Solar Energy Materials and Solar Cells 176 (2018) 427–434

Contents lists available at ScienceDirect

Solar Energy Materials and Solar Cells

journal homepage: www.elsevier.com/locate/solmat

Facile synthesis of mesoporous VO_2 nanocrystals by a cotton-template method and their enhanced thermochromic properties

Shaowen Wu[a], Shouqin Tian[a,b,*], Baoshun Liu[a], Haizheng Tao[a], Xiujian Zhao[a,*], R.G. Palgrave[b], G. Sankar[b], I.P. Parkin[b]

[a] State Key Laboratory of Silicate Materials for Architectures, Wuhan University of Technology (WUT), No. 122, Luoshi Road, Wuhan 430070, PR China
[b] Department of Chemistry, Materials Chemistry Centre, University College London, 20 Gordon St., London WC1H 0AJ, UK

ARTICLE INFO

Keywords:
VO_2 film
Mesoporous structure
Thermochromic property
Solar modulation ability

ABSTRACT

As a very promising thermochromic material, VO_2 (M/R) (Monoclinic/Rutile) has not been widely applied in smart windows due to its intrinsic low solar modulation (ΔT_{sol}) and low luminous transmission (T_{lum}). To address this issue, porous structures have been introduced into the VO_2 film. Herein, mesoporous VO_2 powders with pore size of about 2–10 nm were synthesized using cotton as template by hydrothermal methods. The pore and crystal size of the synthesized VO_2 powders can be reliably controlled by the hydrothermal temperature. The mesoporous VO_2 powders were mixed with PVP to prepare the VO_2-based nanocomposite films by spin coating. The VO_2-based films show a better performance between ΔT_{sol} and T_{lum} than that appeared in previous reports. Especially, a larger pore size could lead to a higher visible transmittance and a larger crystal size would facilitate the enhancement in the solar modulation. In this sense, the VO_2-based film obtained at the hydrothermal temperature of 180 °C exhibits an outstanding thermochromic performance with ΔT_{sol} of 12.9% and T_{lum} up to 56.0% due to a larger crystal size and pore size. Therefore, this synthetic route shows a potential method for the application of mesoporous VO_2 powders for solar control coatings.

1. Introduction

Monoclinic/rutile (M/R)-phase vanadium dioxide (VO_2) undergoes a fully reversible metal-semiconductor transition (MST) at a critical temperature (T_c) of *ca.* 68 °C [1]. This phase transition results in dramatic changes in the optical and electrical properties [2–5]. Below the T_c, VO_2 displays monoclinic crystal structure, which is transparent to near-infrared light due to semiconducting property. Above the T_c, VO_2 displays the rutile crystal structure and is highly reflective to near infrared light while maintaining visible-light transparency due to semimetallic property. This property could make VO_2 a promising material for smart windows [6–9]. However, thin films of VO_2 suffer from poor visible light transmission due to strong inner-band absorptions for both the metallic and semiconducting states [1,6]. In addition, the low solar modulation (ΔT_{sol}) of VO_2 also limits its application [1]. To date, a number of chemical and physical approaches have been employed to improve luminous transmission while maintaining high solar modulation [10–31], including film thickness optimization [32], doping [21–23,33,34], multilayer-stack design [27,28,35], introducing pores [28,36,37] and the formation of composite films [16,18,23,25,30,31,38]. Optical calculations suggest that VO_2 nanoparticles dispersed in a dielectric host are more advantageous than VO_2 continuous thin solid films in smart window applications [39] because they can offer much higher luminous transmission (T_{lum}) and enhanced ΔT_{sol}. Liu et al. [40] prepared the composite films with VO_2 powders dispersed in Si-Al composite sol. The T_{lum} and ΔT_{sol} of these composite film reached 61% and 12%, respectively. Gao et al. [30,41] prepared composite films with VO_2@SiO_2 powders dispersed in aqueous solution containing polyurethane (PU). In this study, it is shown that the visible transparence and solar modulation ability of the VO_2 films can be enhanced by the addition of the PU resulting in a composite. Therefore, VO_2 nanoparticles distributed in another dielectric matrix can offer a novel perspective to achieve high values for T_{lum} and ΔT_{sol}.

