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A Simple PVA/Cu(OAc)₂ Thermogel with Inherent Near-Infrared Light Response and Its Applications in Smart Window and Photoresistor

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Thermogel is one kind of smart materials, characterized by in situ sol-gel transition upon temperature increasing. Currently, most of them are constructed by thermosensitive polymers, which often require tedious chemical synthesis. Besides, it is difficult to precisely control the gel properties through remote stimuli like near-infrared (NIR) light. In this work, we have prepared a thermogel with inherent NIR photothermal responsive feature by simply mixing hydrophilic polyvinyl alcohol (PVA) with Cu(OAc)₂ in deionized water. Without the incorporation of extra reagents and the chemical modification of PVA, the PVA/Cu(OAc)₂ thermogel exhibited the high photothermal conversion efficiency and reversible sol-gel transition behavior. Because of the inherent NIR absorption and optical conversion abilities, the PVA/Cu(OAc)₂ thermogel can be used as a smart window material to effectively absorb sunlight and prevent the rise of indoor temperature. In addition, its photosensitive conductivity also gave the potential as a photoresistor. As far as we know, this is the first PVA-tailored thermogel with inherent NIR light response, which provides an innovative strategy to construct smart materials.

Introduction

As one of the most promising smart materials, stimuli-responsive hydrogels are characterized by their abilities to respond to external stimuli like temperature,^{1,2} ions strength,^{3,4} light,^{5,6} pH,^{7,8} electric/magnetic field⁹⁻¹² and chemical composition.^{13,14} Among them, thermogel has attracted considerable interest because it can undergo physical sol-gel transition once temperature increases over critical point.¹⁵⁻¹⁷ At present, the most frequently adopted strategy to construct thermogel is to incorporate the thermosensitive polymers into the system. For example, poly(*N*-isopropylacrylamide)-derived copolymers have been widely used toward the fabrication of thermogels because they exhibit lower critical solution temperatures (LCST);¹⁸⁻²⁰ aqueous solutions of amphiphilic block copolymers consisting of hydrophilic poly(ethylene glycol) and hydrophobic poly(propylene oxide), poly(glycolide), poly(lactide), or poly(ϵ -caprolactone) can self-assemble into polymeric micelles upon heating, which also induce the reversible sol-gel transition.²¹⁻²³ Nevertheless, this approach has two intrinsic drawbacks: (1) it often requires the tedious synthesis of polymers which is time consuming; and (2) the sol-gel transition is hardly induced by remote stimuli like light,

electricity, and magnetism, which makes it difficult to control the properties of thermogel accurately and remotely.

In order to achieve the controllability by remote stimuli, one of the feasible approaches is to introduce additives with inherent energy transformation abilities into polymeric matrices as they can convert remote energy into local heat.²⁴⁻²⁷ Particularly, near-infrared (NIR) light-induced photothermal conversion reagents such as metal nanoparticles,^{28,29} carbon nanotubes,^{30,31} graphene,^{32,33} and Fe₃O₄ nanoparticles^{34,35} have attracted much attention, because NIR light can be regulated remotely and easily by adjustable wavelength and intensity.^{24,36-38} For example, Liu and co-workers developed a hybrid hydrogel via doping ¹³¹I-labeled copper sulfide (CuS/¹³¹I) nanoparticles, which allowed in vivo gelation remotely by NIR light with an excellent photothermal conversion performance.³⁹ Similarly, Zhang et al. have prepared an analogous hydrogel for tumor therapy by using TiO₂@MWCNT nanocomposite as the photoinitiator and photosensitizer-photothermal agent.⁴⁰ However, due to the poor solubility of photothermal conversion reagents in polymeric matrices, this physical doping strategy suffers from a dilemma that the increase of doping percentages normally causes the phase segregation, whereas lowering the doping percentages would reduce the photothermal conversion efficiency. Thus, the fabrication of a thermogel with inherent NIR light response without the tedious polymer synthesis still remains a challenge.

Herein, we discovered a novel NIR light-responsive thermogel by simply mixing hydrophilic polyvinyl alcohol (PVA) and copper acetate [Cu(OAc)₂] in deionized water (Scheme 1). Upon irradiation of NIR light (808 nm), the blue PVA/Cu(OAc)₂

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Scheme 1 Schematic illustration of the sol-gel transition of PVA/Cu(OAc)₂ thermogel and its applications in smart window and photoresistor.

