Thermal stability of $\gamma$-Fe$_2$O$_3$ nanoparticles and their employment for sensing of acetone vapours

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Abstract. Stability of $\gamma$-Fe$_2$O$_3$ nanoparticles-based films upon an isochronal annealing in air was investigated by x-ray diffraction, differential scanning calorimetry, and thermogravimetry. The $\gamma\rightarrow\alpha$ transformation temperature increased owing to the nanoscaling of Fe$_2$O$_3$; the higher stability of the $\gamma$ phase was explained on the ground of the surface free energy of nanoparticles (with the size of about 6.4 nm). Further, chemiresistors based on the Fe$_2$O$_3$ nanoparticle bilayer prepared by the Langmuir-Schaefer method were fabricated and examined in terms of their sensitivity to acetone vapours down to 500 ppb concentration in air.

1. Introduction

Among hundreds of volatile organic compounds (VOCs) involved in a human exhaled breath, various of them—referred to as biomarkers—were associated with a specific disease [1]. This makes the detection of breath biomarkers applicable in non-invasive screening and real-time monitoring of particular diseases. For example, diabetes patients exhibit a higher acetone concentration in their breath: whilst the values lower than 0.76 ppmv were associated with healthy persons, acetone in diabetics’ breath exceeds about 1.7 ppmv [2].

Contrary to an expensive and complicated instrumentation, solid-state chemiresistor sensors of acetone vapours may dispose of a manufacture potential for fabrication of simple and affordable and thereby personal monitoring device providing an alternative to standard blood analysis. Considering the mentioned concentration range, the sensitivity down to sub ppm range is required. Various semiconducting—often nano-scaled—metal oxides have been used in the role of sensing elements, such as Fe$_2$O$_3$ [3-8], WO$_3$ [9-11], SnO$_2$ [3,12], TiO$_2$ [13], CeO$_2$ [14], and ZnO [15], or related compounds [5,16] and/or activated by impurities [3] being the most popular ones. An operating temperature of a few hundred degrees is typically necessary by virtue of the adsorption/desorption kinetics of detected molecules, and/or technology and application issues; optimal temperatures, i.e. corresponding to the highest response, were reported to range from 175°C to 500°C [3-8,13].
Fe₂O₃ can occur in the α- and γ-phase, whilst the phases display reverse conductivity behaviours [17]. The γ-Fe₂O₃ undergoes a transformation to α-Fe₂O₃ above a transformation temperature ($t_t$) (reported to be of 481°C for γ-Fe₂O₃ NPs (8-20 nm) [18]) impairing the sensitivity and selectivity to reducing gases [19]. Thereby, the necessity of the elevated working temperatures up to $t_t$ of γ-Fe₂O₃-based sensors arises a question on stability of γ-Fe₂O₃. In recent works, $t_t$ was increased by doping of Fe₂O₃ by e.g. Pt [18] or Mn [20]. In this study, the achievement of higher $t_t$ with pure Fe₂O₃ NPs will be demonstrated.

2. Experimental

The Fe₂O₃ nanoparticles (NPs) have been synthesized via reaction between Fe acetylacetonates with 1,2-hexadecanediol, and oleic acid and oleyl amine in the role of the surfactant precursor in phenyl ether. The average NP diameter has been of 6.4±0.6 nm including the surfactant thickness being of about 1 nm. Mixtures of Fe₂O₃/Pd nanoparticles with ratios of 100/1 and 100/5 were prepared. Whereby the Pd NPs (6-7 nm) covered by oleyl amine were purchased from PlasmaChem.

The NP films intended for characterization of sensing properties were prepared by the modified Langmuir-Schaffer (LS) deposition [21] of colloid NPs from the water subphase onto encased alumina substrates (2×2 mm) equipped with interdigitated electrodes with the channel length of 50 μm allowing the film resistivity determination. The investigated films consisted of arrays of two sequentially deposited NP monolayers. The deposited films were annealed at 400°C in dry air for 30 min to stripe off the insulating organic surfactant.

