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2018

Liu, C., Wang, S., Zhou, Y., Yang, H., Lu, Q., Magdassi, S., ... Long, Y. (2018). Index-tunable anti-reflection coatings : maximizing solar modulation ability for vanadium dioxide-based smart thermochromic glazing. *Journal of Alloys and Compounds*, 7311197-1207.
doi:10.1016/j.jallcom.2017.10.045

<https://hdl.handle.net/10356/88925>

<https://doi.org/10.1016/j.jallcom.2017.10.045>

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Index-tunable Anti-reflection Coatings: Maximizing Solar Modulation Ability for Vanadium Dioxide-based Smart Thermo-chromic Glazing

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Abstract

Vanadium dioxide (VO_2) nanoparticles with reversible semiconductor-metal phase transition holds the tremendous potential as a thermochromic material for the energy-saving smart glazing. However, the trade-off between improving the luminous transmittance (T_{lum}) while sacrificing the solar modulation ability (ΔT_{sol}) hampers its bench-to-market translation. Previous studies of anti-reflection coatings (ARCs) focused primarily on increasing T_{lum} while neglecting ΔT_{sol} , which is a key energy-saving determinant. The intrinsically low ΔT_{sol} ($< 16\%$) is due to the fact that VO_2 has a higher refractive index (RI) from 500 nm to 2200 nm wavelength (λ) below its critical transition temperature (τ_c), which causes excessive reflection at a lower temperature. This study aims to investigate ARCs with tunable RI (1.47 – 1.92 at $\lambda=550$ nm) to improve the antireflection effect at a lower temperature, thereby maximizing ΔT_{sol} for various VO_2 nanosubstrates, e.g. continuous thin films, nanocomposites, and periodic micro-patterning films. We showed that the best performing coatings could maximize ΔT_{sol} (from 15.7% to 18.9%) and increase $T_{\text{lum(avg)}}$ (from 39% to 44%) simultaneously, which surpasses the current bench-mark specifications ever reported for ARC-coated VO_2 smart glazing. In addition, the cytotoxicity analyses evidence that ARCs are feasible to improve the cyto-compatibility of VO_2 nanoparticles-based nanocomposites. The presented RI-tunable ARC, which circumvents the complex materials selection and optical design, not only paves the way for practical applications of VO_2 -based smart windows but also has extensive applications in the field of solar cells, optical lenses, smart display, etc.

1. Introduction

Man-made buildings is a major contributor to climate change and accounts for as much as 30% of the total global greenhouse gas emissions and consume 40% of all energy [1]. The lion's share of the emissions could be attributed to the combustion of fossil fuel to regulate the ambient temperature within the buildings. vanadium dioxide (VO_2) nanoparticles based thermochromic glazing may provide an energy-saving solution via “smart-modulation” of light and heat entering a building, thereby eliminating the need for external energy sources to control the interior temperature. Based on highly reversible semiconductor-metal phase transition at a critical transition temperature (τ_c) of 341 K (68 °C) [2], VO_2 could inhibit energy in-flow from infrared (IR) region when it behaves as metallic materials [VO_2 rutile phase, VO_2 (R)] at high temperature, while the semiconductor state [VO_2 monoclinic phase, VO_2 (M)] at low temperature transmits IR to warm up indoor space when the ambient temperature is lower than τ_c [2, 3]. The luminous transmittance (T_{lum} , from 380 nm to 780 nm) remains unchanged at both cold and hot stages.

Although τ_c could be reduced to near room temperature by doping with metal ions of high valence [4-8], two significant shortcomings of VO_2 thermochromic materials that obstruct the way towards possible commercialization are low T_{lum} [9] and insufficient solar modulation ability (ΔT_{sol}) [10]. Different approaches such as doping with large radius rare earth metal ions [11] and two-dimensional nanostructures [12, 13] have been investigated with the focus mainly on increasing T_{lum} , whereas ΔT_{sol} is hard to control since it is related to solar response difference of two states. For instance, the average luminous transmittance [$T_{\text{lum(avg)}}$, the average of T_{lum} at 20° ($T_{\text{lum}(20^\circ\text{C})}$) and T_{lum} at 90° ($T_{\text{lum}(90^\circ\text{C})}$)] increases from 34.8% to 38.6% with F-doping [14] and from 41% to 51% with Mg-doping [15] but not jeopardizing IR switching ability. Nanogirded film is a reliable method to tune both T_{lum} and ΔT_{sol} due to the combination effect between nano-sized open and patterned VO_2 grid. We designed the VO_2 nanogrided film with enhanced $T_{\text{lum}}=79\%$ and $\Delta T_{\text{sol}}=14\%$ [16]. Later, Lu et al. fabricated the periodic micro-patterned VO_2 thin film based on our concept via mesh printing method[17]. Meanwhile,

