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Mesoporous SiO_2/VO_2 double-layer thermochromic coating with improved visible transmittance for smart window

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ABSTRACT

Thermochromic vanadium dioxide (VO_2) film is a potential material for smart-window. But the high refractive index (> 2) of VO_2 coating in visible band resulted in strong reflection and low visible transmission. If another coating with a definite low refractive index is laid on VO_2 film to construct a gradient index multilayer system, the total reflection could be effectively reduced. Therefore in this paper we designed a mesoporous SiO_2/VO_2 double-layer system in which the mesoporous SiO_2 layer possessed an index adjustable from 1.243 to 1.354 to reduce the surface reflection of VO_2-based smart window. The mesoporous structure has been investigated through several techniques including 2D GISAXS, TEM and N_2 ad/desorption. More important, a facile, safe and low-cost solution method was employed to prepare VO_2 film with 60 nm thickness directly from ammonium citrato-oxovanadate (IV) compound that was reported by us previously. On this newly designed mesoporous SiO_2/VO_2 double-layer coating, the integral visible transmittance at 25 °C ($T_{vis,L}$) increased to 80.0% from 69.8% of pure VO_2 coating while the corresponsive integral visible transmittance at 90 °C ($T_{vis,H}$) increased to 78.9% from 67.6% of pure VO_2 coating, if the index of mesoporous SiO_2 layer was optimized to 1.299. Simultaneously, the near infrared switching ability at 2000 nm (ΔT_{2000}) reached 29.0% and solar energy modulation (ΔT_{sol}) was maintained at 10.2%. The phase transition temperatures (T_t) for VO_2 coating and the optimized SiO_2/VO_2 double-layer coating were 51.9 °C and 53.8 °C respectively, far below 68 °C of bulky VO_2. This optical performance should be very attractive for application in the further smart window because of little increased cost and greatly enhanced property.

1. Introduction

Recently thermochromic materials have aroused great attention because they could exhibit a temperature-induced switch for the transmission/reflection of infrared irradiation [1,2]. With this regard, the thermochromic materials could be applied as smart-window coatings to intelligently regulate the amount of solar radiation entering a building according to the environment temperature, therefore, relieving extra energy (heating, lighting or cooling) consumption [3,4]. For ideal thermochromic coating, a large solar modulation above and below the critical temperature was desirable for energy saving purpose, while visible transmission should remain high to ensure good indoor visibility [5]. Vanadium dioxide (VO_2), as a typical thermochromic material, became more attractive in research due to its reversible metal-insulator phase transition (MIT) at a phase transition temperature of 68 °C [6]. Accompanying this phase transition, VO_2 exhibited a drastic change in near-infrared optical transmittance, that is, transmissive to NIR light below 68 °C but reflective above 68 °C. And this MIT phenomenon was simply determined by environmental temperature and occurred quickly [7–9]. These characteristic features made VO_2 promising in the application of thermochromic coating [10].

In order to promote the application of VO_2-based smart windows, many efforts have been made to achieve VO_2 coating on transparent substrate [11–14]. However, relatively low visible transmission due to high refractive index of VO_2 coating still hindered its application. To improve the visible-light transmission, several methods have been

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reported, including fabricating porous VO_2 films, reducing the thickness of the continuous film of VO_2 to less than 80 nm, or depositing multilayer films. However, pore formation or thickness decrease would reduce VO_2 amount, thus leading to lower NIR reflection [15–17]. The deposition of multilayer film on VO_2 film may be an effective method to obtain a balance between visible transmittance and thermochromic switch efficiency, and the depositing an additional layer may also protect VO_2 from oxidation. Kakiuchida et al. fabricated a multilayer structure composed of amorphous silica and VO_2 by reactive magnetron sputtering, which showed an increase in visible transmission and maintained thermochromism [18]. Five-layered $TiO_2/VO_2/TiO_2/VO_2/TiO_2$ film made by magnetron sputtering showed a relatively higher visible transmittance and solar modulating ability, but fabrication of multilayer structure (> 3 layer number) was complex [19]. Multifunctional $VO_2/SiO_2/TiO_2$ coating fabricated by atmospheric pressure chemical vapor deposition (APCVD) was designed to integrate the typical thermochromic property of VO_2 with the photocatalytic property of TiO_2, but the introduction of TiO_2 layer further lowered the visible light transmission because of its high refractive index [20]. In addition, above vapor-based deposition methods were proved to be complicated and expensive due to the difficulty in controlling variable valence of V ions. Therefore, how to enhance the visible light transmission with little sacrifice of solar modulation ability and lower cost of large scale coating are still two major challenges for researchers.

Some calculations have shown that the incorporation of VO_2 in dielectric materials with low refractive index, such as SiO_2, could increase visible-light transmission of the VO_2 films [12,21,22]. If SiO_2 as an antireflection coating was coated on VO_2 coating, it could permit more visible light transit, and reduce the surface reflection. Herein we employed a safe and low-cost solution method to fabricate thermochromic VO_2 film directly from ammonium citrato-oxovanadate (IV) compound reported by us previously [23]. Sequentially, mesoporous SiO_2 antireflection coating was coated on VO_2 film. This solution-based method was applied to fabricate mesoporous SiO_2/VO_2 double-layer film with excellent visible transmittance and thermochromic property successfully.

