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Fully Printed Flexible Smart Hybrid Hydrogels

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Keywords: 3D printing, hydrogel, PNIPAm, smart windows, thermochromics

A printable hybrid hydrogel is fabricated by embedding Poly(N-isopropylacrylamide) (PNIPAm) microparticles within a water-rich silica-alumina(Si/Al)-based gel matrix. The hybrid gel holds a water content of up to 70 wt%, due to the unique Si/Al matrix. The hybrid hydrogel can respond to both heat and electrical stimuli, and can be directly printed layer-by-layer using a commercial 3-dimensional printer without requiring any curing. The hybrid ink is printed onto a transparent flexible conductive electrode composed of silver nanoparticles, and it sustains bending angles of up to 180°, which enables patterning of various flexible devices such as a smart windows and a 3D optical waveguide valve.

1. Introduction

Hydrogels are formed through cross-linking of hydrophilic polymeric chains dissolved within an aqueous solution, which renders broadly tunable chemical and physical properties,^[1] particularly the intriguingly smart functionalities which can be activated by various external stimuli.^[2] The versatility of hydrogels has gained popularity in applications such as tissue engineering,^[3] drug delivery,^[4] soft electronics,^[5] smart devices^[6] and sensors;^[7] in which the smart functionality of the hydrogel is a must. For example, poly(N-isopropylacrylamide)

(PNIPAm) is a widely explored hydrogel, having a lower critical solution temperature (LCST) around 32 °C and is often used as an active matrix, responsive to temperature, pH and light irradiation,^[8] in applications such as drug delivery^[9] and smart windows.^[6a, 9] However, due to limitations of mechanical ^[10] and visco-elastic properties ^[11] during coil-to-globule transition, the processing and deposition methods of PNIPAm hydrogel are limited, especially for fabrication of complex structure patterning on flexible substrates.

Printing of hydrogels enables freedom-of-design, for fabrication of various patterns which are responsive to external stimuli, such as heat, that can yield a thermochromic response. Much effort has been devoted to developing printable hydrogel applications, including electrochemical devices ^[12] and biomaterials.^[13] One of the most well-known classes of printable hydrogels is based on photopolymers such as Polyethyleneglycoldiacrylate (PEGDA) which requires a photopolymerization processes.^[14] If the printing is performed by a layer-by-layer approach, it enables forming 3D objects with high aspect ratio, a process known as 3D or additive manufacturing (AM). To enable 3D printing, maintaining the smart functionality and reducing the water evaporation, a new and facile route is presented here, by embedding PNIPAm micro-sized particles within a printable Si/Al based gel matrix. The water-rich microenvironment is essential for the functionality of the hydrogel as well as to achieve tunable viscosity required for the printing.

The traditional 3D printing technologies for hydrogels include stereolithography and nozzle-based printing.^[15] As introduced by Zhang *et al.*,^[16] and Ouyang *et al.* ^[17] for 3D printing of hydrogels, cross-linking processes (physical, chemical or photo cross-linking) is required to achieve their designed functions during and/or the deposition process. Unlike previous reports of hydrogels 3D printing, here we show the printing of PNIPAm particles which are used as a functional additive and are dispersed within a printable Si/Al-based gel to form a PNIPAm Si/Al hybrid hydrogel (PSAHH). This hybrid can be printed directly on a flexible substrate to

achieve the designed function of thermochromism and optical switch, without any further crossing-linking process.^[16]

By either passive heating or electrical heating of the printed device, the water molecules which are trapped in the PNIPAm particles are extruded to the Si/Al sol gel matrix. This results in an optical change from a transparent to opaque state due to the dehydrated PNIPAm particles that act as light scattering centers. For electrically triggered heating, the hybrid ink is directly printed onto a flexible transparent conductive grid, which is composed of self-assembled silver nanoparticles (**Figure 1**).^[18] During the heating process, the Si/Al gel matrix retains the 3D structure and does not show any shrinkage, contrary to what is observed in pure PNIPAm hydrogels. As shown schematically in **Figure 1**, the new hybrid hydrogel can be deposited in various patterns by using a direct-write dispenser without the need for a further curing process.

