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Human and Animal Physiology

Photocatalytic Activity and Environmental Toxicity of ZnO Microcrystals with Different Morphologies

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This paper deals with the rising problem of water purification using the catalyst-assisted photodegradation process. The catalytic activities of ZnO microcrystals with different morphologies were studied. ZnO microcrystals, microspheres and hexagonal disks were used for the photocatalytic degradation of Methylene Blue dissolved in water. It was found that the degradation rate of ZnO depends not only on the specific surface area of the catalyst but also on the total area of chemically active crystal planes, which are exposed to the light source. For the water solution of Methylene Blue with the concentration of 100 mg/L, the photodegradation rate was highest (~50%) when the hexagonal ZnO disks were used as catalysts. Environmental toxicity of the developed nanomaterials in comparison with Ni-Cu magnetic nanoparticles usually utilized for the magnetic hyperthermia was tested using continuous monitoring of behavioral and physiological parameters of white rats exposed to injections of dispersions of ZnO microcrystals in saline solutions. *© 2022 Bull. Georg. Natl. Acad. Sci.*

ZnO microcrystal, microsphere, hexagonal disk, photodegradation, acute toxicity

Zinc oxide is a remarkable semiconductor, which finds multifunctional applications because of its unique optical and electronic properties [1,2]. Besides, it has long been known that ZnO possesses excellent biocompatibility, antimicrobial, antibacterial and catalytic activity [3-6]. The last item is quite important for environmental protection and human needs, as it enables the effective purification of water by photocatalytic degradation of pollutants. The application of micro- and nanodispersed ZnO materials further enhances their functionality due to the increased activity and the appearance of new, nano-size-related properties. The morphology of nano- and microparticles also has a great influence on their physical and chemical properties [7-9].

The purpose of this work was to study the morphology of vapor synthesized ZnO microcrystals, and to evaluate their photocatalytic activity and toxicity.

Experimental

The micro- and nanocrystals were grown using the pyrolytic technology, based on the application of

gaseous products, formed after thermal decomposition of ammonium chloride. After reacting with Zn and ZnO source powders the volatile precursors were produced, which provided the mass transfer to Si substrate, located in the cold zone of the quartz reactor and heated up to 410°C. More details on the developed technology can be found elsewhere[10]. ZnO crystals with different morphologies were produced depending on the growth time and substrate temperature.

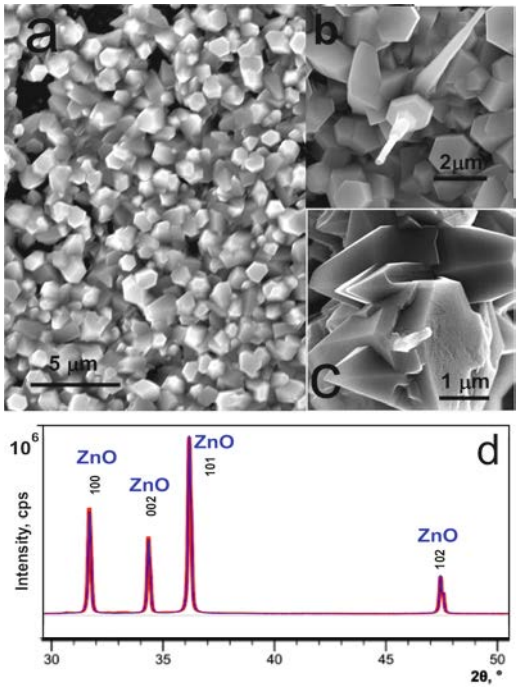

Fig. 1. Plane view SEM image of ZnO microcrystals (a); Nanowire growing on the tip of MC (b); enlarged view of MC (c); the background subtracted XRD pattern of MC (d).

For the evaluation of catalytic activity, the deposited ZnO was scratched off the substrate and mixed in the dark with the solution containing the known concentration of Methylene Blue. The concentration of catalyst in the solution was kept at 100 mg/L. The suspension was irradiated with Xe lamp ДКсШ-50 during the pre-defined time and distance of 20 cm, then placed in the quartz cuvette and analyzed its optical absorbance at λ=664 nm wavelength using UV-Vis spectrophotometer СФ-26. The photodegradation (photodecolorization) rate was calculated as: $R(t)=[1-(A(t)/A(t_0)]\times100\%$, where $A(t)$ and $A(t_0)$ are the absorbance values at time t and t_0 respectively.. The value of R(t) is in fact equivalent to the mole percentage of degraded Methylene Blue. The details of the measurement are described in [11,12].

