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Direct Observation of Ethanol Photocatalysis on Rutile TiO$_2$(110) Surface[†]

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Photocatalytic dissociation of ethanol molecules on the rutile TiO$_2$(110) surface after UV irradiation has been investigated by scanning tunneling microscope at 80 K. Most of the ethanol molecules adsorb molecularly at Ti sites, similar to the case of methanol. After UV irradiation, two different protrusions of products were observed, one of them has been identified by the technique of tip manipulation, which was likely composed of an acetaldehyde in the middle and two bridge-bonded hydroxyls on both neighbored oxygen sites. Multi-time irradiation experiments have also been performed to further understand the relationship between the two protrusions and the process of ethanol photocatalytic dissociation. These results provide detailed insights into the photocatalysis of ethanol on rutile TiO$_2$(110), which would help us to understand how phtotocatalytic reactions of ethnaol proceed at the fundamental level.

Key words: Titanium dioxide, Scanning tunneling microscope, Photocatalysis

I. INTRODUCTION

Titanium dioxide (TiO$_2$) is one of the most important materials in the world, it has been widely used in many fields, such as gas sensors, biocompatible materials, and photocatalysis [1−8]. The potocatalytic property of TiO$_2$ has attracted much attention since the discovery of photocatalytic water splitting on TiO$_2$ electrode in 1972 [9]. In recent years, alcohol/TiO$_2$ systems have become prototype systems in surface science because alcohol molecules can be taken as a model to study the mechanisms of surface catalytic reactions and alcohol decomposition is commonly used as a probe to detect surface reactive sites. Ethanol chemistry on TiO$_2$ surface has also received extensive attentions for its potential use in green chemistry as a renewable energy carrier and a feedstock [10, 11]. Over the last few decades, TiO$_2$ based ethanol potocatalytic reactions have been studied in detail [12−15]. It is therefore interesting to investigate the hydrogen production from ethanol at the single molecular level. The rutile TiO$_2$(110) surface is an ideal system to study ethanol decomposition, because it has been well characterized. Recently, ethanol chemistry on TiO$_2$(110) surface has been investigated by many experimental techniques, such as temperature programmed desorption (TPD) [16−18], two-photo

photoemission spectroscopy (2PPE) [18, 19], X-ray photoelectron spectroscopy (XPS) and scanning tunneling microscopy (STM) [20−23].

TiO$_2$(110) surface is thermodynamically very stable and its structure is clear and rather easy to control. This surface consists of alternating rows of five-foldcoordinated Ti atoms (Ti$_{5c}$) and two-fold coordinated bridge-bonded oxygen (BBO) atoms, with rows of surface oxygen atoms in between. Since bridge-bonded atoms can be removed during UHV annealing, some bridge-bonded oxygen vacancies (BBOv's) can be produced rather easily. Pervious researches have shown that ethanol molecules can be dissociated at BBOv sites via O−H bond scission [24, 25]. Both of molecular and dissociative states have been observed at low temperature using TPD and STM [16, 22].

In reality, oxygen vacancies can be occupied easily in catalytic systems, therefore Ti$_{5c}$ sites were the key sites in the reaction process. The photocatalytic reaction of single ethanol under ultraviolet (UV) irradiation at Ti sites of TiO$_2$(110) surface has been studied by TPD, 2PPE and XPS. The main products are found mainly to be acetaldehyde and hydrogen atoms. But the direct observation of these products on the surface has not been made, and the detailed mechanism of how a single ethanol molecule evolves into the final products at atomic and molecular level is still unclear. Therefore, STM study could provide detailed information of reaction products on the surface [3, 7, 26−29]. The TiO$_2$(110) surface has been studied extensively using the STM technique [30−36]. Consequently, STM coupled with laser irradiation has become a good tool to study photocatalytic reactions of single molecules at real space at the sub-molecular resolution [37−39]. We

can then follow changes of single molecule during the whole reaction process and observe the reaction intermediates clearly.

In this work, we have performed an *in situ* STM experiment which can follow the process of one ethanol molecules from adsorption to the final photocatalytic products at 80 K. Two distinct protrusions of products with different full width at half maximum (FWHM) are observed. In the meanwhile, STM tip manipulation has also been conducted to identify the composition of the products. In a multiple irradiation experiment, the two protrusions show no interconversion, which means those two products are likely two reaction pathways, no two intermediates along one reaction pathways.

