Effective Photocatalytic Hydrogen Evolution by Cascadal Carrier Transfer in the Reverse Direction

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ABSTRACT: Visible-light-responsive photocatalysts used in the highly efficient hydrogen production exhibit several disadvantages such as photocorrosion and fast recombination. Because of the potential important applications of such catalysts, it is crucial that a simple, effective solution is developed. In this respect, in this study, we combined SiC (β modification) and TiO2 with CdS to overcome the challenges of photocorrosion and fast recombination of CdS. Notably, we found that when irradiated with visible light, CdS was excited, and the excited electrons moved to the conduction band of TiO2, thereby increasing the efficiency of charge separation. In addition, by moving the holes generated on CdS to the valence band of SiC, in the opposite direction of TiO2, photocorrosion and fast recombination were prevented. As a result, in the sulfide solution, the CdS/SiC composite catalyst exhibited 4.3 times higher hydrogen generation ability than pure CdS. Moreover, this effect was enhanced with the addition of TiO2, giving 10.8 times higher hydrogen generation ability for the CdS/SiC/TiO2 catalyst. Notably, the most efficient catalyst, which was obtained by depositing Pt as a cocatalyst, exhibited 1.09 mmol g\(^{-1}\) h\(^{-1}\) hydrogen generation ability and an apparent quantum yield of 24.8%. Because water reduction proceeded on the TiO2 surface and oxidative sulfide decomposition proceeded on the SiC surface, the exposure of CdS to the solution was unnecessary, and X-ray photoelectron spectroscopy confirmed that photocorrosion was successfully suppressed. Thus, we believe that the effective composite photocatalyst construction method presented herein can also be applied to other visible-light-responsive powder photocatalysts having the same disadvantages as CdS, thereby improving the efficiency of such catalysts.

1. INTRODUCTION

Because of the fast population increase and technology development experienced nowadays, energy usage is constantly rising. Currently, the main source of energy is fossil fuels, the excessive use of which causes various problems such as energy exhaustion, global warming, and environmental pollution. Therefore, it is crucial to develop a method to generate renewable energy that does not emit pollutants and carbon dioxide. In addition, the formation of hydrogen sulfide is a local problem arising in places such as volcanic zones, geothermal power plants, and oil-refining plants. At present, the main desulfurizing processing method is the Claus process, which includes multiple steps and intense conditions. Therefore, a novel method that employs simpler and milder conditions is required.

In this respect, we propose the use of photocatalytic hydrogen generation and hydrogen sulfide decomposition. A photocatalytic reaction that proceeds under sunlight is very attractive because it can generate hydrogen, which has drawn significant attention as a clean energy source. To achieve an efficient photocatalytic reaction, it is required to utilize not only ultraviolet light with high energy but also visible light. Therefore, we considered the use of cadmium sulfide, which has a strong reducing power and visible light responsiveness. However, cadmium sulfide (CdS) exhibits several disadvantages such as fast recombination due to a narrow band gap and photocorrosion by the shallow valence band (VB) position. As a possible solution to the recombination issue, it has been reported that by combining CdS with TiO2 excited electrons generated on CdS move onto TiO2, thereby increasing the efficiency of charge separation and improving the hydrogen generation ability. However, this solution is not effective in the case of sulfur decomposition.

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in the system employed in these studies, TiO₂ has been used as an acceptor that only receives electrons, which eventually leads to lack of separation of the holes on CdS. In addition, reports have indicated the suppression of photocorrosion using graphene sheets or shells of specific materials, such as K₂[ CdFe(CN)₆]₄ or SiO₂. However, in these cases, it is possible that the charge transfer in the sheet or the shell slows down the reaction. Furthermore, these methods require complete surface coverage and morphology control. Therefore, simpler approaches for the suppression of photocorrosion are needed.

