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One-step hydrothermal synthesis of Rare Earth/W-codoped VO$_2$ nanoparticles: reduced phase transition temperature and improved thermochromic properties

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Abstract. As a reversible thermochromic material, vanadium dioxide (VO₂) is a promising candidate for smart window applications. The trade-off between the integrated visible transmission (T_lum) and the solar modulating ability (ΔT_sol), as well as the high phase transition temperature (τ_c~68 °C) are regarded as the main obstacles for practical applications of pure VO₂ nanomaterials. The combination of both high τ_c reducing efficiency of W and improving T_lum/ΔT_sol properties of RE (rare earth: Eu, Tb), herein lies the purpose of RE/W-codoping to enhance the thermochromic performance. The RE/W-codoped VO₂ nanoparticles were synthesized under hydrothermal conditions, and exhibited grain size of less than 100 nm. The smart window which was fabricated by coating RE/W-codoped VO₂ nanoparticles onto glass, exhibits a thermochromic performance with a combination T_lum = 40%, ΔT_sol = 6.3%, τ_c = 40.8 °C or T_lum = 63%, ΔT_sol = 3.6%, τ_c = 31.9 °C, indicating the largely reduced absorption compared with the single W doping. Under the RE/W-codoping conditions, it was found that the ionic radius of the RE³⁺ cations controlled the crystallinity of the VO₂ particles and the electron/hole carrier counteraction as well as the competition between the strain and the hole carrier played a vital role in modulating the τ_c of the VO₂ products. The findings should be meaningful for investigating the codoping mechanisms for VO₂ nanomaterials.

Keywords. Vanadium dioxide; Solar modulation; Hydrothermal synthesis; Thermochromic smart window; Doping.

1. Introduction

Vanadium dioxide (VO₂) is a well-known thermochromic material, exhibiting a solar modulating ability across its phase transition temperature (τ_c=68 °C), i.e. the high transmission and the high absorption/reflection could be obtained below and above the τ_c, respectively [1-7]. In light of the solar modulating ability, VO₂ has been intensely investigated for applications in smart...
window. It permits the transmission of visible and IR light below \(\tau_c\), and selectively blocks the IR radiation above the \(\tau_c\), thus maintaining a comfortable in-door temperature [8-10]. However, the requirements for practical applications of the smart window (high visible transmission \((T_{\text{lum}}>70\%))\), large solar modulating ability \((\Delta T_{\text{sol}}>10\%))\), near ambient \(\tau_c\), etc.) are difficult to achieve for normal VO\(_2\) materials, due to a trade-off between the \(T_{\text{lum}}\) and the \(\Delta T_{\text{sol}}\), and the high \(\tau_c\) which is far off from 25 °C [11-13].

As for the thermochromic performance, the high \(T_{\text{lum}}\) is to get the clear vision while the large \(\Delta T_{\text{sol}}\) is to promise the enough energy saving efficiency. In order to improve the thermochromic performance of VO\(_2\) nanomaterials, several techniques have been applied to modify the physical and/or chemical characteristics of VO\(_2\) nanomaterials. This includes the porous assembly [14-17], nanocomposite [18-22], patterning [11, 23, 24], antireflection coating [25, 26] as well as the doping[3, 27]. Among these techniques, doping is an easy-to-control and cost-effective choice for tailoring the thermochromic properties of VO\(_2\). As reported in literatures, doping by the cations with the valence state larger than 4+ and/or with the ionic radius larger than 0.58 Å could reduce the \(\tau_c\) [28]. On the other hand, doping by the cations with the valence state less than 4+ or with the ionic radius smaller than 0.58 Å could be used to increase the \(\tau_c\) [28]. Notably, the W\(^{6+}\) doping was reported to show the highest experimental \(\tau_c\) reducing rate 20-26 °C/at% [29-31]. With respect to the integrated visible transmittance \((T_{\text{lum}})\) and the integrated solar modulating ability \((\Delta T_{\text{sol}})\), Mg doping was found to be able to improve the \(T_{\text{lum}}\) by widening the band gap of VO\(_2\)(M) at a rate of 3.9 eV/at.% [32], the Zr doping could enhance the \(T_{\text{lum}}\) by a relative percentage of 65%[33] and the RE (rare earth: Eu, Tb, La) doping[34-36] has the ability to increase the \(T_{\text{lum}}\) and the \(\Delta T_{\text{sol}}\) simultaneously. However, it is challenging to obtain a largely reduced \(\tau_c\) and improved \(T_{\text{lum}}\) as well as \(\Delta T_{\text{sol}}\) concurrently through single doping. In recent studies, it was reported that Mg/W-codoping could exhibit low \(\tau_c\) and enhanced \(T_{\text{lum}}\)/\(\Delta T_{\text{sol}}\) by
combining the advantages of Mg and W doping in $T_{\text{lim}}$ increasing and $\tau_c$ reducing respectively [37] and W/F-codoped VO$_2$ thin films could also show the reduced $\tau_c$ and improved visible transmittance [43]. Besides, the Cr/Nb-codoping was reported to be helpful in achieving the large TCR (temperature coefficient of resistance) with no thermal hysteresis [44]. Therefore, codoping may be a promising approach to optimize the thermochromic performance of VO$_2$ smart windows.

