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Array adsorbent-coated lead zirconate titanate (PZT)/stainless steel cantilevers for dimethyl methylphosphonate (DMMP) detection

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Abstract

Piezoelectric cantilever sensors consisting of a piezoelectric layer bonded to a non-piezoelectric substrate are sensitive to minute mass changes at the cantilever tip. With simple electrical actuation and sensing, they can be easily miniaturized for array detection. We demonstrated room-temperature detection of dimethyl methylphosphonate (DMMP), a simulant of the nerve agent, sarin, using array lead zirconate titanate (PZT)/stainless steel cantilevers coated with different metal oxide adsorbents. Binding of DMMP molecules to the adsorbent surface at the cantilever tip increases the cantilever mass and decreases the cantilever resonance frequency. Detection of DMMP is achieved by monitoring the cantilever resonance frequency shift. Exposed to DMMP, a microporous-SiO_2-coated cantilever exhibits a sharp resonance frequency decrease that saturates within minutes. A mesoporous-Al_2O_3-coated cantilever shows a sluggish resonance frequency shift that does not saturate after an hour. An uncoated PZT/stainless steel cantilever shows no resonance frequency shift when exposed to the DMMP vapor. The combination of the three vastly different DMMP adsorption behaviors on silica, alumina, and stainless steel offers a unique pattern for DMMP recognition, which was demonstrated by the present array sensing using PZT/stainless steel cantilevers. In addition, the microporous SiO_2 coating can be regenerated at room temperature for repeated use and the sensor system can be easily portable.

Keywords: Piezoelectric cantilever; Gas sensor; DMMP; Microporous silica; Mesoporous alumina; Array sensors

1. Introduction

In recent years the need to develop chemical sensors for the detection of air-borne species has increased rapidly. In particular, after 9/11, the need for portable, low-cost, and easily deployable chemical and biological sensors becomes even more urgent. The traditional analytical techniques such as gas chromatography–mass spectrometry (GC/MS) [1], passive Fourier transform infrared spectroscopy (FTIR) [2], and Raman spectroscopy [3] are bulky and expensive, unfit for portable chemical detection. Development of alternative chemical sensors includes surface acoustic wave (SAW) devices [4], silicon-based microcantilever sensors [5], and chemiresistive sensors such as semiconducting metal oxide (SMO) sensors [6,7]. The disadvantage of SMO sensors is that detection must be done at an elevated temperature [6]. SAW devices are in the centimeter size range, a disadvantage for array sensing. Silicon-based micro-cantilever sensors rely on a complex external optical detection system for signal transduction [5,8,9], unsuitable for portable applications.

The purpose of this paper is to demonstrate room-temperature detection of dimethyl methylphosphonate (DMMP) using array piezoelectric cantilevers coated with microporous silica (MIPS) and mesoporous alumina (MEPA). The piezoelectric cantilevers used consist of a piezoelectric layer, i.e., lead zirconate titanate (PZT), bonded to a non-piezoelectric layer, i.e., stainless steel (Fig. 1(a)). When an ac voltage is applied to the thickness direction of the PZT layer, it will elongate or shrink along the length and width directions due to its piezoelectric characteristics. However, the non-piezoelectric stainless steel layer does not deform thereby constraining the movement of the PZT layer, resulting in the alternative bending (vibration) of the cantilever structure. The resonance frequencies of this vibration are determined by the effective mass and elastic modulus of the cantilever. Therefore, any minute mass change on the cantilever

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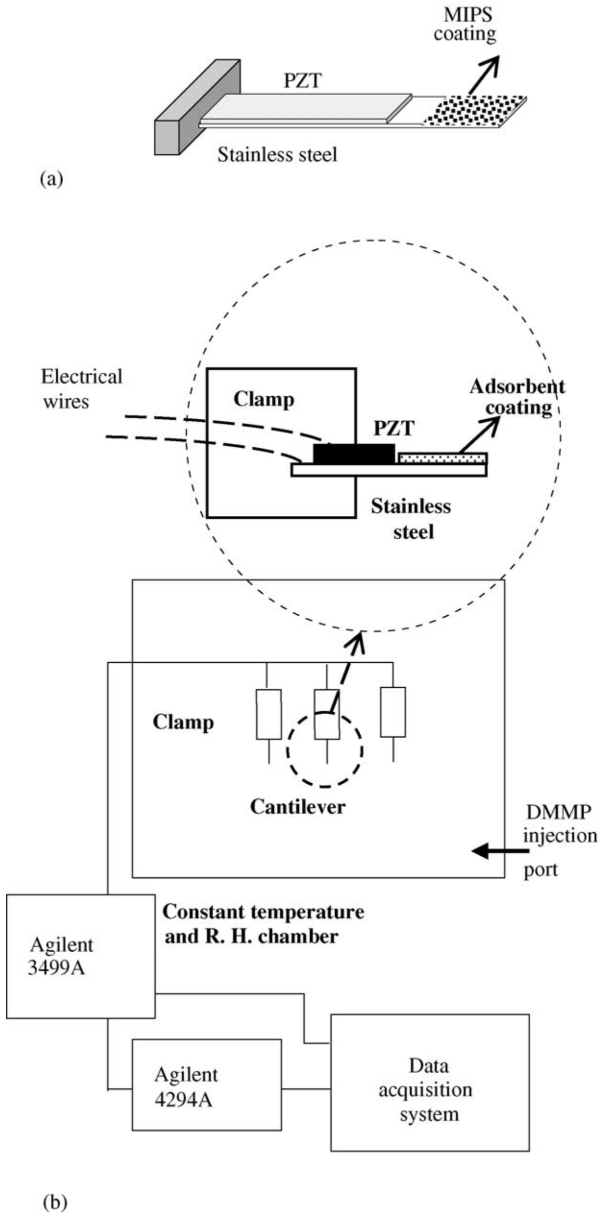

