Supplementary Information

Identifying structural distortion in doping VO_2 with IR spectroscopy

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Experimental Procedure:

Analytical grade vanadyl acetylacetonate ($VO(acac)_2$) and sodium tungstate (Na_2WO_4) were purchased from Sigma Aldrich and used without further purification. In a typical synthesis, the following chemicals were added to a Teflon-lined stainless autoclave with capacity of 50 mL: 1 mmol $VO(acac)_2$, an appropriate amount of Na_2WO_4 and 40 mL of distilled water. After the mixture was stirred to a dark-green suspension, the autoclave was sealed and heated at 200 °C for 24 hours and cooled to the room temperature afterwards. Dark-blue precipitate was washed with water and ethanol several times, and then dried at 60 °C for 6 hours. This precursor was heated at 600 °C for 12 hours in a flowing Ar atmosphere. The product was obtained through this thermal treatment process. VO_2 products with different tungsten doping concentrations were prepared by add Na_2WO_4 in the Teflon-lined: sample (a) with 2 ml of Na_2WO_4 solution, sample (b) with 4.5 ml of Na_2WO_4 solution and sample (c) with 5 ml of Na_2WO_4 solution. The concentration of Na_2WO_4 solution was 0.01 mol/L.

Instrumentation:

XRD patterns were recorded on a Philips X'Pert Pro Super diffractometer with Cu Kα radiation (λ=1.54178 Å). Differential scanning calorimetry (DSC) analysis was carried out on a Netszch DSC 200F3 in a high-purity N_2 flowing atmosphere in a temperature range from 0 to 80 °C. Fourier transform infrared (FTIR) spectroscopy was carried out on a Nicolet 8700 FTIR in a KBr pellet scanning from 4000 to 400 cm^{-1} and in a polypropylene pellet scanning from 500 to 200 cm^{-1}, respectively. FTIR measurements were performed at several fixed temperature as follows: 25 °C, 40 °C, 60 °C, 62 °C, 64 °C, 66 °C, 68 °C, 70 °C, 75 °C and 80°C. The concentrations of elements were measured with a Thermo Scientific PlasmaQuad 3 inductively-coupled plasma mass spectrometry (ICP-MS) after dissolving them with a mixture of HCl and HNO_3 (3:1, volume ratio).

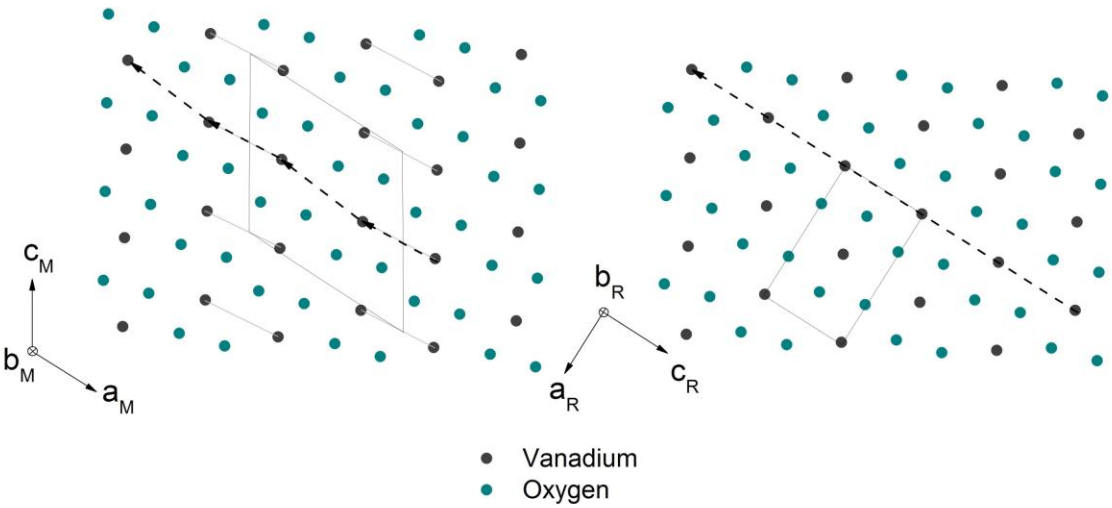

Fig. S1. Microscopic structure of monoclinic and rutile VO_2 projected along [010] axis.

