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Hydrogen production from photo-driven electrolysis of biomass-derived oxygenates: A case study on methanol using Pt-modified WO₃ thin film electrodes

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ABSTRACT

In this paper, we demonstrate the feasibility of H₂ production from biomass-derived oxygenates with photoelectrochemical cells (PECs) based on the tandem cell hybrid photoelectrode configuration. As a proof of concept, we have studied the simplest oxygenate, methanol, which is photoelectrochemically oxidized at thin film tungsten oxide (WO₃) photoelectrodes. When the methanol oxidation reaction (MOR) is coupled with the hydrogen evolution reaction (HER), this process is known as methanol electrolysis. We demonstrate that catalytic modification of the WO₃ surface by the electrodeposition of Pt particles can greatly increase MOR activity at the photoanode, resulting in a significant increase in H₂ production rates from methanol electrolysis. This improvement is greatest at low overpotentials and high Pt loadings, with the demonstrated MOR current density of Pt–WO₃ being nearly four times that of the oxygen evolution reaction (OER) on WO₃ at a potential of 0.8 V vs. the Reversible Hydrogen Electrode. We also illustrate how the increase in WO₃ photocurrent and the decrease in the oxidation onset potential, compared to the OER, make it possible to use WO₃-based photoelectrodes in a simple tandem cell configuration whereby a common PV component such as a-Si can provide the remaining voltage to achieve unassisted methanol electrolysis. Results from methanol electrolysis reveal the potential to utilize a similar approach for larger biomass-derived oxygenates, which could be a promising pathway to H₂ production from renewable feedstock using photo-driven electrolysis.

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1. Introduction

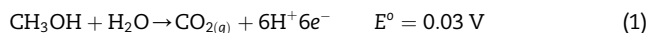
Hydrogen (H₂) is an attractive fuel for the future because it represents a high energy density, mobile energy carrier that produces only water at end use. However, 95% of the hydrogen produced in the U.S. is currently made from nonrenewable

fossil fuel feedstocks such as methane [1], and a low-cost means to produce H₂ using renewable energy inputs has yet to be demonstrated. In recent years, a promising route to renewable H₂ production has been proposed that involves using photoelectrochemical cells (PECs) to produce H₂ from biomass-derived oxygenates (C_xH_yO_z species) [2,3]. Compared

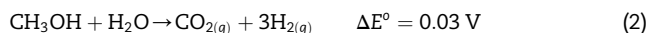
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to conventional biomass-to-H₂ conversion processes [4–6], this PEC-based process can take place at much lower temperature, at smaller scale, and with easy product gas separation [2]. In this paper, we explore this novel route to H₂ production by using Pt-modified WO₃ photoelectrodes (PEs) to oxidize methanol, a commonly-studied oxygenate molecule whose oxidation proceeds as follows:



Methanol is an appropriate starting point for this study because it contains the characteristic –CH₂OH unit that is present in larger biomass-derived oxygenates, making it an excellent probe molecule to evaluate photoelectrodes for the photo-driven electrolysis of more complex molecules. When the methanol oxidation reaction (MOR) is paired with the hydrogen evolution reaction (HER), the overall reaction is given by Eqn. (2), which has been termed methanol electrolysis [7,8]:



As illustrated in Fig. 1a, one of the benefits of producing H₂ from oxygenate species such as methanol is that the thermodynamic voltage requirement, $\Delta E^\circ = E_{\text{C}_x\text{H}_y\text{O}_z}^\circ - E_{\text{H}_2/\text{H}^+}^\circ$ can be significantly smaller than that required for H₂ production from water electrolysis, $\Delta E^\circ = E_{\text{H}_2\text{O}/\text{O}_2}^\circ - E_{\text{H}_2/\text{H}^+}^\circ = 1.23 \text{ V}$ [8]. In PECs, an additional benefit of producing H₂ from electrolysis of oxygenate species is improved reaction kinetics compared to the oxygen evolution reaction (OER), which results in suppressed electron/hole pair recombination at the photoelectrode [9]. Many researchers have demonstrated enhanced PEC H₂ production rates from oxygenate-containing solutions [9–11], but most studies have focused on using dispersed powder catalysts commonly made of TiO₂, which is only active in the UV wavelengths. Furthermore, the use of dispersed powder catalysts creates challenges for product gas separation in real PEC devices. To overcome these issues and achieve more efficient PEC conversion of oxygenates, our efforts are centered on the use of a tandem photoelectrode configuration comprised of a semitransparent thin film photoelectrode placed in tandem with a lower band gap PV component (Fig. 1b). In this configuration, commonly referred to as a hybrid photoelectrode [12,13], the photo-voltages generated by the series PV (V_{PV}) and PE (V_{PE}) components are added, and the photocurrent is limited to the current produced by the component generating the lowest current. Importantly, the hybrid photoelectrode design allows for significant harvesting of visible light photons from the PV component while easily collecting product gasses in divided anode and cathode compartments. Although application of the hybrid photoelectrode concept has been focused on water splitting [12–15], this architecture may prove to be even more useful for PEC conversion of oxygenates because the lower required photovoltage will allow for high-efficiency, low band gap, semiconductors to be used as the bottom cell.