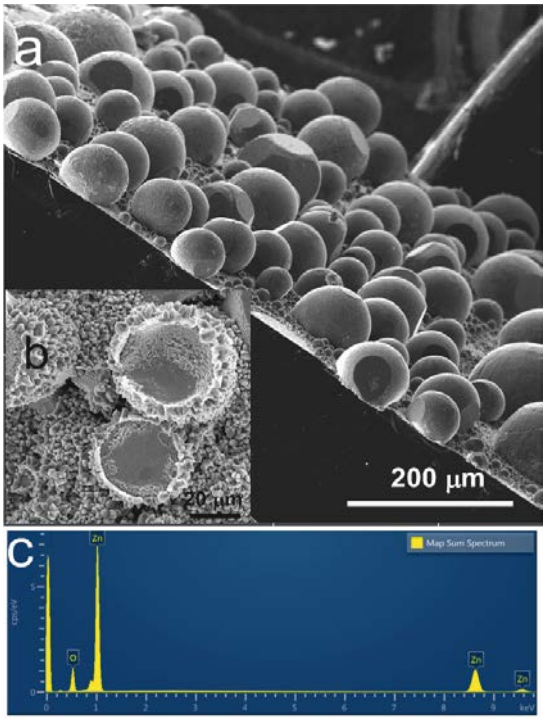

Fig. 2. The cross-sectional view of ZnO microspheres (a); SEM image of hollow and partially filled microspheres (b); EDS spectrum of microspheres (c).

The structure and morphology of ZnO crystals were studied by XRD method on Rigaku SmartLab-10 instrument and on Scanning Electron Microscope (SEM, Tescan Vega-3 XMU) equipped with Oxford Systems Energy Dispersive Spectrometer (EDS).

Taking into account the environmental application of the developed materials a proper attention was given to laboratory testing of the acute toxicity of developed microcrystals against the white rats by means of a long-term (14 days) continuous observation of a number of behavioral (number of mistakes and decisions, total time of passage through the maze, time intervals spent in the dark and lighted parts of the maze) and

physiological (blood pressure, body temperature, blood oxygen saturation) parameters of the exposed test animals passing through the elevated branched maze [13, 14] in comparison with $Ni_{0.7}Cu_{0.3}$ spherical nanoparticles [14].

Results and Discussion

The SEM image of ZnO microcrystals (MC) produced in the initial growth stage is presented in Fig 1. The layer comprises elongated prisms with distorted hexagonal cross sections. The mean sizes of crystals are 1.7 micrometer. On the top of several microcrystals the secondary growth of one dimensional nanowires with diameters close to 100 nm are observed (Fig. 1 b). The tapering of crystals can be clearly seen in Fig. 1 c. XRD pattern of produced layer matches with the standard PDF Card No.:01-070-8072 of a pure hexagonal ZnO (Fig. 1 d). As it is well known, for hexagonal ZnO the fastest growing facet is the (001) basal plane. This Zn terminated plane also has the highest chemical activity and the highest surface energy (σ=2.0 J/m^2), while the prism planes are characterized by low energy (σ=1.2 J/m^2 for (100) plane) and low chemical activity [15]. In the kinetically controlled fast process, the growth proceeds along the *c*–axis, which is perpendicular to the basal plane, and causes the vanishing of this plane. As a result, the elongated and tapered ZnO microcrystals are growing on the substrate. The tapering of ZnO microcrystals, depicted in Fig. 1 c, is a manifestation of a high growth rate that was achieved by using the developed technology.

ZnO microspheres (MS) were the second type of material selected for the evaluation of the catalytic activity. The morphology of MS is shown in Fig.2 a,b. The diameters of microspheres vary in a wide range beginning from single micrometers up to 90 μm. The XRD pattern of this material coincides with that of microcrystals, which was discussed above. The EDS spectrum of MS is presented in Fig. 2 c. The ratio of Zn and oxygen atomic contents is close to unity, once again indicating the formation of stoichiometric ZnO microspheres. Some of MS are hollow or partially filled with ZnO, as it is shown in Fig. 2.b. The mechanism of their formation was explained in [10].

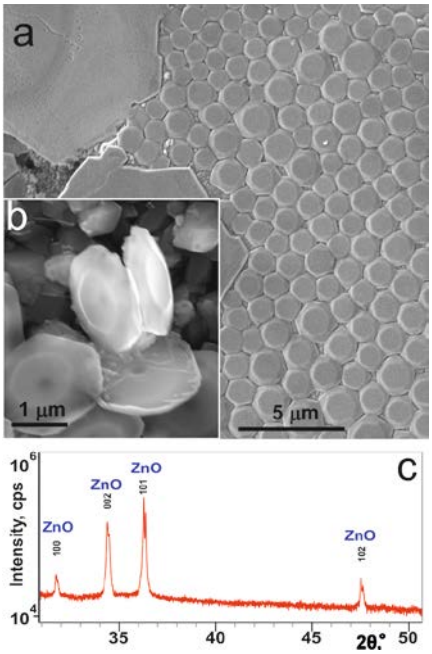

Fig. 3. SEM image of hexagonal ZnO disks (a) and their enlarged view (b); XRD pattern of the layer formed by hexagonal ZnO disks (c).

The third morphology that was analyzed in our experiments was material, consisting of ZnO plane hexagonal disks (HD) presented in Fig. 3 a, b. The diameters of disks were in the range of 1.5 μm, while their thickness was approximately 100 nm. The disks were growing together with microcrystals. However, the coverage of Si surface by disks was higher, reaching~80%. In some regions of the substrate the disks formed the regular, self organized layer, which is shown in Fig.3 a. The comparison of XRD patterns of MC and plane disks (Fig.3 c) clearly shows the increase of the (002) plane-related peak, indicating a predominance of the basal plane in the produced layer.

