A smart polymer with a high sensitivity to temperature and humidity based on polyacrylamide hydrogel doped with polyiodide†

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Herein, we propose a novel strategy involving polyiodide ions to design multifunctional smart hydrogels with high temperature sensitivity. We used iodide ions for in situ fabrication of the non-conductive polyacrylamide (PAM) hydrogel to obtain lyophilized PAM hydrogel doped with polyiodides (PPI) that exhibited negative temperature coefficient (NTC) behavior with high temperature sensitivity. Moreover, the PPI also exhibits special humidity-response behavior, with moisture sensitivity being greatly enhanced compared to hydrogels with common electrolytes (such as LiClO4). The simple and scalable fabrication process, high temperature and humidity responsivity, and intrinsic flexibility are important for the development of smart wearable electronics.

Fig. 1 depicts the fabrication process of PPI wire. PAM hydrogel was first synthesized according to a reported method with some modifications.6 The water content of the synthesized hydrogel was measured to be 88% (wt/wt) by swelling and drying (ESI,† Fig. S1). The PAM gel with a length of 10 cm in plastic tubes (ø = 4 cm) was prepared in the plastic tube following a reported method (Fig. 1a)

A smart polymer is developed by in situ fabrication of polyacrylamide hydrogel with polyiodide. The resulting PAM hydrogel doped with polyiodide showed a high sensitivity to temperature and humidity. Its special humidity-response behavior with high responsivity makes the described hydrogel a highly promising material for building temperature- and humidity-control switches.

Hydrogels are polymeric networks that possess numerous useful properties—including the three-dimensional (3D) microstructures and capability of absorbing large amounts of water—which lend them to various applications in bioengineering, medicine, food industry, water purification, and separation processes.2 In the past few decades, smart hydrogels have been widely researched due to their ability to respond to external stimuli such as light, temperature, electrical field, pH, and even specific biomolecules (antigen).3 Moreover, the 3D hierarchically porous structure of swelled hydrogels allows the permeation of ions and small molecules for in situ modification.

Iodine is a well-known electron acceptor that can produce iodide and polyiodide anions in the interaction with strong electron donors. The Lewis acid acceptor iodine and the Lewis base donors I– or I3– can be regarded as the fundamental building blocks of polyiodides. Polyiodide species can also be formed in the reaction of iodine with nucleophiles (such as phosphine selenides/sulfides and amines). Due to their special electronic properties, iodine and polyiodides are used in many different areas. The discovery of high (metallic) conductivity of polyacetylene after iodine doping has led to the Nobel Prize in Chemistry in 2000.4 Some reports also indicate that the polyiodides can increase the conductivity of polymers.5 Also, polyiodides are essential components of dye-sensitized solar cells, as a reversible redox couple, and of organo-lead perovskites as a structural element of these inorganic frameworks.

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and then dried at 80 °C for 24 h (Fig. 1b). Next, the tube was filled with the aqueous solution of hydrogen polyiodide (ca. 1 M) (Fig. S2, ESI†). After swelling in the solution of hydrogen polyiodide, the color of the PAM hydrogel changed from colorless (Fig. 1a) to dark brown (Fig. 1c), indicating homogeneous dispersion of polyiodide ions in the hydrogel. Finally, the PPI-impregnated rod was obtained after lyophilizing and tailoring (Fig. 1d).

To study the thermistor performance of the PPI, we used chronoamperometry in a two-electrode configuration. To exclude the influence of humidity and flow of air, PPI devices were sealed with Kapton adhesive tapes (Fig. 1e). We used a touchless temperature perturbation to prevent the effect of strain-induced resistance change and blew hot and cool air using a hair dryer (Fig. 1e). A typical heating perturbation period of 10 s was employed. We found that the current increases sharply with increasing temperature (Fig. 1f), after which the device was allowed to recover to its background temperature (25 °C) by blowing cool air. Fig. S3 (ESI†) illustrates the detailed views of a single cooling response; the recovery process is below 10 s. The PPI showed good stability for the repeated temperature responses (Fig. 1f). The lyophilized PAM hydrogel without polyiodide showed a very low current and no response to temperature (Fig. 1f). The thermistor behavior of PPI could likely be attributed to the semiconducting property of polyiodides, in which an increase in conductivity is induced by thermally activating the carriers (see below).† Therefore, the current-time curve confirms that polyiodides increase the conductivity of PAM.

