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ARTICLE TYPE

A Synergy Effect of Sodium on the Phase Transition of Tungsten-doped Vanadium Dioxide

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A synergy effect of sodium on the metal-insulator transition temperature reduction of tungsten doped vanadium dioxide is noted. With the assistance of sodium, doping with tungsten yields an extra depression in the phase temperature of 6-12°C over that of 20-26°C per at% of tungsten.

Vanadium dioxide (VO₂), owing to its inherent insulator-metal transitions (MIT) properties¹, has drawn continuous attention as a remarkable candidate for “smart” optical and electrical materials, such as thermochromic coatings and temperature-sensing switchings.² However, the critical temperature (T_C) of its MIT at ~67°C restricts its further applications in those fields, which usually require the regulation of T_C over a wider range, especially to room temperature efficiently. Amongst several strategies (doping, stress and finite size) to regulate the T_C for VO₂ MIT, doping with some donor impurity atoms is the most effective and readily realized. In particular, substitutional doping of the vanadium (V) with tungsten (W) is the most prominent, which yields a reduction of T_C in the phase transition by ~20 to 26 °C per at% of W.³ The reason was proved to originate from the charge transfer from W ions to V weakens the V-V pairs.⁴ In our earlier work, W-doped vanadium dioxide have been successfully synthesized by thermal reduction and annealing.⁵ However, it always requires relative high dose of W dopants to realize efficient reduction of T_C at room temperature. In this case, more structural distortion and impurities are brought to impact materials performance negatively.^{6,7} To solve this problem, co-doping with W and other elements, has been investigated recently.⁸ Such as, Co-doping with W and Mo showed a superior property in lowering phase transition temperature, and W-F and W-Ti co-doped VO₂ having better infra-red transmittance and electrical resistivity.⁹ Tang et al. discovered a charge compensation between W ion and V ion due to replacing the V⁴⁺ sublattice with W⁶⁺ in VO₂ system. Nevertheless, alkali elements (such as sodium) never have been considered as co-doping of VO₂ with W, although alkali metals have been widely used considering their capability of charge compensation on rare earth doped phosphor materials, which generally induce the enhancement of the intensity of the luminescence.¹⁰ Therefore, it is feasible that the charge transfer of W doped VO₂ system would be influenced via co-doping with sodium, and some worthwhile results would be expected. In this communication, we present our results to show the reduction of T_C of VO₂ induced by W and sodium co-doping.

Herein we have tried to use sodium tungstate (Na₂WO₄) as the full dopant that both sodium (Na) and W elements could be introduced into the final product via high temperature melt and thermal reduction. This is not possible for several reported approaches, such as hydrothermal synthesis and thermolysis, where sodium ions were generally removed during washing step.^{5, 6} Notably, it is found that Na₂WO₄ as a dopant makes doping the V sublattice with W lower the phase transition temperature more efficiently. This is the first time Na metal used as co-doping for W-doped VO₂, which plays a vital role in the process of the phase transition.

Doped VO₂ powders were characterized via X-ray diffraction (XRD). The XRD patterns of doped VO₂ with various extents of Na₂WO₄ are depicted in Figure 1(a). All of the main diffraction peaks can be indexed to monoclinic VO₂ (M1) (space group: *P21/c*, *a*=5.752 Å, *b*=4.538 Å, *c*=5.383 Å, Joint Committee on Powder Diffraction Standards (JCPDS) No. 043-1051). The strong intensity of the (011) points to the preferential growth direction of these crystal structures, as noted formerly for VO₂ materials prepared by solvothermal, thermolysis, etc.^{5,11} From the detail of XRD patterns, with increasing the adding amount of Na₂WO₄, the 2θ value of the most prominent reflection was shifted from the (011) plane of M1 down to the (110) reflections attributed to the R phase (space group: *P42/mnm*, *a*=4.554 Å, *c*=2.855 Å, JCPDS No. 044-0253), as depicted in figure 1(b). As shown in Figure 1(b), the rutile phase has been observed in the samples doped with high amount of Na₂WO₄ (more than 1 at. %) at room temperature. Raman spectroscopy analysis (Figure S1 ESI†) confirm further the stabilization of the rutile phase at room temperature. Additionally, there is no any diffraction peaks assigned to other vanadium compound or tungsten compound in XRD patterns of all the samples. This result indicates that there is no any foreign crystalline phase matter in this doping process. The characteristic diffraction peaks of the XRD patterns shown in the Figure S2 ESI† are assignable to the monoclinic phase for undoped, doped VO₂ samples with other dopants were synthesized by the same approach, suggesting as a monoclinic structure

