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Extended Abstract

Nanocrystalline $LaCoO_3$ Modified by Ag Nanoparticles with Improved Sensitivity to H_2S †

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Summary

Nanocrystalline $LaCoO_3$ was synthesized by sol-gel method and functionalized by Ag nanoparticles via impregnation. An improved sensitivity to H_2S gas was detected for the Ag/$LaCoO_3$. The nanocomposite sensors showed lower cross-sensitivity to CO and NH_3, in comparison to pure $LaCoO_3$. The role of Ag nanoparticles in promotion of the H_2S adsorption and oxidation on the surface of $LaCoO_3$ was elucidated using diffuse reflectance infrared Fourier-transformed (DRIFT) spectroscopy.

Motivation and Results

As a semiconductor metal oxide with perovskite structure, $LaCoO_3$ is of interest for chemical sensors. The hole-type conduction occurs via Co–O framework. The surface of $LaCoO_3$ nanostructures exhibits different adsorption sites (La^{3+} and Co^{3+}) and active sites (chemisorbed oxygen, lattice anions) for gas molecules reception. The sensing mechanisms with $LaCoO_3$ and its nanocomposites are unclear. In this work we obtained nanocrystalline $LaCoO_3$ modified by Ag nanoparticles with improved sensitivity and selectivity to H_2S, characterized the microstructure and surface sites of materials, and proposed the sensing routes during gas-solid interaction.

Nanocrystalline $LaCoO_3$ with particle size 30–80 nm (Figure 1) and specific surface area 5–10 m^2/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 La^{3+}, Co^{3+}, O^{2-} 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 $LaCoO_3$. The Ag/$LaCoO_3$ nanocomposites demonstrated higher sensitivity to 0.2–5 ppm H_2S at 200 °C, in comparison to pure $LaCoO_3$ (Figure 2). Cross-sensitivity tests showed about 10-times higher sensor response of Ag/$LaCoO_3$ to 2 ppm H_2S, as opposed to 20 ppm CO and NH_3 (Figure 3). On DRIFT spectra of the samples Ag/$LaCoO_3$ exposed to H_2S at 200 °C the evolution of peaks was observed relevant to adsorbed H_2S, Ag_2S and SO_4^{2-} groups (Figure 4a). Thus, the sensing process occurred via H_2S adsorption favored by Ag nanoparticles and oxidation to sulfur oxide and sulfate species on the $LaCoO_3$ surface. The reaction products, except SO_4^{2-}, disappeared during further exposure in air, which accounts for sensor recovery (Figure 4b). The persistent sulfate species were likely inactive by-products that did not affect the sensors behavior.

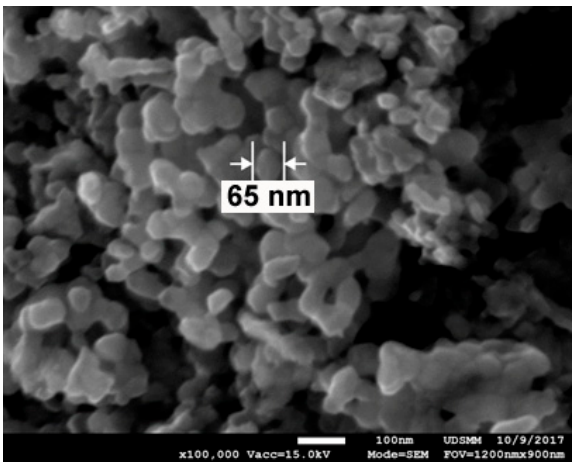

Figure 1. SEM image of $LaCoO_3$ annealed at 600 °C for 9 h.

