

*Electronic Supplementary Information*

**Fabrication of Stable CdS Photoanode for Photoelectrochemical CO<sub>2</sub>**

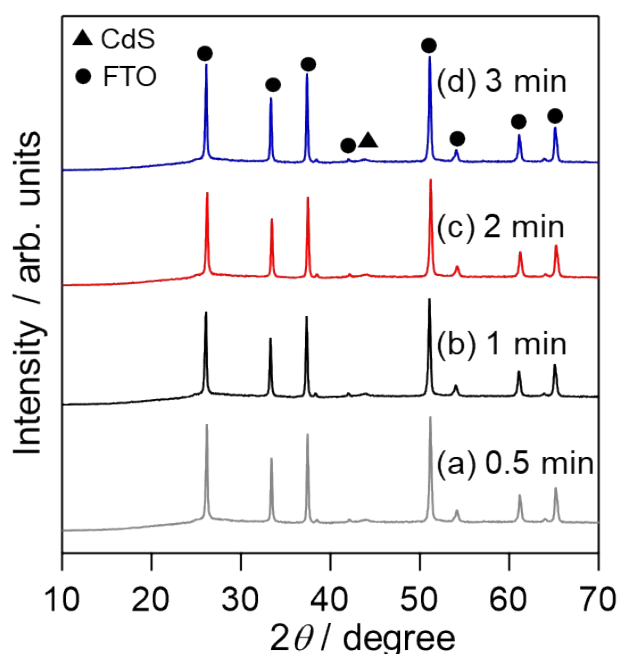
**Reduction under Visible-Light Irradiation**

Masanobu Higashi,<sup>\*a</sup> Itsuki Tanaka,<sup>b</sup> Yutaka Amao,<sup>a</sup> and Tomoko Yoshida<sup>a</sup>

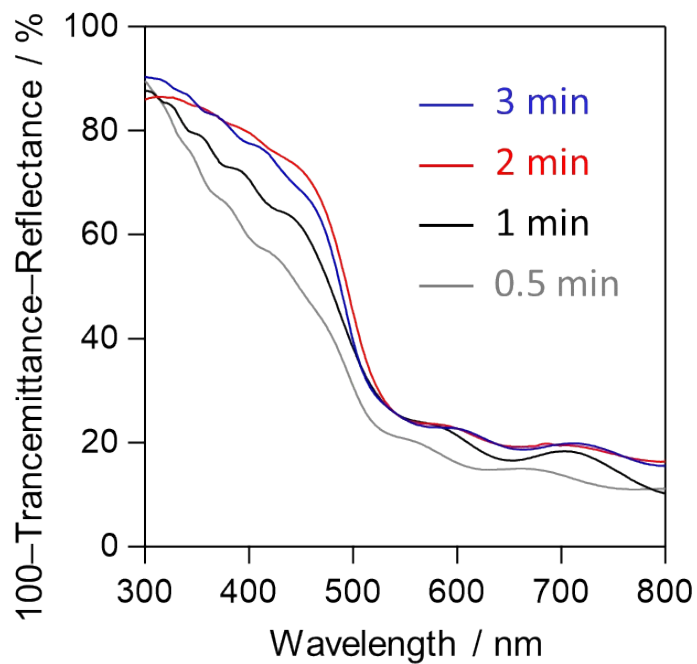
<sup>a</sup>Research Center for Artificial Photosynthesis (ReCAP), Osaka City University, 3-3-138 Sugimoto, Sumiyoshi-ku, Osaka 558-8585, Japan

<sup>b</sup>Graduate School of Engineering, Osaka City University, 3-3-138 Sugimoto, Sumiyoshi-ku, Osaka 558-8585, Japan

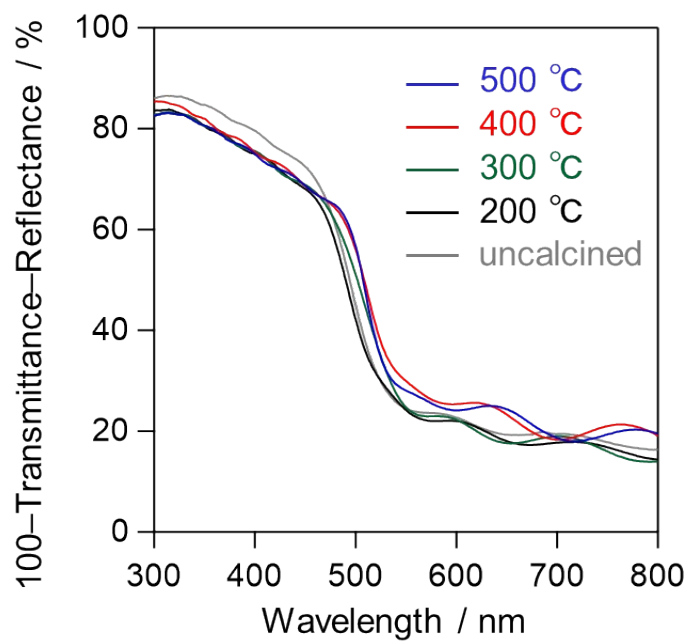
Author to whom correspondence should be addressed: [east@osaka-cu.ac.jp](mailto:east@osaka-cu.ac.jp)



