



Interfacial Schottky junctions modulated by photo-piezoelectric band bending to govern charge carrier migration for selective H₂O₂ generation

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ABSTRACT

A major challenge faced by most systems is the dissociation of O–O bonding on H₂O₂ by subsequent electron (e⁻) reduction. This study investigates interfacial charge transfer by manipulating e⁻ flows through a deflexed band potential on polarized piezoelectric BiFeO₃ (BFO). The H₂O₂ accumulation via coupling with the photocatalyst BiOCl/BiVO₄ (BCV) was highly effective since the Schottky barrier height (SBH) formed within the heterojunction composite shifted according to the surface polarity of BFO. Additionally, the constant alternating surface charge on BFO, reduced the SBH, forcing the photoexcited e⁻ to flow from BCV→BFO for effective H₂O₂ production, while restricting decomposition of H₂O₂ during downshifted band potential (positive surface) as high SBH discontinuing the electrons flow from BCV→BFO. The high interfacial charge transfer resistance (R_{ct}) was also critical for H₂O₂ accumulation, since it is unfavorable for H₂O₂ dissociation (H₂O₂/·OH, +0.39 V) despite the presence of a high band potential (+0.16 eV) on the opposite surface's upshifted band. The formation rate (k_f: 1.13 μmol L⁻¹ min⁻¹) of H₂O₂ was calculated much higher than decomposition rate (k_d: 0.01 min⁻¹). Additionally, the RRDE results indicated favorable 2e⁻ transfer with > 90 % selectivity for H₂O₂. Results from ESR DMPO-·OH adduction and atrazine degradation show an insignificant concentration of ·OH has been produced. This work provides an effective strategy to regulate semiconductors' surface junction by piezoelectric polarization for selective H₂O₂ generation.

1. Introduction

Hydrogen peroxide (H₂O₂) is a versatile oxidizing agent used in a variety of applications, including water treatment, chemical manufacturing, and medical purposes [1–3], owing to its high oxidation potential and benign byproducts. Additionally, H₂O₂ has generated considerable interest as a potential alternative to fossil fuels as a source of clean energy [4]. Compared with compressed H₂ gas, H₂O₂ is more convenient for transportation and storage [5]. Currently, only one major method is used for industrial production of H₂O₂, namely anthraquinone oxidation, which is typically associated with a high energy input and the production of toxic byproducts [6,7]. To meet global demand without entirely relying on fossil fuels, an alternative fuel source such as an H₂O₂

fuel cell (1.09 V) is desirable, as it has a comparable output potential to a hydrogen fuel cell (1.23 V) [8]. As a result, environmentally friendly and cost-effective manufacturing processes are highly attractive, particularly those that do not require sacrificial chemicals, expensive noble metals, or involving evolution of CO₂ gas.

Light-driven catalysts were considered ideal strategies for addressing the aforementioned issues, with considerable effort being made to improve performance efficiency while maintaining a high selectivity for H₂O₂ production [9]. However, photocatalytic generation of H₂O₂ is still constrained by a number of factors, including low light absorption, low electron separation efficiency, the requirement for sacrificial agents, and undesirable decomposition of H₂O₂ by inappropriate conduction band (CB) position (H₂O₂/·OH, +0.39 V vs. NHE) [10–12]. Apart from

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