AMTC Letters
Vol. 2 (2010)

In-situ TEM/STEM Observation of Photocatalytic Reactions of Titanium Oxide Materials

N. Tanaka[1] and K. Yoshida[2]

[1] Ecotopia Science Institute and Crystalline Materials Science,
Nagoya University, Nagoya, 464-8603, Japan
[2]Nanostructures Research Laboratory, Japan Fine Ceramics Center, Nagoya, 456-8587, Japan

In-situ electron microscopy with various kinds of physical operations such as gas-injection, light-illumination and application of electric current and mechanical force is undoubtedly one of advanced electron microscopy in the next decade. The method is now more developed than previous one for observation of phase transformation of metal/ceramic samples by using a heating holder etc. We have been developing related techniques for in-situ high-resolution electron microscopy since the middle of 1990's, by which the world first observations of surface diffusion of tungsten atoms on MgO (001) surfaces[1], grain boundary migration of MgO[2], metal mediated crystallization of germanium[3], nano-beam processing[4], cross sectional observation of gold nano-tips like in STM[5], growth of carbon nanotubes from β-SiC[6] and absorption process of hydrogen into $LaNi_5$[7] were realized

Recently, our in-situ observation has been focused to photocatalytic materials such as titanium dioxide (TiO_2) related materials. The TiO_2 with useful self-cleaning, deodorizing and antibacterial functions by help of ultraviolet (UV) light has been a strong subject of investigation since its discovery of photo-dissolving phenomenon 35 years ago[8]. These materials have been investigated separately in the structures and properties for a long time, but the relationship with the photocatalytic reaction is now necessary to be elucidated in atomic or molecular level. For this purpose, we have developed a dedicated TEM instrument for in-situ observation of photocatalytic reactions on TiO_2 particles by introduction of UV light into TEM column using an optical fiber[9] (Fig. 1). Also in-situ observation of nucleation process of gold clusters onto TiO_2 particles in liquid was for the first time performed using an ionic liquid including tetrachloro gold ions [10].

Fig. 2 shows TEM micrographs of a hydrocarbon/TiO_2 film irradiated with UV light in TEM. Fig. 2(b) shows a high-resolution image of the square-surrounded area in Fig. 2(a) before the irradiation. We can not observe detailed structures of the TiO_2 film due to overlapped hydrocarbons. Fig. 2(c) shows another high-resolution image after the irradiation for 3hrs. Lattice fringes of TiO_2 are now clearly observed. These changes of the images suggest a decomposition of the organic material with irradiation of UV light. We quantified the activity in the submicron area by using electron energy loss spectroscopy (EELS)[11]. Through the photo-decomposition process, crystalline titanium oxide changed to poly-crystals. Titanium oxide films became gradually network aggregates. A detailed analysis of the EELS spectra revealed that origin of these changes was participation of the lattice oxygen in the decomposition reaction. It was thus considered that main active species of this reaction were the hydroxyl radical (・OH) and an oxygen anion radical (・O^-).

As the next step for in-situ observation in Nagoya, we have developed a 1 MV TEM/STEM for various reaction science(Fig. 3)[12] and in-situ aberration corrected TEM at 300 kV. The former enables one to perform higher resolution electron microscopy by stronger transmission of electrons through thicker gaseous layer, and the latter, clear-cut observation of surfaces of catalytic particles without Fresnel fringes due to aberration correction[13]. Our Nagoya research group has a big advantage from these advanced in-situ electron microscopes, which are indeed open to world prominent researchers of nano materials.

The present authors would like to acknowledge many collaborators and graduate students of Nagoya University engaging in the present study.

