Electronic Supplementary Information

Shining a light on fungicide-water: Enhanced photocatalytic degradation with CoTiO$_3$/CaTiO$_3$ nanocomposite and its experimental and theoretical viewpoint of improved intervalence charge transfer of O^{2-} to Ti^{4+} and Co^{2+} to Ti^{4+} ion pairs and spatial charge transfer

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1. Photocatalyst characterization

The crystalline structure of the generated samples was determined using X-ray diffraction (XRD) patterns on an X'pert^3 powder XRD instrument (Malvern Panalytical, UK) equipped with a Cu K radiation (l = 1.5406) source. HR-TEM (JEOL, JEM-2100f) and HR-SEM (Thermo Scientific Apreo) were utilized to evaluate the microstructure and morphology of structural applications. X-ray photoelectron spectroscopy (PHI VersaProbe 4 (XPS)

Microprobe with Al Kα radiation source) was used to identify sample surface characteristics. The carbon tape was utilized as a standard to calibrate the binding energy of XPS results. The UV-vis spectra were collected using a Shimadzu UV 3600i Plus at room temperature. Raman spectra were collected using a HORIBA scientific spectrometer with a 532 nm laser (LabRAM HR Evolution, Horiba.). The surface textural characterization was determined by the BET and BJH method of the N_2 adsorption-desorption isotherms using a Quantachrome Autosorb IQ. PL measurements were collected in the FLS1000 (Edinburgh Instruments) spectrometer. In the photocatalytic test, a 300 W Xenon lamp light source was used. An electrochemical workstation, Shanghai Chenhua CHI-660D, was used to conduct EIS and Mott-Schottky analysis using a three-electrode system of glassy carbon, Ag/AgCl, and Platinum electrodes and 0.1 mol L^{-1} Na_2SO_4 (pH ≈ 6) electrolyte. The working electrodes were prepared by sonicating catalysts in a 1:1 combination of ethanol and distilled water with 5 μL Nafion for 30 min. The resulting sludge was then air-dried after a slowing drop cast on a glassy carbon electrode.

Table S1 Calculated Crystallite size and Lattice strain of bare $CoTiO_3$ and CCO 75:25 composite.

| Sample code	2-Theta (Degree)	Crystallite size (nm)	Lattice strain (%)
CoTiO$_3$	32.813	107.6	0.114
CCO 75:25	33.181	33.8	0.359

2. Validation of actual weight ratio using ICP-OES and EDAX analysis

To validate the actual weight ratio of the prepared CCO composites, we conducted inductively coupled plasma-optical emission spectroscopy (ICP-OES) and high-resolution scanning electron microscopy energy-dispersive X-ray spectroscopy (HR-SEM EDAX)
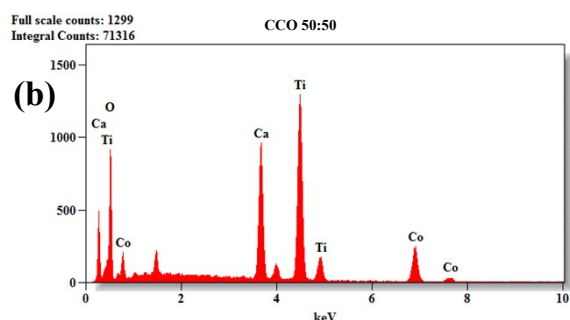
analyses. For the ICP-OES analysis, the composite was initially digested in an HNO_3 solution and then diluted to a volume of 100 mL using deionized water. In the HR-SEM EDAX analysis, the composite was coated in aluminum foil using ethanol.

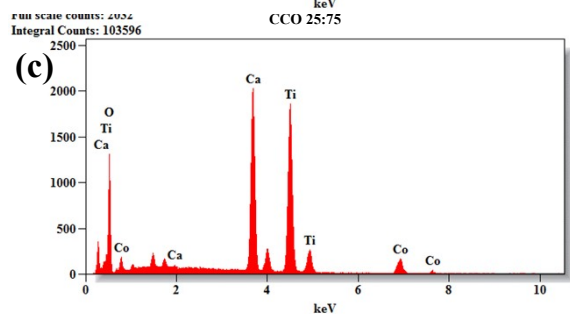**Table S2** The content of Co and Ca in the CCO composite was determined in ICP-OES analysis.

