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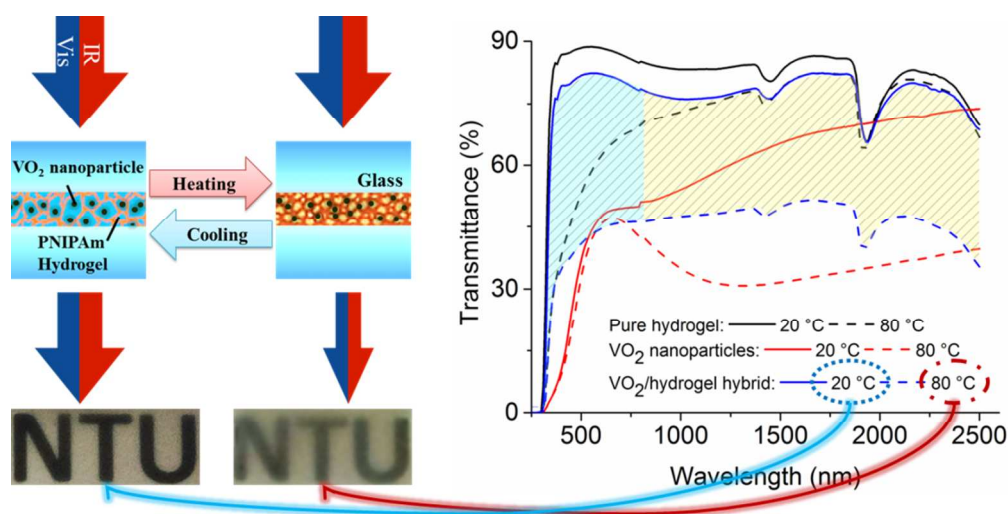


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A novel thermochromic VO₂/hydrogel hybrid was successfully synthesized. At 20 °C the hybrid remains both luminance and IR transparent while at 80 °C, the hybrid turns into translucent which gives large contrast in the visible range (ΔT_{lum}) as highlighted in light cyan (right picture) and this is mainly contributed by hydrogel. Meanwhile the prominent contrast of hybrid in the IR range (ΔT_{IR} , shaded yellow, right picture) is attributed by largely enhanced IR absorption of VO₂ at 80 °C. Both enhanced ΔT_{lum} and ΔT_{IR} give rise to extremely high solar modulating ability $\Delta T_{\text{sol}} \sim 34.7\%$ with salient averaged luminance transmittance (T_{lum}) of 62.6%.

VO₂/hydrogel hybrid nanothermochromic material with ultra-high solar modulation and luminous transmission

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Vanadium dioxide (VO₂) is the most well studied thermochromic material limited by its intrinsic properties of low solar modulation (ΔT_{sol}) and low luminous transmission (T_{lum}) arising from the high luminous absorption of VO₂ at both high and low temperature and more reflective characteristic at low temperature. Different approaches including nanothermochromism, nanoporosity, moth eye nanostructuring and antireflection have been deployed but none of them, by experiments or by simulation, could even reach half of the ΔT_{sol} (~35%) with high averaged T_{lum} (>60%) as produced by our firstly fabricated VO₂/hydrogel hybrid. The hydrophilic-to-hydrophobic phase transition of PNIPAm at ~30 °C predominantly controls the luminous modulation while the monoclinic-to-rutile phase transition of VO₂ nanoparticles at ~68 °C mainly contributes to the infrared modulation. This is the first reported hybrid integrating inorganic with organic thermochromic materials, which gives the unprecedented good thermochromic properties and opens a new research direction.