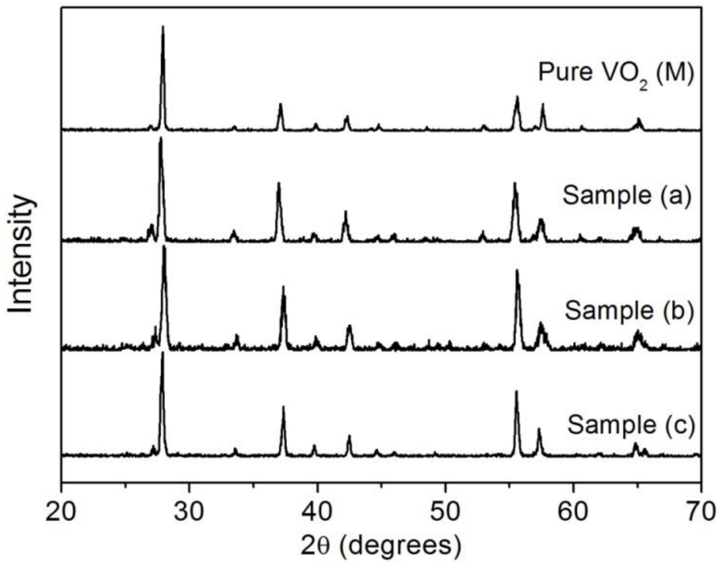

Fig. S2. Powder X-ray diffraction pattern for VO_2 (M) and $V_{1-x}W_xO_2$ doped samples with different doping dose: (a) x=0.0017; (b) x=0.0038; and (c) x=0.0069. The patterns can be clearly indexed to monoclinic VO_2 (M) (Joint Committee on Powder Diffraction Standards, JCPDS No. 82-0661) with the space group $P2_1/c$. There was no peak that can be detected and assigned to other crystal phases of vanadium oxides or tungsten oxides, indicating that the doping of tungsten brings no impurities into the final products. Moreover, no obvious peak shifting has been observed in the XRD patterns accompanied with the doping process.

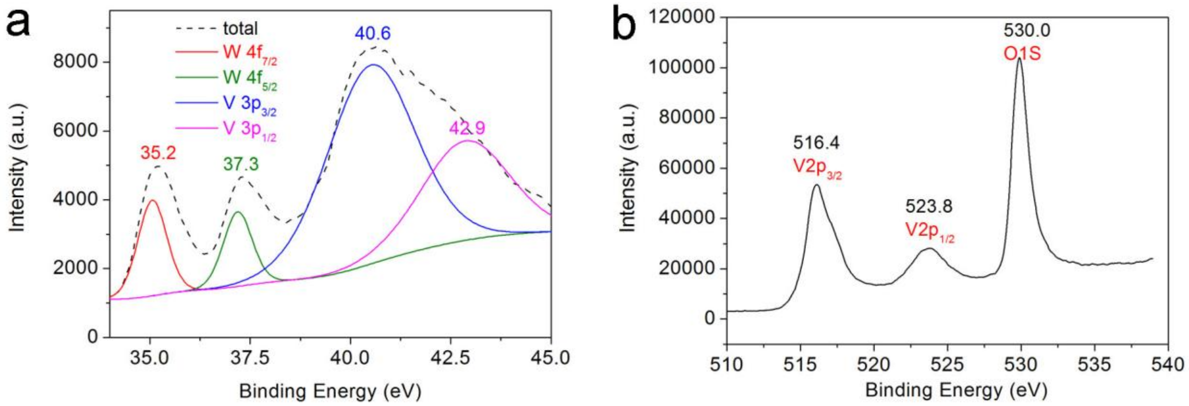

Fig. S3. X-ray photoelectron spectroscopy (XPS) data of doped VO_2 sample (a). The V2p corelevel spectrum shows that the observed value of the binding energy (516.4 eV) for $V2p_{3/2}$ is in good agreement with the literature value of bulk-phase V^{4+}. In addition, the binding energy difference (Δ) between the O1s and $V2p_{3/2}$ levels was used to determine the oxidation state of the vanadium oxide. The Δ value of 13.6 eV in our sample approaches that reported in the literature for V^{4+}. Thus the XPS spectra clearly reveal that vanadium is in the +4 valence state in the as-obtained sample, without any presence of the +5 valence state. Overall, XPS data confirm that all the vanadium remains the oxidation state of V(IV) in the doped sample. The oxidation state of tungsten has been determined to W(VI).

1. C. D. Wagner, W. M. Riggs, L. E. Davis and J. F. Moulder, *Handbook of X-Ray Photoelectron Spectroscopy*, Ed: G. E. Muilenberg, Perkin-Elmer, 1979.
2. G. A. Sawatzky and D. Post, *Phys. Rev. B*, 1979, **20**, 1546.

Table S1: Calculation results for atom site and displacement in absolute coordinates for different modes of pure VO_2 (M). X, Y and Z denote the absolute coordinates of atom locations, and dx, dy and dx denote the displacement of atoms.

