

V₂O₅ nanofibres: novel gas sensors with extremely high sensitivity and selectivity to amines

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Abstract

Chemiresistor-type gas sensors were fabricated by depositing vanadium pentoxide (V₂O₅) nanofibres from aqueous suspension onto silicon substrates. Electrical contact was made through gold electrodes. Due to the sufficiently high conductivity of the fibres, the sensors could be operated at room temperature. Extremely high sensitivity was measured for 1-butylamine (limit of detection (LOD) below 30 ppb) and moderate sensitivity for ammonia. In contrast, only very little sensitivity was observed for toluene and 1-propanol vapours. The sensitivity to 1-butylamine increased linearly when increasing the relative humidity (rh) of the carrier gas from 0 to 60%. Contacting the fibres with either top or bottom electrodes dramatically changed the response characteristics. Based on these results, the sensing mechanism is discussed in terms of intercalation of the amine into the layered structure of the nanofibres and sorption at the nanofibre/electrode interface.

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1. Introduction

Advanced applications for chemical gas sensors, such as medical diagnosis, quality control, detection of explosives and other warfare agents, require the development of novel materials with extremely high chemical sensitivity and selectivity. As a consequence of their high surface-to-volume ratio, nanoparticles [1,2] and nanotubes/fibres [3–5] are especially suitable for this purpose. In particular, the well-known gas sensing properties of metal oxide semiconductors have stimulated the development of novel gas sensors from respective nanofibre materials [3,6]. So far, however, the use of gas sensors comprising metal oxide nanofibres was limited to the detection of highly reactive analytes requiring operation at elevated temperatures [3], or regeneration by UV-irradiation [6]. Here we report on the application of individual V₂O₅ nanofibres as well as nanofibre networks for reversible gas/vapour sensing at room temperature.

V₂O₅ nanofibres form a unique nanostructured material, which is obtained via self-assembly in aqueous solution. These fibres have a bilayered structure, which can incorporate a significant amount of water between the layers [7]. The cross-section of individual fibres is rectangular, with dimensions on the order of ~1.5 by ~10 nm. Their length can vary from several hundreds of nanometers to several micrometers and is controlled by the preparation procedure. The nanofibre samples studied here were prepared by a wet chemical process based on the polycondensation of meta(vanadate) ions [8]. The as-prepared V₂O₅ nanofibres are n-type semiconductors [9] with an electronic conductivity on the order of 0.5 S cm⁻¹ at room temperature. The charge transport proceeds via electron hopping between V^{IV} (impurities) and V^V centres, in accordance with the Mott model [9]. This property makes the fibres well suited for the construction of functional materials or novel devices, which can be operated under ambient conditions. For example, thick films of V₂O₅ fibre networks are employed as anti-static protection layers in photographic industry, and as charge storage material in batteries [7].

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Our interest in V_2O_5 nanofibres for chemical gas sensing is motivated by their high affinity to organic amines [10]. These analytes are important marker compounds for quality control in food industry [11] and medical diagnosis [12,13]. The main goal of our present study was to investigate the sensitivity and selectivity of the fibres for this class of compounds. For that purpose, a chemiresistor-type configuration was employed, which allows for simple read-out of electrical resistance changes as the sensor signal.

2. Experimental section

2.1. Sensor fabrication

V_2O_5 nanofibres were prepared by reacting 0.2 g ammonium (meta)vanadate (NH_4VO_3 , Aldrich) with 2 g of an ion exchange resin (50WX8-100 DOWEX, Aldrich) in 80 ml water. The obtained solution was kept under ambient conditions for at least 3 months in order to obtain fibres with a length exceeding several μm . The silicon substrates used for device preparation were functionalised with amino groups to provide an adhesion layer for fibre deposition. This was achieved by treating the substrates with a solution of 50 μl 3-aminopropyltrimethylethoxysilane (ABCRCR, Germany) in 5 ml toluene at 60 °C. The fibres were either contacted using lithographically defined bottom electrodes (device Type I), or top electrodes (device Types II and III). As bottom electrodes, interdigitated gold structures were used (50 finger pairs, an overlap length of 1800 μm and a gap of 10 μm). As top electrodes, we either used interdigitated gold structures (50 finger pairs, 900 μm overlap length, and a gap of 5 μm ; Type II) or single finger pairs of gold with an overlap length of 2 μm and a gap of 150 nm (Type III). The electrode structures were produced by conventional photo- or e-beam lithography. The fibres were deposited onto the substrates by dip-coating using a 1/10 diluted dispersion of the as-prepared solution.