Thus, in this work, we have combined SiC and TiO₂ with CdS in an effort to overcome the fast recombination and photocorrosion challenges. SiC is a stable photocatalyst, which contains no heavy metals and has attracted an increasing amount of attention in the recent years for its use in semiconductor devices. In addition, TiO₂, the most well-known photocatalyst, is a stable and inexpensive material with a conduction band (CB) position suitable for hydrogen production. Figure 1 displays the schematic illustration of hydrogen evolution with the photocatalyst prepared in this study, in which SiC acted as a sink for the photogenerated holes on CdS. Indeed, there are studies, which have reported the movement of the hole to the VB of SiC. Notably, the reaction scheme of the SiC composite photocatalyst was discussed in detail, with a focus on the movement of the hole to the VB of SiC. Notably, the apparent quantum yield was 24.8%.

2. RESULTS AND DISCUSSION

2.1. XRD Patterns of the Prepared Photocatalysts. Figure 2 displays the XRD patterns of the prepared CdS/SiC/TiO₂ (1:1:1) composite and the respective pure materials. The characteristic diffraction peaks of CdS were detected at 2θ angles of 26.6°, 43.9°, and 52.1°, which can be indexed to the (111), (220), and (311) crystal planes, respectively, of β-CdS (cubic) (JCPDS PDF no. 04-006-3897). In the case of SiC, the characteristic peaks found at 2θ angles of 35.6° and 41.3° were indexed to the (111) and (200) crystal planes, respectively, of β-SiC (cubic) (JCPDS PDF no. 00-029-1129). However, very small peaks from hexagonal SiC appeared at 33.6° and 37.9° and corresponded to the (101) and (103) crystal planes, respectively, of α-SiC (hexagonal) (JCPDS PDF no. 00-022-1273). In the case of TiO₂, the diffraction peaks detected at 2θ angles of 25.3°, 37.9°, 48.0°, 54.2°, and 54.8° were indexed to the (101), (004), (200), (105), and (211) crystal planes, respectively, of tetragonal anatase TiO₂ (JCPDS PDF no. 00-064-0863). Considering the peaks of the CdS/SiC/TiO₂ (1:1:1) composite photocatalyst and corresponding pure materials, it can be assumed that the prepared composites consist of β-CdS, β-SiC, and TiO₂. Furthermore, the peak detected at 28.2° suggested that a small part of anatase TiO₂ was transferred to rutile TiO₂.

The XRD patterns for the CdS/SiC composite photocatalysts with different composite ratios are shown in Figure S1. As can be observed, the proportion of CdS increased with the weakening of the peak intensity of SiC. In addition, because the CdS peak appeared rather wide, it was assumed that the crystallite size was larger than that of SiC. Moreover, from the XRD patterns of the photocatalysts in combination with TiO₂ (Figures S2 and S3), it can be seen that the peak intensity changes according to the composite ratio. However, in the case of the TiO₂ composite, a crystal transition took place, as shown in Figure 2, because of the sintering operation, and crystallites grew, thereby making the CdS peak sharp. The same tendency was observed also in the case of the CdS/TiO₂ composite, which did not contain SiC (Figure S4).
2.2. Ultraviolet–Visible DRS. DRS spectra of the prepared composites and the respective pure materials are shown in Figure 3. The absorbance of each composite was a combination of the absorbances of the individual pure materials. The band gap and absorption edge of each pure material were estimated by extrapolation from the intersection of the slope and the flattened line of the spectra (Figures S5–S7). The calculated band gaps of CdS, SiC, and TiO₂ were found to be 2.12, 2.52, and 3.23 eV, respectively, from which the absorption edges were calculated to be 587, 494, and 385 nm, respectively. Figure 3 shows that SiC absorbs at a wavelength longer than 494 nm, which does not contribute to the reaction characteristics for the indirect band gap. Therefore, the band gap of the main absorption between the VB and the CB was found to be 2.52 eV. In the photocatalytic hydrogen generation experiment, a light source with a wavelength longer than 420 nm was employed to confirm that there was no photoexcitation on TiO₂, and the main charge separation was performed on the CdS photocatalyst.

