



# Preparation of transparent, hard thermochromic polysiloxane/tungsten-doped vanadium dioxide nanocomposite coatings at ambient temperature

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## ABSTRACT

Polysiloxane/tungsten-doped vanadium dioxide [VO<sub>2</sub>(W)] nanocomposite coatings were prepared by de-agglomerating and modifying the self-made VO<sub>2</sub>(W) particles with 3-methacryloxypropyltrimethoxysilane in butyl acetate, then mixing MPS-functionalized VO<sub>2</sub>(W) nanoparticles with polysiloxane oligomers and curing the product at ambient temperature with the aid of 3-aminopropyltriethoxysilane. The VO<sub>2</sub>(W) particles were obtained by hydrolysis of vanadyl sulfate mingled with tungstate dopant and subsequent calcination. The structure and properties of the VO<sub>2</sub>(W) particles and nanocomposite coatings were characterized by X-ray diffraction analysis, differential scanning calorimetry, visible-near infrared spectroscopy, pendulum hardness tests, and nanoindentation. The effects of the synthesis conditions and the de-agglomeration process on the properties of the VO<sub>2</sub>(W) particles were investigated. Crystalline VO<sub>2</sub>(W) particles were obtained only with an appropriate amount of air and temperature during the calcination step and were easily reduced to nanometer size by bead-milling. The obtained nanocomposite coatings exhibited high transparency, good thermochromic performance, and ultra-high hardness (~1.0 GPa).

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## 1. Introduction

Vanadium dioxide (VO<sub>2</sub>) has intrigued researchers due to its thermochromic properties at a relatively low transition temperature ( $T_c = \sim 68^\circ\text{C}$ ) [1]. Moreover, the transition temperature can be adjusted to near room temperature through doping [2,3], demonstrating its promising application in resistive switching elements, thermal relays, optical-switching devices, variable reflectivity mirrors, smart-window coatings, holographic recording media, and so on [4–7]. Generally, VO<sub>2</sub> or doped VO<sub>2</sub> is fabricated in the form of thin films by sputtering [8–11], chemical vapor deposition [12–14], pulsed laser deposition [15,16], or sol–gel processes [17–20]. However, the first three methods are gas phase-based routes that have to employ special equipment and the area of the film is limited. As for the sol–gel method, the high-temperature annealing process restricts the in situ application of this method on windows. The low luminous transmittance (usually <50%) is another significant problem for practical application of VO<sub>2</sub> films on windows.

Up to now, many approaches have been tried to improve the luminous transmittance. Decreasing the thickness of the VO<sub>2</sub> film may be the simplest method of enhancing the transparency, but this method invariably deteriorates the thermochromic properties of the film in the near-infrared region [21]. Doping of the film with fluorine or magnesium is another method of increasing the visible transmittance [22,23]. Also, deposition of a proper anti-reflection layer (i.e., SiO<sub>2</sub>, CeO<sub>2</sub>, or TiO<sub>2</sub>) has been frequently reported to improve the luminous transmittance

[6,24–28]. Recently, Gao et al. employed poly(vinylpyrrolidone) to aid the formation of a film from a VOCl<sub>2</sub> solution. The doped VO<sub>2</sub> film displayed both excellent luminous transmittance and solar-modulating ability [29,30]. However, an annealing process is still necessary in their solution-based approaches, and the visible transparency at a wavelength of 550 nm is still less than 60% for most of the thermochromic films reported.

VO<sub>2</sub>-containing organic coatings may be an ideal alternative for fabrication of thermochromic coatings at mild conditions. Because the filler, consisting of doped or undoped VO<sub>2</sub> particles, is prepared ex situ, the annealing process can be eliminated in the formation of thermochromic films, which is absolutely beneficial for their in situ application on windows. In addition, it has been theoretically proven that the VO<sub>2</sub> nanoparticles in dielectric hosts can improve the luminous transmittance relative to VO<sub>2</sub> films [31]. So far, very little attention has been paid to the fabrication of organic coatings containing VO<sub>2</sub> particles. Valmalette et al. [32] embedded VO<sub>2</sub> pigment into a polymeric coating and analyzed the optical thermochromic behavior of the coating. In a previous work, we primarily prepared an acrylic resin/tungsten-doped VO<sub>2</sub> [VO<sub>2</sub>(W)] coating with 2 wt.% of VO<sub>2</sub>(W) particles in order to demonstrate the thermochromic properties of the VO<sub>2</sub>(W) particles, but the transmittance (550 nm) of the coatings was as low as 45% and did not meet the requirements desired [33].

