Nitric Dioxide and Acetone Sensors Based on Iron Oxide Nanoparticles

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The Fe₂O₃ and CoFe₂O₄ nanoparticle-based Langmuir–Blodgett films for sensing of nitric dioxide (NO₂) and acetone vapours have been explored. Both the sensitivity of the chemiresistors and dynamic properties, such as the response/recovery time, have been probed in dependence of the number of nanoparticle monolayers and working temperatures. The response of 23 at the NO₂ concentration of 1 ppm, i.e., approaching the canine detection limit, has been monitored implying the appropriateness for the detection of nitrate-based explosives.

Keywords: Gas Sensor, Chemiresistors, NO₂, Acetone Vapours, Nanoparticle Arrays, Langmuir–Blodgett Films.

1. INTRODUCTION

The real-time and areal monitoring of environmentally hazardous gases (e.g., CO, CO₂, NO, NO₂, O₃, SO₂, Cl₂) and detection of various gaseous markers (e.g., NO_x of explosives) demand the development of affordable highly-sensitive sensors capable of detection of certain gases in the ppm- and sub-ppm range. Particularly the chemiresistors, i.e., the solid-state gas-sensing devices changing their resistance upon the exposure to traces of a particular gas have received considerable attention.¹ Sensing properties of the solid-state sensors prevalently based on resistive metal oxides, such as Ag₂O,² Fe₂O₃,³ In₂O₃,^{4,5} SnO₂,^{6,7} TiO₂,⁸ WO₃,^{9–12} and ZnO,¹³ are advanced by the nanostructuring of the sensing material (nanotubes, nanoparticles). On one hand, the nanostructuring increases the aspect ratio, i.e., the surface-to-volume ratio, besides it can lead to size-controlled specific effects.¹⁴

In this work, we will demonstrate the sensing properties of chemiresistors based on particular number of Fe₂O₃- and CoFe₂O₄-nanoparticle (NP) self-assembled monolayers toward NO₂ and acetone vapours, the latter being applicable for the breath analysis of glycaemia patients. The sensing films have been prepared by means of the Langmuir–Blodgett (L–B) method, which allows the sequential preparation of particular nanoparticle

monolayers and thereby the controlled formation of the sensing film with targeted number of monolayers enabling to explore the effect of the film thickness on sensing properties.

2. EXPERIMENTAL DETAILS

The Fe₂O₃ and CoFe₂O₄ NPs have been synthesized via reaction between Fe and Co acetylacetonate with oleic acid and oleylamine being the surfactant precursor in phenyl ether.

The average NP diameters have been of 6.4 ± 0.6 nm and 7.6 ± 0.6 nm for Fe₂O₃ and CoFe₂O₄, respectively, including the surfactant thickness of about 1 nm. The sensing NP films have been prepared by the L–B deposition of colloid NPs onto alumina substrates equipped with interdigitated electrodes intended for the film resistivity determination. The investigated films consisted of arrays of 1, 2, 4, 7, and 10 sequentially deposited NP monolayers. Particular monolayers were prepared from the water subphase at the surface pressure of 20 mN/m.

The X-ray diffraction characterization was performed at grazing incidence (the incidence angle of 1 degree) using D8 Discover SSS (Bruker AXS) with rotating Cu anode.

The X-ray absorption near-edge structure (XANES) characterization was carried out in fluorescence mode at station C (CEMO) at the beamline DORIS III at

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HASYLAB of Deutsches Elektronen-Synchrotron (DESY) in Hamburg, Germany.¹⁵

The samples intended for the characterization of the sensing properties have been either annealed at 400 °C or UV-irradiated for 20 min in a reactor equipped with ozone generating mercury lamp ($h\nu = 4.9$ eV, irradiation power of 2 mW/cm²) to stripe the organic surfactant.

The current response of NP layers was characterized upon the 100-sccm flow of dry air mixed with the required amount of NO₂ or acetone vapours. The elevated working temperature has been attained by means of planar heaters fabricated on the back side of the alumina substrates.

3. RESULTS AND DISCUSSION

3.1. Structural Properties of Films

Figure 1(a) presents the scanning electron microscopy (SEM) mapping of one self-assembled nanoparticle monolayer. The stripping of the insulating surfactant (either by the UV irradiation exposure or by annealing) eventuates in discontinuities in 1 ML-thick films (Fig. 1(b)) and accordingly in the current response in the sub-nA range at the supply voltage of 5 V. Employment of 2 and more ML of NPs preserves the continuous films even after the surfactant stripping and the current response increases to the 1 μ A range.

