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$ZnO/CsPbBr_3$ NANOCOMPOSITES for GAS SENSING APPLICATIONS

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Abstract:
It this work were synthesized nanocomposites based on nanocrystalline ZnO thick films and colloidal perovskite $CsPbBr_3$ nanocubes (NCs), and the sensor measurements were performed to NO_2, SO_2 and H_2S at room temperature under periodically blue light illumination (LED with λ_{max}=470 nm). The crystal structure of ZnO and $CsPbBr_3$ was determined by X-ray diffraction, the absorption and photoluminescence spectra of $CsPbBr_3$ colloidal NCs were obtained in UV-vis range. The morphology and size of nanocrystals were defined by HAADF-TEM investigations. $ZnO/CsPbBr_3$ nanocomposite shows increasing of conductance under blue LED illumination, what can be explain by photosensitizing action of $CsPbBr_3$ NCs. The level of photoconductance depends reversible on NO_2 and SO_2 concentration in air, but the sensor response to H_2S is non-reversible. Investigated nanocomposites have a good stability during the measurements and photoconductance very slowly depends on O_2 concentration.

Key words: gas sensor, room temperature, light activation, perovskite, nanocomposite

Introduction

One of the actual ways to improve the selectivity and sensitivity of metal oxide gas sensors, as well as to reduce energy consumption is the activation by light. In various studies, the influence of UV radiation on the sensor properties of ZnO SnO_2, WO_3 and other metal oxides was studied. It was demonstrated that the sensory response to certain gases during irradiation may occur at room temperature. Significant interest is also the study of the effect of visible spectrum radiation on the sensor characteristics of metal oxides. This is a promising way to reduce the energy consumption of the sensor. However, for effective absorption of visible light, wide-gap metal oxides must be combined with photosensitizers such as narrow-gap semiconductors or dyes.

In this work, we used colloidal NCs $CsPbBr_3$ to sensitize the gas sensor properties of nanocrystalline ZnO under visible light irradiation. Lead halide perovskites currently attract exceptionally high attention as materials for solar energy, light-emitting devices but their use in other areas of material science is rarely studied.

Experimental

The colloidal perovskite NCs were synthesized by hot-injection method using Schlenk line according to Protesescu et al. Cs oleate solution in ODE was injected in the reaction mixture at 170°C. $CsPbBr_3$ NCs was separated by centrifugation and redispersed in hexane.

Nanocrystalline ZnO was synthesized in aqueous media at 25°C by precipitation method from $Zn(CH_3COO)_2$ and NH_4HCO_3 as precursors. Obtained white precipitate ($Zn_x(OH)_y(CO_3)_z$) was annealed at 300°C on air during 24 h to form nanocrystalline ZnO.

To perform the sensor measurements the thick film of ZnO was prepared by mixing nanocrystalline ZnO powder with α-terpeniol. The resulting paste was placed to a plate equipped with two measuring Pt electrodes, and the film was sintered at 350°C on air. Next the $CsPbBr_3$ NCs hexane dispersion was dropped on the ZnO film. The resulting $ZnO/CsPbBr_3$ nanocomposite film was dried 6 h at 70°C.

All sensor measurements were carried out by flow through technique at room temperature under periodically (2 min is on, 2 min is off) blue

LED illumination (λ_{max}=470 nm). The atmosphere composition was pre-assigned by means by electronic mass-flow controllers (constant flux 100 ml/min). The certified bottles of gas mixtures was used (20 ppm NO_2 in N_2, 96 ppm SO_2 in N_2, 10 ppm H_2S in N_2, Ar 99,999%, synthetic dry air).

Results

According the X-ray diffraction data, synthesized ZnO has a wurtzite structure. As can be seen from the HAADF-TEM images, ZnO crystallites have a near spherical shape with average crystallite size 20-25 nm. Synthesized colloidal $CsPbBr_3$ NCs belong to cubic perovskite phase (Pm3m, a=5.847 Å) and have a cubic shape with average edge size 10-15 nm. The absorption edge of colloidal $CsPbBr_3$ NCs is located near 510 nm, PL maximum is observed at 517 nm with FWHM=20 nm (Fig 2).

Synthesized ZnO/$CsPbBr_3$ nanocomposite shows increasing electrical conductance under blue LED illumination, while the pure ZnO do not show the photoresponse in some conditions. Following to the periodic illumination, the dependence of the resistance of the samples on time scale also assume a periodic character, having local maxima (R_{dark}) and minima (R_{light}) (Fig. 3). The arrounding atmospheric composition influences on photoconductance of ZnO/$CsPbBr_3$ structures. In the presense of NO_2 resisitance of nanocomposite increases, and the R_{dark}/R_{light} ratio increases too.