nanoporous film structure could achieve a good thermochromic combination of $T_{\text{lum(avg)}}=42\%$ and $\Delta T_{\text{sol}}=14.1\%$ as a result of the insertion of air phase in the form of pores [18]. The organic hydrogel system showed a superior ΔT_{sol} of 59% [19] but it suffered from the the lack of durability and translucent state at high temperature. In 1987, the studies reported by S. M. Babulanam *et al.* proposed the idea of anti-reflection coating (ARC), which facilitates the increment of T_{lum} from 39% to 45% by applying a single layer of SiO_2 , but with the almost complete loss of ΔT_{sol} [20]. Recently, various ARC materials have been laminated with the basis of continuous VO_2 thin films to acquire high $T_{\text{lum(avg)}}$ and ΔT_{sol} , as summarized in Table 1. TiO_2 is used as a multifunctional ARC topcoat in the double-layered film structure by Jin *et al.*, which showed both increments in T_{lum} and ΔT_{sol} [21]. ZrO_2 [22] and CeO_2 [23] have also been used as ARCs. However, the depositions of those overcoats are energy-consuming and expensive. Low-cost sol-gel methods have been adopted to fabricate SiO_2 and TiO_2 overcoats [24], but it only works on continuous VO_2 films. Moreover, the multilayered ARCs have been experimented with TiO_2 and SiO_x [19–21][25–27], with the drawbacks of costly deposition methods, intricate optical design and non-guaranteed enhancements of both T_{lum} and ΔT_{sol} . It is worth noting that compared with other ARCs, the Si-Al gel [28] shows *ca.* 29% improvements of T% contrast (@ $\lambda=2000$ nm) as well as the significant increments of both T_{lum} and ΔT_{sol} .

As summarized in Table 1, only RI-fixed ARCs on the continuous VO_2 films were investigated previously, and none of the studies focused on enhancing ΔT_{sol} to tackle the intrinsic physical limitation of VO_2 , as it has undesirable higher reflectance at lower temperature in the wavelength (λ) from 500 nm to 2200 nm [29]. Here we propose a facile way to produce RI-tunable ARCs by just changing the annealing temperature and the compositions of sol-gel based overcoats to preferentially offer more anti-reflection to the cold state as compared with the hot state (as illustrated in Scheme 1). The results finally lead to the increase of ΔT_{sol} since ΔT_{sol} is the difference between solar transmittance at low temperature and high temperature.

Table 1Recent studies of ARCs on the continuous VO₂ thin film

Double-layered films with ARC	Fabrication techniques		$T_{\text{lum(avg)}} (\%)$		$\Delta T_{\text{sol}} (\%)$		$T\% \text{ contrast}^* @ \lambda = 2000 \text{ nm} (\%)$	
	VO ₂ film	ARC	w/o ARC	w/ ARC	w/o ARC	w/ ARC	w/o ARC	w/ ARC
TiO ₂ /VO ₂ (2002)[21]	RF-sputtering	RF-sputtering	32	47 ↑	4.4	7.0 ↑	53	39 ↓
ZrO ₂ /VO ₂ (2004)[22]	RF-sputtering	RF-sputtering	32	51 ↑	-	-	45	39 ↓
SiO ₂ /VO ₂ (2011)[24]	Sol-gel and thermal-annealing	Sol-gel	40	51 ↑	5.9	7.2 ↑	54	48 ↓
TiO ₂ /VO ₂ (2011)[24]	Sol-gel and thermal-annealing	Sol-gel	42	47 ↑	13.2	15.1 ↑	56	46 ↓
Si-Al/VO ₂ (2013)[28]	Sol-gel and thermal-annealing	Sol-gel	44	48 ↑	6.0	7.7 ↑	<u>14</u>	<u>18 ↑</u>
CeO ₂ /VO ₂ (2013)[23]	Pulse Laser Deposition	Pulse Laser Deposition	30	31 ↑	11.6	15.3 ↑	48	46 ↓

Multi-layered films with ARCs	Fabrication techniques		$T_{lum(avg)} (%)$		$\Delta T_{sol} (%)$		T% contrast* @ $\lambda = 2000$ nm (%)	
	VO ₂ film	ARC	w/o ARC	w/ ARC	w/o ARC	w/ ARC	w/o ARC	w/ ARC
TiO ₂ /VO ₂ /TiO ₂ (2003)[25]	RF-sputtering	RF-sputtering	31	56 ↑	3.9	2.9 ↓	51	36 ↓
α -SiO _x /VO ₂ / α -SiO _x where $x = 0.3$ (2008)[26]	RF-sputtering	RF-sputtering	31	35 ↑	6.5	4.5 ↓	43	20 ↓
TiO ₂ /VO ₂ /TiO ₂ (2009)[27]	Reactive DC Magnetron Sputtering	Reactive DC Magnetron Sputtering	44	60 ↑	4.5	6.0 ↑	47	26 ↓
TiO ₂ /VO ₂ /TiO ₂ / VO ₂ /TiO ₂ (2009)[27]	Reactive DC Magnetron Sputtering	Reactive DC Magnetron Sputtering	41	44 ↑	6.7	12.1 ↑	39	38 ↓

Note: *T% contrast indicates the absolute transmittance difference between low temperature (20 °C) and high temperature (90 °C) at a specific wavelength.

Moreover, the RI tunability of the ARCs can be extensively applied to not only the VO₂ continuous thin films but also to the nanocomposites and micro-patterned VO₂ films to enhance the nanothermochromism effect [30]. Furthermore, VO₂ is not the most thermodynamic stable phase in the air [28, 31-33]. Therefore, an anti-oxidation overcoat is essential, especially for nanocomposites containing high surface energy nanoparticles dispersed in the transparent matrix.

