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Observation of photo-decomposition process of poly-hydrocarbons on catalytic TiO_2 films detected in dedicated *in-situ* TEM

K. Yoshida,* T. Nanbara,* J. Yamasaki,** and N. Tanaka**

* Department of Crystalline Materials Science, Nagoya University, Nagoya 464-8603, Japan
** Ecotopia Science Institute, Nagoya University, Chikusa-ku, Nagoya, 464-8603, Japan

Titanium dioxide (TiO_2) materials with useful self-cleaning, deodorizing and antibacterial functions by help of ultraviolet (UV) light have been a strong subject of investigation since their discovery of photo-dissolving effect 30 years ago[1]. These kinds of materials have been investigated in separated viewpoints of 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. In the present study, for studying the potocatalytic reaction in atomic level by physical science techniques, we have developed a new kind of transmission electron microscope (TEM) system. We introduced UV light into the column by using an optical guide. This system enables us to observe the photocatalytic reactions dynamically. We observed photocatalytic decomposition reactions of hydrocarbons on TiO_2 films by using the *in-situ* HRTEM system[2].

In the present experiment, we observed successfully the change of crystal structures and shapes of grains in the TiO_2 films in photocatalytic process. Triple-layer samples were prepared for the measurement. The first layer was a poly-hydrocarbons film of 30 nm thickness and the second was a thin crystalline film of rutile TiO_2, both of which were supported on a copper (Cu) microscopic grid covered with a collodion film. The titanium oxide thin films were prepared by a laser-ablation method using Nd:YAG Laser (Spectra-Physics INDI-40). The sample was irradiated UV light inside the *in-situ* TEM. The intensity of the light was measured to be 10 mW/cm^2 (λ= 360 nm) on the sample plane. Photocatalytic reaction was observed continuously using the HRTEM system during the course of the experiment. In the same time we measured EELS spectra from some areas on the sample. We also observed them three-dimensionally by 3D electron tomography.

Figure 1 shows TEM micrographs of the sample irradiated with UV light. Fig. 1(a) shows a low-magnification image. A ripped area as indicated by 'vacuum' is observed in the center area of the sample. Fig. 1(b) shows a high-resolution image of the square-surrounded area in Fig. 1(a) before the irradiation. We can not observe detailed structures of the TiO_2 thin films due to overlapped hydrocarbons. Fig. 1(c) shows another high-resolution image after the irradiation for 3hrs. It can be seen from the micrograph that lattice fringes are now clearly observed which we've never observed before the irradiation. These changes of the images suggest a decomposition of the organic material with irradiation of UV light. In the next stage, we quantified the activity in the submicron area by using electron energy loss spectroscopy (EELS) as shown in Fig.2[3]. Through the photo-decomposition of hydrocarbon and collodion films, crystalline titanium oxide changed to poly-crystals. Titanium oxide films gradually became network aggregates as shown Fig 3(a). Fig 3(b) and Fig 3(c) are higher magnification images of the square-surrounded areas. We observed super lattice fringes which explain changes of TiO_2 photocatalyst.

A detailed analysis of electron energy loss spectroscopy (EELS) spectra revealed that the 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 ($\cdot O^-$) [4].We considered a relationship between the size of titanium oxide and the sustainability of photocatalysis.

References

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[5] We would like to thank Professor Nobuaki Sato of Tohoku University for providing TiO_2 samples. The present study was supported by a Research Fellowship of the Japan Society for the Promotion of Science for Young Scientists.