2.2. Chemical sensitivity

To investigate the chemical sensitivity of the fibres the sensor substrates were mounted in a test cell made from Teflon. The sensors were operated by applying a constant direct current (SMU 236, Keithley) and measuring the change of voltage across the electrodes (MM 2002, Keithley) whilst switching between pure carrier gas and the analytes. Test gases and vapours were generated using commercial gas calibration systems (Kalibriersystem MK15/MK5 or MK15-DDS-RL/MK5, Umwelttechnik MCZ GmbH, Ober-Mörlen, Germany). Ammonia (Messer, Germany), ethylamine (Linde, Germany) and trimethylamine (Messer, Germany) were taken from gas cylinders with a concentration of 1% (v/v) in N_2 (5.0). Dilution of these gases was done with purified and dried air (dew point -70 °C), which was provided by a commercial zero-gas generator (Nullgasanlage MD2000-25,

Umwelttechnik MCZ), equipped with a catalytic purification unit. Vapours of the organic analytes 1-butylamine, 1-propanol, and toluene were generated by bubbling the carrier gas through the respective liquids. The actual vapour concentrations were calculated using the Antoine equation and the dilution factors adjusted by the gas calibration system. A photoacoustic detector (1314 Photoacoustic Multi-Gas Monitor, INNOVA AirTech Instruments) was used to verify the settings of the mass flow system. Analyte concentrations in the sub-ppm regime were generated using the second dilution unit of the gas calibration system MK5, which comprises a further cascade of three mass flow controllers. The influence of humidity on the sensitivity of the fibres was investigated by humidifying the test gases and the reference carrier gas using a commercial humidifier unit (Umwelttechnik MCZ GmbH). After changing the humidity level the sensors were equilibrated under reference gas atmosphere for at least 1 h before starting the dose–response measurement. All measurements were performed at room temperature (ca. 22 °C).

2.3. Microscopy

The nanofibre samples were characterised using a TECNAI G2 F20 (FEI) transmission electron microscope (TEM). For these measurements the fibres were deposited onto holey carbon films on copper grids (PLANO) by drop coating. A Leo Gemini 1530 field emission scanning electron microscope (FE-SEM) was used to image the fibres after deposition onto the silicon substrates. Further imaging of the fibres was done using a Digital Instruments Multimode atomic force microscope (AFM). The images were acquired in “tapping mode”.

3. Results and discussion

The transmission electron microscopy (TEM) micrograph depicted in Fig. 1(A) shows individual V_2O_5 nanofibres and nanofibre bundles. In accordance with the literature [9] the image shows individual fibres with a width of ~ 10 nm. Fig. 1(B) shows a field emission scanning electron microscopy (FE-SEM) image of a V_2O_5 fibre network contacted by a pair of electrodes. To use the fibre network as a chemiresistor-type sensor a constant direct current was applied, resulting in a voltage drop across the 10 μm electrode gap of about 100 mV, before dosing with test analytes. The response characteristics of the sensor to volatile organic amines was first tested by applying 1-butylamine vapour. Ambient conditions were simulated by adjusting the relative humidity (rh) to 40%. Fig. 2(A) and (B) shows the transient responses, which were obtained by dosing the sensor depicted in Fig. 1(B) with 1-butylamine in the concentration range between 30 ppb and 9.5 ppm. As seen, the analyte caused an increase of the initial baseline resistance by up to 500%. The limit of detection (LOD), defined as the concentration at which the signal is three times larger than the noise level,

