# REVIEW

By assoc. prof. Dr. Nikolay Alexandrov Grozev, Department of "Physical chemistry", Faculty of chemistry and pharmacy, Sofia University "St. Kliment Ohridski".

Concerning the competition for the academic position "Associate professor", field of higher education 4. Natural sciences, mathematics and informatics; professional direction 4.2. Chemical sciences (Solid State Chemistry), announced in State Gazette №. 65 on 28.07.2023; Order by the Rector of the SU "St. Kliment Ohridski", RD - 38 - 526 / 01. 09. 2023 and decision of FA - FCP, protocol No. 28 / 25.08.2023

For the competition announced in the Official Gazette (№. 65/28.07.2023) for the academic position "Associate professor", the only candidate is PhD Veselina Tocheva Rangelova, currently chief assistant professor at the Department of "Applied Inorganic Chemistry" at the Faculty of chemistry and pharmacy at the SU "St. Kliment Ohridski". Dr. Veselina Rangelova has submitted an electronic copy of all necessary documents, according to the current legal framework (ZRASRB, Rules for the implementation of ZRASRB, Rules for the conditions and procedure for acquiring scientific degrees and occupying academic positions at SU "St. Kliment Ohridski" and Recommended criteria for acquiring scientific degrees and occupying academic positions at SU "St. Kliment Ohridski" for professional direction 4.2 "Chemical Sciences" and 7.3 "Pharmacy" of FCP).

**1. Short CV of the candidate**

Dr. Veselina Rangelova completed her higher education in 1996 at the Faculty of chemistry and pharmacy (then Faculty of chemistry) with “Master’s degree in chemistry” (with specialization: Ultrapure substances and materials based on them). In 2004, she defended her doctoral dissertation at Supreme Attestation Commission and obtained the educational and scientific degree "Doctor" (Ph.D.) in the scientific specialty 01.05.18 „Solid state chemistry”. The dissertation’s title was "Amorphous and nanocrystalline Mg-Ni alloys for hydrogen storage". After the successful defense, she started working at the Department of "Applied inorganic chemistry" at the Faculty of chemistry and pharmacy at SU as assistant professor, senior assistant professor and chief assistant professor, respectively. Dr. Veselina Rangelova's scientific interests are in the field of materials science, catalysis and inorganic synthesis.

**2. Research activity of the candidate**

Dr. Veselina Rangelova is co-author of 18 scientific papers (15 are listed in Scopus database, 2 are in journals without impact factor, quartile or SJR and 1 article is in conference proceedings). According to Scopus database the total number of citations of Dr. V. Rangelova is 174 and her h-index is 5. She was a project leader of three internal projects at the SU Scientific Research Fund as well as she was a team member in other 7 projects (2 international, 4 national and 1 internal at SU). Some of the scientific results were presented at 6 different conferences as sectional reports.

**3. Teaching activity and work with students**

In addition to the research work, Dr. Veselina Rangelova actively participates in teaching at the Faculty of chemistry and pharmacy - she conducts lectures and practical classes on Inorganic chemical technologies for students in the specialty Chemistry, full-time and part-time studies; as well as Chemical Technologies for the specialty Engineering Chemistry and Modern Materials, full-time study. Her teaching activity is also related to work with students and doctoral students, which is evidenced by her scientific supervision of three graduate theses of students, as well as her participation in author collectives for the writing of a textbook and study aid for 10th grade students from secondary education.

**4. Evaluation of the materials for participation in the competition for the position "Associate professor"**

Dr. V. Rangelova participates in this competition with 1.) a habilitation work - a monograph (printed at the Sofia University Publishing House) and 2.) other 14 scientific publications (listed in file "10B.SelectedPublicationsList.pdf") - 12 in refereed and indexed journals and 2 in journals without IF (Q or SJR, namely № 11 in Sofia University "St. Kl. Ohridski" Faculty of chemistry and pharmacy Yearbook, 2009 and № 10 in Nanoscience & Nanotechnology (2015)). The scientific papers are distributed as follows: 3 (Q1), 4 (Q2), 5 (Q3). Co-authors of Dr. V. Rangelova are scientists (including students) from the Faculty of chemistry and pharmacy, the Bulgarian academy of sciences and from abroad. The total number of citations on the articles submitted for participation in the competition is 48. The total number of citations of all scientific works of Dr. V. Rangelova is 174 citations according to Scopus and h-index 5.

The Habilitation thesis (indicator B) as well as the 12 publications (all in Indicator Г) are devoted to modern scientific topics such as the development of new materials for: 1. hydrogen storage, 2. energy storage (reusable batteries) and 3. catalysts for solid fuels. This is the subject of Dr. V. Rangelova's research during her long career at the Department of Applied inorganic chemistry, which began with her doctoral dissertation. This fact on its own says that during this period of time she was formed as a specialist in this field.

