Mg-doped VO₂@ZrO₂ core-shell nanoflakes for thermochromic smart windows with enhanced performance

Wen, Zuohao; Ke, Yujie; Feng, Chengchen; Fang, Shuliang; Sun, Miuyang; Liu, Xinghai; Long, Yi

2021

Wen, Z., Ke, Y., Feng, C., Fang, S., Sun, M., Liu, X., & Long, Y. (2021). Mg-doped VO₂@ZrO₂ core-shell nanoflakes for thermochromic smart windows with enhanced performance. *Advanced Materials Interfaces*, 8(1), 2001606-. doi:10.1002/admi.202001606

<https://hdl.handle.net/10356/145941>

<https://doi.org/10.1002/admi.202001606>

This is the accepted version of the following article: Wen, Z., Ke, Y., Feng, C., Fang, S., Sun, M., Liu, X., & Long, Y. (2021). Mg-doped VO₂@ZrO₂ core-shell nanoflakes for thermochromic smart windows with enhanced performance. *Advanced Materials Interfaces*, 8(1), 2001606-. doi:10.1002/admi.202001606, which has been published in final form at <https://doi.org/10.1002/admi.202001606>. This article may be used for non-commercial purposes in accordance with the Wiley Self-Archiving Policy [<https://authorservices.wiley.com/authorresources/Journal-Authors/licensing/self-archiving.html>].

Mg-Doped VO₂@ZrO₂ Core/Shell Nanoflakes for Thermochromic Smart Windows with Enhanced Performance

Zuohao Wen,[#] Yujie Ke,[#] Chengchen Feng, Shuliang Fang, Miuyang Sun, Xinghai Liu^{} Yi Long^{*}*

[#] Zuohao Wen and Yujie Ke contributed equally to this work.

Z. Wen, C. Feng, S. Fang, M. Sun, Prof. X. Liu
School of Printing and Packaging, Wuhan University, Wuhan 430072, China
liuxh@whu.edu.cn

Dr. Y. Ke, Dr. Y. Long
School of Materials Science and Engineering, Nanyang Technological University, 639798, Singapore

Dr. Y. Long
Singapore-HUJ Alliance for Research and Enterprise (SHARE), Campus for Research Excellence and Technological Enterprise (CREATE), Singapore, 138602, Singapore.

Dr Y. Long
Sino-Singapore International Joint Research Institute (SSIJRI), Guangzhou, 510000, P. R. China.
longyi@ntu.edu.sg

Keywords: Vanadium dioxide, UV-curing, nanocrystals, thermochromic, solar energy.

The VO₂-based smart windows can dynamically and reversibly adjust the indoor solar irradiation to reduce the energy consumption for building glasses. The paper reports the first successful preparation of Mg-doped VO₂@ZrO₂ core-shell nanocrystals with promoted thermochromic performance as well as tunable appearance and wettability. To our knowledge, the achieved combination of T_{lum} of 52.4% and ΔT_{sol} of 7.1% is comparable to the best-reported results of VO₂-based core-shell rod structures. The thickness of ZrO₂ shell is tunable between 3-14 nm, resulting in a slightly hydrophobic surface and a slight color change toward blue-green and brighter produced films. The preparation method based on hydrothermal and UV-curing methods is facile. The work may inspire future development of VO₂ synthesis,

their structure-property, and the application the thermochromic films for energy-saving purposes in buildings or automobiles.

1. Introduction

Reducing the energy consumption of buildings has attracted increasing research interest since it contributes to a significant section (~40%) of the total energy consumption of the society.^[1]

Energy-saving windows can reflect the sunlight in a certain range of wavelengths to reduce the energy used to maintain the indoor environment.^[2, 3] However, the problem is that the optical properties are fixed, which can not adjust the indoor solar radiation to meet the needs in different seasons. The smart window emerges as a promising solution to adjust the indoor solar radiation in a dynamic and controllable way to save the building energy.^[3-6]

Vanadium dioxide (VO_2) is the most-investigated material for the thermochromic smart window. It undergoes a reversible semiconductor-metal phase transition (MIT) at ~68 °C.^[7-10]

$\text{VO}_2(\text{M})$ is a monoclinic structure in the low-temperature insulation phase with space group $\text{P}2_1/\text{c}$, and $\text{VO}_2(\text{R})$ is a tetragonal structure in the high-temperature metal phase with space group $\text{P}4_2/\text{nm}$.^[8] The optical properties, especially the infrared region (IR), can be suddenly changed from high to low transmission under increasing temperature.^[11-14] The phase transition mechanism is still under debate. It is generally considered that it is caused by a strong electron-electron correlation related to the Mott transition or an electron-phonon interaction related to the Peierls transition.^[12, 15]

In recent years, researchers have developed many methods for preparing VO_2 films.