Furthermore, when applied as window coatings, it is very likely that the nanomaterials may come into contact with the human skin and may potentially [34] result in undesired nanotoxicological effects due to the cell-nanomaterials interaction [34-36]. For instance, cellular internalization of engineered nanoparticles can induce autophagy in primary human keratinocytes [37], impair cell sheet migration [34], augment cellular metabolism [38] and even disrupt endothelial barrier function [39]. Therefore, it is imperative to consider the well-documented adverse effects that are associated to the use of the VO₂ nanoparticle-based smart windows with ARCs.

Scheme 1 Schematic illustrating the concept of the RI-tunable ARC applied on the VO₂ substrate, which could preferentially offer better anti-reflection effect at low temperature as compared with that at high temperature.

2. Experimental

2.1. Sample preparation

Two different types of ARC solutions, Si-Al based and TEOS based, were prepared *via* sol-gel methods. The concentrated Si-Al based solution was synthesized as described in our previous work [28]. For having prepared TEOS based solution, a tetraethyl orthosilicate (TEOS, Sigma Aldrich) precursor was firstly diluted to 30 wt% TEOS in the solvent of mixed ethanol (95% analytical grade, Sigma Aldrich) and deionized (DI, 18.2 M Ω) water according to the molar ratio of ethanol: DI water = 4:1. Hydrochloric acid (HCl, 37%, Sigma Aldrich) was added to the mixture dropwise until pH<2. The solution was stirred for 2 h and followed by aging for 24 h before dip coating on VO₂ continuous thin films. Moreover, for applying ARCs on the VO₂ micro-patterning coatings or nanocomposites, the concentrated Si-Al solution was further diluted to 50% of its original concentration by using ethanol (99% analytical grade, Sigma Aldrich), while 30 wt% TEOS solution was diluted to 22 wt% TEOS by adding the corresponding amount of ethanol and DI water. All diluted solutions were magnetically stirred for at least 6h to form homogeneous suspensions.

Continuous VO₂ thin films were deposited on quartz substrates as illustrated in the relevant paper [33]. A 0.5 wt% VO₂/Si-Al gel mixture was prepared as reported [40], which serves as the structural support to the VO₂ micro-patterning films upon drying. Moreover, for nanocomposites samples, VO₂ nanoparticles (Jingcheng Chemicals Co., Ltd, China) were uniformly dispersed in DI water after surface modification by poly(vinyl pyrrolidone) (PVP K30), bar coated on washed soda-lime microscopic glass slides (BK7), and then dried at 50 °C for 15 min to form nanocomposite glass coatings. ARCs were dip coated on the top of bare VO₂ continuous thin films, micro-patterning films and nanocomposites at the withdrawing rate of 50-100 mm/min and dried in air at room temperature for at least 24 h before heating to evaporate unnecessary solvents. All the dip-coated ARC layers at the back side of VO₂ substrates were removed using ethanol. Different temperatures (100-300 °C) were employed in the following

ARC heating process with the same ramping rates of 1 °C/min to obtain the fine quality of overcoats.

For implementing the cytotoxicity analyses, all the polymeric and/or VO₂ samples were first deposited on glass slides with sample amount corresponding to 0.5 mg of VO₂ nanoparticles for experimental group. The sample bound glass slides were then mounted onto 3D-printed sample holders for further analysis. Human dermal fibroblasts were seeded at a density of 10 K/cm² using a 12 well plate culture plate in high glucose DMEM (Hyclone, SH30243.01) supplement with 10% FBS (PAA Laboratories, A15-151) and 1% Penicillin-Streptomycin (Hyclone, SV30010). After overnight culturing, the cells were washed thoroughly 3 times with ice cold PBS to remove unattached cells and replenished with 1ml of fresh cell culture medium. The sample holders were then inserted into 12-well plates, making sure that samples deposited on the glass slides were submerged in the cell culture medium (as demonstrated in Fig. 9B). After 24 h of continuous exposure to the ARC specimens, the sample holders were removed and the cells were collected for cell viability test. For cells collection, cell culture medium was first collected, together with PBS for cell washing to retrieve floating cells. After trypsinization to collect attached cells, both floating cells and attached cells were pooled for cell viability test. For cell viability test, cells were centrifuged down and stained with 1:1000 diluted propidium iodide (PI, Thermo, H3566) in PBS for 5 mins in dark. Propidium iodide (PI) is a red-fluorescent nuclear dye targeting dead cells in a population because it is not permeant to live cells. Cell viability were determined using the Tali® Image-Based Cytometer (Thermo, T10796). Normal cultured fibroblasts serve as untreated controls. Cells treated with 0.2% Triton X-100 (Biorad, 1610407), in PBS for 5mins before PI staining serves as positive controls. Cell viabilities were calculated using the following Eq. 1:

$$Cell\ viability = \frac{N_0 - N_1}{N_0} * 100\% \quad (1)$$

where N₀ denotes the total number of cells and N₁ indicates the number of cells stained positive for PI. A cell viability index of 100% signifies all cells are alive. Cell viability index of all

groups were further divided by that of untreated control to get normalized cell viabilities. The experiment was replicated 3 times for each group.