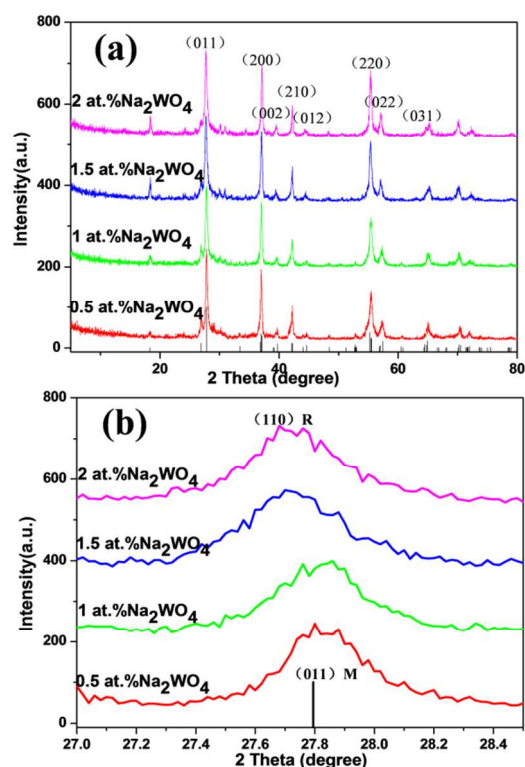


Figure 1 (a) X-ray diffraction pattern measured at room temperature for doped VO₂ samples with different Na₂WO₄ addition. (b) A magnified version of the XRD data with different Na₂WO₄ doping contents in the 27.0° ≤ 2θ ≤ 28.5° range. The vertical lines indicate the (011) peak positions expected for monoclinic VO₂ from JCPDS Card no. 043-1051.

In order to investigate the detailed compositions of doping VO₂ powders, X-ray photoelectron spectroscopy (XPS) measurements were performed. Figure 2 shows the XPS pattern of the 1.5 at.% Na₂WO₄ doped VO₂ sample synthesized by our ammonia reduction scheme. According to the spectra in Figure 2(a), elements, such as carbon, vanadium, oxygen, tungsten and sodium are observed where the carbon may be attributed to surface contamination.¹² while the peaks assigned to W_{4f} and Na_{1s} are quite weak due to the low doping content. On the other hand, vanadium, oxygen and tungsten are studied by fitting the high-resolution XPS spectra of V_{2p}, O_{1s} and W_{4f} respectively. The peaks are shown as in Figure 2(b), at 517.4 eV and 516.0 eV are associated with V_{2p_{3/2}}, and the peaks at 524.8 eV and 523.1 eV are assigned to V_{2p_{1/2}}. According to the spectra, two clear vanadium valence (V⁴⁺ and V⁵⁺) states are observed due to the oxidation of V⁴⁺ on the surface of the sample.¹² The result of O_{1s} has been shown in figure 1(c). The binding energy at 530.1 eV attributed to VO_x. While the other two peaks located at higher binding energies (around 531.8 and 533.9 eV) are attributed to OH or H₂O. In Figure 2(d), the peaks at 37.1 eV and 35.0 eV are attributed to W_{4f_{5/2}}⁶⁺ and W_{4f_{7/2}}⁶⁺,¹³ separately, indicating the valence of W⁶⁺ in the doped VO₂ powder, which is in agreement with the result of Tang et al.¹⁰

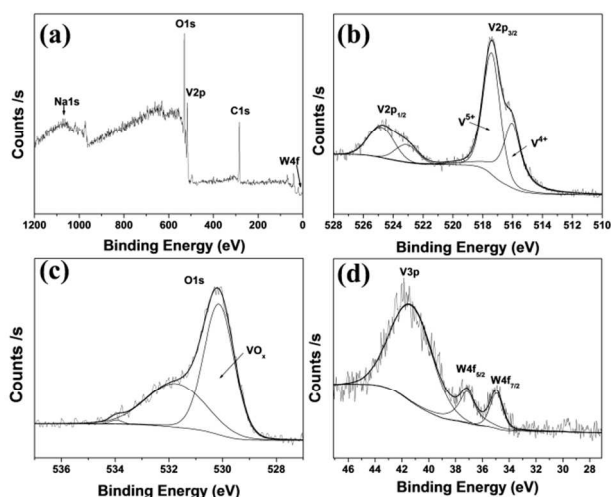


Figure 2 X-ray photoelectron spectroscopy pattern of 1.5 at.% of Na₂WO₄ doped VO₂ sample: (a) wide scan spectra, high-resolution XPS profiles of (b) V_{2p}, (c) O_{1s} and (d) W_{4f} for 1.5 at.% of Na₂WO₄ doped VO₂.

