Decoupling the Lattice Distortion and Charge Doping Effects on the Phase Transition Behavior of VO₂ by Titanium (Ti⁴⁺) Doping

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The mechanism for regulating the critical temperature (T_C) of metal-insulator transition (MIT) in ions-doped VO₂ systems is still a matter of debate, in particular, the unclear roles of lattice distortion and charge doping effects. To rule out the charge doping effect on the regulation of T_C, we investigated Ti⁴⁺-doped VO₂ (TiₙV₁₋ₙO₂) system. It was observed that the T_C of TiₓV₁₋ₓO₂ samples first slightly decreased and then increased with increasing Ti concentration. X-ray absorption fine structure (XAFS) spectroscopy was used to explore the electronic states and local lattice structures around both Ti and V atoms in TiₓV₁₋ₓO₂ samples. Our results revealed the local lattice evolution from the initial anatase to the rutile-like structure around the Ti dopants. Furthermore, the host monoclinic VO₂ lattice, specifically, the VO₆ octahedra would be subtly distorted by Ti doping. The distortion of VO₆ octahedra and the variation of T_C showed almost the similar trend, confirming the direct effect of local structural perturbations on the phase transition behavior. By comparing other ion-doping systems, we point out that the charge doping is more effective than the lattice distortion in modulating the MIT behavior of VO₂ materials.

Vanadium dioxide (VO₂), a strongly correlated electron and metal-insulator transition (MIT) material, is an extremely interesting material suitable for many technological applications. The most striking features of VO₂ are its abrupt first-order MIT near 68°C, exhibiting a large change in the resistivity (up to five orders of magnitude) and the infrared transmittance/reflectivity in the sub-picosecond time scale. Simultaneously, the crystal structure transforms from a high-temperature tetragonal rutile (R) structure characterized by a single V−V distance of 2.85 Å and linear chains of edge-shared Jahn−Teller-distorted VO₆ octahedra, to a low-temperature monoclinic (M1) structure containing V⁴⁺−V⁴⁺ pairs forming a zigzag chain with alternating V−V distances of 2.65 and 3.12 Å and more distorted VO₆ octahedra (see Figure 1). Moreover, different external stimuli such as thermal, electrical, optical, or magnetic field can trigger the MIT in VO₂. These unique characteristics make VO₂ suitable for application such as smart windows, memory devices, uncooled microbolometers, electronic/optical switch devices, thermal/chemical sensors, etc.

The typical MIT temperature of the pure VO₂ is ~68°C, which unfortunately is not ideal for practical applications. Much effort has been devoted to regulate the MIT critical temperature (T_C) of VO₂. An effective route for regulating the T_C is doping with metal ions, in addition to adding internal/external stress or controlling the microstructure and defects. In the available literatures, it was shown that the T_C could be decreased by doping large dopants ions with higher-valence such as W⁶⁺, Mo⁷⁺ and Nb⁵⁺, or increased by small dopants ions with lower-valence (Al³⁺, Ga³⁺, and Ga⁵⁺)12,18–23. In this framework, the still open challenge is the deeper understanding of the intrinsic mechanism for the regulation of T_C by ions-doping, which have an important significance in VO₂ based functional devices.

