

## Structural Changes of Ta<sub>2</sub>O<sub>5</sub> Photocatalyst under Reaction Conditions

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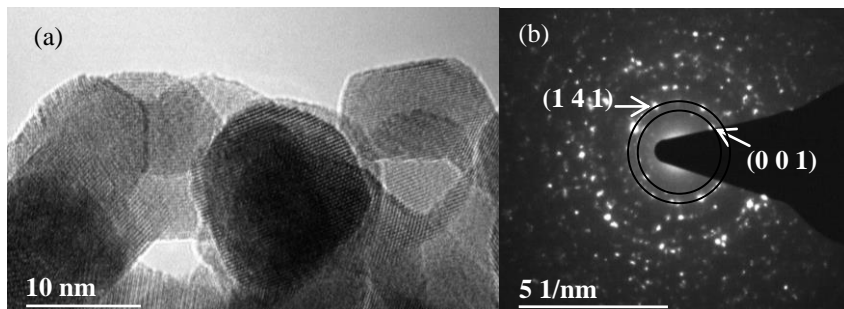
Water splitting using a powdered photocatalyst is a promising clean energy system for converting solar energy into the chemical energy of H<sub>2</sub> molecules. Either ultraviolet (UV) or visible light is required to generate electron-hole pairs in the catalyst which further reduce/oxidize the water into H<sub>2</sub>/O<sub>2</sub>. 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<sub>2</sub>O<sub>5</sub> as a model material to investigate the structural changes under different reaction environments since tantalum based photocatalysts have been reported to show very high photocatalytic activities in the UV [1].

The Ta<sub>2</sub>O<sub>5</sub> nanopowders were synthesized using a solvothermal method described elsewhere [2]. The resulting powders were then calcined at 600°C and 800°C for 5 hours to give a better crystallinity and morphology in the initial photocatalyst. A 450 Watt xenon arc lamp (UV enhanced) with a mirror selecting the wavelengths from 260 to 320 nm was used to excite the electrons over the bandgap of Ta<sub>2</sub>O<sub>5</sub> which is approximately 3.9 to 4.3 eV wide. The initial catalyst was exposed to four different types of environment: (i) liquid water with no UV illumination for 5 hours; (ii) water vapor with no UV illumination for 5 hours; (iii) liquid water with UV illumination for 3, 6, 9 hours; (iv) water vapor with UV illumination for 3, 6, 9 hours. An FEI Tecnai F20 environmental transmission electron microscope (ETEM) was employed to obtain high resolution images of both the initial and the treated catalyst.

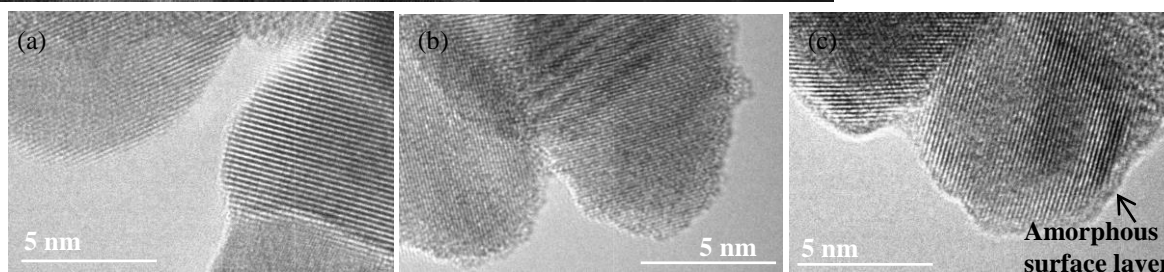
The high resolution image (Fig. 1) of the initial material shows reasonably well-defined morphology of the nanoparticles where clean and smooth surfaces were observed. Electron and X-ray diffraction patterns revealed an orthorhombic structure of Ta<sub>2</sub>O<sub>5</sub>. Materials that underwent treatment (i) show variations of the surface morphology where clean surfaces, rough surfaces as well as amorphous surface layers were observed (Fig. 2). However, such variation was not seen in the catalyst exposed only to water vapor (treatment (ii)) where most of the surfaces remain clean. Figure 3 shows both rough and clean surfaces were present in catalyst that underwent treatment (iii). And for materials that were exposed to UV light in water vapor (treatment (iv)), amorphous surface layers were again found (Fig. 4a). In some particles, new lattice spacings from 3.43 Å to 3.58 Å were found in the treated catalysts that were not previously observed in the initial particles. These spacings could not be assigned to the orthorhombic Ta<sub>2</sub>O<sub>5</sub> structure showing a structural transformation may occur in some catalyst particles under reaction conditions. Also, the nanoparticles that have these new lattice spacings tend to be more sensitive to the 200 kV electron beam than the initial material. Fig.4(a) and (b) shows the morphology of a nanoparticle is dramatically changed from an initially highly crystalline structure to a more disordered structure after several seconds' exposure to the electron irradiation. This may be due to an overall structural modification caused by light and water induced oxygen vacancies formation in the material. Additional *in situ* experiments will be carried out to understand the fundamental structural evolution of the Ta<sub>2</sub>O<sub>5</sub> photocatalyst. Electron energy loss spectroscopy (EELS) will be employed to determine if oxygen vacancies are present. Photocatalytic activity will also be measured to correlate the structure changes with the catalyst performances to better study the structure-activity relationship of the material.

