Nanoscale manipulation of the Mott insulating state coupled to charge order in $1\text{T-TaS}_2$

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The controllability over strongly correlated electronic states promises unique electronic devices. A recent example is an optically induced ultrafast switching device based on the transition between the correlated Mott insulating state and a metallic state of a transition metal dichalcogenide $1\text{T-TaS}_2$. However, the electronic switching has been challenging and the nature of the transition has been veiled. Here we demonstrate the nanoscale electronic manipulation of the Mott state of $1\text{T-TaS}_2$. The voltage pulse from a scanning tunnelling microscope switches the insulating phase locally into a metallic phase with irregularly textured domain walls in the charge density wave order inherent to this Mott state. The metallic state is revealed as a correlated phase, which is induced by the moderate reduction of electron correlation due to the charge density wave decoherence.

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The electron motion as represented by the bandwidth $W$ is strongly limited by the on-site Coulomb repulsion $U$ and a Mott insulating state develops by the localization of electrons near the Fermi energy ($E_F$) when $U/W$ exceeds a critical value. In the Mott insulator $1T$-TaS$_2$, a unique correlated insulating state is brought on by the spontaneous formation of the charge density wave (CDW) order, which substantially reduces the bandwidth $W$ when $U/W$ exceeds a critical value. The Mott phase becomes metallic upon increasing the temperature above $T_c$, where the CDW order melts into small domains textured by nearly commensurate domain wall networks. The metallic phase with the textured CDW can be generated not only by thermal excitation but also by chemical doping, photoexcitation, pressure, carrier injection and the reduction of thickness.

While these studies demonstrate the macroscopic controllability of the correlated Mott insulating phase by the CDW order, the origin of the excited metallic phase, the textured CDW phase, has been elusive. The metallicity was attributed to the metallic domain wall themselves, the metallization of the Mott-CDW domains due to the screening by free carriers of domain walls, or the change of the interlayer stacking order. However, there has been no experimental verification of these scenarios and no direct information on the electronic structure of the domain wall.

In the present study, we have succeeded in the nanoscale manipulation of the metal–insulator transition of the Mott insulating phase of $1T$-TaS$_2$. The metallic domains can reversibly be formed and erased with an atomically abrupt phase boundary by applying voltage pulse from a scanning tunnelling microscope (STM) tip. The spectroscopic measurements with atomic resolution rule out the existence of substantial free carriers along domain walls and unveil the correlated nature of the metallic phase.

**Result**

**Phase manipulations of the charge ordered Mott insulator.** Figure 1a illustrates the CdI$_2$-type crystal structure of $1T$-TaS$_2$ with Ta atoms octahedrally coordinated by S atoms. A unit layer consists of one Ta layer sandwiched between two S layers. Within the insulating phase at low temperature, $1T$-TaS$_2$ develops a long-range ordered CDW accompanied with the David-star distortion; 12 Ta atoms shrink towards the centre Ta atom and 12 S atoms expand away from the centre S atom.

Before the STM images of Figure 1d, e, g voltage pulses are applied with an amplitude of $+2.0$, $+2.10$ and $+2.35$ V with a duration of 100 ms at the central, upper-left (orange arrow in d) and lower-right (magenta arrow in f) sites, respectively. The dashed lines and arrows indicate the pulse-induced evolution of domains. Scale bar, 20 nm.
S layers swell up along the c axis. Such a deformation forms a commensurate $\sqrt{13} \times \sqrt{13}$ triangular superlattice ($a_{\text{CDW}} \sim 12.1 \text{ Å}$; Fig. 1b)\textsuperscript{21}. The lattice deformation brings about the charge localization at the centre of David-star, which is clearly resolved in the STM image of the CDW phase (Fig. 1c)\textsuperscript{22}.

The manipulation of the Mott-CDW phase was realized by applying a positive voltage pulse ($V_p \geq +2.0 \text{ V}$ and $\Delta t = 100 \text{ ms}$) within a typical STM set-up at $T = 4.3 \text{ K}$ (Fig. 1c; Methods). A pulse creates a textured CDW domain of a few tens of nanometres with an irregular domain wall network inside. The additional pulse nearby (solid arrows in Fig. 1d,f) can also reduce the size of a pre-existing textured CDW domain (dashed arrows in Fig. 1e,g). The higher a pulse voltage is, the bigger textured domain is formed. At this temperature, the large textured CDW domains are rather stable but the smaller one can be gradually reduced by the STM imaging with a moderate tunnelling current (Fig. 1h–k). This indicates the metastability of domain walls in the textured CDW phase (Fig. 1h–k).

