

Supporting Information

Photoelectrochemical Study of Carbon-Modified *p*-type Cu₂O Nanoneedles and *n*-type TiO_{2-x} Nanorods for Z-scheme Solar Water Splitting in Tandem Cell Configuration

Nelly Kaneza, Pravin S. Shinde, Yanxiao Ma, Shanlin Pan*

Department of Chemistry and Biochemistry, The University of Alabama, Tuscaloosa, Alabama 35487

*Corresponding Author: span1@ua.edu, 1-205-348-6381

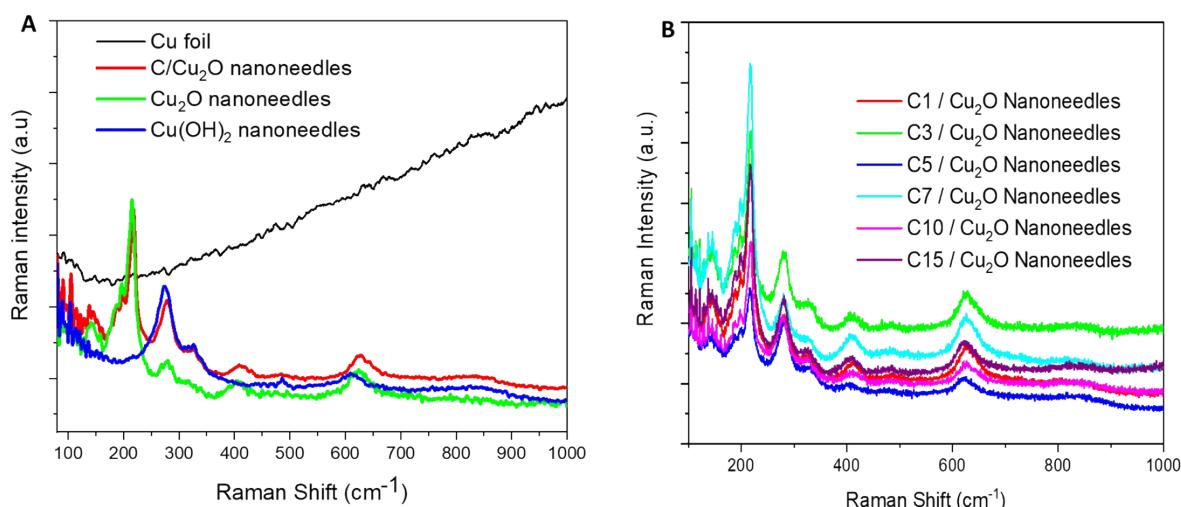


Fig. S1: (A) Raman spectra of Cu foil, Cu(OH)₂ NNs, Cu₂O NNs and C/Cu₂O NNs. (B) Raman spectra of different carbon-modified (1-15 mg mL⁻¹)/Cu₂O NNs. Laser excitation wavelength=532 nm.