Introduction

The global contribution from buildings towards energy consumption has steadily increased reaching figures between 20% and 40% in developed countries¹ and has exceeded transportation and industrial sectors. Among building services, the growth in air-conditioning system energy use is particularly alarming (50% of building consumption), which leads to substantial emission of greenhouse gases.^{1, 2} Smart window can control solar transmission under the application of voltage (electrochromism)³, light (photochromism)⁴ or heat (thermochromism). Among them, thermochromic materials are most attractive since they can be utilized without extra energy input, which can regulate the solar transmission through adaptive response to weather conditions.⁵ The requirements for ideal thermochromic smart-window films are multifold: a large solar modulation (ΔT_{sol}) between above and below critical temperature (τ_c) is desirable for energy saving purpose; meanwhile the luminous transmission (T_{lum}) should remain high (preferably larger than 60%) to ensure good indoor visibility.⁶

Vanadium dioxide (VO₂) has been the most widely investigated thermochromic material in energy-saving smart windows applications.⁶⁻¹⁰ VO₂ could to some extent block infrared (IR) transmission (T_{IR}) at a temperature above τ_c (~68 °C) and allow the IR transmitted below τ_c , where the reversible monoclinic-to-tetragonal phase transition takes place⁷⁻⁹. The intrinsic physical properties of the higher refractive index of VO₂ at low temperature compared with high temperature and large luminous absorption at

both states¹¹ pose a veritable challenge to attain large ΔT_{sol} and high T_{lum} simultaneously. Numerous efforts such as employing doping¹²⁻¹⁵, antireflective coating^{16, 17}, nanoporous structuring^{18, 19}, nanoparticle-based composites^{11, 20-22} and biomimetic nanostructuring^{23, 24} have been investigated in VO₂ to enhance thermochromism (both enhanced ΔT_{sol} and T_{lum}). Table 1 summarizes the best performing experimental and simulation results via those approaches and one of the best reported result for VO₂ based material is ΔT_{sol} =22.3% with averaged T_{lum} =42.8% which still cannot match the requirement for practical usage.²⁵

Moreover, larger T_{lum} and ΔT_{sol} are the everlasting pursuit for smart windows to maximize the energy saving. To address this critical issue, temperature responsive hydrogels as a new candidate for the organic thermochromic smart windows has been recently reported by our group.⁵ Poly (N-isopropylacrylamide) (PNIPAm) hydrogel's hydrophilic-to-hydrophobic phase transition (lower critical solution temperature, LCST ~32 °C) was utilized to bring solar modulation ability.^{30, 31} By tuning the thickness of PNIPAm hydrogel, unprecedented ultra-high thermochromic properties (T_{lum} = 70.7%, ΔT_{sol} = 25.5%) could be obtained compared with any VO₂ based materials.

To further enhance the ΔT_{sol} , VO₂ nanoparticles, which has much stronger IR modulating ability (ΔT_{IR}) than hydrogel, for the first time, are integrated with PNIPAm hydrogel to form a hybrid thermochromic material. The evenly dispersed VO₂ nanoparticles dramatically increase hybrid's ΔT_{IR} , consequently giving rise to even

Table 1 Different approaches to enhance both ΔT_{sol} and T_{lum} and best performing coatings in each category

Approaches		ΔT_{sol}	T_{lum}	Remarks
Doping	Experiment	6.7%	53.8%	Eu doping, T_c decrease to 47.5 °C ¹⁴
	Experiment	4%	51%	Mg doping, T_c decrease to 45 °C ¹⁵
Porosity	Simulation	20%	45%	155nm Thickness with 50% porosity ²⁶
	Experiment	14.1%	41.6%	Polymer-assisted deposition ²⁶
	Experiment	14.7%	50%	Freeze Drying ²⁷
Nanothermo-chromism	Simulation	20%	48%	Oval shape ¹¹
	Experiment	12%	59.1%	VO ₂ /Si-Al nanocomposite foils ⁶
	Experiment	11.7%	51.4%	Sb: SnO ₂ (ATO)/PU matrix ²⁸
	Experiment	22.3%	42.8%	VO ₂ /PU nanocomposite foils ²⁵
Moth-eyed nanostructure	Simulation	15%	70%	Pitch size = 180 nm ²⁴
	Experiment	7.1%	44.5%	Pitch size = 210 nm ²³
Anti-Reflective overcoat	Experiment	12%	43.5%	Five-layered TiO ₂ /VO ₂ /TiO ₂ /VO ₂ /TiO ₂ films ²⁹

Note: All the experiments' testing temperature ranges are 20 °C - 90 °C, except for citation 15 (22 °C-100 °C)

higher ΔT_{sol} up to ~35%, while still maintaining higher average T_{lum} (~63%) than that of any VO₂ based inorganic materials. By tuning the thickness of the hybrid material, it is possible to subtly tune the overall performance by compromising between T_{lum} and ΔT_{sol} to meet various demands for smart window applications.