2.2. Characterization

The crystalline phases of VO₂ commercial nanopowder were determined by X-ray diffraction (XRD) using the D8 Advance diffractometer (Bruker AXS, USA). The dimensions of nanoparticles, as well as the homogeneity of nanocomposites, were characterized by extremely high-resolution scanning electron microscopy (XHR-SEM, Magellan, FEI company, USA). The Nano-ZS analyzer (Malvern Instruments, UK) was employed to analyze the size distribution and surface potential of VO₂ nanoparticles, which were dispersed in pure DI water. The optical transmittance in the range of 250-2500 nm was measured using a UV-Visible-Near IR spectrophotometer (UV-Vis-NIR, Lambda 950, Perkin Elmer, USA) equipped with a Linkam PE120 system Peltier heating and cooling stage.

The T_{lum} , luminous reflectance (R_{lum}), IR transmittance (T_{IR}), IR reflectance (R_{IR}), as well as solar transmittance (T_{sol}) and solar reflectance (R_{sol}) were calculated based on the measured transmittance and reflectance spectra using the following expression as Eq. 2 and Eq. 3, while the corresponding modulation abilities of transmitted and reflected energy in the different spectrum regions were characterized as ΔT_{lum} , ΔT_{IR} , ΔT_{sol} and ΔR_{lum} , ΔR_{IR} , ΔR_{sol} as indicated in Eq. 4 and Eq. 5.

$$T_{lum/IR/sol} = \frac{\int \phi_{lum/IR/sol}(\lambda)T(\lambda)d\lambda}{\int \phi_{lum/IR/sol}(\lambda)d\lambda} \quad (2)$$

$$R_{lum/IR/sol} = \frac{\int \phi_{lum/IR/sol}(\lambda)R(\lambda)d\lambda}{\int \phi_{lum/IR/sol}(\lambda)d\lambda} \quad (3)$$

$$\Delta T_{lum/IR/sol} = T_{lum/IR/sol(low)} - T_{lum/IR/sol(high)} \quad (4)$$

$$\Delta R_{lum/IR/sol} = R_{lum/IR/sol(low)} - R_{lum/IR/sol(high)} \quad (5)$$

where $T_{lum/IR/sol}$ and $R_{lum/IR/sol}$ represent the measured spectral transmittance and reflectance for luminous, IR and whole solar spectrum range, respectively. Φ_{lum} is the standard luminous

efficiency function of photonic vision [41] for λ in the range of 380-780 nm, and $\Phi_{\text{IR/sol}}$ is the IR/solar irradiance spectrum distribution for air mass 1.5 [42] and it represents an overall yearly average for mid-latitudes including diffuse light from the ground and sky on a south facing surface tilted 37° from horizontal. The λ ranges used for $T_{\text{IR/sol}}$ or $R_{\text{IR/sol}}$ calculations are 780-2500 nm and 250-2500 nm, respectively. $\Delta T_{\text{lum/IR/sol}}$ or $\Delta R_{\text{lum/IR/sol}}$ are the difference of integrated spectral transmittance or reflectance for luminous, IR and solar spectrum, respectively. $T_{\text{lum/IR/sol(low)}}$ and $R_{\text{lum/IR/sol(low)}}$ is the luminous/IR/solar transmittance and reflectance that measured at low temperature (20 °C). Similarly, $T_{\text{lum/IR/sol(high)}}$ and $R_{\text{lum/IR/sol(high)}}$ are the transmittance and reflectance that measured at high temperature (90 °C).

The transmittance of single layer ARCs deposited on quartz slides was measured for the calculations of refractive index of ARC (n_{ARC}), which is based on the multi-layer optical theory with Swanepoel method [43] and transfer-matrix method [44, 45]. The optical constants of quartz substrate were extracted from the literature [46], where refractive index of substrate (n_{sub}) is a series of values varied with λ and the extinction coefficient, k_{sub} , is approximately equal to zero throughout the spectrum (250-2500 nm).

3. Results and discussion

3.1. The concept of RI-tunable sol-gel based ARCs

Fig. 1 (A) Spectral RI of continuous VO_2 thin films (from Ref. [29]) at both low (solid blue line) and high (solid red line) temperature with the corresponding square root values (dashed lines) are shown in

the λ range of 250-2500 nm. The green shaded area indicates the RI envelope formed by refractive index of bare VO₂ at 20 °C ($n_{VO_2 (low)}$) and refractive index of bare VO₂ at 90 °C ($n_{VO_2 (high)}$). The yellow-colored area denotes spectral solar irradiance. (B) Thermochromic properties at different temperature, which are calculated from the measured transmittance and reflectance of the diluted Si-Al ARC coated VO₂/Si-Al nanocomposites; (C) RI (at $\lambda=550$ nm) of concentrated Si-Al and 30 wt% TEOS-based ARCs change as a function of ARC annealing temperature. The red dashed segment indicates the abrupt increment of n_{ARC} due to the degradation of polymer components in the Si-Al ARCs.

