REVIEW

of the materials submitted for the **competition for the academic position of „Associate Professor”** in the Faculty of Chemistry and Pharmacy, St. Kliment Ohridski University of Sofia in Higher education professional field 4.2. Chemical Sciences (Inorganic Chemistry) from **Prof. DSc Dimitar Stefanov Todorovsky**, pensioner, former professor in the Faculty of Chemistry and Pharmacy, St. Kliment Ohridski University of Sofia

1. Administrative remarks

Announcement of the Competition*:* Darzhaven vestnik (State Gazette) No 21/15.03.2022.
Rector’s order for the constitution of the Scientific jury: РД-38-175/01.04.2022.
Appointment of D. Todorovsky as a reviewer: Protocol No 1/30.05.2022 of the Scientific jury.
Candidate in the competition: **Dr. Nina Veselinova Kaneva-Dobrevska**, Chief Assist. Prof. in the Department of Inorganic Chemistry of the Faculty of Chemistry and Pharmacy, St. Kliment Ohridski University of Sofia; ORCID No: 0000-0002-2010-7118.

2. Brief biographical data for the candidate

Mrs. Nina Kaneva was born in 1988.

Education. She is graduated as a Bachelor in Computer Chemistry and Teacher in Chemistry and Environmental Protection (2011) and Master in Medical Chemistry (2012) at the Faculty of Chemistry, St. Kliment Ohridski University of Sofia. In 2016 she defended PhD dissertation on the „Synthesis and characterization of pure and modified nanoscale ZnO for photocatalytic application” under the supervision of Assoc Prof. Dr. Karolina Papazova and Dr. Asya Bozhinova.

Professional experience: 2011-2012: chemist, Institute of Molecular Biology, Bulgarian Academy of Sciences.

2015–2021: Teacher in Chemistry and Environmental Protection - National Gymnasium of Natural Sciences and Mathematics.

Since 2015: Assist. Prof., since 2016 - Chief Assist. Prof. in Department of Inorganic Chemistry, Faculty of Chemistry and Pharmacy, Sofia University.

Specializations and international visits: Faculty of Science, Charles University, Prague (2008, 1 week); Department of Chemistry, Saitama University, Saitama (2009, 1 month); Bar-Ilan University, Israel (2011, 1 week), Michigan State University (2011, 2012 - participation in international seminars „Contaminants in the environment and their remedation” and „Fundamentals in understanding water quality”).

Scientific awards: Annual awards of the Sofia University for scientific achievements (2010, 2011); Rostislav Kaischev Fellowship (Chemistry) of Evrica Foundation for young scientist (2011); Prof. Yanko Dimitriev’s Award for PhD student and young scientist in materials science and nanocomposites (2017).

Memberships: Bulgarian Catalytic Society.

3. General description of the deposited materials

The deposited materials are listed in the Application form for participation in the competition and meet the requirements of article 107(1) of the Regulations for the Conditions and Order for Acquiring of Academic Degrees and Academic Positions in the Sofia University. The documents reveal the divers scientific and teaching activities of the applicant.

Dr. Kaneva presents a list of 74 scientific publications, incl. - according to the applicant - 41 in journals with impact-factor or impact rank. Dr. Kaneva reports for 332 independent citations and h-index 12 (Scopus).

3.1. Dr. Kaneva participates in the competition with:

- *19 scientific papers* published in the period 2009-2020. Their distribution between the ranks of the journals is shown on the following Table. Most of the papers are published in specialized journals including highly appreciated Journal of Alloys and Compounds, Applied Surface Science, Applied Surface and Coatings Technology, Colloids and Surface A, Reaction Kinetics, Mechanisms and Catalysis. The papers are not presented in the PhD obtaining procedure.

- List of 47 *citation* of one paper presented for fulfillment of the requirements of indicator „Д".

- List of titles of 93 *reports* (including 14 oral) on scientific forums (2008-2022) (without bibliographic description and abstracts).

- Documents showing her participation in *10 scientific and educational projects* (2007-2024), financed by the Bulgarian National Science Fund (5 projects), European programs (4 projects) and foreign research foundation (1 project).

- *Habilitation thesis*.

