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Disposable optochemical sensor chip for nitrogen dioxide detection based on oxidation of *N*,*N*′-diphenyl-1,4-phenylenediamine

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Abstract

We report on a novel optochemical sensor chip for nitrogen dioxide (NO_2) based on the indicator reagent *N*,*N*′-diphenyl-1,4-phenylenediamine (DPPD). The sensor chip was manufactured by immobilising DPPD in a highly permeable polymeric layer made from polydimethylsiloxane-polycarbonate block copolymer (PDMS-PC). The presence of NO_2 causes oxidation of DPPD, which thereby changes its visible spectrum. The best wavelength for determining NO_2 was 480 nm. To realise short measuring times (e.g. 23 s to determine 5 ppm NO_2), a measuring procedure was chosen that enables a linear correlation between the rate of change of the transmission of DPPD and the concentration of NO_2. A linear calibration function was obtained in the range from 0.1 to 25 ppm NO_2. The limit of quantitation (LOQ) was 0.12 ppm and the accuracy exceeds 6%. The stability of the sensor chips, the effect of internal parameters (indicator reagent concentration and thickness of the polymeric layer) and the effect of external parameters (relative humidity (RH), temperature and gas flow) on the sensor chip response were investigated.

No cross-sensitivities were observed at concentrations lower than 0.1 ppm ozone (O_3), 0.2 ppm chlorine (Cl_2) and 250 ppm nitrogen monoxide (NO).

The application area of the developed sensor chips is environmental and working place analysis of NO_2. For this purpose, the sensor chips will be integrated into a lightweight portable photometer made of semiconductor components.

Keywords: Gas sensor; Optochemical sensor; Nitrogen dioxide detection; Indicator reagents; UV–vis spectroscopy

1. Introduction

Nitrogen oxides (NO_x) are primarily generated while the combustion of fossil fuels in stationary and mobile sources. Normally these processes release nitrogen monoxide (NO) into the atmosphere. Here, under the influence of sunlight and in the presence of molecular or atomic oxygen, ozone or organic radicals, NO is oxidised to NO_2 [1]. NO_2 is known to cause environmental problems, such as acidic rain, photochemical smog and metal corrosion. NO_2 is an irritant gas and a high health risk because exposure for long periods can affect the respiratory tract. For exposures ranging from minutes up to 1 h, a level of 50–100 ppm of NO_2 causes inflammation of lung tissue. Assimilated quantities of 500 ppm NO_2 or more generally lead within days to a pulmonary edema and to death [2]. Therefore, for pollution control and air quality monitoring, e.g. at the working place, there is a strong demand for instruments that are cheaper and smaller than the classical analytical instruments based mostly on spectrophotometric methods, such as chemiluminescence and Saltzman method [3–6] and that can determine NO_2 more accurately than passive sampling devices or detector tubes [7,8].

One promising way to measure NO_2 concentrations in the environment and at the working place is the usage of inexpensive and small gas sensors. Many studies on NO_2 sensors have been reported so far [4,9]. Nevertheless, many of these sensors exhibit low sensitivity, long measuring times (many minutes) and high measuring errors [10–12].

Our aim was to develop an optochemical sensor chip that can be used in a portable device to measure NO_2 concentrations in the range of the occupational exposure limit (OEL = 5 ppm in Germany) [13].

For this study, sensor chips based on redox indicators were used from the group of aromatic amines: *N*,*N*′-diphenyl-1,4-phenylenediamine (DPPD), *o*-dianisidine, *N*,*N*′-diphenylbenzidine (DPB) and *N*,*N*,*N*′,*N*′-tetramethyl-1,4-phenylened-

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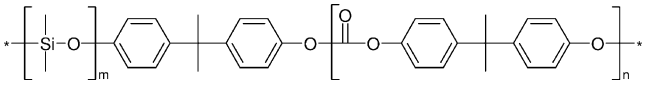

Fig. 1. Structure of polydimethylsiloxane-polycarbonate (PDMS-PC) block copolymer.

iamine (TMPD). These indicator reagents were immobilised in a gas-permeable polymeric layer of polydimethylsiloxane-polycarbonate block copolymer (PDMS-PC). From preliminary studies with other indicator reagents from the group of aromatic amines it became apparent that this was a promising approach for fast, sensitive and specific NO_2 detection.

