



Title	Deciphering Adsorbate-Adsorbate Interactions from Scanning Tunneling Microscopy Images : Integrated Topological, Statistical, and First-Principles Analysis of Methoxy Adsorbates on Pt/TiO ₂ (110)
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Deciphering Adsorbate–Adsorbate Interactions from Scanning Tunneling Microscopy Images: Integrated Topological, Statistical, and First-Principles Analysis of Methoxy Adsorbates on Pt/TiO₂(110)

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Detection of the methoxy species by persistent homology analysis with superlevel set method:

The persistent homology (PH) analysis with superlevel set method was applied to grayscale STM images in this study.^{1,2} The filtrations of pixels are considered to detect the islands for the binarized images in 0-dimensional persistent homology. The 0-dimensional persistent homology with the superlevel set method uses the brightness of the grayscale image, corresponding to the height in STM image, instead of the pixels in the binarized image. The threshold to detect the islands was moved from 255 to 0 brightness with checking the birth of “islands” and the death of “islands” (Figs. 2(a), and S1(a)). The island birth, corresponding to Pt particles, in the early stage of the threshold brightness and then the islands come from methoxy adsorbates birth because the Pt particles are higher than methoxy adsorbates in STM image (Fig. 2(a)). These islands are dead at the terrace of the substrate. Then, the persistence diagram (PD) is obtained; for example, Fig. S1(b) shows the PD corresponding to Fig. 2(b).

The x - and y - axes correspond to birth and death brightness (or height) of islands. As shown in Fig. S1(c), the Pt particles and the methoxy adsorbates give different birth values from the difference in brightness corresponding to the height in real space. On the other hand, the differences in death values come from the differences in the terrace. In this study, the PD in Fig. 2(b) gives not points like Fig. S1(b) but has distribution due to the tilting of the substrate. The PH analysis was carried out after denoising but not background subtraction. In addition, even though the methoxy species are on different terraces, they can be detected and distinguished as shown in Fig. 2(b). The lifetime of an island, defined by (birth-death) of each island, gives the height of its island in case of STM image. Almost 50 (corresponding to ~ 0.3 nm) is the upper threshold to distinguish the Pt nanoparticles from the methoxy species, though the absolute height was a little different depending on the image. On the other hand, the lower threshold of a lifetime of more than two for removing the noise. Finally, the islands in the highlighted region in PD (Fig. 2(b)) corresponded to the methoxy species were picked up. The birth positions of islands which are the highest positions of the methoxy adsorbates were shown in Fig. S1(c). Most of the methoxy adsorbates were successfully identified even though the Pt nanoparticles were co-present and they were distributed on different terrace surfaces. However, the methoxy adsorbates located close to the Pt nanoparticles failed to detect (210 spots), and the TiO_x species having similar height with that of methoxy adsorbates were mistakenly recognized (129 spots), as shown in Fig. 2(c). Frequency of these failures and

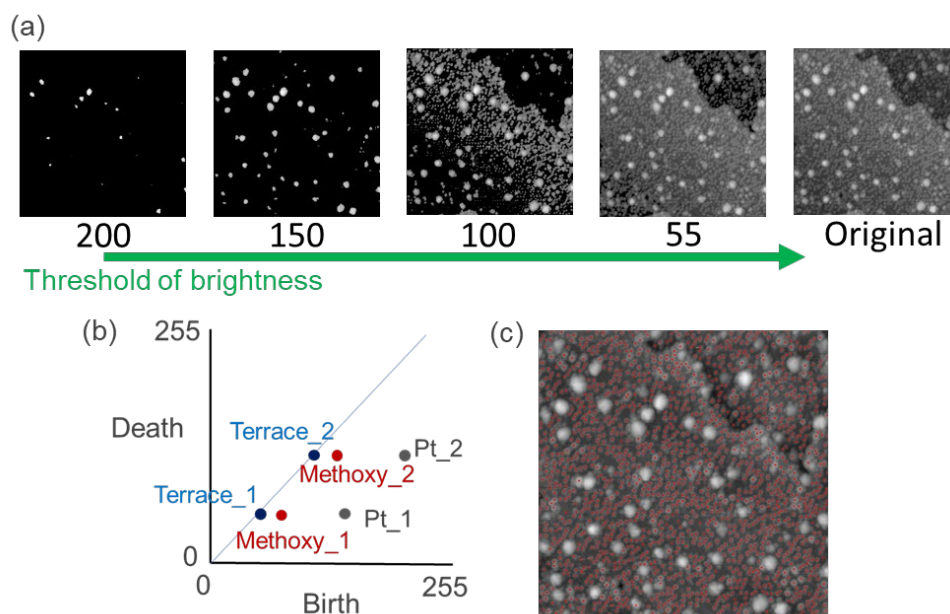


Figure S1. Strategy of detecting methoxy species on the Pt/TiO₂(110) surface by persistent homology analysis. (a) Application of the threshold of brightness to the STM image of methoxy adsorbates on the Pt/TiO₂(110) surface. (b) 0-dimensional persistence diagram (PD) for Fig.2(a). (c) Plot of the birth positions of the data points located within the highlighted region in Fig.2(b).

mistakes should depend on the densities of the Pt nanoparticles and TiO_x species. The non-detection of the methoxy adsorbates located near the Pt nanoparticles was probably due to the Gaussian blur filtering pretreatment for denoising of the STM images. This caused the boundary between a Pt nanoparticle and the adjacent methoxy adsorbates to become ambiguous, and consequently, the Pt nanoparticle and the adjacent methoxy adsorbates were identified as a single large Pt nanoparticle. Such non-detection of the methoxy adsorbates may be decreased by further optimization of the denoising processes of the STM images. The false detection caused by the presence of TiO_x could be suppressed by applying additional persistent homology analysis considering the diameter difference since the lateral sizes of the methoxy adsorbates and the TiO_x species are 0.5 and ~ 1.3 nm, respectively.

Plot of the pair-interaction energy (E_{int}) as a function of the separation distance (d) between the two methoxy species and fitting with a power function:

The E_{int} values obtained from the DFT calculations (see Table1) were plotted as a function of the separation distance (d) between the two methoxy species, as shown in Fig. S2. Fitting with a power function ($E_{int} = \alpha d^\beta$, with α and β being the fitting parameters) was conducted at $d \geq 0.6$ nm although the number of the data points is limited. α and β were estimated to be 16 ± 4 and -2.5 ± 0.6 , respectively.

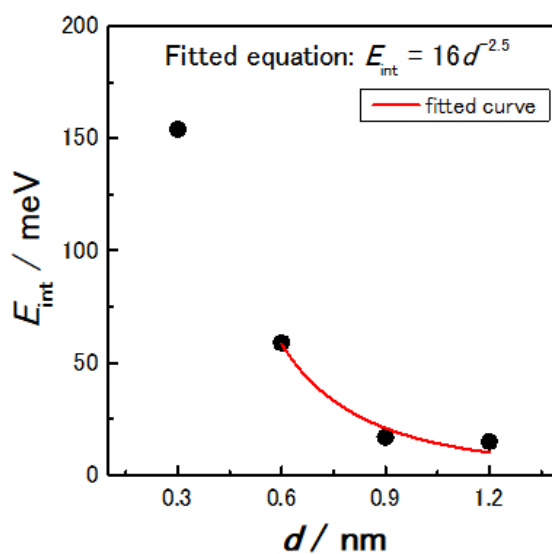


Figure S2. Plot of the pair-interaction energies (E_{int}) obtained from the DFT calculations as a function of the separation distance (d) between the two methoxy species, and fitting with a power function.

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