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1. Introduction

Vanadium dioxide (VO₂) is a well-known inorganic thermochromic material, which exhibits an abrupt reversible semiconductormetal transition (SMT) at around 68 °C.¹ The low-temperature monoclinic VO₂(M) is a semiconductor and infrared (IR) transparent, while the high-temperature rutile VO₂(R) is metallic and exhibits a high IR reflectance.² This distinctive phase transition occurs with an abrupt change in the optical properties, which enables the VO₂ films to automatically switch between a transparent state and a dark state in response to environmental temperature without the use of any external switching device. The special characteristics of VO₂ make it more promising in applications as smart windows as compared to other inorganic and polymeric thermochromic materials.³

Furthermore, organic pollutants as a by-product of rapid industrial development are a serious threat to human health



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Hierarchical VO₂(M)–ZnO dandelions with ZnO nanorods grown radially on VO₂(M) nanoparticle cores have been successfully fabricated for the first time. In these dandelions, the VO₂(M) NPs were prepared by a TiO₂ seed-assisted hydrothermal method and the dandelion-like ZnO nanorods were formed over two steps: heteroseed-induced nucleation and the subsequent heteroepitaxial growth processes. The coupled ZnO could increase the chemical stability of VO₂(M) at relatively high temperatures. In addition, the VO₂(M)–ZnO composite film with decreased phase transition temperature ($T_c = 62.6$ °C) simultaneously displayed an enhanced visible transmission ($T_{vis-l} = 52.2\%$) and solar modulating ability ($\Delta T_{sol} = 9.3\%$) as compared with the pure VO₂(M) film. Besides, the VO₂(M)–ZnO dandelions also exhibited improved photocatalytic performance, likely due to the synergistic effect of the VO₂(M)–ZnO heterojunction, unique dandelion-like hierarchical structure and high specific surface area. This is the first report of such a single VO₂(M)–ZnO dandelions structure with energy saving and environmental protection effects that offer significant potential for creating a multifunctional smart coating.

> and the environment. It is known that photocatalysis is effective for the degradation of organic waste because it is economic, simple and can completely eliminate toxic chemicals from wastewater.^{4,5} Zinc oxide (ZnO) nanomaterials with a wide band gap energy ($\sim 3.37 \text{ eV}$) are potential semiconductor photocatalysts⁶⁻⁸ and have attracted intense research attention in recent years.^{9–12} It is interesting that a composite material with a combination of VO₂ and ZnO would present both energy saving and environmental protection properties.

> For the practical application of VO₂-based smart windows, low visible transmission (T_{vis}) , poor solar modulating ability (ΔT_{sol}) and weak chemical stability are the major drawbacks.^{13,14} Single VO₂ films have a high reflectance and strong absorption due to their larger refractive index (RI) $(n(VO_2(M)) = 2.7-2.8 \text{ and})$ $n(VO_2(R)) = 2.0-2.5)^{15,16}$ and large absorption coefficient, resulting in an insufficient optical properties. According to the previous reports and optical calculations,¹⁷ involving an additional antireflection layer or dispersing the VO₂(M) nanoparticles in a dielectric matrix could improve the optical properties; e.g., TiO₂/VO₂/glass multilayer structure,^{18,19} ZnO:Al/VO₂ doublelayered film,²⁰ ZnO/VO₂/ZnS sandwiched structure²¹ and VO₂-ZrV₂O₇ composite film.²² However, it is difficult to incorporate dielectric layers with a certain refractive index and appropriate thickness into complicated stack structures¹³ and the abovementioned structures are either expensive or they barely demonstrate photocatalytic performance. Besides, VO₂ is gradually



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oxidized into toxic V_2O_5 in a wet ambient atmosphere, which leads to a considerable deterioration of its thermochromic properties. Enhancing the chemical stability of VO_2 against oxidation is also urgently required. Although a series of studies reported by our group have demonstrated that $VO_2(@SiO_2^{23,24}$ and $VO_2(@TiO_2^{25}$ core–shell structures can modulate the optical properties and enhance the chemical stability of $VO_2(M)$, there are no reports on the production of the hierarchical $VO_2(M)$ – ZnO dandelions with enhanced thermochromic and photocatalytic performance, along with a high chemical stability.