II. EXPERIMENTS

The STM-photocatalysis experiments were performed in an UHV chamber equipped with a low temperature scanning tunneling microscopy (Omicron, MATRIX), which had a base pressure lower than 4×10^{-11} mbar. In order to get an ideal vacuum, more than 100 h baking was carried out mainly to eliminate the residue water in the chamber. The $TiO_2(110)$ sample (Princeton Scientific Corp., 5 mm×10 mm×2 mm, both sides polished) was cleaned by repeated Ar^+ icons sputtering (1000 eV, 10 min) and annealing (900 K, 30 min) in the UHV chamber. After that, the sample was transferred to the scanning stage which had been cooled to 80 K using liquid nitrogen. Before adsorption, the ethanol (Sigma-Aldrich) was purified by several freeze-pump-thaw cycles using liquid nitrogen to remove impurities in the sample. The ethanol molecules were then dosed onto the rutile $TiO_2(110)$ surface through a calibrated doser with a pinhole on the top end, the distance between the top of the doser and the TiO_2 sample is about 5 cm. All the images were obtained in constant current mode and the tunneling voltage and tunneling current were +1.25 V and 100 pA, respectively. Electrochemically etched tungsten tip was used in all the STM experiments.

The UV light used in our experiments was a 355 nm ns-laser (HIPPO, Spectra-Physics), which had a diameter of 5 mm. The duration of the laser was 12 ns and the repetition was 50 kHz, the high repetition could ensure that the surface was not damaged by the UV laser. During laser irradiation the STM tip was retracted about 20 μm to avoid shadow effecting and the sample's temperature increase was less than 1 K after laser irradiation in all experiments.

III. RESULTS AND DISCUSSION

A. Ethanol adsorption on TiO$_2$(110) surface at 80 K

The adsorption of ethanol had been studied in detail by STM from 120 K to 160 K, both of molecular and dissociated states had been observed at Ti sites [22]. In order to investigate the photocatalytic dissociation of ethanol molecule we conducted a series of experiments at a lower temperature of 80 K. Interestingly, only molecular ethanol molecules were observed from our STM images, which was not changed even after long time scanning. This suggests that the ethanol molecules are molecular adsorbed on the surface at the low temperature of 80 K.

The detailed information of ethanol adsorption at 80 K is shown in Fig.1. Because STM image contrast is determined predominantly by the tunneling electric current rather than real geometry effect, the topography of $TiO_2(110)$ is illustrated along with the realistic surface geometry (Fig.1(a)), the bright rows represent five-fold Ti sites while the dark rows represent two-fold oxygen rows. The bright protrusions on the dark rows are the BBOv's, which has a concentration of 0.08 ML (1 ML=5.2×10^{14} cm^{-2}). After about 0.04 ML ethanol dosing, many bright protrusions appeared on the surface, most of the spots were located at bright rows which represent ethanol molecules adsorbed on Ti_{5c} sites (Fig.1(b)). In this image, the existence of one BBOv adsorbed ethanol molecule has also been observed, which appeared as a big bright spot on oxygen row, as marked by a dashed black circle. Because Ti_{5c} sites are considered as photocatalytic active sites, we concentrate our attention on the Ti_{5c} sites adsorbed ethanol molecules in this work. An enlarged picture of one Ti_{5c} site adsorbed ethanol molecules is shown in Fig.1(c), the STM image of the ethanol molecule appears to be an elliptical image, which has a long axis along the [001] direction of the $TiO_2(110)$ surface, that is consistent with the orientation of the C−C bond. The most stable configuration of ethanol adsorption on the Ti_{5c} site is illustrated in Fig.1(d) with oxygen atom binding to the Ti_{5c} site, the binding energy of this configuration is 0.72 eV as calculated in a previous work [22], very close to the case of methanol adsoprtion.