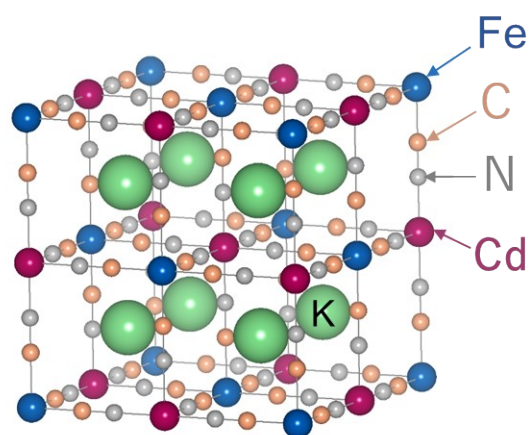
**Figure S1** XRD patterns of CdS electrode prepared by CBD method for (a) 0.5, (b) 1, (c) 2, and (d) 3 min.



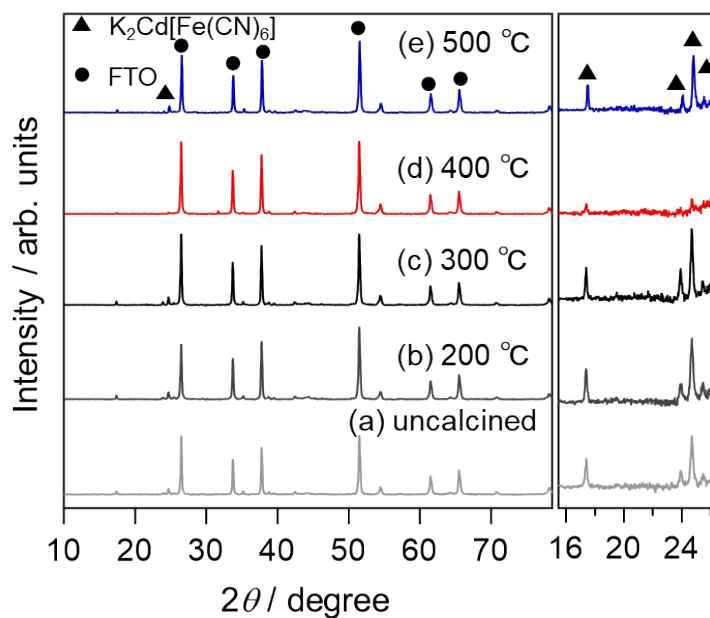
**Figure S2** Photoabsorption spectra of CdS electrodes prepared by CBD for 0.5, 1, 2, and 3 min.



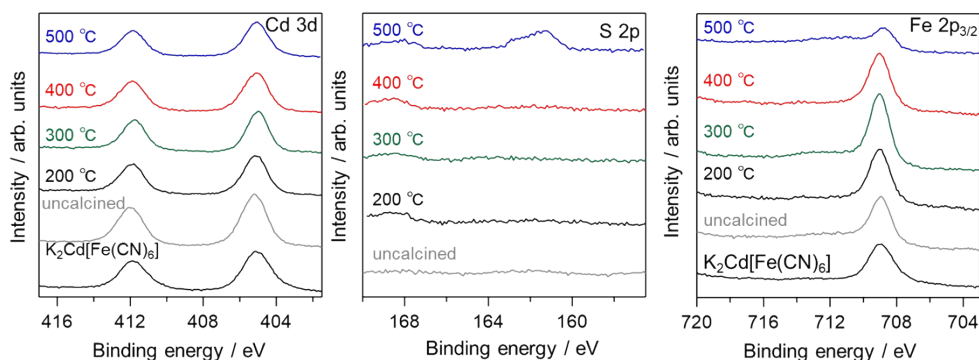
**Figure S3** Photoabsorption spectra of CdS electrodes before and after calcination in  $N_2$  flow at 200, 300, 400, and 500 °C for 30 min.



