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Electronic Supplementary Information

Infra-Red Modulation via Near Room-Temperature Phase Transitions of Vanadium Oxides & Core-Shell Composites

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Materials, Methods, Experimental Section, and Materials Characterization

<u>Materials</u>

Oxalic acid dihydrate (C₂H₂O₄.2H₂O) (ACS reagent) and \geq 99% and Vanadium(V) oxide (V₂O₅) (\geq 99.6% trace metals basis) were purchased from Sigma-Aldrich through Merck Australia.

Methods

Synthesis of crystalline VO₂ and VO_x hydrate nanoparticles

VO_x nanoparticles are synthesized using a benchtop wet chemical process based on the reduction of V₂O₅ powder in ambient pressure. V₂O₅ is reduced using oxalic acid dihydrate $(C_2H_2O_4.2H_2O)$ in a water solution. The reagents are heated on a hotplate set to 240 °C and stirred vigorously at 450 rpm, in a reflux reaction for 48 hours. While in this reflux reaction water will evaporate at approximate 100 °C, the surface of the V_2O_5 particles will reach slightly above this temperature due to their insolubility in water, leading to reactive sites for VO_{x} . nH_2O formation. As the water is the solvent, the reflux reaction offers a constant temperature environment of ~100 °C (near the local boiling point of water) without the need to conventional hydrothermal autoclave reactions used in VO_x nanoparticles synthesis as well as hyper hydration of synthesized metal oxides. The products are then washed and centrifuged before evaporating the excess water. A subsequent annealing step is needed to achieve VO_x powders with different levels of oxygen vacancies. Annealing is carried out in ambient air in in partial air at 550 °C for 90 minutes produces a mix phase of vanadium oxide hydrates, while, annealing in an evacuated environment further dehydrates the nanoparticles to produce VO₂ nanoparticles. This dehydration introduces intrinsic strain to VO₂, which we expect to lower IMT temperatures.

Figure S1. demonstrates the vacuum and high pressure-free synthesis used in this work to produce crystalline VO_x nanoparticles with different oxygen vacancies and hydration levels.

Silica-coating VO_x crystals

Part of the mechanism in controlling the critical temperature of insulator-to-metal transition (IMT) in vanadium oxides is imposed internal strain on the lattice structure of VO_x.¹ Consequently, we use silica spheres as a source of external strain to drive IMT in VO_x to lower critical temperatures. Here, VO_{2-x} and *VO_x.nH₂O* are used as seeds and anchors for the hydrolysis process require to form silica shells. VO_{2-x} and *VO_x.nH₂O* are added to ethanol/water mixture with a ratio of 90:10 (V/V) to achieve a final solution of 10 g/L. Once the seeds are dispersed, tetraethylorthosilicate (TEOS) (98%, 1 mL per 1 g seeds) was added swiftly via syringe and mixed into the solution with gentle agitation. Once the TEOS is mixed in, ammonia (25 wt% in water, 2 mL per 1 g seeds) was poured in and mixed into the solution with gentle agitation. The solution was left unstirred overnight at room temperature for the silica coating to proceed. Additional TEOS is at regular intervals of 30 minutes to form thicker silica shells. Once the silica growth is complete, the sample is washed via centrifugation several times with water to remove excess TEOS and ammonia.

Experimental section

X-ray photoelectron spectroscopy (XPS)

The XPS measurements were performed using a Kratos AXIS SUPRA PLUS instrument with a monochromatic Al K α x-ray source (hv = 1486.6 eV) operated at 10 mA emission current and 12 kV anode potential. The electron collection spot size was ~700 × 300 µm2. A pass energy of 160 eV was used for the survey scans and 20 eV for the high-resolution scans.

X-ray diffraction (XRD)

The XRD measurements were performed using a Bruker D8 Advance Powder Diffractometer with a zero-background sample holder using the copper (Cu) X-ray source.

In-situ Raman spectra

Raman spectroscopy was performed using a Raman InVia Spectrophotometer (Renishaw) equipped with a Renishaw Centrus 1C4A75 detector. The samples were mounted into a Linkam heating/cooling stage set to heat at 2°C min⁻¹ to 80°C and cool at 2°C min⁻¹ back to room temperature. During this heating/cooling ramp cycle, Raman spectra were obtained using 50x objective, a 532 nm laser with a 5 s x 6 exposure time at 1% power, and an 1800 lines mm⁻¹ grating. One spectrum was recorded every minute corresponding to a spectrum every 2°C. Data was collected using the WiRE 5.3 software.