The intuitive understanding is that the regulation of the T_C by metal doping inside the VO₂ lattice depends on the relative size and the relative valence of the dopant ion compared to that of the V⁴⁺ ion. The substitution may give rise to the changes of lattice structure and carrier density (or the conductivity) in parent VO₂. In the case of the W⁶⁺-doping, it has been considered that the W⁶⁺-doping can donate two extra-electrons to the VO₂...
host if considering the charge neutralization. The increase of the electron density affects the band structure and the activation energy, facilitating the transformation to the metallic phase\textsuperscript{23,26}. Moreover, each W dopant is doped substitutionally and disrupts the dimeric $V^{4+}$-$V^{4+}$ bond to form $W^{6+}$-$V^{3+}$ and $V^{4+}$-$V^{3+}$ pairs. This replacement destabilizes the monoclinic phase and thus lowers the energy barrier for the transition to the rutile structure\textsuperscript{26,28}. The different contributions finally result in the reduction of $T_C$. Other researchers focused on the influence of local structure perturbations induced by dopant ions\textsuperscript{23,28}. They suggested that the $T_C$ was not affected by the carrier density variation in VO\textsubscript{2}, but by the lattice distortion induced by the dopants with different ion radius. The change trend of $T_C$ can be correlated with the relative size of the dopant ion compared to that of the V$^{4+}$ ion. Booth et al\textsuperscript{28} claimed that the effect of W$^{6+}$ dopants on neighboring cells would be only structural. Based on EXAFS data, they concluded that a local rutile structure was formed around W$^{6+}$ dopants and a significant expansion in the [110] and [110] directions induced by W$^{6+}$ dopants broke the dimeric homopolar V-V pairs due to the decreasing $d_{\pi}$ orbital overlap, showing the lattice deformations towards the high-temperature rutile structure, and thus resulting in the reduction of $T_C$. Recently, a combination of XANES and EXAFS spectra has been used to characterize the electronic contribution and the local structure perturbations on the host VO\textsubscript{2} upon W$^{6+}$-doping, which indicates that both contributions are responsible for the reduced $T_C$\textsuperscript{29}.

The detailed mechanisms involved in the increase of $T_C$ by doping trivalent ions: Al$^{3+}$, Cr$^{3+}$ and Ga$^{3+}$ in VO\textsubscript{2} are complex to describe since more phases will be involved. Indeed a substitution of Al$^{3+}$ or Cr$^{3+}$ dopants for V$^{4+}$ in VO\textsubscript{2} gives rise to additional insulating phases: two specific monoclinic (M2 and M3) and a triclinic (T) phases, apart from the most common monoclinic (M1) phase\textsuperscript{29–31}.

From the literatures, considering the atomic radius and the valence states of each dopant, it is clear that the regulation of $T_C$ by doping ions is always associated with the lattice distortion and the carrier density change. The change in the carrier density of VO\textsubscript{2} inevitably occurs when the dopant ion is not tetravalent, which means that a donor/acceptor-type doping (i.e., charge doping) of the VO\textsubscript{2} band structure may occur. Nevertheless, which factor plays the critical role in the $T_C$ behavior is still unclear.

In order to reveal the intrinsic mechanism for the regulation of $T_C$ by ions-doping, it is mandatory to identify the roles of the lattice distortion and the charge doping caused by dopants, and which one plays the main role in this mechanism. To this purpose, considering that tetravalent ions-doping may rule out the carrier contribution of tetravalent dopant ions to neighboring vanadium ions, i.e., to minimize the charge doping effect, we choose Ti$^{4+}$ ion as the dopant. In Ti$^{4+}$-doped VO\textsubscript{2} system, it is imperative to clarify the behavior of Ti$^{4+}$ dopants and their influence on the host VO\textsubscript{2} lattice. To address the above issues, the most suitable tool is the X-ray absorption fine structure (XAFS) spectroscopy, because of its specific element selectivity and the sensitivity to the local structure (2–5 Å) around the absorber atoms as well as the electronic structure\textsuperscript{30}.

In this work, Ti\textsubscript{x}V\textsubscript{1-x}O\textsubscript{2} nanopowders were prepared by a hydrothermal method with a subsequent Ar annealing treatment. We systematically explored the electronic and local geometric structure of both the Ti dopants and the host V atoms in Ti\textsubscript{x}V\textsubscript{1-x}O\textsubscript{2} samples using XAFS spectroscopy at both Ti and V K-edges. A combined experimental and theoretical analysis of the mechanism of the regulation of $T_C$ by Ti-doping was performed for the first time. In addition, a comparative analysis of different ion-doping systems was also performed to identify the critical factors in regulating the $T_C$ in ions-doped VO\textsubscript{2} systems.