solution rapidly changed into a green gel with a dramatic temperature increase, while returned to its initial blue sol state again in absence of NIR light. During the irradiation process, copper ions (Cu^{2+}) absorbed NIR light and converted it into heat, which not only raised the solution temperature, but also promoted the hydrolysis of Cu^{2+} into copper hydroxide [$\text{Cu}(\text{OH})_2$] clusters. Subsequently, PVA and $\text{Cu}(\text{OH})_2$ clusters co-aggregated into clathrate complexes mainly driven by hydrophobic interactions, where the flexible chains of PVA projected hydroxyl groups outside while $\text{Cu}(\text{OH})_2$ clusters located in the center of the tangled chains.^{41–44} Consequently, these clathrate complexes gradually formed the three-dimensional (3D) thermogel network. On account of the absorption of NIR light and the intrinsic temperature sensitivity, this PVA/Cu(OAc)₂ thermogel showed a promising application in the fields of smart window and photoresistor (Scheme 1). Notably, different from other reported PVA-based hydrogels which either required the tedious modification of PVA or the extra harsh basic condition,^{45–47} our PVA/Cu(OAc)₂ thermogel was induced by NIR light directly without additional chemical modification of PVA or incorporation of extra reagents. In this system, Cu^{2+} acted as a photothermal reagent and a crosslinker simultaneously. To our best knowledge, this is the first PVA-tailored inherent NIR light-responsive thermogel without the tedious chemical synthesis.

Experimental section

Materials

Polyvinyl alcohol (PVA, M_w : 67,000 Da, hydrolysis degree: 87–89%,) and copper acetate monohydrate [$\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$, AR, 99%] were purchased from Shanghai Aladdin Bio-Chem Technology Co. Other reagents were purchased and used without further purification.

Fabrication of PVA/Cu(OAc)₂ window

Firstly, a hollow double-layer PMMA window with a gap of 5 mm was prepared by using PMMA plates with a thickness of 5 mm. After that, the PVA/Cu(OAc)₂ solution was injected and sealed by glue to afford a PVA/Cu(OAc)₂ window. Similarly, the

Cu(OAc)₂ window as a control was prepared by sealing pure Cu(OAc)₂ solution in the same way.

Fabrication of PVA/Cu(OAc)₂ photoresistor

Firstly, one end of a transparent PMMA tube (length 5 mm, inner diameter 3 mm) was sealed with a metal wire, and then the PVA/Cu(OAc)₂ solution was injected from the other end of the tube. After sealing with the same metal wire, the photoresistor was obtained.

Characterization methods

UV-vis spectra were recorded on a G-9 UV-vis spectrophotometer (Nanjing PKILES Instrument Co., Ltd) from 190 to 1100 nm. The test specimens were kept at corresponding temperature (25 and 80°C) for 5 min before testing. The optical path of quartz cuvette was 1 cm.

Electron spin resonance (ESR) spectrometer (JES-FA200, JEOL Ltd.) with a 100 kHz field modulation was used to measure ESR spectra of PVA/Cu(OAc)₂ and pure Cu(OAc)₂ solutions at 25 and 80°C, respectively. All ESR samples were kept at the testing temperature for 5 min before testing. The center field of magnet field was 300 mT. The sweep time and sweep width (+/-) were 5 min and 150 mT, respectively.

Temperature-dependent ¹H NMR spectra were recorded on a Bruker AV400 spectrometer (400 MHz) operating at the temperature from 25 to 80°C. D₂O was used as solvent, and DMSO-*d*₆ was added as an internal standard.

Hydrodynamic sizes of samples were investigated by dynamic light scattering (DLS) on a Zeta sizer Nano-ZS90 (Malvern Instruments, UK). The concentration of PVA in all samples was 1.0 wt%. Molar ratio of Cu^{2+} to hydroxyl was 3/20.

Morphologies were studied by scanning electron microscopy (SEM, JSM-7610F with 5 kV acceleration voltage) and transmission electron microscopy (TEM, Hitachi HC-1 with 80 kV accelerating voltage). To obtain SEM samples of PVA/Cu(OAc)₂ thermogel, 2 mL of PVA/Cu(OAc)₂ solution was first placed in an oven at 80°C for 10 min to promote the formation of thermogel, and then quickly transferred into liquid nitrogen for rapid freezing. After that, the frozen sample was freeze-dried by a freeze dryer. The sample was coated with gold before the test. For preparing TEM samples, the original solution was diluted 50

times with deionized water and heated at 80°C for 15 min. Then, the liquid was adsorbed on copper grids in an oven at 80°C until it was completely dry.

The pH variation of the solution was recorded with a pH meter (PHS-3E, INESA Analytical Instrument Co., Ltd) at the range of 25 to 80°C. Before the test, the solution (concentration of PVA was 10 wt% and the molar ratio of hydroxyl group/metal ion was 20/3) was diluted 2 times with deionized water, and then 40 mL of the diluent was taken and placed into a beaker. The solution was heated by a magnetic agitator (Dragon Laboratory Instruments Ltd.).

Viscoelasticity was explored by rheological testing via a Thermo HAAKE MARS 60 with a 16 mm coaxial cylinder in the oscillation mode. The temperature sweep was performed from 25 to 80°C (3 °C min⁻¹) at a frequency of 1 Hz and a strain of 5%. Dynamic temperature sweep rheological measurements were measured from 25 to 80°C to gain insights into the reversible sol-gel transition of PVA/Cu(OAc)₂ thermogel. Storage modulus (*G'*) and loss modulus (*G''*) were recorded during the cyclic temperature changes between 25 and 80°C at a strain of 5% and a frequency of 1 Hz.

