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An Extended-gate Organic Field-Effect Transistor toward Food Freshness Sensing

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Abstract

As part of our ongoing program to develop organic field effect transistor (FET)-based sensors for health care, we report histamine detection using an extended-gate organic FET. Histamine is contained in spoiled fish, which causes foodborne illness known as scromboid poisoning. The new organic FET possesses an extended-gate functionalized by carboxyalkanethiol that can interact with histamine. As a result, we have succeeded in detecting histamine in water through a shift of threshold voltage. This indicates the potential utility of the designed organic FET for food freshness sensing.

1. Introduction

The development of monitoring methods of food freshness is very important because food safety is closely related to health conditions. Foodborne diseases are caused by consuming contaminated foods and beverages. For example, foodborne diseases are estimated to cause 6 million to 81 million illnesses each year in the United States [1]. In the case of Japan, the number of patients with food poisoning is more 20-thousand per year. One of the well-known foodborne diseases is scromboid poisoning [2]. The most common symptoms of this poisoning are itching, faintness, dizziness, a burning sensation in the mouth, and the inability to swallow. Scromboid poisoning is generally caused by having spoiled fish with elevated histamine levels. Histamine exists in species of the scombridae family such as tuna, mackerel, blue fish, and sardine, which is derived from decarboxylation of histidine by bacteria with amino acid decarboxylase (Fig. 1 (a)). Hence, the concentration of histamine is regarded as a freshness criterion. Conventionally, quantitative determination of histamine relies chiefly on solid-phase extraction followed by high-performance liquid chromatography [3]. Nevertheless, this method is not easily amenable to simple and low-cost monitoring of histamine.

To develop easy-to-use and low cost food freshness sensors, we believe that organic FET based sensors are one of the best candidates [4]. Because the organic FETs fabricated on a thin plastic film substrate possess their mechanical flexibility, the organic FET sensors could be attached on food or food packages. Furthermore, the organic FET sensors can be fabricated with printing process. However, organic semiconductors are degraded readily by water, unfortunately [5]. Therefore, we designed an extended-gate type organic FET-based sensor, which allows us to not only use stable transistor operation but to detect analytes in aqueous media. The surface of the extended-gate Au electrode was functionalized with a self-assembled monolayer (SAM) of carboxyalkanethiol. The terminal of carboxylate group can recognize histamine via electrostatic and/or hydrogen-bonding interactions (Fig. 1(c)) [6]. The captured histamine causes the charge carrier concentrations in semiconductor layers, therefore, the histamine concentration can be determined quantitatively. Here, we report first extended-gate type organic FET sensor for histamine in water.

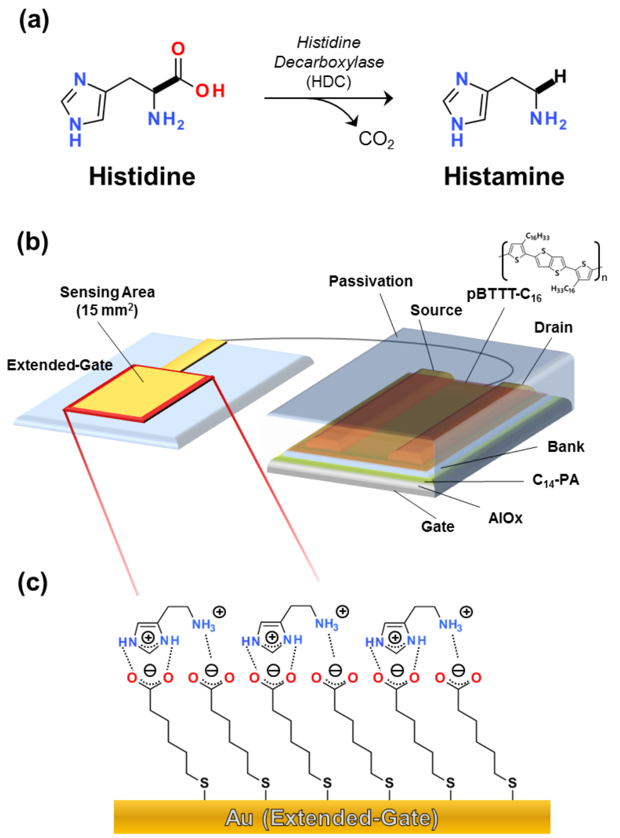

Fig. 1 (a) Biological conversion of histidine to histamine by bacteria with histidine decarboxylase in fish. The amount of histamine is one of the freshness criteria. (b) Schematic structure of the designed extended-gate type organic FET. (c) A plausible model for histamine recognition.

