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WEARABLE MICRO-FLUIDIC pH SWEAT SENSING DEVICE BASED ON COLORIMETRIC IMAGING TECHNIQUES

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In this work we present a flexible and wearable micro-fluidic device for the continuous monitoring of pH changes in sweat during exercise. The sensing capability is based on ionogels, ionic liquid polymer gels, containing pH sensitive dyes capable of reporting pH activity in the range from pH 3 to pH 8. Optical detection is performed using a mobile phone camera with subsequent image processing and analysis. Previously, we reported a wearable micro-fluidic barcode platform capable of measuring the pH of sweat in real time [1]. Here we have improved the device in terms of wearability, physical robustness, chemistry of the sensor and its optical response by using a mobile phone for data collection and a more accurate algorithm for colorimetric image analysis.

The ionogel is a solid, flexible and easily patterned material generated by UV-photopolymerisation from the tetrabutylphosphonium dicyanamide (dca) ionic liquid and a hydrogel polymer (*N*-isopropylacrylamide and *N,N*-methylene-bis(acrylamide)), Figure 1. After polymerization four different pH sensitive dyes are incorporated in the polymer matrix by drop casting. Due to ion-pair interactions between the various pH indicators and the ionic liquid that forms the ionogel structure, there is no leaching of pH dyes, enabling long analysis times without compromising the sensitivity of the system [2].

Delamination of the swollen ionogel from the micro-fluidic device during measurements is prevented by covalent immobilisation of the ionogel on the surface of the poly(methyl methacrylate) (PMMA) substrate. The PMMA is first surface activated using water-vapor plasma, ensuring a good hydroxylation of the surface [3]. Then, an alkenyl terminated self-assembled monolayer (SAM) is deposited using the silane-coupling agent 7-octenyltrichlorosilane, see the scheme in Figure 2-left. The presence of a terminal double bond in the alkyl chains ensures the integration of the SAM in the network of the ionogel by covalent attachment via radical polymerization. Figure 2-right shows a fully swollen, drop shaped ionogel covalently bonded to PMMA after storage in ethanol for 5 hours.

Figure 3 shows the micro-fluidic device placed on the arm of an athlete. Its circular configuration improves the wearability of the device and reduces discomfort by eliminating sharp corners. pH changes in sweat during exercise can be easily monitored by harvesting digital pictures of the ionogel barcodes over time. The images are subsequently processed using a combination of segmentation, labeling and colour space conversion algorithms programmed using the OpenCV computer vision library. Figure 4 depicts calibration response curves of each respective pH dye from pH 3 to pH 10 when analysed using the Hue component of the HSV colour space. Each pH dye shows excellent correlation to a sigmoidal regression model i.e. with an R^2 value of greater than 0.995 in each case.

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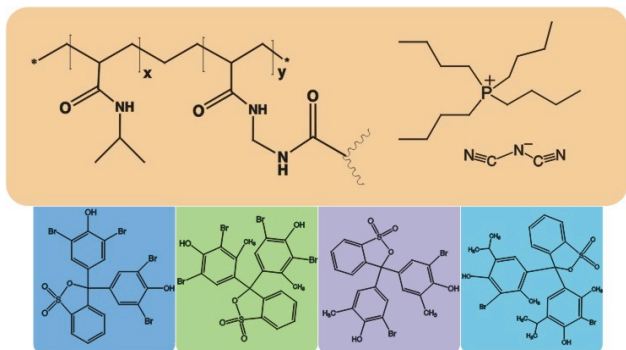


Figure 1: Chemical structures of the hydrogel and the tetra-butyl phosphonium dca ionic liquid (top) and the four chemical structures of the pH sensitive dyes (bottom). From left to right: Bromophenyl Blue, Bromocresol Green, Bromocresol Purple and Bromothymol Blue.

