Supplementary Information

Tungsten-Doped VO_2/Starch Derivative Hybrid Nanothermochromic Hydrogel for Smart Window

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1. X-ray diffraction pattern and phase transition behavior of VO_2(M)

The XRD spectra of monoclinic VO_2(M) (JCPDS card No. 43-1051) and W-VO_2(M) were given in Fig. S1. According to our previous work [1], even when W content was increased to 1.0%, only a slight shift of the M (011) peak was observed for W-doped VO_2(M) samples, which was also confirmed in our experiments. Both XRD results exhibit monoclinic crystal phase without any shift observed. The DSC result clearly shows that the phase transition temperature of W-doped VO_2(M) was reduced from 68 to 39 °C which is close to room temperature and LCST (lower critical solution temperature) of HBPS.

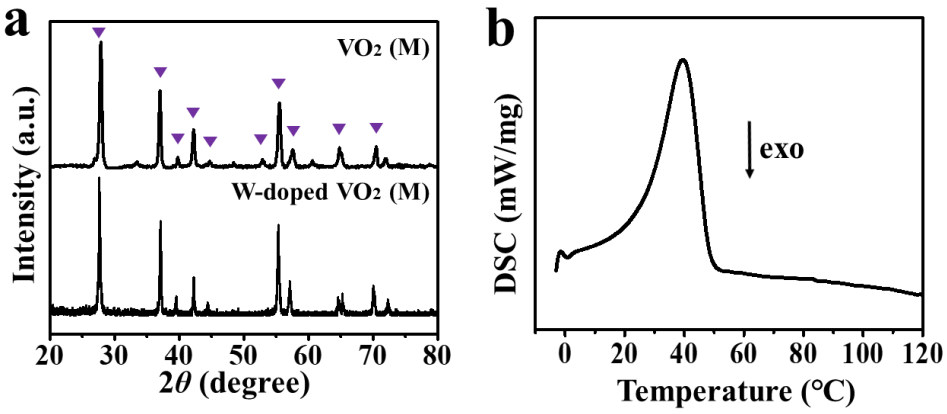

Figure S1. (a) XRD results of the VO_2(M) NPs and the W–VO_2(M) NPs. (b) DSC curve as function of temperature upon heating of W-doped VO_2(M) NPs.

2. Description of the different organic-inorganic hybrid samples

The actual contents of V and W-doped VO_2(M) in the composite film are shown in Table S1.

Table S1. Description of the two different organic-inorganic hybrid thermochromic films investigated in this work.

Sample	C_{HBPS-1} [a]	C_V [b]	$C_{W\text{-doped }VO2(M)}$ [c]
Composite-1	5 g/L	14.85 mg/L	24.18 mg/L
Composite-2	5 g/L	47.05 mg/L	76.62 mg/L
Composite-3	5 g/L	77.67 mg/L	126.48 mg/L

[a] The actual HBPS-1 NP content in the hybrids;.[b] The actual V content in the hybrids determined by ICP;.[c] The actual content of W-doped VO_2(M) calculated from C_V.

3. Morphology of W-doped VO_2 in Composite-2

To obtain a uniform hybrid of W-doped VO_2/starch derivative, zirconia pellet with 0.5 mm diameter was used for grinding to achieve the deaggregation of W-doped VO_2. As shown in the insert picture of Fig. S2a. the zirconia pellet was added into W-doped VO_2 suspension, and the mixture was stirred for 24 hours. Fig. S2a shows that the hydraulic radius of W-doped VO_2 before and after stirring was reduced from 278.3 nm to 98.7 nm. Then, the zirconia pellet was filtered out and the resulted W-doped VO_2 nanosuspension was directly dispersed into the starch derivative matrix. As shown in Fig. S2b, the W-doped VO_2 was well dispersed in the starch derivatives and the diameter of the W-doped VO_2 was 20-60 nm.