In this paper, the RE/W-codoping is proposed for the first time to enhance the thermochromic performance of VO$_2$ by utilizing the large $\tau_c$ reducing ability of W and the $T_{\text{lim}}/\Delta T_{\text{sol}}$ increasing capability of RE. The RE/W-codoped VO$_2$ nanoparticles were hydrothermally assembled to fabricate the thin film smart windows, which were expected to show a low $\tau_c$ and improved $T_{\text{lim}}$ as well as $\Delta T_{\text{sol}}$. The possible mechanism for the RE/W-codoping effect is also discussed in detail.

2. Materials and methods

All chemicals used in this paper, V$_2$O$_5$ (Alfa Aesar, 99.6%), Tb$_2$O$_3$ (Alfa Aesar, 99%), Eu$_2$O$_3$ (Alfa Aesar, 99%), H$_2$WO$_4$ (Alfa Aesar, 99.6%), H$_2$O$_2$ (Sigma-Aldrich), polyvinylpyrrolidone (PVP, 99%, Sigma-Aldrich) and N$_2$H$_4$·H$_2$O (Alfa Aesar, 99.9%) were used as received without any further purification.

Hydrothermal synthesis of RE/W-codoped VO$_2$ nanopowders. 5 mL 30 wt% H$_2$O$_2$ solution was preheated at 90 °C for 3 min in a 300 mL glass beaker. 233 mg V$_2$O$_5$, 6.4 mg H$_2$WO$_4$ and weighed Tb$_2$O$_3$/Eu$_2$O$_3$ powders based on the Eu/Tb doping level 1-6 at% were then added into the hot H$_2$O$_2$ solution. After a vigorous evaporation, the yellowish precursor was chemically reduced by 45 μL N$_2$H$_4$·H$_2$O. It was then transferred and sealed into a 50 mL stainless-steel autoclave with a Teflon liner. After heating at 260 °C for 24h in an oven and then cooling to room temperature in
the air, the products were collected by centrifuging (10000 rpm) 3 times with 10 mL acetone and drying overnight in a vacuum oven.

Fabrication of thin films. 50 mg of RE/W-codoped VO₂ nanoparticles were dispersed in 15 mL of ethanol with ultrasonic irradiation for 10 min. Thereafter 40 mg of PVP was further added into the dispersion to improve the dispersion viscosity and stirred for 5 min. The obtained brown-colored VO₂ dispersion was then knife casted onto glass substrate to get the thin film. An additional annealing at 400 °C for 1h in Ar atmosphere was ultimately applied to increase the adhesion and the film crystallinity. The sample names (0Eu0W-3Tb1W) under different RE/W atomic doping levels have been clarified in Table 1.