## References:

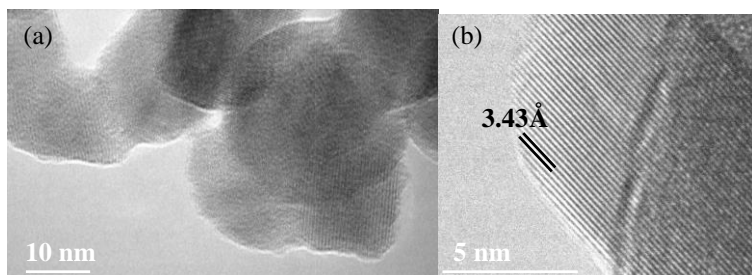
- [1] A. Kudo and Y. Miseki, *Chem. Soc. Rev.*, **38** (2009), 253.  
 [2] J. Buha *et al*, *Phys. Chem. Chem. Phys.*, **12** (2010), 15537.  
 [3] The support from US Department of Energy (DE-SC0004954) and the use of ETEM at John M. Cowley Center for HR Microscopy at Arizona State University is gratefully acknowledged.



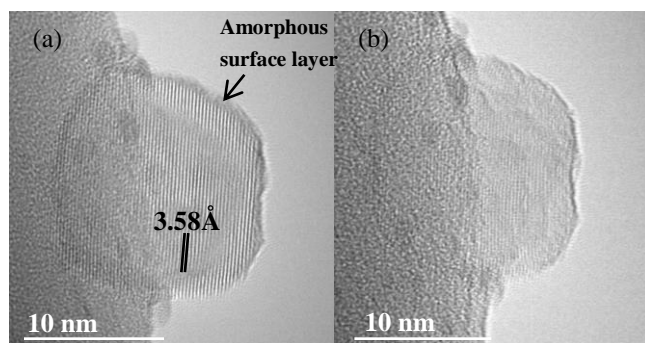
**Figure 1.** (a) Initial Ta<sub>2</sub>O<sub>5</sub> photocatalyst showing clean surfaces. (b) Diffraction pattern of the same area revealing an orthorhombic structure of Ta<sub>2</sub>O<sub>5</sub>.



**Figure 2.** Treated photocatalysts that were kept in liquid water with no UV illumination for 5hr showing various surface morphologies. (a) Clean surfaces. (b) Rough surfaces. (c) Amorphous surface layer on the particles.



**Figure 3.** (a) Treated photocatalysts that were exposed to UV light for 3hr in liquid water showing rough surfaces. (b) Treated photocatalysts that were exposed to UV light for 6hr in liquid water showing a new lattice spacing of 3.43 Å.



**Figure 4.** (a) Treated photocatalysts that were exposed to UV light for 9hr in water vapor. A new lattice spacing (3.58 Å) and an amorphous surface layer are present. (b) The same particle after several seconds of 200kV electron irradiation showing the treated material is beam sensitive.