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Liquid crystal-based sensors for selective and quantitative detection of nitrogen dioxide

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Abstract

A highly sensitive nitrogen dioxide (NO₂) sensor based on orientational transition of a thin film of liquid crystal (LC) supported on a gold surface is reported. Transport of NO₂ molecules through the LC film to the LC-gold interface induces an orientation transition in the LC film. The dynamic behavior of the sensor response exhibits a concentration-dependent response rate that is employed to generate an algorithm for quantitative determination of unknown concentrations. Sensitive, selective and reversible detection with minimal effects of environmental fluctuations suggest that these sensors can be used for quantitative NO₂ detection for a number of applications.

Keywords

Sensors; liquid crystals; nitrogen dioxide; interfaces; surface modification

1. Introduction

Nitrogen dioxide (NO₂), one of the ubiquitous environmental pollutants, is acutely toxic. A prolonged exposure to NO₂ at low concentration can result in bronchospasms and pulmonary edema whereas inhalation of high concentrations can lead to death [1]. The severity of adverse health effects associated with exposure to NO₂ in occupational settings has prompted several governmental regulatory agencies to establish recommended personal exposure limits. For example, in the United States, the National Institute of Occupational Safety and Health has set a 15 minute short term exposure limit (STEL) of 1 parts per million (ppm) for NO₂ [2]. In addition, based on controlled human exposure studies and the growing evidence of the health risks associated with NO₂, the American Conference of Industrial Hygienists and Environmental Protection Agency, have recently proposed the threshold limit value (TLV) for NO₂ exposure to be set at 0.2 and 0.1 ppm, respectively [3]. Various detection technologies based on different physico-chemical signal transduction mechanisms, (such as colorimetric, metal-oxide, electrochemical, chemiluminescence and semiconductor), have been developed to measure the concentration of NO₂ for real-time detection or personal exposure assessment [4–11]. While some of these technologies have been developed and commercialized [12], they are limited in their application either due to the lack of required sensitivity, selectivity or portability needed to measure an adverse level of NO₂ in a complex occupational environment for personal exposure assessment. This

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paper reports functional attributes of NO₂ sensors based on analyte-induced ordering transition in a thin film of liquid crystal (LC) supported on chemically functionalized surface [13]. Using a thin film of nematic LC supported on a gold coated substrate we have developed NO₂ sensors that are highly sensitive, selective and reversible. These sensors are immune to a host of potential interfering compounds (PICs), including high humidity. A measurement of polarized light intensity through sensor provides facile method to quantify the sensor response. Upon exposure to NO₂, the sensor response rate follows a predictable power law dependence on concentration that has been used to determine an unknown concentration of NO₂ with high accuracy. The sensors are functionally stable for at least six months when stored in an inert environment. These results, when combined, demonstrate that the LC-based sensing technology can form the basis of low power, low cost, lightweight, and easy to use sensors suitable for variety of applications in occupational settings.

2. Materials and Methods

2.1 Materials

All the materials in this study were used as received without further purification unless indicated otherwise. LC E7, a mixture of cyano-biphenyl and terphenyls, was purchased from EMD Chemicals (Gibbstown, NJ). Absolute ethanol (anhydrous, 200 proof) was purchased from Pharmco-AAPER. Titanium (99.995%) and gold (99.999%) used for e-beam deposition were obtained from Kamis Incorporated (Mahopac Falls, NY). Glass substrates were supplied by Corning Inc. (Corning, NY). The polymer micro-pillars were fabricated and supplied by Microfabrication Solutions (Cleveland, OH) on the glass substrate using standard wet photolithography with a proprietary polymeric material.

