



Balancing photovoltage generation and charge-transfer enhancement for catalyst-decorated photoelectrochemical water splitting: A case study of the hematite/MnO_x combination

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ABSTRACT

To improve semiconductor-based water-splitting performance, one popular approach is to modify the electrode surface with catalysts. The strategy is to increase charge-transfer kinetics and, hence, to reduce overpotential requirements. Relatively underwhelming attention has been paid to how such surface treatments influence the nature of the semiconductor/solution interface so as to reduce photovoltage generated by the photoelectrode. Using atomic layer deposition-grown (ALD) MnO_x on hematite (α -Fe₂O₃) as an example, here, we show that increased charge-transfer kinetics does not necessarily lead to improved overall performance. Compared to bare hematite, MnO_x-decorated photoelectrode exhibits significant anodic on-set potential shift. The phenomenon is understood as a substantial reduction in photovoltage generation by hematite, and the origin is identified as Fermi-level pinning effect due to MnO_x introduction. This work sheds light on the importance of maintaining band-edge pinning for semiconductor-based photoelectrochemical reactions.

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1. Introduction

Water splitting is an important reaction that can be used to harvest and store solar energy [1,2]. In nature, the process produces reactive protons, building up a concentration gradient to power dark reactions which turn CO₂ to organic molecules [3]. In laboratories, a simplified version of the reaction has been conceived to produce O₂ and H₂, the latter promising a solution to problems caused by the combustion of fossil fuels [4]. In a variation, artificial CO₂ reduction can in principle be powered by sunlight to produce solar fuels [5]. Although the detailed chemical mechanisms of these reactions vary, they share the same key features of harvesting solar energy and storing it in chemicals. Essential components necessary to enable the conversion include an antenna to absorb photons and to produce excited electrons, a mechanism to physically move the excited electrons away from the site where they are generated, and an efficient catalyst to drive chemical reactions selectively [6,7]. Because of the existence of a band gap and the typical band bending formed when in contact with an electrolyte, semiconductors are good candidates for solar water splitting or CO₂ photoreduction [7,8]. Other appealing aspects of using semiconductors for solar fuel

production include durability, low cost, and ease of device fabrication [2].

Since the first demonstration by Honda and Fujishima in 1972 [1], semiconductor-based photoelectrochemical (PEC) water splitting has received significant research attention. For comprehensive explanations about fundamental principles governing PEC water splitting, readers are referred to recent reviews cited herein [2,7]. Among these considerations, two important ones are highlighted here. Our goal is to focus on the semiconductor/water interface [9]. As shown in Fig. 1, for an n-type photoanode, the band bends upward near the interface, allowing one to describe the electrode's optoelectronic behaviors using models built for Schottky-type diode. The origin of the band bending, which is key to discussions about semiconductor-based PEC water splitting, lies in the so-called band-edge pinning [10]. It refers to the effect that the electron affinity (*A*) of the semiconductor on the surface remains unchanged relative to the electrochemical potential (*F*_{redox}) of the solution before and after contact. When in contact, two equilibria are established. At the interface, the electronegativity of the semiconductor (χ) equilibrates with *F*_{redox}. In the body of the semiconductor, χ remains unchanged relative to *A*. Because for equilibrium, χ is flat; through the system, we see that a downward bending of *A* from the surface into the body, and hence, the energy band of the semiconductor (Fig. 1a) is necessary. The bending is important because it provides a built-in field to facilitate separation of photo-

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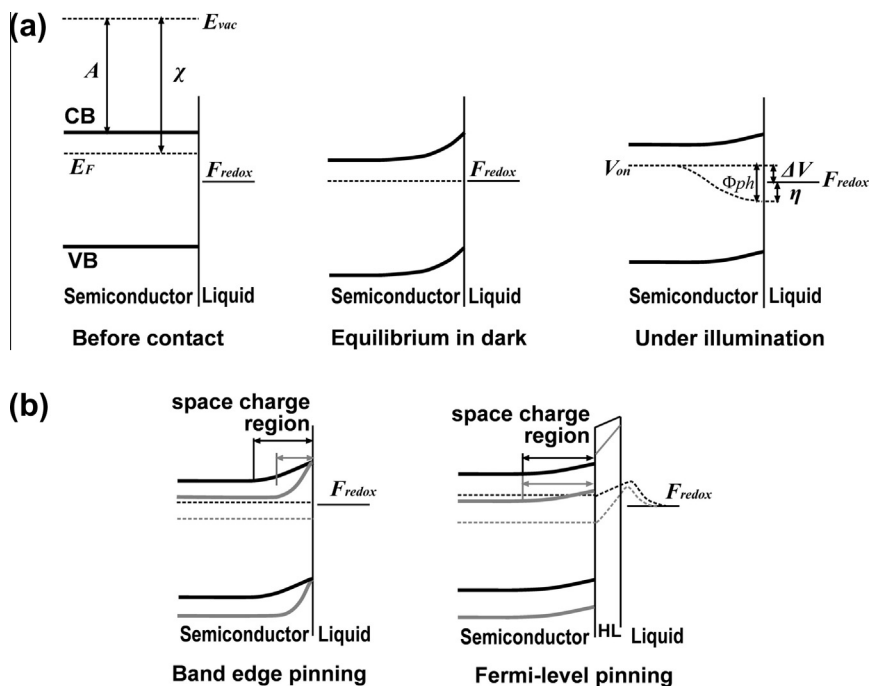


