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Reviewer report to the PhD thesis entitled *"Study of microstructure and real structure of nanoparticles prepared by gas aggregation cluster source"*

by

RNDr. Tereza Košutová

Author:	RNDr. Tereza Košutová
Thesis title:	Study of microstructure and real structure of nanoparticles prepared by gas aggregation cluster source
Thesis title in Czech:	Studium mikrostruktury a reálné struktury nanočástic připravených pomocí plynového agregačního zdroje
Thesis subject area:	Fyzika nanostruktur a nanomateriálů, P4F13
Submission year:	2023
Supervisor:	RNDr. Milan Dopita, Ph.D.
Department:	Department of Condensed Matter Physics

The main aim of the submitted PhD thesis of RNDr. Tereza Košutová is to investigate the microstructure and real structure of various types of homogeneous nanoparticles (NPs), such as Au, Ag, Cu, Nb, heterogeneous core@shell NPs, *etc.* produced by aggregation from the gas phase. These various types of NPs are of great interest due to their peculiar properties arising from different phenomena, such as localized surface plasmon resonance in Ag and Au, superconductivity of Nb and niobium oxide or combined and enhanced properties in core@shell systems, having potential applications as sensor material, in biomedicine, catalysis.

The thesis consists of two main parts. The initial part examines the concepts of microstructure and real structure, with a primary focus on gas aggregation synthesis. Furthermore, another chapter highlights the different techniques utilized for characterizing nanoparticles, with a particular emphasis on X-ray scattering methods (PXRD/SAXS/BCDI), size distribution terminology, electron microscopy, and optical properties. The thesis topic and content are relevant to the research field area, and the overall approach and methods used are appropriate.

The second part of the PhD thesis is dedicated to discussing and interpreting the research findings. It is divided into four main groups, focusing on homogeneous and heterogeneous

NPs, NPs in liquid polymer, and other NPs systems. Each subchapter within these groups is further divided into sections dedicated to different types of nanoparticles. The chapter on homogeneous NPs focuses on investigating real and complex systems under high-temperature conditions in a statistical manner. The results obtained from varying substrate coverage with NPs are compared, with particular attention paid to the thermal evolution of microstructure and morphology. The study meticulously examines parameters such as crystallite size, microstrain, density of structural disorders (twinning and intrinsic stacking faults), preferred orientation, structural phase, and growth mechanisms. Additionally, any changes in microstructure and morphology are related to differences in optical properties. The part of heterogeneous nanoparticles consists of the investigation of Ag@ppHMDSO and Ag@TiO_x core@shell. The research puts emphasis on analyzing the influence of the concentration of HDMSO in the gas mixture on the final microstructure, including the size distribution and coherent domain size. Thermal stability of Ag inclusion is also a concern. Regarding Ag@TiOx core@shell, the study shows that the shell thickness varies due to different deposition parameters. Additionally, the research includes a study on the thermal evolution of TiO_2 phases. The part about NPs in liquid polymers was dedicated to the long- and short-term stability of NPs in PEG mainly studied by SAXS. Finally, the study explores the microstructure of several NPs systems, namely Ni@Ti, Fe-C:H, VxOy, and Ta_3NyOx NPs. The initial results of the study are shown in these various topics.

The formal appearance and level of the PhD thesis is of high quality. The PhD thesis is well-structured, with 130 pages including 91 Figures, 1 Table, and 248 literature resources, and well-written in English.

The PhD thesis contains many original results discussed in great detail, well described, well-argued, and compared with relevant published literature. A large part of the results came from PhD thesis of RNDr. T. Košutová led to scientific outcomes published in good-designated internationally impacted journals, wherein three of them, RNDr. T. Košutová is the first author:

T. Košutová, L. Horák, P. Pleskunov, J. Hanuš, D. Nikitin, P. Kúš, M. Cieslar, I. Gordeev, S. Burazer, A. Choukourov, M. Dopita, *Mater. Chem. Phys.* (2021) 125466.
T. Košutová, J. Hanuš, O. Kylián, M. Cieslar, I. Khalakhan, A. Choukourov, H. Biederman, *J. Phys. D. Appl. Phys.* 54 (2021).
T. Košutová, L. Horák, A. Shelemin, M. Vaidulych, J. Hanuš, H. Biederman, O. Kylián, P. Solař, M. Cieslar, A. Choukourov, M. Dopita, *Surf. Interface Anal.* 52 (2020) 1023–1028.

Additionally, many of the results presented within this thesis were published in peer-reviewed international journals with RNDr. T. Košutová as a co-author (7 manuscripts):

A. Hanková, **T. Košutová**, *et al. Mater. Chem. Phys.* 301 (2023).
K. Biliak, D. Nikitin, S. Ali-Ogly, M. Protsak, P. Pleskunov, M. Tosca, A. Sergievskaya, D. Cornil, J. Cornil, S. Konstantinidis, **T. Košutová**, *et al. Nanoscale Adv.* (2023).

P. Pleskunov, V. Prysiazhnyi, D. Nikitin, **T. Košutová**, *et al. Appl. Nano Mater.* (2022).
A.M. Ahadi, H. Libenská, **T. Košutová**, *et. al J. Phys. D. Appl. Phys.* 55 (2022).
A. Hanková, A. Kuzminova, J. Hanuš, **T. Košutová**, *et al. Surf. Coatings Technol.* 431 (2021) 128015.
P. Pleskunov, **T. Košutová**, *et al. Appl. Surf. Sci.* 559 (2021).
H. Libenská, J. Hanuš, **T. Košutová**, *et al. Plasma Process. Polym.* (2020) 1–11.

Furthermore, RNDr. T. Košutová also contributed to research on different topics, where she is the author or coauthor of another 17 published research papers. So far, the 23 indexed publications of RNDr. T. Košutová have been cited 135 times, and she achieved the H-index 7 according to WOS.

To conclude, the findings obtained within the PhD thesis of RNDr. T. Košutová are novel and will provide significant knowledge in the research field area.

I have found several typos and mistakes within the PhD thesis; as an example, a few are listed below:

Page 26: In Fig. 8 a) there is missing scale bar

Page 34: ʻʻ…see SEM micrographs in Fig. 13. c)ʼʼ – but in Fig. 13. c) caption is written AFM micrographs

Page 43: ʻʻ… density of stacking faults in shown inʼʼ instead of in should be is

Page 47: "…SEM micrographs for bare gold and silver NP…" the word gold and silver are exchanged as in a) is silver and b) is gold presented

Page 50: ʻʻ…. Is confirmed by the SEM and TEMʼʼ instead of TEM should be STEM

Page 90: ʻʻ….. an increase in the Ti/Ag rationʼʼ should be ratio not ration

At the end, I would appreciate more detail discussion on the following topics during the PhD defense:

1. Looking at most of the SAXS data collected and presented (as an example, Fig. 69), the high Q-range part does not follow Q^{-4}. What is the reason?
    a. Did you consider the background as the fit parameter to describe data adequately? If yes, what could be the meaning behind this enormous background contribution?
    b. Could it arise from not proper data reduction and correction?
    c. Did you also try to consider a structure factor into a fit to catch a low Q-range?
2. Page 55 – Can you discuss how the initial crystallite size in the Cu_2O phase is larger than the obtained physical shell thickness of 2.2 nm from SAXS?

Tereza's PhD thesis not only meets all the requirements for the degree, but also showcases her exceptional independence, creativity, and critical thinking. I wholeheartedly recommend awarding Tereza with a well-deserved Ph.D. degree after her successful defense.

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