Supporting Information for

Reduced Titania@Layered Double Hydroxide Hybrid Photoanode for Enhanced Photoelectrochemical Water Oxidation

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Experimental Details

Oxygen detection: The measurement of the photoelectrochemically generated O_2 was carried out in a home-made airtight transparent electrochemical cell using a three-electrode configuration connected with the electrochemical workstation (CHI 660C, CH Instruments Inc., Shanghai). The illumination geometrical area of the photoanode was ~0.54 cm^2. PEC water oxidation measurements were performed in a 1.0 M KOH aqueous solution using bulk electrolysis method at 1.23 V vs. RHE under an illumination of 150 W Xe lamp (100 mW cm^{-2}). Prior to the measurement, the electrolyte was thoroughly degassed by purging argon for 30 min. The formation of O_2 was detected by injecting the gas into a gas chromatograph (GC-7890II; Techcomp. Co., Ltd.) equipped with a semicapillary column and a thermal conductivity detector (TCD).

Supplementary Figures

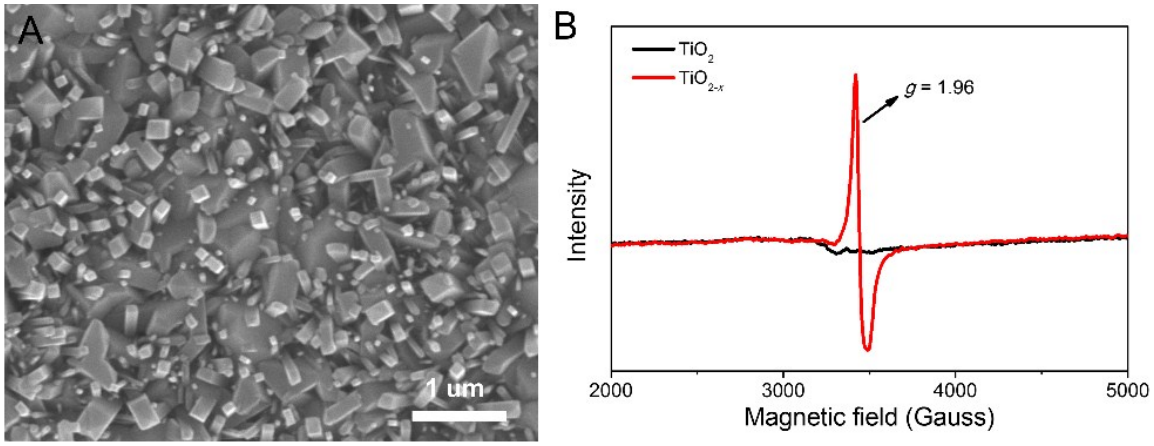

Figure S1. (A) Typical SEM image and (B) ESR spectra of Ti-TiO_2 and Ti-TiO_{2-x}.

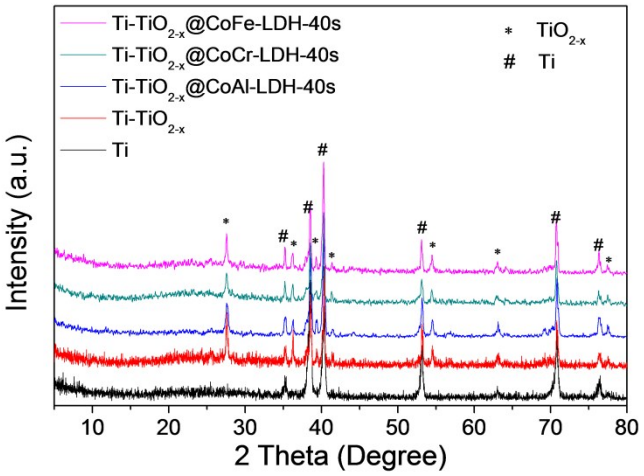

Figure S2. XRD patterns of Ti foil, Ti-TiO_{2-x}, Ti-TiO_{2-x}@CoAl-LDH-40s, Ti-TiO_{2-x}@CoCr-LDH-40s and Ti-TiO_{2-x}@CoFe-LDH-40s.