2. Experimental details

2.1. Materials

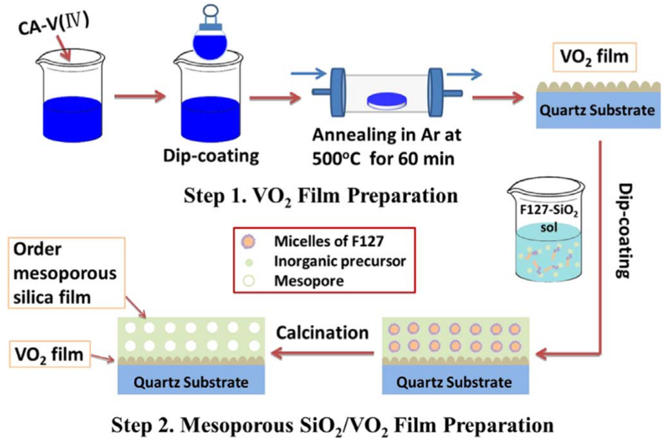
All the chemicals were used without further purification. Ammonium citrato-oxovanadate (CA-V(IV)) was synthesized by a simple solution method based on the procedures from our previous work [23]. Tetraethyl orthosilicate (TEOS) was purchased from Acros. Ethanol and Hydrochloric acid (HCl, 37%) was purchased from Beijing Chemical works. Pluronic F127 ($HO(C_2H_4O)_{106}(C_3H_6O)_{70}(C_2H_4O)_{106}H$, M_w=12600) was purchased from Sigma Aldrich.

2.2. Preparation of VO_2 film

In a typical synthesis showed by Step 1 of Schemes 1, 0.0870 g CA-V(IV) was dissolved into a mixture of deionized water and ethanol. After aging for several days, the coating precursor solution was deposited on clean quartz or Si substrate by dip-coating. Then the obtained film was dried at 60 °C for 10 min. After annealed in Ar flow at 500 °C for 60 min, the CA-V(IV) film was transformed to thermochromic VO_2 film.

2.3. Preparation of mesoporous SiO_2/VO_2 film

The SiO_2 sol used for mesoporous film was synthesized using the following preparation. Triblock copolymer F127 as a template was dissolved in a mixed solution of ethanol, HCl and H_2O. After stirring for 2 h, TEOS was added to the above mixed solution. The final sol, with the molar ratio of TEOS: F127: ethanol: HCl: H_2O=1: x: 30: 0.02: 7, was stirred for 12 h and aged for a week at room temperature. The molar ratio of TEOS and F127 (x) were 0.0090, 0.0057, 0.0049, 0.0042 and 0.003, and the obtained mesoporous SiO_2 film were defined as S90, S57, S49, S42 and S30, respectively.



Scheme 1. The preparation procedure of mesoporous SiO_2/VO_2 film.

Mesoporous SiO_2/VO_2 film was synthesized by dip-coating the SiO_2 sol on the VO_2 film. The as-prepared coating was dried at 80 °C for 1 h in an oven and then calcined at 280 °C for 30 min to remove the surfactant. The final obtained double layer coatings were defined as VS90, VS57, VS49, VS42 and VS30. The preparation procedure is exhibited in Scheme 1.

2.4. Characterizations

Crystalline phase of film was identified by Raman spectra and grazing incidence X-ray diffraction (GIXRD). The Raman spectra were recorded on a Horiba LabRAM HR800 spectrometer using 514 nm argon ion laser. GIXRD patterns were measured at BL14B1 beamline of Shanghai Synchrotron Radiation Facility (SSRF) and 1W1A beamline of Beijing Synchrotron Radiation Facility (BSRF). The ordered mesostructure in film was investigated by 2D Grazing Incidence Small-angle X-ray Scattering (GISAXS) experiments, which was performed at BL16B1 beamline of SSRF in China. The morphology of VO_2 nanoparticles was characterized by transmission electron microscope (TEM, JEM-2100F). The pore structure of the top-layer mesoporous silica film was observed on TEM. The cross-sectional morphology of film was taken on a scanning electron microscope (SEM, JSM-7001F, JEOL). The films were coated on a silicon wafer prior to SEM imaging. The surface morphology of film was measured using an atomic-force microscopy (AFM, XE-100, PSIA). The depth-profiles of V, Si and O elements in coating were measured on a time of flight secondary ion mass spectrometry (TOF-SIMS, TOF. SIMS 5–100). The nitrogen ad/desorption experiment was carried out at −196 °C on an ASAP 2020 instrument. The surface area was measured by Brunauer-Emmett-Teller formalism and the pore size distribution was calculated using a Barrett-Joyner-Halenda (BJH) model for the adsorption branch isotherm. The refractive index and physical thickness of SiO_2 films were measured by using a SE 850 spectroscopic ellipsometer at 70° incidence, with a relative measurement error of about 1%. The thermochromic switching performance of film was monitored using a UV–Vis–NIR spectrophotometer (UV-3150, Shimadzu) from 300 nm to 2500 nm equipped with a homemade heating unit. Thermal hysteresis loops were measured by recording the transmittance at a fixed wavelength of 2000 nm at an interval of 5.0 °C.