The phase transition temperature of doped VO₂ with different extents of Na₂WO₄ using is evidenced by the differential scanning calorimetry (DSC) curves shown in Figure 3(a). It indicates that the T_C for the monoclinic → tetragonal transition is reduced from 49.0 to 4.3°C, with increasing the concentration of Na₂WO₄ from 0.5% to 2.0%, the linear fitting curve is obtained as shown in Figure 3(b) giving rising to the reduction efficiency is about 32°C per at% of W. This result an excellent among reported data.

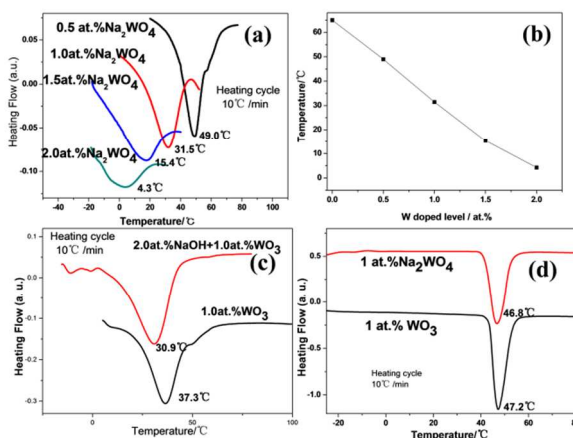


Figure 3 (a) DSC curves of doped VO₂ samples with different amount of Na₂WO₄; (b) Relationship between Na₂WO₄ adding level and the phase transition temperature of VO₂; (c) DSC curves of doped VO₂ sample with 1 at% WO₃ added and VO₂ sample doping with 2 at.% NaOH and 1 at% WO₃ successively; (d) DSC curve of the 1.0 at.% Na₂WO₄ doped and 1.0 at.% WO₃ doped VO₂ samples have been annealed in N₂ at 700 °C for 5h, and further annealed in N₂ at 1100 °C for 2h.

As a comparison, the sample doping with WO₃ exhibits quite different results shown in Figure 3(c) for 1 at.% WO₃ doping sample. The MIT was only shifted down to ~37.3°C in the heating cycle, which was about 6°C higher than doping with 1 at.% Na₂WO₄. On the other hand, VO₂ samples with only doping sodium hydroxide (NaOH) showed similar thermal behaviour compared with pure VO₂ sample (Figure S3 ESI†),

indicating the single element of Na barely affects the phase transition temperatures. Interestingly, the sample, doped successively with 2at.% NaOH and 1 at% WO₃, shows a peak attributable to the phase transition at ~30.9 °C during the heating cycles, which is equivalent with the effect of doped with 1at.% Na₂WO₄. Accordingly, all above results demonstrated that Na dopant play a role to facilitate the effect of W doped in the phase transition of VO₂.

To further exploring how Na dopant affects the MIT properties, the existing state of Na ions in samples is the key problem. In this case, XRD patterns for V₂O₅ precursors obtained upon the fusion of V₂O₅ with different tungsten doping agents are firstly explored (Figure S4 ESI†). It is found that no segregated WO_x phases are detected in doped V₂O₅ precursor. However, it exhibits three characteristic diffraction peaks (asterisks) assignable to the monoclinic phase of Na_{0.33}V₂O₅ (JCPDS-48-0382) for the sample doping with 1 at% Na₂WO₄, suggesting that Na ions just intercalate into layers of V₂O₅ precursors not replacing V as W atom did.¹⁴ Moreover, only diffraction peaks corresponding to the phases of VO₂ are observed in XRD patterns of all doped VO₂ samples, suggestive of the formation of homogeneous solid-solutions. Similarly, only diffraction peaks corresponding to the phases of VO₂ is observed in XRD patterns of doped V₂O₅ precursor, suggestive of the formation of homogeneous solid-solutions. It indicates Na atoms may be interstitial atoms in VO₂ solid-solution, which could be existed in lattice defects or interstitial positions near W atoms rather than replace V sites.

Meanwhile, the energy dispersion spectroscopy (EDS) results have revealed the surface composition of the VO₂ samples with a addition of 1at.% Na₂WO₄ (Figure 4). It is strong evidence about the presence of metal elements of W, V, and Na in the particle surface and the detailed data are summarized in Table 1. The contents of Na and W are determined to be 2.58 and 1.35 at% respectively, which are somewhat more effective result than the actually data, because small quantities of Na₂WO₄ impurity atoms (including Na and W) did not locate in the lattice, deposition occur in the particle surface. Particularly under high temperature annealing, a noticeable shift of surface composition is recorded on the doped VO₂ particle surface, together with changing the morphology from nano-aggregates to bulk shown in Figure 4 (c) and (d). It shows that huge quantities of Na atoms and small amounts of W atoms migrated from inside to the surface of the doped VO₂ particles during thermal treatment processing. Furthermore, as shown in Figure 3(d), after high temperature annealing treatment, the phase transition temperature shift up to ~46.8°C which is close to the T_C of 1 at.% WO₃ doped VO₂. This result clearly indicates that the effect of Na in W doped VO₂ for the temperature of MIT depressed due to the migration of Na atoms at high temperature. It also proved that doping with Na₂WO₄ can get extra reduction in the phase temperature due to the effect of Na atoms in W-doped VO₂. Figure 5 shows a credible mechanism of the atomic migration of doped VO₂ in high temperature annealing.

