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Development of VO₂ Nanoparticles Based Metal-Insulator Transition Electronic Ink

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The phase-change property, known as the metal-insulator transition (MIT), of vanadium dioxide (VO₂) materials has facilitated many exciting applications. Among the various crystal phases of VO₂, the monoclinic (M) phase is the only one that demonstrates low-temperature (~68 °C) MIT behavior. However, the synthesis of pure VO₂ (M) is challenging because various polymorphs, such as VO₂ (A), VO₂ (B) and VO₂ (D), are also typically formed during the process. Furthermore, to achieve the pure crystalline VO₂ (M) phase, very long reaction times, up to 2–4 days, are typically required. Finally, most of the VO₂ (M)-based films are realized through expensive and complex deposition techniques. In this work, we introduce an additional annealing step, post nanoparticle preparation, which not only reduces the complete synthesis time from days to only 6 h but also removes the impure phases and helps in achieving the desired pure VO₂ (M) phase. This work covers the complete synthesis and characterization details of as-prepared nanoparticles. The nanoparticles demonstrate a clear phase transition during the thermal analysis, with the endothermic peak at ~68 °C during heating and the exothermic peak at ~50 °C while cooling. Based on these VO₂ (M) nanoparticles, an ink has been formulated for the inkjet printing of films with controlled thicknesses. The inkjet-printed films have been investigated for their electrical conductivity with external stimuli such as temperature and electrical current. These printed films have

demonstrated electrical conductivity of ~ 1 S/m at room temperature (insulator state), which increases to 150–200 S/m through thermal or electrical stimuli (metal state). To demonstrate the application of the VO_2 ink, a fully printed antenna has been devised that can change its frequency based on the different states of the VO_2 film.

1. Introduction

The rapid development of modern technology requires smart electronic materials that can tune their properties on demand. Vanadium oxide is among these smart materials which can tune its electrical and optical properties by applying external stimuli, such as heat or pressure.^[1–3] Vanadium oxides usually possess several oxide phases, including VO , VO_2 , V_2O_3 , V_2O_5 , V_3O_7 , V_4O_9 and V_6O_{13} .^[4] Among these oxides, vanadium dioxide (VO_2) has received increased attention because it exhibits metal-insulator transition (MIT) in a reversible fashion at relatively lower temperature.^[5] In particular, VO_2 is an insulator at room temperature, but it undergoes a phase transition to a metallic state when heated to its phase-change temperature. In addition, VO_2 also possesses different polymorphisms, including VO_2 (A),^[6] VO_2 (B),^[7, 8] VO_2 (D),^[9] VO_2 (M),^[10] VO_2 (R)^[11] and VO_2 (P).^[12] Among them, the VO_2 monoclinic (M) phase is the most attractive due to its MIT behavior at a relatively low temperature of 68°C .^[13] However, the simultaneous creation of polymorphs results in a mixture phase and makes it extremely difficult to achieve a pure VO_2 (M) phase. The MIT temperature of VO_2 (M) can also be further reduced by doping^[14] and by varying the particle sizes.^[10, 12] This makes VO_2 a promising material for many practical applications, including sensors,^[15] thermochromic smart windows,^[16] field effect transistors,^[17] radio-frequency switches,^[18] terahertz nanoantennas,^[19] reconfigurable antennas,^[20] memory^[21] and energy^[22, 23].

Due to the exciting applications mentioned above, considerable effort has been devoted to producing VO_2 (M) in the form of a thin film, primarily with a dry vapor process using chemical vapor deposition,^[24] sputtering,^[25] metalorganic molecular beam epitaxy (MOMBE) deposition,^[26] pulsed laser deposition (PLD),^[27, 28] e-beam evaporation^[29] and by electric

field inducing ions migration.^[30] On the other hand, several bulk nanomaterials in solution processes with different shapes and sizes using sol-gel^[31] and hydrothermal synthesis^[32] are reported. The VO₂ thin-film deposition techniques using dry vapor processes require an ultra-high level of vacuum conditions (10⁻⁶ Torr) and sometimes very high processing temperatures (400–600 °C). The process also requires expensive masks and nanolithography for device prototyping. However, the solution-based VO₂ preparation processes are the simplest, require lower processing temperatures and are highly scalable. Among the solution-based processes, hydrothermal synthesis is the most widely adopted technique due to its high-quality and pure-phase VO₂ nanomaterial production.^[33] The only disadvantage of hydrothermal synthesis is the longer reaction time required, up to 2–4 days, to achieve pure VO₂ (M). For practical applications, VO₂ (M) nanostructures must be deposited in the form of films. Spin-coating is one technique to realize VO₂ films, but large-area processing and direct patterning are not possible.^[31] With the surge in inkjet printing, which is extremely low cost, completely digital and highly suitable for rapid prototyping or large-scale manufacturing, realizing VO₂ film through inkjet printing can be very beneficial. Thus, pure phase VO₂ (M) nanoparticles must first be synthesized without the mixture of polymorphs. Second, the synthesis time must be reduced from days to hours. Finally, the ink formulation of VO₂ (M) nanoparticles and their inkjet printing are required for high-quality film deposition without the need for expensive and complex deposition techniques. It should be noted that VO₂ (M) ink of this sort is not commercially available. Recently, for the first time, our group has produced preliminary work on a VO₂-based printed radio-frequency (RF) switch.^[18]

