One-Step Hydrothermal Synthesis of W-Doped VO₂ (M) Nanorods with a Tunable Phase-Transition Temperature for Infrared Smart Windows

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ABSTRACT: Vanadium dioxide (VO₂), with reversible metal–semiconductor transition near room temperature, is a compelling candidate for thermochromic windows. Nano-composite coatings derived from VO₂ nanoparticles are particularly superior to VO₂ films due to their advantages in large-scale preparation, flexible shaping, and regulation of optical properties. In this work, we developed a novel method for one-step hydrothermal synthesis of W-doped VO₂ (M) nanorods and studied their application in large-scale infrared smart windows. On introducing tartaric acid as a new reductant, VO₂ underwent a two-stage phase evolution from the pure phase comprising VO₂ (A) nanobelts to VO₂ (M) nanorods, instead of the conventional three-stage B–A–M phase evolution during hydrothermal synthesis. This transition is very favorable for the large-scale hydrothermal synthesis of VO₂ (M). The phase-transition temperature of VO₂ (M) nanoparticles can be regulated systematically by W doping, with a reduction efficiency of about 24.52 °C/atom % W. Moreover, VO₂ (M) composite films were fabricated using a convenient roller coating method, which exhibited significant midinfrared transmission switching up to 31%, with a phase-transition temperature of about 37.3 °C. This work demonstrates the significant progress in the one-step hydrothermal synthesis of VO₂ (M) nanorods and provides significant insights into their applications in infrared smart windows.

1. INTRODUCTION

Vanadium dioxide (VO₂) is an excellent tunable functional material with complex polymorphs. Until now, more than 10 kinds of crystalline phases of VO₂ (phases B, M, R, A, C, and so on) have been reported.¹ However, among all of these polymorphs, VO₂ (M) is the most meaningful one because only VO₂ (M) undergoes a fully reversible first-order metal–semiconductor transition (MST) near room temperature (RT) (Tc = 68 °C).² This transition is accompanied by dramatic changes in the electrical and optical properties from a low-temperature monoclinic semiconductor phase (M phase) to a high-temperature tetragonal rutile metallic phase (R-phase).³ Meanwhile, the Tc of VO₂ (M) can be regulated by doping or stress.⁴ As a consequence, VO₂ (M) has been attracting increasing attention for its potential applications in infrared smart windows, switches, sensors, data storage devices, field-effect transitions, and so forth.⁵⁶⁷⁸ Because of these attractive properties and applications, various kinds of approaches were explored to fabricate VO₂ (M). However, it should be noted that most of the reported methods are focused on the preparation of VO₂ films. By contrast, VO₂ (M) nanoparticles can significantly lessen the stress for phase transformation, satisfy the need for a large area, flexible and special shape substrates coating by adding appropriate organics, and improve both ΔT lum and ΔT sol by dispersing in a dielectric host.¹⁰ Therefore, seeking a suitable method to prepare VO₂ (M) nanoparticles is highly desired and urgently needed.

Nowadays, several approaches have been developed for preparing VO₂ (M) nanoparticles, such as pyrolysis of vanadium-containing precursors, microemulsion-based methods, the solution combustion process, the vapor transport approach, hydrothermal synthesis, and so forth.¹¹⁻¹⁶ Among all of the above methods, the hydrothermal synthetic process is the most commonly used method to synthesize VO₂ (M) nanoparticles due to its simple route of synthesis, low cost, lower required temperature, and comparatively environmentally friendly reaction conditions. Normally, the metastable phase, VO₂ (B), acts as the final product in the hydrothermal reaction, which can then be transformed to VO₂ (M) by the postheating treatment.¹⁷⁻¹⁸ However, postheating annealing might lead to serious aggregation; thus, the corresponding thermochromic properties were seriously deteriorated. Encouragingly, there have been several reports on synthesizing VO₂ (M) through a one-step hydrothermal reaction. For instance, Son et al. synthesized asterisk-shaped VO₂ (M) nanocrystals using VO(SO₄)₂ hydrazine, and NaOH, but the secondary phase, VO₂ (B), always exists.¹⁷ Cao et al. fabricated W-doped VO₂
(R) snowflakes by hydrothermal treatment with $V_2O_5$ and oxalic acid at 240 °C over a reaction time of 7 days.1 Hollow microspheres of VO2 (M) were also obtained by the reaction of $V_2O_5$, PVP, and oxalic acid at 300 °C for 6 h.18 It is obvious that the high temperature and long reaction time will result in energy consumption. Furthermore, some researchers have confirmed that introducing doping additives, such as W, Mo, Sb atoms, would promote the generation of pure phase of VO2 (M) through the hydrothermal reduction of $V_2O_5$ by oxalic acid.1,19−21 Unfortunately, as far as we know, the synthesized pure VO2 (M) particles easily develop a snowflake morphology and the amount of product formed is always small, which limits their dispersion and transparency and makes them unsuitable for large-scale production.19 Recently, Li et al. fabricated asterisk-shaped Mo-doped VO2 (M), with a Mo doping concentration higher than 5.62 atom % and a change in the infrared transmittance of Mo-doped VO2 (M) of only about 10%.20 Chen et al. reported a one-step hydrothermal method for the growth of VO2 (M/R) nanorods, using $V_2O_5$, oxalic acid, and ammonium tungstate as raw materials. They indicated that the W dopant was a crucial parameter for the shape-controlled hydrothermal synthesis of VO2 (M/R), but it was noted that most of the products were still in the shape of a snowflake at a low doping concentration.21