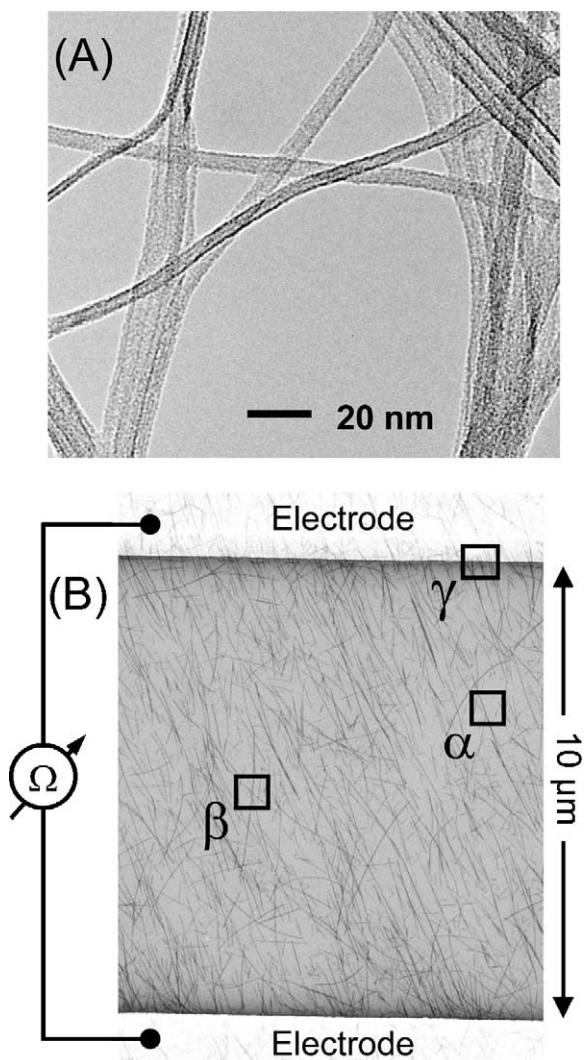


Fig. 1. Bright field TEM micrograph showing individual V_2O_5 nanofibres and fibre bundles (A). FE-SEM image of a chemiresistor device with a thin network of V_2O_5 nanofibres bridging two electrodes (B). The resistance of this sensor device was monitored while dosing it with the analytes. Three different sites are indicated at which the analyte can interact with the device and change the device's resistance. First, the analyte can change the conductivity by interaction with the nanofibres themselves (sites α). Second, adsorption of the analyte can modify the inter-fibre contacts (sites β) and, third the analyte can change the fibre/electrode contact resistance (sites γ).

was below 30 ppb, as apparent from Fig. 2(B). Fig. 2(C) displays the response amplitudes (measured after 300 s of analyte exposure) as a function of analyte concentration for three different humidity levels (5, 20 and 40% rh). The most striking observation is the strong increase in sensitivity (defined as the relative change of resistance at a given analyte concentration) with increasing humidity. Furthermore, at higher humidity the sensor displays a very broad dynamic range, which spans more than three orders of magnitude in analyte concentration, as consistent with Fig. 2(A) and (B). A closer investigation of the influence of humidity on the sensing properties revealed that the sensitivity to 1-butylamine increased linearly with increasing humidity, as shown in Fig. 2(D).

Table 1
Selectivity of V_2O_5 chemiresistors

Analyte	Concentration (ppm)	$\Delta R/R_{ini}$ (%)
1-Butylamine	10	+42
Ammonia	10	+1.8
1-Propanol	1000	+0.4
Toluene	1000	+0.17

Responses ($\Delta R/R_{ini}$) of a V_2O_5 nanofibre network based chemiresistor to different analytes at 40% rh, measured after 300 s exposure.

