

Atomic Level *In Situ* Observation of Surface Amorphization in Anatase Photocatalyst During Light Irradiation in Water Vapor

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Photocatalysts are important for environmental cleanup of undesirable organic compounds and have potential applications for solar fuel generation either through water splitting or CO₂ reduction. TiO₂ is a promising photocatalytic material for water splitting partly because it is earth abundant and very stable under reaction conditions [1]. It is now recognized that atomic level *in situ* observations of catalytic nanomaterials are critical for understanding structure-reactivity relations because the active form of the material may exist only under reaction conditions. For photocatalysts, this requires that the nanomaterial be observed not only in the presence of reactant and product species but also during *in situ* light illumination. An *in situ* atomic level investigation of the surface structure of anatase nanocrystals has been conducted under conditions relevant to gas phase photocatalytic splitting of water with an illumination intensity of approximately 10 suns [2].

In situ observations were carried out using a Tecnai F20 (FEI) environmental electron transmission microscope (ETEM) equipped with a differentially pumped environmental cell operated at 200KV. The ETEM was modified so that samples could be illuminated with UV and visible light from a bright, broadband source [3]. Different experiments were conducted in which the electron dose, reactive gas and light flux were varied to ensure that materials changes of were not mistakenly attributed to photon irradiation. Pure crystallized and shape controlled anatase particles were transformed from Evonik P25 particles (80% anatase and 20% rutile) using a hydrothermal method [4]. To facilitate the TEM analysis, anatase powders were dispersed onto Stober silica spheres and the spheres then dispersed over Pt grids using a drop casting method. The Pt grid was loaded into a Gatan hot stage and the *in-situ* TEM was performed at a temperature of 150°C to simulate the conditions for vapor phase water splitting.

A typical set of images before and after exposure to light and water is shown in Figure 1. The initial particle shown in Figure 1a appears crystalline on the surface and the surface is smooth and atomically abrupt. Figure 1b shows a crystal after 12 hrs exposure to water and light without prior exposure to the electron beam. When the titania is exposed to light and water vapor, the initially crystalline surface converts to an amorphous phase one to two monolayers thick. The amorphous layer is stable and does not increase in thickness with time. This disorder layer will be present on the anatase surface under reaction conditions relevant to photocatalytic splitting of water. Control experiments were done to ensure that the amorphization is attributed to light and water. Figure 2 shows smooth and ordered surfaces after 40 hrs in H₂ gas with 20 hrs light exposure. This proves that the amorphization only happens in the presence of water and light. The amorphous surface monolayer should be hydroxylated TiO₂ containing titanium in a +3 oxidation state which has been detected by electron energy loss spectrum (EELS) and x-ray photoelectron spectroscopy (XPS) as shown in Figure 3. The energy doses of the electron beam and light were calculated to be comparable. Energy transferred by elastic scattering and also inelastic scattering were calculated and possible damage processes will be discussed. Further characterization of modified TiO₂ materials like noble metal loaded and semiconductor sensitized TiO₂ photocatalyst under light exposure will also be discussed [5].

References

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 [2] Zhang, L.; Miller, B.K.; Crozier, P.A. *Nanoletter* 2013, DOI: 10.1021/nl304333h
 [3] Miller, B.K.; Crozier, P.A. *Microscopy and Microanalysis* 2013, DOI: 10.1017/S1431927612014122.
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 [5] 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.

