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# PNIPAM-based ionic hydrogels for enhanced privacy smart windows and flexible sensor

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## HIGHLIGHTS

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# G R A P H I C A L A B S T R A C T

- PNIPAM based ionic hydrogels smart window for privacy protection.
- Energy saving, anti-freezing, wide temperature range thermal responsiveness.
- Ultraviolet/near-infrared light blocking performance, long-term stability.
- PNSP hydrogel has excellent conductivity and solvation effect, making it suitable for flexible sensor.



#### ARTICLE INFO

Keywords: PNIPAM Ionic hydrogel Smart windows Privacy protection Flexible sensor

# ABSTRACT

The thermochromic materials are widely used in the smart window field because they can efficiently regulate solar radiation with temperature changes. Currently, most smart windows switch back and forth between opaque and transparent states to control solar radiation, which is very disadvantageous for the visibility of enclosed environments. Herein, in a binary solvent of ethylene glycol-water (EW), we are developing a series of thermoresponsive ion hydrogels suitable for smart windows by in-situ free radical polymerization of the thermoresponsive monomer N-isopropylacrylamide (NIPAM) and ionic monomers (amphiphilic, anionic, cationic). These smart windows exhibit excellent one-way transparency for privacy protection, allowing observation from a relatively dark private space to a public space outside the smart window during the day, while preventing a view from the relatively bright public space into the private space. Furthermore, these hydrogels demonstrate efficient blocking of ultraviolet / near-infrared radiation, low temperature resistance ( $\sim -40$  °C), wide temperature range thermal responsiveness ( $\sim -25-60$  °C), enabling effective regulation of solar heat radiation. Additionally, the anionic-NIPAM complex hydrogel possesses a high diffusion coefficient of water and excellent conductivity of 13.38 mS cm<sup>-1</sup>, which can be expanded its application in the field of flexible ion-conductive sensors.

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#### 1. Introduction

The global energy crisis and extreme climate change caused by energy consumption in human life have had a negative impact on human activities, embracing green living and energy conservation is in the common interest of humanity. Buildings account for 50 % of global energy demand [1,2], and windows are one of the major contributors to energy loss in buildings, accounting for 60 % of building losses [3]. Smart windows are becoming increasingly popular for improving building energy efficiency, it can freely switch their light transmittance performance according to various external environmental changes, such as heat [2,4], electricity [5,6], light [7], and mechanical [8], dynamically modulating solar radiation. Compared to electrochromic, photochromic, and mechanochromic materials, thermochromic materials have the advantage of directly utilizing the heat from solar radiation to more effectively regulate light transmittance performance. As a result, research on thermochromic smart windows has gained increasing attention [2,4,9–11].

Thermoresponsive smart windows are primarily composed of two glass layers with a layer of thermoresponsive material sandwiched in between. Common thermoresponsive materials include vanadium dioxide [12,13], perovskite [14], nanoparticles [15], and polymer hydrogels [10,16–18]. The lower critical solution temperature (LCST) of poly(N-isopropylacrylamide) (PNIPAM) hydrogel is around 32 °C, which is close to the comfortable temperature range for human sensory perception [19]. Therefore, research on PNIPAM hydrogel smart windows has attracted widespread attention [20]. Various studies have successfully developed PNIPAM smart windows with excellent visible light transmittance and solar modulation capabilities, some studies have also enhanced the freeze resistance and physical crosslinking of hydrogels by adding small amounts of organic solvents [10,21]. However, the co-nonsolvency effect caused by the preferential interaction between water and organic solvents in the presence of a large amounts of organic solvents can lead to the loss of temperature responsiveness and light transmittance performance in PNIPAM [21-24]. Therefore, how to optimize the performance and application of PNIPAM hydrogel under the influence of co-nonsolvency effect is a difficult point in current research.

Privacy protection ranks among the top concerns for individuals, making it a key area of research for the development of next-generation smart windows. Most thermochromic smart windows transition from transparent to opaque as the temperature increases, achieving high-temperature privacy protection and resistance against solar heat radiation. Conversely, other hydrogel-based smart windows undergo a transition from transparent to opaque as the temperature decreases, offering privacy protection at low temperatures [25–27]. However, these smart windows, while protecting privacy, also block external light sources, which is not only detrimental to the visibility in enclosed spaces but also requires additional energy for indoor lighting. Therefore, designing a privacy-protecting smart window that can achieve both privacy protection and provide good visibility conditions is a significant challenge.

In this study, thermoresponsive monomer N-isopropylacrylamide (NIPAM) polymerized separately with zwitterionic monomer sulfobetaine methacrylate (SBMA), or anionic monomer potassium 3-sulfopropyl methacrylate (SPMA), or cationic monomer methacryloyloxyethyl trimethylammonium chloride (MTAC) to fabricate thermoresponsive ionic hydrogels in a binary solvent of ethylene glycol-water (EW). Due to the competitive interaction between N-isopropyl groups in the side chains and water (H<sub>2</sub>O) or ethylene glycol (EG), the phase transition temperature of the ion-thermoresponsive hydrogels were tuned in a wide temperature range of -25-60 °C, resulting in a gradient transparency. Thus, a series novel multifunctional ion-thermoresponsive hydrogels, including zwitterionic PNSB, anionic PNSP, and cationic PNMT, were developed, which would endow hydrogel smart windows with excellent one-way transparency for privacy-protecting during daytime and also moderate gradient

atomizing for energy-saving performance as the ambient temperature increased. Moreover, these hydrogel windows possessed anti-freezing capabilities, being able to withstand temperatures below -40 °C, dynamically regulated infrared blocking capability for effectively control of solar thermal radiation. In addition, the smart window has a UV blocking performance of over 99.7 %, which is significantly higher than similar products currently available on the market [28]. Although both PNSP and PNMT hydrogels possessed outstanding ion conductivity due to the presence of free ions, PNSP hydrogel exhibited a much higher conductivity of 13.38 mS cm<sup>-1</sup>, which would expand its application in the field of PNIPAM-base sensors [29,30]. The larger coordination number of K<sup>+</sup> ions with water and higher water diffusion coefficient in PNSP hydrogel matrix obtained from the molecular dynamic simulation, clarified the huge swelling ratio and the excellent ion conductivity of PNSP hydrogels in a microscopic level. PNSP hydrogel has the ability to withstand fatigue tensile strain over a thousand times and can stably monitor the activities of human joint organs.