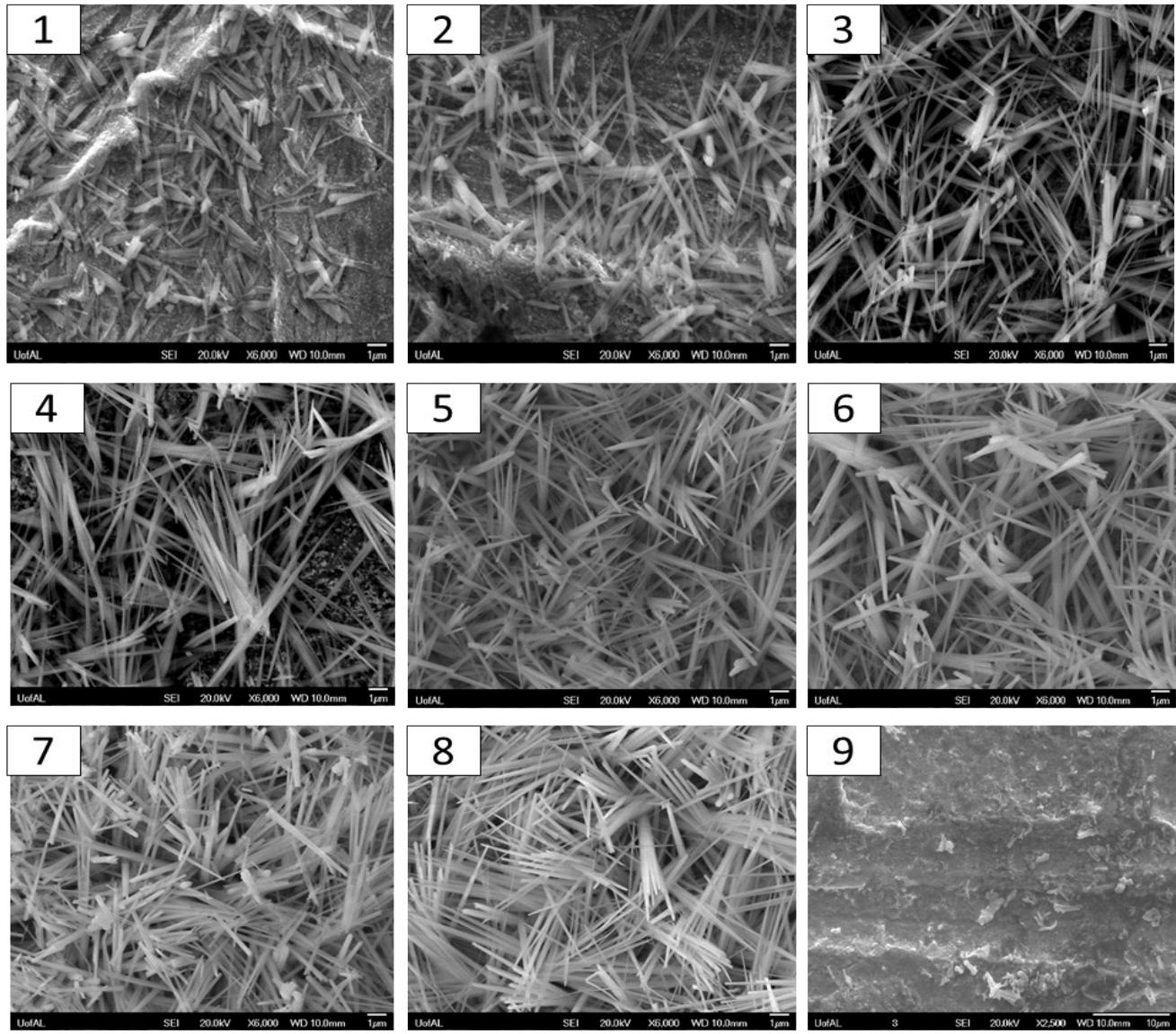


Fig. S2: SEM images of $\text{Cu}(\text{OH})_2$ NNs synthesized at 2.0 V and 10 mA for different anodization durations (1-9 min) in 2 M KOH.