B. Photocatalysis of single ethanol molecule on TiO$_2$(110) surface

Since the band gap of rutile TiO_2 is about 3.1 eV, the wavelength of the incident light must be shorter than 400 nm in order to initiate photocatalytic process. In our experiments, a third-harmonic (355 nm) output of a 1064 nm laser was used. After 20 min laser irradiation, clear changes of the ethanol STM images have been observed. Some ethanol molecules appear to be stretched in the STM images (Fig.2(b)). This phenomenon is similar to the first dissociation step of methanol on the same substrate [38]. The stretched features can be divided into two types (I and II) according to their FWHMs by adding cut profile along [1$\bar{1}$0] direction (Fig.2(c)). After aligning the small peak beside the main peak which represents the BBO rows, we found
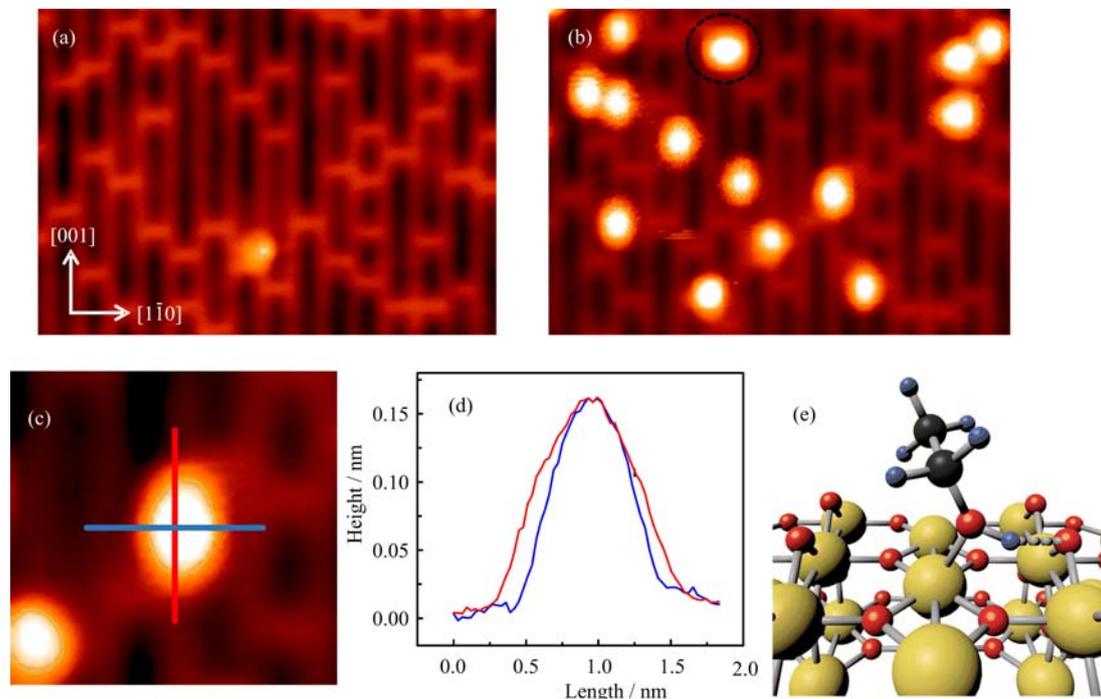
FIG. 1 Ethanol molecules adsorption on TiO$_2$(110) surface. STM images (size 9.5 nm×6.5 nm) of (a) bare TiO$_2$(110) surface and (b) surface after ethanol adsorption, the dashed black circle represents a BBOv adsorbed ethanol molecule. (c) Enlarged image and (d) the cut profiles of one Ti$_{5c}$ site adsorbed ethanol molecule. (e) The schematic drawing of a molecular adsorbed ethanol molecule at Ti$_{5c}$ site, Ti, O, C, and H atoms are shown in yellow, red, black, and blue, respectively.

the image of type I looks more symmetric than type II and the FWHMs of them are 1.10 and 0.95 nm, respectively. After counting more than 50 reacted molecules, the rate of the two types after irradiation is about 1:1 in statistical result.

