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## Electrical mapping of thermoelectric power factor in $\text{WO}_3$ thin film

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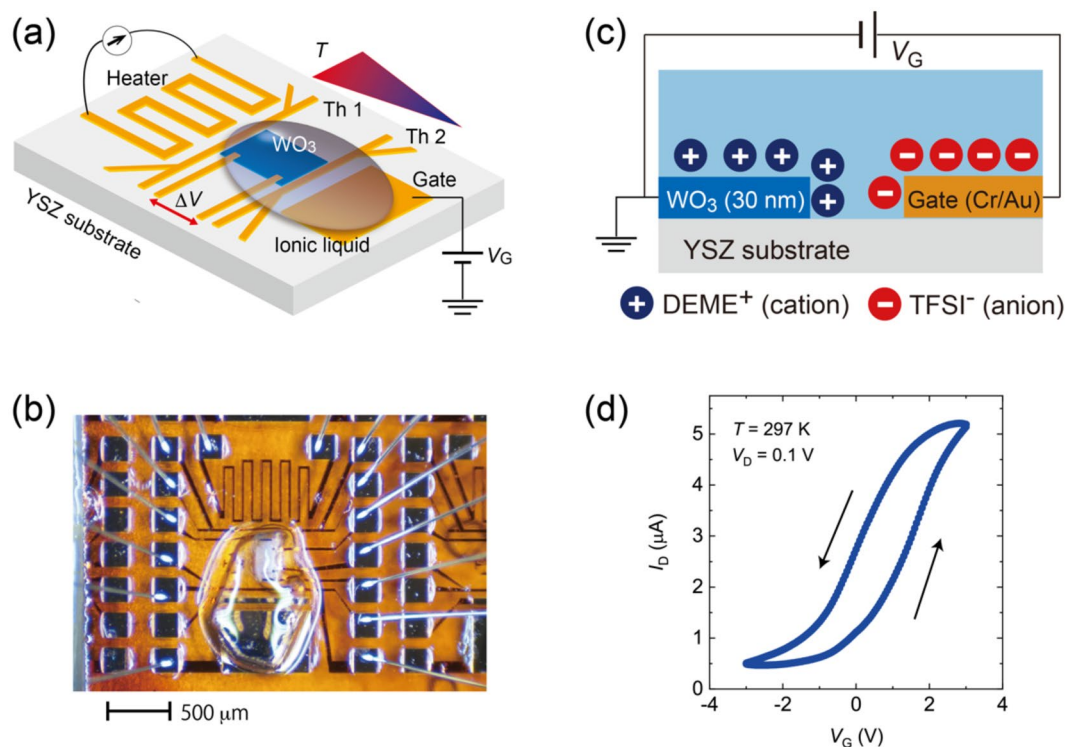
With growing environmental awareness and considerable research investment in energy saving, the concept of energy harvesting has become a central topic in the field of materials science. The thermoelectric energy conversion, which is a classic physical phenomenon, has emerged as an indispensable thermal management technology. In addition to conventional experimental investigations of thermoelectric materials, seeking promising materials or structures using computer-based approaches such as machine learning has been considered to accelerate research in recent years. However, the tremendous experimental efforts required to evaluate materials may hinder us from reaping the benefits of the fast-developing computer technology. In this study, an electrical mapping of the thermoelectric power factor is performed in a wide temperature-carrier density regime. An ionic gating technique is applied to an oxide semiconductor  $\text{WO}_3$ , systematically controlling the carrier density to induce a transition from an insulating to a metallic state. Upon electrically scanning the thermoelectric properties, it is demonstrated that the thermoelectric performance of  $\text{WO}_3$  is optimized at a highly degenerate metallic state. This approach is convenient and applicable to a variety of materials, thus prompting the development of novel functional materials with desirable thermoelectric properties.

