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Colorimetric detection of volatile organic compounds using a colloidal crystal-based chemical sensor for environmental applications

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Abstract

The detection of pollutants such as volatile organic compounds (VOCs) is of significant importance for environmental protection. However, conventional monitoring methods are often time consuming and require expensive equipments. In this study, a colloidal crystal-based colorimetric chemical sensor was developed for environmental applications. The device consists of a glass substrate with a three-dimensional colloidal crystal and poly(dimethylsiloxane) (PDMS) elastomer. Such a colloidal crystal was generated by infiltrating the voids within an opaline lattice of polystyrene nanoparticles with a liquid prepolymer to PDMS, followed by thermal curing. When a sample solution such as benzene, toluene, or xylene, capable of swelling the elastomer matrix, was applied to the surface of this crystal, the lattice constant and thus the wavelength of Bragg diffracted light was increased. On the basis of this mechanism, we demonstrated the colorimetric detection of VOCs. As a result, the colloidal crystal-based chemical sensor could be used to specifically determine VOC concentrations. Additionally, using this colloidal crystal-based chemical sensor, the change in the optical characteristics could be observed with the naked eye. Therefore, this chemical sensor can be applicable to on-site monitoring for environmental applications.

Keywords: Colloidal crystal; Nanoparticles; Chemical sensor; Poly(dimethylsiloxane); Environmental application; Volatile organic compounds (VOCs)

1. Introduction

During recent decades, volatile organic compounds (VOCs) have been commonly found in the environment, in the soil, groundwater, and atmosphere [1,2]. Therefore, humans are easily exposed to these chemicals through the skin, by breathing, and by eating, and even at low concentrations this exposure can present long-term health risks. Among the VOCs, benzene and its derivatives such as benzene, toluene, and xylene (BTX), were confirmed to be human carcinogens, and could cause diversiform cancers, for example, lymphatic and hematopoietic cancers. Furthermore, ingestion of drinking water containing VOCs may lead to liver and kidney damage, and disorders of the immune system, nervous system, and reproductive system as well as several types of cancers [3]. The fact that these VOCs have very different toxicities has meant that society has dealt with each one of them differently. From the viewpoint of environmental protection, it has become a matter of high priority to address the issue of the detection of these compounds. An important and non-trivial first step is to identify sites of pollution, and perform on-field monitoring, which requires a simple, economical, and rapid test for the detection of these compounds in samples taken from industrial processing, soils, human and animal tissues, and foodstuffs. This fact stimulates the development of measurement methods and techniques for environmental pollutant monitoring. With this background, there is an increasing interest in the development of a sensor for VOC detection [4–7]. There are many fields in which these kinds of sensors can be used, such as environmental applications, electronic noses, and in chemical industries, and in fact, many sensors have already been developed. However, the present sensors used for environmental applications, such as gas chromatography/mass spectrometry (GC/MS), require a relatively long assay time that involves troublesome liquid handling and many expensive reagents and apparatus [8,9].

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To overcome these disadvantages, several groups have developed different detection methods for sensors in environmental applications. Mitsubayashi et al. reported the development of an enzyme-based formaldehyde biosensor that detected low concentrations of acetaldehyde using an electrochemical detection method [10]. Mascini et al. developed a dioxin biosensor based on a piezoelectric sensor [11]. In addition, a microfluidic environmental sensor fabricated using microelectromechanical system (MEMS) technology has also been reported [12–14]. However, almost all conventional sensors for environmental applications involve high-cost apparatus that are difficult to use. Therefore, there is a demand for a more convenient and cost-effective sensor system. Hence, we targeted the development of the colloidal crystal-based chemical sensor towards this requirement.

Colloidal crystals are three-dimensionally periodic lattices of mono-dispersed, spherical colloids such as polystyrene and silica. The periodic lattices of the colloidal crystal will diffract incident light in accordance with Bragg's law [15]. The reflected light in the visible spectrum is called the structural color. Additionally, the optical characteristics of colloidal crystals are related to their lattice constants. A millimeter-sized periodic structure can act as a colloidal crystal in millimeter wavelengths; a submicrometer-sized structure, in a visible light region; and the nanometer-sized ones, in the X-ray region. Hence, the resulting colloidal crystals diffract UV, visible, or near-IR light, depending on their lattice constants. A colloidal crystal diffracts light according to the Bragg equation (Fig. 1(a)):

$$m\lambda_{\text{peak}} = 2\, d_{1\,1\,1}\, (n_{\text{eff}}^2 - \sin^2\theta)^{1/2} \quad (1)$$

where m denotes the order of diffraction; λ_{peak} the wavelength of the diffraction peak; $d_{1\,1\,1}$ the spacing between (1 1 1) planes; θ the angle between the incident light and the normal to the diffraction planes; and n_{eff} is the mean refractive index of the crystalline lattice. Based on these features, the colloidal crystal is an ideal candidate for fabricating optical sensors that can be used to determine environmental changes in terms of color changes.

