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**The dispersion of TiO$_2$ modified by the accumulation of CO$_2$ molecules in water: An effective medium for photocatalytic H$_2$ production**

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(Abstract)

The photocatalytic H$_2$ production from water with TiO$_2$ can be noticeably enhanced by the presence of both dense phase CO$_2$ and a surfactant of sodium dodecyl sulfate, being larger by more than one order of magnitude than that from water with TiO$_2$ alone. The surface of TiO$_2$ may be modified by the accumulation of CO$_2$ molecules assisted by the TiO$_2$- and CO$_2$-philic surfactant, changing its photocatalytic activity.

Introduction

Recently, H$_2$ has been investigated as a storable, clean, and environmental-friendly fuel for future energy systems.\(^1\) Photocatalytic water splitting into H$_2$ has been considered as a significant and attractive solution to solve the global energy and environmental problems.\(^2\) It is well known that TiO$_2$ is a cheap, nontoxic, stable and efficient photocatalyst. However, the intrinsic activity of TiO$_2$ is not sufficient due to the facile recombination of photo-generated electron-hole pairs, which is thermodynamically favored\(^3-5\) and TiO$_2$ is to some extent constrained by its wide band gap (3.2 eV), which requires ultraviolet irradiation for photocatalytic activation. In order to solve these problems, many researchers have paid much attention to the modification of electronic and optical properties of TiO$_2$, such as surface modification via organic
materials/semiconductor coupling and band gap modification with metal and nonmetal dopants. In addition, various oxidizing sacrifice agents are used in order to suppress the reverse reaction of \( \text{O}_2 \) and \( \text{H}_2 \) formed back to \( \text{H}_2\text{O} \).

The present authors have been investigating the effects of dense phase \( \text{CO}_2 \) in different chemical reactions, which can act as a promoter as well as a solvent. One of significant findings is that \( \text{CO}_2 \) molecules dissolved in organic substrates and solvents interact with some particular functional groups of substrates and modify their reactivity. This does promote the reaction rate and change the product selectivity in hydrogenation reactions of \( \alpha,\beta \)-unsaturated aldehydes and aromatic nitro compounds. Heck coupling and Diels-Alder reaction. Furthermore, the \( \text{CO}_2 \) molecules could affect the properties of supported metal particles as suggested by \textit{in situ} high pressure optical absorption measurements in dense phase \( \text{CO}_2 \) medium.

Those previous works with either \( \text{TiO}_2 \) or dense phase \( \text{CO}_2 \) have stimulated us to investigate the possibility of synergistic effects of the two species in the production of \( \text{H}_2 \) by photocatalytic water splitting. In the present work, the production of \( \text{H}_2 \) has been studied with different media including \( \text{TiO}_2 \), dense phase \( \text{CO}_2 \), and/or surfactant. The surfactant has been used to form \( \text{CO}_2 \) micelles, which are adsorbed on the surface of \( \text{TiO}_2 \). This work will report an interesting result that the \( \text{H}_2 \) production can be promoted by synergistic effects of dense phase \( \text{CO}_2 \) and a surfactant of sodium dodecyl sulfate (SDS) by more than one order of magnitude compared to the medium with \( \text{TiO}_2 \) alone.