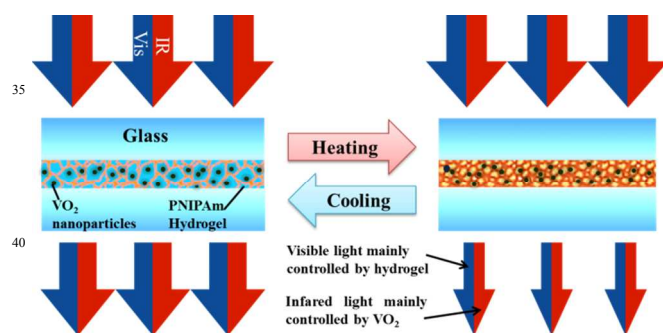
Experimental details

Materials and Equipment

Vanadium (IV) oxide powder (VO₂, 99.99%, Alfa Aesar), Dipropylene glycol methyl ether (DPM, 4.5 wt%, Disperbyk 180), N-isopropylacrylamine (NIPAM, ≥ 98%, Wako Pure Chemical Industries Ltd), N, N'-methylenebis(acrylamide) (≥ 99%, crosslinker, Sigma-Aldrich), polyvinyl alcohol (PVA, M_w = 61,000, Sigma-Aldrich) and N,N,N',N'-tetramethylethylenediamine (TEMED, accelerator, 99%, Sigma-Aldrich), ammonium peroxydisulfate (initiator, 98%, Alfa Aesar) and multipurpose sealant (Selleys All Clear) were used without further purification. Deionized water (18.2 MΩ) was used throughout the experiments.

Preparation of the VO₂/hydrogel hybrids

The fabrication of VO₂ nanoparticles could be found in previously reported paper⁶ and the nanoparticle content was determined to be ~2.6 wt% by thermo-gravimetric analyzer (Q500, TA Instrument, USA) under N₂ protection. The supernatant was used for hybrid synthesis.

**Fig. 1** Solar modulating mechanism of VO₂/hydrogel hybrid

Preparation of the VO₂/hydrogel hybrids

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The hybrid was synthesized by in-situ polymerization of monomer in deionized (DI) water in the presence of VO₂ nanoparticle. In this case, 7.91 g (0.07 mol) N-isopropylacrylamide (NIPAM), 1.32 g (0.03 mol) polyvinyl alcohol (PVA), and 215.6 mg (0.0014 mol) N,N'-methylenebis(acrylamide) were dissolved in 70 °C DI water to make a homogenous 100 ml aqueous solution. After the homogeneous and transparent solution was obtained, the temperature was reduced to 25 °C and this solution was purged with N₂ for 30 minutes. After homogeneous solution containing NIPAM, PVA and N,N'-methylenebis was obtained, 260.0 μL of this solution was pipetted into a 1 mL centrifuge tube. Then 43.3 μL of DPM/VO₂ (DPM: aqueous solution = 1:6, vol %) were added into the centrifuge tube with vibration. 3.0 μL N,N,N',N'-Tetramethylethylenediamine (TEMED, catalyst) and 7.0 μL ammonium persulfate (APS, initiator) were added in sequence to the centrifuge tube with vigorous vibration on vortex for 10 seconds. The solution was transferred in between 2 pieces of clean glass slides to make a sandwich structure after the reaction completed at room temperature for 24 hours. Samples with thickness of 13 μm, 26 μm and 52 μm were successfully made and the sealant was applied at the edges to prevent mass exchange with outside environment. Pure hydrogel sample fabrication process is nearly same as the hybrids, which is without the DPM/VO₂ addition. Fig. 1 shows the mechanism of forming the laminated VO₂/hydrogel hybrid thin film.

