REVIEW

of the competition for the academic position "Associate Professor" in the professional field **4.2. Chemical sciences (Inorganic chemistry),** announced in the **State Gazette no. 21/13.03.2020** by Sofia University "St. Kliment Ohridski" for the Faculty of Chemistry and Pharmacy

Reviewer: Prof. Dr. Ekaterina Zhecheva from the Institute of General and Inorganic Chemistry of the Bulgarian Academy of Sciences

By order of the Rector of Sofia University "St. Kliment Ohridski" (SU) N RD-38-161/10.04.2020 I was appointed to be a member of the Scientific Jury for selection of an Associate Professor in Professional Field 4.2 Chemical Sciences (Inorganic Chemistry). The only applicant is Assist.Prof. Dr. Martin Petrov Tsvetkov from the Department of Inorganic Chemistry at the Faculty of Chemistry and Pharmacy of SU. The submitted materials are in accordance with the Act on Development of the Academic Staff in the Republic of Bulgaria (ADASRB), the Regulations for the application of the ADASRB, the Regulations for the terms and conditions for acquiring academic degrees and occupying academic positions at the Sofia University "St. Kliment Ohridski" and the Recommendations on the criteria for acquiring scientific degrees and occupying academic positions at the Sofia University for the professional field " Chemical Sciences", related to the procedure for occupying the academic position"Associate Professor".

1. Brief biography of the applicant

Assistant Professor Dr. Martin Tsvetkov was born in 1987. In the year of 2010 he graduated from the Faculty of Chemistry of Pharmacy of SU (FChPh-SU) as Bachelor in Nuclear Chemistry and in 2011 he received the Master degree in Nuclear Chemistry. In 2016 he defended at FChPh - SU a PhD thesis in Inorganic Chemistry entitled "Mixed oxides MFe₂O₄ (M=Zn(II), Ni(II), Co(II)) – synthesis, characterization, catalytic properties" under the supervision of Prof. Dr. Maria Milanova. During 2011-2017 he was appointed as a chemist in the Laboratory of X-ray Diffraction Methods and Computed Tomography at the Institute of Physical Chemistry of the Bulgarian Academy of Sciences. Since 2017 he has been working as an Assistant Professor at the Department of Inorganic Chemistry of FChPh - SU. Assist.Prof. Dr. M. Tsvetkov has worked several times at the Joint Institute of Nuclear Research in Dubna, Russia: in November 2016 and October 2019 he was a visiting researcher at the Laboratory of Neutron Physics, and during February-April 2017 and January-April

2018 he was a Research Associate at the Laboratory for Nuclear Problems at the same Institute. The research interests of the candidate are in the field of materials science, photocatalysis and inorganic synthesis.

2. Description of the submitted documents

Assist.Prof. M Tsvetkov has presented the list of publications of his total scientific output, a list and copies of scientific publications with which he participates in the current competition and habilitation work. He is co-author of a total of 23 scientific works on which, according to the applicant, were noted 95 independent citations. In the competition he participates with 19 scientific papers. These papers are distributed according to the rank of the journal in which they were published as follows: 5 in journals with rank Q1 (Journal of Materials Science with IF₂₀₁₉=3.553, Catalysis Communications with IF₂₀₁₉=3.612, Materials Letters with IF₂₀₁₉=3.204, 2 papers in Catalysis Today with IF₂₀₁₉=5.825); 5 in journals with rank Q2 (Materials Chemistry and Physics with IF₂₀₁₉=3.408, American Mineralogist with IF₂₀₁₉=2.518, Superlattices and Microstructures with IF₂₀₁₉=2.120, Journal of Molecular structure with IF₂₀₁₉=2.463, Journal of Solid State Chemistry with IF₂₀₁₉=2.726); 3 in journals with rank Q3; 5 in journals with rank Q4; 1 paper in a journal with SJR but without IF. The habilitation work includes results from 5 papers, 3 of them are published in Q1 journals.

It is noted in the application that 80 citations (Scopus and Web of Science) were noticed on the publications for the competition. However, the candidate participates in the competition with 50 citations, which is visible from the submitted list of citations. Further, Dr. Tsvetkov has recorded in his application documents a Hirsch factor of 4, but the list of citations defines a higher Hirsch factor -5.

According to the Information system "The Authors" of Sofia University, Dr. Tsvetkov participated in a total of 13 research projects, in 4 of which he was project-leader. In the competition for Associate Professor he participates with 7 projects - 4 projects, of which he was the project-leader (1 project funded by National Science Fund and 3 projects funded by SU), as well as 3 projects, of which he was a member of the research-team (2 the project financed by National Asience Fund and 1 project funded by SU).