# 2. Materials and methods

#### 2.1. Materials

N-isopropylacrylamide (NIPAM, 98 %, Shanghai Macklin), methacryloyloxyethyl sulfonic betaine (SBMA, 98 %, ENERGY-CHEMIAL, Shanghai), 3-sulfopropyl methacrylate potassium salt (SPMA, 98 %, BOER Chemical, Shanghai), methyl acryloyloxyethyl trimethylammonium chloride (MTAC, 75 %, BOER Chemical, Shanghai), N,N'-methylenebisacrylamide (MBA, 99 %, Sigma-Aldrich, Shanghai), ammonium persulfate (APS, 98 %, Sigma-Aldrich, Shanghai), N,N,N',N'-tetramethylethylenediamine (TEMED, 99 %, Sigma-Aldrich, Shanghai), ethylene glycol (EG, 99 %, ENERGY-CHEMIAL, Shanghai), Vaseline (China National Pharmaceutical Group, Shanghai). Deionized water (18.2 M $\Omega$ ) was used in the experiment.

#### 2.2. Synthesis of hydrogels

All the hydrogels were prepared from the similar procedure with different formulations listed in Table S1. Briefly, a certain amount of monomer was dissolved in deionized water or ethylene glycol-water mixture to prepare monomer solution at room temperature. The cross-linking agent MBA, catalyst TEMED, and initiator APS were added sequentially by continue stirring. After all the components were completely dissolved, the reaction solutions were poured into a pre-made mold with a sandwich structure (double layer glass with a poly-vinyl chloride interlayer, all with a thickness of 1 mm). The polymerization reaction carried out at room temperature for 1 hour.

#### 2.3. Transmittance measurement of the hydrogels

The hydrogel smart window is placed in a water bath and heated or cooled. Then, the transmittance of the hydrogel at that temperature is measured using a solar film spectrophotometer. The temperature range for measurement is 5–60 °C. The UV transmittance at 365 nm, visible light transmittance in the range of 380–760 nm, and near-infrared transmittance at 940 nm are measured. The hydrogel is prepared into thin sheets with dimensions of 20 mm  $\times$  20 mm  $\times$  1 mm. The UV-visible-near-infrared spectrophotometer (Lambda 950, Varian, USA) is used to measure the transmittance of UV–visible-near-infrared light (wavelength range: 200–2000 nm). The hydrogel is also prepared into thin sheets with dimensions of 30 mm  $\times$  10 mm  $\times$  1 mm, and its transmittance of UV–visible light (wavelength range: 300–800 nm) is measured using a UV–visible spectrophotometer (UV-2450, Shimadzu Corporation).

## 2.4. FT-IR spectrum characterization

The FT-IR spectrum of the hydrogel is measured using a Fourier Transform Infrared spectrometer (Nicolet Magna-IR 550, Thermo Fisher Scientific). The wavenumber range for the measurement is  $500-4000 \text{ cm}^{-1}$ .

#### 2.5. Microscopic morphology characterization

Firstly, the hydrogel is swollen at room temperature. Then, the swollen hydrogel is fractured using liquid nitrogen, and the fractured hydrogel is freeze-dried. The microscopic morphology of the fracture surface of the hydrogel is then measured using a Tungsten filament Scanning Electron Microscope (S-3400 N, Hitachi).

#### 2.6. Water contact angle characterization

The hydrophilicity of the hydrogel is measured at 25 and 45  $^{\circ}$ C using an optical contact angle tester (JC2000D, Shanghai Zhongchen Digital Technology Equipment Co., Ltd.).

#### 2.7. Thermal performance characterization

The thermal performance of the hydrogel is measured using a differential scanning calorimeter (DSC8500, PerkinElmer). The heating rate of the sample is 10 °C min<sup>-1</sup>, and the detection range is from -40–40 °C.

#### 2.8. Mechanical performance characterization

The mechanical performance of the hydrogel is measured using an electronic universal testing machine (CMT4204, MTS Systems Corporation Co., Ltd., China). The hydrogel is prepared into a dumbbell-shaped tensile specimen (with a gauge length of 40 mm, width of 5 mm, and thickness of 2 mm) for uniaxial tensile testing. The stretching rate is 200 mm/min, and the test is terminated when the hydrogel ruptures.

#### 2.9. Molecular dynamics simulation (MD)

The mass transfer behavior and hydrogen bond network in the hydrogel system were studied by molecular dynamics (MD) simulation. We set up three different systems according to the molar concentrations of hydrogel components in the experiment (Table S2). The first system consists of 33 NIPAM molecules, 4 SBMA molecules, 81 EG molecules, and 278 water molecules to simulate PNSB hydrogel system. The second system comprises 22 NIPAM molecules, 10 SPMA molecules, 81 EG molecules, 278 water molecules, and 10 potassium ions to simulate PNSP hydrogel system. The third system consists of 33 NIPAM molecules, 6 MTAC molecules, 81 EG molecules, 278 water molecules, and six chloride ions to simulate the PNMT hydrogel system. The force field parameters is OPLS-AA force field which was taken from the GROMOS force field [31]. All MD simulations were performed with the GROMACS package [32]. A cubic periodic boundary condition box and the SPC/E water model are used. The long-range electrostatic interactions were handled by the particle-mesh Ewald (PME) method with a cutoff radius of 1.4 nm [33]. The LINCS algorithm constrains the bonds containing hydrogen atoms [34]. The Verlet algorithm was used as an integrator of Newton's equation of motion [35]. The time step is set as 1 fs for all the simulations. The systems were first subjected to energy minimization by the steepest descent and conjugate gradient method. Then, the systems were heated slowly to 310 K in 200 ps and equilibrated for 20 ns in an NPT ensemble with a v-rescale thermostat [36] and Berendsen barostat [37]. The stability of the system is demonstrated through the analysis of trajectory data in the NPT ensemble.