According to the reaction medium, the preparation methods can be divided into two categories based on gas and solution deposition, including the gas-based deposition includes chemical vapor deposition (CVD)^[16, 17] and physical vapor deposition (PVD),^[18, 19] as well as

the solution-based deposition including sol-gel,^[20] hydrothermal process^[21-23] and polymer-assisted deposition.^[24, 25]

The development of core-shell structures to encapsulate the VO₂ crystals can enhance their stability and the thermochromic performance.^[11] The VO₂ can be oxidized to V₂O₅ in the air environment after long-term service since the V is a multivalent element as a transition metal.^[13] This will greatly affect the thermochromic performance of VO₂ and limit their application in smart windows.^[5] One potential solution is to coat the surface of VO₂ with inert oxide shells or layers.^[11, 26-28] Also, the core-shell nanocrystals can also adjust the refractive index (RI) of the internal nanofiller, which can reduce the scattering caused by reducing the RI mismatch cross the interface of the nanocrystals and their polymer matrix.^[29] There have been studies on the core-shell structure of VO₂, such as SiO₂,^[30, 31] TiO₂,^[32] ZnO,^[33, 34] and ZnS^[35] deposited on the surface of VO₂. Among them, SiO₂ is a commonly-used shell since it is optically transparent and chemically inert, protecting the core from oxidation.

In this work, the ZrO₂ is applied as the shell layer and Mg as a doping element to form Mg-doped VO₂@ZrO₂ nanocrystals. Because Mg doping can enhance the visible transmittance by widening the bandgap of VO₂.^[36, 37] ZrO₂ is a common anti-reflective material with a number of advantages.^{Error! Reference source not found.}^[38] First, the thermal expansion coefficient of ZrO₂ ($10.3 \times 10^{-6} \text{ K}^{-1}$)^[39] is close to that of the VO₂ monoclinic phase ($6.4 \times 10^{-6} \text{ K}^{-1}$) and tetragonal phase ($17.1 \times 10^{-6} \text{ K}^{-1}$). Second, ZrO₂ has good thermal environment adaptability, low diffusivity at high temperature, and high transmittance in the visible light region. Third, the ZrO₂ is non-toxic and environmentally friendly.^[40] Finally, further functionalization of the ZrO₂ shell allows it to be well incorporated into the polymer matrix.

To our knowledge, the work firstly reports that the successful preparation of VO₂@ZrO₂ core-shell nanocrystals. The XRD, FTIR, TEM, WDS, and EDS results showed that the ZrO₂ shell layer can be coated on the surface of the Mg-doped VO₂ nanocrystal cores without changing the VO₂(M) crystal. The thickness of the ZrO₂ shell can be controlled by adjusting the amount

of Zr precursors. The films have demonstrated with the enhanced thermochromic performance for energy-saving smart windows, resulting in an optimizing T_{lum} of 52.4% and ΔT_{sol} of 7.1%, surpassing or at least being comparable to the best-reported results of VO₂-based core-shell rod structures.

3 Results and discussion

The proposed method is presented in **Schematic 1** to prepare Mg-doped VO₂@ZrO₂ thermochromic thin films on a glass substrate. Firstly, poly(vinylpyrrolidone) (PVP) was coated onto the Mg-doped VO₂ nanocrystals pre-prepared through a one-step hydrothermal method.^[41] Secondly, ZrOCl₂ ethanol and water solution are added to form the ZrO₂ shell. The chemical equation during the reaction is as follows.

Thirdly, the Mg-doped VO₂@ZrO₂ nanocrystals in PVP ethanol solution undergo a mechanical milling process for several hours for a better dispersion. This treatment can increase the dispersion of nanocrystals in the polyurethane acrylate (PUA). Finally, the suspension is cast on the glass substrate through spin coating, followed by a UV-curing process to prepare a VO₂-based composite film.

The Mg-doped VO₂ and Mg-doped VO₂@ZrO₂ powder are produced with a different mass ratio of Zr:V, shown as the XRD patterns in **Figure 1a**. All peaks of the four kinds of particles correspond to monoclinic VO₂(M) (JCPDS no. 43-1051) without any other impurity peaks detected. The Mg-doped VO₂@ZrO₂ has a higher intensity than the uncoated nanocrystals, which may be due to the additional hydrothermal reaction for ZrO₂ shell, leading to an enhanced crystallinity of the Mg-doped VO₂. However, the diffraction peak of ZrO₂ is not clearly shown, because ZrO₂ in core-shell structure is most likely to be amorphous and cannot be detected by XRD. Besides, the diffraction peaks of coated VO₂ tend to broaden,

indicating that the grain size of Mg-doped VO₂@ZrO₂ decreases. The average size (D) of the powder sample is calculated by the Debye Scherer equation:

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (3)$$

Where K = Scherer constant (0.9), λ is the X-ray wavelength of CuK α radiation (1.5406 nm), β is the diffraction angle of the peak, and θ is the full width at half maximum of the maximum intensity of the diffraction peak. The average crystallite size of Mg-doped VO₂ nanocrystals is calculated to be ~2479 Å, while the average crystallite size of Mg-doped VO₂@ZrO₂-4 nanocrystals is ~335 Å. That shows that the core-shell structure will greatly affect the particle size, which may be because heat treatment makes VO₂ nanocrystals crushed, reducing the size of Mg-doped VO₂@ZrO₂. **Figure 1b** shows that the FTIR patterns of ZrO₂, Mg-doped VO₂, and Mg-doped VO₂@ZrO₂ with Zr/V mass ratio of 1/4. The characteristic absorption peak of the Mg-doped VO₂ sample at 525 cm⁻¹ is attributable to the V-O-V long-distance tensile vibration, which is consistent with the previous reports.^[42] ZrO₂ crystals were also identified with a transmittance valley at ~525 cm⁻¹ due to its strong Zr-O vibration of monoclinic ZrO₂. The characteristic band of zirconia appears in the FTIR image of the Mg-doped VO₂@ZrO₂-4 sample with 1041 cm⁻¹ about the bending vibration of the -OH of the chemical bond O-Zr-OH. But it does not show the bending vibration peak at 450 cm⁻¹ of O-Zr-O and other absorption peaks of zirconia. The identified transmittance valleys at this wavenumber is weak in Mg-doped VO₂@ZrO₂ samples may due to relatively poor crystallinity of ZrO₂ shells and some potential damage to VO₂ crystallinity during the shell preparation process. Both the characteristic peaks related to ZrO₂ and VO₂ nanocrystals are observed, indicating the Mg-doped VO₂@ZrO₂ has two oxide structures. Besides, absorption bands of 3437 cm⁻¹ and 1623 cm⁻¹ are also observed, which are -OH tensile vibration peaks and bending vibration peaks of free hydroxyl groups and hydrogen bond surface hydroxyl groups, should being attributed to the hydroxyl groups on the crystal surface.