In this study, we have reported a successful attempt to fabricate the hierarchical VO₂(M)–ZnO dandelions for the first time. The VO₂(M)–ZnO nanoparticles exhibited multiple functions: thermochromism from the VO₂ for solar energy modulation, photocatalytic properties from the ZnO for environmental purification, and highly enhanced chemical stability of VO₂(M). The enhanced thermochromic properties may arise from the anti-reflection effect and good dispersibility introduced by the transparent ZnO, and the higher photocatalytic activity could be ascribed to the unique VO₂–ZnO heterojunction and high specific surface area. The abovementioned technique breakthroughs will play a role in obtaining the composite materials with integrated energy-saving and environmental protection functions for building applications.

2. Experimental section

2.1. Synthesis of VO₂(M) nanoparticles

All the reagents were of analytical grade and used without further purification. $VO_2(M)$ nanoparticles were prepared *via* a rutile TiO₂ seed-assisted hydrothermal synthesis as reported in the literature.²⁶ In a typical procedure, V_2O_5 and $H_2C_2O_4$ · $2H_2O$ powders (1:(1–3) molar ratio) were directly added to 50 ml deionized water with continuous stirring. Then, an appropriate amount of rutile TiO₂ was added to the abovementioned solution. After adequate ultrasonication of the reaction mixture, the resulting solution was transferred into a 100 ml Teflon-lined autoclave and maintained at 240 °C for 24 h. The final products were washed, collected and dried for further use.

2.2. Synthesis of VO₂(M)-ZnO dandelions

Briefly, 0.05 g of the obtained VO₂(M) particles was dispersed in 100 ml of deionized water with adequate ultrasonication. Then, 20 ml of a 0.1 M C₆H₅Na₃O₇·2H₂O (sodium citrate) solution was added into the VO₂(M) suspension for further modification. After stirring for 10 h, the obtained NaCA-capped VO₂(M) particles were centrifuged and washed, and then dispersed in 100 ml of Zn(CH₃COO)₂ ethanol solution (0.02 M). Under stirring for 1 h, 50 ml of a KOH–ethanol solution (0.04 M) was introduced. The mixed solution was transferred to a water bath and heated to 60 °C. After allowing it to stand at 60 °C for 2 h, the obtained products were rinsed and redispersed in 200 ml of deionized water containing Zn(CH₃COO)₂ and HMT (C₆H₁₆N₄) (1:2 molar ratio). The mixed solution was heated to 90 °C and maintained at this temperature for 2 h. The final VO_2 -ZnO dandelions were washed, collected and dried for characterization.

2.3. Characterization

The crystalline structures of the as-prepared crystals were investigated using powder X-ray diffraction (XRD, Model D/max 2550 V, Rigaku, Japan) using $Cu_{K\alpha 1}$ ($\lambda = 1.5418$ Å). The morphology was observed by field-emission scanning electron microscopy (FE-SEM, HITACHI S-3400, Japan) and transmission electron microscopy (TEM, JEM-2010, JEOL, Japan) equipped with energy dispersive spectroscopy (EDS). The attachments of highresolution transmission electron microscopy (HRTEM) images and selected area electron diffraction (SAED) of JEM-2010 were used to obtain the crystallographic information. The compositions of the powders were detected by X-ray photoelectron spectroscopy (XPS, Axis Ultra DLD, Kratos, England). Zeta potential measurements were recorded on a ZetaPALS Zeta potential analyzer. Specific surface area was measured on an ASAP2010 (Micromeritics, USA) instrument using the N2 adsorption method with BET analysis. The optical transmission and absorption spectra were recorded on a UV-Vis spectrophotometer (HITA-CHI U-3010, Japan). The photoluminescence (PL) spectra of the photocatalysts were detected using a Perkin Elmer LS-50B spectrometer.

2.4. Photocatalytic measurements

The photodegradation reactions were carried out under atmospheric conditions using a 300 W Xe lamp (240 nm–2 μ m) as the irradiation source. The as-fabricated photocatalyst (0.03 g) was added to a cylindrical container containing 100 ml of rhodamine B (RhB) aqueous solution (10⁻⁵ M). Before irradiation, the solution was stirred in the dark for 20 min to obtain a good dispersion and to reach an adsorption–desorption equilibrium between the organic molecules and the catalyst surface. To minimize the effects of heating, the photoreactor was fixed in a glass jacket and cooled using flowing water. For every 10 min irradiation intervals, about 3 ml of the suspension was collected and separated by centrifugation. The residual concentration of RhB in the supernatant was measured using a UV-vis spectrometer at a maximum absorption wavelength of around 554 nm.

