REVIEW

on competition for academic position **professor** in a professional direction 4.2. Chemical sciences, scientific field "Physical chemistry", announced in SG, no. 79 of 04.10.2022.

Assoc. Prof. Daniela Karashanova, IOMT, BAS.

Reviewer: Prof. Bogdan Ranguelov, IPC, BAS

One candidate only participates in this competition, namely Assoc. Prof. Daniela Karashanova, PhD. The presented materials for participation in the competition procedure are complete, very well structured and collected, described in details with attached evidence materials and in accordance with the National requirements and the Rules for Academic Development in IOMT, BAS, thus allow evaluation of the candidate participating in the competition.

I. Short bio and analysis of the career profile of the candidate

Daniela Karashanova graduated in 1987 at the prestigious Ninth French language high school in Sofia, then in 1994 she graduated from with a master's degree in Physics at the Faculty of Physics, Sofia University "St. Cl. Ohridski". She started working in the Central Laboratory of Photoprocesses at the Bulgarian Academy of Sciences (currently the Institute of Optical Materials and Technologies "Acad. Yordan Malinovski", BAS) in the Laboratory of Electron Microscopy and in 2005 she defended PhD Thesis entitled "Vacuum deposited silver sulfide thin films: epitaxial growth and surface electron properties". She has successively held the positions of physicist, research associate, assoc. prof. at CLAFOP/IOMT, and since 2010 she has been appointed for Head of electron microscopy laboratory of IOMT, responsible for general studies of the structure, morphology and phase composition of nanomaterials, mainly using transmission electron microscopy and electron microdiffraction techniques.

Daniela Karashanova is a member of the permanent scientific-expert commission for chemical sciences at the National Science Fund, and from 2021 she is also the vice-president of the commission for chemical sciences. She is a representative in the Program Committee of the FP Horizon 2020, for area "Nanotechnologies, advanced materials, biotechnologies, advanced manufacturing and advanced processing".

During 2007, Daniela Karashanova specialized for whole year (after obtaining her PhD at IOMT) at the Interdisciplinary Center for Nanosciences of Marseille (CINaM), where she worked in the group of Jean-Jacques Metois and Pierre Muller. The expertise and the qualification she received is of utmost importance for her subsequent work as Head of the electron microscopy laboratory at IOMT. In this period, Daniela Karashanova acquired qualification in a very difficult method of electron microscopy, namely reflection electron microscopy, a method that allows real-time observation of the dynamics of monatomic steps on vicinal crystal surfaces. Last but not least is the mastered qualification on the special sample preparation techniques necessary for the successful observation of instabilities during growth and/or evaporation of Si(111) and Si(100) crystal surfaces.

II. General description of the presented data materials

Assoc. Prof. Daniela Karashanova has submitted all the necessary documents and the corresponding evidences to them according to the requirements of the law and the regulations of the IOMT: resume/abstracts, PhD diploma document, list and articles for habilitation work, list of publications, list of citations and reviews, list of participations in international and national projects, reference to original scientific contributions, summaries and copies of publications, etc.

The submitted materials are complete, well structured, carefully collected and described in detail with attached evidentiary material. Dr. Karashanova participated in the competition with six publications equivalent to a habilitation work published in the last two years, four of them in journals with quartile Q1 and two in journals with quartile Q2. In these articles, the candidate's work is related to the application of TEM in the study of the microstructure and phase composition of innovative catalytic materials. In addition to the habilitation work, 12 publications and 1 patent, published mainly in the period 2019 - 2022, are presented. The patent was applied for in 2019 and received approval from the Patent Office on 21.11.2022. Note: In the document submitted by the candidate - Reference for minimum requirements Appendix 3-5, Group "Г" points are not 280, but 305 (25 points (Q1) omitted in the calculation of total points for Group "Г").