2.2 Sensor Fabrication

Clean aluminosilicate glass substrates were first patterned with polymeric micro-pillars using conventional photolithographic techniques. The 5 μm tall, hexagonally arranged polymeric micro-pillars are 10 μm in diameter with 20 μm center-to-center spacing [Figure 1]. The array of micropillars covers a 5 mm diameter area on an 0.8 cm $\times$ 0.8 cm glass substrate. The micro-pillared substrates are coated with a 20 $\text{\AA}$ thick titanium adhesion layer and then a 100 $\text{\AA}$ thick film of gold both at a rate of 0.2 $\text{\AA}/\text{s}$ using e-beam evaporator (Temescal FC-1800, CA). The gold coated surface provided specific sensing chemistry for NO₂ adsorption [14, 15]. The polymer micro-pillars, coated with gold film, offer a solid support structure to form uniform and stable LC (E7) film by capillary forces. A droplet of LC (E7), when deposited onto the array of micro-pillars is subjected to the capillary forces that cause the LC to spontaneously spread to form a stable film. A QArray spotting instrument (Qarray Lite, Genetix, CA) was used to dispense consistent amount of LC on the sensor array. Thirty two 0.8 cm $\times$ 0.8 cm micro-pillared gold coated substrates were mounted on a metal fixture and LC was dispensed onto them one at a time. The pillar height (5 μm) determines the maximum thickness of a uniform LC film the pillar array can support. The final volume of the LC dispensed on the sensor was determined by dissolving LC in ethanol and measuring its concentration using UV-vis absorption spectroscopy [16]. A quality control (QC) protocol was established and implemented by statistically sampling four sensors each from a lot of 32 and measuring the volume of the LC deposited on each sensor. If the average volume of the LC in four sensors fell within the range of 22–28 nl (corresponding to LC film thickness of $\sim 2 \mu\text{m}$) with less than 8% coefficient of variation (CV), the sensor lot was assumed to pass the QC test and the sensors were stored in an inert environment at room temperature prior to use in exposure studies.

2.3 Sensor Exposure

The exposure studies were performed using a custom built gas delivery-exposure system. The gas delivery setup consist of a gas dilution system (Sabio Instruments, TX), zero air source (Sabio Instruments, TX), solenoid valve (Parker, Cleveland OH), and standard NO₂ gas cylinders (Air Gas North Central, Chicago IL). Zero air source generates dry air free of NO_x, SO₂, O₃ and H₂S from ambient air. Desired concentrations of NO₂ were generated by mixing the NO₂ from certified cylinder with diluent gas (zero air or nitrogen). Unless stated explicitly, the *zero air* was used as a diluent gas. Gas streams at different humidity levels were generated by bubbling diluent gas through water and by mixing it, at appropriate ratios, with NO₂ gas. Different concentrations of NO₂ and PICs were generated either by using standard gas cylinders or by bubbling diluent gas through respective liquids to generate vapors. The stream of different gases was delivered, at a rate of 1 L/minute, to the sensor placed inside a small exposure chamber (2 cm × 2 cm × 2 cm). The exposure chamber, sandwiched between two crossed polarizers, was placed between a light source (LED source or diffuse light box) and a detector (photo diode or CCD camera). The response of the sensor, upon exposure to different analyte, was determined by measuring the amount of light transmitted through the sensor or by capturing the digital image of the sensors and measuring the brightness of the images. The LED/photo-detector setup was placed inside an environmental chamber maintained at a constant temperature to study the effect of temperature on sensor response.

3. Results and Discussion

3.1. Selective detection of NO₂

The film of LC (E7), when supported on the gold coated surface, assumes a preferred alignment that is parallel to the gold coated surface at the LC-gold interface [17] and perpendicular to the air-LC interface [18][Figure 2(a)]. The LC film, therefore, renders an effective optical birefringence in the visible region. When viewed between crossed-polarizers, this configuration of the LC leads to a bright optical appearance of the sensor [Figure 2(b)]. When the sensor is exposed to the test environment containing 5 ppm NO₂, the gas molecules partition across the LC film and bind on to the gold coated sensing surface via O,O-nitrito chelate formation [14, 15]. The binding of NO₂ molecules on to the gold surface reduces the interfacial energy of the gold-LC interface as evidenced by an increase in measured LC contact angle on a gold coated surface by 20° upon exposure to 500 ppm NO₂. As a consequence, the LC molecules at the gold-LC interface align perpendicular to the interface [Figure 2(c)]. Because of the long range orientational ordering of LC, this reorientation propagates through the entire LC film, i.e. the LC molecules in the bulk of the film orient perpendicular to the surface. Similar LC orientational transition, as a result of decrease in surface energy, has been previously reported on surfaces with controlled surface energies using self-assembled monolayers on gold and glass surfaces [19, 20]. The macroscopic re-orientation of the molecules in the LC film manifests as a dark appearance of the sensor placed between two crossed polarizers [Figure 2 (d)]. At the microscopic level, however, the LC molecules at the wall of the gold coated polymer pillars align perpendicular to the polymer pillars as in the case of LC-based sensors for chemical warfare simulants prepared with metal perchlorate salts [21].

