INVESTIGATION OF LASER PRODUCED NOBLE METAL-SEMICONDUCTOR NANOSTRUCTURES

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Received 21 August 2025
Accepted 14 November 2025
DOI: 10.59957/jctm.v61.i1.2026.15

ABSTRACT

The ZnO/noble metal (both individually - Ag or Pd and in combination) nanocomposites are prepared by laser synthesis methods at atmospheric pressure in air. The formation of complex porous nanostructures is carried out by picosecond pulsed laser deposition at room temperature. The effect of post-deposition nanosecond laser annealing on the morphology and optical properties of the nanostructures is studied. The contribution of laser modifications to the change of a surface plasmon resonance (SPR) absorption band, and respectively, to the near-band-edge (NBE) and deep-level photoluminescence emission (DL), is investigated. The resonance absorption properties are obtained for Ag/ZnO nanostructures before and after the laser annealing. While the SPR absorption band appears for mono- and bimetallic samples with palladium after the laser annealing. The plasmon resonance absorption contributes to the enhancement of photoluminescence band-edge UV emission of all samples and suppression of the strong Vis DL emission of monometallic noble metal/ZnO nanocomposites after the annealing. The low level of the DLE emission is observed before the annealing of the bimetallic sample Ag-Pd/ZnO, with annealing slightly affecting it. This sample demonstrates significantly smaller nanoparticles (NPs), as well as a narrower size distribution in comparison to monometallic noble metal/ZnO nanocomposites.

Keywords: nanostructures, noble metals, ZnO, nanocomposites, pulsed laser deposition, laser annealing, SPR, PL.

INTRODUCTION

In recent years, considerable efforts are focused on developing new materials for transparent electronic devices. Zinc oxide (ZnO), a wide band-gap semiconductor with high exciton binding energy, is a promising candidate for various optoelectronic applications [1]. The research emphasizes the design of complex nanosystems, particularly through combining semiconductors with plasmonic noble metals, which enables tuning of optical and electrical properties [2, 3].

The nanocomposites of metal nanoparticles (NPs) in oxide matrices have attracted attention due to their tunable chemical and physical properties, dependent on NP size, shape, and interactions [4 - 7]. Mixing noble metals further enhances optical, catalytic, and sensing functionalities [8, 9]. Integration of noble metals with ZnO, especially via laser-based techniques, can improve photoluminescence (PL) through coupling between the localized surface plasmon resonance (LSPR) of metal NPs and ZnO excitons [10, 11].

Pulsed laser deposition (PLD) allows precise incorporation of noble metals into ZnO, while subsequent laser annealing promotes the formation of NPs, reduces stress, and improves the crystallinity, all of which influence optical behaviour [12 - 14]. The LSPR-exciton coupling enhances near-band-edge ultraviolet emission and suppresses defect-related deep-level emissions, which are associated with defects and non-radiative recombination centers [15, 16]. The enhancement mechanism leads to an increased spontaneous emission rate and enhanced local electromagnetic fields, thereby enhancing the photoluminescence efficiency [16]. The tunable optical properties of noble metal/ ZnO nanostructures have significant implications for various applications, including optoelectronic devices, sensors, and photocatalysts. By controlling NP size, distribution, composition, and annealing conditions, the photoluminescent properties of ZnO nanostructures can be tailored to meet specific application requirements.

The palladium nanoparticles (PdNPs), alongside silver nanoparticles (AgNPs), are promising plasmonic materials due to their tunable LSPR and high refractive index sensitivity [17]. Ag and Pd can form Schottky junctions with ZnO, improving charge separation and photocatalytic activity, relevant for environmental and energy applications [18].

This study aims to synthesize ZnO-based nanocomposites using short and ultrashort pulsed lasers, incorporating Ag, Pd, and combined Ag-Pd, to tune their optical properties.

EXPERIMENTAL

This study demonstrates the effectiveness of ultrashort-pulsed laser deposition of different kinds of composite noble metal /ZnO nanostructures in the atmospheric pressure in air. The influence of ns-laser annealing on the properties of the films is investigated. The produced samples are grown by pulsed laser deposition (PLD) using a picosecond Nd:YAG laser operating at a fundamental wavelength of 1064 nm with a pulse duration of 10 ps and a repetition rate of 1 kHz. The laser fluence is 0.5 J cm^{-2}. The ZnO and noble metals (Ag, Pd, Ag:Pd - 25:75 %) targets are used for laser ablation. The rotated target composed of two sectors is scanned by laser beam for simultaneous deposition of both materials, where the metal plate is placed on the surface of ZnO [13]. The depositions are performed on quartz substrates SiO_2 (001) in ambient air atmosphere. The target to substrate distance is 5 mm. The depositions are carried out at room substrate temperature for 3 min. The laser annealing of deposited samples is performed by nanosecond Nd:YAG laser at the wavelength of 355 nm. The laser fluence is established at 0.7 J cm^{-2}. The samples are modified at 1 pulse in the air.