Nitrogen physisorption measurements were carried out on a Micromeritics ASAP 2020 apparatus. Before measurements, the freeze-dried samples were degassed at 60°C under vacuum. The porosity was determined from the adsorption isotherms by the Brunauer-Emmett-Teller equation.

The simulated sunlight irradiation was provided by a Solar Simulator (SS-F5-3A, Enlitech). A thermocouple thermometer (UT320A, UNI-T) with a K-type thermocouple sensor was used to monitor simulated indoor temperature. The top surface temperature of window was recorded by IR camera (FLIR ONE Pro).

The electrical resistance was measured by using a digital display multimeter (B35T+, OWON) at a working voltage of 3 V. The relative resistance changes of PVA/Cu(OAc)₂ solution was calculated using $\Delta R = R - R_0$, where *R* and *R*₀ represented the real-time resistance and the initial resistance, respectively.

Results and discussion

NIR light-induced PVA/Cu(OAc)₂ thermogel

Initially, PVA was added into deionized water and continuously stirred at 95°C for 2 h to give a homogeneous transparent solution (10 wt%). After cooling to room temperature, Cu(OAc)₂ was added and then a blue solution formed (hydroxyl group/cooper ion = 20/3, molar ratio). Upon remote irradiation by NIR light device (VCL808N1-4.0W) for 300 s, a stable green thermogel of PVA/Cu(OAc)₂ was obtained with a rapid rise of temperature from 27 to 80°C in Fig. 1a. Moreover, this green thermogel gradually returned to its initial blue sol-state again in absence of irradiation. Notably, the direct heating above 70°C also resulted in the formation of PVA/Cu(OAc)₂ thermogel as shown in Fig. S1. After 100 cycles of heating/cooling, PVA/Cu(OAc)₂ thermogel could still recover to its initial state with the good thermal reversibility (Fig. S2).

Fig. 1 (a) Thermal images of PVA/Cu(OAc)₂ solution treated with NIR light irradiation. (b) Photothermal effect of different PVA/metal acetate solutions upon NIR light irradiation. (c) UV-vis spectra of different PVA/metal acetate solutions at room temperature. (d) Temperature variation of different PVA/Cu(II) anion solutions after NIR light irradiation for 420 s. (e) The pH plots of different PVA/Cu(II) anion solutions from 25 to 80°C. Concentration of PVA was 10 wt% in (a), (b), and (d), while 1.25 wt% in (c) and 5 wt% in (e). Molar ratio of hydroxyl group/metal ion was 20/3. Wavelength of NIR light was 808 nm. Laser power was 1.0 W.

In order to illustrate the importance of Cu²⁺ in the photothermal conversion performance, other metal acetates (Li⁺, Na⁺, Mg²⁺, Mn²⁺, Co²⁺, Ni²⁺, Zn²⁺) with equal molar number of Cu(OAc)₂ were added into PVA solution, respectively. Their temperature variations after NIR irradiation were recorded by IR camera (FLIR ONE Pro), as shown in Fig. 1b and S3. Compared with the other PVA/metal acetates, only PVA/Cu(OAc)₂ formed the thermogel with a generation of the largest temperature increase from 33.3 to 76.4°C, which indicated that Cu²⁺ played an irreplaceable role as the photothermal conversion reagent and crosslinker. UV-vis spectra in Fig. 1c revealed that PVA/Cu(OAc)₂ showed a broad absorption feature in NIR window from 650 to 1100 nm, opposite the negligible absorption for the other PVA/metal acetates. It is known that *d* orbit of Cu²⁺ can split into two different degenerate orbits under a specific ligand field, namely *e_g* and *t_{2g}* orbit. Once the energy gap between *e_g* and *t_{2g}* (splitting energy) matches the energy of NIR region, the photothermal conversion occurs.⁴⁸ For PVA/Cu(OAc)₂, the Cu²⁺ complex was able to absorb NIR light to induce the electron transition between *e_g* and *t_{2g}* orbits, and then the electrons in the excited state could be restored to the ground state by non-radiative decay process, thus realizing the transformation of light energy into heat and generating the thermogel.