The TEM images of the Mg-doped VO₂ are exhibited in **Figure 2a, b**. The nanocrystals are rod-shaped or snowflake-shaped and the bright diffraction points in the SAED pattern in the inset of Figure 2a indicates that the VO₂(M) nanocrystals are single crystal and have good crystallinity. One of the selected diffraction points corresponds to the M (011) crystal plane of VO₂ (M). The HRTEM image of single nanocrystals circled in the insets in Figure 2b shows clear and orderly lattice fringes and the crystal plane spacing is about 3.2 Å, corresponding to the M (011) crystal plane. The TEM images of the Mg-doped VO₂@ZrO₂ are exhibited in **Figure 2c-k**. It can be observed from Figure 2c, f, and i that single VO₂ nanocrystal is coated with ZrO₂ shell separately and the thicknesses of the ZrO₂ shell are about 14.18 nm, 4.80 nm, and 2.82 nm corresponding to Mg-doped VO₂@ZrO₂-2, Mg-doped VO₂@ZrO₂-4, and Mg-doped VO₂@ZrO₂-6, respectively, which means that the Mg-doped VO₂ particles are well-protected by ZrO₂ shell. However, the core-shell structures have no obvious lattice fringes, which may be due to the poor crystallinity of the shell, which is consistent with the previous XRD analysis.

The elemental distributions are analyzed using the EDS mapping technique for the Mg-doped VO₂ (**Figure 3a**). It is found that the elements of Mg and V are distributed on the selected snowflake crystals of the Mg-doped VO₂ sample, indicating that Mg is successfully doped into the VO₂ lattice and no other impurities are generated. **Figure 3b** is the EDS mapping results of Mg-doped VO₂@ZrO₂-4 nanocrystal. Zr, V, and Mg elements of the sample are detected on the nanoflake crystals, indicating the successful coating of ZrO₂ on the surface of Mg-doped VO₂ nanoflake crystals to form a core-shell structure.

Besides, **Figure 3c** is the EDS images of Mg-doped VO₂@ZrO₂-4. The nanocrystals show characteristic peaks of about 0.52, 4.98, and 5.45 keV, attributed to the L α , K α , and K β of V, and also show the characteristic emission lines of Zr related to L α and L β are 2.04 and 2.54 KeV, respectively. It is confirmed that there are zirconia and vanadium oxides (ZrO₂ and VO₂) in the synthesized nanocrystals. The table inserted in Figure 3c shows the EDS value of

Mg-doped VO₂@ZrO₂-4 nanocrystals. The actual value of the Zr/V mass ratio is 0.12, far lower than the design value of 0.25. Because in the preparation process of core-shell structure, the centrifugal cleaning process for ammonia and PVP removal will also remove those suspending Zr(OH)₄ that is not attached to the crystals.

The thermochromic performance of the produced samples is evaluated for their potential application in energy-saving smart windows. The light transmittance (T_{lum} , 380-780 nm) and solar transmittance (T_{sol} , 300-2500 nm) are calculated according to the following equation:

$$T_{lum/sol} = \frac{\int \varphi_{lum/sol}(\lambda)T(\lambda)d\lambda}{\int \varphi_{lum/sol}(\lambda)d\lambda} \quad (4)$$

where λ represents the transmittance at the wavelength λ , $\varphi_{lum}(\lambda)$ is the standard luminous efficiency function for human vision, and sol is the solar spectral irradiance with the air quality of 1.5 (the receiving surface is defined as the inclined plane at 37 ° toward the equator). Also, the solar modulation capacity (ΔT_{sol}) is defined as the following equation

$$T_{sol} = T_{sol,M} - T_{sol,R} \quad (5)$$

where $T_{sol, M}$, and $T_{sol, R}$ represent the solar transmittance of the VO₂ film in the 20°C (M phase) and 90°C (R phase) , respectively. **Figure 4a** is the thermochromic performance diagram of Mg-doped VO₂ energy-saving film prepared at different spin-coating speeds and the calculated performance is shown in **Table 1**. The transmittance valley at ~1200 nm for high-temperature samples is due to the localized surface plasmon resonance of VO₂ crystal in the nano-/micro scale, which is consistent with previous reports.^[43-46] It can be seen that ΔT_{sol} is slightly decreasing, but T_{lum} is increased under an increasing spin-coating speed from 1000 to 4000 rpm. At low-temperature states (20°C), T_{lum} is increased from 24.6% on 1000-rpm to 48.3% on 4000-rpm samples. Therefore, it is necessary to choose the appropriate rotation speed to make a balance between the T_{lum} and ΔT_{sol} , and 4000 rpm is applied for the following results.

