In Situ Visualization of Fast Surface Ion Diffusion in Vanadium Dioxide Nanowires

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Supporting Information

ABSTRACT: We investigate in situ ion diffusion in vanadium dioxide (VO₂) nanowires (NWs) by using photocurrent imaging. Alkali metal ions are injected into a NW segment via ionic liquid gating and are shown to diffuse along the NW axis. The visualization of ion diffusion is realized by spatially resolved photocurrent measurements, which detect the charge carrier density change associated with the ion incorporation. Diffusion constants are determined to be on the order of 10⁻¹⁰ cm²/s for both Li⁺ and Na⁺ ions at room temperature, while H⁺ diffuses much slower. The ion diffusion is also found to occur mainly at the surface of the NWs, as metal contacts can effectively block the ion diffusion. This novel method of visualizing ion distribution is expected to be applied to study ion diffusion in a broad range of materials, providing key insights on phase transition electronics and energy storage applications.

KEYWORDS: Vanadium dioxide, metal insulator transition, ionic liquid gating, ion diffusion, scanning photocurrent microscopy, nanowires

Vanadium dioxide (VO₂), an exemplary correlated material, undergoes a metal–insulator phase transition (MIT) accompanied by a structural transition from high-temperature rutile to low-temperature monoclinic lattice when cooled below 340 K.⁴ The MIT exhibits a rapid and drastic change in the electronic and optical properties, based on which novel applications of switching,⁵⁻⁶ sensing,⁷⁻⁸ and resonators¹⁰¹¹,¹² have been intensively pursued. Ultrafast¹³⁻¹⁵ and microscopy²¹⁻¹⁷ techniques, along with improved computational approaches,¹⁸ have been employed to clarify on the phase transition mechanisms. Ionic liquid (IL) gating¹⁹⁻²⁸ and chemical doping²⁹⁻³³ of VO₂ are of particular interest as they can effectively modulate MIT for potential Mott transistors²⁹,³⁴ and create unusual electronic phases.²² Though the underlying mechanism for IL gating is still under debate, diffusion of atoms, either hydrogen diffusion that leads to chemical doping¹⁹⁻²¹ or oxygen diffusion that creates oxygen vacancies,²²⁻³⁵ is generally considered to play a significant role. For example, IL gating induced MIT in VO₂ has been attributed to electrochemical reaction involving oxygen vacancies,²² which have been found to diffuse at least 0.5 μm along the rutile c-axis.²² H atoms also result in the stabilization of the metal phase down to 2 K, and the diffusion constant of H has been determined to be around 10⁻¹⁰ cm²/s at 100 °C along the rutile c-axis and is much slower along the a-axis.²⁹,³⁵

Though the diffusion of atoms in VO₂ is at the heart of the modulation of the MIT through IL gating or doping, their studies have been limited to hydrogen and oxygen to date.

Alkali metals such as Li, Na, and K are also widely used in IL gating.²⁷,²⁸,³⁶⁻³⁹ Exploration of their diffusion in room temperature monoclinic VO₂ not only sheds light on the IL gating mechanism but also provides realistic approaches to manipulate the MIT toward applications. Furthermore, diffusion may occur both in bulk and at surface. As the micro- and nanoelectronic devices approach to ever smaller scale, the surface becomes more important. While our understanding of bulk diffusion in solid has advanced greatly, diffusion at surface is notoriously challenging to investigate,¹⁰ though it is critical to an endless list of phenomena at nanoscale such as catalysis,¹¹ crystal growth,¹²,¹³ and many self-assembly and filtration processes.¹⁴,¹⁵ Surface diffusion is also particularly important to the application of Li and Na batteries,¹⁶ since the electrodes are often made of polycrystalline materials where the ion diffusion is often dominated at the domain boundaries. Sophisticated experimental techniques such as scanning tunneling microscopy (STM),¹⁷,¹⁸ field ion microscopy (FIM),¹⁹,²⁰ and helium atom scattering¹ have been developed to probe the atomic scale absorbate diffusion. However, these techniques generally require ultrahigh vacuum and ultraclean atomically flat surface and thus are challenging to apply to study

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ion diffusion in realistic environment such as in ambient conditions and in electrolyte solution.