In addition, it was found that not all PVA/Cu(II) anion solutions can form thermogel upon NIR light irradiation. As

shown in Fig. S4, the thermal-induced gelation behavior only occurred in PVA/Cu(OAc)₂ solution rather than PVA/Cu(NO₃)₂, PVA/CuCl₂, and PVA/CuSO₄ solutions, although these four solutions exhibited the similar temperature change tendency upon NIR light irradiation as shown in Fig. 1d. Note that the unique difference between these PVA/Cu(II) anion solutions was the pH. As shown in Fig. 1e, the pH value of PVA/Cu(OAc)₂, PVA/Cu(NO₃)₂, PVA/CuCl₂, and PVA/CuSO₄ declined from 5.4, 4.7, 4.6 and 4.0 at 25°C to 4.8, 4.1, 3.8 and 3.6 at 80°C, respectively, while that of pure PVA solution remained unchanged. The decrease of pH can be reasonably explained by the fact that additional H⁺ was produced by the hydrolysis of Cu²⁺ with the rise of temperature. Since the pH value of PVA/Cu(OAc)₂ was higher than those of other PVA/Cu(II) anion solutions at any given temperature from 25 to 80°C, the failure of PVA/Cu(NO₃)₂, PVA/CuSO₄, and PVA/CuCl₂ solutions to form thermogel was mainly attributed to their relative strong acidity.

Microstructure, rheological behavior and photothermal performance of PVA/Cu(OAc)₂ thermogel

Scanning electron microscope (SEM) was applied to explore the microstructures of PVA/Cu(OAc)₂ thermogel. As shown in Fig. 2a, the dense micro-porous structure was observed in thermogel. It was consistent with the results of Brunauer-Emmett-Teller (BET) nitrogen adsorption-desorption isotherms, where a porosity of PVA/Cu(OAc)₂ thermogel was calculated to be 37.9 m²/g as shown in Fig. 2b.

To further investigate the rheological behavior of sol-gel transition, the temperature-dependent storage modulus (*G'*) and loss modulus (*G''*) of PVA/Cu(OAc)₂ solution were measured. As shown in Fig. 2c, the plot of *G''* remained higher than that of *G'* from 25 to 70°C, which accorded with sol-state property. The slight decline of *G'* and *G''* from 25 to 45°C was caused by the fact that the gelation force at low temperature was insufficient to offset the negative effect on viscosity arising from temperature rising. From 55°C, *G'* and *G''* began to increase until they coincided with each other at around 70°C, indicating the appearance of sol-gel transition. At 80°C, *G'* was in the order of 10² Pa, higher than *G''* (10¹ Pa), corresponding to the gel-state of PVA/Cu(OAc)₂. Dynamic temperature sweep rheological measurements in Fig. 2d showed that after four cycle tests between 25 and 80°C, the system was still stable and kept its original rheological properties, further confirming that PVA/Cu(OAc)₂ owned excellent and repeatable sol-gel transition performance.

For assessing the photothermal conversion capability of PVA/Cu(OAc)₂, conversion efficiency η was quantified by eq (1):⁴⁹⁻⁵¹

$$\eta = \frac{hA(\Delta T_{\max, \text{mix}} - \Delta T_{\max, \text{water}})}{I(1 - 10^{-A_\lambda})} \quad (1)$$

In this equation, $\Delta T_{\max, \text{mix}}$ and $\Delta T_{\max, \text{water}}$ are the maximum temperature variation of PVA/Cu(OAc)₂ solution and water, respectively. *I* is the laser power and *A_λ* is the absorbance of PVA/Cu(OAc)₂ solution at 808 nm. *h* is the heat transfer coefficient and *A* is the surface area of the container. Unknown *hA* is calculated from eq (2):

Fig. 2 (a) SEM image and (b) BET nitrogen adsorption-desorption isotherm of PVA/Cu(OAc)₂ thermogel after freeze-drying. (c) Temperature-dependent *G'* and *G''* of PVA/Cu(OAc)₂ solution from 25 to 80°C with a heating rate of 3 °C min⁻¹. Frequency = 1 Hz and strain = 5%. (d) *G'* and *G''* of PVA/Cu(OAc)₂ solution during heating-cooling cycles between 25 and 80°C with a heating/cooling rate of 3 °C min⁻¹. Frequency = 1 Hz and strain = 5%. (e) Temperature variation of PVA/Cu(OAc)₂ solution after irradiating for 660 s (red points) followed by a cooling period from 660 to 1380 s (blue points). Inset showed the time constant (τ_s) for heat transfer, determined by the linear time-dependent data in the cooling period. (f) Temperature curves of PVA/Cu(OAc)₂ solution with repeated irradiation on/off cycles. Concentration of PVA was 10 wt% in (a), (b), (c), and (d), while 1.25 wt% in (e) and (f). Molar ratio of hydroxyl group/metal ion was 20/3. Wavelength of NIR light was 808 nm. Laser power was 1.5 W.

$$\tau_s = \frac{m_D c_D}{hA} \quad (2)$$

where *m_D* is the mass of water in PVA/Cu(OAc)₂ solution, and *c_D* is the heat capacity of water. By making a linear fit of cooling time (*t*) and $-\ln(\Delta T_{t, \text{mix}}/\Delta T_{\max, \text{mix}})$, time constant τ_s can be obtained as the curve slope.

