Facile embedding of single vanadium atoms at the anatase TiO$_2$(101) surface

Supporting Information

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Synchrotron-based XPS data, Bader charge analysis addressing the oxidation state of adsorbed and embedded V, and STM simulations of various structures with embedded V:
The XPS data were collected at the ASTRID 2 synchrotron facility in Aarhus (MatLine). Instead of two preparations as done in the main article, the measurements at the MatLine were conducted on a V / a-TiO$_2$(101) sample prepared by V deposition at 105 K [curve (a) in Figure S1], followed by annealing at RT for 5 min [curve (b) in Figure S1]. Compared to the STM and XPS data presented in the main article the V coverage was higher (~0.3 ML instead of ~0.1 ML). In the XPS experiment at the MatLine, we again found that the V$2p_{3/2}$ peak shifts toward higher BE upon temperature raise. This clear shift by ~1.9 eV is even higher than the one found for low V coverage that is discussed in the main article. The reason for this large shift probably lays in the clustering of V on the a-TiO$_2$(101) surface upon deposition of ~0.3 ML V at LT.

**Figure S1.** XP-V$2p$ spectra acquired following preparations similar to that applied in the STM experiments of figure 2. Spectrum (a) was acquired following ~0.3 ML V deposition onto a-TiO$_2$(101) at 105 K, and spectrum (b) was acquired after subsequent annealing of the sample at RT for 5 min. Spectra were acquired at 105 K and offset for clarity. The energy scale in BE was set using O$1s$ peak positions and by referencing to the Au $4f_{7/2}$ core line at 84.0 eV.
Figure S2. Simulated STM images of several structures of embedded V for scanning voltages of 1V and 2V. a) Structure 1 (see Table 1) with monomeric V at 6f-Ti and the Ti at an interstitial site ($\text{Ti}_{\text{int}}$). b) As structure 1 but without a $\text{Ti}_{\text{int}}$. c) As structure 2 with V at 5f-Ti but without a $\text{Ti}_{\text{int}}$. d) Stoichiometric surface and V at an interstitial site. The following positions are indicated: 6f-Ti and 5f-Ti sites (grey circles), embedded V (blue circles), 2f-O (red circles), $\text{Ti}_{\text{int}}$ (grey diamonds), and $V_{\text{int}}$ (blue diamonds).
Figure S3. Simulated STM images of stoichiometric TiO2(101) for various voltages. a) 1.1 V, b) 1.5 V, c) 2.0 V. 6f-Ti, 5f-Ti sites (grey circles) and 2f-O (red circles) are indicated. The Tersoff–Hamann approximation was used to conduct the STM simulations.
To calculate the Bader charges of relevant models we have used the method of Henkelman et al.\textsuperscript{3} Table S1 summarizes the calculated Bader charges and magnetic moments of structures 1, 2 and 5 listed in Table 1 in the main article. The V atom in structure 5 shows higher values of the Bader charge and the magnetic moment than structures 1 and 2, respectively. This indicates a more reduced state of structure 5 compared to structures 1 and 2. For reference, the Bader charge of a Ti atom in the uppermost layer of an a-TiO$_2$(101) surface is calculated to be $\sim$19.9 e$^{-}$, and that of V in the uppermost layer of V$_2$O$_5$(001) $\sim$21.1 e$^{-}$.

Table S1. Calculated Bader charges and magnetic moments of structures 1, 2 and 5 (see Table 1 of the main article for assignments of the structures).

<table>
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<tr>
<th>Structure</th>
<th>Bader charge (e$^{-}$)</th>
<th>Magnetic moment ($\mu_B$)</th>
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<tr>
<td></td>
<td>V</td>
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<tr>
<td>1</td>
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<td>21.27</td>
<td>20.02</td>
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<tr>
<td>5</td>
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References: