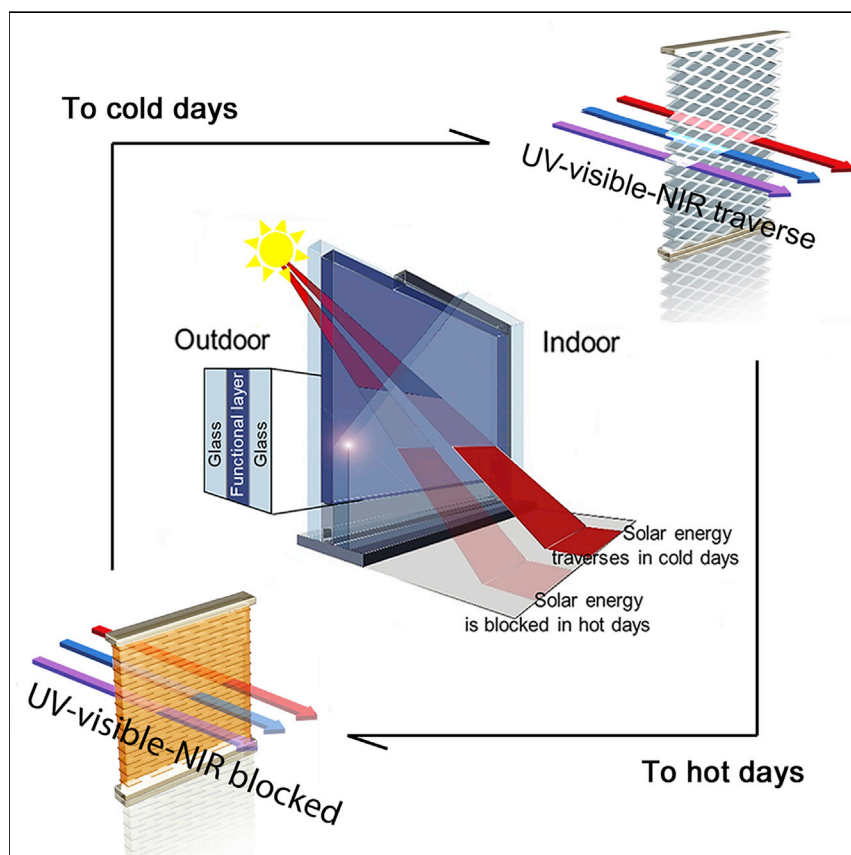


Article

Adaptive Thermochromic Windows from Active Plasmonic Elastomers



Thermochromic windows can smartly modulate the indoor solar irradiation, leading to energy saving for architectural heating and cooling systems. Herein, we integrate the active plasmonic VO₂ nanoparticles in kirigami-inspired reconfigurable elastomers to achieve adaptive, broadband, and highly efficient solar modulation. The smart window promises a UV-visible-NIR traverse state in cold days and a UV-visible-NIR blocked state in hot days to reduce the architectural heating and cooling energy consumption.

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HIGHLIGHTS

The design of smart windows based on plasmonic-enhanced reconfigurable elastomer

A solar modulation of $\Delta T_{\text{sol}} = 37.7\%$ on VO₂-based thermochromic films

The strain- and thermal-responsive localized surface plasmon resonance

A facile method for adaptive, broadband, and highly efficient optical modulation

Article

Adaptive Thermochromic Windows from Active Plasmonic Elastomers

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SUMMARY

Architectural windows that smartly regulate the indoor solar irradiation are promised to economize the building energy consumption. Here, we demonstrate a method for adaptive, broadband, and highly efficient solar modulation for energy-efficient smart windows through active plasmonics in reconfigurable structures. We develop a kirigami-inspired elastomer containing plasmonic vanadium dioxide (VO₂) nanoparticles, in which the geometrical transition and the temperature-dependent localized surface plasmon resonance (LSPR) present dominant controls in ultraviolet-visible and near-infrared regions, respectively. The active LSPR control, via stretch-induced local dielectric changes is mitigated on reconfigurable metamaterials because of their unique strain distributions. This method demonstrated a desirable property in energy-efficient smart windows facilitating improved solar energy modulation (37.7%), surpassing the best-reported modulation in passive and transparent VO₂ thermochromism systems. This first attempt to integrate the plasmonics and reconfigurable structures may inspire developments in smart windows, building energy economization, as well as fundamental studies of plasmonic controls in metastructures.

INTRODUCTION

Architectural windows that smartly regulate indoor solar irradiation have been recognized as a promising solution to economize energy consumption and maintain a comfort level of buildings.¹ Recently, switchable materials that change their transmittance in response to external stimuli have attracted increasing research interests.^{2,3} Among them, the thermal-responsive material is highly competitive for energy-efficient smart window applications because of its low cost, passivity, as well as the rationality of thermal-induced stimulus-response for indoor temperature control.^{1,4,5} The ultimate goal in thermochromic materials is to continuously improve the solar modulation and luminous transmission, which, however, are considerably limited by materials' intrinsic properties.¹ Here, we report a new concept of a mechano-thermochromic smart window inspired by the ancient art of paper cutting, kirigami.

Kirigami has been transitioning to the toolbox of modern materials design.^{6–8} The cut patterns endow materials with unusual mechanical properties such as the 2D-to-3D transformation,^{9,10} predictive deformation,^{7,11} and extensibility enhancement with negligible impact on conductance of a material,¹² thereby promoting the quick development in stretchable electronics,⁶ sensors,¹³ wearable devices,^{12,14} as well as in energy conversion and storage applications.^{12,15} Kirigami-inspired metamaterials can programmatically switch their physical properties by changing the

Context & Scale

Thermochromic windows can smartly modulate the indoor solar irradiation, leading to energy saving for architectural heating and cooling systems. Adaptive solar energy modulation with a high on-off ratio is the key; enhancing the performance, however, is an inevitable challenge as it is limited by materials' intrinsic properties. Conventional improvement methods are to develop the multilayer, porosity, composite, grid, and biomimetic structures. Herein, we are thinking out of the box by integrating the active plasmonic VO₂ nanoparticles in kirigami-inspired reconfigurable elastomers to achieve adaptive, broadband, and highly efficient solar modulation. The smart window demonstrates a high solar energy modulation ($\Delta T_{\text{sol}} = 37.7\%$), outperforming those methods, and has exhibited superior performance in Houston, Hong Kong, and Madrid.

configurations. Recently, these materials have been exploited on optical devices for dynamic light tracking and manipulation.^{15–18} Current studies only apply the non-responsive composition to the kirigami structures serving as the scaffold to integrate with complex optical devices or interact with the incident light by simple reflection or diffraction.^{15–18} Integration with stimuli-responsive additives promises the multiple stimuli-responsive functionalities toward a broadband optical modulation.

Active plasmonics is another important technology for light manipulation, attracting extensive research attention in the past decade.^{19,20} Localized surface plasmon resonance (LSPR) occurs when the resonance frequency of the electrons in metallic nanoparticles (NPs) is coupled with the irradiation wavelength. The electron oscillation leads to a strong electromagnetic field confined in the vicinity accompanied with strong plasmon absorption. The plasmon resonance can be converted into light,^{21,22} chemical energy or hot electron,^{23–26} thermal energy,^{27,28} electric energy,²⁹ and so on.³⁰ Actively tuning LSPR can be achieved by dynamically controlling dielectric surroundings, gap distances between two nanostructures, or carrier density in self-tunable structures,¹⁹ which mainly relies on sophisticated devices,³¹ such as the battery-type electrochemical device for the *in situ* oxidation-reduction reaction,³² which significantly limits their potential to combine with other technologies.

