Instytut Niskich Temperatur i Badań Strukturalnych PAN
im. Włodzimierza Trzebiatowskiego
we Wrocławiu

Adres Instytutu: ul. Okólna 2, 50-422 Wrocław
Tel.: +48 71 343 50 21, Fax: +48 71 344 10 29
E-mail: intibs@intibs.pl | Internet: www.intibs.pl

Reviewer´s report on the habilitation thesis

Author (name and surname): Surjyakanta Rana

Author´s affiliation (institution): Department of Functional Materials, Alexander Dubček University of Trenčín, Slovakia.

Field of habilitation: *Inorganic Technology and Materials*

Title of habilitation thesis: "Graphene-Based Metal Nanocomposites: Harnessing the Synergy of Graphene and Metal Nanoparticles in Coupling Reactions"

Reviewer (name, surname, titles): Assoc. Prof. Włodzimierz Miśta

Reviewer´s affiliation (institution): Institute of Low Temperature and Structural Research of the Polish Academy of Sciences, INTiBS PAN, Wrocław, Poland.

Introduction

Dr. Surjyakanta Rana is a researcher in the Department of Functional Materials at FunGlass, Alexander Dubček University of Trenčín, Slovakia. He is applying for the title of Associate Professor (Docent) in Inorganic Technology and Materials. His habilitation thesis is titled "Graphene-Based Metal Nanocomposites: Harnessing the Synergy of Graphene and Metal Nanoparticles in Coupling Reactions".

He finished his PhD thesis titled „Development of modified mesoporous materials towards various organic transformation reactions" in the Colloids and Materials Chemistry Department, Institute of Minerals and Materials Technology, Bhubaneswar-751013, Orissa, India, in 2013.

His main research activities in Materials Science focus on heterogeneous catalysis, functionalized materials, organic–inorganic hybrid materials, mesoporous materials, nanomaterials, semiconductor materials, and 3D-printing materials.

Assessment of the pedagogical activities of the candidate

Dr. Surjyakanta Rana has demonstrated a sustained commitment to higher education and academic training, with teaching experience extending well beyond the minimum requirements for appointment as Associate Professor. His principal pedagogical activities were conducted at the University of KwaZulu-Natal, South Africa, where he taught Physical Chemistry, Research Methodology, and Nanomaterials to Honors, Master's, and doctoral students.

Dr. Rana's mentoring record includes supervising four Ph.D. students at the University of KwaZulu-Natal and currently co-supervising one Ph.D. student at FunGlass, Slovakia. He has also supervised or mentored five Master's students and three Bachelor's students across institutions in Belgium, South Africa, and Spain. These experiences indicate the extent of international scientific cooperation in research and education.

Assessment of the publication activities of the candidate

Dr. Surjyakanta Rana has established an outstanding scientific record that clearly exceeds the habilitation criteria.

Scientific Papers: Dr. Rana has published 60 scientific papers, including 57 in journals indexed in the Web of Science and Scopus databases.

Citations: The impact of his research is reflected by 1,449 citations excluding self-citations and an h-index of 25 (Scopus) and 23 (Web of Science).

Monographs and Projects: Dr. Rana has also authored two chapters in scientific monographs published by Springer and IntechOpen, and has participated in 11 competitive research projects, serving as the investigator or Principal Investigator on each.

Professional Service: Dr. Rana's contributions to the scientific community extend beyond research output. He holds editorial responsibilities as Associate Editor of Frontiers in Chemistry and serves on the editorial boards of prestigious journals, including Scientific Reports (Nature Portfolio). In addition, he acts as a reviewer for a wide range of high-impact-factor international journals.