In this work, we employed an ambient-curable polysiloxane binder and VO<sub>2</sub>(W) particles in order to fabricate thermochromic nanocomposite coatings with high visible transmittance (~60% at a wavelength of 550 nm), good solar-modulation ability (23.2% at a wavelength of 2500 nm), excellent mechanical properties, and a

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transition temperature near room temperature. The VO<sub>2</sub>(W) particles were synthesized by hydrolysis of vanadyl sulfate mingled with a tungstate dopant and subsequent calcination and de-agglomeration in butyl acetate (BAC) via bead-milling in the presence of 3-methacryloxypropyltrimethoxysilane (MPS). The effect of the de-agglomeration process on the properties (crystal size, particle size, and surface character) of VO<sub>2</sub>(W) particles, as well as the thermochromic and mechanical properties of the polysiloxane/VO<sub>2</sub>(W) coatings, was investigated in detail.

## 2. Experimental details

### 2.1. Materials

Vanadyl sulfate hydrate (VOSO<sub>4</sub>·xH<sub>2</sub>O, 23.5 wt.% V content) was obtained from Shanghai Luyuan Fine Chemical Factory. Ammonium bicarbonate (AR), sodium tungstate dehydrate (AR), aqueous ammonia solution (28 wt.%), absolute ethanol, BAC (CR), n-octane (CR), and 3-aminopropyltriethoxysilane (APS, 98%) were all purchased from Sinopharm Chemical Reagent Co., Ltd. 3-Methacryloxypropylmethylmethoxysilane (MPDS, 98%), MPS (98%), and methyltriethoxysilane (MTES, 98%) were obtained from Zhangjiagang Guotai-Huarong New Chemical Materials Co., Ltd. of China.

### 2.2. Preparation of VO<sub>2</sub>(W) crystals

The crystalline VO<sub>2</sub>(W) powder was prepared as follows. A stoichiometric volume of aqueous sodium tungstate solution (0.50 M) was first dropped into an aqueous solution of VOSO<sub>4</sub> (0.1 mol dissolved in 150 mL deionized water), followed by addition of an aqueous solution of ammonium bicarbonate (0.2 mol dissolved in 150 mL deionized water) using an automatic syringe pump over a period of 1.5 h at room temperature. The slurry-like suspension was magnetically stirred for another hour and subsequently filtered with a #4 sand funnel. The as-obtained precipitate was carefully washed with deionized water and absolute ethanol until no sulfate was detected, and then it was dried at 40 °C under vacuum for about 4 h. The dried precursor (~11.0 g) was put in ceramic boats and further moved to a quartz glass tube (87 × 1300 mm). The quartz glass tube was purged with nitrogen and then heated to 800 °C at a heating rate of 10 °C min<sup>-1</sup> under a flow of nitrogen. Subsequently, a certain amount of air was injected into the tube within 1 min and thereafter the nitrogen flow was stopped. The temperature was held at 800 °C for another 2 h. Crystalline VO<sub>2</sub>(W) powder was obtained through thermal decomposition of the precursor.

### 2.3. Preparation of MPS-functionalized VO<sub>2</sub>(W) nanoparticles

The MPS-functionalized VO<sub>2</sub>(W) [MPS-VO<sub>2</sub>(W)] nanoparticles were obtained as follows. VO<sub>2</sub>(W) powder (7 g) was mixed with 70 g of pre-made BAC/MPS solution. The mixture was sonicated at room temperature for about 30 min and then bead-milled for about 10 h at a rotation speed of 3000 rpm using zirconia beads with diameters of 300 μm. MPS was added into the slurry in three batches, namely, 50, 25, and 25% of the total MPS [MPS/VO<sub>2</sub>(W) = 0.2:1 mol/mol] at 0, 4, and 7 h of milling time, respectively. The temperature of the slurry was carefully controlled in the range of 20–30 °C using an ice/water bath. The as-obtained VO<sub>2</sub>(W) slurry was then centrifuged at either 8000 rpm or 14,000 rpm for 10 min to remove any large aggregates. The supernatant fluid was then precipitated with an approximately fivefold volume of n-octane, then centrifuged to get the MPS-VO<sub>2</sub>(W) nanoparticles. The obtained nanoparticles were further washed with n-octane three times to remove the residual MPS molecules and dried at 40 °C for 2 h under vacuum to evaporate the remained n-octane.