Inspired by this concept, highly porous VO_2(M) films have been synthesized. Xie et al. prepared a periodic porous thermochromic VO_2(M) film [37]. The two-dimensional periodic porous VO_2(M) film exhibited high T_{lum} (81% maximum). However, the solar modulation ability was only 7.9% due to the large pore size (~ 200 nm). Kang et al. [39] employed polymer-assisted deposition technique to obtain a nanoporous film with an average pore size of ~ 28 nm, which exhibited a high ΔT_{sol} of 14.1%. The value of T_{lum}, however, was only 41% probably

* Corresponding authors.
E-mail addresses: tiansq@whut.edu.cn (S. Tian), opluse@whut.edu.cn (X. Zhao).

http://dx.doi.org/10.1016/j.solmat.2017.11.001
Received 14 August 2017; Received in revised form 29 October 2017; Accepted 1 November 2017
Available online 08 November 2017
0927-0248/

because of the small pores. In this sense, it is a great challenge to control the pore size in the VO_2 film to obtain a good balance between visible transparency and solar modulation. Especially, most works are focused on the pore size between VO_2 nanoparticles in the film [28,36,37]. However, the effect of pore size in the VO_2 nanocrystals on the thermochromic properties of films based on the VO_2 nanocrystals has not been reported so far, to our knowledge. Therefore, it is of great importance to investigate the effect of pore size in the VO_2 nanocrystals on the thermochromic properties of VO_2 films consisted of nanocrystals.

In this work, porous VO_2 nanocrystals with 2–10 nm in pore size have been prepared by a facile hydrothermal method using cotton as a template. A post heat treatment under ammonia gas produced from ammonium bicarbonate (NH_4HCO_4) yields porous VO_2 powders. The crystallinity and pore size of the VO_2 nanocrystals appears to be controlled through the hydrothermal reaction temperature. Spin coated thin films from the VO_2 powders exhibit a good balance between visible transparence (T_{lum} = 56.0%) and solar modulation ability (ΔT_{sol} = 12.9%) due to the introduction of the porous structure and creating a composite with PVP in the film preparation stage.

2. Experiments and characterization

2.1. Preparation of mesoporous VO_2 nanoparticles

All reagents were purchased from the Sinopharm Chemical Reagent Co., Ltd., and were used without further purification. 0.4 g (0.0022 mol) of vanadium pentoxide (V_2O_5) and 0.832 g (0.0066 mol) of oxalic acid were dissolved in 30 ml of water, and then 30 ml of ethylene glycol was added to increase the viscosity of the solution. As the cotton degrades the acidic solutions, 1 ml of ammonia was added to adjust the pH to *ca.* 7. The solution and 0.3 g of cotton were transferred to a 100 ml Teflon-lined stainless-steel autoclave. The autoclave was maintained at a temperature of 180 °C for 20 h and then cooled to room temperature naturally. The black product was separated and washed with water and ethanol, and then dried in air at 80 °C for 24 h. In order to remove the template to get porous powders, the product was heated, in air, at 400 °C for 1 h, ramp rate *ca.* 3 °C min^{-1}. Finally, 0.2 g of the obtained mesoporous V_2O_5 and 0.1 g of NH_4HCO_4 were placed in a vacuum tube furnace for 450 °C for 30 min. Ammonia gas produced from the decomposition of NH_4HCO_4 reduced V_2O_5 to VO_2. The obtained sample was noted as Sample d. As comparison, samples were also prepared at hydrothermal temperature of 120 °C, 140 °C and 160 °C, which are noted as Sample a, Sample b and Sample c.

2.2. Preparation of films

0.5 g of VO_2 nanoparticles were dispersed in ethanol that contained 0.25 g of PVP by grinding. This solution was then sonicated to ensure goo mixing. After centrifugation at 8000 rpm, a suspension was formed. This suspension was then uniformly cast onto a float glass substrate by spin-coating at the speed of 500 rpm for 10 s and then 1000 rpm for 20 s. Finally the ethanol was removed by drying in an oven at 80 °C for 1 min, yielding VO_2-based composite films.

