



Pillar arrays of tethered polyvinyltetrazole on silicon as a visualization platform for sensing of lead ions



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ABSTRACT

Using click reactions, we have grafted *N*-propargyl polyacrylonitrile (PAN) to a dot matrix presenting azido-terminated surfaces on a silicon substrate to generate pillar arrays of two-dimensional photonic crystals (2DPCs). The tethered PAN 2DPCs were then subjected to a cyano-to-tetrazole conversion reaction to generate tethered polyvinyltetrazole (PVT) 2DPCs. Over 88% of the cyano groups on the PAN were converted to tetrazolyl groups, determined according to the change in average molecular weight. The tetrazolyl groups exhibited optimal Pb²⁺ absorption at pH 5.3. Each Pb²⁺ ion was chelated to two or four tetrazolyl groups. In addition, the adsorption of Pb²⁺ to the tetrazolyl groups was highly selective in solutions also containing Na⁺, K⁺, Ca²⁺, and Mg²⁺ ions. The absorption of Na⁺, K⁺, Ca²⁺, Mg²⁺, Fe³⁺, or Zn²⁺ ions resulted in insignificant changes in the effective refractive index of the tethered PVT 2DPC; in contrast, absorbing Pb²⁺ ions led to a dramatic change in effective refractive index, due to the high refractive index of Pb²⁺ ions, resulting in a color change from green to dark red, observable to the naked eye along an incident angle of 50–60°. The tethered PVT 2DPC-based assay exhibited high sensitivity and selectivity in an experimentally simple setup for Pb²⁺ sensing. The color change of the 2DPC should be applicable in the development of other diffraction-based sensing technologies.

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1. Introduction

Environmental contamination by heavy metals poses ecological and public health concerns [1]. Human exposure to heavy metal ions has risen considerably as a result of their increased industrial use [2]. Accordingly, public health considerations have motivated the development of highly sensitive and selective approaches for the detection of heavy metal ions. Lead ions (Pb²⁺) are among the most stable and toxic of the heavy metal ions; they are strong environmental pollutants that can harm the health of humans and other organisms. Even at low concentrations, Pb²⁺ ions can cause serious damage to the central nervous system and lead to high blood pressure and impaired kidney function [3,4]. The most widely used techniques for detecting Pb²⁺ ions are atomic absorption spectrometry [5], inductively coupled plasma/atomic emission spectrometry

(ICP-AES) [6], UV–vis spectroscopy [7], and inductively coupled plasma/mass spectrometry (ICP-MS) [8]. Although these methods can be sensitive, accurate, and reliable for routine analysis, they are primarily available only in laboratory settings because they need expensive instrumentation and trained staff capable of performing pretreatment processes. Thus, convenient, simple, and sensitive approaches for the real-time sensing of Pb²⁺ ions remain highly attractive.

One of the most appealing and effective methods, in terms of ease of operation and simplicity of design, for the real-time detection and monitoring of heavy metal ions involves the use of adsorbents. The quality of these adsorbents is usually measured in terms of their adsorption capacity and selectivity. The interactions between the functional groups of the adsorbents and the adsorbates determine the adsorption selectivity as well as the adsorption mechanism. Adsorption through ion exchange, to attract anionic adsorbates or to chelate cationic metal ions, requires electrostatic interactions, most often using amino, thioamido, imidazolino, and hydrazino groups [9,10]. Amino groups are particularly effective for

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removing pollutants from aqueous solutions [11]. In addition, the density of functional groups on an adsorbent surface also determines the adsorption capacity from a solution. Although various chemical agents can be immobilized onto adsorbent surfaces, the adsorption capacity will remain limited without a suitably rich supply of adsorption sites on those surfaces [12]. Several reports have suggested that polymers presenting cooperative functional groups can improve the adsorption capacity for heavy metal ions by providing a higher density of coordinating sites [13,14]. Several adsorbent surfaces have been prepared based on grafting polymers; for example, through surfaces linked to monomers for the grafting of polymers [15], surfaces modified with initiators for polymerization [16], and surfaces for the chemisorption of reactive polymers [17].

Two-dimensional photonic crystals (2DPCs) have emerged as attractive platforms for fabricating high-quality optical microcavities [18]. A number of 2DPC-based optical gratings have been formed from periodic air hole arrays [19,20]. Recently, pillar arrays have been developed as 2DPCs for sensing applications, including pH sensors [21], sensors for volatile organic compounds [22], DNA detectors [23], and immunosorbent assays [24]. When the dimensional parameters and/or the refractive indices of the pillar materials change upon specific or nonspecific absorption of an analyte, the effective diffractive index of the 2DPC will also typically change [25]. In a previous study, we established a process for the fabrication of pillar arrays and found that 2DPCs could exhibit various colors upon changing their geometrical parameters [26]. Considering these 2DPCs as versatile platforms for detection, in this present study we monitored the variations in refractive indices of the 2DPCs upon absorbing Pb^{2+} ions and their resulting color changes. Accordingly, we used click reactions to graft *N*-propargyl polyacrylonitrile (PAN) to a dot matrix presenting azide-terminated surfaces on a silicon substrate to generate pillar arrays of 2DPCs. The tethered PAN 2DPCs underwent a subsequent cyano-tetrazole conversion to generate tethered polyvinyltetrazole (PVT) 2DPCs. These tethered PVT 2DPCs displayed a high absorption capacity for Pb^{2+} ions, with optical properties that varied depending on the metal ions they adsorbed. Our motivation for this study was to create a visual platform of 2DPCs on highly reflective silicon surfaces with specific absorption functions to allow optical sensing [27].

