Vertically distributed VO₂ nanoplatelets on hollow spheres with enhanced thermochromic properties†

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Vanadium dioxide (VO₂) is a phase-transition material exhibiting great potential in the field of smart windows for energy saving. Herein, VO₂ nanoplatelets vertically distributed on hollow spheres are synthesized via a template-free hydrothermal method. The nanoplatelets are separated and uniformly arranged on the spheres so that the dispersion and optical properties are greatly improved. Compared with the observations for the aggregated sample, visible transmittance (Tvis) and solar modulation (ΔTsol) improve from 33% to 50% and from 5.2% to 11.2%, respectively. Meanwhile, a large contrast transmittance of 60% at 2500 nm is obtained. Tvis increases with gradual reduction in ΔTsol as the film thickness is reduced. Ultrahigh Tvis of 87.2% and satisfactory ΔTsol of 5.3% are obtained. Furthermore, the as-obtained VO₂ hierarchical structure exhibits higher sensitivity than VO₂ nanoparticles owing to 2D-structures of nanoplatelets. This study demonstrates a promising 2D structure for promoting practical applications in smart windows.

1. Introduction

Vanadium dioxide (VO₂) has attracted much attention because of its reversible metal–insulator transition (MIT) at low temperature, which is accompanied by structural transition from a low-temperature monoclinic (M) phase to a high-temperature tetragonal rutile (R) phase in nanoseconds. Furthermore, its electronic and optical properties change tremendously. Therefore, VO₂ can be utilized as a switching element, optical storage medium, lighter modulator, and in energy-saving smart windows.

With the depletion in conventional energy resources and increased pollution, energy saving and environmental protection have become current global concerns. According to statistics, around 30–40% of the total energy consumption is utilized in buildings, of which air conditioning and heating account for about 30%, which is ever-growing. A VO₂ smart window is regarded as a promising solution to address the above-mentioned issues, allowing for the replacement of air-conditioning to save energy. When the environmental temperature is increased to the phase transition temperature of VO₂, the smart window causes abrupt decrease in infrared transmittance while maintaining visible transmittance. However, in VO₂-based energy-saving smart windows, the visible light transmittance (Tvis) of VO₂ film is low. In addition, the two key parameters Tvis and solar energy modification ability (ΔTsol) are commonly waxing and waning, which impede the practical applications.

In this regard, numerous methods including pulsed laser deposition, RF sputtering, and physical/chemical vapor deposition have been developed to reduce film thickness and to improve Tvis; however, the modification ability on solar energy (ΔTsol) deteriorates simultaneously. Multilayer VO₂ with optimized structure shows relatively high Tvis and ΔTsol, but the performance is limited by complicated techniques and high cost. Recently, solution-based methods have proved to be effective for improving the phase transition performance of VO₂. It was also demonstrated that optical performance can be improved by decreasing the particle size. Li et al. fabricated VO₂ nanoparticles of diameter 50 nm and found that Tvis increased to 20.6% from 11.7% when the particles were ~80 nm in diameter, and ΔTsol increased to 7.6% from 7.4%. Further, Tvis and ΔTsol further increased to 40% and 8.7%, respectively, when the particle size was 30 nm. Some computational investigations have suggested that optical properties can be further improved by decreasing the nanoparticle size to less than 20 nm for eliminating the reflection of light. However, it is difficult to further reduce the particle size. Meanwhile, nanoparticles tend
to aggregate. In addition, nanoparticles of diameter less than 50 nm are often accompanied with larger hysteresis widths (30–50 °C).1,2,23 To solve this problem, Xu et al.23 and Li et al.25 prepared flake grain structures and demonstrated substantially narrowed hysteresis widths. Meanwhile, it was predicted that aligned prolate particles and aligned oblate particles exhibited higher visible transmittances and solar modulation abilities than spherical nanoparticles.26 It is inspiring that standing nanoplatelets on hollow spheres may be possible to enhance the thermochromic performance significantly.

Herein, hollow VO2(M) spheres composed of nanoplatelets are prepared through a facile template-free hydrothermal method and subsequent thermal annealing. The VO2 spheres exhibit significantly improved optical properties (∆Tvis = 11.2%, Tvis = 50%, and small hysteresis width of 8.5 °C) owing to highly dispersive nanoplatelets. Furthermore, the Tc value can be well-tuned by W doping, and the Tvis and ∆Tvis values are comparable with those of intrinsic VO2, which is promising for the applications of VO2 in the field of smart windows. The physical mechanisms for the formation of VO2 hollow structures with dispersive distribution of nanoplatelets along with their improved optical properties are discussed.