Samples	Co (mg/L)	Ca (mg/L)
CCO 75:25	25.75	8.64
CCO 50:50	16.1	18.41
CCO 25:75	8.59	25.77

(a) Full scale counts: 2197 / Integral Counts: 112388 / CCO 75:25
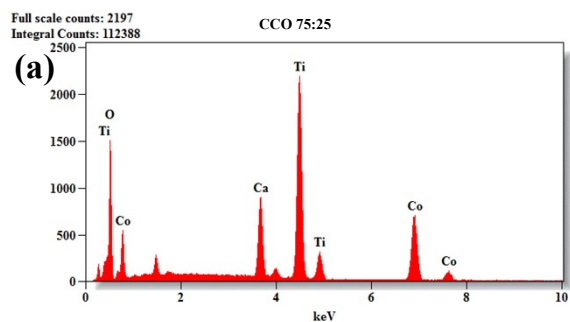
Sample	Co [Weight%]	Ti [Weight%]	O [Weight%]	Ca [Weight%]
CCO 75:25	24.21	30.49	37.91	7.69

(b) Full scale counts: 1299 / Integral Counts: 71316 / CCO 50:50

Sample	Co [Weight%]	Ti [Weight%]	O [Weight%]	Ca [Weight%]
CCO 50:50	13.21	30.98	42.39	13.41

(c) Full scale counts: 2032 / Integral Counts: 103596 / CCO 25:75

Sample	Co [Weight%]	Ti [Weight%]	O [Weight%]	Ca [Weight%]
CCO 25:75	6.16	29.83	44.59	19.42