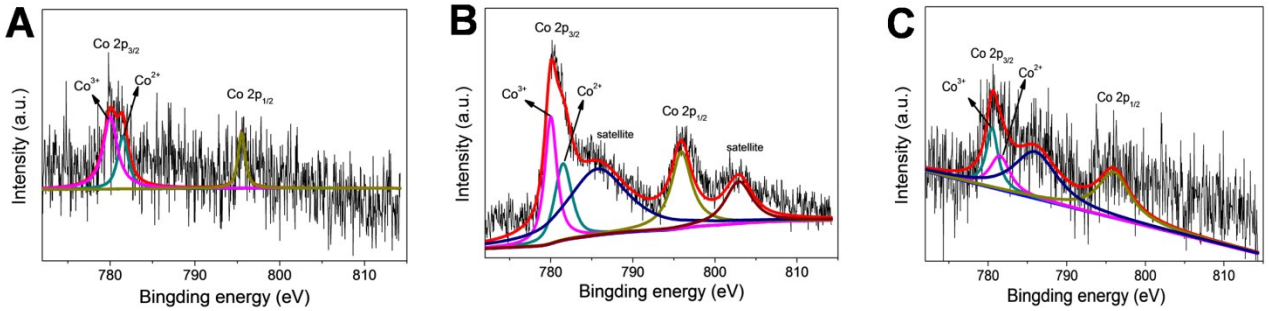

Figure S3. Co 2p XPS spectra of (A) Ti-TiO_{2-x}@CoAl-LDH-40s, (B) Ti-TiO_{2-x}@CoCr-LDH-40s, and (C) Ti-TiO_{2-x}@CoFe-LDH-40s, respectively.

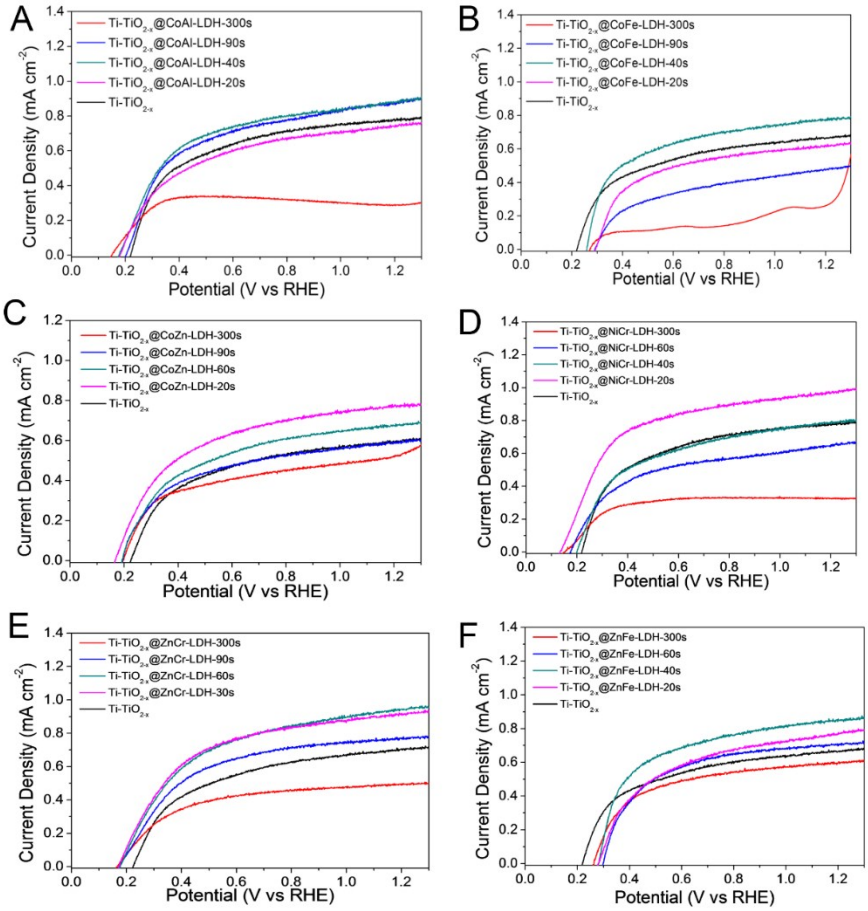

Figure S4. Current-Potential (*J-E*) curves of Ti-TiO_{2-x} and Ti-TiO_{2-x}@LDH respectively modified with different amount of (A) CoAl-LDH, (B) CoFe-LDH, (C) CoZn-LDH, (D) NiCr-LDH, (E) ZnCr-LDH and (F) ZnFe-LDH.