According to the temperature curve of PVA/Cu(OAc)₂ solution in Fig. 2e, τ_s was determined to be 275 s with $R^2 = 0.994$ (inset). Given the mass of water (*m_D*) was 0.5 g and the heat capacity of water (*c_D*) was 4.2 J g⁻¹ K⁻¹, *hA* was calculated to be 7.63 × 10⁻³ W K⁻¹ by using eq (2). In this case, the η of PVA/Cu(OAc)₂ solution was quantified to be 37.8% according to eq (1), where $\Delta T_{\max, \text{mix}}$ value was 59.8°C, $\Delta T_{\max, \text{water}}$ value was 2.7°C (Fig. S5), and *A_λ* was 0.638 determined from UV-vis spectrum (Fig. 1c). Note that this η value was higher than other reported photothermal agents like Au nanorods (21%),⁵² Cu₂-xSe (22%),⁵³ and Cu₉S₅ (26%).⁵⁴ Furthermore, the photothermal stability of PVA/Cu(OAc)₂ was evaluated by the repeated irradiation on/off cycles. As shown in Fig. 2f, no change in the thermal generation ability of PVA/Cu(OAc)₂ was observed within three on/off processes, implying a good photothermal stability. Obviously, PVA/Cu(OAc)₂ possessed a great capability to convert NIR irradiation to heat, which easily facilitated the remote control of reversible sol-gel transition.

Fig. 3 (a) DLS profiles of $\text{Cu}(\text{OAc})_2$ and $\text{PVA}/\text{Cu}(\text{OAc})_2$ solutions at different temperatures. (b) TEM image of $\text{PVA}/\text{Cu}(\text{OAc})_2$ after heating at 80°C for 15 min. (c) ESR spectra of $\text{Cu}(\text{OAc})_2$ and $\text{PVA}/\text{Cu}(\text{OAc})_2$ solutions at different temperature. (d) UV-vis spectra of $\text{Cu}(\text{OAc})_2$ and $\text{PVA}/\text{Cu}(\text{OAc})_2$ solutions at 25°C and 80°C . (e) Temperature-dependent ^1H NMR spectra (400 MHz, D_2O) of $\text{PVA}/\text{Cu}(\text{OAc})_2$ solution with a molar ratio of 20/3. * and Δ represent D_2O and $\text{DMSO}-d_6$, respectively. (f) Temperature-dependent complex viscosity of $\text{PVA}/\text{Cu}(\text{OAc})_2$ solution. (g) Schematic illustration for the formation of $\text{PVA}/\text{Cu}(\text{OAc})_2$ thermogel. (g_1) PVA solution, (g_2) $\text{PVA}/\text{Cu}(\text{OAc})_2$ solution, and (g_3) $\text{PVA}/\text{Cu}(\text{OAc})_2$ thermogel.

Mechanism of NIR light-induced $\text{PVA}/\text{Cu}(\text{OAc})_2$ thermogel

From the standpoint of coordination chemistry, it seems unlikely that aliphatic hydroxyl groups deprotonate at $\text{pH} < 7$ and coordinate with free Cu^{2+} , because of its high $\text{pK}_a \sim 16$.⁴¹ For $\text{PVA}/\text{Cu}(\text{OAc})_2$ solution, its pH value was around 5.4 and would be further decreased with the rise of temperature as shown in Fig. 1e. Therefore, the coordination between free Cu^{2+} and hydroxyl groups cannot occur in $\text{PVA}/\text{Cu}(\text{OAc})_2$ solution, which supported the phenomenon that the addition of $\text{Cu}(\text{OAc})_2$ into PVA solution did not induce the gel formation at room temperature unless extra strong alkaline reagent was added (Fig. S6).

In order to explore the mechanism in depth, temperature-dependent experiments of dynamic light scattering (DLS), electron spin resonance (ESR), UV-vis, ^1H NMR and complex viscosity were carried out. A large number of light-blue suspended particles formed in diluted pure $\text{Cu}(\text{OAc})_2$ at 80°C , and gradually turned into black with the prolongation of heating time (Fig. S7a). During this process, its average particle diameter determined by DLS increased from 50 to 240 nm (Fig. 3a). Since the high temperature can accelerate the hydrolysis of Cu^{2+} into $\text{Cu}(\text{OH})_2$, it was assumed that these particles should be $\text{Cu}(\text{OH})_2$ crystal clusters, which subsequently thermally decomposed to the black copper oxide. Conversely, no precipitation was observed in $\text{PVA}/\text{Cu}(\text{OAc})_2$ solution except the color change

from blue to green upon heating at 80°C (Fig. S7b). Once cooling to the room temperature, it could further return to its initial blue again. Their average particle sizes ranged from 10 to 40 nm at the corresponding temperatures, much smaller than that in pure $\text{Cu}(\text{OAc})_2$ solution, and the transition was reversible (Fig. 3a). This process could be directly revealed by TEM images. As shown in Fig. 3b, a large number of clathrate complexes formed in $\text{PVA}/\text{Cu}(\text{OAc})_2$ solution, whereas only film structures and needle-shaped assemblies were observed for PVA and $\text{Cu}(\text{OAc})_2$ solutions, respectively (Fig. S8). The above results strongly indicated that PVA can stabilize and co-aggregate with $\text{Cu}(\text{OH})_2$ clusters, and further prevent the formation of larger aggregates.

