Supplementary Information (SI) for ChemComm.

Supplementary Information

Morphology optimization of CdS-Pt photocatalyst by photoetching for hydrogen production with high quantum efficiency

Haruki Nagakawa*[a,b,c] and Tetsu Tatsuma*[a]

[a]Institute of Industrial Science, The University of Tokyo, Tokyo 153-8505, Japan.

E-mail: haruki.nagakawa.hb88@vc.ibaraki.ac.jp; tatsuma@iis.u-tokyo.ac.jp

[b]Faculty of Applied Science and Engineering, Ibaraki University, Ibaraki 316-8511, Japan.

[c]Carbon Recycling Energy Research Center, Ibaraki University, Ibaraki 316-8511, Japan.

Experimental procedure

Sample Preparation.

Highly crystalline wurtzite CdS was synthesized by a flux treatment of zincblende CdS. Zincblende CdS particles were prepared by the precipitation method as follows. $Cd(NO_3)_2 \cdot 4H_2O$ (Kanto, 10 mmol) was dissolved in 100 mL of ethanol. Also, $Na_2S \cdot 9H_2O$ (Kishida, 10 mmol) was dissolved in 20 mL of water, and the solution was added dropwise to the $Cd(NO_3)_2$ solution and stirred for 30 min. The particles thus obtained were collected by centrifugation and washed several times with water and ethanol. The resulting product was dried at 60 °C for 1 day and ground in a mortar to obtain precipitated CdS. The prepared zincblende CdS (1.0 g) was mixed with $CaCl_2$ (7.4 g) and NaCl (2.6 g) in a sample tube. The mixture was transferred to an alumina crucible with a lid and the temperature was raised to 600 ºC in 1 h and held for 0 h (<1 min). The mixed salt was left to cool to room temperature, followed by dissolving it in water, and the CdS particles were collected by centrifugation. The particles were washed with water and ethanol at least five times each.

As a co-catalyst for CdS, we selected Pt nanoparticles because they are widely used for photocatalytic studies and therefore enable reliable comparison. Pt co-catalysts were deposited on CdS particles using the electron trap mediated deposition (ETD) method. In the ETD method, 30 mg of CdS particles were suspended in 5 mL of 20 vol% lactic acid solution and irradiated with visible light (430 nm, 48.9 mW cm^{-2}, CL-H1-430-9-1-B, Asahi Spectra) for 30 min. Electrons excited from the CdS valence band to the conduction band were used to reduce Cd(II) ions at the sulfide ion defects of the CdS particles to Cd metal. An H_2PtCl_6 aqueous solution (300 μmol L^{-1}) was added to the dispersion, and it was then stirred under inert gas atmosphere in the dark for 30 min for the galvanic replacement of Cd with Pt. The CdS-Pt particles thus obtained were then collected by centrifugation and washed with water. Since the metallic Cd was fully replaced with Pt, CdS was not covered with metallic Cd.[S1]

The CdS-Pt particles were photoetched by using the same setup as that used in the hydrogen production experiments. A 30 mg of the synthesized CdS-Pt particles was dispersed in 5 mL of 20 vol% aqueous lactic acid solution, and flushed with N_2 or Ar gas. The sample was then irradiated with visible light (430 nm, 48.9 mW cm^{-2}) for 60 min. The photoetched CdS-Pt particles were collected by centrifugation and washed with water.

S1. Y. Chen, W. Zhong, F. Chen, P. Wang, J. Fan and H. Yu, *J. Mater. Sci. Technol.*, 2022, **121**, 19–27.

Characterization.

The prepared photocatalysts were characterized by X-ray diffraction (XRD; Ultima IV, Rigaku), diffuse reflection spectroscopy (DRS; V-670, Jasco), scanning electron microscopy (SEM; JSM-7500FA microscope, JEOL) and X-ray photoelectron spectroscopy (XPS; JPS-9010, JEOL). In the XPS measurements, the samples were adhered to a carbon tape. The obtained spectra were calibrated to align the C 1s peak at 285.0 eV. Curve fitting was performed using a Lorentzian distribution function model. Binding energies of the orbitals used for curve fitting are as follows: Cd (sulfide) $3d_{5/2}$ at 405.2 eV, Cd (sulfide) $3d_{3/2}$ at 411.9 eV, Cd (oxide) $3d_{5/2}$ at 404.6 eV, Cd (oxide) $3d_{3/2}$ at 411.3 eV, S $2p_{3/2}$ at 161.2 eV, S $2p_{1/2}$ at 162.6 eV, Pt $4f_{7/2}$ at 71.0 eV, and Pt $4f_{7/2}$ at 74.0 eV. Corrosion of the particles was analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES; ICPS-7510, Shimadzu). The supernatant of the reaction suspension was collected and filtered after photocatalytic reactions. The sample was then diluted to at least 8 mL, as required for analysis. The analysis was performed three times using the diluted solution, and the average value of the dissolved amount was determined. The dissolution ratio was calculated on the basis of the detected Cd^{2+} ion concentration and the amount of Cd in the particles added to the reaction solution.

Photocatalytic Reactions.

