Significant Effect of Carbonate Ions on the Photooxidation of Water on Mesoporous TiO_2 Film Electrodes

Kazuhiro Sayama, Jan Augustynski,† and Hironori Arakawa
Photoreaction Control Research Center (PCRC), National Institute of Advanced Industrial Science and Technology (AIST), Central 5, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565
†Department of Chemistry, University of Geneva, 1211 Geneva 4, Switzerland

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Carbonate ions cause a net increase of the saturation photocurrent as well as the occurrence of a stepwise photocurrent/potential (I/V) characteristic for the photooxidation of water at a nanocrystalline TiO_2 photoanode deposited on the conducting glass.

Since the report of highly efficient dye-sensitized solar cell by Grätzel et al.,[1,2] the properties of nanostructured TiO_2 semiconductor films supported on conducting glass electrodes have been intensively studied. Such porous TiO_2 films have a large surface area remaining in contact with an electrolyte which can penetrate close to the surface of conducting glass. This is one of the reasons for which the photoelectrochemical properties of the nanostructured TiO_2 electrodes are markedly different from those of single crystal and high-temperature-sintered polycrystalline electrodes.[3–8] In this paper, we report that the presence of carbonate ions in the solution strongly affects both the amount of the saturation photocurrent and the shape of the potential-photocurrent (V-I) curves recorded under the backside (BS) irradiation through the conducting glass. These observations are reminiscent of the significant effect of carbonate anions upon the effectiveness of a Pt-TiO_2 photocatalyst to decompose water into H_2 and O_2 reported earlier (Table 1).[9] It is to be noted that the TiO_2 nanocrystalline electrodes have several common features with the colloidal suspensions of TiO_2 photocatalysts, such as small particle size, large surface area accessible to the electrolyte and the absence of the conventional space-charge layer. Therefore, the studies employing such electrodes are expected to shed also more light on the mechanism of photocatalytic reactions.

Table 1. The saturated photocurrent of the TiO_2 electrode in various electrolyte solutions under the FS and BS irradiation

electrolyte	photocurrent (mA/cm^2)			shape[a]	photocatalyic
	pH	FS	BS	BS	activity[b]
NaOH	13.9	0.23	0.34	Mono	No
Na_3PO_4	13.7	0.20	0.29	Mono	No
Na_2HPO_4	9.1	0.22	0.27	Mono	No
$NaBO_2$	10.9	0.20	0.30	Mono	No
Na_2SO_4	8.0	0.22	0.25	Mono	No
Na_2CO_3	11.1	0.18	0.41	Step	Yes
$NaHCO_3$	9.1	0.15	0.53	Step	Yes
$KHCO_3$	8.6	0.18	0.54	Step	Yes

[a]Mono: The shape of V-I curve was typical and monotonous. Step: The shape of V-I curve was stepwise. [b]The promotion effect on the photocatalytic activity of Pt-TiO_2 for the stoichometric water splitting (Ref. 9).

The TiO_2 electrodes were prepared by coating with a viscous TiO_2 paste (P-25, Degussa) on the SnO_2 conducting glass (F-doped, Nihon Sheet Glass Co., 12 Ω/sq) sheets and calcinating at 500 °C, according to the published procedure.[2] The film thickness after calcination was about 7 μm. The photoelectrochemical experiments were carried out in a Teflon cell equipped with a quartz window. The solutions such as $NaHCO_3$ and NaOH (0.5 mol/l) were carefully deaerated with N_2. The UV light source was an Xe lamp (500 W, USHIO Co.). The counter electrode was a large platinum sheet, and the reference electrode was a Hg_2Cl_2/Hg/Cl^- (1M KCl), normal calomel electrode (NCE, 0.28 V vs NHE). The incident photon-to-current conversion efficiency (IPCE) was measured using a monochromator and a silicon light power meter (Optronic Lab., 730A).

The saturation photocurrents for the TiO_2 electrode, recorded in various solutions under the BS irradiation, are listed in Table 1. Figure 1 shows typical V-I curves obtained in a NaOH and a $NaHCO_3$ solution under the BS irradiation. In the case of NaOH solution (curve a), the photocurrent increased steeply from the onset potential (V_{on}), to reach gradually the saturation at ca -0.2 V, which is a usual behavior for the photooxidation of a number of species including water. On the other hand, the V-I curves recorded in the solutions of carbonate salts exhibited a stepwise rise of the photocurrent (curves b), reaching ca. 1.5 times larger value than in the NaOH solution at higher anodic bias, consistent with the superimposition of a second oxidation process. The stepwise shape of the V-I curve was practically

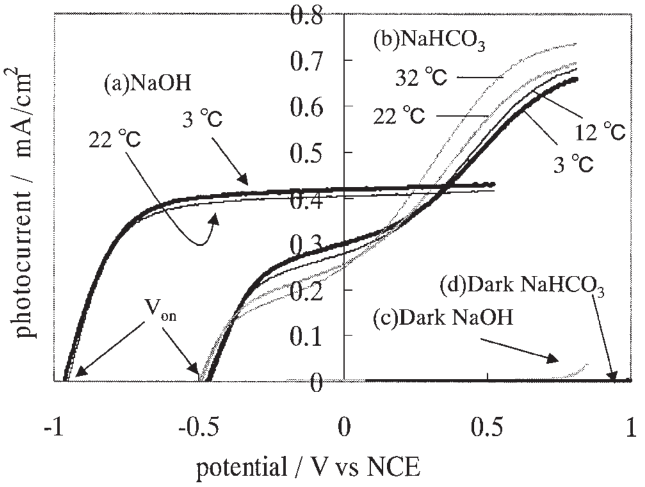

Figure 1. Photocurrent-potential curves recorded in solutions of (a) NaOH and (b) $NaHCO_3$ under the BS irradiation at various solution temperatures. (c) NaOH and (d) $NaHCO_3$ in dark at 22 °C. A special reactor with cooling bath was used.