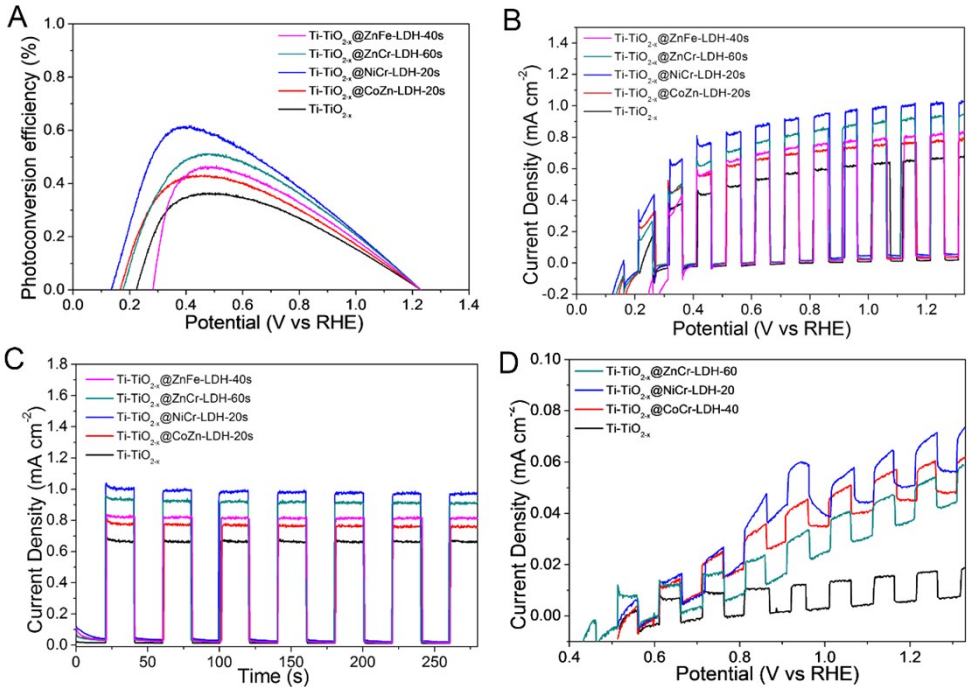

Figure S5. (A) calculated photoconversion efficiency, (B) *J-E* behavior and (C) amperometric Current-Time (*J-T*) curves at a potential of 1.23 V (vs. RHE) under chopped light illumination for the samples of Ti-TiO_{2-x}@LDH; (D) *J-E* behavior under the chopped visible light ($\lambda \geq 400$ nm) illumination for the samples of Ti-TiO_{2-x}, and Ti-TiO_{2-x}@Cr-based LDH.

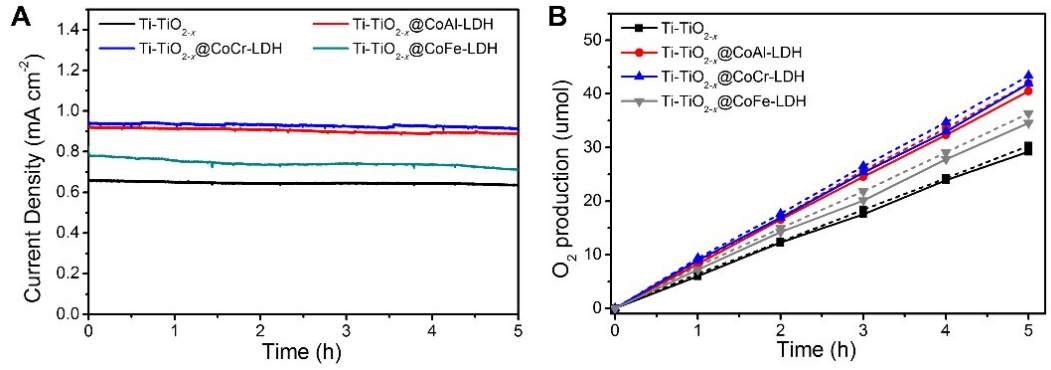

Figure S6. (A) The measured *J-T* curves at a potential of 1.23 V (vs. RHE), and (B) Total O_2 production detected by a gas chromatograph (the dashed lines are the theoretical O_2 production

calculated from the measured photocurrent density assuming 100% faradaic efficiency) for Ti-TiO_{2-x}, Ti-TiO_{2-x}@CoAl-LDH, Ti-TiO_{2-x}@CoCr-LDH, and Ti-TiO_{2-x}@CoFe-LDH.