Comments on the structure and the content of the thesis

(The habilitation thesis is written as a commented collection of previously published scholarly papers of the Author)

The habilitation thesis was designed to accomplish the following specific objectives:

1. Preparation of heterogeneous catalysts with conducting graphene-based support, incorporating both noble and earth-abundant metals such as Pd, Ni, and Cu. The carbon support parent material is graphene oxide (GO), synthesized by the modified Hummers' method [P1] using stoichiometric amounts of graphite powder and the main reagents $NaNO_3$, H_2SO_4, $KMnO_4$, and H_2O_2. The reaction parameters were controlled to ensure safe, controlled oxidation and exfoliation of GO, which was then reduced by $NaBH_4$ or hydrazine hydrate to obtain the final RGO support.
2. Characterization of various physico-chemical properties of the as-prepared materials by techniques such as X-Ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), Raman Spectroscopy, Transmission Electron Microscopy (TEM), along with Selected Area Electron Diffraction (SAED) measurements, Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Spectroscopy (EDS) and X-ray Photoelectron Spectroscopy (XPS) to confirm their successful fabrication.
3. Evaluation of the catalytic performance of these metal-supported graphene-based catalysts towards various industrially important C–C as well as C–heteroatom coupling reactions, *viz.* Ullmann, Suzuki–Miyaura, Mizoroki–Heck, Kumada–Corriu reactions using aryl halides and substituted aryl halides as starting materials; and to assess conversion efficiency and product yield by GC.
4. Investigate all these coupling reactions, covering aspects like the catalyst selection based on state-of-the-art for the individual coupling reactions, varying reaction conditions, reusability study of the catalysts, and the plausible reaction mechanisms

The habilitation thesis consists of seven thematically unified papers that present a comprehensive investigation of the design, synthesis, and catalytic applications of graphene-based metal composites as advanced heterogeneous catalysts for industrially important coupling reactions. In all of these papers, the habilitation candidate is the first Author.

- **P1:** Authors describe the protocol to synthesize active Pd(II) supported on diamine [N-(2- amino ethyl)-3-amino propyl] trimethoxy silane] (AAPTMS) functionalized graphene oxide, providing strong coordination sites to Pd metal particles. This diamine functionalization substantially improved catalyst longevity and reusability, especially evident in the Pd(0)@diamine-RGO system. Catalytic activity was tested by the selective oxidation of benzyl alcohols to benzyl aldehydes with oxygen in aqueous media, using pyridine as a base. There is still strong interest in finding better catalysts and eco-friendly, economical alternative methods in this reaction.
- **P2:** An efficient and easy route to synthesize reduced graphene oxide with well-dispersed palladium nanopartices (7.5nm) is described. Pd^{o}/RGO proved to be an effective, stable, and recyclable catalyst for the Ullmann coupling reaction, with excellent yields of 80-97% in water and good reusability up to 4 cycles, using sodium formate as the reducing agent and potassium hydroxide as the base (80 °C for 5h).
- **P3**: The Author reported the loading of highly air-stable Ni^{o} metal (11nm) on the surface of a reduced graphene oxide RGO prepared by the reduction of Ni(II) deposited on graphene oxide, using hydrazine hydrate. The Ni(0)@RGO catalysts showed superb efficiency in Kumada-Corriu C-C cross-coupling reactions with 92% yield of 4-methyloxybiphenol at 60 °C in THF solvent using Grignard reagent (PhMgCl) in N_2 atmosphere.
- **P4:** The Author reported the catalytic activity of Ni(0)@RGO air-stable (11nm) for the C-S coupling reaction with optimization of reaction conditions in DMF solution using different salts (mainly K2CO3), time, and temperatures of reactions. This catalyst gave excellent yields and conversion (94%) at 90 °C and 3h, giving diphenyl sulfate as a product.
- **P5:** The Author showed the synthesis of highly dispersed palladium nanoparticles (3-7nm) on organo-diamine functionalized graphene, which demonstrates excellent activity

in the Suzuki-Miyaura cross-coupling reaction. The graphene surface, modified with organic ligands such as amines (including Schiff bases and guanidines), serves as a superior support that physically traps the PdNPs, preventing sintering and Ostwald ripening through strong metal-support interaction (SMI). Grafting organic groups (e.g., amine or di-amine groups) onto graphene oxide helps anchor Palladium nanoparticles (Pd^{o}) securely, minimizing metal leaching during reactions. Catalytic activity of Pd(0)AAPTMS@GR with iodobenzene, phenylboronic acid, and K_3PO_4 showed 100% conversion and 98% yield, and the activity remained constant over six cycles. The experiment had an extremely high turnover frequency (TOF = 185,078 h^{-1}) in water at 90 °C and 25min.

