Detection of Carbon Dioxide Using Cucurbit[6]uril-Functionalized Gold Nanorod Gas Sensor Based on Localized Surface Plasmon Resonance

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Seongjae Jo\textsuperscript{a,b,†}, Jinyeong Kim\textsuperscript{a,b,†}, Yejin Kim\textsuperscript{a,c}, and Oh Seok Kwon\textsuperscript{a,b,*}
\textsuperscript{a}Infectious Disease Research Center, Korea Research Institute of Bioscience and Biotechnology (KRIBB), Daejeon 34141, Republic of Korea
\textsuperscript{b}Nanobiotechnology and Bioinformatics (Major), University of Science & Technology (UST), Daejeon 34141, Republic of Korea
\textsuperscript{†}These authors contributed equally to this work.

\textsuperscript{*}Corresponding author E-mail: oskwon79@kribb.re.kr

ABSTRACT

Owing to rapid climate change and increasingly stringent carbon regulations, carbon dioxide detection is becoming more important. In this study, we fabricate a cucurbit[6]uril-functionalized gold nanorod-based localized surface plasmon resonance (LSPR) gas sensor to detect carbon dioxide. The gold nanorods provide a high refractive index unit that enables the measurement of gas molecules with low molecular weights, while cucurbit[6]uril is a chemical receptor that binds to carbon dioxide owing to its structural characteristics. Therefore, cucurbit[6]uril was functionalized through direct adhesion on the surface of gold nanorods, which was replaced with citrate. The manufactured sensor can detect the presence of carbon dioxide at a maximum concentration of 400 ppm in the atmosphere. The high potential applicability of the cucurbit[6]uril-applied LSPR gas sensors is demonstrated in this study.

Keywords: Carbon dioxide, Gold nanorods, Localized surface plasmon resonance, Cucurbituril, Gas sensor

1. Introduction

Among the various gases that constitute the atmosphere, gases such as carbon dioxide, methane, nitrous oxide, freon, hydrofluorocarbons, perfluorocarbons, sulfur hexafluoride, and ozone contribute to the greenhouse effect [1, 2]. The greenhouse effect prevents the release of heat captured from the absorption of solar energy by the Earth [3, 4]. This phenomenon was discovered in 1824 when the French mathematician Joseph Fourier calculated that the Earth would be much colder without an atmosphere [5]. The Swedish scientist Svante Arrhenius reported in 1896 that a warming effect is linked to the increase in carbon dioxide gas from the use of fossil fuels [6]. Likewise, in the 20th century, studies have reported that the increase in carbon dioxide is associated with the increase in global temperature [7, 8]. Recently, researchers have reported that the increase in greenhouse gas concentrations causes critical effects such as extreme weather events, rising sea levels, changes in animal populations, and an increase in the average global temperature [9–11]. Carbon dioxide, methane, nitrous oxide, hydrofluorocarbons, perfluorocarbons, and sulfur hexafluoride were identified as the six major greenhouse gases at the 3rd Conference of the Parties [12]. Among these gases, carbon dioxide accounts for more than 80% of the total greenhouse gas emission and is considered to be the most noteworthy greenhouse gas [5]. In particular, the highest carbon dioxide concentration of 411 ppm was detected in 2018 at the Mauna Loa atmospheric baseline observatory in Hawaii [13]. Because carbon dioxide can remain in the atmosphere for hundreds of years, measures must be taken to slow down global warming [14]. European emission standards are examples of typical carbon dioxide regulation policies [15]. The first stage of these standards was implemented in 1992, and the regulatory standards have now been strengthened to the sixth stage while the implementation of the seventh stage is currently under discussion. Under these policies, the level of carbon dioxide emitted by automobiles was reduced from 130 g/km in 2015 to 95 g/km in 2020 [16]. Carbon dioxide reduction has been discussed and implemented not only in automobile-related policies but also in other fields. Carbon dioxide is mainly produced by the burning of fossil fuels and organic matter such as coal, oil, gas, wood, and solid waste [17]. Because carbon dioxide is produced in almost every essential part of the global economy, including industry, agriculture, transportation, and electricity generation, it is imperative to reduce the use of fossil fuels across all regions [18]. In particular, when Korea joined the Paris Climate Agreement, it set the goal of reducing carbon dioxide production by 24.4% with respect to the carbon dioxide production in 2017 by 2030. Because carbon dioxide accounts for 88.6% of the total greenhouse gas emissions in Korea, the detection of carbon dioxide has gained increased prominence [19]. Sensors that use chemical reactions, which is one of the conventional methods for detecting carbon dioxide, has the disadvantage that the measurement limit is on the order of several ppm [20, 21]. Another method for de-
ecting carbon dioxide is to use a non-dispersive infrared gas sensor. This sensor is based on the principle that each gas has a specific infrared absorption spectrum (e.g., carbon dioxide absorbs at 4.26 μm); hence, it has high selectivity because it detects the gas based on its specific spectrum [22, 23]. Nonetheless, this sensor faces the limitations of being expensive and difficult to miniaturize.