2.10 Moisture retention performance and swelling performance

**characterization.** The hydrogel is placed in a silica gel desiccator (25 °C, 36 % RH) to measure the weight change of the hydrogel within 12 hours. The prepared hydrogel is swollen in deionized water (25 °C, 18.2 MΩ) to reach equilibrium, and then dried in a thermostatic convection drying oven at 60 °C until it reaches equilibrium. The equilibrium swelling ratio of the hydrogel is calculated using the following formula (1), where W<sub>E</sub> represent the mass of the hydrogel at room temperature equilibrium swelling, and W<sub>D</sub> represents the mass of the hydrogel after drying at 60 °C.

Swelling rate 
$$\left(\frac{g}{g}\right) = \frac{W_E - W_D}{W_D}$$
 (1)

#### 2.10. Thermal insulation performance characterization of the hydrogel

A double-glazed window sealed with a PVC circular interlayer is used as a control, and a window injected with the hydrogel is used to simulate an intelligent hydrogel window. The hydrogel has a thickness of 1 mm and a diameter of 30 mm, while the glass has a thickness of 1 mm and a diameter of 35 mm, and the PVC ring has a thickness of 1 mm and a width of 5 mm. A thermal insulation box simulating a building is used, with external dimensions of 12.5 cm  $\times$  16.0 cm  $\times$  22.5 cm, and internal dimensions of 10 cm imes 12.5 cm imes 20.0 cm. A heating lamp with a power of 275 W is used to simulate direct sunlight on the smart window, with the filament located 25 cm away from the intelligent window. The temperature change inside the thermal insulation box is measured in real-time using a built-in temperature detector. The energy-saving efficiency of the intelligent window is calculated using Eq. (2), where Q represents the energy in kJ m<sup>-2</sup>,  $\Delta T$  represents the average temperature difference between the test group and the control group,  $\rho_{air}$  represents the air density of 1.29 kg m<sup>-3</sup>, C<sub>p-air</sub> represents the specific heat capacity of air of 1.004 kJ kg $^{-1}$ K $^{-1}$ , V<sub>box</sub> represents the space of the simulated building, and Swindow represents the effective area of the intelligent window.

$$Q = \Delta T \rho_{air} C_{p-air} \frac{V_{box}}{S_{window}}$$
<sup>(2)</sup>

#### 2.11. Measurement of Conductivity and Sensing Performance of Hydrogel

The resistance R of the hydrogel is measured using a UTR digital bridge, and the length L and cross-sectional area as of the hydrogel are measured using an electronic caliper. Then, the ionic conductivity  $\kappa$  of the hydrogel is calculated using Eq. (3). The hydrogel is encapsulated and connected to copper electrodes using 3 M VHB adhesive. The relative change in resistance during the stretching process of the hydrogel and human motion is measured using a UTR digital bridge. The relative change in resistance is calculated using Eq. (4), where R<sub>0</sub> is the resistance before stretching and R<sub>S</sub> is the resistance after stretching. The gauge factor (GF) was calculated by Eq. (5), where  $\Delta R/R_0$  was the relative resistance change and  $\varepsilon$  was the applied strain.

$$\kappa = \frac{L}{R \cdot A_s} \tag{3}$$

$$\frac{\Delta R}{R_0} = \frac{R_s - R_0}{R_0} \tag{4}$$

$$GF = \frac{\Delta R/R_0}{\varepsilon}$$
(5)

#### 3. Results and discussion

#### 3.1. Structure, morphology and property characterization

The PNIPAM hydrogel smart windows have a reversible transition between transparency and opacity due to the thermo-triggered phase transition at LCST, which will achieve energy-saving. However, the totally opaque windows will highly reduce the light intensity in the room and also obstruct the view of those inside. Achieving effective thermo-chromic performance as well as semi-transparency with gradient changes and one-way transparency of light in hydrogels that are energy-saving and privacy-protection for smart window applications remains a significant challenge. To address this issue, we have developed ion-PNIPAM hydrogels (Scheme 1), which have been prepared using a one-pot method followed different formulations (Figure S1, Table S1, Supplementary). These thermoresponsive ionic hydrogels will provide a solution for achieving both privacy-protection and energy-saving in hydrogel smart windows. Simultaneously, the high ionic conductivity of the ion-PNIPAM hydrogels opens a way for implantable and wearable sensors.

The characteristic functional groups of these hydrogels were measured through Fourier-transform infrared spectroscopy (Fig. 1a). The peaks at  $3343 \text{ cm}^{-1}$  in the five hydrogels are characteristic peaks of -OH stretching vibrations in the hydrogel. Additionally, peaks at  $1472 \text{ cm}^{-1}$  and  $1268 \text{ cm}^{-1}$  correspond to the stretching vibrations of

-CH<sub>2</sub>- and -NH- groups, respectively. The peak at  $1634 \text{ cm}^{-1}$  corresponds to the -C=O stretching vibration characteristic peak of the PNIPAM chain segment in the five hydrogels [17]. The peak at 1728 cm<sup>-1</sup> corresponds to the stretching vibration of the -COO- ester carbonyl group in the side chains of PNSB, PNSP, and PNMT hydrogels, while peaks at 1175 cm<sup>-1</sup> and 1044 cm<sup>-1</sup> correspond to the asymmetric and symmetric stretching vibrations of the -SO<sub>3</sub> groups on the side chains of PNSB and PNSP, respectively [38,39]. The peak at 955 cm<sup>-1</sup> corresponds to the stretching vibration of the quaternary ammonium group on the PNMT side chain [40].

The PNSB, PNSP, and PNMT hydrogels possess different types of porous structures (Fig. 1b) but similar appearance with a milky white color (Fig. 1c). It can be observed that PNSB has larger pore sizes, approximately ranging from  $100 \,\mu\text{m}$  to  $200 \,\mu\text{m}$ , with the self-interaction between zwitterions being the main reason for the low physical cross-linking structure of PNSB hydrogel. The PNSP hydrogel has a very rich porous structure, with pore sizes in the range of  $20{-}50 \,\mu\text{m}$ , while the PNMT hydrogel has an irregular porous structure. EDS analysis shows that all three hydrogels contain significant amounts of C, N, and O



Scheme 1. Preparation scheme, structure and principle of multi-functional privacy protective ionic hydrogel.

