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Crystallised mesoporous TiO_2(A)-VO_2(M/R) nanocomposite films with self-cleaning and excellent thermochromic properties

Zhang Chen,[1] Chuanxiang Cao,[1] Shi Chen, [1] Hongjie Luo,[1,2] and Yanfeng Gao[1,2]*

1 State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai institute of Ceramics, Chinese Academy of Sciences, 1295 Dingxi, Shanghai 200050, China

2 School of Materials Science and Engineering, Shanghai University, 99 Shangda, Shanghai 200444, China

* Author for correspondence. Email: yfgao@shu.edu.ac.cn

Tel/Fax: +86-21-6990-6218

Supporting information

S1 Influence of refractive index of matrix on optical performance of VO_2-based composite film.

Transmittances of VO_2-based composite film with different matrix refractive index (n) were simulated using an optical admittance recursive method[1]. Optical constants of the VO_2-based composite films are calculated using the "effective medium theory"[2]. Luminous transmittance (T_{lum}) and solar energy modification ability (ΔT_{sol}) were calculated according to literature[3]. Different refractive indexes of matrix (from 1.0 to 3.0) were calculated and the results are shown in **Figure S1-1**. As showed in the figure, as the n of matrix increased, ΔT_{sol} decreased for the same T_{lum}. Anatase TiO_2 has a refractive index of about 2.5, even the amorphous TiO_2 xerogel film has an refractive index of about 1.8 to 2.0, the highest ΔT_{sol} could be obtained by TiO_2&VO_2 composite film is less than 18%, much less than that obtain by O-I VO_2 composite coating (about 28 %, when n = 1.52)[4].

The influenence of coating thickness and contents of VO_2 in coatings on T_{lum} and ΔT_{sol} were also simulated with this method. Results are showed in **Figure S1-2**. The results showed that the film thickness and contents of VO_2 in coatings have similar influence on T_{lum} and ΔT_{sol}, especially when the contents of VO_2 in coatings is low. In other words, we could adjust T_{lum} and ΔT_{sol} by both coating thickness and contents of VO_2 in coatings to obtained a optimized value.

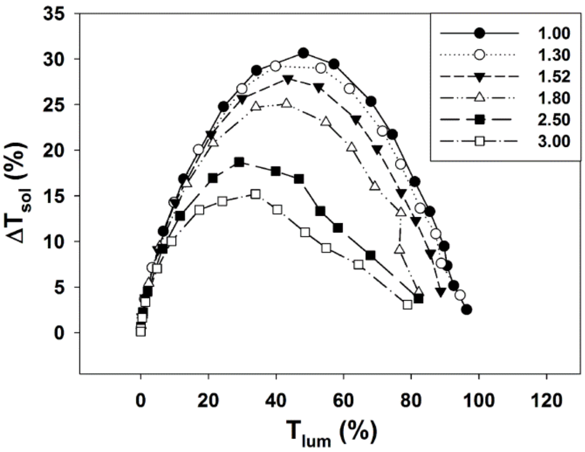

Figure S1-1. The relationship between ΔT_{sol} with T_{lum} under different matrix refractive index (n). The lower n, the better optical performance.

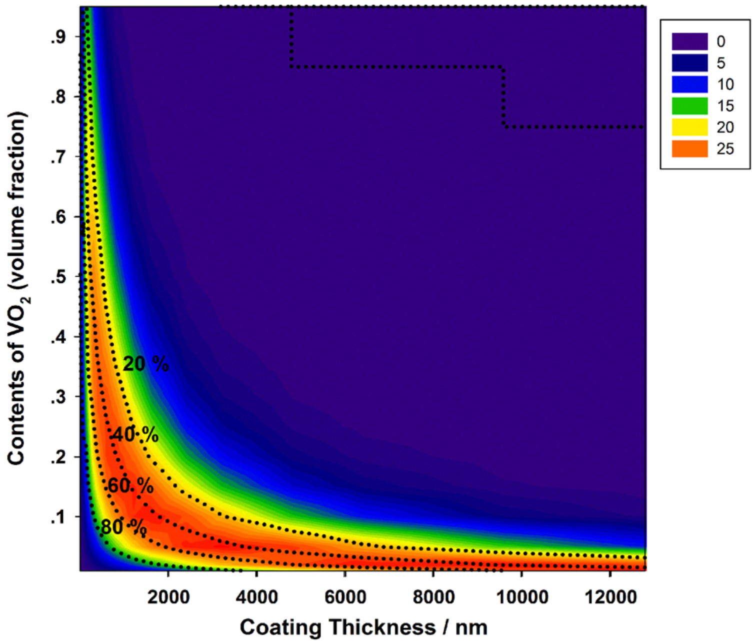

Figure S1-2 A contour map of the relationship between coating thickness and contents of VO_2 in coatings with T_{lum} and ΔT_{sol} of the composite coating when matrix refractive index is 1.52. ΔT_{sol} in the figure is characterized by different color, dash line in the figure is T_{lum}.

S2 Interference analysis of composite films with added P123% during annealing

P123 were added in the TiO_2 sols with VO_2 NPs to create mesoporoes in the TiO_2-VO_2 composite films. Because of the decomposition of P123 and the contraction of the composite film, the optical thickness of the films changed a little, which bring obvious changs in the interference between film interfaces and influence there optical performances. The typical example is the films with 2 wt.% P123 annealed to 300 ºC with different heating speeds.

