Report

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on the materials presented for participation in the competition for the academic position "Associate Professor" in Natural sciences, mathematics and informatics, professional field 4.2. Chemical Sciences (scientific specialty "Solid State Chemistry, nanomaterials and minerals")

1. General presentation of the procedure

This Report is prepared in response to Order № РД-09-28/12.02.2021 and Order № РД-09-35/18.02.2021, issued by the Director of the Institute of Mineralogy and Crystallography, Bulgarian Academy of Sciences (IMC-BAS), following the decision made by the Academic Jury that was held on 23.02.2021.

The only candidate in the competition for "Associate Professor" announced in the State Gazette, issue 106, December 15, 2020 is Assistant Professor Katerina Lubomirova Zaharieva, PhD from the Institute of Catalysis.

The materials presented by Assistant Professor Katerina Zaharieva for participation in the competition fully meet the requirements of the Development of Academic Staff in the Republic of Bulgaria Act (DASRB), the Rules for the Application of the Development of Academic Staff in the Republic of Bulgaria Act, the Rules of BAS and with the Rules set at the Institute of Mineralogy and Crystallography, Bulgarian Academy of Sciences.

2. Applicant's research activity.

The results of the research activity of Assistant Professor Dr. Katerina Zaharieva, have been developed within 13 research projects, of which 9 with national funding from the National Science Fund, 1 under the Operational Program "Human Resources Development" 2007 - 2013 of the European Social Fund, 2 funded by University of Mining and Geology "St. Ivan Rilski" and 1 with internal funding from BAS, headed by Dr. Zaharieva. They are summarized and described in 69 scientific publications, 29 of which are in journals with ISI "impact factor", and 3 in journals only with "impact rank". Among the journals with "impact factor" are the renowned in the field of materials science, physicochemical studies of materials, as well as the synthesis and characterization of ceramic materials: Materials Letters (IF = 3.204 / 2020), Materials Chemistry and Physics (IF = 2.101 / 2015), Ceramics International = 3.450 / 2018). The results were presented also at 117 scientific forums.

For her participation in the announced competition for the position of "Associate Professor" at IMC-BAS, Dr. Zaharieva has presented 54 publications, 32 of which are in journals with "impact factor" or "impact rank", distributed by their quartiles as follows: 3Q1, 5Q2, 3Q3, 18Q4, 3SJR. 11 of them are united in habilitation work, and 21 are presented in addition. The independent citations by other authors, found in the world databases Scopus and Web of Science and presented in the competition are 84. All these quantitative indicators provide the necessary scores, corresponding to the minimal national requirements, mentioned in the Republican regulations for implementation of ZRASRB, as well as in the Regulations of IMC and even exceed them in most of the indicators. The candidate's Hirsch index, according to the Web of Science database, is h = 5.

The part of the research activity of Dr. Zaharieva, published in 11 articles in journals with "impact factor" are the basis of the habilitation work and it is presented under the unifying title "Synthesis and research of oxide nanoscale materials (oxides, mixed oxides, composite materials based on oxides)". Most of the oxide materials described in the applicant's publications are synthesized targeting an application in photocatalysis for the decomposition of organic pollutants and thus they are related to the subject area of great importance and

relevance for research, due to its relationship with the European Union priorities as environmental protection, human health and biodiversity.

The experimental work in the publications presented in the habilitation report includes the synthesis and characterization of a wide range of oxide nanomaterials. The main role of Dr. Zaharieva is in the synthesis of the studied systems, among which: magnesium aluminate ($MgAl_2O_4$), nanosized copper ferrites ($Cu_xFe_{3-x}O_4$, $0 \leq x \leq 1$), mixed cobalt-copper ferrites with different stoichiometric composition: $Co_{0.25}Cu_{0.25}Fe_{2.5}O_4$, $Co_{0.4}Cu_{0.1}Fe_{2.5}O_4$, $Co_{0.5}Cu_{0.5}Fe_2O_4$, single-phase nickel ferrite $Ni_{0.5}Fe_{2.5}O_4$, zinc and manganese ferrite materials - $ZnxFe_{3-x}O_4$, x = 0.5, 1 and $Mn_xFe_{3-x}O_4$, x = 0.25, 0.5, 1, magnesium ferrite materials $Mg_xFe_{3-x}O_4$ (x = 0.25, 0.5, 1), series of nanosized substituted magnetite-type materials deposited on activated carbon from peach pits, nanosized zinc oxide (ZnO), composite materials based on oxides, $NiMnO_3$ / Mn_2O_3, nanocomposites - TiO_2-CeO_2-ZnO, TiO_2-ZnO and TiO_2-CeO_2, etc. For this purpose, the following synthesis methods have been applied - mechanochemical treatment in a high-energy planetary ball mill, melt synthesis, co-precipitation, microwave treatment and their combinations.

