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A Polymer-Based Chip for pH Sensing

Kuo-Feng Chou*, Yu-Chih Lin, Hui-Ying Chen, Shi-Yu Huang, and Chih-Yong Lin

Department of Biomedical Engineering, Yuanpei University, Taiwan

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ABSTRACT

A novel pH sensor consisting of a pH-sensitive hydrogel and conductive polymer layer was developed. Monomers of hydroxyl ethyl methacrylate were polymerized. The sensing principle of the device was based on the piezoresistive effect induced by the swelling behavior of the hydrogel varying with the pH value of the solution contacting the polymer. The correlation between the sensitivity of the device and UV radiation dosages was investigated. The output characteristic of the pH sensor was measured. The pH sensitivity of the specimens was lower with UV radiation exposure, and the effect of temperature on the stability of the device was evaluated.

INTRODUCTION

Many papers on pH sensors based on hydrogels have been published [1–9]. The operating principle of all pH sensors with a hydrogel substrate are based on the bending of a flexible matrix induced by swelling of the gel. The deformation of the geometric structure can be sensed as a change in capacitance or resistance. Herber et al. [2] developed a hydrogel biosensor for monitoring the partial pressure of CO_2 in the stomach. Han et al. [1] combined a pressure transducer and pH-sensitive gel to develop a biosensor for measuring the concentration of glucose in the blood. Trigo et al. [9] investigated the effect of the polymerization condition on the sensitivity and response time, and predicted the characteristics of the sensor using the Mooney-Rivlin model and the finite element method.

Most researchers have chosen PVA-PAA copolymer as the pH-sensitive materials. Our previous study [10, 11] found that the amount of swelling of poly(HEMA) exposed to gamma rays in buffer solutions varied with the pH value of the buffer. Moreover, the pH-sensitive behavior could be modified by the irradiation dosage. However, in this study, we modified poly(HEMA) with ultraviolet irradiation rather than gamma rays in order to maintain the mechanical properties of the hydrogel thin film by avoiding the damage that can be induced by the high irradiation energy.

MATERIALS AND METHODS

Sensing principle. The sensing device comprised a pH-sensitive hydrogel layer [poly(HEMA)], resistance Ag gel layer, and SiO_2 substrate. The operating principle of the sensor is shown in Fig. 1. The swelling of the polymer film induced by absorbing the testing solution varies with the pH value of the solution. This swelling deforms the resistance layer under the hydrogel such that the resistance changes, with a linear relationship between the resistance and strain:

$$\frac{\Delta R}{R} = \varepsilon \qquad (1)$$

The resistance layer is included in a Wheatstone bridge, allowing the change in the resistance of the Ag gel to be calculated from the output voltage of the bridge.

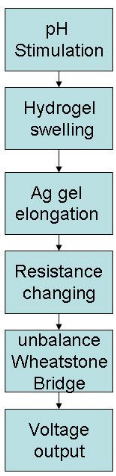

FIG. 1. Operating principle of the pH sensor.

Materials. All chemical reagents were purchased from Tokyo Kasei Kogyo and were used as receiver. Water was distilled and deionized to a specific resistance of 18 MΩ.

Aqueous solutions (10 wt%) of ammonium persulfate (APS) and sodium metabisulfite (SMBS) were used together as initiators and were made immediately prior to each use. All chemicals were used as receiver except where stated otherwise. Ethylene dimethacrylate (EDMA) was used as the cross-linking agent.

Fabrication of the pH sensing chip. The monomer mixture comprised monomer (HEMA), cross-linking agent (EDMA), and solvent (deionized water). HEMA monomer diluted with water (HEMA:water = 60:40). Next, EDMA, APS, and SMBS were added to the solution and mixed by an ultrasonic machine for 5 min. The polymerization of these monomer mixtures were initiated by APS and SMBS at concentrations of 0.5 wt% and 0.2 wt% of the total monomer, respectively. Prepolymerization occurred at 65°C for 30 min. A 10-mm × 10-mm strain gauge was encapsulated into the prepolymer. The thickness of the polymer layer was 500 µm. After prepolymerization, the specimens were exposed to 360-nm UV radiation for 2 hr at a dosage of 72 J/cm^2.

pH measurement system. The setup of the pH measurement system is shown in Fig. 2. The pH sensor contains a sensing chip and Wheatstone bridge. The signal-conditioning section amplifies the output signal and filters it using an AD620 IC. The voltage output is then converted into a digital signal by an NI 6024E DAQ card. Finally, the curve of the pH value versus time is displayed on a PC.

