Solution-Processed VO$_2$-SiO$_2$ Composite Films with Simultaneously Enhanced Luminous Transmittance, Solar Modulation Ability and Anti-Oxidation property

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Recently, researchers spare no efforts to fabricate desirable vanadium dioxide (VO$_2$) film which provides simultaneously high luminous transmittance and outstanding solar modulation ability, yet progress towards the optimization of one aspect always comes at the expense of the other. Our research devotes to finding a reproducible economic solution-processed strategy for fabricating VO$_2$-SiO$_2$ composite films, with the aim of boosting the performance of both aspects. Compare to VO$_2$ film, an improvement of 18.9% (from 29.6% to 48.5%) in the luminous transmittance as well as an increase of 6.0% (from 9.7% to 15.7%) in solar modulation efficiency is achieved when the molar ratio of Si/V attains 0.8. Based on the effective medium theory, we simulate the optical spectra of the composite films and the best thermochromic property is obtained when the filling factor attains 0.5, which is consistent with the experimental results. Meanwhile, the improvement of chemical stability for the composite film against oxidation has been confirmed. Tungsten is introduced to reduce the phase transition temperature to the ambient temperature, while maintain the thermochromism required for application as smart window. Our research set forth a new avenue in promoting practical applications of VO$_2$-based thermochromic fenestration.

With the aim of reducing energy consumption in architectures, energy-efficient windows, especially "smart windows" based on chromogenic materials are considered to be good candidates for energy conservation and have attracted considerable concerns$^1$. Vanadium dioxide (VO$_2$), a representative thermochromic material, can initiate an automatic reversible semiconductor-metal phase transition (SMT) from the monoclinic structure (P2$_1$/c, M1 phase: the most stable monoclinic phase in room temperature) to the tetragonal structure (P4$_2$/mmm, R phase) at ca. 68°C, giving rise to a dramatic modification of the optical properties from infrared (IR) transmitting to IR reflecting, and maintains the visible transparency, which is suitable for the application of energy-efficient windows$^2–^4$. To meet the requirement for large-scale implementation on architectural buildings, VO$_2$-based materials should satisfy the following criteria: the phase transition temperature ($T_t$) closes to the ambient temperature ($<25^\circ$C), the integrated luminous transparency ($T_{lum}$) $\geqslant 40\%$ as well as the solar modulation ability ($\Delta T_{sol}$) $\geqslant 10\%$.$^5$

Generally, doping metal ions with high valence (such as W$^{6+}$, Mo$^{6+}$, Nb$^{5+}$) is confirmed to be an effective way to reduce $T_t$ to room temperature$^5–^8$. Among them, tungsten is proved to be the most effective dopant$. However, $T_{lum}$ is inevitably limited to $<40\%$ if a relative high $\Delta T_{sol}$ is maintained, which cannot balance the requirements for $T_{lum}$ and $\Delta T_{sol}$.$^6$ Therefore, a tougher challenge is to simultaneously and substantially improve both of $T_{lum}$ and $\Delta T_{sol}$ via an economic method. It is believed that the low visible transparency of VO$_2$ film originates from the
strong inner-band and inter-band absorptions in the short-wavelength range \(^{21,22}\). Experiments and calculations have demonstrated that some special dopants (such as F\(^-\) and Mg\(^{2+}\)) can serve to widen the band gap of VO\(_2\) and induce a blue-shift of the absorption edge, leading to an increase of the visible transparency \(^{15,16}\). However, the improvement of \(T_{\text{lim}}\) is usually accompanied by a deteriorated switching behavior. Deposition of single/multi-layer antireflection (AR) layers with high reflective index dielectric materials (i.e., SiO\(_2\), ZrO\(_2\), TiO\(_2\)) is a traditional strategy to enhance \(T_{\text{lim}}\). Nonetheless, it requires additional heating process and the presence of AR layer usually jeopardizes the near infrared (NIR) switching ability. Moreover, film thickness and microstructures markedly affect the optical properties and switching behaviors of VO\(_2\)-based films. The transmittance spectra for VO\(_2\) films with various thicknesses illustrate that the improvement of \(T_{\text{lim}}\) is inevitably at the expense of \(\Delta T_{\text{sol}}\). Zhou et al. have proposed a novel periodic porous structure with an unprecedented high visible light transmittance (81%). However, the switching efficiency is only ca. 23% at 2000 nm\(^\text{}\). To our knowledge, the optical properties of VO\(_2\) films obtained by the above approaches rarely can increase both \(T_{\text{lim}}\) and \(\Delta T_{\text{sol}}\) which otherwise tends to be undesirably low and constitutes a major obstacle for practical implementation of thermochromic fenestration.

