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Description	

STM imaging of a model surface of

Ru(4,4'-dicarboxy-2,2'-bipyridine)₂(NCS)₂ dye-sensitized TiO₂ photoelectrodes

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Abstract

A TiO₂(110)-(1×1) surface was prepared in an ultra-high vacuum, transported in laboratory air, and observed with a scanning tunneling microscope (STM) operated in a vacuum of 10⁻⁴ Pa. Empty state images showed atomically flat terraces separated by single-height steps, on which 5-fold-coordinated surface Ti atoms were observed as spots arranged in a rectangular lattice. The Ru(4,4'-dicarboxy-2,2'-bipyridine)₂(NCS)₂ (N3) dye was adsorbed on the TiO₂ surface by immersing the TiO₂ wafer into an acetonitrile solution of the dye. In the empty state images, individual N3 molecules were observed as oval particles protruding by 0.6 nm from the TiO₂ surface. The oval shape elongated to the [1 $\bar{1}$ 0] directions was attributed to electron tunneling from tip to unoccupied states localized at the two carboxyl groups bound to the TiO₂ surface.

Keywords: STM, titanium dioxide, dye

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Introduction

A dye-sensitized titanium dioxide (TiO_2) electrode is a key component of dye-sensitized solar cells [1-4]. The electrons excited in the light-sensitive dye molecules are delivered to the external circuit through a film of nanocrystalline TiO_2 . The photo-excited electrons transfer through overlapping orbitals between the dye molecules and the TiO_2 surface. The electron transfer is thought to sensitively reflect nanoscale surface structures such as a configuration of the dye molecule and local charge density of the TiO_2 surface. The nanoscale structure of dye-sensitized TiO_2 surfaces may provide clues leading to optimization of the electron transfer and thereby improvement of the solar cells performance as well as a detailed description of the photovoltaic process.

Applying scanning probe microscopes (SPMs) to well-defined model surfaces is a possible approach to the nanoscale structure of the electrode surfaces. Imaging of individual dye molecules on a rutile $\text{TiO}_2(110)$ surface by a scanning tunneling microscope (STM) [5-7] was the beginning of our SPM study of the dye-adsorbed TiO_2 surfaces. In order to transport the $\text{TiO}_2(110)-(1\times 1)$ surface prepared in ultra-high vacuum (UHV) to dye solutions in air without polluting, the surface was covered by a monolayer of pivalate ($(\text{CH}_3)_3\text{CCOO}^-$) molecules prior to being removed from the vacuum. The pivalate monolayer which exposes alkyl groups on the surface top layer passivated the TiO_2 surface against contaminants in laboratory air. A fraction of the pivalates was replaced by dye molecules in the solution [5]. Following the successful imaging of the dye molecules using the pivalate monolayer, lateral distribution of the $\text{Ru}(4,4'\text{-dicarboxy-2,2'\text{-bipyridine}})_2(\text{NCS})_2$ (N3) dye molecules [8] and the effect of deoxycholic acid additives on the aggregation of $\text{Ru}(4,4',4''\text{-tricarboxy-2,2':6',2''-terpyridine})(\text{NCS})_3$ dye (black dye) [9] were examined. A noncontact atomic force microscopy study revealed visible-light-induced work function shifts on the adsorbed N3 molecules [10], which indicated the possibility of an imaging photoelectron injection process for each dye molecule.

The aim of the present study is to prepare a model surface suitable for research on practical dye-sensitized TiO_2 surfaces. Unlike in our previous studies, in this case, the rutile

TiO₂(110)-(1×1) surface was transported from the UHV chamber to the dye solution without the protection of the pivalate which is not usually used in the practical dye-sensitized solar cells. Exposing single crystal surfaces prepared in UHV is conventionally avoided because the atomically well-defined surface is spoiled by the adsorption of the contaminants from the air. It was found that the (1×1) structure of the TiO₂(110) surface was maintained after exposure to the air and that the dye-adsorbed TiO₂(110) surface could be prepared by simply immersing the (1×1) surface to the dye solution. The adsorbed N3 molecules were observed as an oval particle on the pivalate-free TiO₂ surface, which provided experimental support for the theoretically-predicted adsorption configuration of the N3 molecules on the (110) surface [11]. The pivalate-free N3/TiO₂(110) surface would be useful for future studies of the dye-TiO₂ system as a realistic model of the electrode. For example, the shift of the conduction band of the TiO₂ [12] and co-adsorption of the additives and the dye molecules [13-16], which are important factors for the performance of the electrode, can be examined without being perturbed by the pivalate.