2. Results and Discussion

The designed device structure is illustrated in Fig. 1(b). An Al gate electrode was deposited on a glass substrate by thermal evaporation (30 nm). The gate dielectric consisted of a thin-film of AlOx (5 nm) and a tetradecylphosphonic acid (1.7 nm) SAM. Au source-drain electrodes were deposited on the gate dielectric layer by evaporation (30 nm) and patterned using photolithography. The channel width and length were 500 and 20 µm, respectively. For preparation of bank layers, a 1wt% solution of an amorphous fluoropolymer (Teflon® AF1600) in FC-43 was dispensed using a dispenser system. A semiconducting polymer, pBTTT-C_{16} (poly(2,5-bis(3-hexadecylthiophene-2-yl) thieno[3,2-*b*]thiophene)), was drop-casted from a 0.03wt% solution of *o*-dichlorobenzene, and then annealed at 175 ºC

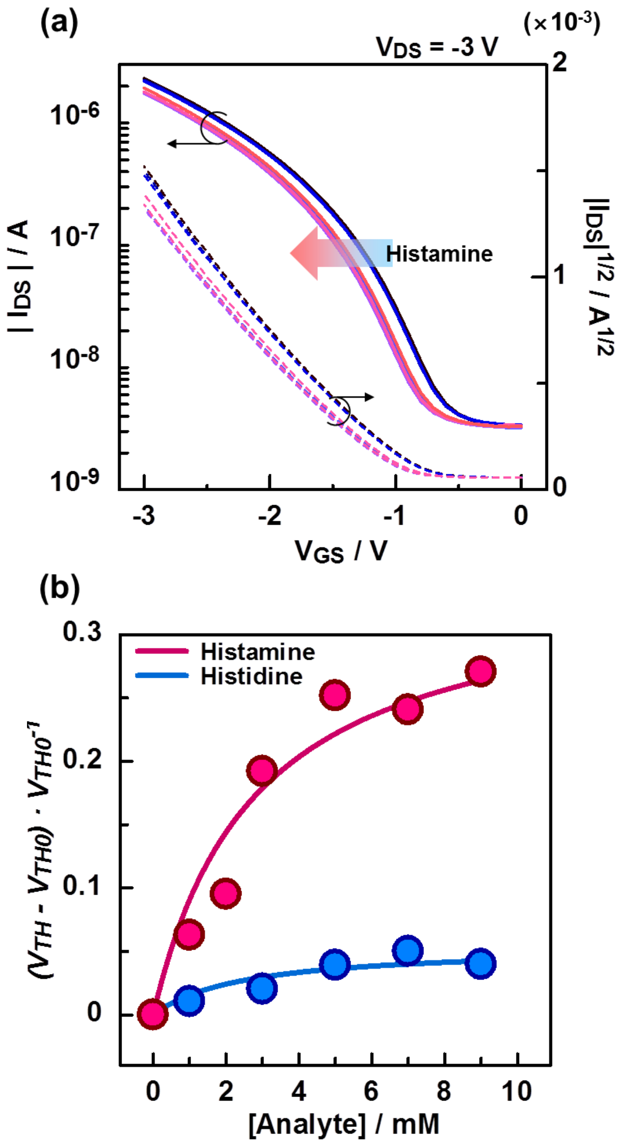

Fig. 2 (a) Transfer characteristics (I_{DS}-V_{GS}) of the organic FET upon titration with histamine in a MES-buffer solution (100mM) with NaCl (500 mM) at pH 5.5. [Histamine] = 0-9 mM. (b) Changes in threshold voltage of the organic FET by analytes at various concentrations in a MES-buffer solution (100 mM) with NaCl (500 mM) at pH 5.5. Histamine (●), histidine (●).

for 30 min under N_2 atmosphere. For passivation of the device, Cytop® (CTL-809M) was spin-coated on the device (100 nm) and baked at 100 ºC for 10 min. An Au extended-gate electrode on a PEN film substrate (125 µm) was prepared by thermal evaporation. The size of sensing area on the extended-gate was 15 mm^2. The Au extended-gate electrode was immersed in a hexane solution containing 1 mM of 5-carboxy-1-pentanethiol for 1 h at room temperature. The SAM-attached electrode was washed by ethanol and water.

The functionalized extended-gate electrode was dipped in a MES (2-morpholinoethanesulfonic acid) buffer solution of histamine and then the extended-gate electrode was connected to the organic FET. As a reference electrode, an Ag/AgCl electrode was employed. The transfer characteristics of the organic FET upon titration with the histamine solution are summarized in Fig. 2(a). In consequence, a shift of the transfer curve with increasing the amount of histamine was observed. To promote a greater understanding of detection mechanism of histamine, the titration of histidine was carried out. As illustrated in Fig. 2(b), much weaker response to histidine was obtained. The presence of a carboxyl group lowers the binding affinity presumably due to electrostatic repulsion between the carboxyl moieties of the SAM and the carboxy oxygens of histidine. These results indicate that the fabricated organic FET sensor can distinguish histamine from histidine, which is very useful to monitor fish freshness.

3. Conclusions

In summary, we have succeeded in detecting histamine in water by the designed organic FET device. To the best of our knowledge, this is the first report of histamine detection utilizing by extended-gate type organic FETs. We are convinced of that this result opens up an avenue for development of future organic FET-based sensors for monitoring of food freshness.

Acknowledgements

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