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Significant Effects of Anion in Aqueous Reactant Solution on Photocatalytic O_2 Evolution and Fe(III) Reduction

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The apparent quantum yield at 365 nm over TiO_2 photocatalyst for O_2 evolution and Fe^{3+} reduction in an aqueous $FeCl_3$–HCl solution was 51%, and more than 15 times higher than in an aqueous $Fe_2(SO_4)_3$–H_2SO_4 solution.

The splitting of water into H_2 and O_2 over photocatalyst has been studied to develop clean and sustainable system for a hydrogen production. It has been reported that some powdered photocatalysts show activity for water splitting under visible light irradiation.[1] However, the present efficiencies are not satisfying for practical use at the present stage. On the other hand, photocatalytic reduction of redox mediators that increases total Gibbs energy is also an attractive artificial photosynthesis reaction because the accumulation of reduced redox mediators and the separation from O_2 gas are easy.[2] Moreover, this uphill reaction can be applied to a photocatalysis–electrolysis hybrid system[3,4] which is a practical water-splitting method. From the standpoints of stability, cost, and absence of side reactions, Fe^{3+}/Fe^{2+} is an excellent redox mediator at the present stage. Precious metals such as Pt are not essential as a cocatalsyst for Fe^{3+} reduction. It has been reported that TiO_2, WO_3, Cs-modified WO_3 (referred to as Cs–WO_3), $BiVO_4$, $BiWO_6$, and BiM_2VO_6 ($M = Cu$ and Zn) showed photocatalytic O_2 evolution and Fe^{3+} reduction.[2,4–12] High crystallinity, small particle size, and structural anisotropy are usually needed to photocatalyst particles by water splitting to achieve high efficiency.[1] In the case of Fe^{3+} reduction; moreover, the condition of reactant solution is also important because Fe^{3+} ions have to preferentially arrive at the photocatalyst surface and receive photogenerated electrons smoothly. Therefore, it is speculated that the state of a Fe^{3+} complex ion affects the photocatalytic activity for Fe^{3+} reduction because the adsorption behavior and the reaction behavior of Fe^{3+} ion would be changed by the state of the Fe^{3+} complex ion. In this study, we found the apparent quantum yield (AQY) at 365 nm of TiO_2 photocatalyst for O_2 evolution and Fe^{3+} reduction in the aqueous $FeCl_3$–HCl solution was very high up to 51%, and more than 15 times higher than in the aqueous $Fe_2(SO_4)_3$–H_2SO_4 solution. It is meaningful to investigate how much AQY for reversible redox reaction will be improved.

TiO_2 powder (Rutile, surface area: $2.6\,m^2\,g^{-1}$, Toho Titanium Co.) was used as the photocatalyst according to previous literature.[6] WO_3 and Cs–WO_3 were prepared by hydrothermal and impregnation methods according to previous literature.[4] To investigate the reaction mechanism, TiO_2 electrodes were prepared from Ti foil purchased by Nilaco (thickness: 40 µm) by calcination at 973 K for 30 min in air. Photocatalytic reaction was conducted in a side-window cell made of Pyrex connected to a gas-closed circulation system with online gas chromatograph. The photocatalyst powder (0.4 g) was dispersed in aqueous Fe^{3+} solution (300 mL) by a magnetic stirrer. The initial pH in the aqueous Fe^{3+} solution was always adjusted to be 2.3. The amounts of Fe^{2+} and Fe^{3+} were determined by color reactions using phenanthroline and acetic acid complex methods, respectively. The amount of evolved O_2 was determined using online gas chromatography (Shimadzu; MS-5A column, TCD, Ar carrier). Apparent quantum yield was measured using a monochromatic light through a band pass filter. The number of incident photons was determined using a Si photodiode that was proofread by NMIJ (National Metrology Institute of Japan). The photoelectrochemical measurements were performed using a potentiostat (BAS Co.) and a Pyrex glass cell. A Pt wire and a Ag/AgCl electrode were used as the counter and reference electrodes, respectively.