Investigations on energy harvesting have become a mainstream in materials science, integrating different research disciplines such as physics, chemistry, electronics, and engineering<sup>1–4</sup>. This trend is motivated partly by the global requirement to develop advanced energy saving technologies<sup>5,6</sup>, aiming to reduce the current considerable carbon emission. Simultaneously, there is an urgent need to provide micro IoT (Internet of Things) sensors with stand-alone power systems<sup>7,8</sup>, the number of which will be skyrocketing in the coming decades. Thermoelectric energy conversion, which is a transformation of waste heat into electricity, has manifested itself as a promising  $\text{CO}_2$ -free technology for generating electricity from environment<sup>9</sup>. In order to realize more useful and efficient thermoelectric energy conversion, new strategies have been proposed, such as flexible devices<sup>10,11</sup>, nano structures<sup>12,13</sup>, and ionic thermoelectric materials<sup>14–16</sup>. Furthermore, besides the continuous experimental efforts, computer-based approaches have emerged and been transforming traditional processes of experimental researches.

For the past decade, high-throughput calculations and machine learning have been advancing dramatically, demonstrating the indisputable utility of these approaches for the exploration of thermoelectric materials<sup>17,18</sup>. Computer-based materials research deductively or statistically investigate materials, structures, and compositions, to predict promising thermoelectric materials that should be evaluated experimentally. Thus, both experimental and computer-based approaches for exploration of thermoelectric materials should proceed together in tandem and feedback the results between them. However, considering the fast growth of computer-based science, experimental side would be required to accelerate; in general, evaluation of the thermoelectric properties requires great experimental effort because the figure of merit or power factor depends on mutually related parameters of the Seebeck coefficient  $S$  and the electrical conductivity  $\sigma$ , which drastically change with the carrier density  $n$ .

Recently, electrolyte gating techniques have been applied to a variety of materials and were found to be very effective for systematically controlling  $n$ <sup>19</sup>. By just applying several volts of the gate voltage  $V_G$ , highly insulating electronic states are converted into conducting metallic states and even superconducting phases in oxides<sup>20–22</sup>, two dimensional materials<sup>23</sup>, and inorganic semiconductors<sup>24</sup>. Furthermore, continuous carrier doping using liquid electrolytes was found applicable to materials in which conventional methods such as bulk chemical doping were ineffective<sup>25–27</sup>. Thus, gate scanning of the thermoelectric properties in a wide temperature  $T$  and  $V_G$  (i.e.,  $n$ ) space would definitely help accelerate thermoelectric researches from an experimental side.

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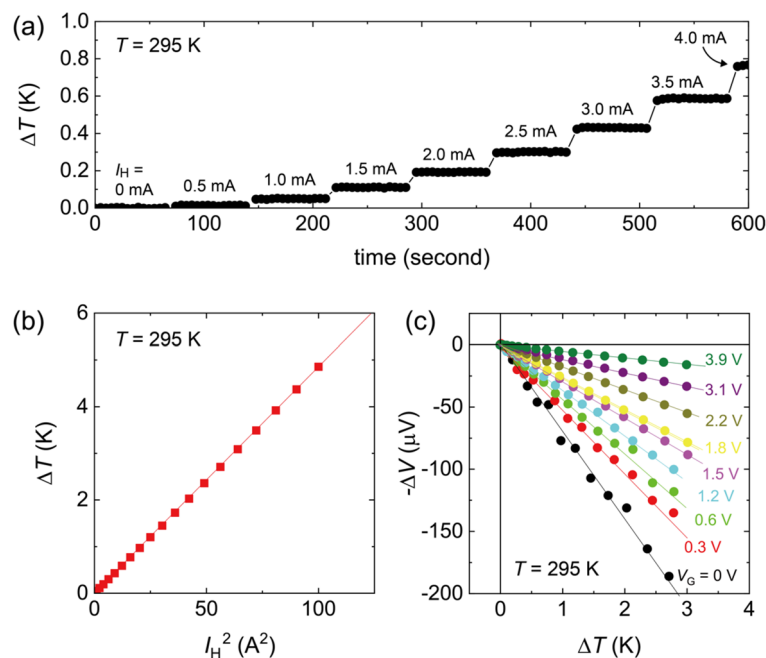