Characterization. The XRD characterization was performed with a Shimadzu XRD-6000 X-ray diffractometer (Cu-Kα, λ = 0.15406 nm) with a voltage 40 kV and a current 30 mA. Raman spectra were recorded with the Confocal Raman Witec alpha300 SR under 785 nm laser at room temperature. The morphology of the products was characterized using a field emission scanning electron microscope (FESEM, JSM-7600F, JEOL, Japan) at an accelerating voltage 5 kV and a probe current 7 μA. The morphology and the crystalline phase were further measured with the transmission electron microscopy (TEM, JEOL-2010, JEOL, Japan) at an accelerating voltage of 200 kV. The elemental analysis of the product were carried out using the EDX equipped on the FESEM and TEM. The phase transition temperature of the codoped VO₂ products was determined with a differential scanning calorimeter (DSC Q10, TA Instruments, USA), and the DSC data were collected in the temperature range 5-60 °C under a N₂ atmosphere. The film thickness and the optical constants were measured with VASE Ellipsometer (VB-400, J.A. Woollam Co., Inc. USA). The UV-Vis-NIR transmittance spectra (250 nm<λ<2500 nm) were recorded using a UV-Vis-NIR spectrophotometer (Cary 5000, Agilent Ltd, USA) equipped with a
Linkam PE120 system Peltier heating & cooling stage. The integrated visible transmittance ($T_{\text{lum}}$, 380 nm<\(\lambda\)<780 nm) and solar transmittance ($T_{\text{sol}}$, 280 nm<\(\lambda\)<2500 nm) were calculated based on the expression

$$T_{\text{lum/sol}}=\int \varphi_{\text{lum/sol}}(\lambda) T(\lambda) d\lambda/\int \varphi_{\text{lum/sol}}(\lambda) d\lambda$$  \hspace{1cm} (1)$$

where $T(\lambda)$ is the recorded %T, $\varphi_{\text{lum}}$ is the standard luminous efficiency function for the photopic vision of human eyes[38] and $\varphi_{\text{sol}}$ is the solar irradiance spectrum for air mass 1.5 (corresponding to the sun standing 37° above the horizon) [39]. $\Delta T_{\text{sol}}$ is calculated as $\Delta T_{\text{sol}}=T_{\text{sol}}(\tau<\tau_c)-T_{\text{sol}}(\tau>\tau_c)$.

3. Results and discussion

3.1 Synthesis of RE/W-codoped VO$_2$ nanoparticles

Figure 1 shows the XRD patterns of the RE/W-codoped VO$_2$ nanoparticles, synthesized hydrothermally. The corresponding formula of the samples 0Eu0W (pure VO$_2$)-6Eu1W (VO$_2$ doped with 6 at% Eu and 1 at% W), 1Tb0W-3Tb1W with different RE/W doping levels has been tabulated in Table 1. The Eu/Tb/W doping levels in the VO$_2$ samples have also been determined by the EDX in terms of Eu (at%)/V(at%), Tb (at%)/V(at%) and W (at%)/V(at%). As shown in Figure 1A, the XRD pattern of the sample 0Eu0W shows the major VO$_2$(M) phase (JCPDS #82-661), and the additional peak at ~27° (2θ) should be attributed to the V$_6$O$_{13}$ impurity. Interestingly, the XRD pattern of the sample 0Eu1W shows the pure VO$_2$(M) phase with the crystalline planes (011), (-102), (-211), (020), (-212), (220) and (002), indicating that the tungsten dopant may help to promote the crystallization of VO$_2$(M). As for the samples 1Eu1W-6Eu1W, an additional EuVO$_4$ phase (JCPDS #15-0809) with the faces (101), (200), (220), (103), (312) and (400) could be
indexed in the XRD pattern. Whereas for the Tb/W-codoped VO$_2$, as shown in Figure 1B, the samples 1Tb0W-3Tb1W exhibit the combination of VO$_2$ (M) phase and the TbVO$_4$(JCPDS #17-0340) impurity in the corresponding XRD patterns. The XRD result reveals that the VO$_2$(M) phase can be successfully attained under the RE/W-codoping hydrothermal conditions, but the impurity (TbVO$_4$, EuVO$_4$) is difficult to be eliminated, which may be due to the high affinity of RE to V in the chemical reaction and/or the extremely low solubility of RE oxides. The phase composition of the pristine VO$_2$ (0Eu0W) was also confirmed by the Raman spectra (Figure 1C), where the peaks at 146 ($A_g$), 196 ($A_g$), 226 ($A_g$), 288 ($A_g$), 403 ($A_g$), and 485 ($A_g$) cm$^{-1}$ could be assigned to the V-O vibration of the monoclinic VO$_2$ (M) phase, and the peaks at 166, 266 cm$^{-1}$ should be attributed to the V$_6$O$_{13}$ impurity.