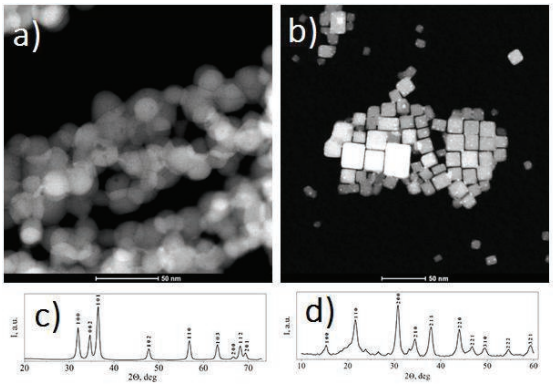

Fig. 1. a) HAADF-TEM image of nanocrystalline ZnO; b) HAADF-TEM image of $CsPbBr_3$ NCs; c) XRD pattern of nanocrystalline ZnO (CuK_α); XRD pattern of colloidal $CsPbBr_3$ NCs (CuK_α).

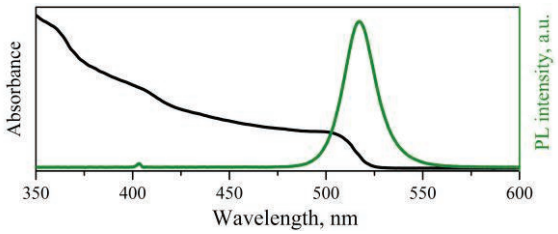

Fig. 2 Optical absorption and PL spectra of colloidal $CsPbBr_3$ NCs in hexane.

Unlike from NO_2, the presence of SO_2 in air leads to decreasing of nanocomposite resistance, but the R_{dark}/R_{light} ratio remain nearly constant. Under the influence of 1 ppm H_2S the resistance of nanocomposite was decreased non-reversible. Variation of oxygen concentration in 18-20 vol.% range had no effect on photoelectrical properties of ZnO/$CsPbBr_3$ nanocomposite.

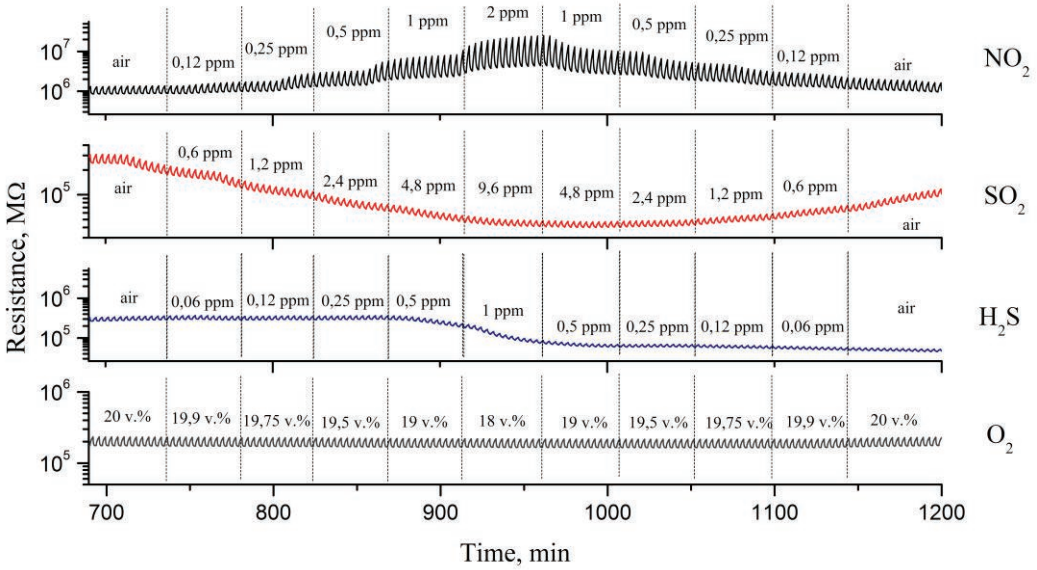

Fig. 3 Sensor measurements to NO_2, SO_2, H_2S and various O_2 concentration at room temperature under periodic blue LED illumination for ZnO/$CsPbBr_3$ nanocomposite .