Fig. S1 HRSEM- EDAX spectra of composites CCO 75:25 (a), CCO 50:50 (b), and CCO 75:25 (c).
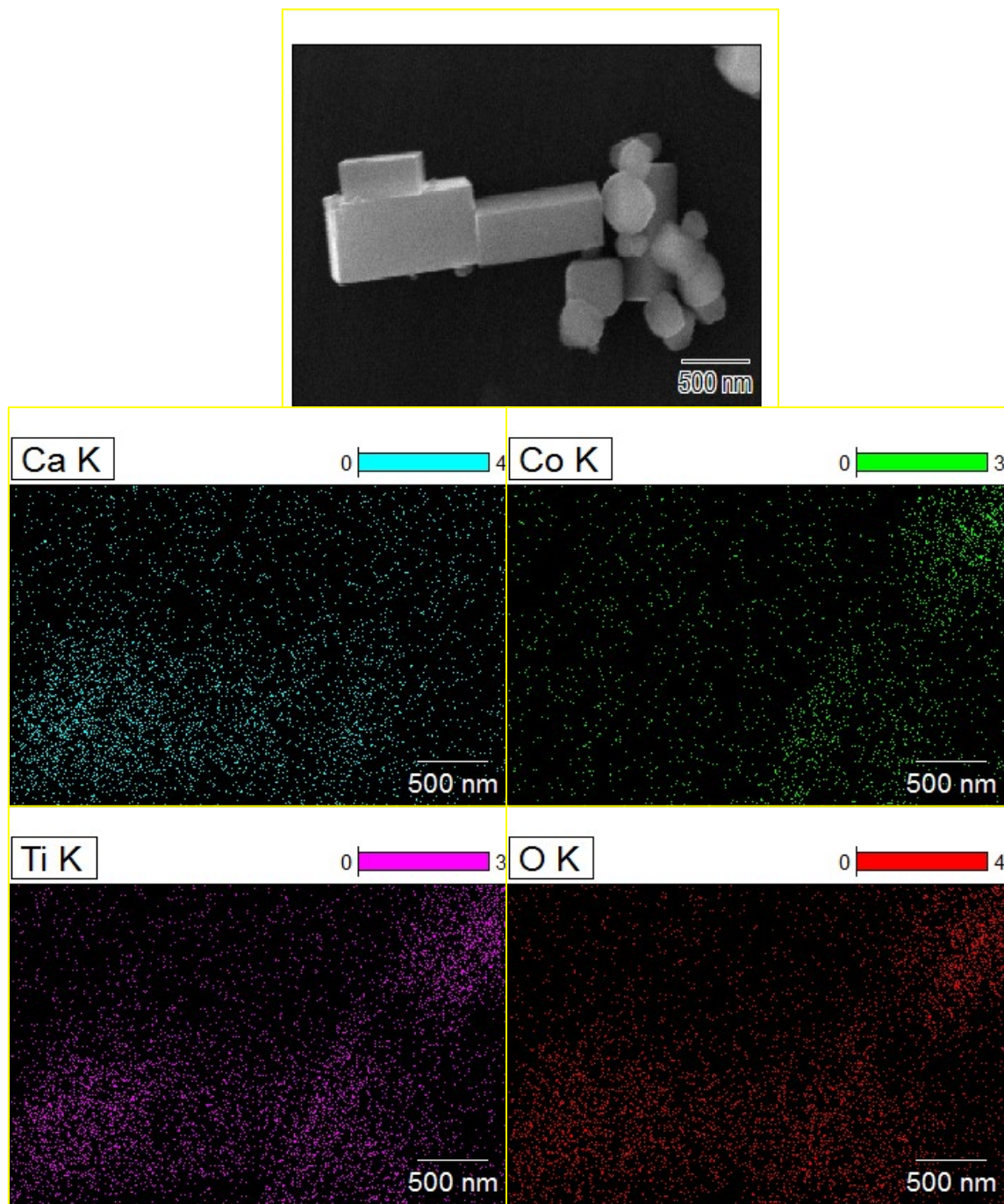
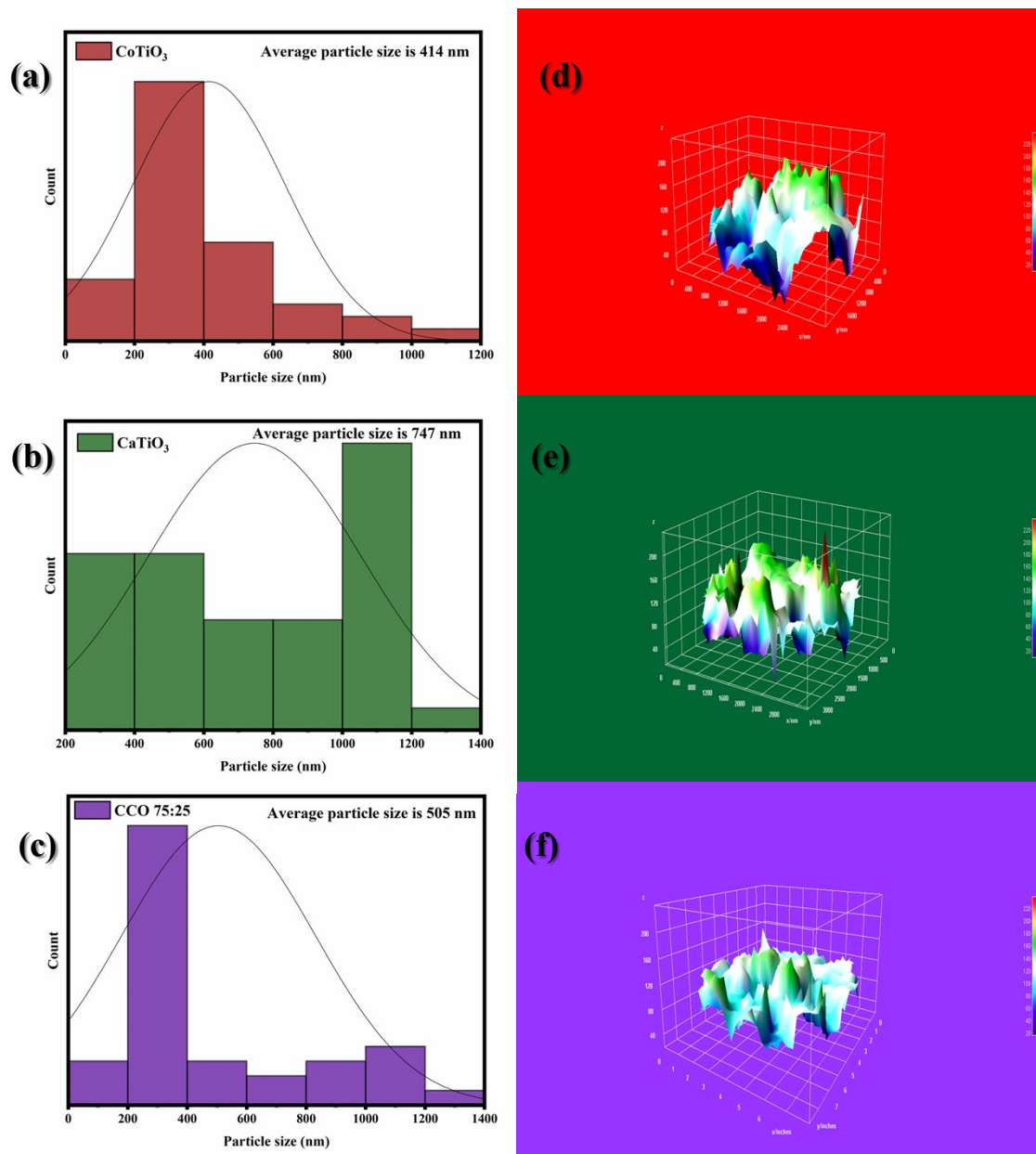**Fig. S2** Elemental mapping analysis of CCO 75:25 composite.