The thermal stability of NP layers has been investigated through the structure characterization by X-ray diffraction (XRD) upon the vacuum anneal up to 700 °C. Figures 2(a) and (b) plot structure evolutions of the CoFe₂O₄- and Fe₂O₃-nanoparticle layers (prepared by drop-casting of NPs dissolved in toluene onto silicon substrates) upon the annealing in vacuum. As for the former (the a panel), the spectra reveal changes at annealing at 500 °C: A new peak at about $2\theta = 45$ degree emerges, which dominates for higher annealing temperatures. The peak is attributed to the reduced Co₃F₇ phase with the primitive cubic cell. The original CoFe₂O₄ phase vanishes almost entirely at 700 °C, as the strongest 311 diffraction is only visible and it is replaced by FeO and CoO phases. Concerning the Fe₂O₃ nanoparticles (the b panel), the slight shift of the 440-peak toward the lower 2θ with the annealing temperature suggests the gradual transformation from the Fe₂O₃

Fig. 1. The SEM mapping of the single Fe₂O₃ nanoparticle arrayed monolayer (a) after the preparation by the L-B method and (b) after the surfactant stripping by UV irradiation.

Fig. 2. The CoFe₂O₄- and Fe₂O₃-nanoparticle structure evolutions (a and b panel, respectively) in dependence of the annealing temperature at pressure of about 10⁻⁶ Pa yielded by X-ray diffraction.

to Fe₃O₄ phase, thereby confirming the partial reduction too. Besides, the formation of a new FeO phase with area-centred cubic lattice is indicated at 700 °C. Both characterizations suggest that the CoFe₂O₄ and Fe₃O₄ nanoparticles are rather stable up to at least about 400 °C and 600 °C, respectively.

Fe₃O₄ oxidizes into Fe₂O₃ upon the annealing in air and/or UV irradiation. The oxidation of Fe₃O₄ to the final Fe₂O₃ phase at the ageing in air was confirmed by the X-ray absorption near-edge spectroscopy (XANES) characterization. This is shown in Figure 3, where the absorbance at the Fe *K*-edge (7112 eV) of a film formed by 10 ML of Fe₂O₃-nanoparticles closely resembles to the spectrum of the Fe₂O₃ powder.¹⁶ The 2 ML- and 5 ML-thick nanoparticle layers have shown virtually the same spectra.

3.2. Sensing Properties

The sensor response, i.e., the resistivity upon the detected gas/vapours exposure, R_{NO_2} or R_{acetone} , ratioed to the resistivity upon the dry air, R_{air} , has been investigated in dependence on the sensor temperature, number of monolayers, and the detected gas concentration.

Fig. 3. The XANES spectra of 10 monolayers of self-assembled Fe_2O_3 -nanoparticle (points) at the Fe K -edge (7112 eV) compared to those of the Fe_2O_3 powder (dotted line), the latter being adopted from Ref. [16]. The spectra have been normalized to allow their detailed comparison.

3.2.1. Response to Acetone Vapours

Figures 4(a), (b) show responses of Fe_2O_3 - and CoFe_2O_4 -films with various thickness in dependence of the acetone concentration at 400 °C (left) and 500 °C (right). The response of the CoFe_2O_4 to acetone vapours is

Fig. 4. The response of the Fe_2O_3 and CoFe_2O_4 NP sensors with 1, 2, 4, and 10 MLs to the varying acetone concentration measured at 400 °C ((a) panel) and 500 °C ((b) panel).

generally lower than that of Fe_2O_3 , while the responses of Fe_2O_3 (except the 1 ML-thick film) and CoFe_2O_4 are reversed; the acetone exposure-belonging to reducing gases-decreases (increases) resistance for the former (latter). In other words, the behaviours of the Fe_2O_3 and CoFe_2O_4 -films have n - and p -type character, respectively. Interestingly, the p -response of the 1 ML-thick Fe_2O_3 film switches to the n -response with the second and more monolayers. The transformation from n - to p -response when going from 1 to 2 ML of Fe_2O_3 films has been observed for all explored working temperatures, i.e., 350, 400, 450, and 500 °C. The n - p conductivity transition in metallic oxides has not been observed seldom; the transformation even for a particular metal-oxide semiconductor (α - Fe_2O_3 , CoFe_2O_4) in dependence of the working temperature^{17,18} and/or the gas concentration.¹⁷ The general ground for the conductivity change has not been clear so far and it has continued to be a matter of discussions.

Figure 5 summarizes the responses of the Fe_2O_3 NP layers toward acetone concentration of 5 ppm in dependence on the working temperature. The response increases with the number of monolayers, while the working temperature markedly affects only the thickest film. The best sensitivity of ca 1.8 is about half order lower than that reported for WO_3 -based nanopowders.⁹

Figure 6 illustrates the time-resolved response of 10 ML Fe_2O_3 film to acetone vapours. The response and recovery time were defined as the time required to reach 90% of the total change. While the response time was about 15 minutes independent of the acetone concentration, the recovery time ranged from about 15 minutes to 55 minutes when going from 5 to 200 ppm of acetone. The response time required to reach 50% of the change maximum was about 5 minutes.

3.2.2. Response to NO_2

The exposure to NO_2 leads to oxidizing reaction, which may cause the increase of depletion layer and thereby the

Fig. 5. The temperature dependence of the response of 2, 4, and 10 ML of Fe_2O_3 NPs layers to the acetone concentration of 5 ppm.