Based on our previous work on methanol photocatalysis, it is certain that the main products of single ethanol photocatalysis under UV irradiation at the Ti$_{5c}$ site are acetaldehyde and bridging hydroxyls [18]. By TPD investigation of high coverage system, the acetaldehyde has been observed from a two-step process, the first step is the breaking of O−H bond and the second step is C−H bond cleavage as same as methanol photodissociation. In Fig.2(c), the unsymmetrical red line missed a part on the left relative to the cut profile of type I. If both neighbored BBO site has H adatoms, the main peak should be symmetric. Obviously, only one H-atom dissociated from the ethanol could lead to asymmetric structure. Therefore, according to their different cut profile property, it is easy to conclude that the type I images are due to an acetaldehyde molecule adsorbed on a Ti$_{5c}$ site with two hydroxyls located separately at different oxygen rows, and the type II image is likely from an ethoxy radical (CH$_3$CH$_2$O) on a Ti$_{5c}$ site and a hydroxyl at the adjacent oxygen row. The results are quite interesting, which means that we have observed the different products: one is with one hydrogen photocatalytically dissociated (type II) and the other is with two hydrogen atoms dissociated to the BBO sites

(type I). This is quite different from our previous STM study on methanol photocatalysis on the same surface, in which we always see dissociated methanol products are with two H-atoms dissociated after light illumination. Considering the similarity between methanol and ethanol, this is certainly quite intriguing. Further experiments are needed to clarify this issue.

C. Tip manipulation of the photocatalytic products

STM tip manipulation has been used to identify atomic and molecular species on single crystal surfaces. The manipulation is obtained by increasing the tunneling current or reducing the tunneling voltage to make the tip go down, then move the tip from a precise orientation. The distance between the tip and surface is extremely close in comparison with normal scanning condition. By the use of this technique, we can accurately move the species at the predefined region without perturbing other places. In this work, we have tried to investigate the composition of the two different features (type I and type II) by the use of this technique, the whole process is displayed in Fig.3.

As shown in Fig.3(b), four ethanol molecules are adsorbed at the Ti$_{5c}$ sites of the TiO$_2$(110) surface after dosing, which appear as elliptic features. Photocatalytic reactions have happened on all of the four molecules after a period of laser irradiation, as evi-
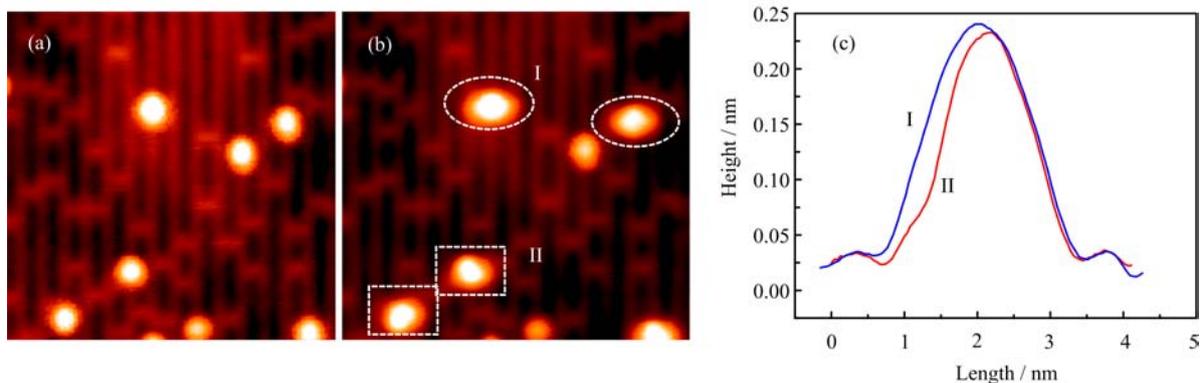
FIG. 2 STM images of ethanol photo-reaction on TiO$_2$(110) surface under 355 nm irradiation (size 9 nm×9 nm). (a) The TiO$_2$(110) surface with ethanol adsorption. (b) Two different changes happened after UV irradiation (10 mW, 20 min), marked by dashed ellipse (type I) and rectangle (type II). (c) The cut profiles along direction of the two different products, the blue cure and the red curve represent type I and type II, respectively.
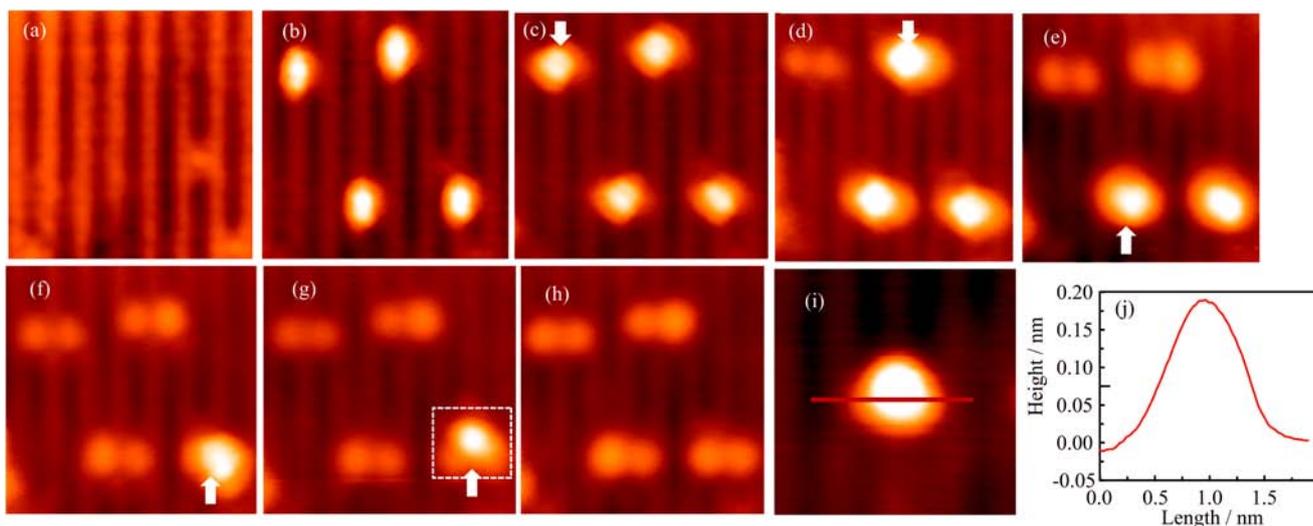