As shown in Fig. 1A, the spectral refractive indices (RI) of continuous VO₂ thin films at both low and high temperature [29] form an envelope in the λ range of 500-2000 nm. The low temperature VO₂ (M) phase has higher RI than the high temperature VO₂ (R) phase (*i.e.*, $n_{VO_2 (low)} \gg n_{VO_2 (high)}$) in the envelope, leading to more solar energy reflection at the cold state as compared with the hot state. High reflection depresses $T_{lum(low)}$ as well as $T_{sol(low)}$ which causes the intrinsic issue of low ΔT_{sol} in VO₂ (refer to Eq. 4). To address such intrinsic issues, an ARC can be carefully designed to suppress more reflection below τ_c than that above τ_c , which induces a higher ΔT_{lum} and thereby results in larger ΔT_{sol} (*i.e.*, widening the T% contrast between low and high temperature). This ARC- ΔT_{sol} relationship can be evidenced practically by applying a diluted Si-Al based ARC on the VO₂/Si-Al nanocomposites. As demonstrated in Fig. 1B, obviously, the ARC decreases R_{lum} from *ca.* 13% to *ca.* 6% and meanwhile ΔT_{lum} and ΔT_{sol} are enhanced due to the reduction of ΔR_{sol} (*i.e.*, the decrease of R_{sol} at low temperature > the decrease of R_{sol} at high temperature).

Based on Fresnel equation, high reflection may be theoretically reduced to minimum by adopting a specific ARC layer on top of the VO₂ substrates, if n_{ARC} could be tuned to the vicinity of $\sqrt{n_{VO_2(high)}}$ [47] (in Fig. 1A: dashed purple line for $\sqrt{n_{VO_2(low)}}$ and dotted pink line for $\sqrt{n_{VO_2(high)}}$). The concept of RI-tunable ARCs can be implemented by low temperature heating of Si-Al or TEOS sol-gel based overcoats. With the consideration of spectral solar irradiance, the RI of the ARCs obtained at the different annealing temperature are compared at $\lambda=550$ nm in this study since the peak of solar irradiance is located at $\lambda \approx 550$ nm. Fig. 1C

reports the proportional relationship between n_{ARC} and annealing temperature. Since most of aqueous solvents evaporated slowly with increasing heating temperature of 1 °C/min, a linear increment of Si-Al based n_{ARC} can be observed from 100 °C to 250 °C, while the abrupt change of RI happens at 300 °C due to the degradation of polymer components in the Si-Al ARCs. The densification process of TEOS sol-gel coatings is gradually completed from 100 °C to 200 °C and the TEOS-based n_{ARC} is stabilized at *ca.* 1.9 from 250 °C onwards. The Si-Al and TEOS-based ARCs are able to provide wide RI availability from 1.47 to 1.92, which effectively circumvent the ARC materials selection and exhibit the potential to satisfy different RI requirements for a wide range of optical applications.

As evidenced in Fig. 2A, by altering the RI of the sol-gel based ARCs close to $\sqrt{n_{\text{VO}_2(\text{low})}}$, more anti-reflection could occur at cold stage compared with hot stage, and consequently a maximized ΔT_{sol} could be obtained. As n_{ARC} (*ca.* 1.68) is approximately identical to the $\sqrt{n_{\text{VO}_2(\text{low})}}$ (*ca.* 1.69) at $\lambda=550$ nm, ΔT_{sol} of VO₂ continuous films is boosted from 4.3% to 6.3% with the increment of *ca.* 47%. The n_{ARC} of *ca.* 1.57 and *ca.* 1.81 are neighboring the value of 1.69 and hence they also enhance ΔT_{sol} significantly but with smaller marginal increments. The insufficient enhancements of ΔT_{sol} are obtained by using 30 wt% TEOS ARCs, because the overcoats offer low RI-tuning range (from 1.47 to 1.57) which is inadequate to meet the requirement for improving thermochromic properties of the VO₂ substrate, but it might be suitable for other RI requirements considering low n_{ARC} . The typical transmittance spectra of VO₂ with or without depositing the concentrated Si-Al based ARC (Fig. 2B) reveals the noticeable increasing of T_{lum} [48].

Fig. 2 (A) Different n_{ARC} of either TEOS-based (black plot) or Si-Al based (blue plot) ARCs offer various influences of ΔT_{sol} . The original ΔT_{sol} of bare VO_2 continuous thin films for coating with TEOS-based ARCs (left black-dashed line) is 4.6%, while that of bare VO_2 for coating with Si-Al based ARCs (right blue-dashed line) is 4.3%. Dash-dotted green line denotes to $\sqrt{n_{\text{VO}_2(\text{low})}} = 1.69$ at $\lambda=550\text{nm}$ (calculated from Ref. 23). (B) The transmittance spectra of continuous VO_2 thin films with or without Si-Al based ARCs.

