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Effect of Carbonate Ions on the Photooxidation of Water over Porous $BiVO_4$ Film Photoelectrode under Visible Light

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Carbonate ions in the aqueous electrolyte solution improved both the photocurrent and the stability of a porous $BiVO_4$ semiconductor electrode used for water splitting under visible light up to 520 nm. The photocurrents in $AHCO_3$ (A = Na and K) solutions at 1.23 V were approximately six times higher than that in Na_2SO_4 aqueous solution. The maximum incident photon-to-current efficiency (IPCE) was 45% at 420 nm without any surface modifications.

Since the photoelectrochemical splitting of water into H_2 and O_2 using a TiO_2 photoelectrode under UV light was first reported,[1] various semiconductor photoelectrodes have been intensively investigated for direct solar energy conversion and storage. In particular, n-type oxide semiconductors with a narrow band gap, such as WO_3 and Fe_2O_3, have been investigated under visible light.[2,3] These oxides are relatively stable, suitable for O_2 evolution and are easily prepared by calcination in air, as compared to nonoxide semiconductors. The structure of the porous thin film on conducting glass is important for improvement of the solar energy conversion efficiency of the semiconductor photoelectrode, because their diffusion lengths of electrons and holes are shorter compared to those in conventional photoelectrodes. Photoelectrochemical water-splitting systems have two limitations: there are few oxide semiconductors activated by visible light, and the efficiencies are inadequate. Recently, $BiVO_4$ semiconductor photoelectrodes with a porous structure have been investigated;[4–7] these photoelectrodes showed a good incident photon-to-current efficiency (IPCE), up to approximately 20% under visible light. The IPCE of the $BiVO_4$ electrode was improved by up to 44%, by surface modification with silver ions;[4] however, it is preferable to avoid the use of a precious metal component.

In this study, we investigated the dependence of photocurrent on the composition of aqueous electrolyte solutions in contact with the $BiVO_4$ electrodes. Na_2SO_4 has generally been used as the electrolyte for the $BiVO_4$ electrodes.[4–7] It has been reported that the photocurrent of a TiO_2 electrode in an aqueous solution of carbonate salts under UV light was improved.[8] Herein, we describe the effect of carbonate anions, both on the photocurrent of the $BiVO_4$ electrodes and on the photocurrent stability. We also propose a reaction mechanism for the carbonate anion effect.

The $BiVO_4$ films were prepared by a modified metal–organic decomposition (MOD) method.[4] $Bi(NO_3)_3 \cdot 5H_2O$ (Kanto Chemical Co.) in acetic acid ($0.66\,mol\,L^{-1}$) and bis(acetylacetonato)oxovanadium(IV) (Azmax Co.) in acetylacetone ($0.08\,mol\,L^{-1}$) were mixed in a 1:1 stoichiometric ratio of Bi to V. The solution was applied to a conducting glass surface (FTO glass, Nippon Sheet Glass Co., F-doped SnO_2, $10\,\Omega\,sq^{-1}$) using a spin coater, and the film was fired at ca. 500 °C in air for 30 min. This process was repeated six times to produce the final film. The photoelectrochemical and capacitance measurements were carried out using a potentiostat (BAS Co.) and a Pyrex glass cell. A Pt wire and a Ag/AgCl electrode (0.21 V vs. NHE, pH 0) were used as the counter and reference electrodes, respectively. The light source was a solar simulator (Sanei Denki Co. AM-1.5, 1 SUN). The semiconductor electrodes were irradiated through the FTO conducting glass. The masked-off irradiated area was $0.28\,cm^2$. The light-harvesting efficiency (LHE) of the electrode was calculated from the transmittance (T) and reflectance (R) using an integrating sphere.