Fig. S3 Particle size distribution of bare CoTiO$_3$ (a), CaTiO$_3$ (b), and CCO 75:25 composite (c) and corresponding Surface occupancy plot (SOP) (d), (e), and (f).
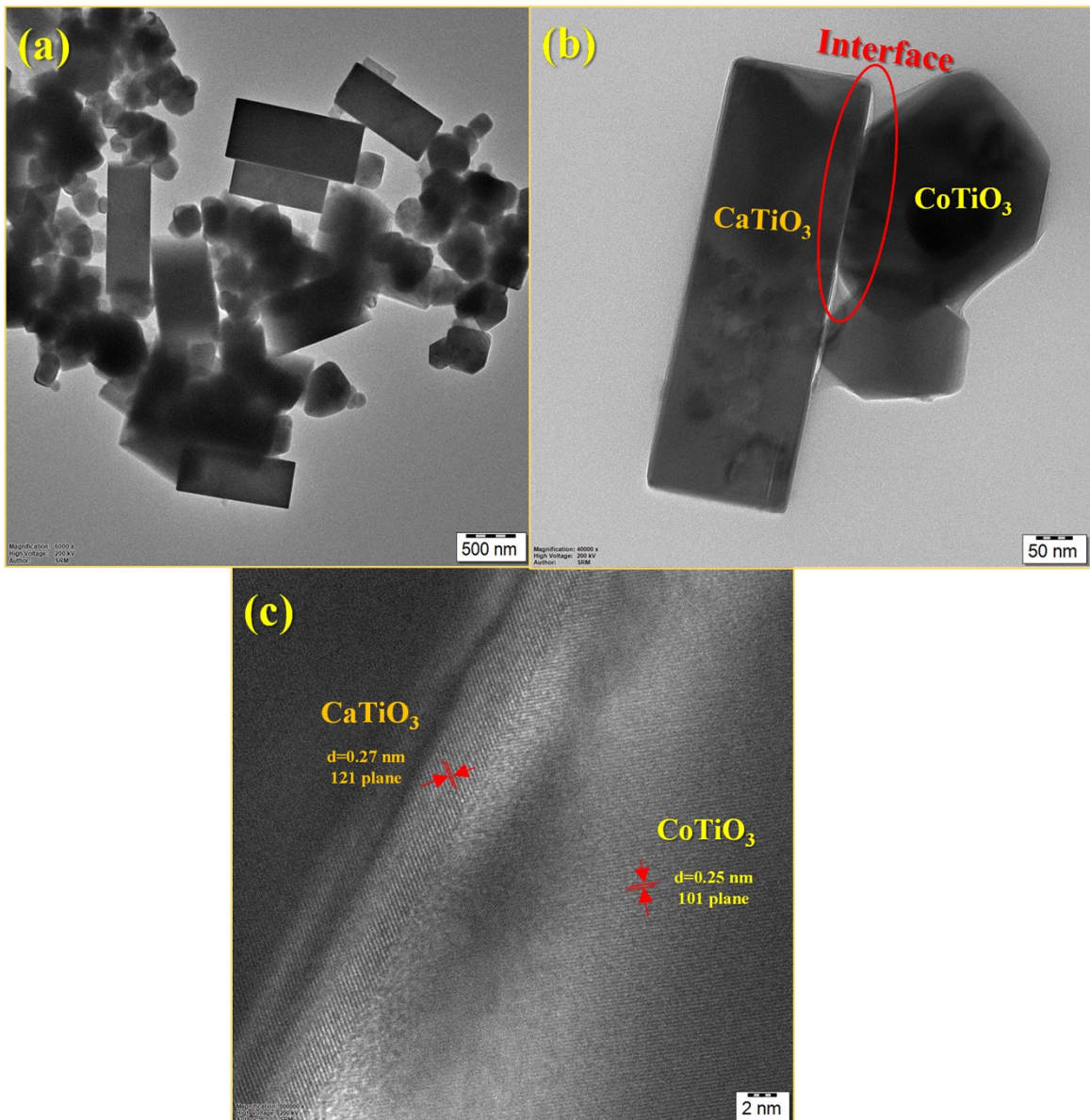
Fig. S4 HRTEM Image of CCO 75:25's interface.