Figure 1 shows models of the TiO₂(110) surface and the N3 dye molecule. On the TiO₂(110)-(1×1) surface, O atoms bridging two Ti atoms (bridge O atoms) are aligned in the [001] direction, and Ti atoms coordinated to five O atoms (5-fold-coordinated Ti atoms) are exposed in the troughs between the rows of the bridge O atoms [17]. The size of the surface unit cell is 0.30×0.65 nm². The N3 dye is a complex of Ru containing two biisonicotinic acid ligands ((C₅H₃NCOOH)₂) and two thiocyanate ligands (NCS). The ligands are coordinated to the Ru center with C₂ symmetry around the bisection of the ∠NRuN angle formed by the N atoms of the thiocyanate groups. The carboxyl groups (COOH) of the biisonicotinic acid ligands are dissociatively anchored to Ti atoms of the TiO₂ surface in a bridge form (Ti-O-C-O-Ti) [18].

Experimental section

A TiO₂(110) wafer was first heated at 1200 K for 1 h in a quartz tube evacuated to 1 Pa to increase the conductivity by producing O defects. An alumel-chromel thermocouple was placed in an electric furnace with the tube to monitor the temperature. The bluish-colored TiO₂ wafer was

introduced into a UHV chamber with a base pressure of 4×10^{-7} Pa. The UHV chamber was equipped with an Ar^+ sputtering gun (EX03, Thermo) and low energy electron diffraction optics (BDL600, OCI). The surface was cleaned by cycles of Ar^+ sputtering and annealing at 1100 K to show the (1×1) diffraction pattern. After being cooled to room temperature, the wafer was transported in laboratory air to a multi-purpose scanning probe microscope (JSPM4200, JEOL) in 10 min. The microscope stage was placed in a glass chamber which can be evacuated to 5×10^{-4} Pa. Adsorption of the N_3 molecule was carried out by immersing the TiO_2 wafer in acetonitrile solution of 3.4×10^{-3} M N_3 followed by rinsing in pure acetonitrile. The STM imaging was performed at a pressure of 5×10^{-4} Pa using a mechanically cut Pt-Ir wire as a probe. Empty state images were obtained in a constant current mode at room temperature in the dark. Stable imaging was accomplished with a sample bias voltage between +1.4 and +2.0 V. STM imaging in air was performed after the imaging in vacuum by filling the glass chamber with laboratory air. The images are presented without filtering, and the cross sections were measured on the images smoothed by a nine-point median filter.

Results and discussion

Figure 2(a) shows the wide scan image of the TiO_2 surface cleaned in UHV. Flat terraces were separated by steps preferentially running along the $\langle 001 \rangle$ and $\langle \bar{1}\bar{1}1 \rangle$ directions, which is typical of the (1×1) surface [19]. The string growing from the step edges indicated by the arrowhead was assigned to Ti_2O_3 . The bright particles indicated by arrows were either TiO_x species or unidentified contaminants. In the close-up view of the terrace, bright spots arranged in a 0.34×0.65 nanometer rectangular array were observed as shown in Fig. 2(b). The spots corresponded to the 5-fold-coordinated Ti atoms. The Ti 3d derived unoccupied orbital contributed to the electron tunneling in the empty state image of the (1×1) surface [20].

The vacancies of the bridge O atoms which were observed as faint spots between two adjacent Ti atom rows in UHV [19] were not observed. The bridge O vacancies would have been filled by dissociative adsorption of H_2O [21] or O_2 [22] during transport in laboratory air. Figure 2(d)

shows the image of the sputter-annealed surface scanned in air. The terraces with an irregular corrugation were observed when a pulsed sample bias voltage of +10 V was applied. The step-terrace structure disappeared in the subsequent scan with an acquisition time of 26 sec per image. It is probable that the H₂O molecules were accumulated on the surface in air, and the H₂O layer was reduced by applying the pulsed voltage.