A measurement of amount of light transmitted through the sensor, placed between crossed polarizers, as a function of time provides the dynamic response of the sensor to NO₂. Figure 3 depicts the dynamic behavior of a sensor flanked by two crossed polarizers, between a light source and a photo detector. The data shows that the sensor yields a measurable response to 5 ppm NO₂ (in dry air) in ~ 25 seconds. When a sensor fabricated *without* a gold film was exposed to 5 ppm NO₂ for 30 minutes, no change in transmitted light intensity was

observed. This result establishes that the NO₂ dissolved in LC alone is not enough to induce a change in the optical properties of the LC leading to the observed change in the transmitted light intensity. When a sensor *with* gold film is exposed, NO₂ molecules enter into the LC film and get adsorbed at the gold-LC interface. Initially, when the surface density of the adsorbed NO₂ molecule is not sufficient to cause a significant change in the interfacial energy, the LC molecules remain parallel to the interface. When the surface density of the adsorbed NO₂ molecules at the gold-LC interface is higher than a threshold value, the change in interfacial energy is large enough to trigger an orientational transition in the LC from parallel to perpendicular alignment and the transmitted light intensity diminishes. The time it takes for surface density to rise above the threshold value depends, among other parameters (e.g. LC thickness, sensor substrate geometry, LC materials), on the concentration of the NO₂ in the gas stream, i.e. the higher concentration gives a faster response. In contrast, when the sensor is exposed to other potential interfering compounds (nitric oxide, carbon dioxide, oxygen etc.), they are either blocked by the organic LC film or get adsorbed at the LC-gold interface but do not induce ordering transition. The data shown in Figure 3 also demonstrates the selectivity of LC sensors for NO₂ against very high concentrations of other gases that may be present in a common work environment. In particular, the LC sensor does not respond when exposed to analytes such as sulfur dioxide or hydrogen sulfide, the most common interferents for widely used electrochemical-based NO₂ sensors [22].

3.2. Dynamic behavior of sensor response and quantitative detection

The intensity of light transmitted through a thin film of LC placed between two crossed polarizers is given by [23],

$$I(t) = I_0 \sin^2[\delta(t)/2],$$

where $\delta(t) = 2\pi\Delta n(t)d/\lambda$ is the optical phase difference introduced by a LC film having a thickness d to an incident light beam with intensity I_0 at a wavelength λ , and $\Delta n(t)$ is the effective optical birefringence of the LC. The effective birefringence, and therefore, the transmission of polarized light through the LC film depend on the orientation of the LC molecules with respect to the surface normal. As a consequence, the dynamic response of the LC-sensor depends on the dynamics of the orientational transition of LC.

When a LC film supported on a gold coated surface is exposed to NO₂, the time required to induce the orientational transition of the LC depends on the strength of interaction between the gold surface and LC molecules, the rate of NO₂ accumulation at the LC-gold interface, and the ease with which the adsorbed NO₂ perturbs the initial alignment. The strength of interaction of the LC with gold and with the adsorbed NO₂ molecules is dependent on the properties of LC material [17]. For a given LC material, dynamic response of the sensor depends, therefore, on the efficiency of transport of NO₂ molecules from the gas stream to the LC-gold interface and the adsorption-desorption kinetics at the interface. Partition of NO₂ into the LC film is governed by the Henry's law: $C(0,t) = K_{LC}C_0$, where C_0 is the concentration of NO₂ in the gas stream, K_{LC} is the gas-LC partition coefficient and $C(0,t)$ is the concentration of NO₂ in the LC at the LC-air interface. The transport of NO₂ molecules across the LC film (typically ~2 μm) is governed by the well-known Ficks' second law of diffusion in one dimension [24]:

$$\frac{\partial C(z,t)}{\partial t} = D \frac{\partial^2 C(z,t)}{\partial z^2} \quad (1)$$