III. Evaluation of the general scientific activity and overall academic career

The entire scientific activity of Dr. Karashanova is related to conducting scientific research with electron microscopy and, in particular, with transmission electron microscopy (TEM). Dr. Karashanova participated in the competition with six publications equivalent to a habilitation work and in addition presented 12 publications and 1 patent. The total number of the candidate's publications after 2012 is also impressive, reaching a total of 111 publications within a period of ten years (until 2022). She is the first/corresponding author in two of these publications, both of which are from 2012. It should immediately be clarified that the role of Dr. Karashanova as a co-author in the presented articles is extremely important - this is her role in planning and conducting the transmission microscopy studies of the materials and systems that are different in their nature, structure and properties, described in the presented publications, as well as in the data analysis of their morphology, microstructure and phase composition. In modern scientific research, especially in the field of synthesis and characterization of new materials, work is carried out in large groups of scientists, and interconnected experiments are almost always carried out by different groups. Although she is not in the role of corresponding/first author in the articles, for me the role and the contribution of Dr. Karashanova are indisputable in terms of the quality of the obtained results.

Here I want to discuss one more aspect of the candidate's activity, namely the pedagogical and organizational activity. Dr. Karashanova gives a course of lectures for PhD students at the BAS Educational Center, 30 hours of lectures entitled "Electron microscopy and electron diffraction in the morphological and phase analysis of materials" and 15 hours of practical exercises. Dr. Karashanova's contribution on the "Interdisciplinary Chemistry" seminars for doctoral students and young scientists (held annually since 2008 - fifteen editions) as the chairman of the organizing committee and main initiator and organizer is enormous. These seminars are a platform, actually well-known platform among PhD students and young scientists, where they present their research orally and also listen to training lectures from well established scientists. In addition, it should be noted that Dr. Karashanova is the main organizer of the International Autumn School of Crystallography and Electron Diffraction, 2017 and of the Training School of Electron Microscopy and its Applications in Materials Science, 2019. Daniela Karashanova is a long-time secretary of the Bulgarian Crystallographic Society (BCS), and from 2021 she is also the Chairman of the BCS.

IV. Evaluation of the main scientific contributions

As it was mentioned, the entire scientific activity of Assoc. Prof. Karashanova is related to conducting scientific research with electron microscopy and, in particular, with transmission electron microscopy (TEM). This also determines the relatively broad thematic spectrum by which the candidate's scientific and scientific-applied contributions can be determined. The main part of the contributions are related to the TEM study of the microstructure and phase composition of innovative catalytic materials, synthesized and applied in various reactions/processes – from hydrogen production, synthgas and phenol, to neutralization of volatile organic compounds and the decomposition of formaldehyde and methanol. Significant contributions have been made in the use of TEM on graphene and thin-film based materials, as well as metal and composite nanoparticles obtained by laser ablation in various media.

With regard to innovative catalytic materials, the work of Associate Professor Karashanova is related to microscopic observations of the active phases in the atomic resolution mode (HRTEM), as well as to the diffraction modes of the so-called selective small area diffraction (SAED), which enables determination of the microstructure and phase composition within even individual nanoparticles. It is in these two specific modes of observation that one can see the experience and the skill of working with TEM, as well as the "feeling" for choosing precisely the right/important part of the sample that will give the necessary information - I mean in particular the images and diffractions in articles A1 (figs. 4 and 5), A2 (figs. 3 and 4), A3 (fig. 5), A5 (fig. 4). Right away, the following should be noted: although one of the best modern transmission electron microscope models (JEM 2100) is used in all studies, this does not mean that all results are obtained automatically, on the contrary, it is the human factor that because of which the best of a given device can be "shown" - in this case resolution in the subnanometer scale. Regarding SAED diffraction, it should be noted that the identification of phases/compounds is not a simple task, but is based on a heavy and time-consuming procedure of very precise measurement of distances on the diffraction pattern and subsequent precise work with the so-called COD (Crystallography Open Database) files.
According to the shape and type of the active phase, as well as depending on the type of support (substrate), the catalysts studied by Associate Professor Karashanova can be divided into two groups - (i) applied metal catalysts and (ii) metal oxides on porous supports. In supported metal catalysts, the active phase is metal in the form of nanosized particles that are finely dispersed on the surface of the support.

Here follows a brief reference to the main contributions of the candidate in the submitted for review works - the contributions are clasified among the determination of the morphology and phase composition of the metal nanoparticles, as well as the structure of the substrate used.

