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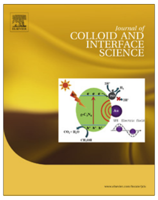

Regular Article

High performance flexible pH sensor based on polyaniline nanopillar array electrode

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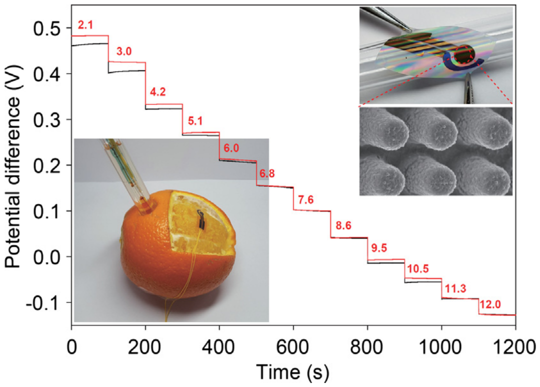
GRAPHICAL ABSTRACT

Flexible and thin pH sensors were fabricated using a two electrode configuration comprised of a polyaniline nanopillar array working electrode and an Ag/AgCl reference electrode, showing excellent sensor performances in terms of pH sensitivity, response time, reversibility, repeatability, selectivity, and stability.



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ABSTRACT

Flexible pH sensor technologies have attracted a great deal of attention in many applications, such as, wearable health care devices and monitors for chemical and biological processes. Here, we fabricated flexible and thin pH sensors using a two electrode configuration comprised of a polyaniline nanopillar (PAN) array working electrode and an Ag/AgCl reference electrode. In order to provide nanostructure, soft lithography using a polymeric blend was employed to create a flexible nanopillar backbone film. Polyaniline-sensing materials were deposited on a patterned-nanopillar array by electrochemical deposition. The pH sensors produced exhibited a near-Nernstian response (~60.3 mV/pH), which was maintained in a bent state. In addition, pH sensors showed other excellent sensor performances in terms of response time, reversibility, repeatability, selectivity, and stability.

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1. Introduction

pH sensors provide a logarithmic measure of hydrogen ion concentration and are essential analytical tools in laboratories, clinics, and industries [1–5]. Since many biological and chemical reactions are dependent on pH level, pH sensors are widely used in continuous processes to ensure human health care, water quality, food quality, and to monitor chemical or biological reactions [1–5]. Recently, flexible/wearable sensors have received a great deal of attention for the continuous monitoring of human health [6–12]. For instance, Wang et al. devised bandage-based pH sensors for a real-time wound pH monitoring [10]. Diamond et al. developed textile-based pH sensors for measuring the pH of sweat, and suggesting a correlation exists between pH and sweating rate [13]. Clinics and quality control laboratories require point of care testing (POCT) technologies because they provide test results quickly, do not require user-expertise, and are relatively cheap [14–17]. Davis et al. described the fabrication of POCT pH sensors based on disposable capillary fill system for monitoring wound pH [16]. The most common commercial pH sensors are based on conventional glass-type electrodes due to their sensitivities, stabilities, and longevities. However, these pH sensors cannot fully meet the requirements of the abovementioned applications because of the brittleness of glass, size limitations, and lack of structure transformation. For these reasons, pH sensor developments are focused on advanced sensing materials, miniaturization, mechanical properties, cost, and scalability for mass production.

Numerous pH sensitive materials based on metal oxides, such as IrO_2 [18], TiO_2 [19], RuO_2 [20], ZnO [21], Co_3O_4 [22], WO_3 [11], and CuO [23], have been developed for many applications. These materials showed pH sensitivities between 28 and 69 mV per pH. Yang et al. reported that heat-treated iridium oxide films exhibit high pH sensitivity (59.5 mV/pH), a wide pH range (2.38–11.61), and a rapid response time ($\sim$2 s) [18]. Chou et al. fabricated RuO_2 thin films as the pH sensing layer, and reported high pH sensitivity, but with enhanced drift and hysteresis effects [20]. Although these metal oxide based sensors offer promising alternative materials to glass electrodes, their non-guaranteed mechanical properties and high cost limit their usages as flexible/wearable sensors. Conducting polymers are also capable of providing pH sensing ability due to the protonation/deprotonation of functional groups at different pH levels [24–26]. Moreover, conducting polymer-based sensors have the advantages of simplicity, environmental processability, mechanical flexibility, high electrical conductivity, and low cost. Wang et al. described fabrication methods for preparing polyaniline-based wearable sensors to measure pH values in the physiological range, and demonstrated near-Nernstian response ($\sim$58 mV/pH) [10]. Furthermore, as compared with bulk macroscopic structured materials, nanomaterials offer potential advantages because their large surface-to-volume ratios enhance charge transfer abilities, which improve pH sensitivities and response times.