**Results**

The influence of Ti$^{4+}$-doping on phase transition properties of VO\textsubscript{2}. Figure 2 shows the DSC curves of Ti\textsubscript{x}V\textsubscript{1-x}O\textsubscript{2} samples with different Ti concentrations. At low Ti concentrations, as shown in Figure 2 (left), during the heating process the $T_C$ slowly decreases with increasing Ti concentration. It reaches a minimum at the Ti concentration of 2.8%. During the cooling process the starting phase transition temperature is almost unchanged, and after the starting phase transition a broad exothermic peaks subsequently appear, indicating the occurrence of a non-uniform phase transition. At the higher Ti concentrations, e.g., 5.0%, 6.1%, and 8.1%, as shown in Figure 2 (right), during the heating process the $T_C$ increases with increasing Ti concentration. The same trend of the $T_C$ is also observed during the cooling process. In addition, the double endothermic/exothermic peaks appear during the heating/cooling process, probably due to the non-uniform doing or the polydispersity in the size distribution\textsuperscript{19}.

Generally, the endothermic peaks appearing during the heating process are used to determine the $T_C$ of the ions-doped VO\textsubscript{2}. The $T_C$ of the Ti\textsubscript{x}V\textsubscript{1-x}O\textsubscript{2} samples slowly decreases reaching a minimum and then gradually increases with increasing Ti concentration, in agreement with data of Betelle \textit{et al} \textsuperscript{22}. Previous researches did not show a unique behavior of the Ti$^{4+}$-doping on regulating the $T_C$. 

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Figure 1 | The crystal structures of low-temperature monoclinic (space group P2\textsubscript{1}/c) and high-temperature tetragonal rutile (space group P4\textsubscript{1/2}mm) phases of VO\textsubscript{2}. 

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Most of researches reported the increase of T_C, however, only showed the increase of T_C in high Ti concentration (>=3%) due to weak ability of Ti dopants to regulate the T_C. In addition, it was found that the T_C saturated at around 80°C when the Ti doping concentration reaches to a higher level [35]. From the current results, it seems that the T_C decreases in initial low Ti concentration, while it increases gradually with further increasing Ti concentration in a certain concentration range.

Although Ti doping did not regulate the transition temperature significantly, Ti doping can effectively modify the thermochromic properties of VO_2, such as the decrease of hysteresis sloop width of phase transition, the improvement of the temperature coefficients of resistance, and the enhancement of visible transmittance (T_vis, 380–780 nm) and solar transmittance (T_sol, 240–2600 nm) [33-37].

The influence of Ti-doping on the crystalline structure of VO_2. Ion-doping inevitably modifies the host VO_2 lattice structure, e.g., the phase transformation from a monoclinic to a rutile structure in the N_xV_1-xO_2 systems (N = W, Mo or Nb) [39-41], and the formation of stabilized M2, M3, or T phases in the M_xV_1-xO_2 systems (M = Al or Cr) [29,31]. However, the Ti-doping did not change the kind of crystal lattice of Ti_xV_1-xO_2 samples, a local structure phase transition from the monoclinic to the rutile structure may occur in some regions of the samples with increasing Ti concentration. In addition, several diffraction peaks gradually shift to lower diffraction angles, e.g., the peaks in Figure 3b, pointing out upon Ti^{4+}-doping a continuous increase of the interplanar spacing due to the larger radius of the Ti^{4+} ion (0.0605 nm) compared to the V^{4+} ion (0.058 nm). The opposite trend was observed when VO_2 was doped with Al^{3+} ions (0.054 nm) [32].

The morphology and microstructure of Ti_xV_1-xO_2 samples. Figure 4a–e show SEM images of Ti_xV_1-xO_2 and undoped VO_2 samples after the Ar annealing treatment. Ti_xV_1-xO_2 samples are actually composed of nanoparticles (100–300 nm), compared with microparticles (1–10 μm) present in undoped VO_2 sample. Moreover, the Ti doping had a strong effect on the morphological evolution of Ti_xV_1-xO_2 samples. The Ti_xV_1-xO_2 nanoparticles gradually reduce their mean particle size with increasing Ti concentration, due to the reduced crystallization ability (i.e., enhanced heterogeneous nucleation process) of Ti_xV_1-xO_2 nanoparticles by Ti doping [35]. The same situation occurred in other ions-doped systems [21].