Resistance NP layers was examined at voltage of 1 V upon varying concentration of acetone vapors in dry air. This was achieved by mass flow controller-controlled mixing of dry air and a certified mixture of 20 ppm acetone vapors in dry air. The total medium flow of 10 or 100 sccm was kept constant for any acetone concentration. The elevated working temperature of the sensing layer was attained by means of planar resistive heaters incorporated on the back side of the alumina substrates.

The NP films intended for structural characterization were drop-casted onto polished silicon substrates. The x-ray diffraction (XRD) characterization was performed using D8 Discover SSS (Bruker AXS) facility with rotating Cu anode.

The differential scanning calorimetry (DSC) and thermogravimetry (TG) measurements were performed using TA Instruments Q 200 and SDT Q 600 facilities, respectively, in Ar ambient with heat ramps of 1, 10, and 40 K/min.

3. Results and discussion

3.1. Structural properties of Fe₂O₃ nanoparticles

The γ-α transformation is the phase change from cubic γ-Fe₂O₃ (maghemite) to rhombohedral α-Fe₂O₃ (hematite). The phase transformation of NPs is generally affected by the NP preparation, supporting substrate, size, doping, and heating rate. Randrianantoandro et al. [22] reported that γ-Fe₂O₃ NPs with size from 5 to 30 nm are stabilized owing to the high surface free energy, and even a reverse α→γ transition was achieved by ball milling. 8-20 nm γ-Fe₂O₃ NPs transformed to α phase at 481°C and $t_t$ increased to 547°C upon the doping of NPs with 0.25 wt % of Pt [18].

Here, the γ→α transformation was investigated by means of XRD and DSC-TG methods. The probed NPs did undergo isochronal annealing durative one hour in air at temperatures ranging from 500°C to 770°C. Figure 1 contrasts the XRD of the Fe₂O₃ NPs annealed at 550°C and 600°C. Apparently, the γ-Fe₂O₃ phase preserves up to at least 550°C, the annealing at 600°C reveals the mixed phase, as features pertaining to the α-Fe₂O₃ appear. It means that 550°C < $t_t$ < 600°C. On the other side, the features indicative α-Fe₂O₃ appeared already at 500°C for both the 100/1 and 100/5 Fe₂O₃/Pd mixtures (not shown here) suggesting that the presence of Pd decreases the transformation temperature by at least 50°C. Accordingly, Pd shows an adverse effect in comparison to Pt [18].
In parallel, the $\gamma$-$\alpha$ transformation was examined by the DSC-TG method. Figure 2a presents DSC dependences taken on couples of the pure and Pd-doped Fe$_2$O$_3$ samples. The dependences reveal peaks at about 560 K, which is associated by dramatic weight loss in TG (Figure 2b). This suggests that the surfactant is removed in two steps.

Figure 1. X-ray diffractogram of Fe$_2$O$_3$ nanoparticles annealed one hour at 550°C or 600°C with labelled features indicative of $\alpha$- and $\gamma$-Fe$_2$O$_3$ phases, and the substrate (s).

Figure 2. The differential scanning calorimetry (a) and the thermogravimetry (b) dependences taken with the ramp rate of 10 K/min for three couples of samples: undoped Fe$_2$O$_3$ nanoparticles, and Fe$_2$O$_3$/Pd nanoparticle mixtures.
Similar two steps TG weight loss was reported for $\gamma$-Fe$_2$O$_3$ NPs covered by oleic acid surfactant earlier [20]. Authors assumed that the first and second weight loss correspond to weakly bound secondary and to the strongly bound primary surfactant layer, respectively. Double or even triple peaks are present at higher temperatures (Figure 2a). We presume that the peaks between 700 and 760 K are related to the crystallization, which was supported by XRD characterization (not shown here), while the features around 800 K correspond to the $\gamma \rightarrow \alpha$ transformation. This—in terms of the pure Fe$_2$O$_3$—is finished at about 870 K, thus complying to about 600°C arising from the XRD measurements. In terms of the Fe$_2$O$_3$/Pd samples, the transformation is shifted down by about 30°C. Since these peaks are related to the phase transition, no weight losses are expected, as indicated by plateaus of the TG dependences in the same temperature region (Figure 2b). The further weight loss observed above 900 K (Figure 2b) is not understood at this moment.