3. Results and discussion

3.1. Preparation of VO₂(M)-ZnO dandelions

The X-ray diffraction (XRD) patterns of the as-prepared samples are shown in Fig. 1. All the diffraction peaks in Fig. 1a could be perfectly indexed as the monoclinic phase of VO₂ synthesized by a TiO₂(R) seed-assistant hydrothermal synthesis. Rutile TiO₂ has the same space group and similar lattice parameters as found for VO₂(R), thus the rutile TiO₂ can be used as seeds to promote the formation, control the morphology and reduce the size of VO₂(M).²⁶ As observed in Fig. 1b, two sets of diffraction peaks exist for the VO₂(M)–ZnO sample, which were correspondingly ascribed to the hexagonal wurtzite ZnO (JCPDS 36-1451) and VO₂(M) (JCPDS 43-1051). The diffraction peaks



Fig. 1 XRD patterns of the as-prepared products: (a) VO_2(M) and (b) VO_2(M)-ZnO.

were sharp and intense, indicating the highly crystalline character. Furthermore, no characteristic peaks for impurities, such as $Zn_2V_2O_7$ and $Zn_3(OH)_2V_2O_7 \cdot 2H_2O$, were observed, suggesting that the compositions of the abovementioned samples were ZnO and VO₂.

Fig. 2a–e present the representative SEM and TEM images of the abovementioned two samples. According to Fig. 2a, the synthesized $VO_2(M)$ nanoparticles were grown into quasi-spherical shape with a size of around 50–100 nm. Fig. 2b and c are the low- and high-magnification SEM images of the $VO_2(M)$ –ZnO crystals, respectively. It could be seen that the product consisted of relatively uniform dandelion-like assemblies that were about 400 nm in size. From the enlarged SEM image shown in Fig. 2c,

we found that the radially arrayed ZnO nanorods grew around a core to form the "dandelion" structures, and that each nanorod was 20-50 nm in diameter and about 200 nm in length. The typical TEM image shown in Fig. 2d further reveals that the average diameter of the core was about 100 nm, which is in accordance with the size of the initially prepared $VO_2(M)$ NPs. Moreover, a high-resolution TEM (HRTEM) of the ZnO nanorod is shown in Fig. 2e. The fringe spacing of 0.52 nm agreed well with the spacing of the (001) lattice planes of ZnO_{27}^{27} and the diffraction spots of the corresponding selected area electron diffraction (SAED) pattern could be indexed as the (001), (101) and (100) reflections (inset in Fig. 2e). This demonstrated that the ZnO nanorods were structurally uniform and can be described as single crystals with a [100] growth direction. In addition, the EDS measured in one signal dandelion (the red oval in Fig. 2d) showed that the VO₂(M)-ZnO dandelions were composed of Zn, V, Ti and O, which is consistent with the XRD results.

Different amounts of the VO₂(M) NPs were introduced to obtain the optimal VO₂(M)–ZnO dandelion structure. As seen in Fig. S1b (ESI[†]), when 0.1 g of VO₂(M) NPs were used in the experiment, the products consisted of inhomogeneous nanosheets and dandelions. The intensity of the ZnO diffraction peaks was weaker. Upon decreasing the amount of VO₂(M) NPs, the nanosheets were gradually decreased and uniform VO₂(M)–ZnO dandelions were formed. When the usage of the VO₂(M) NPs was set as 0.05 g, products with good morphology and high crystallinity were obtained, as shown in Fig. S1d (ESI[†]).

To investigate the chemical state of the as-synthesized $VO_2(M)$ -ZnO dandelions, X-ray photoelectron spectroscopy (XPS) was carried out, and the corresponding results are shown in Fig. 3. The full-scan spectrum (Fig. 3a) demonstrates that V,



Fig. 2 (a) TEM image of the $VO_2(M)$ NPs, (b and c) Low- and high-magnification SEM images, (d) TEM image, (e) HRTEM image and SAED patterns (inset), and (f) EDS patterns of the $VO_2(M)$ -ZnO dandelions.



Fig. 3 XPS patterns of the VO₂(M)–ZnO dandelions: (a) XPS full spectrum, (b) V_{2p} spectra, (c) Zn_{2p} spectra, and (d) O_{1s} spectra.