Herein, we report the development of a polyaniline nanopillar (PAN) array-based disposable and flexible pH sensor. Soft lithography using a polymeric blend was employed to prepare flexible nanopillar backbone film. Polyaniline was used as a working electrode and silver/silver chloride (Ag/AgCl) as a reference electrode and these were deposited on patterned-nanopillar backbone films by stencil lithography. Furthermore, the method used is simple and scalable and has a high reproducibility. The produced PAN pH sensors demonstrated high pH sensitivity, good reversibility, rapid response time, good ion selectivity, and low potential drift.

2. Experimental

2.1. Reagents and materials

Aniline (99.5%), sulfuric acid, hydrogen chloride, sodium hydroxide, potassium hydrogen phthalate, potassium dihydrogen phosphate, tris(hydroxymethyl)aminomethane, borax, potassium chloride, calcium chloride, magnesium chloride, and ammonium chloride were obtained from Sigma-Aldrich. Sodium chloride was purchased from Junsei. A dielectric ink ESL 242-SB was obtained from ElectroScience.

2.2. Fabrication of PAN sensor

Polymeric nanopillar arrays were fabricated using silicon mold and soft lithography process using mixture of polyurethane acrylate and NOA63, and were then transferred on Polyethylene terephthalate (PET) film as described in our previous report [27]. For the construction of pH sensor electrode configuration, thin layers of gold/titanium and silver/titanium were deposited by vacuum sputtering under a patterned mask. Ag/AgCl reference electrodes were completed by electroplating chloride on silver. As-obtained Ag/AgCl reference electrodes were coated with dielectric ink ESL 242-SB mixed with KCl (30 wt%). The samples were then cured at 125 °C during 10 min [28]. Polyaniline sensor materials were electrochemically deposited on gold/titanium layer by cyclic voltammetry technique of 30 cycles in a potential range of -0.1 to $+0.8$ V under a three-electrode system. The electrolyte was a mixture of 0.5 M H_2SO_4 containing 0.25 M aniline monomer. The prototype PAN sensor had a device size of 11.5 × 36 mm (Fig. 1a). The pH buffer solution was prepared by mixing 5 mM potassium hydrogen phthalate, 5 mM potassium dihydrogen phosphate, 5 mM tris(hydroxymethyl)aminomethane, 2.5 mM borax, and 100 mM sodium chloride. In order to measure pH of flexible PAN sensor, PAN sensor was fixed on a glass rod with respect to a bending radius of 4 mm (Fig. 4a).

2.3. Characterization and measurements

Scanning electron microscope (SEM, Hitachi S-4800) was performed to investigate the morphology and microstructure of PAN array. Fourier transform infrared spectroscopy (FTIR) spectra were recorded using a FTIR-4600 (Jasco, Japan). To evaluate pH response, potential difference between PAN and Ag/AgCl electrodes was measured using a CHI 760 E (CH Instruments, USA). During the measurements, pH values of buffer solutions were manipulated by adding 1 M HCl and 1 M NaOH. Meanwhile, the pH level was confirmed by a commercial pH meter (Orion™ Star A211).

3. Results and discussion

Fig. 1a and 1b shows a schematic of prototype PAN sensor of size 11.5 × 36 mm. The sensor is flexible and is easily bent without breaking because of the mechanical support provided by the polymeric nanopillar arrays (Fig. 1a). To configure the two-electrode pattern, a gold layer was firstly deposited by stencil lithography. Polyaniline and Ag/AgCl layers were used as working and reference electrodes, respectively. The polyaniline layer was electrochemically deposited on nanopillar array using 30 cycles of cyclic voltammetry in a three electrode system. The electropolymerization of polyaniline has been reported to provide a highly conformal and effective polyaniline coatings, the thicknesses of which can be controlled by varying deposition time. In this work, the coating thickness of polyaniline was $\sim$53 nm (Fig. S1). Fig. 1c and d shows SEM images of the surface morphology of a PAN sensor. PAN sensor