This work reports the synthesis of VO₂ (M) nanoparticles with a hydrothermal technique in a shorter reaction time, compared to 2–4 days. The nanoparticles have been synthesized in 6 h and further annealed for 3 h in vacuum, a crucial step to achieve pure phase nanoparticles. The novelty of our preparation approach as-compared to reported literature work is also summarized in supporting information Table S1. The VO₂ (M) nanoparticles have been

characterized in detail for their morphology, as well as their crystalline, chemical and thermal properties. It has been confirmed that as-prepared nanoparticles possess similar material properties to 24- h reaction products. The as-prepared pure phase VO₂ (M) nanoparticles have been used for ink formulation to demonstrate their functionality as an electronic ink. The electronic ink has been characterized in detail for its viscosity, surface tension and printing properties. The functionality of the as-formulated ink has been assessed by printing several overprinted layers to determine its electrical characterization. The as-printed films have demonstrated decent electrical conductivity of ~1 S/m at room temperature and 150–200 S/m when applying external stimuli such as temperature or electrical current. Finally, a frequency-reconfigurable patch antenna, printed on a glass substrate along with printed VO₂ films, has been devised as a proof of concept. The performance of printed VO₂ films is encouraging and can be useful for a number of tunable and reconfigurable devices, as well as many other applications in the field of optical and energy related devices.

2. Results and Discussion

2.1. Synthesis and Characterization of VO₂ Nanoparticles

The VO₂ nanoparticles were prepared by a hydrothermal-based solution process, with full details provided in the experimental section. We designed experiments with different reaction times, including 3, 6 and 24 h, and their products were investigated by XRD (X-ray diffraction) analysis. The XRD spectra for as-synthesized nanoparticles are displayed in Figure 1(a); it can be observed in the XRD spectra that the as-synthesized nanoparticles are a mixture of undesired VO₂ (A) and desired VO₂ (M) phases, with similar crystalline intensity for the 6- and 24- h reaction times. In addition to the VO₂ (A) and VO₂ (M) phases, some unresolved peaks at 20.87, 33 and 49.84° are also observed. To achieve a pure VO₂ (M) phase, we have exposed as-synthesized nanoparticles in different annealing environments, including variable temperature, time and atmosphere. It is well known that vanadium dioxide

is prone to oxidation; thus, we have annealed the as-synthesized sample in vacuum conditions.

The XRD spectra demonstrated in Figure 1(b) clearly reveals that annealing at 300 °C in a

Figure 1. The XRD patterns of (a) as-synthesized and (b) annealed VO₂ nanoparticles with different reaction time.

vacuum has produced a pure VO₂ (M) phase for all the samples synthesized with 3-, 6- and 24- h reaction times. The XRD peaks observed at 27.84, 37.01, 42.19 and 55.56° correspond to the [011], [-211], [-212] and [-222] crystal planes, respectively, which is well matched to JCPDS No. 72-0514.^[34] It is interesting to note that the sample synthesized for 3 h followed by annealing has demonstrated low-intensity XRD peaks, while the 6- and 24- h reaction time samples have demonstrated higher intensity with similar intensity peaks. It is thus concluded that the sample synthesized with a 6 h reaction time and an annealing at 300 °C is optimal to

achieve pure and high-quality VO₂ (M) nanoparticles. In addition, it was investigated that annealing for 3 h is best as compare to 1 h, higher intensity peaks were observed in the XRD spectra (for supporting information, see Figure S1[a]). Similarly, the annealing temperature of 300 °C was more optimal than 400 or 500 °C. The XRD spectra, displayed in Figure S1(b) in the supporting information, have revealed that for higher annealing temperatures such as at 400 °C, XRD peaks are further narrowed and expected to possess larger nanoparticles. The XRD peaks for the sample at 500 °C had nearly completely deviated from the original VO₂ (M) phase to unresolved phases.