VO_{x-2} and VO_x.nH₂O planner channel fabrication

Planar channel devices investigated here were fabricated on Si using conventional photolithography, electron-beam metal deposition (~10 nm Cr/ ~100 nm Au) and lift-off. The two-terminal here has a channel length of ~1 mm and width of ~5 μ m. VO_{x-2} and VO_x.nH₂O are dispersed isopropyl alcohol (IPA) and 2-butanol mixture similar to inks developed by by Hu *et al.* which is characterized to be a universal recipe for nanoparticle suspensions.² and drop cast between the two terminal devices to achieve a thickness of ~200 nm.

Transmission electron microscopy (TEM) and energy dispersive X-ray (EDX)

The TEM images and the EDX elemental mapping were taken using a FEI Tecnai F20 microscope at 200 kV High voltage (Ian Holmes Imaging Center, Bio21). The TEM samples were prepared by dropping 6 μ L of sample dispersion on TEM grids (300 mesh copper grid).

Fourier-transform infrared spectroscopy (FTIR)

IR transmittance spectroscopy is carried out using a FTIR spectrometer (Frontier, Perkin Elmer) equipped with deuterated triglycine sulfate detector. The samples are mounted on a temperature controlled environmental chamber (Linkam Scientific Instruments) with an aperture of 2 mm in diameter. During the heating and cooling experiments, transmittance spectra are measured at a spectral resolution of 4 cm⁻¹, in steps of 10° C until a maximum of 100 °C of the stage temperature. A separate calibration experiment is carried out to corelate the stage temperature to the sample temperature. Transmittance spectra are normalized to a reference undoped silicon substrate, identical to the ones that the materials are drop cast upon. The lower and upper wavelength limit of the measured spectra are determined by the limitations of the black body IR source and the glass window on the environmental chamber, respectively.

Longwave infrared imaging

Vanadium oxide particles are drop-cast onto double-side polished, undoped silicon wafer chips. These chips along with a reference chip without any particles, are attached to the edges of a glass microscope slide and mounted 5 cm above a silicon wafer on a hotplate. The silicon wafer is used as a hot object and imaged using a FLIR Lepton camera module, in a temperature linear mode. The temperature of the hotplate is increased from 50 ° to 300 °C in steps of 50 °C. The perceived temperature of the object through the synthesized vanadium oxide particles are compared, to assess their thermal camouflage capabilities in the longwave infrared region. <u>Material characterization</u>

X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and Raman spectra

XPS is used here to both study the oxidation state of as synthesized VO_x nanoparticles and the silica coated VO_x nanoparticles. **Figure S2**a, b and c show the survey spectra VO_x nanoparticles as well as silica coated VO_x nanoparticles with expected V2p, O1s, Si2p, OKLL peaks. Figure

S2c shows as synthesized VO_x shows core-shell peaks for O1*s* at ~529, 531.2, and 533 eV and $V2p_{3/2}$ at ~516.1 and 517.7 eV. The O1*s* can be deconvoluted into three components with contributions from –O, –OH, and H₂O. These three components are present in many vanadium oxide and other metal oxides hydrates.³⁻⁶ The presence of H₂O and dominance of V–OH and H₂O–OH indicate that the nanoparticles synthesized here are $VO_x.nH_2O$. This is a product of reducing V₂O₅ powder in a well hydrated reflux environment followed by annealing in air. V2p_{3/2} peaks are attributed to V⁴⁺ and V⁵⁺ respectively, which are a property of crystalline vanadium oxides.^{7, 8} The slight shift in V⁴⁺ and V⁵⁺ values to higher binding energy is a common property of vanadium oxide hydrates and is due to the layered nature of those hydrates.^{3, 4} Figure S2d and e show the O1*s* at and V2*p*_{3/2} core-shell peaks, however they are dominated by the ~532 eV peak characteristic to SiO₂. Although O1*s* andV2*p*_{3/2} relevant to VO_x nanoparticles are present they are not resolved because the dominant SiO₂ peak limits the possibility to further extrapolate on vanadium oxidation states with great accuracy. Figure S2f and g show the Si2*p* peak centered at ~104 eV in agreement with works in literature.⁹⁻¹¹