**4.1. Habilitation thesis (Group of indicators B)**

The habilitation thesis was submitted for printing at the Sofia University Publishing House, which is certified with an official note. ISBN 978-954-07-5810-7 has been issued. The official note is also accompanied by the required review, in this case by a specialist in the field Prof. Georgi Tsvetkov. The book consists of 127 pages (without title pages and table of contents – 120 pages) and meets the requirement of being over 100 pages, as well as having the specified number of characters per page (in average). There are only 5 figures, which is perhaps a little sparse.

The thesis is fascinatingly written without losing consistency or scientific accuracy and is based on a huge number of cited sources – 282, the majority of which are articles from the last 15 years. The title is “MOFS. Storage of Gases in Porous Materials'. MOFS is an abbreviation of Metal Organic Frameworks, these are modern synthetic materials for storing hydrogen, carbon dioxide and fossil fuels in a gaseous state. They can also be used to purify gaseous mixtures. These materials allow a structure to be predetermined that has the desired porosity and ratio of crystalline (presence of long-range order) to amorphous part (presence of near-range order), i.e. to obtain a flexible structure "in which there are no useless volumes" (quote). This is a consequence of the interaction of metal ions and organic separators ("linkers") in MOFS composition. In this way, certain functional groups can deliberately be introduced into the pores to interact with a specific guest molecule. Thus, metal-organic mesh materials exhibit high selectivity and retention capacity in the processes of storage or separation of gaseous mixtures. This scientific subject is from the end of the 20th century and the beginning of the 21st century, i.e. the scientific researches of Dr. V. Rangelova and co-authors are in a rapidly developing contemporary and highly competitive environment, and contribute to obtaining new facts, enriching existing knowledge and theories, and having immediate opportunities for application in practice.

The work is very well structured and allows a non-specialist to navigate very easily. The introductory part motivates the writing of the present monograph and clearly indicates its place in the scientific literature - "...to present the current progress and the main problems in this still developing research area, as well as to outline possible strategies for improving the sorption characteristics of this new class of materials.". I believe that the goal set has been convincingly achieved and the monograph has earned its right to exist.

The chapter "Storage of gases in the solid phase" follows - a more general description of the need for gas storage in porous bodies, as well as a brief historical overview of porous bodies - zeolites, porous coordination polymers and metal-organic network materials, so-called MOFs.

The reader, already prepared with the basic knowledge, in the next two chapters moves on to become familiar with specific examples of the application of MOFs - hydrogen and carbon dioxide storage. Each chapter is written self-consistently, i.e. the problem is considered from the beginning (the need to store these gases), the ways of obtaining (respectively trapping), a description of more conventional storage materials and finally MOFs - attention is paid here to sorption processes and methods for their characterization, their design (based on different compounds) and concludes with strategies to improve the capacity of these materials.

The thesis could benefit both laymen with an interest in the field and specialists (due to the availability of a rich and reliable source for what has been done up to date in the field).

**4.2. Articles (Group of indicators Г)**

The articles presented in the competition are different from the articles used to obtain the scientific and educational degree "doctor" in year 2004.

The articles are divided into 2 groups that correspond to the candidate's scientific interests: the first and main group refer to amorphous and crystalline materials with the potential to store hydrogen in the solid phase - thanks to metal alloys (articles 3, 6-9, 13, 14) and MOFs (articles 10, 11 and 12), in addition article 4 is included which describes other functional materials – Zr-based glasses (alloys); the second group is devoted to the catalytic decomposition of ammonium perchlorate (articles 1, 2 and 5). All of them "...include the synthesis of new materials with the definition of functional properties, their morphological, microstructural and thermal design, as well as the determination of the reduction of technical properties leading to practical applications.". I use this

quote from the candidate's text, because it (the quote) very precisely and clearly defines the essence of scientific works of Dr. V. Rangelova.

Various techniques were used for the synthesis, some of them were innovative for their time - fast-fast melting from a melt ($10^5$-$10^6$ K/sec), mechanical alloying and reactive mechanical alloying using ball mills and high-frequency induction melting. Methods such as transmission electron microscopy, scanning electron microscopy, X-ray and electron diffraction, dynamic scanning calorimetry, thermogravimetry are used for microstructural characterization of the samples. The studies of hydrogen sorption properties were conducted with appropriate methods - in gas phase saturation and in electrochemical conditions.

Unfortunately, of the articles devoted to MOFs, only one article (12) carries points in the contest. Two other papers (10 and 11) are presented for completeness because they still contain interesting results.

**4.2.1. Main results**

What follows are some of the scientific contributions that have made the greatest impression on me.

**4.2.1a. Solid phase materials with hydrogen storage potential**

The research on the hydrogen-sorption properties of materials characterized by the presence of an amorphous and nanocrystalline structure aims to establish a relationship between the morphology of the alloys, their microstructure and their capacity, as well as hydrogenation/dehydration kinetics.

