Synthesis of optosensitive structures based on zinc oxide

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Abstract. In the research, light-sensitive structures based on a heterostructure of ZnO-nanorods/PbS colloidal quantum dots (CQDs) were fabricated. The paper describes technological features of obtaining coatings by the low-temperature hydrothermal method and fabrication of a ZnO-nanorods/PbS CQDs heterostructure. It is shown that this structure is capable of converting light into electrical energy. These structures are promising for use as gas sensors functioning at temperatures close to room temperature.

1. Introduction
Nanostructured materials based on zinc oxide, due to their large specific surface and semiconductor properties, find applications in photocatalysis [1], gas sensors [2, 3], photovoltaic cells [4–7], and piezoelectric nanogenerators [8]. The use of zinc oxide in the form of filamentary nanocrystals is of special interest due to their high crystalline qualities and high charge carrier mobility.

Presently, gas sensors based on metal oxides generally operate at high temperatures (about 400 °C). The need for heating oxide gas sensors leads to an increase in energy consumption, which is unacceptable for stand-alone and mobile devices. A new approach to solve this problem is the replacement of heating by light irradiation [9]. The sensitization of zinc oxide nanostructures by colloidal quantum dots (QCDs) is promising for the use of optical and infrared radiation. The appearance of an electric current upon irradiation of the ZnO/QCDs structure can be a sign of the effective injection of charge carriers into the conduction band of zinc oxide, that is, the operation of this structure as a photovoltaic cell. In this paper, heterostructures of ZnO nanorods/PbS QCDs were fabricated. The colloidal quantum dots of lead sulphide were chosen due to their widely tuned band gap (0.71–1.28 eV) [10]. PbS QCDs with a band gap of 1.35 eV were also studied in this paper.

2. Experiment
The fabrication of ZnO-nanorod/PbS QCD heterostructures can be divided into three consecutive stages: the formation of ZnO seed layers, the synthesis of coatings based on ZnO nanorods by the low-temperature hydrothermal method, and the deposition of PbS colloid quantum dots. In this work, the seed layers were formed by the ultrasonic spray-pyrolysis method. The main advantage of this method is the simplicity of the equipment, which determines the low cost of the technology. The spray pyrolysis method is based on thermal decomposition of solution aerosols. The use of ultrasonic spraying, as a rule, leads to the creation of aerosols from smaller droplets, which ultimately leads to more uniform coatings. Thus, an aqueous solution of zinc acetate Zn(CH₃COO)₂·2H₂O with a concentration of 0.05 M was used as a spray solution. The temperature of the heating element was maintained at 380 °C. At present, the low-temperature hydrothermal method has become one of the
main methods for the synthesis of nanorods, since the use of alkaline reagents allows synthesis at temperatures below 100 °C and does not require complicated equipment. An aqueous solution with equimolar concentrations (0.025 M) of hexamethylenetetramine (HMTA) and zinc nitrate was used as a solution for the synthesis of ZnO nanorods. To form the ZnO–nanorods/PbS QCD structure, a dispersion of colloidal quantum dots was introduced onto ZnO nanorods by spin coating at 2500 rpm for 20 seconds.

3. Results and discussion
The morphology of a typical ZnO seed layer obtained by ultrasonic spray pyrolysis is shown in figure 1.

![AFM image of a seed layer obtained by ultrasonic spray pyrolysis](image)

The image shows that a uniform seed layer of zinc oxide consisting of ~ 30 nm crystallites with a small spread in height is formed.