Hydrogen adatoms on the bridge O atom rows [21] and O adatoms on the Ti atom rows [22], which are formed by dissociation of H₂O and O₂ at the bridge O vacancies, respectively, and are occasionally observed as faint spots in the STM images in UHV, were not observed. Imaging of the H and O adatoms seemed to have been disturbed by the residual H₂O in the microscope chamber. The scratch noises and cloud-like features shown in Fig. 2(b) suggest the migration of H₂O molecules. When the surface temperature was lowered to 200 K, adsorbed H₂O molecules were identified as spots on the Ti atom rows [21,23]. Other air-component gases were unlikely to be adsorbed on the (1×1) surface. No adsorbate was observed in the noncontact atomic force microscope images of the (1×1) surface obtained under the atmospheric pressure of pure N₂ gas [24]. The CO₂ molecules adsorbed on the 5-fold-coordinated Ti atoms and the bridge O vacancies were desorbed at a temperature lower than 270 K [25].

After immersion in the N₃ solution, bright particles appeared on the sputter-annealed surface. Figure 3(a) shows the STM image of the surface immersed for 1 min. The number density of the particles was 0.04 nm⁻². Seventy percent of the single N₃ molecules were recognized as oval particles elongated to the $[1\bar{1}0]$ direction. When the immersion time was extended to 11 min, the number density increased to 0.08 nm⁻² (Fig. 3(b)). The particles were not observed on the surface immersed in pure acetonitrile as shown in Fig. 3(c). We therefore assigned the particles to the adsorbed N₃ molecules. The particles with a minimum diameter of approximately 2.0 nm were single N₃ molecules, and the larger particles were aggregates of the N₃ molecules. Some of the single molecules and the N₃ aggregates are indicated in the images by arrows and arrowheads, respectively. The aggregation was responsible for the nonlinear increase of the particles with the immersion time.

The number density of the adsorbed N3 molecules after a 1 min immersion was half that of our previous study using the pivalate-covered TiO₂ surface [5], though the concentration of the N3 solution was equal in both experiments. The concentration of the N3, which was probably hydrophobic due to the aromatic ligands, was able to be locally enhanced on the pivalate-covered TiO₂ surface relative to the pivalate-free surface. After an 11 min immersion, the N3 molecules tended to be located nearby, and the aggregates were enlarged. The aggregation of the N3 molecules was also observed on the pivalate-covered TiO₂ surface when the number density of the N3 molecules reached 0.08 nm⁻². The UHV-STM image of the pivalate-covered TiO₂ surface immersed in the N3 solution for 1 min is shown in Fig. 3(d) for reference. The N3 molecules were observed as bright particles and located adjacent to each other. On the basis of the lateral distribution analysis, we proposed that the trapping of an N3 molecule in the solution by a preadsorbed N3 molecule was a driving force for the aggregation on the pivalate-covered surface [8]. In the proposed aggregation process, the pivalate molecule does not take part in the aggregation. The N3 molecules would be expected to aggregate in a similar manner on the pivalate-free TiO₂ surface.

Figure 4(a) shows a close up of the single N3 molecule. The schematic model of the image is presented in Fig. 4(b), where the outlines of the N3 molecule and the surface Ti atoms are represented by a dotted-line circle and a solid-line circle, respectively. The oval particle corresponding to the N3 molecule extends over three Ti atom rows. In the pivalate monolayer, the N3 molecules did not show such a distinct oval shape as shown in Fig. 3(d). The cross sections along the solid lines in the model are presented in Fig. 4(c). The lateral dimension of the oval was approximately 1.1 and 1.8 nm in the [001] and the [1 $\bar{1}$ 0] directions, respectively. The height from the TiO₂ surface was approximately 0.6 nm. The spots assignable to the acetonitrile molecules were not observed. The dark spots which appeared in the pivalate monolayer after immersion in acetonitrile were tentatively assigned to the acetonitrile molecules [5]. It is possible that the acetonitrile molecules were stabilized in the pivalate monolayer but not on the pivalate-free (1×1) surface.