The particles sizes and shapes were confirmed by their corresponding transmission electron microscopic (TEM) images. Figure 2 displays low resolution and high-resolution TEM images of the samples synthesized with a 6 h reaction time (a-c) and annealed at 300 °C (d- f) for 3 h. The inset in (a) and (d) displays the selected area electron diffraction (SAED) pattern for as-synthesized and annealed samples, respectively. From the TEM images, it has been confirmed that the nanoparticles are primarily spherical in shape but are aggregated,

Figure 2. The low and high-resolution TEM images of (a-c) as-synthesized and (d-f) annealed VO₂ nanoparticles. The inset in (a & d) and (c & f) displays the corresponding SAED pattern and high-resolution TEM images, respectively.

with average aggregate size between 20–50 nm (a and d). The distance between two crystal planes has been observed as 0.32 nm, which corresponds to (011) crystal plane, as shown in the insets of (c) and (f).^[31] The SAED pattern has confirmed the poly-crystalline phase of annealed VO₂ (M) nanoparticles, which is well matched with its corresponding XRD spectra and d-spacing value. In comparison to annealed sample (d-f), as-synthesized VO₂ NPs sample did not show any distinct particle size change except low crystalline scattered ring pattern in SAED spectra (inset of a), which confirmed the mixture of phases. The particles sizes and shapes have been further confirmed by their corresponding SEM images, displayed in Figure S2 in the supporting information. It can be seen in TEM (Figure 2) and SEM (Figure S2) images that nanoparticles are usually aggregated thus it is difficult to count the particle size distribution. We have calculated average particles size from XRD peak at 27.8 degree, which correspond to (011) plane, using Scherrer equation and displayed in Figure S3 in supporting information. Based on full width at half maximum (FWHM) for peak at 27.8, the calculated particle sizes are in the range of 10-12 nm which are lower than the aggregated particle size observed in the SEM and TEM images.

2.2. Chemical and Surface Analysis of VO₂ Nanoparticles

The quality and chemical compositions of as-synthesized (non-annealed) and annealed VO₂ nanoparticles were further examined by Fourier transform infrared (FTIR) spectroscopy in transmission mode and are displayed in Figure S4 in the supporting information. In the as-synthesized sample, weak adsorption bands appeared at 532 and 768 cm⁻¹, and a strong adsorption band appeared at 1,001 cm⁻¹. For the annealed sample, these bands shifted to 531, 716 and 995 cm⁻¹, and new bands appeared at 421 cm⁻¹. The as-observed bands for the annealed sample could be considered intrinsic to vanadium dioxide, which matched well with previous reports.^[34] In particular, bands at 531 and 421 cm⁻¹ are attributed to the V-O-V

octahedral bending mode, and bands at 716 and 995 cm^{-1} are due to coupled vibrations of V=O.

Usually, during growth or annealing processes, a number of vanadium oxides, with their respective oxidation states, such as VO (V^{2+}), V_2O_3 (V^{3+}), VO_2 (V^{4+}) and V_2O_5 (V^{5+}), are prone to be formed. Thus, it is important to characterize the annealed VO_2 sample with X-ray photoelectron spectroscopy (XPS) measurements for surface composition and chemical elemental valence state. The XPS spectra are displayed in Figure 3. No elemental peaks other than C, V and O are observed on the survey spectrum (Figure 3[a]). The signal from the peak of carbon 1s could be attributed to unintentional contamination from the ambient environment. The carbon 1s peak is assumed to possess binding energy at 284.8 eV, which has been used as a calibration for the binding energies of V and O. To get the precise valence state of vanadium in oxide, a high-resolution XPS spectrum focusing between 510–540 eV is

Figure 3. The XPS spectra of annealed VO_2 nanoparticles: (a) survey spectrum and (b) high-resolution XPS scan of O 1s and V 2p.

displayed in Figure 3 (b). Two peaks, centered at 516 and 523.6 eV, are associated with the spin-orbit splitting of $\text{V}2\text{p}_{3/2}$ and $\text{V}2\text{p}_{1/2}$, which are in good agreement with the V^{4+} oxidation state.^[36–38] In addition, the peak at 529.9 eV is associated with O 1s corresponding to the binding energy of V-O. After fitting the XPS spectra, some uncertainty on the valence state of