In this study, we fabricated a gas sensor based on localized surface plasmon resonance (LSPR) that is capable of detecting carbon dioxide. Cucurbit[6]uril (CB6) molecules are applied on a gold nanorod (AuNR) substrate to form the sensor. Because of their structural characteristics, gold nanorods have a higher refractive index unit than the more widely used gold nanoparticles (AuNPs) [24–26]. This allows the nanorods to be used for the sensitive detection of gases such as carbon dioxide (CO₂). Cucurbituril is a pumpkin-shaped macrocyclic molecule that contains glycouryl monomers linked by a methylene bridge. The cucurbituril molecules are named according to the number of linked glycouryl monomers (e.g., cucurbit[5]uril, cucurbit[6]uril, cucurbit[7]uril). Each molecule has its own characteristics. In particular, cucurbit[6]uril possesses alkyl chains that form hydrophobic cavities and allow for hydrophobic interactions. Cucurbit[6]uril interacts with cationic guests through the cationic dipole interaction at a carbonyl portal. These characteristics allow cucurbit[6]uril to detect various gases, such as carbon dioxide, and have great promise in the field of gas encapsulation and storage because they enable the sequestering of specific molecules within intrinsic internal cavities [27]. In this study, the detection of standard carbon dioxide gas by a cucurbit[6]uril-functionalized gold nanorod-based LSPR gas sensor prepared in the above method is demonstrated. In addition, the possibility of detecting carbon dioxide present in exhaled breath using the LSPR gas sensor is also confirmed. The above experimental results illustrate the effectiveness of the cucurbit[6]uril-functionalized gold nanorod-based LSPR sensor and its considerable potential for carbon dioxide detection.

2. Experimental details

2.1. Materials and reagents

All chemical reagents [gold(III) chloride trihydrate (HAuCl₄), trisodium citrate, cetyltrimethylammonium bromide (CTAB), sodium borohydride (NaBH₄), ascorbic acid, silver nitrate (AgNO₃), polystyrene sulfonate (PSS), hydrogen peroxide (H₂O₂), sulfuric acid (H₂SO₄), 3-aminopropyltrimethoxysilane (APTMS), cucurbit[6]uril (CB6), deionized water (DW), dimethylformamide (DMF), and toluene] were purchased from Sigma Aldrich.

2.2. Synthesis of gold nanoparticles and gold nanorods

AuNPs were synthesized using a previously published protocol [24]. First, 150 mL of TSC (2.2 mM) was heated to 100 °C, and 1 mL of HAuCl₄ (25 mM) was added. After 10 min, when the seeds of the particles were formed and the solution color turned to soft pink, the solution temperature was decreased to 90 °C. To develop the seeds, 1 mL of HAuCl₄ (25 mM) was injected into the solution and allowed to react for 2 min. Next, the APTMS-functionalized gold nanorod-based LSPR gas sensor was prepared in the above method. The light that penetrated the substrate placed on the stage of the LSPR system. The light that penetrated the substrate was analyzed using a spectrometer (QEPRO-ABS, Ocean Optics). The LSPR spectra at different regions of all the AuNR substrates were measured at least five times to confirm the reproducibility and repeatability of the LSPR gas sensor measurements.

3. Results and discussion

3.1. Strategy for carbon dioxide detection via a cucurbit[6]uril-functionalized gold nanorod LSPR gas sensor

The fabrication method of the CB6-functionalized AuNR-based LSPR gas sensor and the strategy for detecting carbon dioxide are described in Fig. 1. Plasmons were induced using the AuNRs to apply the LSPR substrate as a gas sensor. Although AuNRs are com-