The photocurrents of $BiVO_4$ electrodes, the conductivity and the pH in various electrolyte solutions are shown in Table 1, and some typical potential–current curves of $BiVO_4$ electrodes in $KHCO_3$ and Na_2SO_4 electrolyte solutions are shown in Figure 1. We found that the photocurrents in carbonate solutions such as $AHCO_3$ (A = Na and K) were higher than those in other solutions. The CO_2 bubbling into carbonate solutions improved the photocurrent. The photocurrents in $AHCO_3$ solutions with CO_2 bubbling at 1.23 V were approximately six times higher than that in aqueous Na_2SO_4 solution. The photocurrents in sodium dihydrogen phosphate or sodium borate solution, which have a buffer effect, were much lower than those in carbonate solutions. It is suggested that the improvement of the photocurrent by carbonate salts is not related to the buffer effect. The photocurrent was not dependent on the concentration of Na_2SO_4; on the other hand, it was improved by increasing the concentration of carbonate ions up to the point of saturation or by bubbling CO_2 gas into the solution. The maximum photocurrents at 1.23 V (RHE of O_2/H_2O) and 1.9 V were approximately 1.67 and $2.57\,mA\,cm^{-2}$, respectively. It is noteworthy that the shapes of the potential versus photocurrent curves had a steep upslope from the open circuit potential in carbonate solutions compared to those in other solutions. The conductivity of the solution was influenced by the concentration of the electrolytes, but a direct relationship between the conductivity and photocurrent was not observed. The photocurrent in Na_2CO_3 was higher than the photocurrents in noncarbonate electrolytes solutions but was lower than that in $NaHCO_3$. The carbonate salt has two acid dissociation constants ($K_{a1}(pK_{a1}) = 4.47 \times 10^{-7}$ (6.35), $K_{a2}(pK_{a2}) = 4.68 \times 10^{-11}$ (10.33)). Therefore, most of the carbonate ions were present as hydrogencarbonate ions (HCO_3^-) in pH 7 to 9, so CO_3^{2-} and H_2CO_3 were present in negligible amounts (H_2CO_3/HCO_3^- and CO_3^{2-}/HCO_3^- were 2.2×10^{-2} and 4.7×10^{-3} at pH 8). In Na_2CO_3 solution at pH 11.8, most carbonate ions were present as CO_3^{2-}, so HCO_3^- and H_2CO_3 were present in negligible amounts (H_2CO_3/HCO_3^- and CO_3^{2-}/HCO_3^- were 3.6×10^{-6} and 29). We also ensured that the ratio of H_2 and O_2 was almost two (28 and $14\,\mu mol\,h^{-1}$) under Xe

Table 1. The photocurrents of $BiVO_4$ electrodes and the pH in various electrolyte solutions

Electrolyte	Concentration /mol L^{-1}	Conductivity[b] /mS cm^{-1}	pH	Photocurrent/mA cm^{-2} at 1.23 V[d]	Photocurrent/mA cm^{-2} at 1.9 V[d]
$NaHCO_3$	0.1	7.3	8.7	0.89	2.04
$NaHCO_3 + CO_2$	0.1	7.3	6.9	1.09	2.24
$NaHCO_3 + CO_2$	S(approx.1.0)[a]	53	7.8	1.59	2.47
Na_2CO_3	0.1	14.6	11.8	0.32	1.69
$KHCO_3 + CO_2$	0.1	9.7	6.9	0.94	2.36
$KHCO_3 + CO_2$	S(approx.2.8)[a]	148	8.2	1.67	2.57
Na_2SO_4	0.1	15.9	6.5	0.25	1.36
Na_2SO_4	1.0	86	6.9	0.26	1.53
$NaH_2PO_4 + NaOH$[c]	0.1	10.2	6.9	0.21	1.66
$NaBO_2 + H_3BO_3$[c]	0.1	5.4	7.5	0.29	1.63

[a]Saturated solution (S). [b]The error of the conductivity was large, more than 20 mS cm^{-1}. [c]pH was adjusted at around neutral. [d]RHE.

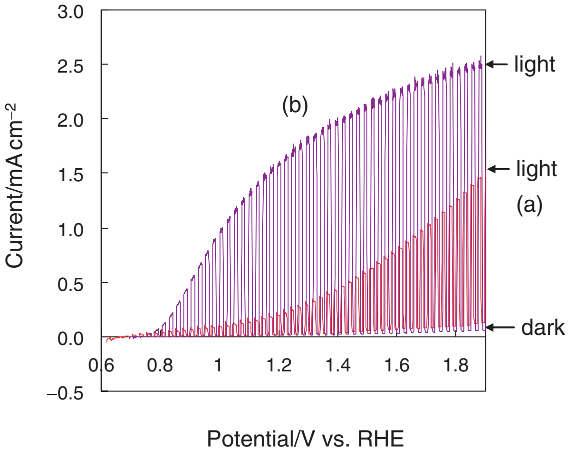

Figure 1. Typical potential vs. current curves of $BiVO_4$ electrodes in various aqueous electrolyte solutions under solar simulated light (AM-1.5, 1 SUN) using a light chopper. 0.01 V s^{-1}, anode sweep. (a) Na_2SO_4 (1 mol L^{-1}), (b) saturated $KHCO_3$ with CO_2 bubbling.