Table 1. Photocatalytic O_2 evolution on TiO_2, WO_3, and Cs–WO_3 photocatalysts in various reactant solutions[a]

Catalyst	Reactant solution		Incident light	Activity /µmol h^{-1}
	Fe^{3+} source	Additive acid		
TiO_2	$Fe_2(SO_4)_3$	H_2SO_4	>300 nm	23
TiO_2	$FeCl_3$	H_2SO_4	>300 nm	119
TiO_2	$FeCl_3$	HCl	>300 nm	285
WO_3	$Fe_2(SO_4)_3$	H_2SO_4	>420 nm	63
WO_3	$FeCl_3$	HCl	>420 nm	120
Cs–WO_3	$Fe_2(SO_4)_3$	H_2SO_4	>420 nm	196
Cs–WO_3	$FeCl_3$	HCl	>420 nm	240

[a] Catalyst: 0.4 g, reactant solution: 4.2 mM Fe^{3+} 300 mL, light source: 300-W Xe-arc lamp, reaction cell: side-irradiation cell. [b] Initial pH of reactant solution was always adjusted to be pH 2.3 using an additive acid.

Table 1 shows the photocatalytic O_2 evolution over TiO_2, WO_3, and Cs–WO_3 in various reactant solutions. These photocatalysts showed activities as reported previously.[4,6] The total amount of O_2 gas reached 315 µmol over Cs–WO_3, agreeing with the stoichiometric amount expected from Fe^{3+} (1260 µmol) in aqueous $Fe_2(SO_4)_3$–H_2SO_4 and $FeCl_3$–HCl solutions. The stoichiometric amount of Fe^{2+} was detected in the solution after photoreaction by the phenanthroline method, while Fe^{3+} was not detected at all. These activities strongly depended on kinds of iron source and acid using for pH adjustment. It is surmised that the Fe^{3+} complex ion formed in the aqueous $FeCl_3$–HCl solution differed from that in the aqueous $Fe_2(SO_4)_3$–H_2SO_4 solution.

Table 2 shows the dependences of AQYs of TiO_2 and Cs–WO_3 photocatalysts for O_2 evolution on wavelength of incident light. The AQY of TiO_2 at 365 nm was 12% in the case of using the aqueous $FeCl_3$–H_2SO_4 solution as a reactant solution. This AQY was at the same level compared with the value reported by Ohno and coworkers[6] previously (10%) under the same TiO_2 and reactant solution. When the aqueous $FeCl_3$–HCl solution was used as a reactant solution, the AQY at 365 nm of TiO_2 was enhanced to 51%. It should be stressed that the high efficiency was achieved only changing the condition of reactant solution without changing photocatalyst itself. The AQY of Cs–WO_3 in the case of using the aqueous $FeCl_3$–HCl solution as a reactant solution became high as the wavelength of incident light became short. In contrast, the order of the AQYs for the aqueous $Fe_2(SO_4)_3$–H_2SO_4 solution differed from that for the aqueous $FeCl_3$–HCl solution; the AQY at 365 nm was lower than that at 420 nm. It has been reported that Fe^{3+} complex ions have absorption bands in UV light region.[12–14] The two strong absorption bands in the UV light region were also observed both Fe^{3+} complex ions

Table 2. Dependences of apparent quantum yields for Fe^{3+} reduction and O_2 evolution over photocatalyst on wavelength of incident lights[a]

Catalyst	Reactant solution		Incident light	AQY /%
	Iron ion source	Additive acid[b]		
TiO_2	$Fe_2(SO_4)_3$	H_2SO_4	365 nm	3
TiO_2	$FeCl_3$	H_2SO_4	365 nm	12
TiO_2	$FeCl_3$	HCl	365 nm	51
Cs–WO_3	$Fe_2(SO_4)_3$	H_2SO_4	365 nm	10
Cs–WO_3	$Fe_2(SO_4)_3$	H_2SO_4	420 nm	15
Cs–WO_3	$Fe_2(SO_4)_3$	H_2SO_4	460 nm	7
Cs–WO_3	$FeCl_3$	HCl	365 nm	24
Cs–WO_3	$FeCl_3$	HCl	420 nm	19
Cs–WO_3	$FeCl_3$	HCl	460 nm	9

[a] Catalyst: 0.4 g, reactant solution: 4.2 mM Fe^{3+} 300 mL, light source: 300-W Xe-arc lamp, reaction cell: side-irradiation cell. [b] Initial pH of reactant solution was always adjusted to be pH 2.3 using an additive acid.

