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Electronic Supplementary Information

Periodic Porous Thermochromic VO_2(M) Film with Enhanced Visible Transmittance

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1. Experimental Section.

Fabrication of Polystyrene Colloidal Crystal Templates: The quartz glass had been cleaned under ultrasonication by sequentially immersing in ethanol, acetone and distilled water, and then treated with the 98% H_2SO_4/H_2O_2 (3:1, in volume) solution and ultrapure water (Milli Q) to make them uniformly hydrophilic. Large-area well-ordered monolayer colloidal crystal templates (MCC) comprising polystyrene (PS) spheres were fabrication on these quartz glass slides using a method as previously reported.[1] The transmittance of quartz glass is shown in **Fig. S1**. For the preparation of the MCC template, 10 μL of water/ethanol dispersion containing monodisperse polymer colloidal spheres were dropped onto the top surface of a 1×1 cm piece of glass located at the mid-bottom of a Petri dish. The dispersion spread freely on the water surface until it covered nearly the whole surface area, resulting in a colorful MCC film. Then the MCC film was picked up with a quartz glass, and the patterned substrate covered with MCC was kept in vacuum prior to use.

Fabrication of Periodic Porous VO_2 (M) Films: As shown in Scheme S1, a 0.2 mol·L^{-1} $VOSO_4$ aqueous solution was prepared from $VOSO_4$ hydrate dissolved in ultrapure water/ethanol (1:1 in volume) as precursor solution. The glass slides with the MCC templates consisting of PS spheres were immersed into the solution at a certain angle, as illuminated in **Scheme 1**. This MCC hard template is immersed into the precursor water/ethanol mixed solution ($VOSO_4$ as vanadium source and then NH_4HCO_3 as precipitator, Caution: without NH_4HCO_3, the pure VO_2(M) phase cannot be obtained after annealing.) at a certain angle to form floating MCC template. Subsequently, the floating template can be picked up with a specific-required substrate, such as a quartz glass or some other substrates with flat or curved surface. After drying in vacuum overnight and annealing at 500 °C in Ar at a ramping rate of 2 °C /min, periodic porous VO_2 (M) film is finally achieved on quartz glass. A multilayer template can be fabricated by repeating the previous strategy. At the final lift-off step, the dried substrate covered with the monolayer or multilayer template can serve as a substrate to pick up another colloidal monolayer floating on the NH_4HCO_3 solution.

Characterization: The X-ray diffraction (XRD) were recorded by using a Philips XQPert Pro Super diffractometer with CuKα radiation (λ=0.154178 nm). Raman spectra were recorded at room temperature with a LABRAMHR Confocal Laser MicroRaman Spectrometer. The field emission scanning electron microscopy (FESEM) was performed by using a JEOLJSM-6700F field emission scanning electron microscope (15 kV). All the optical spectra were recorded on a Perkin Elmer Lambda 950 UV/Vis-NIR spectrophotometer with the variable temperature accessory (Specac).

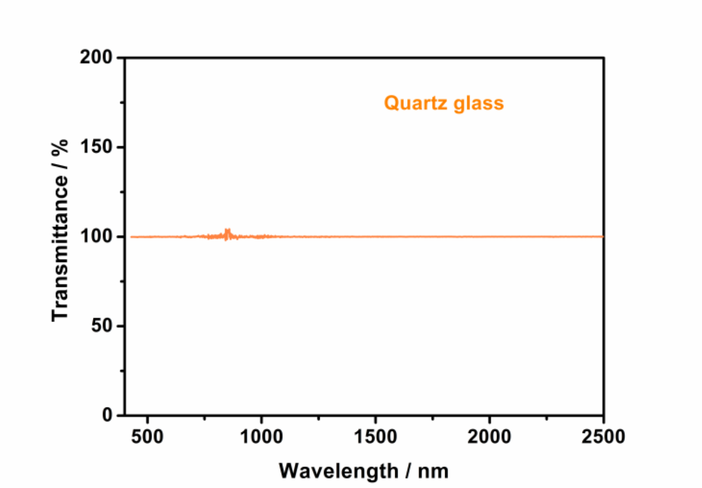
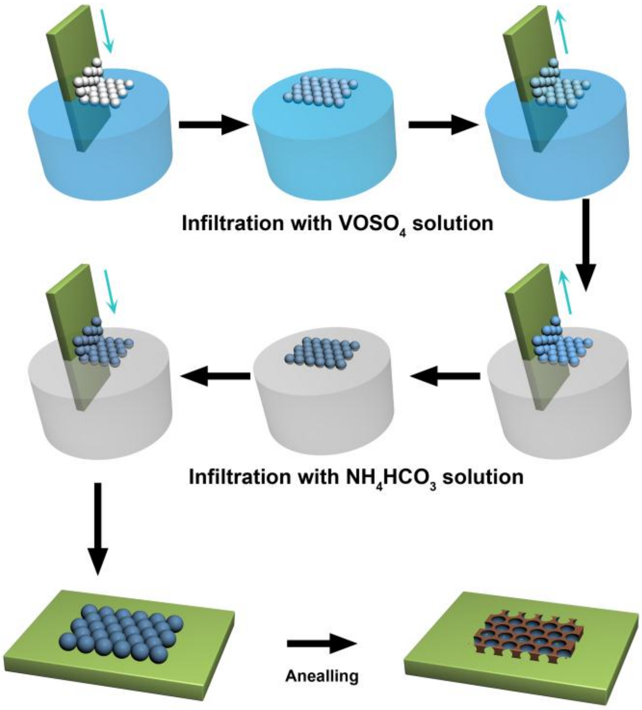


Fig. S1 Optical transmittance spectra of quartz glass.