As showing in **Figure S2**, there might be two AR peaks for 2% P123 sample before annealing, the first one is around 1600 nm, the second one is not obvious, but should be addressed in visible region[3]. This is the reason that 2% P123 sample had the highest T_{lum} and ΔT_{sol}[3]. During annealing, AR peaks would move to short wavelength due to mass loss and film contraction. As discussed in paper, sample annealed at 10 ºC /min had larger film contraction, and it is oblivious in **Figure S2**: the first AR peak at 2 ºC/min is around 1250 nm, while at 10 ºC /min it is around 1000 nm. For 2 ºC /min sample, the first AR peak enlarged ΔT_{sol} but the second AR peak moved out visible region, so it had lower T_{lum}; for 10 ºC /min sample, the second AR peak also moved out visible region, but the first AR peak made up part of the T_{lum} lost, bringing it higher T_{lum} but also lost ΔT_{sol}.

Table S2. Luminous transmittance (T_{lum}) and solar energy modification ability (ΔT_{sol}) of films with different amounts of P123 annealed with different processes

		Room temperature	2 ºC/min to 300 ºC	10 ºC/min to 300 ºC	Two-step annealing
T_{lum}	20 ºC	63.0	52.7	57.4	60.4
(%)	90 ºC	60.0	51.7	56.3	58.8
ΔT_{sol} (%)		13.3	9.7	7.0	8.4

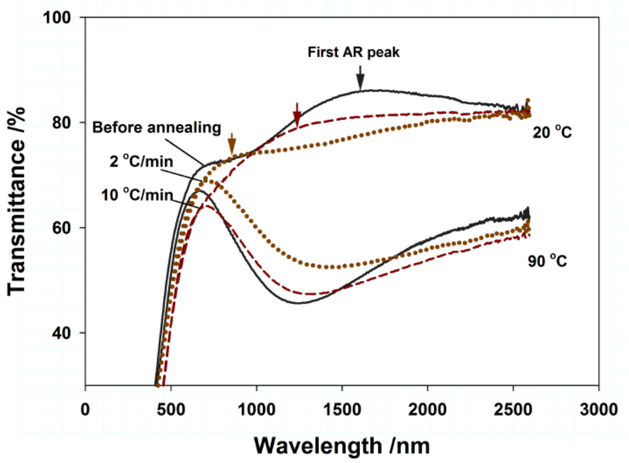

Figure S2. Transmittance (at 20 and 90 ºC) of sample with 2% P123 annealed at different heating speed. Arrows mark the position of first AR peak, which moves with film thickness and density change.

S3 Transmittance and reflectance curves of the best sample.

Reflectance curve shows clear valleys induced by interference. Film thickness could be estimated with the position of these valleys. There is relationship between wavelength of the first valley and films refractive index (ignoring extinction coefficient because it is small for VO_2 (M)):

$$\lambda = 2\pi nd$$

Where λ is the wavelength of the valley, n is refract index of the films and d is film thickness. As SEM showed in the paper, thinner sample with 4% P123 and annealed with two-stepped process has an thickness of about 270 nm, and its first valley in reflectance curve is at 800 nm. Wavelength of the first valley of the best sample is at about 1500nm, thus the thickness of the best sample may be twice as thick as that of the thinner one, about 500-600 nm.

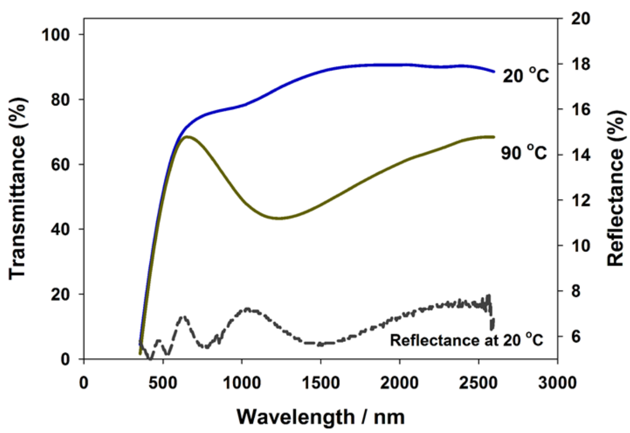

Figure S3. Transmittance and room temperature reflectance of the best sample.

S4 Transmittance changes of samples at 20 ºC after ultraviolet irradiation

Contaminated samples were irradiated with ultraviolet light (SUV110GS-36L, PL17) centered at 254 nm, which is much more powerful on photocatalytic efficiency than the reported (centered at 302 nm). Transmittance of samples were measured after irradiated very 30 s by a Hitachi U-4100 UV-visible-near-IR spectrophotometer. As showed in **Figure S4**, transmittance of sample with 4% P123 (b) and without P123 (c) at 660 nm have a change of more than 10 % after immersing into MB solution, but the black substrate has change only 3%.

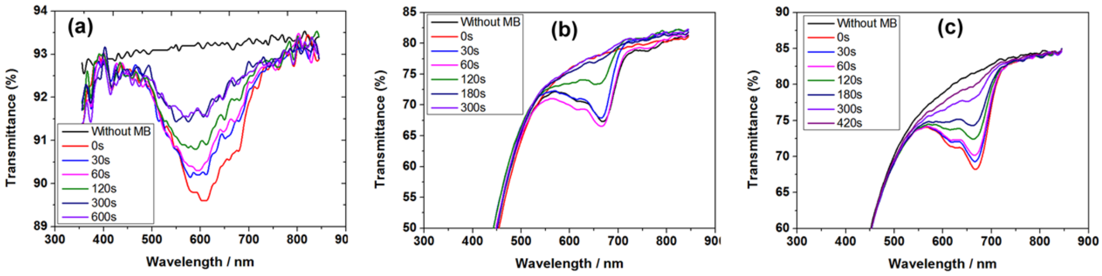

Figure S4. Transmittances of black substrate (a) and sample with 4% P123 (b) and without P123 (c) under UV irradiation after immersing them into a 30 μM MB solution for 10 min.

References

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