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Polymeric cantilever sensors functionalized with multiamine supramolecular hydrogel

Yan Zhang, Hyung H. Kim, Bong H. Kwon, Jeung S. Go*

School of Mechanical Engineering, Pusan National University, Busan, Republic of Korea

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ABSTRACT

This paper presents a multiamine supramolecular hydrogel (SH) modified SU-8 cantilever sensor. A chemical process to integrate the SH on the surface of SU-8 cantilever is developed to improve the stability and reusability of the functionalized cantilever sensor, instead of physical surface functionalization methods such as direct coating and self-assembly. The network structure of the SH is formed through a ring-opening and amine-substituted reaction in epoxy groups of the SU-8. The surface functionalization of the SU-8 cantilever is characterized by using scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). The modified SU-8 cantilever sensor has been successfully applied for real-time measurement of metal ions concentration in aqueous solutions. Responses from the cantilever due to surface stress are induced by the axial coordination of ferric ions to amino groups of the SH and the chemical energy is converted into the mechanical energy which can be measured by a piezoresistive sensor. The concentration-dependent performance of the sensor is demonstrated and discussed, indicating a potential use of SH functionalized cantilever sensors.

1. Introduction

Polymeric cantilever sensors have been developed and demonstrated to have low noise level and high sensitivity due to small Young's modulus compared to silicon cantilever sensors [1,2]. Also, the transition from semiconductor materials to polymers allows simple fabrication process and shorter fabrication time. In specific, SU-8 polymer contains reactive epoxy functionalities for a high degree of cross-linking after photo-activation and high flexibility of surface chemistry and is a mechanically robust material among the available photo-patternable polymers. These characteristics have attracted increasing attention in physical [3], chemical [4] and biological applications [5–8].

As a chemical or biological sensor, the surface of the polymeric cantilever is usually modified by an appropriate coating which is highly sensitive to target analytes. The SU-8 cantilever is commonly pre-modified with a robust monolayer to withstand further functionalization such as alkanethiol compounds on gold [3] and ceric ammonium nitrate [7] by adsorption, surface coating, plasma treatment [5] or polymerization [4,6]. The functionality species and the corresponding modification methods are significantly important to obtain the sensitivity of the cantilever sensor and to enhance the stability of sensing process.

To make a sensitive and stable functionalized cantilever sensor, one of the most promising technologies is to combine a synthesized material and surface modified layer [9,10]. As a smart material, the supramolecular hydrogel (SH), composed of gelator molecules and water molecules, has drawn an attention recently because of good feature preserving biologically active proteins for catalysis and scaffolds in tissue engineering [11]. It is also sensitive to pH [12,13], temperature [14,15] and even specific molecules [16–19]. The corresponding techniques to convert a non-electrical change into an electrical signal involve optical [20], conductometric [21], oscillating [22] and magneto-elastic transducers [23]. Since most hydrogels are too brittle to be used as a compliant cantilever [24], the hydrogels are usually deposited [25] or bonded on the cantilever or plate surface and their analyte-dependent swelling is monitored by using piezoresistive [13,26,27], optical [15] or capacitive sensors [28].

Powerful means to develop a SH functionalized cantilever sensor are to introduce new gelators and chemical modification technique. In this work, we have developed a multiamine SH functionalized cantilever sensor for chemical and biological application. The developed hydrogelator with fast response to external stimuli is based on aminoalkyl phosphoamide compounds prepared by reacting phosphoryl trichloride with diamines in a basic condition [29]. Unlike traditional protocols, the multiamine SH is integrated onto the upper surface of the SU-8 cantilever through chemical reaction

* Corresponding author at: School of Mechanical Engineering, Pusan National University, 63 Beon-gil 2, Busandaehag-ro, Geumjeong-gu, Busan 609-735, Republic of Korea. Tel.: +82 51 510 3512; fax: +82 51 512 5236.
E-mail address: micros@pusan.ac.kr (J.S. Go).

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processes without the pre-treatment of SU-8 surface and specific conditions. Modified SU-8 cantilever has higher stability and reusability as a cantilever sensor. The formed gel layer with reactive —NH groups provides attachment to target species such as proteins and metal ions. It has been demonstrated that the amino groups interact strongly with metallic cations [30], and the introduction of multiple functional groups will improve the absorption capacity, which can be proven effectively to remove metal ions in a waste water sample by using multiamine functionalized mesoporous silica [31,32]. As a demonstration of the potential use of the multiamine SH modified SU-8 cantilever sensor, the absorption performance to ferric ions was also investigated in this work.

2. Experiment

2.1. Sensor operational principle

The cantilever sensor was composed of two triangular cantilevers as illustrated in Fig. 1a. One is modified with the SH and the other is the reference cantilever without surface modification. The cross section view of the SH modified cantilever is shown in Fig. 1b. In this work, triangular cantilevers rather than rectangular ones with the same width at the base were designed and fabricated to improve the sensitivity of the cantilever sensor.

To examine the swelling behavior of the SH modified SU-8 cantilever, the commercial waterproof strain gauges (N11-FA-1-120-11, Magus Trading Corporation) were used. Two strain gauges with resistance of R1 and R2 were bonded onto the bottom and top surfaces of the SH modified cantilever with details in the Supporting Information. In the reference cantilever, the other two waterproof strain gauges with resistance of R3 and R4 were bonded on both sides of the cantilever surface respectively, to compensate the influence of liquid flow on cantilever deflection. The four strain gauges constitute a half Wheatstone bridge circuit (Fig. 1c). The cantilever deflection will cause a stress change on the base surface of the cantilever and therefore a resistivity change of the strain gauge, resulting in proportionally the output voltage of the sensor (see the derivation in Supporting Information).

