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The dispersion of TiO₂ modified by the accumulation of CO₂ molecules in water: An effective medium for photocatalytic H₂ production

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(Abstract)

The photocatalytic H₂ production from water with TiO₂ can be noticeably enhanced by the presence of both dense phase CO₂ and a surfactant of sodium dodecyl sulfate, being larger by more than one order of magnitude than that from water with TiO₂ alone. The surface of TiO₂ may be modified by the accumulation of CO₂ molecules assisted by the TiO₂- and CO₂-philic surfactant, changing its photocatalytic activity.

Introduction

Recently, H₂ has been investigated as a storable, clean, and environmental-friendly fuel for future energy systems.¹ Photocatalytic water splitting into H₂ has been considered as a significant and attractive solution to solve the global energy and environmental problems.² It is well known that TiO₂ is a cheap, nontoxic, stable and efficient photocatalyst. However, the intrinsic activity of TiO₂ is not sufficient due to the facile recombination of photo-generated electron-hole pairs, which is thermodynamically favored³⁻⁵ and TiO₂ 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 TiO₂, such as surface modification via organic

materials/semiconductor coupling and band gap modification with metal and nonmetal dopants.⁶⁻⁹ In addition, various oxidizing sacrifice agents are used in order to suppress the reverse reaction of O₂ and H₂ formed back to H₂O.^{10,11}

The present authors have been investigating the effects of dense phase CO₂ in different chemical reactions, which can act as a promoter as well as a solvent. One of significant findings is that CO₂ 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 α,β -unsaturated aldehydes^{12,13} and aromatic nitro compounds,^{14,15} Heck coupling¹⁶ and Diels-Alder reaction.¹⁶ Furthermore, the CO₂ molecules could affect the properties of supported metal particles as suggested by *in situ* high pressure optical absorption measurements in dense phase CO₂ medium.¹⁷

Those previous works with either TiO₂ or dense phase CO₂ have stimulated us to investigate the possibility of synergistic effects of the two species in the production of H₂ by photocatalytic water splitting. In the present work, the production of H₂ has been studied with different media including TiO₂, dense phase CO₂, and/or surfactant. The surfactant has been used to form CO₂ micelles, which are adsorbed on the surface of TiO₂. This work will report an interesting result that the H₂ production can be promoted by synergistic effects of dense phase CO₂ and a surfactant of sodium dodecyl sulfate (SDS) by more than one order of magnitude compared to the medium with TiO₂ alone.

Results and discussion

The authors tested different reaction media in the presence of dense phase CO₂ and/or a surfactant of SDS. The results obtained are shown in Figure 1. The rate of H₂ production observed in the present reaction runs was small. The authors used a laboratory designed high pressure stainless steel reactor of 50 cm³ 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 H₂ production obtained. The rate of H₂ 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 CO₂ was introduced to pure water. Interestingly, the rate of H₂ 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 CO₂ and SDS was indispensable for promoting the photocatalytic H₂ production with TiO₂ in aqueous

medium. When dense phase CO₂ is present, the pH of the aqueous medium decreases and some acidic species such as H₂CO₃ and HCO₃⁻ are formed¹⁸; the pH decreases to about 3 at CO₂ pressures > 3 MPa.¹⁹⁻²⁰ The pH and the formation of these acidic species may be important factors determining the rate of photocatalytic H₂ production.²¹⁻²⁴ When SDS surfactant is used, TiO₂ powders can be dispersed well in water. From the results of Figure 1, however, the acidic nature and the stable TiO₂ dispersion are not responsible for the even larger H₂ production in the presence of both dense phase CO₂ and SDS, which should act in a synergistic way in modifying the properties of TiO₂. We conducted control reaction runs using Ar instead of CO₂ under the same conditions. The reactions were made with TiO₂ in H₂O-SDS-Ar medium at Ar pressures of 3 and 1.5 MPa. The H₂ production was observed to be very small compared to that in H₂O-SDS-CO₂ but comparable to those in H₂O and H₂O-SDS media. This indicates the importance of a chemical species of CO₂ for the higher H₂ production observed in the H₂O-SDS-CO₂ medium.