More evidence came from ESR spectroscopy in Fig. 3c. With temperature rising from 25 to 80°C , a decrease in ESR intensity was observed for $\text{Cu}(\text{OAc})_2$ solution (brown and purple dashed lines), which is due to the reduction of Cu^{2+} caused by the aggravation of hydrolysis. Nevertheless, the addition of PVA into $\text{Cu}(\text{OAc})_2$ solution at 25°C also resulted in a slight decrease in ESR intensity (blue solid line), which further declined to a lower level at 80°C (red solid line). Given that no coordination between hydroxyl group and free Cu^{2+} existed in $\text{PVA}/\text{Cu}(\text{OAc})_2$ solution, this slight change was probably due to PVA bonded with trace $\text{Cu}(\text{OH})_2$ in $\text{PVA}/\text{Cu}(\text{OAc})_2$ solution at 25°C , thus promoting the hydrolysis reaction and the decrease of Cu^{2+} .

In addition, UV-vis and ^1H NMR spectra were further used to demonstrate the interaction between PVA and $\text{Cu}(\text{OH})_2$ clusters.

As shown in Fig. 3d, $\text{Cu}(\text{OAc})_2$ solution showed a broad absorption peak at 770 nm due to the $d-d$ electron transition of hydrated Cu^{2+} (brown dashed line), and red-shifted to 773 nm resulting from the formation of $\text{Cu}(\text{OH})_2$ clusters at 80°C (purple dashed line). However, upon addition of PVA, the absorption peak underwent a slight blue-shift from 770 to 766 nm (blue solid line), and further blue-shifted to 758 nm at 80°C (red solid line). This implied that there was an interaction between PVA and $\text{Cu}(\text{OH})_2$ clusters which caused the environment change around $\text{Cu}(\text{OH})_2$ clusters. Through a continuous heating process from 25 to 80°C, the absorption peak in PVA/ $\text{Cu}(\text{OAc})_2$ solution showed a continuous blue-shift and would return to the initial position after cooling (Fig. S9), which illustrated that the interaction between PVA and $\text{Cu}(\text{OH})_2$ clusters was reversible and heavily dependent on temperature. Moreover, the interaction also can be reflected from the results of ^1H NMR. As shown in Fig. 3e and Fig. S10, proton peaks of methine ($\text{CH}-$) and methylene (CH_2-) in PVA chains broadened either with increasing the temperature or the molar ratio of Cu^{2+} /hydroxyl group. On the contrary, proton peaks of pure PVA solution became gradually sharpened with the raise of temperature (Fig. S11). It is known that the broadening of proton peaks implies that insoluble polymer segments form or polymer chains are kinetically limited in solution, as ^1H NMR signals arise only from protons in a liquid-like fraction.⁴⁵ Therefore, it was deduced that the generated $\text{Cu}(\text{OH})_2$ clusters can be surrounded by PVA hydrophobic backbones to form a green clathrate complexes $[\text{Cu}(\text{OH})_2\text{-PVA}]$ via hydrophobic forces, similar to the report by Yokoi.^{41,42} In this case, PVA chains fixed by $\text{Cu}(\text{OH})_2$ clusters had undetectable ^1H NMR signals while $\text{Cu}(\text{OH})_2$ clusters surrounded by PVA chains were difficult to aggregate into larger-sized precipitates. This deduction can be further confirmed by temperature-dependent viscosity of PVA/ $\text{Cu}(\text{OAc})_2$ solution from 25 to 80°C. As shown in Fig. 3f, the viscosity underwent a slight decrease from 25 to 45°C due to the weak interactions between PVA and $\text{Cu}(\text{OH})_2$ clusters, whereas began to rise dramatically after 45°C, which revealed the monotonic enhancement of hydrophobic interactions between PVA and $\text{Cu}(\text{OH})_2$ clusters as a function of the concentration for $\text{Cu}(\text{OH})_2$ clusters.

Taking all above results together, the formation process of PVA/ $\text{Cu}(\text{OAc})_2$ thermogel was proposed in Fig. 3g. Initially, upon addition of $\text{Cu}(\text{OAc})_2$, PVA could stabilize the trace hydrolyzed $\text{Cu}(\text{OH})_2$ clusters in PVA/ $\text{Cu}(\text{OAc})_2$ solution at room temperature. But because of the low degree of hydrolysis, the amount of $\text{Cu}(\text{OH})_2$ clusters was insufficient to form strong hydrophobic interactions with PVA chains, which would not induce significant changes in the solution state (Fig. 3g₁ and 3g₂). Subsequently, NIR light irradiation induced the rise of solution temperature that accelerated the hydrolysis of Cu^{2+} with generating more $\text{Cu}(\text{OH})_2$ clusters. These clusters were surrounded by PVA hydrophobic backbones to form a green clathrate complexes $[\text{Cu}(\text{OH})_2\text{-PVA}]$ via hydrophobic forces, where the hydrophilic hydroxyl groups in PVA chains toward the outside and $\text{Cu}(\text{OH})_2$ clusters located in the center of the tangled chains. Consequently, the 3D cross-linked network of thermogel