2. Experimental

2.1 Preparation of VO2 nanoplatelets

All reagents were of analytical grade and used without further purification. Ammonium vanadate (NH4VO3) and ammonium tungstate ((NH4)6W12O41·xH2O) were stirred in 35 ml ethyl alcohol (C2H5OH) and deionized water (DI water) for 30 min and then sonicated by a sonifier cell disrupter for 2 min. After shredding, 2 ml ethylene glycol (EG), 2 mmol oxalic acid (H2C2O4), and 1 ml HNO3 were separately added to the above-mentioned solution under stirring for 4 h. After that, the solution was transferred to a 50 ml Teflon-lined stainless steel autoclave and kept at 200 °C for 24 h; then, it was cooled to room temperature naturally. The final precipitate was separated by centrifugation and washed thrice with deionized water and absolute ethanol before drying in vacuum at 60 °C for 6 h. Finally, nanoporous VO2 hollow spheres were obtained after thermal annealing in argon (Ar) at 450 °C for 2 h at a heating rate of 5 °C min⁻¹.

2.2 Preparation of VO2 thin films

The suspension of as-prepared particles was dispersed ultrasonically in deionized water for 20 min without the ball-milling treatment. Then, an appropriate amount of salinе coupler KH-570 was added under stirring. After that, polyurethane (PU, DISPERCOLLU 54, Bayer) was added with stirring for 10 min. Finally, the mixture was uniformly cast onto a quartz glass using an automatic coating machine and dried at 80 °C for 1 min.

2.3 Characterization

The morphology of VO2 particles was characterized by high-resolution transmission electron microscopy (HR-TEM, JEOL JEM 2100F) and field-emission scanning electron microscopy (FESEM, JSM-7000F). The phases were determined by X-ray diffraction (GXRD, Shimadzu XRD-7000) with Cu-Kα radiation (λ = 0.154 nm) at a fixed incident angle of 0.5° and 2θ scanning rate of 8° min⁻¹. Raman spectra were examined using a Horiba HR800 spectrometer with 633 nm laser as the excitation light source. Differential scanning calorimetry (DSC, DSC204F1, NETZSCH, Germany) was measured at 0–100 °C with a heating rate of 5 °C min⁻¹ under a nitrogen flow. The elemental component and chemical valence states were determined by X-ray photoelectron spectroscopy (Thermo Scientific K-Alpha, XPS). Transmittance spectra were obtained in the range from 250 nm to 2500 nm at normal incidence using a Hitachi U-4100 spectrometer.

3. Results and discussion

Fig. 1 schematically displays the synthesis process of VO2(M). Fig. 2(a) shows the FESEM image of the as-prepared sample. Clearly, the spheres have interior hollow structures, which is confirmed by the TEM image inserted in Fig. 2(a). The powder is annealed at 350, 400, 450, and 500 °C. As shown in Fig. 2(b)–(d), the surface morphologies change slightly when the samples are annealed at temperatures lower than 450 °C. Nanoplatelets are uniformly distributed on the hollow spheres, but the nanoplatelets melt into spheres when the annealing temperature is elevated to 500 °C, as clearly shown in Fig. 2(e) and the inset of Fig. 2(e) (TEM image). As shown in Fig. 2(f), only the diffraction peaks of VO2(B) (JCPDS Card No. 25-1003, space group: C2/m (12), a = 12.030, b = 3.693, c = 6.420 Å) are identified for the as-prepared samples, and only the diffraction peaks of the VO2(M) phase (JCPDS Card No. 43-1051, space group: P21/c (14), a = 5.752, b = 4.538, c = 5.383 Å) are identified for the four annealed samples. The intensities of peaks increase with the annealing temperature, indicating improved crystallinity. As shown in Fig. 3(a)–(c), the samples annealed at 350, 400, and 450 °C maintain their hollow structures. The large-area TEM...
image of VO$_2$ annealed at 450 °C is inserted in Fig. 3(c). Fig. 3(a’)-(c’) display HRTEM images of Fig. 3(a)-(c), respectively. The sample annealed at 350 °C exhibits poor crystallinity with blurry lattice fringes and point defects [Fig. 3(a’)], but its crystallinity improves to some degree when it is annealed at a higher temperature [Fig. 3(b’)] and (c’)]. The interplanar distance of $d = 3.14$ Å can be indexed to the (011) plane of monoclinic VO$_2$, as shown in Fig. 3(a’)-(c’).