Figure S3a, b and c show VO_{2-x} nanoparticles as well as silica coated VO_{2-x} nanoparticles with expected V2*p*, O1*s*, Si2*p*, and OKLL peaks similar to $VO_x.nH_2O$. Figure 3c shows as synthesized VO₂ shows core-shell peaks for O1*s* at ~530 and 531.2 eV and V2*p*_{3/2} at ~515.8 and 517.1 eV. V2*p*_{3/2} peaks are attributed to V⁴⁺ and V⁵⁺ respectively which are a property of crystalline vanadium dioxide.^{7, 8} The additional peak in the O1*s* region at ~ 531.2 eV is attributed to the – OH contribution in the bulk of the nanoparticles synthesized.¹² We note here the absence of the H₂O and the substantial H₂O–OH the peaks present in the *VO_x.nH₂O* nanoparticles. Annealing reduced VO_x powder in low oxygen environment is utilized to both provide preferential crystallization of VO_{2-x} as well as drive water molecules from the layered VO_{2-x} structure. The

notable V⁵⁺ satellite peak is due rapid oxidation of vanadium oxides and is commonly present in untreated surfaces of the vanadium oxides.¹³ The intensity of the V⁵⁺ satellite peak is dependent on a rage of factors such as substrates, the length of time the surface of the nanoparticle's is exposed to an air environment, and artificial oxidation that occurs due to X-ray source during XPS measurements. Resembling $VO_{x.nH2O}$ nanoparticles figure S3d and e show the O1s at and V2p_{3/2} core-shell peaks with a dominant SiO₂. Figure S3f and g show the Si2p peak as expected indicating the success and consistency of the silica formation process. Concurrently, V2p_{3/2} relevant to VO₂ are present but not resolved.

Figure 4Sa show *in-situ* Raman spectra of both the VO_{2-x} nanoparticles and the *VO_x.nH₂O*. Here, we study the phase changes in Raman spectra with temperature. The temperature study of phase change for both particles will be used confirm the impact and dominance of VO_{2-x} monoclinic grains and their transformation to rutile grains. Figure 4Sc shows Raman peaks at 140, 195 (A_g), 225 (A_g), 264 (B_g), 306 (A_g), 337 (B_g), 395 (A_g), 439 (B_g), 489 (B_g), and 615 (A_g) cm⁻¹ which are characteristic of monoclinic VO₂¹⁴⁻¹⁶. Figure 4Sb shows Raman peaks for VO_x hydrate with peaks at 144, 195 (A_g), 284 (B_g), 304 (A_g), 403 (A_g), 482 (B_g), 529 (A_g), 701, 995 cm⁻¹. 144, 195, 304, 403, 482, 529, and 701 peaks are VO₂(M) peaks while 284 and 995 are V₂O₅ peaks.¹⁷

X-ray diffraction diffractograms have been reported to show both the crystallinity and the evolutions of phase transitions in vanadium oxides. The insulator-to-metal transition (IMT) process is a structural change in the type of crystal and is observed through changes in the monoclinic (M) peaks of vanadium dioxide.¹⁸ Any notable strain exhibited by the silica coated will predominantly affect the location and intensity of VO₂ (M) since those peaks are more sensitive to external stimuli that alter the IMT temperatures of vanadium oxides such.^{19, 20} **Figure S4**c and d show the XRD diffractograms of both VO_{2-x}, *VO_x.nH₂O*, and their silica coated

nanoparticles. Figure S4a shows a VO₂ (M) phase consistent with (VO₂(M): JCPDS, No. 72-514) and existing literature.^{21, 22} The silica shells formations around the VO₂ in figure S4c exhibit a shift in the (011) peak by ~ 0.25° across both silica shells in this work. This shift will differentiate the silica coated nanoparticles and increase their sensitivity to stimuli as well as the rapidness of crystal transformation and recovery since the crystal structure will experience simultaneous sources for changes in their crystal structures.

Figure S4d show mixed phases of V₂O₅ (V₂O₅: JCPDS, No. 00-041-1426), VO_{2.*n*H₂O (VO_{2.*n*H₂O: JCPDS, No. 18-1445), and VO₂ (M). Mixed phases are inherent in metal oxide hydrates and this highlights nature of the nanoparticles synthesized in an air environment. The impact of the silica shell strain is seen in the shift of the VO₂ (M) (011) peak by \sim 2°. This shift is more prominently that the shift in silica coated pristine VO_{2-x} The intermixed nature of VO_{2-x}, V₂O₅ and VO_{2.*n*H₂O provide much larger crystals structure making shifts along the [011] plane more dramatic.}}}

Transmission electron microscopy (TEM), energy dispersive X-ray (EDX), and scanning electron microscopy (SEM)

