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Full Paper

Single-crystalline W-doped VO₂ nanobeams with highly reversible electrical and plasmonic responses near room temperature

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Single-crystalline vanadium dioxide (VO₂) nanostructures are of great interest because of their single-domain metal-to-insulator transition. In this paper, single-crystalline W-doped VO₂ nanobeams were synthesized for optical and electrical applications. As a result of differences in the polarization of the beams along their transverse and longitudinal axes, dual surface plasmon resonance peaks at 1344 and 619 nm are generated, resulting in an increase in the solar modulating abilities of the VO₂ nanobeams. The conductivity of the single crystalline W-doped VO₂ nanobeams changes by 3–4 orders of magnitude at the transition temperature, which is of great importance for electrical applications.

1. Introduction

Vanadium dioxide (VO₂) is a smart material that is characterized by a reversible phase transition from an insulating monoclinic phase (VO₂ (M), $P 2_1/c$) to a metallic rutile phase (VO₂ (R), $P 4_2/mnm$) at ~68 °C.^[1-6] During the metal to insulator transition (MIT), a sudden drop in infrared transmittance upon heating above the transition temperature τ_c makes it a

promising candidate for use in thermochromic smart windows.^[7-11] Recently, there has been some newly reported VO₂ nanostructures (W-doped VO₂@SiO₂ nanoparticles,^[11b] VO₂ nanonets,^[11c] TiO₂(R)/VO₂(M)/TiO₂(A) multilayer film^[11d]) in smart window applications, where the nanoparticles, nanonets and multilayer films showed $T_{\text{lum}}/\Delta T_{\text{sol}}=50.6\%/14.7\%$, $46.3\%/10.7\%$, $29.0\%/10.2\%$, respectively. VO₂ nanostructures have also been found to promising candidates for sensors and other device applications, including single domain switches,^[12] flexible strain sensors,^[13] field-effect transistors,^[14] solid-state thermal memories^[15] and batteries.^[16] As a result, the low temperature synthesis of crystalline VO₂ nanostructures is of great importance. In addition, τ_c for pure VO₂ is too high to be used in smart applications. An efficient way to reduce τ_c is to dope VO₂ with high valence metal cations. ^[17-21] Tungsten (W⁶⁺) cations have been found to be the most efficient dopants for lowering τ_c at a rate of $\sim 20\text{-}28$ K/at.%.^[22]

In the past, high temperature evaporation,^[23-26] sol-gel methods^[27] and magnetron sputtering^[28] have been used to fabricate nanostructured VO₂ materials using complex equipment. In contrast, hydrothermal synthesis is an alternative facile method to prepare nanostructured metal oxides at relatively low temperatures (< 300 °C), owing to the increased solubility of oxides in hot water under a high autogenous vapor pressure.^[29] Nanostructured VO₂ materials, including nanopowders^[30,31] and nano-asterisks,^[33] have been synthesized under hydrothermal conditions below 300 °C with polycrystalline characteristics, complicating studies of the single domain metal-insulator phase transition. Hydrothermally synthesized nanorods^[32] have previously been reported to be micron-sized or larger in length, limiting their use in smart applications. To the best of our knowledge, there is still no report of the hydrothermal synthesis and investigation of uniform single-crystalline W-doped VO₂ nanobeams that are below 100 nm in width and 500 nm in length, although high temperature evaporation has been used to fabricate similar structures.^[34]

In this paper, we report a simple hydrothermal process to synthesize W-doped single-crystalline VO₂ nanobeams and propose a rolling mechanism to explain their structural evolution from the starting 2D V₂O₅-H₂O₂ layered material to vanadium oxide nanowires/nanobeams and nanopowders. A uniform distribution of W dopants in the VO₂ nanobeams results in a high doping efficiency and a unique surface plasmon resonance (SPR). The SPR is favored in thermochromic smart window applications to enhance their solar modulation ability ΔT_{sol} (defined as the solar transmission difference above and below τ_c). It occurs only in the metallic state of VO₂, leading to enhanced absorption at high temperature and consequently reducing transmission above τ_c without compromising the transmission in the insulating state below τ_c .

