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Visible light responsible catalysis on a TiO_2(001) surface studied by STM

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Photocatalysis has long been studied from fundamental interests of photochemical reactions at surfaces as well as the viewpoint of energy resource problem for sustainable human life. Most of the studies on photocatalysis have been devoted to photocatalyitc phenomenon by UV irradiation, where many photocatalytic materials and effective systems have been developed and proposed.

TiO_2 is a typical oxide effective for photocatalysis, particularly for oxidative decomposition of organic pollutants by UV irradiation. Recently, visible light responsible TiO_2 has accepted much attention due to the high efficiency of sun light utilization. However, TiO_2 has band gaps of 3.0-3.2 eV for the rutile or anatase cystrals, so that UV lights with higher energy than the band gap can promote the photocatalysis of TiO_2. To develop visible light responsible TiO_2, transition metal ions such as Fe, Ni, Cr, etc., main elements such as C, S, N, etc. have been doped into TiO_2 bulk. Formation of Ti^{3+} ions by reduction has also been attempted to promote the photocatalysis. The part of theses modifications has been suggested to be associated with formation of oxygen vacancies in TiO_2. These modifications of TiO_2 decrease the band gap energy or create new energy levels in the bad gap.

Despite the success of geometric and electronic modifications of TiO_2, the surface structure of TiO_2 photocatalysts has not been studied by surface science so much. The surface property related to photocatalysis depends on the geometric and electronic structures of TiO_2 at the surface. The surface structure of TiO_2 photocatalysts has not been illustrated definitely in an atomic scale.

This paper reports the first example of visible light responsible chemical reactions on a TiO_2 single crystal surface without any doping. TiO_2(110) surface which is most stab le among rutile surfaces, but this surface was inactive for decompositions of formic acid and methanol by both UV and visible light irradiations. We have found that TiO_2(001) surface is active for visible light induced reactions by imaging the change of individual adsorbed species by STM as shown in Fig.1. Formic acid dissociatively adsorbs to form formate ion on the surface. The formats decomposed to OH species by visible light irradiation. Oxygen is indispensable for the visible light responsible decomposition reaction. The photochemical reaction was proportional to the concentration of formats and the pressure of oxygen. The TiO_2(001) surface was also active for oxidative decomposition of methanol by visible light. We have also studied the surface structure of the visible light responsible TiO_2(001) surface by STM. The detail of STM topographic analysis, LEED pattern, and use of probe molecules that selectively adsorb on 4-fold and 5-fold coordinated Ti^{4+} ions reveal a latticework-step structure as illustrated in Fig.2. Preliminary DFT calculations indicate that 4-fold coordinated Ti^{4+} ions on the top place and 2-fold coordinated O^{2-} ions on the side plane are responsible for visible light responsible chemical reactions.

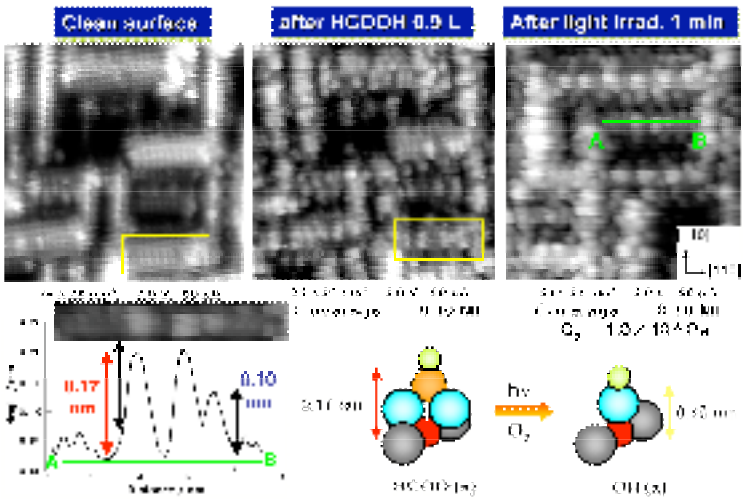

FIG. 1. STM images of the clean TiO_2(001) surface, after HCOOH exposure, and after visible light irradiation for 1 min. The bottom (left) is the topographic profile for the irradiated surface which shows two bright contrasts with 0. 17 nm height for formates and a bright contrast with 0.10 nm height for hydroxyl. The bottom (right) shows illustration of the reaction step..

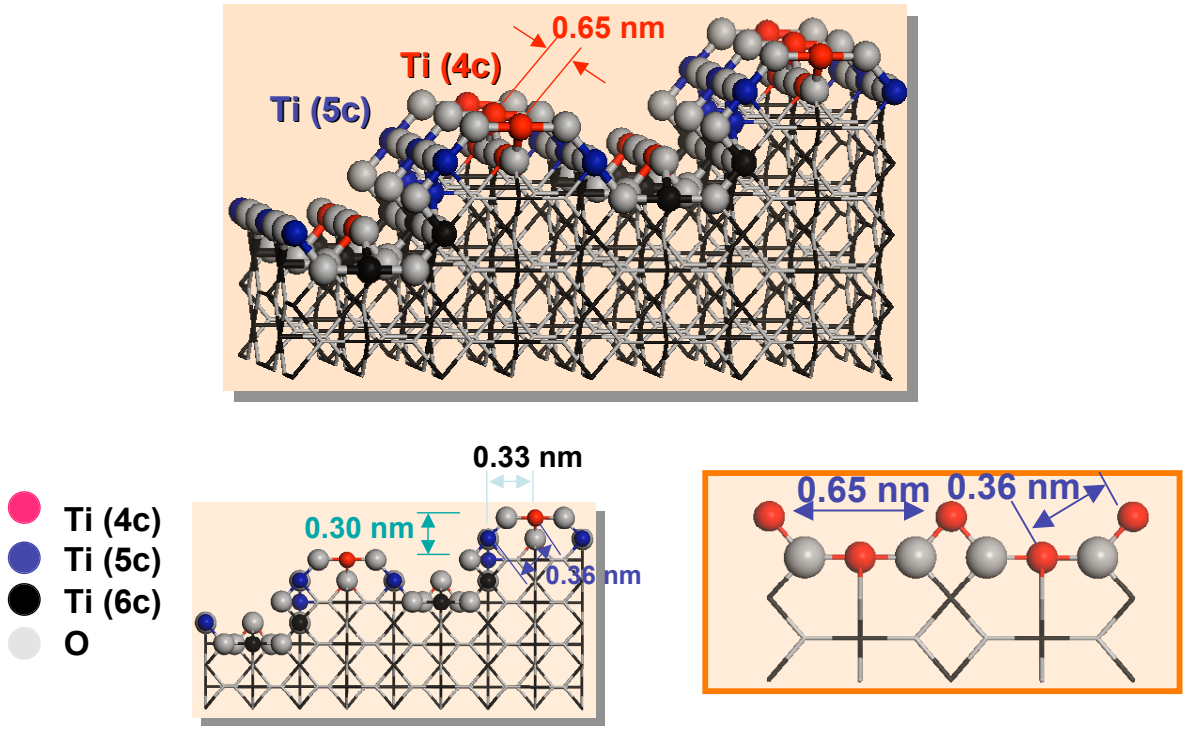

FIG. 2. Proposed structure model of TiO_2(001) surface by STM, LEED, and probe molecules. The model structure is based on a (114) facet plane and added rows composed of three Ti rows and side planes. (upper) three-dimensional structure; (bottom, left) side view; (bottom, right) side view along (110) direction.

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