Gas chromatographs (490 micro GC, Agilent Technologies; GC-2014AT, Shimadzu) were used for determination of the amount of hydrogen gas evolved in the photocatalytic reactions. A High Performance Liquid Chromatograph (LC-40 system with CDD, Shim-pack SCR-102(H), Shimadzu) was used for determination of the amounts of pyruvic acid, acetic acid and formic acid as oxidation products.

The external quantum yield (EQE) was evaluated on the basis of eq (1).

$$EQE = \frac{The\ number\ of\ reacted\ electrons}{The\ number\ of\ incident\ photons} \times 100\ [\%] \# (1)$$

The number of incident photons was measured using a spectroradiometer USR-45V-14 (Ushio). The number of reacted electrons was calculated from the amount of hydrogen evolved by the two-electron reduction.

Optimization of the Reaction Conditions.

The concentration of $[PtCl_6]^{2-}$ for the Pt deposition process and the concentration of lactic acid for the photoetching process were optimized in terms of the resultant hydrogen evolution rate under light irradiation (430 nm, 12.1 mW cm^{-2}) for 60 min (Fig. S4).

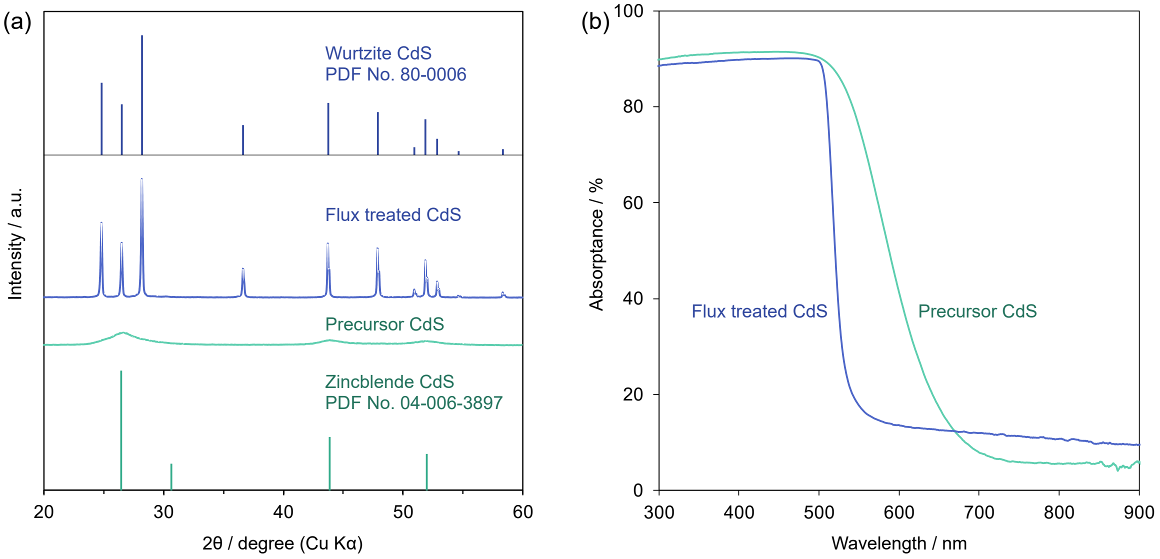

Fig. S1 (a) XRD patterns and (b) diffuse reflection spectra of the CdS particles before and after the flux treatment.

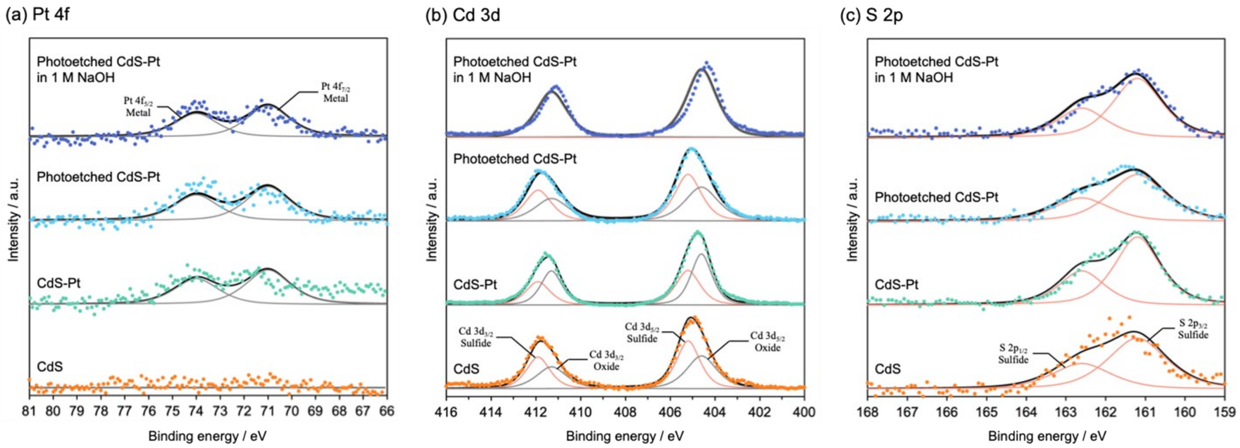

Fig. S2 XPS spectra in the (a) Pt 4f, (b) Cd 3d and (c) S 2p regions of the prepared CdS, CdS-Pt and photoetched CdS-Pt photocatalysts.