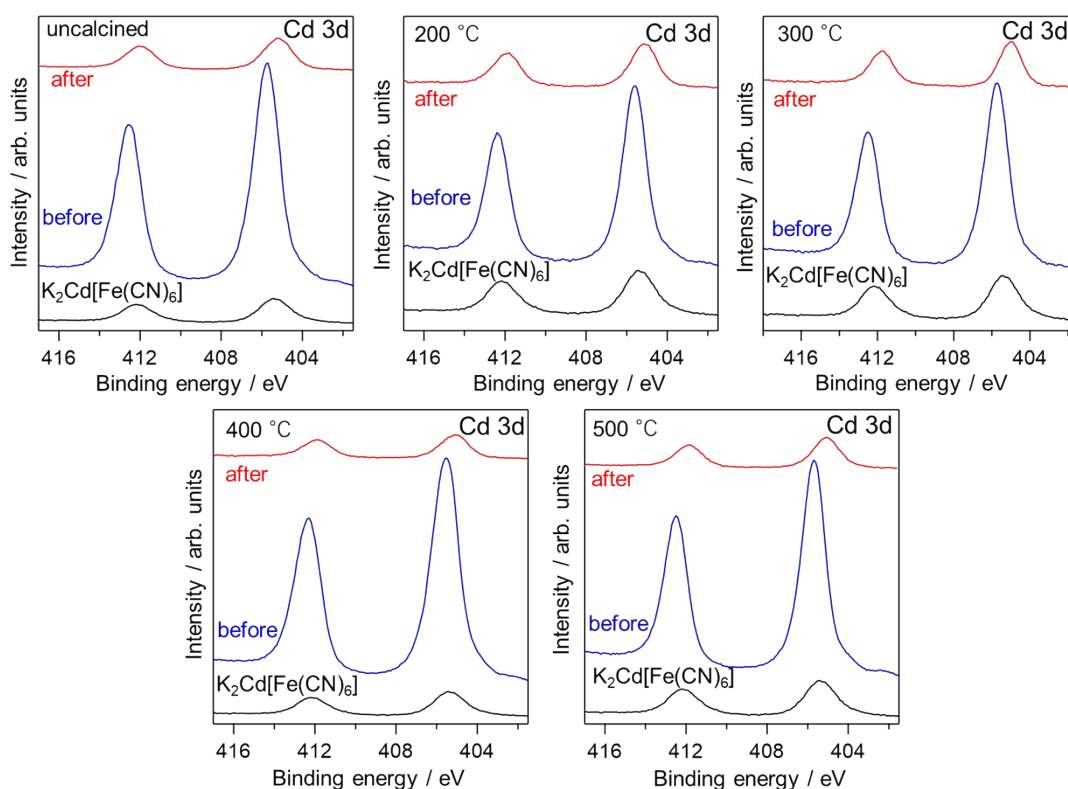
**Figure S4** Crystal structure of  $K_2Cd[Fe(CN)_6]$ .



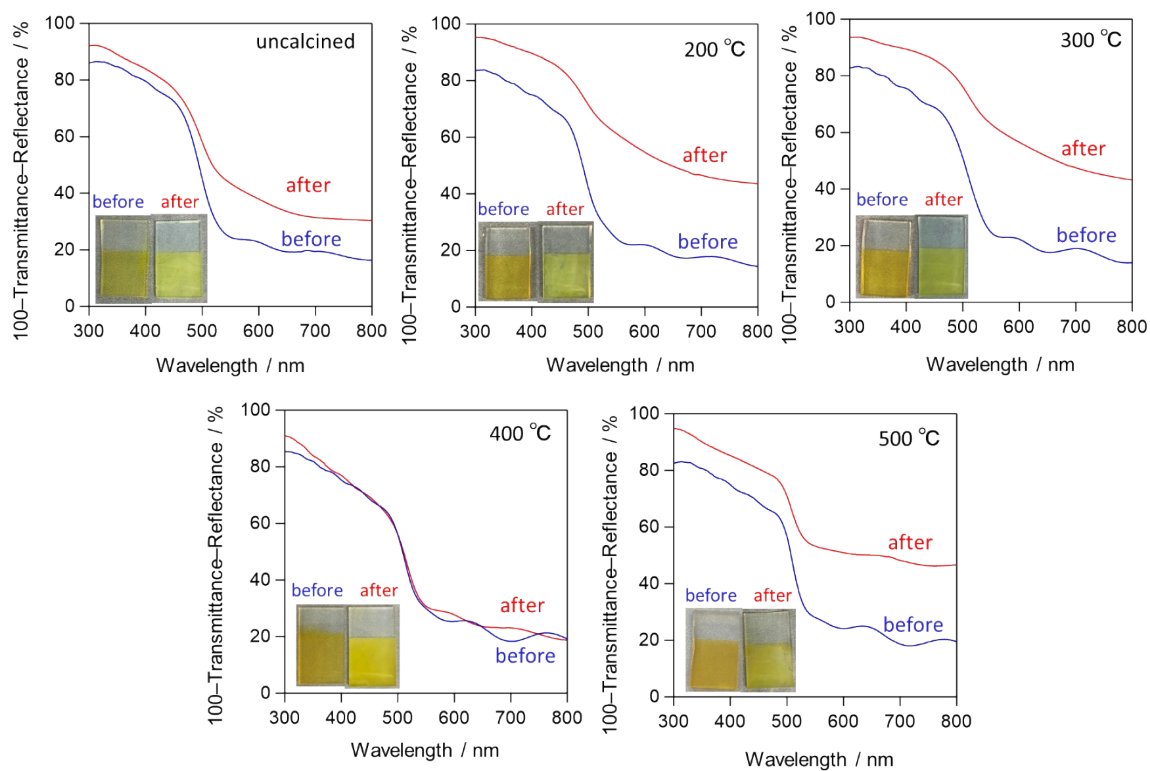
**Figure S5** XRD patterns of CdS electrodes prepared by CBD for 2 min with and (a) without the calcination in  $N_2$  flow at (b) 200, (c) 300, (d) 400 and (e) 500 °C for 30 min after chronoamperometry measurement in borate buffer solution (pH 8) containing  $K_4[Fe(CN)_6]$  (0.1 M) at  $-0.5$  V vs. Ag/AgCl under visible-light irradiation.



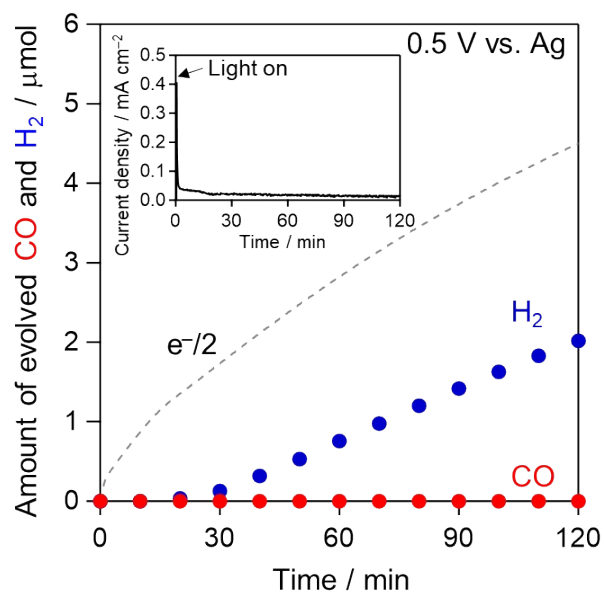
**Figure S6** XP spectra of Cd 3d, S2p and Fe 2p<sub>3/2</sub> region for CdS electrodes prepared by CBD for 2 min with and without the calcination in N<sub>2</sub> flow at 200, 300, 400 and 500 °C for 30 min after chronoamperometry measurement in borate buffer solution (pH 8) containing K<sub>4</sub>[Fe(CN)<sub>6</sub>] (0.1 M) at -0.5 V vs. Ag/AgCl under visible-light irradiation.



**Figure S7** XP spectra of Cd 3d region for CdS electrodes prepared by CBD for 2 min with and without the calcination in N<sub>2</sub> flow at 200, 300, 400 and 500 °C for 30 min before and after chronoamperometry measurement.



**Figure S8** Photoabsorption spectra of CdS electrodes before and after the reaction, along with photographs of CdS electrodes.



**Figure S9** Time course of gas evolution over the CoO<sub>x</sub>-loaded TaON electrode system under visible-light irradiation with an applied bias of 0.5 V vs. Ag counter electrode. Anode side: borate buffer solution containing 0.1 M K<sub>4</sub>[Fe(CN)<sub>6</sub>], CO<sub>2</sub> bubbling (pH 6.8). Cathode side: borate buffer solution, CO<sub>2</sub> bubbling (pH 6.8). The inset shows the changes in the photocurrent.