DRS spectra with different composite ratios are shown in Figures S5–S8. When SiC was included in the composite, the CdS absorption became weaker with the increasing proportion of SiC (Figure S8). Similarly, in the case of TiO₂, the absorption of CdS and SiC became weaker as the proportion of TiO₂ increased (Figures S9–S11).

2.3. Fluorescence Spectroscopy Analysis. From the fluorescence spectra displayed in Figure 4, it can be seen that the CdS fluorescence appearing from 510 to 550 nm was quenched by the presence of SiC or TiO₂ in the composite. The quenching due to the presence of TiO₂ suggests that the electrons excited by CdS were transferred to the CB of TiO₂ (Figure 1). By contrast, the quenching due to the presence of SiC indicates that the hole generated in CdS moved to the VB of SiC. We concluded that the electrons and holes were inactivated after the transfer because of nonradiative inactivation.

2.4. Transmission Electron Microscopy (TEM) Images and Models of the Prepared Photocatalysts. Figure 5 displays the TEM images of the prepared composite photocatalysts and energy-dispersive X-ray spectroscopy (EDS) mapping of the CdS/SiC/TiO₂ composite (1:1:1, containing 1 wt % Pt). The TEM image of pure CdS (Figure 5a) clearly showed an agglomeration of fine particles of about 5–20 nm. After compositing with SiC (Figure 5b), the fine CdS particles with a diameter of about 5–20 nm were deposited on the SiC nanoparticles with a size of about 50–200 nm, thereby indicating that there was no change in the particle size of CdS before and after the composite formation. The TEM image of CdS/SiC/TiO₂ shows fine TiO₂ particles with a size of about 5–20 nm on the CdS/SiC photocatalyst (Figure 5c). Furthermore, the TEM and EDS mapping images of the CdS/SiC/TiO₂ composite loaded with Pt (Figure 5d) indicated that CdS dispersed through SiC in the core and subsequently precipitated and that TiO₂ was composited in a way that it partly covered the CdS/SiC composite. We concluded that a part of the Pt is distributed around SiC, most specifically around CdS, because of the use of a visible-light-induced (λ > 420 nm) photodeposition method, with CdS absorbing most of the irradiated light. However, as TiO₂ was composited to cover CdS, the area where TiO₂ was present was considered to have received electrons from CdS (Figure 1), leading to the precipitation of Pt. In other words,
although the distribution of Pt depended on the position of CdS, Pt was deposited on the TiO$_2$ surface because of electron transfer from CdS, which occurred in the area covered with TiO$_2$. Another important observation from the TEM images was that, in all composite forms, the SiC surface was partially exposed. Considering the photocatalytic reaction occurring on the prepared composite photocatalyst, we concluded that it would be necessary to expose the SiC surface because the oxidation reaction proceeds on SiC.

2.5. Photocatalytic Activity. Figure 6 presents the relationship between the photocatalyst combination ratio and the hydrogen production amount. As can be seen, the most effective combination ratio was that of the CdS/SiC/TiO$_2$ (1:1:1) composite photocatalyst. Generally, it was found that when either SiC or TiO$_2$ was combined with CdS, the amount of hydrogen generation increased. Furthermore, when both were present in the composite, a further improvement of the hydrogen production amount was observed. However, an excessive amount of SiC caused weakening of the CdS absorption and a decrease in the amount of hydrogen production (Figure S8). By contrast, deficient SiC led to insufficient transfer of holes generated on CdS and poor SiC surface exposure where the oxidation reaction takes place, thereby reducing the hydrogen generation efficiency. Moreover, an excessive amount of TiO$_2$ also caused decreased hydrogen generation efficiency because of the weak CdS absorption and the relatively smaller SiC surface on which the oxidation reaction can proceed (Figures S9–S11). By contrast, an insufficient composite amount of TiO$_2$ caused the separation of excited electrons to become deficient and the efficiency of charge separation to decrease. Therefore, the visible-light absorption was mainly carried out by CdS, whereas the oxidation and reduction reactions proceeded on the SiC and TiO$_2$ surfaces, respectively, because of the carrier movement.

