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).[1] 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.

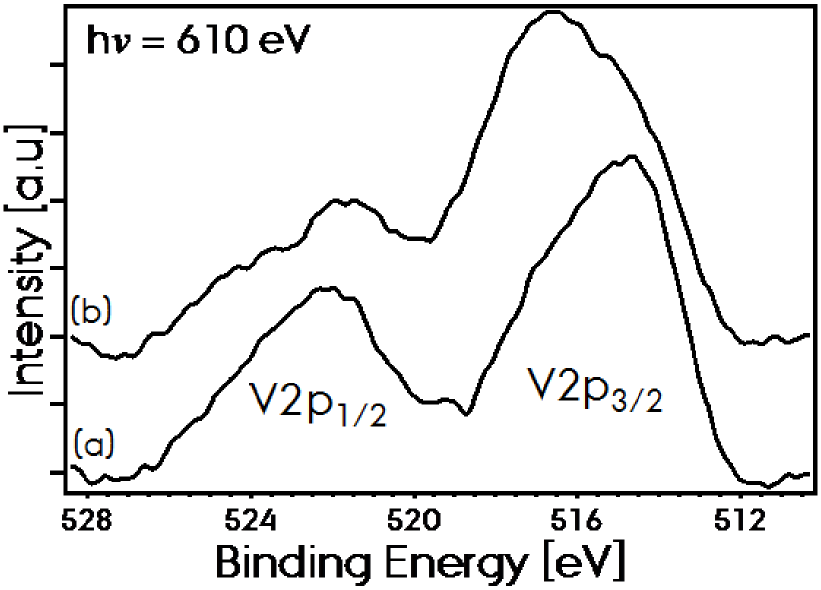


Figure S1. XP-V*2p* spectra acquired following preparations similar to that applied in the STM experiments of figure 2. Spectrum (a) was acquired following ~0.3 ML V deposition onto a-TiO_2(101) at 105 K, and spectrum (b) was acquired after subsequent annealing of the sample at RT for 5 min. Spectra 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.

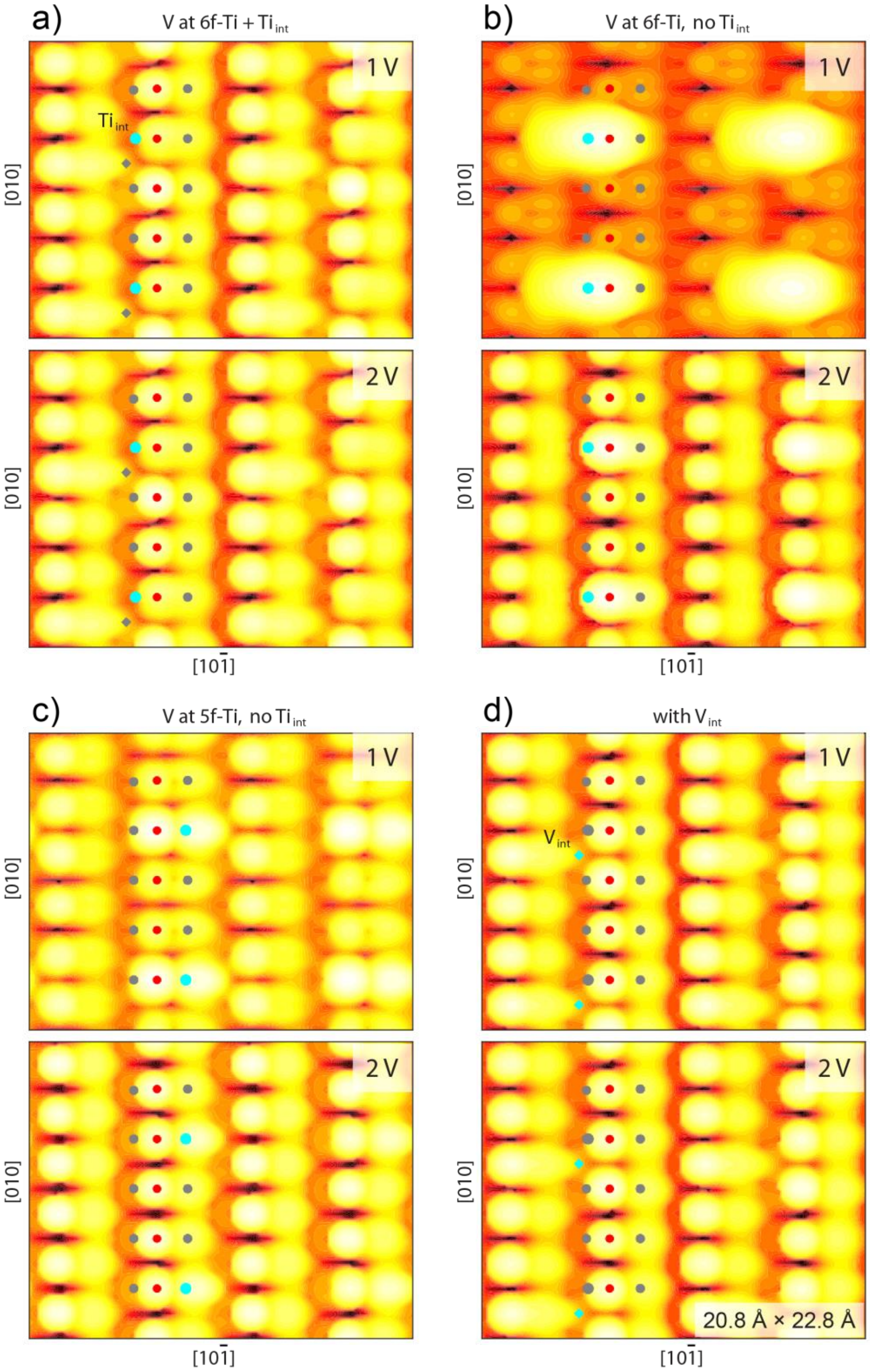


Figure S2. Simulated STM images of several structures of embedded V for scanning voltages of 1V and 2V. a) Structure 1 (see Table 1) with monomeric V at 6f-Ti and the Ti at an interstitial site (Ti$_{int}$). b) As structure 1 but without a Ti$_{int}$. c) As structure 2 with V at 5f-Ti but without a Ti$_{int}$. 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), Ti$_{int}$ (grey diamonds), and V$_{int}$ (blue diamonds).

