REVIEW

for a competition for the academic position "Professor" in the professional field 4.2. Chemical sciences, scientific specialty "Physicochemistry", announced in State Gazette No. 79 of 04 October 2022 for the needs of the Institute of Optical Materials and Technologies (IOMT) - BAS

Candidate: Dr. Daniela Bogdanova Karashanova, Associate Professor at IOMT - BAS

Reviewer: dr Dragomir Mladenov Tachev, professor at the Institute of Physical Chemistry - BAS

1. Brief biographical details of the applicant

The only candidate in the competition is Dr. Daniela Bogdanova Karashanova, Associate Professor at the Institute of Optical Materials and Technologies, IOMT-BAS. She is a graduate of the Faculty of Physics of Sofia University "St. Kliment Ohridski" with a degree in Physics and specializations in Meteorology and Pedagogy of 1994. She received the educational and scientific degree "Doctor" (PhD) in 2005 at the Central Laboratory of Photoprocesses "Acad. Jordan Malinowski" - Bulgarian Academy of Sciences. She defended his thesis on "Physicochemical properties of vacuum-deposited silver sulfide thin films: epitaxial growth and surface electrical properties". Since 1995 Dr. Karashanova has been working at the Institute of Optical Materials and Technologies, IOMT-BAS (formerly the Central Laboratory of Photoprocesses "Acad. Jordan Malinowski",) holding successively the positions of "Physicist", "Senior Assistant" and "Associate Professor". Since 2010, she has been in charge of the Electron Microscopy Laboratory of the Institute.

Associate Professor Karashanova also has scientific and organizational experience. Between 2014 and 2020 she was a Representative in the Program Committee of the FP Horizon 2020 at the Ministry of Science and Education, and since 2019 she has been a Member of the Permanent Scientific Expert Committee on Chemical Sciences at the Research Fund.

2. Evaluation of the submitted materials

Associate Professor Karashanova has submitted a complete set of documents for participation in the competition in accordance with the requirements of the Regulations for the Implementation of the Law for the Development of Academic Staff in the Republic of Bulgaria and the Regulations for the Conditions and Procedure for the Acquisition of Scientific Degrees and the Occupation of Academic Positions at IOMT - BAS. The documents are accurately formatted and provide the necessary information for the evaluation of the scientific research activity of Associate Professor Karashanova.

The candidate participates in the competition with 18 publications, of which 6 are equivalent of habilitation thesis (group of indicators "B", indicator "4") and 12 in group of indicators "Г", indicator "7". It is noteworthy that all but one of the submitted articles were published after 2019. The articles submitted as the equivalent of a habilitation thesis are thematically related under the title "Transmission electron microscopy of materials with catalytic applications" and concern the characterization mainly of graphene-like carbon phases.

Of the first 6 publications, 4 were in Q1-ranked journals and 2 in Q2-ranked journals. Of the second 12 publications, 6 are in journals with Q1 rank, 2 with Q2 and one with Q3. One patent is also listed. Thus, the applicant scored 140 points out of 100 required for the group of indicators "B" and

305 points in „Г" out of 220 required by the Law on the Development of Academic Staff in the Republic of Bulgaria (LDASRB) and the Regulations for its implementation in IOMT-BAS.

84 citations of publications involving the applicant were submitted for the competition, which earned her 158 points on the "Д" indicators against the required 120. The citations are of articles involving the applicant no older than 2012, again with a preponderance of articles published after 2019.

Daniela Karashanova has participated in 12 national and 5 international scientific or educational projects. She has been the leader of two national projects. This asset brings her a total of 260 points in Group „E".

In this way, Dr. Daniela Bogdanova Karashanova gained a total of 923 points with the required 640, which significantly exceeds the minimum requirements for the academic position of "professor", set out in the Law on the Development of Academic Staff in the Republic of Bulgaria and the Regulations on the Conditions and Procedure for the Acquisition of Scientific Degrees and Academic Positions at IOMT-BAS.

The oldest of all the articles presented, including as cited paper, was published in 2012, two years after the acquisition of the academic position of "Associate Professor" and 7 years after receiving the ESD "Doctor". Therefore, the publications and citations of the applicant included in the present competition were not used by her either in obtaining the Ph.D. or in being awarded the academic position of Associate Professor.

