

Soft Matter

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COMMUNICATION

Light Responsive Two-Component Supramolecular Hydrogel: A Sensitive Platform for Humidity Sensors

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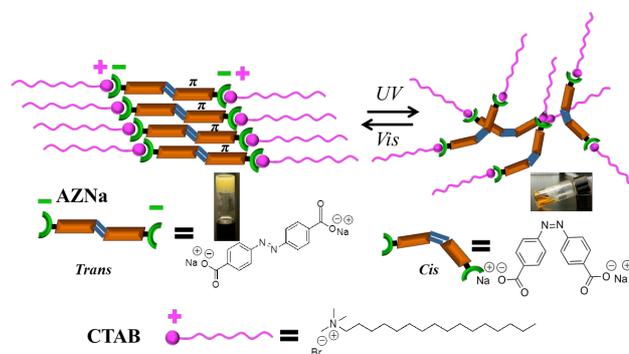
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The supramolecular assembly of anionic azobenzene dicarboxylate and cationic cetyltrimethylammonium bromide (CTAB) formed a stimuli responsive hydrogel with a critical gelation concentration (CGC) of 0.33 wt%. This self-sustainable two-component system was able to repair damage upon light irradiation. Moreover, it was successfully employed in the fabrication of highly sensitive humidity sensors for the first time.

Employing low-molecular-weight gelators (LMWGs) to prepare supramolecular gels has recently received substantial interest as these gelators are held together by common non-covalent interactions such as hydrogen bonding, π - π interactions, dipole-dipole, donor-acceptor, solvophobic interactions, and electrostatic interactions.^[1] In particular, two-component gelator composed of two different molecules is of significant importance as particular functionalities can be easily introduced by one component that ultimately transfers this property over the whole self-assembled system.^[2] Adding functionality or stimuli responsiveness to a gel system is now easily achieved yielding a plethora of 'smart' soft materials. These systems can respond to a wide range of stimuli such as temperature, light, magnetic field, electric field, pH, mechanical stress and chemical stimuli.^[3] Among these stimuli, light has many advantages including wide availability, ease of manipulation, and clean operation. Although light responsive gels are well established in literature, developing general and versatile methods for two-component gel formation as well as methods to control gel properties is still lacking. Supramolecular assembly of azobenzene and α -

cyclodextrin has been reported^[4] as well as the photo responsiveness of azobenzene containing polymeric systems.^[5] However, to the best of our knowledge, there are no reports on the supramolecular assembly of a two-component gelator system to form a photoresponsive and self-sustaining gel with very low CGC (critical gelation concentration) value. Thus, spontaneous self-assembly of a two-component gelator based on anionic azobenzene dicarboxylate (AZNa) and cationic surfactant cetyltrimethylammonium bromide (CTAB) to afford a supramolecular functional hydrogel is presented (**Scheme 1**). The azobenzene chromophore is an established photoresponsive moiety that can undergo photo-isomerization, which ultimately leads to the anticipated phase transition. Moreover, it contains an aromatic backbone that can promote supramolecular self-assembly. CTAB is employed as a complementary charged species with an amphiphilic character. The hydrogel was very stable for several months at normal conditions (22–25 °C) and it could be synthesized at large scale in a similar manner. It also presented impressive mechanical properties in addition to thermal and light responsiveness making it both self-sustaining and damage repairing. Moreover, we investigated the use of this system for the first time in humidity sensors where the impedance characteristics of the hydrogel film were examined and evaluated with changing relative humidity.



Scheme 1. Proposed mechanism of self-assembly and light-triggered disassembly of two-component hydrogel.

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The mechanism of self-assembly is mainly driven by the electrostatic interactions of anionic AZNa with cationic CTAB in addition to π - π stacking of the AZNa aromatic rings (**Scheme 1**). Oppositely charged molecules assembled one after another with the help of π - π interactions forming one-dimensional gel fibers. Subsequently, the one-dimensional gel fibers were intertwined into three-dimensional network structure, which created a plethora of voids and channels for holding water molecules. As expected, the hydrogel exhibited photoinduced phase transition upon UV irradiation (365 nm, 70 mW cm⁻², 5-6 min) where the thick gel (1.65 wt%) collapsed gradually to a clear orange solution (**Scheme 1**). Upon visible light exposure (> 450 nm) for 15-20 min, the clear solution reverted back to its former gel phase. The photo-isomerization causes an alternation of the distance between para carbon atoms of the azobenzene group from 9.0 Å in the *trans*- form to 5.5 Å in the *cis*- form. Consequently, the dipole moment of the two isomer changes from no dipole moment in *trans*- form to 3.0 D in *cis*-form.^[7] Literature reports confirm that the change in dipole moment is believed to disrupt the hydrophobic/hydrophilic balance.^[8]

