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Electronic structure and surface properties of non-stoichiometric $Fe_2O_{3-\delta}$ (α and γ) and its application in gas sensing

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Abstract

Crystalline nanoparticles of γ-Fe_2O_3 and α-Fe_2O_3 as candidates for gas sensing were synthesized by flame spray process (FSS). γ-Fe_2O_3 was obtained in a one step process, while α-Fe_2O_3 was obtained after heat-treatment of as-prepared γ-Fe_2O_3 nanoparticles. With a combination of diffuse reflectance spectroscopy (DRS), X-ray photoelectron spectroscopy (XPS), advanced near edge X-ray absorption fine structure (NEXAFS) spectroscopy, we probed the electronic structure and described the mechanisms of reducing gas sensing at the molecular scale and correlated the sensing property with charge transfer and valence band characteristics. The surface composition was determined by the XPS and resonance RBS (Rutherford backscattering spectrometry). The core level and valence band spectra of mild-oxidized and mild-reduced samples revealed the non-stoichiometric character of Fe_2O_3 and contribution of electronic surface defects. These two polymorphic forms of Fe_2O_3 exhibit significant differences of the chemical surface composition, electronic structure and resulting sensing properties.

Keywords: nanoparticles; Fe_2O_3; hydrogen sensing; XPS; NEXAFS; electronic structure; band gap

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1. Introduction

The search for affordable materials for high performing gas sensors is an ongoing quest. In order to obtain a promising material for sensing application it is necessary to control crystallinity and phase composition. Flame spray synthesis (FSS) yields metal oxide nanoparticles for the next generation of chemical sensors. Fe_2O_3 is one of the semiconducting metal oxides, which is of great interest as a solid state gas sensor [1]. α-Fe_2O_3 hematite and γ-Fe_2O_3 maghemite are two crystal phases of ferric oxide, which are mainly investigated for gas sensor applications as they have a narrow band gap, good chemical stability, low cost and broad applications. Recently, switching of conductivity type, which depends on the material doping, working conditions, has also attracted considerable attention [1]. This effect can have significant impact on the gas sensing properties of iron oxides. Non-stoichiometric Fe_2O_3 nanoparticles are the promising semiconducting materials not only for gas sensing of different gases but have already found an application in other fields e.g. photoelectrochemistry [2], ferromagnetism [3] and photocatalysis [4] due to their favorable electronic, magnetic and optical properties. Hematite and maghemite are the polymorphs exhibiting different type of conductivity, what can be exploited for theirs selectivity towards either reducing or oxidizing gases.

In our work we approached the reducing gas sensing properties of the two different polymorphic forms of non-stoichiometric $Fe_2O_{3-\delta}$ with the extended spectroscopic investigation of its surface composition, electronic structure and charge transfer properties.

2. Experimental

Two polymorphic forms of Fe_2O_3 were prepared by flame spray synthesis from metal-organic precursor solution (0.5 mol/dm^3 ferrocene). In direct one-step synthesis maghemite phase was obtained, while thermal post-treatment at 823 K of as-prepared nanoparticles resulted in phase transformation towards hematite. As-prepared nanoparticles were subjected to the phase composition analysis by X-ray diffraction (XRD), specific surface area (SSA) determination by Brunauer-Emmett-Teller (BET) adsorption isotherms, and optical band gap determination by diffuse reflectance spectroscopy (DRS). The surface composition of mild-oxidized samples (given to heat treatment at 673 K at air condition) and mild-reduced (after Ar^+-ion sputtering) was investigated with the X-ray photoelectron spectroscopy (XPS) and was supported with the resonance Rutherford backscattering spectrometry (RBS) for mild-oxidized samples. The electronic structure was probed with the near-edge X-ray absorption fine structure spectroscopy (NEXAFS) along with the XPS. The electrical resistance response ($\Delta R/R_0$) of disc-shaped sensors (pellets) was determined against the hydrogen and ammonia exposure over a wide range of the concentration) and under different operating temperatures. The sensor response is defined as $S=(R-R_0)/R_0$, where R_0 is a baseline resistance in reference air atmosphere and R is a resistance in detected gas atmosphere.

3. Results and discussion

Nanoscaled particles of Fe_2O_3 were obtained in direct one-step high temperature flame assisted combustion process of ferrocene. XRD show that the as prepared brownish nanoparticles consist of maghemite (γ-Fe_2O_3) with low crystallinity. Thermal post-treatment at 823 K under air caused a phase transformation towards hematite orange-red nanoparticles (α-Fe_2O_3), accompanied by an increase of the crystallinity. The average particle size (d_{TEM}) was roughly 12 nm for as-synthesized spherical particles of (only some with hexagonal shape) Fe_2O_3. In the case of post-treated nanoparticles, a substantial increase of particles size was observed caused by sintering effect with a formation of prolate worm-like structures,

with an arithmetic average length of roughly 157 nm and an average arithmetic width of roughly 42 nm. Inspection of the DRS spectra given to differential analysis (not presented here) revealed four transition energies for both γ-Fe_2O_3 and α-Fe_2O_3. Predominant peaks are attributed to the overall band gap energy which is 1.82 eV and 2.12 for γ-Fe_2O_3 and α-Fe_2O_3, respectively.