To explore the effect of the ZrO₂-shell on the thermochromic performance of VO₂ energy-saving films, the transmittance spectra of the Mg-doped VO₂ and Mg-doped VO₂@ZrO₂-4 samples are recorded (**Figure 4b**) and their thermochromic performance is summarized in Table. 1. It can be found that the ZrO₂ shell has a great influence on the thermochromic properties. After ZrO₂ coating Mg-doped VO₂ nanocrystals, T_{lum} and ΔT_{sol} are changed from 48.3% and 4.7% to 50.6% and 6.2%, respectively. This is because the better dispersion of the core-shell crystals than the bare Mg-doped crystals in the matrix, and the aggregation of VO₂ crystals may lower the thermochromic performance by reducing the transmittance contrast at dense solar energy region of ~1000 to 1500 nm.^[47]

We further investigate the effect of ZrO₂ coating thickness on the thermochromic performance of Mg-doped VO₂@ZrO₂ core-shell structure film, **Figure 4c** and **Table 2** are the transmittance spectra and the values of the thermochromic performance of Mg-doped VO₂ with different ZrO coating amount under the same spin coating conditions (4000 rpm for 30 s). As the Zr/V ratio increases, the visible light transmittance increases from 33.9% to 62.1% for T_{lum} at low temperatures. The optimizing performance is found on Mg-doped VO₂@ZrO₂-4 sample ($Zr/V = 1/4$), ΔT_{sol} of the film reaches maximum value is 7.1%, and the light transmittance is higher than 50%. To our knowledge, the performance outperforms or at least be comparable to the best-reported results of VO₂-based core-shell rod structures^[31, 32, 48-51] and nanoparticles (NP)^[11, 32, 33, 52] (**Figure 4d**).

The ZrO₂ shells to the wettability of VO₂ crystals are further investigated. **Figure 5** shows the contact angle results on the surface of the Mg-doped VO₂ and Mg-doped VO₂@ZrO₂ samples. It is found that the core-shell structure films have a larger contact angle than the uncoated VO₂ film. As the ZrO₂ coating amount increased, the contact angle gradually increases from 59.3° to 73.7°, an increase of about 19.5%, indicating that the core-shell structure tends to lead a more hydrophobic surface. The hydrophobic surface is beneficial to maintain the

isolation of VO₂ from water and protect the coating from oxidation, which can improve the environmental stability of the VO₂ coating for long-term service.^[53]

The prepared films are shown in **Figure 6** and their color is analyzed for Mg-doped VO₂ and Mg-doped VO₂@ZrO₂ films in the CIE lab system (**Figure 7**). Combined with the visual experience and the Lab value in **Table 3**, the color of the films gradually becomes light yellow, and the transparency is significantly enhanced. The a* and b* chromaticity coordinates of the films change from (0.08, 31.01) to (-2.61, 23.23) corresponding to the color shift of red to green and yellow to blue, and the parameter L* is increased from 40.32 to 66.40, corresponding to the increase in the brightness of the film. This color change leads to a blue shift of the absorption edge from 490nm to 440nm. This color change may make the Mg-doped VO₂@ZrO₂ energy-saving film more suitable for windows.

4 Conclusion

In summary, transparent Mg-doped VO₂@ZrO₂-based thermochromic films are prepared for the first time. These films switch from a low-temperature infrared transparent state to a high-temperature infrared blocking state, accompanied by an optimizing T_{lum} of 52.4% and ΔT_{sol} of 7.1%, outperforming or at least being comparable to the best-reported results of VO₂-based core-shell rod structures. The XRD, FTIR, TEM, WDS, and EDS results showed that the ZrO₂ shell layer can be coated on the surface of the Mg-doped VO₂ nanocrystal cores without changing the VO₂(M) crystal.

The thickness of the ZrO₂ shell layer varies between 3-14 nm. After ZrO₂ coating, the color of the films shifts towards blue-green and brighter, and the change in contact angle showed that the films changed to the hydrophobic direction to isolate the core and water to improve environmental stability. The work may inspire the future development of VO₂ synthesis and thermochromic smart windows.

2. Experimental and characterization procedures

Preparation of Mg-doped VO₂ nanocrystals. Mg-doped VO₂ nanocrystals were synthesized by the one-step hydrothermal method. In a typical procedure, 1.365 g of V₂O₅ powder (99.99%, Sarn Chemical Technology (Shanghai) Co., Ltd.) and 0.0479 g of Mg(NO₃)₂·6H₂O powder (99.99%, Sinopharm Chemical Reagent Co., Ltd.) was added into 75 ml of oxalic acid dihydrate (AR, Sinopharm Chemical Reagent Co., Ltd) aqueous solution with a concentration of 0.22 M to form a yellowish slurry. The atomic molar ratio of Mg to V is 3%. The slurry was stirred for 30 mins and then transferred to a 100-ml Teflon-lined stainless-steel autoclave. The autoclave was maintained at 280 °C for 48 hr and then air-cooled to room temperature. The mixed solution was taken out, and the powder was repeatedly washed six times using water and ethanol. The powder was vacuum dried at 60°C for 12 hr, followed by a grind process to obtain 3 at% Mg-doped VO₂ powder.