- *The author's reference* - comprehensive and detailed, clearly presenting the scientific contributions of the applicant.

3.2. The fulfillment of the official minimal requirements for the acquiring the academic position of „Associate Professor" (according to both the national legislation and the specific recommendations of the Faculty of Chemistry and Pharmacy) is seen in the following Table.

Table. Fulfillment of the official minimal requirements for the acquiring the academic position „Associate Professor"and some scientometric data for the published papers

Indicator	A	В				Г					Д	Ж
Points												
National requirements	50	100				200					50	-
Faculty recommendations	50	100				220					70	70
Dr. N. Kaneva	50	104[1]				249[2]					94	165
Journal rank		Q1	Q2	Q3[1]	Q4[1]	Q1	Q2	Q3	Q4	Book chapter[2]		
Number of publications		1	2	-	3	3	4	3	2	1		

[1] The quartile of paper № 4 (from the list presented in file 10б from the applicant's documents) is Q4 for the year of publishing (SJR metrics), not Q3 as shown by Dr. Kaneva. The reduction of 3 points for Indicator „В" does not change the fact that the points for this indicator meet the requirements.

[2] Dr Kaneva presents as a Book chapter the publication "Photocatalytic efficiency of zinc oxide films obtained at different annealing temperatures", published in The Book of Full Text, BLACK SEA NETWORK FOR INTERCULTURAL COMMUNICATIONS (BIC), 5 (2020) 171-179. ISPEC Publishing House, Editors Dr. Bulent Haner and Zhuldyz Sakhi. ISBN: 978-625-7720-11-3,

The book represents full text proceedings of the International Black Sea Coastline Countries Symposium-5, held on 28-29.11.2020. The paper of Dr. Kaneva et al. presents the results of a particular investigation (with 14 cited references) and her claim to be included in Indicator „Г8. Published book chapter or collective monograph" is unacceptable. In the file „11.Scientific contribution of Dr. Kaneva" (from the documents presented by the applicant) the paper is presented (incorrectly to my opinion) in Section „Book chapters" and (correctly) in Section „Conference participations". The reduction of 25 points for Indicator „Г" does not change the fact that the points for this indicator meet the requirements.

3.3. Habilitation thesis

The habilitation thesis entitled „Purification of waters from organic pollutants by means of heterogenic catalysis" (31 pages, 23 references) is worked out on 6 papers (2010-2017) of the applicant; in 4 of them she is 1-st and in one - 2-nd author. These papers have 35 citations. The reported results will be discussed in more details in point 4 of the review.

The thesis is appropriately constructed. It reveals the significance of the problem; short description of the investigateded pollutants azo-dyes and pharmaceuticals and general principles of the heterogenic photocatalysis are given.

Methods are described for: (i) preparation of ZnO as a photocatalyst: sol-gel in few modifications and chemical deposition combined with two methods for films deposition, (ii) mechanoactivation of commercial ZnO in planetary ball mil, (iii) determination of crystal structure, crystallites size, morphology and specific surface area of the prepared materials.

Experimental results from the photocatalytic degradation of the investigated pollutants are presented, the kinetics of the processes is determined and the influence of few factors on the photocatalysts activity is discussed:

- Films morphology and crystallites size resulted in different sol synthesis methods.
- Chemical nature of the pharmaceuticals.
- Mechano- and thermal activation. The problem is of interest because, along with other changes, these treatments might cause changes in defect concentration.

The authors explain the increase of the photocatalytic activity of ZnO films at the increase of annealing temperature with the exponential increase of the defect concentration.

The reported experimental results show not synonymous effect of the mechanoactivation on the photocatalytic activity (as shown in other studies). Indeed, the defects could possess different role – as absorption centers in the visible spectrum and adsorption centers but - as charge carriers recombination centers, also. Thus, they may have positive or negative effect on the activity. The influence of the medium and the time of the activation shown in Dr. Kaneva's works can be related to their influence on the type and concentration of the induced defects. The possible concurrence between the increase of the specific area and of the defect concentration - both results in the mechanotreatment - is correctly mentioned in the habilitation thesis

From the established higher activity of the products activated in ethanol than of those activated in air, one could speculate that the dispersion of the material is more important than the defect concentration. However, the lower results achieved after activation in methanol suggests that the process is probably more complicated.