A thrilling concept that nanocomposites materials comprising VO\(_2\) nanoparticles and highly transparent materials is providing an intriguing interest due to the unique properties. Optical calculations have confirmed that VO\(_2\) nanoparticles distributed in a dielectric matrix exhibit higher \(T_{\text{lim}}\) and better \(\Delta T_{\text{sol}}\) than pure VO\(_2\) films, which offers a novel perspective to achieve a favorable optical performance\(^2\). Inspired by this concept, some pioneering researches have devoted to fabricate VO\(_2\)-based composite particles and/or to cast them on glass or flexible substrate to obtain films with excellent thermochromic properties. Li et al. fabricated core-shell VO\(_2\)/TiO\(_2\) composite nanopowders with both thermochromic and photocatalytic properties\(^2\). Gao et al. prepared flexible VO\(_2\) nanocomposite foils based on SiO\(_2\)/VO\(_2\) core/shell structures with an improved \(T_{\text{lim}}\) from 29.2% to 55.3%, while \(\Delta T_{\text{sol}}\) exhibited a decrease from 13.6% to 7.5%\(^2\). Core-shell VO\(_2\)(M)/SiO\(_2\) films on a transparent Teflon film were obtained by casting the hydrothermal synthesized composite nanoparticles to gain an increased visible transmittance from 31.72% to 35.96%, accompanied by a significant increase in \(\Delta T_{\text{sol}}\) of 8.4%\(^2\). VO\(_2\) nanocrystals dispersed in SiO\(_2\) matrix are highlighted to be a new pathway to exhibit superior visible transmittance without compromising the NIR modulation ability as compared to conventional VO\(_2\) thin films\(^2\), offering a multitude of possibility for energy conservation.

To our knowledge, the V-O system is a complex binary system which contains a variety of compounds including V\(_2\)O\(_3\), VO\(_2\), V\(_2\)O\(_5\) and so on. Moreover, the various polymorphs of VO\(_2\), including VO\(_2\) (R), VO\(_2\) M1, VO\(_2\) (B) and VO\(_2\) (A), introduce a series of difficulties to fabricate pure VO\(_2\) films with thermochromic properties\(^2\). As a result, an accurate control of annealing atmosphere is vital to the formation of pure VO\(_2\) (M1). The majority of the fabrications of pure VO\(_2\) (M1) usually demand on high-vacuum equipment, and it inevitably increases the fabrication cost and raises the complexity of the operation, which is unsuitable for the large-scale fabrication of VO\(_2\)-based intelligent window. Additionally, as we can see, previous studies on VO\(_2\)-based composite structure mainly focuses on a prior preparation of pure VO\(_2\) (M1) particles followed by the formation of a composite structure due to the difficulties of direct fabrication of VO\(_2\)-based composite structure, which are closely related to the hard-controllable annealing atmosphere. Due to the above reasons, it is really significant and challengeable to develop an available pathway for directly fabricating VO\(_2\)-based composite films without the complex vacuum process, thus offering a unique opportunity to the practicable application of thermochromic coatings as “smart windows”.

Differ from the composite structure usually obtained via a two-step process, here we present a direct synthesis of VO\(_2\)-SiO\(_2\) composite films on glass substrate through an economic solution-based method and a relationship is drawn between the film products and the annealing conditions. With no need of a laborious vacuum processing, pure VO\(_2\)-SiO\(_2\) composite films (M1 phase) with different molar ratios of Si/V can be easily obtained by simply varying the gas flow of nitrogen. The influence of SiO\(_2\) on the structure, morphology as well as optical properties are detailed evaluated. We simulate the optical spectra of the composite films based on the effective medium theory and obtain a relationship between the volume filling factor \((f)\) and \(\Delta T_{\text{sol}}\). Next, we focus on the thermochromic properties of VO\(_2\)-SiO\(_2\) films in the function of SiO\(_2\) contents. Our results provide a series of well-formed composite films with simultaneously enhanced \(T_{\text{lim}}\) combined with \(\Delta T_{\text{sol}}\). The obtained results are in good agreement with our calculations. The anti-oxidation property of the composite film has also been investigated. Tungsten is introduced to reduce \(T_{\text{f}}\) of the composite film to the vicinity of room temperature, while maintain an excellent thermochromic property. Our work hence shortens the distance of VO\(_2\)-based thermochromic films towards smart window coatings for improved building energy conservation.

**Results**

**Optimization of annealing parameters.** To obtain the pure M phase (M1) of VO\(_2\) thin films, the appropriate annealing parameters are investigated. Fig. 1 shows the XRD patterns of films prepared at various annealing temperatures and times. As shown in Fig. 1 (a), for film annealed at 400 °C, it exhibits apparent diffraction peaks which can be indexed to the pure monoclinic structure. The

![Figure 1](scientificreports/srep07000/afigure1.png)

**Figure 1** | XRD patterns of films prepared at different annealing conditions. (a) The annealing time is kept at 1 hour and the annealing temperature varies from 400 °C to 500 °C; (b) The annealing temperature is kept at 450 °C and the annealing time varies from 0 hour to 2 hours.
Intensities of the diffraction peaks significantly increase as enhancing the annealing temperature to 450 °C, indicating an improved crystallinity of the film. Some additional diffraction peaks which can be attributed to NaV₆O₁₅ appear when the annealing temperature further increases to 500 °C. The emergence of NaV₆O₁₅ could be particularly originated from the diffusion of Na⁺ from glass substrates as increasing the annealing temperature 2. Fig. 1 (b) shows the XRD patterns of films annealed at 450 °C for different annealing times. The nitrogen atmosphere, which contains ca. 0.01% O², greatly affects the oxidation state of the films. The main products with different annealing times are V₂O₅, VO₂ and V₆O₁₃, respectively. Additionally, NaV₆O₁₅ appears when the annealing time is long. Based on the above discussion, the optimized annealing temperature and time to obtain pure M1 phase VO₂ thin film are 450 °C and 1 hour, respectively.