3. General characteristics of the candidate's scientific research, applied scientific and pedagogical activities

The research activity of Assoc. Prof. Dr. Karashanova since 2010 is concentrated around transmission electron microscopy (TEM) and related electron diffraction (SAED). As a universal method in materials science, TEM is used to characterize the nanostructure of a wide range of new materials. This is also the case of Assoc. Karashanova's research - they cover supported metal catalysts, oxides on porous substrates, graphene and thin film materials, metal and composite nanoparticles, in a variety of media. Candidate's scientific activity consists in preparation of samples of different nature and properties for their investigation with TEM, planning and conducting the experiment, and analyzing the results for their structure morphology and phase composition.

The total number of articles featuring the candidate in the Scopus database is currently 120, 104 of which have been published since 2012. Obviously, the growth of the publication activity of Assoc. Prof. Karashanova is positively influenced by the successful management of the Electron Microscopy Laboratory at IOMT-BAS, which she was entrusted with in 2010. The citations without self-citations of all co-authors, again in the Scopus database, of all papers involving Assoc - Prof. Karashanova is 540 and the Hirsch index is 11.

The teaching activity of Assoc. Prof. Dr. Karashanova includes a course of lectures for PhD students at the Training Center of BAS with the title "Electron microscopy and electron diffraction in morphological and phase analysis of materials". The duration is 30 hours of lectures and 15 hours of exercises. She was also the supervisor of one thesis for the Bachelor's degree and the co-supervisor of two theses for the Master's degree.

4. Main scientific and applied contributions

The main scientific contributions of the works presented as the **equivalent of a habilitation thesis** concern the study of the microstructure and phase composition of innovative catalytic materials.

A classical gold catalyst on a support containing cerium oxides was investigated with TEM. The size, 3-4 nm, of the gold nanoparticles as well as their affinity for Ce_2O_3 are determined by TEM. The existence of a non-stoichiometric phase $Ce_{11}O_{20}$, which is an intermediate in the reduction of CeO_2 to Ce_2O_3, has also been shown to be relevant to the formation of the gold particles. It was found that the addition of potassium to the substrate did not change its phase composition. It was shown for the first time that when alumina and alumina oxyhydroxide exist in the substrate, gold nanoparticles are formed on the surface of the former and in close proximity to the latter. The quaternary system of Co_3O_4, CeO_2 and γ-Al_2O_3 + γ-AlOOH was first proposed for the oxidation of formaldehyde to carbon dioxide and water.

A mixture of CeO_2 and γ-Al_2O_3 has also been used as a copper catalyst support, and in some cases γ-Al_2O_3 is doped with Yttrium. The difference in the phase compositions of the substrates obtained differently was established by TEM, which explains the different catalytic behavior of the respective catalytic systems.

Another nanocatalyst studied with TEM is a system of metals: Ni, Ru and Pt, singly or in combination of two metals: Ni-Pt and Ru-Pt, deposited on a porous beta zeolite substrate. The zeolite particles used were found to have an elliptical shape, in contrast to the spherical shape reported in the literature. The zeolite was characterized as a beta type with a tetragonal lattice. The metal particles have been characterized in the high resolution mode of the microscope as the sizes found are again below 5 nm. Electron diffraction also detected oxides of Ni and Ru due to the larger amount of these metals in the catalyst. The metal-containing particles are located on the zeolite surface.

A series of catalysts, in which the active phases are oxides of Co, Mn and mixtures thereof, were deposited on macro-mesoporous silica. Details of the substrate structure, the phase composition of the active components and their distribution on the substrate surface have been established with TEM. In the simultaneous presence of the two metals in a 1:1 or 2:1 ratio, stable mixed oxides of the type $Mn_xCo_{3-x}O_4$ were detected by electron diffraction and high resolution. The position of the metal nanoparticles on the mesoporous silica was determined. The sizes found are again between 2 and 5 nm, with clustering also observed in the case of pure Cobalt. An important result is the loss of catalytic activity when some of the particles enter the mesopores of the substrate.