Figure 1 mechanism and structure of flexible electro-thermochromic device (FETD). Top images represent the printing of the hybrid hydrogel at room temperature (left) and high temperature or applied voltage on the grid (right). At low temperature, the visible light wavelength can pass through the hybrid hydrogel (middle left), and when it is heated the light is scattered (middle right) by the PNIPAm particles without any shrinkage of the hybrid hydrogel. The mechanism is shown in the two bottom schemes. At room temperature, the water molecules are within the PNIPAm particles. Once heated (bottom right), the water molecules will be released from the PNIPAm and the shrinkage particles will cause scattering of the light.

2. Results and discussion

Figure 2a shows a scheme describing the designed printed pattern and deposition mechanism of the PSAHH gel onto a flexible transparent conductive grid. The printhead is moving along the X-Y axis, and after each layer is finished the build platform is lowered at the Z axis for the next layer to be printed. As can be seen in **Figure 2b** and **2c**, the layer-by-layer printing enables printing of patterns having a height of 2 mm. This height was obtained by printing four layers. Due to the suitable viscosity (50-100 PaS, **Figure S1**), the gel maintained its shape after each

layer of printing. **Figure 2d** shows the same pattern after heating to 35 °C, which becomes translucent due to the PNIPAm dehydration process.

Figure 2. a Schematic 3D printing; b Side view of printing process; c Printed hydrogel onto the transparent electrode at low temperature; d Printed hydrogel onto the transparent electrode at 35°C.

Another geometry is presented in **Figure S2a, b** which shows the different optical response before and after heating.

In order to show the applicability of the new material and method we have used it for fabrication of a flexible electro-thermochromic device (FETD) and a flexible optical waveguid valve. As seen in **Figure 3 a (i) (ii)**, while applying a current of 1.8 Amp on the two edges of the transparent grid, the PSAHH heats up and the contrast of the device changes from transparent to opaque, due to the behaviour of PNIPAm above the LCST. It should be noted that the time required for the device to return to its transparent state is just a few seconds, as seen in Video S1 (Supporting Information).

Figure 3 a (i) FETD without applied voltage at room temperature and (ii) with 1.8 A steady current applied; b FETD with 1.8 A steady current applied 180° bending; c Schematic of FETD to bend to 180°; d Response time of FETD with different applied current and embedded pictures (embedded pictures show the FETD at transparent state ~ 0 amp, translucent state ~ 0.6 amp, and opaque state ~ 1.8 amp); e reported ETDs response time and applied voltage, f Thermo-durability of FETD, g Pictures of straight

line composed of a segmented SiAl matrix and PSAHH (marked in dashed yellow line) printed on glass substrate at room temperature f(i) and 60°C f(ii) with green laser illumination, h Pictures of straight line of a segmented SiAl matrix and PSAHH printed on a transparent flexible electrode at room temperature while bending twisting (i) during laser illumination.

The direct contact of the hybrid hydrogel with the grid enables high flexibility of the full FETD device, as can be seen in **Figure 3b** and video S1. 400 μm thick samples were tested at various bending angles (from 0 to 180 °) and there were no short-circuit of the transparent grids under applied voltages up to 8 V. It should be noted that even at bending angles of over 180°, the transparent electrode continued to heat, indicating flexibility of the transparent conductor. The device was tested for 100 cycles of 90 degrees bending without any noticeable change in the heating temperature or applied current. This high flexibility of the device is attributed to the direct contact between the gel and transparent electrode, which makes the gel adapting to the same geometry of the transparent electrode, as shown schematically in **Figure 3c**. This is in contrast to our control experiment that was performed with pure PNIPAm gel only, which delaminated upon bending.

Due to the direct contact of the hybrid gel with the electrical grids, the response time significantly decreased compared with previous report.^[6b] The response time is directly depends on the applied current, which decreased from 35 to 17 s, while the current increased from 0.6 to 1.8 Amps (2 ~ 6 V) (**Figure 3d**). **Figure 3e** compares the response time with other reported ETDs ^[6b, 19], showing that the new FETD has a faster response with relatively low energy consumption. As seen in **Figure 3d**, the visible transmittance is also dependent on the applied current, while after applying 0.6 amp on FETD, the device will turn from transparent to translucent, and only when the current is increased to 1.8 amp, the FETD will turn to completely opaque. This was observed as well for the reverse case from opaque to transparent.

