

SrTiO₃ Surface Post Photocatalytic Water Oxidation: TEM Chemical and Structural Analyses

Sadegh Yazdi and Tanja Cuk

University of Colorado Boulder, Boulder, Colorado, United States

Photoelectrochemical water splitting is a promising renewable approach for generating zero-emission hydrogen fuel economically. The solar energy is used to dissociate water molecules into oxygen and hydrogen in a photoelectrochemical cell. The photocatalyst reactions occur at the electrode–electrolyte interface and often alter the electrode surface. The morphology can affect the durability and lifetime of photoelectrochemical cells. Here, we apply advanced transmission electron microscopy (TEM) techniques to study the surface of the single crystal n-SrTiO₃ after being used as a photoanode in water oxidation under pulsed laser excitation.

Nb-doped single crystal SrTiO₃ was used as the working electrode in a photoelectrochemical cell with a Pt wire as the counter electrode in 0.1 M NaOH. Optically pumping the Schottky barrier across the SrTiO₃ – aqueous interface with a 266 nm ultrafast pulsed laser initiated the reaction with a reasonably high surface excitation (~3% of O-surface sites). While the ultrafast pulse yields an immediate surface excitation, the charge-separation efficiency was maintained (75 %) and led to Faradaic O₂ evolution from the working electrode (see ref [1] for details). The SrTiO₃ surface, however, changes during water oxidation. To interrogate the surface, we prepared cross-sectional TEM specimens from the affected area using focused ion beam (FIB) milling in an FEI Nova 600 DualBeam system. The morphology and composition of the surface layer were analyzed in a Thermo Fisher probe-corrected Titan Themis S/TEM equipped with a Super-X EDS detector at 300 keV.

The photo-excited surface layer appears darker than surrounding intact SrTiO₃ in secondary electron images in SEM. Cross-sectional specimens were prepared from the center of the dark region (Fig. 1a). High angle annular dark field scanning transmission electron microscopy (HAADF-STEM) images (Fig. 1b) revealed the layer to be amorphous and porous with a rough spiky interface with the crystalline SrTiO₃ substrate (Fig. 1c). The bright contrast on the SrTiO₃ region near the layer shows the presence of lattice strain close to the interface. Chemical analysis of the layer by energy dispersive X-ray spectroscopy in STEM (STEM-EDS) showed that material loss within the layer is likely due to the leaching of mainly Sr during photocatalysis. Spectra in Fig 2.b shows that the Sr to Ti and Sr to O X-ray peak ratios drop significantly as moving from the SrTiO₃ bulk to the affected layer. Quantified EDS maps and their corresponding profiles in Fig. 2 show that the weight percent of Sr in the damaged layer decreases by over 50%, whereas Ti and O weight percent increase. We found that the thickness of the photo-excited layer and its chemical composition depend on different parameters including the exposure time to the laser, in other words, the photocatalysis reaction period.

Further chemical analyses of the photo-excited surface by electron energy loss spectroscopy (EELS) and X-ray photoelectron spectroscopy (XPS) are in progress that will be presented in the meeting. Detailed structural and compositional analysis of the surface of SrTiO₃, as a model photoanode material, will be a significant step forward in understanding the surface rearrangement of chemical bonds occurring during photocatalysis reactions at this and other surfaces [2].