In this Letter, we report the direct visualization of ion diffusion in single crystalline VO₂ nanowires (NWs) by taking advantage of the drastic change in charge carrier concentration associated with ion doping. The ions are injected from electrolyte into an exposed segment of a VO₂ NW by electrochemical gating, while the direct ion doping of the other part of the NW is prohibited by an ion barrier. The diffusion of the ions from the exposed segment to the covered segment along the NW axis significantly increases the local electron concentration. The imaging of such change is then made possible by using scanning photocurrent microscopy (SPCM), where photocurrent generated by local illumination is mapped as a function of laser position. Using this novel method, we image the ion transport in VO₂ NWs in situ and extract diffusion constants for Li, Na, and H ions at room temperature.

Single crystalline VO₂ NWs are synthesized by a chemical vapor deposition (CVD) method following our previous work as briefed in the Methods section. Figure S1 shows the morphology of the as-grown VO₂ NWs. The NWs have rectangular cross sections and are typically 300–500 nm in width and 100–300 nm in height and tens of micrometers long. They grow along the [100] direction of the monoclinic (M1) phase, which corresponds to the c-axis of the high temperature rutile phase. The as-grown NWs are then transferred to 300 nm SiO₂ covered Si substrates, where single NW field effect transistor (FET) devices are fabricated using a standard electron beam lithography (EBL) process. To enable local injection of ions into the NW, a poly(methyl methacrylate) (PMMA) layer is spin-coated on top of the FET device and is partially removed by EBL to expose only a segment of the NW. Finally, an IL droplet of polyethylene glycol (PEO) with 5 wt % of LiClO₄ is applied to the NW device (the detailed information on chemicals can be found in Methods).

Figure 1a shows the schematic drawing of a complete device. Optical images of a typical device before and after the application of IL are shown in Figure 1b and c. A window is clearly seen in Figure 1b where the PMMA is locally removed and the NW is exposed. This window cannot be seen in Figure 1c after a droplet of LiClO₄/PEO is placed on the device because the refractive index of PEO matches well with that of PMMA. The IL is only in direct contact with the exposed NW segment while the other part of the NW is protected by the PMMA layer.

We first compare the IL gating effects in a fully exposed channel and a partially exposed channel in a VO₂ NW device (Device #1, reflection image shown Figure 2b). Electrochemical gate sweeps of this three-probe device are shown in Figure 2a. As the gate voltage (V₉) is increased to 1 V, the conductance of the fully exposed section (G23) is enhanced by over 30 times, indicating the insulator-to-metal phase transition. On the contrary, the conductance of the partially exposed section (G12) is only doubled, indicating that the resistance of the NW segment covered by PMMA is unaffected by gating.

SPCM measurements are then performed to extract the gate-induced doping distribution. SPCM provides spatially resolved photocurrent mapping and has been used to explore charge carrier transport in various nanostructures. Recently, SPCM has also been applied to devices under IL gating. The experimental setup is briefly described in the Methods and detailed in our previous work. All measurements are performed in air and at room temperature. Though pure PEO solidifies at room temperature, it stays in the liquid phase after adding salt such as LiClO₄ and remains transparent, allowing photocurrent imaging. In the SPCM measurements, electrodes 1 and 3 are short-circuited, while electrode 2 is floating. At V₉ = 0 V, photocurrent spots of opposite polarities are observed near metal–NW contacts (Figure 2b), attributed to photovoltaic effects at Schottky junctions. Polarieties of the spots indicate upward band bending toward the metal electrodes. Then a SPCM image is taken immediately after V₉ is increased to 1 V, in which the photocurrent spots at the contacts exposed to IL disappear, while the photocurrent spot at the contact covered by PMMA (spot A in Figure 2b) remains. This is because gating only induces insulator-to-metal phase transition in the exposed NW segment and eliminates the Schottky junction at the corresponding contacts. The photocurrent magnitude at spot A is also increased from 35 to 80 pA, because the total channel resistance is reduced. In addition, another photocurrent spot appears near metal electrode 2, attributed to photovoltaic effects at Schottky junctions.