Figure 1

Other surfactants, listed in Table 1, were also tested for comparison (Figure 2). The comparison of H₂ production in the presence and absence of dense phase CO₂ imply that 3 MPa CO₂ has some positive effect on the H₂ production; however, the couples of CTAB, DTAB, and NaHS with dense phase CO₂ cannot improve the H₂ 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 CO₂-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 TiO₂ 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 TiO₂ powders with SDS was more stable compared to the other surfactants; it was more difficult to separate the SDS-stabilized TiO₂ powders by simple filtration. The chemical nature of SDS should be important for the enhanced H₂ production.

Table 1, Figure 2

Then, the influence of either CO₂ pressure or SDS concentration and the

catalyst stability were further investigated for the medium including TiO₂, dense phase CO₂, and SDS. Figure 3a shows the effect of CO₂ pressure on the H₂ production, which increased largely from 365 $\mu\text{L g}^{-1} \text{h}^{-1}$ at 0.5 MPa to 3185 $\mu\text{L g}^{-1} \text{h}^{-1}$ at 1.5 MPa but then decreased with the pressure. Very small amounts of CO and CH₄, which were less than 5 ppb against H₂, were also detected under the conditions used, and the rates of CO and CH₄ production decreased as CO₂ pressure increased. Figure 3b gives the effect of SDS concentration, indicating that the H₂ 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 H₂ 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 TiO₂ was durable.

Figure 3

Those results show that the presence of *both dense phase CO₂ and SDS* is required for enhancing the photocatalytic H₂ production. The noticeably larger H₂ 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 TiO₂ in water in the presence of dense phase CO₂ and surfactants. In these UV/Vis experiments, a thin film TiO₂ on a quartz plate was used instead of TiO₂ powders (see Experimental Section). Figure 4a shows UV/Vis spectra collected for the TiO₂ film in different aqueous solutions compressed by 3 MPa CO₂. In the SDS solution, TiO₂ 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 H₂ production. But, similar UV/Vis spectra were obtained for the TiO₂ film in aqueous solutions including SDS (20.25 mM) compressed by CO₂ at different pressures of 1 – 12 MPa although the H₂ production was maximal at a certain pressure (Figure 3a).

Figure 4

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, H₂O-CO₂-SDS, H₂O alone, and H₂O-CO₂-CTAB were used. The rates of H₂ 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 H₂ production decreased by 63%, 33%, and 21% for H₂O-CO₂-SDS, H₂O alone, and H₂O-CO₂-CTAB, respectively. Namely, the most significant decrease appeared for the most active system of H₂O-CO₂-SDS (-TiO₂). These results also indicate the importance of the modification of TiO₂ by CO₂ 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 CO₂ and SDS, the coexistence of these two components is indispensable for noticeably enhancing the H₂ production over TiO₂. In the presence of SDS, CO₂ molecules are emulsified in SDS micelles and those CO₂ micelles should exist in contact with the surface of TiO₂ powders, as illustrated in Figure 5. The accumulation of CO₂ molecules on TiO₂ 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 TiO₂ 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 TiO₂. In contrast, CTAB and DTAB containing tetraalkylammonium anions are less likely to have such interactions²⁵ and so TiO₂ 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 CO₂ molecules and the interactions should be stronger than that with the cationic surfactant. So, these TiO₂- and CO₂-philic natures of SDS should be crucial for the larger H₂ production in the presence of dense phase CO₂ and SDS. For TiO₂ modified by the CO₂ 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 CO₂ micelles should occupy a larger area of the surface of TiO₂; when the whole area is covered by the micelles, however, the contact of TiO₂ 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 TiO₂ used is 11 m² g⁻¹ and the total area of TiO₂ powder used (0.10

g) is 1.1 m^2 . Under the conditions used, the number of SDS molecules present in water of 20 cm^3 is 0.162 mmol at its CMC (8.1 mM).²⁶ Assuming the area occupied by one SDS molecule at the surface of micelles is 0.65 nm^2 , the surfactant used can cover an area of 64 m^2 . Possibly, the amount of SDS surfactant molecules is so sufficient at CMC that a sufficient number of CO_2 molecules may accumulate on the surface of TiO_2 and change its properties. The influence of CO_2 pressure is also maximal at a certain pressure (Figure. 3a). When CO_2 pressure is raised, the number and/or volume of the micelles in contact with TiO_2 could increase. Some fraction of the surface of TiO_2 is required to be exposed free of CO_2 micelles for the photocatalysis and so a certain pressure may give a maximum effect. The CO_2 micelles, adsorbed on TiO_2 and present freely in water, might work as a pool for H_2 .