\textbf{Results and discussion}

The authors tested different reaction media in the presence of dense phase \( \text{CO}_2 \) and/or a surfactant of SDS. The results obtained are shown in Figure 1. The rate of \( \text{H}_2 \) production observed in the present reaction runs was small. The authors used a laboratory designed high pressure stainless steel reactor of 50 cm\(^3\) as described in Experimental section. The reaction mixture was illuminated by a high-pressure Hg lamp through a quartz window of 1 cm in diameter attached to the reactor. Therefore, the whole volume of reaction mixture was not necessarily illuminated. This is a main reason for the small rate of \( \text{H}_2 \) production obtained. The rate of \( \text{H}_2 \) production was enhanced from 93 \( \mu \text{L g}^{-1} \text{ h}^{-1} \) to 158 \( \mu \text{L g}^{-1} \text{ h}^{-1} \) when 3 MPa \( \text{CO}_2 \) was introduced to pure water. Interestingly, the rate of \( \text{H}_2 \) production was noticeably increased to 1285 \( \mu \text{L g}^{-1} \text{ h}^{-1} \) when SDS was also added to the medium. The presence of both dense phase \( \text{CO}_2 \) and SDS was indispensable for promoting the photocatalytic \( \text{H}_2 \) production with \( \text{TiO}_2 \) in aqueous
medium. When dense phase CO$_2$ is present, the pH of the aqueous medium decreases and some acidic species such as H$_2$CO$_3$ and HCO$_3^-$ are formed$^{18}$; the pH decreases to about 3 at CO$_2$ pressures > 3 MPa.$^{19-20}$ The pH and the formation of these acidic species may be important factors determining the rate of photocatalytic H$_2$ production.$^{21-24}$ When SDS surfactant is used, TiO$_2$ powders can be dispersed well in water. From the results of Figure 1, however, the acidic nature and the stable TiO$_2$ dispersion are not responsible for the even larger H$_2$ production in the presence of both dense phase CO$_2$ and SDS, which should act in a synergistic way in modifying the properties of TiO$_2$. We conducted control reaction runs using Ar instead of CO$_2$ under the same conditions. The reactions were made with TiO$_2$ in H$_2$O-SDS-Ar medium at Ar pressures of 3 and 1.5 MPa. The H$_2$ production was observed to be very small compared to that in H$_2$O-SDS-CO$_2$ but comparable to those in H$_2$O and H$_2$O-SDS media. This indicates the importance of a chemical species of CO$_2$ for the higher H$_2$ production observed in the H$_2$O-SDS-CO$_2$ medium.

Figure 1

Other surfactants, listed in Table 1, were also tested for comparison (Figure 2). The comparison of H$_2$ production in the presence and absence of dense phase CO$_2$ imply that 3 MPa CO$_2$ has some positive effect on the H$_2$ production; however, the couples of CTAB, DTAB, and NaHS with dense phase CO$_2$ cannot improve the H$_2$ production so significantly as observed with SDS as shown in Figure 1. The authors further tested a nonionic surfactant P123 and fluorinated ones of APFO and AHPFO, which were more CO$_2$-philic than the above-mentioned ones. Unfortunately, the degradation of those surfactants was observed to occur to some extent. For example, about 23% of the initial amount of APFO decomposed under the same reaction conditions. However, no decomposition of SDS was observed and very small fractions, less than 0.5% of the initial quantities, decomposed for the other surfactants of CTAB, DTAB, and NaHS. The TiO$_2$ powders were observed to be dispersed well in water in the presence of these surfactants as well except for the cationic ones. But, the dispersion of TiO$_2$ powders with SDS was more stable compared to the other surfactants; it was more difficult to separate the SDS-stabilized TiO$_2$ powders by simple filtration. The chemical nature of SDS should be important for the enhanced H$_2$ production.

Table 1, Figure 2

Then, the influence of either CO$_2$ pressure or SDS concentration and the
catalyst stability were further investigated for the medium including TiO$_2$, dense phase CO$_2$, and SDS. Figure 3a shows the effect of CO$_2$ pressure on the H$_2$ production, which increased largely from 365 $\mu$L g$^{-1}$ h$^{-1}$ at 0.5 MPa to 3185 $\mu$L g$^{-1}$ h$^{-1}$ at 1.5 MPa but then decreased with the pressure. Very small amounts of CO and CH$_4$, which were less than 5 ppb against H$_2$, were also detected under the conditions used, and the rates of CO and CH$_4$ production deceased as CO$_2$ pressure increased. Figure 3b gives the effect of SDS concentration, indicating that the H$_2$ production was maximal at a certain concentration comparable to its critical micelle concentration (CMC). The rate of CO production is independent of the concentration of SDS. The reaction was tested for longer reaction times under the standard conditions. The production of H$_2$ was observed to occur at a constant rate during the reaction up to 14 h (Figure S1 in Supporting Information); namely, the photocatalytic activity of TiO$_2$ was durable.