Preparation of Mg-doped VO₂@ZrO₂ nanocrystals. Mg-doped VO₂@ZrO₂ nanocrystals were synthesized through the thermal decomposition method. First, the Mg-doped VO₂ nanocrystals were pretreated using PVP (99.99%, Sinopharm Chemical Reagent Co., Ltd). 0.5 g of Mg-doped VO₂ powder and an appropriate amount of PVP were dispersed in 30 ml of ethanol (AR, Sinopharm Chemical Reagent Co., Ltd) and fully stirred to ensure that the PVP could attach onto VO₂ crystals. Then, the Mg-doped VO₂@ZrO₂ core-shell structure was prepared by the hydrolysis of ZrOCl₂·8H₂O (99.99%, Sinopharm Chemical Reagent Co., Ltd). Different amounts of ZrOCl₂·8H₂O were dispersed in a mixed solution of ethanol and water and added to the above solution, where the mass ratios of V and Zr were variable from 2:1, 4:1 to 6:1. Then ammonia water (AR, Sinopharm Chemical Reagent Co., Ltd) was added at 60 °C and continued to react for 2 hr to motivate the hydrolysis of ZrOCl₂·8H₂O. After fully cooling down to room temperature, the powder was obtained by high-speed centrifugation to remove excess PVP and ammonia water, and then added 60 ml of ethanol

and water solution. The mixed solution was stirred for 30 min and then transferred to a 100 ml Teflon-lined stainless-steel autoclave. The autoclave was maintained at 240°C for 24 hr and then was air-cooled to room temperature. After the reaction, the produced powder was washed by high-speed centrifugation with water and freeze-dried for 48 h to obtain Mg-doped VO₂@ZrO₂ core-shell structure powders.

Preparation of Mg-doped VO₂@ZrO₂/PUA composite film. The 0.5 g of as-prepared crystals and 0.25 g of PVP were dispersed ultrasonically in 16 ml of ethanol for 8 h by mechanical ball milling. The polyurethane acrylate (PUA) is prepared by adding the anhydrous toluene-2,4-diisocyanate (TDI, CAS# 91-08-7, Sinopharm Chemical Reagent Co. Ltd.) drop-by-drop into the anhydrous polyethylene glycol (PEG, CAS# 25322-68-3, Sinopharm Chemical Reagent Co. Ltd.), followed by adding 17.0 g of hydroxyethyl acrylate (HEA, CAS# 868-77-9, Sinopharm Chemical Reagent Co. Ltd.) at elevated temperature of 75 °C and reacting for ~7 hrs. Before that, the distillation processes are applied for commercial TDI (9.42 g) and HEA (9.84 g) to remove the water. Then, an appropriate amount of PUA, trimethylolpropane triacrylate (TMPTA, CAS# 15625-89-5, Aladdin), tripropylene glycol diacrylate (TPGDA, CAS# 42978-66-5, Alladin), 1,6-hexanediol diacrylate (HDDA, CAS# 13048-33-4, Alladin), and diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TPO, CAS# 75980-60-8, Alladin) were added and stirred for 6 h. Finally, 0.2 ml of the mixture was uniformly cast onto the glass substrate and spin-coated at different speeds (1000-4000 rpm) for 10 s. Composite films were formed after curing for 20 s under UV light. The films produced at 4000 rpm is identified with a thickness of ~70 μm.

Characterization. The crystalline phases of the powder were analyzed by X-ray powder diffraction (XRD, D8 Focus, Bruker, Germany). The morphology and elemental composition of the powder were determined by Transmission Electron Microscope (TEM, 2100F, JEOL,

Japan) and Electron Probe Micro Analysis (EPMA, JXA-8530F Plus, JEOL, Japan), respectively. The optical transmittance characteristics were obtained by UV-vis-NIR spectrophotometer (UV-3600, SHIMADZU, Japan) in the wavelength range of 300-2500nm equipped with a film heating-cooling accessory. The contact angles were measured by a fully automatic contact angle meter (SL200KS, Kino, USA) to evaluate the hydrophilicity of the films. The film colors were measured by the Spectro EYE spectrophotometer (X-Rite, USA) with L (brightness), a (red-green), and b (yellow-blue) values of color parameters.

Acknowledgments

Zuohao Wen and Yujie Ke contributed equally to this work. X. Liu acknowledges the study is supported by the financial support of this work by NSAF (Grant No. 51776143). The use of SEM, XPS, TEM, and AFM was funded by the Open Subsidies for large-scale Equipment of Wuhan University (Grant No. LF20181061). Y. Long thanks to the funding support by the National Research Foundation, Prime Minister's Office, Singapore under its Campus for Research Excellence and Technological Enterprise (CREATE) programme and Sino-Singapore International Joint Research Institute for funding support.

Conflicts of interest

The authors declare no conflict of interest.

Received: ((will be filled in by the editorial staff))

Revised: ((will be filled in by the editorial staff))

Published online: ((will be filled in by the editorial staff))

References

- [1] Y. Ke, C. Zhou, Y. Zhou, S. Wang, S. H. Chan, Y. Long, *Adv. Funct. Mater.* **2018**, 28, 1800113.
- [2] G. Cai, J. Wang, P. S. Lee, *Acc. Chem. Res.* **2016**, 49, 1469.
- [3] Y. Ke, J. Chen, G. Lin, S. Wang, Y. Zhou, J. Yin, P. S. Lee, Y. Long, *Adv. Energy Mater.* **2019**, 9, 1902066.
- [4] G. Cai, X. Cheng, M. Layani, A. W. M. Tan, S. Li, A. L.-S. Eh, D. Gao, S. Magdassi, P. S. Lee, *Nano Energy* **2018**, 49, 147.