- **P6**: The Author reported a highly effective, eco-friendly, diamine functionalized graphene supported palladium (5.5nm) (Pd(0)-AAPTMS@GR) catalyst for the Mizoroki-Heck coupling reaction using triethylamine (Et_3N) as a base and DMF as a solvent, which facilitates the formation of the C-C bond between aryl halides and olefins. For optimization, he performed a coupling reaction (iodobenzene and methyl acrylate) using different solvents and bases. Finally, he observed a 100% yield of coupling product using DMF with Et_3N at 110 °C for 4h.
- **P7:** The Author described the synthesis of coupling catalyst with Cu nanoparticles (4-6.5nm) well-dispersed on different diamine-functionalized supports (GO, mesoporous silica MCM-41, mesoporous zirconia ZrO2, and mixed RGO-MCM-41) using natural leaf extract from Wallich Spurge plant as a green, reducing agent. These bioactive compounds act as both reducing agents and capping agents (stabilizing the nanoparticles and preventing metal particle aggregation and leaching). The 5Cu(0)-AAgPTMS@GO-MCM-41 composite material displayed excellent catalytic activity towards all the C-C, C-O, and C-N Ullman coupling reactions. In general, for supported metal catalysts to be effective, the metal must be highly active and strongly bound to the support (strong metal support interaction, SMSI) to minimize metal leaching and maximize recyclability. This research opens up a novel method for the *in situ* generation (in a one-pot strategy) of transition metal NPs on rGO nanosheets. The main advantage of these methods is the elimination of toxic reducing agents and the avoidance of harsh experimental conditions.

This greener approach may find applications across various medicinal and technological fields, and the catalyst produced by this method can be reused without significant loss of activity.

The specific role of the habilitation thesis is also that cross-coupling reactions are among the most significant carbon-carbon and carbon-heteroatom bond-forming reactions in organic synthesis. Cross-coupling reactions have been widely used for the preparation of various important pharmaceutical products, molecular organic materials, and bioactive compounds.

In the habilitation thesis, the Author focused on the development, synthesis, and comprehensive characterization of graphene-based metal nanocomposites for use as advanced heterogeneous coupling catalysts. The research includes the preparation of both noble-metal (Pd) and non-noble-metal (Cu and Ni) nanoparticles supported on reduced graphene oxide, amine-functionalized reduced graphene oxide, and amine-functionalized reduced graphene oxide and mesoporous silica matrices.

He described, according to the classical mechanism of coupling, that the reaction takes place through an oxidative addition of halide compounds to the Pd(0) metal complex to provide a Pd(II) complex intermediate, and, in general, the reaction ends with a reductive elimination reaction to produce the coupling compounds to close the red-ox Pd(0) ⇔ Pd(II) cycle.

Meanwhile, the Author focused mainly on the catalytic efficiency, stability, and recyclability of the prepared materials in important cross-coupling reactions. The catalysts exhibited promising performance in Mizoroki–Heck, Suzuki–Miyaura, Ullmann, and Kumada–Corriu reactions.

