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HCl gas adsorption/desorption properties of poly(*N*-isopropylacrylamide) brushes grafted onto quartz resonator for gas-sensing applications

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ABSTRACT

Poly(*N*-isopropylacrylamide) (PNIPAM) chains were grafted onto a quartz resonator using surface-initiated atom transfer radical polymerization (SI-ATRP). The PNIPAM loading was varied by changing the grafting time and the monomer concentration. AFM analysis revealed that the increase in PNIPAM loading was attributable to increases in the chain length and in the corresponding brush height. The HCl gas adsorption/desorption properties of the resulting PNIPAM brushes were measured by a quartz crystal microbalance (QCM) technique. The PNIPAM brushes adsorbed large amounts of HCl gas, and the adsorption capacity was linearly related to the PNIPAM loading, indicating the homogeneous adsorption of HCl gas inside the PNIPAM brushes. On the other hand, the rate of desorption of the HCl molecules was lower than that of the adsorption process, and slowed with increases in chain length. Reversibility was insufficient, especially at longer chain lengths due to the difficulty of the diffusion of gas molecules from inside the brushes. The reversibility was improved by raising the measuring temperature from 30 °C to 50 °C, but it was still up to 80%, suggesting the irreversibility of the adsorption.

1. Introduction

Hydrogen chloride (HCl) gas is produced primary by burning fuels that contain chlorine and incinerating waste that contains plastics [1]. Since HCl gas is toxic to the human body, reliable detection of HCl gas is required from the stand points of emission control and air-quality monitoring in workplaces. There is thus an increasing need for simple, inexpensive gas sensors. Among the materials that have been used for gas sensing, polymers have attracted attention because of their low cost and the simplicity of film-fabrication techniques, the ease of deposition on various types of substrates, and the wide choice of chemical structures. It is therefore highly desirable to develop practical polymer-based HCl gas sensors with high sensitivity and selectivity as well as good reversibility. Various types of HCl gas sensors using polymers have been investigated so far. As sensing films for optochemical-type sensors, porphyrin derivatives dispersed in a biodegradable polymer [2], a nanofibrous porphyrinated polyimide [3], and copolymers consisting of a fluorescently active co-oligomer [4] have been reported. Multiwalled carbon nanotubes embedded in poly(2,5-dimethylaniline) [5] and polyaniline nanofibers [6] were utilized for a conductometric sensor, and amino-functional copolymers [7] and poly(acrylamide) derivatives [8] were utilized for QCM-based sensors.

The performance of a gas sensor is related to the gas adsorption/desorption properties of its sensing film, irrespective of its sensing mechanism. Since the gas adsorption/desorption properties of a polymer film are affected by its morphology, control of the morphology of a sensing film is important for the development of practical polymer-based gas sensors. In a previous study, we investigated the HCl gas adsorption/desorption properties of poly(*N*-isopropylacrylamide) (PNIPAM) with a nanoparticle form as well as a thin film form using a quartz crystal microbalance (QCM) technique [9]. The results showed that PNIPAM with the nanoparticle form had a completely reversible adsorption, irrespective of the PNIPAM loading on the quartz resonator, whereas the adsorption of the HCl gas of the thin film form was slow and the reversibility was poor. From those results, we concluded that the method by which a PNIPAM films is produced significantly influences its gas-sensing properties.

Many reports have dealt with the grafting of PNIPAM onto surfaces, leading to the applications based on smart surfaces [10–20], but very few reports have studied PNIPAM brushes

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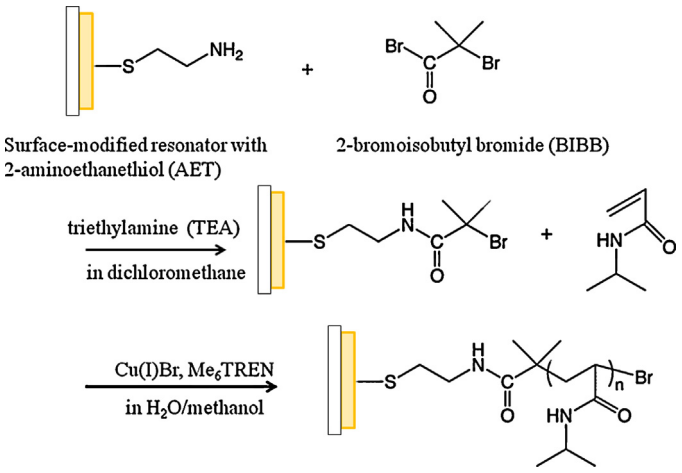

Scheme 1. Preparation pathway of PNIPAM brushes onto a gold electrode of quartz resonator.

for gas sensing [21]. In recent years, PNIPAM has been grafted onto quartz crystal surfaces to explore the collapse and swelling behavior of PNIPAM brushes in water [22–24]. In this work, we also grafted PNIPAM chains onto the gold electrode surface of a quartz resonator, but the purpose is to apply it to an HCl gas sensor. The effects of grafting time and measuring temperature on the HCl gas adsorption/desorption properties of PNIPAM brushes were investigated using the QCM technique. The properties of these brushes were also compared with those of the nanoparticle and thin film forms reported previously [9].