- [5] X. Cao, T. Chang, Z. Shao, F. Xu, H. Luo, P. Jin, *Matter* **2020**, 2, 862.
- [6] Y. Gao, H. Luo, Z. Zhang, L. Kang, Z. Chen, J. Du, M. Kanehira, C. Cao, *Nano Energy* **2012**, 1, 221.
- [7] Y. Cui, Y. Ke, C. Liu, Z. Chen, N. Wang, L. Zhang, Y. Zhou, S. Wang, Y. Gao, Y. Long, *Joule* **2018**, 2, 1707.
- [8] K. Liu, S. Lee, S. Yang, O. Delaire, J. Wu, *Mater. Today* **2018**, 21, 875.
- [9] L. Xiao, H. Ma, J. Liu, W. Zhao, Y. Jia, Q. Zhao, K. Liu, Y. Wu, Y. Wei, S. Fan, K. Jiang, *Nano Lett.* **2015**, 15, 8365.
- [10] M. Li, X. Wu, L. Li, Y. Wang, D. Li, J. Pan, S. Li, L. Sun, G. Li, *J. Mater. Chem. A* **2014**, 2, 4520.
- [11] Y. F. Gao, S. B. Wang, H. J. Luo, L. Dai, C. X. Cao, Y. L. Liu, Z. Chen, M. Kanehira, *Energy Environ. Sci.* **2012**, 5, 6104.
- [12] Y. Ke, S. Wang, G. Liu, M. Li, T. J. White, Y. Long, *Small* **2018**, 14, 1802025.
- [13] T. Chang, X. Cao, N. Li, S. Long, Y. Zhu, J. Huang, H. Luo, P. Jin, *Matter* **2019**, 1, 734.
- [14] M. E. A. Warwick, R. Binions, *J. Mater. Chem. A* **2014**, 2, 3275.
- [15] S. Biermann, A. Poteryaev, A. I. Lichtenstein, A. Georges, *Phys. Rev. Lett.* **2005**, 94, 026404.
- [16] M. Wilkinson, A. Kafizas, S. M. Bawaked, A. Y. Obaid, S. A. Al-Thabaiti, S. N. Basahel, C. J. Carmalt, I. P. Parkin, *ACS Comb. Sci.* **2013**, 15, 309.
- [17] R. Shi, X. Cai, W. Wang, J. Wang, D. Kong, N. Cai, P. Chen, P. He, Z. Wu, A. Amini, N. Wang, C. Cheng, *Adv. Funct. Mater.* **2019**, 29, 1900527.
- [18] J. B. Kana Kana, J. M. Ndjaka, B. D. Ngom, N. Manyala, O. Nemraoui, A. Y. Fasasi, R. Nemutudi, A. Gibaud, D. Knoesen, M. Maaza, *Thin Solid Films* **2010**, 518, 1641.
- [19] T. D. Vu, Z. Chen, X. Zeng, M. Jiang, S. Liu, Y. Gao, Y. Long, *J. Mater. Chem. C* **2019**, 7, 2121.

- [20] Y. Jiazhen, Z. Yue, H. Wanxia, T. Mingjin, *Thin Solid Films* **2008**, *516*, 8554.
- [21] S. R. Popuri, M. Miclau, A. Artemenko, C. Labrugere, A. Villesuzanne, M. Pollet, *Inorg. Chem.* **2013**, *52*, 4780.
- [22] M. Li, S. Magdassi, Y. Gao, Y. Long, *Small* **2017**, *13*, 1701147.
- [23] Z. Chen, Y. Gao, L. Kang, C. Cao, S. Chen, H. Luo, *J. Mater. Chem. A* **2014**, *2*, 2718.
- [24] L. Kang, Y. Gao, H. Luo, Z. Chen, J. Du, Z. Zhang, *ACS Appl. Mater. Interfaces* **2011**, *3*, 135.
- [25] M. Liu, B. Su, Y. V. Kaneti, Z. Chen, Y. Tang, Y. Yuan, Y. Gao, L. Jiang, X. Jiang, A. Yu, *ACS Nano* **2017**, *11*, 407.
- [26] T. Chang, X. Cao, L. R. Dedon, S. Long, A. Huang, Z. Shao, N. Li, H. Luo, P. Jin, *Nano Energy* **2018**, *44*, 256.
- [27] T. Chang, X. Cao, N. Li, S. Long, X. Gao, L. R. Dedon, G. Sun, H. Luo, P. Jin, *ACS Appl. Mater. Interfaces* **2017**, *9*, 26029.
- [28] I. Top, R. Binions, M. E. A. Warwick, C. W. Dunnill, M. Holdynski, I. Abrahams, *J. Mater. Chem. C* **2018**, *6*, 4485.
- [29] Y.-Q. Li, S.-Y. Fu, Y. Yang, Y.-W. Mai, *Chem. Mater.* **2008**, *20*, 2637.
- [30] R. Li, S. Ji, Y. Li, Y. Gao, H. Luo, P. Jin, *Mater. Lett.* **2013**, *110*, 241.
- [31] Y. Zhou, A. Huang, Y. Li, S. Ji, Y. Gao, P. Jin, *Nanoscale* **2013**, *5*, 9208.
- [32] Y. Li, S. Ji, Y. Gao, H. Luo, P. Jin, *ACS Appl. Mater. Interfaces* **2013**, *5*, 6603.
- [33] Y. Chen, X. Zeng, J. Zhu, R. Li, H. Yao, X. Cao, S. Ji, P. Jin, *ACS Appl. Mater. Interfaces* **2017**, *9*, 27784.
- [34] H. Yin, K. Yu, C. Song, Z. Wang, Z. Zhu, *Nanoscale* **2014**, *6*, 11820.
- [35] H. Ji, D. Liu, C. Zhang, H. Cheng, *Sol. Energy Mater. Sol. Cells* **2018**, *176*, 1.
- [36] N. Wang, S. Liu, X. T. Zeng, S. Magdassi, Y. Long, *J. Mater. Chem. C* **2015**, *3*, 6771.
- [37] S.-Y. Li, N. R. Mlyuka, D. Primetzhofer, A. Hallén, G. Possnert, G. A. Niklasson, C. G. Granqvist, *Appl. Phys. Lett.* **2013**, *103*.

