Printed, Flexible pH Sensor Hydrogels for Biomedical Applications

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Introduction: Current sensors for monitoring environmental signals, such as pH, are often made from rigid materials that are incompatible with soft biological tissues. The high stiffness of such materials sets practical limitations on the *in situ* utilisation of sensors under biological conditions. To this end, various innovative concepts have been introduced to develop more flexible sensors for wearable devices, textiles, bionics, soft electronics, and soft robotic systems. Yet, the majority of these methods are cumbersome, inconvenient, and often expensive.

In this study, we demonstrated an elegant approach for rapid manufacturing of highly flexible pH-sensitive hydrogels based on poly(3,4-ethylenedioxy thiophene) (PEDOT) doped with negatively charged poly(styrenesulfonate) (PSS) and robust hydrophilic polyurethanes (HPU). PEDOT that is *p*-doped with PSS is a hole conductor material. Given the complex nature of PEDOT:PSS, its electronic characteristics are sensitive to pH. By optimising the composition of the PEDOT:PSS/HPU inks, we were able to utilise 3D printing for the fabrication of pH sensitive PEDOT:PSS/HPU hydrogel sensors in one step (Figure 1).

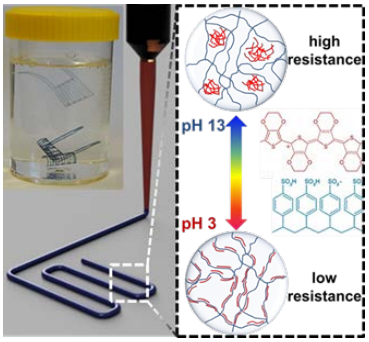


Figure 1. An image of pH sensor hydrogels with schematic illustration of their pH sensing mechanism.

Materials and Methods: The HPU used in this study was based on poly(ethylene oxide) soft chains (PEO) and cyclohexylisocyanate hard segments. Depending on the length of PEO blocks, the HPU macromolecules are soluble in certain concentrations of water and ethanol (EtOH) mixture but remain insoluble in pure water or EtOH. For ink formulation, first a 5w/v% HPU solution was made in a 95:5 EtOH:water solvent. To this solution, various amounts of the 1.1 wt% PEDOT:PSS aqueous dispersion (Sigma Aldrich) was added. The PEDOT:PSS/HPU conductive inks were then 3D printed using the EnvisionTEC 3D-Bioplotter® (Figure 2a).

Results and Discussion: A linear and reversible correlation between the conductivity of fully swollen PEDOT:PSS/HPU hydrogel sensors and the pH was observed, which is attributed to the pH-sensitivity of the PEDOT:PSS element (Figure 2b). The electrical resistance of hydrogel sensors was not affected by extreme bending and twisting, and consecutive tensile cycling – up to 400 cycles of 50% extension. The 3D printed, hydrogel-based pH sensors remained functional after two months of storage in Milli-Q water. The inherently low modulus of hydrogels developed in this work (~10^3 kPa) is 10^2 to 10^4 times lower than most materials traditionally used in sensor technology. The combination of low modulus and the sub-millimetre thickness of hydrogel sensors has enabled us to create pH sensors with flexural stiffness at the order of 1 μN m. As a comparison, human skin has a flexural stiffness of ~10^2 μN m.

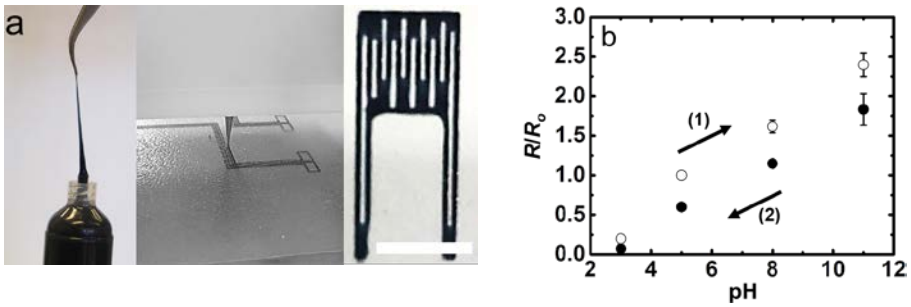


Figure 2. (a) Printable inks used for 3D gel printing of pH sensor hydrogels (scale bar is 10 mm). (b) The electrical response of printed pH sensor hydrogels to ascending and descending pH change. R_o is the resistance between two legs of the pH sensor shown in (a) in Milli-Q water.

Conclusions: Optimised formulations of PEDOT:PSS/HPU inks were developed to fabricate highly flexible pH sensors that linearly respond to pH in wet environments. Such printable inks that can produce biosensors using a one-step fabrication method eliminate the cumbersome and inconvenient processing of rigid materials that are used in the manufacturing of conventional pH sensors.