Here, we develop a kirigami-inspired elastomeric metamaterial containing phase-change vanadium dioxide (VO₂) NPs for adaptive, broadband, and highly efficient solar modulation targeting energy-efficient smart windows. The phase transition of VO₂ to metallic state releases the free electrons to support the plasmon resonance at high temperatures (above ~65°C), resulting in distinguishing absorption in the near-infrared (NIR) region.³³ The geometrical transition and the temperature-dependent LSPR present dominant controls in UV-visible and NIR ranges, respectively. Besides the thermal- and aggregation-induced LSPR tunability, we also demonstrate a novel LSPR control based on stretch-induced local dielectric changes. This stretch-induced LSPR change is observed on planar films, while it is quenched on kirigami structures because of their unique strain distributions. In addition, the metamaterial exhibits an ultrahigh solar energy modulation ($\Delta T_{\text{sol}} = 37.7\%$) while adopting to energy-saving smart window applications, which surpasses the best results of VO₂-based thermochromism.

RESULTS

Concept and Material Design

Active modulation of optical transmittance can be achieved by either the structural transition or active LSPR of VO₂ NPs under external stimuli. These two methods are complementary to each other to enhance the transmittance modulation in a broad range of the spectrum. The strain-induced transition to a compact state remarkably reduces UV-visible transmittance but provides limited NIR control because of the relatively high transparency of the VO₂-elastomer composite in the NIR region (Figure 1A1). On the contrary, the switch-on of LSPR under elevated temperature induces a strong transmittance decrease in the NIR spectrum range while offering a negligible effect in UV-visible regions (Figure 1A2). The integration of the active LSPR of VO₂ NPs with the reconfigurable structures is able to independently control the light transmittance in UV-visible and NIR range, leading to a broadband transmittance modulation (Figure 1A3).

The NPs are demonstrated as monoclinic VO₂ (Figure 1B), and they are characterized as the quasi-sphere morphology (Figure 1C) with a narrow size distribution and an

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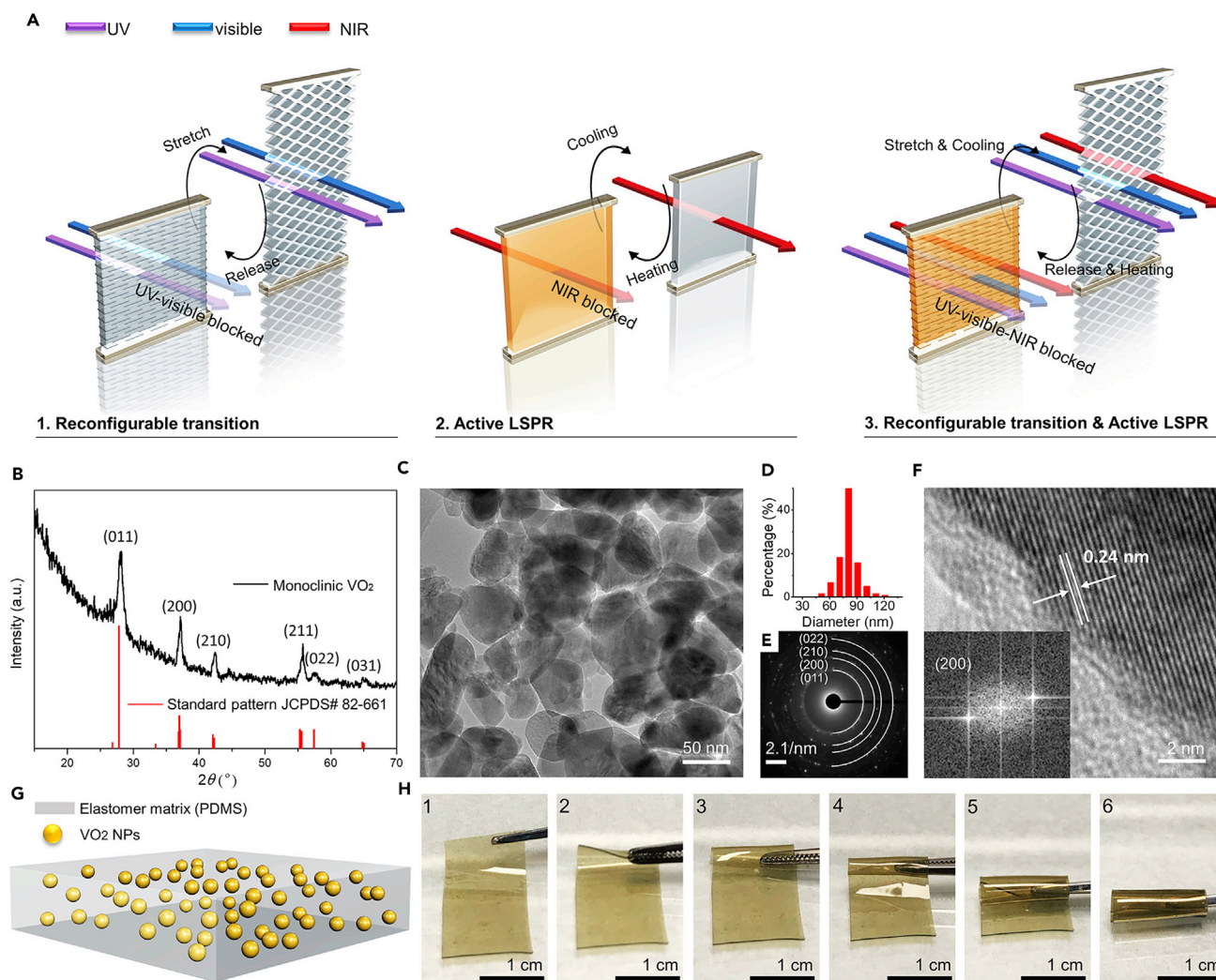


Figure 1. Concept and Material Design

(A) Schematic of transmittance modulation methods based on (A1) reconfigurable metamaterials, (A2) active LSPR, and (A3) the integration of active LSPR and reconfigurable metamaterials.

(B) X-ray diffraction (XRD) pattern of the VO_2 NPs with identified planes based on the PDF card No. JCPDS# 82-661.

(C) TEM image of quasi-sphere VO_2 NPs.

(D) The size distribution diagram.

(E) The SAED pattern of monoclinic VO_2 .

(F) HRTEM image of a VO_2 NP on edge and the corresponding fast Fourier transition (FTT) image as the inset.

(G) Illustration of the produced composite film consisted of well-dispersed VO_2 NPs in the PDMS matrix.

(H) Photographs of the roll-up process of the yellow-brown composite film from figures on the left to right (H1–H6).

average diameter of ~ 80 nm (Figure 1D). In the selected area electron diffraction (SAED) pattern, four bright rings are identified to be the (022), (210), (200), and (011) planes of monoclinic VO_2 (Figure 1E). An interplanar spacing of 0.24 nm is observed by high-resolution transmission electron microscopy (HRTEM), corresponding to the (200) plane of monoclinic VO_2 (Figure 1F and the inset). These NPs are dispersed in poly(dimethylsiloxane) (PDMS) matrices (Figure 1G) with a very low concentration (nominal 0.75‰–2.25‰) to maintain the mechanical property of the elastomer as well as offer sufficient optical property of VO_2 . PDMS is applied because of its high transparency in the UV-vis-NIR spectrum (Figure S1). The

composite film displays a yellow-brown appearance and is easily rolled up by a tweezer, demonstrating its flexibility (Figures 1H1–1H6). It is also stretchable, benefitting from the elastomer PDMS matrix (Figure S2).

Active Localized Surface Plasmon Resonances

On the composite film, a temperature-dependent LSPR on-off character is demonstrated. The LSPR is totally quenched at room temperature, whereas its intensity gradually increases with an increase in temperature (Figure 2A). This is attributed to the thermal-induced crystal phase transition of VO₂.^{34,35} Upon increasing temperature, the crystal phase changes from insulating monoclinic to metallic rutile states, releasing the free electrons to support the plasmon resonance, resulting in an increased absorption in the NIR region. In addition, an LSPR red-shift is observed when temperature is increased (Figure 2A), which is consistent with the previous report on 2D-patterned VO₂ NPs on quartz substrates.³³ The gradual emergence of LSPR in 70°C–90°C corresponds to the hysteresis loop under increasing temperature (Figure 2B). The crystal phase transition is further identified by the temperature-dependent X-ray diffraction (XRD) (Figure S3). These intermediate states during the transition display a gradient of metallic fraction,³³ resulting in a gradual LSPR change. The critical temperature of VO₂ (~65°C) is maintained in the PDMS matrix (Figure S4). The LSPR on-off ratio is dependent on the quantity of VO₂ NPs. Both the transmittance contrast in the NIR range and the ΔT_{sol} increase with increasing VO₂ concentration from nominal 0.75% to 2.25% (Figures 2C and S5). Reported methods for active control of LSPR usually result in peak shifts, accompanied by peak width changes,¹⁹ while the thermal-induced LSPR intensity control is distinct and facile.