The obtained RE/W-codoped VO$_2$ nanoparticles were further characterized with TEM. As depicted in Figure 2A-P, all the undoped (0Eu0W, Figure 2A, B) and Eu/W-codoped (0Eu0W-6Eu1W, Figure 2C-P) VO$_2$ samples show the morphology of nanoparticles with the size below 100 nm. The VO$_2$ (M) phase was further confirmed by the SAED patterns (inset in Figure 2) and the HRTEM images (Figure 2B, D, F, H, I, L, N, P) which can be indexed with the standard VO$_2$ (M) crystalline faces (011), (-211) and (200). In addition, the EuVO$_4$ impurity could also be indexed in the SAED patterns of the Eu/W-codoped samples. The V/Eu/W elemental mapping for the sample 5Eu1W was performed representatively to identify the dopant distribution in the nanoparticles. As shown in Figure 2Q, the signal of Eu-L$\alpha$ and W- L$\alpha$ in the VO$_2$ nanoparticles where V-K$\alpha$ populated is distributed continuously, revealing the efficient Eu/W doping for the sample. Due to the disturbance of EuVO$_4$ impurity, the unexpected concentrated Eu-L$\alpha$ signal at the impurity position could be pointed out in the mapping. Similarly, the morphology and the crystalline phase of the Tb/W-codoped VO$_2$ nanoparticles were also validated in the TEM images as shown in Figure 3. The VO$_2$(M) crystalline phase could be easily indexed in the HRTEM images.
(Figure 3B, D, F, H, J, L, N) and the TbVO₄ impurity could be figured out in the corresponding SAED patterns (inset figure). The continuous Tb/W-codoping was also observed in the V/Tb/W elemental mapping for the sample 3Tb1W as illustrated in Figure 3O. Due to the impurity of TbVO₄/EuVO₄ in the products, the doping level of the RE/W-codoped VO₂ were roughly determined using the EDX equipped in the TEM by focusing on the selected pure phase VO₂ nanoparticles (Table 1).

Figure 1 XRD patterns of the Eu/W codoped (A) and Tb/W-codoped VO₂ nanopowders (B). (C) Raman spectra of the pristine VO₂ sample (0Eu0W). Laser wavelength=785 nm.
3.2 Phase transition of RE/W-codoped VO₂ nanoparticles