To examine the improvement of efficiency in greater detail, the cocatalyst was deposited on the main composite, and the action spectra were recorded. Table 1 shows the hydrogen production rates obtained using the synthesized composite photocatalysts: pure CdS, CdS/TiO$_2$ (1:1), CdS/SiC (1:1), and CdS/SiC/TiO$_2$ (1:1:1), both with and without the Pt cocatalyst. We found that the CdS/TiO$_2$ (1:1) composite exhibited 5.6 times higher hydrogen evolution rate (85.2 μmol h$^{-1}$ g$^{-1}$) than pure CdS. This improvement was due to transfer of excited electrons from CdS to the CB of TiO$_2$, thereby preventing recombination on CdS and increasing the efficiency of charge separation. This assumption was supported by the photoluminescence spectra shown in Figure 4.

For CdS/SiC, considering the relative positions of the CdS and SiC bands, we can conclude that efficiency improvement was caused by the transfer of holes generated on CdS to the VB of SiC. Therefore, the CdS/SiC composite exhibited hydrogen generation ability of 65.6 μmol g$^{-1}$ h$^{-1}$, which is 4.3 times higher than that of pure CdS. However, Figure 3 shows that because SiC has absorption of 494 nm, efficiency may also be improved by the influence of electrons excited by SiC. This assumption is supported by the action spectra of CdS and CdS/SiC (Figure 7), which show that although no SiC excitation occurred at wavelengths of $\lambda = 500$ and 540 nm, the efficiency of CdS/SiC was improved compared to that of pure CdS. On the basis of this observation, we concluded that the hole transfer to SiC VB was responsible for improving the efficiency of hydrogen evolution.

On the basis of the above observations, we proposed two possible mechanisms for hydrogen evolution and sulfide...
decomposition: one that includes SiC excitation (Figure 8a) and the other occurring in a wavelength region that does not excite SiC (Figure 8b). The hydrogen generation ability can be explained not only by SiC excitation but also by the fact that holes tend to move to more stable band positions. Because SiC is an n-type semiconductor,45 holes cannot move in SiC. However, when the substance to be oxidized approaches within the effective particle diameter of holes present on SiC, the reaction can proceed. Thus, the CdS/SiC/TiO2 photocatalyst clearly showed higher activity in terms of hydrogen production ability and quantum yield than the other two kinds of composites shown in Figures 7 and 8 because the carriers moved in the opposite direction, as the destination for electron transfer was the CB of TiO2 and that for hole transfer was the VB of SiC (Figure 8).

For the photocatalysts after Pt deposition, the hydrogen generation ability was the same as that before Pt deposition, improved with the combination of TiO2 and SiC, and further improved upon formation of a tricomposite photocatalyst. However, after Pt deposition, the photocatalysts, in which TiO2 was composited, showed smaller improvement than the ones that did not contain TiO2. Although Pt acts as an electron acceptor, promotes charge separation, and lowers overvoltage, it is assumed that such a tendency was obtained because charge separation promotion induced by Pt was the same as that of TiO2. The most efficient CdS/SiC/TiO2 composite photocatalyst with the Pt cocatalyst exhibited hydrogen production ability of 1090.4 μmol g−1 h−1, which is 7.4 times higher than that of pure CdS with the Pt cocatalyst. In addition, the apparent quantum yields of all composite photocatalysts reached 0% at 580 nm, indicating that hydrogen was produced by the excited electrons produced by absorption of CdS, whereas the absorption derived from the indirect band gap of SiC was not used to excite electrons.