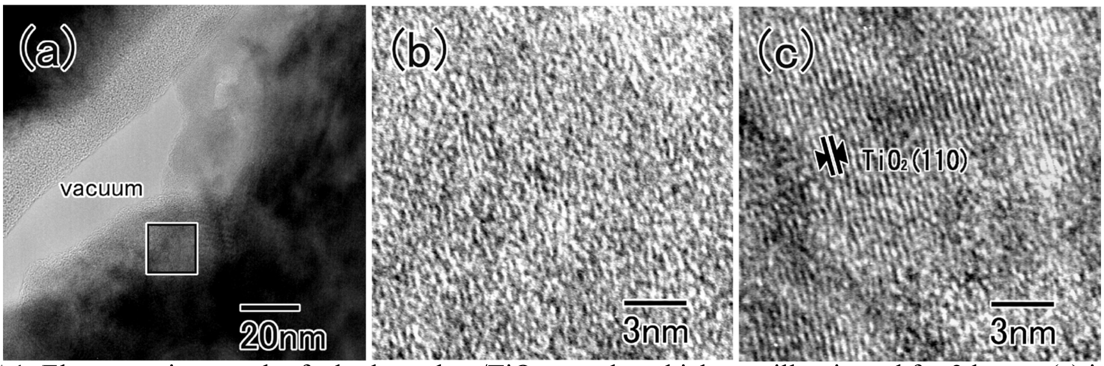

FIG.1: Electron micrograph of a hydrocarbon/TiO_2 sample which was illuminated for 3 hours. (a) is a low-magnification image after UV irradiation. (b) is a high-magnification image before irradiation. (c) is a high-magnification image after irradiation.

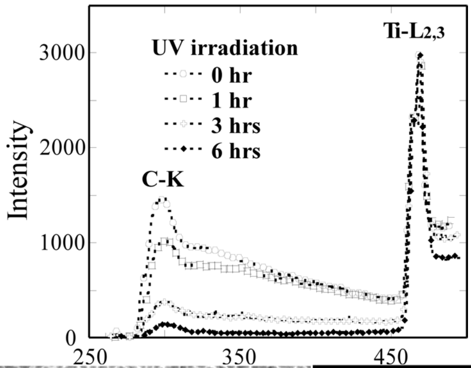

FIG.2: EELS spectra with UV irradiation. The peak of carbon-K edge, which shows the existence of organic materials, decreased with the irradiation.

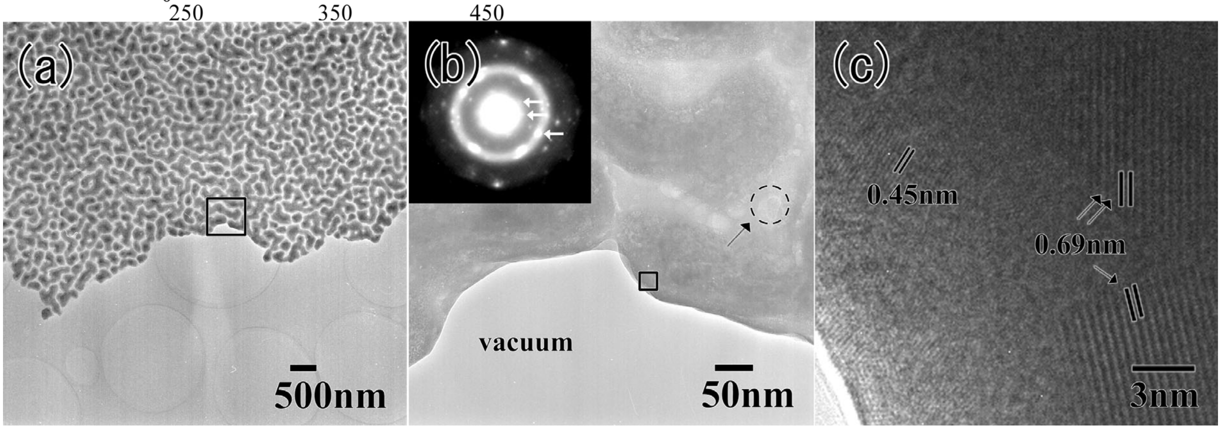

FIG.3: Electron micrograph of a hydrocarbon/TiO_2 sample which was illuminated for 1 week. (a) is a low-magnification image after UV irradiation. A high-magnification image (b) and A high-resolution image (c) of square-surrounded areas.

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