Figure 4 shows the phase transition of the RE/W-codoped VO₂ nanopowders determined by DSC cycling measurement. Due to the low crystallinity of as-prepared products, the Eu/W-codoped VO₂ nanoparticles were tested after an additional annealing at 400 °C for 1 h in Ar flow. As shown in Figure 4A and Table 1, to begin with 1 at% W doping (0Eu1W), the phase transition temperature \( \tau_c \) could be decreased from the pristine 61.7 °C (0Eu0W) to 42 °C in accordance with the reported \( \tau_c \) reducing efficiency of W doping [29]. Upon increasing the Eu doping level from 0 (0Eu1W) to 1 (1Eu1W) and 2 at% (2Eu1W), the \( \tau_c \) was slightly increased from 42 to 46.7 and 49.2 °C, respectively, mainly owing to the neutralization of free electron carrier from the W⁶⁺ doping by the introduced hole carrier from the Eu³⁺ doping. However, upon increasing the doping level of Eu to 3 at% (3Eu1W) and 4 at% (4Eu1W), the \( \tau_c \) began to decrease to 48.6 and the minimum 38.1 °C, respectively, which indicates the dominant role of the extra strain from the lattice distortion of Eu/W-codoped VO₂ under both the doping levels. With further increasing the Eu doping level to 5 at% (5Eu1W) and 6 at% (6Eu1W), the largely increased hole carrier density from Eu³⁺ doping started to control the \( \tau_c \) modulation, which resulted in the slight increase of \( \tau_c \) to 47.2 and 48.2 °C, respectively. However, the \( \tau_c \) reduction by hole carriers incorporated into the \( d_\parallel \) sub-bands has been reported by Zhang et al. [46]. Therefore, the increase of \( \tau_c \) by hole carriers in the Eu³⁺ highly doping conditions should be due to the incorporation of hole carriers into the \( d_\parallel \) or \( \pi^* \) sub-bands, which will be confirmed by the future studies. With respect to the Tb/W-codoped VO₂ nanoparticles, as shown in Figure 4B and Table 1, the single Tb doping (1Tb0W-7Tb0W) could reduce the \( \tau_c \) from 61.7 °C of pristine VO₂ (0Eu0W) to around 50 °C at the single Tb doping level of 5 at%. Under Tb/W-codoping conditions, upon increasing the Tb doping level from 1 (1Tb1W), 2 at% (2Tb1W) to 3 at% (3Tb1W), the \( \tau_c \) had steadily decreased to 40.8, 36.5 and 31.9 °C respectively, mainly ascribed to the extra strain.
arising from the Tb doping in the lattice. Moreover, the latent heat of phase transition for the sample 1Tb0W can reach 35.83 J/g, which is comparable to the value 41.87 J/g for commercial VO$_2$ product (Alfa-Aesar)[40], revealing the high crystallinity of the product. Even at the Tb/W-codoping conditions, the phase transition latent heat could also remain 12.51 J/g for 1Tb1W, 15.93 J/g for 2Tb1W and 5.81 J/g for 3Tb1W. The higher crystallinity of Tb doped VO$_2$ than that of Eu doped ones should be due to the smaller ionic radius of Tb$^{3+}$ (0.92 Å) than that of Eu$^{3+}$ (0.95 Å), since the crystallinity could be reduced by the significant deformation of the lattice.

3.3 Thermochromic properties

Figure 5A shows the UV-Vis-NIR transmittance spectra of the RE/W-codoped VO$_2$ thin films prepared by casting powder products onto glass substrates. All the VO$_2$ thin films show the solar modulations across the cold (20 °C) and hot (90 °C) conditions in the near infrared (NIR) region. The %T contrast at the wavelength 2500 nm could be increased from 37.5% for pristine VO$_2$ (0Eu0W) to 37.8% and 38.5% when the VO$_2$ was doped with Eu/W (2Eu1W) and Tb/W (1Tb1W), respectively. Moreover, the Tb/W-codoping (1Tb1W, 2Tb1W, 3Tb1W) was found to be able to improve the visible transmission by 100% or higher compared with the pristine VO$_2$. The integrated visible transmission ($T_{\text{lum}}$) and the solar modulating ability ($\Delta T_{\text{sol}}$) for the RE/W codoped VO$_2$ thin films were calculated based on the %T spectra, and have been tabulated in Table 1. As depicted in Table 1, the pristine VO$_2$ (0Eu0W) showed the largest $\Delta T_{\text{sol}}$=7.3% and a low $T_{\text{lum}}$(20/90 °C)=20.3%/21.2%. With single 1 at% W doping, the annealed sample 0Eu1W showed an increased $T_{\text{lum}}$(20/90 °C)=50.4%/52.5% and a largely reduced $\Delta T_{\text{sol}}$=2.8%. With Eu/W-codoping, the annealed 5Eu1W and 2Eu1W could recover the $\Delta T_{\text{sol}}$ to 4.6% and 5.2% respectively, but the $T_{\text{lum}}$(20/90 °C) was largely reduced to corresponding 15.2%/18.1% and 16.5/18.6%. Comparatively, the Tb/W-codoping (1Tb1W, 2Tb1W, 3Tb1W) was found to be effective in
enhancing the $T_{\text{lum}}$ and increasing the $\Delta T_{\text{sol}}$. For the sample 1Tb1W, the $\Delta T_{\text{sol}}$ could be recovered to 6.3%, nearly 90% of the pristine VO$_2$, and the $T_{\text{lum}}(20/90 \, ^\circ\text{C})$ was increased to 37.5%/43.1%, which is ~2 times larger than that of the pristine VO$_2$. As for the sample 3Tb1W, the $T_{\text{lum}}$ was further increased to 60.9%/65.0%, almost 3 times larger than that of the pristine VO$_2$, but the $\Delta T_{\text{sol}}$ was reduced to 3.6%. Although the thermochromic properties cannot reach the best reported values for the VO$_2$ nanoparticles ($T_{\text{lum}}=\sim50\%, \Delta T_{\text{sol}}=\sim20\%$)[41], this first investigation on the RE/W-codoping should be meaningful for maintaining proper thermochromic performance when reducing the $\tau_c$ to near room temperature, and should be useful for studying the doping mechanism in VO$_2$ materials.

