

Investigating solar degradation mechanisms of the Ta₃N₅ photoelectrode by in-situ transmission electron microscopy

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Background incl. aims

Photoelectrochemical water splitting is a clean and renewable method to directly convert green energy carrier from solar light into hydrogen. Ta₃N₅ is a promising photocatalytic material for use as a photoanode, with suitable bandgap (2.2 eV), and with the conduction band (CB) and valence band (VB) energy levels appropriately straddling the water redox potentials [1]. By applying only 1.23 V of overpotential, the photocurrent density under 1 Sun illumination reaches the theoretical limit of approx. 13 mA.cm² [2, 3]. However, during operation when the photoelectrode is exposed to water, sunlight, and biasing conditions, photocorrosion has shown to occur. This reduces the stability of the device significantly and degrades the material by oxidizing the surface. In order to utilize this material as a stable and efficient photoanode, it is important to understand and prevent the solar degradation process. We have previously investigated the stability of the electronic band structure of Ta₃N₅ using operando ambient pressure X-ray photoelectron spectroscopy (AP-XPS) at the HIPPIE beamline at the MAX IV synchrotron in Lund using the “dip and pull” setup for pure Ta₃N₅ as well as NiOx coated materials and found Fermi-level pinning to occur, and a significant improvement was made by stabilizing the surface. We then wanted to investigate the dynamic structural changes that occur to Ta₃N₅ during the degradation process when Ta₃N₅ is exposed to water vapor, biasing conditions, and light.

Methods

Ta₃N₅ thin films on glass substrates were made with pulsed vapor deposition of metal Ta, following a nitridation process. Some samples were also made with a protective NiOx coating. The ex-situ characterization work was done using a FEI Titan G2 transmission electron microscope (TEM), DCOR Cs probe corrector, Super-X EDS detector, and Gatan GIF Quantum 965 electron energy loss (EELS) Spectrometer at SINTEF in Oslo. While the in-situ TEM characterization was carried out using an environmental transmission electron microscope a Titan E-Cell 80-300ST TEM at DTU. The TEM sample was made with a focused ion beam and connected to a heating and biasing chip with a diode placed on top of the extra contacts.

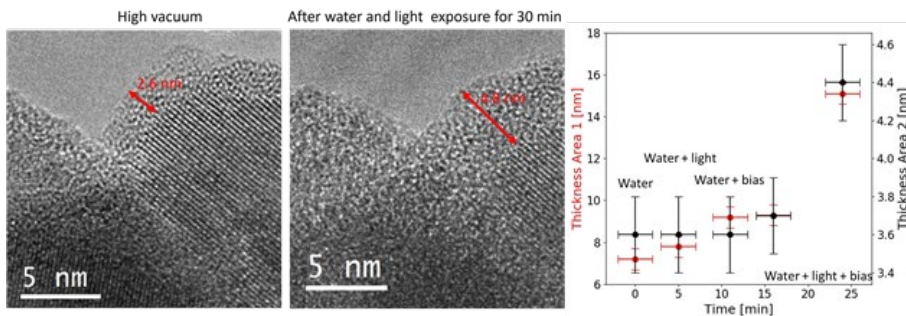
Results

During the degradation process, an amorphous layer is formed at the surface. The surface layer formation is highest when combining water, light, and biasing of the sample. The process seems to first make small nanocrystals of Ta₃N₅. After some time, they are amorphized, and new nanocrystals are formed. This process continues till we have a stable uniform surface layer.

Conclusion

The surface degradation process creates an amorphous layer, and is most pronounced when combining water, light, and bias. The degradation first makes small nanocrystals of Ta₃N₅, for then to amorphized them separately.

Graphic:



Keywords:

Degradation, TEM, operando, Ta₃N₅, Hydrogen

Reference:

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