Here are my comments about the synergistic properties between graphene and the active palladium center. In general, researchers describe graphene as a „**solid-state ligand**“ in Pd/graphene (palladium-on-graphene) catalysts for coupling reactions, meaning that graphene actively influences the chemical behavior of the deposited palladium nanoparticles. Instead of merely acting as an inert physical support to hold only the deposited metal, graphene chemically communicates with the palladium to accelerate the coupling reaction. Next, graphene doping, functionalization, and defect creation represent a critical opportunity to develop the next generation of highly active and selective catalysts. The high activity was attributed mainly to the defect site formed on graphene's surface during the synthesis stage. Pd metal atom strongly interacts (SMSI) with functionalities present in the GO surface and also with vacancies situated in the basal plane of RGO using the synergistic electron exchange activity of rGO and Pd (charge transfer of graphene and metal). The integration of metal nanoparticles onto graphene or graphene oxide (GO/rGO) creates a highly active catalytic environment. This synergistic coupling works in several ways:

- **Enhanced Electron Transfer:** Graphene's unique sp^2-hybridized carbon hexagonal network, with C=C bonds within the graphene matrix, acts as an electron-rich reservoir. It facilitates swift electron transfer to and from the metal nanoparticles, lowering the activation energy for C-C and C-heteroatom bond formation (donor/acceptor concept).
- **Defect Engineering:** When materials (such as palladium) are deposited onto graphene, the interaction relies heavily on graphene's structural defects. These defective sites anchor palladium securely via strong metal-support interaction (SMI) while modulating its electronic properties, much as a traditional molecular ligand (e.g., phosphine) does in solution. Strong covalent metal–d–graphene π hybridization (d-π) is observed after deposition of metal on the graphene surface. The formation of chemical bonds and perturbations of the π-electron cloud at the graphene-metal interface can substantially modify graphene's properties, enabling continuous charge transfer across the interface when SMSI is present. All active metals in the coupling reaction (Ni, Co, Pd, Ru, and Ti) are strongly coupled to graphene (chemisorbed). In contrast to the strong hybridization observed for the metals noted above (Ag, Al, Au, Cd, Cu, Ir, Pt), metals are weakly physisorbed onto graphene. Interfacing a transition metal with graphene is central to fundamental science for studying the catalytic and transport properties of graphene. It is also imperative for technological applications of this material, including catalysis, microelectronics, and spintronics. Up to now, graphene research has been on the rise, with no plateau in sight in the near future.
- **Adsorption Capacity:** Graphene's basal plane pre-concentrates reactants (e.g., aryl halides and terminal alkynes) in closed proximity to the active metal sites by π-π interaction.
- **High Surface Area:** Provides a large, accessible interface for high-density dispersion of metal nanoparticles.

In general, a combination of crystal engineering and the support of metallic Pd nanostructures on a conductive catalyst support (few-layered graphene (FLG)) leads to highly enhanced catalytic activity. Graphene oxide (**GO**), with oxygen functional groups and double bonds, can effectively stabilize active metals, transfer electrons, and minimize mass-transfer resistance, making it a promising support for coupling reactions.

The experimental work demonstrates a high level of experimental rigor by applying complementary structural (XRD, TEM, SEM-EDX) and spectroscopic (FTIR, Raman, XPS) characterization techniques.

My only comment concerns the lack of sufficient surface testing methods. The XRD method is not intended for testing surfaces but rather for examining the bulk structure of the sample (article P7, section 3.1: **surface characterization?**). The Author used only one surface analysis by XPS spectroscopy. The only major drawback is the lack of characterization of the support texture and porosity by N_2 adsorption-desorption at 77 K (S_{BET} and pore volume), which could characterize the degree of dispersion of nanographene platelets (i.e., the degree of exfoliation and re-aggregation of graphene sheets due to π–π stacking). To more accurately characterize the dispersion degree of palladium metal, CO chemisorption measurements would be useful. The measurement of average particle size by XRD using the Scherrer equation, or TEM evaluation, is not very detailed. Of course, this relates to the availability of equipment, which would enable the Author to more precisely characterize synergistic effects between the graphene support and the supported metal in hybrid catalysts in the future.