**Article 3** - an interesting fact is found that small differences in the composition of the alloys do not change the parameters of the crystal lattice of $LaNi_5$, but some electrochemical characteristics turn out to be sensitive - for example, in alloys with a lower content of Al (x = 0.04. .0.08) a higher capacity was measured (or as the Al content increases, the battery capacity decreases), which is also characteristic of alloys with a much higher Al content (x>0.1). In all, the capacity decreases after conducting 50 charge/discharge cycles.

In **Article 12**, studies of the thermal and hydrogen sorption properties of newly synthesized MOFs of Cu-4,4′-(perfluoropropane-2,2-diyl)diphthalic acid are presented. It was found that the use of $Cu(OH)_2$ leads to the formation of a product with a higher rate and stability.

**Paper 14** includes the results obtained on the hydrogenation of rapidly cooled amorphous alloys $Ni_{81.5}B_{18.5}$ and Fe-B-Si. The amorphous Ni-B alloy was found to absorb larger amounts of hydrogen than the Fe-B-Si-based metallic glass, with the initial kinetics of hydrogen absorption and desorption for the two alloys being comparable (which is very clearly seen in Fig. 2 of article 14).

**4.2.1b. Materials for the catalytic decomposition of ammonium perchlorate**

It is peculiar observation that the mesoporous materials serving as catalysts for the decomposition of ammonium perchlorate have the morphology of flora species. Perhaps this similarity is a necessary condition for the manifestation of catalytic properties?

In **Article 1** submicron $\beta - Ni(OH)_2$ particles were obtained shape as sand-rose. The addition of 5% (wt) of $\beta - Ni(OH)_2$ to ammonium perchlorate was found to significantly lower the decomposition temperature (by about 69 degrees), and the heat energy released was almost twice that of pure ammonium perchlorate.

**Article 5** is devoted to the synthesis and characterization of new mesoporous cauliflower-like structures consisting of aggregated $CuO/Cu(OH)_2$ nanoparticles. The new material was shown to exhibit excellent catalytic activity for the decomposition of ammonium perchlorate close to that of the best copper catalysts.

**5. Critical notes and recommendations on the presented works**

Note: **Publication 1** in the files "17.PublicationsSummary.pdf" and "10B.SelectedPublicationsList.pdf" is "Sand-rose shaped β-$Ni(OH)_2$ microspheres...", while in the document "14.Contributions.pdf" as publication 1 is considered "Mesoporous cauliflower-like $CuO/Cu(OH)_2$ hierarchical structures" (which is actually publication 5, i.e. in "14.Contributions.pdf" the numbering of publications 1 and 5 has been changed), which does not change essentially the consideration.

Often in the chemical formulae, subscripts are not placed as subscripts.

Some sources in the "Literature" section of the thesis are formatted differently (see for example [14] and [15], [218] and [219]) and often contain as a citation not only one source, but several different ones (for example [ 239] contains source [240]). Source [29] appears between [253] and [254], etc.

There are inevitably typographical errors in a text. For example:

Стр. 11 – „Лабораторно, синтетични зеолити са получени едва в средата на 20 век, като специфичната им структура се охаракеризира с развитите вече дифракционни методи за анализ [9, 10].“

Стр. 13 – „…характеристики на порестата им структура спрямо свойствата на конкретната молекула, която има да бъде адсорбирана.“

Стр. 49 – „водрод – влияние на катализатор, полярност на връзките и т.н.“

My advice is if there is an opportunity, the thesis to be corrected before printing, as it would only benefit from these corrections.

**6. Questions**

In connection with the fact (found in article 3) that small amounts of aluminum change the electrochemical properties of alloys, in the procedure of grinding the particles to nano-size using ball mills with steel balls, are there small amounts of iron/carbon released, that would affect the behavior of the alloys?

**7. Conclusion**

It can be summarized that according to the individual minimum national requirements, Dr. V. Rangelova shows the following results (Group of indicators):

A. (Ph.D.), 50 points, against the required 50

B. Habilitation thesis, 100 points, out of 100 required

Г. Scientific publications excluding those in the habilitation thesis, 230 points, against the required 220

Д. Citations /SCOPUS/, 348 points, against the required 70. Clarification: here are included all the citations so far, not only that of the presented 12 articles (with 48 citations), still if we took just them into consideration the requirements are again exceeded.

Ж. h-index = 5, participation in projects, introduced new courses, graduates – 155 points, against the required 70.

It should also be noted the participation of Dr. V. Rangelova in writing a textbook and study aid for students of the 10th grade of secondary education, as it is very important for specialists to be able to convey their knowledge in an understandable manner to the students and so to form the curiosity and interest in the subject "Chemistry" so necessary for future scientific researchers.

In conclusion, I express my inner conviction that chief assistant professor Veselina Tocheva Rangelova, Ph.D., meets all the requirements of the Law on the Development of the Academic Staff in the Republic of Bulgaria (ZRASRB) and other normative documents. In this regard, I recommend Dr. Veselina Tocheva Rangelova to take the academic position of "assoc. professor" in professional field 4.2. Chemical Sciences (Solid State Chemistry).

Sofia, 14.11.2023

Signature: Nikolay Grozev

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