MICROWAVE-ASSISTED SYNTHESIS OF CERIUM DOPED ZNO NANOSTRUCTURES AND ITS OPTICAL PROPERTIES

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Abstract In this research we attempted to synthesize zinc oxide nanostructures doped with REE cerium by microwave-assisted method. The article presents the results obtained with different pH values of the processed solutions, the time of exposure to microwave irradiation, as well as the results of the application of cyclic irradiation exposure. Samples studied by fluorescence spectroscopy and scanning electron microscopy.

1. Introduction

Synthesis of nanoparticles with desired geometric parameters and the respective physical and chemical properties have great scientific importance. One of the most popular materials for producing nanoparticles in the scientific community is a wide gap (3.37 eV), zinc oxide semiconductor. In recent years, a growing number of works devoted to the doping of zinc oxide nanoparticles with rare earth elements due to 4f levels of REE³⁺ shielding which causes the narrow optical transitions. One of such rare-earth elements is cerium, which oxide is well known for its optical properties in UV region. Polymer nanocomposites with zinc oxide nanoparticles containing cerium oxide were used to remove organic pollutants from industrial wastewater [1, 2].

Nevertheless, at the moment there is a lack of scientific research on the synthesis of cerium-doped zinc oxide nanoparticles. Perhaps because of the large number of geometric variations as a zinc oxide - nanoparticles, wires, tubes, rings, spirals / springs, etc. or a variety of synthesis methods such as laser or chemical vapor deposition, catalysis-driven molecular beam epitaxy, thermal evaporation, sonochemical method, electrochemical deposition [3], etc.

At the moment, the most popular is the hydrothermal method with various additives such as organic additives, such as organic ones PVP, PEG, SDS and CTAB [4] to control the morphology and growth of nanostructures but their exact working mechanism guiding the growth of ZnO is still under discussions. Microwave synthesis is a relatively young method, but it is much cheaper and safer, both for the environment and for scientists than any other method. The only problem is to get optimal conditions for synthesis such as pH, solvent, additives, irradiation power and time [5, 6].

In our research we used a microwave method assisted with ultrasound and report an optical properties of nano and microparticles of ZnO doped with cerium for three different pH values, two dopant concentration and irradiation time and cyclicality.
2. Experiment
All chemicals were analytical grade reagents, and used as received without further purification. The required amount of zinc acetate dihydrate (Zn(CH₃COO)₂·2H₂O, Sigma-Aldrich 99.9%) and cerium(III) acetate hydrate (Ce(CH₃COO)₃·xH₂O Sigma-Aldrich) were used for the preparation of the Ce-doped ZnO nanoparticles. According to dopant’s concentration salts mixtures were dissolved in 100ml of distilled water by sonication for 30 min (42 kHz, 60W). The final solution was adjusted to alkaline conditions (pH 9.5; 10.0; 10.5; 11.0) by adding dropwise 8.5-10 ml of aqueous ammonia solution during mixing.

The obtained solutions were separated and irradiated in a microwave oven at 200 W, with different irradiation times of 5, 10, 15 min. Several solutions were irradiated cyclically by interval exposure for 10/20 sec power on/off.

Microwave-treated solutions were studied by fluorescence spectroscopy (Shimadzu RF5301), and also applied by spincoating method onto silicon wafers and examined by electron microscopy (Tescan MIRA3). Origin Labs 8.1 software was used for data processing.

3. Results and discussion
The use of microwave irradiation allows to obtain fluorescent nanoparticles in a short period of time (~1 hour). PH, exposure time and microwave power have a significant effect on the product of the synthesis – it could change optical properties and morphology. The structure of a wurtzite consists of two close-packed hexagonal structures with the positions t₁ = (0, 0, 0) and t₂ = (0, 0, s/2) occupied by different atoms. It creates variations in the position of the cerium atom in the zinc oxide standard, affecting energy transitions. Emission spectra found in the literature [7], however, shows only two peaks in cerium emission located in the region of 395-400 nm and 425-430 nm in UV and one single wide peak for cerium in visible region with a maximum of about 480-500 nm. It could be explained in the case of crystals doped with the Ce⁺³ ion, excitation bands corresponding to the excited 5d states of the ion and emission bands corresponding to transitions from the lowest 5d level to the 2F₅/₂ and 2F₇/₂ ground states.

We found a hypsochromic displacement of the luminescence bands to 360 nm and 380 nm (fig.1) respect to the values found in the literature but in case of 2% doping (fig. 1 a) a broad peak of fluorescence of 350-480 nm with a pronounced maximum of 420 nm and a shoulder of 385 nm was obtained.

Fig.1 Emission spectra of doped zinc oxide with cerium:
a) pH 9.5 cycled irradiation 10 min (1), 5 min (2); 2% of dopant (3)  b) pH 10.3 10min (1) and pH 9.7 15 min cycled irradiation (2) and permanentt irradiation for pH 9.7 (3), pH 10.3 (4)
Previously we examined the effect of high concentrations of dopant [8], which showed parabolic dependences on the increase in the number of REE ions. An increase in dopant leads to an intense precipitation of its own oxide precipitate, which in turn can be solved by adding various precursors, such as glycols or MEA.

