Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Impacts on Carbon Dioxide Electroreduction of Cadmium Sulfides via Continuously Surface Sulfur Vacancy Engineering

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Experimental Methods

1 Electrocatalyst synthesis.

The nanorod-like CdS electrocatalysts were prepared by a one-step solvothermal method. In a typical procedure for synthezing 0-CdS without surface S_v, 1 mmol of cadmium chloride and 2 mmol of thiourea were dissolved in 30 mL of ethylenediamine. The mixture was transferred into a Teflon-lined autoclave, sealed, and maintained at 150 ^oC for 24 hours. After cooling to room temperature, the resulting yellow solid products were collected by centrifugation, washed with distilled water and ethanol three times each. The product was then vacuum-dried at 60 ^oC overnight. To produce 0.05-CdS, 0.09-CdS, 0.15-CdS and 0.18-CdS samples, only the mole ratio of cadmium chloride and thiourea are changed into 1:1, 2:1, 3:1 and 4:1, respectively.

2 Electrode fabrication.

Typically, the carbon paper was cut into 0.5×2 cm^2 pieces, washed in boiling distilled water for 1 hour, and dried in an oven overnight. 10 mg of sample and 40 μl of Nafion solution (5 wt%) were dispersed in 1 ml of ethanol solution by sonicating for 30 min to form a homogeneous ink. 100 μl of the resulting catalyst ink was drop-dried onto the each side of carbon paper substrate to ensure full coverage of the substrate (0.5×1 cm^2).

3 Materials characterizations.

The crystal structure was determined using X-ray diffraction (D/MAX 2550 VB/PC). The structure of the catalysts was examined by TEM (TECNAI F-30, 300 kV). Further, the chemical states of the elements in catalysts were studied by XPS (ESCALAB 250Xi), and the binding energy of the C 1s peak at 284.8 eV was taken as an internal reference. The photoluminescence was measured in room temperature using a double grating spectrofluorometer (HORIBA, FL3-22).

4 Electrocatalytic tests.

Ag/AgCl (3 M KCl) and carbon rod (diameter of 5 mm) were used as the reference electrode and the counter electrode, respectively. Electrochemical measurements were performed by using a Model CHI 660E potentiostat in a two-compartment electrochemical cell, and Nafion 117 was used to separate the catholyte and the anolyte. The electrolyte solution (0.5 M $KHCO_3$) was purged with high-purity CO_2 (99.99%)

gas for at least 20 min, and the pH of the electrolyte was 7.2 after saturation. The CO_2 reduction reaction were measured by using chronoamperometry at each fixed potential and gaseous products (i.e., H_2 and CO) were quantified using a gas chromatography (GC) system (RAMIIN, GC2060) that was equipped with a flame ionization detector (FID) and a thermal conductivity detector (TCD). Ultrahigh purity argon gas (Ar, 99.99%) was used as the carrier gas. The average CO_2 flow rate was 5 sccm, which was measured by a universal flow meter (Alicat Scientific, LK2) at the entrance of the electrochemical cell.

5 DFT calculations.

During the electrochemical reduction of CO_2, the free energies were computed based on a computational hydrogen electrode (CHE) model proposed by Nøskov et al. The CHE model defines that the chemical potential of protons/electrons ($H^+ + e^-$) in solution is equal to half the chemical potential of the gas phase H_2. According to the definition of Gibbs free energy, $G = E_{DFT} + E_{ZPE} + \int CpdT - TS$. Due to the error of functional for CO_2, a +0.33 eV correction for CO_2 was introduced to match the gaseous free energy of the experimental result. To consider the influence of the degree of acidity or alkalinity on the selectivity, the calculated limiting potential at pH = 8 was with reference to standard hydrogen electrode (SHE). The calculated lattice constants for CdS can be 4.159 Å × 4.159 Å × 6.752 Å, which are in good agreement with the respective experimental values of 4.150 Å × 4.150 Å × 6.737 Å.

We calculated the change in Gibbs free energy on CdS electrocatalysts with different surface S vacancies. The reaction energy ΔE is calculated based on DFT. Where E is the total energy of the DFT, E_{ZPE} is the zero-point vibrational energy, $\int CpdT$ is the enthalpic correction, and S is the entropy, and T is the system temperature (298.15 K, in our work). Zero-point vibrational energies are calculated with the vibrational frequencies of adsorbates and molecules as calculated within DFT. Under the condition of 298.15 K, $\int CpdT$ and S can be obtained by reference (C. J. Cramer, Essentials of Computational Chemistry: Theories and Models, John Wiley & Sons. 2013).