lamp (300 W) with external bias (2.0 V vs. counter electrode) using a closed gas-circulation system with an online gas-chromatograph (TCD). By considering all the above-mentioned results, we concluded that this large improvement of photocurrent for O_2 evolution in $AHCO_3$ solutions is related to concentration of the carbonate anions, especially the HCO_3^- ion and not directly related to pH, conductivity, and cations. It has been reported that the photocurrent of $BiVO_4$ in Na_2SO_4 solution was improved by Ag^+ treatment;[4] however, this treatment was not effective in carbonate solutions.

Figure 2 shows the LHE and IPCE spectra of the $BiVO_4$ electrodes in saturated aqueous $NaHCO_3$ solution with CO_2 gas bubbling. Both the thresholds of the wavelength for LHE and IPCE spectra were observed at about 520 nm. The band gap estimated by this threshold value was approximately 2.4 eV, which was the same as the reported band gap of the monoclinic $BiVO_4$.[9] The IPCE increased with an increase in the applied bias, and the IPCEs of 420 nm at 1.23 V (reverse hydrogen electrode, RHE) and 1.9 V were approximately 32% and 45%, respectively. The absorbed photon to current efficiency (APCE = IPCE/LHE) at 420 nm, corrected for the reflection loss of the Pyrex glass cell window, the absorption loss of the FTO glass and the transmissive loss of the electrode, was appoximately 44% at 1.23 V and 62% at 1.9 V. The photocurrents in noncarbonate solutions such as Na_2SO_4, NaH_2PO_4, and $NaBO_2$ decreased quickly (Figure 3). On the other hand, the photocurrent in $NaHCO_3$ was more stable compared to that of the other solutions. It is significant that both the photocurrent and the stability of the $BiVO_4$ electrode were improved simply by the presence of carbonate ions, without modification with a noble metal, such as Ag^+.[4]

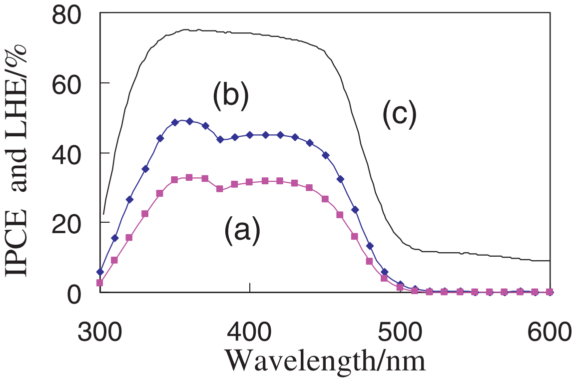

Figure 2. IPCE and LHE spectra of the $BiVO_4$ electrodes. IPCE was measured in saturated aqueous $NaHCO_3$ solution with CO_2 gas bubbling. (a) IPCE at 1.23 V (RHE), (b) at 1.9 V. (c) LHE.

The improvement effect of the photocurrent by HCO_3^- ion has also been reported on porous TiO_2 photoelectrodes under UV light.[8] Moreover, the activity increase caused by carbonate ions was also observed over various photocatalysts, such as TiO_2, Ta_2O_5, ZrO_2, and others, under UV light.[10–12] The HCO_3^- ion was more effective than CO_3^{2-} ion over a ZrO_2 photocatalyst.[11] The reaction mechanisms over photocatalysts have been explained by two effects: the suppression of the reverse reaction and/or the acceleration of O_2 evolution through carbonate radicals and peroxocarbonates.[8,11,12] The improvement of the photocurrent over a $BiVO_4$ electrode by HCO_3^- ion in this study can be explained by the presence, or absence, of