Here we consider the adsorption configuration of the N3 molecule on the basis of the STM images. The oval shape of the N3 molecules reflects the lateral distribution of unoccupied molecular orbitals contributing to the electron tunneling. Figure 5 shows two adsorption configurations of the N3 molecule, where free N3 molecules were simply superimposed above the TiO₂(110) surface. Configuration (i) uses two carboxyl groups of the same biisonicotinic acid ligand for adsorption, and configuration (ii) uses two carboxyl groups from each biisonicotinic acid ligand. In the two configurations, the mismatch between the C-C distance of the two carboxyl groups and the site-to-site distance for the carboxyl groups is less than 10% [5]. The density functional theory (DFT) calculation predicted that configuration (i) was energetically more stable than configuration (ii) and was further stabilized by bonding between the S atom of one thiocyanate ligand and the bridge O atom [11]. In Fig. 5(a), the thiocyanate ligand indicated by an arrowhead is closer to the surface than the other and forms the S-O bonding. In such a case, the free biisonicotinic acid ligand is relaxed around the Ru atom in the direction indicated by an arrow in the top view and aligned to the [001] direction. The S-O bonding was indicated by core level photoemission spectroscopy on the N3 monolayer prepared by injecting N3 solution onto the TiO₂(110) surface in the vacuum by using a homemade spray deposition system [11].

In adsorption configuration (i), the two anchored carboxyl groups are separated by 0.30 nm in the [001] direction and 0.65 nm in the [110] direction. Electron tunneling to the orbitals around the anchored biisonicotinic acid ligand resulted in an STM image elongated to the $[1\bar{1}0]$ direction. It is likely that the LUMO of the N3 molecule is localized around the anchored biisonicotinic acid ligand on the analogy of the DFT calculation for the N3 molecule attached to an anatase TiO₂ cluster [26-28]. Tunneling to the orbitals around the free biisonicotinic acid ligand, which results in an STM image elongated to the [001] direction, may have minor contribution to the tunneling current at the bias voltage where N3 molecules are visualized with 5-fold-coordinated Ti atoms. The image height of the N3 molecule which was lower than the geometric height from the TiO₂ surface is accounted for by the dominant contribution of the orbitals around anchored biisonicotinic acid ligand.

In adsorption configuration (ii), anchoring of two carboxyl groups limits the relaxation of the molecular structure. The two anchored carboxylate groups are separated by 0.9 nm in the [001] direction and 0.65 nm in the $[1\bar{1}0]$ direction. Assuming the electron tunneling to the orbitals around the anchored two isonicotinic acid ligands (C_5H_3NCOOH), the image of the N3 molecule is likely to be elongated to the [001] direction. Two non-anchored isonicotinic acid ligands are aligned parallel to the [001] direction, and the carboxyl groups of the ligands are laterally separated by 0.9 nm. Hence, the non-anchored isonicotinic acid ligands would not contribute to causing the STM image to be elongated to the $[1\bar{1}0]$ direction. Thus configuration (ii) is less likely to produce the oval shape in the STM images.

It is possible that the N3 molecules embedded in the pivalate monolayer in configuration (i) were observed as circular particles. The pivalates forming the monolayer on the $TiO_2(110)$ surface were observed as closely packed spots. The unoccupied orbital around the alkyl group at the surface top layer contributed to the empty state imaging of the pivalate [29]. The alkyl groups were closer to the tip end than the anchored carboxyl groups of the N3 molecules. Therefore, the images of the pivalates were likely to overlap the neighboring N3 molecules. In such a case, the oval shape of the image of the N3, which originates from the dominant contribution of the orbitals around the two anchored carboxyl groups to the electron tunnel, would be made unnoticeable.

Conclusion

It was found that the rutile $TiO_2(110)-(1\times 1)$ surface prepared in UHV was retained after short exposure to laboratory air. An adsorption of the N3 molecules on the (1×1) surface was prepared by simple immersion of the surface to the dye solution in air. Imaging the N3 molecules on the (1×1) surface revealed an anisotropic shape in the STM image, which was related to the adsorption configuration of the N3 molecule. The present results offer a preparation method of a model surface of the dye-sensitized TiO_2 electrode and promote microscopic analysis of the dye- TiO_2 interface.

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Figure captions

Figure 1 (a) A ball model of the $\text{TiO}_2(110)-(1\times 1)$ surface including monatomic steps. Small and large spheres represent Ti and O atoms, respectively. The O atoms are shaded according to their depth. (b) A stick-and-ball model N3 molecule.

