

# Cys-modified zinc oxide 1D-nanostructures formation for gas sensors application

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## Abstract

In this work, the ZnO-based materials were synthesized for gas sensors applications. The nanostructures formation was carried out by mild hydrothermal synthesis with the variations in surfactant concentration. The qualitative and quantitative analysis of the surface states in ZnO nanocrystals was performed. The effect of surfactant (cysteine) adsorption on ZnO 1D-nanostructures growth and the distribution of acid-base adsorption sites on nanostructures surface were investigated. The control of the nanorods aspect ratio (about 0.4 at cystein concentration of 5 mM/l) leads to the changes in the Zn<sup>2+</sup>/O<sup>2-</sup> ions proportion, emerging on the surface. High cysteine concentrations resulted in the formation of Brønsted acid and Lewis base adsorption sites.

**Keywords:** Zinc oxide ZnO, surfactants, cysteine (Cys), adsorption sites, gas sensors.

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## 1. Introduction

Nowadays intensive industry development results in increasing environmental pollution. One of the devices for the most effective monitoring of hazardous compounds are gas sensors. At present the design of gas sensor based multisensor systems of the “electronic nose” type is under active research [1]. In this case, simultaneous processing of the response of all sensors is impossible without the use of artificial neural networks. The learning opportunities in these systems play a key role due to the multidimensionality of the gas sensorics tasks.

The operation principle of the resistive gas sensor is based on the active layer conductivity changes in gas adsorption-

desorption processes on the surface. Metal oxide semiconductors (*n*- and *p*- type) are often used as an active layer of the gas sensors due to oxidation-resistivity. Various types nanostructures application allows increasing gas sensors sensitivity. Surface dangling bonds, structure defects, as well as adsorbed radicals, can act as adsorption sites. Thus, varying type and concentration of ions it is possible to change gas sensor selectivity [2].

Effective method for analysis of surface acid-base properties and quantitative identification of adsorption sites of different functional materials is based on adsorption of acid-base indicators [3-6]. Investigation of surface adsorption sites could be of interest to both assessing the interaction of surfactants with the surface of the nanostructures (when controlling morphology during synthesis process) and

predicting selectivity and sensitivity of resistive gas sensors active part.

To control the morphology of zinc oxide various complexing agents and surfactants like polyvinylpyrrolidone (PVP) [7], cetyltrimethylammonium bromide (CTAB) [8], polyethyleneimine (PEI) [9], polyvinyl sulfonic acid PVS [10] etc. are used. One of the surfactants of significant interest for use is cysteine, acting as a zwitterionic surfactant due to the presence of several functional groups. There are various articles dedicated to the Cys use for the ZnO nanoparticles and QDs stabilization in a solution [11-13], however, there are no data on its application for the surface modification of zinc oxide nanorods. In this paper, morphology changes and the types of adsorption sites of ZnO nanostructures was achieved by using cysteine, acting as a surfactant that adsorbs on the "solution-nanorod" interface.

The purpose of the present work was to study a cysteine influence on the morphology and distribution of the adsorption sites on zinc oxide nanorods obtained by hydrothermal method.

## 2. Experimental

Nanostructures formation was carried out via mild hydrothermal synthesis [14-17] at the low temperature ( $T=85^{\circ}\text{C}$ ) within 60 min. 25 mM hexamethylene tetramine was used as a weak alkali, while zinc nitrate equimolar solution  $\text{Zn}(\text{NO}_3)_2$  was a  $\text{Zn}^{2+}$  precursor. The pH of the growth solution at  $T=25^{\circ}\text{C}$  was 5.5.

$\text{Zn}^{2+}$  cations produced during the zinc salt hydrolysis react with the alkali  $\text{OH}^-$  anions forming various hydroxides:  $\text{ZnOH}^+$ ,  $\text{Zn}(\text{OH})_2$ ,  $[\text{Zn}(\text{OH})_3]^-$  and  $[\text{Zn}(\text{OH})_4]^{2-}$ . Due to the pyroelectric effect in ZnO seed crystallites, charged zinc hydroxocomplexes are adsorbed on the corresponding negatively charged oxygen grain  $\text{O}^{2-}$  and positively charged zinc  $\text{Zn}^{2+}$  grain with subsequent condensation in oxide form. Zinc hydroxide  $\text{Zn}(\text{OH})_2$  is not involved in the growth of 1D-nanostructures of ZnO, because of the charge absence. Nanostructures growth occurs along the  $6_v$  axis.

For the surface modification via surfactant molecules adsorption cysteine (Cys) with a 0.25 – 0.5 mM concentration was used. Upon synthesis completion samples were washed and dried at room temperature. Finally, obtained samples were annealed in a UV chamber (at a wavelength  $\lambda=253.7$  nm with a lamp power of  $P = 8$  W) for 5 hours to remove adsorbed Cys molecules removal from the nanorods surface.

Surface sites analysis of the obtained ZnO nanostructures was carried out via acid-base indicators adsorption method [18]. Weak organic acids and bases are used as indicators. During the indicators adsorption process a change occurred in the optical density of the solution is captured using the UV-Vis spectrophotometer (ECROSKHIM PE-5400UV) at a given wavelength (table 1).

