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Inter-molecular Control of Poly-ion complex LB Films with Fullerene Molecules for Molecules Size Recognition

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Inter-molecular Control of Poly-ion complex LB Films with Fullerene Molecules for Molecules Size Recognition

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Gases with different molecular sizes were successfully distinguished by the spatially controlled the LB films using fullerene molecules. By depositing the 200 layers of LB films with the spacer molecules using polyelectrolyte subphase, the quartz crystal microbalance (QCM) type gas sensors with high sensitivity and high durability for molecular size recognition were fabricated.

Keywords LB film; polyelectrolyte; poly-ion complex; molecular size ; recognition; fullerene: quartz crystal microbalance; sensor

INTRODUCTION

Recently, the gas or smell sensor using a quartz crystal microbalance (QCM) [1-3] increase its importance because of its sensitivity to measure the mass of the chemical substance with 1-ng order accuracy. These sensors are formed by coating the electrodes with sensing thin films. These sensing films are empirically chosen and there are few reports on the optimum conditions for the fabrication of the structure of sensing films. Therefore we proposed the new sensing film using spatially controlled LB films with spacer molecules. With this method, larger odor molecules can be caught by this LB film, which means the higher sensitivity as gas sensor[4-7]. In this study, we added Poly(allylamine) hydrochrolide (PAH) at every bilayer as polymer backbone to strengthen the LB film and have succeeded in depositing 200-Layer LB film, which was impossible to deposit without the help of polymer backbone.

The sensitivity of the sensor using the 200-layer LB films as sensing film was improved drastically than that of the thin LB films

EXPERIMENTAL

LB films consisted of 20 or 200 monolayers containing spacer fullerene molecules (C_{60}) were deposited on a QCM silver electrode (10MHz). The transfer of the monolayers to the substrate was made with a moving-wall type LB trough (Nippon Laser and Electronics Lab.,). The schematic illustrations of a molecular sifter by LB films containing spacer molecules are shown in Fig.1. As shown in this figure, polymer backbones were added to the LB films with spacer molecules just like the cytoskeleton in the biological cell membrane. These backbones are introduced by adding the polyelectrolyte, PAH, into the water subphase during the deposition of the LB films.

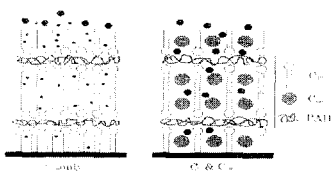

Fig.1 Schematic illustrations of the spatially controlled LB films with polymer backbones between bilayers.

RESULTS AND DISCUSSIONS

When the LB film contained C_{60} as the spacer, we could not succeed in depositing more than 60 layers. However, when the PAH was melted in the water subphase, it was very easy to deposit up to 200 bilayers. These results indicate that the molecular arrangement of the LB films including spacer

We consider that this organization was caused because the C_{20} molecules in the LB films was anchored with each other by the polymer thread.

The changes of the sensor responses in a static system as the increase of

the number of layers are shown in Fig.2. As the increase of the number of layers, the sensor response increased drastically.

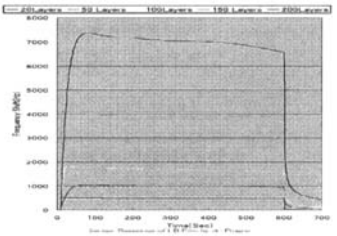

Fig.2 The changes of the sensor responses as the increase of the number of layers of LB films (static system).

Therefore, we consider that the sensor response increased drastically because the intermolecular space , the path for the gas molecules into the LB films, was secured as the increase of the number of layers. Another reason to be considered for the drastic sensitivity improvement of the sensing film as the increase of the number of layers is that the gas molecules can stay longer in a very stable state at the deep part in the sensing film. Generally, the molecules near the surface of the sensing film are considered to be very unstable and occasionally repeat adsorption and desorption. On the other hand, however, the gas molecules inside of the sensing film can stay longer in the sensing film because they strongly trapped to the film molecules by the obstacles of the other trapped gas molecules. Nevertheless, the very quick recovery characteristics of the sensors are also can be seen in the Fig.2. These experimental facts of the quick responses of the sensors support the highly organized molecular arrangement in the sensing films as shown in Fig.1.

The sensor responses to various the gas molecules were examined in a gas flow system. The results are shown in Fig.3. The 3-D chemical structures of the gas molecules used in this study are also shown in the right side. As shown in this figure, the sensor showed the highest response to benzene, the smallest gas molecule in this experiment. And the order of the response was

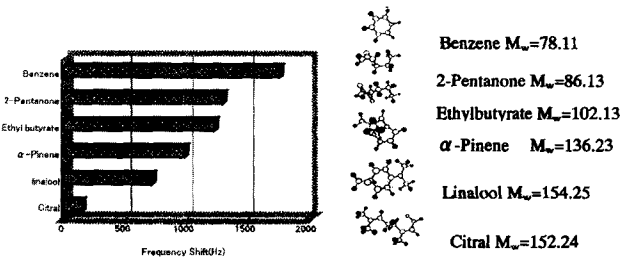

Fig.3 Sensor responses to the gas molecules with various chemical structures

exactly in accordance with that of the size of the gas molecules. Consequently, high selectivity of the newly developed sensing film was clearly demonstrated in a gas flow system

CONCLUSIONS

It was demonstrated that by controlling the molecular organization in the sensing film using spacer molecules and polyelectrolytes, high performance sensing film with high sensitivity and molecular shifter function for gas or smell sensor was established. The molecular arrangement design in the self assembly film is very promising for the molecular size recognition.

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