**Figure 1.** Structure and typical transistor operation of ion-gated device based on  $\text{WO}_3$  thin film. **(a)** Schematic device structure to measure the Seebeck effect under gate voltage  $V_G$ . In this configuration, the resistance and the Seebeck coefficient are simultaneously measured. Here, Th1(Th2),  $T$ , and  $\Delta V$  stand for the resistive thermometer, temperature, and thermoelectric voltage, respectively. A drop of an ionic liquid was deposited to cover the  $\text{WO}_3$  channel and the gate electrode. See the “[Experimental section](#)” for more details of the device structure. **(b)** Optical image of  $\text{WO}_3$  device with ionic liquid on top. **(c)** Schematic diagram of alignment of ions under  $V_G$ . When a positive  $V_G$  is applied to the gate electrode, the cations align on the surface of the  $\text{WO}_3$  thin film to form the electric double layer, which could trigger both the electrostatic carrier accumulation and electrochemical doping. **(d)** Typical transfer characteristics (drain-source current  $I_D$  versus  $V_G$ ). The values of  $I_D$  increases with increasing  $V_G$ , showing that the electron carriers are doped under positive  $V_G$ . The drain voltage  $V_D$  was 0.1 V.

In this study, we present the gate control of thermoelectric properties in  $\text{WO}_3$ , a functional oxide semiconductor that has been attracting attention<sup>28–34</sup>. Although thermoelectric measurements in  $\text{WO}_3$  and related materials have been conducted especially in the last decade<sup>28,35</sup>, basic characteristics such as  $n$  and  $T$  dependences have not been investigated systematically, which makes  $\text{WO}_3$  the best choice to study the effect of electrolyte gating. We synthesized  $\text{WO}_3$  thin films with the thickness of 30 nm on a substrate of yttria stabilized zirconia (YSZ). The synthesis process and the X-ray diffraction (XRD) data (see Supplementary Figure S1) were reported elsewhere<sup>36</sup>. An electric double layer transistor structure was fabricated by depositing a drop of an ionic liquid on the  $\text{WO}_3$  thin film, as shown in Fig. 1a and b. We systematically investigated the thermoelectric power factor of  $\text{WO}_3$  and mapped the data for a wide range of  $T$  and  $V_G$ . The results demonstrate how the thermoelectric properties develop against carrier doping, providing a solid guideline for the investigation of much higher thermoelectric performance in  $\text{WO}_3$ .

## Results and discussion

The details of the device structure and the concept behind its fabrication are summarized in Fig. 1. The device was patterned using the standard photolithography technique. As seen in Fig. 1a, b, and Supplementary Figure S2, a drop of the ionic liquid covered the  $\text{WO}_3$  thin film and the gate electrode, forming the electric double layer on the surface of  $\text{WO}_3$ . Figure 1c schematically shows that the application of the positive gate bias causes the cations align on the surface of  $\text{WO}_3$ , inducing a strong electric field on the interface. A typical transfer characteristic ( $V_G$  dependence of the drain source current  $I_D$ ) at 297 K is given in Fig. 1d, suggesting that electron carriers were induced under the positive gate bias. The hysteresis was observed possibly due to the slow re-formation of ions against  $V_G$ . Two resistive thermometers and a heater were prepared by the metal evaporation on the same substrate. The heater was placed in the immediate vicinity of  $\text{WO}_3$  to induce a thermal gradient along the channel. The local temperatures were monitored using the two thermometers, Th1 and Th2, and the thermoelectric voltage  $\Delta V$  was measured using the electrodes connected to both ends of the channel (See Supplementary Notes). Therefore, the device structure prepared for this study allows for the evaluation of thermoelectric properties under the application of gate electric field (See “[Experimental section](#)”)<sup>37</sup>.