To investigate the growth mechanism of the optimized structure, controllable experiments were designed. We believed that ethyl alcohol (C$_2$H$_5$OH) could possibly promote the formation of nanoplatelets (Fig. S1, ESI†). As the volume percentage of C$_2$H$_5$OH increased from 0% to 100%, the morphology of the product changed from aggregated nanowires to nanoplatelets. As shown in Fig. S2 (ESI†), both ethylene glycol (EG, H$_2$C$_6$O$_2$) and oxalic acid (H$_2$C$_2$O$_4$) played key roles in the morphologies of the products. EG was more likely to promote the formation of a spherical structure, whereas H$_2$C$_2$O$_4$ was more influential in the formation of a hollow structure. When the volume percentage of EG was below 2.8% or above 11.4%, aggregated nanoplatelets [Fig. S2(h), ESI†] and solid spheres [Fig. S2(a), ESI†] were obtained, respectively. In the absence of H$_2$C$_2$O$_4$, self-assembled solid microspheres composed of nanoplatelets were formed (Fig. S3, ESI†). As H$_2$C$_2$O$_4$ increased, the morphology evolution underwent two stages including the formation [Fig. S2(b), (f) and (i), ESI†] and the collapse of hollow spheres [Fig. S2(c), (g) and (j), ESI†].
This implied that $\text{H}_2\text{C}_2\text{O}_4$ promoted the formation of the hollow structure at a certain content, which may be due to the gas generated from the redox reaction. In addition, the diameters of the hollow spheres could be controlled from 500 to 1300 nm by adjusting the precursor concentrations of NH$_4$VO$_3$ from 0.025 to 1 mol L$^{-1}$. The SEM images and size distributions are clearly shown in Fig. S4 (ESI†). Oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$) as the reducing reagent has been widely applied to reduce metal salts (V(V)) to low-valence metals. The reaction between NH$_4$VO$_3$ and oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$) was as follows: 27,28

$$2\text{NH}_4\text{VO}_3 + 4\text{H}_2\text{C}_2\text{O}_4 \rightarrow (\text{NH}_4)_2[(\text{VO})_2(\text{C}_2\text{O}_4)_3] + 2\text{CO}_2 + 4\text{H}_2\text{O},$$

(1)

$$\text{(NH}_4)_2[(\text{VO})_2(\text{C}_2\text{O}_4)_3] \rightarrow 2\text{VOC}_2\text{O}_4 + 2\text{NH}_3 + \text{CO} + \text{CO}_2 + \text{H}_2\text{O},$$

(2)

$$\text{VOC}_2\text{O}_4 \rightarrow \text{VO}_2 + \text{CO} + \text{CO}_2,$$

(3)

Fig. 4 schematically illustrates the process of the formation of hollow spheres. The hollow spheres are formed as a result of outward Ostwald ripening by dissolution of the inner part and growth of the outer shell.29–32 The hydrolysis of VOC$_2$O$_4$ leads to VO$_2$ nanoparticles; then, the nanoparticles recombine to minimize the surface energy, resulting in solid spheres.33–38 During the subsequent hydrothermal process, recrystallization occurs at the interface between the solid and liquid, that is, on the outermost surface. However, the inner regions of solid spheres tend to dissolve because of their loosely packed features. Such a ripening process, that is, dissolution and then recrystallization, gradually proceeds from the outermost region towards the interior. At the same time, small holes in the spheres assemble into a large gap between the yolk and the shell. As a result, the solid spheres are transformed to yolk-shelled structures (stage I).39–42 When the reaction time is extended, secondary Ostwald-ripening occurs on the pre-formed solid cores, and further dissolution and re-crystallization of less stable interior architectures result in the formation of completely hollow microspheres (stage II). In addition, the reduction reaction accelerates the dissolution of interior cores and thus promotes Ostwald ripening. The gas product may also make the nanoplatelets grow vertically on the surface of the spheres.