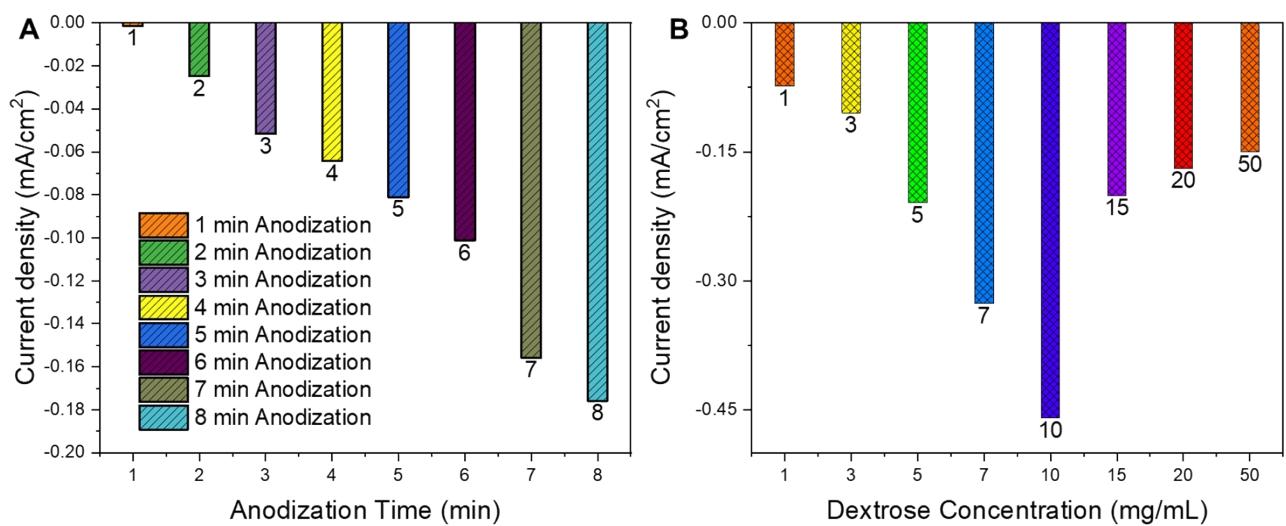


Fig. S3: (A) Photocurrent responses of C/Cu₂O NNs obtained from Cu(OH)₂ NNs anodized at different durations (1-8 min) and (B) Effect of dextrose concentration (1- 50 mg mL⁻¹) on formation of C_d/Cu₂O NNs from Cu(OH)₂ NNs anodized at 8 min. All current densities were recorded at -0.50 V vs. Ag/AgCl.