The process of electrocatalytic reduction of CO_2 can be regarded as the process of electron coupling and proton transfer, which can be divided into the following three steps:

(1) $*CO_2 + H^+(aq) + e^- \leftrightarrow *COOH$

(2) $*COOH + e^- + H^+(aq) \leftrightarrow *CO + H_2O$

(3) $*CO \leftrightarrow CO(g) + *$

The reaction energy ΔE can be directly determined by analyzing the total energy of the DFT. For example, the E required for the first step of electrocatalytic reduction of CO_2 can be defined as E_1, and * represents the catalyst adsorbed by various intermediate substances. $E_1 = E(*COOH) - E(*) - E(CO_2) - 1/2\ E(H_2)$; The reaction energy required for the second step of the reaction is $E_2 = E(*CO) + E(H_2O) - E(*) - E(CO_2) - E(H_2)$; The reaction energy required for the third step of the reaction is $E_3 = E(CO) + E(H_2O) - E(CO_2) - E(H_2)$.

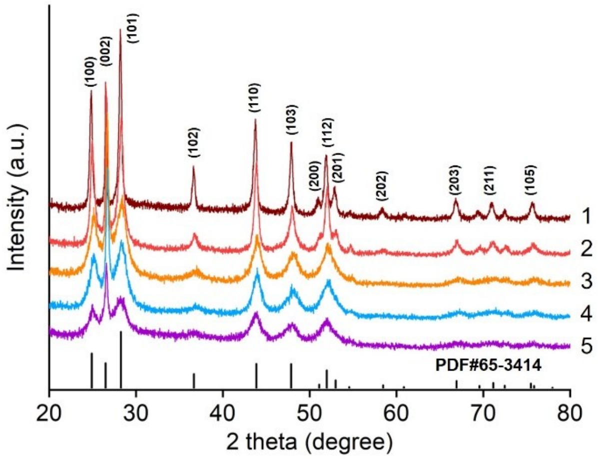

Figure S1. XRD pattern of the as-prepared CdS electrocatalysts. The curves 1-5 present 0-CdS, 0.05-CdS, 0.09-CdS, 0.15-CdS and 0.18-CdS samples, respectively.

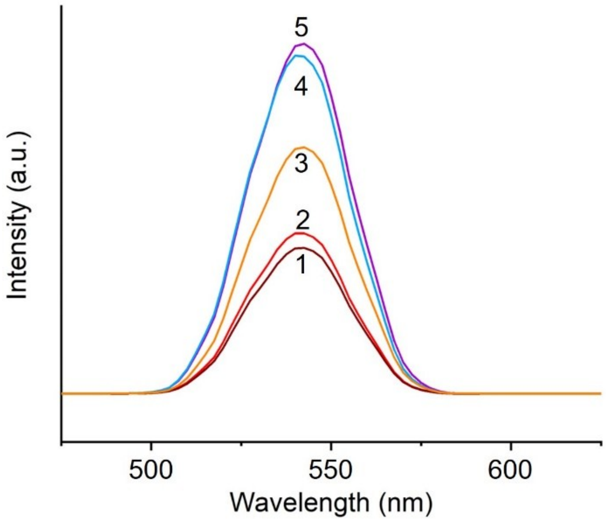

Figure S2. The room temperature photoluminescence of CdS samples under the excitation of 400 nm. The wavelength emission around 530 nm can be related to the surface S_v contents. The curves 1-5 present 0-CdS, 0.05-CdS, 0.09-CdS, 0.15-CdS and 0.18-CdS samples, respectively.

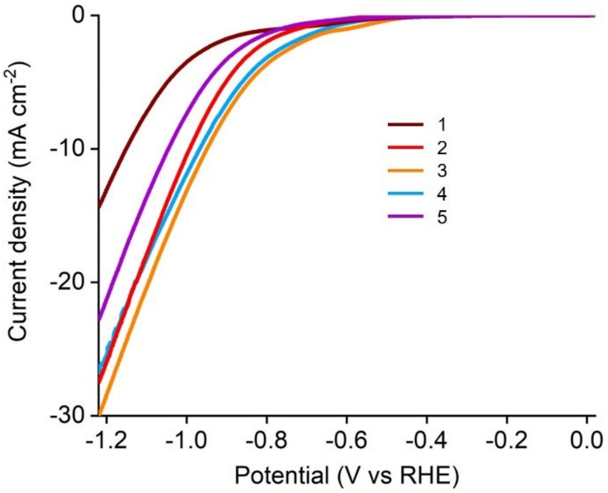

Figure S3. Comparison of the current density profiles for CdS electrocatalysts in CO_2-saturated solution. The curves 1-5 present 0-CdS, 0.05-CdS, 0.09-CdS, 0.15-CdS and 0.18-CdS samples, respectively.