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**Fig. 1.** (a) FT-IR spectra of PNIPAM0, PNIPAM, PNSB, PNSP, and PNMT hydrogels. (b) SEM images of (I) PNSB, (II) PNSP, and (III) PNMT hydrogels. (c) Photographs of (I) PNSB, (II) PNSP, and (III) PNMT hydrogels. (d) Differential scanning calorimetry (DSC) curves, (e) Tensile stress-strain curves, (f) Moisture retention performance, and (g) Equilibrium swelling ratio (SR<sub>E</sub>) of PNIPAM0, PNIPAM, PNSB, PNSP, and PNMT hydrogels.

elements and typical characteristic elements S in PNSB hydrogel, K and S in PNSP hydrogel, and Cl in PNMT hydrogel, respectively (Figs. S2–4, Supplementary).

Differential scanning calorimetry (DSC) analysis was employed to detect the phase transition behaviors of PNIPAM-based hydrogels within the temperature range of -40 °C to 40 °C (Fig. 1d). For PNIPAM0 hydrogel, two endothermic peaks were observed at 0 °C and 29.02 °C, respectively. The former was attributed to the freezing point peak of PNIPAM hydrogel at low temperatures, with an energy of 1472 mJ, while the latter was attributed to the characteristic phase transition peak of PNIPAM, with an energy of only 29.2 mJ, much smaller than the freezing point peak. It is of note that no endothermic peak was detected in the case of PNIPAM, PNSB, PNSP, and PNMT hydrogels with ethylene glycol-water binary solvent in this entire temperature region. This is

because the presence of ethylene glycol greatly enhances the freeze resistance of the hydrogels, allowing all four hydrogels to withstand temperatures below -40 °C without exhibiting a freezing point peak. These unique thermal transition behaviors were also confirmed by the transparency appearances of these PNIPAM-based hydrogels at different temperatures (Figure S5, Supplementary). PNIPAM0 hydrogels with water as solvent exhibited an opaque-to-transparent transition, while PNIPAM hydrogel with ethylene glycol-water binary solvent exhibited a transparent-to-opaque transition as the temperature increased from -25-25 °C, respectively.

The transparency of PNSB, PNSP, and PNMT ionic hydrogels varies slightly, showing a much weaker temperature sensitivity compared with PNIPAM hydrogels, and the widened temperature response range significantly reduces their phase transition endothermic peaks, thus no phase transition peaks is observed. Although the PNIPAM hydrogel becomes transparent at -25 °C and exhibits the phenomenon of LCST upon heating, the weak phase transition heat cannot be detected due to the influence of the ethylene glycol-water binary composition. This is consistent with the fact that the introduction of polyhydric alcohol solvents lowers the LCST of PNIPAM and weakens the phase transition peak, as reported in previous studies [21]. The mechanical properties of hydrogels were further evaluated through tensile and stress tests. The stress–strain curve (Fig. 1e) shows that the PNIPAM0 hydrogel has a high tensile strength of 1.73 MPa. However, introducing ethylene glycol solvent in the hydrogel greatly changed the mechanical properties of PNIPAM hydrogel, by decreasing the tensile strength to 0.69 MPa and significantly improving the tensile strains from 239 % to 755 %. The ultimate tensile strains and stresses of



**Fig. 2.** (a) Schematic illustration of the privacy protection hydrogel's effectiveness. Photos of smart windows with PNSB (left) and PNIPAM (right) hydrogels in bright environment (I) and dark environment (II) and their principles diagram of light regulation (III). (b) Transmittance performance of PNIPAM0, PNIPAM, and PSBMA hydrogels in the visible light range (380–760 nm) as a function of temperature (5–60 °C). (c) Ultraviolet-visible-near-infrared transmittance spectra of PNIPAM0, PNIPAM0, PNIPAM, PNSB, PNSP, and PNMT hydrogels. Ultraviolet-visible transmittance spectra of PNSB (d), PNSP (e), and PNMT (f) hydrogels at 25 °C. Temperature responsiveness of PNSB (g), PNSP (h), and PNMT (i) hydrogels under ultraviolet / visible / near-infrared light in the temperature range of 5–60 °C (inset: water contact angles on the corresponding hydrogels at 25 and 45 °C).

the PNSB, PNSP and PNMT ion hydrogels were similar or a little smaller than that of PNIPAM hydrogel with the same binary solvent. It is evident that the introduction of an ethylene glycol-water binary solvent system significantly increases the tensile strain while markedly decreasing the tensile stress of the hydrogels. The moisture retention performance of hydrogels in a silica gel desiccator (25 °C, RH=36 %) exhibited significant differences (Fig. 1f). After 12 hours, the mass retention rates of PNIPAMO, PNIPAM, PNSB, PNSP, and PNMT hydrogels were detected to be 39.05 %, 76.07 %, 84.68 %, 88.38 %, and 86.45 %, respectively. This shows that the moisturizing performance of the PNIPAM hydrogel, which incorporates ethylene glycol as a moisturizer, is significantly superior to that of the PNIPAMO hydrogel. Furthermore, the PNSB, PNSP, and PNMT hydrogels exhibit even stronger moisturizing properties than the PNIPAM hydrogel, attributed to the ionic functional groups (-SO3, -N  $(CH_3)_3^+$ ) possessing a stronger binding capacity with the ethylene glycolwater mixture.

We observed significant differences in the swelling properties of hydrogels by immersing in deionized water (Figure S6 and Movie S1, Supplementary). The equilibrium swelling ratios (SR<sub>E</sub>) of ion hydrogels were obviously higher than that of PNIPAM hydrogel. Especially for PNSP hydrogel, the SR<sub>F</sub> was detected as high as 544.78 g  $g^{-1}$ , almost 40 times that of PNIPAMO hydrogels (Fig. 1g). PNSP hydrogel is capable of absorbing water hundred times its own skeletal mass due to the hydrophilicity of the networks and abundant and highly flexible SO3 groups. The large number of oxygen atoms in the SO<sub>3</sub> groups can form strong hydrogen bonds with water molecules, imparting super-swelling characteristics to the hydrogel. While PNSB hydrogel also contains a significant amount of SO3 groups, the interactions between the zwitterionic groups constrain its water absorption capacity. Moreover, molecular dynamics simulations revealed significantly more solvent molecules around the polymer backbone of PNSP hydrogels, indicating a stronger solvation effect (Table S3, Supplementary). Therefore, PNSP hydrogels exhibit superior performance in moisturizing and water absorption.