2. Results and Discussion

N₂H₄·H₂O is an effective reagent to synthesize VO₂ by reducing the V₂O₅ starting material ($2\text{V}_2\text{O}_5 + \text{N}_2\text{H}_4 \cdot \text{H}_2\text{O} \rightarrow 4\text{VO}_2 + \text{N}_2 + 3\text{H}_2\text{O}$).^[35] However, residual H₂O₂ in the precursor can also react with the N₂H₄·H₂O ($2\text{H}_2\text{O}_2 + \text{N}_2\text{H}_4 \cdot \text{H}_2\text{O} \rightarrow \text{N}_2 + 5\text{H}_2\text{O}$). Therefore, the amount of N₂H₄·H₂O is critical for the synthesis of the VO₂ phase. Figure 1a shows X-ray diffraction (XRD) patterns of W-doped-VO₂ hydrothermal products, showing phase evolution with increasing amounts of N₂H₄·H₂O. When the addition of N₂H₄·H₂O was below 30 μL, a mixture of V₆O₁₃ and VO₂(R) was formed, primarily owing to the consumption of N₂H₄·H₂O by the residual H₂O₂ in the precursor. After increasing the amount of N₂H₄·H₂O to 35 μL, a highly crystalline VO₂ (R) phase (JCPDS #79-1655) was synthesized successfully. Upon further increasing the amount of N₂H₄·H₂O to 50 and 100 μL, the products were gradually reduced to V₆O₁₁ and V₂O₃, respectively. Only the intermediate VO₂(A) phase, which crystallized in tetragonal form with space group *P*4₂/ncm (JCPDS #42-876), could be obtained under the same hydrothermal conditions without W doping, suggesting that W doping reduces the energy barrier for VO₂(R) phase formation. A similar phenomenon has been observed in the synthesis of Mo-doped VO₂(M) nanorods, where only the VO₂(B) phase

(monoclinic $C2/m$, JCPDS #81-2392) could be obtained without the addition of molybdic acid.^[36]

The morphology of the vanadium oxide products is shown in Figures 1 (b-f). Along with the phase evolution ($V_6O_{13} \rightarrow VO_2 \rightarrow V_6O_{11} \rightarrow V_2O_3$), the morphology gradually changed from nanowire (V_6O_{13}) to nanobeam (VO_2) to nanoparticle, with a continuous reduction in aspect ratio. As shown in Figure 1b, the V_6O_{13} nanowires are ~ 50 nm in width, with a length in the micron-size range and an aspect ratio of >50 . With increasing reducing agent, the V_6O_{13} nanowires reduce in length (Figure 1c). $VO_2(R)$ nanobeams with a low aspect ratio ($\sim 4-8$) could be obtained by further increasing the amount of the reducing agent, with the width and length of nanobeams (Figure 1d) falling into the ranges 90-100 nm and 400-800 nm, respectively. Finally, V_6O_{11} and V_2O_3 nanoparticles with mean grain sizes of ~ 50 nm were obtained as observed in Figure 1e and f, respectively. It is of interest that the morphology of the VO_2 product could be tailored by the W doping level as shown in Figure S1 (see the supporting information), where the nanobeams could be changed to the mixture of nanobeam and nanoparticles.

A rolling mechanism is proposed to explain the structural transformation from the layered starting material to the final low-dimensional nanostructures.^[37] As illustrated in Figure 2a and Figure S6 (see supporting information), the $V_2O_5 \cdot H_2O_2$ precursor has a two-dimensional sheet structure and a chemical composition of $V_2O_5 \cdot 1.6H_2O$, as confirmed by XRD (JCPDS #40-1296) and selected area electron diffraction (SAED), consistent with previous experimental results.^[38] As the amount of reducing agent $N_2H_4 \cdot H_2O$ ($[N_2H_5]^+ \cdot OH^-$) is steadily increased, the product is gradually reduced, following the phase evolution $V_6O_{13} \rightarrow VO_2 \rightarrow V_6O_{11} \rightarrow V_2O_3$. With increasing temperature and pressure during the hydrothermal process, the lamellar structure tends to curl into one-dimensional V_6O_{13} tubular structures, some of which continue to grow into solid V_6O_{13} nanowires by lateral growth (Figure 2b). As VO_2 , V_6O_{11} and V_2O_3 do not have enough solubility to grow via Oswald

ripening mechanism that would allow mass transfer from smaller nanocrystals to larger ones, the VO₂ nanobeams were formed with relative low aspect ratios (Figure 2c and 1d), and the V₆O₁₁/V₂O₃ nanopowders with the lowest solubility were obtained from the collapse of nanowires/nanobeams. To summarize, starting from a layered V₂O₅-H₂O₂ gel, nanostructured vanadium oxide can transform into one-dimensional nanotubes/nanowires/nanobeams through rolling and finally collapsing into nanoparticles, through the phase evolution V₂O₅ → V₆O₁₃ → VO₂ → V₆O₁₁ → V₂O₃ (Figure 2c).