Figure 1. VO₂ NW device configuration with an ion-injection window. (a) Schematic drawing of the device, where a VO₂ NW (red line) is electrically connected to Cr/Au contacts (golden bars) and partially covered by PMMA (light blue layer). An IL droplet (half dome) is then applied to cover the entire device but is only in direct contact to a segment of the VO₂ NW through a window. Panels b and c are optical images of a typical device before and after applying IL. The scale bar denotes 5 μm.
been shown in a recent study of ion transport in \( \text{H}_2\text{V}_3\text{O}_8 \) NWs.\(^6\)

After demonstrating the ion blocking capability of PMMA, we now present the results for ion diffusion in another VO\(_2\) NW device (device no. L2). As \( V_g \) is increased to 1 V in this device, a photocurrent spot is immediately observed at the window edge (Figure 3a), consistent with the results in device no. L1. Strikingly, when \( V_g \) is fixed at 1 V for a few minutes, we notice the appearance of an additional photocurrent spot of opposite polarity, which gradually broadens and shifts from the window edge (Figure 3b).

**Figure 2.** Electrochemical gating and SPCM characterizations of a single VO\(_2\) NW FET device (device no. L1) partially covered by PMMA. (a) The conductance between contacts 1 and 2 (G12) and the conductance between contacts 2 and 3 (G23) as a function of \( V_g \). The arrows indicate the scan direction. Scan rates for both curves are 20 mV/s. (b) Photocurrent images of the device at different \( V_g \). The scale bar at the bottom is 2 \( \mu \)m, and the color scales are in pA. The laser at 532 nm has a peak intensity of 30 kW/cm\(^2\). The yellow shaded areas indicate the positions of the electrodes. The band bending diagrams are overlay with the photocurrent images. The bottom panel shows the reflection image before applying IL.

**Figure 3.** SPCM visualization of the Li\(^+\) ion transport in a VO\(_2\) NW device (device no. L2). (a) Photocurrent images at \( V_g = 1 \) V and \( V_{SD} = 0 \) V as a function of gating time. The scale bar denotes 2 \( \mu \)m, and the color scale is in pA. (b) Photocurrent cross sections (solid lines) along the NW axis extracted from panel a and the calculated electric field distributions (dashed lines) at different time. The yellow shaded areas indicate the positions of the electrodes and the dashed line indicates the window edge. (c) Photocurrent images at \( V_{SD} = 0.1 \) V taken at \( V_g = 0 \) V, immediately, and 40 min after \( V_g \) is increased to 1 V, respectively. (d) The peak position of the shifting photocurrent spot as a function of gating time. The red solid line is the calculated peak position values using parameters \( D = 1.0 \times 10^{-10} \) cm\(^2\)/s and \( n_i/n_0 = 13 \). This calculated curve overlaps perfectly with a simple square root fitting \( (x_{peak} = \sqrt{D^*t}) \), where \( D^* = 3.1 \times 10^{-10} \) cm\(^2\)/s. (e) Schematic illustrating ion injection into the exposed NW and subsequent diffusion into the covered NW. S and D are source and drain metal contacts, respectively. (f) Electron density \( (n_e) \) and ion density \( (n_i) \) as a function of position away from the window, at two different gating times.
window moves across the entire NW channel (∼8 μm long). After that, Vg is decreased to zero, and then the photocurrent spot disappears (Figure S3). As a side note, photocurrent is also observed along the edge of the right electrode under Vg = 1 V, presumably caused by the light induced electrochemical reaction on metal. The long-time gating does not affect the morphology of the VO2 NW. The atomic force microscopic (AFM) images of the device before and after applying Vg = 1 V for 1 h look identical (Figure S4). Careful examination reveals that there is a slight height reduction about 2–4 nm in the exposed 270 nm thick NW segment, likely caused by electrochemical etching of the surface. But the PMMA covered NW segment has no change in height at all.