Supplementary material related to this article can be found online at doi:10.1016/j.colsurfa.2024.134775.

#### 3.2. Optical and thermal response

We successfully synthesized a series privacy protection thermoresponsive ionic hydrogels smart window. Taking PNSB hydrogel as an example, its transmittance is affected by the ratio of reactants and the thickness (Figure S7 - S8 and Table S4, Supplementary). Therefore, this work fixed the thickness of the hydrogel at 1 mm. The PNSB zwitterionic hydrogel smart window, with privacy protection function, renders the images behind it unobservable in bright environments but allows clear observation in dark environments (Fig. 2a (I, II)). Similarly, the PNSP anionic hydrogel and PNMT cationic hydrogel also exhibit advanced privacy protection performance. Conversely, the PNIPAM hydrogel smart window renders images unobservable in both conditions (Figure S9, Movie S2, Supplementary). When the ambient brightness changes, the smart window can either display or block images behind it. When light enters from the bright A region, long-wavelength visible light will enter the relatively dark B region, allowing objects in the A region to be observed. Short-wavelength visible light will be reflected by the smart window, causing only the blue-white color of the smart window to be seen in the A region (Fig. 2a (III)). Although visible light in the B region also plays a similar role, both the long-wavelength visible light passing through the smart window and the short-wavelength visible light reflected back are diluted to an extent that is difficult to observe due to the incident and reflected light in the A region. Therefore, when these special transmittance performance hydrogels are applied to smart windows, it ensures that people in relatively dark private spaces can observe scenes in external public spaces, while people in relatively bright public spaces cannot see that in the dark private space (Figure S9 and Movie S2, Supplementary). We demonstrated the light transmittance of PNSB and PNIPAM hydrogels indoors to view outdoor scenes (Figure S10, Supplementary). Compared to other hydrogels that sacrifice visibility to achieve privacy protection [25,27,41], PNSB (PNSP, PNMT) hydrogels provide excellent visibility while ensuring privacy protection. This provides a new perspective for the development of privacy protection hydrogels. By the transparency changes of PNI-PAM hydrogel at a low temperature of -25 °C to an indoor temperature of 25 °C, it appears that the slightly transparent PNIPAM hydrogel at low temperatures becomes completely opaque at room temperature (Figure S5 and Movie S3, Supplementary). This is attributed to the co-nonsolvency effect of PNIPAM in ethylene glycol-water binary solvent.

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PNIPAM and PSBMA are thermo-responsive polymers with lower critical solution temperatures (LCST) and upper critical solution temperatures (UCST), respectively [20,42,43]. Therefore, we examined the changes in visible light transmittance of PNIPAMO, PNIPAM, and PSBMA hydrogels at different temperatures (Fig. 2b). At 20 °C, the visible light transmittance of PNIPAMO hydrogel is 86.5 %, which decreases to around 1.0 % as the temperature rises to 35 °C, consistent with previous studies [44]. PNIPAM hydrogel exhibits almost 1.5 % transmittance in the temperature range of 5-60 °C, demonstrating a completely opaque behavior due to the weakening of its temperature responsiveness and light transmittance. PSBMA hydrogel is opaque at -25 °C due to the electrostatic aggregation among zwitterionic groups, and fully transparent at 25 °C, and exhibits varying degrees of blue-white coloration during the temperature range (Figure S11 and Movie S4, Supplementary). This is because the hydrogel reflects more blue light and other low-wavelength light under these conditions, resulting in different shades of blue and white. Similarly, PSBMA hydrogel also provides unilateral light transmission for privacy protection under low-temperature conditions. When light passes through the hydrogel, more visible light in the shorter wavelength range is reflected by the hydrogel, making the hydrogel appear milky white in the direction of incident light, while longer wavelength visible light can penetrate the hydrogel, allowing observation of objects in the direction of incident light from the other side of the hydrogel. Likewise, anionic PNSP and cationic PNMT hydrogels exhibit the same unilateral light transmittance properties as zwitterionic PNSB hydrogels. Therefore, this study proposes zwitterionic PNSB, anionic PNSP, and cationic PNMT hydrogels for smart windows with privacy protection suitable for a wide temperature range, greatly expanding the new applications of ionic hydrogels. Furthermore, these series of hydrogels can be rendered in various colors to enrich their application scenarios (Figure S12, Supplementary).

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By observing the ultraviolet-visible-near infrared transmission spectra (200–2000 nm) of PNIPAM0, PNIPAM, PNSB, PNSP, and PNMT hydrogels, all hydrogels show similar transmittance curves in the nearinfrared region (>800 nm) apart from PNIPAM hydrogel, which exhibits near-zero transmittance across the entire wavelength range (Fig. 2c). The transmittance of PNSB, PNSP, and PNMT hydrogels demonstrates an exponential growth trend in the 200–800 nm range, while PNIPAM0 hydrogel shows a slow increase in transmittance in this range, consistent with the objective principle that longer wavelength light has greater penetration power than shorter wavelength light. The transmittance differences of hydrogels in the ultraviolet-visible light region may be related to their privacy protection properties.

To explore the privacy protection mechanisms of PNSB, PNSP, and PNMT hydrogels, we conducted a more detailed analysis of the ultraviolet-visible transmission spectra of these hydrogels in the range of 300–800 nm at 25 °C (Fig. 2d-f). The ultraviolet-visible transmission spectra of PNSB, PNSP, and PNMT hydrogels at 25 °C exhibit exponential curves with rapid increasing slopes from zero at short

wavelength range to semi-transparency at long wavelength range. This allows longer-wavelength visible light to penetrate through the hydrogel, while shorter-wavelength visible light is reflected by the hydrogel.