Electronic structure of the textured CDW domain. The domain walls themselves are well resolved in the STM images (Fig. 2). The phase of the CDW changes abruptly across the domain walls as shown in Fig. 2d. They form disordered networks in contrast to the hexagonally ordered domain walls of the nearly commensurate CDW phase\textsuperscript{8,25}. This difference is apparently related to the quenched nature of the present textured CDW domains, being far away from the thermal equilibrium. The present case would be closer to the metallic phase induced by the laser excitation from the low temperature phase. This work called the metallic phase a hidden, thermodynamically unreachable, order state and assumed a triangular lattice of the domain walls without any microscopic information\textsuperscript{13}.

Most of the previous studies considered the conducting channel along a domain wall as the origin of the metallic property\textsuperscript{9,14,26}. Nevertheless, there has been a lack of direct spectroscopic information on domain walls. The present study rules out a dominating metallic nature of the domain wall denying most of the previous metallization scenarios for various textured CDW phases. In the STM image, the contrast of domain walls is suppressed close to $E_F$ (Fig. 2b) and enhanced at $V_T = +0.20 \text{ V}$ (Fig. 2c) with their own reconstruction different from a David-star. This indicates that a domain wall has little density of states near $E_F$ with its own electronic state at $+0.20 \text{ eV}$, which is more directly verified by the spatially resolved $dI/dV(r, V)$ curves (green curves in Fig. 3d,e). In addition, as shown in Fig. 2d, the common domain walls consist of even number (12 + 12) Ta atoms so that the number of electrons within the domain wall is even. Thus, the metallic character of the domain wall\textsuperscript{26} is not expected \textit{a priori}. This point will be detailed elsewhere.

The zero-bias conductance profile ($dI/dV(0, 0)$) in Fig. 3c distinguishes the metallic and insulating regions sharply. Note that it is peaked on the CDW maxima within the textured CDW domain. They originate from a pronounced spectral feature close to $E_F$ (white arrows in Fig. 3b, the grey regions in Fig. 3d and the black arrow in Fig. 3e). In addition, the tunnelling spectra in the textured CDW phase exhibit broad features centred at $-0.12$ and $+0.14 \text{ eV}$. They are similar to the Hubbard states in the Mott-CDW phase but shifted slightly towards $E_F$ with a substantial reduction of the intensity and a noticeable broadening (1.3–1.6 times larger than the bandwidth of Hubbard states). On the other hand, the top of the valence subband is also shifted substantially towards $E_F$ (orange arrows in Fig. 3e).

Electronic structure of the domain walls. The domain walls are well resolved in the STM images (Fig. 2). The phase of the CDW changes abruptly across the domain walls as shown in Fig. 2d. They form disordered networks in contrast to the hexagonally ordered domain walls of the nearly commensurate CDW phase. This difference is apparently related to the quenched nature of the present textured CDW domains, being far away from the thermal equilibrium. The present case would be closer to the metallic phase induced by the laser excitation from the low temperature phase. This work called the metallic phase a hidden, thermodynamically unreachable, order state and assumed a triangular lattice of the domain walls without any microscopic information.

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half filling. Our theoretical calculations based on spin-liquid physics (Methods) reveals a metal–insulator transition as a function of $U/t$, which captures the major experimental findings; the weakening and broadening of the Hubbard states together with the reduction of the Mott gap and the appearance of the sharp peak near $E_F$ (Fig. 3d). This peak was assigned as the coherent resonance of correlated electrons in the previous dynamic mean field theory calculations. These theories assure that the present textured CDW phase is a correlated metallic state close to the critical regime of the Mott transition ($U/t \approx 1.4$ in Fig. 3f and Supplementary Fig. 2). Deviating marginally from the theory, the coherent peak assigned in the experiment has an asymmetric shape and is located slightly below $E_F$. The previous STS results of a correlated metal showed very consistent spectra. While we attribute those deviations to the interference effect caused by the tunnelling current, a further study on the spectral details is desirable.