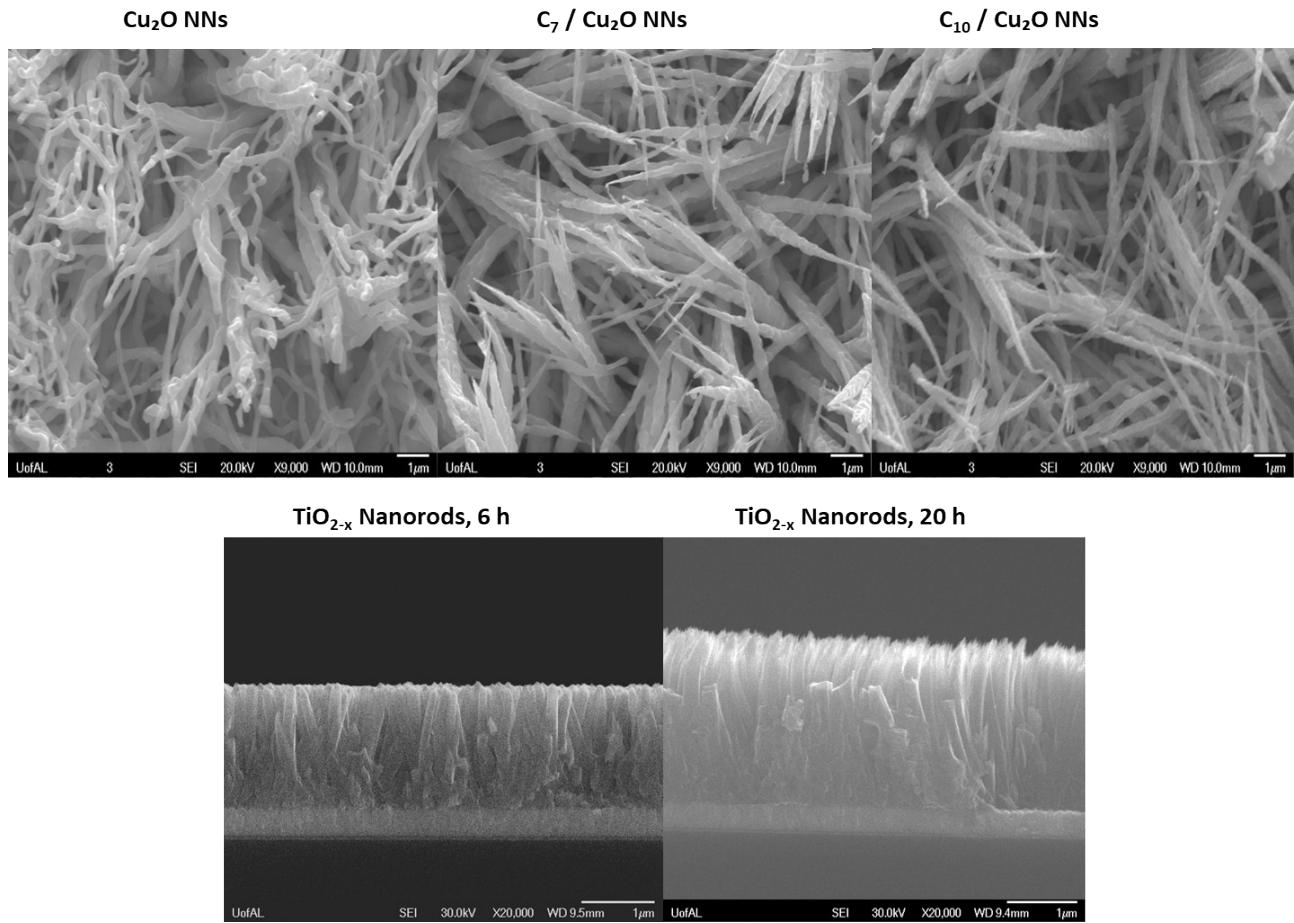


Fig. S4: SEM images of Cu₂O, C₇/Cu₂O, and C₁₀/Cu₂O NNs obtained from Cu(OH)₂ NNs anodized for 8 min; and cross-sectional SEM images of oxygen deficient TiO_{2-x} NRs hydrothermally grown for 6 and 20 h.