Table 1. Data of indicators used in adsorption method

Indicators	pKa	$\lambda_{\text{max}}$ , nm
Methyl orange	3.46	460
Bromocresol purple	6.4	540
Brilliant green	1.3	610
Neutral red	6.8	540
Indigo carmine	12.8	610
Bromthymol blue	7.3	430
Rosaniline hydrochloride	2.1	540
Methyl red	5	430
Bromophenol blue	4.1	590
Thymol blue	8.8	430
Ethylene glycol	14.2	200

After calculating the concentration of the sites for all indicators, the distribution curve  $q = f(\text{pKa})$  was plotted. A detailed description of the experimental and calculation methods is given in [19, 20].

Obtained ZnO nanocrystals were investigated using scanning electron microscopy method (Quanta Inspect, FEI).

## 3. Results and discussion

Cysteine is an amino acid with a thiol, carboxyl and amine radicals (the structural formula is presented in fig. 1, a).

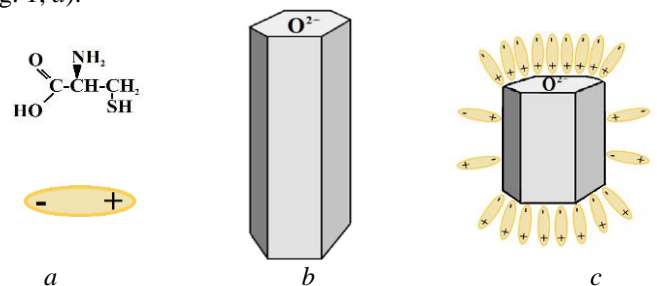


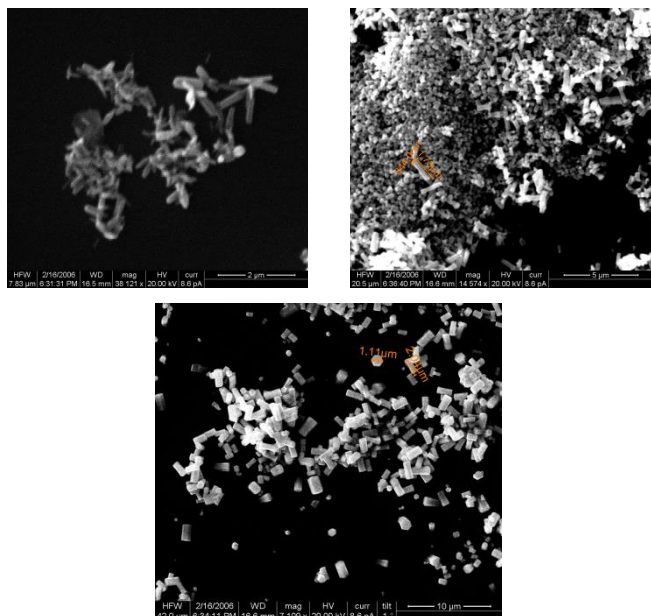
Figure 1. Cys molecule structural formula and the scheme on the growth scheme (a); the mechanism of nanorods growth in the absence (b) and in the presence of Cys (c)

Cysteine aqueous solution has buffer properties. At the solution pH corresponding to the initial solution for a mild hydrothermal synthesis at  $T=25^{\circ}\text{C}$  the ionization of amino ( $\text{NH}_3^+$ ) and carboxyl ( $\text{COO}^-$ ) groups occurs. Since the growth of ZnO nanostructures ends with  $\text{O}^{2-}$  ions (Fig. 1, b), an increase in pH value ( $\text{pKa}(\text{NH}_2)=10.25$ ) leads to the preferential diffusion of cysteine molecules to the (0001) faces and adsorption on their surface. Adsorbed cysteine molecules in growth solution can be represented as a dipoles combination (with  $\text{NH}_3^+$  and  $\text{COO}^-$  ionized groups) (Fig. 1, c).

With the  $\text{NH}_4\text{OH}$  addition into the initial solution (which leads to alkaline medium formation) the ZnO nanorods are faceted with  $\text{Zn}^{2+}$  edge. The radical ionization occurred at the solution pH reaches  $\text{pKa}(\text{COOH})=2.05$  and

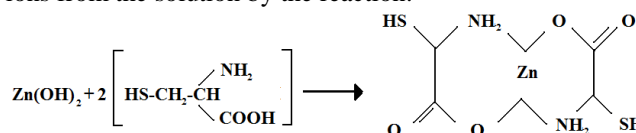
$pK_a(SH)=8.0$ . Accordingly, using a solution with  $pH > 8.0$  also deteriorates aspect ratio.

Microphotographs of ZnO nanorods obtained at different concentrations of Cys in a weak-acid solution ( $pH = 5.5$ ) are shown in Fig. 2.