Non-covalent interactions such as hydrogen bonding and π - π interactions can be studied by recording NMR spectra at different temperatures where the line width of NMR peaks can be used to distinguish between aggregated and free molecules.^[9] The recorded NMR spectra demonstrate that, below 45 °C, the aromatic region in the gel state showed two broad peaks corresponding to H_a and H_b of the azobenzene rings due to self aggregation (**Fig. 1**). The supramolecular self-assembled structure was retained upto 43 °C as evident by the broad and gradual down field shift of peaks. Further gradual increase in temperature to 45 °C resulted in the appearance of sharp and clear two doublet peaks providing a clear evidence of disassembly of gel phase and the formation of free state monomeric azobenzene moieties (**Fig. 1**). Temperature responsiveness (gel-sol transition temperature, T_{gel}) as well as chemical stability were also studied and reported in **Fig. S1**.

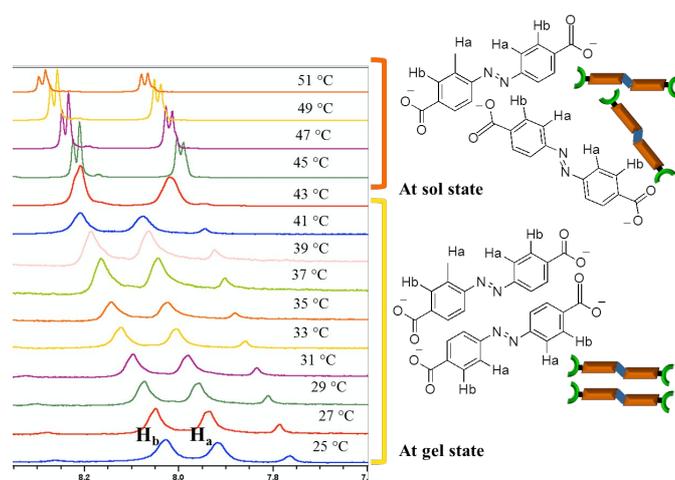


Fig. 1 Variable temperature ¹H NMR studies of hydrogel (1.6 wt %) in D₂O.

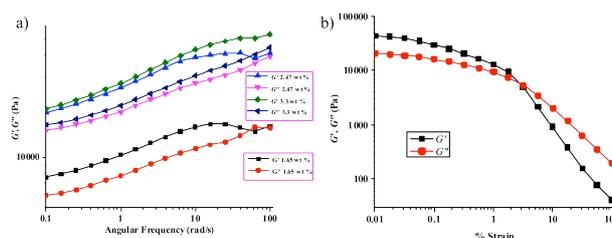


Fig. 2 a) Frequency sweep measurement of hydrogels with three different gelator concentration; b) amplitude sweep measurement of hydrogel at 1.65 wt%

The microstructure of the hydrogel was thoroughly examined with various microscopic techniques to obtain a visual image of the aggregation mode in the gel. Scanning electron microscopy (SEM), transmission electron microscopy (TEM), and confocal laser scanning microscopy (CLSM) experiments revealed that the gel have a fiber like morphology (**Fig. S2**). Such a supramolecular 3D network structure clearly depicts the better entrapment of solvent molecules.

Dynamic rheological measurements were performed for hydrogel samples with three different concentrations to demonstrate how the rheological behaviour changes with gelator concentrations. The storage modulus (G') and loss modulus (G'') with respect to applied stress (amplitude sweep) and applied frequency (frequency sweep) were measured for 1.65 wt%, 2.47 wt% and 3.3 wt% hydrogel samples. **Figure 2a** describes the frequency sweep measurement of three hydrogel samples. It can be seen that at lower frequency region G' is greater than G'' indicating true gel-like material. In all three cases, both G' and G'' are increasing with increasing frequency and in case of 1.65 wt% gel, one cross-over point appeared at a particular frequency, indicating decrease in elastic character in the gel system. This may be due to the fact that at higher frequency region the fiber network structure is no longer intact and the gel matrices breakup into smaller units. With gradual increase in gelator concentration the crossover point disappeared, demonstrating the gradual increase in gel network structure. Furthermore, the firmness or rigidity of the gel material is often expressed by $G'-G''$ value (**Table S1**). Analysis of these values suggests that the 3.3 wt% gel exhibits higher firmness (10147 Pa) while 1.65 wt% gel has lower firmness (2861 Pa). The variation of G' and G'' with applied stress (amplitude sweep) at a constant frequency (1 %) for 1.65 wt% gel is shown in **Figure 2b**. Above a critical value, both G' and G'' fall abruptly to a very low value indicating the free flow of the gel. This critical value is known as yield stress (σ_y). The σ_y values for all three gel samples are summarized in **Table S1**.