2. Experimental

2.1. Materials

N-isopropylacrylamide (NIPAM: Wako Pure Chemicals, Tokyo), 2-aminoethanthiol (AET: Tokyo Kasei, Tokyo), ethanol (Wako Pure Chemicals), 2-bromoisobutyl bromide (BIBB: Tokyo Kasei), copper(I) bromide (Cu(I)Br: Wako Pure Chemicals), dichloromethane (Wako Pure Chemicals, Tokyo), triethylamine (TEA: Nacalai Tesque, Tokyo), tris[2-(dimethylamino)ethyl] amine (Me6TREN: Sigma–Aldrich Japan, Tokyo), and methanol (Wako Pure Chemicals) were used without further purification.

2.2. Preparation of PNIPAM brushes

PNIPAM brushes were prepared by grafting linear PNIPAM chains onto the gold electrode of the AT-cut quartz resonator (9 MHz) using surface-initiated atom transfer radical polymerization (SI-ATRP) according to the literature [15,19,24]. Scheme 1 illustrates the preparation of PNIPAM brushes onto the quartz resonator.

First the ATRP initiator, BIBB, was immobilized onto the resonator surface before the PNIPAM was grafted throughout the two-step procedure. In the first step, the gold electrode of the resonator surface, previously cleaned with piranha solution, was modified with AET by immersing the resonator in 26 mM AET solution in ethanol for 2 h. An assembled monolayer (SAM) of AET formed spontaneously during this procedure. The resultant resonator was rinsed repeatedly with ethanol and distilled water to remove the physically adsorbed AET on the surface. The AET-modified resonator was then dried under vacuum at 30 °C for 1 h. In the second step, the amino groups immobilized on the surface were reacted with BIBB. The resonator modified with AET was first put

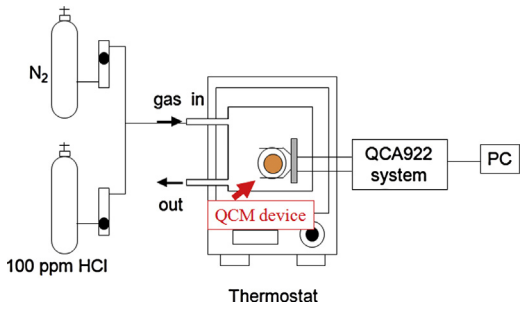

Fig. 1. Experimental setup used for HCl gas adsorption/desorption measurements.

into 25.2 ml of dry dichloromethane containing dry triethylamine (4 vol%), followed by the addition of 0.5 ml of BIBB dropwise into the solution. The resonator was kept in solution for 1 h with an ice bath, and the reaction was further carried out for 3 h at room temperature. The resultant resonator modified with BIBB was then rinsed by sonication in ethanol for 1 min, and dried under vacuum at 30 °C for 1 h.

The PNIPAM brushes were fabricated by reacting the bromo groups immobilized on the surface with NIPAM monomers during the subsequent ATRP. The resonator modified with BIBB was immersed in either of two degassed solutions of NIPAM with different monomer concentrations (0.80 mol dm^{-3} and 1.60 mol dm^{-3}). The degassed NIPAM solution was a mixture of 6.3 g (56 mmol) or 12.6 g (112 mmol) of NIPAM, 43.8 ml of H_2O and 26.3 ml of methanol containing 0.021 g of Cu(I)Br and 40 μl of tris[2-(dimethylamino)ethyl] amine (Me6TREN), with CuBr being used as a catalyst and Me6TREN as a ligand [25]. The grafting was performed at 20 °C for different grafting times under a N_2 stream. Since the reaction conditions of AET immobilization were not varied in this study, the resulting grafting density was assumed to be constant. Consequently, varying the grafting time can alter the molecular weight of the grafted PNIPAM and the corresponding brush height. After the polymerization, the PNIPAM-grafted quartz resonator was rinsed by sonication in methanol for 1 min, and the surface-modified quartz resonator with PNIPAM brushes was then dried under vacuum at 30 °C for 1 h.

2.3. Measurements

The setup used for HCl gas adsorption measurements is shown in Fig. 1. All quartz resonators modified with PNIPAM brushes were set in a thermostated vessel, and measurements were performed at 30 °C or 50 °C in flows of 100 ppm of dry HCl gas diluted with N_2.

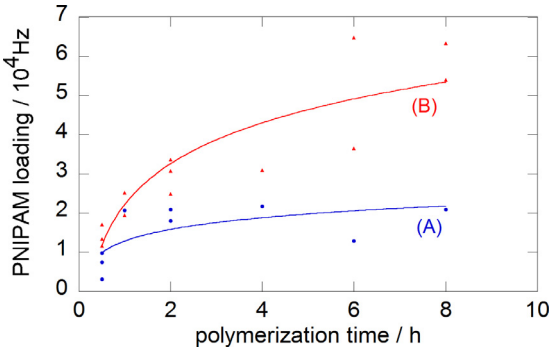

Fig. 2. Dependence of PNIPAM loading on the grafting time for PNIPAM brushes prepared from different monomer concentrations: (A) c_{NIPAM} = 0.80 mol dm^{-3} and (B) 1.60 mol dm^{-3}.