Figure 2 (a) Wide scan image of the sputter-annealed TiO_2 surface ($70\times 70 \text{ nm}^2$). Sample bias voltage (V_s) = +1.4 V, tunneling current (I_t) = 0.5 nA. (b) Narrow scan image of the terrace ($8\times 8 \text{ nm}^2$). $V_s = +1.7 \text{ V}$, $I_t = 0.5 \text{ nA}$. (c) Cross sections obtained along the solid lines in image (b). The lines below the cross sections indicate the positions of the 5-fold-coordinated Ti atoms. (d) The sputter-annealed TiO_2 surface observed in air ($70\times 70 \text{ nm}^2$). $V_s = +1.7 \text{ V}$, $I_t = 0.4 \text{ nA}$.

Figure 3 (a)-(c) STM images of the TiO_2 surfaces ($70\times 70 \text{ nm}^2$). (a) after immersion in the N3 solution for 1 min. $V_s = +1.6 \text{ V}$, $I_t = 0.7 \text{ nA}$. (b) after immersion in the N3 solution for 11 min. $V_s = +1.6 \text{ V}$, $I_t = 0.3 \text{ nA}$. The spots assigned to isolated N3 molecules and N3 aggregates are indicated by arrows and arrowheads, respectively. (c) after immersion in pure acetonitrile for 11 min. $V_s = +1.7 \text{ V}$, $I_t = 0.7 \text{ nA}$. (d) UHV-STM image of the pivalate-covered (1×1) surface immersed in the N3 solution for 1 min ($20\times 20 \text{ nm}^2$). $V_s = +1.0 \text{ V}$, $I_t = 1.0 \text{ nA}$.

Figure 4 (a) A close-up STM image of the adsorbed N3 molecule ($8\times 8 \text{ nm}^2$). $V_s = +1.6 \text{ V}$, $I_t = 0.7 \text{ nA}$. (b) A schematic model of the image (a). The solid-line circles and the dotted-line circle represent the 5-fold-coordinated Ti atoms and the outline of the N3 molecule, respectively. (c) Cross sections obtained along the dash-dotted lines in model (b).

Figure 5 Possible configurations of N3 molecule on the (1×1) surface. The thiocyanate ligand closer to the TiO_2 surface in configuration (i) is indicated by an arrowhead. The arrow in the top view of configuration (i) indicates the direction of the relaxation of the biisonicotinic acid ligand

accompanying the formation of the S-O bonding.

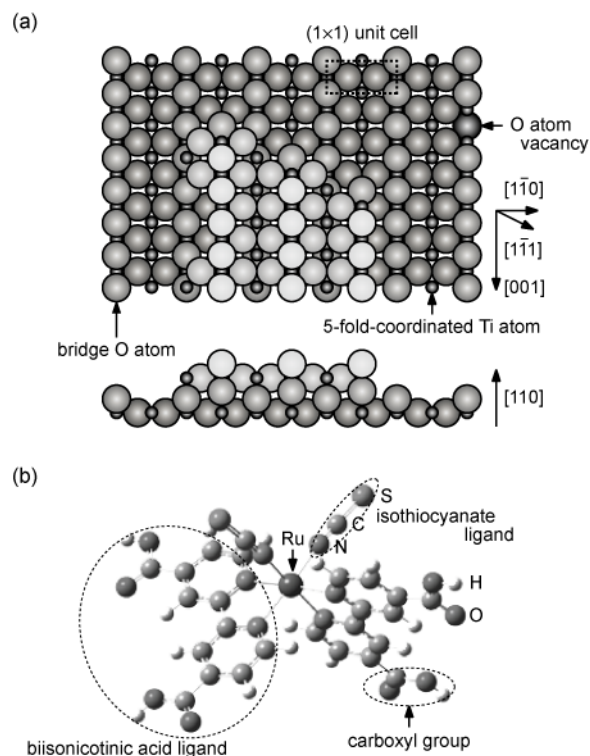


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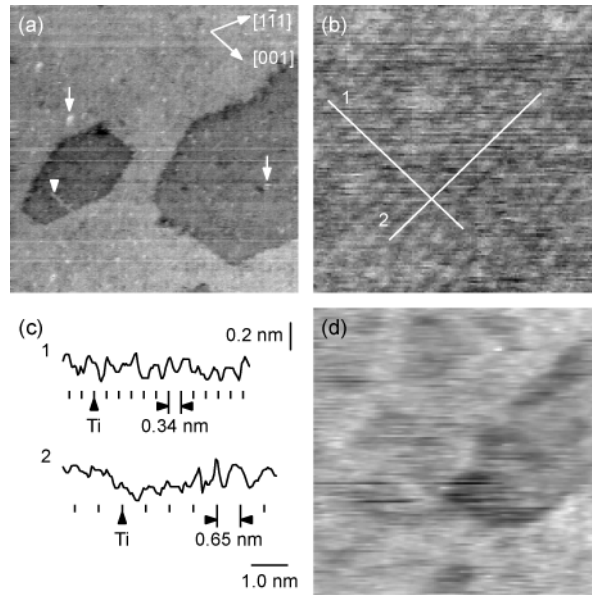


