Zinc oxide hierarchical nanostructures for photocatalysis

O Yukhnovets, A A Semenova, E A Levkevich, A I Maximov, V A Moshnikov

Department of Micro- and Nanoelectronics, St Petersburg Electrotechnical University "LETI", Saint-Petersburg 197376, Russia

E-mail: iuhnovec@gmail.com

Abstract. In this work, we perform the study of zinc oxide hierarchical structures synthesized by the low-temperature hydrothermal method. The paper considers morphological properties of obtained structures. Photocatalytic activity of samples was analysed by methyl orange degradation under UV irradiation. The sufficient decrease in methyl orange has been demonstrated.

1. Introduction
The topic of water and air environment purification from organic impurities is currently relevant. A great alternative to classical refining methods is the photocatalysis [1]. This process can be described as the change of chemical reactions rate under the light excitation in the presence of the photocatalyst which is involved in chemical transformations of the reaction participants [2].

Among the wide variety of materials for photocatalytic performance zinc oxide (ZnO) can be emphasized on due to the ecological safety of formation and utilization, technological ease of preparation [3]. In comparison with the widespread titanium dioxide (a wide bandgap semiconductor with $E_g = 3.0-3.3$ eV [4]), zinc oxide ($E_g = 3.36$ eV) is characterized by a higher quantum yield of phototransformation, which is associated with a low degree of charge carriers recombination and high adsorption capacity [1].

In the transition to nanoscale conditions the activity of photocatalytic materials increases. This effect is achieved by increasing the specific surface area and reducing the recombination of charge carriers [3].

With the use of wet chemistry techniques it is possible to obtain different morphologies of ZnO nanostructures: nanoneedles, nanobelts, nanodendrites et al [5]. In this paper, porous zinc oxide nanospheres consisting of 2D-plates were synthesized. These structures are characterized by developed surface and enhanced photocatalytic properties.

2. Experimental section

2.1. Synthesis of ZnO hierarchical structures
Zinc oxide was synthesised under mild hydrothermal conditions. Adjusting pH of a solution, temperature and precursor concentrations it is possible to change the morphology of a structure in a wide range. Among other methods, soft surfactant templating proved to be an effective approach for tailoring complex 3D hierarchical structures via oriented self-assembly of nanobuilding sub-units [6, 7].
To synthesize zinc oxide hierarchical structures (ZnO HSs) 0.5 ml of 0.5 M zinc nitrate solution (Zn(NO$_3$)$_2$$\cdot$6H$_2$O) was mixed with 30 ml distilled water containing 0.5 g of cetyl-trimethyl-ammonium-bromide (CTAB), followed by adding 5 ml of NaOH solution. The concentration of NaOH solution was estimated on the assumption of $[\text{Zn}^{2+}]:[\text{OH}^-]=1:10$ ratio. The solution was mixed in an ultrasonic bath (100 W), vigorously stirred for 5 minutes and transferred to the thermostat (90$^\circ$C) for 2 hours. Products were collected by centrifugation and washed for 3 times in distilled water. ZnO powder then was dried at 80$^\circ$C and annealed at 350$^\circ$C for 20 minutes.

2.2. Photodegradation experiment
To perform photodegradation reaction 10 ppm solution of methyl orange was mixed with photocatalyst and stirred in the dark for 1 hour to reach adsorption-desorption equilibrium between dye and ZnO HSs. The suspension was placed under UV irradiation. To analyse changes of methyl orange concentrations adsorption spectra of a solution were taken at regular time intervals.

3. Results and discussion

3.1. Morphology of ZnO hierarchical structures
Under hydrothermal conditions, ZnO tends to form one-dimensional structures due to the greater growth rate of (0001) plane [6]. It is possible to achieve the formation of complex 3D-nanostructures by adjusting synthesis conditions (temperature, precursor concentrations, growth time, pH), using surfactants as a soft template or applying ultrasonic irradiation.

Figure 1 (a, b) demonstrates the results of synthesis in alkaline media with polyvinylpyrrolidone (PVP). Figure 2 shows the structures obtained under ultrasonic irradiation.

![Figure 1. SEM images of ZnO HSs structures grown with PVP.](image1)

![Figure 2. SEM images of ZnO HSs grown under ultrasonic irradiation.](image2)
Within the frame of this work the formation and photocatalytic properties of ZnO HSs synthesized with CTAB were considered in details.

Figure 3 (a, b) shows scanning electron microscopy of hierarchical ZnO nanostructures. It is seen that structures appeared to be porous spheres composed of 2D petals merged by the oriented self-assembly process. The exact formation mechanism of hierarchical structures is still undefined. However, it is assumed that the driving force for nanocrystals assembly is the anisotropic hydrophobic attraction and electrostatic interactions derived from surface charges.

At the first stage, the formation of ZnO clusters (30-40 atoms) occurs. Clusters are stabilized by CTAB micelles and aggregate into plates merging to form spherical structures in order to minimize surface energy. Hence, CTAB acts as a coordinating agent for colloidal nanoclusters and enables to grow oriented nanostructures by simple wet chemistry methods [7].

![Figure 3. SEM images of ZnO HSs grown with CTAB.](image)

3.2. Photocatalytic activity

It is expected that zinc oxide hierarchical structures are to demonstrate enhanced photocatalytic properties due to unique morphology that provides high surface-to-volume ratio, inhibits charge carriers recombination and powder aggregation.

In order to activate the photocatalytic process, the amount of energy should be equal or more than the band gap energy of photocatalysts, so that the electrons of valence band can be excited and moved to the conduction band. This energy is the minimum threshold intensity of radiation for activating and starting the photocatalytic process.

The idea of photocatalytic oxidation is to convert hazardous organic dyes to harmless or less harmful intermediates. The last stage of oxidation is a conversion of organic dye to carbon dioxide and water.

In this paper, the photocatalytic activity of ZnO HSs was analysed by degradation of methyl orange dye under UV irradiation. In order to perform photocatalytic reaction 80 mg of photocatalysis were mixed with 10 ppm methyl orange solution. To analyse changes of methyl orange concentrations adsorption spectra of a solution were taken at regular time intervals. Figure 4 shows the degradation process of dye with the presence of ZnO HSs under UV irradiation. Spectra reveal a feature at 360 nm which corresponds to ZnO nanoparticles adsorption band. It can be seen that methyl orange concentration has sufficiently decreased during the photocatalytic reaction. Besides, the colour of a solution changed from orange to almost clear. This result indicates a great perspective of zinc oxide hierarchical structures for photocatalytic applications.
4. Conclusions
Applying such approaches as pH changes, surfactant addition, ultrasonic irradiation enables to obtain complex structures with high surface-to-volume ratio. In this paper, we discuss the formation of 3D hierarchical structures by simple low-temperature hydrothermal synthesis with CTAB surfactant added. It is assumed that ZnO colloidal clusters are stabilized by CTAB micelles and aggregate into spheres by oriented self-assembly. The developed morphology of synthesized structures is expected to enhance photocatalytic properties of ZnO. In our experiments, the sufficient decrease in methyl orange dye concentration during photocatalytic reaction has been demonstrated.

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