Figure 5

In conclusion, the photocatalytic H_2 production from water with TiO_2 can be noticeably enhanced by the presence of *both dense phase CO_2 and SDS surfactant*, by more than one order magnitude as compared to that in neat water. The surface properties of TiO_2 photocatalyst should be modified by the accumulation of CO_2 micelles (nano bubbles). This is a new type of the chemical function of dense phase CO_2 as promoter and modifier. The dense phase CO_2 accumulating on the surface of TiO_2 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 CO_2 and SDS in our laboratory.

Experimental section

General

Anatase TiO_2 (particle size 217 nm , surface area $11 \text{ m}^2 \text{ g}^{-1}$) and several types of surfactants were purchased from Aldrich and used without further purification. Distilled water (Wako) and CO_2 (99.99%) were used as delivered.

Photocatalytic hydrogen production

The photocatalytic reactions were carried out in a 50 cm^3 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 $360\text{-}370 \text{ nm}$, $400\text{-}410 \text{ nm}$, and $430\text{-}440 \text{ nm}$. In a typical run, a weighed amount of surfactant and

water (20 cm³) were added into the reactor and the mixture was stirred for 2 min. Then, the mixture was loaded with 100 mg TiO₂ and further stirred for 2 min. After sealed, the reactor was flushed with Ar and CO₂ for media without CO₂ and those with CO₂, 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, CO₂ was introduced up to the desired pressure and the reaction mixture was illuminated by turning on the lamp. After the reaction, the gases (mainly H₂, CO₂, CO, CH₄) evolved were collected in a gas trap. The amount of H₂ was determined by gas chromatography (Shimadzu GC-8A, molecular sieve 5A packed column, TCD detector, N₂ carrier) and CO, CO₂, and CH₄ by another gas chromatography (Shimadzu GC-8A, Porapak Q packed column, FID detector, N₂ carrier) with a methanizer converting those gases into CH₄. The reaction was also tested without TiO₂ in the presence of dense phase CO₂ and surfactant under illumination and with TiO₂ 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 TiO₂ in water compressed by CO₂ were examined by *in situ* high pressure UV/Vis spectrometer (Jasco Model V-570).¹⁷ We failed to collect good spectra for TiO₂ powders due to their light scattering; our UV/Vis cell did not have an integrated mirror ball to gather sufficient effluent light. So, thin TiO₂ 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.

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Figure Captions

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.

Figure 2. Comparison of photocatalytic H₂ production from water with different surfactants in the presence and absence of dense phase CO₂. Reaction conditions: TiO₂ 100 mg, H₂O 20 cm³, CO₂ 3 MPa, 323 K, 8 h. The concentrations of the surfactants used are 2.5 times of their CMCs.

Figure 3. Effect of CO₂ pressure (a) and SDS concentration (b) on photocatalytic H₂ production in the presence of both SDS and dense phase CO₂. Reaction conditions: TiO₂ 100 mg, H₂O 20 cm³, CO₂ 3 MPa, SDS 20.25 mM, 323 K, 8 h.

Figure 4. UV/Vis spectra of TiO₂ film (a) in water (1) and in different aqueous solutions with CTAB (2), DTAB (3), NaHS (4), and SDS (5) at a CO₂ 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 CO₂ pressure of 3 MPa.

Figure 5. Illustration of the reaction medium including TiO₂ powder, SDS surfactant, and dense phase CO₂. The properties of TiO₂ photocatalyst may be modified by the accumulation of CO₂ molecules on its surface assisted by the surfactant.