the same for the forward and the back scan of the potential, and remained unchanged even under a very weak UV illumination. As expected, because of a decrease of pH, the photocurrent onset in carbonate solutions was shifted towards more positive potentials. Note also that the dark current (curves c and d) was negligible over the entire potential region. The photoresponse of the F-SnO_2 conducting glass without a TiO_2 film was negligibly small. The IPCE's corrected for the single-pass absorption of the conducting glass, not corrected for the light scattering, at 310 nm in NaOH and $NaHCO_3$ solutions reached 64% and 87%, respectively. On the other hand, in the case of the front side (FS) irradiation, the shapes of the V-I curves were monotonous in all solutions including carbonate salts solutions, and the photocurrents under the FS irradiation were smaller than those under the BS irradiation. Evidently, the photocurrent generation was more efficient close to the back contact, which is consistent with a lower extent of charge recombination due to a shorter diffusion length.[4] Under the FS irradiation, the photocurrents in carbonate solutions were small compared to those in other solutions. All these results suggest that a highly effective area for electron generation exists close to the conducting glass especially in the carbonate solution under larger positive potentials.

Importantly, the specific effect of carbonates upon the anodic photocurrent at the TiO_2 electrode was suppressed by increasing pH of the solution above 12, even in the presence of a large concentration of CO_3^{2-} ions. It is to be recalled in this connection that carbonate anions undergo adsorption on the TiO_2 surface at $pH < 12$, to form various surface species.[9,10] It has also been shown by Eriksen et al., that carbonate anions react with $OH^{\bullet}$ radicals to form OH^- ions and carbonate radicals.[11] Accordingly, one may expect such a reaction to occur between surface-bound $OH^{\bullet}$ radicals, formed in the process of water photooxidation at TiO_2, and the adsorbed carbonate species.

The photocurrents recorded in NaOH and other salt's solutions, except carbonate solutions, slightly increased with decreasing the temperature, both under the BS and FS irradiation. The same trend was also observed under the FS irradiation in carbonate solutions. Such an effect may be assigned to a decrease of the recombination rate with decreasing the temperature. As shown in Figure 1(b), the effect of temperature upon the amount of photocurrent was more complex in the case of the BS irradiation in carbonate solutions. Although the photocurrent at the first plateau (between -0.2 and $+0.2$ V) of the stepwise V-I curve increased with decreasing the temperature, this trend became inverted at larger anodic potentials with the saturation photocurrents at the second plateau ($>+0.5$ V) clearly decreasing with decreasing the temperature. This suggests the possible occurrence, in the potential region corresponding to the second plateau, of an electron injection process in addition to the hole transfer. As the dark current remained negligible over the entire range of potentials, the second plateau of the V-I curve is necessarily associated with the oxidation of the intermediates formed through the process of hole transfer (which occurs already in the range of potentials corresponding to the first plateau in Figure 1(b)). Assuming that the electron injection from the intermediates into the conduction band of TiO_2 occurs principally close to the back contact of the film, one may expect the photocurrent to be affected by the diffusion rate of the intermediates toward the conducting glass. This might be the reason for the observed increase of the photocurrent with the temperature. Moreover, the increase of the temperature is expected to produce an increase of the rate constant, leading to an increase of the current, like for most of electrochemical reactions. From the above results, the following mechanism is suggested. One of the candidates among the intermediates responsible for the electron injection may be the adsorbed $CO_3^{\bullet -}$ radical anion produced either through the oxidation of carbonate/bicarbonate ions by the holes or by the photogenerated $OH^{\bullet}$ radicals.

$$CO_3^{2-} + h^+ \text{ (or } OH^{\bullet}) \rightarrow CO_3^{\bullet -} \qquad (1)$$

The adsorbed carbonate radical ions may subsequently recombine to form peroxocarbonate species such as $C_2O_6^{2-}$ and CO_4^{2-}.[11]

$$2CO_3^{\bullet -} \rightarrow C_2O_6^{2-} \qquad (2a)$$

$$CO_3^{\bullet -} + OH^{\bullet} \rightarrow CO_4^{2-} + H^+ \qquad (2b)$$

These peroxocarbonate species undergo a rapid decomposition into O_2 and CO_2 under UV illumination. However, considering relatively weak photocurrents observed in the initial part of the I-V curve under slightly positive potentials ($<+0.3$ V), the adsorbed $CO_3^{\bullet -}$ radical species are also expected to act as effective recombination centers for the photogenerated electrons via the backward reaction of the eq (1). We assign the increase of the current observed in the second part of the I-V curves, under higher positive potentials ($>+0.3$ V), to the spontaneous electron injection by the carbonate radical anions into the conduction band of TiO_2 close to the back contact and/or directly to the SnO_2 conducting glass, assuming that the redox potential of $CO_4^{2-}/CO_3^{\bullet -}$ is located at ca. $+0.3$ V.

$$CO_3^{\bullet -} + H_2O \rightarrow CO_4^{2-} + 2H^+ + e^- \qquad (3)$$

On the other hand, the Fermi level on the outer side of the mesoporous TiO_2 film is expected to be unaffected by the potential applied to the back contact.[7] Therefore, the electron injection might mainly occur close to the conducting glass surface.

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