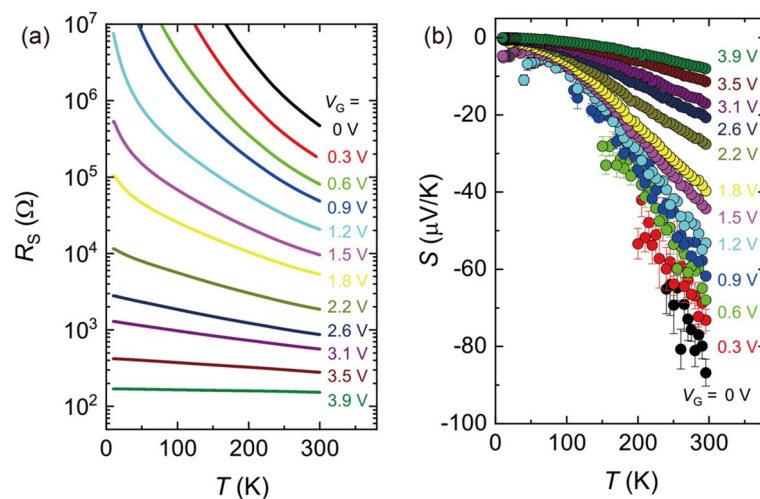


**Figure 2.** On-chip thermoelectric measurements of  $\text{WO}_3$  thin film. (a) Temperature difference  $\Delta T$  for different heater current  $I_H$ . When  $I_H$  was applied to the heater in Fig. 1a,  $\Delta T$  was induced between the edges of the channel due to the Joule heating of the heater. The values of  $\Delta T$  increased with increasing  $I_H$ . (b) Heater power dependence of  $\Delta T$ . The values of  $\Delta T$  linearly increased against  $I_H^2$ , confirming that the temperature gradient on the sample is solely attributed to the Joule heating of the heater. (c) Thermoelectric voltage  $\Delta V$  under  $\Delta T$  in  $\text{WO}_3$  thin film. The measurements were performed at 295 K. The slope of the  $\Delta V - \Delta T$  plot was systematically suppressed with increasing  $V_G$ .

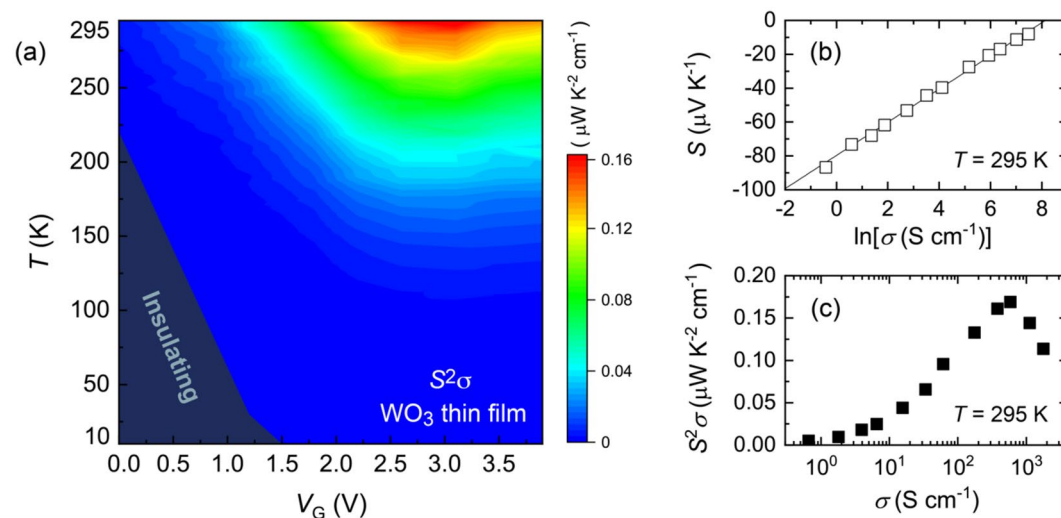
The thermoelectric effect was measured in this on-chip device structure (Fig. 1a and b) and systematically controlled under the gate bias. Figure 2a shows the temperature difference  $\Delta T$  between Th1 and Th2 (see Supplementary Figure S2) for different values of the heater current  $I_H$ . The values of  $\Delta T$  showed a stepwise increase with increasing  $I_H$ ;  $\Delta T$  was stable for a fixed value of  $I_H$ . It was also confirmed from Fig. 2b that  $\Delta T$  was proportional to  $I_H^2$ , validating that the thermal gradient on the  $\text{WO}_3$  thin film was induced solely by the Joule heating of the heater. Figure 2c shows the  $\Delta V - \Delta T$  plot of the  $\text{WO}_3$  thin film for different  $V_G$  at 295 K. The values of  $\Delta V$  linearly increased with  $\Delta T$ , indicating that the thermoelectric effect was correctly measured. The slope of the  $\Delta V - \Delta T$  plot was continuously suppressed with increasing  $V_G$ , which shows that the absolute values of  $S$  were suppressed. It is worth noting that the change of the thermoelectric response seen in Fig. 2c is consistent with the gate induced  $I_D$  modulation seen in Fig. 1d. Generally, in semiconductors,  $|S|$  is suppressed by the shift of the Fermi level to higher energy regions<sup>38</sup>. Thus, both results in Figs. 1d and 2c are the direct outcome of the gate-induced electron doping into the  $\text{WO}_3$  thin film.