In contrast, the ultraviolet-visible transmission spectra of PNIPAM, PSBMA, PSPMA, and PMTAC hydrogels at 25 °C show a trend of slow increase in slope, attributed to their stronger transmittance capability for longer wavelength light. These types of hydrogels exhibit either completely transparent or blurry transparency, but none demonstrate the unique unidirectional light-transmitting property. Comparing the ultraviolet-visible transmission curves of PNSB, PNSP, and PNMT hydrogels at 25  $^\circ\text{C}$  and 45  $^\circ\text{C},$  it reveals a significant variation in the transmittance of PNSB hydrogel at different temperatures, indicating a strong thermal responsiveness. Whereas, the transmittance of PNSP and PNMT hydrogels shows minimal changes with temperature, as the anionic / cationic groups in the hydrogels are more independent compared to zwitterionic groups. The interactions and competitive attraction among the anionic / cationic groups, N-isopropyl segments, and ethylene glycol-water binary solvent significantly weaken the thermal responsiveness of the PNIPAM chains.

Given the stronger thermal responsiveness exhibited by PNSB hydrogel, we employed molecular dynamics simulation to investigate the relationship between the number of hydrogen bonds and temperature at the molecular level (Figure S13, Supplementary). As the temperature increases from 25 °C to 45 °C, the number of hydrogen bonds between PNIPAM segments and water molecules significantly decreases, while the number of hydrogen bonds between PSBMA segments and water molecules remains almost unchanged. This microscopic explanation elucidates how the transparency of PNSB hydrogel undergoes significant changes with temperature variations.

To gain a deeper understanding of the thermal responsiveness of PNSB, PNSP, and PNMT hydrogels, we measured the transparency performance of the hydrogels in the temperature range of 5–60 °C (Fig. 2g-i). The transmittance of the hydrogels decreases slowly with increasing temperature, which is attributed to the presence of ion-containing polymer segments in the hydrogels. Unlike PNIPAM hydrogels, which show sharp phase transitions only near their LCST, PNSB, PNSP, and PNMT hydrogels display a slow and weak responsiveness in a wide temperature range. On the other hand, changes in surface wettability also demonstrate the temperature response of the hydrogel. With increasing temperature, the hydrophobic effect at the interface strengthens, leading to a significant increase in the water contact angle (inset in Fig. 2g-i).

By observing the transparency performance of PNSB, PNSP, and PNMT hydrogels at -25 °C (low temperature) and 25 °C (room temperature), it is evident that the hydrogels exhibit significant thermal responsiveness (Figure S5, Supplementary). At 25 °C, the transmittance of PNSB, PNSP, and PNMT hydrogels at an infrared wavelength (940 nm) are 42.2 %, 54.4 %, and 60.6 %, respectively. The ultraviolet transmittance (365 nm) for all three hydrogels is below 0.3 %. These different types of ion hydrogels exhibit over 99.7 % protection against ultraviolet (365 nm) radiation and efficient protection against infrared light (940 nm) within the temperature range of 5-60 °C. PNSB hydrogels display significant temperature responsiveness, effectively blocking more solar radiation at high temperatures and allowing more solar heat radiation to pass through at low temperatures. This helps maintain the ambient temperature within a range suitable for human activities and provides uncompromised privacy protection under normal temperature conditions. On the other hand, PNSP and PNMT hydrogels exhibit lower temperature responsiveness, resulting in more stable privacy protection and regulation of solar heat radiation.

#### 3.3. Thermal stability and resistance to infrared radiation heating

The practical application of smart windows should adhere to requirements such as reducing solar thermal radiation and maintaining stability [45]. Using a home-made device as the simulated building equipped with a hydrogel smart window (Fig. 3a, Figure S14, Supplementary), indoor temperature regulation and energy saving effect were detected. Prior to heating, the initial indoor temperature was stabilized at 22.4 °C ( $\pm$  0.3 °C). Then, solar radiation was simulated by an infrared heating lamp and the compartment with the smart window was heated for a certain period until the indoor temperature reached a steady state. In this process, temperatures inside the compartment were monitored by using a built-in thermo-sensor.

We analyzed the thermal insulation efficiency of three types of smart windows (Fig. 3b). In the control group experiment, i.e., using a regular window with air instead of hydrogel, the indoor temperature rapidly increased and stabilized at 40.5 °C, with a  $\Delta$ T of 18.1 °C. When simulating the experiment with PNSB hydrogel smart windows, the indoor temperature stabilized at 30.6 °C, with a  $\Delta$ T of 8.2 °C. Correspondingly, the indoor temperatures stabilized at 32.4 °C with a  $\Delta$ T of 10.0 °C for PNSP hydrogel window and at 34.5 °C with a  $\Delta$ T of 12.1 °C for PNMT hydrogel window.

In comparison to the regular window control group, the experimental groups of PNSB, PNSP, and PNMT hydrogel smart windows showed excellent temperature regulation effects with temperature reductions of  $\Delta T=9.9$  °C,  $\Delta T=8.3$  °C, and  $\Delta T=6.0$  °C, respectively (Fig. 3c). The thermal resistance values per unit area relative to regular windows were calculated to be 11.34, 9.28, and 6.87 kJ m<sup>-2</sup> for PNSB, PNSP, and PNMT hydrogel smart windows, respectively, with the corresponding heat absorption values of 9.93, 11.45, and 13.86 kJ m<sup>-2</sup>. Based on these calculations, the energy-saving efficiency of the three types of smart windows in the simulation experiment was determined to be 54.7 %, 44.8 %, and 33.1 % for PNSB, PNSP, and PNMT hydrogel smart windows, respectively. Notably, compared to other works, the PNSB (PNSP, PNMT) hydrogel smart windows do not sacrifice visibility while providing efficient energy savings and temperature regulation [4, 7,45]. The high energy-saving efficiency allows these privacy-protecting hydrogel smart windows to reduce solar heat radiation during hot summers, maintaining stable indoor temperatures and thus reducing energy consumption. Furthermore, visible light can still penetrate through these hydrogel smart windows, which can save additional energy consumption generated by lighting.