Another metastable polymorph, VO2 (A), was reported as an intermediate phase during the transformation from VO2 (B) to VO2 (M) by Théobald.22 This polymorph also exhibited a similar reversible phase-transition property from low-temperature tetragonal VO2 (A) to high-temperature body-centered tetragonal VO2 (A$_{14}$) at 162 °C.23 VO2 (A) is a thermodynamically stable phase compared with VO2 (B), which may be beneficial in the generation of VO2 (M). However, this metastable phase has not been studied widely until now because the growth conditions of VO2 (A) are so harsh that this metastable phase is usually missed during the preparation of the VO2 polymorph.24−27

In this study, we introduced a new reductant, tartaric acid (TA), instead of the conventional reductant, oxalic acid, in the hydrothermal synthesis of VO2 nanoparticles. TA is a typical α-hydroxycarboxylic acid, which has been successfully applied to the hydrothermal synthesis of TiO2, Fe3O4, In2O3, Sb2S3, WO3, Bi2S3, and so forth.28−33 The hydroxyl and carboxyl groups in TA endow it with suitable hydrophilic characteristics and can promote the reduction of vanadium oxides and formation of VO2 eventually during the hydrothermal process in the present system. In our study, we developed a novel one-step TA-assisted hydrothermal synthesis method to prepare VO2 (A) nanobelts and then transformed them to VO2 (M) nanorods through W doping. It was inspiring to discover that the VO2 (M) nanoparticles possessed high purity, good crystallinity, and a stable morphology, and the $T_c$ of VO2 (M) could be simply tuned to a comfortable temperature by adjusting the doping concentrations of ammonium tungstate. Composite films obtained by mixing these nanoparticles with a polymer matrix and then roller coating this mixture onto a polyethylene terephthalate (PET) substrate exhibited significant midinfrared transmission switching properties and demonstrated great application potential in infrared smart windows.

**Figure 1.** (a) XRD patterns of hydrothermal reaction products with different $V_2O_5$/TA molar ratios; (b) DSC curve of VO2 (A); (c, d) SEM images of VO2 (A) at low and high magnifications, respectively; the inset is the TEM image.
absence of any other phase or impurities illustrates that the as-obtained VO₂ (A) has a high purity. Upon further increasing the amount of TA, V₂O₅ is further reduced to V₅O₉. This indicates that there is a reduction process: V₂O₅ → V₃O₇·H₂O → VO₂ (A) → V₅O₉ → V₂O₃, with TA as the reducing reagent during this reaction. According to the above results, a V₂O₅/TA molar ratio of 5:1 is optimal for the synthesis of pure-phase VO₂ (A). The morphology of pure-phase VO₂ (A) was studied by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) (inset of Figure 1d). Obviously, it can be seen from Figure 1c,d that the product exhibits a clear beltlike morphology, with a width of 200–300 nm and a length of up to several tens of micrometers. Differential scanning calorimetry (DSC) analysis of the VO₂ (A) nanobelts clearly shows a noticeable endothermic peak at 169 °C, as shown in Figure 1b, which can be assigned to the phase transition of low-temperature tetragonal VO₂ (A) to high-temperature body-centered tetragonal VO₂ (A₉).  

