Electronic State Modulation Interfaced with Interfacial Electric Fields: Ca Site Activation Promoting Photocatalytic Hydrogen Evolution in CdS/$Ca_2Co_2O_5$ S-Scheme Heterojunction

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Characterizations

The morphology and microstructure of the materials were characterized by means of a transmission electron microscope (TEM, JEM-2100) and a scanning electron microscope (SEM, field emission type Apreo 2). The crystal structure of the samples was investigated via X-ray diffraction (XRD, Rigaku INT-2000), with a scanning rate of 10 ° per minute and a scanning range from 5° to 80°. The elemental composition, electron transport performance, and valence state of the catalyst were analyzed through X-ray photoelectron spectroscopy (XPS ESCALAB 250Xi). The ultraviolet-visible diffuse reflectance spectra of the prepared catalysts were recorded on a Shimadzu UV-2550 spectrophotometer, with BaSO4 serving as the reference background. The photoluminescence (PL) and time-resolved photoluminescence (TRPL) spectra were measured using a FluoroMAX-4 (France, Horvalla) spectrometer to conduct further characterization of the catalyst. The zeta potential of the samples was determined by using a Litesizer 500. The hydrogen content was analyzed using a gas chromatograph (GC7900, manufactured by Techcomp Company), with high-purity nitrogen gas serving as the carrier gas.

Electrochemical test

Electrochemical tests were carried out on a three-electrode electrochemical workstation (VersaStat 4-400, AMETEK) following a self-regulating standard. The prepared catalyst was electrochemically characterized with indium tin oxide (ITO) conductive glass (1×1 cm^2) serving as the working electrode and a 0.2-molar sodium sulfate solution as the electrolyte. The specific procedure was as follows: 5 mg of the catalyst was dispersed in 300 μl of a 10% Nafion ethanol solution, and then ultrasonic treatment was applied to ensure homogeneity. The resulting suspension was coated onto the ITO conductive glass to fabricate the working electrode. Subsequently, the transient photocurrent response was measured under the irradiation of a 300 - watt xenon lamp.

DFT calculation

The first-principles calculation was conducted within the framework of density functional theory (DFT). Specifically, the Perdew-Burke-Ernzerhof (PBE) functional under the generalized gradient approximation (GGA) was utilized to address the exchange - correlation interactions. The momentum energy cutoff value for the plane-wave basis set of the extended Kohn-Sham electronic wave function was set at 300 eV. Given that the Co ions in $Ca_2Co_2O_5$ feature unpaired d-electrons and pronounced electron correlation effects, spin polarization was enabled throughout all calculations. Owing to the non-negligible weak interlayer interactions at the CdS/$Ca_2Co_2O_5$ heterojunction interface, the Tkatchenko-Scheffler (TS) dispersion correction method was adopted to accurately characterize the influence of van der Waals forces on the geometric structure and electronic properties of the system. To eliminate spurious mirror interactions induced by periodic boundary conditions, a sufficiently thick vacuum layer of 15 Å was introduced during the construction of the heterojunction model. For CdS, bulk $Ca_2Co_2O_5$, and the constructed heterojunction model, k-point grids of 7×7×4, 5×5×3, and 1×1×1 were utilized respectively, to ensure sufficient sampling for Brillouin zone integration.

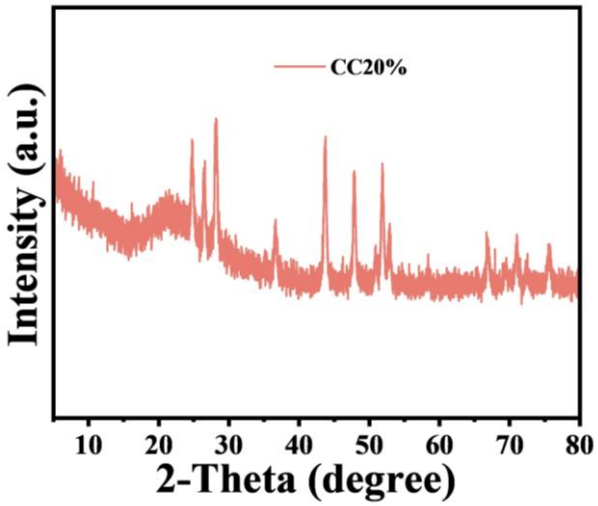

Fig. S1 XRD of CC20%.

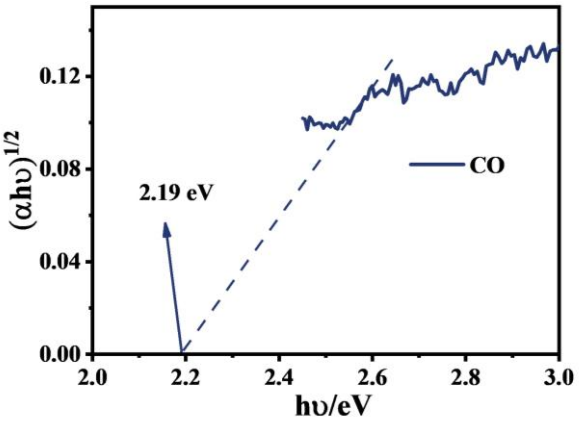

Fig. S2 Band gap of CO.