Fig. 4 (a) Transmission spectra of PVA/ $\text{Cu}(\text{OAc})_2$ solution at 25 and 80°C. Insets are digital photos of PVA/ $\text{Cu}(\text{OAc})_2$ solution at 25°C (left) and 80°C (right). (b) Time-dependent transmittance of PVA/ $\text{Cu}(\text{OAc})_2$ solution at 485 nm under different temperatures. (c) Schematic illustration of the lab-made model house used for the measurement of indoor temperature upon sunlight irradiation. (d) Time-dependent indoor temperature in model house covered by PMMA window, $\text{Cu}(\text{OAc})_2$ window and PVA/ $\text{Cu}(\text{OAc})_2$ window upon one sun irradiation (1000 W m^{-2}).

formed (Fig. 3g₂ and 3g₃). While, once NIR irradiation for PVA/ $\text{Cu}(\text{OAc})_2$ solution was removed, the reverse reaction of Cu^{2+} hydrolysis would be enhanced, which gave rise to the dissolution of $\text{Cu}(\text{OH})_2$ clusters. As a result, the PVA chains fixed by $\text{Cu}(\text{OH})_2$ clusters previously were restored to the original free state, resulting in the collapse of gel structures (Fig. 3g₃ and 3g₂).

Application on smart window and photoresistor.

Considering that PVA/ $\text{Cu}(\text{OAc})_2$ solution possessed high absorption performance in UV and NIR light range (190–380 nm and 650–1100 nm) and allowed for the high visible light transmission in the visible region as shown in Fig. 4a, its potential application as the smart window material was investigated. With the temperature rising from 25 to 80°C, the light transmittance of PVA/ $\text{Cu}(\text{OAc})_2$ solution dramatically declined from 85% to 32% at 485 nm with the gradual color change from blue to green (Fig. 4a and S12). Moreover, the higher the solution temperature, the faster the color change. As shown in Fig. 4b, the light transmittance of PVA/ $\text{Cu}(\text{OAc})_2$ solution at 80°C sharply decreased from 85% to 32% within 300 s, strongly revealing the good optical conversion performance of PVA/ $\text{Cu}(\text{OAc})_2$. In order to simulate the effect of PVA/ $\text{Cu}(\text{OAc})_2$ to reduce the indoor temperature under sunlight, a PVA/ $\text{Cu}(\text{OAc})_2$ window was made by injecting PVA/ $\text{Cu}(\text{OAc})_2$ solution into a hollow double-layer PMMA window (Fig. S13), and then installed it on a model house as shown in Fig. 4c, where a thermocouple thermometer was used to monitor the change of indoor temperature upon sunlight irradiation. As shown in Fig. 4d, after irradiating for 3600 s, the steady-state indoor temperature with PMMA window was 53.0°C because of its high light transmittance, while 36.9°C for $\text{Cu}(\text{OAc})_2$ window. Conversely, the steady-state indoor temperature with PVA/ $\text{Cu}(\text{OAc})_2$ window was much lower ($\sim 33.5^\circ\text{C}$) accompanying with a top surface temperature around 54.3°C .

(Fig. S14), which was contributed to its NIR absorption property as well as the decrease in transmittance. The above results indicated the PVA/Cu(OAc)₂ window with high NIR shielding and reversible optical conversion property can reduce the indoor temperature effectively under sunlight irradiation by blocking the sunlight both in the NIR and visible region.

Besides, benefiting from intrinsic conductive quality of free Cu²⁺ and photothermal ability of PVA/Cu(OAc)₂ solution, the conductivity of PVA/Cu(OAc)₂ solution was deeply affected by sunlight irradiation. As shown in Fig. 5a, the conductivity of PVA/Cu(OAc)₂ solution reached 2.84 mS/cm at 70°C from 2.18 mS/cm at 25°C, revealing that a higher temperature of solution corresponding to a lower resistivity due to the accelerated migration rate of Cu²⁺ with the increase of temperature. Based on this change, a PVA/Cu(OAc)₂ photoresistor was fabricated by encapsulating PVA/Cu(OAc)₂ solution into a PMMA tube and then connected to a circuit for adjusting the current (Fig. S15). When the photoresistor was irradiated by sunlight, the current rapidly flowed across the PVA/Cu(OAc)₂ solution and the light-emitting diode (LED) gradually brightened (Fig. 5b). In addition, the photoresistor was connected with a multimeter to record the changes of resistance upon sunlight irradiation (1000 W m⁻²). As shown in Figure 5c, the resistance signal of the PVA/Cu(OAc)₂ photoresistor showed repeatable variations during the treatment with irradiation on/off cycles, which exhibited a great potential application prospect in optical control devices.