The electronic structure of VO_{2-x}, *VO_x.nH*₂*O*, and silica coated nanoparticles were analysed using high resolution transmission electron microscopy (HRTEM), selected area electron diffraction (SAED) and energy dispersive X-ray (EDX). HRTEM and SAED patterns were analysed and interpreted utilizing CrystTBox software. **Figure S5**a-f show HRTEM images of the nanoparticles studied in this work. The calculated lattice spacing of the *VO_x.nH*₂*O* and VO_{2-x} nanoparticles is ~3.2 Å and ~2.7 Å, respectively. This is in agreement with monoclinic VO_{2-x} literature reports.²³ Silica coated VO_{2-x} nanoparticles show a reduction in D-spacing with increasing amount of TEOS added and by extension the thickness of the silica shell with the calculated spacing further reducing to ~ 1.8 Å. Similar patterns are observed to a lesser extent in silica coated $VO_x.nH_2O$. This is due to the presence of water molecules that both limit the impact of extrinsic strain on the lattice structure and drive thicker silica shells formation. This is seen in the failure to observe a SAED for silica coated VO_x.nH₂O in figure S5d and f. Moreover, HRTEM show the shape and size of the VO_{2-x}, VO_{x.nH2O}, and their silica coated core-shell structures. VO_{2-x} nanoparticles in Figure S5a are overlapping spheres caused by the conglomeration of nanoparticles in their suspension. The silica coated VO_{2-x} nanoparticles show both the formation of spherical silica shells with thicknesses of ~ 27 nm and ~ 37 nm when using 1% and 1.6% TEOS, respectively. On the other hand, $VO_x \cdot nH_2O$ in Figure S5d show a nanobeam shaped nanoparticles while the silica coated core structures show spherical silica formation with with thicknesses of ~86 nm and ~131 nm when using 1% and 1.6% TEOS, respectively. Although those thicknesses do not represent the thicknesses of all core-shell structures here, they reflect a general trend that is supported by subsequent characterisation and nanoparticles behaviour. Here, the spherical silica formation is expected since the Stöber process conventionally producing silica spheres around seed particles ^{24, 25}. We also note the presence of more silica shells when using VO_x.nH₂O, which is due the further utilisation of TEOS cause by more water molecules during the hydrolysis reaction during the Stöber process. To further understand the particle shape and size scanning electron microscopy (SEM) is used. Figure S6 shows the overall morphology of films fabricated using our nanoparticles. Although the shape observed in TEM cannot be observed here, we note that the nanoparticles are assembled to form consistent films. Figure S6a-c show VO_{2-x} films and their silica coated variation without much distinction between the films due the silica shells being thin that it does not have much impact on the morphology of the nanoparticles. The impact of silica shells is seen

more clearly in between $VO_{x.nH_2O}$ and its silica coated variations in Figure S6d-f. The thicker silica shell formed when using the hydrate as seed particles show a more ceramic-like surface.

Figure S1.



Figure S1. Synthesis of crystalline VO_{2-x} and VO_x.nH₂O nanoparticles. Note that the

temperatures quoted refer to the set temperature of the hotplate and not the solution. The solution will remain at the boiling point of the solvent-solute mixture at ~ 100 $^{\circ}$ C.





Figure S2. Survey Spectra for (a) $VO_{x.}nH_2O$, (b) Silica coated $VO_{x.}nH_2O$ nanoparticles using 1% TEOS, and (c) Silica coated $VO_{x.}nH_2O$ nanoparticles using 1.6% TEOS. XPS spectra of vanadium (V2p_{3/2}) and oxygen (O1s) for $VO_{x.}nH_2O$ nanoparticles (c) as synthesized shows peaks at ~529, 531.2, and 533 eV, which indicate the V–O, V–OH, H₂O–OH, and H₂O bonding respectively, and peaks at ~517.1 and 515.8 eV, which indicate vanadium in the V⁵⁺ and V⁴⁺ oxidation states, respectively. (d) Silica coated $VO_{x.}nH_2O$ nanoparticles using 1% TEOS and (e) Silica coated $VO_{x.}nH_2O$ nanoparticles using 1.6% TEOS show oxygen (O 1s)

at ~532 eV, which is attributed to dominant SiO₂ features of Silica shells. XPS spectra of silicon (Si2*p*) for (g)Silica coated $VO_{x.}nH_2O$ nanoparticles using 1% TEOS, and (h) Silica coated $VO_{x.}nH_2O$ nanoparticles using 1.6% TEOS show oxygen (O 1s) at ~104 eV.