In the above discussion for the fabrication of pristine VO₂ film, we choose the nitrogen gas as the annealing atmosphere with a gas flow of 0.200 L·min⁻¹. However, this annealing parameter suitable for pristine VO₂ film is inapplicable for VO₂-SiO₂ composite films. For example, when Si/V = 1.0, the composite film annealed under this gas flow is characterized as an amorphous carbon film with gray color. The formation of this amorphous film can be possibly attributed to the carbon residues in the films due to the incomplete degradation of the organic matter originating from the addition of SiO₂ sols. The production of carbon residues possibly results in a reduction effect on the resulting amorphous films. To consume the carbon residues, a certain amount of oxygen is required to fabricate a composite film with pure M1 phase. As we have referred, the annealing treatment is operated without a vacuum supply process. Additionally, the nitrogen gas also contains a certain amount of O₂. Consequently, in the following experimental, we can adjust the content of oxygen acted on the residual carbon substance by simply varying the gas flow of the nitrogen and the crystallization to VO₂-SiO₂ composite film (Si/V molar ratio = 1.0) occurs when the gas flow is 0.525 L·min⁻¹. As such, we discuss the appropriate atmosphere for other composite films and the detailed gas flow of nitrogen for each film is listed in Table 1.

### Table 1 | The molar ratios of Si/V in the films prepared on aluminium foils and the thicknesses of the composite films on glass substrates with different Si/V molar ratios as well as the calculated filling factor according to the molar ratios of Si/V based on the EDX results. The area selected for investigation of EDX spectra is 60 × 60 μm²

| Si/V molar ratio in the solution | Gas flow (L·min⁻¹) | Si/V molar ratio in the films | Filling factor (f) | Film thickness (nm) |
|---------------------------------|-------------------|-----------------------------|-------------------|-------------------|
| 0.0                             | 0.200             | 0                           | 0                 | 102               |
| 0.2                             | 0.250             | 0.23                        | 0.261             | 109               |
| 0.4                             | 0.300             | 0.45                        | 0.408             | 117               |
| 0.6                             | 0.375             | 0.62                        | 0.487             | 128               |
| 0.8                             | 0.450             | 0.83                        | 0.560             | 136               |
| 1.0                             | 0.525             | 1.12                        | 0.623             | 144               |

Film morphology. The morphology of the prepared films is of paramount importance to obtain the desired optical properties, and the changes in the particles size and morphology of the films induced by the addition of SiO₂ can be observed via SEM images. Fig. 3 exhibits the morphology evolution of the composite films upon enhancing the Si/V molar ratio. For pristine VO₂ film, the film is composed with uniform and well-formed grains. Clear grain boundaries appear between the particles. Upon the addition of SiO₂, the particle sizes are apparently depressed in Fig. 3 (b), (c) and (d), which is consistent with the earlier report 2. The size reduction can also be confirmed in the cross-sectional SEM observation of the VO₂ film and VO₂-SiO₂ composite film (Si/V = 0.8), as illustrated in Fig. 3 (e) and (f). Compared to the pristine VO₂, the VO₂-SiO₂ composite film shows relative homogenous and narrow particle size distributions, indicating that the SiO₂ in the composite film play a crucial role to reduce the degree of growth and agglomeration of VO₂ particles. According to these observations, it may be concluded that SiO₂ particles are well formed and a composite structure is obtained in the film. With the aim to determine the effective molar ratios of Si/V in the composite films, we fabricate the films on the aluminum foils (to exclude the influence of the Si in the glass substrate) under the same procedure discussed above and the followed EDX analysis results are demonstrated in Table 1. The atomic percent ratios of Si/V are respectively ca. 0, 0.23, 0.45, 0.62, 0.83, 1.12, which are in close proximity to the initial ratios in the deposition solutions.

**Film structure.** Fig. 2 depicts the typical XRD patterns of VO₂-SiO₂ composite films with different Si/V molar ratios, which can be used to further evaluate the evolution of the phase composition, grain size, and crystallinity of the films. It is revealed that all films exhibit the typical diffraction peaks of M1 phase VO₂ (JCPDS card no. 72-0514, P₂₁/c, a = 0.5743 nm, b = 0.4517 nm, c = 0.5375 nm, and β = 122.61°). Since the annealing temperature is far below the crystallization point of SiO₂, it is most likely that the SiO₂ in the composite films is amorphous, which cannot be detected by XRD. Additionally, no evidence can be seen for other crystalline phases, such as V₂O₅, V₆O₁₃ or VSi₅O₁₅, indicating the purity of the composite films. None of the diffraction peaks exhibit significant migration with increasing the molar ratio of Si/V. However, a broadening and weakening tendency of the diffraction peak of (011) crystalline plane is observed, which is largely due to the grain refinement as increasing the molar ratio of Si/V.
To further detect the microstructure of the composite film, high-resolution transmission electron microscopy (HRTEM) images and corresponding selected area electron diffraction (SAED) patterns are collected for the VO₂-SiO₂ composite film (Si/V molar ratio 0.8). As shown in Fig. 4 (a), the film is composed of well-fined particles, which is in agreement with the SEM images observed previously. The crystallized VO₂ and the amorphous SiO₂ particles are distributed as separate phases as shown in Fig. 4 (b). A more detailed microstructural analysis further confirms that the sample is crystallized into monoclinic VO₂. As is found in the SAED patterns (Fig. 4 (d)), bright diffraction rings evident the polycrystallinity nature of the sample, which is consistent with the XRD results. In Fig. 4 (c), clear and ordered lattice fringes are observed in the HRTEM images, corresponding to the (011) crystalline plane. The distributions of VO₂ and SiO₂ are examined by scanning transmission electron microscopy (STEM) and elemental mapping measurements. The annular dark-field (ADF) image of VO₂-SiO₂ (Fig. 4 (e), (f)) and the elemental maps respectively corresponding to V, Si and O (Fig. 4 (g), (h), (i)) further illustrate the inhomogeneous distribution of VO₂ and SiO₂ nanoparticles in the composite film. The particle sizes of VO₂ range from 30 to 100 nm, which is in good agreement with the SEM images.