Characterization

The morphology of milled VO₂ nanoparticles in PNIPAm monomer solution was observed by transmission electron microscopy (TEM) and the micrographs were collected using a Carl Zeiss LIBRA[®] 120 in-column energy filter TEM equipped with an integrated OMEGA filter.

The dynamic rheological tests were performed with 40 mm parallel plate on Discovery hybrid Rheometers (DHR-3, TA

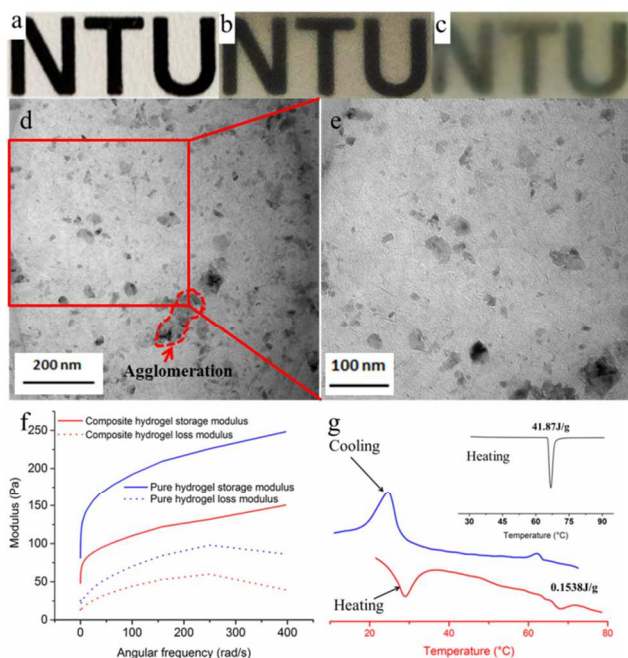


Fig. 2 (a) Pure hydrogel thin film at room temperature (25 °C), (b) VO₂/hydrogel hybrid at room temperature, (c) VO₂/hydrogel hybrid at 35 °C, TEM image of VO₂ nanoparticles at (d) 31500× and (e) 50000×, (f) Angular frequency dependence of storage modulus and loss modulus for pure hydrogel and VO₂/hydrogel hybrid at 25 °C, (g) DSC of VO₂/hydrogel hybrid and commercial VO₂ powder (inset).

instruments, USA) at room temperature (25 °C). To investigate the linear viscoelastic regime, amplitude sweeps were performed and strain of 10% was chosen for both samples. Frequency sweep tests were conducted from 0.01 rad/s to 400.0 rad/s with fixed gap of 500 μm.

Swelling ratios of both hydrogels were measured by the weight ratio of equilibrium swollen hydrogels to dry hydrogels. Hydrogels were allowed to immerse into DI water for 3 days and DI water was changed every 12 hours. The weight of W_g as the swollen hydrogel weight was obtained. Then the hydrogel was put into dry box at 50 °C until constant weight of the dry gel, W_d , was obtained. Swelling ratio (q) of pure hydrogel and hybrid can be calculated by $q = \frac{W_g}{W_d}$.

The specific heat flow of PNIPAm/VO₂ hybrid and pure VO₂ were characterized with a N₂-protected Q10 differential scanning calorimeter (TA Instruments, USA), with ramping rate set as 3 °C/min. The enthalpy of the phase transition was calculated by Thermal Advantage Software (TA Instruments, USA).

The transmittance spectra in 250 nm – 2500 nm wavelength range were collected on a UV-Vis-NIR spectrophotometer (Cary 5000, Agilent, USA) at normal incidence. The spectrophotometer is equipped with a heating and cooling stage (PE120, Linkam, UK). The integral luminous transmittance T_{lum} (380–780 nm), IR transmittance T_{IR} (780–2500 nm) and solar transmittance T_{sol} (250–2500 nm) were calculated by equation 1:

$$T_{lum/IR/sol} = \frac{\int \varphi_{lum/IR/sol}(\lambda) T(\lambda) d\lambda}{\int \varphi_{lum/IR/sol}(\lambda) d\lambda} \quad (1)$$

where $T(\lambda)$ denotes spectral transmittance, $\varphi_{lum}(\lambda)$ is the standard luminous efficiency function of photopic vision³² in the wavelength range of 380–780 nm, $\varphi_{IR}(\lambda)$ and $\varphi_{sol}(\lambda)$ is the IR/solar irradiance spectrum distribution for air mass 1.5

