Overestimated solar water splitting performance on oxide semiconductor anodes

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Water oxidation is a 4-electron uphill energy process that largely limits the overall water splitting reaction thermodynamically and kinetically [1]. Photocurrent measurement is one of the most important approaches to evaluate the performance of a photoanode. It has been well realized that photocurrent may render exaggerated performance when photocorrosion of electrode occurs, such as the case of ZnO and CdS or when sacrificial reagents are present in the electrolyte. However, the choice of electrolyte could be another very important but easily overlooked issue for the valid interpretation of photocurrent.

Pioneering findings by Choi [2,3] and Mi [4,5] have demonstrated the existence of competing side reactions in various aqueous and non-aqueous electrolytes using WO₃ as the photoanode, where the actual O₂ evolution amount was measured and compared with photocurrent. It has been shown that the side reaction is more of a problem when 1) acidic or neutral aqueous electrolyte is used; 2) the photoanode semiconductor possesses a low valence band (VB) edge that generates highly oxidative holes. When acidic anions, such as Cl⁻, HSO₄⁻, SO₄²⁻, ClO₄⁻ exist in the aqueous electrolyte, the oxidation of these anions will compete with the oxygen evolution reaction (OER) for photogenerated holes. The oxidation of many acidic anions is thermodynamically less favourable than the OER, thus these competing side reactions are rarely of a concern for an electrolysis system in the dark. Under illumination, however, photogenerated holes would have enough energy to overcome the overpotential for the oxidation of acidic anions when the anode semiconductors possess the VB edges low enough to generate highly oxidative holes [3]. In addition, these competing side reactions are kinetically

more favourable than the sluggish 4-electron O₂ evolution process. For TiO₂ photoanode, lower O₂ evolution amount compared with the amount calculated from photocurrent was also reported with O₂ Faradaic efficiencies of 9%–35% in 0.2 mol L⁻¹ H₂SO₄ under Xe arc lamp illumination [6]. In this consideration, it might be misleading to evaluate the performance of a photocatalytic water oxidation system without measuring the actual O₂ evolution rate.

Recently, Niederberger and colleagues [7] have clearly pointed out this important yet easily overlooked issue for photoelectrochemical water splitting, i.e., photocurrent alone is insufficient to fully evaluate the performance of a photoanode. In their experiments, four aqueous electrolytes (1 mol L⁻¹ CH₃SO₃H, 1 mol L⁻¹ H₂SO₄, 0.1 mol L⁻¹ Na₂SO₄ at pH 3, and 0.1 mol L⁻¹ Na₂SO₄ at pH 5.5) were used to explore the influence of the competing reactions over the OER on WO₃ photoanodes. The WO₃ photoanodes prepared from the same condition exhibited noticeably different photocurrent density-potential characteristics in these four aqueous electrolytes under AM 1.5G illumination. When 1 mol L⁻¹ CH₃SO₃H was used as the electrolyte, a photocurrent density of 3.5 mA cm⁻² at 1.23 V vs. reversible hydrogen electrode (RHE) was achieved, followed by 3.2 mA cm⁻² in 1 mol L⁻¹ H₂SO₄, 2.4 mA cm⁻² in 0.1 mol L⁻¹ Na₂SO₄ (pH 3), and 2.0 mA cm⁻² in 0.1 mol L⁻¹ Na₂SO₄ (pH 5.5), respectively, at 1.23 V vs. RHE. This significant photocurrent difference clearly suggests that different surface reactions are involved in these four electrolytes on the same photoanode material.

To reveal the actual reaction pathway, the authors measured the O₂ evolution rate, which could be compared with the theoretical O₂ evolution amount calculated from the

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photocurrent. When $1 \text{ mol L}^{-1} \text{CH}_3\text{SO}_3\text{H}$ was used as the electrolyte, no O_2 was observed (Fig. 1a), indicating the absence of water oxidation reaction in spite of the high photocurrent. When $1 \text{ mol L}^{-1} \text{H}_2\text{SO}_4$ was used as the electrolyte, which yielded the second highest photocurrent, O_2 could be detected, but with a very slow evolution rate compared to the theoretical value calculated from the photocurrent (Fig. 1b). The resulting O_2 Faradaic efficiency is only 8% for WO_3 anode in $1 \text{ mol L}^{-1} \text{H}_2\text{SO}_4$. Compared the high photocurrent and the zero or extremely low O_2 evolution rate for WO_3 anodes in $\text{CH}_3\text{SO}_3\text{H}$ and H_2SO_4 , it can be inferred that serious side reactions exist, which largely suppress the OER and consume the majority of photogenerated holes. Specifically, CH_3SO_3^- anions could be oxidized to $\text{CH}_3(\text{SO}_3)_2$ in $1 \text{ mol L}^{-1} \text{CH}_3\text{SO}_3\text{H}$, and HSO_4^- anions to $\text{S}_2\text{O}_8^{2-}$ in $1 \text{ mol L}^{-1} \text{H}_2\text{SO}_4$. In this sense, it could be misleading to evaluate the performance of the WO_3 photoanode simply using photocurrent as the only indicator.