Table 1 Metal atoms compositions of 1.0at.% Na₂WO₄ doped VO₂ sample: (a) annealed in N₂ at 700 °C for 5h, (b) further annealed in N₂ at 1100 °C for 2h

Sample	Content of Na (at. %)	Content of W (at. %)	Content of V (at. %)
(a)	2.58	1.35	96.07
(b)	12.35	1.51	86.24

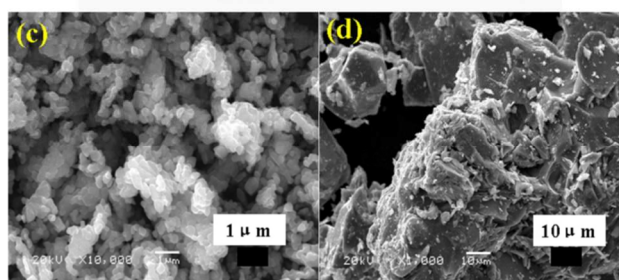
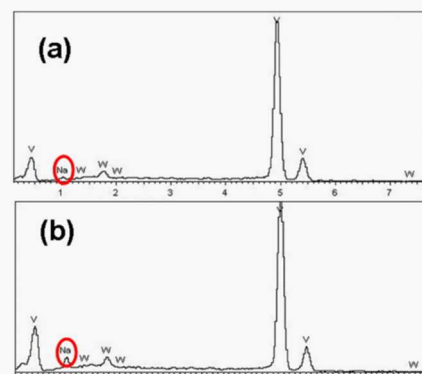


Figure 4 EDS spectrum of 1.0at.% Na₂WO₄ doped VO₂ samples: (a) annealed in N₂ at 700 °C for 5h, (b) further annealed in N₂ at 1100 °C for 2h; SEM images of 1.0at.% Na₂WO₄ doped VO₂ samples (c) have been annealed in N₂ at 700 °C for 5h and (d) further annealed in N₂ at 1100 °C for 2h.

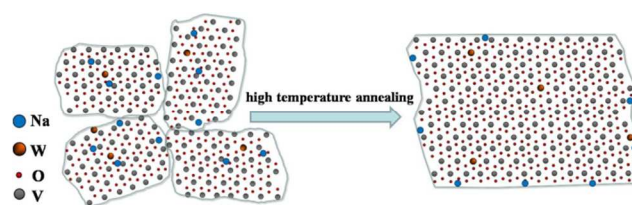


Figure 5 Schematic of ions motivation at high temperature annealing for Na₂WO₄ doping VO₂ powder

With above results in hand, we can deduce preliminarily the plausible mechanism. In the relevant literatures, it has been established that a charge transfer occurs and results in the pile-up of itinerant electrons around the W dopant,^{3, 10} when doping W⁶⁺ substitutional with V⁴⁺. This provides a chance to incorporate Na ions as the charge compensation reagent, just like the effects of alkali metal ions for rare earth doped phosphor system.⁹ While W as substitutional dopants replaces the V sublattice, the Na ions as interstitial impurity are mainly distributed around W dopant in Na₂WO₄ doped VO₂. It is reported that the local structure of W dopants have an symmetric tetragonal-like structure, which lead to locally nucleate rutile-like regions giving rise to the reduction of the thermal activation energy of MIT.^{15, 16} In our case, Na ions around W dopants might expand the scope of rutile-like regions

in the host matrix and introduce more crystal defects^{16,17}. Therefore, the T_C is even more lowered by ancillary effect of doping with Na.

In summary, we have successfully synthesized W-doped VO₂ by reduction of doped V₂O₅ using Na₂WO₄ as a full dopant. Under the presence of Na, an impressive depression of the phase transition temperature (about ~32°C per at% of tungsten dopant using) has been obtained. We have observed that Na has synergic effect on the MIT behaviour for W doped VO₂. It is instructive and meaningful for improving the preparation technologies of low temperature thermochromic materials and understanding the mechanism of the reduction of critical temperature triggered by doping for VO₂ metal-insulator transition. Further work will focus on the detail mechanism and development of new co-doping system of alkalis and other dopants.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Supplemental data of powder X-ray diffraction pattern, differential scanning calorimetry curves and electron microscopy images. See DOI: 10.1039/b000000x/

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