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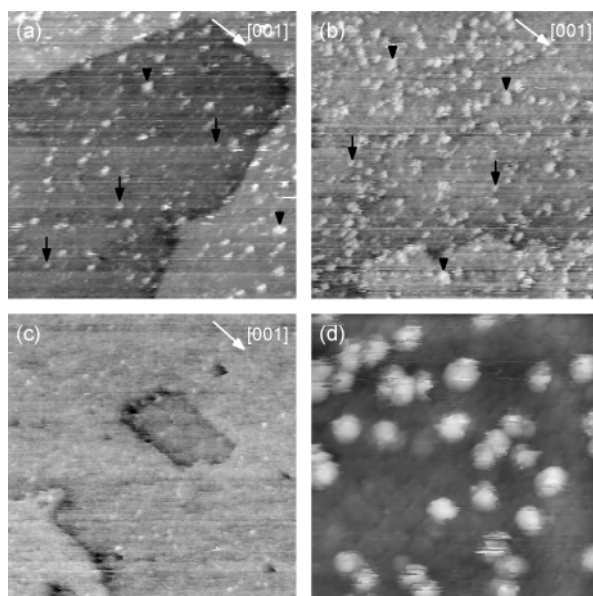


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Sasahara et al. Figure 3

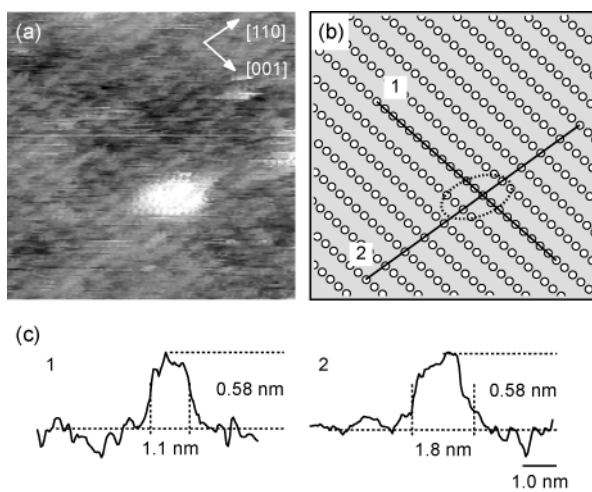


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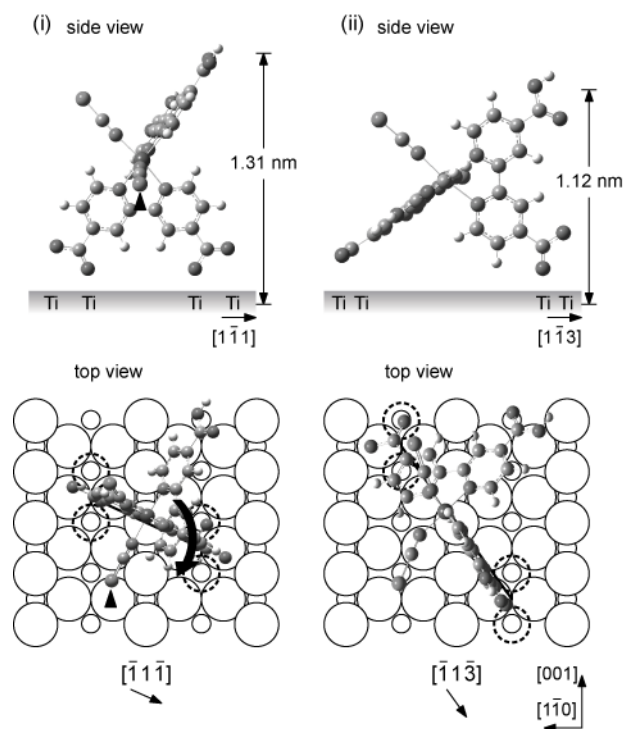


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