

Structure of Defects on anatase TiO₂(001) Surface

Supporting Information

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1. Spatial orbital distribution calculated by PBE and HSE functional.

We compared the spatial orbital distribution calculated by PBE and HSE functional. As shown in Figure S1, the difference between them is insignificant. Therefore, in our work we use PBE and (4×8) unit cell to simulate the STM image for different O_V and Ti_{ini} structures.

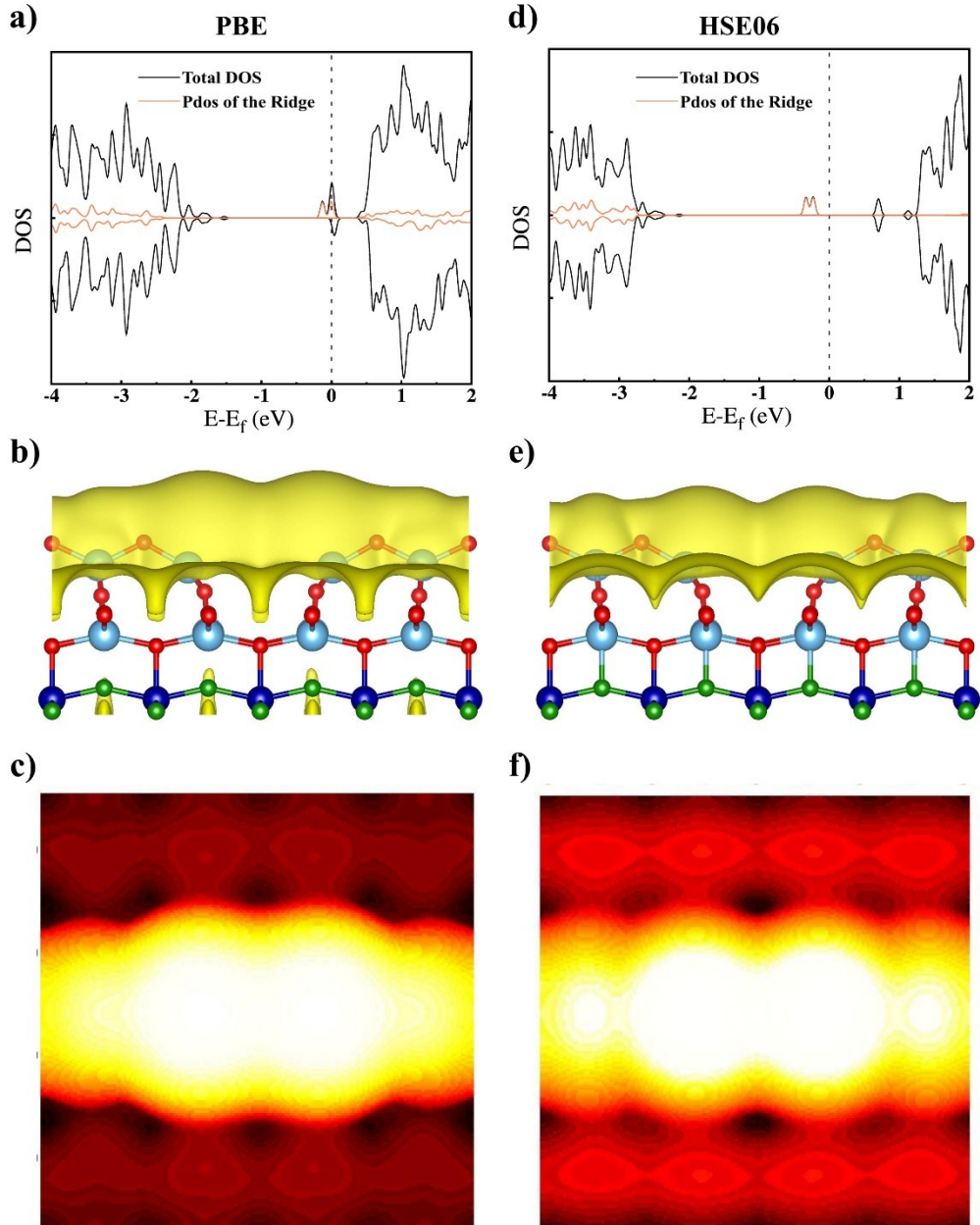


Figure S1. The DOS, orbital spatial distribution and simulated STM image of O_V_I structure obtained by PBE (a-c) and HSE06 (d-f).

2. Conversion energy barrier of the equivalent oxidized structures.

$1/2ML(D)$ and $1ML(M)$ structures have four equivalent structures. The conversion barrier between them is shown in Table S1. Both the conversion barrier of $1/2ML(D)$ and the conversion barrier across the ridge of $1ML(M)$ are smaller than 0.26eV. But the the conversion barrier parallel the ridge of $1ML(D)$ is larger than 1eV. Therefore in our work we average the four equivalent structures of $1/2ML(D)$ and two equivalent structures of $1ML(M)$ to get the simulated STM images.

Barrier(eV)	$1/2ML(D)$	$1ML(M)$
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Across the ridge	0.040	0.086
Parallel the ridge	0.251	1.01

Table S1. The calculated energy barrier between the oxidized structure and its symmetrical image across and parallel the ridge.

3. Observations in the STM measurements.

In the work by Wang et al.¹, the dark spot, bright spot and half-dark-half-bright spots have been observed. We marked the three kinds of different defects in Figure S2.

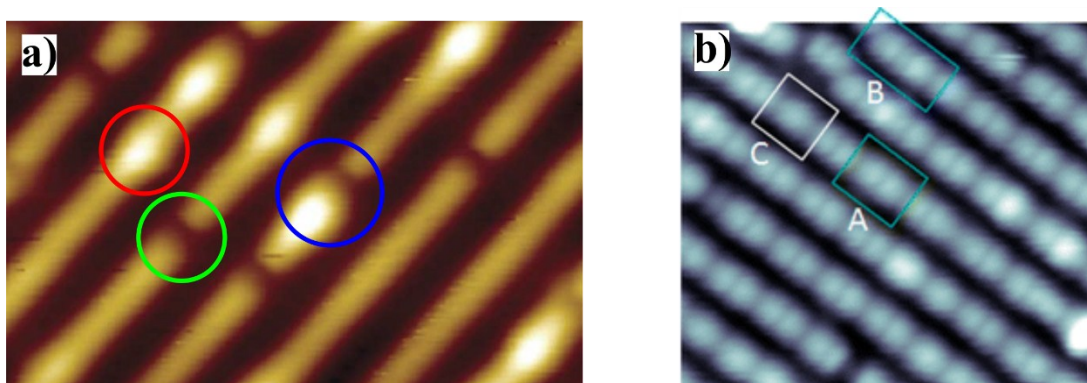


Figure S2. (a) High-resolution STM images of the reduced anatase $\text{TiO}_2(001)-(1 \times 4)$ surface, which is from Figure 2(a) of reference¹. We mark bright, dark and half-bright-half-dark defect with red, green and blue circles, respectively. (b) Figure 2(a) of reference², three type of feature (A, B, C).

1. Y. Wang, H. Sun, S. Tan, H. Feng, Z. Cheng, J. Zhao, A. Zhao, B. Wang, Y. Luo, J. Yang and J. G. Hou, *Nat. Commun.*, 2013, **4**, 2214.