Zn, O, and C exist in the products. The C element could be attributed to adventitious carbon-based contaminants, and the binding energy for the C_{1s} peak was 284.6 eV, which was used as the reference for calibration. The Ti element from the $TiO_2(R)$ seeds was unobserved due to the deep level and weak signal. As shown in Fig. 3b, the peak located at 516.3 eV corresponded to $V_{2p3/2}$, which is in agreement with a previous study²⁸ and indicates that the vanadium was in +4 state. Fig. 3c shows the Zn_{2p} spectrum of the VO₂(M)-ZnO dandelions, which contains two representative peaks located at 1021.4 and 1044.5 eV, corresponding to $Zn_{2p3/2}$ and $Zn_{2p1/2}$ of Zn^{2+} , respectively. The shape of the O_{1s} spectrum shown in Fig. 3d was asymmetric, which indicates that there is more than one chemical state according to the binding energy. Thus, the region of O_{1s} is divided into two peaks. The main peak centered at 530.2 eV is attributed to O^{2-} ions on the crystal lattice of the Zn^{2+} and V^{4+} ion array (O_{Zn-O} and O_{V-O}).²⁹ The shoulder at 531.5 eV is associated with hydroxide interactions such as the adsorption of OH groups.³⁰

3.2. The formation mechanism of the $VO_2(M)$ -ZnO dandelions

To investigate the formation mechanism of the VO₂(M)–ZnO dandelions, three other samples were prepared for comparison: ZnO NRs, VO₂(M)–ZnO without Na-CA and VO₂(M)–ZnO without ZnO seeds. The XRD patterns (Fig. S2a, ESI†) indicated that the samples consisted of ZnO and VO₂(M) without other impurities.

As seen in Fig. S2b (ESI⁺), the pure ZnO NRs had a size of around 150 nm in diameter and 1-2 μ m in length. If the VO₂(M) were not modified with sodium citrate, the final product consisted of much more single ZnO NRs and the dandelion-like NPs with an uneven morphology that were seriously aggregated (Fig. S2c, ESI[†]). Furthermore, when the experiment was conducted in the absence of ZnO seeds, the ZnO mainly grew into hexahedron shape with a size of around 1 µm and was partially formed into nanosheets coated on the surface of the $VO_2(M)$ NPs, as shown in Fig. S2d (ESI[†]). The surface preparation and subsequently introduced ZnO seeds are important for the generation of the hierarchical VO₂(M)-ZnO dandelions. The surface preparation might be beneficial for modifying the Zeta potential of $VO_2(M)$ (from -8.76 to -49.21 mV, Table 1), which could promote the electrostatic attractions between the Zn^{2+} ions and the $VO_2(M)$ NPs. The introduced ZnO seeds were beneficial for epitaxial growth and the formation of rod-like ZnO.

Therefore, based on the abovementioned results and discussion, we proposed a tentative mechanism for the formation of the

Table 1	The Ze	eta	potential	data	of	the	products	at	different	synthesis
stages										

Products/ethanol	VO ₂ NPs	Na-CA capped VO ₂ NPs	Zn ²⁺ adsorbed VO ₂ NPs	ZnO seed coated VO ₂ NPs
Zeta potential (mV)	-8.76	-49.21	5.56	-6.15



 $\label{eq:scheme1} \begin{array}{l} \text{Scheme1} & \text{Schematic illustration of the heteroseed assembly induced} \\ \text{formation of VO}_2(M) - ZnO \mbox{ dandelions}. \end{array}$

VO₂(M)–ZnO dandelions, which was similar to that reported previously.³¹ As illustrated in Scheme 1, first, when the modified VO₂(M) NPs were dispersed in the ZnAC₂ solution, Zn²⁺ ions were captured by the negatively charged VO₂(M) NPs due to electrostatic attractions. Then, the Zn²⁺ ions loaded VO₂(M) NPs with positively charged surface (5.56 mV, seen in Table 1) acted as the cores for the formation of the ZnO seeds after the addition of KOH. Besides, the excess KOH added would further switch the surface charge from positive to negative (from 5.56 to -6.15 mV, Table 1), which actively led to the spontaneous self-assembly of the primary VO₂(M)–ZnO heteroseeds to the VO₂(M)–ZnO core–shell heteroseeds. Finally, the VO₂(M)–ZnO hanorod arrays and eventually lead to the formation of VO₂(M)–ZnO dandelions.

3.3 Antioxygenic and thermochromic properties

The VO₂(M) and VO₂(M)–ZnO were annealed in air at different temperatures for 15 min at a heating rate of 10 $^{\circ}$ C min⁻¹ to study the antioxygenic properties. The phase evolution after being annealed at different temperatures is shown in Fig. 4.