The indicator reagents were chosen because of their reactivity towards oxidising substances as a result of a comprehensive study of the literature. Their reaction pathways and products as well as their characteristic absorption spectra are described in the literature (for detailed references see Section 3).

The silicone-polycarbonate block copolymer has already been used as an immobilising matrix in a disposable optochemical chlorine gas sensor that was developed by our group [14]. It has a high gas permeability (according to the datasheet 7.275×10^{-11} cm^3(RTP) cm cm^{-2} s^{-1} Pa^{-1} for CO_2) and is soluble in common organic solvents. Because of its transparency, it is possible to carry out spectrophotometric measurements in transmission mode, which is an advantage for optochemical sensors [15,16].

2. Experimental

2.1. Materials

The basic elements of the sensor chip are a solid glass carrier, a polymeric layer and a sensitive indicator reagent. We used $0.7 \times 1.5 \times 0.1$ cm^3 glass sheets as solid carrier. The polymer used was the polydimethylsiloxane-polycarbonate block copolymer SSP-M213 supplied by Specialty Silicone Products (Ballston Spa, USA).

All indicator reagents were supplied by Sigma–Aldrich (Steinheim, Germany). Organic solvents, chloroform and tetrahydrofuran (both p.a. grade), were supplied by Merck (Darmstadt, Germany) and used without further treatment (Figs. 1 and 2).

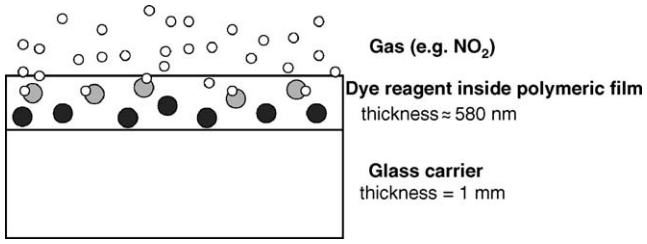

Fig. 3. Schematic cross-section of a sensor chip: (●) indicator reagent molecules before the reaction; (◔) indicator reagent molecules after the reaction; (◯) NO_2 molecules.

2.2. Sensor chip preparation

The sensor chips were manufactured by using a self-designed spin-coating equipment with a fixed number of revolutions of 4500 rpm. For this, a solution of 60 mg ml^{-1} (unless otherwise noted) of PDMS-PC in the organic solvent tetrahydrofuran (in the case of DPB as indicator reagent) or chloroform (in the case of every other indicator reagent) containing different amounts of indicator reagent was prepared. Then, 40 μl of this solution were pipetted onto a rotating glass sheet to obtain a thin, homogenous layer after evaporation of the organic solvent. For a cross-section of such a sensor chip see Fig. 3.

All steps were carried out under exclusion of ultraviolet light to avoid photooxidation of the dissolved indicator reagent.

The thickness of the polymeric layers was controlled by using a profilometer P-11 Long Scan Profiler (KLA Tencor, USA). For this purpose, the polymer layer was partially scratched from the glass sheet and the profile was scanned across the scratch. The thickness of the layers was adjusted in the range of 580 ± 80 nm (at 60 mg ml^{-1} polymeric solution).

2.3. Gas preparation and measuring system

NO_2, NO and Cl_2 were added from test gas cylinders (Messer Griessheim, Germany). O_3 was generated by an Ozomat

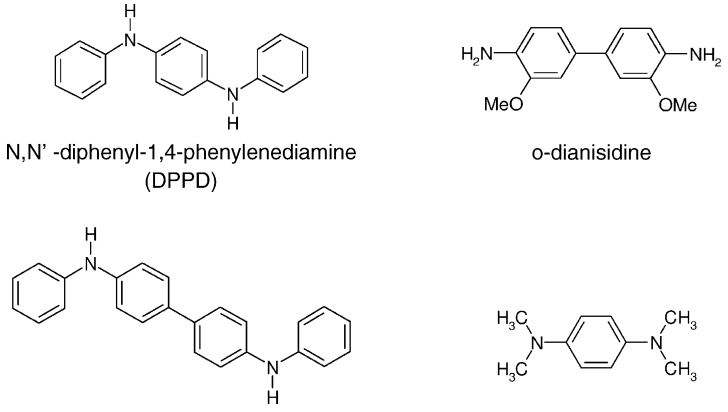

Fig. 2. Investigated indicator reagents for NO_2 detection.