Assoc.Prof. Tsvetkov has 17 contributions to scientific forums, which is visible from the Information system "The Authors". However, details on venues and co-authors is missing. He is the guest editor of the special issue "Rare-earths doped materials" of the open-access journal Crystals.

A reference concerning the pedagogical activity of the candidate is attached.

All documents submitted by Dr. Tsvetkov fit the topic of the competition. A check-up of compliance with the Minimal national requirements and with the Recommendations of the

Sofia University for occupying the academic positions "Associate Professor" for the professional field "Chemical Sciences" is presented. The breakdown of indicators is as follows: indicator A - 50 points; indicator C - 105 points (100 required); indicator D - 235 points (220 required); indicator E - 100 points (70 required); indicator G - 95 (70 required). As can be clearly seen, scientometric data of Assist.Prof. M. Tsvetkov satisfy the requirements.

3. General characteristics of the research activity and personal contribution of the applicant

The scientific publications of Martin Tsvetkov in this competition are in the field of inorganic materials science and namely photocatalysis, heterogeneous catalysis and rare-earth chemistry. For the most part, they are thematically homogeneous and include studies on the synthesis and properties of new or modified materials with photocatalytic properties that are based on transition metal oxides (14 papers). The publications from the habilitation work fall into this topic (papers No 1, 11, 15, 18, 19). This work is entitled "Advanced oxidation processes for removal of organic pollutants in water" and summarizes some of the candidate's studies on the complete mineralization of organic compounds by hydroxyl radicals that are generated in the course of photocatalytic processes or Fenton reactions. Different approaches have been applied to control the effectiveness of photocatalysts and catalysts. The effect of the gamma-irradiation on the defect structure and photocatalytic properties of TiO₂ has been studied. Nanocomposites with improved photocatalytic properties containing two semiconductors are obtained - g-C₃N₄ and NiO or CuO, as well as nanocomposites of the type semiconductor - metal, such as ferrites and Ag. New catalysts based on CuO have been investigated in Fenton-like reactions in pH-neutral water solutions. In the habilitation work, results from a candidate's contribution on a scientific forum are also included, but the full text (at least summary) of this contribution as well as name and venue of the conference are not attached.

Beyond the habilitation work, a series of publications are devoted to the potential of ferrite materials as photocatalysts and photo-Fenton catalysts for purifications of water from organic contaminants (papers No. 4-10, 17). Most of these papers present joint studies with colleagues from the Institute of Catalysis of Bulgarian Academy of Sciences. Multicomponent ferrites that contain Zn, Cu, Co, Ni, Mg were prepared (pure or doped with rare earths or modified with metal nanoparticles) and their photocatalytic properties have been investigated. Catalysts based on magnetite are studied for photo-Fenton degradation of an organic dye.

The publications No. 3 and 14 are in the field of heterogeneous catalysis and consider the catalytic neutralization of volatile organic compounds in air. Complete oxidation of benzene and ethyl acetate on gold catalysts/cobalt modified ceria and cobalt ferrite modified with Hf(IV) are investigated.

The papers No. 12, 13 and 16 reflect the candidate's interests in the rare earth chemistry and contain results on the effect of lanthanide ions on the structural features of complex oxides such as zirconium tungstate and ferrites. The papers on the doped ferrites (No. 13 and 16) are a result of the collaboration of the candidate with colleagues from the Joint Institute for Nuclear Studies in Dubna.

All of Assist.Prof. Tsvetkov's publications for the competition are with co-authors. Martin Tsvetkov has performed mostly the photocatalytic studies and, in a number of papers, the synthesis as well as the phase and structural characterization of the materials. This lead to conclude that Mr. Tsvetkov's personal contribution to these studies is clearly significant. However, I think that the attached author's reference of the scientific contributions could be organized in a more appropriate way to emphasize better the logical links between the various studies.

4. Major scientific contributions

The major scientific contributions of Martin Tsvetkov can be summarized as follows:

The effect of the gamma-irradiation on the defect structure and photocatalytic properties of TiO_2 depends on the "history" of the material. The trade product of TiO_2 Degussa P25 that was gamma-irradiated with small doses (28 kGy) displays an enhanced rate of degradation for the model dye Malachyte Green in the ultraviolet and visible spectral range. Gamma-generated Ti^{3+} ions are revealed in these samples. On the contrary, the gamma-irradiated TiO₂ that was prepared by the sol-gel method (anatase) exhibits a reduced photocatalytic activity and Ti^{3+} ions are not detected.