2. Theoretical calculation

The band structure and density of states were calculated using the CP2K package[1] with the exchange-correlation function set as generalized gradient approximation (GGA) parameterized by the Perdew-Burke-Ernzerhof (PBE) (GGA-PBE) functional.[2] The electronic wave function was described using the TZVP-MOLOPT-SR-GTH basis set.[2] Geometry optimization was performed using the BFGS optimization algorithm,[3] with a convergence threshold of 1.0E-6. The Quickstep method[2] was utilized to calculate the total energy and

electronic structure of the systems. Spin-polarized parametrization was taken into account during the calculations. The energy cut-off was set to 400 eV for all samples, and SFC tolerance and k-point were set to be 2×10^{-6} eV atom^{-1} and $1 \times 2 \times 1$, respectively. The CoTiO$_3$/CaTiO$_3$ model was built by placing the CaTiO$_3$ model 2.1 Å beneath the CoTiO$_3$ to form a heterogeneous structure. The ionic cores were set as ultrasoft pseudo-potentials to promote transferability and decrease the number of plane waves required to expand the Kohn-Sham orbitals. A vacuum space of more than 15 Å was introduced to avoid interference between neighboring systems.
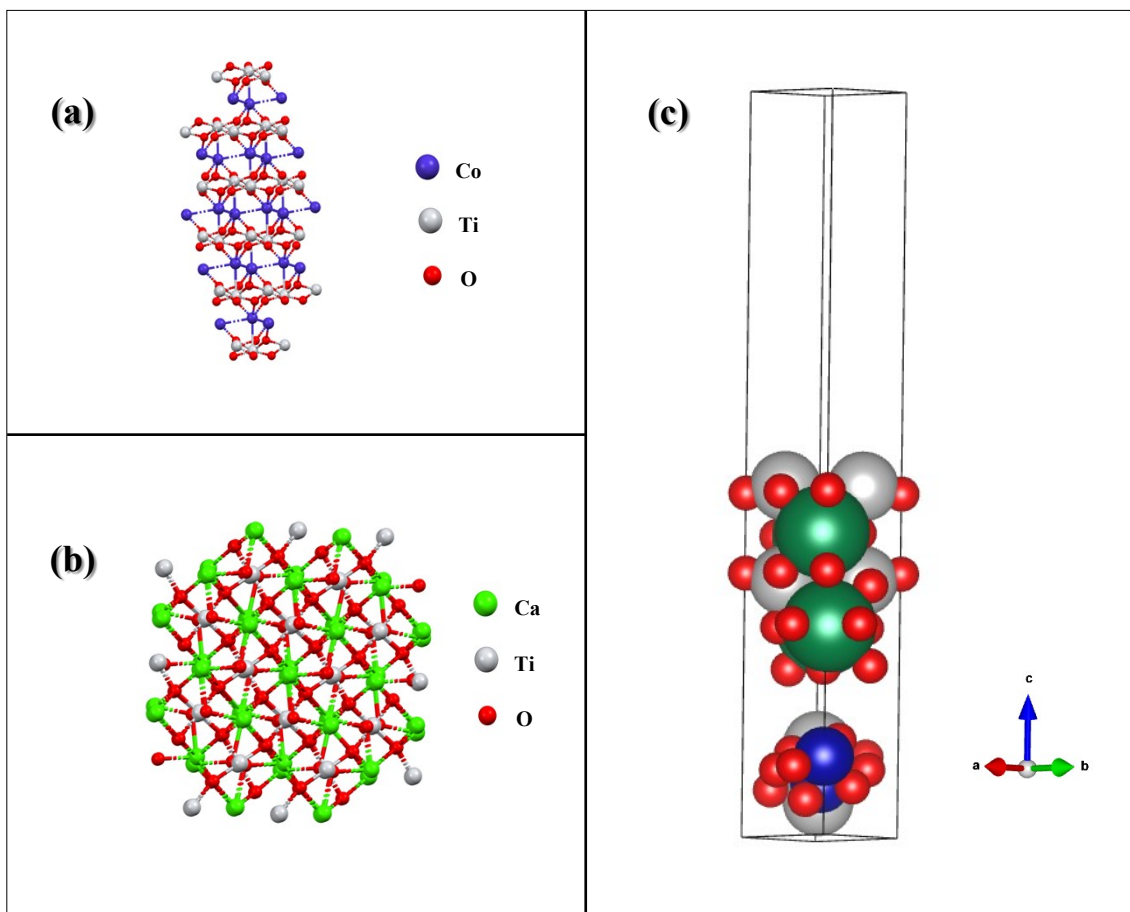