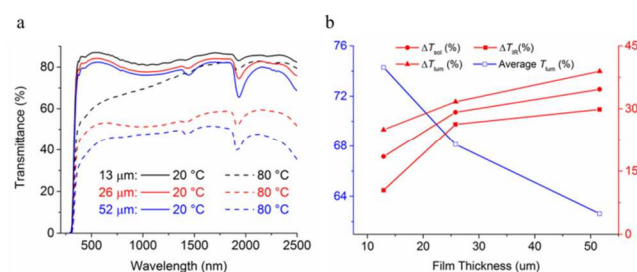


Fig. 3 (a) Optical transmittance spectra of the three samples with different thicknesses between 20 °C and 80 °C; (b) Trend of ΔT_{sol} , ΔT_{lum} , ΔT_{IR} and average T_{lum} between 20 °C and 80 °C for different thicknesses.

(corresponding to the sun standing 37° above the horizon with 1.5 atmosphere thickness, corresponds to a solar zenith angle of =48.2)³³. $\Delta T_{lum/IR/sol}$ is obtained by $\Delta T_{lum/IR/sol} = T_{lum/IR/sol, 20\text{ °C}} - T_{lum/IR/sol, 80\text{ °C}}$.

Results and discussion

At room temperature, pure PNIPAm hydrogel is colorless transparent (Fig. 2a), while VO₂/hydrogel hybrid is brownish transparent due to the presence of VO₂ nanoparticles (Fig. 2b) and starts to appear translucent when temperature increases to 35 °C (above LCST). The TEM images at different magnifications (Fig. 2d, e) show that the milled nanoparticles are irregular, non-spherical and well dispersed within matrix. Agglomeration is sparsely observed and the particle size ranges approximately from 20 to 100 nm. Both the storage and loss modulus of hybrid are lower than those of pure hydrogel (Fig. 2f), indicating that the effective crosslinking density is reduced in the hybrid. The role of VO₂ nanoparticle in reducing crosslinking density can also be proven in swelling ratio tests that pure PNIPAm hydrogel has an equilibrium swelling ratio of 6.12 g/g while VO₂/hydrogel hybrid assumes a larger swelling ratio of 13.58 g/g. However, the storage modulus of hybrid hydrogel is still higher than loss modulus over the observed frequency range and this is a confirmative indication of crosslinked hydrogel.³⁴ The critical transition temperatures of both hydrogel matrix (~32 °C) and VO₂ (~68 °C) have been preserved in the hybrid as shown in Fig. 2g. It is worthwhile to mention that the phase transition specific enthalpy of hybrid at ~68 °C is only ~0.154 J/g and the nanoparticle concentration in hydrogel is ~0.372% as calculated from TGA result, which gives the VO₂ nanoparticles in hydrogel 41.39 J/g (0.154/0.372%) phase transition enthalpy. This is very close to the phase transition enthalpy of commercial VO₂ micro-sized powders (41.87 J/g) (Fig. 2g inset) and it proves that the hydrogel matrix does not affect the VO₂ nanoparticle phase transition at 68 °C.

For VO₂/hydrogel hybrid, two transmittance valleys at ~1430 nm and 1930 nm (Fig. 3a) indicate typical absorption of water at these two wavelengths. The 1400 nm peak is due to the O-H stretch in the water molecule, while 1900 nm valley is a combination of O-H stretch and H-O-H bending. At low temperature, more hydrogen bonds exist between water and crosslinked chains; these hydrogen bonds are gradually broken with increasing temperature, which indicates a continuous phase separation.⁵

Both luminous and IR transmission of VO₂/hydrogel hybrid is lessened with increasing thickness. As demonstrated in Fig. 3a

Table 2 Comparison between different thicknesses of hybrid with VO₂/DPM to monomer solution ratio 1:6.