In A1, a catalytic material is investigated in which the active phase of a noble metal is replaced by copper nanoparticles, and one of the metastable phases of alumina is used as supports, namely the polymorphic phase gamma-Al_2O_3 in a mixture with CeO_2 and γ-Al_2O_3 as well as CeO_2 and Yttrium-doped γ-Al2O3. Preparation of the substrate was carried out by two methods - by impregnation of γ-Al_2O_3 and by mechanochemical mixing of the two components. The contributions of the electron microscopic study are related to the definition of the differences in the phase composition and the structure of the substrates obtained by the two methods, which explains their different behavior in the catalytic reaction. Mechanochemical mixing was shown to promote the coexistence of CeO_2 and Y_2O_3 phases and thus leads to better catalytic activity compared to the imregnation method.

In A2, the active phases of the catalysts are oxides of Co, Mn and their mixtures in different ratios, the support is macro/mesoporous silica (MMS), and the catalysts are tested on the oxidation of CO and n-hexane. Information is obtained on the structure of the substrate, the phase composition of the active components and their distribution on the surface of the substrate for a metals ratio of 1:1 and 2:1 in favor of cobalt. The structure of the native and mixed oxides of the metals is determined, and the distribution of the metal phases on the porous substrate is also investigated. The catalytic activity on complete oxidation reactions of CO and n-hexane is shown to be highest for the pure cobalt catalyst and lowest for the manganese-only one.

In A3, the active components of the catalysts are Cobalt-Zinc ferrites, and the substrate is a porous modified carbon foam, on which the ferrite nanoparticles from salts of the three metals (Co, Zn, Fe) are synthesized by wet impregnation. In the study, it is interesting to note the leading role of transmission electron diffraction and microscopy and its complementation with the results of Mössbauer spectroscopy. The phase composition of the catalyst are determined - hematite, magnetite and cubic spinel ferrites of cobalt and zinc. The catalyst is studied in a methanol decomposition reaction until the so-called synthgas is obtained. It is shown that the highest degree of methanol conversion - over 90% is achieved at 670 - 690°C with pure cobalt ferrite, as well as with a low content of Zn (Co:Zn=8:2) in the mixed ferrite material, where, however, the catalytic activity decreases due to separation of less active catalytic phases.

Publication A4 presents a study of supported metal catalysts, in which nanosized metals Ni, Ru and Pt, singly and in combination of two metals: Ni-Pt and Ru-Pt, on a porous zeolite support were used as the active phase. Structurally, the zeolite has been identified as a "beta" type zeolite, with a tetragonal crystal lattice. The sizes of the metal particles and their locations on the surface of the zeolite aggregates were determined. Catalytic materials are applied in a catalytic reaction to produce phenol.

The catalyst in A5 is a gold catalyst, but in the form of nanoparticles, for which the TEM study shows dimensions of the order of 3 to 4 nm and structure of cubic gold. Three compositions were used for the substrate: a) combination of Co_3O_4 and CeO_2, b) the same mixture with added potassium, and c) a quadruple oxide-hydroxide mixture of Co_3O_4, CeO_2 and β-Al_2O_3. For substrate a) - electron diffraction showed the presence of a non-stoichiometric phase of cerium oxide: $Ce_{11}O_{20}$, which is assumed to be formed as an intermediate step in the reduction of $CeO_2 \rightarrow Ce_2O_3$. The presence of gold nanoparticles was established on this phase, too. For substrate c) - important data were obtained on the interaction of the active phase and the substrate. The deposition of gold nanoparticles both on aluminum oxide, where they are captured on the surface thanks to hydroxyl groups, and in close proximity to aluminum oxyhydroxide, which was established for the first time in the scientific literature, has been demonstrated. The catalysts were applied in a reaction for the complete oxidation of formaldehyde to carbon dioxide and water.

Publication A6 investigates mixed manganese-cerium (Mn-Ce) oxides synthesized directly on mesoporous amorphous silica. The catalytic material is targeting on air pollutants and on volatile organic compounds. The hexagonal arrangement of the mesopores of the substrate was confirmed, as well as the fact that this structure is preserved, both after the deposition of the active phase at high temperature and after the participation of the catalyst in the reaction for which it was proposed. The distribution of the active components on the carrier and the phase composition of the material at different ratios of the precursors of the two metals are demonstrated.