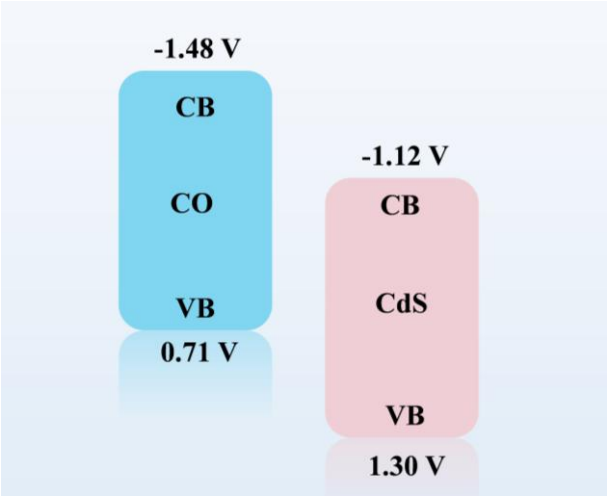

Fig. S3 Band structure of CO and CdS.

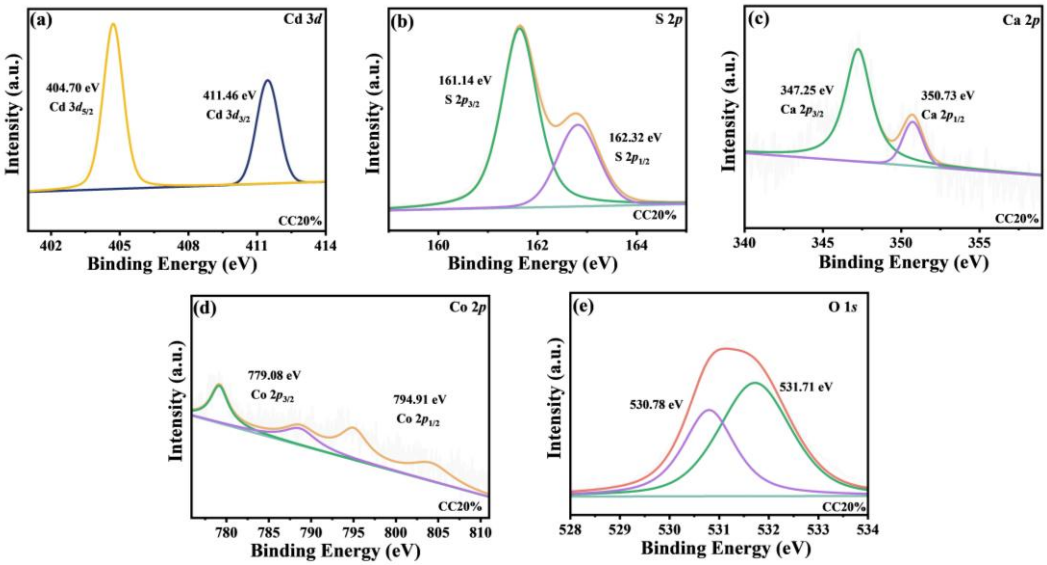

Fig. S4 XPS fine spectra of Cd 3d, S 2p, Ca 2p, Co 2p, and O 1s after hydrogen production.

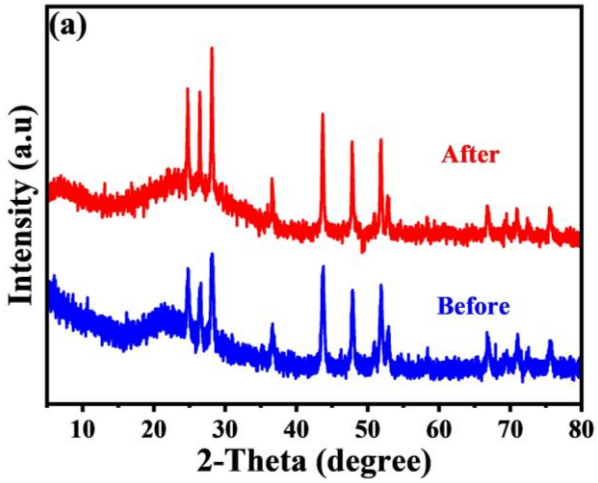

Fig. S5 XRD of CC20% after hydrogen production.

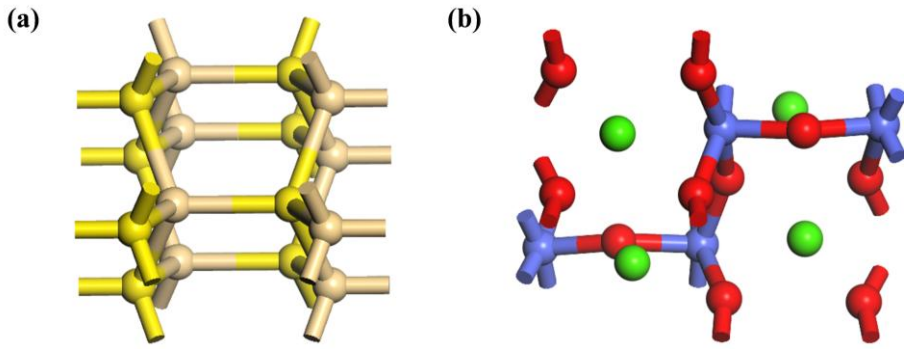

Fig. S6 DFT calculation models of CdS and CO.