Thickness	T_{lum} (20 °C)	T_{lum} (80 °C)	ΔT_{lum}	Average T_{lum}	T_{sol} (20 °C)	T_{sol} (80 °C)	ΔT_{IR}	ΔT_{sol}
13 μ m	86.8	61.8	25	74.3	84	56.5	10.5	18.5
26 μ m	84	52.3	31.7	68	80.7	51.5	26.3	29.2
52 μ m	82.1	43.2	38.9	62.6	78.9	44.2	29.9	34.7

and Table 2, T_{lum} slightly decreases with thickness at 20 °C with negligible amount and still maintains at a relatively high level of 82.1% for sample with thickness of 52 μ m. As the particle size is ~20-100 nm (Fig. 2 e) which is much smaller than the visible wavelength, this does help to minimize the scattering of visible light, thereby maintaining high T_{lum} . However at 80 °C, T_{lum} prominently decreases from 61.8% to 43.2% with thickness increasing from 13 μ m to 52 μ m which is mainly due to the higher blocking effect of thicker hydrogel,⁵ resulting more prominent luminous transmission difference (ΔT_{lum}) as shown in Fig. 3b. Although the T_{lum} of 43.2% at 80 °C is relatively low, the ultra-high T_{lum} of >80% at 20 °C gives average T_{lum} higher than 62%, which is superior to almost any known thermochromic VO₂ materials (Table 1). Furthermore, the hybrid's infrared modulation (ΔT_{IR}) and ΔT_{sol} increase with increasing thickness (Fig. 3b) and this is mainly contributed by the combined effects of more IR absorption of larger amount VO₂ and more scattering from crossed-linked hydrogel at high temperature.

The VO₂ nanoparticles dispersed in DPM with the same amount of solid loadings in hybrid and the pure hydrogel with same thickness as hybrid were used as reference samples. The three UV-Vis spectra for pure hydrogel, VO₂ nanoparticles and VO₂/hydrogel hybrid are shown in Fig. 4.

Compared with the pure VO₂ nanoparticles in DPM (red lines), VO₂/hydrogel hybrid (blue lines) has a blue shift in the visible range and increases overall solar transmission of most spectra (T_{sol} , 250-2500 nm) below and above τ_c (Fig. 4), which gives higher T_{lum} (62.6% vs. 42.5% Table 3). This may be due to the fact that VO₂ nanoparticles are much more sparsely distributed in the hydrogel matrix with the minimized scattering of light, which allow more solar transmission between VO₂ nanoparticles.

Meanwhile there is a negligible ΔT_{lum} of 2.4% for pure VO₂ but giant contrast in the near IR range (780-2500 nm) with 22.2% ΔT_{IR} . Contrarily, there is a large contrast in the visible range (380-780 nm wavelength) for the pure hydrogel (black lines) as confirmed by large ΔT_{lum} of 29.7% and relatively small in the near IR range with 9.5% ΔT_{IR} . Thus the gigantic contrast in the VO₂/hydrogel hybrid occurs in both visible and IR range with correspondingly much enhanced ΔT_{IR} (light yellow region ~29.9%) and ΔT_{lum} (light cyan region ~38.9%) gives an unprecedented high ΔT_{sol} (34.7%) while maintaining moderate T_{lum} (62.6%) as shown in Table 3 and Fig. 4.

Compared with best reported VO₂ sample,²⁵ the VO₂/hydrogel hybrid has a much higher T_{lum} at 20 °C (82.1% vs. 45.6%) and slightly higher T_{lum} (43.2% vs. 40%) at 90 °C, which gives ~42.6% increment in averaged T_{lum} (62.6% vs. 42.8%) and large ΔT_{lum} (38.9% vs. 5.6%). Since visible range spectrum has higher $\phi_{sol}(\lambda)$ (solar spectral irradiance distribution) compared with infrared range as shown in grey shaded area (Fig. 4), the large transmission difference in the visible range of the hybrid (light

