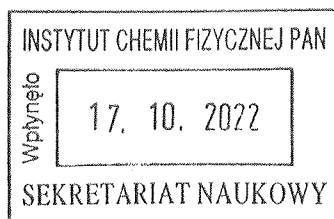


Prof. dr hab. Szczepan Zapotoczny
Uniwersytet Jagielloński, Wydział Chemii
ul. Gronostajowa 2, 30-387 Kraków
Tel.: 12 686 2530
E-mail: zapotocz@chemia.uj.edu.pl



UNIwersYTET
JAGIELLOŃSKI
W KRAKOWIE

Wydział Chemii

Review of the Ph.D. thesis

"Synthesis, characterization, and testing of catalytic nanomaterials – greener route to synthetic methods"

by Alcina Johnson Sudagar

M.Sc. Alcina Johnson Sudagar has prepared the presented doctoral dissertation under the supervision of Prof. Włodzimierz Kutner and auxiliary supervision of Dr. Krzysztof Noworyta at the Institute of Physical Chemistry, Polish Academy of Sciences in Warsaw in collaboration with Prof. Francis D'Souza group at the University of North Texas in Denton. The dissertation covers the synthesis and characterization of nanomaterials for catalytic applications, particularly molecularly imprinted polymer (MIP) films and silver-based hybrid systems obtained following some principles of green chemistry. Fabrication of such catalytic systems is a subject of contemporary studies aiming at achieving more efficient, selective, and "greener" synthetic methodologies. In my opinion, the chosen topics are challenging, and the presented results are important for developing MIP systems serving as catalytic platforms and using industrial wastes for useful synthetic processes as alternatives to their simple disposal.

The dissertation consists of 5 chapters and is written in English. The first chapter classically covers an introduction followed by defining the major aims of the thesis. Fundamental issues on catalysis in general, as well as fabrication and catalytic applications of MIPs, are presented together with current literature background on the fabrication of nanomaterials for catalysis, particularly produced in green chemistry approaches. This part is

well-written, referring to the historical background and supported by the comprehensive list of relevant recent literature. It shows that the Ph.D. candidate has deepened the subject of the doctoral dissertation and provides the reader with an excellent background for the motivation of the undertaken research and an introduction to the issues described below. I would also like to emphasize the nice and legible editing of the entire dissertation using, e.g., helpful color codes for selected abbreviations and informative schemes.

Chapter 2 presents a detailed description of the experimental methods and techniques used by the Ph.D. candidate in her experimental studies. This chapter is a rather extensive part of the dissertation (more than 50 pages) with detailed descriptions and numerous illustrative schemes/figures of ca. 15 various techniques spanning from theoretical simulations, electrochemical techniques, various spectroscopies and microscopies, and dynamic light scattering to analytical techniques. This part indicates a broad range of research tools mastered by the student and described with good level of understanding the physicochemical background of those methods.

The following chapter describes the results of computer simulations and experimental work related to the formation and characterization of MIPs. The research aimed to develop MIPs for the selective electrosynthesis of 2,2'-biphenols, a common molecular motif in natural or synthetic biologically relevant compounds. The application of properly designed MIPs was supposed to enhance the selectivity and efficiency of such syntheses. The selection of functional monomers and crosslinking agents for a given template molecule (3,3',5,5'-tetramethyl-2,2'-biphenol, TMBh) was supported by the density functional theory calculations. Two types of films based on diphenylamine-2-carboxylic acid (MIP-1) and tri-thiophene derivative of methylbenzoic acid (MIP-2) were selected and formed by electropolymerization while MIP-2 was further studied due to poor stability and performance of MIP-1. Importantly, non-imprinted polymers (NIPs) with relevant compositions were also formed and used as control systems. The MIPs were carefully characterized using spectroscopic (e.g., UV-vis spectroscopy), electrochemical (e.g., CV and DPV), and microscopic (e.g., AFM) techniques. The whole approach, including optimization of the formation of MIPs, removal of the template, and performing and optimizing the synthesis of TMBh, was clearly described, and the results were carefully analyzed. As a promising achievement, an increased selectivity in the electrosynthesis of TMBh from the 2,4-dimethylphenol reagent was observed, in spite of limited yield related to stability issues

of the imprinted films under conditions of potentiostatic electrosynthesis applied. Thus, improvement of the MIP stability may be treated as an important pathway for further development of MIPs for such electrosyntheses.