The LSPR position in the produced film is dependent on the ways to disperse VO₂ NPs during film preparation (unless specifying, the LSPR of VO₂ is measured on 95°C). The fabrication process includes stir, ultrasonic, and standing (Note S1). The LSPR position is observed to be blue-shift from ~1,380 to ~1,260 nm when introducing the ultrasonic process or prolonging the standing duration (Figure 2D). The blue-shift could be explained by the decrease of NPs' aggregation degrees (Figure S6), which decreases the distance between NPs. Plasmonic coupling arises when rutile VO₂ NPs come close to each other in nanoscale, inducing the red-shift of LSPR. To further understand the plasmonic coupling effects of VO₂, the extinction spectra of two VO₂ NPs (spheres of 80 nm in diameter) are calculated under a varied gap from 20 to 200 nm. It was observed that the extinction peak shifts from ~1,390 to ~1,250 nm at the gap of 20 and 200 nm, respectively, resulting in increasing intensity of the electric field in the gap (Figure S7). This simulation result may partially explain the aggregation effect in the experiment, which also observed the blue-shift (Figure 2E). In the experiment, the ultrasonic procedure facilitates the separation of aggregated NPs to individuals, while the standing process can precipitate aggregated NPs and reduce their amount in final films. Controlling the dispersion condition is considered as a static method because the LSPR is fixed on a produced sample. The static tunable LSPR is important, for example, in bio-sensing, imaging, and therapy as well as in solar energy-related applications.³¹

It is worth mentioning that an LSPR shift is also observed when a film is stretched (Figure 2F). On the sample prepared via 1-week standing, the LSPR position of the unstretched film is ~1,260 nm and shifts to a shorter wavelength of ~1,230 nm under a strain of 33%; however, increasing the strain to 67% or 100% does not induce further position change (Figure 2G). This stretch-induced LSPR shift is quite interesting. Previous studies of elastomerically active plasmonics

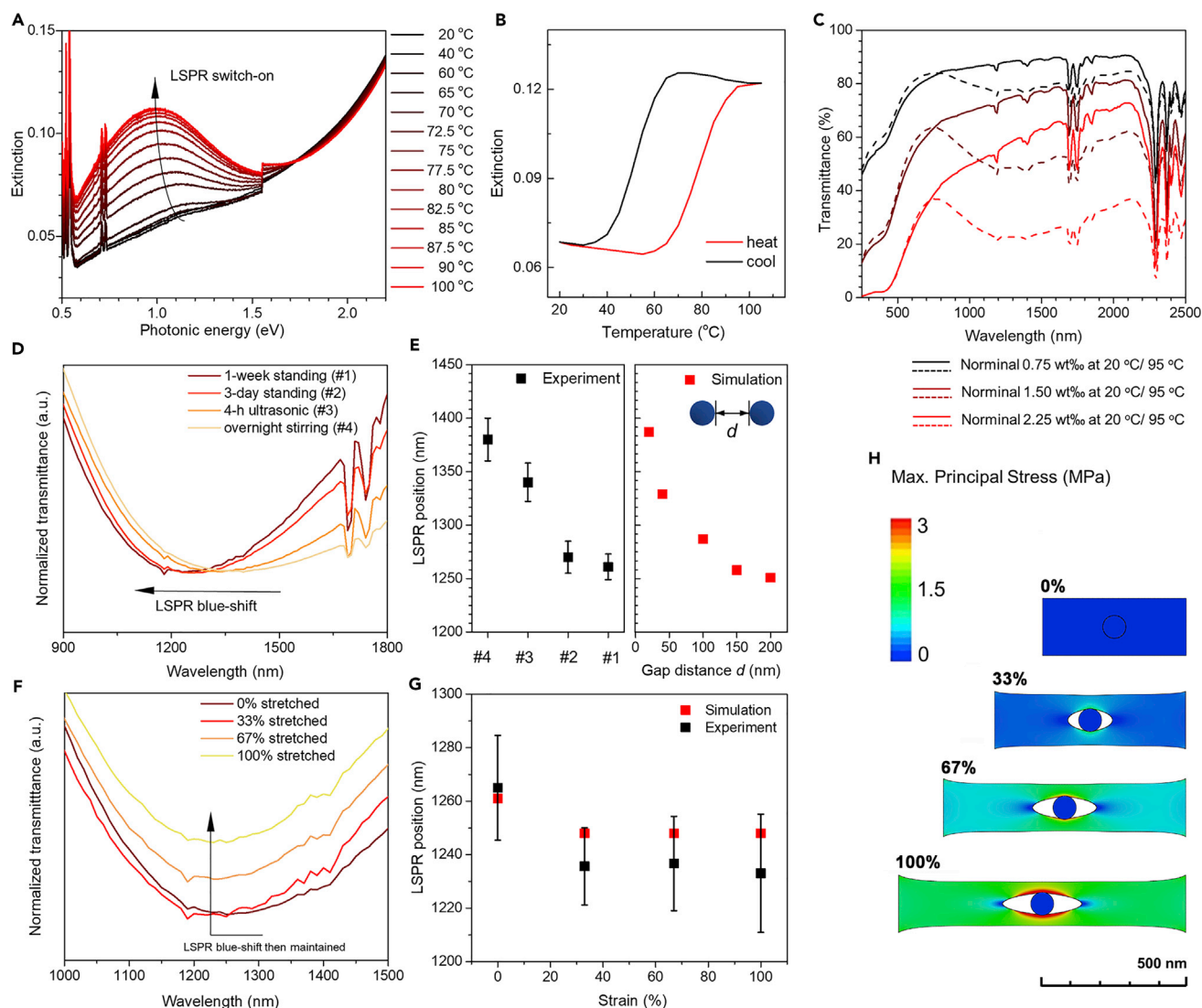


Figure 2. Active Localized Surface Plasmon Resonances

(A) Temperature-dependent extinction spectra of VO₂-PDMS composite under increasing temperature.
 (B) The hysteresis loop of extinction intensity at 1,260 nm (0.98 eV) during a heating and cooling process.
 (C) Transmittance spectra of the composite films with different VO₂ concentrations at 20°C and 95°C.
 (D) Normalized transmittance spectra of the samples under different dispersion conditions (sample #1–4).
 (E) Experimental LSPR positions on the sample #1–4 and calculated results on two VO₂ NPs with a gap varied from 20 to 200 nm. Error bars, SD. n = 3. Inset is the illustration of the gap (d).
 (F) Normalized transmittance spectra of the composite film under strains of 0%, 33%, 67%, and 100%.
 (G) Experimental and simulated LSPR positions under the strains. Error bars, SD. n = 3.
 (H) Simulated configuration transition of a VO₂ NP in PDMS matrix under an increasing strain, illustrated by four simulated stress contours under the strains of 0%, 33%, 67%, and 100%.

commonly report on dynamically tuning the gap in the nanoscale between two patterned plasmonic nanostructures on an elastomer surface.^{19,36} However, the case here may be different. The well-dispersed VO₂ NPs with a very low concentration (much lower than 1%) in the elastomer exhibit long distances (≥ 200 nm) next to each other (Figure S6A). Tuning gaps in such distances do not contribute to the coupling effect,^{19,33} eliminating the possibility of gap-dependent LSPR position as in previous reports.