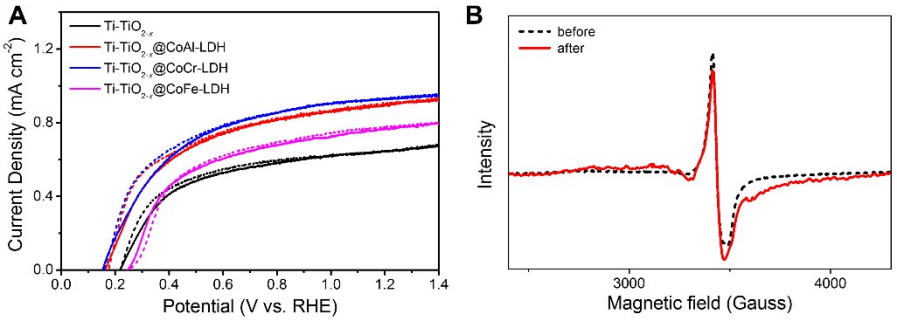

Figure S7. (A) *J-E* curves before (the dashed lines) and after 5 h PEC tests for Ti-TiO_{2-x}, Ti-TiO_{2-x}@CoAl-LDH, Ti-TiO_{2-x}@CoCr-LDH, and Ti-TiO_{2-x}@CoFe-LDH, respectively; (B) ESR spectra of Ti-TiO_{2-x} before and after PEC measurement.

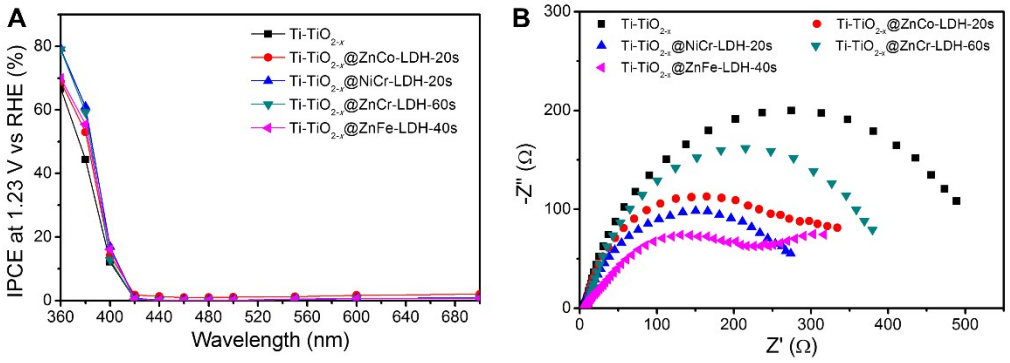

Figure S8. (A) IPCEs measured at an applied voltage of 1.23 V (vs. RHE), and (B) electrochemical impedance spectra (EIS) measured at the open circuit potential under illumination for the samples of Ti-TiO_{2-x}, Ti-TiO_{2-x}@ZnCo- LDH-20s, Ti-TiO_{2-x}@NiCr-LDH-20s, Ti-TiO_{2-x}@ZnCr-LDH-60s and Ti-TiO_{2-x}@ZnFe-LDH-40s.