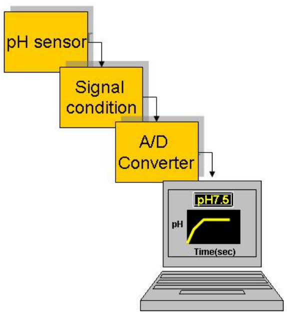

FIG. 2. Setup of the pH measurement system.

RESULTS

Effect of UV radiation on the chip sensitivity. The specimens exposed to UV radiation (360 nm, 0–432 J/cm^2) were immersed in buffer solutions with pH values of 1–8 for 60 min. The weights of samples were measured at certain time points. The amount of swelling was quantified as

$$swelling\ degree = \frac{W_t - W_0}{W_0} \qquad (2)$$

where W_t is the sample weight at time t, and W_0 is the weight of the dry sample.

The relationship between the amount of swelling and the pH value of the solution is shown in Fig. 3. The amount of swelling of poly(HEMA) decreased as the pH value increased. The slope of the regression line was lower for specimens exposed to UV radiation, which implies that acid functional groups and cross-linking structures were induced by the UV radiation.

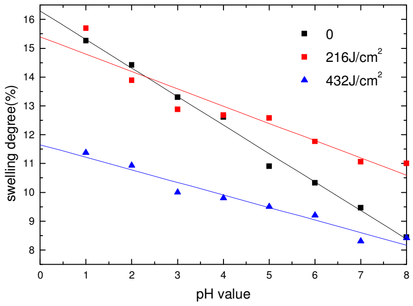

FIG. 3. Amount of swelling of poly(HEMA) versus the solution pH for different UV radiation exposures.

Output characteristic of the pH sensing chip. The sensing chip was connected to the measurement system and immersed in solutions with various pH values. The output voltage of the measurement system recorded after 60 min is shown in Fig. 4. The relationship between output voltage and pH value of the solution was linear, with the regressed line having a slope and intercept of 0.3001 and –0.0165, respectively; that is, the sensitivity of the chip was 0.0165 V/pH.

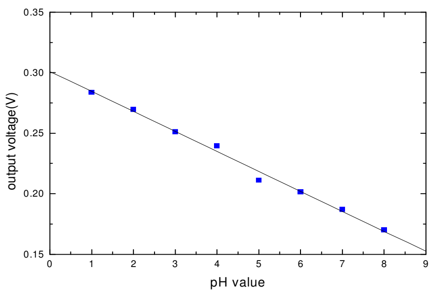

FIG. 4. Output voltage of measurement system versus the solution pH.

Effect of temperature on the chip stability. Three samples of the chips were immersed in deionized water at 30 °C, 40 °C, and 50 °C for 3 hr. The output voltage of sensing device was measured at certain time points. Fig. 5 shows that the output curves did not differ markedly with the testing temperature, indicating that the sensing chip is thermally stable in the range of 30–50 °C.

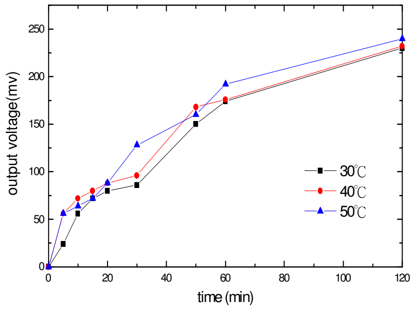

FIG. 5. Output voltage of measurement system versus time for different temperatures.

DISCUSSION

A novel pH sensor has been developed whose sensitivity varies with the dosage of UV radiation. The pH sensor consisting of a strain gauge encapsulated with pH-sensitive poly(HEMA) was fabricated and tested. The output voltage increased when the pH value of the solution decreased. The sensitivity of the device was 0.0165 V/pH. The specimens exposed to UV radiation contained acid functional groups and cross-linking structures, which decreased their sensitivity. The experimental data also indicate that the output behavior of the sensor is not influenced by temperature.

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FOOTNOTES

* Corresponding author. Mailing address: Department of Biomedical Engineering, Yuanpei University, 306 Yuanpei St., Hsin-Chu, 30015 Taiwan, Phone: 886 3 610 2346. Fax: 886 3 610 2347. E-mail: kuofeng@mail.ypu.edu.tw

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