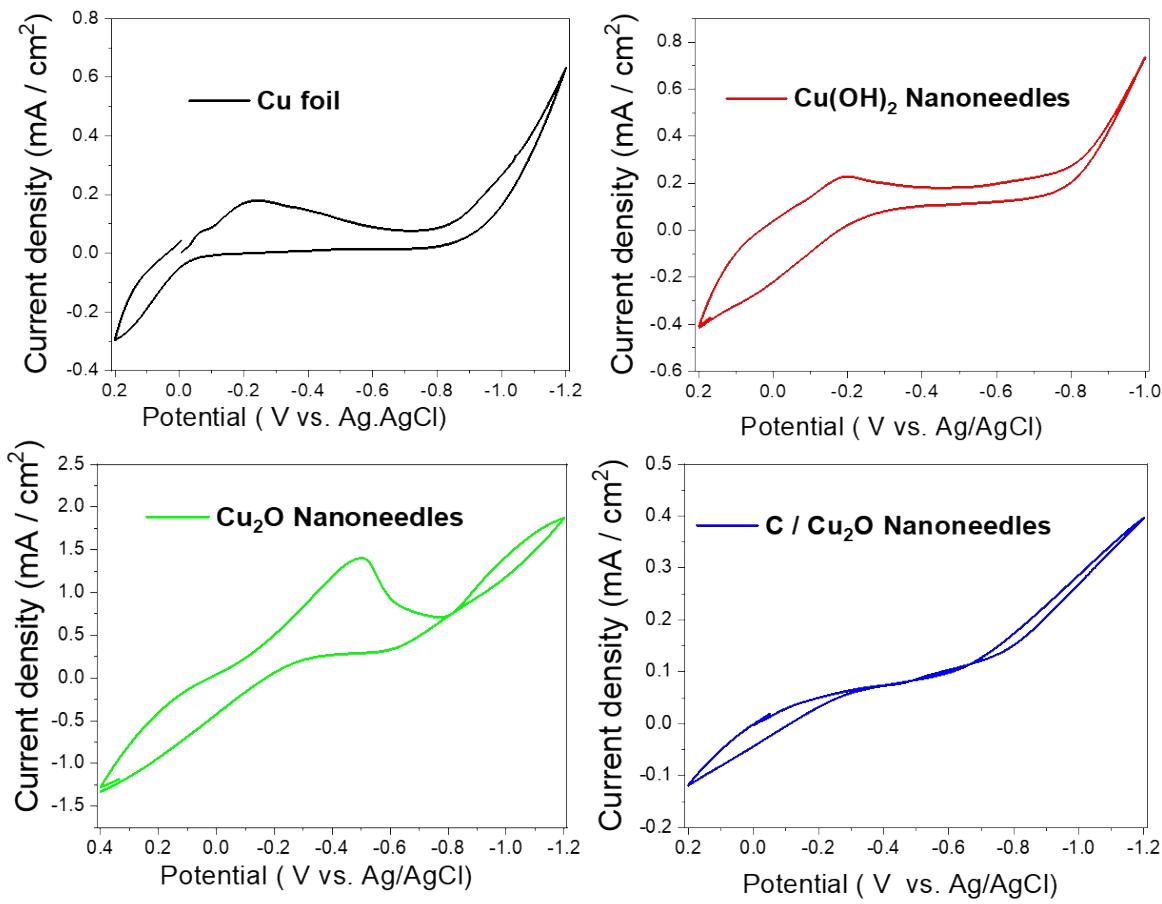


Fig. S5: Cyclic voltammetry of (A) Cu foil, (B) Cu(OH)₂ NNs, (C) Cu₂O NNs, and (D) C/Cu₂O NNs in 0.5 M Na₂SO₄ and 0.1 M KH₂PO₄ at a scan rate of 100 mV s⁻¹. Experimental data was measured in a three-electrode setup with Ag/AgCl as the reference electrode and graphite as the counter electrode.

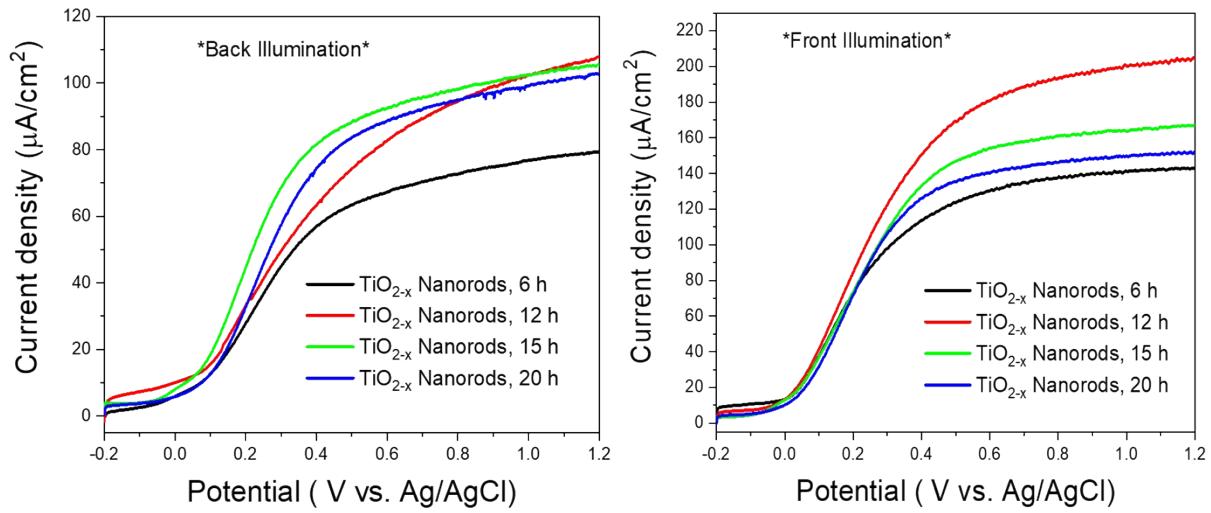


Fig. S6: J - V curves of oxygen-deficient TiO_{2-x} nanorods hydrothermally grown for different durations (6–20 h) in N_2 -purged 0.5 M Na_2SO_4 and 0.1 M KH_2PO_4 (pH 5.0) under simulated 1 sun illumination (A.M 1.5). Front illumination: nanorods side; Back illumination: FTO side.