Table 1. Surfactants used in the present work.

Surfactant	Abbr.	Molecular formula	CMC ^[a] (mM, 298 K)
Sodium dodecyl sulfate	SDS	$\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3\text{Na}$	8.1
1-Hexadecanesulfonic acid sodium salt	NaHS	$\text{CH}_3(\text{CH}_2)_{15}\text{OSO}_2\text{Na}$	0.7
Dodecyltrimethylammonium bromide	DTAB	$\text{CH}_3(\text{CH}_2)_{11}\text{N}(\text{CH}_3)_3\text{Br}$	15
Hexadecyltrimethylammonium bromide	CTAB	$\text{CH}_3(\text{CH}_2)_{15}\text{N}(\text{CH}_3)_3\text{Br}$	0.92
Poly(ethylene oxide)-poly (propylene oxide)- poly (ethylene oxide)	P123	$\text{HO}(\text{CH}_2\text{CH}_2\text{O})_{20}(\text{CH}_2\text{CH}(\text{CH}_3)\text{O})_{70}(\text{CH}_2\text{CH}_2\text{O})_{20}\text{H}$	0.052
Ammonium pentadecafluorooctanoate	APFO	$\text{CF}_3(\text{CF}_2)_6\text{COONH}_4$	30~34
Ammonium heptadecafluorooctanesulfonate	AHPFO	$\text{CF}_3(\text{CF}_2)_7\text{SO}_3\text{NH}_4$	—

[a] Data of critical micelle concentration (CMC) from Ref. [26].

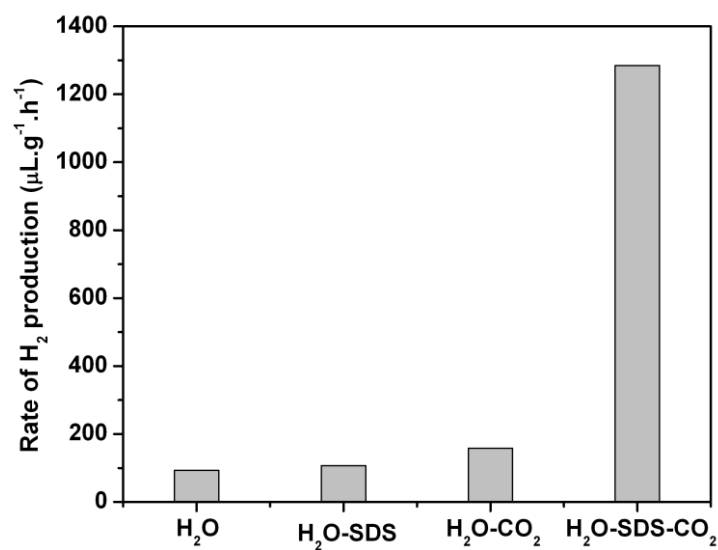


Figure 1. Rate of photocatalytic H₂ production from water with TiO₂ in different aqueous media. Reaction conditions: TiO₂ 100 mg, H₂O 20 cm³, CO₂ 3 MPa, SDS 20.25 mM, 323 K, 8 h.