2.6. Photocorrosion Suppression. In the synthesized photocatalysts, CdS was sandwiched between SiC and TiO2, thereby reducing CdS exposure, which enabled suppression of photocorrosion and recombination between the CB of TiO2 and VB of SiC. To confirm the stability of the composite photocatalyst, a hydrogen production experiment was conducted for 24 h using the most efficient composite photocatalyst (CdS/SiC/TiO2 1:1:1 with Pt 1 wt %). Figure 9 shows the relationship between the hydrogen evolution amount and the reaction time. The presence of a sacrificial reagent in the experiment confirmed that the hydrogen production rate remained constant.

The stability of the photocatalyst in pure water and the extent of photocorrosion suppression were examined by visible-light irradiation (λ > 420 nm). Hydrogen was not detected from the reaction using either photocatalyst under visible-light irradiation, probably due to both kinetic and thermodynamic factors. In particular, the VBs of CdS and SiC were shallower than those of the oxide photocatalysts, which weakened the driving force. Furthermore, as the potential could not reach that of the oxygen generation reaction proceeding with two electrons, the holes were not consumed and no hydrogen evolution occurred. In addition, although the generally assumed oxygen generation reaction proceeded with four-electron oxidation, which explains the VB position of CdS and SiC from the thermodynamic viewpoint, the reaction did not proceed probably because the electrons were inactivated before storing the four excitation electrons, owing to the insufficient intensity of the irradiation light.46

The X-ray photoelectron spectroscopy (XPS) spectra of the photocatalysts used in this experiment were obtained before and after light irradiation, and the XPS peaks of elemental sulfur are shown in Figure 10. The photocatalyst before use showed a peak corresponding to S2− in the bound state (Figure 10a) and a peak derived from 2p3/2 and 2p1/2. By contrast, the sulfur peak of pure CdS after use shifted to the higher energy side (Figure 10b), indicating that S2− was oxidized by light.
irradiation, thereby leading to the precipitation of single sulfur (S0). However, for the CdS/SiC/TiO2 composite photocatalyst, no such shift was observed because of the elution suppression due to reduced CdS exposure and carrier transport to SiC, such that the generated holes on CdS were no longer used for photocorrosion.

3. CONCLUSIONS

In this study, we successfully improved the efficiency of the hydrogen generation reaction accompanied by sulfide decomposition by compositing SiC and TiO2 with CdS. The most efficient catalyst, which was obtained after depositing Pt as a cocatalyst, achieved 50 times higher hydrogen production rate than pure CdS and 24.8% apparent quantum yield using a 420 nm light source. In this photocatalytic reaction, electrons excited on CdS were separated into the CB of TiO2, and the generated holes were separated into the VB of SiC. Moreover, via this cascadal carrier transport, fast recombination of CdS and photocorrosion was successfully suppressed. All in all, we believe that the photocatalyst construction presented in this study can also be applied to other visible-light-responsive photocatalysts and expect that similar efficiency improvement and photocorrosion suppression would be observed.

4. EXPERIMENTAL SECTION

4.1. Materials. The synthesis of the photocatalysts was carried out according to a previously reported simple two-step method. The CdS/SiC nanocomposites were prepared via a facile wet chemistry approach. A requisite amount of SiC powder (β modification, Wako Pure Chemical Industries Ltd., Tokyo, Japan) was dispersed in 100 mL of 0.1 M NaOH ethanol solution and mechanically stirred for 1 h. Then, 3.08 g of Cd(NO3)2·4H2O (Kanto Chemical Co., Inc., Tokyo, Japan) was fully dissolved in ethanol (100 mL) and added to the SiC dispersed mixture. The resulting suspension of SiC and cadmium ions was mechanically stirred for 1 h. Thereafter, 20 mL of an aqueous solution containing 2.4 g Na2S·9H2O (Wako Pure Chemical Industries Ltd., Tokyo, Japan) was added dropwise to the aforementioned mixture, and the agitation was continued for 1 h. The formed composite powder was filtered, washed with pure ethanol and ultrapure water, and dried at 353 K for 24 h.