Figure 3a and 3b show high resolution X-ray photoelectron spectroscopy (XPS) V 2p and W 4f scans of the W-doped VO₂ product, respectively. The binding energy for V 2p_{3/2} was located at 516.3 eV, indicating a V⁴⁺ valence state and confirming the phase purity of the VO₂. According to a calculation based on the V 2p and W 4f peaks, the W⁶⁺ doping level is measured to be 2.45 at.%. Energy dispersive X-ray secondary electron microscopy (EDX-SEM) analysis of the W-doped VO₂ nanobeams, shown in Figure 3d, indicates a doping level of ~2 at.% W, consistent with the value expected from the precursor solution and similar to the value of 2.45 at.% obtained using XPS. Figure 3c shows a differential scanning calorimeter (DSC) curve recorded from the 2 at.% W-doped VO₂ product upon heating and cooling in the temperature range 5-60 °C under N₂ flow. The endothermic and exothermic peaks upon heating and cooling indicate a latent heat of $\Delta H=15.14/18.97$ J/g, compared to the commercial product with $\Delta H=38.7/41.87$ J/g,^[35] resulting from a lattice distortion arising from the W⁶⁺ doping, since the energy barrier for the phase transition is closely related to the stability of the structure. As observed in the DSC curve, the phase transition temperature during heating and cooling is $\tau_{c,h}=23.1$ °C and $\tau_{c,c}=14.9$ °C, respectively, giving a τ_c of 19 °C, consistent with the τ_c reducing rate of W⁶⁺ (20-28 °C/at.%) for a doping level of 2.45 at.%. The W doping level can be controlled by the doping source H₂WO₄, and the τ_c for 1/1.5 at.% W doped VO₂ is 42.5/34.4 °C (Figure S2, see supporting information).

Figure 4a shows an SAED pattern recorded from a single VO₂ nanobeam. Two sets of diffraction spots are identified as the VO₂(R) and VO₂(M) phases and are indicated using black and red indices. A corresponding bright-field transmission electron microscope (BF-TEM) image in Figure 4b shows that the growth direction of the nanobeam is along the [001] direction. Corresponding dark-field (DF) TEM images along the (001) and (010) directions are shown in Figure 4c and d, respectively. Brighter layers with widths of a few nanometers, which are visible in Figure 4c, are attributed to slight misorientation of the (020) planes in the lateral direction. Interestingly, the DF-TEM image in the (010) direction has a smaller outer contour compared to the BF and DF (100) TEM images, suggesting that the (010) planes are not diffracting strongly, for a similar reason to the misorientation observed in the DF (100) TEM image. SAED patterns did not change when the electron beam was moved along each nanobeam, revealing their invariant crystalline nature. Figure 5 shows high-angle annular DF scanning TEM (HAADF STEM) and EDX STEM maps of VO₂ nanobeams. Figure 5a shows a low magnification HAADF STEM image of several VO₂ nanobeams, in which whiter areas correspond to the superposition of more than one nanobeam. The image confirms that the nanobeams have widths of ~100 nm and lengths below ~800 nm, in accordance with the SEM results. A high resolution HAADF STEM image shown in Figure 5b gives an indication of the replacement of V by W atoms in the VO₂ lattice, as marked by arrows, indicating efficient doping by W⁶⁺, where the W atoms with larger atomic number are brighter than the V atoms, arising from their different contributions to the elastic scattering signals collected by the detector. Moreover, as shown in the EDX STEM maps (Figure 5d-e), the W atoms are dispersed uniformly in the nanobeam.