We will first provide a qualitative physical picture to explain the observed shifting photocurrent spot. The occurrence of this photocurrent spot in the PMMA covered VO2 NW segment indicates that an internal electric field is developed by gate induced ion injection. As the direct vertical Li+ ion injection is blocked by the PMMA layer, ions must diffuse from the exposed segment along the NW axis. The ion concentration is high in the exposed NW segment and gradually drops over distance moving into the covered region. As the positive ions induce free electrons in the NW, this ion concentration gradient leads to an electron concentration gradient and an internal electric field. At fixed gate voltage, more ions diffuse into the covered NW segment and result in broadening and shift of the photocurrent spot. At 40 min, the negative photocurrent spot shifts all the way to the left electrode, suggesting ions diffuse through the entire NW channel. Therefore, these sequential photocurrent images allow one to observe the in situ ion diffusion in motion. The photocurrent peak position (xpeak) as a function of gating time can be fit nicely by a square root function (xpeak = Dn tw), where Dn = 3.1 × 10−10 cm2/s is the apparent diffusion constant (Figure 3d).

The SPCM images under nonzero VSD (Figure 3c) further confirm this physical picture. Since photocurrent distribution reflects the local electric field distribution, at nonzero VSD, the most resistive part of the NW has the largest potential drop and hence the strongest photocurrent. Before Vg is applied, the photocurrent is uniform under VSD = 0.1 V, indicating a uniform distribution of electric field. Immediately after Vg is 1 V is applied, the photocurrent in the exposed segment disappears, since this segment is switched to metal phase and its resistance is greatly reduced. After fixing Vg = 1 V for 40 min, the photocurrent is also greatly suppressed in the covered NW segment close to the window, indicating Li+ diffuses into this region and leads to a resistance reduction.

To quantitatively understand the measured photocurrent profiles and to more accurately extract the ion diffusion constant, we provide a simple model based on 1D ion diffusion along the NW axis. The ion concentration (ni) along the NW axis is expected to be governed by Fick’s second law,

\[
\frac{\partial n_i}{\partial t} = D \frac{\partial^2 n_i}{\partial x^2}
\]  

(1)

where D is the diffusion constant, t is time, and x is the distance. The solution is,

\[
n_i(x, t) = n_{i0} \operatorname{erfc} \left( \frac{x}{2\sqrt{Dt}} \right)
\]  

(2)

where ni0 is the ion concentration at the boundary (x = 0) and erfc is the complementary error function. Assuming each positive ion induces a free electron and ni0 is the electron concentration before Vg is applied, the total free electron concentration is then \( n = n_{i0} + n_i \). The erfc distributions of n and ni are plotted in Figure 3f. At t = 60 s after gating, the exposed NW segment is switched to metal phase when \( n > n_i \) (ni is the critical electron concentration to induce insulator-to-metal transition), leading to a drastic increase of n to about 10^2 ni. A junction is then created between the metal and insulator domains, which explains the positive photocurrent spot observed at the window edge. The distribution of n caused by the ion diffusion explains the negative photocurrent spot inside the covered segment. At t = 2400 s (40 min), ions further diffuse into the covered NW segment. This leads to a slight expansion of the metal domain into the covered segment, while most of the NW segment covered by PMMA remains insulating. This is evidenced by the slight shift of the positive photocurrent spot at the window edge (Figure 3a) and the fact that the dark conductance is only increased by 3 times 40 min after applying Vg = 1 V (conductance is expected to increase by 30 times if the entire NW undergoes insulator-to-metal phase transition as shown in Figure 2). It also results in a shift and broadening of the negative photocurrent spot as the distribution of n extends further into the covered segment. If n is low compared with the density of states (\( N_c \)), we can use Boltzmann distribution to calculate the local electric potential \( \varphi \) by,

\[
n(x, t) = N_c \exp \left[ - \frac{E_c - E_F - \mu \varphi}{k_B T} \right]
\]  