In order to investigate the selectivity of the sensors, our studies were extended to ammonia, 1-propanol and toluene. Ammonia was chosen as the inorganic complement of 1-butylamine. 1-Propanol was used as a model compound representing the class of volatile hydroxylic organics with amphiphilic character, and toluene was chosen as a model compound for the class of non-polar, hydrophobic analytes. The corresponding response amplitudes detected at 40% rh are summarised in Table 1 for one specific sensor device. Although the absolute values varied among different sensors, the same characteristic trend was observed in all cases. It is apparent that ammonia and 1-butylamine lead to significantly stronger responses compared to 1-propanol and toluene, even if the former are supplied in two orders of magnitude lower concentrations. Moreover, the sensitivity to other organic amines, such as ethylamine and trimethylamine, was found to be comparable to those of ammonia and 1-butylamine. These results clearly demonstrate the high selectivity of V_2O_5 nanofibre chemiresistors for ammonia and, especially, organic amines. As described above in the case of 1-butylamine, the sensitivity to other amines investigated also increased with increasing relative humidity. However, this effect was not observed for toluene and 1-propanol.

The sensing mechanism was investigated by changing the contact configuration of the sensor devices. Sensors of Type I correspond to above described chemiresistors, which employ interdigitated electrodes located underneath the fibres. For the other type of sensors, by contrast, the electrodes were placed on top of the fibre network (Type II) or onto individual fibres (Type III). Fig. 3 shows the responses of the sensors of Type II and III to 1-butylamine at a concentration of 240 and 9.5 ppm and 40% rh, respectively. The inset of the figure shows an atomic force microscopy (AFM) image of the Type III sensor based on individual fibres. Table 2 compiles the major results obtained with the three different sensor types. In striking contrast to the behaviour of sensor Type I, both types of sensors with electrodes on top of the fibres responded with a decrease in resistance upon exposure to 1-butylamine. In addition, the sensitivity was at least one order of magnitude lower.

Three different sites for analyte sorption appear relevant for the sensing mechanism (Fig. 1(B)). Specifically, the analyte can intercalate into the layered structure of the fibres or adsorb on their surface (sites α). Also, the analyte can adsorb between the inter-fibre contacts (sites β), or adsorb between the fibres and the electrode surface (sites γ). While