Zinc nitrate serves as a source of Zn$^{2+}$ ions in the low-temperature hydrothermal method. HMTA, first of all, serves as a source of hydroxyl group OH$^-$, and secondly, it acts as a buffer, slowly releasing OH$^-$. The rate of hydrolysis of HMTA decreases with increasing pH and vice versa. However, nucleation in the bulk of the solution is observed in the synthesis process, which leads to the contamination of the sample surface, rapid depletion of the solution and, accordingly, a relatively low growth rate of nanorods. To suppress nucleation in the volume of the solution, ammonium hydroxide and polyethyleneimine were used. Ammonium hydroxide, forming complexes with zinc ions, reduces the degree of supersaturation in zinc, and polyethyleneimine molecules adsorbed on the nuclei due to the steric effect prevent the achievement of the critical size of ZnO nuclei, at which further growth becomes thermodynamically stable. So polyethyleneimine (0.005 M) and ammonium hydroxide (0.66 M) were added to the growth solution with equimolar concentrations (0.025 M) of HMTA and zinc nitrate. In this case, suppression of bulk nucleation and an increase in the growth rate of ZnO nanorods (figure 2 (b)) were observed.
Figure 2. SEM images of: a sample without suppression of bulk nucleation (a); a sample with suppression of bulk nucleation (b). The duration of the synthesis was 60 minutes.

Figure 2 shows that suppression of bulk nucleation leads to an increase in the length of ZnO nanocrystals by approximately 4 times. The shape of the nanorods also changes, which is due to the gradual depletion of reagents in the solution. The suppression of bulk nucleation also avoids the contamination of the growing ZnO nanorod arrays by agglomerates appearing in the solution.

The optical absorption spectrum of colloidal quantum dots is shown in figure 3.

![Optical absorption spectrum of colloidal quantum dots.](image)

Figure 3. Optical absorption spectrum of colloidal quantum dots.

The exciton peak of absorption of the PbS QCDs is ~ 920 nm, which corresponds to a band gap of 1.35 eV. To improve transport in the QCDs layer, long molecules of oleic acid were replaced with short ligands, which were tetrabutylammonium iodide (TBAI), because PbS QCDs were stabilized with oleic acid and dispersed in toluene. The solution of tetrabutylammonium iodide in methanol was introduced to the PbS layer by spin coating, followed by washing in methanol. With a different number of deposition cycles of colloidal quantum dots, the values of the short-circuit current changed. However, the values of the open-circuit voltage $V_{oc}$ remained almost unchanged (~ 50 mV). The SEM image of the sample with the highest value of the short-circuit current is shown in figure 4.
Figure 4. SEM image of the measured structure.

Figure 5. Schematic representation of the measured structure with clamping contacts.

Figure 4 shows that there is a second phase on the ZnO nanorods — the PbS QCDs. Measurement of the voltage-current characteristics of the heterostructure was carried out using clamping gold contacts (figure 5). One contact was fed to the layer of colloidal PbS quantum dots, and the second to the FTO coating.

The energy parameters of the measured structure are shown in figure 6. The electronic affinity for the FTO was adopted at 4.4 eV [11]. The electron affinity for ZnO in the direction (000-1), (0001) usually lies in the range 4.44 - 4.2 eV [12]. The value of the work function was adopted at 4.3 eV [13]. A value of the zinc oxide band gap was taken at 3.4 eV. The electron affinity for PbS usually takes the value of ~ 4.3 eV [7]. The position of the Fermi level is influenced by the type of ligands. So in [7] the position of the Fermi level was at 0.51 eV below the bottom of the conduction band in the case of using TBAI.

![Energy Diagram](image)

Figure 6. Energy parameters of the ZnO/PbS heterostructure materials.

The current-voltage characteristic of the sample showed that there is a nonzero current at zero voltage both under illumination and without illumination (figure 7).
Figure 7. Voltage-current characteristic of the heterostructure.

Generation of an electric current without illumination can be related to the background of infrared radiation. During illumination, the short-circuit current increased, while voltage remained unchanged at $V_{oc} \sim 50$ mV. Thus, the structure of ZnO-nanorods/PbS-colloidal quantum dots is sensitive to radiation in the optical and infrared regions of the spectrum.

4. Conclusion
The use of hydrothermal synthesis makes it possible to form dense arrays of zinc oxide nanowires that are promising for creating highly sensitive gas sensors. The heterojunction of ZnO nanorods / PbS-QCDs is designed to activate the gas sensitive layers operating at temperatures close to room temperature by irradiating the structure and injecting the charge carriers into the zinc oxide conduction band. Irradiation of the structure leads to an increase in the electron concentration in zinc oxide crystals and to an increase in its catalytic activity.

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