Fig. 6. The time-dependent response of the 10 ML- Fe_2O_3 NPs layers in dependence on the acetone concentration. The hatched rectangles depict the time-controlled acetone concentration of sensor's ambient.

height of potential barrier, eventually resulting in the resistance increase. Figure 7 plots the response of Fe_2O_3 films consisting of 2, 4 and 10 ML to different concentrations of NO_2 in dependence of the working temperature. The response $R_{\text{NO}_2}/R_{\text{air}}$ increases with the numbers of monolayers and it is the highest at temperature range of about

Fig. 7. Responses of Fe_2O_3 films with 2, 4, and 10 nanoparticle monolayers toward NO_2 with the concentration of 2, 4, and 8 ppm.

Fig. 8. The temperature dependence of the NO_2 response of 10 ML-thick Fe_2O_3 NP layers.

300–400 °C. The responses for the 10 ML Fe_2O_3 , i.e., the films with the highest response, are redrawn in Figure 8. The response of ca 23 to 1 ppm NO_2 detected by means of 10 ML-thick film would suggest a good response for the sub-ppm range; the response would rate to usually yielded ones for metal oxide-based sensors.¹ Concerning NO_2 , no p – n transformation has been observed. The characterization of dynamic properties (not shown here) suggest the response/recovery times of about 20 minutes in the concentration range from 1 to 8 ppm NO_2 .

4. SUMMARY

The sensing properties of Fe_2O_3 - and CoFe_2O_4 -nanoparticle Langmuir–Blodgett films toward acetone and NO_2 have been investigated. Among the explored films with 1, 2, 4, 7, and 10 nanoparticle monolayers, ten Fe_2O_3 monolayer-thick films have demonstrated the highest sensitivity, namely of 150 and 23 for 8 and 1 ppm of NO_2 , respectively. Notably, the good response to NO_2 approaching the ppb-range suggests the appropriateness for the detection of nitrate-based explosives. The sensitivity toward acetone concentration in the ppm-range was in the range of units only. The Fe_2O_3 and CoFe_2O_4 films displayed the reverse conductivity-type behaviour, while the conductivity-type switch was observed for the Fe_2O_3 films when going from the one to more monolayers.

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References and Notes

1. A. Afzal, N. Cioffi, L. Sabbatini, and L. Torsi, *Sens. Actuators B* 171–172, 25 (2012).
2. M. M. Rahman, S. Bahadar Khan, A. Jamal, M. Faisal, and A. M. Asiri, *Chem. Engn. J.* 192, 122 (2012).

3. S. Luby, L. Chitu, M. Jergel, E. Majkova, P. Siffalovic, A. P. Caricato, A. Luches, M. Martino, R. Rella, and M. G. Manera, *Vacuum* 86, 590 (2011).
4. M. W. K. Nomani, D. Kersey, J. James, D. Diwan, T. Vogt, R. A. Webb, and G. Koley, *Sens. Actuators B* 160, 251 (2011).
5. Z. Yidong, J. Gangcheng, W. Ka Wai, and Z. Zhi, *Sensor Lett.* 8, 355 (2010).
6. H. Liu, J. Park, and G. Wang, *Sensor Lett.* 8, 243 (2010).
7. S. F. Bamsaoud, S. B. Rane, R. N. Karekar, and R. C. Aiyer, *Sens. Actuators B* 153, 382 (2011).
8. D. Wang, A. Chen, and A. K. Jen, *Phys. Chem. Chem. Phys.* 15, 5017 (2013).
9. L. Wang, K. Kalyanasundaram, M. Stanacevic, and P. Gouma, *Sensor Lett.* 8, 709 (2010).
10. D. Meng, N. M. Shaalan, T. Yamazaki, and T. Kikuta, *Sens. Actuators B* 169, 113 (2012).
11. L. You, X. He, D. Wang, P. Sun, Y. F. Sun, X. S. Liang, Y. Du, and G. Y. Lu, *Sens. Actuators B* 173, 426 (2012).
12. C. Zhang, M. Debliquy, A. Boudiba, H. Liao, and C. Coddet, *Sens. Actuators B* 144, 280 (2010).
13. S. B. Khan, M. Faisal, M. M. Rahman, and A. Jamal, *Talanta* 85, 943 (2011).
14. N. P. Zaretskiy, L. I. Menshikov, and A. A. Vasiliev, *Sens. Actuators B* 170, 148 (2012).
15. K. Rickers, W. Drube, H. Schulte-Schrepping, E. Welter, U. Brüggmann, M. Herrmann, J. Heuer, and H. Schulz-Ritter, *AIP Conf. Proc.* 882, 905 (2007).
16. M. Newville, XAFS Data Library, Argonne National Laboratory, Argone (URL <http://cars9.uchicago.edu/cgi-bin/newville/Model-Search.cgi>).
17. A. Gurlo, M. Sahm, A. Oprea, N. Barsan, and U. Weimar, *Sens. Actuators B* 102, 291 (2004).
18. X. Chu, D. Jiang, Y. Guo, and C. Zheng, *Sens. Actuators B* 120, 177 (2006).
19. J. Luo, L. Wang, X. Shi, J. Yin, E. Crew, S. Lu, L. M. Lesperance, and C. J. Zhong, *Sens. Actuators B* 161, 845 (2012).