Those results show that the presence of both dense phase CO$_2$ and SDS is required for enhancing the photocatalytic H$_2$ production. The noticeably larger H$_2$ production observed (Figure 1) should result from some synergistic effects of these two components. In situ high pressure UV/Vis spectroscopy was used to examine the properties of TiO$_2$ in water in the presence of dense phase CO$_2$ and surfactants. In these UV/Vis experiments, a thin film TiO$_2$ on a quartz plate was used instead of TiO$_2$ powders (see Experimental Section). Figure 4a shows UV/Vis spectra collected for the TiO$_2$ film in different aqueous solutions compressed by 3 MPa CO$_2$. In the SDS solution, TiO$_2$ shows absorption in a wide range of wavelength being tailed to a larger wavelength compared to the other surfactants. The spectrum with NaHS also has a wider absorption but to a lesser extent compared to SDS. The spectrum with DTAB is similar to that in pure water and the one with CTAB has a narrower absorption. The UV/Vis spectra were further collected at different SDS concentrations (Figure 4b). A wider absorption spectrum was obtained at a concentration of 8.1 mM compared to those at 4.05 mM and 20.25 mM. Comparison with the results of Figures 1, 2 and 3b suggests that a wider UV/Vis absorption is beneficial to a larger H$_2$ production. But, similar UV/Vis spectra were obtained for the TiO$_2$ film in aqueous solutions including SDS (20. 25 mM) compressed by CO$_2$ at different pressures of 1 – 12 MPa although the H$_2$ production was maximal at a certain pressure (Figure 3a).
Additional reaction experiments were made using a cutoff filter through which the reaction mixture was illuminated by the light of a selected range of 230-410 nm in wavelength. Three reaction systems, H$_2$O-CO$_2$-SDS, H$_2$O alone, and H$_2$O-CO$_2$-CTAB were used. The rates of H$_2$ production were observed to decrease in all these systems as compared to those obtained without the cutoff filter. It is important to note, however, that the extent of decrease depends on the system examined; the rate of H$_2$ production decreased by 63%, 33%, and 21% for H$_2$O-CO$_2$-SDS, H$_2$O alone, and H$_2$O-CO$_2$-CTAB, respectively. Namely, the most significant decrease appeared for the most active system of H$_2$O-CO$_2$-SDS (-TiO$_2$). These results also indicate the importance of the modification of TiO$_2$ by CO$_2$ molecules on its surface, showing the larger extension of light absorption at wavelength > 360 nm (Figure 4a).

Although the details are still unclear about the effects of dense phase CO$_2$ and SDS, the coexistence of these two components is indispensible for noticeably enhancing the H$_2$ production over TiO$_2$. In the presence of SDS, CO$_2$ molecules are emulsified in SDS micelles and those CO$_2$ micelles should exist in contact with the surface of TiO$_2$ powders, as illustrated in Figure 5. The accumulation of CO$_2$ molecules on TiO$_2$ is assisted by the presence of SDS and this should modify its surface properties, as suggested by UV/Vis spectroscopy (Figure 4). The surface of TiO$_2$ may be positively charged under the reaction conditions used because its point zero charge is at a pH value of about 6.18,23 The anionic SDS surfactant is likely to have electrostatic and hydrogen bonding interactions between its sulfate head group with the positively charged surface of TiO$_2$. In contrast, CTAB and DTAB containing tetraalkylammonium anions are less likely to have such interactions 25 and so TiO$_2$ powder could not be well dispersed in the water phase in the presence of these surfactants. Another feature of SDS is the occurrence of interactions with the electron deficient CO$_2$ molecules and the interactions should be stronger than that with the cationic surfactant. So, these TiO$_2$- and CO$_2$-philic natures of SDS should be crucial for the larger H$_2$ production in the presence of dense phase CO$_2$ and SDS. For TiO$_2$ modified by the CO$_2$ accumulation, it is speculated that the photo-excitation generating electron and hole may occur by the light in a wider wavelength (in a wider energy) being tailed to longer wavelength (lower energy) (Figure 4) and/or the recombination of electron and hole formed may be slowed down. When the SDS concentration is increased, the CO$_2$ micelles should occupy a larger area of the surface of TiO$_2$; when the whole area is covered by the micelles, however, the contact of TiO$_2$ with water molecules should become difficult. Therefore, the positive effect of SDS may be maximal at a certain concentration (Figure 3b). The BET surface area of TiO$_2$ used is 11 m$^2$ g$^{-1}$ and the total area of TiO$_2$ powder used (0.10
g) is 1.1 m². Under the conditions used, the number of SDS molecules present in water of 20 cm³ is 0.162 mmol at its CMC (8.1 mM). Assuming the area occupied by one SDS molecule at the surface of micelles is 0.65 nm², the surfactant used can cover an area of 64 m². Possibly, the amount of SDS surfactant molecules is so sufficient at CMC that a sufficient number of CO₂ molecules may accumulate on the surface of TiO₂ and change its properties. The influence of CO₂ pressure is also maximal at a certain pressure (Figure 3a). When CO₂ pressure is raised, the number and/or volume of the micelles in contact with TiO₂ could increase. Some fraction of the surface of TiO₂ is required to be exposed free of CO₂ micelles for the photocatalysis and so a certain pressure may give a maximum effect. The CO₂ micelles, adsorbed on TiO₂ and present freely in water, might work as a pool for H₂.