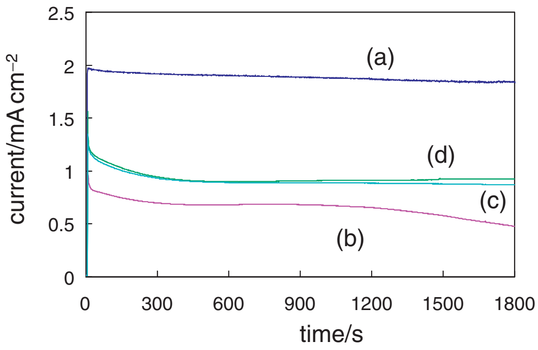

Figure 3. Time course of photocurrent of the $BiVO_4$ electrodes in (a) $NaHCO_3$ with CO_2 gas bubbling (pH 6.9), (b) aqueous Na_2SO_4 (pH 6.5), (c) $NaH_2PO_4 + NaOH$ (pH 6.9), and (d) $NaBO_2 + H_3BO_3$ (pH 7.5) solutions. The concentration was $0.1\,mol\,L^{-1}$. The applied potential was 1.0 V (Ag/AgCl).

hole transfer from the $BiVO_4$ surface to the HCO_3^- ion. We speculate that in the case without hole transfer the mechanism of the reverse reaction (the reduction of O_2 into H_2O by the electron from $BiVO_4$) was suppressed by the presence of HCO_3^- ion. In this case, the evolved O_2 gas cannot re-adsorb on the $BiVO_4$ surface because of steric hindrance by the adsorbed HCO_3^- ion. We measured the cathodic current of the O_2 reduction over the $BiVO_4$ electrode in various solutions under negative bias without light irradiation. As a result, we found that the cathode current of the O_2 reduction in $NaHCO_3$ was not smaller than the cathode current in other solutions, such as Na_2SO_4 and NaH_2PO_4.[16] Therefore, it is clear that the improvement of the photocurrent by HCO_3^- ion cannot be explained on the basis of the suppression effect of the reduction of O_2 by the adsorbed HCO_3^- ion without hole transfer.

In the case of the reaction mechanism with hole transfer from the $BiVO_4$ surface to HCO_3^- (electron transfer from HCO_3^- to $BiVO_4$), O_2 gas is formed by way of some carbonate radicals or peroxocarbonates.[8,10,11,13–15] Eriksen et al.[13] studied the behavior of $HCO_3^{\bullet}$ and $CO_3^{\bullet -}$ radicals in aqueous $NaHCO_3$ solution using a pulse radiolysis system, and they demonstrated that most $OH^{\bullet}$ radicals were consumed by HCO_3^- and that the self-recombination of $CO_3^{\bullet -}$ radicals to form peroxocarbonates had a negative apparent activation energy. Peroxocarbonate has been synthesized from Na_2CO_3 and H_2O_2 at low temperature.[14] Furthermore, the peroxocarbonates can also be synthesized by electrolysis of highly concentrated aqueous carbonate solutions at low temperature.[15] Most of the anions around neutral pH in carbonate solution are HCO_3^-, and the amounts of CO_3^{2-} and OH^- are negligible. We hypothesized that the h^+ in the valence band can react with the HCO_3^- anion having negative charge, preferentially, compared to neutral H_2O molecule at this pH. The electron transfer from the HCO_3^- ion is more favorable with increase in the concentration of HCO_3^- ion. The photocurrent of $BiVO_4$ increased with increasing concentration of HCO_3^- ion. It was speculated that in the case of the TiO_2 electrode some carbonate radicals and peroxocarbonates might be formed and that these species might inject electrons into the conduction band of TiO_2 only under highly positive bias,[8] because the potential versus photocurrent curve had a unique stepwise shape and the photocurrent of the second step above +0.8 V (RHE) was very large. On the other hand, the potential versus photocurrent curve of the $BiVO_4$ electrode was not stepwise in $AHCO_3$. The conduction band of $BiVO_4$ was more positive than that of TiO_2,[4] and the photocurrent of $BiVO_4$ was observed above +0.8 V (RHE), the same region as in the second step using TiO_2. There is a possibility that electron injection from the carbonate radicals and peroxocarbonates into the conduction band of $BiVO_4$ took place at all potential levels above +0.8 V. On the other hand, there is another explanation for the increase of photocurrent through peroxocarbonates without electron injection process as follows. The O_2 gas evolution takes place with CO_2 gas evolution concomitantly in this case, through the carbonate radicals and peroxocarbonates. The decomposition of the carbonate radicals and peroxocarbonates is irreversible. Therefore, it is surmised that desorption of O_2 gas from the $BiVO_4$ surface occurs easily and is free from the O_2 reduction by an electron from $BiVO_4$. The CO_2 gas can dissolve quickly and is reconverted to HCO_3^-, behaving like a catalyst for effective O_2 evolution.

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