The gate-induced carrier doping is much clearly illustrated in the  $T$  dependence measurements of the electrical and thermoelectric transports. Figure 3a shows the  $T$  dependence of the sheet resistance  $R_s$  of the  $\text{WO}_3$  thin film for different  $V_G$ . When  $V_G = 0$  V,  $R_s$  showed a large value of  $\sim 0.5$  M $\Omega$  at 295 K and semiconducting behavior against  $T$ . With increasing  $V_G$ ,  $R_s$  systematically decreased, accompanied by a transition from an insulating to a metallic state<sup>33,36</sup>. The lowest value of  $R_s$  obtained here was  $\sim 200$   $\Omega$  for  $V_G = 3.9$  V, which is comparable to the previous reports on ion-gated  $\text{WO}_3$ <sup>30,31,36</sup>. As shown in Fig. 3b, we simultaneously evaluated the thermoelectric response of  $\text{WO}_3$  with the measurement of  $R_s$ . The values of  $S$  were gradually suppressed with increasing  $V_G$  in the entire measured  $T$  range. For low  $V_G$  values,  $S$  was obtained only at high temperatures because the resistance between the voltage probe for  $\Delta V$  measurements including the contact resistance became too high ( $> \sim$  M $\Omega$ ), which made it difficult to reliably measure  $\Delta V$  at low temperatures. For large  $V_G$  values,  $S$  approached zero with decreasing  $T$ , which is typical behavior in metallic semiconductors<sup>38</sup>. Here we note that the systematic modulation of  $S$  in bulk  $\text{WO}_3$  has never been realized by conventional chemical doping method; the electric double layer doping is a unique approach to explore the thermoelectric properties of semiconductors.

The overall thermoelectric property of the  $\text{WO}_3$  thin film is electrically visualized in a wide  $T$  and  $V_G$  space. Figure 4a shows the contour plot of the thermoelectric power factor  $S^2\sigma$ , using the data from Fig. 3. The electrical conductivity  $\sigma$  was estimated as  $\sigma = 1/(d \times R_s)$ , where  $d$  is the thickness of the thin film,  $\sim 30$  nm. Here, we assume that the carrier accumulation layer thickness is the same with  $d$ . Generally, in field effect transistors, only the topmost layer as thin as several nanometers is affected by the gate electric field. However, it has been reported that electrolyte gating can uniformly dope electrons into the whole  $\text{WO}_3$  thin film, even for thick films having a thickness of 70 nm<sup>30,33</sup>. This suggests that the electron doping does not proceed electrostatically but occurs electrochemically in the ion-gated  $\text{WO}_3$  thin film<sup>30,33</sup>.



**Figure 3.** Gate induced transition from insulator to metal in  $\text{WO}_3$  thin film. (a) Temperature  $T$  dependence of sheet resistance  $R_s$  under gate bias. The values of  $R_s$  are suppressed by the application of gate voltage  $V_G$ .  $R_s$  showed insulating behavior at  $V_G=0$  V, whereas a flat  $T$  dependence was observed at  $V_G=3.9$  V. (b)  $T$  dependence of Seebeck coefficient  $S$  under gate bias. The values of  $S$  were gradually suppressed with increasing  $V_G$  in the entire measured  $T$  region. For low  $V_G$  values,  $S$  was obtained only at high temperatures because the resistance between the voltage probe for  $\Delta V$  including the contact resistance was too high ( $> \sim \text{M}\Omega$ ). For large  $V_G$  values,  $S$  approached zero with decreasing  $T$ , which is typical behavior in metallic semiconductors. The error bars correspond to the standard error in the linear fitting of  $\Delta V$ - $\Delta T$  plot.