In order to verify the optical transmittance stability under temperature variations, 100 cycles of cooling-heating (from 25 °C to 45 °C) were conducted on PNSB, PNSP, and PNMT hydrogel smart windows (Fig. 3d-f). It can be observed that after 100 cooling-heating cycles, all three types of hydrogel smart windows maintained their initial light transmittance properties. For PNSB hydrogel, the visible light transmittance change remained at  $\Delta T_{vis}$  (25–45 °C) = 3.0 %, with minimal impact on its privacy protection performance. The near-infrared light transmittance change was maintained at  $\Delta T_{IR}$  (25–45 °C) = 14.5 %. The PNSB hydrogel smart window allows more infrared light transmission at low temperatures and blocks more infrared light at high temperatures. For PNSP hydrogel, the visible light transmittance change remained at  $\Delta T_{vis}$  (25–45 °C) = 2.9 %, and  $\Delta T_{IR}$  (25–45 °C) = 3.1 %. While for PNMT hydrogel, the visible light transmittance change remained at  $\Delta T_{vis}$ (25–45  $^\circ C)$  = 4.9 %, and  $\Delta T_{IR}$  (25–45  $^\circ C)$  = 6.6 %, both a little higher than that of PNSP ones. More importantly, PNSP hydrogel smart windows showed negligible temperature variations over a wider temperature range, resulting in stable privacy protection performance and controlled infrared light incidence.

Meanwhile, the optical transmittance stability of PNSB, PNSP, and PNMT hydrogel smart windows in ambient environments were also monitored (Fig. 3g-i). The ultraviolet (365 nm) / visible (380–760 nm) / near-infrared (940 nm) transmittance was measured every 10 days (the hydrogel smart window is adjusted to 25 °C during the test). Through 180 days of continuous observation, the ultraviolet /visible / near-infrared light transmittance of all three hydrogel smart windows remained stable at their initial transmittance levels without any decay of their performance. It is demonstrated the reliable long-term stability of these hydrogel smart windows.



**Fig. 3.** (a) Simulation of architectural thermal insulation device. (b) Heating curves of PNSB, PNSP, and PNMT smart windows under simulated conditions. (c) Thermal radiation blocking, thermal radiation absorption, and temperature regulation capability relative to ordinary glass of PNSB, PNSP and PNMT smart windows. Stability over 100 cycles of cooling-heating (25–45 °C) for (d) PNSB hydrogel, (e) PNSP hydrogel, (f) PNMT hydrogel. Ultraviolet (365 nm) / visible (380–760 nm) / near-infrared (940 nm) transmittance stability of (g) PNSB hydrogel, (h) PNSP hydrogel, (i) PNMT hydrogel smart windows placed outdoors for 180 days in Shanghai, China. (The light transmission performance is detected at 25 °C).

#### 3.4. Ionic conductivity and microscopic molecular dynamics simulation

Using molecular dynamics simulation, the solvation structures of potassium and chloride ions in the PNSP and PNMT hydrogels were analyzed. From the radial distribution function (RDF) g(r) and coordination number N(r) of free ions in PNSP and PNMT hydrogels (Fig. 4a-d), two sharp peaks in the calculated RDF profiles were observed

corresponding to the coordination between  $K^+/Cl^-$  ions and oxygen atoms in  $H_2O$  and that between  $K^+/Cl^-$  ions and oxygen atoms in EG molecules in both systems, indicating the formation of solvated structures between free ions and binary solvents. According to the coordination number, the K ion is surrounded by about five water molecules and one EG molecule. Furthermore, there was no significant change in both g(r) and N(r) for PNSP system at different temperatures. This



**Fig. 4.** Radial distribution function and coordination number of PNSP hydrogel (a, b) and PNMT hydrogel (c, d) at 25 °C (a, c) and 45 °C (b, d). (e) Mean square displacement (MSD) of PNSB, PNSP, and PNMT hydrogels. (f) Ionic conductivity of PNIPAMO, PNIPAM, PNSB, PNSP, and PNMT hydrogels. Molecular dynamics (MD) simulations of 3D snapshots and partially enlarged microstructure diagrams of PNSB (g), PNSP (h), and PNMT (i) hydrogels.

indicates that the solvated ions are not sensitive to temperature and exhibit good thermal stability, in good agreement with the negligible impact of temperature variations on the light transmittance performance of PNSP hydrogel.

Comparing the g(r) and N(r) of ions in PNSP and PNMT hydrogels at 25 °C (Fig. 3a, c), it can be observed that both g(r) and N(r) of K<sup>+</sup>-H<sub>2</sub>O (O) are greater than that of Cl<sup>-</sup>H<sub>2</sub>O(O), while g(r) of K<sup>+</sup>-EG(O) is lower than that of Cl<sup>-</sup>EG(O). The N(r) of K<sup>+</sup>-EG(O) is almost identical to that of Cl<sup>-</sup>EG(O). This suggests that the interaction between K<sup>+</sup> and water in PNSP hydrogel is stronger than that between Cl<sup>-</sup> and water in PNMT hydrogel. The activity of water molecules in solvated structure is higher than that of free water molecules, which drives ion diffusion and increases the conductivity of the system. Thus, the stronger solvation and the larger coordination number of K<sup>+</sup> induced a higher conductivity of the PNSP hydrogel.

From the mean square displacement of water molecules in the three hydrogels (Fig. 4e), diffusion coefficients (D) of water molecules in PNSB, PNSP, and PNMT hydrogels were calculated to be  $0.0958 \times 10^{-5}$ ,  $0.1563 \times 10^{-5}$ , and  $0.1135 \times 10^{-5}$  cm<sup>2</sup> s<sup>-1</sup>, respectively. It is observed that the mobility of water molecules is in the order of  $D_{PNSP} > D_{PNMT} > D_{PNSB}$ , indicating that the highest conductivity of PNSP hydrogel. This is consistent with the conclusions drawn from RDF g(r) and coordination number N(r) of ions with water in PNSP and PNMT hydrogels.