To investigate the stretch-induced LSPR change, we further simulate the structural change of a VO₂ NP (diameter of 80 nm) embedded in the PDMS matrix under different stretching strains (Figure 2H). Upon increasing the stretch, the VO₂ NP was observed to delaminate from the interfacial boundary with the PDMS matrix in highly stressed regions, generating an ellipsoidal void around the NP due to the weak adhesion force between hydrophobic PDMS and hydrophilic VO₂.³⁷ Similar local delamination has also been observed on SiO₂ microspheres (hydrophilic) in a stretched PDMS matrix (hydrophobic).³⁸ The void forms and elongates along the stretching direction under increasing strain (Figure 2H), leading to the dielectric change on the surface of VO₂ NPs. The change from PDMS (reflective index of 1.4) to the air (reflective index of 1) leads to the blue-shift of LSPR peak position. We further calculated the extinction spectra of a VO₂ NP in the stretched PDMS matrix (Figure S8). We found that as the strain increases from 0% to 33%, a blue-shift of LSPR is also observed but remains unchanged with a further increase of strain. This is consistent with the experiment result (Figure 2G). The slight deviation from the experiment may be attributed to the oversimplified model of a single NP in the simulation, which cannot perfectly present the collective NPs in the experiment, including the imperfect surface property of NPs, anisotropic morphologies of NPs rather than perfect spheres, or non-sufficient local strains. The small shift in the spectrum region with relatively sparse solar energy distribution provides a negligible contribution to the solar energy modulation (Figure S9).

Kirigami-Inspired Reconfigurational Structures

The composite films (unless specifying, nominal 2.25‰ is applied) are further tailored by a cutter into various shapes, including the complex curve designs of “lion,” “butterfly,” and “flower”-like shapes (Figure 3A). The darkness variation in samples is due to the different VO₂ concentration. They are further developed to kirigami patterns. Figure 3B shows a design with alternant parallel line cuts. The patterned cuts gradually decouple from each other under an axial stretching, transforming to the non-compact configuration as cuts open up (Figure 3B). A 2D-to-3D transformation is also achievable by a kirigami design with perpendicularly crossed line cuts (Figure 3C). This planar design is transformed programmatically to a 3D architecture with buckling through a similar process as the cuts open up (Figure 3C). Specific geometric designs of these two kirigami patterns are indicated in Figures S10 and S11.

To better understand the effects of kirigami patterns and VO₂ nanocomposite films on the mechanical properties, we measured the stress-strain curves of the pure PDMS, the VO₂-PDMS composite, and the kirigami-patterned VO₂-PDMS composite. The kirigami design in Figure 3B is applied in the following discussion. Similar stress-strain curves are observed on PDMS and VO₂-PDMS samples (Figure 3D) and samples with VO₂ concentration from a nominal 0.75‰ to 2.25% (Figure S12), demonstrating that the incorporation of such low concentrations induces little effect to mechanical properties of PDMS (Figure 3E). However, the introduction of kirigami patterns augments the strain from 100% to 260% and dramatically reduces stress and stiffness (Figure 3D). Compared with the other two, the kirigami-patterned VO₂-PDMS film displays significantly lower Young's modulus and toughness (Figure 3E). The stretchability enhancement is strongly related to the cutting design, especially the cut length (*l*) (Figure S10).³⁹ More importantly, such low stress is due to the configuration transition, resulting in very low local strains on the materials. We further applied a finite element simulation to investigate the local strain distribution. Under a strain of 100%, a very low local strain (less than 5%) is observed to be distributed along the majority of belt structures, and it is less than 10% even at cut tip

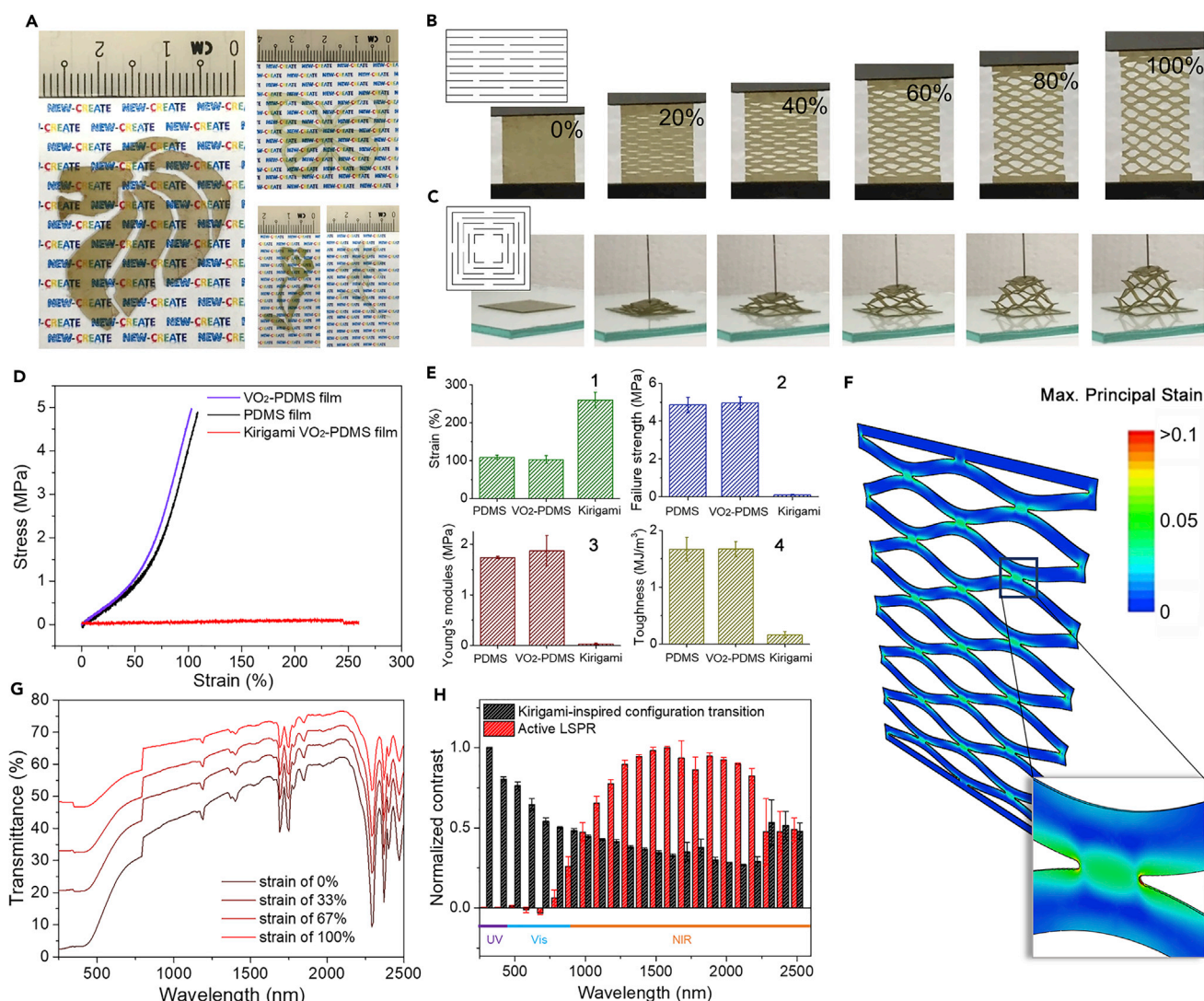


Figure 3. Kirigami-Inspired Reconfigurational Structures

(A) Photograph of the curved designs prepared by tailoring the VO₂-PDMS films, including “lion,” “butterfly,” and “flowers.” VO₂ concentration is nominal 1.50‰ and 0.75‰ for the (A2) and the (A4), respectively.

(B and C) Kirigami designs and their configurational transitions under stretch. (B) Illustration of the design with alternant parallel line cuts and the photograph of its configurations under an in-plane axial strain from 0% to 100%. (C) Illustration of the design with perpendicular crossed line cuts and the photographs of its 2D-to-3D configurations transitions under out-plane stress.

(D) Measured uniaxial stress-strain curves of the planar PDMS, the planar VO₂-PDMS composite, and the kirigami VO₂-PDMS films with the design in Figure 3B.