**Figure 4.** Optimization of thermoelectric power factor in  $\text{WO}_3$  thin film. (a) Mapping of thermoelectric power factor  $S^2\sigma$  against temperature  $T$  and gate voltage  $V_G$ . The value of  $S^2\sigma$  increased with increasing  $V_G$  and showed a maximum at  $V_G \sim 3.1$  V. (b) Evolution of  $S$  against electrical conductivity  $\sigma$ . The values of  $S$  change linearly with  $\ln(\sigma)$ , which holds for a variety of semiconductors<sup>45</sup>. (c) Optimization of  $S^2\sigma$  of  $\text{WO}_3$  at room temperature.

The systematic modulation of the thermoelectric property in Fig. 4a suggests the continuous change in the electronic structure for the  $\text{WO}_3$  thin film. In the low  $V_G$  region,  $R_s$  increased with decreasing  $T$ , as shown in Fig. 3a, suggesting that the  $\text{WO}_3$  thin film is nondegenerate with an activation energy  $E_a$ <sup>39,40</sup>. The relationship between  $\sigma$  and  $T$  can be expressed with an Arrhenius type equation,

$$\sigma = \sigma_0 \exp\left(-\frac{E_a}{k_B T}\right) \quad (1)$$

where  $\sigma_0$  is a pre-exponential factor, and  $k_B$  is the Boltzmann constant. We applied Eq. (1) to the experimental curve of  $R_s$  for the most resistive state with  $V_G=0$ , according to the analysis conducted by Mattoni *et al.*<sup>40</sup>. The estimated value of  $E_a$  was  $\sim 106$  meV (see Supplementary Figure S5), which is one order of magnitude smaller

than the insulating gap of  $\text{WO}_3$ ,  $\sim 3.0 \text{ eV}^{28,41-43}$ . This suggests that, at  $V_G = 0 \text{ V}$ , a shallow donor level exists below the conduction band bottom due to oxygen vacancies in the film<sup>40</sup>. On the other hand, in the large  $V_G$  region,  $R_s$  was drastically suppressed and showed a flat  $T$  dependence, as shown in Fig. 3a. A systematic trend can be also seen in the thermoelectric response in Fig. 3b. The absolute value of  $S$  was gradually suppressed with increasing  $V_G$  due to the increase in the carrier doping level. These suggest that the  $\text{WO}_3$  thin film was highly doped and degenerate.

Our electrochemical approach modifies  $S$  of  $\text{WO}_3$  in a similar manner with the bulk chemical doping on other inorganic semiconductors. The relationship between  $S$  and  $\sigma$  in doped semiconductors is described by the following expression<sup>44-46</sup> as

$$S = -\frac{k_B}{e} \times \left( -\ln \sigma + \ln [N_c e \mu] + \frac{5}{2} + r \right) \quad (2)$$

where  $N_c$ ,  $\mu$ , and  $r$ , are the effective density of states for the conduction band, the carrier mobility, and the scattering parameter, respectively. Equation 2 suggests that  $S$  is proportional to  $\ln \sigma$  when the  $n$  dependence of  $\mu$  is moderate. This condition would hold in transition metal oxides with low carrier mobility at room temperature<sup>47,48</sup>. Actually, the linear relationship between  $S$  and  $\ln \sigma$  has been confirmed for a variety of semiconductors although the slope of the plot often varies from  $k_B/e$  for each material<sup>45</sup>. Figure 4b shows the change in  $S$  as a function of  $\sigma$  for the  $\text{WO}_3$  thin film, which demonstrated that a good linearity between  $S$  and  $\ln \sigma$  reasonably held in  $\text{WO}_3$  as well. When we plot  $S^2\sigma$  as a function  $\sigma$ , a peak was observed at  $\sigma = 585 \text{ S cm}^{-1}$ , as shown in Fig. 4c. The value of  $S^2\sigma$  was modulated and optimized through the continuous carrier modulation from an insulating to a metallic region, which has never been found in the studies of bulk  $\text{WO}_3$ . Here, it would be noted from Fig. 4a that the highest  $S^2\sigma$  would exist above room temperature. Expanding this approach toward much higher temperatures would be more useful for the investigation of novel thermoelectric materials.