Fig. 4 presents the results of our experiments on the photodegradation (decolorization) of

Methylene Blue using ZnO with different morphologies. As we outlined previously, the illumination was performed using the Xe lamp, which has an emission spectrum close to the natural sunlight. The first measurement was performed after 10 minutes of irradiation, while the following measurements were done with 15-min interval. The cumulative exposure time was 100 min. For all samples the photocatalytic activity increases with time and then reaches a saturation value after approximately 70 minutes of exposure. The observed saturation in catalytic decomposition may be related to the breakdown of ZnO in the water based solution [16].

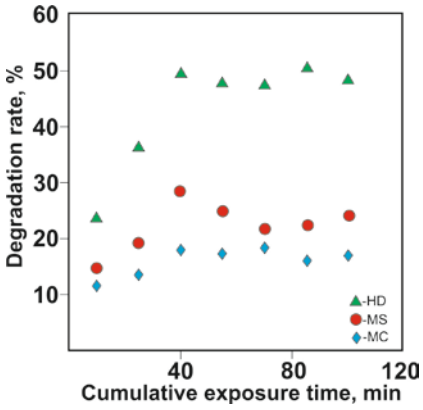

Fig. 4. The dependence of the photodegradation rate on the cumulative UV light exposure time.

According to Fig. 4 the hexagonal ZnO disks have the highest photocatalytic activity, followed by the activities of microspheres and microcrystals. This is consistent not only with the values of the specific surface areas of analyzed materials but also with the chemical activities of different crystal facets. The closely packed hexagonal disks (Fig. 3 a) have the lowest specific surface area among other microstructures. However, the high chemical activity of basal planes of HD prevails over the low surface area and yields the highest catalytic activity. Comparing the activities of MC and MS materials, it should be noted that both of them have the same crystal structure with the same percentage of exposed crystal facets. Nevertheless, the specific surface area of microspheres, particularly those with hollow and semi-filled inner spaces (Fig. 2 b), is higher than that of the microcrystalline layer. This causes the observed slightly higher catalytic activity of MS in comparison with MC.

Conclusions

ZnO microcrystals with three distinct morphologies were studied for the catalytic decomposition of Methylene Blue dissolved in water. The photodegradation was performed by irradiating the solution with UV lamp, having the emission spectra close to the natural sunlight. The photodegradation experiments revealed that, in spite of a small specific surface area, the hexagonal ZnO disks with exposed (001) basal planes had the highest catalytic activity, with the degradation rate close to 50%. Such a high rate was caused by the chemical activity of the basal plain in comparison with other planes. The degradation rate of ZnO microspheres and microcrystals slightly differ from each other and was approximately 20%. The saturation of the photodegradation process was observed for all samples, which was explained by the degradation of ZnO itself, caused by the prolonged UV light illumination.

The determined acute toxicity of all tested microcrystals within the experimental error (8-11 %) was practically equal to the acute toxicity of $Ni_{0.7}Cu_{0.3}$ spherical magnetic nanoparticles.

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ადამიანისა და ცხოველთა ფიზიოლოგია

სხვადასხვა მორფოლოგიის მქონე თუთიის ოქსიდის მიკროკრისტალთა ფოტოკატალიტიკური აქტივობა და ტოქსიკურობა

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**აკადემიის წევრი, ივანე ბერიტაშვილის ექსპერიმენტული ბიომედიცინის ცენტრი, თავის ტვინის სისხლის მიმოქცევის და მეტაბოლიზმის განყოფილება, თბილისი, საქართველო
§ივანე ჯავახიშვილის თბილისის სახელმწიფო უნივერსიტეტი, ე. ანდრონიკაშვილის სახ. ფიზიკის ინსტიტუტი, თბილისი, საქართველო

ნაშრომი ეხება დაბინძურებული წყლის გაწმენდას კატალიზატორით გამოწვეული ფოტოდეგრადაციის მეთოდით, რაც მზარდ პრობლემას წარმოადგენს. შეფასებულია ZnO–ს მიკრონაწილაკების, მიკროსფეროებისა და ჰექსაგონალური ბრტყელი დისკების ფოტოკატალიტიკური აქტივობა მეთილენის ლურჯის 100მლ/ლ კონცენტრაციის წყალხსნარის ფოტოდეგრადაციისთვის. ფოტოდეგრადაციის სიჩქარე მაქსიმალური (~50%) იყო ჰექსაგონალური თუთიის ოქსიდის დისკების გამოყენებისას. ZnO-ს მიკრომასალების ტოქსიკურობა შეფასდა მათი თეთრი ვირთაგვების სისხლში ინიექციისა და შემდგომი ქცევითი და ფიზიოლოგიური პარამეტრების შესწავლით. შედეგები შედარდა კიბოს მაგნიტური ჰიპერთერმიისთვის ფართოდ გამოყენებული Ni-Cu მაგნიტურ ნანონაწილაკების ტოქსიკურობას.

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