

# Elucidating Photoelectrocatalytic Mechanism Related To The Reconstructed Interfaces of Ternary Nanostructured $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/Au/TiO<sub>2</sub> Photonanode by X-ray Spectroscopies

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## Abstract

Hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) has increasingly paid wide attention as one of the most promising photoanode materials in semiconductor-based sunlight-driven photoelectrocatalytic water splitting devices. However, the full exploitation of solar-to-hydrogen conversion efficiency of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> water splitting cell is still finite by poor majority carrier conductivity, short hole-diffusion lengths, and sluggish kinetics for the oxygen evolution reaction (OER) at the photoelectrode/electrolyte interface. In this study, we reported that adjusting the composition of the electrolyte with the integrating a crystalline  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> core, metallic Au nanoparticles, and an amorphous TiO<sub>2</sub> overlayer could be as a strategy to enhance photocatalytic performance. Under simulated solar illumination, the photoelectrocatalytic performance of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/Au/TiO<sub>2</sub> was significantly improved with the photocurrent density was found to be 4-fold greater than that of pure  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> at 1.23 V versus RHE. X-ray absorption spectroscopy (XAS) was performed to investigate the electronic properties of the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and how it was modified with Au and TiO<sub>2</sub> decoration. The significant improvement could be attributed to the relayed pumping of photogenerated charge carriers through the photoelectrode/electrolyte interface reconstructed by Au nanoparticles and TiO<sub>2</sub> overlayer. Using the power of scanning transmission X-ray microscopy (STXM) as a spectromicroscopic technique, the photohole transport mechanism was revealed and accordingly provide insight into the impact of material heterogeneities on its performance.