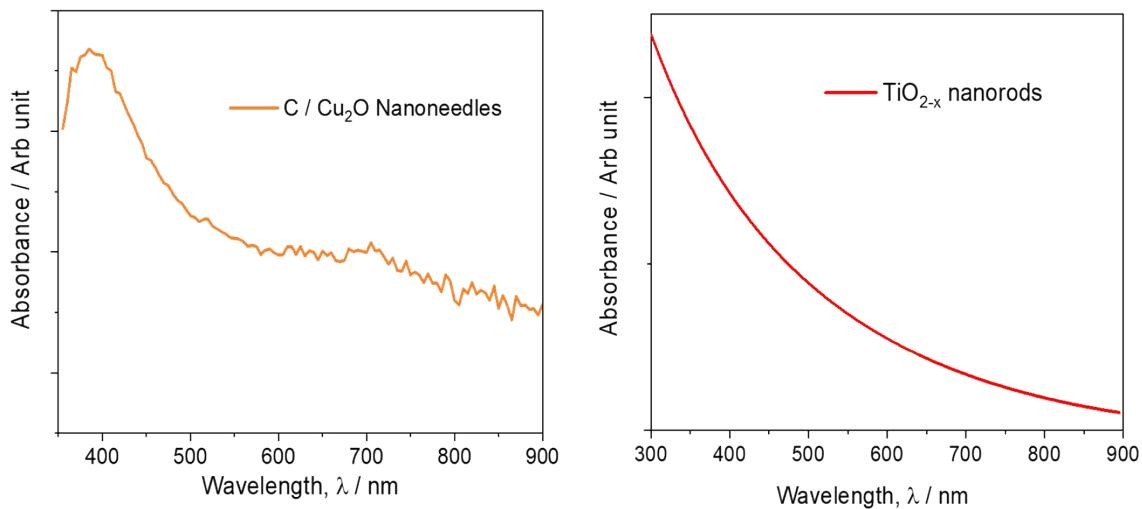


Fig. S7: UV-Vis diffuse reflectance spectra (DRS) of $\text{C}/\text{Cu}_2\text{O}$ NNs and TiO_{2-x} NRs.

Table S1: Electrochemical impedance spectroscopy (EIS) parameters obtained for TiO_{2-x} NRs fabricated with hydrothermal growth times of 12 and 20 h.

Sample	R_s (Ω)	R_{ct} (Ω)	CPE or C_{dl} (μF)
12 h TiO_{2-x} NRs Dark	496.5	1,90,130	2.259
12 h TiO_{2-x} NRs Light	495.2	20,949	6.366
20 h TiO_{2-x} NRs Dark	492.9	98,155	3.443
20 h TiO_{2-x} NRs Light	497.4	12,542	11.083

Table S2: Electrochemical impedance spectroscopy (EIS) parameters obtained for Cu_2O NNs with and without a protective carbon layer.