2.1. Optical Properties

Temperature-dependent UV-Vis-NIR spectra were recorded in the temperature range 10 - 40 °C and plotted in the form %T (transmission) vs λ , as shown in Figure 6a. As reported in the literature,^[39] plasmonic metal nanobeams can exhibit two SPR peaks due to polarization

along their transverse and longitudinal axes. When the VO₂ nanobeams were heated from 20 to 40 °C, a pair of extinction peaks at 619 nm and 1344 nm was observed and attributed to transverse ($\lambda_{\text{SPR,T}}=619$ nm) and longitudinal ($\lambda_{\text{SPR,L}}=1344$ nm) SPR bands of metallic VO₂ above 20 °C, which is quite different from the single SPR peak around 600 nm for VO₂ nanoparticle patterns.^[40] As the short-wavelength incidence in the NIR region carries more energy, the expanded %T contrast in this region arising from the SPR should contribute largely to the enlargement of ΔT_{sol} , which has also been proved in the VO₂@SiO₂ nanostructures.^[41] Owing to the wide length distribution of the nanobeams, the full width at half maximum (FWHM) of the longitudinal SPR band at 1344 nm is 567.9 nm, which is much wider than that of the transverse SPR band at 619 nm (FWHM= 278.3 nm) (Figure 6b). To the best of our knowledge, this is the first report of temperature-dependent dual SPR peaks in VO₂ nanostructures. This dual SPR peaks could offer the tunability of the transmission contrast at different wavelength, which could be explored for other applications.^[12b-12d] The largely depressed SPR intensity (4.0 % to 2.8 % and 2.7 % to 1.3 % for transverse and longitudinal SPR, respectively) from 40 to 20 °C suggests a progressive transition from the metallic phase to the semiconducting phase, with a τ_c of 19 °C. Upon further cooling, the SPR disappeared at 15 °C, indicating the completion of the MIT. By reducing the W doping level from 2 at.% to 1.5/1.0 at.%, the morphology was changed from nanobeams to the mixture of nanobeams and nanoparticles (Figure S1), and the positions of the SPR peaks were blue shifted from 1344/619 nm to 1290/530 nm (Figure S3, see supporting information), mainly owing to the decrease of aspect ratio. As shown in Figure 6c, the IR transmittance contrast ($\%T_{\tau=10\text{ °C}}-\%T_{\tau>10\text{ °C}}$) at a wavelength of 2500 nm first increased rapidly upon heating below 20 °C and then reached a stable value above 30 °C, which also indicated an MIT transition at a relatively low temperature. The %T hysteresis loop at 2500 nm was measured in the temperature range 10 to 40 °C. As shown in Figure 6d, transition on heating/cooling gradually proceeds in the range from 15 to 30 °C/30 to 10 °C, with maximal change happening around

22/15 °C. The best-fitting result to the heating and cooling %T data gives $\tau_{c,h}=21.6$ °C, $\tau_{c,c}=14.4$ °C and $\tau_c=(\tau_{c,h}+\tau_{c,c})/2=18$ °C, similar to the DSC result. The MIT sharpness (~ 2.0) is comparable to the reported results. The τ_c reduction of the W doped VO₂ should be ascribed to the generated free electron carriers^[4] as well as the extra strains resulted from the atom replacement of V⁴⁺ by W⁶⁺.^[42]

Figure 7a shows the temperature-dependent T_{lum} and ΔT_{sol} for the VO₂ nanobeams. On cooling from 40 to 13 °C, T_{lum} shows a slight change from 26.3% to 27.8%, while ΔT_{sol} increases steadily from 2.1% to a peak value of 5.0% at 15 °C, before dropping to 4.0% at 13 °C. The sharp decrease in ΔT_{sol} above 15 °C is ascribed to the obvious %T bump at around 800 nm, since a sharp increase in %T in the metallic state can reduce the ΔT_{sol} value seriously. ΔT_{IR} also exhibits a peak value (6.8%) at 15 °C, as shown in Figure 7b, which can also be attributed to the %T bump in the metallic state arising from the two SPR peaks from the VO₂ nanobeams. However, the thermochromic properties ($T_{lum}=26.0\%$, $\Delta T_{sol}=5.0\%$) of the thin film composed of beams cannot reach the highest value ($T_{lum}=56.0\%$, $\Delta T_{sol}=8.7\%$) as reported for the W-doped VO₂ nanoparticles.^[11b] It is of interest that after adding additional 30 μ L NH₃·H₂O (30 wt.%) into the precursor, the hydrothermal product could be transformed from VO₂ nanobeams to VO₂ nanoparticles (average grain size ~ 30 nm), and the latter exhibited better performance with $T_{lum}=31.2\%$, $\Delta T_{sol}=6.4\%$ (Figure S8), which is still lower than the best result, mainly due to the larger grain size (30 v.s. 18.9 nm).