Fig. 2 shows the assembled cantilever sensor for metal ions detection installed in a microfluidic reservoir. To introduce the target analyte solutions, the microfluidic reservoir with the volume of 0.8 ml was fabricated using polydimethyl siloxane (PDMS). The inlet/outlet holes were formed by drilling with a sharp stainless needle through the side walls of the PDMS reservoir. The modified and reference cantilevers were integrated into the reservoir, which were bonded on the PDMS handling layer. The reservoir was sealed with an additional PDMS layer.

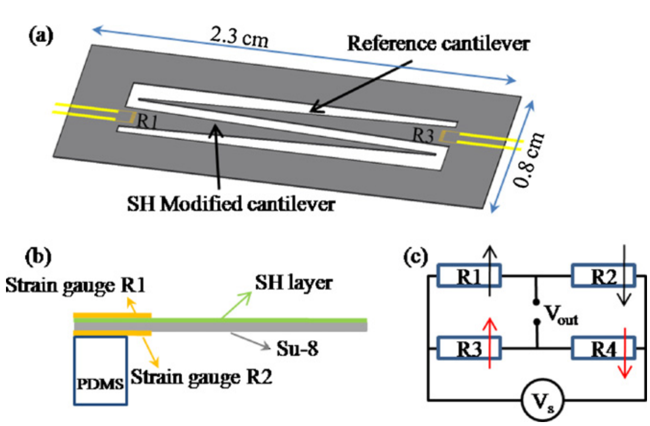

Fig. 1. Schematic diagrams: (a) top view of the SU-8 cantilevers bonded with strain gauges, (b) cross sectional view of the SU-8 cantilever with surface modification, and (c) half Wheatstone bridge circuit to measure electrical output.

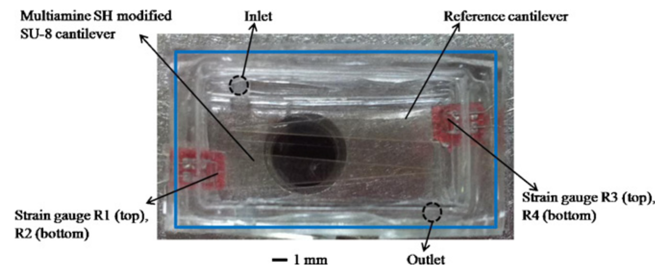

Fig. 2. Optical image of the assembled cantilever sensor for metal ion detection.

2.2. Fabrication of the SU-8 cantilever

The fabrication started with coating of an anti-stiction monolayer of dichlorodimethylsilane (hereafter, DDMS) on Si substrate, to release the fabricated SU-8 cantilever layer in the end. The SU-8 (SU-8 2050, Microchem) was spin-coated on the Si substrate. Triangular cantilevers were patterned by irradiating UV with the length, thickness and width of 16 mm, 0.1 mm and 3 mm at the base, respectively. Some patterned cantilevers were mechanically released from the DDMS-treated Si substrate by using a tweezer. Others were released after the surface modification process. The DDMS-based release layer has an additional advantage to be used as a protective layer to make the modification only on the top surface of the SU-8 cantilever. Thus the bottom surface is inert while the top surface exhibits a high affinity to the target analyte, which results in a difference in surface stress that can be measured in the static operation mode of the cantilever sensor.

2.3. Functionalization of the SU-8 cantilever

The surface modification of SU-8 cantilever with multiamine SH is based on the ring-opening reaction of free epoxy groups and the following condensation reaction [29,33]. Typically, for the opening reaction of the free epoxy groups, the propane-1,3-diamine (1 ml, 12 mmol) and lithium perchlorate ($LiClO_4$, 6.3 mg, 60 mmol) were dissolved in ether (10 ml) in a vial (20 ml) at a room temperature. The silicon wafer with patterned SU-8 was then dipped into the solution. The vial was sealed and kept for 10 h to avoid fast volatilization of the solvent due to the fast volatility of the ether. Then, the wafer was carefully flushed by ethanol and dried in air. For the subsequent condensation reaction, the wafer was again dipped into the solution of 0.5 ml phosphorous chloride ($OPCl_3$) mixed with 8 ml tetrahydrofuran. After 30 min, 0.5 ml propane-1,3-diamine was added for further cross-linking. The wafer was then washed by sodium ethoxide/ethyl alcohol (EtONa/EtOH) solution to release amido/amine groups and dried in air. The chemical modification process is illustrated in Scheme 1. Finally the SH modified SU-8 cantilevers on the wafer were mechanically released from the silicon substrate.

2.4. Sensing measurements

The detection capability of the SH functionalized SU-8 cantilevers was demonstrated by measurement of metal ions concentration. Deionized water (DI-water) was firstly injected into the reservoir to impregnate the hydrogel and kept for 10 h until a stable baseline was obtained. The buffered solutions of $Fe_2(SO_4)_3$ with various concentrations (5–35 mM) were used to examine the performance of the multiamine SH modified SU-8 cantilever sensor. The piezoresistive response was measured by the half Wheatstone