The main contributions of Dr. Zaharieva in the habilitation report refer to finding the appropriate experimental conditions - temperature, speed and duration of milling, ratios of the initial components on the one hand and for obtaining nanoscale materials with improved properties (larger specific surface area, higher dispersion and better photocatalytic activity to the decomposition of dyes in aqueous solutions under the action of UV light compared to studies by other authors), as well as to improve the synthesis technology (lowering the temperature of the thermal treatment), and on the other hand to establish the influence of these parameters on the structure and morphology of the materials, and respectively on their properties, with special attention to photocatalytic activity.

The publications, presented in addition to the habilitation report are described as belonging to 4 thematic areas:

1. Photocatalytic studies of NiO0.8ZnO0.2/ZnO, calcium titanate dopped with phosphorus TiO_2, abiotic, biogenic material, lepidocrocite and hybrid nanocomposites (polybenzimidazole-ZnO, polydiphenylacetylene-ZnO in polystyrene matrix and ZnO/ polystyrene.
2. Mechanochemical activation of pure and Ag, Ni or Co-doped zinc oxide, calcium titanate and magnetite-type materials.
3. Studies related to the phase composition and/or structure of photocatalysts and other materials.
4. Synthesis of ferritic catalytic nanomaterials, nanosized iron oxyhydroxides and composite photocatalysts based on nickel oxide and zinc oxide.

In these studies, the main contribution of the candidate is the selection and application of synthesis methods for the production of nanoscale ferritic catalytic materials, iron oxyhydroxides and composite photocatalysts based on nickel oxide and zinc oxide. activation.

The photocatalytic behavior of various oxide, hybrid and composite materials in the decomposition reactions of various model organic dyes - malachite green, methylene blue, methyl orange, reactive black 5 was also studied in details and their improved activity against certain pollutants was demonstrated compared to similar materials synthesized by other authors. For example, high photocatalytic activity was found to degrade the three studied dyes (malachite green, methylene blue and methyl orange) from hybrid photocatalysts - PBI / ZnO due to the synergistic effect between the inherent properties of the photoactive semiconductor ZnO and polybenzimidazole.). Polydiphenylacetylene-ZnO nanocomposites in polystyrene matrix show 88% degradation of Malachite green as a result of synergy between the polymer components.

Mechanochemical activation as a method for improving the properties of materials, obtaining nanosized materials with new properties that are not typical for massive samples was also studied. It is applied for pure and Ag, Ni and Co-dopped ZnO, as well as for CaTiO3 and leads to an increase in the photocatalytic ability of the samples especially in the case of

Ag-dopped ZnO, due to the higher degree of crystallinity and small crystallite size (22 nm). A decrease in the average crystallite size of the studied materials after mechanochemical activation was proved.

The phase composition of the catalytic materials was determined and discussed on the basis of the data from the X-ray phase analysis of ZnO and 1.5 wt. % lanthanum doped ZnO thermally treated at 350oC, 450oC and 500oC, and also dopped with 1.5 wt. % Ag and termally treated at 500 ° C. The presence of ZnO phase has been confirmed.

In general, the scientific contributions from the research conducted by the candidate can be divided into the following areas:

• Identification and application of experimental schemes and approaches in the synthesis of various oxide nanoscale materials.

• Establishing the optimal conditions for the synthesis of oxide nanoscale materials with new and improved characteristics and properties.

• Clarification of the relationships between the synthesis method, structure, composition and photocatalytic efficiency of the synthesized oxide nanoscale materials.

CONCLUSION

Presented by the candidate in the competition, Assistant Professor Katerina Lyubomirova Zaharieva, PhD, documents and materials meet the requirements of the Law on the Development of Academic Staff in the Republic of Bulgaria, the Regulations for its implementation and the relevant Rules of IMC-BAS and the topic of the announced competition for "Associate Professor" in the part "Solid State Chemistry, nanoscale materials".

I give my positive assessment of the work and activities presented in the competition and I recommend to the esteemed members of the Scientific Jury to prepare a report-proposal to the Scientific Council of IMC-BAS, Assistant Professor Katerina Lyubomirova Zaharievada to be elected for the academic position of "Associate Professor" at IMC-BAS, in professional field 4.2. Chemical sciences (Solid state chemistry, nanoscale materials and minerals).

20.04.2021 assoc. prof. Daniela Karashanova