The effect of the hybrid gel thickness on the optical and thermochromic properties of the FETD were further studied. **Figure S3a, b** shows optical spectra and thermochromic properties of FETD composed of thickness of 100 μm , 200 μm , 400 μm and 800 μm (sample A, B, C, and

D in sequence) of PSAHH film with and without applied current. As shown in **Figure S3b**, T_{lum} decreases as the thickness increases at both 20 °C and 60 °C, which is different from pure PNIPAm hydrogel. As temperature increases, for pure PNIPAm hydrogel, there is negligible T_{lum} decrease below LCST.^[6b] As can be seen in **Figure S3b**, 400 μ m films obtained the highest ΔT_{lum} of 80.1% and ΔT_{IR} of 66.15% between 20 °C and 60 °C, which leads to an extremely high solar modulating ability (ΔT_{sol}) of 73.5%, while at the same time, T_{lum} of 400 μ m film is still higher than 80% at 20 °C, which is just slightly lower than 100 and 200 μ m films. Correspondingly, 400 μ m films showed the largest contrast in transmittance at 600 nm, which is about 80%. It should be noted that an important advantage in printing the hydrogel is that the layer thickness can be easily tuned by simply controlling the number of printed layers.

An interesting phenomenon was observed in **Figure S4a**, where T_{lum} samples of grid with SAPHH had higher transparency than empty silver grid (73.7%), except for sample D. This may be largely due to the direct contact and filling of the silver grid voids by the PSAHH (**Figure S4b**). The height of silver grid lines is about 1 micrometers (**Figure S4c**), while the space between the lines is 50 μ m (**Figure S4d**), thus grids are a bit translucent due to the light scattering at the grid void areas (**Figure S4e**). As shown in **Figure S4f**, once PSAHH covers the grids voids, the space between grids will be filled with a transparent and homogenous layer of gel formed (**Figure S5**), which could enhance transmittance. It is worth noting that this direct contact of water based hydrogel with the conducting silver grid without short-circuit is bennifted from the novel water encapsulation ability provided by Si-Al gel matrix.

The long-term performance of the FETD was evaluated by a cycling durability test. As shown in **Figure 3f**, the transmittance at 600 nm under 60 °C (1.8 amp applied, for 400 μ m film thickness) were almost constant after 100 cycles, while T_{lum} at 20 °C (no current applied) was slightly decreased from 88% to 72%. Meanwhile the contrast at 600 nm also decreased with the cycles, but still 64% of the contrast remained.

This hybrid hydrogel can also act as an optical switch in a printed waveguide. We printed waveguides with different shapes, composed of three segments: pure Si/Al gel, PSAHH and pure Si/Al gel. As can be seen in **Figure 3g**, during illumination by a green laser, the light passes thorough the whole waveguide (**3g(i)**). Whereas, after heating the printed waveguide to 60°C, the green light is blocked by the PSAHH segment (**3g(ii)**). This is due to the light scattering resulting from the de-hydrated PNIPAm particles. Since the hybrid hydrogel is flexible, we further demonstrated that the printed flexible waveguide continues to function while bending (**Figure 3h**) and twisting (**Figure 3i**) under laser illumination.

Unlike the pure PNIPAm hydrogel which has a significant disadvantage of volume shrinkage while heating due to the deswelling of the water in the hydrogel (**Figure S6a, b**), the hybrid PSAHH did not show any shrinkage and deformation during heating (**Figure S6c, d**). The main reason for this is that the water is retained within the Si-Al gel matrix (**Figure 1**).

