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REVIEW OF THE DOCTORAL DISSERTATION SUBMITTED BY
***mgr inż.* NINA TARNOWICZ-STANIAK (M.Sc. Eng.)**

The doctoral dissertation entitled „*Gold Nanoparticles as Components of Advanced Hybrid Materials Employing Light to Control the Course of Chemical Processes*" has been prepared by *mgr inż.* Nina Tarnowicz-Staniak (M.Sc. Eng.) at Institute of Advanced Materials, Faculty of Chemistry, Wrocław University of Science and Technology, Poland under supervision of *prof. dr hab. inż.* Katarzyna Matczyszyn (Wrocław University of Science and Technology) as Supervisor (thesis advisor) and *dr* Marek Grzelczak (Centro de Física de Materiales, CSIC-UPV/EHU, San Sebastian, Spain) as Co-Supervisor. The dissertation has been pursued within BioTechNan - the programme of interdisciplinary cross-institutional post gradual studies KNOW in the field of Biotechnology and Nanotechnology.

The doctoral dissertation of Nina Tarnowicz-Staniak is at the boundary of chemical sciences and materials engineering, and it refers to the concepts of preparation of advanced materials capable of using light to control the course of chemical processes. Among important issues is the feasibility of application of plasmonic nanostructures, such as gold nanorods which could provide both catalytic surfaces and strong interactions with light. While gold nanoparticles have been chosen as a key component of the materials examined in the dissertation, the cellulose in a form of nanofibers has been proposed as the second important component of the hybrid materials considered in the study. It is noteworthy that cellulose nanofibers enable efficient immobilization and stabilization of gold nanostructures as well as control of their optical properties. On the whole, the dissertation significantly contributes to the development, preparation, characterization and performance of hybrid, plasmonic and plasmonic-photochromic materials based on cellulose nanofibers. On fundamental grounds, gold nanostructures existing in the presented systems provide control of chemical processes through light-induced plasmonic effects. Immobilization of gold nanostructures on cellulose nanofibers improves the stability and plasmonic properties under intense illumination even at elevated temperatures or in the broad range of pH's. Furthermore, particular emphasis has centered on the fabrication of composites of nanocellulose with plasmonic Au-nanostructures and organic dyes, as well as on the development of hybrid materials based on azobenzene derivatives and nanostructures of gold. The successful approaches have involved introduction of azobenzenes to prompt catalytic enhancement of their photoinduced and thermal isomerization. Finally, the observations concerning temperature changes occurring at the nanoscale as well as the feasibility of application of azobenzene-type dyes as molecular thermometers under different conditions within the proposed frameworks also seem to be of primary importance.

The doctoral dissertation is organized in a way that it consists of three parts (*Introduction; Results, Discussion and Methodology; and Summary – Conclusions and Perspectives*), preceded by *Acknowledgements, Table of Contents, Abbreviation List,* as well as *Summary in English* and *in Polish*. The first scientific part of *Introduction* refers to motivation, objective, research hypotheses and emphasizes the importance and novelty of the pursued research (Chapter 1). Later, in Chapter 2, the author provides general literature review with crucial items of information concerning plasmonic nanoparticles, synthesis and properties of gold nanorods, the feasibility of chemical transformations triggered by light in the context of the plasmon-mediated reaction mechanisms, generation of highly energetic charge carriers, and plasmon-related effects as important catalytic tools, as well as consideration of thermal effects and discussion of inter-band transitions. Here the author mentions own approach based on cellulose as the component of advanced materials, describes nanocellulose with synthetic and mechanistic details related to impregnation with dyes, mentions its hierarchical structure, and addresses the feasibility of *in-situ* reduction of gold complexes and formation of gold nanostructures. At this stage, the author introduces the concept of fabrication of hybrid materials based on cellulose and dyes through application of azobenzenes and gold nanoparticles. In Chapter 3 of *Results, Discussion and Methodology*, the utility of cellulose nanofibres as robust inert scaffolds for plasmonic nanoparticles, enabling stabilization of their optical properties, is addressed. The actual designs are based on cellulose nanofibers decorated with Au or bimetallic AuPd nanorods. The resulting systems are evaluated toward the photocatalytic regeneration of cofactor (oxidized form of nicotinamide adenine dinucleotide, NAD^+) molecules. Here, to facilitate the NAD^+ cofactor reduction, coupling of the reaction with sodium formate as hydride donor is explored. It is noteworthy that Pd-coated Au-nanorods supported on nanocellulose scaffolds have been used as efficient and reusable photocatalysts under illumination with visible light. Details of unique silver-assisted synthetic methodology are also provided and well-documented. The proposed systems have been thoroughly characterized using various analytical technique, such as scanning transmission electron microscopy, UV-Vis-NIR spectrophotometry, and X-ray photoelectron spectroscopy. Among other important issues is the fact that prepared hybrid systems have exhibited practical stability and durability of plasmonic properties under intense illumination, elevated temperatures, and at wide ranges of pH's. In this respect, advantages coming from the application of cellolose nanofibers as an inert scaffold should be emphasized

In Chapter 4, the author describes current challenges in the area of plasmonic-photochromic hybrid systems by presenting a general protocol for the preparation of multifunctional, water-dispersible, cellulose-stabilized hybrid plasmonic-photochromic materials. Technical details of preparative procedures are provided and carefully described. In addition, this chapter examines the mutual interactions between dye and cellulose nanofibers, as well as gold nanorods and certain photochromic derivatives of azobenzenes. In addition to stability of the proposed systems, among important features of the proposed formulation is the ability of the efficient transfer of the dye into aqueous phase. Despite complexity, the proposed materials exhibit well-defined optical characteristics and maintain plasmonic and photochromic features. These facts constitute a significant achievement in the area.