where $C(z,t)$ is the concentration of NO₂ at time t in the LC film at a distance z below the LC-air interface and D is the diffusion coefficient that typically depends on the molecular

structure of the LC. At the LC-gold interface, assuming that the diffusion across the thin gold film is negligible, the time dependence of the surface concentration $C_s(t)$ of NO_2 can be described by the reversible molecular adsorption [15]:

$$\frac{\partial C_s(t)}{\partial t} = k_a C(L, t) [N - C_s(t)] - k_d C_s(t) \quad (2)$$

where $C(L, t)$ is the concentration of the NO_2 at the LC-gold interface, k_a and k_d are adsorption and desorption coefficients, respectively and N is the total number of adsorption sites available per unit area. With proper boundary conditions, equation (2) can be solved analytically for $C_s(t)$ i.e., the surface concentration of the adsorbed NO_2 molecules. An order of magnitude estimate of the time required for NO_2 molecules to diffuse through a $\sim 2 \mu\text{m}$ thick LC film is on the order of 4.8 milliseconds. The typical switching time for LCs, used in LC displays, to reorient along the direction defined by an external electric field or the surface treatment is on the order of milliseconds [23]. However, as shown in Figure 3, the response time of the LC-based NO_2 sensor is at least two orders of magnitude higher than these characteristic times. Therefore, the dynamic behavior (e.g. the response time, rate of response) of the sensor is not limited by the diffusion or the LC switching processes but is controlled by partition of NO_2 through air-LC interface and adsorption kinetics at LC-gold interface, both of these processes are dependent on the concentration of NO_2 in the stream. We note that the LC alignment and adsorption kinetics at the gold-LC interface might be influenced by the microscopic structure of the gold film.

As described above, the dynamic response from the LC sensor depends on a number of parameters including the material properties of LC, the concentration of NO_2 in the stream, the thickness of the LC film, the flow rate, and the geometrical parameter of the sensor substrate. With all other experimental parameters fixed, the response time exhibits a power law dependence on concentration (i.e. the response time decreases with concentration). We have recently reported similar characteristics for LC-based organophosphonate sensors [21]. Additionally, once the sensor starts to respond, the rate of response (i.e. the slope of the response curve as depicted by dashed lines in Figure 3) also exhibits a predictable concentration dependence behavior over a wide range. Therefore, by measuring the response rate following an exposure, one can determine the concentration of NO_2 present in an unknown environment using an algorithm based on a calibration curve. To validate this approach, a calibration curve was generated by exposing six sensors each from three independent lots at each concentration. Four sensors from a fourth independently fabricated lot were then exposed to each of the eight unknown concentrations of NO_2 and the response rates were measured and plotted as a function of concentration [Figure 4(a)]. These measured response rates were used to generate an algorithm that correlates the response rate with the concentration and the algorithm was implemented to determine the unknown concentration. Figure 4(b) shows the variation of the measured concentration against the set concentration. The strong correlation between the measured and the set concentrations demonstrates that the LC sensors can be used to accurately determine an unknown concentration of the analyte using a simple algorithm.

3.3. Effect of humidity and sensor reversibility

The response from sensors based on most of the existing sensing technologies exhibit effect of humidity in that either they give false positive signal or significantly impede the response. In order to test the effect of humidity on the response from LC-based NO_2 sensors, we exposed six identical sensors each to three different concentrations of NO_2 at two extreme humidity levels (0 and 90% RH). Using the exposure results from six sensors at each condition we determined the average response rate and standard deviations.

Figure 5 shows the measured response rate at different concentrations. It is clear from the figure that the humidity causes the sensor to respond at a slower rate in high humidity than in dry air. While this effect seems to be statistically significant at lowest concentration tested (1 ppm) it is negligible at high concentrations. We also note that these sensors did not show any false positive signal when exposed to high humidity (90% RH) alone.