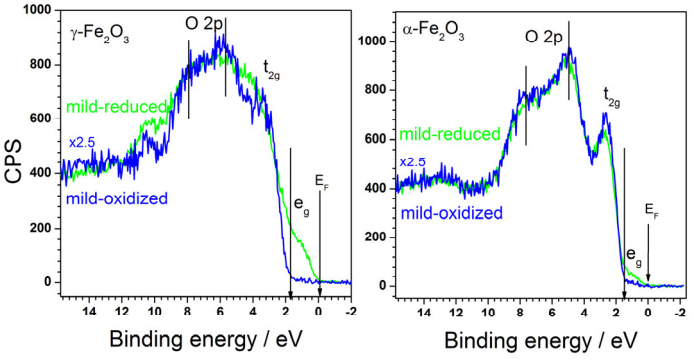

Fig. 1. XPS valence band spectra of mild-oxidized and mild-reduced γ-Fe_2O_3 and α- Fe_2O_3

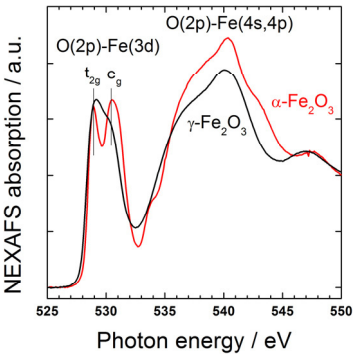

Fig. 2. Normalized O K-edge NEXAFS spectra of γ-Fe_2O_3 and α- Fe_2O_3

By subjecting samples to mild-oxidizing and mild-reducing ex-situ condition we have probed the surface stoichiometry. As observed within the valence band region (Fig. 1.) the non-stoichiometry of surface develops when samples' surrounding condition change from mild-oxidizing to mild-reducing. The contribution of surface defect states near the Fermi energy level F_E up to 2 eV range can be seen as a higher spectral weight. This means that when samples are exposed to the reducing gas atmosphere, while sensing operation, the surface defects strongly develop (mostly oxygen vacancies) inducing the resistance change. This process can be reversed by the introducing oxidizing gas atmosphere, when created oxygen vacancies can be filled and thus the resistance changes in the opposite direction. The spectral weight of the spectroscopic feature corresponding to the surface defects is more pronounced for γ-Fe_2O_3, what can be correlated to the different conductivity type of these two polymorphs of Fe_2O_3. These results were confirmed with the resonance RBS. Refilling of the oxygen vacancies in samples given to mild-oxidizing condition is much efficient in the case of α-Fe_2O_3, where the oxygen content $O_{3-\delta}$ was found to be 3.07±0.12, while in case of γ-Fe_2O_3 was 2.94±0.12. Significant decrease of the non-stoichiometric oxygen contribution under mild-reducing condition was also found from the O 1s core level analysis for both Fe_2O_3 forms. Moreover, Fe 2p core level analysis provided us with the information that under mild-reducing condition both Fe^{3+} and Fe^{2+} valence states are present and higher contribution of Fe^{2+} was observed for γ-Fe_2O_3. Pre-edge region of NEXAFS O K-edge (Fig. 2) with the low energy transition to unoccupied O(2p) hybridized with Fe3(d) positioned at 530 eV show double peak character, however with significant differences in overall spectral shape for both phases. This splitting originates from the t_{2g} and e_g states. These two peaks seem to overlap stronger for γ-Fe_2O_3, confirming the presence of Fe^{2+} next to Fe^{3+}. Differences found in the electronic structure can be correlated with differences in the intrinsic properties of these two forms of Fe_2O_3, mainly in electrical transport and eventual gas sensing behavior. Non-stoichiometric α-Fe_2O_3 and γ-Fe_2O_3 responded to a wide concentration range of the H_2 and NH_3, with favorable sensing of H_2 (Fig. 3.). The highest response was achieved at 523 K for α-Fe_2O_3, however at higher operating temperatures the sensor response remained linear within the whole concentration range. The direction of the dynamic changes of the resistance change upon exposure to reducing gas

indicates that γ-Fe_2O_3 shows n-type semiconductor behavior up to 573 K, while α-Fe_2O_3 shows p-type behavior.

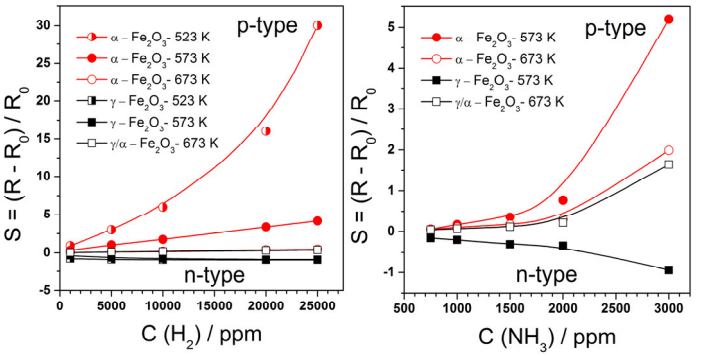

Fig. 3. Change of the relative resistance as a function of the gas concentration (H_2 and NH_3) and operating temperature

4. Conclusions

Nanoscaled γ-Fe_2O_3 phase was synthesized with the FSS. Thermal post-treatment induced the phase transformation towards α-Fe_2O_3, with improved crystallinity. Substantial differences found in the stoichiometry of both polymorphs of Fe_2O_3 strongly affects the electronic structure and related material properties, mainly electrical transport, what has a reflection in the eventual gas sensing behavior towards reducing gases. Nanosensors obtained from non-stoichiometric α-Fe_2O_3 and γ-Fe_2O_3 responded significantly and fast to a wide concentration range of the H_2 and NH_3, with favorable sensing of H_2 at 523 K and 573 K. The direction of the dynamic changes of the electrical resistance under hydrogen exposure showed that as-synthesized γ-Fe_2O_3 and post-treated α-Fe_2O_3 semiconductors have different type of conductivity. γ-Fe_2O_3 is an n-type semiconductor up to 573K and α-Fe_2O_3 is a p-type semiconductor.

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