TGA analysis was performed for all the samples at 25 to 60 °C, while holding the temperature at 25, 40 and 60 °C for 30 minutes at each temperature. As can be seen in the TGA curves (**Figure 4a**) of pure PNIPAm, PSAHH and Si/Al matrix (without PNIPAm), there is a dramatic weight loss of 30 wt% at 25°C and a total weight loss of 90 wt % at 60 °C, due to the evaporation of water from the pure PNIPAm sample, while for the hybrid gel only 31% total weight loss is observed up to 60 °C (total water content was 67.5 wt%). It can be seen that a similar weight loss was observed for the matrix without PNIPAm (blue line) and for the PSAHH, indicating that the water retention is mainly attributed to the Si/Al matrix.

Figure 4 a Weight loss of both pure PNIPAm hydrogel and PSAHH in heating process, b UV-Vis-NIR spectrum of both pure PNIPAm hydrogel and PSAHH, c Hysteresis loop and derivative of both pure PNIPAm hydrogel and PSAHH.

UV-Vis-NIR measurement was performed on 400 μm thickness film samples. As seen in **Figure 4b**, two distinct valleys can be seen in the transmittance spectrum at 1400 and 1900 nm for both pure PNIPAm hydrogel and hybrid PSAHH; These valleys are attributed to the IR light absorption of O-H stretching and bending of water molecules at these wavelengths.^[20] The intensity of the transmittance valleys are negatively dependent on temperature,^[21] therefore the valley intensity decreases after heating. During heating, water molecules are released from the PNIPAm, which is reflected in the low intensity valleys of the O-H stretching ^[6a]. The solar transmittance spectra of pure PNIPAm and PSAHH samples are nearly the same at both room temperature and 60 °C. This implies that the optical response of both hybrid and pure PNIPAm hydrogel are the same and the heat stimulated smart function is maintained. Furthermore, the coloration contrast of PSAHH is more than 80% at 600 nm, with an extremely high solar modulating ability, 72.7%, showing similar transmittance and solar modulating ability of pure PNIPAm.

The transmittance hysteresis loop at 600 nm was recorded during a heating and cooling cycle within the temperature range of 20 °C to 60 °C for the 400 μm thick sample (**Figure 4c**). The inset of **Figure 4c** shows the derivative graph of the LCST of PSAHH compared to that of pure PNIPAm which was used to calculate the average LCST. Interestingly, the average LCST of PSAHH was 32.5 °C, which is higher than that of the pure PNIPAm hydrogel at 28 °C. This is probably due to the poor thermal conductivity of the inorganic Si/Al matrix as opposed to that

of the pure PNIPAm hydrogel. Overall it can be concluded that after embedding the PNIPAm particles within the Si/Al matrix, the heat response of the hydrogel is maintained.

All the samples were dried, followed by SEM, EDX, FTIR and Raman characterization. As can be seen in the SEM image in **Figure S7a** and **Figure 5a**, the PANIPAm is present as small irregular particles in the size range of tens of micrometers. EDX chemical mapping (**Figure 5b**) confirm that these particles are composed of PNIPAm, since they do not contain any Si. Figure S7b shows the porous structure of pure Si/Al matrix after freeze-drying, where the pores were formed due to the evaporation of water from the Si-Al gel. As seen in **Figure 5c**, the microstructure of the surface of the PNIPAm microparticles does not change after being embedded in the Si-Al gel matrix, compared with freeze-dried PNIPAm particles dispersed in DI water (**Figure 5c inset**) as the porous structure on the surface remains.

Figure 5 a SEM image of individuals PNIPAm particles, b EDX mapping of Si in Si-Al matrix, c SEM image of PNIPAm microparticles embedded in the Si/Al gel matrix after freeze-drying. Inset image shows pure PNIPAm micro pieces after freeze-drying in the same scale. d FTIR spectrum of freeze-dried pure PNIPAm hydrogel, pure Si-Al gel matrix and PSAHH, e Raman spectrum of pure PNIPAm hydrogel, pure Si-Al gel matrix and PSAHH.