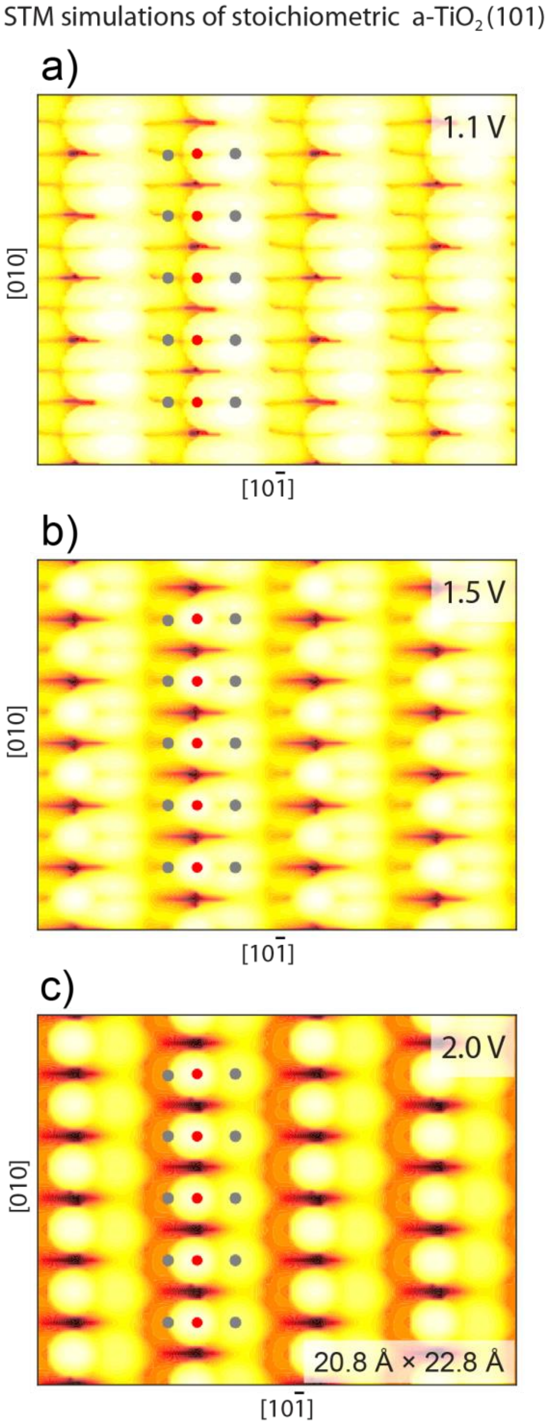
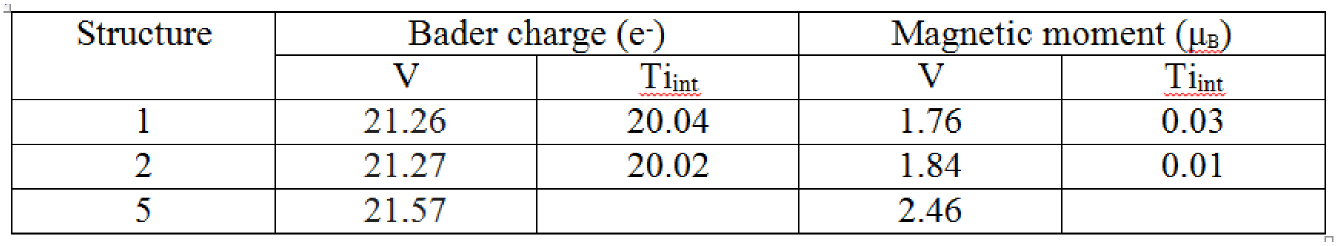


Figure S3. Simulated STM images of stoichiometric TiO2(101) for various voltages. a) 1.1V, b) 1.5 V, c) 2.0 V. 6f-Ti, 5f-Ti sites (grey circles) and 2f-O (red circles) are indicated. The Tersoff–Hamann approximation[2] was used to conduct the STM simulations.

To calculate the Bader charges of relevant models we have used the method of Henkelman *et al*.[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 ~19.9 e^-, and that of V in the uppermost layer of V_2O_5(001) ~21.1 e^-.



Structure	Bader charge (e^-)		Magnetic moment (μ_B)	
	V	Ti_{int}	V	Ti_{int}
1	21.26	20.04	1.76	0.03
2	21.27	20.02	1.84	0.01
5	21.57		2.46	

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

References:

1 ISA, Centre for Storage Ring Facilities, Aarhus, http://www.isa.au.dk/.

2 J. Tersoff and D. R. Hamann, *Phys. Rev. B* 1985, **31**, 805–813.

3 G. Henkelman, A. Arnaldsson and H. Jonsson, *Comp. Mater. Sci.* 2006, **36**, 354–360.