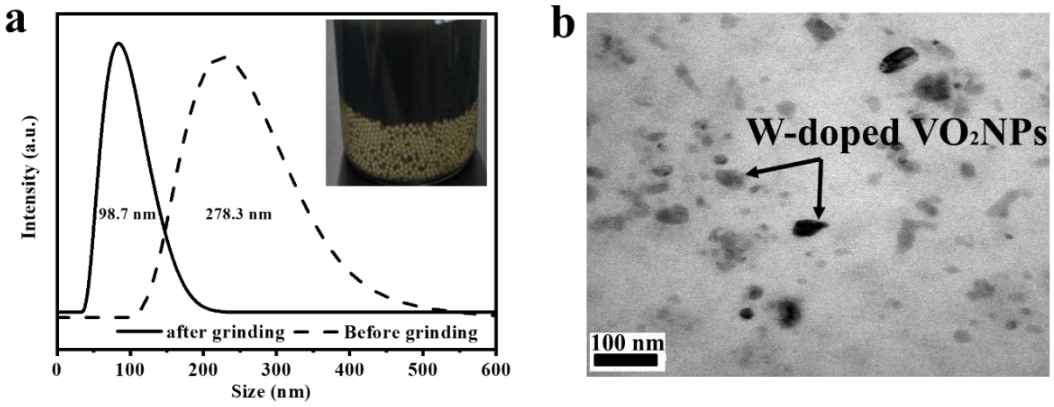

Figure S2. (a) Diameter of W-doped VO_2 NPs before (dash line) and after (solid line) grinding, and the insert picture shows the W-doped VO_2 suspension with white zirconia pellets. (b) TEM image of Composite-2.

4. Hysteresis loop of Composite-2

The transmittance at a fixed wavelength of 550 nm in the temperature range 20 to 45 °C for Composite-2 was recorded in a heating and cooling cycle and plotted versus temperature in Fig. S3. It can be seen that the hysteresis loop for Composite-2 had a relatively narrow loop gap. And the cloud point temperature of composite-2 was determined to be about 33 °C for the cooling and heating cycle with a T_{lum} decrease from 96% to 17%.

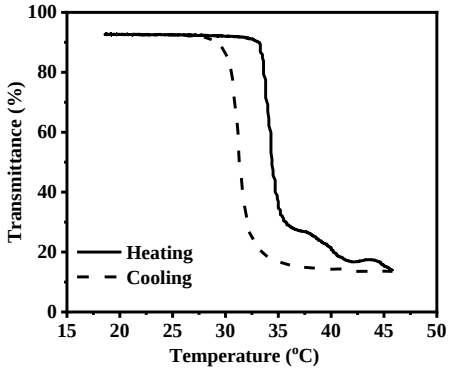

Figure S3. Hysteresis loop for the temperature-dependent transmittance of the Composite-2 at a wavelength of 550 nm.

5. Comparison of optical performance between previously reported smart window system and our system

As shown in Table S1, comparing with the result of the literature listed, our composite film shows excellent solar modulation properties (ΔT_{sol} = 34.3%) with high luminous transmittance ($T_{lum,\ average}$ = 78.7%). Also, the high $T_{lum,\ average}$ value of our composite indicates that we do not need extra energy to maintain good visibility indoors.

Table S2. Comparison of my hybrid sample with other thermochromic materials (note: "–" means data not available).

Category			Modulated solar spectrum (nm)	T_{lum} (%)	$\triangle T_{sol}$ (%)	Ref.
Thermal-responsive materials	VO_2	VO_2	700-2500	45.6	22.3	2
	Hydrogels	W + Zr-doped VO_2	700-2500	56.4	12.3	3
		PNIPAm	250-2200	70.7	25.5	4
		Modified cellulose	250-2200	67.4	25.7	5
		Modified starch	250-2200	87.7	40.1	6
	Metamaterials	Kiri-Kirigami metamaterials	200-2200	-	-	7
	Perovskites	Halide perovskite	400-700	-	-	8
	Liquid crystals		400-2200	-	-	9
VO_2 based hybrid thermochromic material	Non-responsive	VO_2/PU	700-2500	45.6	22.3	2
		VO_2/Si-Al gel	700-2500	59.1	12.0	10
		VO_2/PDMS	700-2500	85.0	-	11
		VO_2/TiO_2	700-2500	61.2	14.6	12
	responsive	VO_2/PNIPAm	250-2500	62.6	34.7	13
		VO_2/HPC	250-2500	56.0	36.0	14
		VO_2/NLETS	500-2500	71.0	18.2	15
		VO_2@SiO_2/PNIPAm	250-2500	75.6	62.7	16
		Our composite VO_2/Statch	250-2500	78.7	34.3	

6. References

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