## Conclusions

In conclusion, we revealed the systematic evolution of thermoelectric properties of  $\text{WO}_3$  against electrochemical carrier doping. Ion gating is a versatile technique in carrier doping and continuously modulated  $n$  of the  $\text{WO}_3$  thin film. The value of  $S^2\sigma$  was optimized to have  $\sim 0.16 \mu\text{W K}^{-2} \text{ cm}^{-1}$  in a highly electron-doped region, where  $\text{WO}_3$  exhibited the metallic electrical and thermoelectric transports. These findings could serve as an important guideline for exploring much higher thermoelectric performance in bulk  $\text{WO}_3$  and its related materials such as nanocrystalline  $\text{WO}_3$  and  $\text{WO}_3$ -based composites<sup>28,49,50</sup>. The current approach, the  $T - V_G$  (i.e.,  $n$ ) mapping of  $S^2\sigma$ , is applicable to various functional materials other than  $\text{WO}_3$  as well. Its synergetic combination with other approaches such as computation and machine learning would make that a powerful tool, leading to the emergence of high performance multifunctional thermoelectric materials hidden in unexplored materials groups.

## Experimental section

**Thin film growth.** The hexagonal  $\text{WO}_3$  film were grown on a YSZ(111) substrate by evaporating tungsten via RF sputtering with a RF power of 30 W. We followed the same procedure that was reported elsewhere<sup>36</sup>. The  $\text{O}_2$  partial pressure was controlled at  $\sim 2.2 \text{ mTorr}$  in the growth chamber, and the Ar partial pressure was maintained at  $\sim 8 \text{ mTorr}$ . Supplementary Figure S1 in Supplementary Information shows the XRD curves of out-of-plane and in-plane configurations, which confirmed that the hexagonal structure of  $\text{WO}_3$  was realized. The thickness of the film was controlled by the deposition time and was estimated with X-ray reflectometry. The film thickness was estimated to be  $\sim 30 \text{ nm}$ .

**Fabrication of ion gated device.** To control the electron carrier density in the  $\text{WO}_3$  thin film, an electric double layer transistor structure was fabricated, which is schematically shown in Fig. 1a. The optical image of the device is shown in Fig. 1b and Supplementary Figure S2. The channel length and width were  $300 \mu\text{m}$  and  $100 \mu\text{m}$ , respectively. The electrodes and the channel were patterned using standard photolithography techniques. All the electrodes required for the ion gating experiments were prepared by the evaporation of Cr/Au with the thickness of 3/35 nm. In addition, the resistive thermometers, Th1 and Th2, and a heater were also prepared using the same procedure. A small amount of an ionic liquid  $N,N$ -dimethyl- $N$ -(2-methoxyethyl)- $N$ -methylammonium bis-(trifluoromethylsulfonyl)-imide (DEME-TFSI) was deposited to cover both the channel and the gate electrode in order to conduct gating experiments with a side gate configuration. DEME-TFSI has the glass transition temperature at 182 K, below which the polarization of ions is fixed and cannot be modulated by  $V_G$ <sup>51,52</sup>. Throughout the experiments,  $V_G$  was applied and changed at 300 K.

**Thermoelectric measurements.** As schematically shown in Fig. 1a, we prepared a heater in close vicinity of one end of the  $\text{WO}_3$  channel; it produced a thermal gradient  $-\nabla T$  from the heater to the other edge of the channel<sup>37</sup>. Two resistive thermometers, Th1 and Th2, monitored the  $T$  differences, which was induced by the Joule heating of the heater (See Fig. 2). The values of  $S$  were estimated as  $-E/|\nabla T|$ , where  $E$  is the electric field induced through the Seebeck effect, by measuring the thermoelectric voltage between both ends of the  $\text{WO}_3$  channel. The calibration of resistive thermometers is described in detail in Supplementary Notes.

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## Author contributions

T.K., G.O. and K.T. synthesized the thin films. S.S. and T.K. fabricated the devices. S.S. and S.O. constructed the measurement system. S.S., K.T. and S.O. planned the study and carried out the electrical and thermoelectrical measurements. K.T. performed the XRD measurements and analyzed the data. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

## Competing interests

The authors declare no competing interests.

## Additional information

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