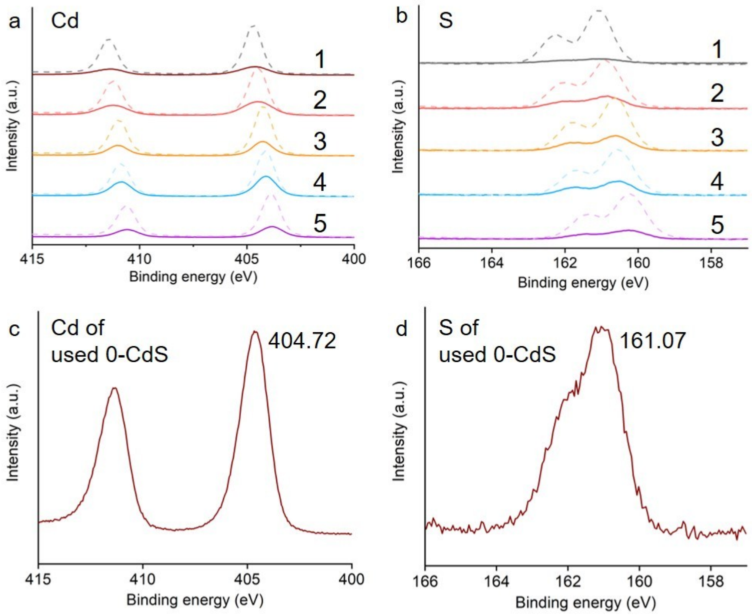

Figure S4. Cd 3d (a) and S 2p (b) XPS spectra of the as-prepared CdS electrocatalysts before (dotted lines) and after (solid lines) electrocatalytic tests. Cd 3d (c) and S 2p (d) XPS spectra of used 0-CdS sample. The curves 1-5 present 0-CdS, 0.05-CdS, 0.09-CdS, 0.15-CdS and 0.18-CdS samples, respectively.

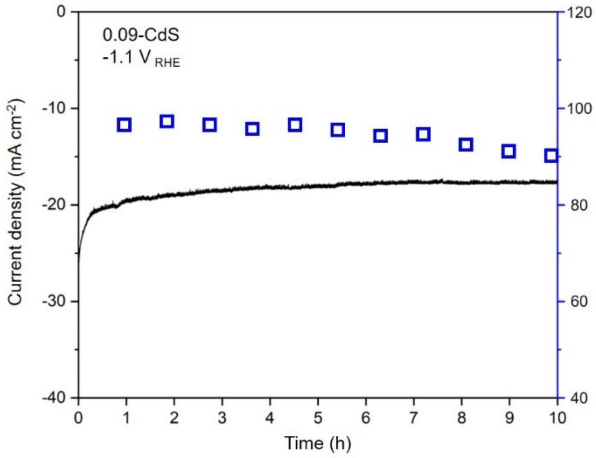

Figure S5. Current density (black line) and product faradaic efficiency (blue square) for 0.09-CdS electrocatalyst, depending on time. The potential in was maintained at -1.1 V_{RHE}.

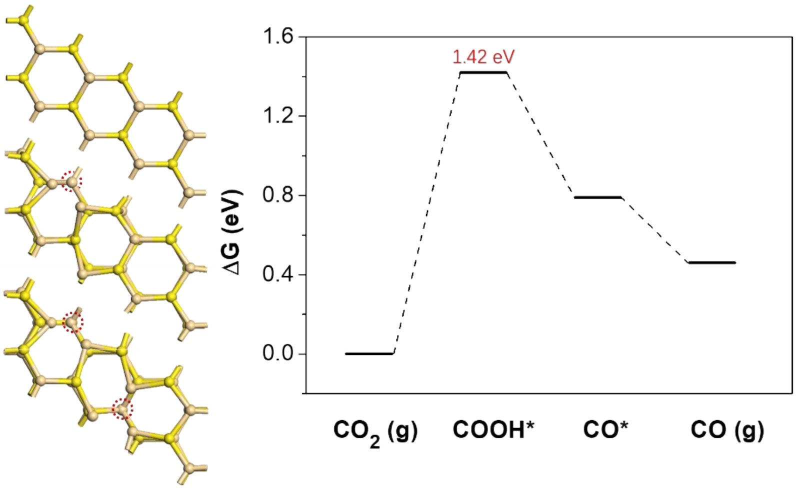

Figure S6. The adsorption binding energies of CO_2 on the CdS with two sulfur vacancies.