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Nanocrystalline LaCoO₃ modified by Ag nanoparticles with improved sensitivity to H₂S

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As a semiconductor metal oxide with perovskite structure, LaCoO₃ is of interest for chemical sensors. The hole-type conduction occurs via Co-O framework. The surface of LaCoO₃ nanostructures exhibits different adsorption sites (La³⁺ and Co³⁺) and active sites (chemisorbed oxygen, lattice anions) for gas molecules reception. The sensing mechanisms with LaCoO₃ and its nanocomposites are unclear. In this work we obtained nanocrystalline LaCoO₃ modified by Ag nanoparticles with improved sensitivity and selectivity to H₂S, characterized the microstructure and surface sites of materials, and proposed the sensing routes during gas-solid interaction.
Nanocrystalline LaCoO3 with particle size 30-80 nm (Fig. 1) and specific surface area 5-10 m2/g was obtained by sol-gel synthesis using ethylenediamine as a coordination ligand. The samples were impregnated by Ag nanoparticles with the size increasing in the range 30-60 nm on increasing silver percentage 2-5 wt.%. XPS spectroscopy demonstrated the presence of La³⁺, Co³⁺, O²⁻ ions in the bulk along with a large fraction of chemisorbed oxygen species. Metallic Ag nanoparticles were observed by XPS and XRD. The DC-resistance increased in presence of Ag due to electrons donation into p-type LaCoO₃. The Ag/LaCoO₃ nanocomposites demonstrated higher sensitivity to 0.2-5 ppm H₂S at 200 °C, in comparison to pure LaCoO3 (Fig. 2). Cross-sensitivity tests showed about 10-times higher sensor response of Ag/LaCoO₃ to 2 ppm H₂S, as opposed to 20 ppm CO and NH₃ (Fig. 3). On DRIFT spectra of the samples Ag/LaCoO₃ exposed to H₂S at 200 °C the evolution of peaks was observed relevant to adsorbed H₂S, Ag₂S and SO₄²⁻ groups (Fig. 4a). Thus, the sensing process occurred via H₂S adsorption favored by Ag nanoparticles and oxidation to sulfur oxide and sulfate species on the LaCoO₃ surface. The reaction products, except SO₄²⁻, disappeared during further exposure in air, which accounts for sensor recovery (Fig. 4b). The persistent sulfate species were likely inactive by-products that did not affect the sensors behavior.

Summary

Nanocrystalline LaCoO₃ was synthesized by sol-gel method and functionalized by Ag nanoparticles via impregnation. An improved sensitivity to H₂S gas was detected for the Ag/LaCoO₃. The nanocomposite sensors showed lower cross-sensitivity to CO and NH₃, in comparison to pure LaCoO₃. The role of Ag nanoparticles in promotion of the H₂S adsorption and oxidation on the surface of LaCoO₃ was elucidated using diffuse reflectance infrared Fourier-transformed (DRIFT) spectroscopy.

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