2.2. Electrical Properties

As described above, the W doped VO₂ has the room temperature τ_c , which motivates us to fabricate Mott field-effect transistors (FETs) to induce the phase transition by applying a gate voltage. Figure 8a shows the temperature-dependent electrical resistance of the film composed of W-doped VO₂ nanobeams. The low phase transition temperature of ~ 19 °C can be seen from the hysteresis loop of the resistance, which is consistent with the optical and DSC measurements. It is similar to reports of pure VO₂ nanobeams in the literature,^[43] which

exhibit a large resistance reduction (>3 orders of magnitude) across the phase transition that is much sharper than that of the W-doped VO_2 nanobeams (by ~ 2 orders of magnitude). This large difference is due to the single crystalline nature of the as-fabricated nanobeams. The inset in Figure 8d shows the FET device geometry used in this study, in which the VO_2 nanobeams were dispersed in ethanol and coated onto a Si substrate with an ~ 120 nm SiO_2 layer on top. Figures 8b-d show the field emission properties of the devices fabricated with a channel of W-doped VO_2 nanobeams. Under a gate voltage of 2V and below 11 $^\circ\text{C}$, the drain current increases slowly with drain voltage (Figure 8b). When combined with the I *v.s.* V_G curves (Figure 8c), this result indicates that the drain current increases sharply above 12 $^\circ\text{C}$. Moreover, the temperature-dependent drain current for $V_D=1\text{V}$ and $V_G=2\text{V}$ increases sharply for temperatures above 12 $^\circ\text{C}$ (Fig. 8d), indicating the MIT at this temperature. The decrease of drain current with increasing the gate bias above 12 $^\circ\text{C}$ should be due to the gate-source leakage, arising from the transition from insulator to metal of the nanobeams. No leakage current through the dielectric SiO_2 layer can be found in the test. For these FET measurements, τ_c is measured to be ~ 12 $^\circ\text{C}$. Since the measurement was performed at the near ambient temperature, the extra strain from the thermal mismatch between the nanobeams and the substrate should be neglected. The reduction of τ_c from 19 to 12 $^\circ\text{C}$ should be mainly ascribed to the applied electric field. Therefore, the FET device fabricated with a channel of W-doped VO_2 nanobeams shows the advantages of a large magnitude resistance reduction, as well as a lower electrically-measured value of τ_c .

3. Conclusion

In summary, nanostructured W-doped vanadium oxide materials have been synthesized using a hydrothermal approach from a layered $\text{V}_2\text{O}_5\text{-H}_2\text{O}_2$ gel. By tuning the addition of $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$, the evolution of phase and morphology from V_6O_{13} (nanotubes/nanowires) to VO_2 (nanobeams) to V_6O_{11} (nanopowders) to V_2O_3 (nanopowders) during the hydrothermal process could be observed. A rolling mechanism is proposed to explain the synthesis of such

nanotube/nanowire/nanobeam structures from two-dimensional precursors, as confirmed by TEM images. W doping is found to be critical for the formation of the VO₂(R) phase, since only the intermediate VO₂(A) could be obtained under the same synthesis conditions without doping, suggesting a reduction in phase formation energy barrier with doping. Uniform single-crystalline VO₂ nanobeams showed a pair of SPR peaks in the metallic state arising from polarization along the transverse and longitudinal axes. The single-crystalline W-doped VO₂ nanobeams exhibit an increase in electrical conductivity across τ_c by 3-4 orders of magnitude, i.e., 1-2 orders of magnitude higher than usually reported. The low-temperature synthesis of uniform single crystalline VO₂ nanobeams should facilitate their room temperature applications in a variety of areas of research, such as thermochromic windows, FET devices and smart sensors.