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Figure 1. Schematic illustration of the detection strategy of cucurbit[6]uril-functionalized gold nanorod-based LSPR gas sensors for measuring carbon dioxide.
monly stabilized with CTAB or polyethylene glycol (PEG), here, we used PEG-free AuNRs based on our previously published study [24]. The AuNRs were immobilized on a bare glass substrate. In addition, cucurbit[6]uril was used as a key component for the detection of carbon dioxide. CB6 is composed of six glycouryl monomers linked by a methylene bridge. The high electron density of the carbonyl portal in CB6 allows electrostatic interactions with materials such as cations and metal surfaces. These features have gained increasing attention in applications that range from nanoparticle synthesis and assembly to plasmon-assisted molecular sensing. The direct interaction of cucurbit[n]uril with gold was first established through the transmission electron microscopy and ultraviolet-visible characterization observations of coagulate formation in which cucurbit[n]uril acted as an adhesive between adjacent gold nanoparticles [28]. The interparticle spacing between neighboring nanoparticles was found to be approximately 0.9 nm, which is consistent with the height of the cucurbit[n]uril molecule [29]. A CB6-functionalized AuNR-based LSPR gas sensor was fabricated using the above process. The LSPR absorbance peak is sensitive to the plasmons formed in the environment around the gold nanorod. As a result, carbon dioxide can be detected by analyzing the absorbance wave-

3.2. LSPR effect of gold nanorods substrate

The performance of AuNRs as LSPR gas sensors was evaluated through a comparison with AuNPs. Figure 2 shows the absorbance wavelengths of the AuNRs and AuNPs measured using a UV-Vis spectrometer. The maximum peak wavelength of the AuNPs was 520 nm. The diameter of AuNPs with the maximum peak wavelength of 520 nm is widely known to be 20 nm, as can be verified in Figs. 3(a) and 3(b). The gold nanorods exhibited two structural peaks at 512 and 785 nm. The two peaks indicate that the nanostructure had a rod-like shape, as can be confirmed from Figs. 3(c) and 3(d). Figure 3 shows scanning electron microscopy images of the fabricated AuNP and AuNR substrates, from which it can be confirmed that uniformly synthesized nanostructures were well dispersed on the substrates.

A representative indicator for evaluating the performance of a nanoplasmonic substrate is the refractive index unit. The absorption wavelength of the nanostructure changes sensitively with changes in the surrounding environment. The performance of the substrate can therefore be evaluated by comparing the differences in the absorption wavelength in different surrounding environments. Figure 4 shows the absorbance spectra of the AuNR and AuNP substrates measured in air (refractive index: 1), DW (refractive index: 1.33), DMF (refractive index: 1.43), and toluene (refractive index: 1.50). The refractive index units were calculated from the measured absorbance spectra. i) According to the Drude model for the electronic structure of metals, the LSPR peak wavelength has an approximately linear relation with the refractive index [26]. ii) Accordingly, a graph can be drawn with the peak wavelengths of the absorbance spectra measured from different refractive media (e.g., air, DW, DMF, and toluene) on the y-axis and the refractive indices of the media on the x-axis. iii) A steeper gradient in the resultant graph corresponds to a larger peak shift, which in turn indicates a larger LSPR effect. The gradient obtained for the AuNR substrate was more than four times greater than that for the AuNP substrate. This indicates the superior performance of the AuNR substrate over the AuNP substrate. We therefore used AuNR substrates in the LSPR gas sensors for measuring carbon dioxide.

3.3. Mechanism of carbon dioxide capture by cucurbit[6]uril

The nanoplasmonic substrate was functionalized with CB6 to detect carbon dioxide. Figure 5 shows the characterization of CB6. The size of cucurbituril molecules is typically on the order of 10 Å. The cavity of CB6 has a height of approximately 9.1 Å, an outer diameter of approximately 5.8 Å, and an inner diameter of approximately 3.9 Å. Mohan et al. [30] recently performed quantum mechanical calculations to investigate the adsorption strength and selective adsorption of carbon dioxide in CB6 cavities. They found that although both the interior and exterior of CB6 can adsorb carbon dioxide, the most powerful adsorption site is at the center of the pores. This implies that the interior of CB6 is more important than the exterior for detecting carbon dioxide. In other words, the efficiency of carbon dioxide detection is maximized when the CB6 molecules are densely arranged.

Following a previous study [30], we immobilized CB6 directly on...
gold nanorods. In Fig. 6, we analyze CB6 in various reacting time to determine the saturation condition. In the experiment, a 6.33±0.57 nm peak shift occurred in 3 h, a 9.38±0.68 nm shift in 6 h, a 13.37±0.69 nm shift in 12 h, and a 16.76±0.45 nm shift in 24 h. The maximum peak wavelength shift (Δλ_{max}) was calculated from the LSPR spectra measured using the custom lab-made LSPR system. The relative shift was calculated as Δλ_{max} (nm) = λ_{max (AuNR-CB6)} - λ_{max (AuNR)}, where λ_{max (AuNR-CB6)} is the maximum peak wavelength of the CB6-functionalized AuNR and λ_{max (AuNR)} is the maximum wavelength of the bare AuNR. As a result, we applied 24 h condition to the nanoplasmonic substrate for the fabrication of the CB6-functionalized AuNR-based LSPR gas sensor.