(E) Mechanical property analysis of stress, strain, Young’s modulus, and toughness. Error bars, SD. n = 3.

(F) SEM-simulated strain distributions of the kirigami VO₂-PDMS film and the magnified strain contour on a cut tip area as the inset.

(G) Transmittance spectra of kirigami-patterned VO₂-PDMS film under strains of 0%, 33%, 67%, and 100%.

(H) Normalized transmittance contrasts in the wavelength range from 250 to 2,500 nm. Error bars, SD. n = 5.

area (Figure 3F and the inset), which is the area that is subject to the maximum stress.¹⁷ The low local strain under stretch leads to the significant low stress as well as enhanced stretchability.

The local strain has been demonstrated to affect the LSPR position as shown in Figures 2F and 2G. Compared to the film without the kirigami pattern, the drastic lower local strains prevent the formation of air voids around the VO₂ NPs. Thus, the

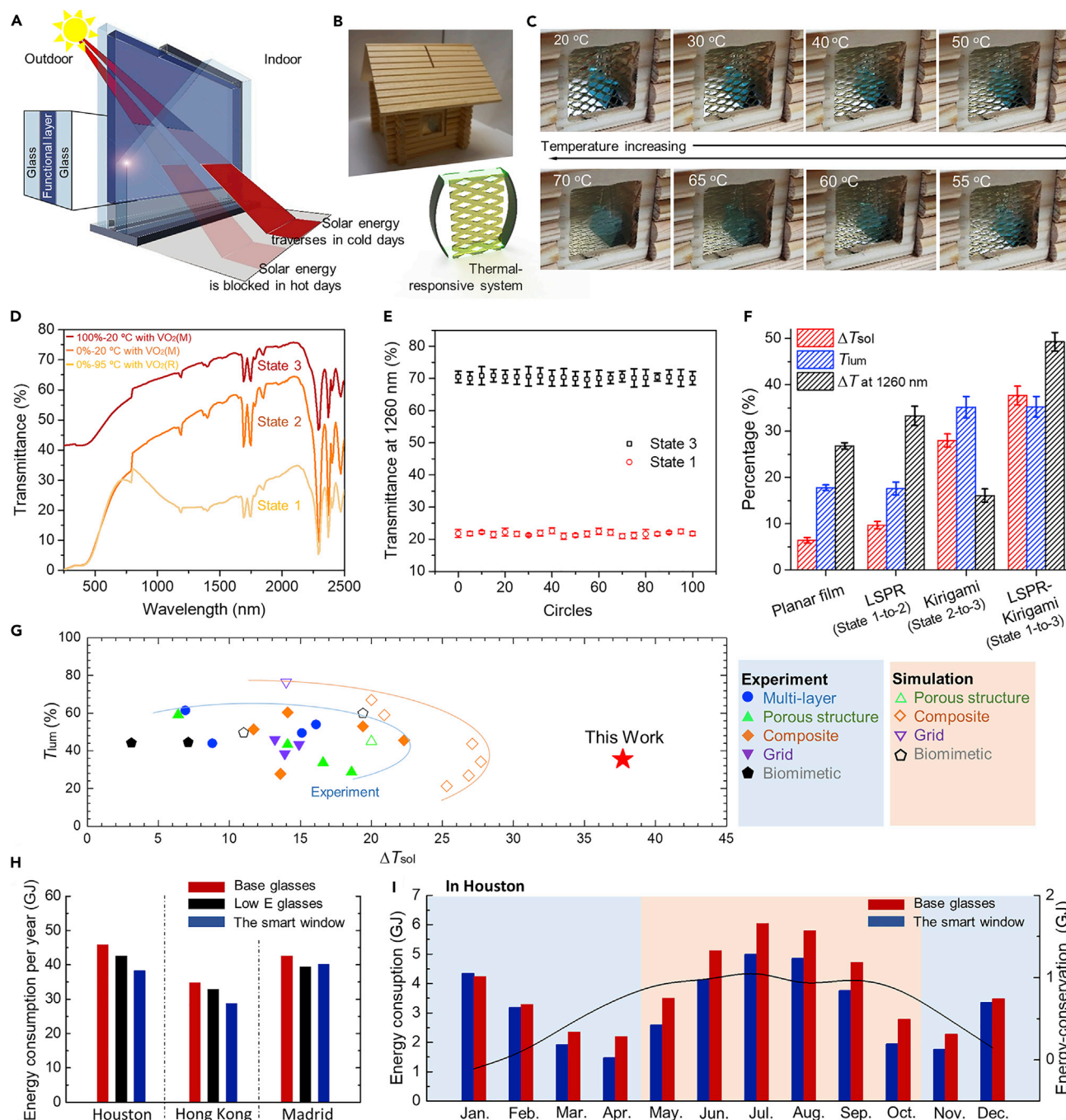


Figure 4. Smart Windows toward Energy Efficiency

(A) Illustration of an energy-saving smart window that adaptively reduces the indoor solar energy irradiation under elevated temperature.

(B) The photograph of the house model and a schematic of the thermal-responsive system for the smart window demo.

(C) The configuration transition of the smart window model under increasing temperature. The fully thermal responsive system is applied.

(D) Transmittance spectra of the film at (state 1) 90 °C with compact configuration, (state 2) 20 °C with compact configuration, and (state 3) 20 °C with non-compact configuration (strain of 100%).

(E) Cycling test of the film switching between states 1 and 3. Error bars, SD. $n = 3$.

(F) Calculated ΔT_{sol} , T_{lum} , and $\Delta T_{1260\text{ nm}}$ of the film in states 1–3 and the reference film based on planar VO_2 and PDMS, respectively. Error bars, SD. $n = 3$.

Figure 4. Continued

(G) Comparison of this work with the best-reported experiment and simulation works regarding the T_{lum} and ΔT_{sol} .^{33,40–55} Reported methods of VO₂-based transparent thermochromism systems are classified and denoted using different colors on the right of (G).

(H and I) Simulation results of building heating and cooling energy. (H) Calculated energy consumptions per year for the material applied in Houston, USA; Hong Kong, China; and Madrid, Spain, respectively, comparing to the base and low E glasses. (I) Comparison of the monthly energy consumption of the material and base glasses applied in Houston.

introduction of kirigami pattern can maintain an unchanged LSPR position during the film stretch.

The stretch-induced reconfigurable structures also bring about dynamic transmittance control. It is demonstrated that the transmittance of normal incidence gradually increases by stretching the kirigami VO₂-PDMS film in an in-plane axial direction (Figure 3G). This can be attributed to the decrease of the effective areas under increasing strains from 0% to 100%.

We further examine the modulation effectiveness in different wavelengths for stretch-induced structural transition and thermal-induced active-LSPR methods, respectively (Figure 3H). The analysis is based on the transmittance spectra in Figures 2C and 3G by calculating the normalized transmittance contrast in different wavelengths under the respective stimuli. It is observed that the structural transition and the thermal-induced active-LSPR present dominant controls in UV-visible and NIR ranges, respectively (Figure 3H). In the UV-visible region, the VO₂-PDMS film shows a high absorption that is sensitive to the effective area change. In the NIR region, the film with relatively high transparency displays less sensitivity to the effective area change but very high sensitivity to the temperature-dependent LSPR. These two are complementary to each other, contributing toward a broadband tunability covering a 250–2,500 nm spectrum range.