3.2. Sensing performance of Fe2O3 nanoparticle films

Polycrystalline films Fe$_2$O$_3$ can manifest electrical resistance of hundreds MΩ [3,18]. Even though resistance decreases upon reducing acetone exposure, chemiresistors with the extremely low conductivity are rather precluded from standard laboratory characterization. Resistance of the layers examined here was about 6 MΩ at the operating temperature, which allowed the characterization at voltage of 1 V. The sensor response, i.e., the resistivity measured in dry air, $R_{air}$, ratioed to resistivity detected upon precisely controlled trace concentrations of acetone vapours, $R_{acet}$, was examined in dependence on acetone concentration, operating temperature, and total gas flow.

Figure 3 shows the response to 1 and 0.5 ppm acetone vapors in air upon the constant total gas mixture flow of 100 sccm. The sensor temperature was kept at 420°C, since the highest response was observed in the temperature range from about 370 to 450°C (not shown here). The concentration change in the testing cell is not immediate upon the switching the probed mixture; it depends on the total flow of the medium and the volume of the testing chamber. Given the filling time of the employed testing cell (with volume of about 25 cm$^3$) being about 15 seconds upon the flow of 100 sccm, the onsets of the responses suggest that rate of the response is virtually determined by the time necessary to establish the requested acetone concentration in the testing cell. The response saturates at about 7.5% upon acetone concentration of 500 ppb.

![Figure 3](image_url)  
Figure 3. Response $R_{air}/R_{acet}$ of two arranged monolayers of Fe$_2$O$_3$ nanoparticles upon 5 minute exposures of 0.5 and 1 ppm acetone vapours with the preserved total gas flow of 100 sccm. Vertical dash bars indicate the switching ON and OFF of the acetone vapours. The sensor temperature was kept at 420°C.
The time necessary for the response saturation upon the probed mixture makes the sensor rather slow. The response time can be shortened by employment of a higher gas flow, yet, that augments the cooling of the sensor, which affects the response. Therefore, the operation at a lower total gas flow would be preferable. Figure 4 shows the responses upon one-minute durative exposure of various concentrations of acetone vapours with the preserved total gas flow of 10 sccm. Such flow results in the filling time of about 2:30 minutes. The dependences suggest that employment of such stringent conditions, i.e. both the short exposure period and the very low total gas flow, allows to obtain response near to the diabetes diagnosis threshold.

![Graph showing response R_air/R_acet of two monolayers of Fe$_2$O$_3$ nanoparticles upon various concentrations of acetone vapours allowed flowing for one minute with the constant overall gas flow of 10 sccm. Numbers next to the dependences indicate the acetone concentrations in ppm. The switching ON and OFF of the acetone vapours are indicated by vertical bars.]

4. Summary
The $\gamma \rightarrow \alpha$ transformation temperature of Fe$_2$O$_3$ nanoparticles was investigated by combination of the x-ray diffraction, the differential scanning calorimetry, and the thermogravimetry methods. It was demonstrated that the $\gamma$-Fe$_2$O$_3$ phase preserves up to at least 550°C, the magnitude sufficient for the operating temperature of a gas sensor. The doping of Fe$_2$O$_3$ nanoparticles by Pd ones decreases the $\gamma \rightarrow \alpha$ transformation temperature of Fe$_2$O$_3$ NPs by about 50°C. The Fe$_2$O$_3$ films formed by two monolayers of arranged nanoparticles proved to detect acetone vapours down to 500 ppb. The sensor appear sufficient swift to detect acetone concentration near to the diabetes diagnosis threshold within one minute.

Acknowledgments
We acknowledge the support via APVV-14-0891, VEGA 2/0010/15 and CNR-SAS 2016-2018 grants.

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