In Figure 4f, the Energy dispersive X-ray (EDX) fluorescence spectrum obtained from SEM analysis shows the Ti, V, O, and Si char-

Figure 2 | Comparison of DSC curves of Ti_xV_1-xO_2 samples and an undoped VO_2 (M1) sample during heating and cooling cycles.
acteristic peaks. Actually, the Si peak appears also due to the scattering induced by Si substrate. In Figure 4i, the EDS spectrum obtained from TEM analysis shows no Si peak since a Cu grid was used for supporting the sample, and clearly shows Ti, V, O, and Cu peaks. The Cu peaks are clearly due to the scattering induced by the Cu grid. Therefore, both EDS spectra obtained from TEM and SEM analysis confirm that Ti$_x$V$_{1-x}$O$_2$ nanoparticles contain only Ti, V, and O elements.

Figure 4g shows the TEM image of Ti$_x$V$_{1-x}$O$_2$ nanoparticles ($x = 5.0\%$). The corresponding SAED pattern (Figure 4h) is in agreement with the diffraction pattern along the [211] crystal axis of the M1 phase (JCPDS No. 72-0514), showing the monoclinic single-crystal nature of the Ti$_x$V$_{1-x}$O$_2$ nanoparticles. In addition, the measured interplanar spacings are 0.10–0.12 Å larger than theoretical values, due to the lattice expansion when Ti ions were incorporated into the VO$_2$ lattice.
**XAFS analysis.** To clarify the behavior of Ti dopants and their influence on the host VO₂, the local structures of both Ti and V atoms in the TiₓV₁₋ₓO₂ samples, as well as their chemical states, were systematically investigated by XAFS spectroscopy at Ti and V K-edges.

Figure 5a shows V K-edge XANES spectra of TiₓV₁₋ₓO₂ and undoped VO₂ (M1) samples. For vanadium oxides, the energy positions of the threshold, the pre-edge peak and the absorption-edge exhibit a monotonic dependence on the oxidation states of the absorber atoms according to Kunzl’s law. For TiₓV₁₋ₓO₂ samples (x = 0.6%, 1.7%, 8.1%), the energy positions of the threshold, the pre-edge peak and the absorption-edges are almost the same and coincide with that of the undoped VO₂ (M1), pointing out the tetravalent valence of V ions in the TiₓV₁₋ₓO₂ samples. In addition, the pre-edge peak can be used to evaluate the changes in the local symmetry of V atoms, due to its sensitivity to the local coordination environment of the absorber atoms and the electron density of d states. Pre-edge peak intensity increases with a lower local symmetry while decreases for a higher local symmetry of the absorber atoms. As an example, the pre-edge peak intensity is negligible in VO characterized by a regular octahedral symmetry (Oₖ) around the absorber V atoms, while increases if the local symmetry is lower than the Oₖ symmetry such as in VO₂, V₂O₅, and V₂O₃, reaching the maximum for vanadates with a tetrahedral coordination (Td). At low Ti concentrations (0.6% and 1.7%), TiₓV₁₋ₓO₂ samples show an increased pre-edge peak intensity. However, a decreased intensity occurs at high Ti concentration, e.g., at 8.0% Ti concentration, and the pre-edge peak intensity decreases back to close to that of VO₂ (M1). The change of the pre-edge peak intensity indicates that with increasing Ti concentration, the distortion of the VO₆ octahedra around V atoms firstly increases to a maximum from the initial VO₆ octahedra of VO₂ (M1) and then decreases back to the VO₆ octahedra of VO₂ (M1).

V K-edge EXAFS data confirm the evolution of the local structure around V atoms. Figure 5b and c show V K-edge EXAFS oscillations [k²γ(k)] and their Fourier transforms (FTs), respectively. In Figure 5b, the 8.1% Ti sample shows similar EXAFS oscillations with the undoped VO₂ (M1) sample, while 0.6% and 1.7% Ti samples show significantly different EXAFS oscillations respect to the VO₂ (M1). Likewise, in Figure 5c, the FTs curves clearly demonstrate a similar local structure around V atoms for the 8.1% Ti sample and the VO₂ (M1), in agreement with the theoretical spectrum of the VO₂ (M1), i.e., their FTs curves exhibit the four characteristic peaks of M1 phase: the two peaks at ~1.33 and 1.75 Å, corresponding to the first V–O coordination shell, and other two at ~2.15 and 2.95 Å associated to the V–V₁M and V–V₃M shells. On the contrary, the low Ti concentration samples (0.6% and 1.7%) show FTs curves significantly different with that of VO₂ (M1), compatible with local structures different from the standard M1 phase structure. Therefore, the local structure around V atoms deviates from the standard M1 phase structure first in the initial Ti doping process. With the further increase of the Ti concentration, the local structure around V atoms will return back to the M1 phase structure. This is accord with the change trend of VO₆ octahedra in above V K-edge XANES analysis.