It was found that the $VO_2(M)$ in our study remained unchanged at 290 °C and then oxidized into V2O5 at 320 °C (Fig. 4a), while the pure $VO_2(M)$ reported in the literature²⁵ partly changed into V₃O₇ and V₂O₅ at 290 °C. The increased stability may due to the existence of the TiO₂(R) seeds. On the contrary, VO₂(M)-ZnO still remained in its original phase compositions after being annealed at 380 °C (Fig. 4b), indicating its good chemical stability. Upon further increasing the annealing temperature to 430 °C, VO₂(M) just reacted with the ZnO at the interface to form Zn₂V₂O₇ without the existence of V₂O₅. The abovementioned phenomenon indicated that the VO₂(M)-ZnO composite exhibited enhanced stability at high temperatures. The enhancement may be ascribed to the two aspects: one was the existence of the $TiO_2(R)$ seeds and the other was the protection from the coupled ZnO. TiO₂ and ZnO are more stable than VO₂(M) at a relatively high temperature. The $TiO_2(R)$ seeds could increase the structural stability and the dense ZnO could act as an effective barrier layer to prevent the diffusion of oxygen into the VO₂ lattice. This result was superior to the previously reported $VO_2(a)SiO_2$ and VO₂(a)TiO₂ structures.^{24,25}

The reversible phase transition temperature of the pure VO₂(M) and VO₂(M)-ZnO composite powders were measured using differential scanning calorimetry (DSC) and the curves are shown in Fig. 5a. It was found that the endothermic peak in the heating process of pure VO₂(M) was located at 67.8 °C. However, the phase transition temperature of the heterostructured VO₂(M)–ZnO dandelions was decreased to 62.6 °C. This result was lower than the previously reported VO₂@SiO₂ nanorodbased powders³² and VO₂(M)@C belt-like structure.³³ After coating the powder onto a float glass substrate, the films were prepared and then inserted into the UV-Vis spectrophotometer to measure the transmittance at a low (20 °C) and a high temperature (90 °C). The optical transmittance spectra are shown in Fig. 5b. It can be clearly seen that the VO₂(M)–ZnO composite film exhibited perfect optical properties. It reached a sufficiently high visible transmission (T_{vis-1} = 52.2%) and still retained an excellent solar modulating ability (ΔT_{sol} = 9.3%), which are better than that found for a pure VO₂(M) film (T_{vis-l} = 35.0% and ΔT_{sol} = 8.5%), as shown in Table 2.



Fig. 4 XRD patterns of the samples after heat treatment at different temperatures for 15 min: (a) VO₂(M) and (b) VO₂(M)–ZnO.



Fig. 5 (a) DSC curves and (b) optical transmittance spectra at a low (20 °C) and a high temperature (90 °C) for the VO₂(M) NPs and VO₂(M)–ZnO dandelions.

 Table 2
 The optical properties, binding energy and specific surface area of the samples

Sample	$T_{\rm c}$ (°C)	$T_{\rm vis-l}$ (%)	$\Delta T_{\rm sol}~(\%)$	$\lambda_{\text{c-l}} (\text{nm})$	$E_{\rm g}~({\rm eV})$	$S_{\rm BET} \left({{{\rm{m}}^2}\;{{\rm{g}}^{ - 1}}} \right)$
VO_2	67.8	35.0	8.5	498	2.27	_
ZnO	_	_	_	_	2.95	34.5
VO ₂ -ZnO	62.6	52.2	9.3	475	2.67	69.5

The solar transmittance was calculated by the formula $T_{\rm sol} = \int \varphi(\lambda) T_{\rm r}(\lambda) d\lambda / \int \varphi(\lambda) d\lambda$ and the solar transmittance modulation efficiency was calculated using $\Delta T_{\rm sol} = T_{\rm sol_20^\circ C} - T_{\rm sol_90^\circ C} \cdot \varphi(\lambda)$ is the solar irradiance spectrum for air mass 1.5 corresponding to the sun standing 37° above the horizon and $T_{\rm r}(\lambda)$ is the transmittance of our sample.³⁶

In addition, the existence of ZnO could widen the optical band gap from 2.27 eV in a pristine VO₂ film to 2.67 eV in the VO₂(M)–ZnO heterostructured film, as shown in Fig. S3 (ESI†). For a direct semiconductor, the band gap energy, E_g , can be determined as follows:

$$(\alpha h\nu)^2 = A(h\nu - E_{\rm g}) \tag{1}$$

where α , ν , E_g and A are the absorption coefficient, light frequency, band gap energy and constant, respectively.³⁴ By linear extrapolation of $(\alpha h\nu)^2$ against $h\nu$, the value of the E_g was obtained as the intercept at the $\alpha = 0$ axis.

