

Opportunities and Challenges for *In-Situ* Characterization of Photocatalysts in Environmental TEM.

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Photocatalytic water splitting has been considered a promising technology for generating sustainable clean energy. Essentially, photocatalytic materials enable the process of converting and storing solar energy in the form of H₂ molecules. It is now recognized that atomic level *in-situ* observations of catalytic materials are critical for understanding structure-reactivity relationships and deactivation processes such as photocorrosion. For photocatalysts, this requires that the system be observed not only in presence of reactant and product species but also during *in-situ* light illumination. Here opportunities and challenges associated with building a “photo-reactor” inside an environmental TEM (ETEM) are discussed.

An optical fiber-based *in-situ* illumination system was developed and installed in an FEI Tecnai F20 ETEM with light intensity close to 10 suns [1]. The ETEM has a differential pumping system which allows up to 10 Torr gas pressure around the TEM sample. TiO₂ based and Ta₂O₅ based UV absorption photocatalysts were chosen as model systems for *in-situ* and *ex-situ* characterizations. TiO₂ is relatively abundant with simple crystal structures while Ta₂O₅ is very efficient with more complicated structures. The oxides are functionalized with Ni-NiO core-shell nanoparticles, which have been reported to be one of the most efficient surface co-catalysts when loaded onto TiO₂ or Ta₂O₅. The combination of heat, light, and reactant gas stimuli allows the structural evolution of a photocatalyst to be followed through activation, reaction, and deactivation. Figure 1 shows the activation of a Ni metal co-catalyst on TiO₂ involving *in-situ* reduction at 400 °C in 1 Torr for 4 h. Interestingly, the Ni metal becomes coated with a thin amorphous TiO_x layer during the reduction step. During the subsequent Ni oxidation step to form the Ni-NiO core-shell structure, this TiO_x mixes with NiO layer. Additional experiments have confirmed that the Ni/TiO₂ catalyst reduced *ex-situ* is also covered with TiO_x layer.

We have shown that subtle changes may take place under photoreaction conditions. For example, *in-situ* observation of TiO₂ nanocrystals under water and light exposure shows the formation of amorphous surface layers less than 0.5 nm in thickness [2]. We are currently installing an optical fiber into an FEI Titan ETEM equipped with an image corrector to enable sub-angstrom *in-situ* imaging of photocatalysts under reaction conditions (using the objective aperture port (Fig. 2)). Using EELS and residual gas analysis to detect gas molecules inside the microscope, we are also pursuing operando TEM to directly detect hydrogen during *in-situ* illumination of the photocatalysts in a water vapor atmosphere.

For water splitting it is important to understand the difference in deactivation mechanisms under liquid and vapor phase reaction conditions. As shown in Fig. 3, photo corrosion was observed *ex-situ* as a transformation of the Ni/NiO core-shell structure to a void-shell

structure due to dissolution of Ni under liquid water and UV exposure from a xenon lamp [3-4]. This photocorrosion mechanism does not occur during *in-situ* experiments with 18 Torr of water vapor and up to 16 h UV light exposure. This highlights the difference between liquid and gas phase reaction conditions. For the low pressure conditions present in the differentially pumped ETEM, *operando* measurements are critical to connect structure and reactivity. For catalytic activity measurements from *ex-situ* liquid cell photoreactors, *in-situ* measurement should ideally be performed in a liquid cell environment to correlate structure and reactivity. Practical issues including electron beam effects, light source alignment, sample stability, etc. must also be understood and controlled. This presentation will discuss many of the technical and scientific opportunities and challenges for *in-situ* characterization of photocatalysts with emphasis on solar hydrogen production.

References:

- [1] B.K. Miller et al, Microscopy and Microanalysis 2013, **19**, 461-469
- [2] L. Zhang et al, Nano Lett. 2013 **13** (2), 679-684
- [3] Q. Liu et al, Appl. Catal. B 2015 **172-173**, 58-64
- [4] L. Zhang et al, J. Phys. Chem. (under review)
- [5] The support from US Department of Energy (DE-SC0004954) and the National Science Foundation (CBET-1134464) and the use of TEM at John M. Cowley Center for HR Microscopy at Arizona State University is gratefully acknowledged.

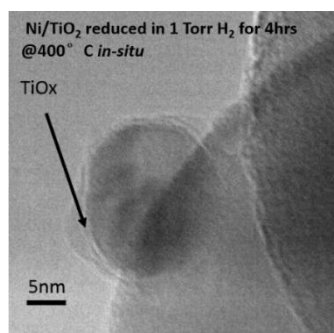


Figure 1 Ni/TiO₂ reduced in 1 Torr flowing H₂ for 4 h *in-situ*

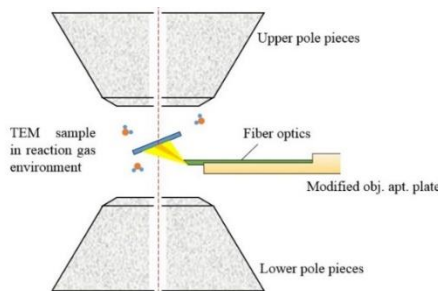


Figure 2 Schematic drawing of the development of light illumination system on objective aperture rod for FEI TITAN

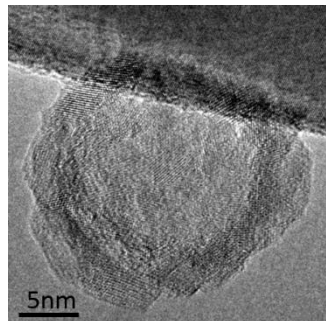
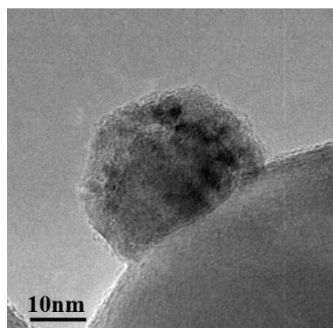


Figure 3: a) Ni-NiO core-shell structure maintained after 16 h water vapor and light exposure *in-situ*. b) Ni-NiO core-shell structure transformed to void-shell after *ex-situ* exposure of 6 h light exposure in liquid water.