Review report

for a contest for the academic position "Professor" in a professional field 4.2. Chemical sciences for the scientific specialty "Inorganic Chemistry", for the needs of the Faculty of Chemistry and Pharmacy of Sofia University "St. Cl. Ohridski", announced in the State Gazette, issue № 96 of 19.11.2021 and with a candidate **Assoc. Prof. Dr. Penka Vasileva Tsanova**

Reviewer: Professor Konstantin Todorov Balashev, DSc

1. General requirements and brief description of the candidate

The only candidate in the contest for professor of Inorganic Chemistry at the Faculty of Chemistry and Pharmacy of Sofia University is Assoc. Prof. Dr. Penka Vasileva Tsanova. She graduated in 1981 the Faculty of Chemistry of Sofia University "St. Cl. Ohridski", majoring in Inorganic Chemistry and after that almost all her professional career has passed in the same faculty. Assoc. Prof. Vasileva started in 1982 as a chemist at the Laboratory for Highly Pure Substances (later "Institute for Pure and Highly Pure Substances") at the faculty of chemistry at Sofia University and was at this position until 1989, when she was promoted as an assistant professor at the Department of General and Inorganic Chemistry. Then, after acquiring the academic positions of Senior assistant (1992-2003) and Chief Assistant Professor (2003-2012), in 2012 she was tenured as an associate professor in the department, a position she currently holds.

2. Description of the presented materials

Assoc. Prof. Vasileva has prepared and presented in tabular form a report on the implementation of the minimum national requirements for the scientific position "Professor". She participates in the contest with scientific production, which is published in leading specialized international journals, chapters in books, textbooks, teaching and methodological materials or one that is reported at relevant scientific forums. As of today (March 14, 2022), 37 articles by Assoc. Prof. Vasileva and 452 citations have been found in the Scopus database. Her H-index is 10, without taking into account the self-citations of all co-authors.

The presented list, containing 36 publications, for participation in the contest, Assoc. Prof. Vasileva has divided into 6 categories: publications in peer-reviewed scientific journals, refereed and indexed - 16, published chapters from books - 3, publications related to the International Chemistry Olympiad - 3, publications referenced in Chemical Abstracts from scientific forums- 3, textbooks, teaching and methodological materials-11.

The publishing activity of Assoc. Prof. Vasileva clearly shows her profound scientific and pedagogical competence. Most of the publications presented in the general list are in distinguished, specialized journals, which are leading in the field of inorganic and analytical chemistry, as well as in the contemporary nanotechnology, such as: Molecules, Heliyon, Microchemical journal, Journal of Materials Science, Colloids and Surfaces A etc. All submitted publications entirely match the scope of the announced contest.

Assoc. Prof. Vasileva presented a habilitation thesis titled "Design and characterization of new nanomaterials for special analysis of mercury, chromium and iron", which within 89 pages summarizes her main scientific contributions based on the articles from the list of publications for participation in the contest that are included in group "B" indicators (A1, A3, A4, A7, A12).

A list of 34 research projects dating back to 1984, that are funded by state funds or the Ministry of Education and Science or European and international programs is presented. From these projects, 11 are conducted by Dr. Vasileva after her habilitation either as a leader (6 projects) or as a participant.

The indicators for the academic activity of Assoc. Prof. Vasileva significantly exceed the minimum national requirements and those of the Faculty of Chemistry and Pharmacy for the scientific activity of the candidates required for the academic position “Professor.” This is shown in the table:

Group indicators	National requirements	Requirements of the Faculty of Chemistry and Pharmacy	Point acquired by the candidate
А	50	50	50
В	100	100	100
Г	200	220	279
Д	50	60	72
Е	150	150	168.5
Ж	-	120	268

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

Assoc. Prof. Vasileva's research and pedagogical activity are within the scientific fields: Science and Technology of Nanomaterials [A1-A16, B34-B36, D52-D54], Chemical Education for Chemistry Training for participation in the International Chemistry Olympiads [C37-C39] and Methodology of chemistry education in secondary school [E1-E11].

In the first of the above-mentioned areas, two scientific topics can be considered, the first one is new methods for the synthesis of nanoparticles and nanocomposites, while the second is related to their potential application. The first one is devoted to synthetic procedures of silver and gold nanoparticles in aqueous dispersions [A1, A4, A6, A13, A14, B34, B36, D52, D54], metal oxide nanocomposite particles [A2, A3, A10, A12, A15, B36, D53] and hybrid organic-inorganic nanocomposite materials [A5, A7, A9, A11]. New "green" chemical methods for the synthesis of nanoparticles and their composite nanostructures as well as their physicochemical characterization have been developed and optimized. Analytical applications of metal nanoparticles and their composite nanostructures for special analysis of toxic and essential elements, such as silver nanoparticles as selective and sensitive optical sensors for the determination of Hg (II), Cr (VI) and Fe (III) are proposed within the second topic [A1, A4, A6, A8, B34, B35]. Metal oxide nanocomposite particles and hybrid organic-inorganic nanocomposite films as effective nanosorbents for solid phase extraction and special analysis of mercury and chromium [A3, A5, A7-A9, A11, A12, A15, B35] are also studied, as well as, the biological [A13, A14, B36] and (Photo)catalytic activity [A2, A10, D53, D54] of the synthesized nanoparticles and nanocomposite materials.