**Optical properties.** Fig. 5 depicts the variation of visible transmittance of VO₂-SiO₂ composite films in response to the variation of Si/V molar ratios. It is clearly that the maximum visible transparency greatly enhances from 41.9% to 64.7% at 630 nm as increasing the proportion of SiO₂ in the film. Compare the insert images which represent the photographs of VO₂ and VO₂-SiO₂ films (Si/V molar ratio = 0.8), a significant enhancement of the visible transparency is observed. Lopez et al. have previously revealed that the scattering effect of VO₂ gradually decreases with the reduction of the particle size, indicating that the transmittance would reasonably increase. The addition of SiO₂ restricts the growth and aggregation of VO₂ particles, and further reduces the initial reflectance of particles and thus inherits a better high luminous optical property, which is in consistent with the previous report. In addition, the visible transmittance is enhanced possibly through an AR effect. Upon the addition of SiO₂ in the composite films, SiO₂ stack on the surface of VO₂ particles and serve as the AR layer, which can effectively affect the reflected light from the air-coating and coating-substrate interfaces, leading to a higher transmittance over the visible region spectrum. Wavelength dependent refractive indices (n) and extinction coefficient (k) of VO₂-SiO₂ composite films with various Si/V molar ratios are plotted in Fig. 6. Expectedly, both the n and k of the composite thin films exhibit a significant depression in whole measured wavelength upon the increase of SiO₂ addition. Fig. 7 illustrates the reflectance spectra of VO₂-SiO₂ composite films of the semiconductor state. Upon the addition of SiO₂ in the composite film, the reflectance shows a significant depression in the whole wavelength. According to the Fresnel’s equation, the reduced n (2.58 for VO₂ film and 2.30 for

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**Figure 3** The surface morphology of films with various Si/V molar ratios. Si/V = (a) 0; (b) 0.4; (c) 0.6; (d) 0.8. The cross sectional of pristine VO₂ film (e) and VO₂-SiO₂ composite film with Si/V = 0.8 (f).

**Figure 4** The TEM image (a), HRTEM (b, c), SAED patterns (d), ADF (e, f) images of the VO₂-SiO₂ composite film (Si/V = 0.8) and the elemental maps respectively corresponding to V, Si and O ((g), (h), (i)).
VO₂-SiO₂ film with Si/V = 1.0) contributes to a decreased reflectance of the film. The spectral transmittance of VO₂-SiO₂ composite films of the semiconductor state ranges from 250 nm to 2500 nm are characterized as shown in Fig. 8. VO₂ thin film exhibits salient switching of the NIR transmittance, indicating a good thermochromic property. Especially, the composite films show better optical performance with a larger transmittance change in 2000 nm (ΔT₂₀₀₀ nm) upon the increase in the addition of SiO₂, as shown in Table 2. The phenomenon is consistent with the previously studies that not only the luminous transmittance but also the transmittance change upon the phase transition greatly increase with the decrease of VO₂ particle size30. To further quantify the potential application of the composite films as coatings on smart windows, we calculate the integral luminous transmittance (Tlum) and solar transmittance (Tsolar), 250–2500 nm) of all the composite films based on the measured spectra using the following expression:

\[ T_{\text{lum}} = \int \varphi_{\text{lum/air}}(\lambda)T(\lambda)d\lambda \int \varphi_{\text{lum/air}}(\lambda)d\lambda \]

where \(T(\lambda)\) denotes the transmittance at wavelength \(\lambda\), \(\varphi_{\text{lum}}\) is the standard luminous efficiency function for the photopic vision of human eyes and \(\varphi_{\text{sol}}\) is the solar spectral irradiance for the air mass 1.5 (The receiving surface is defined as an inclined plane at 37° tilt toward the equator)33. The luminous transmittance modulation (ΔTₗum) and solar energy modulation (ΔTₙsol) are defined as:

\[ \Delta T_{\text{lum}} = T_{\text{lum,s}} - T_{\text{lum,m}} \]

Figure 5 | The luminous transmittance of films with different Si/V molar ratios ranges from 380–780 nm measured at 30°C. The insert images correspond respectively to photographs of the pristine VO₂ film (below) and VO₂-SiO₂ composite film (Si/V = 0.8) (upper).

Figure 6 | The wavelength dependent refractive index (a) and extinction coefficient (b) of films with different Si/V molar ratios. All of the optical constants are measured at 30°C.

Figure 7 | The reflectance spectra measured at 30°C of VO₂-SiO₂ composite films with different Si/V molar ratios range from 250 to 2500 nm.