3.2. *VO₂ nanocomposites substrate with diluted sol-gel based ARCs*

3.2.1. *Characterization of VO₂ nanoparticles and nanocomposites*

The XRD patterns of commercial VO₂ nanopowder (Fig. 3A) reveal the characteristic crystallographic diffraction peaks of monoclinic phase VO₂ crystals (M1, PDF number 01-082-0661) with Scherrer crystallite size of 19.39 nm, which implies good formation of crystal lattice that is one of the criteria for acquiring outstanding nano-thermochromism [30]. The high XRD peak intensity suggests the high degree of crystallinity of VO₂ nanoparticles, which plays an important role in the phase transition properties of VO₂. According to low magnification XHR-SEM image (Fig. 3B) and dynamic light scattering (DLS) measurement (the inset of Fig. 3B), VO₂ nanoparticles present a wide size distribution (by volume) from 10 nm to 500 nm when they are dispersed in pure DI water (1 wt%) without stabilizer. This may due to the particle agglomeration when the surface potential of *ca.* -39.7 mV is not enough to restrict the combination of neighboring nanoparticles. The average particle size is approximately 100 nm with two peaks appearing at *ca.* 20 nm and *ca.* 80 nm, which could be correlated to the averaged lateral and longitudinal dimensions of short rod-like nanoparticles respectively as displayed in Fig. 3C. Meanwhile, high magnification XHR-SEM image (Fig. 3C) shows VO₂ nanoparticles mixing with 5-7 nm width VO₂ nanofibers, which may contribute to the small size part in the DLS plot (the inset of Fig. 3B). With the stabilizer of PVP K30, nanoparticles are uniformly dispersed and encapsulated in the polymer matrix (semi-transparent substances appeared in Fig. 3D).

Fig. 3 (A) XRD patterns of commercial VO₂ nanopowder (black) are associated with typical crystallographic peaks of VO₂ monoclinic phase (red). XHR-SEM images show: (B) VO₂ nanopowder. The inset is particle size distribution by volume according to dynamic light scattering measurement; (C) Morphologies of VO₂ nanoparticles and nanofibers; (D) 1 wt% VO₂ nanoparticles well-dispersed in the PVP K30 polymer matrix.

3.2.2. The effects of compositions on ARC performance

Fig. 4 Concentrations of Si-Al (A) and TEOS (B) based ARCs influence on thermochromic properties of VO₂ nanocomposites.

As illustrated in Fig. 4A, the concentrated Si-Al based ARCs (red bars) lead to detrimental effects on both ΔT_{IR} and ΔT_{sol} with negligible marginal increments of $T_{lum(avg)}$ and ΔT_{lum} . Similarly, if maintaining the same concentration of TEOS based ARCs (yellow bars) as used for continuous thin films, the anti-reflection effect only participates in increasing $T_{lum(avg)}$. This phenomenon implies that more anti-reflection is given to the VO₂(R) state at a higher

temperature (*e.g.* 90 °C) instead of the VO₂ (M) state at a lower temperature (*e.g.* 20 °C), thereby decreasing all energy modulation abilities including ΔT_{lum} , ΔT_{IR} as well as ΔT_{sol} (see Fig. 4B). This may be due to the fact that the nanocomposite VO₂ coatings have overall lower RI compared with continuous VO₂ films since the polymer matrix have lower RI. Therefore, the diluted formulations of sol-gel based ARCs are required to accommodate the reduced overall composite RI of the substrate. As shown in the lower part of Fig. 4A and 4B, both diluted Si-Al (green bars) and 22 wt% TEOS ARCs (blue bars) have remarkable anti-reflection effects throughout the solar spectrum (250-2500 nm) and they reveal the strong capabilities to simultaneously enhance $T_{\text{lum(avg)}}$, ΔT_{lum} , ΔT_{IR} and ΔT_{sol} of VO₂ nanocomposites.

3.2.3. Optimization of nanothermochromic properties and anti-oxidation

Fig. 5 Relationship between thermochromic properties and the increasing heating temperature of diluted Si-Al (A) or 22 wt% TEOS (C) based ARCs; Spectral transmittance of the optimized thermochromic performances VO₂ nanocomposites with the facilitations of diluted Si-Al ARCs (B) heated at 100 °C or 22 wt% TEOS ARCs (D) at RT*

22 wt% TEOS ARCs (D) maintained at room temperature (RT) respectively; The insets of (B) and (D) show the transparency differences before and after applying diluted Si-Al or 22 wt% TEOS ARCs, respectively. Note: * denotes ARCs without heat treatments before UV-Vis-NIR measurements.

As compared with continuous film substrate (Fig. 2A), VO₂ nanoparticles dispersed in the polymer matrix could offer both higher $T_{lum(avg)}$ (38.6% vs. 37.5%) and much larger ΔT_{sol} (15.7% vs. 4.3%) due to the ‘nanothermochromism’ [30]. As shown in Fig. 5A and 5C, the nanothermochromic properties could be further enhanced by tuning the ARC heating temperature to acquire optimized combinations of T_{lum} and ΔT_{sol} . According to Table 2, increasing heating temperature ensures promoting T_{lum} at both low and high temperature, but the downward development of $\Delta T_{lum/IR/sol}$ with increasing temperature is due to larger enhancement of $T_{lum/IR/sol}$ at high temperature as compared with $T_{lum/IR/sol}$ at low temperature (refer to Eq. 3). The maximized nanothermochromic combinations could be obtained at 100 °C ARC heating temperature for the diluted Si-Al encapsulated nanocomposites, while 22 wt% TEOS coated VO₂ shows the optimized results when it is maintained at room temperature without post ARC heat treatment. As displayed in Fig. 5B, Si-Al based ARCs in the dilution form could effectively facilitate the enhancement of spectral transmittance ($T_{lum/IR/sol}$) at low temperature throughout the solar spectra, while the diluted TEOS-based ARCs present the large anti-reflection effects with the most focus on the visible-near IR region (Fig. 5D)