4. Scientific activity

The **scientific field of Dr. Kaneva is clearly defined** – synthesis of powders and thin films of pure and modified/doped ZnO and their application for photocatalytic purification of waters from dyes and pharmaceuticals.

The applicant's investigations, reported in papers presented in the present competition, are developed in ***two closely connected directions***:

4.1. Fine inorganic synthesis and materials characterization of pure and modified ZnO powders and thin films as photocatalysts

The influence of the composition of the produced materials and of number of factors influencing the crystal structure, the morphology, some physico-chemical properties and – as a result – the photcatalytic activity of the prepared materials is studied.

a) Powders. Commercial TiO_2 (anatase) and ZnO are used [13][1]. ZnO powders are modified by: (i) thermal activation (1 h, 100-500 ^oC) [2], (ii) mechanical activation (by planetary ball mill with agate or stainless steel triboreactors at 200-400 min^{-1} at weight powder/balls ratio of 1:3–1:10 for 1-60 min in air or as ethanol/methanol suspension) [2,3],

[1] The numbers follow numbering in the list of papers given in file 10б in the documents submitted by the applicant. The paper presented as book chapter is denoted with № 19.

(iii) mixing with $ZnFe_2O_4$ [10] or with oxides of La and Eu and nitrate of Ce(III) (mixing at sonification, dried at 100 ^oC) [18].

b) Thin films preparation

- *Initial sol* is prepared by variants of the sol-gel methods [4,5,16,17,19]. Usually $Zn(CH_3COO)_2 \cdot 2H_2O$ as a Zn source is used. The synthesis is performed in presence of polymeric or complexing additives. Microwaves assisted sol-gel preparation is applied for TiO_2 modified ZnO [12-14]. The influence of the preparation method [1,15] and of the various solvents tested [1,5,17] on the films morphology is shown.
- Glass *substrates* are usually used [1,4-6,8,11,14,15,16,17,19]. Al-folio is also tested but the roughness of its surface make results to worse [8,16].
- Few *film deposition methods* are applied: dip-coating [1,4,5,8,10,16,17,19], spin-coating [1,6], spray-pyrolysis [12], chemical deposition (for nanowires preparation) [6,13]. The later method (used in other paper with the applicant's participation) consist in two steps: modification of the glass substrates with a thin layer of ZnO (produced by heating of spin coated layer of $Zn(CH_3COO)_2 \cdot 2H_2O$) followed by hydrothermal growth of ZnO nanowires in aqueous solution of $Zn(NO_3)_2$ and methenamine at 87 ^oC in closed vessel. In the ZnO-TiO_2 experiments, nanowires with length of 3–3.5 μm, diameter of 100–150 nm and TiO_2 particles of about 0.05 μm distributed between the ZnO nanowires are produced [13].

The sprayed films, obtained from in the presence of polymer modifier possess a porous structure, while the sol–gel films have ganglia-like hills with a width of 0.5–1 μm [8].

- *Post-deposition annealing* is performed at 100, 300, 500 ^oC [4,19]; 500 ^oC [16]. AFM images show that the surface morphology of the films strongly depends on the annealing temperature; the size of the crystallites and of the surface ganglia structures increase with annealing temperature increase [19].
- *Modification* of ZnO films is performed with: (i) Ni^{2+} (0-15%) [7], (ii) $ZnFe_2O_4$ [10,11], (iii) TiO_2 (0–100 mol%). It is shown that the titania dopant causes significant changes in the crystal structure and morphology of the films and leads to the formation of hexagonal nanorods on the ZnO surface [12]. TiO_2 doped ZnO nanowires thin films [13] and multilayered sol-gel ZnO/TiO_2/glass structures [14] are produced.

c) Characterization of the prepared materials

Number of analytical technique is applied for characterization of the produced photocatalysts:

- Crystal structure – X-ray difractometry [1,2,4-8,10,11,13,14,18].
- Morphology - SEM [2,4-7,10,11,13,15,16,18,19], TEM [18], AFM [19].
- Spectral properties – FTIR- [5], UV/Vis- [6,11,15,16,18] spectroscopy and XPS [1,8,12,14].
- Composition and electronic properties - X-ray photoelectron spectroscopy [12].
- Specific surface area - BET [10,18].

d) Preparation of Cu-doped ZnO thin films for ethanol vapours sensing

The electrical and gas-sensing properties of nanostructures formed of two overlaping layers of pure and Cu-doped ZnO are investigated. Nonlinear dependence of the potential difference on ethanol concentration at constant temperature is found [9].