Figure 3 | Direct comparison of electronic structures between commensurate and textured CDW phases. (a) STM image of a crossover region between the commensurate and textured CDW phase ($I_t = 10$ pA, $V_s = -1.20$ V and $L^2 = 45 \times 45$ nm$^2$). Scale bar, 10 nm. (b) The differential conductance $dI/dV$ data measured along the arrow in a. The white dashed lines and arrows highlight the bandwidth broadening and the coherent peaks, respectively. (c) The magenta and blue curve each correspond to the STM topographic line profile (Z-height) and the $dI/dV$ intensity at $E_F$ along the given lateral positions. The domain walls (a point defect) are marked by green(orange) arrows. (d) $dI/dV(V)$ curves along the black arrow shown in b. Each curve is averaged within each CDW cluster and shifted for comparison. The spectra in green are for the domain walls in the textured CDW region. Coloured regions highlight the prominent peaks indicated by arrows in e. (e) Spatially averaged $dI/dV(V)$ curves of the insulating commensurate CDW phase (magenta), the metallic domain (blue) and the domain wall (green). The horizontal dashed lines mark the zero conductance. Blue (red), yellow and green arrows indicate the lower (upper) Hubbard state, the topmost valence subband, and the domain wall state, respectively. (f) Theoretically calculated spectral function for different correlation $U/t$ in a triangular lattice.

Figure 4 | Existence of the subdomains and the stacking order. (a) High- and (b) low-bias STM image of the textured CDW domain ($I_t = 10$ pA, $V_s = -1.20$ V and $+0.15$ V and $L^2 = 62 \times 62$ nm$^2$). The relatively large CDW domains (red dashed lines) within a texture CDW domain and the insulating subdomains (yellow solid lines) within them. The black arrows indicate the domain walls in the sublayers. Scale bar, 10 nm.
Discussion
What remains to be explained is the origin of the reduced correlation $U/t$ to drive the transition. The screening by free carriers of domain walls is not likely as shown by the lack of $E_F$ weight in the $dI/dV$ data. Instead, we note that the long-range CDW order is lost within the textured CDW domain. The reduced CDW order would naturally decrease the CDW band ordering. The reduced correlation energy $U(1)$ slave-rotor representation for the Mott transition discussed previously. In addition, the domain walls can act as the disorder potential, which can also drive the metallization of a Mott insulator. The low-bias images and the spectroscopy data indicate clearly that the reduced CDW order induces the reduced width $W$ and at the same time the reduced $U$, which drives the Mott-CDW state into the critical regime of a correlated metallic state.

While the STM images we showed so far only deal with the lateral CDW ordering, we also notice that the vertical CDW stacking order has a crucial impact on this transition. Figure 4 shows that a relatively large domain within the metallic domain has extra but weak domain walls inside (black arrows in Fig. 4a), which is assigned as the domain wall existing in the sublayer(s). The low-bias images and the spectroscopy data indicate clearly that this domain harbours insulating subdomains as defined by the sublayer domain walls. One can straightforwardly deduce that these subdomains correspond to different interlayer stacking of the CDW; the interlayer CDW stacking order is lost by the formation of the irregular domain wall networks in each layer except for those metallic subdomains. This suggests that not only the intralayer but also interlayer CDW order has to be taken into account to explain the reduced electron correlation for the Mott transition. The importance of the interlayer CDW stacking order was recently discussed, while the direct experimental evidence for the interlayer CDW stacking order was recently shown in the textured CDW state, we take the U(1) slave-rotor representation for possible spin-liquid physics at least in the intermediate temperature regime. It is straightforward to perform the saddle-point analysis based on an ansatz for spin-liquid physics, which leads us to confirm the existence of a metal-insulator transition from a spin-liquid-type Mott insulating state to a correlated metallic phase at critical value of $U/t$ (details shown in Supplementary Note 1).

Theoretical calculations. The CDW-Mott state in 1T-TaS$_2$ can be described by an effective one-band Hubbard model on the triangular lattice at half filling

$$H = -t \sum_{\langle ij \rangle} \left( c_i^\dagger s_i + c_i s_j \right) - \mu \sum_i n_i c_i^\dagger c_i + U \sum_i n_i n_i^\dagger,$$

where $c_i$ is an electron annihilation operator with spin $s$ at site $i$, identified with each centre of David-star. Hinton from the observation that the coherently peaked states emerge in the textured CDW state, we take the U(1) slave-rotor representation for possible spin-liquid physics at least in the intermediate temperature regime. It is straightforward to perform the saddle-point analysis based on an ansatz for the spin-liquid physics, which leads us to confirm the existence of a metal-insulator transition from a spin-liquid-type Mott insulating state to a correlated metallic phase at critical value of $U/t$ (details shown in Supplementary Note 1).

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