To understand the intrinsic local structure change around the host V atoms within the doping process, we then focus on the local structure around Ti dopants. Figure 6a and b show Ti K-edge XANES spectra and their EXAFS oscillations [k²γ(k)] of TiₓV₁₋ₓO₂ samples, respectively, which both depict the evolution of the local structure around Ti dopants. The 0.6% and 1.7% Ti samples show similar XANES spectra with TiO₂ (A) except for the pre-edge structure (Figure 6a). When the Ti concentration increases to 8.1%, the XANES spectrum matches well with that of TiO₂ (R). This remarkable and systematic evolution also appears in the Ti K-edge EXAFS oscillations. As shown in Figure 6b, the 0.6% and the 1.7% Ti samples exhibit the characteristic EXAFS oscillations of TiO₂ (A) while the 8.1% Ti sample exhibits the characteristic EXAFS oscillations of TiO₂ (R). Therefore, Ti K-edge XANES and EXAFS data both indicate that the local structure around Ti dopants changes from the TiO₂ (A)-like to the TiO₂ (R)-like structure with increasing Ti concentration (see Figure 6c). Namely, at the initial low Ti concentration, the local anatase structure around Ti dopants is formed in the host monoclinic VO₂ structure, and subsequently a local rutile structure around Ti dopants is gradually formed with increasing Ti concentration. The local structure dynamics of Ti dopants ought to be responsible for the local structure change of the host V atoms. Moreover, the local rutile structure around Ti dopants perfectly account for the appearance of two peaks in the range 63.5° < 2θ < 66.0° in the XRD patterns at high Ti concentrations. In addition, the energy positions of the absorption-edges of the TiₓV₁₋ₓO₂ samples are constant and coincide
with those of TiO$_2$ (A) and TiO$_2$ (R), pointing out the tetravalent valence of Ti ions in the Ti$_x$V$_{1-x}$O$_2$ samples.

**Discussion**

Based on our XAFS results, it seems that the doping VO$_2$ with Ti$^{4+}$ ions has a position between clearly donor- and acceptor-like defects, due to the same valence between the Ti$^{4+}$ dopant and the V$^{4+}$ ion. To confirm this scenario, we performed electron density of states (DOS) calculations using the projector augmented wave (PAW) method implemented in the Vienna *Ab-initio* Simulation Package (VASP)

The PBE form of the generalized gradient approximation (GGA) and the DFT scheme$^{2}$ (U = 4.0 and 6.6 eV for V and Ti atoms, respectively) were used to describe the electron exchange-correlation interaction. A $2 \times 2 \times 1$ supercell with 48 atoms containing 15 V atoms, 32 O atoms and 1 Ti atom, corresponding to $\sim$6.25% Ti concentration was used. For comparison, we also performed the similar DOS calculations of W-doped VO$_2$, except $U = 0$ eV for W atom.

Figure 7 compares the total and partial DOS of undoped VO$_2$, 6.25% Ti-doped VO$_2$, and 6.25% W-doped VO$_2$. It can be observed that below the Fermi level, the total DOS and the partial V-3d/O-2p DOS do not show clear differences between the undoped VO$_2$ and the 6.25% Ti-doped VO$_2$ (Figure 7a and 7b), indicating the negligible influence of Ti$^{4+}$ dopants on the valence band structure of VO$_2$. But for W-doped VO$_2$, the DOS (Figure 7c) shows the Fermi level in the bottom of the conduction band, indicating the electron doping of VO$_2$ due to a charge transfer between W$^{6+}$ and V$^{4+}$ ions, in accord with the detection of reduction of V$^{5+}$ to V$^{3+}$ ions in W-doped VO$_2$. Therefore, from the above DOS calculations, we confirm that the incorporation of Ti$^{4+}$ ions in VO$_2$ basically do not induce a donor or acceptor doping of the VO$_2$ band structure due to the lack of a charge transfer between Ti$^{4+}$ and V$^{4+}$ ions. This DOS calculations result can match with the constant valences of V and Ti ions from above XANES spectra, and the XPS spectra reported by Chen et al.$^{37}$, which also showed the unchanged valence states of V$^{5+}$ and Ti$^{4+}$ in Ti-doped VO$_2$. All of these indicate that the carrier concentration experience no significant change in Ti$_x$V$_{1-x}$O$_2$ system. Accordingly, the charge doping effects caused by Ti$^{4+}$ doping almost can be ruled out, and only the local structure perturbations can be considered to...
Table 1 | Comparison of the radius of different doped ions with V$^{4+}$ ion