Fig. 5(a) shows temperature-dependent optical transmittance spectra of 7.8 μm thick films composed of VO$_2$(M) hollow spheres annealed at different temperatures. The films composed of aggregated nanoplatelets are prepared under the same conditions but without $\text{H}_2\text{C}_2\text{O}_4$, and they are annealed at 450 °C for comparison. Fig. 5(c) displays $T_{\text{vis}}$, $\Delta T_{\text{sol}}$ and near-infrared contrast at 2500 nm. As the annealing temperature is increased from 350 °C to 400 °C, the $T_{\text{vis}}$ and $\Delta T_{\text{sol}}$ values improve from 49.1% to 50.8% and from 7.8% to 8.6%, respectively, due to the enhanced crystallinity of VO$_2$(M), and $\Delta T_{\text{sol}}$ increases to 11.2% at the annealing temperature of 450 °C. However, $T_{\text{vis}}$ and $\Delta T_{\text{sol}}$ reduce to 23.2% and 2.1%, respectively, at the annealing temperature of 500 °C due to amalgamation and growth of nanoplatelets [Fig. 2(e)]. The film composed of aggregated nanoplatelets exhibits $T_{\text{vis}}$ of 34.6% and $\Delta T_{\text{sol}}$ of 5.2%, which are lower than those of the hollow structure with separate nanoplatelets. It is demonstrated that enhanced optical properties are observed due to high crystallinity, small size and good dispersion of the nanoplatelets. To further study the optical properties of the films, samples of different thicknesses are prepared; the cross sections of the samples are displayed in Fig. S5(a) (ESI†). Fig. 5(b) shows transmittance spectra of the samples of different thicknesses. The VO$_2$ composite coatings are uniform and well-dispersed in the PU matrix, as shown in Fig. S(6) (ESI†). The optical properties of the films are summarized in Fig. 5(d). $T_{\text{vis}}$ decreases with increasing film thickness owing to increased absorption. It is worth noting that the changes between $T_{\text{vis}}$ and $\Delta T_{\text{sol}}$ are more balanced as compared with the previously reported results.13,14 As shown in Fig. 5(b) and (d), higher $T_{\text{vis}}$ can be obtained by decreasing the film thickness with gradual decrease in $\Delta T_{\text{sol}}$; $T_{\text{vis}}$ increases to 87.2% for the 2.6 μm thick film, and $\Delta T_{\text{sol}}$ of 5.3% is maintained. The balance between $T_{\text{vis}}$ and $\Delta T_{\text{sol}}$ can be due to high dispersion and 2D structures of the nanoplatelets.

Simulations were performed using the COMSOL Multiphysics software. Models were established with reference to the literature,43–45 and detailed parameters are expounded in the ESI†. Fig. 6(a) and (c) show simulation models of the composite films composed of dispersed and aggregated nanoplatelets, respectively. As shown in Fig. 6(a), nanoplatelets that were 50 nm long, 30 nm wide and 7 nm thick were vertically arranged on hollow spheres. In contrast, the nanoplatelets aggregated into a solid sphere, as shown in Fig. 6(c). Fig. 6(b) and (d) show the simulated transmittances of the composite films at low and high temperatures using the published optical index.26 It can be seen that the composite films composed of dispersed nanoplatelets exhibited better performance than the aggregated nanoplatelets. It was demonstrated that good dispersion of nanoplatelets is essential for excellent thermochromic performance of the VO$_2$ composite film.

Tungsten (W) doping is utilized to reduce the $T_{\text{vis}}$ value. The synthesis method for W-doped VO$_2$ sample is the same as that of intrinsic VO$_2$, but additional ammonium tungstate as the tungsten source is also added to the reaction liquid; also, VO$_2$(M) with different W contents can be obtained by controlling the molar ratio of ammonium tungstate to NH$_4$VO$_3$. Fig. 7(a) shows XRD patterns of the annealed samples with different W contents; all the diffraction peaks can be indexed to VO$_2$(M). As shown in Fig. 7(b),
the peak of the (011) plane shifts towards a small angle with increasing W content because the diameter of W$^{6+}$ ions is larger than that of V$^{4+}$ ions. Fig. 7(c)–(e) show the SEM images of the samples; the morphology changes slightly upon doping.
Fig. 7  (a) XRD patterns and (b) magnified patterns of the (011) peak of the annealed samples with different W contents; (c)–(e) SEM images of the samples.

Fig. 8 (a) TEM image of the W-doped VO₂(M) hollow microsphere and the EDS mapping of V, O and W elements. XPS spectra of 2 at% W-doped VO₂: (a) survey spectrum, (b) and (c) core-level spectra for V₂p and W₄f, respectively.

Fig. 8(a) displays the EDS mapping results of V, O and W in the hollow sphere. Clearly, V, O and W are uniformly distributed on the nanoplatelets. Fig. 8(b)–(d) show XPS spectra of doped VO₂(M).