It is important to emphasize the contribution of Assoc. Prof. Vasileva in education and promotion of chemistry among high school students in our country, especially for her participation in training and educating Bulgarian Olympians students and for their excellent performance at the International Chemistry Olympiads [C37-C39, E1, E2, E4, E5].

4. Main scientific and applied scientific contributions

The contributions of Assoc. Prof. Vasileva can be summarized according to the above-mentioned areas of her research, as follows:

• Design of gold and silver nanoparticles in stable aqueous dispersions

An original "green" synthesis of silver [A1, A3, A4, A6, A12, A13, A14, D52] and gold [A3, B34, B36, D54] nanoparticles has been developed and optimized.

• Functional properties of metal nanoparticles

It has been shown for the first time that starch-coated silver nanoparticles can be used as an LSPR-based optical nanosensor for selectively detection of Hg (II) and Fe (III) in aqueous samples from the environment. The conditions for direct quantification of both analytes have been optimized, and mechanisms of selective sensory activity have been proposed. It has been shown that the sensory activity of silver nanoparticles is selective for the chemical form Fe (III) and for Hg (II). Simple, fast and low-cost analytical procedures have been developed for easy and sensitive quantification of Hg (II). The analytical applicability of the developed analytical procedures for simple and fast field screening of Hg (II) and Fe (III) in groundwater and drinking water, and for determination of Hg in wastewater [A6, A4] has been confirmed. A new, fast and effective strategy for direct and selective determination of the toxic chemical form of chromium Cr (VI) in aqueous samples has been developed [A1, B34]. Precise optimization of the response time of the optical sensor demonstrates for the first time the possibility of selective, accurate and reliable determination of Cr (VI) in the presence of high concentrations of Cr (III). The proposed analytical procedure is feasible during sampling and is applicable for rapid screening for Cr (VI) of groundwater from contaminated regions [A1].

• Biological activity of metal nanoparticles

In vitro experiments have shown a different effect of the two types of silver nanoparticles synthesized with different stabilizing agents (starch or raffinose) on the "isolated heart" of a frog. It has been found that silver nanoparticles with a less dense coating than the raffinose trisaccharide have a positive inotropic effect (increase in the strength and speed of heart contractions). As is a result of the denser coating of starch polysaccharide, due to their reduced reactivity, no effect of nanoparticles on heart rate was found. It has been shown that in the presence of adrenergic receptor blockers (prazosin and propranolol), the positive inotropic effect of nanoparticles is partially reduced due to nonspecific activation of adrenoceptors on cardiac cell membranes [A13]. For the first time, the biological activity on cellular and subcellular components of raffinose-coated silver nanoparticles was studied. A dissociative effect on intact mitochondria from liver cells with an inhibitory effect on ATPase activity has been demonstrated and the ability of silver starch-coated nanoparticles to pass through the inner mitochondrial membrane has been demonstrated [A14].

• Catalytic activity

High catalytic activity of the synthesized gold nanoparticles coated with raffinose was found and it was shown that the fraction of gold nanoclusters present in the dispersion of nanoparticles is responsible for this phenomenon. Homogenization of the nanoparticles in size was found to be a result of Ostwald ripening and preparation of a monodisperse suspension. This process has been shown to be associated with a tenfold decrease and stabilization of the catalytic activity of nanoparticles [D54].

• Design of metal oxide nanocomposite materials

A three-stage synthesis for the production of nanocomposite "core-shell" materials has been developed and optimized. Physicochemical characterization has shown that the final stage of "colloidal mixing" produces discrete metal-oxide nanocomposite particles consisting of pre-synthesized and surface-functionalized monodisperse submicron SiO_2-NH_2 spheres ("nuclei") and disc-arranged on the surface of the "cores" silver and gold nanoparticles ("shell") [A3, A12, A15]. A new effective two-stage "solution-solid" method for the synthesis of nanocrystalline ZnO and composite metal-oxide nanocrystals Au/ZnO in a starch matrix has been developed and optimized. The critical experimental conditions for achieving the desired physicochemical and functional characteristics of the product of this synthetic method have been established [A2, A10, D53]. It has been shown that the gold nanoparticles in the Au / ZnO nanocrystalline composite are formed in the first stage (solution phase), while the ZnO nanophase is formed in the second stage (solid phase). The nanocrystalline nature of the gold and oxide nanophases has been established [A2].