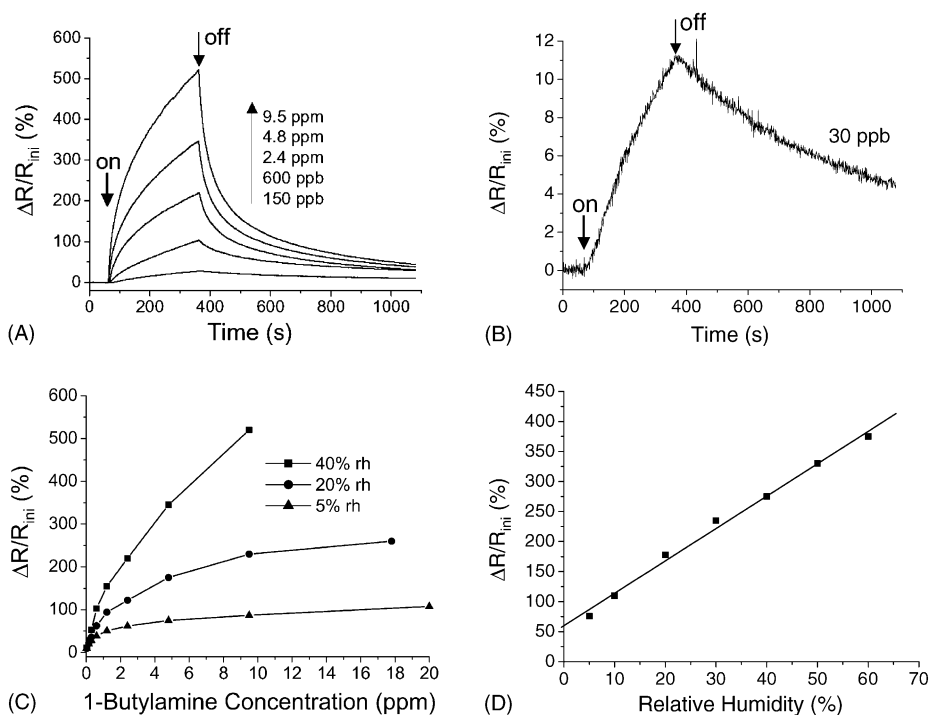


Fig. 2. Response transients ($\Delta R/R_{ini}$) of the V_2O_5 chemiresistor shown in Fig. 1 (Type I) at 40% rh to 1-butylamine between 150 ppb and 9.5 ppm (A) and at 30 ppb (B). Part (C) shows the response amplitudes measured after 300 s analyte exposure as a function of the 1-butylamine concentration, at 5, 20 and 40% rh. Part (D) shows how the response amplitude to 1.2 ppm 1-butylamine vapour increases linearly by 5.4% with increasing humidity by 1%. All measurements were performed at room temperature.

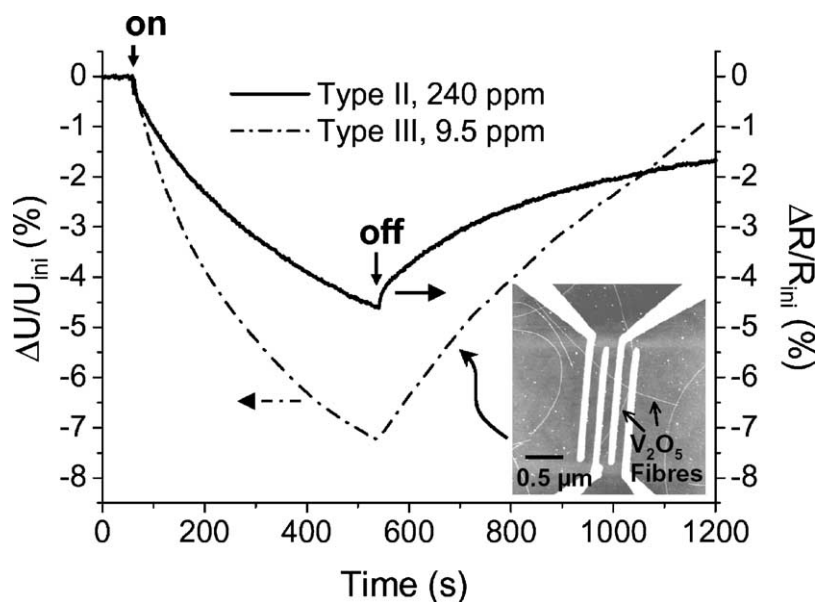


Fig. 3. Response to 1-butylamine at 40% rh for two V_2O_5 chemiresistors (Types II and III) with the electrodes placed on top of the nanofibres. Sensor Type II, which is based on a thin network of nanofibres, was exposed to 240 ppm of 1-butylamine vapour. This device showed ohmic conductivity and, thus the response, $\Delta R/R_{ini}$, is identical to $\Delta U/U_{ini}$. The inset shows an AFM image of the chemiresistor, Type III. This sensor, which is based on two individual V_2O_5 nanofibres (only the two middle electrodes were employed), was exposed to 9.5 ppm of 1-butylamine vapour. Because of the low conductance this device was operated at a bias of 3 V (150 nm electrode gap). As this voltage falls into the range in which the sensors show non-ohmic behaviour, the response is given as the relative change in voltage $\Delta U/U_{ini}$. All measurements were performed at room temperature.