Figure 8 | Transmittance spectra of VO₂-SiO₂ composite films upon increasing Si/V molar ratios in the wavelength ranges from 250 nm to 2500 nm. Solid line: 30°C, Dash line: 100°C. The gray area indicates the normalized values of the solar spectral irradiance (\(\varphi_{\text{sol}}\)).
\( \Delta T_{\text{vol}} = T_{\text{vol,s}} - T_{\text{vol,m}} \) \hspace{1cm} (3)

\( T_{\text{hyst,s}}, T_{\text{hyst,m}}, T_{\text{vol,s}} \) and \( T_{\text{vol,m}} \) denote as the luminous transmittance and solar transmittance at the semiconducting state and the metallic state, respectively. The obtained results are elaborated in Table 2. It is clear that the \( \Delta T_{\text{vol}} \) greatly increases from 9.7% for \( VO_2 \) thin film to a maximum of 15.7% when \( Si/V \) molar ratio attains 0.8, accompanied by a huge increment of \( T_{\text{hyst,s}} \) from 29.6% to 48.5%. The obtained values are the best among the reported values of \( T_{\text{hyst}} \) and \( \Delta T_{\text{vol}} \) for a typical single-layered \( VO_2 \) film (41.0%, 6.7%)\(^{23}\), \( TiO_2/VO_2 \) double-layered films (46.0%, 7.0%)\(^{23}\), \( TiO_2/VO_2/TiO_2/VO_2/TiO_2 \) five-layered films (44%, 12.1%)\(^{23}\), \( VO_2-Sb:SnO_2 \) composite films (49.8%, 11.7%)\(^{24}\) and core-shell \( VO_2 (M) @SiO_2 \) casted foils (35.9%, 8.4%)\(^{22}\).

### Phase transition temperature

The switching characteristics of the composite films are investigated by recording the temperature-dependent optical transmittance during the heating and cooling process at 2000 nm as illustrated in Fig. 9. Detailed parameters of the hysteresis loops are obtained as follows. Briefly, a plot of \( d(Tr)/d(T) \) &\( T \) is obtained from each hysteresis loop, yielding two peaks with a well-defined maximum. \( Tr \) and \( T \) denote as the transmittance and temperature, respectively. Each \( d(Tr)/d(T) \) &\( T \) curve has been fitted with a Gaussian function using the Origin pro 8.0 software, as shown in Fig. 10. The temperature corresponding to the maximum of each \( d(Tr)/d(T) \) &\( T \) curve is defined as the phase transition temperature of heating and cooling branch, denote as \( T_h \) and \( T_c \), respectively. The phase transition temperature (\( T_T \)) of the film is defined as:

\[ T_T = (T_h + T_c)/2 \] \hspace{1cm} (4)

The hysteresis loop width (\( \Delta T_T \)) is defined as the difference between \( T_h \) and \( T_c \). The sharpness of the phase transition for heating or cooling run is characterized by the full width at half maximum (FWHM) of the \( d(Tr)/d(T) \) &\( T \) curve, smaller value means sharper change of the slope. The detailed parameters are summarized in Table 3.

As we can see, a large hysteresis of the pristine \( VO_2 \) thin film, of around 9.9°C, is directly related to the nanoparticle microstructure\(^{11}\). Broader hysteresis loops are obtained for samples with the addition of \( SiO_2 \). It is striking to notice that by continuously increasing the \( Si/V \) molar ratios, \( T_T \) of the film shows no obvious variation, while \( T_h \) exhibits a progressive increase. Meanwhile, the transition sharpness becomes smoother (expressed as the apparent enhancement of FWHM) upon enhancing the \( Si/V \) molar ratio. We ascribe this phenomenon to the surrounding \( SiO_2 \), which helps to absorb the locally induced stresses among \( VO_2 \) lattices during the phase transition\(^{21}\).

### Anti-oxidation properties

The poor long-term oxidation resistance is another obstacle to the application of smart windows due to the thermodynamically instability of \( VO_2 \). It has been previously reported that \( VO_2 \) is gradually oxidized into toxic \( V_2O_5 \) when it is exposed to the air for a long period or abused at high temperature above 300°C\(^{38-37}\), which leads to a considerable deterioration of the thermochromic properties. In this case, improving the chemical stability of \( VO_2 \) against oxidation is urgently required. The anti-oxidation properties of the film after the addition of inert \( SiO_2 \) are investigated compared with the pristine \( VO_2 \) thin film. As illustrated in Fig. 11, after exposing the films in air at room temperature for 6 months, the pristine \( VO_2 \) film cannot maintain the original pure monoclinic phase with the (011) peak weakens while some additional peaks assigned to \( V_2O_5 \) appear. For the composite film \( (Si/V \) molar ratio = 0.8), the XRD pattern shows no obvious change and all peaks can be assigned to the monoclinic \( VO_2 \). The results firmly confirmed that the addition of \( SiO_2 \) in the composite structure can effectively protect \( VO_2 \) from being oxidized, offering a similar anti-oxidation protection comparable to the anti-reflection layer\(^{27}\).

**Table 2 | Optical parameters during the phase transition of \( VO_2-SiO_2 \) films with different \( Si/V \) molar ratios**

| \( Si/V \) molar ratio | \( T_{550 \text{nm}} \) | \( \Delta T_{2000 \text{nm}} \) | \( T_{\text{hyst,s}} \) | \( T_{\text{hyst,m}} \) | \( \Delta T_{\text{hyst}} \) | \( T_{\text{vol,s}} \) | \( T_{\text{vol,m}} \) | \( \Delta T_{\text{vol}} \) |
|------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 0                      | 32.5            | 54.2            | 29.6            | 26.8            | 2.8             | 35.2            | 25.5            | 9.7             |
| 0.2                    | 37.9            | 56.8            | 33.7            | 30.4            | 3.3             | 39.7            | 27.8            | 11.9            |
| 0.4                    | 47.5            | 56.7            | 40.7            | 36.3            | 4.4             | 44.9            | 31.8            | 13.1            |
| 0.6                    | 51.3            | 57.7            | 44.5            | 39.5            | 5.0             | 48.8            | 34.0            | 14.8            |
| 0.8                    | 53.9            | 57.4            | 48.5            | 43.2            | 5.3             | 52.9            | 37.2            | 15.7            |
| 1.0                    | 50.5            | 60.7            | 46.4            | 42.5            | 3.9             | 54.2            | 38.8            | 15.4            |