(3)

where \( E_c \) is the energy level of the conduction band edge, \( E_F \) is the Fermi level, \( \mu \) is the absolute value of electron charge, \( k_B \) is the Boltzmann constant, and T is the temperature. Therefore, the local electric field caused by the gate-injected ions is

\[
E(x, t) = - \frac{d}{dx} \varphi = - \frac{k_B T}{\mu \varphi} \frac{d}{dx} \ln \left( \frac{n}{N_c} \right)
\]  

\[
= - \frac{k_B T}{\mu \varphi} \frac{d}{dx} \ln \left( \frac{n_i + n_{i0}}{N_c} \right) \operatorname{erfc} \left( \frac{x}{2\sqrt{Dt}} \right)
\]  

(4)

As photocurrent is proportional to the local electric field, we can make a direct comparison of the measured photocurrent distribution and the electric field distribution calculated from the above model. As shown in Figure 3b, the calculated electric field follows the observed photocurrent curves quite well at various gating times.

After understanding the photocurrent distribution, we now use the above model to more accurately extract the diffusion constant. Figure 3d shows the time-dependent photocurrent peak position, which corresponds to the position where electric field reaches maximum. We can then determine the D value through best fitting of the experimental data using numerically obtained electric field maximum position from eq 4. It turns out that the extraction of D depends on the value of \( \Delta n/n \), which can be estimated from the photocurrent images taken under bias since,

\[
\Delta j = \Delta \sigma E = \frac{j \Delta \sigma}{\sigma} = \frac{j \Delta n}{n} \propto \frac{1}{n}
\]  

(5)
where $\Delta j$ is the photocurrent density, $\Delta \sigma$ is the laser-induced increase in conductivity, and the photogenerated carrier concentration $\Delta n$ is expected to be independent of injection position. Therefore, we may estimate $\Delta j$ by the ratio of photocurrent, which is about 13 using the photocurrent data at 40 min in Figure 3c (more details can be found in Figure S5 in the Supporting Information). By using $\frac{\Delta j}{n_0} = 13$ and $D = 1.0 \times 10^{-10} \text{ cm}^2/\text{s}$ the calculated $x_{\text{weak}}$ matches very well the experimental curve (Figure 3d). We note that this model-determined $D$ value is on the same order of magnitude but is expected to be more accurate than the simple square fit value ($D^* \pm$). Upon the four measured VO$_2$ NW devices, we obtained $D$ values ranging from $2.2 \times 10^{-11}$ to $1.0 \times 10^{-10} \text{ cm}^2/\text{s}$ for Li$^+$ (see Table S1 in Supporting Information for a summary of $D$ values measured in all devices).