The habilitation thesis by Dr. Surjyakanta Rana is part of a global research trend to develop industrial catalysts based on Pd, Ni, and Cu, supported on GO/RGO conducting supports, for coupling reactions. These works constitute a thematically coherent series of studies, with the guiding principle being to find optimal synthesis parameters to improve the efficiency, increase yields close to the stoichiometric yield of the desired product, and reduce the number and amount of unwanted products or decrease the energy and costs involved in several industrial catalytic coupling processes, making the processes sustainable.

My conclusion is that the inclusion of seven high-quality, high-impact-factor publications provides strong evidence of the research's originality, continuity, and international visibility, while highlighting the central theme of exploiting the synergistic interplay between graphene and metal nanoparticles to enhance coupling catalysis.

Assessment of the formal side of the work (language, style, structure)

The habilitation thesis is written in English and is clearly and logically organized, facilitating comprehension of the scientific content. The document follows a well-structured format, comprising sections dedicated to the scientific background, research objectives, principal findings, mechanistic interpretations, and a comprehensive Slovak-language summary. The presentation is characterized by scientific accuracy, clarity, and consistency. The candidate demonstrates the ability to synthesize extensive analytical and characterization data into a comprehensive and well-reasoned discussion. The originality check conducted through the AIS system yielded a similarity rate of 4.43%, well within acceptable limits and confirming adherence to the principles of academic ethics and proper citation practices.

Reviewer´s questions for discussion to be answered during the thesis defense

Based on the scope, objectives, and outcomes of the presented research, the following questions are proposed:

1. What properties of supported transition metals make them effective catalysts, particularly in coupling reactions? What is the role of support, and which experimental parameters strongly influence activity in coupling reactions when you must optimize the process?

2. What is the opinion of the Author about whether a vigorous debate exists over whether these supported Pd species act through a truly heterogeneous process, or via a homogeneous process involving leached low-coordination Pd in solution or surface of amorphous PdOx, which could be in trace amounts? Up to now, the lack of a fundamental understanding of the relationship between the properties of the nanoparticle, the support, and the catalytic activity has hindered the development and optimization of high-performance supported catalysts, whose performance is a multi-parameter function of preparation and activation parameters (which key parameters are the most important?), and using many traditional catalyst support systems and a variety of synthetic techniques. Generally speaking, for supported catalysts to

be effective, the metal must be highly active and strongly bound to the support to minimize metal leaching and maximize recyclability. What is the opinion that their effectiveness is related to the nature of the support, which plays a decisive role in connection with the amount of palladium released into the solution?

3. What is your opinion about the possible composition of the active palladium catalytic center? Is it possible that Pd^{o}/PdO_x can exist with Pd(0), Pd^{+2}, or $Pd^{\delta+/-}$ oxidation state? It is obvious that in catalytic systems and nanoparticles, palladium frequently exists as a dynamic mixture of metallic palladium Pd(0) and an oxidized state $Pd^{\delta+}$ fractional charge.
4. Please describe the role of size effect (SAC, cluster, nanoparticles), shape, weak and strong metal support interaction, and preferential crystallographic facet exposed of metal nanoparticles on the reactivity of metal/ graphene catalysts.

Conclusion (Explicitly expressed proposal for the award of the scientific-pedagogical title of associate professor):

Habilitation thesis of Dr. Surjyakanta Rana, titled „Graphene-Based Metal Nanocomposites: Harnessing the Synergy of Graphene and Metal Nanoparticles in Coupling Reactions", fulfills the requirements for the habilitation in the field „Inorganic Technology and Materials ".
I strongly recommend acceptance of the habilitation thesis for the habilitation procedure at the Alexander Dubček University of Trenčín and, after its successful defense, awarding Dr. Surjyakanta Rana the scientific – pedagogical title of "associate professor" in the field of "Inorganic Technology and Materials".

Place and Date: Wrocław 10.06.2026

Reviewer´s Signature

[redacted]

Instytut Niskich Temperatur
i Badań Strukturalnych
im. Włodzimierza Trzebiatowskiego
Polskiej Akademii Nauk
50-422 Wrocław, ul. Okólna 2
tel. 071 3435021, NIP: 896-00-07-258