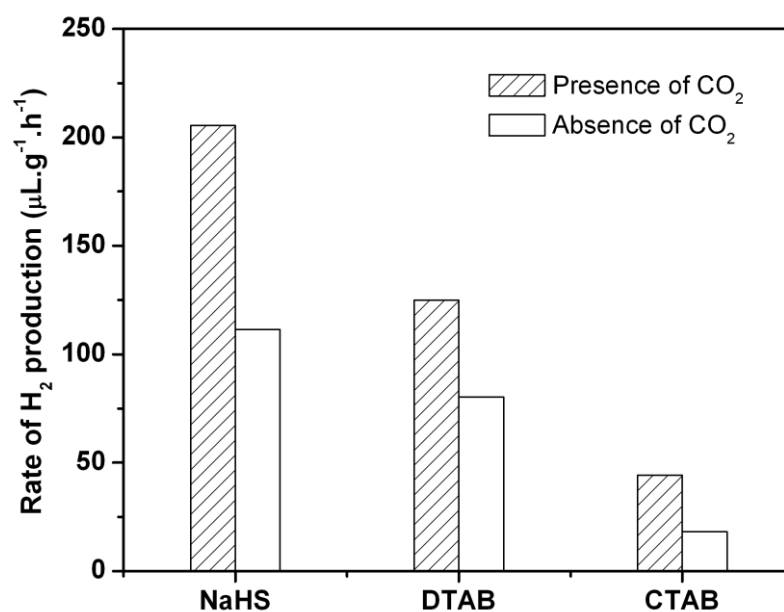


Figure 2. Comparison of photocatalytic H₂ production from water with different surfactants in the presence and absence of dense phase CO₂. Reaction conditions: TiO₂ 100 mg, H₂O 20 cm³, CO₂ 3 MPa, 323 K, 8 h. The concentrations of the surfactants used are 2.5 times of their CMCs.

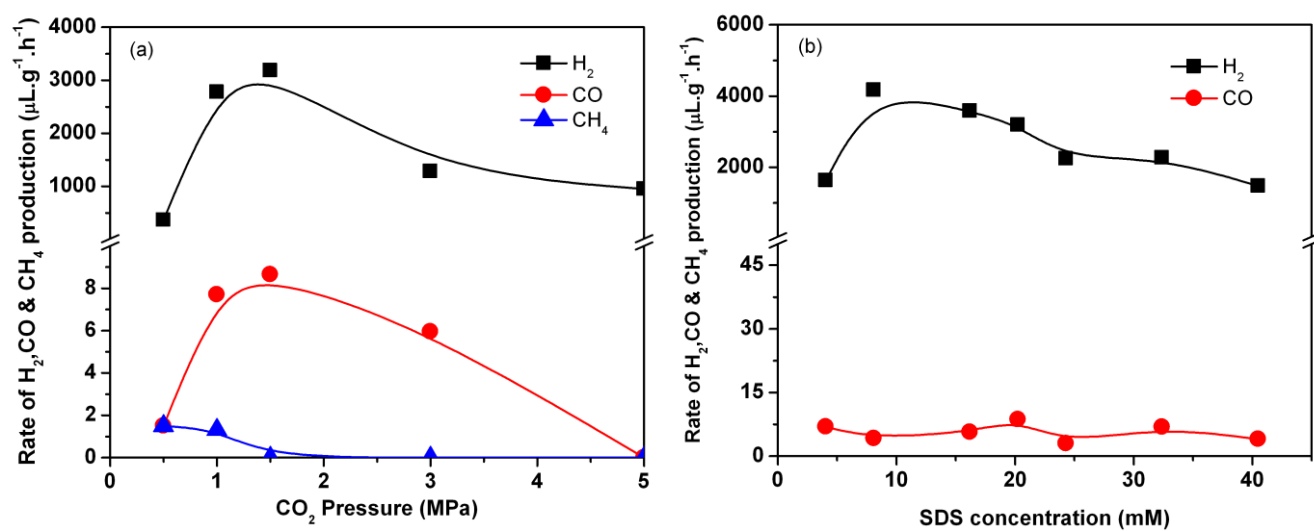


Figure 3. Effect of CO₂ pressure (a) and SDS concentration (b) on photocatalytic H₂ production in the presence of both SDS and dense phase CO₂. Reaction conditions: TiO₂ 100 mg, H₂O 20 cm³, CO₂ 3 MPa, SDS 20.25 mM, 323 K, 8 h.