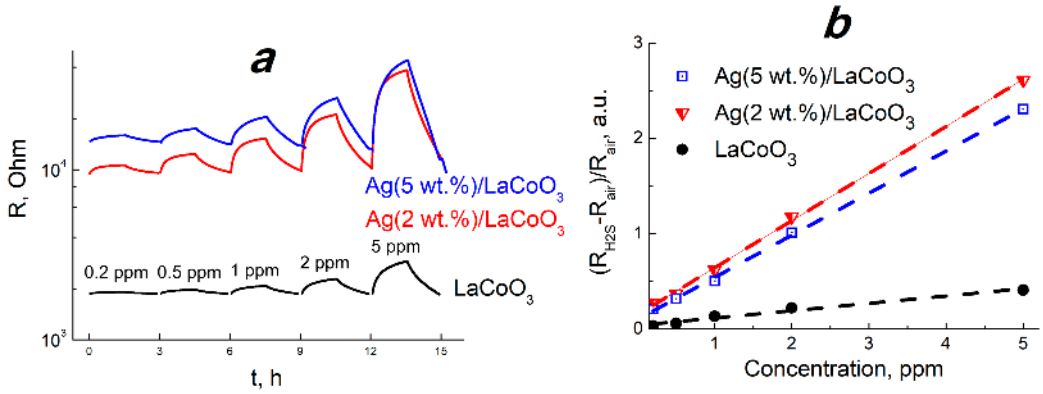

Figure 2. Dynamic response (**a**) and sensor signals (**b**) of $LaCoO_3$ and $Ag/LaCoO_3$ to 0.2-5 ppm H_2S at 200 °C.

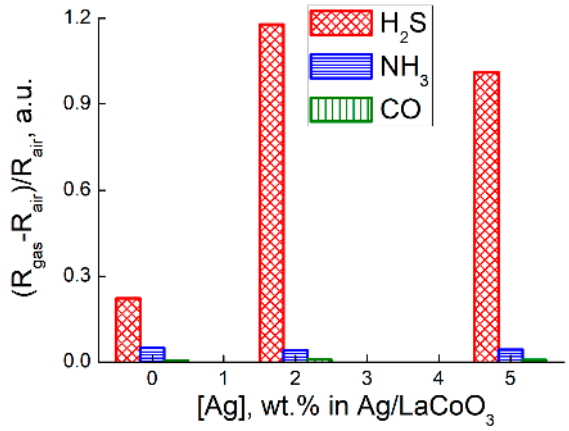

Figure 3. Comparison of sensor signals of $LaCoO_3$ and $Ag/LaCoO_3$ to 20 ppm CO, 20 ppm NH_3 and 2 ppm H_2S at 200 °C.

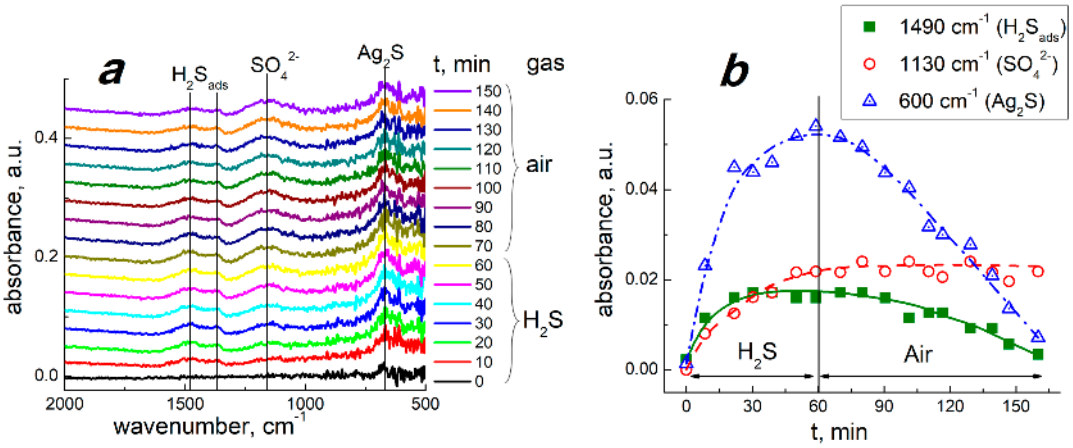

Figure 4. DRIFT spectra of Ag/$LaCoO_3$ exposed to 20 ppm H_2S at 200 °C for 60 min and to air at 200 °C for further 90 min (**a**), and absorption intensities of the peaks of adsorbed H_2S, SO_4^{2-} and Ag_2S (**b**).

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Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.