vanadium arises. For example, peaks for $V2p_{3/2}$ and $V2p_{1/2}$ display slight shoulder peaks at 517.1 and 524.94 eV, respectively, which may correspond to a certain amount of the V^{5+} oxidation state. E. Hryha et al. have discovered that all standard vanadium oxides are usually covered with a thin layer ($\text{\AA}$ thin) of vanadium pentoxide, regardless of high chemical purity and storage under argon.^[39] Thus, it is believed that as-observed shoulder peaks at 517.1 and 524.94 eV are due to the V^{5+} oxidation state of vanadium from the surface; furthermore, no other valence state of V was detected. It is interesting to note that we have not observed the vanadium pentoxide phase during the XRD analysis, as displayed in Figure 1(b) and in Figure S5 in the supporting information, probably due to the sensitivity limit of the XRD tool for thin layers of vanadium pentoxide. It has been established that the binding energy difference between O1s and $V2p_{3/2}$ ($\Delta = B(O1s) - BE(V2p_{3/2})$) can also be used to determine the oxidation state of vanadium. In this regard, we have calculated the binding energy span as 13.9 eV, which is well matched with the reported pure VO_2 phase.^[39] The composition of V:O was determined to be 1:2.2, which further confirmed that the as-annealed sample is bulk-form, pure-phase vanadium dioxide (VO_2). The surface states of as-synthesized and annealed VO_2 nanoparticles, in comparison with pure V_2O_5 powder (99.6%), were further investigated with Raman spectroscopy and are displayed in Figure S6 in the supporting information. In the as-synthesized sample, Raman peaks appear at 162, 194, 260, 475, 513, and 618 cm^{-1} which confirms the mixture phase of VO_2 (M),^[32] VO_2 (A),^[40] and mixed valence states of V^{4+}/V^{5+} ^[41]. For the annealed sample, Raman peaks appear at 192, 222, 260, 341, 383 and 615 cm^{-1} , which could exclusively be assigned to pure monoclinic VO_2 (M) phase^[32, 42-44]. It should be noted that none of the V_2O_5 peaks (143, 195, 282, 302, 405, 480, 528 and 700 cm^{-1})^[45] have been observed in the annealed sample which further confirms the purity of VO_2 (M).

2.3. Thermal Analysis of VO_2 Nanoparticles

It has been confirmed by XRD and FTIR analyses that the as-annealed sample is pure, with a high-quality VO_2 (M) phase. However, XPS analysis has resulted in the possibility of a V^{5+}

(V_2O_5) oxidation state in addition to the desired V^{4+} (VO_2). Due to the different composition of vanadium oxides and their phases, the possibility existed that the MIT characteristics (at 68°C) might be seriously degraded. Therefore, thermal analysis was necessary to study the

Figure 4. Differential scanning calorimetry analyses of (a) as-synthesized and (b) annealed VO_2 nanoparticles.

MIT behavior of the as-annealed sample. The reversible phase transitions (with heating–cooling) of the as-synthesized and annealed VO_2 nanoparticles were conducted using differential scanning calorimetry (DSC), as displayed in Figure 4. No exothermic or endothermic peaks are observed for the as-synthesized VO_2 nanoparticles between room temperature and 120°C , as demonstrated in Figure 4(a). However, clear MIT peaks at 68°C

during heating (endothermic) and 50 °C during cooling (exothermic) are observed for annealed sample, as displayed in Figure 4(b). The DSC analysis confirms the hysteresis-based reversible phase transition characteristics from monoclinic to tetragonal structures. The monoclinic phase corresponds to an insulator characteristic; however, the tetragonal, or rutile, phase corresponds to a metallic characteristic. The calculated thermal hysteresis phenomenon with transition width between heating and cooling curves was 18 °C, which corresponds to a first-order phase transition.

2.4. Ink Formulation of VO₂ Nanoparticles and their Characterization

To evaluate the functional properties of the as-prepared VO₂ nanoparticles (reaction time 6 h, annealed at 300 °C), ink formulation has been performed. Using a typical ink formulation, 200 mg annealed VO₂ (M) nanoparticles were mixed in 50 ml ethanol followed by addition of 200 µL dispersant. The resultant mixture was ultrasonicated for 1 h to disperse the nanoparticles in solvent. After sonication, the resultant solution was centrifuged at 5,000 rpm for 15 min and then washed with ethanol one to two times per cycle to remove access dispersant or surfactant. The resulting VO₂ nanoparticles were then formulated as an ink in the mixture of 87.5 vol% of 2-methoxy ethanol, 7.5 vol% chlorobenzene and 5 vol% ethanol. The formulated ink was subsequently filtered by 1 µm polypropylene Whatman paper before jetting. The resultant ink solution is displayed in the inset of Figure S7(a) in the supporting information. The observed viscosity of the as-formulated ink for inkjet printing was ~2.19 cP, using a spindle speed of 200 rpm with a shear rate of 132 s⁻¹ and shear stress of 2.89 dyne/cm² at room temperature, as displayed in Figure S7(a) in the supporting information. The measured density of ink was ~1.0525 gm/cm³. The as-formulated ink exhibited an SFT of ~28.26 mN/m, which is good for stable jetting performance, as displayed in Figure S7(b) in the supporting information.