Hydrogel erosion kinetics was measured in order to demonstrate the gel's stability under water. Distilled water (2.3 mL) was added on top of the gel (0.7 mL of 3.3 wt%) and erosion was monitored under water at room temperature over a period of 25 days by measuring absorbance at 334 nm (**Fig. S3**). Interestingly, the two-component hydrogel was extremely stable under water over a long time at room temperature. The self-sustaining nature of the gel was verified by transferring

the gel (1.65 wt%) from a vial to a petri dish to observe the integrity of the as-prepared system. Interestingly, this soft gel retained its cubic shape as seen in **Fig. 3a**. The bulk gel material was then cut into two pieces with a blade followed by manually bringing the two pieces together with a moderate press (**Fig. 3b**). The system was then covered with a glass slide and left standing for 24 hrs at room temperature. **Fig. 3c** shows that the two blocks completely fused together and can be suspended in air. Moreover, we concluded that the time needed for full coalescence can be tuned by varying the gelator concentration (data not shown). We hypothesize that the regeneration of attractive electrostatic interactions between the two gel blocks is promoting the self-sustaining process upon physical contact as illustrated in **Fig. 3**.

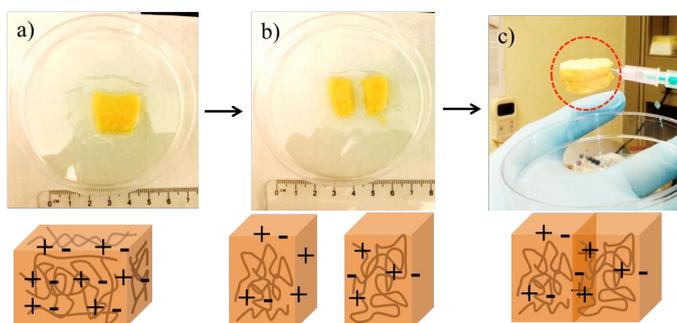


Fig. 3 a) Self-sustaining nature of the gel; b) gel is cut into two pieces; c) gel blocks completely coalesce after 24 h.

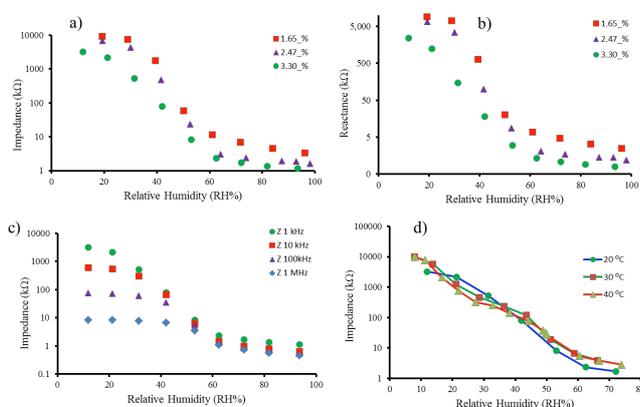


Fig. 4 a) Impedance b) reactance at 1 kHz for 3 gel concentrations; c) frequency dependence of the measurements for the concentration of 3.3%; d) hydrogel humidity response at different operating temperatures at 1 kHz in logarithmic scale.

Although this system is self-sustaining by nature, it is also photo triggered due to the presence of azobenzene. Yoshida et al. has documented photochemical surface healing using an azobenzene dopant of a microparticle/liquid-crystal (LC) composite gel.^[10] Thus, we ventured to investigate if we can promote faster damage repair when our system is coated on a surface utilizing external stimuli. Our gel solution shows absorption maxima at 330 nm and shoulder band at around 430 nm (**Fig. S4a**). The strong absorption band at 330 nm