Fig. 1. A schematic of: (a) a piezoelectric cantilever coated with microporous silica (MIPS) at the tip and (b) the experimental setup for the DMMP detection test.

can be detected by monitoring the resonance frequency shift. The mass detection sensitivity, $\Delta f/\Delta m$, was shown to increase sharply with a decreasing cantilever size, where Δm and Δf are, respectively, the mass change and the associated resonance frequency shift [10]. Piezoelectric cantilever sensors have the advantages of small size, simple electrical actuation and detection, low power consumption, and the convenience for array detection. Earlier studies have demonstrated the use of piezoelectric cantilevers for mass sensing [10], in situ cell detection [11], and ethanol and water vapor detection [12]. In addition, gold-coated piezoelectric cantilevers were also shown to detect mercury by monitoring the stiffening effect on the cantilever resonance frequency due to the adsorbed mercury [13].

In order to apply the mass sensing mechanism to gas detection, the surface of the cantilever has to be functionalized by an adsorption layer to selectively capture the target gas molecules inducing the mass change on the cantilever. To detect dimethyl methylphosphonate, a simulant of nerve gas—sarin, self-assembled monolayers (SAM) [4], or polymer thin films [14] are widely used as the adsorption layer. Recent reports showed that DMMP exhibited different adsorption behaviors on different metal oxide surfaces [15,16]: non-destructive adsorption on SiO_2 and destructive adsorption on Al_2O_3, indicating the potential of creating a selective DMMP detection pattern by combining detection signals from array cantilever sensors coated with different metal oxides. In addition, the metal oxide adsorbents offer the advantage of high specific surface areas and chemical stability, which can further enhance the detection sensitivity and permit the sensor to withstand harsh environmental conditions.

2. Experimental procedures

2.1. Sensor preparation

A schematic of the experimental setup is shown in Fig. 1. The PZT/stainless cantilevers used have a PZT layer (T105-H4E-602, Piezo System Inc., Cambridge, MA) 0.7 mm long, 1.8 mm wide, and 0.127 mm thick bonded to a 0.05 mm thick stainless steel layer (Alfa Aesar, Ward Hill, MA) using a conductive epoxy (GC Electronics, Rockford, IL). The stainless steel layer was extended at the free end (see in Fig. 1(a)) to form a 1.9 mm long stainless steel tip which was cleaned with acetone and subsequently coated with sol–gel derived MIPS or MEPA. The MIPS and the MEPA used have a specific surface area of ~800 and ~380 m^2/g and an average pore size of 10 and 61 Å, respectively [17]. The coating was achieved by repeatedly depositing 1 μL of a 3 mg/mL metal oxide powder suspension. For better coating uniformity, a deposited suspension was allowed to dry on the cantilever tip before the next droplet was deposited.

2.2. Gas detection

The detection setup is schematically shown in Fig. 1(b). Cantilever sensors were placed in a closed chamber where the temperature was held constant at $22.2 \pm 0.3\,^{\circ}C$. The relative humidity (RH) in the chamber was maintained at $11.2 \pm 0.1\%$ using Drierite desiccant (W.A. Hammond Drierite, Xenia, OH). Ten milliliters of liquid DMMP (Alfa Aesar) was sprayed into the chamber to simulate the sudden exposure to the vapor of a nerve agent during a terrorist attack in the civilian environment [18]. The resonance frequency of the cantilever was monitored using an impedance analyzer (Agilent 4294A, Agilent, Palo Alto, CA) at an interval of 10 s. For array sensing, the impedance analyzer was connected to a switch box (Agilent 3499A, Agilent) which swapped among the sensors. In addition, ammonia solutions (5.0N, Alfa Aesar) were sprayed instead of liquid DMMP to investigate the response of the sensors to different vapors.