Mixed manganese-cerium oxides on mesoporous amorphous silica were also investigated. It was found that the procedure of preparing the oxides directly on the silica did not change its structure. With TEM and EDS, it was shown that manganese and cerium are uniformly dispersed on the surface and in the pores of the mesoporous silica without clogging the latter. Since the oxide particles are too small, a satisfactory diffraction pattern is not obtained by either X-ray diffraction or scanning electron diffraction (SAED). For this reason, for the samples with two different molar ratios of Mn:Ce metals, 2:1 and 1:2, Fourier transformation of images taken in high resolution mode was used to identify the MnO_2 phase. This demonstrates the presence of Manganese of the fourth valence, which plays an essential role in the catalytic ability.

Characterization of a catalyst with an active component of mixed $Co_xZn_{1-x}Fe_2O_4$ ferrites deposited on modified carbon foam was also performed. A highly developed surface of the carbon support was found with TEM, making it suitable for use in a catalytic system. The active phase consisted of spherical particles of 5-10 nm in size, but clusters of more than 20 nm were also found. A significant number of phases involving Co, Zn and Fe have been recorded.

In summary, the contributions of the candidate presented as a habilitation thesis are the characterization by TEM and electron diffraction of catalytic systems characterized by extremely small amounts and sizes of the active component, which is dispersed on a support with a large surface area.

The determination of the size, location and phase composition of the active component as well as the morphology of the support are of utmost importance for the catalytic properties of the system. These factors determine both the importance of the contributions made and the necessity of using advanced experimental practices, which the candidate clearly possesses.

The scientific and applied contributions of the works **outside the habilitation thesis** of Assoc. Prof. Dr. Karashanova are divided thematically into two areas: 'Transmission electron microscopy of graphene and thin-film materials' and 'Transmission electron microscopy of metallic and composite nanoparticles obtained by laser ablation in different media', the unifying one again being transmission electron microscopy.

The TEM observations are part of an effort to produce graphene and graphene-like carbon layers with potential applications in microelectronics and optoelectronics. The descent in size to an atomic monolayer predestines transmission electron microscopy as an indispensable tool for determining the relationship between preparation conditions and the result obtained. Herein lies the main contribution of the candidate. The studied methods of preparation of graphene and graphene-like phases are chemical vapor deposition (CVD) laser ablation of various graphite targets with deposition on several types of substrates and water and direct irradiation of graphite-containing suspension with laser.

The wide variety of preparation methods and parameters predetermines the wide variety of carbon phases to be characterized, and the nanoscale dimensions and the different type of carrier, substrate or suspension, imply maximum effort and knowledge in planning and performing the experiment. According to what has been found with TEM, vapor phase deposition on copper foil offers layer-by-layer formation of graphene planes, and bilayer graphene has been demonstrated to be obtained over larger areas in an advanced manner. By electron diffraction, it is shown that the observed graphene is bilayered, and the rotation of the second plane with respect to the first is determined. By the rotation, the moment of obtaining a third graphene plane is also determined.

When carbon is deposited on a silicon substrate by laser ablation, no ordered graphene planes are formed. The contribution here is the tracking of the initial stages of nanocrystalline graphite layer formation. The variation of the crystallographic orientation of the growing particles is traced.

It was also found that laser ablation of a graphite target in water formed mainly graphite phases and diffraction from a selected region revealed a diffraction pattern typical of single crystal graphite. Replacing the graphite target with a graphite suspension and varying the irradiation conditions including irradiation of a flowing stream from the suspension results in the production of multiple graphene-like phases, among which reduced graphene oxide, defective graphene, graphene oxide, graphite microparticles, amorphous carbon and fullerene C60. These phases were identified and distinguished by TEM and electron diffraction in a selected area. Thin and relatively transparent carbon flakes of micrometer dimensions, bulb-like shaped nanosized formations and amorphized nanosized carbon were observed. The most commonly observed forms are carbon flakes.

The second topic in the works presented outside the habilitation thesis concerns the characterization of nanoparticles obtained by pulsed laser ablation under a wide variation of both the irradiation conditions and the irradiated material and the medium in which the particles are formed. The mode of production involves small amounts of material, often insufficient for X-ray diffraction, which highlights the importance of electron diffraction in TEM observations. The contributions of Assoc. Prof. Karashanova are in the electron microscopic characterization of the nanoparticles thus obtained, which is a necessary step in the optimization of the preparation process.