(Figure S1).[15] The absorbance of the aqueous $Fe_2(SO_4)_3$–H_2SO_4 solution was higher than that of the aqueous $FeCl_3$–HCl solution. Thus, the AQYs of Cs–WO_3 were changed depending on the difference of the light shield effects between the aqueous $Fe_2(SO_4)_3$–H_2SO_4 and $FeCl_3$–HCl solutions. Here, the AQYs at 420 and 460 nm of Cs–WO_3 for the aqueous $FeCl_3$–HCl solution were higher than that for the aqueous $Fe_2(SO_4)_3$–H_2SO_4 solution, although the shield effects of these reactant solutions were negligible in the visible light region. Moreover, the AQY at 365 nm of TiO_2 for the aqueous $FeCl_3$–HCl solution was high more than 15 times compared with that for the aqueous $Fe_2(SO_4)_3$–H_2SO_4 solution while the AQY at 365 nm of WO_3 was high only 2.5 times. The adsorption amounts of Fe^{3+} complex ions in the aqueous $FeCl_3$–HCl solution for TiO_2 and Cs–WO_3 were 23 and 13 μmol g^{-1}, respectively. These adsorption amounts were not changed compared with that of Fe^{3+} complex ions in the aqueous $Fe_2(SO_4)_3$–H_2SO_4 solution for both photocatalysts. Therefore, it is speculated that additional factors affecting photocatalytic performance strongly may be present, except for the light shield effects and the adsorption amounts.

Figure 1 shows the typical potential–current curves of a TiO_2 electrode. The photocurrent of the TiO_2 electrode was not changed in aqueous Na_2SO_4–H_2SO_4 and NaCl–HCl solutions, indicating that the oxidation reaction of H_2O into O_2 is not affected by the kind of anion at all. On the other hand, the Fe^{3+} reduction current of the TiO_2 electrode in the aqueous $FeCl_3$–HCl solution was much higher than that in the aqueous $Fe_2(SO_4)_3$–H_2SO_4 solution. This difference was also supported by the results of measurement of the cyclic voltammetry of the Fe^{3+} complex ions at a Pt electrode in the aqueous $Fe_2(SO_4)_3$–H_2SO_4 and $FeCl_3$–HCl solutions (Figure S2)[15] and the measurement of the typcal potential–current curves of a WO_3 electrode (Figure S3).[15] Therefore, it was considered that the Fe^{3+} complex ions in the aqueous $FeCl_3$–HCl solution are reduced easily compared with that in the aqueous $Fe_2(SO_4)_3$–H_2SO_4 solution on the TiO_2 electrode, and this difference was the major factor affecting photocatalytic performance.

In conclusion, it was found that the activities over TiO_2, WO_3, and Cs–WO_3 for Fe^{3+} reduction were changed greatly depending on the condition of reactant solution. There is a difference of the shield effects between aqueous $Fe_2(SO_4)_3$–H_2SO_4 and $FeCl_3$–HCl solutions. Moreover, Fe^{3+} complex ions in the aqueous $FeCl_3$–HCl solution are reduced easily compared with that in the aqueous $Fe_2(SO_4)_3$–H_2SO_4 solution. The AQY at 365 nm of TiO_2 was enhanced to 51% (more than 15 times) only changing the condition of the reactant solution without changing the photocatalyst itself. This clearly indicates that the powdered photocatalyst can show remarkably high AQY for the Fe^{3+} reduction reaction. The TiO_2 powder was used as commercialized here; therefore, AQY will be improved more by modification of the photocatalyst.

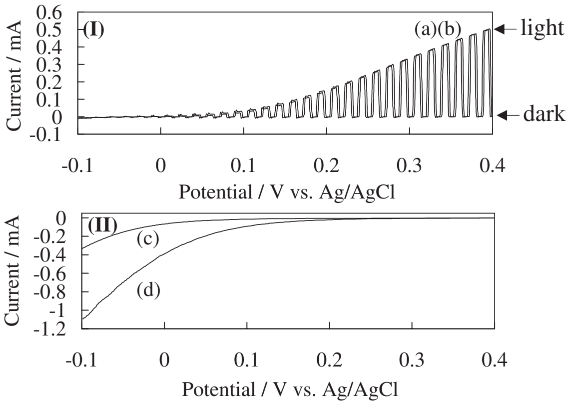

Figure 1. The potential–current curves of TiO_2 electrode. (I): Photocurrent curves for O_2 evolution in aqueous (a) H_2SO_4–Na_2SO_4 and (b) HCl–NaCl solutions under UV light using a light chopper, (II) Fe^{3+} reduction current curves in aqueous (c) $Fe_2(SO_4)_3$–H_2SO_4–Na_2SO_4 and (d) $FeCl_3$–HCl–NaCl solutions. The pH was adjusted to be pH 2.3.

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