Generally, hydrothermal reduction of V₂O₅ to VO₂ follows the following phase evolution: VO₂ (B) → VO₂ (A) → VO₂ (M/R).  

The formation energy of the VO₂ (A) phase has been demonstrated to be higher than that of VO₂ (B). This indicates that VO₂ (A) is a more thermodynamically stable phase compared with metastable VO₂ (B). In this regard, VO₂ (A) is more beneficial for the generation of VO₂ (M) than VO₂ (B) during hydrothermal synthesis. To analyze the relative stabilities of VO₂ (B) and VO₂ (A) more visually, the crystal structures of VO₂ (B) and VO₂ (A) were compared. As displayed in Figure 2, both of them are layered structures and are composed of VO₆ octahedra basic units. In the structure of VO₂ (B), vanadium atoms are no longer in the center of the VO₆ octahedra, causing the VO₆ octahedra to get slightly distorted. For VO₂ (A), the VO₆ octahedra are less deformed. In addition, the V–O–V bond angle in the structure of VO₂ (B) is nearly vertical, which leads to the generation of intense structural tension and electronic repulsion. By contrast, the structure of VO₂ (A) shows less electronic repulsion, thus reducing the structural tension. Overall, it can be indicated that VO₂ (A) has a more thermodynamically stable structure than VO₂ (B). In this work, TA was employed to be the reductant instead of the conventionally used oxalic acid, and VO₂ (A) but not VO₂ (B) was formed indirectly. So, we state that the yield of VO₂ (M) was 4 times higher than that obtained by the other research groups.
It has been reported that introducing doping additives could promote the generation of VO₂ (M). In this work, we choose ammonium tungstate to support the synthesis of VO₂ (M). Figure 3a shows the XRD patterns of W-doped VO₂ nanoparticles, with a doping content from 0.5 to 2 atom %. It is worth noting that W doping has a significant influence on the preparation of pure-phase VO₂ (M). For the sample with the addition of 0.5 and 1 atom % W, the product is a mixture of VO₂ (A) and the main phase, monoclinic VO₂ (M) (JCPDS no. 43-1051, space group P2₁/c, a = 5.752 Å, b = 4.538 Å, c = 5.383 Å). On increasing the amount of W to 1.5 atom %, the diffraction peaks of VO₂ (A) vanish and all peaks can be indexed to VO₂ (M), illustrating that pure-phase VO₂ (M) (T₀ ∼ RT) is successfully synthesized. However, Cao et al. reported that pure-phase W-doped VO₂ (M) could only be obtained when the reaction time reached 7 days and the W-doping content was 4 atom %. Upon continuously increasing the W-doping content to 2 atom %, pure-phase VO₂ (M) (JCPDS no. 76-0675, space group P4₂/mmm, a = 4.556 Å, b = 4.556 Å, c = 2.860 Å) is obtained at RT (T₀ ≤ RT). No peaks of any other phase are observed, revealing that the products are well crystallized, with high purities. In addition, there are no peaks related to ammonium tungstate or its derivatives, suggesting that the W atoms are incorporated into the crystal lattice of VO₂ (M), forming a substitutional solid solution. Magnifications of the (011) peak for VO₂ (M) and (110) peak for VO₂ (R) are displayed in Figure 3b. Significant shifting of the M (011) peaks to smaller angles is detected, which indicates a slight increase in the interplanar spacing. This can be attributed to the substitution of V atoms with W atoms of a larger atomic radius. Moreover, more V atoms would be substituted on increasing the W-doping content. This result could further confirm that W was successfully captured into the crystal lattice of VO₂ (M). In addition, it could be concluded that W doping can promote the transformation from VO₂ (A) to VO₂ (M). As we know, VO₂ (M) is more thermodynamically stable than VO₂ (A), which makes the synthesis of VO₂ (M) require more energy. On doping with W, the VO₆ octahedron is distorted by the partial substitution of V atoms with W atoms, which makes the interconnections between different VO₆ octahedra break more easily, as the atomic radius of W atoms is larger than that of V atoms. This mechanism offers not only oxygen vacancies but also the energy required for the formation of pure-phase VO₂ (M). Therefore, VO₂ (A) transforms to VO₂ (M) completely when the W-doping content reaches a certain value.