Sample	R_s (Ω)	R_{ct} (Ω)	CPE or C_{dl} (μF)
Cu_2O NNs Dark	427.5	6720	8.118
Cu_2O NNs Light	430.7	2308	179.390
C/ Cu_2O NNs Dark	429.5	3509	22.697
C/ Cu_2O NNs Light	425.7	2091	230.150

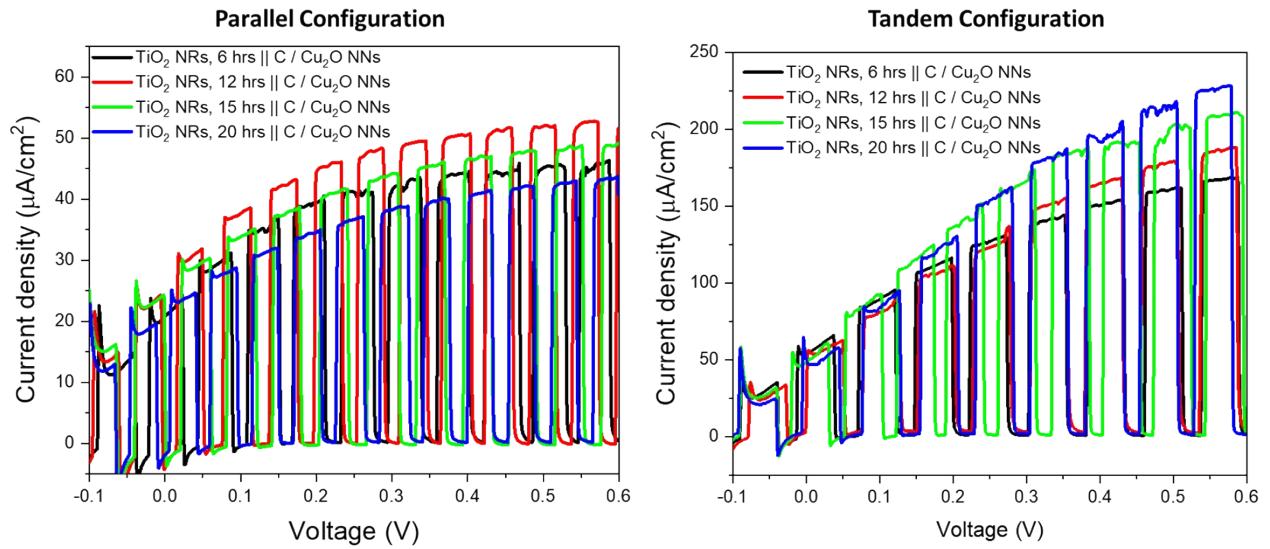


Fig. S8: J-V curves of *p*-type C/Cu₂O NNs/*n*-type TiO_{2-x} NRs (6–20 h) tandem cells in N₂-purged 0.5 M Na₂SO₄ and 0.1 M KH₂PO₄ electrolyte (pH 5.0) under simulated 1 sun illumination (A.M 1.5). The proposed tandem cells were placed in parallel or tandem configuration.