### 2.4. Synthesis of polysiloxane oligomers

Polysiloxane oligomers were synthesized as per our previous method [34]. That is, a 50 mL round-bottom flask equipped with a condenser was put in an oil bath. Then 2.32 g (0.01 mol) of MPDS and 7.12 g (0.04 mol) of MTES were added into the flask and magnetically stirred, followed by dropwise addition of a diluted aqueous ammonia (0.1 mol/kg, 0.9 g)/ethanol (1 g) solution over 15 min at room temperature. Afterwards, the reaction mixture was heated to about 90 °C and refluxed for 4 h to obtain the polysiloxane oligomers.

### 2.5. Preparation of polysiloxane/VO<sub>2</sub>(W) nanocomposite coatings

The MPS-VO<sub>2</sub>(W) nanoparticles were re-dispersed in BAC based on a solid content of 10% and then mixed with the as-obtained polysiloxane oligomers (theoretical solid content: 83.25%). The mass ratio of the MPS-VO<sub>2</sub>(W)/BAC dispersion to the as-obtained polysiloxane oligomer was set as 5.7/50, 14.5/50, 23.6/50, 29.8/50, 45.9/50, 62.9/50, and 141.6/50, corresponding to the VO<sub>2</sub>(W) content of 1.0, 2.5, 4.0, 5.0, 7.5, 10.0, and 20.0 wt.% in the dried films. The mixture was then sonicated for about 20 min and evaporated under vacuum at room temperature (or further charged with a certain amount of BAC) to obtain coatings with a solid content of about 50%. After 30 wt.% of APS was added (based on the weight of the as-obtained polysiloxane oligomer solution), the coating was cast on glass slides using a #8 wire-wound applicator (about 80 μm in wet film thickness) and dried at room temperature for one week. The samples were then used for further optical and mechanical measurements.

### 2.6. Characterization

Fourier transform infrared (FTIR) spectra were obtained using a Nicolet Nexus 470 spectrometer (ThermoFisher, USA) in the wavenumber range of 400–4000 cm<sup>-1</sup> with a resolution of 4 cm<sup>-1</sup> and accumulation of 32 scans. Liquid MPS solution was dropped onto the surface of NaCl plate and quickly dried by infrared irradiation for direct characterization. The dried nanoparticles were blended with KBr to form sample flakes.

X-ray powder diffraction (XRD) measurements were carried out at room temperature using a Bruker Nanostar U System, with incident X-ray wavelength (λ = 0.1542 nm). The collimation system consisted of two cross-coupled Gobel mirrors and four pinholes. A Hi-Star two-dimensional (2-D) area detector (Siemens) filled with pressurized xenon gas was used to record the one-dimensional (1-D) XRD patterns at a voltage of 40 kV and a current of 40 mA.

Transmission electron microscopy (TEM) was performed on an H600 transmission electron microscope (Hitachi Corp., Japan) at an accelerated voltage of 100 kV. The as-prepared VO<sub>2</sub> dispersion was diluted with BAC and directly dried on copper grids.

The particle size and distribution of the MPS-VO<sub>2</sub>(W)/BAC dispersions were detected by a Nano ZS90 particle-size analyzer (Malvern Instruments Co., Ltd., U.K.).

Thermogravimetric analysis (TGA) was carried out using a PerkinElmer TGA-7 instrument (USA) from ambient temperature to 750 °C at a heating rate of 20 °C/min under ultrapure nitrogen atmosphere.

Differential scanning calorimetry (DSC) was performed on a PerkinElmer Pyris 1 system with a heating rate of 10 °C/min and ultrapure nitrogen protection.

Thermochromic switching characteristics were monitored on a Hitachi U-4100 UV-visible-near IR (NIR) spectrophotometer equipped with a film-heating unit. The transmittance spectra at normal incidence were recorded in the wavelength range of 400–2600 nm at a scanning rate of 600 nm/min. Hysteresis loops were measured by collecting the transmittance of the films at a fixed wavelength (1550 nm) at approximate intervals of 2.0 °C. The diffuse reflectance at normal incidence

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