Smart Windows toward Energy Efficiency

The kirigami VO₂-PDMS film (nominal 2.25%) is demonstrated as a smart window. Among various types of smart windows, the thermochromic-based one promises a passive way to reduce the building energy consumption by passively modulating the indoor solar energy in response to environmental temperature (Figure 4A).^{1,5} The fully thermal response is achieved on produced sample by, for example, integrating with thermal-shrinkable tapes made of polyolefin (Figure S13). The adaptive thermal-responsive system was applied in a house demo to demonstrate the potential for the thermochromic smart window (Figure 4B). It was observed that the film changed from a non-compact (strain of 100%) to a compact (strain of 0%) state through a gradual close up of kirigami cuts under increasing temperature, accompanied with a less-clear image of the indoor clamp (Figure 4C). To examine the performance when applying to energy-saving smart windows, we further measured the transmittance spectra of the film in the thermal-responsive system at 20°C and 95°C temperatures. The film at 95°C (state 1 in Figure 4D) demonstrated a significantly lower transmittance in UV-vis-NIR regions than the film at 20°C (state 3 in Figure 4D). This is because the film exhibits a compact structure with an “on” state of LSPR, while it displays a non-compact structure with an “off” state of LSPR. The transmittance spectra at intermediate temperatures are recorded as in Figure S14 with/without compact configurations, of which both display decreasing NIR transmittance under increasing temperatures. The film is stable during the switch between these two states and no obvious contrast decrease is observed on 1,260 nm after making a switch 100 times between these two states (Figure 4E). This good stability is attributed to the good cyclicity of VO₂ NPs and kirigami structures (Figure S15).^{12,33}

Respective contributions of the active LSPR and the kirigami structure are identified by comparing the transmittance spectrum of the 0%-stretched film at 20°C (state 2 in Figure 4D). More specifically, the contributions of active LSPR, kirigami, and their synergistic effects are calculated based on the contrasts of states 1 to 2, 2 to 3, and 1 to 3 in Figure 4D, respectively. The results of ΔT_{sol} , average visible transmittance (T_{lum}), and the transmittance contrast at 1,260 nm ($\Delta T_{1260 \text{ nm}}$) are presented in Figure 4F (detailed calculation methods are described in Note S2). It is demonstrated that sole active LSPR and kirigami structure effects contribute to ΔT_{sol} of 9.7% and 28.0%, respectively. The combined effect of the LSPR and kirigami structures gives record-high ΔT_{sol} up to 37.7%, as well as a significantly enhanced T_{lum} from 17.6% (plasmonic sample) to 35.2% ("plasmonic-kirigami sample" as shown in Figure 4F). Meanwhile, the introduction of active LSPR largely enhances the NIR controllability; for example, the contrast at 1,260 nm ΔT_{1260} increases from 16.1% on the kirigami sample to 49.3% on the plasmonic kirigami sample (Figure 4F). All three parameters, ΔT_{sol} , T_{lum} , and ΔT_{1260} , are enhanced simultaneously by such a simple approach.

The produced reconfigurable metamaterial with active LSPR displays ~490% greater ΔT_{sol} and ~100% higher T_{lum} than the reference of a planar thermochromic VO₂ film (Figures 4F and S16). The achieved ΔT_{sol} of 37.7% surpasses the results in reported works among VO₂-based transparent thermochromism systems. Compared with reported works, the method here provides a significantly greater ΔT_{sol} than other approaches targeting performance enhancement as summarized in Figure 4G.^{33,40–51} The experimental results even break the theoretical limitations simulated based on these methods (Figure 4G).^{41,49,52–55} Shortages remain such as the visible reconfigurable transition and additional space required when applying in practice. These may be solved by reducing the dimension of kirigami cuts and the delicate design of windows.

The electric conservation ability of the smart window was evaluated by application to architecture in Houston, US; Hong Kong, China; and Madrid, Spain. The building (Figure S17) with smart windows demonstrated 7.54, 6.05, and 2.41 GJ lower energy consumption per year than with those with base glasses in Houston, Hong Kong, and Madrid, respectively (Figure 4H). Compared with low emissivity (low E) glasses, this material also displayed better energy conservation for buildings in Houston and Madrid (Figure 4H). To further assess its performance in a year, we calculated monthly energy consumption for heating and cooling of the room in Houston (Figure 4I). The room with such smart windows showed less energy consumption than that with base glasses from February to December (Figure 4I). Moreover, we calculate the energy conservation by plotting the energy consumption difference between the smart window and base glasses as the black line in Figure 4I. The smart window displays peak energy conservation during the summer (pink area in Figure 4I), which demonstrates that the smart window can significantly reduce the energy for cooling in summer. We further demonstrated that the integration of reconfiguration and active LSPR displays significant enhancement in energy conservation than the individual one, attributing to the benefits of the reconfiguration and active LSPR in cold seasons and hot seasons, respectively (Figure S18). Although the optical response at 95°C was used in the simulation, it is ready to achieve similar performance with doped VO₂ NP with much reduced τ_c .¹ This calculation demonstrates the great potential of the concept of active plasmonics in kirigami configurations for smart windows toward adaptive energy saving over years.

DISCUSSION

Promoting the thermochromic performance has consumed long-lasting research efforts; however, it is considerably limited by materials' intrinsic properties. Here, we

are thinking out of the box by introducing the kirigami structures. To our knowledge, the method of integrating the active LSPR of VO₂ with reconfigurable metamaterials has not been reported yet, though the VO₂ is the most studied materials for thermo-chroic smart windows.⁵ The reconfigurable structure transition display dominated controls in UV-vis spectrum range, while the thermal-induced switchable LSPR of VO₂ offers remarkable tunability in NIR range, resulting in a decent ΔT_{sol} (37%), outperforming the best reports based on multilayer, porosity, composite, grid, and bio-mimetic structures.¹ The achieved thermo-mechanical system can also be designed to be fully thermal responsive. We further demonstrated that the smart window promises great potential to lower the annual energy consumption of buildings in Houston, Hong Kong, and Madrid. Though the size of the kirigami structures and the applied strain (100%) may not be preferred for practical applications, further improvement in methods may aid and the concept may accelerate the development on high-performance energy-efficient smart windows, for example, by introducing stimuli-responsive metamaterials.

The method for tuning the plasmonics through the strain-induced local dielectric changes is facile, robust, and inexpensive and, to our knowledge, has not been reported in literature. Reported methods require either sophisticated devices or complicated and expensive fabrication processes for materials, such as an electro-chemical system for dynamic redox reactions³² or electron-beam lithography for metasurface fabrications.⁵⁶ The simple void-induced dielectric change under stretch may be further improved and applied to diverse plasmonic materials.³¹ Besides, we also envision the study may inspire further investigations of plasmonics on kirigami metamaterials, such as dynamically tilting the anisotropic plasmonic nanocrystals in kirigami metamaterials or tuning the surface plasmons in kirigami-inspired nano/micro-structures.

In summary, we demonstrate a facile method for solar modulation toward the high-performance smart window. A kirigami-inspired reconfigurable metamaterial is developed using a stimuli-responsive composite consisting of elastomer and well-dispersed VO₂ NPs, exhibiting adaptive, broadband, and high-contrast solar modulation. The thermal-, aggregation-, and strain-induced LSPR changes are demonstrated. This method exhibits an ultra-high ΔT_{sol} (37.7%) when applied to thermochromic-based smart windows. This synergetic thermo-mechanical system may inspire developments in smart windows, building energy economization, as well as fundamental studies of plasmonic controls in metastructures.

EXPERIMENTAL PROCEDURES

Preparation of Composite Films

Composite films are prepared by curing the pre-mixed NPs with the precursor and curing agent of PDMS gel (SYLGARD 184, Dow Corning). In detail, VO₂ NPs (Jincheng, China) and the precursor and curing agent of PDMS gel are mixed with 54 mL hexane (Aik Moh, Singapore) in a glass bottle. The quantities of the precursor and the curing agent are fixed to 2.0 and 0.2 (weight ratio of 10:1). The VO₂ NPs are weighted to be 15, 30, and 45 mg as nominal 0.75 wt %, 1.5 wt %, and 2.25 wt % for samples with different VO₂ concentration. The mixture was blended by a magnetic stirrer, followed by an ultrasonic and/or a standing process to reduce the concentration of aggregated VO₂ NPs. All samples were stirred overnight, while durations for ultrasonic and standing processes were varied for samples; details are presented in the next paragraph. After that, 18 mL supernatant of the suspension was transferred to a glass Petri dish with a diameter of 5.6 cm. The hexane is removed by overnight

evaporation at room temperature in a fume hood. After hexane removal, the stiff mixture was cured in an oven at 100°C for 30 min, and thereafter at 150°C for 10 min. The produced VO₂-PDMS film is easily peeled off from the Petri dish using a tweezer. A cutter is used directly to fabricate kirigami patterns on produced films.