corresponds to $\pi\text{-}\pi^*$ transition of the *trans*- isomer and the weak absorbance at around 430 nm corresponds to $n\text{-}\pi^*$ transition of the *cis*- isomer. Upon UV light irradiation (365 nm), the 330 nm absorption band decreases remarkably and concomitantly the shoulder band increases slightly, which indicates the progress of the photo-isomerization from *trans*- to *cis*- isomer. Subsequently under visible light irradiation, the $\pi\text{-}\pi^*$ absorption increases with slight decrease in $n\text{-}\pi^*$ absorption, corresponding to the photoisomerization of azo group from *cis*- back to *trans*- state. Photo-isomerization between *cis*- and *trans*- isomers of the binary self-assembled system could be recycled many times without decomposition of the components (**Fig. S4b**). The gel was coated on a metal surface and 2 similar cuts were induced on the surface. One side was irradiated with a UV lamp (365 nm, 70 mW cm⁻²) followed by visible light exposure while the other cut was not UV irradiated. The irradiated surface completely healed after just 2 mins of irradiation (**Fig. S4c**). We believe that upon irradiation, the gel is partially transformed to sol state permitting the gelator networks to reorient and redisperse in the damaged area. Subsequent visible light exposure of the UV-illuminated area resulted into *cis*- to *trans*- photoisomerization and repaired the damaged area by reordering the gel network structure. It is important to note that the above process was not due to a thermal effect but strictly due to photo-isomerization as during experimental time the gel surface temperature was increased to 22.6 °C from 19 °C, which is lower than the gel-sol phase transition temperature.

The porosity and the fibrous network of the hydrogel have prompted us to explore its potential for use in humidity sensors. Moreover, Literature shows that most of the polyelectrolyte based humidity sensors contained quaternary ammonium group as one of the common groups in their structural unit.^[11] Three different gel samples (1.65 wt%, 2.47 wt% and 3.3 wt%) were prepared to be tested for humidity sensing. The film was immobilized on gold interdigitated electrodes as previously described.^[12] A decreasing trend in the impedance with the increase of the relative humidity is shown in **Fig. 4a**. The reason for this is based on the fact that water molecules diffuse in the pore of the gel network, changing the materials properties. Thus, the film is becoming more conductive and the impedance decreases. Moreover, lowering the gel concentration gave higher impedance values. The higher the concentration is, the higher the capacitance gets since the absolute value of the reactance is inversely proportional to the capacitance (**Fig. 4b**). This is based on the fact that higher gel concentration has higher relative permittivity. **Fig. 4c** demonstrates the sensor response at different reading frequencies of the LCR (1 kHz, 10 kHz, 1 MHz) and it is plotted in logarithmic scale. It has been shown that the measurements are frequency dependent. Applying an AC signal, the capacitor will accumulate specific amount of charge before the sign change of the potential difference and the charge dissipates. The higher the frequency, the less charge will accumulate and the smaller the opposition to the current. The impedance readout at low frequencies provides ample time for water dipoles to orient to

a large extent in the material. For this reason, the water molecules absorbed by the pores of the gel fiber networks can achieve higher polarization at lower frequencies. Another way of measuring the sensors's output is by using simple IC circuitry.^[13] Finally in order to test the sensor at different operating temperatures, the testing chamber was placed above a hot plate (with temperature control). As concluded from Fig. 4d for a concentration of 3.3 wt%, varying temperature did not affect the sensor's operation. Thus, this material can provide a wide range of temperature operation, which is the most common for indoors and outdoors monitoring.

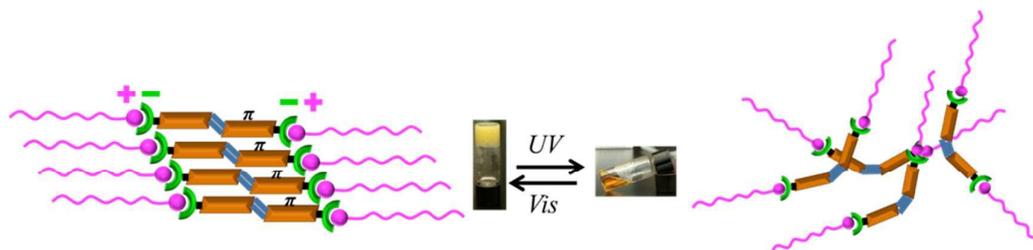
In summary, spontaneous self-assembly of a two-component hydrogel afforded a stimuli responsive hydrogel at room temperature. Self-sustaining nature of the hydrogel was verified and showed to be dictated by the oppositely charged nature of the two components. Light-triggered phase transition of the hydrogel was also utilized for repairing surface coating. The hydrogel was then coated on gold interdigitated electrodes and tested as a humidity sensor where it showed high sensitivity and reproducibility due to the ability of the hydrogel to uptake water molecules at relatively low frequencies. To the best of our knowledge, this is the first report on the use of stimuli responsive two-component hydrogel in humidity sensors. It is envisioned that self-assembled soft materials could be further extended for the development of many smart systems due to their straightforward fabrication and ease of manipulation and design.

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TOC Entry



Supramolecular self-assembly of a two-component hydrogel afforded a stimuli responsive hydrogel at room temperature.