Mode no. 1:

	X	Y	Z	dx	dy	dz
V	1.118434	4.539165	-0.57041	-0.07503	0.134447	-0.18603
V	3.66241	2.22205	0.248908	0.075034	0.134447	0.186031
V	3.715416	0.095064	2.976174	-0.07503	0.134447	-0.18603
V	1.17144	2.412178	2.156853	0.075034	0.134447	0.186031
O	0.523744	0.996852	0.84834	-0.16467	-0.00456	-0.04612
O	1.920627	3.23531	0.452643	-0.27251	-0.24862	-0.16233
O	4.2571	3.313967	-1.16985	0.164672	-0.00456	0.046119
O	2.860216	0.918196	-0.77415	0.272508	-0.24862	0.162325
O	4.310106	3.637376	1.557421	-0.16467	-0.00456	-0.04612
O	2.913222	1.398918	1.953117	-0.27251	-0.24862	-0.16233
O	0.57675	1.320262	3.575606	0.164672	-0.00456	0.046119

Mode no. 2:

	X	Y	Z	dx	dy	dz
V	1.118434	4.539165	-0.57041	0.169492	-0.29789	-0.10059
V	3.66241	2.22205	0.248908	0.169492	0.297889	-0.10059
V	3.715416	0.095064	2.976174	0.169492	-0.29789	-0.10059
V	1.17144	2.412178	2.156853	0.169492	0.297889	-0.10059
O	0.523744	0.996852	0.84834	-0.12909	-0.16291	0.023916
O	1.920627	3.23531	0.452643	-0.17993	-0.15464	0.149518
O	4.2571	3.313967	-1.16985	-0.12909	0.162908	0.023916
O	2.860216	0.918196	-0.77415	-0.17993	0.154641	0.149518
O	4.310106	3.637376	1.557421	-0.12909	-0.16291	0.023916
O	2.913222	1.398918	1.953117	-0.17993	-0.15464	0.149518
O	0.57675	1.320262	3.575606	-0.12909	0.162908	0.023916

Mode no. 3:

	X	Y	Z	dx	dy	dz
V	1.118434	4.539165	-0.57041	-0.19317	-0.29969	0.118239
V	3.66241	2.22205	0.248908	-0.19317	0.299686	0.118239
V	3.715416	0.095064	2.976174	-0.19317	-0.29969	0.118239
V	1.17144	2.412178	2.156853	-0.19317	0.299686	0.118239
O	0.523744	0.996852	0.84834	0.175131	-0.15545	-0.11969
O	1.920627	3.23531	0.452643	0.172251	-0.00927	-0.09988
O	4.2571	3.313967	-1.16985	0.175131	0.155449	-0.11969
O	2.860216	0.918196	-0.77415	0.172251	0.009267	-0.09988
O	4.310106	3.637376	1.557421	0.175131	-0.15545	-0.11969
O	2.913222	1.398918	1.953117	0.172251	-0.00927	-0.09988
O	0.57675	1.320262	3.575606	0.175131	0.155449	-0.11969

Mode no. 4

	X	Y	Z	dx	dy	dz
V	1.118434	4.539165	-0.57041	0.021622	-0.0351	0.165412
V	3.66241	2.22205	0.248908	-0.02162	-0.0351	-0.16541
V	3.715416	0.095064	2.976174	0.021622	-0.0351	0.165412
V	1.17144	2.412178	2.156853	-0.02162	-0.0351	-0.16541
O	0.523744	0.996852	0.84834	-0.04421	-0.0767	0.155486
O	1.920627	3.23531	0.452643	-0.36886	0.135652	0.185654
O	4.2571	3.313967	-1.16985	0.044205	-0.0767	-0.15549
O	2.860216	0.918196	-0.77415	0.368859	0.135652	-0.18565
O	4.310106	3.637376	1.557421	-0.04421	-0.0767	0.155486
O	2.913222	1.398918	1.953117	-0.36886	0.135652	0.185654
O	0.57675	1.320262	3.575606	0.044205	-0.0767	-0.15549

Mode no. 5:

	X	Y	Z	dx	dy	dz
V	1.118434	4.539165	-0.57041	0.047299	0.072851	-0.01648
V	3.66241	2.22205	0.248908	-0.0473	0.072851	0.016475
V	3.715416	0.095064	2.976174	0.047299	0.072851	-0.01648
V	1.17144	2.412178	2.156853	-0.0473	0.072851	0.016475
O	0.523744	0.996852	0.84834	-0.28416	0.029075	0.077619
O	1.920627	3.23531	0.452643	0.15089	-0.16559	0.323073
O	4.2571	3.313967	-1.16985	0.284164	0.029075	-0.07762
O	2.860216	0.918196	-0.77415	-0.15089	-0.16559	-0.32307
O	4.310106	3.637376	1.557421	-0.28416	0.029075	0.077619
O	2.913222	1.398918	1.953117	0.15089	-0.16559	0.323073
O	0.57675	1.320262	3.575606	0.284164	0.029075	-0.07762