4.2. Photocatalytic properties of the prepared materials for water purification from azo-dyes and pharmaceuticals

a) Pollutants. Two types of organic pollutants of waters are objects of the performed photocatalytic investigations:

- azo-dyes: Malachite Green [1,7,10,12,14,15,16,17]; Brilliant Green [3], Reactive Black [8,11,19], Orange II [13];

- pharmaceuticals: Chloramphenicol [2,6,18], Paracetamol [2,6,18].

The experiments are carried out with initial pollutants concentrations in the interval 3-20 ppm, for example: 20 ppm Orange II for slurry experiments and 10 ppm for film photocatalysis [13]; 3, 5, 10 ppm Malachite Green [7,15,16] or Reactive Black [19].

b) ***Illumination***. Along with UV-illumination [1,3,4,6,7,10,11,13,16,17,19] (maximum emission wavelength, as an example, 365 nm [15]), visible radiation [3,7,11,13] is also applied. Experiments in darkness [1,7,11,17,19] are performed to elucidate effect of the pollutant adsorption on the catalyst.

c) The influence of number of factors on the photocatalytic activity of the produced materials is established:

- Initial sol preparation method.

- *Complexing agent presence.* The higher photocatalytic activity against Malachite Green solution (5 ppm, 94% degradation after 3 h) of ZnO samples obtained in presence of monoethanolamine is attributed to the greater number of active sites on the surface, while the polymer solution leads to aggregation of the ganglia [15].

- *The influence of few solvents* on the photocatalityc activity is tested and advantages of 2–propanol and especially of 2-metoxyethanol are shown [1,5,17].

- *The microwave irradiation* leads to a formation of poorly crystallized multilayers with very small crystallites and enhanced surface roughness. This results in a higher photocatalytic activity of these structures than the conventionally prepared samples [14].

- Films thickness and type of the substrate

Thicker films of ZnO (prepared by 5 immersions of the substrate in ZnO polyethyleneglycol/ethanol suspension) show higher activity against Malachite Green than films produced by one immersion [10].

The ZnO film on glass *substrate* is more effective for dye decolorization than that on Al-foils [16].

Generally, it is shown that films preparation mode influences photocatalytic activity through its significant effect on the films morphology and crystal structure [1,5,15,17,19].

- Thermal treatment

- *The* ZnO *powders annealed at 100 ^oC* show highest rate constant and 96% mineralization after 1 h of drug irradiation, which authors relate to the smaller size of the crystallites and their better developed surface. Further increase of the temperature to 200, 300, 400 and 500 ^oC leads to decrease of the photocatalityc activity [2].

- A positive effect on the sol-gel/dip-coating produced ZnO films activity with *annealing temperature increase* from 100 to 300 and 500°C towards azo-dyes [19] and pharmaceuticals [4] is established. According to the authors the effect is due to increase of the crystallites/ganglia sizes [19] and to the crystallization of amorphous films and the exponential increase of the defects concentration [4].

- It is shown that the optimal *thermal treatment temperature* depends on the films production mode due to its effect on the crystal structure and morphology, also. ZnO sprayed films, treated at 350 °C, have a higher activity than the sol–gel produced ones. The increase of the temperature to 450 °C leads to a deterioration of the morphology and to significantly decreased activity. On the opposed, the thermal treatment of the sol–gel films at 450 °C leads to a higher crystallinity, which results in faster decomposition of the dyes [8].

Generally, it is shown that films annealing temperature influences photocatalytic activity through its effects on: (i) the crystal structure and the morphology [8], (ii) the size of *crystallites/ganglia [2,19], (iii) the surface area [2], (iv) the crystallization of amorphous films and, mainly, to the exponential increase of the defects concentration [4].*

- Mechanoactivation.