Figure 5

In conclusion, the photocatalytic H₂ production from water with TiO₂ can be noticeably enhanced by the presence of both dense phase CO₂ and SDS surfactant, by more than one order magnitude as compared to that in neat water. The surface properties of TiO₂ photocatalyst should be modified by the accumulation of CO₂ micelles (nano bubbles). This is a new type of the chemical function of dense phase CO₂ as promoter and modifier. The dense phase CO₂ accumulating on the surface of TiO₂ would promote the photo-excitation generating electron and hole or retard the recombination of the electron and hole formed. Further experiments of photocatalytic reactions under different conditions and in situ high pressure UV/Vis and FTIR spectroscopy are in progress to clarify the synergistic effects of CO₂ and SDS in our laboratory.

Experimental section

General
Anatase TiO₂ (particle size 217 nm, surface area 11 m² g⁻¹) and several types of surfactants were purchased from Aldrich and used without further purification. Distilled water (Wako) and CO₂ (99.99%) were used as delivered.

Photocatalytic hydrogen production
The photocatalytic reactions were carried out in a 50 cm³ stainless steel autoclave with a quartz window (diameter 1 cm), using a 500 W high-pressure Hg lamp (Ushio USH-500SC). This lamp emits predominantly in the wavelength range of 360-370 nm, 400-410 nm, and 430-440 nm. In a typical run, a weighed amount of surfactant and
water (20 cm$^3$) were added into the reactor and the mixture was stirred for 2 min. Then, the mixture was loaded with 100 mg TiO$_2$ and further stirred for 2 min. After sealed, the reactor was flushed with Ar and CO$_2$ for media without CO$_2$ and those with CO$_2$, respectively, for three times to remove the air. The reactor was placed on a heating plate and bound with a heating tape. The temperature was monitored by a thermocouple embedded in the reactor wall. When the reactor was heated and the temperature reached to a reaction temperature of 323 K, CO$_2$ was introduced up to the desired pressure and the reaction mixture was illuminated by turning on the lamp. After the reaction, the gases (mainly H$_2$, CO$_2$, CO, CH$_4$) evolved were collected in a gas trap. The amount of H$_2$ was determined by gas chromatography (Shimadzu GC-8A, molecular sieve 5A packed column, TCD detector, N$_2$ carrier) and CO, CO$_2$, and CH$_4$ by another gas chromatography (Shimadzu GC-8A, Porapak Q packed column, FID detector, N$_2$ carrier) with a methanizer converting those gases into CH$_4$. The reaction was also tested without TiO$_2$ in the presence of dense phase CO$_2$ and surfactant under illumination and with TiO$_2$ in dark. No products were detected in these reactions. The reactions runs were repeated under the same conditions to ensure the reliability of data collection.

In-situ high pressure UV/Vis measurement
The properties of TiO$_2$ in water compressed by CO$_2$ were examined by in situ high pressure UV/Vis spectrometer (Jasco Model V-570). We failed to collect good spectra for TiO$_2$ powders due to their light scattering; our UV/Vis cell did not have an integrated mirror ball to gather sufficient effluent light. So, thin TiO$_2$ film on a quartz plate was used, which was prepared by vacuum evaporation of Ti in a thickness of 10 nm on the plate (about 5 mm x 25 mm) followed by oxidation in air at 723 K for 5 h.