Figure 5d shows the FTIR spectra of Si/Al matrix (blue), PSAHH (black) and the pure PNIPAm hydrogel (red). The three large absorption peaks at 1540 cm⁻¹ (amide II group), 1650 cm⁻¹

(amide I group) and 1460 cm^{-1} (-C=O bond) can be observed in pure PNIPAm sample, which are the three characteristic peak ^[22] of PNIPAm. Another absorption peak at 3300 cm^{-1} attributed to -NH bond, is partially merged with another peak at 3440 cm^{-1} , which is a significant peak of -OH .^[23] For PSAHH sample (black) the amide II, amide I and -C=O peaks were clear. This is due to the unevaporated water left in PSAHH sample, and the existence of strong intramolecular hydrogen bonding formed between -C=O groups or -NH groups of PNIPAm and -OH groups of Si/Al matrix^[24]. Furthermore, FTIR measurement of three samples before and after the UV exposure (**Figure S8**) shows that the three characteristic peaks remain nearly intact suggesting that hybrid gel has the same UV stability as the pure PNIPAm.

Figure 5e shows the Raman spectra of the Si/Al matrix (blue), PSAHH (black) and the pure PNIPAm hydrogel (red). As can be seen for the Si/Al matrix, the Si-(OR)_4 stretching peak is at around 400 cm^{-1} and a typical Al-(OH)_3 stretching is $\sim 3600\text{ cm}^{-1}$.^[25] It is interesting to note that the Si-OR peak can be well observed after the addition of the PNIPAm particles, however the Al-OH stretching peak is merged by the PNIPAm organic large stretching peak around $3300\text{-}3600\text{ cm}^{-1}$. This peak can also be observed for the pure PNIPAm, which is due to stretching of -OH in water^[26] and has extremely large intensity than other significant peaks in PNIPAm. The Raman spectra shows that the PSAHH is a combination of the pure PNIPAm embedded in a Si/Al matrix without any additional covalent bond.

3. Conclusion

A new hybrid hydrogel ink was fabricated and printed layer-by-layer directly onto a flexible substrate and a transparent electrode. The new and simple approach involves a printable Si/Al-based gel matrix with embedded smart hydrogel polymeric particles. The hybrid ink printed structures sustained bending angles of up to 180° and enabled patterning of various flexible electro-thermochromic devices such as a flexible smart window and an optical waveguide switch. We expect that this new approach will pave the way for fabrication of smart optical

devices by additive manufacturing processes, and for printing other materials with high water-loading.

4. Experimental Section

N-isopropylacrylamide (NIPAm, 98%, Wako Pure Chemical Industries Ltd), N, N – methylenebis (acrylamide) (99%, Sigma-Aldrich), N,N,N,N-tetramethylethylenediamine (TEMED, accelerator, 99%, Sigma-Aldrich), ammonium peroxydisulfate (98%, Alfa Aesar), (3-Glycidyloxypropyl)trimethoxysilane (GPTMS, 98%, Sigma-Aldrich); trimethoxymethylsilane (MTMS, 98%, Sigma-Aldrich), Aluminum-tri-sec-butoxide (ATSB, Sigma-Aldrich), Polyvinylpyrrolidone (PVP40, Sigma-Aldrich), Nitric acid (HNO₃, 70%, Sigma-Aldrich), Methanol (99.9%, Sigma-Aldrich), Verowhite (Stratasys), and Loctite 3414 were used without further purification. Deionized water (18.2 MU), Ethanol (99.8%, Sigma-Aldrich) was used throughout the experiments.

Preparation of liquid PNIPAM-hydrogel

The synthesis of the liquid PNIPAM-hydrogel follows the synthesis of pure PNIPAM-hydrogel^[6a]. 3.164g (0.14 mol) of PNIPAM and 862.4mg (0.028 mol) of N,N'-methylenebis(acrylamide) were dissolved in D.I. water at 25 °C to make 400 mL homogenous aqueous solution. Then 6.15 mL of TEMED (catalyst) was added, followed by mixing at 600rpm for 30 mins. Finally, 12.3 mL of APS (initiator) was added into the solution. In order for the reaction to be completed, the solution was left stirring for at least 24 hours. The whole procedure (including completion of the reaction) was conducted at room temperature (25 °C). Then the homogenous liquid underwent pre-freezing-freeze-drying process by liquid nitrogen and dried by vacuum at -50 °C for 72 hours. After freeze drying, the PNIPAm powder was directly dispersed into 20 ml DI water by using vortex for 1 min, then the PNIPAm liquid

hydrogel was made. This pure PNIPAm liquid hydrogel is transparent at room temperature and will turn to opaque, when the temperature is above LCST (**Figure S9** a and b).