Chapter 4 focuses on the syntheses and catalytic applications of silver-based hybrid nanomaterials obtained by the treatments of brewery wastes (collected at different stages of brewing) with silver cations. It begins with a detailed characterization of selected brewery wastes that is important for further conclusions about the influence of the waste composition on the content and size of the obtained nanomaterials. Polyphenols, (poly)saccharides, peptides, and selected inorganic anions present in the wastes seemed to be mostly involved in the reactions with silver cations and the formation of complex hybrid nanostructured materials. The main silver-based components identified in the hybrid materials were Ag_3PO_4 , AgCl , and Ag metallic nanoparticles. The student studied how the reaction conditions (temperature, time) influenced the final composition and the implied properties of the nanomaterials leading to various activities in electrocatalytic oxygen reduction reactions. She has shown that the samples combining all three silver-based components exhibited the highest photocurrent of all studied samples. That pointed to more complex relationships in the hybrid materials leading to more efficient performance than that observed for pure Ag_3PO_4 or AgCl . Notably, the selected nanostructured composite systems favored the two-electron oxygen reduction process. They positively shifted the oxygen reduction reaction (ORR) potential by ca. 100 mV, making those materials promising for electrocatalytic applications.

The last chapter summarizes the achievements presented in the dissertation and describes the future perspective for the studied systems. This chapter is a concise but essential part showing the ability of the Ph.D. candidate to critically analyze her own research results and envision possible improvements of the studied materials. While a significant increase in the desired product yield accompanied by an increase in the reaction selectivity was achieved, the student also mentioned the need to solve stability issues and develop more cost-efficient monomers for scaling up the formation of MIP films. Moreover, she emphasized that the proposed approach for generating silver-based catalytic materials enables the utilization of some industrial wastes that are cost and environmentally efficient. While she realized the organic surface capping might be necessary for overall catalytic

activity, further processing of the obtained materials converting these organic layers into carbon nanomaterials may be beneficial for the catalytic applications.

The presentation of the results and their discussion in the experimental chapters of the dissertation indicate that M.Sc. Alcina Johnson Sudagar is able to plan the research, ask relevant research questions, and apply adequate methods to answer those questions. She acquired the data using numerous methods (she also clearly mentioned collaborative works), properly presented the data, analyzed them, and plainly described the results. Some of the results presented in the dissertation have already been published (2 papers in Nanomaterials), while the part related to MIPs is in preparation.

The dissertation contains several valuable research results mentioned above, but due to my role as the reviewer, I would also like to add some comments and possible corrections that the candidate may address during the defense of the thesis.

(1) P. 94. It is said that the supernatant obtained after synthesizing silver-based nanomaterials was discarded. Has its composition been analyzed? Could you comment on the level of organic and inorganic matter collected from the wastes in the formed silver-based nanomaterials?

(2) Figure 3.5 b and d as well as Figure 3.8 b, d, and f. Application of the same x-scale would be suggested for the presentation of the results for their easier comparison.

(3) Table 3.2. How the roughness values were calculated, and how do these values refer to the respective film thicknesses? What is the physical meaning of the phase values presented in the table?

(4) Could you propose any methods for improving (lowering) the roughness of the deposited MIP films and eventually decreasing its thickness that may both be important for the overall catalytic performance of the systems?

(5) I would suggest using for controls, in addition to non-imprinted polymer systems, also imprinted films based on molecularly different templates that would not fit the desired product. It would help to distinguish the effects of enhanced selectivity related to the imprinting phenomenon from the effects related to, e.g., different film densities or mechanical properties (see Table 3.3.)

In summary, M.Sc. Alcina Johnson Sudagar has confirmed her competency in synthesizing and characterizing nanomaterials for catalytic applications, including usage of advanced synthetic and characterization techniques. The research methodology was clearly

described, and the results were analyzed with the high care expected for a Ph.D. dissertation, leading to reasonable conclusions. Thus, in my opinion, the reviewed thesis fulfills the criteria set for Ph.D. dissertations in the Act of 20 July 2018 - Law on Higher Education and Science (a current reference to the legal act - uniform text: Journal of Laws of 2022, item 574, as amended) and I ask for admission of M.Sc. Alcina Johnson Sudagar to the public defense of the dissertation.

A handwritten signature in black ink, appearing to read 'Szczepan Zapotoczny', with a stylized, flowing script.

Szczepan Zapotoczny