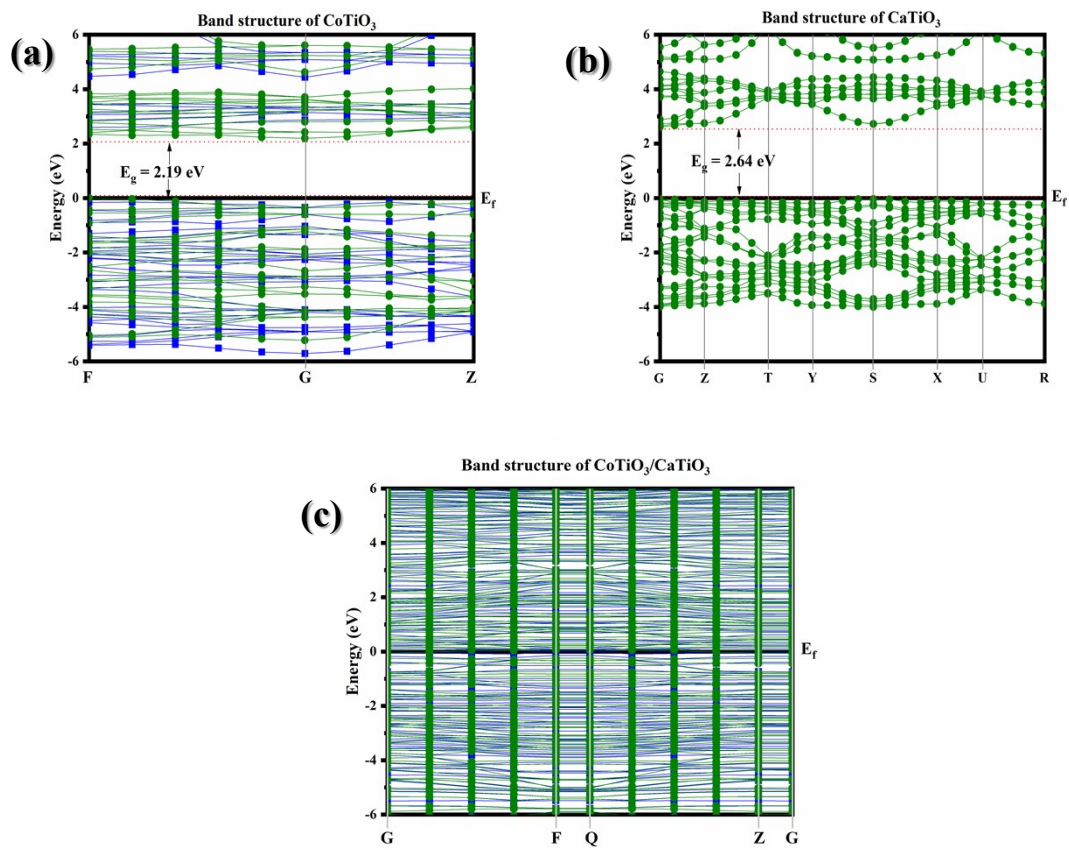**Fig. S5** Optimized structures of CoTiO$_3$ (a), CaTiO$_3$ (b), and CoTiO$_3$/CaTiO$_3$ (c).