FIG. 3 Imaging tip manipulation on the photo-catalytic product of type I (size 5 nm×5 nm). (a) Bare TiO$_2$(110) surface. (b) STM image of the surface after UV irradiation. (c)−(g) The progress of tip manipulation, the white arrows indicate the direction of tip manipulation. (h) Image of the surface after tip manipulation, only OHs left on the surface. (i) STM image and the cut profile of a acetaldehyde molecule adsorbed on TiO$_2$(110) surface.

denced in Fig.3(c). All of them are stretched after light illumination and belong to the type I. To further confirm the composition of these bright spots, tip manipulation was performed. One of the four type I features was pulled by the STM tip along a certain orientation as marked by a white arrow in Fig.3(c). A remarkable change of the image occurred, the big bright spot was missing and two faint bright protrusions left on the surface. The two spots can be identified as two bridge bonded hydroxyls (BBOH), using a technique developed previously in which hydrogen atoms on BBO can be easily removed by voltage above 2 V [40]. We have repeated this manipulation on three other type I protrusions (Fig.3 (d)−(g)). All of those three images show the same change that is with two BBOHs remained on the neighbored BBO sites. In these manipulations, it

means that an acetaldehyde molecule was pictured by the STM tip.

We have also done another manipulation on the image. A different result has been obtained from this manipulation. A triangle intermediate feature has been observed during this tip manipulation, which is marked by a dashed square in Fig.3(g). The changed triangle image seems to consist of one big bright spot in the middle and two lower dim bright spots on both sides. We assign the bright spot in the middle to an acetaldehyde molecule and the two faint spots are the two BBOHs left in the final picture. In this manipulation, it seems that the acetaldehyde molecule was kicked to a neighboring Ti$_{5c}$ site. The similarity between this image and the image of acetaldehyde molecule adsorbed on the TiO$_2$(110) surface (Fig.3(i)) clearly supports our assign-

ment in Fig.3(g). Therefore, the STM tip manipulation pulled the acetaldehyde molecule from the original site to a neighboring Ti$_{5c}$ site along the Ti row.

We have also tried to manipulate the type II image using the STM tip. After the tip manipulation of type II, only one BBOH left was observed at some manipulations. This picture seems to fit our assumption that the type II image in the intermediate of the ethanol dissociation process, which consists of a CH$_3$CH$_2$O molecule and one H-atom on BBO. However, result of multiple irradiation experiment described in the next seems to indicate otherwise. Further manipulations of some type II images, however, result in the type I image with two BBOHs left. This suggests that the tip induced further dissociation of the ethoxy radical on the surface.