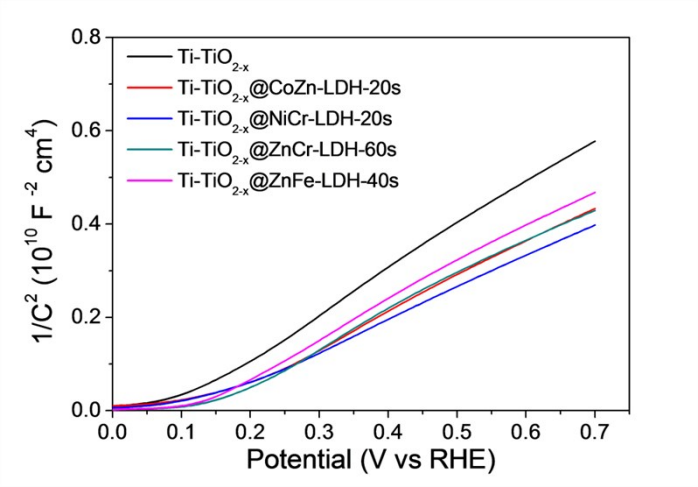

Figure S9. Mott-Schottky plots collected at a frequency of 5 kHz in the dark for the samples of Ti-TiO_{2-x}@CoZn- LDH-20s, (B) Ti-TiO_{2-x}@NiCr-LDH-20s, (C) Ti-TiO_{2-x}@ZnCr-LDH-60s and (D) Ti-TiO_{2-x}@ZnFe-LDH-40s comparing with Ti-TiO_{2-x}.

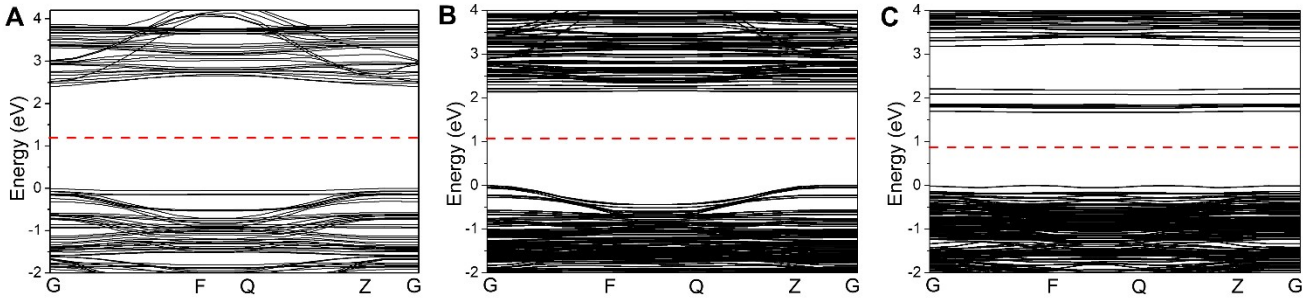

Figure S10. The band structure of (A) CoAl-LDH, (B) CoCr-LDH, and (C) CoFe-LDH, respectively. The red dashed line represents the Fermi level. The energy of CB minimum and VB maximum are calculated by the equations E_{CB}=-W+0.5E_g and E_{VB}=-W+0.5E_g, respectively.

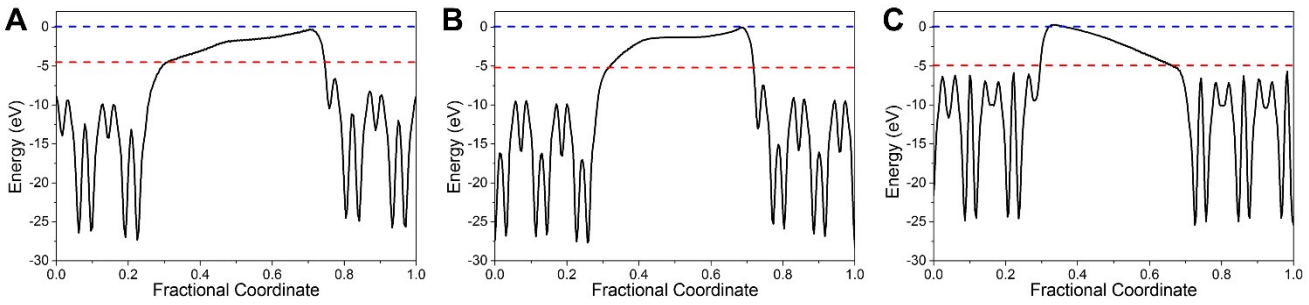

Figure S11. The work function of (A) CoAl-LDH, (B) CoCr-LDH, and (C) CoFe-LDH, respectively. The blue dashed line represents the vacuum level and the red dashed line represents the Fermi level.