Water splitting using a powdered photocatalyst is a promising clean energy system for converting solar energy into the chemical energy of H$_2$ molecules. Ultraviolet (UV) or visible light is required to generate electron-hole pairs in the catalyst which further reduce/oxidize the water into H$_2$/O$_2$. However, the photocatalyst may undergo a structural transformation under reaction conditions and the structure-activity relationship has not yet been fully understood. In this study, we use Ta$_2$O$_5$ based catalysts as the model material to investigate the structural changes under reaction environments.

The Ta$_2$O$_5$ nanopowders were synthesized using a solvothermal method described elsewhere [1]. The resulting powders were then calcined at 600°C and 800°C for 5h to give a better crystallinity and morphology in the initial photocatalyst. A 450 Watt xenon arc lamp with a mirror selecting the wavelengths from 260 to 320 nm was used to excite the electrons over the bandgap of Ta$_2$O$_5$ which is approximately 3.9 to 4.3 eV wide. The initial Ta$_2$O$_5$ nanopowders were then exposed to UV light for 9h in water vapor. An FEI Tecnai F20 environmental transmission electron microscope (ETEM) was employed to obtain high resolution images of both initial and treated material. The high resolution image (Fig.1) of the initial material shows reasonably well-defined morphology of the nanoparticles where clean and smooth surfaces were observed. Electron and x-ray diffraction patterns revealed an orthorhombic structure of Ta$_2$O$_5$. However after the treatment, the initially clean surfaces were found to be more disordered and amorphous surface layers were present (Fig.2). Also, new lattice spacings from 3.43 Å to 3.58 Å were found in some treated particles that were not previously observed in the initial catalyst.

The functionalization of the catalyst by loading NiO on Ta$_2$O$_5$ was also investigated. The NiO (5 wt%)/Ta$_2$O$_5$ catalysts were synthesized using an impregnation method and were pretreated by H$_2$ reduction at 673K for 1h and subsequent O$_2$ oxidation at 473K for 0.5h. The structure of this reduction-oxidation treated catalyst is shown in Fig. 3a. Photocatalytic reactions of both NiO/Ta$_2$O$_5$ and pure Ta$_2$O$_5$ catalysts were carried out in a glass reactor with a quartz window in a gas-closed system. The evolved H$_2$ gas was detected by a gas chromatography (GC) and Fig.3b shows the H$_2$ peak intensities from the two catalysts. The H$_2$ production was calculated for each catalyst and it was significantly improved from 26 to ~220 μmol/h/g by the NiO loading. Additional in situ experiments will be carried out to understand the fundamental structural evolution of these photocatalysts correlated with their photocatalytic performances.

References:

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Fig. 1: (a) Initial Ta$_2$O$_5$ photocatalyst showing clean surfaces. (b) Diffraction pattern of the same area revealing an orthorhombic structure of Ta$_2$O$_5$.

Fig. 2: Treated photocatalysts that were exposed to UV light for 9hr in water vapor. A new lattice spacing (3.58Å) and an amorphous surface layer are present.

Fig. 3: (a) The structure of the 5 wt% NiO/Ta$_2$O$_5$ catalyst after reduction-oxidation pretreatment. (b) The H$_2$ peak intensities of both NiO/Ta$_2$O$_5$ and pure Ta$_2$O$_5$ catalysts from the GC.