The VO₂ ink was inkjet printed under constant printing conditions, with full details provided in the experimental section. To assess the ink formulation, several dots and line

Figure 5. Inkjet-printed VO₂ dot patterns: (a) low and (b) high-resolution SEM images, (c) 3D surface profile for dots and (d) cross-sectional 2D surface profile of single printed dot.

patterns were printed on the glass substrate, and the ink-solvents were then dried at 200 °C. The printed ink formed arrays of dots on the glass substrate, which are characterized by the SEM 3D and 2D profiler, as displayed in Figure 5. The SEM (a and b) and 3D (c) images display the uniform dot pattern, with a decent density of nanoparticles covering the entire dot area. The printed dots also demonstrate a uniform dot width of ~95 μm. The cross-sectional thickness of the printed dots was measured by the 2D profiler, with a resultant thickness of ~1 μm (d). To further study the effect of overprinting on the thickness and density of printed films, line patterns with a drop spacing (DS) of 30 and 40 μm were printed on glass substrates while varying the number of overprinting layers. 2D and 3D surface profiling was conducted for the line patterns printed with DS of 30 μm (a) and 40 μm (b), as shown in Figure S8 in the supporting information. The printed lines produced a width of ~100 μm, which further broadened to ~150 μm as the number of overprinting layers increased (a and b). The thickness

for one-layer printing with $DS=30\ \mu\text{m}$ is usually higher than for $DS=40\ \mu\text{m}$, which further increases as the number of overprinting layers increases. It is believed that the initial layer of printing is directly related to the ink interaction with the target substrate. The ink compatibility with the substrate is usually governed by the surface tension of the ink and the surface energy of the substrate. It is also believed that with successive overprinting, one can densify the printed film with more nanoparticles and eventually print a more uniform pattern. As demonstrated in Figure S8 (a and b) in the supporting information, line uniformity and density were substantially enhanced by increasing the number of overprinted layers from one to five. It is observed that the printed lines do not display coffee-ring effects or line bulging.

2.5. DC Characterization of Printed VO_2 Nanoparticle-Based Film

In the previous section, we confirm that our prepared VO_2 nanoparticles display a clear phase transition with thermal application (Figure 4). It is thus crucial to evaluate the electrical behavior for printed VO_2 nanoparticle-based films while applying different temperatures. To characterize the printed VO_2 film, current-voltage (I-V) measurements have been performed

Figure 6. DC characterization of as-printed VO_2 films with different overprinted layers as a function of thermal triggering.

to extract the resistance and conductivity. The VO_2 films with 1–40 layers (which is an arbitrary choice of printed layers) have been printed between the defined gap area of electrodes. To test the electrical tuning with phase transition, the temperature of a hot plate

was varied from room temperature to 100 °C. For a one-layer printed film, at room temperature, the observed resistance was around 685 k Ω , which displays an insulating behavior. As the temperature was increased, a slight decrease in resistance was observed. At 60 °C, the resistance of the printed film begins to decrease quickly, as demonstrated in Figure 6. Increasing the temperature beyond this point further reduced the resistance. At temperatures from 80–100 °C, the resistance becomes constant at a value around 3.6 k Ω . When the temperature was reversed from high to low (cooling stage), the resistance recovered its initial value. The resistance changes by two orders of magnitude from room temperature to 100 °C, with the phase transition occurring at $\sim$ 68 °C during heating cycle and $\sim$ 60 °C during the cooling cycle. It is obvious that as the number of printed layers is increased, resistance at room temperature (also called OFF resistance) and at high temperature (also called ON resistance) were improved. It is interesting to note that similar thermal hysteresis behavior is observed for all printed layers. The observed ON–OFF resistances and calculated conductivities are also summarized in Table S2 and Figure S9 in the supporting information, respectively. From supporting information Table S2 and Figure S9, it can be seen that all overprinted VO₂ films possess nearly identical ON–OFF conductivity, except for the one-layer printed film. In particular, printed films with 5–40 layers display OFF conductivity of $\sim$ 1.2–1.4 S/m and ON conductivity of 150–200 S/m, with an ON/OFF ratio of 10². From this electrical characterization, it can be concluded that the printed VO₂ film possesses similar MIT characteristics as previously reported.^[16, 46–48] However, it is also observed that ON/OFF ratio of 10² of printed film is lower as compared to the films deposited through dry vapor processes like RF magnetron^[49] and non-patterning route of sol-gel process.^[50] It is primarily due to lower film quality (porosity, roughness, etc) leads to lower ON/OFF ratio and non-sharp transition. However, it must be stated that the above mentioned methods do not do direct patterning like inkjet printing. We expect the quality of the film to be improved in our future research by optimizing nanoparticles size, ink-formulation, loading of VO₂

nanoparticles and exploring different sintering technique (such as laser, photonic, etc) to densify the printed film without affecting underneath substrate.

A similar response has also been observed for the same printed film with electrical triggering, as displayed in Figure 7. For a five-layer printed VO₂ film, the resistance drops from 37 k Ω to 235 Ω when the supplying current changes from 0.001 to 30 mA. As the number of printed layers (thickness) increases, resistance drops. For a ten-layer printed VO₂ film, the resistance drops from 12 k Ω to 68 Ω when the supplying current changes from 0.001 to 60 mA. Similarly, for 20 and 40 layers, ON resistances of 46 and 19 Ω are observed with supplying currents of 80 and 100 mA, respectively. It is notable that for electrical triggering, the measurement test current has been limited to certain values to avoid the VO₂ film burning due to the Joule heating. It is interesting to note that the resistance change occurs in a repetitive manner with electrical triggering and recovers its initial value. For electrical triggering, the ON/OFF resistance ratio is 10², which is consistent with its thermal heating. It is believed that the driving mechanism for MIT is either a strong electron correlation (Mott–Hubbard transition) or an electron–lattice coupling (Peierls transition), or both.^[51] The exact mechanism is still debated.