Simulations

A three-dimensional finite-different-time-domain (3D FDTD) method was used to calculate LSPR of VO₂ NPs. Commercial Finite Element software (ABAQUS) was used to simulate the mechanics of both local VO₂/PDMS unit and global kirigami structure. Building energy usage was calculated using Energyplus with an air conditioner (Table S1). For details of simulation methods, please refer to the Supplemental Information.

SUPPLEMENTAL INFORMATION

Supplemental Information includes Supplemental Experimental Procedures, 18 figures, 1 table, and 2 notes and can be found with this article online at <https://doi.org/10.1016/j.joule.2018.12.024>.

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AUTHOR CONTRIBUTIONS

Y.L. proposed and guided the project. Y.K. designed and performed most of the experiments and drafted the manuscript. Y.Z. and S.W. assisted in the mechanical property measurement and analysis. P.H. and S.W. assisted in the transmission electron microscopy measurement and analysis. Y.Y. and X.W. performed the FDTD simulation. Q.Z. and Y.T. performed the finite element method (FEM) simulation. Y.T. performed the building energy simulation. S.W., T.J.W., J.Y., J.P., Q.X., D.Z., and Y.L. discussed and revised the manuscript. All authors checked the manuscript.

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REFERENCES

1. Cui, Y., Ke, Y., Liu, C., Chen, Z., Wang, N., Zhang, L., Zhou, Y., Wang, S., Gao, Y., and Long, Y. (2018). Thermochromic VO₂ for energy-efficient smart windows. *Joule* 2, 1707–1746.
2. Barile, C.J., Slotcavage, D.J., Hou, J., Strand, M.T., Hernandez, T.S., and McGehee, M.D. (2017). Dynamic windows with neutral color, high contrast, and excellent durability using reversible metal electrodeposition. *Joule* 1, 133–145.
3. Llordés, A., Wang, Y., Fernandez-Martinez, A., Xiao, P., Lee, T., Poulain, A., Zandi, O., Saez Cabezas, C.A., Henkelman, G., and Milliron, D.J. (2016). Linear topology in amorphous metal oxide electrochromic networks obtained via low-temperature solution processing. *Nat. Mater.* 15, 1267–1273.
4. Lin, J., Lai, M., Dou, L., Kley, C.S., Chen, H., Peng, F., Sun, J., Lu, D., Hawks, S.A., Xie, C., et al. (2018). Thermochromic halide perovskite solar cells. *Nat. Mater.* 17, 261–267.
5. Ke, Y., Zhou, C., Zhou, Y., Wang, S., Chan, S.H., and Long, Y. (2018). Emerging thermal-responsive materials and integrated techniques targeting the energy-efficient smart window application. *Adv. Funct. Mater.* 28.
6. Blees, M.K., Barnard, A.W., Rose, P.A., Roberts, S.P., McGill, K.L., Huang, P.Y., Ruyack, A.R., Kevek, J.W., Kobrin, B., Muller, D.A., et al. (2015). Graphene kirigami. *Nature* 524, 204–207.
7. Shyu, T.C., Damasceno, P.F., Dodd, P.M., Lamoureux, A., Xu, L., Shlian, M., Shtein, M., Glotzer, S.C., and Kotov, N.A. (2015). A kirigami approach to engineering elasticity in nanocomposites through patterned defects. *Nat. Mater.* 14, 785–789.
8. Xu, L., Shyu, T.C., and Kotov, N.A. (2017). Origami and kirigami nanocomposites. *ACS Nano* 11, 7587–7599.
9. Castle, T., Sussman, D.M., Tanis, M., and Kamien, R.D. (2016). Additive lattice kirigami. *Sci. Adv.* 2, e1601258.