A promising PE material to be used in the hybrid photoelectrode configuration is WO₃, a semiconducting material that exhibits excellent stability in acidic solutions [16] and has a band gap ($E_g = 2.6 \text{ eV}$) that allows it to absorb substantially more light under AM 1.5 illumination than TiO₂ ($E_g = 3.2 \text{ eV}$)

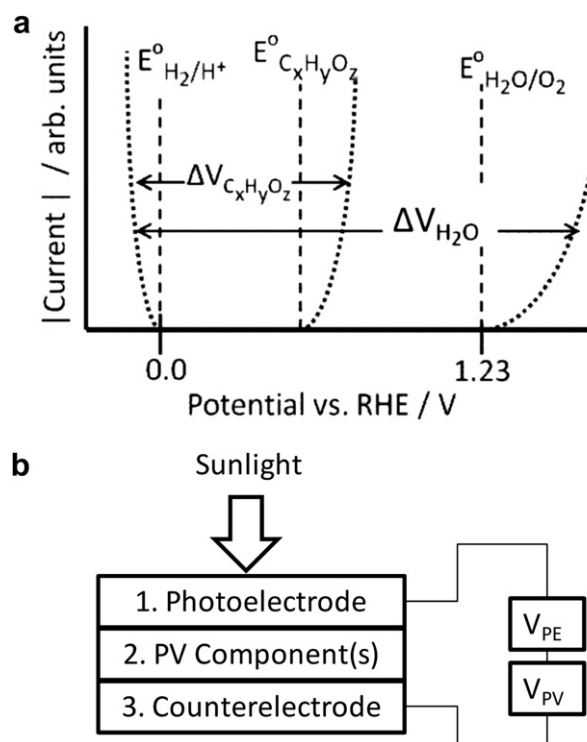


Fig. 1 – a.) Schematic current/potential diagram showing the voltage required to produce hydrogen through conventional water electrolysis ($\Delta V_{\text{H}_2\text{O}}$) or through an alternate pathway in which an electron donor species is oxidized in place of water ($\Delta V_{\text{C}_x\text{H}_y\text{O}_z}$). Dashed lines mark the reversible Nernstian potentials for each half cell reaction and the dotted curves show the operating curve for each electrode. Deviation of an electrode operating curve from the Nernstian potential represents an overpotential, or efficiency loss, which results from poor kinetics and/or mass transfer limitations at the electrode surface. b.) Schematic diagram of a hybrid photoelectrode device consisting of monolithically integrated photoelectrode, photovoltaic, and counterelectrode components. The series addition of the photo-voltages generated by the photoelectrode (V_{PE}) and photovoltaic (V_{PV}) components is often necessary to achieve $\Delta V_{\text{H}_2\text{O}}$ or $\Delta V_{\text{C}_x\text{H}_y\text{O}_z}$.

[17]. WO₃ is not active toward the MOR in the dark, but shows good photocatalytic activity toward the MOR under illumination, achieving photocurrents of $\sim 4.5 \text{ mA cm}^{-2}$ that far exceed that obtained from the oxygen evolution reaction (OER) [18]. The enhanced photocurrent has been attributed to improved kinetics compared to the OER, as well as the occurrence of photocurrent multiplication whereby one photon is able to create two or more electrons through the direct injection of secondary electrons from adsorbed reactive intermediates into the semiconductor bulk [19]. These factors are especially beneficial for large band gap photoelectrode materials such as WO₃ or TiO₂, which are normally limited to low current densities ($< 3 \text{ mA/cm}^2$) due to optical absorption constraints.

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