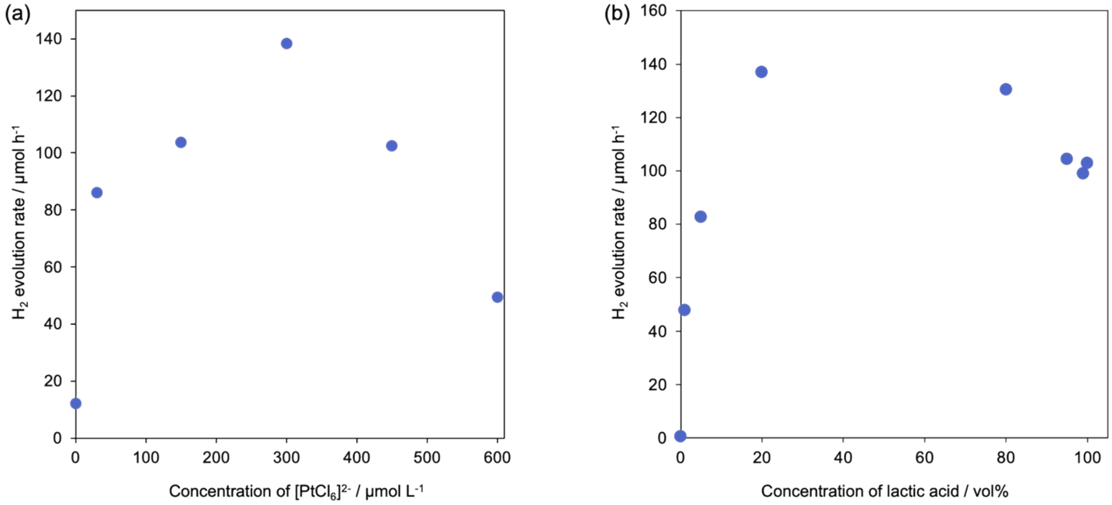

Fig. S3 Hydrogen evolution rates of the CdS-Pt photocatalysts. (a) Dependence on the $[PtCl_6]^{2-}$ concentration during the Pt loading process. Hydrogen evolution rates were measured in a 20 vol% lactic acid solution. (b) Dependence on the lactic acid concentration during the photoetching process. Pt was deposited in a solution containing 300 µmol L^{-1} $[PtCl_6]^{2-}$ and 20 vol% lactic acid.

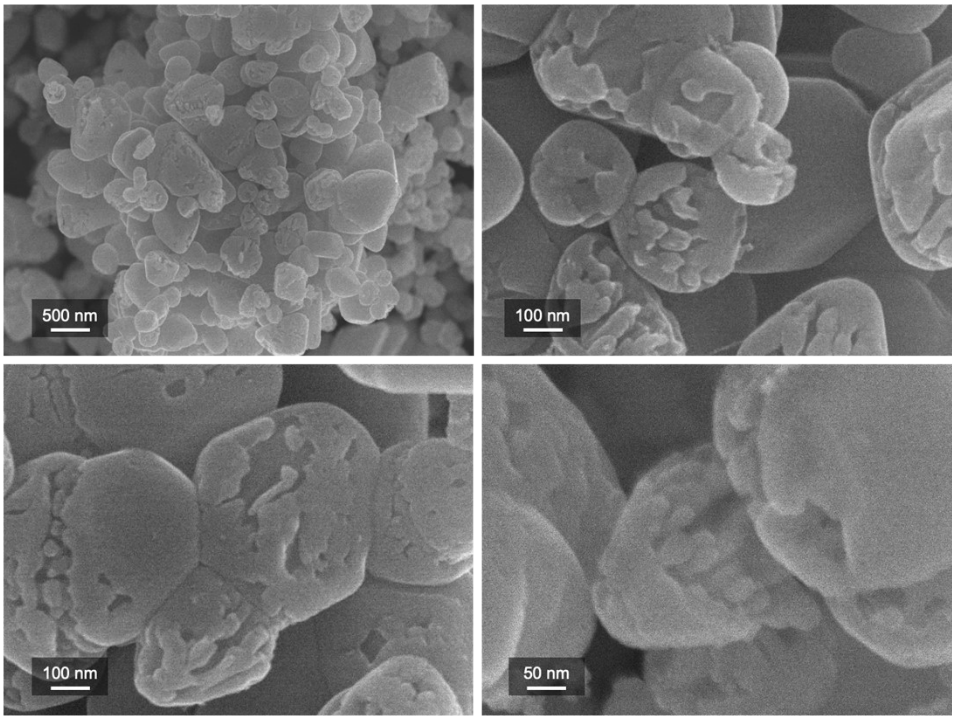

Fig. S4 SEM images of CdS-Pt photoetched in the presence of 20 vol% lactic acid for 60 min under 48.9 mW cm^{-2} visible light (430 nm).