| Element | Valence state | Ionic radius (pm) |
|---------|--------------|------------------|
| V       | +4           | 58               |
| Ti      | +4           | 60.5             |
| Nb      | +5           | 64               |
| Mo      | +6           | 59               |
| W       | +6           | 60               |

The ionic radius data was quoted from the literature of Shannon.65

have the dominated effect on the regulation of $T_c$ in $\text{Ti}_x\text{V}_{1-x}\text{O}_2$ nanopowders samples. Therefore, the two trend of the local structure change around $V$ atoms induced by Ti-doping (from above V K-edge XAFS spectra), roughly corresponds to the two observed changes of the $T_c$. On the basis of experimental and theoretical results, we consider that the mechanism of the regulation of $T_c$ by $\text{Ti}^{4+}$ doping is mainly associated with the local structure perturbations induced by $\text{Ti}^{4+}$ dopants.

Our DSC results showed that the $T_c$ slightly decreases in low Ti concentration level (within about 3% Ti concentration), while a small amount of W doping (within 3.4% W concentration) will result in a distinct $T_c$ decreasing (Figure S1). Previous literatures also showed that the ability to regulate the $T_c$ in the $\text{Ti}_x\text{V}_{1-x}\text{O}_2$ system was smaller than the $\text{M}_x\text{V}_{1-x}\text{O}_2$ ($\text{M} = \text{W}^{6+}, \text{Mo}^{6+}$ or $\text{Nb}^{5+}$) systems.12,19,26,33,36,43

Table 1 shows the radius of several dopant ions and the $V^{4+}$ ion. $\text{Ti}^{4+}$ and $\text{W}^{6+}$ ions have the radius close to each other, but $\text{W}^{6+}$ ions have the considerably larger ability to regulate the $T_c$ of VO$_2$, i.e., a reduction in $T_c$ by 20 to 30 K at.% W for the bulk and by ~50 K at.% W in nanostructures.11,24,34,44

In the case of W-doping, the VO$_6$ octahedra shows a distortion trend with increasing W concentration, until the concentration of 1.7% (Figure S2). However, it cannot be suggested that the gradually decreasing of $T_c$ (Figure S1) is mainly attributed to the distortion of VO$_6$ octahedra since the electron doping of $W^{6+}$ ions in VO$_2$ is also conducive to the reduction of the $T_c$.11,18,26. In $\text{Ti}_x\text{V}_{1-x}\text{O}_2$ system, the charge doping effects caused by Ti$^{4+}$ doping can be ignored, i.e., decoupling the lattice distortion and charge doping effects on the phase transition behavior of VO$_2$.

Due to the large ion size, when W or Ti atoms occupy the V sites, the substitution doping will yield the detwisting of the nearby monoclinic VO$_2$ lattice in the similar way especially within low doping concentration. This type of lattice detwisting induces the decreasing $V-V$ pairs tilting, depairing of dimerized $V-V$ pairs, and distorting the VO$_6$ octahedra in surrounding monoclinic structure.16,24,28

The distortion of VO$_6$ octahedra induced by ions-doping can change the hybridization between V 3$d$ and O 2$p$ orbitals, resulting in the shift of $\pi$ and $\pi^*$ bands near the Fermi level in the band structure of VO$_2$, that finally changes the energy gap.24

The above comparative analysis suggested us that the charge doping (i.e., donor/acceptor doping) in VO$_2$ plays a more fundamental role in the regulation of the $T_c$, although the local structure perturbations induced by dopants has an inevitable influence on the $T_c$. Actually, the smaller ability to regulate the $T_c$ in the $\text{Ti}_x\text{V}_{1-x}\text{O}_2$ system is most likely due to the negligible charge doping effect upon $\text{Ti}^{4+}$-doping.