X-ray photoelectron spectroscopy (XPS) was performed to investigate the composition and chemical state of the W-doped VO₂ sample. Figure 4a shows a wide-range survey spectrum of 2 atom % W-doped VO₂ (M). It reveals that the sample consists of vanadium, oxygen, carbon, and tungsten, where the peak of carbon is attributed to the hydrocarbon contamination on the sample surface. In Figure 4b, the O1s and V2p peaks were fitted with a Shirley function. The peak located at 530.3 eV can be assigned to O²⁻ in V−O, which is in good accordance with the structural information on the VO₂ (M) structure. Additionally, the V2p3/2 peak is separated into two peaks, meaning two valence states of vanadium (+4 valence and +5 valence) exist in the sample. The binding energy of 516.5 eV corresponds to V⁴⁺, which is slightly higher than 515.8 eV for pure VO₂ but is consistent with the value for W-doped VO₂ (M) obtained in previous reports, suggesting that the binding energy of the +4 valence state of V₂P₃/₂ increases slightly after W-dopant introduction. In addition, the binding energy of 517.7 eV is assigned to V⁵⁺ due to oxidation at the surface of the sample when exposed to air. The difference between the binding energies of O1s and V2P₃/₂ is 13.8 eV, consistent with
the value of 14.2 eV reported in the literature. Figure 4c shows binding energies of 35.22 and 37.38 eV for W 4f7/2 and W 4f5/2, respectively, revealing that the existing form of W ions in this sample is W6+ instead of the other valence form. This result confirmed that the W atom was actually doped into the VO2 nanoparticles.

Typical SEM and TEM images of VO2 powders with different W-doping contents are presented in Figure 5. Both beltlike and rodlike morphologies are observed for 0.5 atom % doping in this work (Figure 5a). With 1 atom % doping (Figure 5b), the nanorod particles in the sample increase obviously. For the sample with 1.5 atom % W doping (Figure 5c), the former belt crystals disappear and all of the particles show a rodlike shape, with a typical width of 100−200 nm and an uneven length. Subsequently, as the W-doping content is increased to 2 atom % (Figure 5d and its inset), the powders exhibit uniform nanorods and the length increases up to several micrometers. The aspect ratio of the nanorods increases noticeably. This result suggests that increasing the W-doping content could promote not only the generation of VO2 (M) but also the growth of nanorods.

As far as we know, VO2 (M) particles synthesized by a one-step hydrothermal reaction with oxalic acid as a reductant always show a snowflake shape.1,19,21 By contrast, one-dimensional (1D) nanostructures, such as nanorods, nanobelts, and nanowires, have raised great interest because they present novel characteristics, owing to their small radial dimensions, while retaining their longitudinal connectivity. As a kind of 1D nanostructure, nanorods can be used for investigating specialized applications and in fundamental research, such as assessment of the phase-transition temperature and phase-transition mechanism of VO2 (M).46 Normally, W-doped VO2 (M) nanorods were fabricated through a two-step hydrothermal method. There are a few studies on the preparation of W-doped VO2 (M) nanorods via a one-step hydrothermal method.21,47,48 For instance, Chen et al. reported that W doping plays a crucial role in the growth of W-doped VO2 (M) nanorods.21 In our study, TA is not only a reductant but also a
kind of alternative template reagent. The presence of TA was crucial in obtaining nanorods, owing to the capping effect. A probable mechanism for the evolution of nanorods is presented in Figure 6. The VO₂ grains grow, with the reaction proceeding continuously. Simultaneously, TA may play a certain role as a capping agent, which is adsorbed onto the surface of VO₂ and controls the overall growth kinetics. The lateral growth of VO₂ is restricted due to hindrance of the capping agent. These result in the growth of the products only to specific facets and in obtaining nanorods eventually.