In order to further investigate the RE/W-codoping effects, the optical band gap ($E_g$) was determined by fitting the linear part of the curve $(\alpha \omega)^2$ v.s. $\omega$ (Figure 5B) according to the expression

$$(\alpha \omega)^2 = A(\omega-E_g) \quad (2)$$

Where $\alpha$ is the absorption coefficient [$\alpha d=-\ln(T/1-R)$], $A$ is a constant and $\hbar \omega$ is the photon energy ($\hbar \omega/eV = \frac{1240}{\lambda/\text{nm}}$). As seen in Figure 5B, the annealed single W-doped VO$_2$ (0Eu1W) showed an increase of band gap ($E_g=2.50 \, \text{eV}$) compared with the annealed pristine VO$_2$ (0Eu0W, $E_g=2.33 \, \text{eV}$) which should attribute to the increase of the $T_{\text{lum}}$, and is not consistent with the band gap narrowing effect of the W doping[42]. This should be due to the reduction of the lattice distortion arising from the W doping during the annealing process [41], since the lattice distortion is proportional to the band gap narrowing, and the band gap widening could give rise to the increase of $T_{\text{lum}}$. As for the as-prepared Tb/W-codoping (1Tb1W, 2Tb1W, 3Tb1W), $E_g$ was gradually increased from 2.24 to 2.30 eV along with the continuous Tb doping, in accordance with the band gap widening effect of RE doping[34], which also gave rise to the increase of $T_{\text{lum}}$. 
as described above. The Eg of the as-prepared Tb/W-codoped VO$_2$ is slightly lower than the pristine VO$_2$, which should be due to the band gap narrowing effect of the W doping [42].

The complex refractive index ($N=n+ik$) for the RE/W codoped VO$_2$ was also determined using ellipsometry. As shown in Figure 6B, comparing with the pristine VO$_2$ (0Eu0W), the refractive index ($n$) of 2Tb1W was evidently reduced above 600 nm, which should contribute to the largely enhanced $T_{\text{lum}}$ as indicated in Table 1 and Figure 6A. The 2Eu1W did not show apparent changes of the refractive index compared with 0Eu0W, which indicated the weak $T_{\text{lum}}$ modulation, in accordance with the %T measurement in Table 1. Based on the Ravindra relation [45], the band gap could be expressed as $N=4.16-0.85 \text{Eg}$, where $N=(n^2+k^2)^{1/2}$. According to the Eg expression, the calculated Eg ($\lambda=1290$ nm) for the samples 0Eu0W, 2Eu1W and 2Tb1W is 2.39 eV, 2.41 eV and 2.40 eV, respectively, which is similar to the value fitted from the UV-Vis-NIR spectra, further proving the RE/W-codoping effect on the Eg of VO$_2$. 
Figure 2 Bright-field TEM images (A, C, E, G, I, K, M, O) and the corresponding SAED patterns (inset) as well as the HRTEM images (B, D, F, H, J, L, N, P) for the samples 0Eu0W (VO₂, A, B), 0Eu1W (V₀.₉₉W₀.₀₁O₂, C, D), 1Eu1W (V₀.₉₈Eu₀.₀₁W₀.₀₁O₂, E, F), 2Eu1W (V₀.₉₇Eu₀.₀₂W₀.₀₁O₂, G, H), 3Eu1W (V₀.₉₆Eu₀.₀₃W₀.₀₁O₂, I, J), 4Eu1W (V₀.₉₅Eu₀.₀₄W₀.₀₁O₂, K, L), 5Eu1W (V₀.₉₄Eu₀.₀₅W₀.₀₁O₂, M,
N) and 6Eu1W (V\textsubscript{0.93}$\text{Eu}_{0.06}\text{W}_{0.01}\text{O}_2$, O, P) nanoparticles. (Q) FESEM image and the corresponding V-K\textalpha{}, Eu-L\textalpha{} and W-L\textalpha{} elemental mapping of the 5Eu1W nanoparticles.