- [38] J. A. Rodríguez, M. Fernández-García, *Synthesis, Properties, and Applications of Oxide Nanomaterials*, Wiley, **2007**.
- [39] N. I. Lazukova, V. A. Gubanov, *Solid State Commun.* **1976**, *20*, 649.
- [40] H. Zong, C. Geng, C. Zhang, H. Liu, J. Wu, Z. Yu, G. Cao, C. Kang, M. Li, *Appl. Surf. Sci.* **2019**, *487*, 138.
- [41] A. Bai, H. Song, G. He, Q. Li, C. Yang, L. Tang, Y. Yu, *Ceram. Int.* **2016**, *42*, 7583.
- [42] F. Guinneton, L. Sauques, J. C. Valmalette, F. Cros, J. R. Gavarri, *Journal of Physics and Chemistry of Solids* **2001**, *62*, 1229.
- [43] Y. Ke, X. Wen, D. Zhao, R. Che, Q. Xiong, Y. Long, *ACS Nano* **2017**, *11*, 7542.
- [44] Y. Ke, Q. Zhang, T. Wang, S. Wang, N. Li, G. Lin, X. Liu, Z. Dai, J. Yan, J. Yin, S. Magdassi, D. Zhao, Y. Long, *Nano Energy* **2020**, *73*, 104785.
- [45] S. Long, X. Cao, R. Huang, F. Xu, N. Li, A. Huang, G. Sun, S. Bao, H. Luo, P. Jin, *ACS Appl. Mater. Interfaces* **2019**, *11*, 22692.
- [46] S. Dou, J. Zhao, W. Zhang, H. Zhao, F. Ren, L. Zhang, X. Chen, Y. Zhan, Y. Li, *ACS Appl. Mater. Interfaces* **2020**, *12*, 7302.
- [47] Y. Ke, Y. Yin, Q. Zhang, Y. Tan, P. Hu, S. Wang, Y. Tang, Y. Zhou, X. Wen, S. Wu, T. J. White, J. Yin, J. Peng, Q. Xiong, D. Zhao, Y. Long, *Joule* **2019**, *3*, 858.
- [48] N. Wang, M. Duchamp, C. Xue, R. E. Dunin-Borkowski, G. Liu, Y. Long, *Adv. Mater. Interfaces* **2016**, *3*, 1600164.
- [49] Y. Zhou, S. Ji, Y. Li, Y. Gao, H. Luo, P. Jin, *J. Mater. Chem. C* **2014**, *2*, 3812.
- [50] Y. Li, S. Ji, Y. Gao, H. Luo, M. Kanehira, *Sci. Rep.* **2013**, *3*, 1370.
- [51] A. Huang, Y. Zhou, Y. Li, S. Ji, H. Luo, P. Jin, *J. Mater. Chem. A* **2013**, *1*, 12545.
- [52] J. Zhu, Y. Zhou, B. Wang, J. Zheng, S. Ji, H. Yao, H. Luo, P. Jin, *ACS Appl. Mater. Interfaces* **2015**, *7*, 27796.
- [53] N. Maximous, G. Nakhla, W. Wan, K. Wong, *J. Membr. Sci.* **2010**, *352*, 222.

Scheme 1. Preparation procedure for Mg-doped $\text{VO}_2@ZrO_2$ nanocrystals and flexible composite films

Figure 1. (a) XRD patterns of Mg-doped VO_2 and Mg-doped $\text{VO}_2@ZrO_2$ powder with a different mass ratio of Zr:V. (b) FTIR patterns of ZrO_2 , Mg-doped VO_2 , and Mg-doped $\text{VO}_2@ZrO_2$ powder with Zr/V mass ratio of 1/4

Figure 2. (a and b) TEM and HRTEM images of Mg-doped VO₂, the inset in (a) is the SAED image of Mg-doped VO₂; (c, d, and e) TEM and HRTEM images of Mg-doped VO₂@ZrO₂-2; (f, g, and h) TEM and HRTEM images of Mg-doped VO₂@ZrO₂-4; (i, j and k) TEM and HRTEM images of Mg-doped VO₂@ZrO₂-6 (Mg-doped VO₂@ZrO₂-2, Mg-doped VO₂@ZrO₂-4, Mg-doped VO₂@ZrO₂-6 indicate the V/Zr mass ratio is 2, 4 and 6, respectively)