3.4. Detection capability of LSPR gas sensor for standard carbon dioxide

To detect carbon dioxide, we applied CB6 to a LSPR gas sensor and evaluated the detection capability of the CB6-functionalized AuNR-based LSPR gas sensor. The LSPR spectra of bare AuNR substrates before the attachment of CB6, CB6-functionalized AuNR substrates, and CB6-functionalized AuNR substrates after reaction with carbon dioxide are analyzed in Fig. 7(a). The gray plot is the maximum peak wavelength of the AuNR substrate. A second peak wavelength appeared at 710.3±0.6 nm, as shown in Fig. 7(b). Because the gas measurement was performed on a substrate in the dry state, the environment of the bare AuNR substrate corresponded to the air state. This validity of the second peak wavelength at 710.3±0.6 nm was confirmed by the second peak wavelength of 785 nm shown in Fig. 2 and the refractive index unit shown in Fig. 4. The dark gray plot shows the maximum peak wavelength of the CB6-functionalized AuNR substrate and has a second peak wavelength at approximately 722.1±0.5 nm. It can thus be confirmed that the 24 hours condition was used in the immobilized CB6 (Fig. 6). The blue plot is the maximum peak wavelength of the CB6-functionalized AuNR substrate after reaction with carbon dioxide. The measurement was performed after exposing the substrate to 100% (v/v) carbon dioxide for 5 min using a commercial CO₂ gas cylinder. The first peak wavelength was observed at 450 nm, but it was difficult to observe a distinct peak shift in this signal. The second peak wavelength occurred at 727.5±0.5 nm, and a peak shift of 4.4 nm compared to the CB6-functionalized AuNR substrate was confirmed. These results indicate that the CB6-functionalized AuNR-based LSPR gas sensor can overcome the limitations of the conventional LSPR sensor, which cannot easily detect light molecules such as carbon dioxide or produce meaningful measurements.

3.5. Detection of carbon dioxide in exhalation using LSPR gas sensor

In this section, the actual carbon oxide detection ability of the CB6-functionalized AuNR-based LSPR gas sensor is analyzed. Because carbon dioxide occupies approximately 0.04% of the entire atmosphere, carbon dioxide is gradually attached to CB6 when the LSPR gas sensor is exposed to the atmosphere, and the peak wavelength shifts. Converting the volume of carbon dioxide in the atmosphere to ppm using 1% = 10,000 ppm, the LSPR gas sensor can detect the 400 ppm concentration of carbon dioxide in the atmosphere. However, because the gas exposure and desorption time are not controlled in atmospheric exposure, a closed system with a chamber must be used to consistently detect carbon dioxide. Figure 8 shows an actual application in which the carbon dioxide in exhaled breath is analyzed rather than the carbon dioxide in the nonuniform atmosphere. Carbon dioxide (4%) is present in exhaled breath at a concentration of 40 ppm. The experiment was performed by blowing exhaled breath at a board for 10 s, pausing for a short release time, and then blowing exhaled breath again for three repetitions. Additionally, the measured concentration was converted into the relative concentration Δλ_{max} (%) = Δλ_{max (interfering divider)/Δλ_{max (carbon dioxide)}}. In consideration of changes caused by the water vapor in exhaled breath. In the experimental re-
In this work, we devised a cucurbit[6]uril-functionalized gold nanorod-based LSPR gas sensor that can detect carbon dioxide. Gases such as carbon dioxide are difficult to detect with high sensitivity because of their low molecular weights, but can be successfully detected by using the high plasmonic properties of gold nanorods. Cucurbit[6]uril was adopted as a chemical receptor because of its structural characteristics, which enable the trapping of carbon dioxide in its internal cavity. The manufactured LSPR gas sensor can detect not only standard carbon dioxide, but also carbon dioxide in exhaled breath. The strategy employed can enable sensitive carbon dioxide analysis in conventional LSPR sensors, which are otherwise difficult to apply as gas sensors. This pilot study demonstrates the promising applicability of cucurbit[6]uril-functionalized gold nanorod-based LSPR gas sensors for carbon dioxide detection.

4. Conclusions

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Conflicts of Interest

The authors declare no conflicts of interest.

ORCID

Seongjae Jo https://orcid.org/0000-0003-2864-9162
Jinyeong Kim https://orcid.org/0000-0001-6451-4631

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