Figure S3. Survey Spectra for (a) VO_{2-x} , (b) Silica coated VO_{2-x} nanoparticles using 1% TEOS, and (c) Silica coated VO_{2-x} nanoparticles using 1.6% TEOS.XPS spectra of vanadium ($V2p_{3/2}$) and oxygen (O1s) for VO_{2-x} nanoparticles (a) as synthesized shows peaks at ~530 and 531.2 eV, which indicate the V–O and V–OH bonding respectively, and peaks at ~517.1 and 515.8 eV, which indicate vanadium in the V⁵⁺ and V⁴⁺ oxidation states, respectively. (b) Silica coated VO_{2-x} nanoparticles using 1% TEOS (c) Silica coated VO_{2-x} nanoparticles using 1.6% TEOS show oxygen (O 1s) at 532 eV, which is attributed to dominant SiO₂ features of

Silica shells. XPS spectra of silicon (Si2*p*) for (g)Silica coated VO_{2-x} nanoparticles using 1% TEOS, and (h) Silica coated VO_{2-x} nanoparticles using 1.6% TEOS show oxygen (O 1s) at ~103.5 eV.

Figure S4.



Figure S4. The in-situ Raman spectra at a range of temperatures from 20°C to 80°C of (a) VO_{2-x} nanoparticles; (b) $VO_{x.}nH_2O$ nanoparticles. X-ray diffractograms of (c) VO_{2-x} nanoparticles (black), Silica coated VO_{2-x} nanoparticles using 1% TEOS (cyan), Silica coated VO_{2-x} nanoparticles using 1.6% TEOS (light blue). (d) $VO_{x.}nH_2O$ (dark yellow), Silica coated $VO_{x.}nH_2O$ nanoparticles using 1% TEOS (cyan), and Silica coated $VO_{x.}nH_2O$ nanoparticles using 1.6% TEOS (light blue).







Figure S5. Transmission electron microscopy (TEM) images, selected area electron diffraction (SAED) patterns (inset), high-resolution transmission electron microscopy (HRTEM) image, and the Inverse Fast Fourier Transition (IFFT) of the HRTEM of (a) VO_{2-x} nanoparticles, (b) Silica coated VO_{2-x} nanoparticles using 1% TEOS, (c) Silica coated VO_{2-x} nanoparticles using 1.6% TEOS, (d) *VO_x.nH₂O*, (e) Silica coated *VO_x.nH₂O* nanoparticles using 1.6% TEOS.

Figure S6.



Figure S6. Scanning electron microscopy (SEM) images of (a) VO_{2-x} nanoparticles, (b) Silica coated VO_{2-x} nanoparticles using 1% TEOS, (c) Silica coated VO_{2-x} nanoparticles using 1.6% TEOS, (d) $VO_{x.}nH_2O$, (e) Silica coated $VO_{x.}nH_2O$ nanoparticles using 1% TEOS, and (f) Silica coated $VO_{x.}nH_2O$ nanoparticles using 1.6% TEOS.





Figure S7. Heating and cooling of vanadium oxide nanoparticles and the measured IR transmittance spectra between 25 °C and 75 °C for (a) VO_{2-x} nanoparticles, (b) Silica coated VO_{2-x} nanoparticles using 1% TEOS, and (c) Silica coated VO_{2-x} nanoparticles using 1.6% TEOS.

Figure S8.



Figure S8. *In-situ* IR transmittance spectra as a function of temperature and wavelength in (a) $VO_{x.}nH_2O$ nanoparticles, (b) Silica coated $VO_{x.}nH_2O$ nanoparticles using 1% TEOS, and (c) Silica coated $VO_{x.}nH_2O$ nanoparticles using 1.6% TEOS. Transmittance at λ = 4.5 µm upon heating and cooling, (d) $VO_{x.}nH_2O$ nanoparticles, (e) Silica coated $VO_{x.}nH_2O$ nanoparticles using 1% TEOS, and (f) Silica coated $VO_{x.}nH_2O$ nanoparticles using 1.6 % TEOS.





Figure S9. Heating and cooling of vanadium oxide nanoparticles and the measured IR transmittance spectra between 25 °C and 75 °C for (a) $VO_{x.n}H_2O$ nanoparticles, (b) Silica coated $VO_{x.n}H_2O$ nanoparticles using 1% TEOS, and (c) Silica coated $VO_{x.n}H_2O$ nanoparticles using 1.6% TEOS.

Table S1.

Nanoparticles	Peak position (2θ)	FWHM	Microstrain (<i>ɛ</i>)	Microstrain (µɛ)
VO ₂	28.05	0.2481	0.0043	4.3
1% VO ₂ :SiO ₂	27.83	0.3740	0.0066	6.6
1.6% VO ₂ :SiO ₂	27.83	0.4002	0.0070	7.0
VO _x .nH ₂ O	26.16	0.1324	0.0025	2.5
1% <i>VO_x.nH₂O</i> :SiO ₂	28.18	0.2408	0.0042	4.2
1.6% <i>VO_x.nH₂O</i> :SiO ₂	28.20	0.2369	0.0041	4.1

Table S1. Microstrain along the (011) access using Wilson's equation for lattice distortions.

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