Based on the original preparative technique "synthesis through ammonia evaporation", a new method has been elaborated for the preparation of 3D mesoporous composites NiO/g- C_3N_4 and CuO/g-C₃N₄ as photocatalysts in the visible spectral range. A synergetic effect for the adsorption and photocatalytic degradation of the toxic dye Malachite Green is observed that was provoked by the well-developed contacts between the components in the composite. Superoxide radicals (•O₂⁻) and photo-generated holes (h+) were found to be the active species in the process

The synthesis of binary and ternary ferrites has been advanced as an effective route to improve the effectiveness of magnetite-based photocatalysts. Materials have been obtained whose rate constants for azo-dyes degradation are close or higher to that of the reference material TiO_2 Degussa P25. Eu(III) and Tb(III) additives have a positive effect on the

photocatalytic activity of NiFe₂O₄ μ Zn_{0.5}Ni_{0.5}Fe₂O₄ for Malachite Green degradation in the visible spectral range.

The effect of the modification of binary ferrites MFe_2O_4 (M= Zn,Mg, Co) with Ag nanoparticles forming nanocomposites depends on the nature of the divalent metal in the ferrite structure. Silver nanoparticles improve significantly the photocatalytic activity of magnesium ferrite but a negative effect is observed with zinc ferrite. Due to the lower band gap energy, cobalt ferrite displays a low photocatalytic activity which is not affected by the silver additives.

CuO microparticles with a "hierarchical"- type structure have been synthesized by hydrolysis of a copper-ammonia complex at underwater dynamic Leidenfrost conditions and it was proven that they degrade completely in the dark and in neutral medium micro-pollutants of caffeine via H₂O₂.activation.

A hydrothermal method has been applied for the synthesis of $Zr_2W_2O_8$ modified with Eu(III). Small amounts of Eu(III) raise the temperature of the order-disorder phase transition between the alpha- and beta-phase, reduce the thermal expansion coefficient and expand the optical band gap.

The incorporation of very small amounts of rare earths $(10^{-9} - 10^{-6} \text{ wt. \%})$ into the structure of binary ferrites was studied by the Time Differential $\gamma\gamma$ -Perturbed Angular Correlation Method. Results show that nuclides preferentially occupy octahedral sites in the spinel structure.

5. Impact of publications in the literature

As already mentioned, Assist.Prof. Tsvetkov has not submitted the complete citation list of the papers for this competition but a list with only 50 citations. This makes it difficult to evaluate his papers with the widest impact in the literature. According to the attached list, the most cited publication is No 7 in Materials Chemistry and Physics, which deals with the synthesis and photocatalytic properties of nanosized copper ferrites (22 citations). There are 13 citations for the publications included in the candidate's habilitation works, but it should be noted that only one of the publications from the habilitation work was published before 2018.

6. Pedagogical activity

Dr. M. Tsvetkov has a significant teaching and pedagogical activity. His teaching load during the last 3 years, when he was an Assistant Professor, was about 400 hours per year. Dr. Tsvetkov leads exercises and seminars for the courses in "General Chemistry" and "Inorganic Chemistry" for various specialties in FChPh. In addition, from 2019 he gives the lectures of two compulsory courses - "General Chemistry" for the specialty "Teacher of Natural

Sciences" at the Faculty of Physics at Sofia University and "Methods for characterization of substances and materials (X-ray structural analysis)" for a master's program in FChPh. He also leads lectures and exercises for the elective courses "Equilibrium physical properties of single crystals" and "Single crystals and materials for fiber optics". In addition, he was the supervisor of 15 students courseworks.

7. Critical notes

I have no general objections to the research work of Assist.Prof, Martin Tsvetkov.

CONCLUSION

Assistant Professor Dr. Martin Tsvetkov participates in the competition with an asset that fulfills the requirements for occupying the academic position of Associate Professor at Sofia University "St. Kliment Ohridski" in the professional field Chemical Sciences. The documents presented prove that he is a productive young researcher in the field of inorganic chemistry with established qualities and a promising career who combines academic and teaching activities. Based on all of the above, and namely topical thematic area with prospects for future research, quantity and quality of papers and their impact in the literature, his scientific contributions and engagement in research projects as well as his pedagogical activity, I strongly recommend Assist.Prof. Dr. Martin Tsvetkov to be appointed at the academic position of Associate Professor in the professional field 4.2. Chemical Sciences (Inorganic Chemistry) at the Faculty of Chemistry and Pharmacy of SU.

> Reviewer: Prof. Dr. Ekaterina Zhecheva

Sofia, 21.08.2020