• Functional properties of metal oxide nanocomposites.

Metal oxide nanocomposite particles of SiO_2 / AgNPs and SiO_2 / AuNPs were synthesized for non-chromatographic special analysis of mercury. Different chemical affinities of the two types of nanocomposites to Hg (II) and $CH_3 Hg^+$ [A3, A12, A15] have been achieved. Optimal conditions for quantitative sorption of Hg (II) and CH_3Hg on the surface of nanocomposite particles, respectively, have been established and mechanisms for sorption activity and their high selectivity have been proposed [A12, A3].

• Antibacterial activity of metal nanoparticles and their metal oxide nanocomposites

The toxic effects of different types of nanomaterials (silver nanoparticles, carbon nanostructures, nanoparticles of metal oxides) from contemporary articles on the mechanisms of antimicrobial activity of metal-based nanomaterials are systematized and summarized in a chapter entitled "Nanoparticles and Nanoparticles and [B36].

• Photocatalytic activity

High photocatalytic activity of the samples of nanocrystalline photocatalyst ZnO synthesized in a starch matrix was found [A10, D53]. The size and shape of ZnO nanocrystals have been shown to be essential for the observed high photocatalytic activity [A10]. An optimal starch-Zn (II) ratio at which the maximum catalytic efficiency of the nanocrystalline ZnO photocatalyst is achieved, has been established [D53].

• Design of hybrid organic-inorganic nanocomposite materials

A procedure has been developed for the production of a new hybrid organic-inorganic composite material based on SiO_2 of the "core-shell" type [A5]. An environmentally compatible method for obtaining hybrid nanocomposite films with homogeneous structure, high stability and good mechanical properties has been developed [A7, A9, A11].

• Functional properties of hybrid organic-inorganic nanocomposite materials as nanosorbents for solid phase extraction in special and multi-element analysis procedures

Hybrid organic-inorganic microspheres of SiO_2 have been shown to be an effective sorbent for the rapid and selective quantification of Cr (VI) [A5]. It has been also shown that hybrid chitosan nanocomposite films with embedded silver nanoparticles coated with raffinose are an effective sorbent for multi-element solid phase extraction and enrichment of Al (III), Cd (II), Co (II), Cr (III), Cu II), Fe (III), Ni (II), Pb (II) and Zn (II). An analytical method for the determination of Al (III), Cd (II), Co (II), Cr (III), Cu (II), Fe (III), Ni (II), Pb (II) and Zn (II) has been developed [A9]. A validated analytical procedure for the determination of Al (III), Cd (II) and Pb (II) has been established [A11]. An analytical method for the determination of Cr (VI) in waters using hybrid nanocomposite films as an effective and selective sorbent of Cr (VI) in the presence of Cr (III) has been also proposed [A7].

• Dental composite materials

For four dental composites, the relationship between composition and morphological characteristics, the degree of photopolymerization and the amount of residual monomer released in aqueous solution is shown. It has been found that a higher degree of conversion does not necessarily result in a lower amount of the released residual monomer [A16].

6. Critical remarks and recommendations to the scientific works of the candidate

I have no critical remarks to Assoc. Prof. Vasileva and to the applied documentation. It is presented correctly and in accordance with the requirements of the law and the regulations of Sofia University.

7. Personal impressions of the reviewer about the candidate

I know Assoc. Prof. Vasileva very well and I highly appreciate her competence as a specialist and responsiveness of a colleague. I can say that thankfully to the various discussions and seminars we have had in our joint participation in some of the faculty research projects, her advices, comments and recommendations about the synthesis of nanoparticles have been extremely valuable when we needed to overcome and solving our important tasks related to experimental details, data interpretation and proposing new kinetic models.

CONCLUSION

The documents presented by Assoc. Prof. Vasileva, as the only candidate in the announced contest for the academic position "Professor" in the professional field 4.2. Chemical sciences for the scientific specialty "Inorganic Chemistry" meet and further exceed the requirements of the Law and the Regulations on the terms and conditions for acquiring scientific degrees and holding academic positions at Sofia University "St. Kliment Ohridski". Her contributions are undeniable and clearly discernible in the scientific community.

The analysis of overall research work, scientific and pedagogical activity of Assoc. Prof. Dr. Penka Vasileva Tsanova gives me the confidence to support her candidacy and to recommend to the Honorable Jury to propose to the Faculty Council of Faculty of Chemistry and Pharmacy **to award her the academic position "Professor"** in a professional field 4.2. Chemical sciences for the scientific specialty "Inorganic Chemistry".

14.03.2022 г.

Sofia

(prof. Konstantin Balashev, DSc)