Acknowledgements
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References


149-153.


**Figure Captions**

Figure 1. Rate of photocatalytic H\(_2\) production from water with TiO\(_2\) in different aqueous media. Reaction conditions: TiO\(_2\) 100 mg, H\(_2\)O 20 cm\(^3\), CO\(_2\) 3 MPa, SDS 20.25 mM, 323 K, 8 h.

Figure 2. Comparison of photocatalytic H\(_2\) production from water with different surfactants in the presence and absence of dense phase CO\(_2\). Reaction conditions: TiO\(_2\) 100 mg, H\(_2\)O 20 cm\(^3\), CO\(_2\) 3 MPa, 323 K, 8 h. The concentrations of the surfactants used are 2.5 times of their CMCs.

Figure 3. Effect of CO\(_2\) pressure (a) and SDS concentration (b) on photocatalytic H\(_2\) production in the presence of both SDS and dense phase CO\(_2\). Reaction conditions: TiO\(_2\) 100 mg, H\(_2\)O 20 cm\(^3\), CO\(_2\) 3 MPa, SDS 20.25 mM, 323 K, 8 h.

Figure 4. UV/Vis spectra of TiO\(_2\) film (a) in water (1) and in different aqueous solutions with CTAB (2), DTAB (3), NaHS (4), and SDS (5) at a CO\(_2\) pressure of 3 MPa. The concentrations of the surfactants used is 2.5 times of their CMC. (b) Spectra for the aqueous solutions with SDS at different concentrations of (1) 4.05 mM, (2) 8.1 mM, and (3) 20.25 mM at a CO\(_2\) pressure of 3 MPa.

Figure 5. Illustration of the reaction medium including TiO\(_2\) powder, SDS surfactant, and dense phase CO\(_2\). The properties of TiO\(_2\) photocatalyst may be modified by the accumulation of CO\(_2\) molecules on its surface assisted by the surfactant.
Table 1. Surfactants used in the present work.

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Abbr.</th>
<th>Molecular formula</th>
<th>CMC[^{[a]}] (mM, 298 K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium dodecyl sulfate</td>
<td>SDS</td>
<td>CH(_3)(CH(<em>2))(</em>{11})OSO(_3)Na</td>
<td>8.1</td>
</tr>
<tr>
<td>1-Hexadecanesulfonic acid sodium salt</td>
<td>NaHS</td>
<td>CH(_3)(CH(<em>2))(</em>{15})OSO(_2)Na</td>
<td>0.7</td>
</tr>
<tr>
<td>Dodecyltrimethylammonium bromide</td>
<td>DTAB</td>
<td>CH(_3)(CH(<em>2))(</em>{11})N(CH(_3))(_3)Br</td>
<td>15</td>
</tr>
<tr>
<td>Hexadecyltrimethylammonium bromide</td>
<td>CTAB</td>
<td>CH(_3)(CH(<em>2))(</em>{15})N(CH(_3))(_3)Br</td>
<td>0.92</td>
</tr>
<tr>
<td>Poly(ethylene oxide)-poly (propylene oxide)-poly (ethylene oxide)</td>
<td>P123</td>
<td>HO(CH(_2)CH(<em>2))(</em>{20})(CH(_2)CH(_2))(_7)(CH(<em>3)O)(</em>{70})(CH(_2)CH(<em>2)O)(</em>{20})H</td>
<td>0.052</td>
</tr>
<tr>
<td>Ammonium pentadecafluorooctanoate</td>
<td>APFO</td>
<td>CF(_3)(CF(_2))(_6)COONH(_4)</td>
<td>30–34</td>
</tr>
<tr>
<td>Ammonium heptadecafluorooctanesulfonate</td>
<td>AHPFO</td>
<td>CF(_3)(CF(_2))(_7)SO(_3)NH(_4)</td>
<td></td>
</tr>
</tbody>
</table>

[a] Data of critical micelle concentration (CMC) from Ref. [26].
Figure 1. Rate of photocatalytic H₂ production from water with TiO₂ in different aqueous media. Reaction conditions: TiO₂ 100 mg, H₂O 20 cm³, CO₂ 3 MPa, SDS 20.25 mM, 323 K, 8 h.
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