The main result of these investigations is the conclusion that mechanoactivation leads to various phenomena that can have an opposite effect on the photocatalytic activity of the material. The mechanoinduced effects can be dependent on the (even relatively short) activation times (1-60 min) leading to different photochemical behavior of the catalyst - the degradation rate of Acetaminophen and Chloramphenicol by commercial ZnO powder riches a maximum at mechanoactivation time of 30 min in air and then decreases. Effect of the milling media is studied. Activation as suspension in ethanol is more effective than air milling and leads to degradation of 85% of the Paracetamol and 54% of the Chloramphenicol [2]. The effect (on the degradation of Brilliant Green) is different under UV- or visible light irradiation for 1 – 7 min [3].

- Chemical nature of the pollutant.

Following literature data, the higher photocatalytic activity of ZnO films in degradation of Reactive Black 5 (compared to the effect on Malachite Green) is explained with the weaker N=N bond in the Reactive Black 5 in comparison with the C-C bond between the central carbon atom and N,N-dimethylaminobenzyl in Malachite Green which affects the formation of intermediates [8].

It is experimentally shown that the Chloramphenicol is more pliable to photocatalytic degradation under UV-light irradiation than Paracetamol by ZnO thin and nanowires films [6]. The same conclusion is drawn from the results of the treatment with sol-gel produced film under 315–400 nm illumination by a Sylvania 18 W lamp [4].

- Dopants.

- Increasing of the amount (0-15%) of **Ni^{2+}-ions** in ZnO sol-gel/deep-coating films lowers the crystallites and ganglia sizes and the photocatalytic activity in comparison with the pure ZnO films [7]. The respective publication has 47 citations.

- The **$ZnFe_2O_4$**-films have lower photocatalytic efficiency (in Reactive Black bleaching) than pure ZnO films. Its mixture with ZnO has 3 times higher activity than films from pure ferrite [11]. *Negative effect* of the $ZnFe_2O_4$ for both films and powders under UV illumination – the increase of the relative amount of the dopant (1, 5, 10%) in ZnO lowers the photocatalytic activity [10].

- *Synergetic interaction between* TiO_2 and ZnO is observed in TiO_2 doped ZnO films - they show higher photocatalytic activity than that of the undoped ZnO and TiO_2 samples. The films obtained in presence of TiO_2 (molar part 50%) showed the fastest bleaching of the Malachite Green [12].

- Chemically deposited *nanowires* ZnO/TiO_2 show significantly increased activity towards Orange II under UV and visible light illumination than pure ZnO nanowires. It is believed that this is due to increase of the illuminated area and more effective charge separation [13].

- The novelty in [14] is that in the course of sol-gel/deep-coating producing of ZnO/TiO_2 nanostructures *microwave treatment* is applied for drying and heating. So obtained samples show more developed surface, very small crystallites (8 nm) and higher photocatalytic activity, compared to those obtained by the conventional method.

- **Lanthnoids** (oxides/salts) *(mol part 2%)*-ZnO *powder mixtures* manifest faster degradation of Paracetamol than of Chloramphenicol under UV-illumination. The effect depends on the nature of the lanthanoids. The highest effect exhibits the La_2O_3/ZnO mixture degradation of 96% of Paracetamol and 81% of the Chloramphenicol after 4 h photocatalytic treatment) followed by Eu_2O_3/ZnO (88% and 77% for the respective pharmaceuticals) and by the $Ce(NO_3)_3 \cdot 6H_2O/ZnO$ mixture. The authors explain the lanthanoids effect with the more effective separation of the charges carriers and, respectively, higher yield of free radicals [18].

First order kinetics of the studied photocatalytic processes is established.

4.3. Basic scientific contributions

Few ***important characteristics*** of the presented works should be mentioned:

- Investigation of pharmaceuticals as water pollutant, along with the wide-spread azo-dyes, is, undoubtedly, of interest.
- Adequate methods of characterization of the produced materials are applied.
- Some of the investigations and applied methods are performed for the first time: doping of ZnO with Ni^{2+} [7]; thin films and powders of ZnO mixed with $ZnFe_2O_4$ [10,11]; a combination of microwave and conventional treatment used to dry and heat the multilayered ZnO/TiO_2/glass structures [14].
- Plan for the future work is included in the habilitation thesis: (i) Synthesis of more effective ZnO- and TiO_2-based catalysts.(ii) Synthesis of system semiconductor - co-catalyst aiming increase of the quantum yield. (iii) Photocatalytic experiments with pharmaceuticals as pollutants.