The fact of a 2.5-fold increase in photoluminescence with an increase of the irradiation from 5 to 10 min was established. Also according to the fluorescence spectra, we can conclude the great contribution in increasing the value of pH emissions, while the cyclical emission although is insignificantly compared to the alkalinity of the solution. Thus, the amount of NP’s emission from the solution treated with 9.5 pH constant radiation 80 r.u. (fig 1b (3)), as in the case of cyclic exposure of 10 seconds every 20 seconds is about 410 r.u.(fig.1a (1)).

Samples with the strongest fluorescence intensity at zinc oxide area were selected for morphology studies by SEM (Fig 2). Sample #1(15 min irradiation, pH=9.7) has the strongest fluorescence intensity at zinc oxide emission area – 420 r.u.. In this pattern, we see the presence of different structures: 2 μm width aggregates of rods with directional growth along one plane and chaotic growth in the form of coral (fig. 2a), 350nm diameter rods forming crosshairs (fig. 2b) and the structure consisting of several rods of different diameters (fig. 2c).

For the sample #2 (5 min cycled irradiation, pH=9.5) with almost twice lower than sample #1 emission the porous (~3μm diameter) material with a small claster of zinc oxide rods on the edge of pore was obtained (fig 2 e). Irradiated for 10 min sample #3 (pH=10.3) showed us a sponge-like material [9] with 5 μm length aggregates.

4. Conclusions
Synthesis of nanostructures of zinc oxide doped with cerium using microwave radiation was achieved in a solution of cerium and zinc oxalates in the treatment with radiation for 15 minutes in alkali (pH = 9.7). Structural characteristics are very heterogeneous, particles easily aggregate, rods form structures with different growth directions and different numbers of particles involved. Possibly, the introduction of precursors glycol type aggregation and reduce the overall uniformity of the structures.
A shorter radiation effect on samples leads to the formation of porous structures with a decrease in fluorescence intensity, while it is significantly higher than the pH of solutions, but it is known from the literature that an increase in the formation of zinc hydroxide in solution entails an increase in the number of building blocks for nanostructures and leads to increase their length. Cyclical effects of microwave radiation, apparently, help to reduce the total time of exposure to radiation on the sample.

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6. References

[1] U.K. Gautam, L.S. Panchakarla, B. Dierre, X.S. Fang, T. Sekguchi, Y. Bando, D. Golderg, C.N.R. Rao, Adv. Funct. Mater. 19 (2009) 131.

[2] S.S. Warule, N.S. Chaudhari, B.B. Kale, K.R. Patil, P.M. Kainkar, M.F. More, R. Murakami, J. Mater. Chem. 22 (2012) 8887.

[3] H.N. Chandrakala B, Ramaraj , Shivakumaraiah , Siddaramaiah . Optical properties and structural characteristics of zinc oxide Aceriumoxide doped polyvinyl alcohol films Plastics Rubber and Composites 2015 44(1):33-39.

[4] M.A. Borik, S.I. Bredikhin, V.T. Bublik, A.V. Kulebyakin, I.E. Kuritsyna, E.E. Lomonova, F.O. Milovich, V.A. Myzina, V.V. Osiko, P.A. Ryabochkina, S.V. Seryakov, N.Yu. Tabachkova. Phase composition, structure and properties of (ZrO2)1-xy(Sc2O3)x(Y2O3)y solid solution crystals (x=0.08-0.11; y=0.01-0.02) grown by directional crystallization of the melt. // Journal of Crystal Growth, 2017, Vol. 457, pp. 122-127.

[5] Jacek Wojnarowicz, Tadeusz Chudoba, Stanislaw Gierlotka and Witold Lojkowski, Effect of Microwave Radiation Power on the Size of Aggregates of ZnO NPs Prepared Using Microwave Solvothermal Synthesis, Nanomaterials 2018, 8(5), 343.

[6] Michel J Rossi, Riccardo Iannarelli, F. Weiss, Hinrich Grothe, Metastable Nitric Acid Trihydrate in Ice Clouds, Angewandte Chemie International Edition, 2016.

[7] Ting Lin, Ling Cong Fan, Zhi Bin Xu, Ying Shi, Jian Jun Xie, Lian Yun Deng, Yu Ying Ren. Fabrication and Luminescent Properties of Translucent Ce$^{3+}$:Lu2SiO5Ceramics by Spark Plasma Sintering, Advanced Materials Research, Vols. 295-297, pp. 1300-1304, 2011.

[8] Shulga Aleksandra, Butusov Leonid, NagovitsynIlia, Chudinova Galina, Hayrullina Indira, Kurilkin Vladimir, Kochneva Margarita. NANOCON 2017 - Conference Proceedings, 9th International Conference on Nanomaterials - Research and Application. 2018. 152-156.

[9] Ayca Bal-Ozturk, Oksan Karal-Yilmaz , Zeynep Puren Akguner, Soner Aksu, Arzu Tas, Hulya Olmez, Sponge-like chitosan-based nanostructured antibacterial material as a topical hemostat, J. Appl. Polym. Sci. 2019.