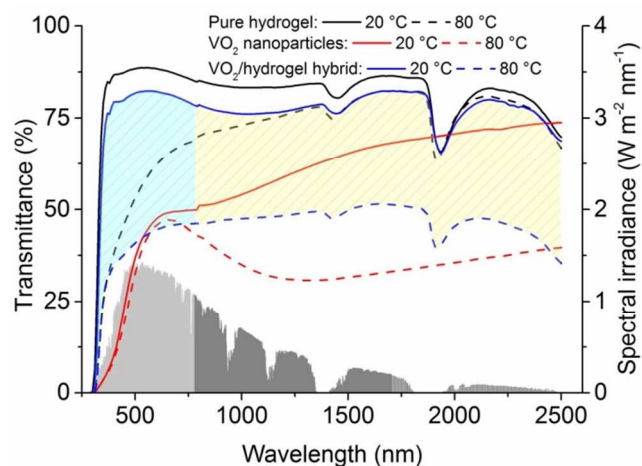


Fig. 4 UV-Vis spectrums of pure hydrogel (black), pure VO₂ (red) and VO₂/hydrogel hybrid (blue) at low and high temperature, the grey area indicates the normalized values of the visible (light) and IR (dark) spectra spectral irradiance. The light cyan area with sparse slashes is the luminous transmission difference and the light yellow area is the IR transmission difference of VO₂/hydrogel hybrid.

cyan) gives rise to largely enhanced ΔT_{sol} . It is of interest to observe that the two water absorption peaks at ~1430 and 1930 nm wavelengths are coincident with two valley of the solar spectral irradiance (Fig. 4), which indicates that the water absorption has the negligible effects on the T_{sol} and ΔT_{sol} . The dramatically enhanced ΔT_{sol} (34.7% vs. 22.3%) arises from large ΔT_{lum} mainly contributed by hydrogel and the large ΔT_{IR} by VO₂. This gives ~56% enhancement in ΔT_{sol} compared with best reported VO₂.

Most researchers focused on nanothermochromic VO₂¹¹ as it gave the best performance compared with other approaches (Table 1) and it predicted that the highest possible ΔT_{sol} is ~20% with ~48% T_{lum} . However, none of the matrix used is solar modulating and it is the first time that thermal responsive hydrogel matrix has been adopted and such hybrid overcomes the physical limitation of nanothermochromism as shown in the simulation. Ultra large ΔT_{sol} contributed from both ΔT_{lum} and ΔT_{IR} could be achieved while high T_{lum} could be maintained. This opens a new avenue for the hybrid nanothermochromic materials.

Table 3 Comparison of thermochromic properties for pure hydrogel thin film, pure VO₂ nanoparticles' made thin film, VO₂/hydrogel hybrid composite thin film and the best reported data in the reference.

Sample	$T_{lum,20\text{ }^\circ\text{C}}$ (%)	$T_{lum,80\text{ }^\circ\text{C}}$ (%)	ΔT_{lum} (%)	$T_{lum,average}$ (%)	ΔT_{IR} (%)	ΔT_{sol} (%)
Pure hydrogel	88.5	58.8	29.7	73.6	9.5	21.4
Pure VO ₂ /DPM	43.7	41.3	2.4	42.5	22.2	11.2
VO ₂ /hydrogel Hybrid	82.1	43.2	38.9	62.6	29.9	34.7
Best reported VO ₂ data ²⁵	45.6	40.0	5.6	42.8	Not Given	22.3

Conclusions

For the first time, we report a novel VO₂/hydrogel hybrid and it gives dramatically high ΔT_{sol} (34.7%), while maintaining moderate average T_{lum} (62.6%), which offers 74% enhancement of ΔT_{sol} and 30% increment of T_{lum} compared with theoretical nanothermochromic value. Meanwhile, it is far better than any organic and inorganic experimental results as ΔT_{sol} is dramatically enhanced via combined effects from luminous regulating organic matrix and IR regulating inorganic nanoparticles. This revolutionary concept of nanothermochromic hybrid opens a new phase in the smart windows applications.

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Notes and references

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