Next, we demonstrate that Li$^+$ ions mainly diffuse at the surface of the VO$_2$ NWs. For this purpose, we design a device (device no. L3) with two separate ion injection windows, with one window (W1) to the left of electrode 1 and the other window (W2) between electrodes 2 and 3 (Figure 4). After $V_6 = 1 \text{ V}$ is applied, a photocurrent spot is observed moving from the edge of W2 away from the window into the PMMA covered NW segment, similar to the behavior in device no. L2. This photocurrent spot moves across the entire channel 2–3 (11.5 $\mu$m) to electrode 2 in 600 min. On the other hand, an ion induced photocurrent spot is not observed in channel 1–2. Though the distance is short from the W1 edge to channel 1–2 (3.2 $\mu$m), ions injected in W1 do not appear to diffuse into the channel. This indicates that Li$^+$ diffusion is blocked by the metal electrode (Cr/Au). Even after applying a higher gate voltage ($V_6 = 1.5 \text{ V}$) for another 300 min, the photocurrent distribution remains the same in channel 1–2, and the ions cannot diffuse across either electrode 1 or 2. The ion diffusion blocking by the metal contacts suggest that ions diffuse dominantly at surface. The ion diffusion in the bulk should not be stopped by the contact, as shown in the case of H$_2$V$_3$O$_8$. The surface diffusion is also supported with the fact that we do not see any optical reflection change of the NW after gating. The insulator-to-metal phase transition is associated with large change in optical reflection. If ions diffuse deep into the NW, the optical reflection is expected to change significantly as observed in the case of H diffusion at elevated temperature. However, in our case, we do not see any change in both PMMA covered segment and exposed segment even after applying $V_6$ for hours, indicating Li doping only occurs at the surface. Furthermore, the contact ion blocking also suggests that the ion diffusion rate at the VO$_2$ surface sensitively depends on whether the surface is covered by polymer or metal. Presumably, Cr makes stronger chemical bonding to the VO$_2$ surface, while the interaction between PMMA and VO$_2$ is likely much weaker, allowing Li$^+$ ions to move across.

Finally, we compare the diffusion rates of different ions at the VO$_2$ surface. We first apply 5.8 wt % NaClO$_4$/PEO to a VO$_2$ NW device with the same configuration (device no. N1), the evolution of SPCM images looks similar to LiClO$_4$/PEO (Figure 5a). The peak positions can also be fit quite well with the simulation to extract the Na$^+$ diffusion coefficient (Figure 5b). In the three devices we measured, we obtained the $D$ values of Na$^+$ from $3.6 \times 10^{-11}$ to $1.6 \times 10^{-10} \text{ cm}^2/\text{s}$, comparable to Li$^+$ (see a summary of diffusion constants measured in all devices in Table S1 in Supporting Information). To test the H$^+$ ion diffusion, we apply PEO with 1 wt % H$_2$O as the gating media to a device (device no. H1). The gating with H$_2$O/PEO also significantly changes the conductivity of VO$_2$ (Figure 5d), akin to LiClO$_4$/PEO and NaClO$_4$/PEO. Similar H$^+$ ion gating effects have been shown previously. However, different from the Li$^+$ and Na$^+$ gated devices, the photocurrent spot in this device does not appear to shift after applying $V_6 = 1 \text{ V}$ for 60 min (Figure 5c). If using the spatial resolution of our SPCM of 200 nm, we determine an upper limit of the $D$ value for H$^+$ ions: $D < 1.1 \times 10^{-13} \text{ cm}^2/\text{s}$, much lower than Li$^+$ and Na$^+$. The slower H$^+$ diffusion may be attributed to the stronger H$^+$ bonding to the VO$_2$ lattice. The sizes of Li ad Na atoms are bigger but their bonds to oxygen are weaker (bond dissociation energy, $D^*_{\text{Li}^+} = 340.5 \text{ kJ mol}^{-1}$, $D^*_{\text{Na}^+} = 11.5 \text{ kJ mol}^{-1}$) and the color scale is in pA. (b) Schematic drawing illustrates the diffusion of Li$^+$ is blocked by metal electrodes.

![Figure 4](image-url)
We report a high diffusion constant of $10^{-10}$ cm$^2$/s for both Li$^+$ and Na$^+$ ions. The diffusion most likely occurs at the VO$_2$ surface evidenced by the effective ion diffusion blocking at the Cr/VO$_2$ interface. The ion diffusion rate of H is much slower.

The observed fast ion surface diffusion in VO$_2$ provides critical insights in understanding the gate induced phase transition and may also have impacts in energy storage applications. The developed experimental method may be applied to study ion diffusion in a broad range of materials.