Figure 7 shows the Fourier transform infrared (FTIR) spectra of the as-synthesized VO₂ powders. The characteristic broad absorption bands that appeared in all samples at 3436 and 1631 cm⁻¹ are assigned to the stretching and bending vibrations of the hydroxyl group (−OH), respectively, resulting from the absorbed H₂O molecules on the surface of VO₂. The absorption band at 2380 cm⁻¹ is due to the asymmetric stretching vibrations of CO₂. In particular, we can clearly see differences among the three phases of VO₂, with a range of 400–1000 cm⁻¹, which can be ascribed to the different vibration modes of the V−O type. For VO₂ (A), the band at 941 cm⁻¹ is assigned to the stretching of short V=O bands and the two peaks at 594 and 557 cm⁻¹ are attributed to the delocalization of the electrons involved in V⁴⁺−V⁴⁺ bonds between VO₆ octahedra, which are characteristic of VO₂ (A). In the typical FTIR spectrum of a monoclinic VO₂ (M) sample, the absorption band at 530 cm⁻¹ could be attributed to the bending vibrations of V−O−V bridges and the broad band at 684 cm⁻¹ is characteristic of the first “rutile packing” of VO₂ octahedra. Additionally, there is no vibrational absorption peak corresponding to rutile VO₂ (R). For VO₂ (M), the electrons involved in the V−V bonds between VO₆ octahedra are localized. However, these electrons are delocalized for VO₂ (R); this delocalization involves a screening effect for the incident photons. Under this circumstance, no vibration absorption band for VO₂ (R) can be observed, which implies a drastic decrease in the transmittance. Therefore, FTIR can be used as a characterization method to distinguish the three phases of vanadium dioxide.

The Tₙ’s of VO₂ nanoparticles with different doping contents were characterized by DSC, as shown in Figure 8a. It can be seen that the Tₙ of VO₂ (M) decreases with an increase in the W-doping content. An increase in the W content from 0.5 to 2 atom % significantly reduces Tₙ from 60.6 to 21.3 °C, which is lower than RT, providing auxiliary evidence for the formation of pure-phase VO₂ (R) at RT with 2 atom % W doping. Moreover, the intensity of the DSC peaks decreases with an increase in the W-doping content. The explanation could be as follows: The low-temperature monoclinic structure of VO₂ (M) demonstrates alternative V−V intervals (2.65 and 3.12 Å), whereas the high-temperature rutile structure of VO₂ (R) has a very symmetric structure, with equidistant V−V intervals (2.87 Å). Partial substitution of the V atoms with large W atoms causes the V−V interval to shrink, leading to a decrease in the structural differences between VO₂ (M) and VO₂ (R) and reducing the MST activation energy accordingly. Figure 8b shows the linear relationship between Tₙ and W concentration (from 0.5 to 2 atom %). The least-squares approximation gives a Tₙ reduction efficiency of 24.52 °C/atom %, which is slightly higher than that obtained by other research groups that synthesized VO₂ (M) by a one-step hydrothermal method but is consistent with that previously reported, revealing that the Tₙ of VO₂ (M) could be easily tuned by adjusting the W-doping content. These results suggest effective W doping in VO₂ and also further confirm the formation of VO₂ (M), which is in accordance with the XRD results.

The 1.5 atom % W-doped VO₂ (M) nanorods were mixed with a polymer matrix and then processed to form a composite film on the PET substrate using a convenient roller coating method, as shown in Figure 9. The film is highly transparent,
flexible, homogeneous, smooth, and light gray-blue in color. Although the infrared spectrum extends across a wide range (0.77–1000 μm), there are only two wavelength ranges that show high infrared transmittance in the atmosphere (3–5 and 8–12 μm). So, we study the phase-transition properties of VO2 films in the infrared region. The optical properties of the VO2 composite film were investigated from variable-temperature infrared spectra (Figure 10). Figure 10a represents the infrared transmittance of the VO2 composite film during the heating process. It can be seen that the transmittance decreases significantly with an increase in temperature, corresponding to the semiconductor–metal phase transition of VO2. Figure 10b displays the hysteresis loop of the normalized transmittance–temperature plot at a fixed wavelength of 9 μm. A significant change in the transmittance up to 31% across the phase transition is observed, suggesting that 1D W-doped VO2 (M) has a good infrared-switching property. The corresponding first-order derivative curves are shown in the inset of Figure 10b. It is worth noting that the phase-transition temperatures of the heating transition and cooling transition are 45.2 °C (T1) and 29.4 °C (T2), respectively. According to the calculated results, the Tc of the film is 37.3 °C (Tc = (T1 + T2)/2); this result is in agreement with that of the DSC analysis shown in Figure 8, and the hysteresis width (ΔT) of the film is 15.8 °C (ΔT = T1 − T2).