Valuable observations, referring to the effect of gold nanorods on the isomerization process of the photochromic component in the hybrid system composed of gold nanorods, cellulose nanofibers and azobenzene-type dye have been described in Chapter 5. Here, the concept of exploring the catalytic properties of Au nanostructures toward the photoinduced isomerization is novel, indeed, as well as it is of potential practical importance. An interesting observation concern the results obtained for samples containing distinct gold nanorods indicating that the catalytic effect of these nanostructures tends to increase with decreasing their sizes. It is noteworthy that a complete set of thermodynamic parameters describing the Au-induced thermal isomerization has also been provided. For example, for all Au-containing samples, thermal relaxations in the dark have been characterized by activation energies lower by 20 kJ/mol, when compared to the performance of the analogous hybrid samples but without Au.

Chapter 6 addresses fundamental aspects of utilization of plasmon-related effects toward indirect control of Z-E isomerization of azobenzene-type photochromes. Furthermore, by considering the kinetic changes permitting quantification the extent of the thermoplasmonic effects, the author proposes the approach permitting assessment of . temperatures of samples at the nanoscale level. The concept based on application of azobenzene-type photochromes to act as molecular thermometers is original and scientifically valuable. Important kinetic and mechanistic items of information have been obtained upon subjecting the water-dispersed hybrid materials to alternating dark and illumination conditions. In particular, the author has reported statistically significant kinetic changes only for Au-containing samples. Based on statistical modeling, a scientifically sound conclusion has been provided about the predominant contribution of the thermoplasmonic effects to the plasmon assisted processes. At the end of the doctoral dissertation, the author summarizes her scientific achievements, as well as provides *Conclusions and Perspectives (Chapter 7*), in addition to *Appendix.*

The research results described in the Nina Tarnowicz-Staniak's dissertation significantly contribute to the state of the art of functionalized Au-nanostructure-containing systems and to the development of related hybrid materials. On the whole, Nina Tarnowicz-Staniak appears as coauthor of six publications, where two out of them (in which she is a first author) are strictly related to her dissertation, in addition to one position which is a chapter in the reviewed conference proceedings. These works have been published in very good journals of international circulation (e.g., *ACS Applied Materials and Interfaces, Small, RSC Advances, Journal of Physical Chemistry C*). There are also two publications under preparation. Numerous contributions (including oral) to international conferences (in addition to some local conferences) should be noted and appreciated.

Going to the substantive evaluation of the dissertation, I would like to mention the importance of observations and achievements described therein. The main accomplishments concern synthesis, thorough characterization, as well as feasibility of applications in the photocontrol of physicochemical transformations of novel scientifically-advanced functional materials composed of cellulose nanofibers and plasmonic nanostructures, particularly gold nanorods. Among other important issues is detailed characterization of developed hybrid materials using various techniques. Furthermore, such issues as stabilization of optical of gold-nanorode-based systems under various conditions should also be noted here.

Upon reading the doctoral dissertation, my general impression is that the work is well-written. Indeed plasmonic effects and related phonomena, gold nanostructures, cellulose nanofibers, hybrid, plasmonic and photochromic materials and their properties are broadly addressed, as well as the results obtained are carefully described and interpreted. Both the results and conclusions are convincing.

I have got a few minor questions or comments that could be easily answered or explained during the doctoral defense.

(1) The section on plasmonic gold nanostructures is extensive and scientifically sound. However, while discussing properties of gold nanoparticles, the information about historically developed and broadly-studied alkanothiolate-modified gold clusters is largely missing. Some critical review would be useful in this respect.

(2) Some additional information about homogeneity (or their lack) of nanodimensional gold-palladium “alloys” would be helpful with respect to discussion of their catalytic properties.

(3) Is there any detailed experimental evidence for long-term stability and durability of operation of the proposed hybrid systems? The term “great” is not always precise.

(4) There is also technical very minor criticism: in some micrographs (e.g., in Figures 5 and 51), scale bars are not clearly visible.

In conclusion, I would like to express my high appreciation to the efforts of the author, emphasize high scientific value of the obtained results and evaluate very positively the doctoral dissertation. Furthermore, I would like to state that the dissertation meets the formal and customary criteria and expectations for doctoral works in the area of exact and natural sciences and chemistry discipline. Thus, I am convinced that Nina Tarnowicz-Staniak should be readily admitted to the public doctoral defense at Wrocław University of Science and Technology.

Having in mind the importance of pursued research, the quality, the high scientific value and the application potential of results obtained (presented in valuable publications onto which the dissertation is based), I would like to recommend awarding the dissertation and conferring the Ph.D. degree to Nina Tarnowicz-Staniak with distinction (honors).

Pawel J. Kulesza