Fig. 5 (a) Conductivity of PVA/Cu(OAc)₂ solution at different temperatures. (b) Photographs of an LED light connected with PVA/Cu(OAc)₂ photoresistor upon sunlight irradiation. (c) Variation in the resistivity of PVA/Cu(OAc)₂ photoresistor after repeated sunlight irradiation on/off cycles.

Conclusions

In summary, we have prepared a novel PVA/Cu(OAc)₂ thermogel with inherent NIR light response via a simple yet cost-effective method. At room temperature, PVA/Cu(OAc)₂ existed in a blue sol-state, while gradually changed into a green gel-state upon NIR light irradiation. During this process, the clathrate complexes [Cu(OH)₂-PVA] were formed mainly promoted by the hydrophobic interactions between Cu(OH)₂

clusters and PVA chains, where the hydrophilic hydroxyl groups in PVA chains toward the outside and Cu(OH)₂ clusters located in the center of the tangled chains, thus resulting in the sol-gel transition. Because of the good inherent photothermal conversion (~37.8%) and high photothermal stability of PVA/Cu(OAc)₂ thermogel, its potential applications have been explored in the fields of smart window and photoresistor. The results showed that the lab-made PVA/Cu(OAc)₂ window was able to effectively maintain the indoor temperature below 35°C under sunlight irradiation, while the as-prepared PVA/Cu(OAc)₂ photoresistor exhibited a sensitive and repeatable responses to sunlight irradiation. In brief, our simple PVA/Cu(OAc)₂ thermogel with inherent NIR light response will be a promising candidate for the future manufacture industry of smart materials.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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Electronic Supplementary Information

A Simple PVA/Cu(OAc)₂ Thermogel with Inherent Near-Infrared Light Response and Its Applications in Smart Window and Photoresistor

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Fig. S1 Optical photographs of PVA/Cu(OAc)₂ thermogel at 70, 80, 90 and 100°C, respectively, as well as its recover to solution after cooling to room temperature.

Fig. S2 Optical photographs of gel-sol transitions of PVA/Cu(OAc)₂ upon 100 heating/cooling cycles.

Fig. S3 Optical photographs of PVA/metal acetate (Cu^{2+} , Li^+ , Na^+ , Mg^{2+} , Mn^{2+} , Co^{2+} , Ni^{2+} , Zn^{2+}) solutions before and after irradiation of NIR light at 808 nm.

Fig. S4 Optical photographs of PVA/Cu(OAc)_2 , $\text{PVA/Cu(NO}_3)_2$, PVA/CuCl_2 , and PVA/CuSO_4 solutions before and after irradiation of NIR light at 808 nm.

Fig. S5 Photothermal effect of PVA/Cu(OAc)₂ solutions and water upon NIR light irradiation.

Fig. S6 Optical photograph of PVA/Cu(OAc)₂ hydrogel with addition of NaOH (concentration was 0.1 M) at 25°C.

Fig. S7 Optical photographs of (a) Cu(OAc)₂ and (b) PVA/Cu(OAc)₂ solution upon heating at 80°C (concentration of PVA was 1.0%, and the molar ratio of hydroxyl group/Cu²⁺ was 20/3).

Fig. S8 TEM images of (a) PVA and (b) $\text{Cu}(\text{OAc})_2$ solutions upon heating at 80°C for 15 min.

Fig. S9 Temperature-dependent UV-vis spectra of PVA/ $\text{Cu}(\text{OAc})_2$ solution (concentration of PVA was 1.25%, and the molar ratio of hydroxyl group/ Cu^{2+} was 20/3).

Fig. S10 ^1H NMR spectra (400 MHz, D_2O) of PVA/ $\text{Cu}(\text{OAc})_2$ solution as increasing the molar ratio of Cu^{2+} /hydroxyl group from 0/20 to 7/20 at 25°C . * and Δ represent D_2O and $\text{DMSO}-d_6$, respectively.

Fig. S11 Temperature-dependent ^1H NMR spectra (400 MHz, D_2O) of PVA solution. * and Δ represent the ^1H NMR peak of D_2O and $\text{DMSO-}d_6$.

Fig. S12 Transmittance variation of PVA/Cu(OAc)_2 solution as a function of temperature at 485 nm.

Fig. S13 The fabrication process and optical photograph of PVA/Cu(OAc)₂ window.

Fig. S14 Time-dependent top surface temperatures of PVA/Cu(OAc)₂ window. Inset is the IR thermal image of PVA/Cu(OAc)₂ window under 1000 W m⁻² sunlight irradiation.

Fig. S15 (a) Schematic illustration and (b) photograph of the PVA/Cu(OAc)₂ photoresistor connected into a circuit.