The **main scientific contributions** can be summarized as follows:

- **Development of fine inorganic synthesis methods for preparation of ZnO-based photocatalysts.**

Determination of the role of:

(i) the synthesis conditions, incl. of the source materials (solvents, complexing and polymeric additives); (ii) the method of thin film deposition (deep coating, spin coating, spray-pyrolysis, chemical deposition; effect of the microwave treatment); (iii) the temperature of the films annealing; (iv) the time and the medium of mechanoactivation; (v) the presence of dopants (Ni(II), $ZnFe_2O_4$, TiO_2, lanthanoid oxides/salts)

on the films thickness, the crystal structure, the morphology, the specific surface area, some spectral properties of the prepared materials.

- **Contribution to the elucidation of the potential of pure and modified ZnO powders and films as photocatalysts for azo-dyes and pharmaceuticals degradation in water.**

- Specific experimental data are provided for the effect of the application of number of ZnO-based photicatalysts for water purification of azo-dyes and pharmaceuticals.
- The effect of the above mentioned factors and of the pollutant chemical nature on the photocatalytic activity.
- The obtained results contribute to more detailed understanding of the relation

preparation method - film deposition technique – activation/modification ► *crystal structure/morphology – photdcatalytic activity.*

Citation. The applicant reports for 177 citations of the papers presented in the competition excluding self citation of all authors.

Personal contribution. The average number of co-authors of the presented papers is 5.7. Dr. Kaneva is 1-st author in 14 and 2-nd in 2 of the all 19 papers and her personal contribution is clearly expressed.

5. Teaching activity

In 3 of the recent 5 years (excluding maternity leave) Dr. Kaneva has an average total employment of 403 academic hours which exceeds the load required by the University regulations. Dr. Kaneva is giving tuition in seminars and laboratory practice for the courses in General Chemistry with Stoichiometric Calculations and in Inorganic Chemistry for students in number of university subjects. She has been supervisor of 13 theoretical and experimental course projects in Inorganic Chemistry.

I highly assess her work (2015 – 2021) as teacher in Chemistry and Environmental Protection in the National Gymnasium of Natural Sciences and Mathematics.

Conclusion

The scientific work of Dr. Kaneva in the field of inorganic synthesis and photocatalysis starts in the time when she is undergraduate student (papers with her co-authorship are published in international journals in 2009; the role of her supervisors and colleagues from Nanoscience and Nanotechnology Laboratory has to be acknowledged), continued with her PhD dissertation and is successfully developed after that.

The materials provided for the competition proves that the scientific and teaching activities of Dr. Kaneva satisfy the requirements of the national law and of the recommended criteria of the Faculty of Chemistry and Pharmacy. They approve Dr. Kaneva as a qualified scientist and university teacher in the field of inorganic chemistry.

Dr. Kaneva takes part in a series of extensive, detailed and carefully interpreted investigations of the synthesis and photocatalytic behavior of ZnO-based catalysts. The results of her scientific activity contribute toward a better assessment of the potential of ZnO as a photocatalyst.

I know Dr. Kaneva as an excellent 1-st year student and I have some contacts with her up to 2010. She is an enthusiastic and promising young scientist and I believe that his promotion will be useful for both his academic carrier and for the further developing of the photocatalytic investigations in the Faculty.

Taking in mind the scientific and teaching activities of Dr. Kaneva as well as my personal opinion I recommend to the Scientific jury ***to propose to the Faculty Council Chief Assist. Prof. Dr. Nina Veselinova Kaneva-Dobrevska to be elected for the academic position of Assoc. Professor*** in the Professional field 4.2. Chemical Sciences, scientific field Inorganic Chemistry at the Faculty of Chemistry and Pharmacy, St. Klment Ohridski University of Sofia.

7.7.2022 Reviewer:

D. Todorovsky