Fig. S6 The calculated band structure of $CoTiO_3$ (a), $CaTiO_3$ (b), and $CoTiO_3/CaTiO_3$.

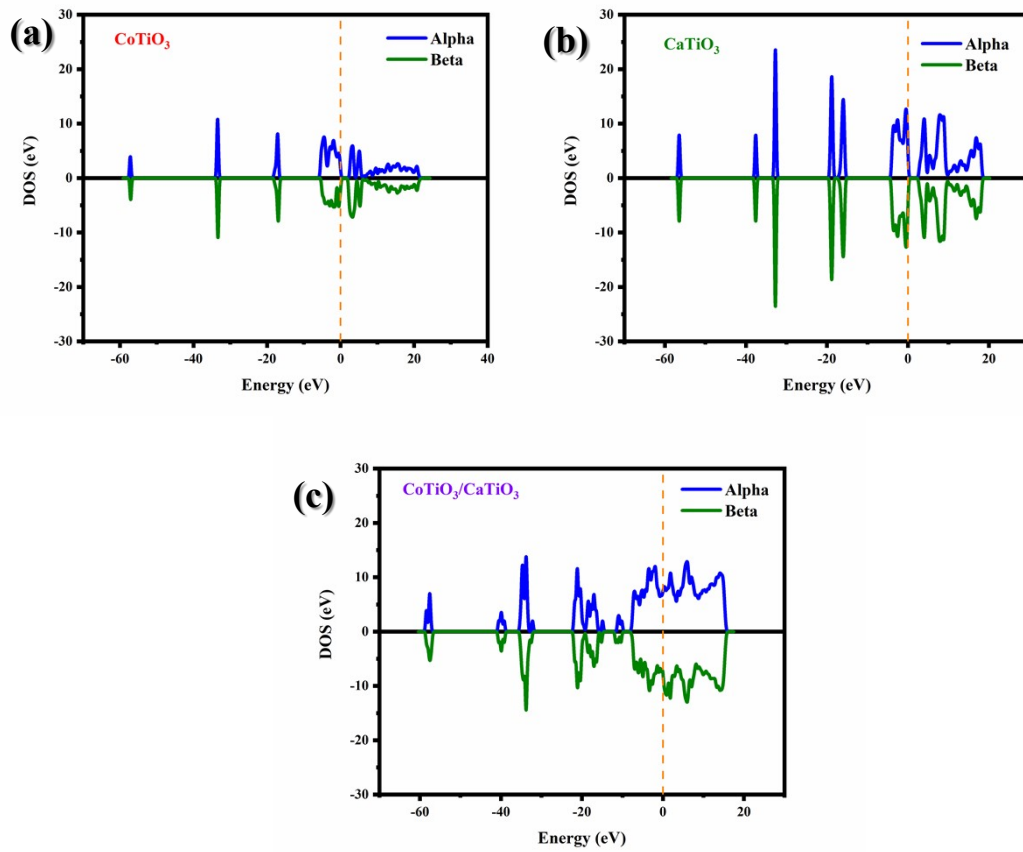**Fig. S7** Calculated total density of states (TDOS) of CoTiO$_3$ (a), CaTiO$_3$ (b), and CoTiO$_3$/CaTiO$_3$.

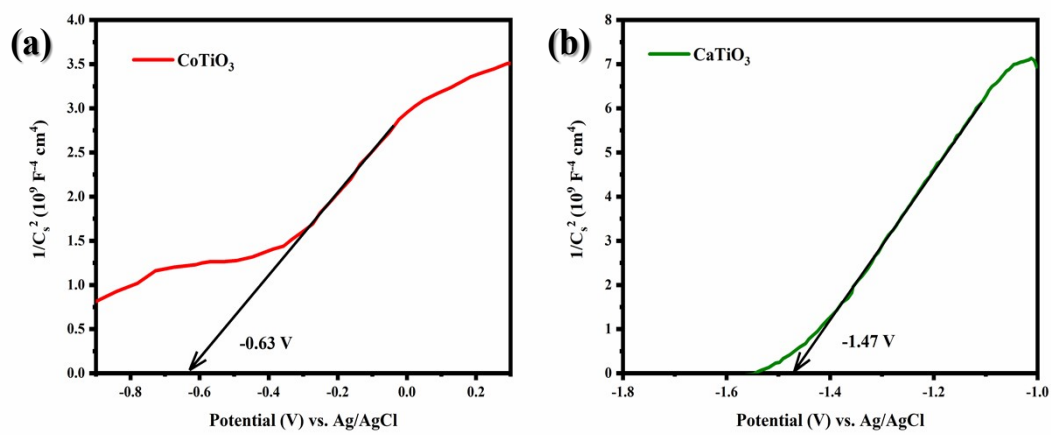## 3. Validation of band edges using the Mott-Schottky analysis