References

[1]N. Tanaka et al., *J. Electron Microsc*., **217**(1996) 311.
[2]T. Kizuka & N. Tanaka, *Mater. Sci. Form*, **233**(1997) 405.
[3]N.Tanaka & M. Kawahara, *Mater. Sci. Eng*., A**312**(2001) 25.
[4]T. Kizuka & N. Tanaka, *Phil. Mag. Lett*.,**76**(1997) 289.
[5]T. Kizuka et al., *Phys. Rev*., B **55**(1997) R7398.
[6]H. Watanabe et al. *J. Microsc*., **203**(2001) 40
[7]N. Tanaka et al., *Proc. 4th PRICM*(2001) pp. 417.
[8]A. Fujishima et al., *J. Electrochem. Soc.* **122** (1975) 1487.
[9]K. Yoshida and N. Tanaka et al., *Appl. Phys. Lett*., **84** (2004) 2542.
[10]K. Yoshida and N. Tanaka et al., *J. Electron Microsc*., **56** (2007) 177.
[11]K. Yoshida and N. Tanaka et al., *Nanotech*., **15** (2004) S349.
[12]N. Tanaka et al., *Proc. IMC17* (2010) , to be submitted.
[13]N. Tanaka, in "*Adv. Imaging & Electron Physics*" Vol.**153** (Academic Press, 2008)

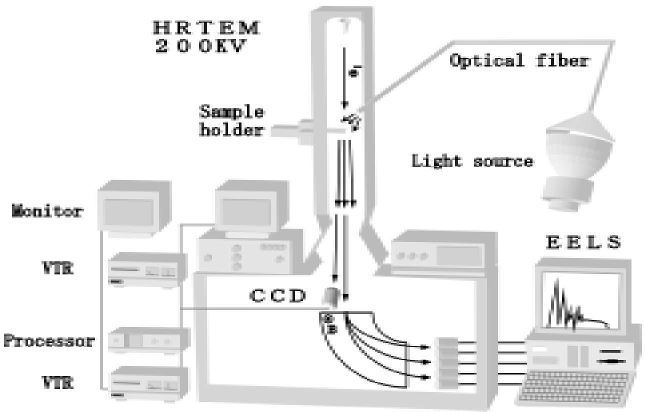

Fig. 1: Dedicated TEM for in-situ observation of photocatalytic reactions with introduction of UV light and reaction gas.

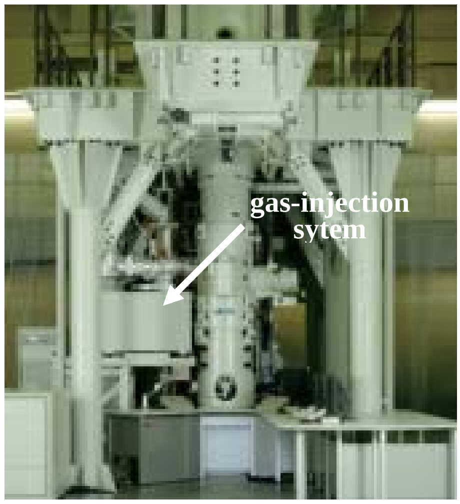

Fig. 3:View of Reaction Science HVEM in Nagoya University.

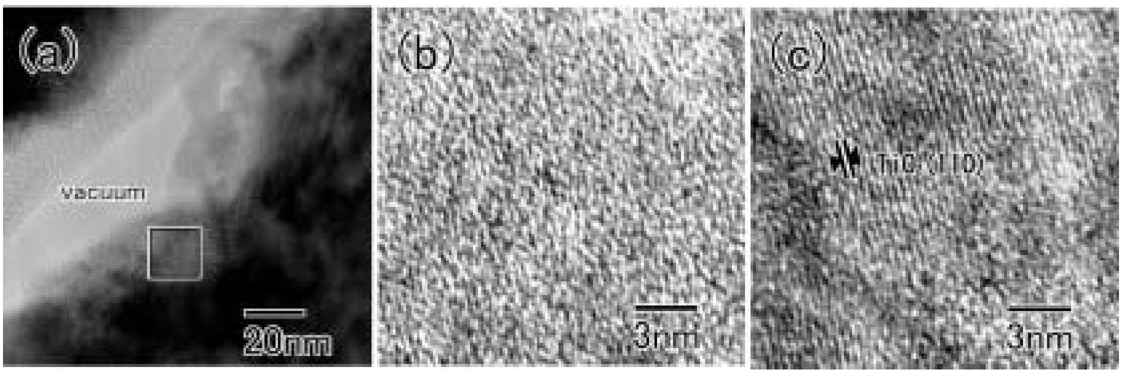

Fig. 2: Change of hydro-carbon deposited surface of a TiO_2 film due to UV irradiation inside the dedicated TEM.