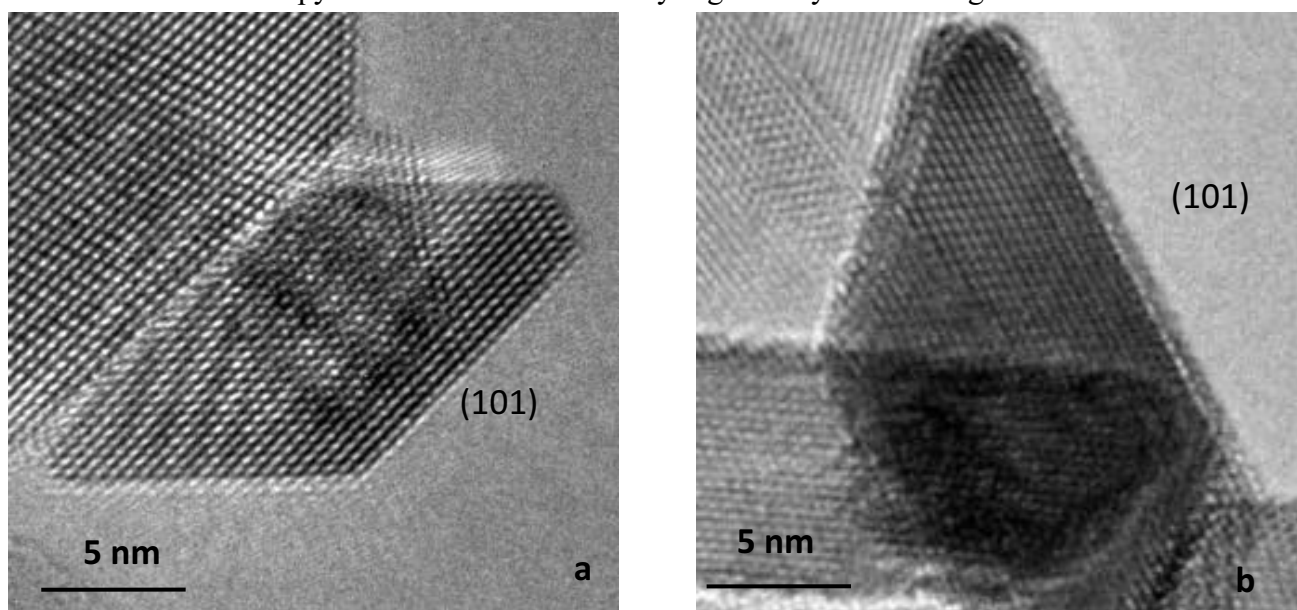


Figure 1. a) Initial anatase crystal at 150°C. b) After 12 hrs light exposure in 1 Torr H₂O.

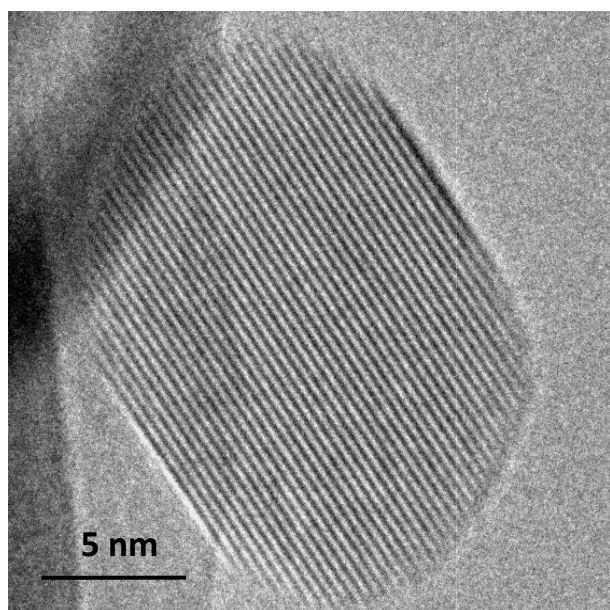


Figure 2. Fresh anatase particles after 40 hrs in 0.5 Torr H₂ gas, 20 hrs light exposure

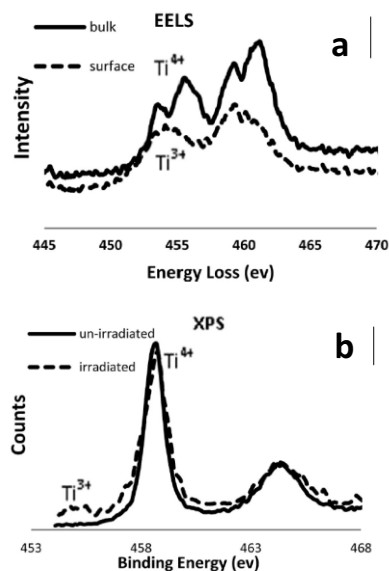


Figure 3. a) EELS spectra from surface and bulk of the irradiated anatase crystal. b) XPS spectra of the irradiated and un-irradiated anatase samples.