In conclusion, $\text{Ti}_x\text{V}_{1-x}\text{O}_2$ nanopowders exhibit two trends for the $T_c$; the $T_c$ slightly decreases to a minimum and then increases with increasing Ti concentration. The behavior of $\text{Ti}^{4+}$ dopants and their influence on the host VO$_2$ lattice has been explored for the first time by XAFS spectroscopy and theory calculations. With increasing Ti concentration, the local structure around Ti dopants displays an evolution from a local anate to a rutile-like structure, which induces a perturbation of the nearby monoclinic VO$_2$ lattice. As a result, the distortion of the VO$_6$ octahedra in the monoclinic VO$_2$ lattice becomes more and more distinct at the initial doping stage. With the further Ti doping, the distorted VO$_6$ octahedra will return to the initial VO$_6$ octahedra together with the appearance of the local rutile structure around Ti dopants. The structure evolution induced by Ti doping is actually considered responsible for the observed trends of $T_c$ in the DSC tests.

Finally, we should underline that, although the current Ti-doping research show a direct influence of the local structure perturbations induced by Ti dopants on the regulation of $T_c$, this modulation effect of the Ti doping strategy on VO$_2$ materials is not such pronounced, in particular if we consider the variation of the phase transition temperature. By comparison of the ability to regulate the $T_c$ in different ions-doping systems, such as W$^{6+}$ dopants, we may claim that the charge doping for VO$_2$ may play a critical role in the effective regulation of the $T_c$ in no tetrahedral ions-doped VO$_2$ systems.

**Methods**

**Synthesis of $\text{Ti}_x\text{V}_{1-x}\text{O}_2$ nanopowders.** The Ti-doped VO$_2$ ($\text{Ti}_x\text{V}_{1-x}\text{O}_2$) samples were synthesized by a hydrothermal method followed by an annealing treatment. The different amount of Ti (SO$_4$)$_2$ aqueous solution (0.01 M) were added to V(acac)$_2$ aqueous solutions under vigorous stirring. The value of $x$ in $\text{Ti}_x\text{V}_{1-x}\text{O}_2$ refers to the Ti atomic percent in the feed. Each of the final solutions was transferred to the Teflon cup, which was later heated in a sealed autoclave at 200°C for 24 hours. After the hydrothermal reaction, the precipitate was collected by centrifugation, washed with copious amounts of deionized water, N, N-dimethylformamide (DMF) and ethanol, and then dried in vacuum at 60°C. Finally, $\text{Ti}_x\text{V}_{1-x}\text{O}_2$ samples were calcined under an argon (Ar) atmosphere at 700°C for 6 hours.

**Characterization.** The crystalline structure of the $\text{Ti}_x\text{V}_{1-x}\text{O}_2$ samples was determined by X-ray diffraction (XRD) using a theta/theta rotating anode X-ray Diffractometer (model: TTR-III, Cu Kα radiation). The morphology and the microstructures were characterized with a Field-emission scanning electron microscope (FE-SEM, JEOL JSM-6700F) and transmission electron microscopy (TEM, JEM-2010HR). The phase transition behavior was studied by differential scanning calorimetry (DSC, Q2000).

**XAFS spectra measurement and analysis.** XAFS spectra were measured at ambient temperature (~24°C) at the beamline 1W2B of the Beijing Synchrotron Radiation Facility (BSRF), using a Si(111) double crystal monochromator with an energy resolution (AE/E) of <1×10$^{-6}$ eV. Ti and V metal foils were respectively used for calibrating energy at the Ti K- and V K-edges. Ti K-edge XAFS spectra were collected in the fluorescence mode using a Lytle detector, while V K-edge XAFS spectra were collected in the transmission mode using ionization chambers filled with Ar/Ne. V K- and Ti K-edges XAFS spectra were collected in the energy range of 5288–6351 and 4768–5419 eV, respectively. In the data processing procedure, the experimental absorption data were processed using the ATHENA module (version 0.8.0.34) implemented in the IFEFFIT package.66–68

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