**Tungsten doped \( VO_2-SiO_2 \) composite film.** For our \( VO_2-SiO_2 \) composite film, the simultaneously enhanced luminous transparency and the solar energy modulation have met the requirements \( (T_{\text{hyst}} \geq 40\%, \Delta T_{\text{vol}} \geq 10\%) \). Although, the \( T_T \) of the composite film increase upon the addition of \( SiO_2 \) it can be readily reduced to the ambient temperature by replacing some vanadium atoms with tungsten. Fig. 12 shows the XRD pattern, transmittance spectra as well as the hysteresis loop of W-doped \( VO_2-SiO_2 \) composite film.

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**Figure 9 |** (a) The hysteresis loops at 2000 nm of \( VO_2-SiO_2 \) composite films with different \( Si/V \) molar ratios. (b) The relationship between the transition temperature and the \( Si/V \) molar ratio during the heating and cooling processes.
The composite film exhibits pure monoclinic structure as well as significant transmittance change in NIR spectrum across the phase transition. The phase transition temperature is successfully reduced to 34.2°C and the hysteresis loop width is also narrowed down by 3.8°C. The NIR switching efficiency is diminished compared with undoped film due to the incorporation of W dopant. Nonetheless, Tlum and Tsol of the W-doped composite film are calculated to be respectively 43.3% and 11.3%, satisfying the requirements for practical thermochromic fenestration.

**Discussion**

In order to give a deeper analysis for the change of optical properties upon the addition of SiO2, we simulate the optical spectra of the composite films as shown in Fig. 13. Clear evidence for thermochromism is seen in reflectance (R) and transmittance (T) regardless of the volume filling factor (f). The R (T) of the semiconductor state exhibits a significant decrease (increase) with enhancing the f, and vice versa. Tlum, Tsol, ΔTlum as well as the ΔTlum of the films correspond to each f are calculated and plotted as shown in Fig. 14. Both Tlum and Tsol demonstrate a progressive increase when f is enhanced. Meantime, not only the Tsol but also the Tlum of the semiconductor state is higher than that of the metallic state, indicating that the thermochromism is not confined to the NIR region but takes place in the whole wavelength. Moreover, it can be referred from Fig. 14 (c) that ΔTsol exhibits a broad maximum of 16.07% when f = 0.5 and is compatible with Tlum = 57.85% and Tlum = 51.22%. The calculation for VO2 particles dispersed in In2O3: Sn performed by Li et al. exhibits a same tendency and ΔTsol displays a broad maximum of ca. 12.8% for f = 0.35, which is close to the value where the VO2 units start to percolate in the Breugeman model.

As we have noted, the ΔTsol greatly increases from 9.7% for VO2 thin film to a maximum of 15.7% when Si/V molar ratio attains 0.8 (corresponds to f = 0.56), accompanied by a huge increment of Tlum from 29.6% to 48.5%. The experimental results are in good agreement with the calculations. The synergistic performances suggest that high Tlum and excellent ΔTsol can be realized simultaneously via optimizing the f of SiO2 in the composite film, which paves a new way for the application of VO2-based smart windows.

**Table 3** The detail parameters derived from the hysteresis loops at 2000 nm of VO2-SiO2 composite films with different Si/V molar ratios

| Si/V molar ratio | Tlum (°C) | Tl (°C) | Tsol (°C) | ΔTlum (°C) | FWHM (°C) |
|------------------|-----------|---------|-----------|------------|-----------|
| 0                | 67.3      | 57.4    | 62.3      | 9.9        | 4.6       |
| 0.2              | 69.7      | 56.9    | 63.3      | 12.8       | 6.5       |
| 0.4              | 70.8      | 56.8    | 63.8      | 14.0       | 7.0       |
| 0.6              | 72.2      | 56.4    | 64.3      | 15.8       | 10.6      |
| 0.8              | 74.5      | 57.1    | 65.8      | 17.4       | 11.3      |
| 1.0              | 76.2      | 57.0    | 66.6      | 19.2       | 12.1      |

**Figure 10** The d(Tr)/d(T)&T plots of VO2-SiO2 composite films with different Si/V molar ratios to describe the transition parameters of heating and cooling branches. The molar ratio of Si/V = (a) 0; (b) 0.2; (c) 0.4; (d) 0.6; (e) 0.8; (f) 1.0. Tr and T represent transmittance and temperature at 2000 nm. Th and Tc express the phase transition temperature of heating and cooling branches, respectively.
Our calculations mentioned above have confirmed that the thermochromism of \( \text{VO}_2 \) occurs in the entire solar range. As a result, \( D_{\text{Tsol}} \) can be described as:

\[
D_{\text{Tsol}} \approx D_{\text{Tlum}} + D_{\text{Tnir}}.
\]  

(5)