The Raman spectra of PPI (Fig. 2a) show four peaks at 218 cm⁻¹, 147 cm⁻¹, 110 cm⁻¹ and 67 cm⁻¹ corresponding to the polyiodide building blocks, I₂ and I₃⁻. The symmetrical ion I₃⁻ normally exhibits one Raman active band, the ν₃ symmetric stretch around 110 cm⁻¹. However, when the ion’ symmetry is broken through interactions with other species (herein –C=O)NH₂ and I₂), the νₛ deformation vibration (70 cm⁻¹) and the ν₃ antisymmetric stretch (130–140 cm⁻¹) also become Raman active. Moreover, in the solid state free I₂ exhibits a single Raman band at 180 cm⁻¹, which moves to a lower wavenumber upon coordination to a donor atom (herein I₃⁻), indicating a reduction in the I-I bond order.† The UV-Vis absorption spectra of PPI thin film are shown in Fig. 2b. The PPI shows wide absorption with an onset at about 1464 nm. The band gap E₉ determined from the absorption edge is about 0.85 eV.

To image the morphology of the hydrogel by Scanning Electron Microscopy (SEM), the swollen gel was frozen by dipping in liquid nitrogen and then freeze dried in vacuum for 48 h. SEM images of the thus-lyophilized hydrogels (partially de-swollen, contraction volume is about 40–50%) show a classic 3D porous foam morphology of both PAM and PPI hydrogels (Fig. 3). The PAM forms a continuous network with micron-sized pores (marked by the white arrows in Fig. 3a). After impregnating with polyiodide, the dehydrated gel turns to a dark color (inset of Fig. 3c), and coral-like dendritic fibers can be observed on the edge of the pores (marked by the white arrows in Fig. 3c and d), probably attributable to polyiodide crystallites. To study the distribution of iodine within the gel, the PPI was subjected to energy dispersive X-ray (EDX) mapping. The results revealed 5.1 atom% (~34 wt%) iodine in the lyophilized PPI (Fig. S4a, ESI†), which was uniformly distributed throughout the hydrogel structure (Fig. S4b, ESI†). We suggest that this uniform functionalization of PAM surface with polyiodides could be attributed to the interaction between the iodine and the amide groups of the polymer (Fig. S4, ESI†).

Hence, we can infer that combining the non-conductive PAM gel with semiconducting polyiodides is responsible for the thermistor behavior of PPI.

To further examine the thermistor performance of the PPI, we studied the conductivity change upon varying the temperature. Fig. 4a shows the I-t curves of the PPI thermistor in the range of 30–100 °C. At 2 V bias, the current of the device increases from 0.15 μA (at 30 °C) to 3.64 μA (at 100 °C)—a clear indicator of negative temperature coefficient (NTC) behavior.† Fig. 4b shows the decrease of resistance variation with increasing temperature. The exponential dependence of resistance on reciprocal temperature is described by an Arrhenius-type equation:

\[
R = R_0 \exp \left( \frac{E_a}{2kT} \right) = R_0 \exp \left( \frac{B}{T} \right)
\]

where \(R\) is the resistance at temperature \(T\), \(R_0\) is the resistance at \(T = \infty\), \(E_a\) is the thermal activation energy, \(k\) is the Boltzmann constant, and \(B\) is the thermal index. Eqn (1) can be rewritten as

\[
\ln(R) = \ln(R_0) + \frac{E_a}{2kT} = \ln(R_0) + \frac{B}{T}
\]
The temperature dependent resistivity is a result of the semiconducting nature of polyiodide, which is controlled by thermally activated charge carriers, leading to the decrease of resistance at higher temperature. Similar to conventional ceramic thermistors, the measured NTC characteristics of our devices indicate their semiconducting behavior. For our PPI thermistors, the high temperature sensitivity results from the lower carrier density in the non-conductive polymer matrix, whereby the thermal activation can induce larger resistance variations.