Figure 3. (a) EDS mapping results of the Mg-doped VO₂ with Mg, V and O elements, respectively; (b) EDS mapping results of the Mg-doped VO₂@ZrO₂-4 with Zr, Mg, V and O elements, respectively; (c) EDS analysis of the Mg-doped VO₂@ZrO₂-4

Figure 4. Transmittance spectra at 20 and 90°C of (a) Mg-doped VO₂-based films at 1000, 2000, 3000, and 4000 rpm, (b) the uncoated Mg-doped VO₂ and Mg-doped VO₂@ZrO₂-4 films at 4000rpm, and (c) the uncoated Mg-doped VO₂ and Mg-doped VO₂@ZrO₂ films with the V/Zr mass ratio of 2, 4 and 6, respectively. (d) Comparison of the work with previous VO₂-based core-shell rod structures [31, 32, 48-51] and nanoparticles. [11, 32, 33, 52]

Figure 5. (a-d) Images of water contact angles of the (a) uncoated Mg-doped VO₂ and (b-d) Mg-doped VO₂@ZrO₂ films with the V/Zr mass ratio of 6, 4, and 2, respectively

Figure 6. The uncoated Mg-doped VO₂ and Mg-doped VO₂@ZrO₂ films with the V/Zr mass ratio of 6, 4, and 2 for samples 1, 2, 3, or 4, respectively

Figure 7. The CIE color analysis of the uncoated Mg-doped VO₂ and Mg-doped VO₂@ZrO₂ films with the V/Zr mass ratio of 6, 4, and 2 for number 1, 2, 3, or 4, respectively in the CIE Lab system

Table. 1 Summary of optical properties in T_{lum} and ΔT_{sol} for as-prepared samples: Mg-doped VO₂-based films at 1000, 2000, 3000, and 4000 rpm and Mg-doped VO₂@ZrO₂-4 films at 4000rpm

Sample name	Speed (rpm)	$T_{lum}(\%)$		$T_{sol}(\%)$		$\Delta T_{sol}(\%)$
		20°C	90°C	20°C	90°C	
Mg _{0.03} V _{0.97} O ₂	1000	24.6	24.1	25.1	20.3	4.8
Mg _{0.03} V _{0.97} O ₂	2000	35.8	35.5	36.0	31.1	4.9
Mg _{0.03} V _{0.97} O ₂	3000	47.5	47.8	47.1	42.9	4.2
Mg _{0.03} V _{0.97} O ₂	4000	48.3	47.8	47.7	43.0	4.7
Mg _{0.03} V _{0.97} O ₂ @ZrO ₂ -4	4000	50.6	50.5	54.8	48.6	6.2

Table. 2 Summary of optical properties in T_{lum} and ΔT_{sol} for as-prepared samples: the uncoated Mg-doped VO₂ and Mg-doped VO₂@ZrO₂ films with the V/Zr mass ratio of 6, 4, and 2, respectively

Sample name	Zr:V mass ratio	ΔT_{2000nm}	$T_{lum}(\%)$		$T_{sol}(\%)$		$\Delta T_{sol}(\%)$
			20°C	90°C	20°C	90°C	
Mg _{0.03} V _{0.97} O ₂	0	15.7	33.9	33.1	34.0	28.5	5.5
Mg _{0.03} V _{0.97} O ₂ @ZrO ₂ -6	1:6	14.5	41.0	40.8	40.9	35.9	5.0
Mg _{0.03} V _{0.97} O ₂ @ZrO ₂ -4	1:4	17.4	52.4	51.6	56.3	49.2	7.1
Mg _{0.03} V _{0.97} O ₂ @ZrO ₂ -2	1:2	11.5	62.1	59.8	62.3	56.3	6.0

Table. 3 The CIE Lab values of the uncoated Mg-doped VO₂ and Mg-doped VO₂@ZrO₂ films with the V/Zr mass ratio of 6, 4, and 2, respectively

Number	Sample name	Zr:V	L*	a*	b*
1	Mg _{0.03} V _{0.97} O ₂	0	40.32	0.08	31.01
2	Mg _{0.03} V _{0.97} O ₂ @ZrO ₂ -6	1:6	43.69	-0.57	32.17
3	Mg _{0.03} V _{0.97} O ₂ @ZrO ₂ -4	1:4	59.24	-1.65	30.53
4	Mg _{0.03} V _{0.97} O ₂ @ZrO ₂ -2	1:2	66.40	-2.61	23.23

Thermochromic smart window is promised to adaptively reduce the building energy consumption. The work reports the successful preparation of $\text{VO}_2@\text{ZrO}_2$ core/shell nanoflakes through the hydrothermal method. A composite thermochromic film is prepared based on such materials and PUA matrix via UV-curing method and is demonstrated with enhanced-performance for the energy-saving smart application.

Zuohao Wen, # Yujie Ke, # Chengchen Feng, Shuliang Fang, Miuyang Sun, Xinghai Liu * Yi Long *

Mg-Doped $\text{VO}_2@\text{ZrO}_2$ Core/Shell Nanoflakes for Thermochromic Smart Windows with Enhanced Performance

ToC figure (55 mm broad $\times$ 50 mm high)