\( D_{\text{Tlum}} \) and \( D_{\text{Tnir}} \) denote as the integral transmittance modulation of the visible and NIR spectra, respectively. It is worthy noted that solar energy between 250–2500 nm constitutes the majorities of the total heat energy in the whole solar irradiance spectra, among which, the heat energy in the visible light and NIR light accounts for ca. 43% and 48%, respectively. Expectedly, not only the transmittance change in the NIR region but also the changes in visible light region of \( \text{VO}_2 \) thin film to undergo the phase transition play an important role in determining the \( D_{\text{Tsol}} \). Previous researches have demonstrated that the change in the luminous transmittance (\( \Delta T_{\text{lum}} \), the difference between \( T_{\text{lum,s}} \) and \( T_{\text{lum,m}} \)) of the film is thickness-dependent. For film with less than 50 nm thick, \( T_{\text{lum,s}} \) of the film is generally lower than \( T_{\text{lum,m}} \) due to the interference effect, and, vice versa. In our experiment, the thicknesses of obtained films are determined to be approximately 102, 109, 117, 128, 136 and 144 nm respectively by the step profiler (listed in Table 1), increases with the enhancement of the molar ratio of Si/V (Higher viscosity of the precursor solution is obtained when increasing the proportion of SiO\(_2\) sols, contributing to a slight increase in film thickness due to the same spin-coating parameters.).

The \( \Delta T_{\text{lum}} \) value of the composite films increases as enhancing the molar ratio of Si/V (from 2.8% for Si/V = 0 to 5.3% for Si/V = 0.8), which is in line with the calculated results. Of note, with enhancing the molar ratio of Si/V in the film, the value of \( \Delta T_{2000 \text{ nm}} \) for the composite film exhibits an obvious improvement compared to the \( \text{VO}_2 \) film, which, to a large extent, determines the \( \Delta T_{\text{nir}} \), giving rise to the increase of \( \Delta T_{\text{sol}} \). The improvement of \( \Delta T_{\text{lum}} \), together with the enhancement of \( \Delta T_{\text{nir}} \), jointly contribute to the larger \( \Delta T_{\text{sol}} \) for films with larger Si/V molar ratio.

For our \( \text{VO}_2\)-SiO\(_2\) composite film, \( T_h \) shows a progressive increase by continuously increasing the Si/V molar ratios, while leaving \( T_c \) unchanged. A similar phenomenon has also been observed in \( \text{VO}_2\)/Pt multi-layers due to the replacement of \( \text{VO}_2\)/air interfaces with \( \text{VO}_2\)/Pt interfaces by Pt deposition, which confirms that the \( \text{VO}_2 \) interact with the surrounding media play a role in modifying the SMT path. To our knowledge, the occurrence of the two transitions is dominated by totally different defects. For the transition from semiconductor phase to metal phase, the vast majority of the newly formed metal-phase \( \text{VO}_2 \) nuclei are located extremely close to grain boundaries due to the surface-localized defects. While for the reversal transition, it is dominated by bulk defects in \( \text{VO}_2 \) particles. The shift of \( T_h \) towards higher temperatures indicates that the SMT is retarded by nucleation of the metal phase after the change of surrounding medium. The diminished availability of defects which can serve as nucleation sites lowers the possibility to trigger the phase transition, contributing to the shift of \( T_h \) towards higher temperatures. As such, the broadening of the hysteresis loops can also be ascribed to it. The shift of \( T_h \) towards higher temperature gives a clue that the chemical stabilization of the semiconductor state is enhanced.

Our research provides a simple and economic solution-based method to fabricate \( \text{VO}_2\)-SiO\(_2\) composite films with the aim to simultaneously improve the luminous transmittance and the solar energy modulation. Differ from the common method to fabricate pure \( \text{VO}_2\),

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**Figure 12** | JCPDS card No. 72-0514 (a), transmittance spectra at 25°C and 100°C (b), hysteresis loop at 2000 nm (c) as well as corresponding \( d(T_r)/d(T) \ & T \) plot of W-doped \( \text{VO}_2\)-SiO\(_2\) composite film (molar ratio: W/V = 0.015; Si/V = 0.8). \( T_r \) and \( T \) represent transmittance and temperature at 2000 nm, respectively.
(M1), we provide an easy-controllable method by simply varying the gas flow of nitrogen and have no requirement of high-vacuum equipment. All of the obtained composite films exhibit pure monoclinic phase structure with excellent crystallinity. According to the TEM results, VO₂ and SiO₂ are distributed as separate phases and the addition of SiO₂ in the films plays an important role in hindering the growth and aggregation of VO₂.

Based on the effective medium theory, we calculate the optical constants and simulate the corresponding optical spectra of the composite films of various filling factors. The calculations illustrate that the composite film exhibits the best thermochromic property when the filling factor attains 0.5, which is consistent with the experimental result. With the exception of the high luminous transmittance and the superior modulation of solar modulation ($T_{\text{lum}} = 48.5\%$, $\Delta T_{\text{sol}} = 15.7\%$), the anti-oxidation property of the composite film is discussed. VO₂-SiO₂ composite film maintains the original monoclinic structure after depositing in air for six months. Tungsten is introduced to effectively reduce the phase transition temperature to the ambient temperature, while retains the thermochromism required for application as smart window. Our VO₂-SiO₂ composite films enable effective tailoring of the optical performance, which open a new horizon of multifunctional coating as the architectural fenestration.

**Method**

**Materials.** All the chemicals of analytical grade were commercially available and used without further purification. Vanadium pentoxide (V₂O₅) was chosen as the source of vanadium and oxalic acid (H₂C₂O₄·2H₂O) was selected as the reducing agent. Tetraethylorthosilicate (TEOS) and hydrochloric acid (HCl, 37%) were used as the silica precursor and hydrolyzing catalyst, respectively. Pluronic F127 (EO₃₅·PO₇₅·EO₃₅, $M_w \approx 12,600$ g/mol) was added as a pore-forming agent. Dehydrates ethanol (EtOH, 95%) was used as solvent in both systems. Ammonium tungstate hydrate ($\left(\text{NH}_4\right)_2\text{H}_2\left(\text{WO}_4\right)\cdot\text{H}_2\text{O}$) was chosen as dopant to lower the phase transition temperature.