Fig. 1. Band structure of n-type semiconductor. (a) Before contact (left panel) and after contact, under equilibrium conditions in dark (middle panel) with an electrolyte system where a single redox pair dominates the electrochemical potentials in the solution. The right panel shows steady-state conditions under illumination. The downward bent quasi-Fermi level represents that of photogenerated holes. An overpotential (η) is necessary to maintain a meaningful photocurrent. ΔV is the measurable difference between the applied potential and F_{redox} . (b) When a positive bias is applied to the semiconductor, the applied bias drops within the semiconductor space charge region to broaden the degree of band bending under band-edge pinning conditions (left panel). Under Fermi-level pinning conditions, the applied bias drops within the Helmholtz layer (HL), leaving the band bending unchanged (right panel). The gray and black lines are under different bias and the bumps between semiconductor and liquid represent potential drop in HL.

generated charges, a basis for semiconductor-based solar energy harvesting [10].

The afore-described model ignores how charge distribution within the electrolyte near the interface is influenced by the semiconductor. Such a simplification is often justified by the fact that, due to high ionic strength of the electrolyte, the potential drop in the solution is typically much smaller than that in the semiconductor [11]. However, when sufficient surface states exist on the semiconductor (e.g., with a density of $\sim 10^{13}$ – 10^{14} cm^{-2}) [12], the potential difference between χ and F_{redox} may result in a non-negligible potential drop within the Helmholtz layer (Fig. 1b) [13]. This effect is known as Fermi-level pinning. Not contributing to charge separation within the semiconductor, Fermi-level pinning effect is negative for PEC water-splitting purposes [13]. Practical devices often exhibit a combination of partial band-edge pinning and partial Fermi-level pinning. The recent literature reports describing PEC performance of various photoelectrodes often fail to highlight the importance of the negative impact of Fermi-level pinning. We hope to correct the deficiency by addressing this issue in this report.

Fermi-level pinning effect negatively impacts PEC performance of a photoelectrode by reducing the measurable photovoltage (Φ_{ph}). This understanding is schematically illustrated in Fig. 1b, where an n-type semiconductor-based photoanode is depicted. Experimentally, the influence is manifested by an increase in the turn-on voltage (V_{on}) of a polarization plot (for a photoanode), where V_{on} is defined as the potential at which anodic current is first experimentally measured and is related to Φ_{ph} , F_{redox} and η (kinetic overpotential) following

$$\Delta V = F_{redox} - V_{on} = \Phi_{ph} - \eta \quad (1)$$

Since ΔV is a loose analog of open-circuit voltage in photovoltaics, there is significant interest to maximize it for higher system efficiency. For example, researchers have been trying to reduce η by

applications of catalysts, on the basis that the semiconductor photoanode alone often requires large overpotentials for water oxidation [14,15]. Attempts of using homogenous catalysts whose water oxidation mechanism is known or heterogeneous ones which have been shown to exhibit low η in oxidizing water have been widely reported [16,17]. A major figure-of-merit used to measure the catalytic effect was how much V_{on} is cathodically shifted in a photoanode-based PEC system [18]. Careful examination of Eq. (1), however, reveals that at least two factors may contribute to a cathodic shift in V_{on} , namely an increase in Φ_{ph} or a reduction in η . For a given system, understanding which factor plays a more important role has significant implications. If it is realized that smaller Φ_{ph} is the main cause of higher V_{on} , research attention should be directed toward modifying the semiconductor/water interface for a reduced surface state density. Efforts focused on catalytically modifying the surface will likely have a limited impact on the overall water-splitting performance enhancement unless the catalyst also happens to reduce surface state densities. On the other hand, when a catalyst is applied to a photoelectrode, great care must be taken to avoid creating high density of states at the interface, which otherwise would lead to smaller Φ_{ph} , negating the gain in η reduction. In this report, we use a hematite/ MnO_x model system to highlight this understanding. It is shown that although MnO_x is effective in increasing water oxidation kinetics, its application onto hematite greatly suppresses the overall PEC performance. The effect is understood as a significant reduction of Φ_{ph} caused by the introduction of MnO_x as thin as that produced by a single cycle of ALD precursor exposure.

Here, hematite ($\alpha\text{-Fe}_2\text{O}_3$) is chosen as a photoanode material for our study because it represents a good platform to understand phenomena related to PEC water splitting [9,19–23]. The main appealing properties held by hematite include abundance, stability against photocorrosion, non-toxicity and suitable optical band gap

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