**Methods.** VO$_2$ NWs were synthesized via a chemical vapor deposition (CVD) method using V$_2$O$_5$ as the precursor in a tube furnace (Lindberg Blue M). V$_2$O$_5$ (Alfa Aesar, 99.99%) powder was adopted as the only precursor and placed in a quartz boat at the center of the tube furnace. An unpolished x-cut quartz substrates (MTI) was placed 7 cm downstream from the boat. The system was first pumped down to a base pressure of $\sim$30 mTorr. The furnace was then heated up to 880 °C and maintained at the peak temperature for 40 min to 2 h. After that, the furnace was cooled down to room temperature over approximately 3 h.

To fabricate single NW field effect transistors (FETs), the free-standing NWs were transferred onto 300 nm SiO$_2$ coated, heavily p-doped Si wafers by directly pressing the Si wafer against the growth substrate. Subsequently, top metal contacts (250 nm Cr/50 nm Au) were made to individual NWs using electron beam lithography (EBL, FEI 430 NanoSem) or sputtering (Lesker). A 1.5 μm thick poly(methyl methacrylate) (PMMA 950, C9, MicroChem) layer was then spin-coated at 4000 rpm on top of the device, followed by baking at 180 °C for 5 min. Then a second EBL was performed, followed by

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**Table 1. Ion Diffusion Constants in Materials**

<table>
<thead>
<tr>
<th>ion</th>
<th>material</th>
<th>$T$ (°C)</th>
<th>$D$ (cm$^2$/s)</th>
<th>surface or bulk</th>
<th>crystal orientation</th>
<th>reference</th>
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</thead>
<tbody>
<tr>
<td>H</td>
<td>ZnO</td>
<td>300</td>
<td>$8 \times 10^{-10}$</td>
<td>bulk</td>
<td>[001]</td>
<td>67</td>
</tr>
<tr>
<td>H</td>
<td>TiO$_2$</td>
<td>20</td>
<td>$1.8 \times 10^{-13}$</td>
<td>bulk</td>
<td>c-axis</td>
<td>68$^a$</td>
</tr>
<tr>
<td>H</td>
<td>VO$_2$ NW</td>
<td>100</td>
<td>$6.7 \times 10^{-10}$</td>
<td>bulk</td>
<td>c-rutile</td>
<td>29</td>
</tr>
<tr>
<td>O</td>
<td>VO$_2$ film</td>
<td>20</td>
<td>$1 \times 10^{-13}$</td>
<td>bulk</td>
<td>c-rutile</td>
<td>25$^b$</td>
</tr>
<tr>
<td>Li</td>
<td>porous V$_2$O$_5$</td>
<td>20</td>
<td>$3.8 \times 10^{-9}$</td>
<td>surface</td>
<td>N.A.</td>
<td>69</td>
</tr>
<tr>
<td>Li/Na</td>
<td>VO$_2$ NW</td>
<td>20</td>
<td>$10^{-10}$</td>
<td>surface</td>
<td>c-rutile</td>
<td>this work</td>
</tr>
</tbody>
</table>

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$^a$Extrapolated from high temperature measurements. $^b$Estimated from data presented in the publication.
developing to partially remove PMMA, to expose the gate electrode and only a part of the NW. Finally, an ionic liquid droplet of polyethylene glycol (PEO, 1000, Alfa Aesar) with 5 wt % of LiClO4 (Alfa Aesar, 99%), 5.8 wt % of NaClO4 (Alfa Aesar, 98%), or 1.0 wt % H2O was applied to the NW device. By controlling the amount of PEO applied to the tip of the micromanipulator, we achieved a small liquid droplet with a size of 20–100 µm to minimize leak current. The gate leak current was substantially smaller than the conduction current in all measurements.

Current–voltage curves were measured through a current preamplifier (DL Instruments, model 1211) and a NI data acquisition system. Scanning photocurrent microscopy (SPCM) measurements were performed using a home-built metal transition for all measurements. The intensity was controlled below the threshold of insulator-to-metal transition for all measurements supported by the Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under contract no. DE-AC02-05CH11231.

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