**Synthesis of VO₂-SiO₂ composite thin films.** The preparation process of the VO₂-SiO₂ composite films is shown schematically in Fig. 15. In a typical synthesis, certain amount of V₂O₅ was reduced by H₂C₂O₄ (molar ratio is 1:3) in EtOH solution. After refluxing at 120 °C for 10 hours (hrs), a transparent blue solution of V(O)₃C₂H₂O (1.0 M) was obtained. For preparing a VO₂-SiO₂ composite solution, a SiO₂ sol was prepared by mixing TEOS, EtOH and H₂O (The pH value was adjusted to 2 with HCl) at a given volume ratio as 1:10:0.2. F127 was added as a pore-forming agent to increase the porosity of the film. The solution was stirred for 1 hour following by aging for at least one day before merging with the V(O)₃C₂H₂O solution. After blending thoroughly for 1 hour, a homogeneous, clear and blue solution was obtained. The final concentration of V(O)₃C₂H₂O was diluted to a constant of 0.5 M by EtOH and the nominal Si/V atomic ratio varied from 0 to 1.0. For tungsten doped sample, the amount of the additive was carefully controlled for the realization of a fixed W doping level up to 1.5 at.%. The precursor solutions were aged for 2 hrs at room temperature before spin coating.

Composite films were deposited on borosilicate glasses (20 × 20 mm²) by a spin-coating technology with the speed of 3000 rpm for 20 s. To analyze the elemental composition and the molar ratio of Si/V in the composite films, films were prepared on aluminum foils under the same procedure. All the substrates were sequentially cleaned by acetone, ethanol and deionized water to remove surface contaminations. After drying at 60 °C for 10 min to remove the excess solvent, the as-prepared films were annealed by the step of 5 °C/min in tube furnace under an appropriate atmosphere.

**Characterization.** The crystal structure of the VO₂-SiO₂ composite films was collected by Glancing Angle X-ray diffractometer (GAXRD, PANalytical Xpert Pro MPD) using Cu-Kα radiation ($\lambda = 1.54$ Å). The operating voltage and current were kept at 40 kV and 40 mA, respectively. The surface morphology and element distributions were characterized by field emission scanning electron microscopy (FESEM, S-4800, Hitachi Japan) and transmission electron microscopy (TEM, 2010F, JEOL and TF20, FEI) equipped with an energy-dispersive spectrometer (EDS, Oxford) attachment. The thicknesses of the composite films were determined by the step profiler (Alpha-Step D-100, KLA-Tencor USA). Specimens for TEM analysis were prepared by cutting, grinding, dimpling and ion-milling (Gatan 691, operated at 3.0 to 0.5 kV and cooled with liquid nitrogen), followed by surface cleaning using an ion cleaner (JIC-410, JEOL, Japan) to remove completely any residual amorphous film. The thermochromic properties of the films were monitored by ultraviolet-visible-near infrared spectrophotometer (UV-Vis-NIR, Lambda 750), from 250 to 2500 nm at temperature 30 °C and 100 °C, respectively. Temperature was measured with the assistance of a temperature sensor in contact with the films which was connected with a temperature controlling unit (FP23, SHIMADEN Japan).
refractive index and extinction coefficient of the films were performed on spectroscopic ellipsometry (SE) (M-2000UI, J.A. Woollam USA) in the spectral range of 245–1680 nm. Hysteresis loops were measured by collecting the transmittance of the films at a fixed wavelength (2000 nm) under variable temperatures at an approximate interval of 2°C. The temperature errors were less than ±1.0°C based on repeated measurements.

Calculation based on the effective medium theory. Based on the effective medium theory, we calculate the optical constants of the composite films. It is considered that there is a random mixture of VO₂ and SiO₂ nanoparticles dispersed in our composite films. Both of the nanoparticles are taken to be spherical with size far less than λ, so that the composite film can be regarded as an “effective medium” model with properties intermediate between those nanoparticles. Assuming that the VO₂ and SiO₂ units are topologically equivalent, it is appropriate to get the effective dielectric function (ε) based on the Bruggeman theory:\[\varepsilon_1 \cdot f \cdot \varepsilon_{SiO_2} + \varepsilon_2 \cdot (1 - f) \cdot \varepsilon_{VO_2} = \varepsilon \cdot \varepsilon_0.\]

Among which,
\[\varepsilon = \varepsilon_1 + i\varepsilon_2 \quad (7)\]
\[\varepsilon_1 = n^2 - k^2 \quad (8)\]
\[\varepsilon_2 = 2nk \quad (9)\]

ε₅₀ and ε₆₀ are the effective dielectric functions of the two nanoparticles, respectively. f denotes as the “filling factor” (i.e., volume fraction) of SiO₂, ε₁ and ε₂ are the real part and the imaginary part of the dielectric function, respectively. The optical constants of VO₂ and SiO₂ are adopted from the literatures. Based on the calculated optical constants of composite films with different f, we simulate the optical spectra of a single-layer composite film on borosilicate glass substrate by the Essential Macleod software.

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"et al" indicates that multiple authors contributed to the work, but specific contributions from each author are not listed individually. The references are cited in the text to provide detailed information on the research and developments in the field of thermochromic materials.