10. Lee, W., Liu, Y., Lee, Y., Sharma, B.K., Shinde, S.M., Kim, S.D., Nan, K., Yan, Z., Han, M., Huang, Y., et al. (2018). Two-dimensional materials in functional three-dimensional architectures with applications in photodetection and imaging. *Nat. Commun.* 9, 1417.
11. Tang, Y., Lin, G., Han, L., Qiu, S., Yang, S., and Yin, J. (2015). Design of hierarchically cut hinges for highly stretchable and reconfigurable metamaterials with enhanced strength. *Adv. Mater.* 27, 7181–7190.
12. Lv, Z., Luo, Y., Tang, Y., Wei, J., Zhu, Z., Zhou, X., Li, W., Zeng, Y., Zhang, W., Zhang, Y., et al. (2018). Editable supercapacitors with customizable stretchability based on mechanically strengthened ultralong MnO₂ nanowire composite. *Adv. Mater.* 30, 1704531.
13. Yamamoto, Y., Harada, S., Yamamoto, D., Honda, W., Arie, T., Akita, S., and Takeji, K. (2016). Printed multifunctional flexible device with an integrated motion sensor for health care monitoring. *Sci. Adv.* 2, e1601473.
14. Guo, H., Yeh, M.H., Lai, Y.C., Zi, Y., Wu, C., Wen, Z., Hu, C., and Wang, Z.L. (2016). All-in-one shape-adaptive self-charging power package for wearable electronics. *ACS Nano* 10, 10580–10588.
15. Lamoureux, A., Lee, K., Shlian, M., Forrest, S.R., and Shtein, M. (2015). Dynamic kirigami structures for integrated solar tracking. *Nat. Commun.* 6, 8092.
16. Xu, L., Wang, X., Kim, Y., Shyu, T.C., Lyu, J., and Kotov, N.A. (2016). Kirigami nanocomposites as wide-angle diffraction gratings. *ACS Nano* 10, 6156–6162.
17. Tang, Y., Lin, G., Yang, S., Yi, Y.K., Kamien, R.D., and Yin, J. (2017). Programmable kiri-kirigami metamaterials. *Adv. Mater.* 29, 1604262.
18. Wang, W., Li, C., Rodrigue, H., Yuan, F., Han, M.-W., Cho, M., and Ahn, S.-H. (2017). Kirigami/origami-based soft deployable reflector for optical beam steering. *Adv. Funct. Mater.* 27.
19. Jiang, N., Zhuo, X., and Wang, J. (2018). Active plasmonics: principles, structures, and applications. *Chem. Rev.* 118, 3054–3099.
20. Schuller, J.A., Barnard, E.S., Cai, W., Jun, Y.C., White, J.S., and Brongersma, M.L. (2010). Plasmonics for extreme light concentration and manipulation. *Nat. Mater.* 9, 193–204.
21. Willets, K.A., and Van Duyne, R.P. (2007). Localized surface plasmon resonance spectroscopy and sensing. *Annu. Rev. Phys. Chem.* 58, 267–297.
22. Emmanuel, F., and Samuel, G. (2008). Surface enhanced fluorescence. *J. Phys. D Appl. Phys.* 41.
23. Hou, W., and Cronin, S.B. (2013). A review of surface plasmon resonance-enhanced photocatalysis. *Adv. Funct. Mater.* 23, 1612–1619.
24. Zhou, L., Swearer, D.F., Zhang, C., Robotjazi, H., Zhao, H., Henderson, L., Dong, L., Christopher, P., Carter, E.A., Nordlander, P., et al. (2018). Quantifying hot carrier and thermal contributions in plasmonic photocatalysis. *Science* 362, 69–72.
25. Brongersma, M.L., Halas, N.J., and Nordlander, P. (2015). Plasmon-induced hot carrier science and technology. *Nat. Nanotechnol.* 10, 25–34.
26. Christopher, P., and Moskovits, M. (2017). Hot charge carrier transmission from plasmonic nanostructures. *Annu. Rev. Phys. Chem.* 68, 379–398.
27. Hao, Q., Li, W., Xu, H., Wang, J., Yin, Y., Wang, H., Ma, L., Ma, F., Jiang, X., Schmidt, O.G., et al. (2018). VO₂/TiN plasmonic thermochromic smart coatings for room-temperature applications. *Adv. Mater.* 30.
28. Zhu, X., Vannahme, C., Højlund-Nielsen, E., Mortensen, N.A., and Kristensen, A. (2016). Plasmonic colour laser printing. *Nat. Nanotechnol.* 11, 325–329.
29. Atwater, H.A., and Polman, A. (2010). Plasmonics for improved photovoltaic devices. *Nat. Mater.* 9, 205–213.
30. Hutter, E., and Fendler, J.H. (2004). Exploitation of localized surface plasmon resonance. *Adv. Mater.* 16, 1685–1706.
31. Agrawal, A., Cho, S.H., Zandi, O., Ghosh, S., Johns, R.W., and Milliron, D.J. (2018). Localized surface plasmon resonance in semiconductor nanocrystals. *Chem. Rev.* 118, 3121–3207.
32. Garcia, G., Buonsanti, R., Runnerstrom, E.L., Mendelsberg, R.J., Llores, A., Anders, A., Richardson, T.J., and Milliron, D.J. (2011). Dynamically modulating the surface plasmon resonance of doped semiconductor nanocrystals. *Nano Lett.* 11, 4415–4420.
33. Ke, Y., Wen, X., Zhao, D., Che, R., Xiong, Q., and Long, Y. (2017). Controllable fabrication of two-dimensional patterned VO₂ nanoparticle, nanodome, and nanonet arrays with tunable temperature-dependent localized surface plasmon resonance. *ACS Nano* 11, 7542–7551.
34. Chen, Y., Wang, Z., Chen, S., Ren, H., Wang, L., Zhang, G., Lu, Y., Jiang, J., Zou, C., and Luo, Y. (2018). Non-catalytic hydrogenation of VO₂ in acid solution. *Nat. Commun.* 9, 818.
35. Sun, K., Riedel, C.A., Urbani, A., Simeoni, M., Mengali, S., Zalkovskij, M., Bilenberg, B., de Groot, C.H., and Muskens, O.L. (2018). VO₂ thermochromic metamaterial-based smart optical solar reflector. *ACS Photonics* 5, 2280–2286.
36. Huang, F., and Baumberg, J.J. (2010). Actively tuned plasmons on elastically driven Au nanoparticle dimers. *Nano Lett.* 10, 1787–1792.
37. Moot, T., Palin, C., Mitran, S., Cahoon, J.F., and Lopez, R. (2016). Designing plasmon-enhanced thermochromic films using a vanadium dioxide nanoparticle elastomeric composite. *Adv. Opt. Mater.* 4, 578–583.
38. Ge, D., Lee, E., Yang, L., Cho, Y., Li, M., Gianola, D.S., and Yang, S. (2015). A robust smart window: reversibly switching from high transparency to angle-independent structural color display. *Adv. Mater.* 27, 2489–2495.
39. Guan, Y.S., Zhang, Z., Tang, Y., Yin, J., and Ren, S. (2018). Kirigami-inspired nanoconfined polymer conducting nanosheets with 2000% stretchability. *Adv. Mater.* 30, 1706390.
40. Zhang, Z., Gao, Y., Luo, H., Kang, L., Chen, Z., Du, J., Kanehira, M., Zhang, Y., and Wang, Z.L. (2011). Solution-based fabrication of vanadium dioxide on F: SnO₂ substrates with largely enhanced thermochromism and low-emissivity for energy-saving applications. *Energy Environ. Sci.* 4, 4290–4297.
41. Kang, L., Gao, Y., Luo, H., Chen, Z., Du, J., and Zhang, Z. (2011). Nanoporous thermochromic VO₂ films with low optical constants, enhanced luminous transmittance and thermochromic properties. *ACS Appl. Mater. Interfaces* 3, 135–138.
42. Gao, Y., Wang, S., Kang, L., Chen, Z., Du, J., Liu, X., Luo, H., and Kanehira, M. (2012). VO₂-Sb:SnO₂ composite thermochromic smart glass foil. *Energy Environ. Sci.* 5, 8234–8237.
43. Gao, Y., Wang, S., Luo, H., Dai, L., Cao, C., Liu, Y., Chen, Z., and Kanehira, M. (2012). Enhanced chemical stability of VO₂ nanoparticles by the formation of SiO₂/VO₂ core/shell structures and the application to transparent and flexible VO₂-based composite foils with excellent thermochromic properties for solar heat control. *Energy Environ. Sci.* 5, 6104–6110.
44. Shen, N., Chen, S., Chen, Z., Liu, X., Cao, C., Dong, B., Luo, H., Liu, J., and Gao, Y. (2014). The synthesis and performance of Zr-Doped and W-Zr-Codoped VO₂ nanoparticles and derived flexible foils. *J. Mater. Chem. A* 2, 15087–15093.
45. Chen, Z., Gao, Y., Kang, L., Cao, C., Chen, S., and Luo, H. (2014). Fine crystalline VO₂ nanoparticles: synthesis, abnormal phase transition temperatures and excellent optical properties of a derived VO₂ nanocomposite foil. *J. Mater. Chem. A* 2, 2718–2727.
46. Zhu, J., Zhou, Y., Wang, B., Zheng, J., Ji, S., Yao, H., Luo, H., and Jin, P. (2015). Vanadium dioxide nanoparticle-based thermochromic smart coating: high luminous transmittance, excellent solar regulation efficiency, and near room temperature phase transition. *ACS Appl. Mater. Interfaces* 7, 27796–27803.
47. Lu, Q., Liu, C., Wang, N., Magdassi, S., Mandler, D., and Long, Y. (2016). Periodic micro-patterned VO₂ thermochromic films by mesh printing. *J. Mater. Chem. C* 4, 8385–8391.
48. Liu, C., Long, Y., Magdassi, S., and Mandler, D. (2017). Ionic strength induced electrodeposition: a universal approach for nanomaterial deposition at selective areas. *Nanoscale* 9, 485–490.
49. Ke, Y., Balin, I., Wang, N., Lu, Q., Tok, A.I., White, T.J., Magdassi, S., Abdulhalim, I., and Long, Y. (2016). Two-dimensional SiO₂/VO₂ photonic crystals with statically visible and dynamically infrared modulated for smart window deployment. *ACS Appl. Mater. Interfaces* 8, 33112–33120.
50. Qian, X., Wang, N., Li, Y., Zhang, J., Xu, Z., and Long, Y. (2014). Bioinspired multifunctional vanadium dioxide: Improved thermochromism and hydrophobicity. *Langmuir* 30, 10766–10771.
51. Chang, T., Cao, X., Dedon, L.R., Long, S., Huang, A., Shao, Z., Li, N., Luo, H., and Jin, P.

- (2018). Optical design and stability study for ultrahigh-performance and long-lived vanadium dioxide-based thermochromic coatings. *Nano Energy* 44, 256–264.
52. Li, S.Y., Niklasson, G.A., and Granqvist, C.G. (2010). Nanothermochromics: Calculations for VO₂ nanoparticles in dielectric hosts show much improved luminous transmittance and solar energy transmittance modulation. *J. Appl. Phys.* 108, 063525.
53. Li, S.-Y., Niklasson, G.A., and Granqvist, C.G. (2011). Nanothermochromics with VO₂-based core-shell structures: calculated luminous and solar optical properties. *J. Appl. Phys.* 109, 113515.
54. Liu, C., Balin, I., Magdassi, S., Abdulhalim, I., and Long, Y. (2015). Vanadium dioxide nanogrid films for high transparency smart architectural window applications. *Opt. Express* 23, A124–A132.
55. Taylor, A., Parkin, I., Noor, N., Tummeltshammer, C., Brown, M.S., and Papakonstantinou, I. (2013). A bioinspired solution for spectrally selective Thermochromic VO₂ coated intelligent glazing. *Opt. Express* 21, A750–A764.
56. Pryce, I.M., Aydin, K., Kelaita, Y.A., Briggs, R.M., and Atwater, H.A. (2010). Highly strained compliant optical metamaterials with large frequency tunability. *Nano Lett.* 10, 4222–4227.