Figure 7. DC characterization of as-printed VO₂ films with different overprinted layers as a function of electrical triggering.

2.6. Fabrication of a Fully Printed Reconfigurable Antenna

In wireless communication, reconfigurable components are increasingly important due to their ability to tune it by external stimuli, such as magnetic fields and thermal, electrical, mechanical and optical factors.^[52–57] For example, smartphones contain multiple antennas that are usually implemented to cover different frequency bands (working frequency determines antenna length), such as GPS, GSM, Wi-Fi, Bluetooth, 2G/3G or 4G LTE. Thus, it is important to install a single antenna system in these wireless devices that can tune to several frequency ranges. So, instead of having multiple bulky antennas on a smartphone, using a “frequency-reconfigurable antenna” (which can tune the frequency on demand) can reduce cost and save precious space inside the smartphone. A VO₂-based film as an RF switch could

be the key to realize the reconfigurable antenna. As a proof of concept, a fully printed reconfigurable patch antenna with VO₂-based printed switches has been designed that can change its operating frequency by applying external heat. The fabricated antenna prototype and its model are displayed in Figure 8(a–c). First, a uniform ground plane with silver paste is printed on the back side of a glass substrate, as shown in Figure 8(a). The patch antenna is designed so that the lengths L1, L2 and L3 determine the operating frequency (Figure 8[c]). In a typical antenna design, the working frequency is inversely proportional to the length. For a shorter length, L1, the antenna works at higher frequency, and for longer lengths, L1+L2+L3, the antenna's working frequency shifts to a lower value. In between lengths L1 and L2, three VO₂ switches were inkjet printed, and between L1 and L3, two switches were printed. The VO₂ switches were modeled with lumped elements: the ON state with 3 Ω , and the OFF state with 0.2 k Ω resistance and 1 pF capacitance. The geometry of the antenna and the detailed dimensions are provided in the experimental section. All five VO₂ switches were used to change the patch antenna's radiating length, but the two closest to the patch antenna feeding port also change the insert slot dimension for matching purposes. The length L3 is optimized

Figure 8. Fully Printed Reconfigurable Antenna: (a) printed ground plane, (b) as-fabricated prototype, (c) as-designed antenna, (d) measured reflection coefficient of the antenna with the VO_2 film at ON/OFF state and (e) measured radiation pattern.

in the simulation to match both bands. At room temperature, VO_2 switches act as an insulator (OFF state), which isolates the lengths $L2$ and $L3$, with effective lengths up to only $L1$, and thus function at higher frequency. When switches are heated to 80°C , VO_2 changes its phase and becomes conductive (ON state). The switches then function as connections between lengths $L1$ and $L2$ and between $L1$ and $L3$; thus, effective length increases, and the antennas begin to function at a lower frequency. By turning the switch from ON to OFF, the effective length can be varied, which in turn shifts the frequency. The as-designed and fabricated frequency-reconfigurable antenna has two bands: one for 3G at 2.1 GHz and the other for Wi-Fi at 2.4 GHz. In simulations, the single patch antenna is impedance matched from 2.31 to 2.45 GHz in the OFF state, and from 1.98 to 2.1 GHz in the ON state; the measured results demonstrate impedance matching from 2.32 to 2.49 GHz and from 1.93 to 2.03 GHz in the

OFF and ON states, respectively. Figure 8(d) demonstrates that the simulation results correlate very well with the measured results. A uniform antenna radiation pattern is displayed in Figure 8(e).

3. Conclusions

In conclusion, this work successfully demonstrates the synthesis of phase pure VO₂ (M) nanoparticles with reaction times much shorter (6 h) than the usual synthesis protocol (2–4 days). The experimental setup, with different reaction times, annealing temperatures and annealing environments, leads us to discover the crucial step to make pure VO₂ (M) nanoparticles without compromising their crystallinity and morphology. The as-synthesized nanoparticles, following annealing at 300 °C for 3 h in a vacuum, display a clear MIT at 68 °C during thermal analysis. The as-annealed nanoparticles have been successfully implemented in the preparation of electronic ink and inkjet printing. The functionality of the as-formulated ink has been assessed by printing different line patterns with varying numbers of overprinted layers, and subsequently its electrical characterization has been performed. The printed VO₂ films have demonstrated a very low electrical conductivity (insulator state) of ~1 S/m at room temperature and 150–200 S/m (metal state) after being either thermally heated to 80 °C or electrically triggered with 100 mA current. Both thermally and electrically triggered samples have demonstrated a 10² ratio of conductivity. Thermally triggered samples have displayed slower recovery with characteristic hysteresis; however, electrical triggering has displayed quick recovery with multiple cycles. To prove the functionality of the ink, a patch antenna design with multiple VO₂ films was implemented, wherein the VO₂ films acted as switches. The fully printed antenna has demonstrated a working frequency of 2.4 GHz when the switch is in the OFF state (at room temperature). By turning the VO₂ switch ON, the electrical length of antenna increases and shifts its frequency to 2.1 GHz. The promising results of this fully printed reconfigurable antenna have confirmed that VO₂-based electronic ink could be explored for several functional printed devices.