4. Experimental Section

All of the chemicals V₂O₅ (99.6%, Alfa Aesar), H₂WO₄ (99.9%, Alfa Aesar), N₂H₄·H₂O (99.9%, Alfa Aesar) and H₂O₂ (30 wt.%, Sigma-Aldrich) were used as received without any further purification.

Hydrothermal synthesis of vanadium oxide materials: V₂O₅ (182 mg) and H₂WO₄ (10 mg) powder were added to H₂O₂ (5 mL, 30 wt.%) preheated at 90 °C with stirring. After vigorous evaporation, a dark brown W-doped V₂O₅-H₂O₂ precursor sol was obtained, followed by the addition of deionized (DI) water (15 mL). The sol was reduced by N₂H₄·H₂O (25/30/35/50/100 μ L) and then quickly sealed in a 100 mL-Teflon-lined autoclave. The hydrothermal reaction was performed at 260 °C for 24 hours in an oven. After cooling in air, the products were collected and washed with copious amounts of DI water and acetone several times by centrifuging (10000 rpm). Ultimately, the products were dried in vacuum at 50 °C for 12 hours.

Characterization: The phase of the products was characterized with a Shimadzu XRD-6000 X-ray diffractometer (Cu-K α , λ = 0.15406 nm) using a voltage of 40 kV and a current of 30

mA at an X-ray grazing angle of 1.0° . Their morphology was determined using a field emission scanning electron microscope (FESEM, JSM-7600F, JEOL, Japan) at an accelerating voltage of 5 kV. For conventional transmission electron microscopy (TEM) studies, i.e., using selected area electron diffraction (SAED), bright field (BF) and dark field (DF) imaging, an FEI Tecnai G2 (FEI Company, Eindhoven, The Netherlands) microscope was used at an accelerating voltage of 200 kV. For high-resolution (HR) high angle annular dark field (HAADF) scanning (S-)TEM and energy-dispersive X-ray (EDX) studies, a probe-aberration-corrected FEI Titan microscope (FEI Company, Eindhoven, The Netherlands) was used at an accelerating voltage of 200 kV. This microscope is equipped with a four quadrant EDX detector and the aberration coefficients of the probe forming system are corrected to fourth order. The elemental chemical states of the samples were measured using X-ray photoelectron spectroscopy (XPS, Kratos Axis Ultra, UK). An Al $K\alpha$ (1486.6 eV) monochromatic X-ray source was used with an emission current of 10 mA and an anode HT of 15 kV. C 1s (284.5 eV) was used for spectrum calibration. DSC data were collected using a differential scanning calorimeter (DSC Q10, TA Instruments, USA) in the temperature range 5-60 $^\circ\text{C}$ under a N_2 atmosphere. Transmittance spectra in the range 250-2500 nm were measured using a UV-Vis-NIR spectrophotometer (Cary 5000, Agilent Ltd, USA) equipped with a Linkam PE120 system Peltier heating & cooling stage. The integrated visible transmittance (T_{lum} , 380-780 nm) and solar/IR transmittance (T_{sol} , 280-2500 nm; T_{IR} , 780-2500 nm) were calculated based on the recorded %T spectra using the expression

$$T_{\text{lum/sol/IR}} = \frac{\int \phi_{\text{lum/sol/IR}}(\lambda) T(\lambda) d\lambda}{\int \phi_{\text{lum/sol/IR}}(\lambda) d\lambda} \quad (1)$$

where $T(\lambda)$ is the recorded film transmittance, ϕ_{lum} is the standard luminous efficiency function for the photopic vision of human eyes^[44] and $\phi_{\text{sol/IR}}$ is the solar/IR irradiance spectrum for air mass 1.5 (corresponding to the sun standing 37° above the horizon).^[45] The hysteresis loop of %T at a wavelength of 2500 nm was measured at temperatures ranging

from 10 to 40 °C. In order to attain the phase transition temperature τ_0 , the temperature-dependent heating and cooling %T(τ) data were fitted using a sigmoidal function of the form:

$$\%T(\tau) = A2 + (A1 - A2) / [1 + \exp(\tau - \tau_c) / B] \quad (2)$$

where τ is the temperature in °C and A1, A2, τ_c and B are fitting parameters. Two phase transition temperatures $\tau_{c,h}$ and $\tau_{c,c}$ were obtained in the heating and cooling cycles, respectively and the average phase transition temperature was defined as $\tau_c = (\tau_{c,h} + \tau_{c,c}) / 2$, $\Delta \tau_c = \tau_{c,h} - \tau_{c,c}$.^[46] The integrated transmittance variation $\Delta T_{lum/sol/IR}$ compared to the transmission at 10 °C is given by the expression $\Delta T_{lum/sol/IR} = T_{lum/sol/IR}(10\text{ °C}) - T_{lum/sol/IR}(\tau)$.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Figure 1. (a) XRD patterns of W-doped vanadium oxide for different amounts of $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ and corresponding field emission SEM images. The $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ additions are: b, 25 μL ; c, 30 μL ; d, 35 μL ; e, 50 μL ; f, 100 μL . In (b) and (c), the nanowires are V_6O_{13} , and the nanobeams are VO_2 . The scale bars are 500 nm in b-f.

Figure 2. a) Bright-field TEM image of a layered $V_2O_5-H_2O_2$ precursor, with SAED and XRD patterns inset. b) Bright-field TEM image of a V_6O_{13} tube and wires, with SAED patterns inset. c) Schematic diagram describing the formation of vanadium oxide nanostructures by a rolling mechanism.

Figure 3. High resolution XPS scan of (a) O1s and V2p and (b) V3p and W4f. (c) DSC curve for the 2.45at.% W doped VO₂ nanobeams. (d) EDX spectrum recorded from a W-doped VO₂(R) nanobeam.

Figure 4. (a) SAED pattern recorded from a single nanobeam. The indices in black and red correspond to the $\text{VO}_2(\text{R})$ and $\text{VO}_2(\text{M})$ phases, respectively. (b) BF TEM and (c-d) DF TEM images of the nanobeam considered in (a). The DF TEM images are recorded along (c) (001) and (d) (010). The outer contour of the DF (001) TEM image is reproduced using dashed lines in (d). The dashed circles in (a) indicate the positions of the objective aperture used to record images (c-d). The scale bars for the DF TEM images are given in (b).

Figure 5. (a) Low magnification HAADF STEM image of an ensemble of VO₂ nanobeams. (b) High resolution HAADF STEM image of a selected area on the edge of a nanobeam. Black arrows indicate atomic columns with higher contrast. (c-e) Simultaneously recorded (c) HAADF STEM and (d, e) EDX maps of (d) V, (e) W and (f) O.

Figure 6. (a) UV-Vis-NIR spectra recorded in the temperature range 10 to 40 °C. (b) SPR peaks of the %T spectra at 20 °C (blue line), with Gauss fitting (black and red lines) and base line subtract. (c) %T contrast ($\%T_{\tau=10^\circ\text{C}} - \%T_{\tau>10^\circ\text{C}}$) at 2500 nm. (d) Temperature-dependent %T hysteresis loop recorded at a wavelength of 2500 nm. The solid line represents a best-fitting result.

Figure 7 (a) Thermochromic properties and (b) IR modulating ability for a thin film deposited on a glass substrate with 2 at.% W-doped VO₂ nanobeams under temperatures from 13 to 40 °C. $\Delta T_{\text{sol/IR}}$ was calculated from $\Delta T_{\text{sol/IR}}(T) = T_{\text{sol/IR}}(10\text{ °C}) - T_{\text{sol/IR}}(T)$.

Figure 8. (a) Hysteresis loop of the temperature-dependent resistance of W-doped VO₂ nanobeams. (b) Temperature-dependent I/V curve measured at a gate voltage of 2 V. (c) Temperature-dependent I/V_G curve measured at a drain voltage of 1 V. (d) Temperature-dependent drain current measured at a gate voltage of 2 V and a drain voltage of 1 V.

Single-crystalline W-doped VO₂ nanobeams with highly reversible electrical and
plasmonic responses near room temperature

Hydrothermal synthesis; Vanadium dioxide; Metal to insulator transition; Nanobeams;

Surface Plasmon Resonance

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Long*

Single-crystalline W-doped VO₂ nanobeams obtained *via* rolling from a 2D precursor,
exhibiting uniform W doping, a low transition temperature and dual SPR peaks.