By using these features, several sensors based on colloidal crystals were fabricated by embedding colloidal crystals in appropriate polymers or hydrogels. These colloidal crystal-based sensors exhibit brilliant colors, which change in response to temperature, pH, ionic species, and glucose levels (Fig. 1(b)) [16,17]. Asher et al. reported the development of a colloidal crystal-based sensor for the detection of creatinine [18] and glucose [19] for medical applications. In all of these studies, the lattice constant, and thus the color exhibited by the colloidal crystal, as determined by the Bragg Eq. (1), varied in response to the environmental changes. In a number of related studies, the change in the refractive index was also demonstrated as a means to detect variations in the environment.

In this study, poly(dimethylsiloxane) (PDMS) was used for the fabrication of colloidal crystal-based chemical sensors for environmental applications. PDMS swells in non-polar organic solvents. In addition, its swelling kinetics differ according to the polarity of the solvent [20]. Using this material, we fabricated a simple, convenient, and cost-effective colloidal crystal-based chemical sensor for the colorimetric detection of VOCs for environmental applications. Previously, for environmental applications, similar detection principles or materials have been used for detection of the various vapors [21,22]. In addition, using this colloidal crystal-based chemical sensor for detection of VOCs, more simplified detection systems can be established.

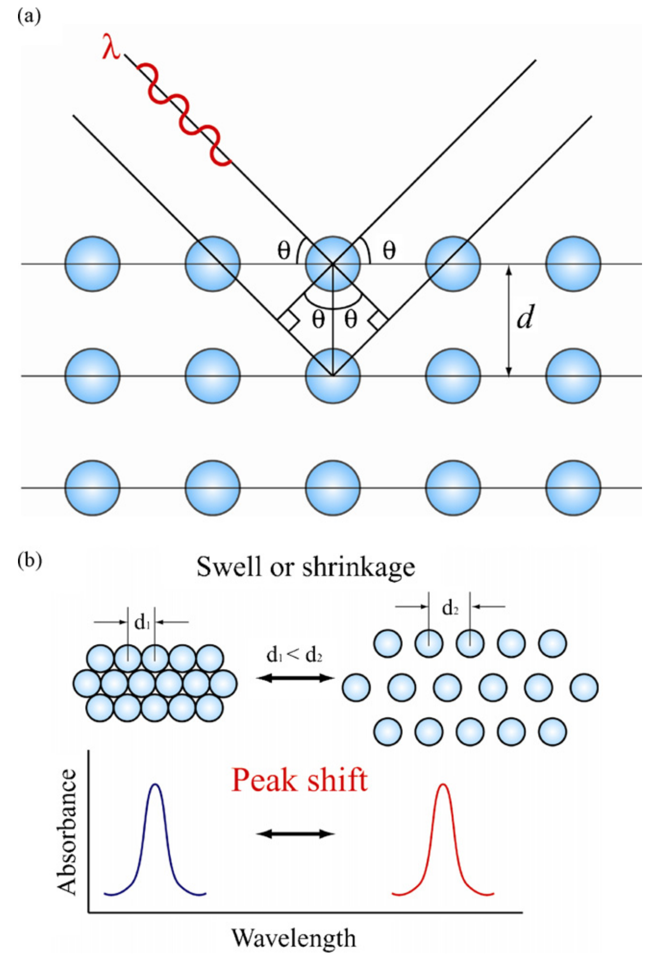

Fig. 1. (a) Theoretical schematic illustration of the colloidal crystal-based chemical sensor. (b) Detection principle of the colloidal crystal-based chemical sensor.

In this report, we fabricated a large-area (up to mm^2), well-ordered, three-dimensional colloidal crystal-based chemical sensor using polystyrene nanoparticles by using the dry-up process of its colloidal dispersion. The optical characteristics of the three-dimensional colloidal crystal-based chemical sensor were evaluated by using a UV–vis spectrometer, and the surface analysis was performed by using atomic force microscopy (AFM). Simultaneously, we performed the evaluation of the selectivity and calibration characteristics of this colloidal crystal-based chemical sensor for BTX.

2. Experimental

2.1. Materials

Polystyrene nanoparticles (diameter: 202 nm, 2.57%, w/v) used for preparing the colloidal crystals were purchased from