The ionic conductivities of PNSB, PNSP, and PNMT hydrogels were detected to be 0.69, 13.38, and 4.00 mS cm<sup>-1</sup>, respectively (Fig. 4f). The presence of free ions confers certain conductivity to hydrogels [46,47]. Due to the separate existence of free K<sup>+</sup> and Cl<sup>-</sup> ions, respectively, PNSP and PNMT hydrogels exhibit higher ionic conductivity. The magnitude of ion conductivity in the three hydrogels is consistent with the diffusion coefficients of water molecule in the hydrogels, indicating that the larger diffusion coefficient of water molecules has a positive effect on the

electrical conductivity of the hydrogels. Combined with the comparison of g(r) and N(r), diffusion coefficients of water molecules and the internal structures (Fig. 4g-i) of PNSB, PNSP and PNMT hydrogels, it confirms that water state has a profound impact on the mobility of water molecules and the conductivity of the hydrogel, suggesting that the pore size is not an essential factor governing the diffusion of water molecules [48]. Additionally, the high hydration of K<sup>+</sup> enhances the interactions with water molecules, which will prevent the formation of ice crystals and evaporation of water, resulting in a freeze-tolerant and anti-icing PNSP hydrogel.

#### 3.5. Flexible sensor application

In view of the larger ionic conductivity, higher diffusion coefficient of water molecules and more thermal stability of PNSP hydrogel, multifunctional PNSP hydrogel can maintain excellent conductivity performance at extreme low temperatures, which will be a potential hydrogel-based flexible wearable sensor. It can be seen that the LED indicator becomes dim when the hydrogel is stretched, which is due to the change in relative resistance ( $\Delta$ R) caused by the deformation of the hydrogel (Fig. 5a). This indicates that PNSP hydrogels can be used for resistance type tensile strain sensors [30,49]. Similarly, the brightness changes during the compression-rebound process demonstrate the potential for compression sensor of PNSP hydrogel (Movie S5, Supplementary).

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The gauge factor (GF) of the PNSP hydrogel sensor was determined to be 3.18 (Fig. 5b), making it highly suitable for applications in the field of hydrogel ion-conductive sensors. During a typical 100 % strain loading-unloading process, the stretch response time of the hydrogel



**Fig. 5.** (a) Changes in LED brightness with PNSP hydrogel at the relaxed (I) and stretched (II) states, with the closed circuit connected to a 4.5 V voltage. (b) Gauge factor of PNSP hydrogel. (c) Response time and recovery time of PNSP conductive hydrogel in a single 100 % tensile-shrinkage cycle. (e) Stability of PNSP hydrogel with over 1000 cycles of 100 % tensile deformation repeated stretching (3.8 s per cycle). Sensor detecting human joint activity signals for (e) throat, (f) wrist, (g) outside of the elbow joint, (h) inside of the elbow joint, (i) fingers, (j) facial muscles. (k) Schematic diagram of the sensor structure (Fig. S15, Supplementary).

sensor is approximately 254 ms, while the recovery time is around 240 ms, demonstrating a rapid responsiveness (Fig. 5c). As the strain sensor, the conductivity stability of hydrogel is also very important for wearable devices. For this purpose, we detected the relative resistance changes of the hydrogel sensor during 1000 stretching cycles under a 100 % strain deformation (Fig. 5d). Each loading-unloading cycle lasts 3.8 s and the testing lasts more than one hour. After 1000 cycles, the relative resistance can still remain stable, suggesting the excellent durability and fatigue resistance performance of PNSP hydrogel. As water content is also affect the conductivity of the hydrogel, the stable cyclic performance indicates an excellent water retention of the PNSP hydrogel, in consistent with the results abovementioned in Fig. 1f.

The real-time activity of various joints in the human body was monitored. Due to its high stretchability, rapid response, and high sensitivity, the real-time  $\Delta R/R_0$  curves of the strain sensor show sharp and rapid responses to the movements of the throat, wrist, elbow, finger, and facial muscles (Fig. 5e-j). It is worth noting that even for the slight throat movement and face smile, the respond signals are strong and stable without any background noise detected. Moreover, when monitoring the inner elbow joint movement, the instrument can output a stable negative signal due to slight compression of the hydrogel inside the sensor during motion. These results indicate that the hydrogel sensor can monitor and distinguish various movements of the human body in both stretching and compressive modes. Therefore, the privacyprotective hydrogel developed in this study can also effectively integrate with human health activities monitoring. Compared to transparent hydrogel sensors, PNSP hydrogel sensors are able to block a substantial amount of solar ultraviolet radiation, enabling it to monitor movement while protecting the skin. Additionally, it exhibits superior conductivity and fatigue resistance without the need for adding any other components, thus providing a theoretical foundation for its application in the field of flexible sensor.

#### 4. Conclusions

In summary, privacy-protective hydrogels (PNSB, PNMT, PNMT) were synthesized by combining the thermosensitive monomer NIPAM with three ionic monomers, i.e., zwitterionic SBMA, anionic SPMA, and cationic MTAC in an ethylene glycol-water binary solvent. These types of ionic hydrogels not only possess the ability to regulate light transmittance over an extremely wide temperature range ( $\sim -25-60$  °C) but also demonstrate exceptional frost resistance ( $\sim-40$  °C) and effective blocking of infrared radiation, enabling them to regulate solar thermal radiation while ensuring privacy protection. Specially, the PNSP hydrogel with an ultra-high ionic conductivity of  $13.38 \text{ mS cm}^{-1}$  enables it a potential application in the field of conductive sensors. The high diffusion coefficient of water molecule, large K<sup>+</sup> ion coordination number with water and stable radial distribution functions of PNSP hydrogel from MD simulation elucidate the mechanism at a microscopic level. We have reason to believe that our ionic hydrogels can be widely applied in the areas of smart windows for buildings and automobiles, as well as in flexible sensors for detecting human health activities.

#### CRediT authorship contribution statement

Honglai Liu: Resources. Xia Han: Writing – review & editing, Writing – original draft, Visualization, Resources, Data curation. Cheng Lian: Software. Chenglin Zhang: Writing – review & editing, Writing – original draft, Visualization, Formal analysis, Data curation. Mochou Liu: Writing – review & editing. Zekai Zhang: Formal analysis.

#### **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Data availability

Data will be made available on request.

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#### Appendix A. Supporting information

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