Figure 10c–e shows that the VO2 composite film displays three switching windows in the middle-infrared region: window I, 3.5–5.5 μm; window II, 8.5–12.5 μm; and window III, 14.5–25 μm. This means that the VO2 hybrid film can achieve middle-infrared switching in multiple regions, and the switching region could be regulated by choosing different polymer matrices. It is worth noting that infrared switching of the composite film at around 37.3 °C is useful for limiting the infrared thermal radiation and thus can be used to regulate RT. Moreover, the employed roller coating method is useful for large-scale fabrication of VO2 composite films. So, we believe that the present work is significant for the practical application of VO2 (M) in infrared smart windows.
3. EXPERIMENTAL SECTION

3.1. Synthesis of W-Doped VO$_2$ (M). A certain amount of TA (C$_{6}$H$_{7}$O$_{7}$ purchased from Pangang Group Steel Vanadium & Titanium Co., Ltd.) was dissolved in 80 mL of deionized water. Then, 1.092 g of vanadium pentoxide and the requisite quantity of ammonium tungstate were added to the solution, with constant magnetic stirring for 1 h. Thereafter, the mixture was transferred to a 100 mL Teflon-lined stainless steel autoclave, sealed, maintained at 240 °C for 48 h, and cooled to RT naturally. The resulting black precipitate was collected by centrifugation and washed two times with deionized water and ethanol, respectively, before drying in a thermostatic drying oven at 60 °C for 12 h.

3.2. Fabrication of VO$_2$ (M) Composite Films. As-prepared W-doped VO$_2$ (M) (5 wt %) was dispersed in tetraethyl orthosilicate with continuous stirring. Then, 2 wt % silane coupling agent and 2 wt % dispersant were added, with constant magnetic stirring for 10 min. Thereafter, an appropriate quantity of poly(ethyl methacrylate) was added gradually into the above solution, which was stirred for another 10 min. Finally, the slurry was uniformly cast onto a PET substrate using a stainless steel coating bar and dried at 80 °C for 1 min.

3.3. Characterization. The crystalline structures of the products were determined by DX2000 X-ray powder diffraction with Cu Kα1, 2 radiation (λ = 0.154056 nm). The morphologies of products were investigated by SEM (S-4800; Hitachi) and TEM (Tecnai G2 F20 S-TWIN; FEI), with an accelerating voltage of 200 kV. The vanadium valence states and chemical composition of W-doped VO$_2$ were detected by XPS (Kratos, England) using an Al Kα ($h\nu = 1486.6$ eV) exciting source. The FTIR spectrum from 400–4000 cm$^{-1}$ was measured on a Tensor 27 (Buker, Germany) spectrometer, using pressed KBr tablets. The phase-transition behavior of the products was analyzed by DSC (DSC1; Mettler toledo) in the temperature range from 0 to 100 or 200 °C, at a heating rate of 10 °C/min using a liquid-nitrogen cooling unit. The optical properties of the films were also investigated by FTIR attached an adapted heating controlled unit, and then the hysteresis loops of W-doped VO$_2$ film was received by collecting the transmittance of films at a fixed wavelength (9 μm).

4. CONCLUSIONS

In summary, the A, M, and R controlled phases of VO$_2$ were prepared for the first time by the one-step hydrothermal synthesis method. TA was used as a new reductant, and W doping was performed to facilitate the formation of VO$_2$ (M) and regulate its phase-transition temperature. The VO$_2$ underwent a two-stage phase evolution from pure-phase VO$_2$ (A) nanobelts to VO$_2$ (M) nanorods, instead of the conventional three-stage B–A–M phase evolution. Furthermore, the T$_c$'s of the VO$_2$ (M) nanorods were regulated systematically, with a reduction efficiency of about 24.52 °C/atom % W. A flexible W-doped VO$_2$ (M) composite film on PET was fabricated using the convenient roller coating method. This composite film exhibited significant middle-infrared transmission switching of up to 31%, with a phase-transition temperature of about 37.3 °C. Moreover, the VO$_2$ composite film can achieve middle-infrared switching in multiple regions. In this work, we developed a one-step hydrothermal method for the synthesis of VO$_2$ (M) nanorods and provided significant insights into their applications in large-scale infrared smart windows.

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Notes
The authors declare no competing financial interest.

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