2.3. Characterization

The crystalline phases of the nanoparticles in the powder form were determined by X-ray diffraction (XRD, D8Advance, CuKα, λ = 0.154178 nm produced under a 3 kW output power). The morphologies of the powders and films were examined by a field emission scanning electron microscopy (SEM, JSM-5610LV, Japan) and field emission transmission electron microscopy (TEM, JEM2100, Japan). Pore size and distribution of the powders were determined by nitrogen adsorption–desorption using a BET analyzer. The compositions of the powders were determined by X-ray photoelectron spectroscopy (XPS). The thermochromic properties of the films from 300 to 2500 nm was measured with ultraviolet–visible–near-infrared spectrophotometer (UV–Vis–NIR, UV-3600) at temperature 20 and 90 °C, respectively.

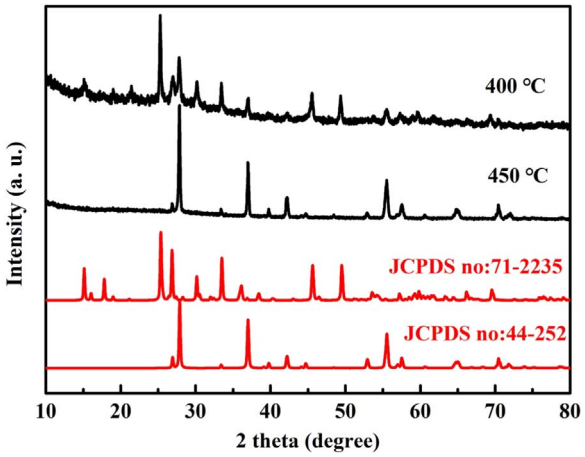

Fig. 1. XRD patterns of Sample d (prepared at the hydrothermal reaction temperature of 180 °C) obtained by annealing V_2O_5 in an ammonia atmosphere at 400 °C and 450 °C for 30 min.

The integrated luminous transmittance (T_{lum}, 380–780 nm) and solar transmittance (T_{sol}, 300 − −500 nm) were obtained from the following equation [42]

$$T_{lum/sol} = \int \varphi_{lum/sol}(\lambda) T(\lambda) d\lambda / \int \varphi_{lum/sol}(\lambda) d\lambda$$

where, T(λ) denotes film transmittance at wavelength λ, $\varphi_{lum}(\lambda)$ is the standard luminous efficiency function for the photopic vision of human eyes, $\varphi_{sol}(\lambda)$ is the solar irradiance spectrum for air mass 1.5 corresponding to the sun standing 37° above the horizon. ΔT_{sol} is attained from ΔT_{sol} = T_{sol} (20 °C) -T_{sol} (90 °C).

3. Results and discussion

3.1. The structure of VO_2 nanocrystals

The XRD patterns of the powder samples obtained by annealing the V_2O_5 in an ammonia atmosphere at 400 °C and 450 °C for 30 min are shown in Fig. 1. In addition to the diffraction peaks corresponding to M-phase VO_2 (JCPDS card no.44-252), additional reflections due to V_6O_{13} (JCPDS card no.71-2235) phase were also seen for samples annealed at 400 °C. Only the M-phase VO_2 was detected when the annealing temperature was raised to 450 °C. This suggests that there is an energy barrier that needs to be overcome to obtain M-phase VO_2.

In order to determine the morphology of the samples synthesized, SEM images of the sample d (produced from hydrothermal reaction at 180 °C and subsequently reduced at 450 °C) are shown in Fig. 2(a), (b). It can be seen from Fig. 2(a) that the samples have a fibrous morphology. The diameter of the VO_2 fibers is estimated to be 5–10 μm. Interestingly, the VO_2 fibers consisted of clusters of small nanoparticles with pores present between the particles is seen in an enlarged image which is shown in Fig. 2(b). Further enlarged TEM images of the same sample shown in Fig. 2(c), show that the samples are clusters of nanoparticles with a diameter *ca.* 60 nm, with mesopores (about several tens of nanometers) present between the nanoparticles. This supports the morphology observed in the SEM images in Fig. 2(b). In Fig. 2(d), the lattice planes are clearly seen, these give an interplanar spacing of d = 0.320 nm corresponding to the (011) plane of monoclinic VO_2. This is consistent with the XRD results. In addition, the clear lattice fringe indicated good crystallinity of the synthesized VO_2.

In order to examine the oxidation states of the vanadium in the synthesized VO_2 powders, XPS measurements were performed and the results are shown in Fig. 3. The full spectra in Fig. 3(a) suggests the presence of oxygen and vanadium in the samples. C1s is used for