The binding energies of elements obtained from XPS analysis are corrected by referencing to that of C₁s (284.6 eV). The full profile of the XPS spectrum in Fig. 8(b) confirms the presence of C,
V, O and W; C originates from surface contamination. The peak at 516.2 eV due to V$_{2p3/2}$ [Fig. 8(c)] and the peak at 41.3 eV due to V$_{3p}$ [Fig. 8(d)] are ascribed to V$^{4+}$. As shown in Fig. 8(d), the W$_{4f}$ peaks with binding energies centered at 35.4 and 37.5 eV are ascribed to W$_{4f7/2}$ and W$_{4f5/2}$, respectively, indicating that W in the powders is in the form of W$^{6+}$.

The phase transition temperature can be investigated by DSC analysis since its first-order reversible phase transition is accompanied with energy absorption and release during heating and cooling processes. Fig. 9(a) shows DSC curves of the samples annealed at different temperatures. For the samples annealed at 450 °C, all DSC curves show endothermic peaks at about 69 °C during the heating period and exothermic peaks at about 60 °C during the cooling period. However, for the sample annealed at 500 °C, two endothermic and exothermic peaks appear during heating and cooling processes, respectively, which are similar to reported results. The multi-peaks can be understood by Dai’s analysis; it points out that a particle size of 13 nm is the critical size when the heating peak is at about 60.5 °C, and the cooling peak decreases to 32 °C. However, above 15 nm, the phase transition properties are in accordance with those of bulk VO$_2$(M). For samples annealed at 500 °C, two kinds of particles with diameters of about 13 nm and 150 nm are obtained, as shown in the TEM image inserted in Fig. 2(e). Fig. 9(b) shows DSC curves of W-doped VO$_2$(M) annealed at 450 °C. $T_c$ of pure VO$_2$(M) is 69.5 °C, as reported previously, and it greatly reduces to 29.8 °C when the content of W is increased to 2%, as shown in Fig. 9(c). The effect of W in reducing $T_c$ is 19.7 °C per %, which agrees well with the reported results. Tan et al. pointed out that doping with W creates locally symmetric domains that are more akin to the high-temperature rutile phase of VO$_2$, thereby lowering the activation energy barrier for the structural transformation to the metallic phase. Meanwhile, W doping weakens the hybridization of V$_{3d}$–O$_{2p}$ and assists in narrowing the characteristic band gap of the low-temperature monoclinic phase. In addition, the hysteresis width of intrinsic VO$_2$(M) is 8.5 °C, which is substantially smaller than the reported values. The optical transmittance spectra of W-doped VO$_2$ at 20 °C and 90 °C are shown in Fig. 10; the optical properties as well as those from references are listed in Table 1 for comparison. As reported previously, the optical properties of VO$_2$ deteriorate due to doping-induced lattice distortion. However, the $T_{vis}$ and $\Delta T_{sol}$ values of W-doped VO$_2$ in this study are almost comparable with those of intrinsic VO$_2$. As the W doping content is increased from 0.0% to 2.0%, the $T_{vis}$ and $T_{sol}$ values decrease from 50.0% to 47.6% and from 11.2% to 8.1%, respectively, exhibiting good balance between $T_{vis}$ and $T_{sol}$. As displayed in Table 1,
the samples with nanoplatelets exhibit better overall performance and thus, they are promising for applications in the field of smart windows.

4. Conclusion

In summary, VO₂(M) nanoplatelets with excellent dispersion, high crystallinity and small dimensions are obtained in this study. Excellent optical properties are achieved with T_{vis} of 50.8% and ΔT_{sol} of 11.2%. Meanwhile, a large contrast transmittance of 60% at 2500 nm is obtained. In addition, T_{vis} increases with the gradual reduction in ΔT_{sol} when the film thickness is reduced. Ultrahigh T_{vis} of 87.2% and satisfactory ΔT_{sol} of 5.3% are obtained. Furthermore, the VO₂ nanoplatelets exhibit higher sensitivities compared to nanoparticles. Thus, VO₂(M) spheres composed of 2D nanoplatelets will promote practical applications in smart windows.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was jointly supported by the National Natural Science Foundation of China (Grant No. 51771144, 51471130), Natural Science Foundation of Shaanxi Province (No. 2017JZ015), and City University of Hong Kong Applied Research Grant (ARG) No. 9667104.

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