2. Experimental section

2.1. Materials

Silicon wafers, Si(100) p-type, polished on one side (diameter: 6 in.) were supplied by Hitachi (Japan). HF solution (10 wt%) was used to clean (10 min, 25 °C) the silicon substrates and remove the silicon oxide film. The HF-treated substrates were immersed (5 min) in a mixture of H_2SO_4 and H_2O_2 (2:1 mol%) and then rinsed three times with distilled water to generate a uniform layer of silicon oxide. The materials for graft polymerization—propargylamine, 2-bromo-2-methylpropionyl bromide (BB), acrylonitrile, copper(I) bromide, (3-bromopropyl)trichlorosilane (BS), triethylamine (TA), copper(II) bromide, and 1,1,4,7,7-pentamethyldiethylenetriamine (PMDETA)—were purchased from Acros Organics. Acrylonitrile, PMDETA, BS, and BB were purified through vacuum distillation prior to use. All other chemicals and solvents were of reagent grade and purchased from Aldrich Chemical.

2.2. *N*-Propargyl poly(acrylonitrile)

A three-neck flask containing a solution of propargylamine (0.556 g) and TA (1.022 g) in THF was cooled in an ice bath

for 30 min, deoxygenated, and then filled with N_2 . A solution of BB (2.356 g) in THF added to the flask under N_2 , resulting in a white precipitate (triethylammonium bromide). The mixture was stirred at 0 °C under N_2 for 24 h. The solids were filtered off; repeated extraction of the mixture gave *N*-propargyl-2-bromo-2-methylpropionamide. Copper(I) bromide (0.134 g), PMDETA (0.348 g), and the as-prepared *N*-propargyl-2-bromo-2-methylpropionamide (0.204 g) were mixed with ethylene carbonate in a reaction vessel under a N_2 atmosphere. After deoxygenation, a solution of acrylonitrile (16 g) in ethylene carbonate was added dropwise into the vessel under a N_2 atmosphere at 70 °C. The resulting propargyl-polyacrylonitrile (propargyl-PAN) was obtained with cleaning of excess methanol and passed through a column of Al_2O_3 to remove the copper ions. The resulting solution was poured into MeOH; the precipitate was placed in a Soxhlet apparatus and treated with MeOH to remove any unreacted materials. Samples of propargyl-PAN were analyzed through gel permeation chromatography (GPC) using a VISCOTEK-DM400 instrument equipped with an LR 40 refractive index detector. Monodisperse polymer standards (Polymer Lab, Agilent) were used to generate a calibration curve.

2.3. Modification of azido-terminated dot matrix on silicon substrate

The fabrication process, using very-large-scale integration, for preparing the patterned polymer brushes as pillar arrays is depicted in Fig. 1 [28,29]. It comprised the following steps: (A) The Si wafer, rich in OH groups on the surface, was treated with hexamethyldisilazane (HMDS) at 95 °C to turn the OH groups on the surface of the wafer to a passive film of $Si(CH_3)_3$; the photoresist was spun on the HMDS-treated Si wafer to pattern a hole array using I-line lithography. (B) The sample was subjected to argon/oxygen plasma treatment (AOP) to form OH groups on the HMDS-treated surface; AOP resulted in the bottom surface becoming chemically modified (strongly hydrophilic or polar) only in the areas not covered by the photoresist; the photoresist was removed from the surface by cleaning with acetone, generating the chemical dot matrix surface. (C) BS units were assembled selectively onto the bare areas of the bottom Si surface after AOP in dry toluene [30]. (D) An azido-terminated surface was obtained after treating the bromo-modified surface with NaN_3 ; the substitution reaction involved exposing the bromo-modified substrates overnight to a saturated solution of NaN_3 in DMSO in a covered vessel; the sample was then rinsed sequentially with DMSO, MeOH, and DI water before drying under a stream of N_2 [31]; the wafers were placed in a Soxhlet apparatus to remove any unreacted materials and dried under a stream of N_2 ; this procedure resulted in surfaces patterned with regions of azido groups and regions of photoresist; the as-prepared propargyl-PAN (0.300 g), CuBr (0.0690 g), and PMDETA (0.498 g) were dissolved in dry DMSO and deoxygenated (repeated evacuation under vacuum), then reacted with the as-prepared azido-terminated Si wafer at 40 °C for 48 h under high-purity N_2 ; this click reaction covalently immobilized propargyl-PAN onto the dot matrix to form pillar arrays, the basic structure of the 2DPC; the samples were removed from the solution and washed repeatedly with acetone. (E) The PAN-terminated surface, NH_4Cl , NaN_3 , and DMSO (150 mL) were stirred (40 min) in a 300-mL vessel and then at 80 °C for 60 min to generate the tethered PVT 2DPC; the samples were rinsed sequentially with water and 0.6 M HCl, then dried in a vacuum oven at 50 °C; the azido-modified surfaces and those clicked with propargyl-PAN were examined using X-ray photoelectron spectroscopy (XPS; Scientific Theta Probe, UK) and an FTIR spectrometer equipped with an attenuated total reflection (ATR) geometry; the morphologies of the photoresist template and pillar array of PVT were analyzed through atomic force microscopy

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