To test the reversibility of LC-based NO₂ sensors, the sensors were exposed to alternate streams of NO₂ free dry zero air (dry air) and a specified concentration of NO₂ diluted with dry N₂. A sensor was first exposed to dry air for two minutes, followed by a two minute 4.2 ppm NO₂ exposure [Figure 6(a)]. After a two minute exposure to NO₂, the sensor was flushed with dry air for ten minutes. During this exposure the sensor remains dark between crossed polarizers indicating that the surface density of NO₂ molecules at the LC-gold interface remains greater than the threshold value needed to align the LC molecules perpendicular to the surface. This suggests that NO₂ molecules in the LC film do not partition back into dry air stream to generate the concentration gradient in the LC film that promotes NO₂ desorption and subsequently induces a change in LC alignment at the LC-gold interface. To delineate these observations further, an identical sensor was exposed for two minutes to dry N₂ and then to 4.2 ppm NO₂ for one minute. The stream of NO₂ was then supplanted with a stream of dry air after one minute when the transmitted light intensity decreased to 50% of the initial value. As shown in Figure 6(a), the sensor response did not change substantially during the exposure. This indicates that even at the moderate surface density of NO₂ molecules that is just enough to induce a tilt (with respect to the surface normal) in the LC orientation, the NO₂ molecules do not partition back to the dry N₂ stream. Once the NO₂ stream is reintroduced, the surface density of NO₂ increases and the LC molecules orient perpendicular to the surface and the transmitted light decreases. These results clearly indicate that the chemical potential prevents NO₂ molecules dissolved in LC film to partition back to the dry air stream. To test the effect of humidity on the reversibility, a sensor was sequentially exposed to alternate streams of humid air for 5 minutes and 5 ppm humid NO₂ for 10 minutes both at 85% RH [Figure 6 (b)]. As anticipated, the sensor did not respond to initial exposure to humid air while it responded to 5 ppm NO₂. However, upon re-exposure to humid air, the sensor recovers to its initial state in 20 minutes. The sensors remain functionally responsive to NO₂ after recovery as shown in Figure 6 (b). Furthermore, a sensor was sequentially exposed to NO₂ free dry zero air for 3 minutes, 1 ppm NO₂ for 20 minutes, NO₂ free dry zero air for 30 minutes, NO₂ free humid air (80% RH) for 60 minutes, and 1 ppm dry NO₂ for 20 minutes. The results showed that after the full response to exposure to dry NO₂, the sensor did not reverse even after 30 minutes of exposure to dry zero air. However, as soon it was exposed to humid zero air it started to reverse within minutes. Once recovered, it again responded to dry NO₂. These results, when combined, indicate that the NO₂ molecules partition back to the humid N₂ stream, creating a concentration gradient in the LC film that promotes desorption of NO₂ molecules at the LC-gold interface and induces LC re-orientation. This prominent effect of humidity on sensor reversibility is most likely due to the higher affinity of NO₂ towards water vapor than dry air and is consistent with slight decrease in sensor response with humidity (Figure 5). These results clearly show that these sensors can be formatted, with proper optimization of the parameters involved, for a reversible response to NO₂.

3.4. Effect of temperature on response

To test the effect of temperature on NO₂ response, four identical sensors were exposed to different concentrations of NO₂ at three different temperatures inside the environmental chamber. The average response rate was then measured as a function of temperature at different concentrations. The result as depicted in Figure 7 shows that an increase in the temperature causes the sensors to respond faster i.e., an increase in response rate. This effect

is more prominent at lower concentrations and less pronounced at higher concentration. The data also show that there is a predictable effect of temperature on the sensor response that can be compensated by using an algorithm. A systematic study that correlates the response rate at different concentrations to develop a temperature compensating algorithm is currently underway.

4. Conclusions

In summary, sensors based on ordering transition in a thin film of LC supported on a gold coated surface exhibit selective detection of NO₂ over a wide dynamic range. The dynamic response of the sensor is primarily dependent on the partition of NO₂ through the LC film and kinetics of adsorption on the gold surface. Measurement of the rate of change of the optical response at different concentrations provides a facile means for quantitative determination of an unknown concentration. The sensor does not respond to humidity alone and exhibits a reversible response to NO₂ at high humidity. These results, combined with minimal and predictable effect of temperature and humidity on the performance of the sensor, suggest that these sensors form the basis for NO₂ detection devices for a number of occupational exposure monitoring applications. Efforts are underway in our lab to further improve the sensitivity of these LC sensors to detect NO₂ at the recently proposed concentration of 0.1 ppm by optimizing sensor configuration (e. g. altering chemical functionality of the sensor surface or varying geometrical parameters).