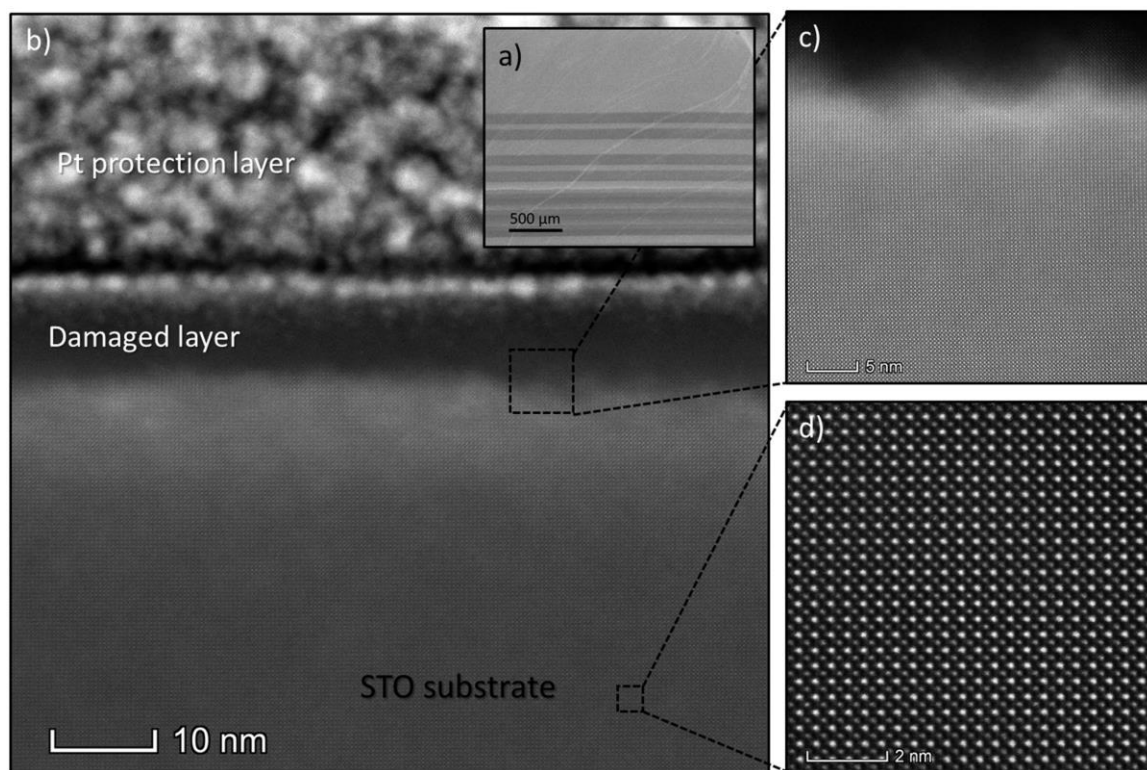


Figure 1. a) An SEM micrograph of the surface of n-SrTiO₃ after photocatalytic water oxidation. The dark horizontal lines show the damaged surface where the pulsed laser was scanned during the water oxidation. b) A typical HAADF-STEM image of a FIB prepared cross-sectional specimen showing a porous and amorphous damaged surface. Higher magnification images from the black dashed boxes in b) are shown in c) and d). The image in c) shows the rough and spiky interface between the SrTiO₃ substrate and the damaged layer. The brighter contrast close to the interface is an indication of strain fields. Atomic resolution image in d) from the SrTiO₃ substrate confirms the defect-free crystalline structure.

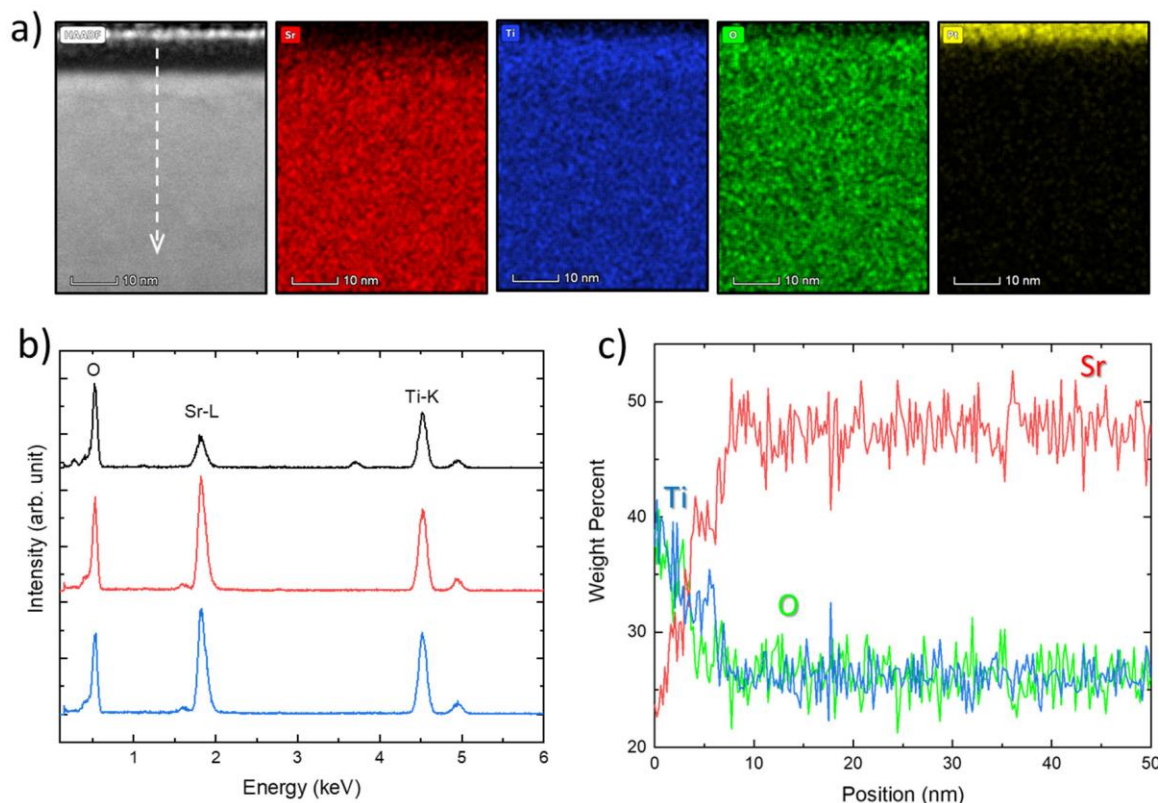


Figure 2. a) HAADF-STEM and its corresponding STEM-EDS weight percent maps of Sr- $K\alpha$, Ti- $K\alpha$, O- K , and Pt. b) shows the EDS spectra from the substrate (blue), the strained region close to the interface (red), and the damaged layer (black). Only part of the spectrum (up to 6 keV) is shown for clarity. The Sr/Ti and Sr/O peak ratios significantly drop as moving to the damaged layer. c) Line profiles from the Sr, Ti, and O maps in a) across the white dashed arrow shown in the HAADF-STEM image. Cliff-Lorimer ratio technique was used for quantification, and spectra from the substrate were used for the precise measurement of k -factors.

References

- [1] D. J. Aschaffenburg, X. Chen, and T. Cuk, *Chem. Commun.*, 2017, **53**, 7254-7257.
- [2] The support from the Facility for Electron Microscopy of Materials at the University of Colorado at Boulder (CU FEMM) is acknowledged.