The CdS/SiC/TiO2 composites were synthesized via a sol-gel process at room temperature through the hydrolysis of titanium isopropoxide (Kanto Chemical Co., Inc., Tokyo, Japan) in the presence of the CdS/SiC composite. First, the CdS/SiC powder was dispersed in 100 mL of isopropanol and stirred for 30 min. Then, the required amount of titanium isopropoxide was added dropwise, and the suspension was stirred for another 30 min. Pure H2O was subsequently added dropwise, and the resulting mixture was stirred for 1 h. The prepared composite powder was filtered, dried, and calcined at 673 K for 2 h under air flow to increase the crystallinity of TiO2. Composites with different molar ratios were fabricated according to this method by adjusting the amounts of SiC powder and titanium isopropoxide used. For comparison, CdS alone was prepared via a similar method, which excluded the addition of SiC. In this approach, 1 wt % Pt was deposited on the composite photocatalysts using H2PtCl6·6H2O (Kanto Chemical Co., Inc., Tokyo, Japan) through a photodeposition method under visible light (λ > 420 nm) in methanol solution.

The synthesized composite photocatalysts were characterized by XRD (sample horizontal type multipurpose X-ray diffractometer, Ultima IV, Rigaku, Tokyo, Japan), DRS (U-3900/3900H spectrophotometer, Hitachi High-Tech Science, Tokyo, Japan), fluorescence spectroscopy (FP-6600 fluorophotometer, JASCO, Tokyo, Japan), TEM/EDS analysis (EM-002BF, Topcon, Tokyo, Japan), and XPS analysis (JPS-9010MC, Mg anode, JEOL Ltd., Tokyo, Japan).

4.2. Photocatalytic Reactions. Photocatalytic experiments were conducted in a gas-closed circulation system equipped with a vacuum line. Each photocatalyst sample (0.4 g) was suspended in 240 mL of aqueous solution containing 0.1 M sodium sulfate and sodium sulfide. A 300 W Xe lamp (Lamp House R300-3J) with an ultraviolet (UV) cutoff filter (λ > 420 nm) was used as a visible-light source. A 3 mL aliquot of the evolved gas was collected through a gas-sampling port that was directly connected to a gas chromatograph (GC-8A Shimadzu, Kyoto, Japan). A Xe lamp with band-pass filters (λ = 420, 460, 500, 540, and 580 nm, Asahi Spectra, Tokyo, Japan) was employed in the determination of the apparent quantum yield, which was calculated according to eq 1.

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\text{Apparent quantum yield} \% = \frac{\text{number of reacted electrons}}{\text{number of incident photons}} \times 100
\]
The number of incident photons was measured using a silicon photodiode detector (S1337-1010BQ, Bunkoukeiki Co., Ltd., Tokyo, Japan), and the number of reacted electrons was calculated from the evolved hydrogen.

4.3. Durability Evaluation. To confirm the photocorrosion suppression, we conducted light irradiation experiments in pure water. Each photocatalyst sample (0.03 g) was suspended in a 23 mL vial bottle containing 15 mL of pure water, followed by degassing the reaction mixture by Ar bubbling. A 300 W Xe lamp with an UV cutoff filter (λ > 420 nm) was used as the visible-light source. A 0.1 mL aliquot of the evolved gas was collected by a gas-tight syringe and then injected into the gas chromatograph for analysis of the generated gas. XPS analysis was performed on the photocatalyst both before and after light irradiation.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b02449.

Supplementary data including XRD patterns, calculated band gaps, and DRS spectra of the composite photocatalysts (PDF)

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Notes

The authors declare no competing financial interest.

■ ABBREVIATIONS

XRD, X-ray diffraction; DRS, diffuse reflection spectroscopy; FE-TEM, field emission-transmission electron microscope; EDS, energy dispersive X-ray spectroscopy; XPS, X-ray photoelectron spectroscopy

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