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Biographies

Avijit Sen received his Ph.D. from the Indian Institute of Science, Bangalore, India, in 1997 and his B.Sc. and M.Sc. degrees, from Jadavpur University, Kolkata, India, in 1989 and 1991, respectively. Currently, he is working as a Senior Scientist at Platypus Technologies LLC. Prior to his employment with Platypus, he worked as a Senior Scientist at the ChemSensing Inc. (Urbana-Champaign, IL).

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Bart A. Grinwald received his B. S. in Electrical Engineering and minor in Physics from the University of Wisconsin – Platteville in 2006. He then joined Plexus Corp., Neenah, WI, as an Analog Design Engineer developing medical and industrial safety products. In 2009 he joined Platypus Technologies LLC where he designs and builds test and measurement systems and develops prototype devices for the LC-based sensors.

Heidi J. VanTreeck received her Bachelor of Arts degree in Biology in 2005 from the University of Wisconsin, Milwaukee. She accepted a position at PPDI (Pharmaceutical Product Development Inc.) in Madison, WI in 2005 where she tested numerous market pharmaceutical drugs. She joined Platypus Technologies LLC in 2008 as a Research Chemist to help develop LC-based chemical and biological sensors that take advantage of the uniqueness of LCs.

Bharat R. Acharya received his doctoral degree in Physics in 2001 from Kent State University, Kent OH, in LC alignment on polymer surfaces used for LC displays. After his graduate work, Dr. Acharya joined Bell Laboratories in Murray Hill, NJ, as a NSF-GOALI post-doctoral fellow. While at Bell Labs, he developed LC-based devices for telecommunication applications. He then joined Platypus Technologies LLC, as a research scientist to develop LC-based chemical and biological sensors. Currently, Dr. Acharya is the Director of Sensor Development and leads an interdisciplinary group of scientists pursuing development of biological and chemical sensors that exploit the unusual behavior of LCs in contact with different interfaces.

Figure 1.
Configuration of the substrates used for LC-based sensors: Scanning electron microscope image of the substrates with polymer micro pillars used for fabrication of LC-based sensors.

Figure 2.

Principle of real-time detection of NO_2 : (a) Organization of LC molecules within a thin film of LC supported on a gold coated substrate. (b) The sensor appears bright when viewed between crossed polarizers. (c) A subtle change in the structure of the interface (i.e., binding of NO_2 at the gold-LC interface) is amplified into a change in the orientation of the LC and (d) the sensor appears dark when viewed between crossed polarizers.

Figure 3. Selective detection of NO₂ using LC-based sensors: Identical sensors optimized for detection of NO₂ were exposed to 5 ppm NO₂ and vapors from common atmospheric chemicals at very high concentrations. The sensors respond to NO₂ while remaining immune to exposure to other chemicals for much longer than 200s depicted in the figure. The dotted triangle shows the segment of the response curve used for measurement of the response rate.

Figure 4. Quantitative detection of NO₂ using LC-based sensors: (a) A dose response curve generated by exposing sensors from three independent lots. The dose response curve was used to develop an algorithm and to determine unknown concentrations using sensors from fourth independent lot. (b) Correlation between the calculated (using the algorithm) and the set NO₂ concentrations.

Figure 5. Effect of humidity on the sensor response: Sensors were exposed to different concentrations of NO_2 at two different humidity levels and the response rates were plotted.

Figure 6. Effect of humidity on reversibility of the sensor response. (a) Sensor shows irreversible response to 4.2 ppm dry NO₂ when flushed with dry N₂. The solid curve shows the response when the sensor is exposed to dry N₂ after it has fully responded to NO₂. The dashed curve shows the dynamic behavior of the sensor when the sensor was exposed to dry N₂ before the response was complete. The solid (dotted) arrow shows the time at which the sensor was exposed to dry NO₂ (dry N₂). (b) Reversible response of the sensor to humid NO₂ when it is exposed to humid (85% RH) N₂. The solid (dotted) arrow shows the time at which the sensor was exposed to humid NO₂ (humid N₂).

Figure 7. Effect of temperature on NO_2 detection at various concentrations. Sensors were exposed to different concentrations of NO_2 at three different temperatures and the response rates were plotted.