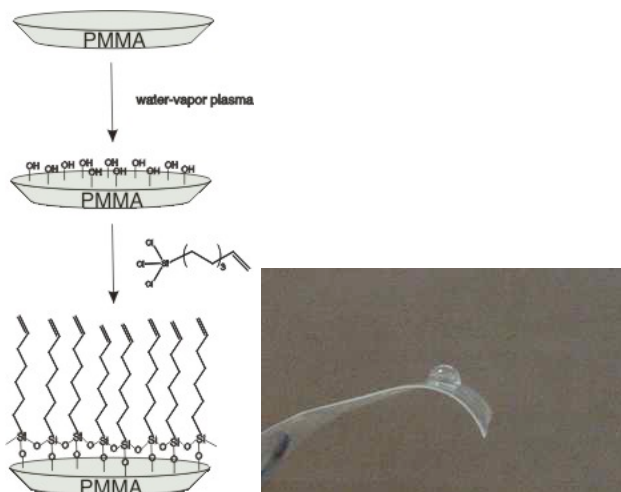


Figure 2. (left) Schematic representation of the PMMA chemical surface modification. (right) Picture of the swollen grafted ionogel on PMMA.

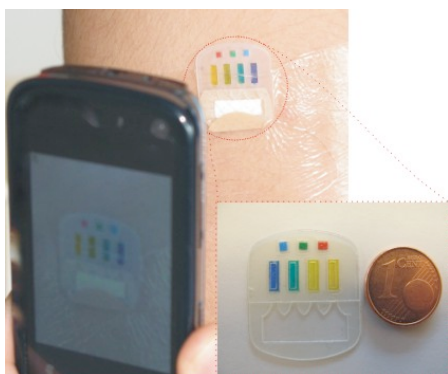


Figure 3. Wearable microfluidic device located on the arm using a high adhesive transparent sweat patch. The camera of a mobile is used to take pictures of the sensing area of the device. The mobile application will be used for real time pH monitoring of sweat during exercise.

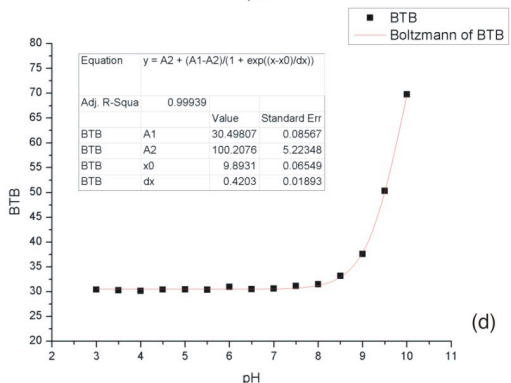
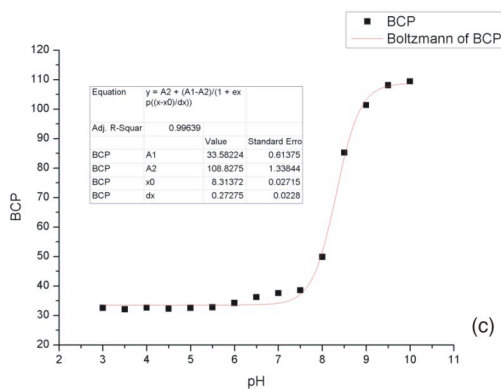
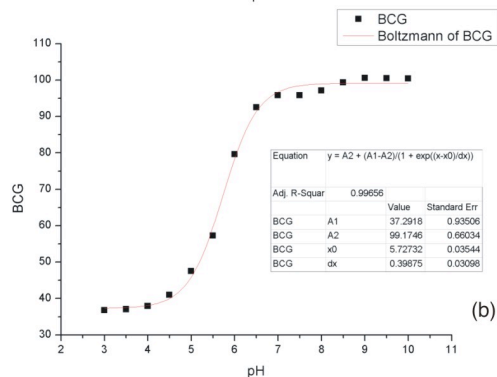
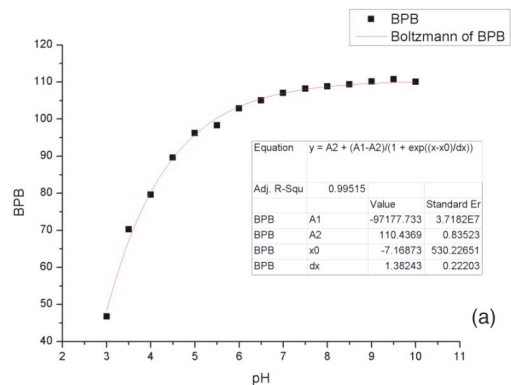


Figure 4. Calibration curves of the camera's response to colorimetric changes in the respective pH dyes: (a) Bromophenyl Blue, (b) Bromocresol Green, (c) Bromocresol Purple, (d) Bromothymol Blue. All have achieved an excellent sigmoidal fit (Boltzmann) i.e. $R^2 > 0.995$, $n = 15$.