The change in E_g reflected the nature and the concentration of the defects. The incorporation of Zn and the interfacial stress induced a distortion in the VO₂ materials and increased the concentration of the defects, resulting in a wider optical band gap and a lower phase transition temperature. The widened optical gap could lead to a blue shift in the absorption edge from 498 to 475 nm, which, in turn, resulted in a significant increase in the visible transmittance (as seen in Table 2). This positive effect of the coupled ZnO on the optical properties and the phase transition temperature of the VO₂(M) film was similar to that previously reported on Zn-doped VO₂(M) films.³⁵ In addition, the refractive index of the ZnO was lower than that found for VO₂(M), the existence of the ZnO can act as an antireflection layer to increase the transmittance.

3.4 Photocatalytic activity

To demonstrate the photocatalytic activities of the as-synthesized VO₂(M)-ZnO dandelions, the photocatalytic decomposition of RhB as a test reaction was carried out under simulated solar light produced using irradiation from a Xe-lamp. As observed in Fig. 6a, the major absorption peaks of RhB at around 550 nm diminished gradually as the irradiation proceeded and almost vanished after 50 min. Correspondingly, the color of the suspension completely transformed from deep pink to translucent at the end (insert in Fig. 6a). These observations revealed that the chromophoric structure of RhB was gradually decomposed during the reaction process. Furthermore, for comparison, pure ZnO NRs were also investigated as a photocatalytic reference. As observed in Fig. 6b, the VO2(M)-ZnO dandelions exhibited the highest photocatalytic activity. After being irradiated for 20 min, the degradation efficiency of the VO₂(M)-ZnO dandelions was of about 80%, whereas the value obtained for the ZnO NRs was about 46%. The degradation process approximately complied with the pseudo-first-order kinetics,³⁷ as shown in formula (2).

$$\ln C/C_0 = -kt \tag{2}$$

where *C* and *C*₀ refer to the remnants and initial concentration of RhB, respectively. *k* is the degradation constant and the values for VO₂(M)–ZnO, ZnO NRs and Blank are 0.0782, 0.03 and 0.005 min⁻¹, respectively, which were calculated from Fig. 6c. Accordingly, the photocatalytic efficiency displayed the following order: VO₂(M)–ZnO > ZnO NRs > Blank.

In addition, to evaluate the stability of the catalyst during the photo-degradation of RhB in an aqueous solution, the reacted VO₂(M)–ZnO catalyst was collected and washed several times with deionized water to remove the residual dye impurities and then dried at 60 °C for 12 h to measure the mass. The mass remained unchanged, which indicated that the VO₂(M)–ZnO catalyst was stable without any dissolution.

The surface structures of the as-synthesized ZnO NRs and $VO_2(M)$ -ZnO dandelions were analysed by nitrogen sorption



Fig. 6 (a) Absorption spectra and photographs of RhB solutions in the presence of the $VO_2(M)$ -ZnO dandelions under UV-vis light at different periods of time. (b and c) Degradation profiles and kinetic linear simulation curves for RhB over different samples: Blank, ZnO NRs and $VO_2(M)$ -ZnO dandelions.

isotherm technique, and the curves are presented in Fig. 7a. Brunauer-Emmett-Teller (BET) analysis revealed that the surface area of the VO₂(M)–ZnO dandelions was 69.5 m² g⁻¹, which was much larger than that found for pure ZnO (34.5 $m^2 g^{-1}$) (Table 2). The special hierarchical structure of the $VO_2(M)$ -ZnO dandelions could both increase the surface area and prevent the aggregation of the catalyst nanoparticles, which are beneficial to increase the active sites and improve the photocatalytic performance. In addition, the composite with narrowed band gap could increase the utilization efficiency of the simulated solar light. Furthermore, the charge separation and recombination properties of the as-prepared samples were investigated using photoluminescence (PL) emission spectroscopy. In Fig. 7b, it indicates that the VO₂(M)-ZnO dandelions exhibited a much lower emission intensity than the pure ZnO NRs. A previous work reported that the PL emission below 413 nm occurred by the recombination of the free excited electrons and holes.³⁸ The lower emission intensity indicated that the recombination of the photogenerated charge carrier was greatly inhibited in the VO₂(M)-ZnO heterostructures.

Based on the results of the abovementioned measurements, it can be inferred that the ZnO NRs were uniformly grafted on the surface of the VO₂(M) NPs to form the VO₂(M)–ZnO heterojunction due to intimate interfacial contacts. Under simulated solar light irradiation, the photogenerated electrons and holes could be stored separately, as shown in Scheme 2. The electrons could reduce the dissolved molecular oxygen to produce $O_2^{\bullet^-}$ superoxide radical anions ($O_2 + e \rightarrow O_2^{\bullet^-}$), while the holes were ultimately trapped by the hydroxyl groups (or H₂O) on the surface to yield OH[•] radicals (h⁺ + HO₂ \rightarrow OH[•] + H⁺). The $O_2^{\bullet^-}$ and OH[•] radicals are strong oxidizing agents that can decompose the organic dye. Furthermore, because of the better separation of photogenerated electrons and holes attributed to the 3D heterojunction structure, more $O_2^{\bullet^-}$ and OH[•] radicals were produced, improving the photocatalytic activity.