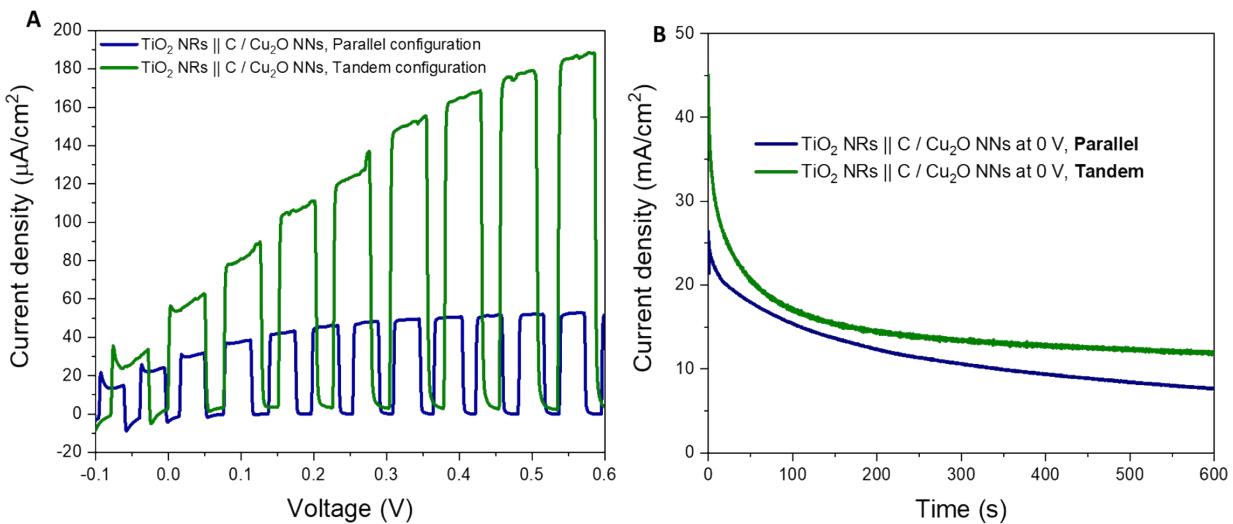


Fig. S9: (A) J-V and (B) J-t curves of *p*-type C/Cu₂O NNs/*n*-type TiO_{2-x} NRs (12 h) tandem cells in N₂-purged 0.5 M Na₂SO₄ and 0.1 M KH₂PO₄ electrolyte (pH 5.0) under simulated 1 sun illumination (A.M 1.5) at zero bias and without any sacrificial reagents.

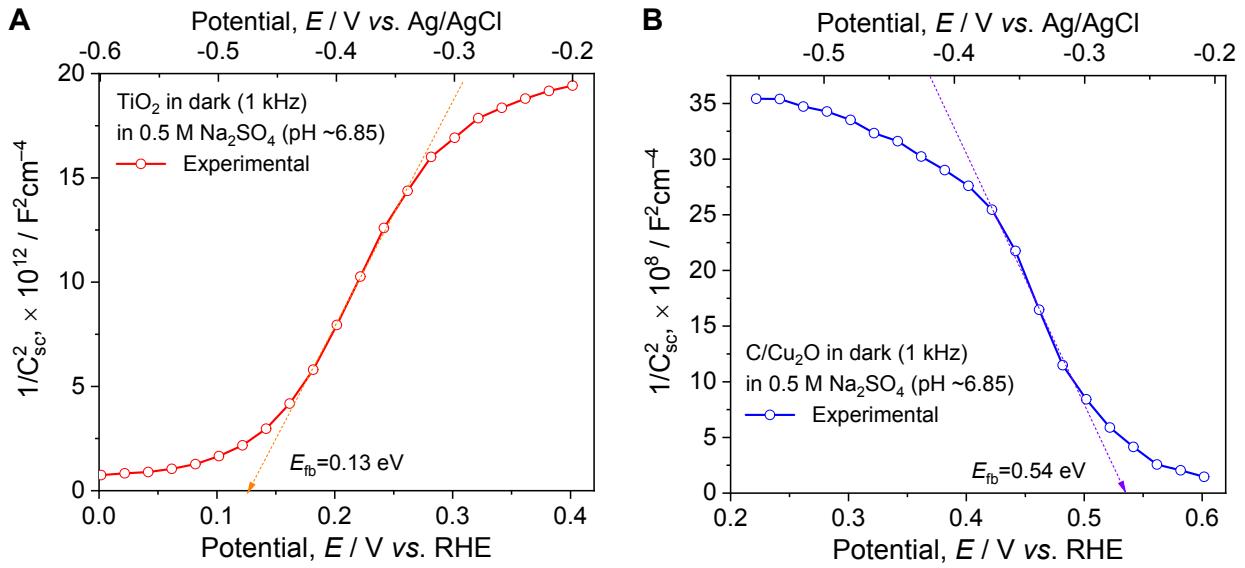


Fig. S10: Mott-Schottky plots of (A) *n*-type TiO_{2-x} NRs and (B) *p*-type C/Cu₂O NNs measured from N₂-purged 0.5 M Na₂SO₄ phosphate-buffered electrolyte (pH 6.85) under dark condition at 1KHz, revealing the flat band potential (E_{fb}) values.