Scheme S1. Outline of fabrication strategy for fabricating periodic ordered porous VO_2 (M) film. A glass covered with MCC template was immersed into the $VOSO_4$ solution first to form a floating template on the surface of the solution. Then the monolayer template was picked up using a substrate. Then the process was repeated on the surface of the NH_4HCO_3 solution. The periodic ordered porous VO_2 (M) film was finally formed after annealing in air.

2. Calculation for the space occupancy of VO_2(M).

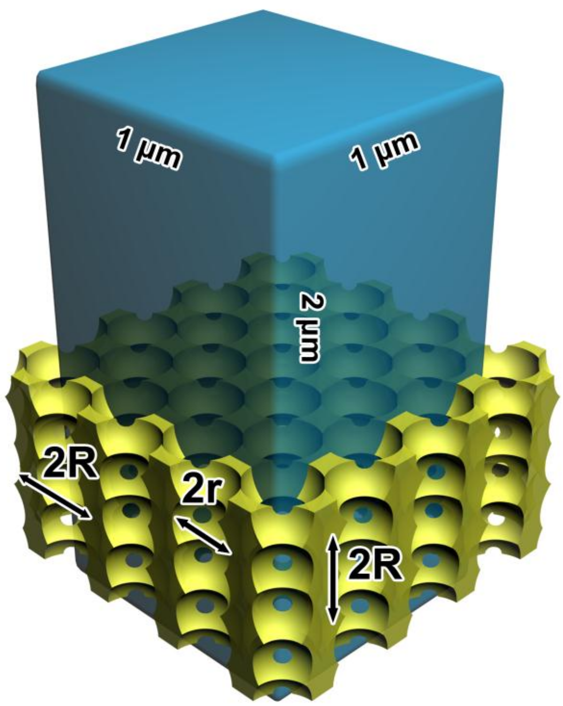


Fig. S2 Diagram showing the model and parameters for calculation of the space occupancy of VO_2(M).

Assuming there is an ideal periodic porous structure as shown in **Fig. S2**, the sum of space occupancy of VO_2(M) and air is 1. Hence we can calculate the space occupancy of VO_2(M) in a fixed space (taking 1000 nm×1000 nm×2000 nm for example) through the space occupancy of air, which is much easier for calculation due to its regular hemispherical shape of air. 2R (420 nm) is the diameter between the centers of neighbored air spheres, in other words, is the distance between the centers of adjacent wall. 2r (406 nm) is the diameter of air pores. So the number of air hemispheres is 1000/2R×1000/2R×(2N-1), where N is the layer number of the template. The actual space occupancy may be lower than this calculated value because here the volume change resulting from interconnection between each sphere is ignored.

$$\text{Space Occupancy of } VO_2(M) = 1 - \frac{\frac{1}{2}\times\frac{4}{3}\times\pi r^3\times\frac{1000}{2R}\times\frac{1000}{2R}\times(2N-1)+1000\times1000\times[2000-(2N-1)R]}{2000\times1000\times1000}$$

3. Optical transmittance spectra of periodic porous VO_2(M) films using the template with different layer number.

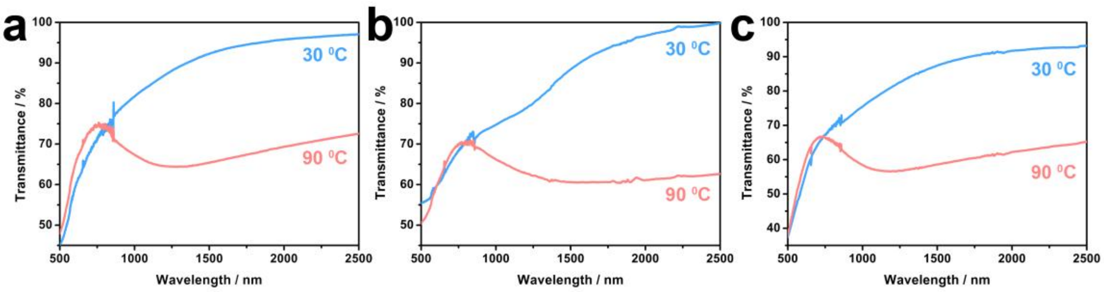


Fig. S3 Optical transmittance spectra of periodic porous VO_2(M) films using the template with different layer number: (a) 2; (b) 3; (c) 4.

Notes and references

1. C. Li, L. Qi, Adv. Mater. 2010, 22, 1494