Figure 3 Bright-field TEM images (A, C, E, G, I, K, M) and the corresponding SAED patterns (inset) as well as the HRTEM images (B, D, F, H, J, L, N) for the samples 1Tb0W (V\textsubscript{0.99}$\text{Tb}_{0.01}\text{O}_2$, A, B), 3Tb0W (V\textsubscript{0.97}$\text{Tb}_{0.03}\text{O}_2$, C, D), 5Tb0W (V\textsubscript{0.95}$\text{Tb}_{0.05}\text{O}_2$, E, F), 7Tb0W (V\textsubscript{0.93}$\text{Tb}_{0.07}\text{O}_2$, G, H), 1Tb1W (V\textsubscript{0.98}$\text{Tb}_{0.01}\text{W}_{0.01}\text{O}_2$, I, J), 2Tb1W (V\textsubscript{0.97}$\text{Tb}_{0.02}\text{W}_{0.01}\text{O}_2$, K, L) and 3Tb1W (V\textsubscript{0.96}$\text{Tb}_{0.03}\text{W}_{0.01}\text{O}_2$, M, N)
nanoparticles. (O) FESEM image and the corresponding V-Kα, Tb-Lα and W-Lα elemental mapping of the 3Tb1W nanoparticles.

Figure 4 Heating and cooling DSC cycles for the RE/W-codoped VO₂ nanoparticles. (A) Eu/W-codoped VO₂ with additional annealing at 400 °C for 1 h. (B) As-prepared Tb/W-codoped VO₂.

Table 1 Thermochromic properties of the RE/W-codoped VO₂ nanoparticles.

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<tr>
<td>2Eu1W</td>
<td>V₀.₉₇Eu₀.₀₂W₀.₀₁O₂</td>
<td>Eu: 2/W: 1</td>
<td>Eu: 1.7/W: 0.9</td>
<td>49.2/ 63</td>
<td>16.5/ 18.6</td>
<td>5.2</td>
<td></td>
</tr>
<tr>
<td>3Eu1W</td>
<td>V₀.₉₆Eu₀.₀₃W₀.₀₁O₂</td>
<td>Eu: 3/W: 1</td>
<td>Eu: 2.9/W: 1.3</td>
<td>48.6/ 77</td>
<td>26.5/ 28.5</td>
<td>2.1</td>
<td></td>
</tr>
<tr>
<td>4Eu1W</td>
<td>V₀.₉₅Eu₀.₀₄W₀.₀₁O₂</td>
<td>Eu: 4/W: 1</td>
<td>Eu: 3.7/W: 1.1</td>
<td>38.1/ 49</td>
<td>12.3/ 9.6</td>
<td>2.4</td>
<td></td>
</tr>
<tr>
<td>5Eu1W</td>
<td>V₀.₉₄Eu₀.₀₅W₀.₀₁O₂</td>
<td>Eu: 5/W: 1</td>
<td>Eu: 5.6/W: 1.2</td>
<td>47.2/ 53</td>
<td>15.2/ 18.1</td>
<td>4.6</td>
<td></td>
</tr>
<tr>
<td>6Eu1W</td>
<td>V₀.₉₃Eu₀.₀₆W₀.₀₁O₂</td>
<td>Eu: 6/W: 1</td>
<td>Eu: 5.3/W: 0.7</td>
<td>48.2/ 68</td>
<td>31.4/ 34.5</td>
<td>-1.3</td>
<td></td>
</tr>
<tr>
<td>1Tb0W</td>
<td>V₀.₉₉Tb₀.₀₁O₂</td>
<td>Tb: 1</td>
<td>Tb: 1.5</td>
<td>52.7/ 80</td>
<td>69.3/ 71.9</td>
<td>1.9</td>
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</tr>
<tr>
<td>3Tb0W</td>
<td>V₀.₉₇Tb₀.₀₃O₂</td>
<td>Tb: 3</td>
<td>Tb: 3.3</td>
<td>55.9/ 78</td>
<td>78.1/ 78.6</td>
<td>2.1</td>
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</tr>
<tr>
<td>5Tb0W</td>
<td>V₀.₉₅Tb₀.₀₅O₂</td>
<td>Tb: 5</td>
<td>Tb: 4.7</td>
<td>49.7/ 49</td>
<td>53.4/ 54.5</td>
<td>0.8</td>
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</tr>
<tr>
<td>7Tb0W</td>
<td>V₀.₉₃Tb₀.₀₇O₂</td>
<td>Tb: 7</td>
<td>Tb: 6.7</td>
<td>52.2/ 42</td>
<td>65.6/ 68.6</td>
<td>2.0</td>
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</tr>
<tr>
<td>1Tb1W</td>
<td>V₀.₉₈Tb₀.₀₁W₀.₀₁O₂</td>
<td>Tb: 1/W: 1</td>
<td>Tb: 0.8/W: 0.9</td>
<td>40.8/ 73</td>
<td>37.5/ 43.1</td>
<td>6.3</td>
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</tr>
<tr>
<td>2Tb1W</td>
<td>V₀.₉₇Tb₀.₀₂W₀.₀₁O₂</td>
<td>Tb: 2/W: 1</td>
<td>Tb: 1.9/W: 0.8</td>
<td>36.5/ 69</td>
<td>54.7/ 59.7</td>
<td>4.7</td>
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</tr>
<tr>
<td>3Tb1W</td>
<td>V₀.₉₆Tb₀.₀₃W₀.₀₁O₂</td>
<td>Tb: 3/W: 1</td>
<td>Tb: 3.1/W: 1</td>
<td>31.9/ 45</td>
<td>60.9/ 65.0</td>
<td>3.6</td>
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</table>