Lewis and co-workers [5] have systematically investigated the photoelectrochemical oxidation of acidic anions. The electrochemical redox potential for HSO_4^- oxidation, $E^0(\text{HSO}_4^-/\text{S}_2\text{O}_8^{2-})$, equals to $2.12 \text{ V vs. normal hydrogen}$

electrode (NHE), while $E^0(\text{CH}_3\text{SO}_3^-/(\text{CH}_3\text{SO}_3)_2)$ was predicted to be less than 2.12 V vs. NHE . Although water oxidation ($E^0(\text{O}_2/\text{H}_2\text{O}) = 1.23 \text{ V vs. NHE}$) is thermodynamically more favourable than the oxidation of HSO_4^- and CH_3SO_3^- anions, the 4-electron OER is kinetically hindered. In addition, the low VB edge of WO_3 makes it possible for photogenerated holes to overcome the overpotential for these two competing reactions. Thus, the O_2 evolution is largely suppressed in $\text{CH}_3\text{SO}_3\text{H}$ and H_2SO_4 electrolytes when using WO_3 as the photoanodes. Similarly, the oxidation of Cl^- anion will completely suppress water oxidation owing to the relatively low redox potential of this 2-electron competing side reaction, where $E^0(\text{Cl}^-/\text{Cl}_2)$ equals to 1.36 V vs. NHE [3].

Sulfate is another commonly used electrolyte. When $0.1 \text{ mol L}^{-1} \text{Na}_2\text{SO}_4$ at pH 3 and pH 5.5 are used for WO_3 photoanode, lower photocurrent compared with $\text{CH}_3\text{SO}_3\text{H}$ and H_2SO_4 is obtained, but the O_2 evolution rate is largely improved (Figs 1c and d). The O_2 Faradaic efficiency reaches 33% and 47% for $0.1 \text{ mol L}^{-1} \text{Na}_2\text{SO}_4$ at pH 3 and pH 5.5, respectively. Like the case for H_2SO_4 , the SO_4^{2-} oxidation competes with OER for photogenerated holes.

Figure 1 Measured O_2 evolution amount compared with the theoretical value calculated from photocurrent for WO_3 photoanodes in the four aqueous electrolytes: (a) $1 \text{ mol L}^{-1} \text{CH}_3\text{SO}_3\text{H}$, (b) $1 \text{ mol L}^{-1} \text{H}_2\text{SO}_4$, (c) $0.1 \text{ mol L}^{-1} \text{Na}_2\text{SO}_4$ at pH 3, and (d) $0.1 \text{ mol L}^{-1} \text{Na}_2\text{SO}_4$ at pH 5.5. Reproduced with permission from [7], Copyright 2016, Wiley-VCH.

Another important concern is the stability of photoanode material in different electrolytes. A stability test over 20 h shows that the WO_3 photoanode loses 44% of its initial photocurrent in 1 mol L^{-1} $\text{CH}_3\text{SO}_3\text{H}$, 59% in 1 mol L^{-1} H_2SO_4 , 81% in 0.1 mol L^{-1} Na_2SO_4 (pH 3), and 89% in 0.1 mol L^{-1} Na_2SO_4 (pH 5.5). The fact that WO_3 is not stable at $\text{pH} > 4$ could explain the low stability in Na_2SO_4 (pH 5.5). However, the low stability of WO_3 photoanode in 0.1 mol L^{-1} Na_2SO_4 (pH 3) and highly acidic 1 mol L^{-1} H_2SO_4 suggests that some new species is formed causing the deactivation. It has been suggested that the formation of persulfate ($\text{S}_2\text{O}_8^{2-}$) is the reason for WO_3 deactivation [8]. While 1 mol L^{-1} H_2SO_4 is expected to result in more persulfate formation than 0.1 mol L^{-1} Na_2SO_4 (pH 3), the stability is higher in the former electrolyte. This indicates that the formation of persulfate might not be the only cause for instability. The deactivation of WO_3 has been attributed to the formation of peroxo species on the WO_3 surface [9]. Hill *et al.* [3] also reported the existence of incomplete water oxidation to peroxide species, accompanying the oxidation of anions in electrolyte.

In conclusion, the work reported by Niederberger and co-workers underlines a very important caution that photocurrent may lead to overestimated performance of a photoanode due to the multiple reaction pathways existing in the electrolyte. The actual O_2 evolution amount and the stability of the electrode should be measured to evaluate how much of the photocurrent is used to oxidize water, the electrolyte, and the anode materials, respectively. This is especially necessary for photoanode materials with a low VB edge position, such as WO_3 , used in electrolytes containing acidic anions with favorable oxidation kinetics. This work

may further help to establish a reliable estimation methodology for photoelectrochemical performance in solar water splitting.

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