4. Experimental

Chemicals: Vanadium (IV) oxide sulfate hydrate ($\text{VOSO}_4 \cdot x\text{H}_2\text{O}$, Sigma-Aldrich, 97% anhydrous), vanadium (V) oxide (V_2O_5 , Aldrich, ≥ 99.6 trace metals basis), urea (NH_2CONH_2 , Fisher Scientific), hydrazine hydrate (N_2H_4 , Sigma-Aldrich, reagent grade, 50–60%), 2-methoxyethanol ($\text{C}_3\text{H}_8\text{O}_2$, Sigma-Aldrich, anhydrous, 99.8%), chlorobenzene ($\text{C}_6\text{H}_5\text{Cl}$, ACS reagent, 99.5%), ethanol (absolute, VWR Chemicals). A nanoparticle dispersant/surfactant (alcohol dispersion) was purchased from US Research Nanomaterials, Inc. These chemicals were used as received without further purification.

Synthesis of VO_2 Nanoparticles: In a typical synthesis process, a 1.8 g urea pellet was dissolved in 150 ml DI water, and 0.1 M of vanadium (iv) oxide sulfate hydrate (2.445 g) powder was subsequently added. The resultant mixture was mixed well until it became a clear-blue colored solution, and then 0.9 ml of 10% hydrazine hydrate solution in water was added drop-wise, while stirring. The final solution was then transferred into a 200 ml PPL high-temperature polymer-liner-based hydrothermal autoclave reactor. The reaction temperature was set at 260 °C. Three sets of experiments were performed, varying the reaction times from 3–24 h. After the completion of the reaction, the resultant blue-black color precipitate was centrifuged, washed with water and ethanol and then dried in a vacuum furnace at 70 °C for 1 h. The obtained dried powder was then post-processed with different annealing temperatures and times in a vacuum furnace to obtain pure VO_2 (M) nanoparticles.

Inkjet Printing Using VO_2 Nanoparticles: The VO_2 dot and line patterns were directly printed on a glass substrate using a drop-on-demand piezoelectric inkjet nozzle (DMP-2831) with a nozzle diameter of 16 μm ; the drop volume was 10 pL. The uniform and continuous ejection of droplets was achieved by adjusting various wave forms while applying a firing voltage of 22 V at a 1-kHz printer velocity. The cartridge temperature was set to room temperature. During the jetting, the plate temperature was set to 50 °C. The detailed jetting waveform is displayed in Figure S10 in the supporting information. The thickness of the as-printed lines

was varied by changing the number of overprinting layers using 20–40 μm DS. After printing the total layers, curing was conducted in the vacuum box for 1 h at 200 °C. This step was critical to further evaporate the solvent and densify the printed layer.

Fabrication of Fully Printed Reconfigurable Antenna: Commercially available conductive silver paste (PE819, purchased from DuPont) was used to print the antenna. The patch antenna was screen-printed on the glass and cured at 150 °C for 30 min with a thickness of $\sim 30\ \mu\text{m}$. The dimension of the design is as follows (in mm): $W=27$, $W_1=6$, $L_1=19$, $L_2=1.6$, $L_3=1.4$, $L_4=2.5$, $G_1=0.2$. To achieve frequency reconfigurability, VO_2 ink was inkjet printed on the gap area using 40 layers of printing for the top three switches and 60 layers printing for the bottom two switches to achieve the required resistance. After VO_2 printing, films were cured at 200 °C for 1 h in the vacuum. A subminiature version A (SMA) connector was mounted afterward at the edge of the antenna using conductive epoxy, which solidifies at a lower temperature in the oven.