We performed control experiments, replacing the polyiodide with a 1 M LiClO4 electrolyte. Fig. 4d shows the I-t curves at different temperature from 30 to 100 °C. In contrast to PPI, very little change of the current was observed up to 60 °C, and above 70 °C the hydrogel became soft leading to a sharp increase of the current. Moreover, the measured current was very unstable and decreased sharply after applying the bias, indicating an ionic nature of conductivity. The decrease of the current can be attributed to the formation of the reverse internal potential ($E^\circ$) with the electrical double layer as the ions with opposite charge diffuse at the applied potential ($E$). At high temperature, the ion diffusion ability in the hydrogel was enhanced because of the increase in the fluidity of the polymer. The proposed mechanisms of temperature-dependent conductivity of PPI and PAM/LiClO4 are described in Scheme 1.

The stability of the thermal-response of PPI devices was demonstrated by varying the temperature between 30 °C and 80 °C (Fig. 5). The current remains stable for cycling between 80 °C heating (20 s) and 30 °C cooling (20 s), indicating a fully reversible conductivity change. Our results suggest that the novel PPI material has high potential to be used in NTC thermistor devices.

Non-encapsulated PPI thermistor devices also reveal a strong response to humidity (Fig. 6a). A simple device was used to adjust and monitor the humidity of environmental conditions of PPI (Fig. S5, ESI†). In the control PAM/LiClO4 devices the current increases only slightly as the humidity increases from 30% to 60% (Fig. 6b). The PPI devices show a similar behavior up to a humidity of ~50%. However, as the humidity is increased above 50%, a two-part linear relationship between $I$ and humidity ($H$) is observed (Fig. 6c): between 50% and 55% the current changes slowly with a slope of ~0.02 μA per %H; above 55%, the current increases more rapidly, with a higher slope of ~0.38 μA per %H. When the humidity is increased to 60%, both hydrogels show characteristic ion diffusion, according to the I-t curves. This is probably due to the formation of aqueous channels within the hydrogel under higher humidity. Notably, the PPI showed a much higher humidity response than PAM/LiClO4. These results indicate that water can greatly enhance the conductivity of polyiodides. Fig. 6d shows the cycling stability of the PPI humidity sensor, between 50% and 57%

**Scheme 1** Proposed temperature-conductive mechanism of PPI and PAM/LiClO4.
humidity. The sharp change in current with the rapid change in humidity between 57% (or higher) and 50% (or lower) indicates the reversibility and stability of PPI devices. The simple linear relationship between $I$ and $H$ makes PPI a promising material for application in humidity-control switches.

Conclusions

In conclusion, we fabricated a novel polymer thermistor by combining PAM hydrogel with polyiodide. This material exhibited typical semiconductor-like NCT behaviors. The device achieved a thermal index (B) as high as 5320 K, which significantly exceeds that of both the conventional ceramic material (typically, transition metal oxides) based thermistor (2000–5000 K)\(^3\) and the recently reported graphene thermistors (847–1860 K).\(^{14,15}\) The excellent thermistor sensitivity can be attributed to the combination of non-conductive property of PAM polymer chains with semiconductivity of polyiodide. Moreover, this hydrogel also showed a special humidity-response behavior with high responsivity. The simple fabrication method, plasticity, low-cost and high sensitivity make PPI hydrogel a promising thermistor material for application in humidity-control switches.

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References

17. C. Yan, J. Wang and P. S. Lee, ACS Nano, 2015, 9, 2130.