Fig. S8 Mott-Schottky plots of CoTiO$_3$ (a), and CaTiO$_3$ (b).

The Mott-Schottky (M-S) plots are used to determine the flat band potential of bare CoTiO$_3$ and CaTiO$_3$ (Fig. S7a and b). The calculated flat band potentials of bare CoTiO$_3$ and CaTiO$_3$ are -0.63 V and -1.47 V (vs Ag/AgCl) respectively.

$$E_{NHE} = E_{SHE} + 0.0591 \times pH + 0.241\,V \tag{1}$$

$$E_{VB} = E_g + E_{CB} \tag{2}$$

Based on the provided values, the conduction band potentials (E$_{CB}$) of bare CoTiO$_3$ and CaTiO$_3$ can be calculated in terms of the normal hydrogen electrode (NHE) using equation 1.[4,5] The E$_{CB}$ values bare CoTiO$_3$ and CaTiO$_3$ are -0.024 V and -0.815 V, respectively. Additionally, based on equation 2,[6] the valence band potentials (E$_{VB}$) for bare CoTiO$_3$ and CaTiO$_3$ are 2.436 V and 2.665 V, respectively.
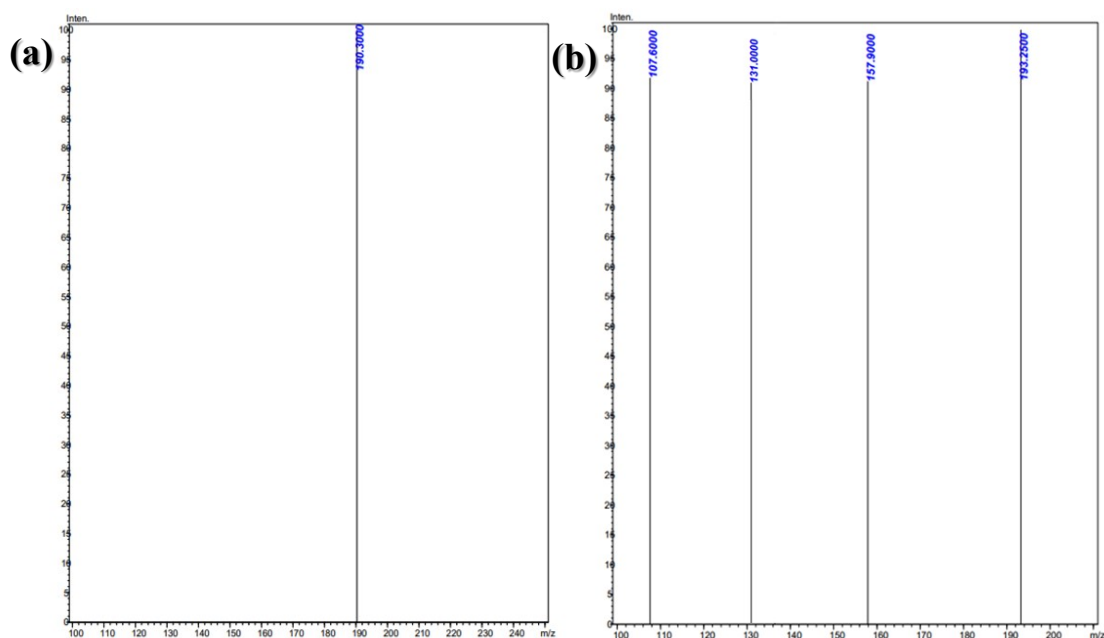

Fig. S9 LC-MS spectra of CBZ before photocatalysis (a), after photocatalysis using CCO 75:25 composite (b).

References

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