Preparation of Si/Al gel

The preparation method of Si-Al gel was reported.^[27] To begin with, 1500 ml DI water was poured into a 2 L three-neck flask on heating mantle. Following process was to heat up DI water to 80 °C while stirring at 200 rpm, then turn off the heating. 400 ml ASB was poured in quickly, under stirring, for 4 minutes. Then, 10 ml HNO₃ was added to adjust pH to 3~4. Then the flask was heated up again to 80 °C under stirring at 200 rpm for about 2 hours to evaporate from 600 ml liquid in the flask. 30 g PVP was added into the flask under stirring, until all PVP dissolved, resulting in “solution A”. 755 ml GPTMS, 218 ml MTMS, 1472 ml ethanol and 512 ml methanol were mixed and agitated ultrasonically for 30 mins to obtain “solution B”. after cooling down solution A to room temperature, it was poured into solution B slowly to obtain “solution C”. Finally, 120 g PVP was dissolved in solution C under ultrasonic agitation for about one hour.

Preparation of the transparent electrical grid

The fabrication of the transparent electrical grid was conducted directly on the polyethylene terphthalate substrate (PET 125 µm, Jolybar Israel). The transparent grid fabrication process was reported previously.^[28] Briefly, a 420 screen printing stainless steel mesh (Ponger 2000 Israel) was placed onto the PET. Next, droplets of the silver nanoparticles (NP) aqueous dispersion^[29] were placed on top of the mesh. During evaporation of the water, the silver NP self-assembled along the walls of the mesh. After 20 min, the mesh was removed, leaving a grid pattern composed of the silver NP. Once the transparent patterns were formed, it was sintered by exposure to HCl vapors for 30 seconds. This was achieved by placing it in a 10 mL glass petri dish, which was placed in a larger petri dish (100 mL) that contained 10 mL of conc. HCl (37 wt%, Aldrich).

Preparation of PNIPAm-Si-Al Hybrid hydrogel (PSAHH) and flexible electro-thermochromic device (FETD)

2 ml PNIPAm liquid hydrogel were mixed into 8ml Si-Al based gel by stirring at 600rpm, heated up to 70 °C until only 2 ml of the PNIPAm-Si-Al gel was obtained. Frames with thicknesses of 100, 200, 400 and 800 µm made of verowhite (staratasys) were 3D printed (Eden printer, Stratasys) and placed directly on the surface of the electrical grid. The PNIPAm-Si-Al gel was placed directly inside the frames with PET thin film cover and Loctite 3414 sealant was applied at the edges.

The pattern formation was formed using a Hyrel (USA) system equipped with a 200 µm needle at a 2.3 pulses/nl rate without heating the printing bed. No waiting time was required between each printed layer. The printed pattern and thickness was defined by using an STL file to about 0.5 mm.

Characterization

The solar transmittance spectra in 250 nm – 2500 nm range were recorded with a UV-Vis-NIR spectrophotometer (Cary 5000, Agilent, USA) at normal incidence, while the detecting distance between light source and samples was 20 cm. The spectrophotometer is equipped with a heating and cooling stage (PE120, Linkam, UK).

The integral luminous transmittance T_{lum} (380–780 nm), IR transmittance T_{IR} (780–2500 nm) and solar transmittance T_{sol} (250–2500 nm) were calculated by equation 1:

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

where $T(\lambda)$ denotes spectral transmittance, $\varphi_{lum}(\lambda)$ is the standard luminous efficiency function of photopic vision^[30] in the wavelength range of 380–780 nm, $\varphi_{IR}(\lambda)$ and $\varphi_{sol}(\lambda)$ is the IR/solar irradiance spectrum for air mass 1.5 (corresponding to the sun standing 37° above the

horizon with 1.5 atmosphere thickness, corresponds to a solar zenith angle of $\approx 48.2^\circ$.^[31]

$\Delta T_{\text{lum/IR/sol}}$ is obtained by $\Delta T_{\text{lum/IR/sol}} = T_{\text{lum/IR/sol}, 20^\circ\text{C}} - T_{\text{lum/IR/sol}, 80^\circ\text{C}}$.^[32]

Current applied on the electrical heater was varied using a Keithly 2401. Temperature was measured and sample was photographed by using a FLIR E4 thermal imager.