An excellent task solved by a team with the participation of Assoc. Prof. Karashanova is the preparation of silver nanoparticles with a given size distribution in a particularly pure medium for application in ophthalmology. In this task, statistical processing of TEM images was applied to determine the size distributions of the silver particles. Thus, dependencies of particle quantity and size on laser wavelength and radiation intensity were established. A significant result is that absorption of laser radiation with the near-wavelength surface plasmon resonance of silver leads to melting and fusion or clumping of nanoparticles and formation of long chains. Using TEM research, a two-step method was developed to produce silver nanoparticles below 10 nm in size, in which laser irradiation of a target produced larger particles, which were subsequently fragmented by a second irradiation with a wavelength close to that of the plasmon resonance. Precise TEM analysis accompanied by statistical image processing was used at each step of the nanoparticle preparation to see how the particle size and size distribution changed and to tune the laser radiation parameters in each subsequent experiment. As a result, with the significant contribution of electron microscopy and the candidate, silver nanoparticles with a size below 10 nm were successfully obtained in an extremely clean environment. From this result, a national patent was successfully issued.

With TEM, gold and silver nanoparticles in a solid SiO_2 or ZnO matrix were characterized. The particles in SiO_2 were obtained by co-precipitation in pulsed laser ablation and in ZnO by ion implantation. Laser irradiation or custom annealing were applied to modify the particles. The sizes of the particles thus obtained were determined to be in the order of a few nm to a few tens of nm, which usually grew after treatment. As an interesting result I would note the detection by electron diffraction of a metastable phase of silver with a hexagonal lattice parallel to the equilibrium cubic one in ZnO with implanted silver. Moreover laser treatment at 355 nm wavelength leads to the disappearance of the equilibrium cubic lattice of silver.

Another scientific contribution of the candidate is the characterization of nickel and iron in combination with silver particles obtained in a liquid or on a substrate by laser ablation, including an applied magnetic field. Again, morphology, size in the nanometer and tens of nanometer range has been determined. Three size orders of the particles, the largest of which is in the micron range, have been identified and related to three different laser ablation products. The magnetic field has an influence only on the large size particles that have ferromagnetic properties.

A significant contribution is the observed growth of a nickel particle with a size below 10 nm in the chamber of the electron microscope under the influence of the electron beam. This is considered to be evidence of the presence of nickel atoms in the liquid that remained on the carbon membrane when the microscope sample was prepared.

5. Significance of the results obtained and personal contribution of the candidate.

Current trends in materials science involve complex physicochemical processes related to the preparation and use of materials with a particular nanostructure leading to favorable electrical catalytic or optical properties. Therefore, collective activities of specialists with knowledge in different fields are a necessity imposed by practice. In this picture, transmission electron microscopy occupies one of the central places. The systems investigated by Assoc. Prof. Dr. Karashanova and the results obtained have made a significant contribution to the field of catalysis and the establishment of methodologies for the preparation of graphene and nanoparticles diverse in composition with the predominant use of laser ablation.

I have known Prof. Dr. Karashanova for more than 10 years as a dedicated, precise and responsible researcher. I have not had the honor to work with her directly, but the feedback from close colleagues with whom she has shared work is extremely positive. The contributions of Assoc. Karashanova are well described and distinguished in the author's reference. I have no doubt in her personal contribution to the scientific results obtained

6. Conclusion

The publications submitted by the candidate are on the topic of the competition and represent original research contributions in the field of applied physicochemistry and in particular in catalysis and preparation of nanomaterials with potential applications in electronics and optoelectronics.

The nature and the result of the scientific activity of Associate Professor Dr. Daniela Bogdanova Karashanova, as well as the presented scientific contributions and formal criteria meet all the requirements for holding the academic position of "Professor" defined by the Law on the Development of Academic Staff in the Republic of Bulgaria and the Regulations on the Conditions and Procedure for the Acquisition of Scientific Degrees and the Holding of Academic Positions at IOMT-BAS.

In connection with the above, I propose that Assoc. Prof. Dr. Daniela Bogdanova Karashanova be elected "Professor" in the professional field 4.2 Chemical Sciences, scientific specialty "Physicochemistry" for the needs of the Institute of Optical Materials and Technologies "Acad. J. Malinowski.

30 January 2023. Reviewer:

/ Prof. Dr. D.Tachev /