Characterization: The morphological properties were examined using scanning electron microscopy (Zeiss Merlin with Gemini 2 column) and transmission electron microscopy (FEI Titan G2 80–300 kV equipped with a $2\ \text{k} \times 2\ \text{k}$ CCD camera model US4000, Gatan, Inc). The phase crystallinity of the VO_2 nanoparticles was examined by XRD (Bruker D8 Advance) in the range of 20–60° with scan rate of 6° per minute at 40 kV. The chemical binding energy was examined by X-ray photoelectron spectroscopy (XPS, Amicus). The chemical nature was also characterized by FTIR spectrometer (Nicolet 6700). The FTIR sample is prepared using the KBr pellet method. Raman spectra were recorded at room temperature with a LabRAM-ARAMIS Raman Spectrometer using a Cobalt laser (473 nm) excitation source with a laser power of $<0.5\ \text{mW}$. The differential scanning calorimetry (DSC) was performed using Discovery DSCTM tool. Furthermore, the viscosity of the ink was measured using a Brookfield Rheometer (DV3T). The surface tension of the ink was measured by using a KRUSS DSA100, based on the pendant drop method. The thicknesses of the printed VO_2 and silver layers was

examined using a 2D surface profilometer (Veeco Dektak 150) and a 3D profilometer (NV7300, Zygo Optical Profiler). I-V measurements were performed using a Keysight B2912A precision source meter on a hot plate probe station capable of temperature control from 25–200 °C. The resistance was extracted by taking the inverse slope of I-V measurements in the linear low voltage regime where the voltage is swept between ± 0.1 V. The VNA from Keysight Technologies was used for the antenna measurement.

Supporting Information

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

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A vanadium dioxide (VO₂) nanoparticles based electronic ink is developed, which has been fully characterized for its material and electrical properties. The electronic ink demonstrates metal-insulator transition (MIT) at 68 °C, suitable for many printed functional devices. The fully printed reconfigurable antenna demonstrates frequency tuning from Wi-Fi band to 3G band with thermal triggering, applicable for wireless communication.

Development of Phase-Change VO₂ Nanoparticle-Based Electronic Ink

M. Vaseem*, S. Zhen, S. Yang, W. Li, A. Shamim

Supporting Information

Development of Phase-Change VO₂ Nanoparticles Based Electronic Ink*Mohammad Vaseem*, Su Zhen, Shuai Yang, Weiwei Li and Atif Shamim***Table S1.** Comparison table for the preparation of VO₂ (M) nanostructures with hydrothermal route

Shape of Nanostructures	Reaction Temperature (°C)	Reaction Time	Post-thermal Treatment (°C) / Time	Inkjet Printing Application	References
cucumber-like	160-220	18 h	500-600 / 3h	no	[9]
nanoparticle	220	48 h	400/ 40 second	no	[12]
nanoparticle	260	24 h	60/ 10 h	no	[32]
belt-like	180	1-7 days	no	no	[58]
nanoparticle	180-400	15 h	no	no	[59]
nanoparticle	240	24 h	no	no	[60]
nanoparticle	280	24 h	60/ 24 h	no	[61]
nanoparticle	260	12 h	90/ 1 h	no	[62]
nanoparticle	260	24 h	60/ 10 h	no	[63]
nanoparticle	240	24 h	no	no	[64]
nanoparticle	240	24 h	50/ 12 h	no	[65]
nanoparticle	240	24 h	60/ 12 h	no	[66]
nanoparticle	260	6 h	300/ 3 h	yes	This work

Figure S1. XRD patterns of annealed VO_2 nanoparticles with (a) different annealing time and (b) different annealing temperature.

Figure S2. SEM images of (a-c) as-synthesized and its corresponding (d-f) annealed VO_2 nanoparticles prepared with different reaction time such as (a) 3, (b) 6 and (c) 24 h.

Figure S3. (a) Particle size calculation from FWHM of XRD peak using Scherrer equation and its corresponding (b) calculated particle size distribution of annealed VO₂ nanoparticles with different reaction time.

Figure S4. FT-IR spectra of as-synthesized (non-annealed) and annealed VO₂ nanoparticles

Figure S5. XRD patterns of annealed VO_2 nanoparticles and its comparison with commercially available V_2O_5 powder (99.6% purity)

Figure S6. Raman spectra of (a) as-synthesized (non-annealed), (b) annealed VO_2 nanoparticles and (c) commercially available V_2O_5 powder (99.6% purity)

Figure S7. (a) Viscosity and (a) Surface tension (SFT) measurement of the ink. The inset in (a) is showing camera image of as-formulated VO₂ ink.

Figure S8. The cross-sectional surface profiler images of as-printed line pattern with (a) drop-spacing, DS= $30\text{ }\mu\text{m}$ and (b) DS= $40\text{ }\mu\text{m}$. The insets are showing its corresponding 3D surface profile.

Figure S9. Calculated conductivity from *DC* characterization of as-printed VO₂ films with different overprinted layers as a function of thermal triggering

Table S2. Summarized conductivity of as-printed VO₂ films with different overprinted layers

# of Printed Layer	OFF Conductivity (S/m)	ON Conductivity (S/m)	ON/OFF Ratio
1	0.39	73.44	186
5	1.23	173.76	141
10	1.16	166.50	142
20	1.35	191.82	142
40	1.42	156.25	110

Figure S10. Jetting waveform for as-formulated VO₂ nanoparticles ink.