TGA Q500 (TA instrument) was used to test the water content of PSAHH and pure PNIPAm hydrogel for 25 to 60 °C. The TGA analysis was performed for all the samples at 25 to 60 °C, while holding the temperature fixed at 25, 40 and 60 °C for 30 minutes at each temperature with ramping temperature of 20 °C per min.

The viscosity and shear stress of NIPAm solution, PSAHH and pure PNIPAm hydrogel were tested by Anton Paar Physica MCR 501 Rheometer, with 1 to 0.1 1/s shear rate.

JSM-5310 and FESEM-6340F were used to capture the scanning electron microscope (SEM) and energy-dispersive X-ray spectroscopy (EDX) images of the sample. Prior to the experiment, Samples were freeze-dried using liquid nitrogen (N₂) before drying in a chamber for 72 hours. Thereafter, the freeze-dried powder was examined using SEM. The Fourier transform infrared spectroscopy (FTIR) data was collected by FTIR Perkin Elmer Spectrophotometer (Spectrum 400 FT-IR). All the samples were pre-freezed in liquid nitrogen and freeze dried at -50 °C in vacuum chamber. 0.01 gram of each sample was milled and mixed with 0.3 gram KBr powder, then pressed into appropriate tablets. All the data were collected by transmittance mode.

Raman spectra was recorded using a Witec alpha300 SR (WITec) Raman microscope configured with a charge-coupled device array detector with the excitation laser line of 488 nm.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Hybrid hydrogel composed of embedded PNIPAm particles within a silicon-based matrix and printing of various functional devices onto flexible transparent electrical heaters. This approach enables fabrication of optoelectronic devices such as smart windows and optical waveguide valve.

Keywords: 3D printing, hydrogel, PNIPAm, smart windows, thermochromic

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Supporting Information

Fully Printed Flexible Smart Hybrid Hydrogels

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S1. Viscosity of NIPAm solution, pure solid PNIPAm hydrogel, PSAHH and shear stress of PSAHH

PNIPAm liquid hydrogel is totally transparent as at below LCST, at this time the liquid hydrogel's phase is homogeneous, while as temperature increasing above LCST, homogeneous phase started to separate, while the color became translucent and finally opaque.

S2: a Unique printed geometry of PNIPAm Si/Al hybrid gel at room temperature, b 1.8 amp steady current applied on Unique printed geometry of PNIPAm Si/Al hybrid gel film.

S3. a Transmittance spectrum of 4 samples with (solid line) and without (dash line) applied current; b Optical properties of 4 samples

S4 a. Luminous transmittance of 4 samples and pure silver grid at 20 °C; b Schometric of PSAHH cover on grids c, d SEM of silver regular grid, e, f Mechanism of high luminous transmittance of FETD.

S5 Microscope image of hybrid gel merged inside the grids. The spacing between the grid lines is 50 micrometers.

S6: a Pure PNIPAm hydrogel at room temperature, b Pure PNIPAm hydrogel heated up to 70 °C for 10 mins (shrinkage and phase separation), c PNIPAm Si-Al hybrid hydrogel at room temperature, d PNIPAm Si-Al hybrid hydrogel heated up to 70 °C for 10 mins (no visible shape change).

S7: a Freeze-dried PNIPAm liquid hydrogel micro pieces, b Porous structure of Si-Al matrix after freeze-drying

S8: a FTIR spectrum of pure PNIPAm hydrogel before and after UV exposure, b FTIR spectrum of pure Si-Al matrix before and after UV exposure, FTIR spectrum of PNIPAm-Si-Al hybrid hydrogel before and after UV exposure.

S9: a. PNIPAm liquid hydrogel at room temperature; b. PNIPAm liquid hydrogel at 60 °C

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