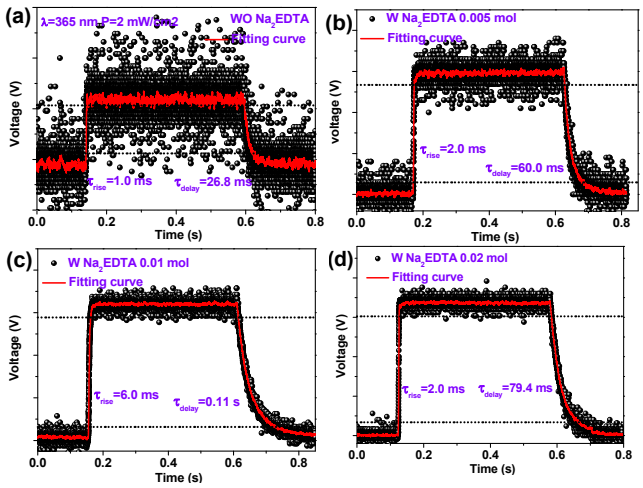

Fig.S7 Photoresponse speed of ZnO NRs/Cu_2O heterojunction devices with different Na_2EDTA additions under 365 nm illumination.

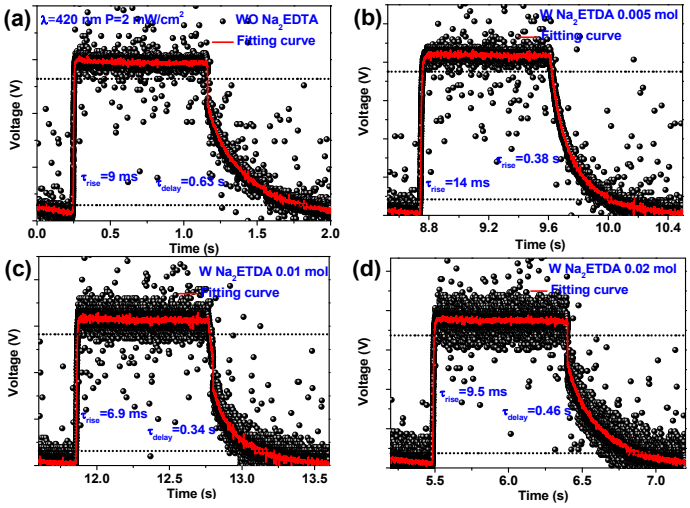

Fig.S8 Photoresponse speed of ZnO NRs/Cu_2O heterojunction devices with different Na_2EDTA additions under 420 nm illumination.

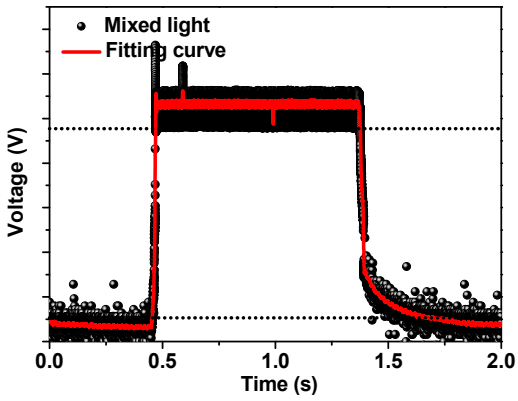

Fig.S9 Photoresponse speed of ZnO NRs/Cu_2O heterojunction device with 0.005 mol Na_2EDTA addition under UV and visible mixed light illumination.

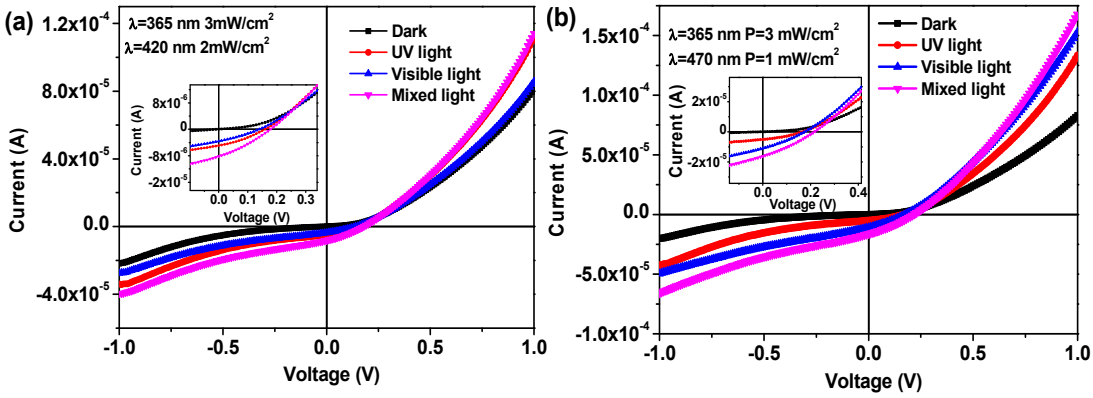

Fig.S9 I-V curve of ZnO NRs/Cu_2O PD under UV and visible monochromatic light and the mixed light illumination.