Table 2

Optimization of thermochromic properties for VO₂ nanocomposite smart window applications by using RI-tunable sol-gel based ARCs

VO ₂ Nanocomposite samples			T_{lum} (%)		ΔT_{lum}	ΔT_{IR} (%)	ΔT_{sol}
			20 °C	90 °C	(%)		(%)
Sample C1	w/o ARC		39.9	37.3	2.6	30.8	15.7
(w/ diluted Si-Al ARCs)	w/ ARCs	RT*	45.4	40.8	4.6	36.2	18.9
		100°C	46.3	41.4	4.9	36.0	18.9
		150°C	44.5	39.9	4.6	34.8	18.2
		200°C	45.2	41.6	3.6	31.4	16.3
		250°C	47.8	45.3	2.5	26.4	13.4
Sample C2	w/o ARC		47.3	44.9	2.4	27.0	13.6
(w/ 22 wt % TEOS ARCs)	w/ ARCs	RT*	52.7	48.7	4.0	31.4	16.4
		100°C	51.3	47.8	3.5	29.4	15.3
		150°C	52.6	49.2	3.3	28.7	14.8
		200°C	52.1	49.1	3.0	27.5	14.1
		250°C	56.3	54.1	2.2	20.8	10.8

Note: * RT denotes ARCs without heat treatments before UV-Vis-NIR measurements.

Fig. 6 Comparisons of current work with the contemporary researches of ARC-coated thermochromic VO₂ thin films (round [15–18,22] and square [19–21]) in terms of ΔT_{sol} and T_{lum} .

As tabulated in Table 2, the highest ΔT_{sol} of *ca.* 18.9% can be achieved with the optimized T_{lum} of 46.3% at low temperature and 41.4% at high temperature by the application of diluted Si-Al based ARCs and heating at 100°C before UV-Vis-NIR measurements. The best combination of thermochromic properties generated by 22 wt% TEOS based ARCs show ΔT_{sol} =16.4% with maximized $T_{\text{lum (low)}}$ =52.7% in the VO₂(M) state and $T_{\text{lum (high)}}$ =48.7% at the VO₂(R) phase. The superior nanothermochromic results obtained by utilizing RI-tunable sol-gel based ARCs have surpassed all the contemporary ARCs investigations on the basis of VO₂-based thin films (red round spots [22-24, 28, 49] and yellow squares [25-27] in Fig. 6. It is also comparable to the recent best reported results ($T_{\text{lum(avg)}}$ =42.8% and ΔT_{sol} =22.3%) with fine crystallized VO₂ nanoparticles in the polyurethane matrix [50].

Fig. 7A shows that without ARC, after heating at 120 °C for 15 min, the VO₂ nanocomposites entirely losses the thermochromic effects and this instability of VO₂ limits its smart window applications. The XRD patterns (Fig. 7B) illustrate that the peak intensity of VO₂ (M) phase is obviously decreased after the heat treatment of bare nanocomposites, which implies poor crystallinity of VO₂ composites due to oxidation without the thermal-protection of RI-tunable ARCs and therefore explains the vanish of thermochromism in Fig 7A. The ARCs can provide anti-oxidation encapsulation for VO₂, especially for the nanoparticles with high surface energy embedded in a composite form as there is no phase change with ARC coated samples which were annealed under same condition (The XRD are not shown here).

Fig. 7 (A) Transmittance spectra and (B) XRD patterns of the bare VO₂ nanocomposites before and after heat treatments.

3.3. Extensive application of diluted Si-Al ARCs on micro-patterned VO₂ films

Fig. 8A demonstrates the effective anti-reflection brought by the diluted Si-Al based ARCs, which is coated on top of micro-patterned VO₂ substrates (Fig. 8C and 8D). It is worth noticing that, prior to heating the ARCs (*i.e.*, “w/ ARC-RT” in Fig. 8A), %R (20°C) is lower than %R

(90 °C) in the UV-visible region, leading to $\Delta R_{\text{lum}} = -0.5\%$, while these 2 factors flip over and cause the increase of ΔR_{lum} (from -0.5% to 0.6%) and ΔR_{sol} (from -0.1% to 0.8%) after slowly heating the ARCs to 100°C (refer to “w/ ARC- 100°C ” in Fig. 8A). As mentioned in Section 1, lower ΔR_{sol} ultimately leads to higher ΔT_{sol} . The diluted Si-Al ARCs without heating (see “w/ ARC-RT” in Fig. 8B) significantly boost ΔT_{sol} from 3.6% to 10.5% with a tremendous enhancement of T_{lum} about 2.5 times ($T_{\text{lum (low)}}$ from 16.8% to 44.4% and $T_{\text{lum (high)}}$ from 16.7% to 42.1%). Therefore, these results evidences that RI-tunable sol-gel based ARCs can be extensively applied to solve the intrinsic problems of VO_2 thereby amplifying the thermochromic performances of various VO_2 substrates.