Regarding graphene and thin-film materials, the candidate's contributions are related to the preparation of the samples, TEM observation using the relevant modes and techniques, analysis and interpretation of the obtained data.

The deposition of double-layer graphene on a copper foil as a substrate by the method of chemical vapor deposition is studied. Laminar or turbulent flow of gases is used. Evidence for the successful deposition of bilayer graphene is provided.

Carbon thin film layers obtained by the laser ablation method - deposition of carbon layers by ablation of microcrystalline graphite on different substrates - were studied. Four of the layers, all deposited on oxidized Si, were examined by TEM, using two different ablation modes - with the same wavelength of 355 nm, but with different generation - continuous and pulsed. The heavy tasked sample preparation should be noted in these studies, especially due to the need to remove the substrate.

Electron microscopic studies were performed on a graphite target subjected to pulsed laser ablation in water. As a result of the 1064 nm irradiation, particles in a large range of sizes – from a few nanometers to tens of microns – are formed in the suspension. In order to obtain in the suspensions particles of increasingly fewer graphite planes and even single-layer graphene, in addition to adjusting the parameters of the laser radiation, an extensive experiment was made using different quality and type of starting graphite materials.

The morphology and phase composition of thin layers of titanium oxide (produced by magnetron sputtering method) doped with a large amount of carbon (up to 3 at. %) were investigated. The morphology of the layers was recorded, showing a grain structure typical of polycrystalline samples. The applied electron diffraction and high resolution mode established the presence of three crystalline phases of TiO_2: anatase and rutile, which have a tetragonal structure and orthorhombic brookite.

Different metallic and composite nanoparticles produced by pulsed laser ablation are studied – nanoparticles from single metals, to their combinations, and also in combinations with oxide compounds. There is a great variety in the media in which the synthesis takes place - from double distilled water and ethanol to vacuum and/or air. Valuable information was obtained on the morphology of the nanoparticles at different ablation energy densities for different laser wavelengths. The morphology of the particles, their shape and size - average size and particle size distribution, their yield, and also their phase composition - were compared. The possibility of using one or another wavelength of laser radiation is shown, depending on the purpose of application of the obtained nanoparticles. Impressive are the studies on the synthesis and subsequent impact with laser pulses of the average size and the size distribution of silver (nano)particles in an aqueous colloid, with the aim of application in ophthalmology as part of a preparation for the treatment of intraocular infections. The synthesized colloid is biocompatible and free of chemical contamination, has particle sizes in the range of up to 10 nm (a two-phase process is used) to cross the intraocular barriers, and exhibits proven antibacterial activity. The results are also protected by a patent.

V. Citataions

The articles submitted for participation in the contest received 84 citations, and in total for the period 2011-2022, the citations on works with the participation of the candidate are 518. This is to prove the extremely good "visibility" of the scientific publications of the applicant, as well as the fact that the they are published in promising scientific fields by using the method of transmission electron microscopy and electron diffraction successfully.

VI. Critics and suggestions

In general, I have no critical notes. I use the case to recommend to the candidate and, in general, to all who are involved in the field of microscopy (especially electron microscopy) - the increasingly successful development of the method and the introduction of newer techniques (including machine learning, neural networks, and even and artificial intelligence) require continuous (self) improvement and acquisition / exchange of knowledge on a global World level.

VII. Personal impression

Dr. Karashanova is an undisputed specialist in conducting research with transmission electron microscopy. At the same time, she has a keen scientific curiosity, which is one of the necessary prerequisites for successful scientific work. Dr. Karashanova also possesses perhaps one of the most necessary qualities for a successful microscopist – the lack of hasting, the ability for consistent and deliberate, purposeful activity, combined with the necessary dose of patience.

OVERALL DECISION

Based on overall evaluation of the presented materials, I give my categorically positive opinion and strongly recommend the members of the Scientific Jury to award Dr. Daniela Karashanova the academic position of "**professor**" in professional direction 4.2. Chemical sciences, scientific field "Physical chemistry".

30/01/2023

This review is prepared by:

Prof. Bogdan Ranguelov