Note: aEDX derivation is ±10%, bτ_c=(τ_c,cool+τ_c,heat)/2, c d is the film thickness, dΔT sol=T sol(20 °C)-T sol(90 °C)
Figure 5 (A) UV-Vis-NIR %T spectra of the annealed 0Eu0W, 0Eu1W, 2Eu1W, 5Eu1W and the as-prepared 1Tb1W, 2Tb1W and 3Tb1W recorded at 20 °C (solid lines) and 90 °C (dash lines), respectively. (B) Corresponding plots of $(\alpha \nu \omega)^2$ v.s. $\hbar \omega$, where the optical band gap $E_g$ was determined by fitting the linear part of the curves.

Figure 6 (A) Averaged $T_{\text{lum}}$ and $\Delta T_{\text{sol}}$ for the annealed 0Eu1W, 2Eu1W and the as-prepared 2Tb1W samples. (B) Corresponding refractive index ‘$n$’ and the extinction coefficient ‘$k$’ tested at room temperature by ellipsometer.

Conclusion

In summary, the effect of RE/W-codoping on modulating the thermochromic properties of VO$_2$ nanomaterials was investigated for the first time. The Eu/W- and Tb/W-codoped VO$_2$ nanoparticles were one-step synthesized by a simple hydrothermal process. Due to the larger ionic radius of Eu$^{3+}$, the obtained Eu/W-codoped VO$_2$ nanoparticles exhibited less crystallinity than the Tb/W-codoped VO$_2$ nanoparticles, which can then be overcome by an additional annealing process. Both the annealed Eu/W- and as-prepared Tb/W-codoped VO$_2$ nanoparticles exhibited reduced $\tau_c$ and proper combination of $T_{\text{lum}}$ and $\Delta T_{\text{sol}}$. The Tb/W-codoping was found to
be effective in improving both the $T_{\text{lum}}$ and $\Delta T_{\text{sol}}$ as compared with single W doping, which provides an alternative approach for enhancing thermoehromatic properties and reducing $\tau_c$ to ambient temperature. Overall, the hydrothermal synthesized RE/W-codoped VO$_2$ nanoparticles successfully overcame the limit of $T_{\text{lum}}$ and $\Delta T_{\text{sol}}$ for single W-doping, which should be of great importance for the practical applications of VO$_2$ in smart windows, and should be meaningful for investigating the codoping mechanisms.

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