In addition, the photo-induced holes have strong oxidability. They could also react with the surface O^{2-} ions on ZnO to release O_2 (ZnO + 2h⁺ \rightarrow Zn²⁺ + 1/2O₂), leading to the dissolution of ZnO.³⁹ Thus, the pure ZnO nanostructures display significant photocorrosion phenomena. For the VO₂(M)–ZnO heterojunction,



Fig. 7 (a) Nitrogen adsorption-desorption isotherm and (b) PL emission spectra of ZnO NRs and VO₂(M)-ZnO dandelions.



Scheme 2 Schematic illustration of the photocatalytic mechanism of the $VO_2(M)$ -ZnO dandelions.

the holes were gathered on the $VO_2(M)$ surface, which may reduce the photocorrosion effect. Besides, the other methods such as N-doping,⁴⁰ coupling with C_{60}^{41} and forming the core–shell structure⁴² are beneficial to prohibit the photocorrosion of the ZnO.

4. Conclusions

In summary, the $3D \text{ VO}_2(M)$ –ZnO dandelions were prepared for the first time. They exhibited unique features: enhanced photocatalytic ability, improved thermochromic properties and chemical stability. The enhanced photocatalytic ability could be primarily attributed to the formation of a heterojunction structure at the interface between ZnO and VO₂(M), which greatly promoted the efficient separation of photogenerated electron–hole charge carriers. The improved thermochromic properties and chemical stability were ascribed to the ZnO. This synthetic process has advantages including simplicity, speed and cost-effectiveness. It is expected to have potential application prospects in energy saving and environmental protection fields.

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Notes and references

- 1 A. Zylbersztejn and N. F. Mott, *Phys. Rev. B: Solid State*, 1975, **11**, 4383.
- 2 S. D. Ji, F. Zhang and P. Jin, Sol. Energy Mater. Sol. Cells, 2011, 95, 3520.
- 3 N. Shen, Z. Chen, X. L. Liu, C. X. Cao, B. R. Dong and Y. F. Gao, *J. Mater. Chem. A*, 2014, **2**, 15087.
- 4 J. S. Lee, O. S. Kwon and J. Jang, J. Mater. Chem., 2012, 22, 14565.
- 5 S. Xie, X. Lu, T. Zhai, J. Gan, W. Li, M. Xu and Y. Tong, *Langmuir*, 2012, **28**, 10558.