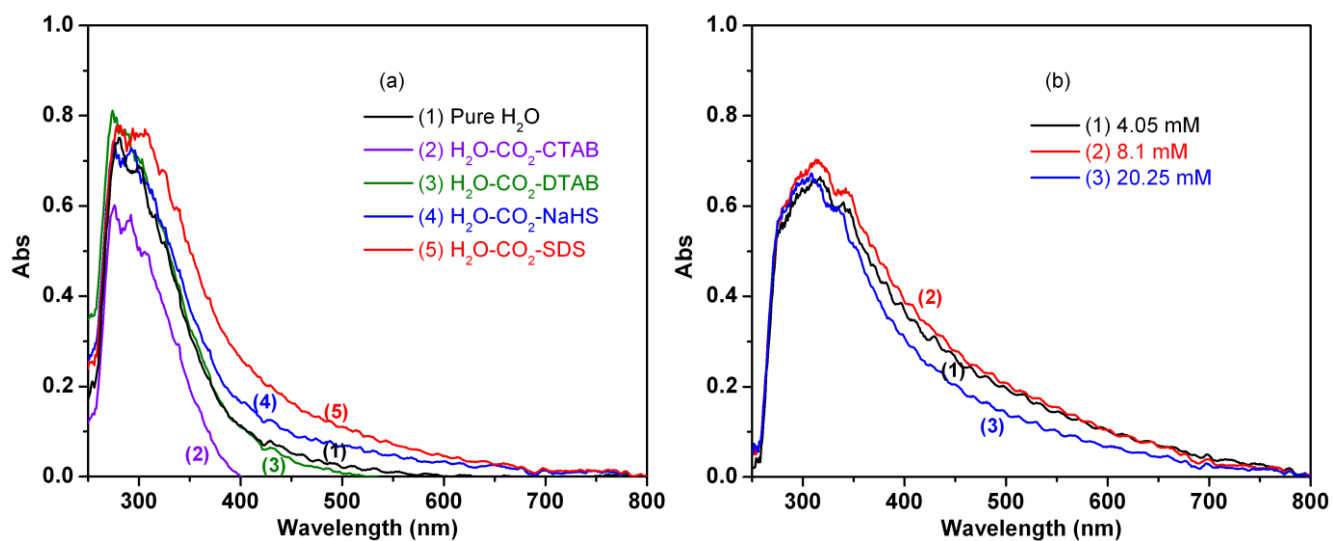


Figure 4. UV/Vis spectra of TiO_2 film (a) in water (1) and in different aqueous solutions with CTAB (2), DTAB (3), NaHS (4), and SDS (5) at a CO_2 pressure of 3 MPa. The concentrations of the surfactants used is 2.5 times of their CMC. (b) Spectra for the aqueous solutions with SDS at different concentrations of (1) 4.05 mM, (2) 8.1 mM, and (3) 20.25 mM at a CO_2 pressure of 3 MPa.

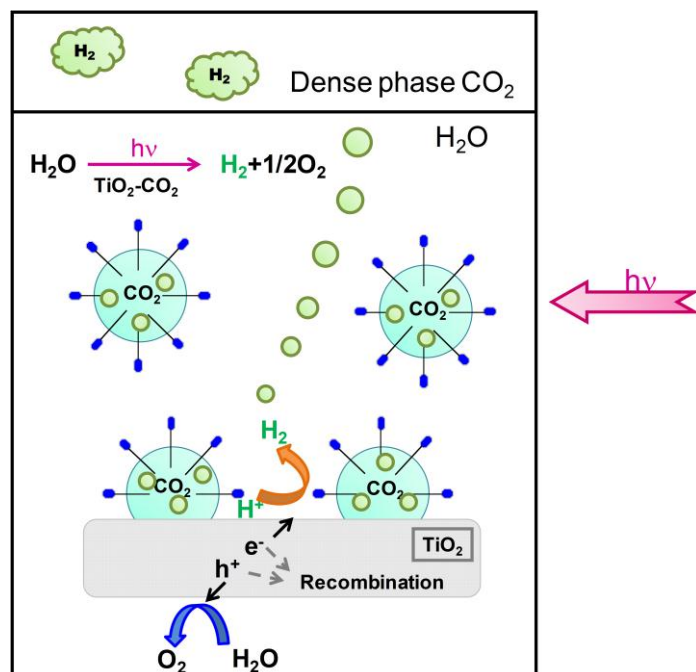


Figure 5. Illustration of the reaction medium including TiO_2 powder, SDS surfactant, and dense phase CO_2 . The properties of TiO_2 photocatalyst may be modified by the accumulation of CO_2 molecules on its surface assisted by the surfactant.