D. Multi-time UV irradiation experiment

To further understand the properties of the product type II, a multi-irradiation experiment was performed by UV laser. Because the final product of acetaldehyde is formed by an O−H bond cleavage followed by a C−H bond breaking. If type II indicates only O−H bond cleavage, the STM image will change into a type I image when the C−H bond cleavage happens after multi-irradiation. The detailed results of our multi-irradiation experiment are shown in Fig.4.

Figure 4(a) shows the STM image of TiO$_2$(110) surface after ethanol adsorption, all of them are adsorbed at the Ti$_{5c}$ sites. After the first time UV irradiation (10 min, 20 mW), there are four type I protrusions and three type II protrusions, as evidenced in Fig.4(b). After another 10 min laser irradiation with higher power of 50 mW, two more ethanol molecules dissociated, the number of type I features increase to six with the three type II spots still unchanged (Fig.4(c)). Then the third time irradiation was performed by an even more powerful light irradiation, 120 mW and 20 min. The STM image is shown in Fig.4(d). Two more ethanol molecules dissociated, but the three type II features are still unchanged as before.

During this multiple time irradiation experiment, new type I and type II images were produced directly from the ethanol molecules, suggesting that ethanol molecules are dissociated into two products. However, interconversion between the two type images has never been detected. We have also performed a much larger sample area, similar results are obtained. This implies that those two products cannot be converted into each other. Therefore, type II image is likely not an intermediate of ethanol photocatalysis, instead it is likely a peculiar reaction product of ethanol photocatalysis on TiO$_2$(110) that with one H-atom on the BBO. And it cannot be converted to the final product (type I) photocatalytically, but can be done with an STM tip manipulation. However, the exact structure of this type II product cannot be derived from this work, further in-
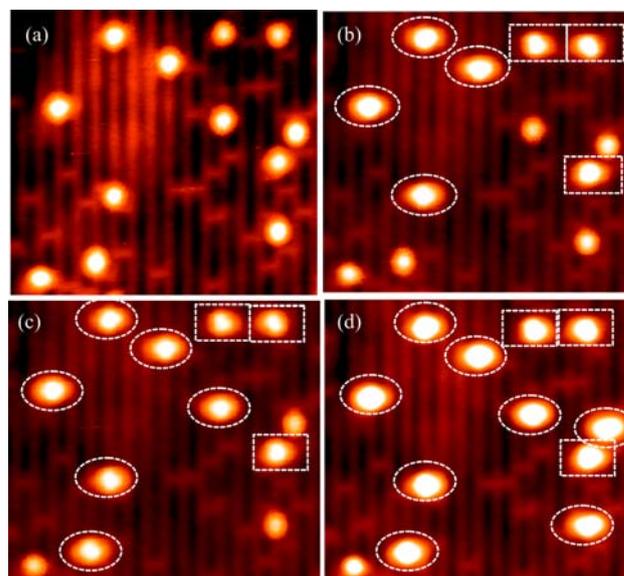

FIG. 4 STM experiment of multi-times light irradiation (size 10 nm×10 nm). (a) The TiO$_2$(110) surface after ethanol adsorption. (b) The surface after the first time UV irradiation (20 mW, 10 min). (c) The surface after the second time UV irradiation (50 mW, 10 min). (d) The surface after the third time UV irradiation (120 mW, 20 min). The dashed ellipse and rectangle represent type I and type II, respectively.

vestigations are certainly needed in order to clarify this issue.

IV. CONCLUSION

Photocatalytic dissociation of ethanol molecules on TiO$_2$(110) surface has been investigated by STM with sub-molecular resolution for the first time. At 80 K, the main adsorption form of ethanol on Ti$_{5c}$ sites is molecular adsorption, which looks like ellipses from the STM image. After UV irradiation, two different protrusions of products have been detected which are classified as type I and type II depending on the FWHM. Type I is clearly composed of an acetaldehyde molecule and two BBOHs, as identified by STM tip manipulation. However, the conversion from type II to type I was not observed through laser irradiation, but can be done with STM tip manipulation. Therefore, the dissociation process of ethanol in low coverage may have two different channels, with one channel of dissociation of two hydrogen atoms from ethanol and the other with one hydrogen atom from ethanol.

V. ACKNOWLEDGMENTS

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