Table 2

Responses ($\Delta R/R_{ini}$ or $\Delta U/U_{ini}$) of three V_2O_5 sensors with different contact configurations to 1-butylamine at 40% rh

Type	Material	Electrode configuration	Response (%)	1-Butylamine concentration (ppm)	Interaction centres
I	Network	Underneath	+520	9.5	α , β , γ
II	Network	On top	−4	240	α , β
III	Individual fibres	On top	−7	9.5	α

Possible sites of interaction between the analyte and the sensor device are the nanofibres themselves (α), the inter-fibre contacts (β), and the nanofibre/electrode interface (γ). Depending on the contact configuration and the ratio of the fibre length/electrode gap, sites β and γ are eliminated and not accessible, respectively.

all three interaction sites are present in Type I sensors, sites γ are absent in the case of fibres contacted with on-top electrodes (both Types II and III). In addition, in the case of the sensor based on single nanofibres with on-top electrodes (Type III), sites β are also absent, and therefore only sites α remain. Since both sensor Types II and III responded to 1-butylamine with a decrease of resistance, it can be concluded that the increase of resistance observed in the case of sensor Type I is caused by the intercalation of analyte between the fibres and the electrode surface (sites γ). This effect apparently dominates other signal components, which arise from analyte adsorption at sites α and β , as demonstrated with sensor Types II and III. The assumption of significant adsorption of 1-butylamine taking place at the fibre/electrode interface is supported by the pronounced affinity of amines reported for both gold [14] and V_2O_5 [10] surfaces.

The change of conductance, which is induced by 1-butylamine adsorption on sensor Types II and III, is possibly a result of adsorption onto the fibre and/or intercalation of the analyte into the bilayered structure of the nanofibres. Intercalation of alkylamines [10] and water molecules [7] into the layered structure of V_2O_5 gels has been reported previously. For example, the intercalation of alkylammonium ions was evidenced by X-ray diffraction measurements, which revealed a significant increase of the distance between the oxide layers [10]. Thus, the increase of conductance shown in Fig. 3 may be attributed to electron transfer from the analyte to the vanadium pentoxide structure, which results in an increased n-doping of the fibres. Evidence for such charge transfer has been reported previously for V_2O_5 nanofibres interacting with aniline [15] or water [16].

The enhancement of sensitivity with increasing humidity suggests that the adsorption of water promotes the intercalation of 1-butylamine at the fibre/electrode interface. Although we currently have no experimental evidence, it seems reasonable to assume that the formation of a thin water film supports the diffusion of 1-butylamine into the interfacial region by dissolving the analyte. Furthermore, the interactions of the amine with the electrode material could be different in the presence of water, as reported previously [14]. To investigate the importance of the electrode/nanofibre interface, other nanofibre or nanotube systems combined with different electrode materials have to be investigated. Furthermore, to understand the effect of humidity on the sensitivity to amines, we are systematically varying the surface properties of the electrode structures and the ratio of fibre length to electrode spacing. In addition, by using amines with different structure

and solubility properties, we intend to gain further insights into the sensing mechanism.

4. Conclusions

In conclusion, vanadium pentoxide (V_2O_5) nanofibre-based sensors have proven capable of detecting organic amines with extremely high sensitivity and selectivity at room temperature. The LOD for 1-butylamine was found to be less than 30 ppb, which is far below the detection limit of the human olfactory system (ranging from around 240 ppb to 13.4 ppm [17]). The high sensitivity to organic amines makes these sensors promising candidates for healthcare applications (e.g. diagnosis of uremia [12] or cancer [12,13]) and food freshness monitoring [11]. On the basis of the results reported here, chemical modification might be used to tailor the surface properties of the V_2O_5 nanofibres and, thereby, to fine-tune the chemical selectivity of such sensors for specific applications. Further advantages of these sensors are the possibility of miniaturisation and their operation at room temperature, as exemplified with the single nanofibre device (Type III). Taken together, these features make V_2O_5 nanofibres well suited for applications in integrated sensor chips.

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Biographies



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T. Vossmeier studied Chemistry at the Philipps-University, Marburg where he received his Diploma in 1992. In 1995, he received his PhD (Dr. rer. nat.) from the Technical University, Berlin. After working as a post-graduate researcher at the University of California at Los Angeles (UCLA) he joined Sony in 1998 and became group leader at the Materials Science Laboratories in Stuttgart. His current research interests are functional nanostructured materials and devices, self-assembly, molecular recognition and design of interfaces, and chemical sensors.