**Figure 2.** ZnO nanorods obtained in the presence of Cys with the concentration: a – 0.25 mM, b – 1 mM, c – 3 mM

Decrease in nanostructures coating density on a substrate with an increase in the cysteine concentration can be associated with the gelation reaction and the capture of zinc ions from the solution by the reaction:



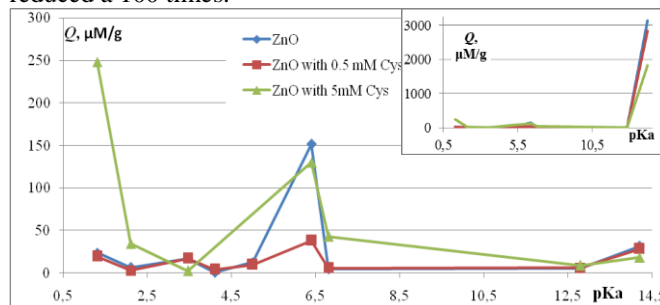
Since the thiol radical in the weak-acid solution is not ionized, cysteine molecules have a large hydrophobicity coefficient (+ 2.5), which can also prevent the diffusion of ions to nanostructures. The structures obtained during the synthesis have a clearly viewed hexagonal cut, with with decreasing of average aspect ratio (ratio of the diameter  $D$  to length  $L$ ) with Cys concentration increasing (table 2).

Table 2. The dependence of the ZnO nanorods aspect ratio on the Cys concentration

Cys concentration, mM/l	Mean aspect ratio ( $D/L$ )
0	0.14
0.25	0.16
0.5	0.18
1	0.2
3	0.38

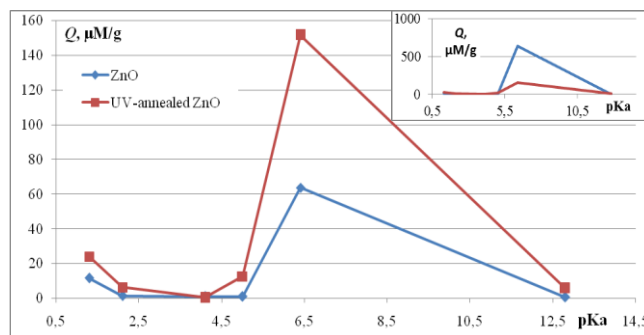
5	0.46
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The results of Cys modified zinc oxide nanorods adsorption sites investigation are presented in Fig. 3. For a visibility, the scale of the peaks corresponding to the  $pK_a=14.2$  is reduced a 100 times.



**Figure 3.** Distribution curves of acid-base sites on the ZnO nanostructures surface obtained at different Cys concentrations (on the insert are shown distribution curves without scaling peaks)

The observed significant changes in the sites distribution (shift into the Brönsted acids area) indicates the preferential effect of adsorbed cysteine. Annealing samples under the UV irradiation leads to a significant decrease in the hydroxyl groups concentration on nanostructures surface compared with the non-annealed samples (Fig. 4).

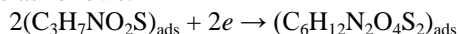


**Figure 4.** Distribution curves of acid-base sites on the ZnO nanostructures surface obtained in the Cys absence (on the insert are shown distribution curves without scaling peaks)

Zinc atoms prevail on the such samples surface, which corresponds to the sites with  $pK_a=14.2$ . This indicates a low surface filling degree with  $OH^-$  groups. With 0.5 mM Cys addition the concentration of sites with  $pK_a=6.4$  decreases, while there is no significant surfactant influence on other sites types. Increasing the Cys concentration to 5 mM leads to a significant increase in the concentration of Brönsted acid sites and a decrease in the concentration of Lewis acid sites. The concentration of sites with  $pK_a=6.4$  increases and becomes closer to the value characterizing the ZnO nanostructures obtained without the Cys addition.

In general, the obtained ZnO nanostructures adsorption sites distribution is typical for most oxides [19]. Analyzing zinc oxide, it should be noticed that  $Zn^{2+}$  atoms in ZnO lattice correspond to acid Lewis sites and  $O^{2-}$  atoms with filled electronic shell, capable to attach proton or Lewis acid correspond to basic Lewis sites. Our experiments have shown that high Cys concentrations result in the formation of Bronsted acid and Lewis base sites.

Under UV irradiation free charge carriers are generated in the ZnO nanostructures. Charge carriers interaction with surfactant adsorbed molecules leads to oxidation of cysteine to cystine as follows:



ZnO role lies in the charge transport to the cysteine adsorbed molecules. Besides, cystine newly formed molecule can act as adsorption center with pKa less than 2.5.

The dimmers obtained on the ZnO nanostructures surface can degrade to  $CO_2$  and  $NH_4$  under continuous thermal and UV treatment. At the same time, sulfide radicals remain on the ZnO nanorods surface.

## Conclusion

ZnO nanostructures were formed in the presence of cysteine to control the morphology of the crystal, type and concentration of adsorption sites. As our experiments have shown, increasing the Cys concentration the aspect ratio decreases and the concentration of Bronsted acid sites increases. The concentration of Lewis base sites is sufficiently decreased with the Cys concentration increase. Obtained results can be useful for regulating the selectivity of resistive gas sensors based on oxide nanostructures.

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