Fig. 8 Spectral reflectance (A) and transmittance (B) of micro-patterning VO_2 films without (“w/o ARC”) or with the diluted Si-Al based ARCs before (“w/ ARC-RT”) and after (“w/ ARC- 100°C ”) heat treatment. The optical microscope images of micro-patterning VO_2 films without (C) and with (D) Si-Al based ARCs.

3.4. Cytotoxicity of VO₂ nanoparticles-based nanocomposites with ARCs

With the smart window applications in mind, we have prepared three different variants of coatings to represent different kinds VO₂ nanoparticles exposure scenarios (Fig. 9A). Thereafter, the prepared coatings were mounted onto our in-house 3D-printed acrylate based sample holder prior to their exposure to a monolayer of human dermal fibroblasts (Fig. 9B). The in-vitro experiment was designed to examine the cytotoxic potential of the coatings. Shown in Fig. 9C is the normalized cell viability of the cells that were exposed to the different experimental groups for 24 hours. Cell death (60%) was observed to be significantly higher for the group that was exposed to the bare VO₂ nanoparticles (refer to the “VO₂ NPs” group in Fig. 9C) compared to the untreated control (without any coatings). This observation is consistent with a recent report demonstrating that direct interaction of the VO₂ nanoparticles with the cells could impair adenosine triphosphate (ATP) synthesis, leading to oxidative stress induced cytotoxicity[51]. In our case, the weak adhesion force between the VO₂ nanoparticles and the glass surface may have led to the sedimentation of VO₂ nanoparticles onto the cell monolayer to facilitate nanoparticles cellular uptake. In stark contrast, cell viability is significantly improved for the VO₂ nanoparticles that were embedded in the polymeric matrix with or without the Si-Al ARCs by approximately 2-fold to a level that is comparable to the untreated control. This could be attributed to the restricted in-solution mobility of the matrix bound VO₂ nanoparticles, thus limiting direct cell-VO₂ nanoparticles interaction. Interestingly, the addition of the Si-Al ARC could further enhance the nanoprotective effects of the VO₂ nanoparticles-based nanocomposites (refer to the “VO₂ NPs+matrix+Si-Al coating” group in Fig. 9C) as evidenced by an increase in cell viability relative to the bare VO₂ nanocomposites (refer to the “VO₂ NPs+ matrix” group in Fig. 9C). Taken together, we demonstrated that our devised Si-Al ARCs are cyto-compatible and that is a feasible strategy to suppress the nanotoxic effects that are inherent to VO₂ nanoparticles.

Fig. 9 Devised Si-Al ARCs are cyto-compatible. (A) Schematic of the coating composition. i) bare VO₂ nanoparticles ii) VO₂ nanoparticles dispersed and encapsulated in polymer matrix and iii) VO₂ nanoparticles dispersed and encapsulated in polymer matrix with another layer of Si-Al ARC are deposited on glass substrate (B) Schematic of sample exposure to cells with the help of 3D-printed sample holder. (C) Normalized cell viability of human dermal fibroblasts exposed to the different variants of VO₂ samples. Untreated samples and cells treated with triton x-100 (0.2% in PBS) serve as negative and positive controls for PI staining respectively. All data are presented as mean $\pm$ SD (n=3). * denotes statistical significance at $p < 0.05$.

4. Conclusions

The trade-off issue between improving T_{lum} and sacrificing ΔT_{sol} has been tackled by employing a novel RI-tunable nano sol-gel based ARCs. VO₂ has a higher RI at low temperature than that at high temperature for most visible and near IR range, which causes higher Fresnel reflection at the lower temperature and this is the one of the main reasons leading to intrinsically low solar modulation ability (ΔT_{sol}) of VO₂. The results suggest that with the specific RI of a tunable ARC coatings, more anti-reflection could be offered to the cold state as compared with hot state, thereby enhancing ΔT_{sol} . The best performing combination of nanocomposite substrate and ARCs could enhance $T_{lum(avg)}$ (from 39% to 44%) and ΔT_{sol} (from 15.7% to 18.9%) simultaneously by simply fine tuning the RI of ARC via annealing and/or concentration dilution. This RI tunable ARC could work on various VO₂ substrates, including

continuous thin films, nanocomposites and micro-patterning VO₂ substrates. It provides a facile approach to obtain various RI of ARC materials without the optical design and complex materials selection work. The cytotoxicity analyses reveal that the Si-Al ARCs are cyto-compatible and feasible to suppress the nanotoxicity of VO₂ nanoparticles. Therefore, the work presented here paves the way for practical applications of VO₂-based thermochromic smart windows in the real life as well as other optical applications.

Acknowledgements

This Research is conducted by NTU-HUI-BGU Nanomaterials for Energy and Water Management Programme under the Campus for Research Excellence and Technological Enterprise (CREATE), that is supported by the National Research Foundation, Prime Minister's Office, Singapore. The characterization works were contributed by the Facility for Analysis, Characterization, Testing and Simulation (FACTS) in Nanyang Technological University, Singapore and The Harvey M. Krueger Family Center for Nanoscience and Nanotechnology of the Hebrew University, Israel. The authors would also like to thank Dr. Yuwei Hu for his contribution to this paper.

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