- 6 L. Lin, Y. Yang, L. Men, X. Wang, D. He and Q. Tang, *Nanoscale*, 2013, 5, 588.
- 7 C. Luo, D. Li, W. Wu, C. Yu, W. Li and C. Pan, *Appl. Catal., B*, 2015, **166**, 217.
- 8 X. Zheng, D. Li, X. Li, J. Chen, C. Cao, J. Fang, J. Wang, Y. He and Y. Zheng, *Appl. Catal., B*, 2015, **168**, 408.
- 9 Z. Chen, N. Zhang and Y. J. Xu, *CrystEngComm*, 2013, **15**, 3022.
- 10 S. Guo, S. Han, H. F. Mao, C. C. Wu and J. Li, *J. Power Sources*, 2014, 245, 979.
- 11 H. Yin, K. Yu, C. Song, R. Huang and Z. Zhu, ACS Appl. Mater. Interfaces, 2014, 6, 14851.
- 12 Z. Zhang, C. Shao, X. Li, L. Zhang, H. Xue and Y. Liu, *J. Phys. Chem. C*, 2010, **114**, 7920.
- 13 L. Kang, Y. Gao, H. Luo, Z. Chen, J. Du and Z. Zhang, ACS Appl. Mater. Interfaces, 2011, 3, 135.
- 14 Z. Zhang, Y. Gao, L. Kang, J. Du and H. Luo, *J. Phys. Chem. C*, 2010, **114**, 22214.
- 15 P. Jin, G. Xu, M. Tazawa and K. Yoshimura, *Jpn. J. Appl. Phys.*, 2002, **41**, 278.
- 16 T. B. Messaoud, G. Landry, J. P. Gariépy, B. Ramamoorthy, P. V. Ashrit and A. Haché, *Opt. Commun.*, 2008, 281, 6024.
- 17 S. Li, G. A. Niklasson and C. G. Granqvist, J. Appl. Phys., 2010, 108, 1.
- 18 N. R. Mlyuka, G. A. Niklasson and C. G. Granqvist, *Phys. Status Solidi A*, 2009, 206, 2155.
- 19 N. R. Mlyuka, G. A. Niklasson and C. G. Granqvist, Sol. Energy Mater. Sol. Cells, 2009, 93, 1685.
- 20 L. Kang, Y. Gao, H. Luo, J. Wang, Z. Zhang and M. Kanehira, Sol. Energy Mater. Sol. Cells, 2009, **95**, 3189.
- 21 Y. Zhao, R. Xu, X. Zhang, X. Hu, R. J. Knize and Y. Lu, *Energ. Build.*, 2013, **66**, 545.
- 22 J. Du, Y. Gao, H. Luo, Z. Zhang, L. Kang and Z. Chen, *Sol. Energy Mater. Sol. Cells*, 2011, 95, 1604.
- 23 A. B. Huang, Y. J. Zhou, Y. M. Li, S. D. Ji, H. J. Luo and P. Jin, J. Mater. Chem. A, 2013, 1, 12545.
- 24 Y. F. Gao, S. B. Wang, H. J. Luo, L. Dai, C. X. Cao and M. Kanehira, *Energy Environ. Sci.*, 2012, 5, 6104.
- 25 Y. Li, S. Ji, Y. Gao, H. Luo and M. Kanehira, *Sci. Rep.*, 2013, 3, 1370.
- 26 D. B. Li, M. Li, J. Pan, Y. Y. Luo, H. Wu and G. H. Li, ACS Appl. Mater. Interfaces, 2014, 6, 6555.
- 27 L. W. Chang, Y. C. Sung, J. W. Yeh and H. C. Shih, J. Appl. Phys., 2011, 109, 1.
- 28 S. Chen, L. Dai, Y. F. Gao, X. L. Liu, Z. Chen and M. Kanehira, *Phys. Chem. Chem. Phys.*, 2013, 15, 17537.
- 29 H. H. Yin, K. Yu, C. Q. Song, Z. L. Wang and Z. Q. Zhu, *Nanoscale*, 2014, 6, 11820.
- 30 M. T. Uddin, Y. Nicolas, C. Olivier, T. Toupance, L. Servant and W. Jaegermann, *Inorg. Chem.*, 2012, **51**, 7764.
- 31 M. Jiang, S. Bao, X. Cao, Y. Li, S. Li, H. Zhou, H. Luo and P. Jin, *Ceram. Int.*, 2014, 40, 6331.
- 32 Y. J. Zhou, A. B. Huang, Y. M. Li, S. D. Ji, Y. F. Gao and P. Jin, *Nanoscale*, 2013, **5**, 9208.
- 33 Y. F. Zhang, M. J. Fan, W. B. Wu, L. Hu, J. C. Zhang and X. H. Liu, *Mater. Lett.*, 2012, 71, 127.
- 34 E. A. Davis and N. F. Mott, Philos. Mag., 1970, 22, 0903.

- 35 Z. Zhang, Y. Gao, L. Kang, Z. Chen, J. Du and H. Luo, *Langmuir*, 2010, **26**, 10738.
- 36 Y. Qin, Y. J. Zhou, J. Li, J. Ma, D. L. Shi and J. H. Yang, J. Colloid Interface Sci., 2014, 418, 171.
- 37 M. S. Lee, S. S. Park, G. D. Lee, C. S. Ju and S. S. Hong, *Catal. Today*, 2005, **101**, 283.
- 38 A. F. Kohan, G. Ceder, D. Morgan and C. G. Van de Walle, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2000, **61**, 15019.
- 39 Y. Q. Cao, J. Chen, H. Zhou, L. Zhu, X. Li and A. D. Li, *Nanotechnology*, 2015, **26**, 1.
- 40 S. Muthulingam, K. B. Bae, R. Khan, I. H. Lee and P. Uthirakumar, *RSC Adv.*, 2015, **5**, 46247.
- 41 C. Han, M. Q. Yang, B. Weng and Y. J. Xu, *Phys. Chem. Chem. Phys.*, 2014, **16**, 16891.
- 42 L. Yu, W. Chen, D. Li, J. Wang, Y. Shao and X. Zheng, *Appl. Catal.*, *B*, 2015, **164**, 453.