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► **To cite this version:**

Stefan Stanescu, Leon Schmidt, Y. J. Dappe, Dris Ihiawakrim, Walid Baaziz, et al.. Enhancement of the solar water splitting efficiency mediated by surface segregation in Ti-doped hematite nanorods. 8th International Conference on Catalysis and Chemical Engineering, Feb 2024, Boston, United States. hal-04907688

HAL Id: hal-04907688

<https://hal.science/hal-04907688v1>

Submitted on 23 Jan 2025

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Enhancement of the Solar Water Splitting Efficiency Mediated by Surface Segregation in Ti-doped Hematite Nanorods

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Abstract

Hydrogen production by solar water splitting is a very attractive idea because it allows storing solar energy in the H₂ molecules using a clean method. First demonstration of water splitting was reported 50 years ago using TiO₂ as photoanode¹. Since then, plethora of studies were reported, owing to materials chemists' infinite imagination, addressing different classes of photosensitive materials including semiconducting oxides, III-V semiconductors², MOF (metal-organic framework) architectures³, ferroelectric materials⁴, etc. Band engineering is often employed targeting the same single aim: enhance the efficiency of the photoelectrochemical (PEC) process, increasing thus hydrogen production efficiency.

We report here a simple band engineering approach applied to one of the most Earth abundant materials, the hematite, using Ti doping³⁻⁶ and tuning annealing conditions: temperature and atmosphere. Enhanced PEC activity was obtained, mediated by surface states, as evidenced using electrochemical impedance spectroscopy. We found strongly enhanced photocurrent, of more than 200 %, for Ti-doped hematite photoanodes annealed under Nitrogen compared to equivalent photoanodes annealed in air⁶. The nanoscale origin of the increased photocurrent was addressed using combined XPEEM, STXM, X-rays spectroptychography and STEM. Shadow XPEEM alone can be used to discriminate surface and bulk contributions of the chemistry and chemical coordination. STXM complement successfully these results evidencing formation of Ti-rich clusters for photoanodes annealed in O₂-free atmosphere. Spectro-ptychography allows to better identify and isolate both spatially and chemically Ti-rich clusters. X-ray spectromicroscopies altogether were confronted with STEM measurements and DFT calculations, the results suggesting formation of pseudo-brookite clusters at the surface of the Ti-doped hematite.

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