The morphology of the as-deposited samples is observed by scanning electron microscopy (SEM) using a LYRA I XMU system (Tescan). The optical properties of the produced nanostructures are analysed based on their transmission spectra taken by an HR 4000 UV-Vis spectrometer (Ocean Optics) in the spectral range of 200 - 600 nm. The photoluminescence (PL) measurements of the samples are conducted on a FluoroLog 3 spectrofluorometer (HORIBA Jobin Yvon) with 325 nm excitation light. The optical properties of the nanocomposites are investigated in terms of their morphology.

RESULTS AND DISCUSSION

To have better knowledge of the behaviour of mono- or bimetallic nanoparticles in ZnO nanostructures, we have compared the mixed ratio of Ag:Pd - 25:75 % with a separately doped silver or palladium in ZnO matrix. The SEM images of the samples before and after the ns-laser annealing are presented on Fig. 1. The highly porous network nanostructures are fabricated on the substrates. The formation process of the homogeneous nanonetwork (NN) layer at a close target-to substrate distance is attributed to the pure nonlinear effect of the picosecond laser, used for deposition. The ps-laser beam interacts with the target and nonlinear ionization is induced to establish surface plasma plume. The plasma vapor quickly cools down and condenses into nanoparticles after leaving the target in a short distance. The condensation occurs, where the nanoparticles merge with each other into nanowires, which stack randomly on the substrate to form the complicated nanonetwork. The aggregations of nanoparticles, which are normally induced by thermal treatments are partially inhibited due to the short pulse duration [19, 20]. In comparison to the conventional ns-PLD, the pure nano morphology at a much closer target-to-substrate distance can be achieved. Observations on nanoparticles are made using the magnified SEM images with the particles' size distribution presented on the histogram insets. The laser treatment leads to formation of distinct spherical nanoparticles with mean diameter of 150 nm for the Ag/ ZnO sample. The samples of Pd/ZnO and Ag-Pd/ZnO

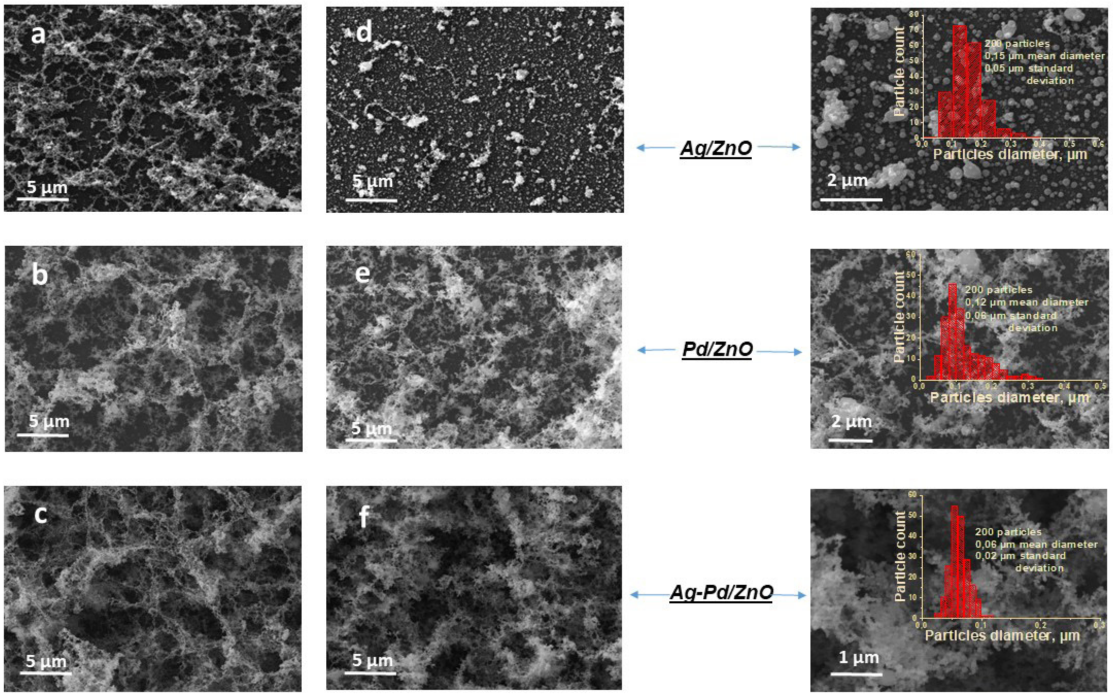

Fig. 1. SEM images of ZnO/noble metal nanostructures (a, b, c) before the laser annealing, (d, e, f) after the laser annealing and magnified SEM images with the histograms of particles size distribution.

demonstrate a nanonetwork morphology consisted of nanoparticles, which retained after the annealing, but a weak agglomeration of NPs is observed. The large porosity of the films deposited in the air is observed. The mean NPs diameter for the Ag-Pd/ZnO sample is about 60 nm, in comparison to the other samples of Pd/ZnO and Ag/ZnO (120 nm and 150 nm, respectively). The narrower NPs size distribution in the range of 20-110 nm is observed for Ag-Pd/Zn sample after the annealing. While the other samples show a wider size distribution in the ranges of 40-340 nm for Pd/ZnO and 30-360 nm for Ag/ZnO.

The noble metal nanoparticles can enhance the light absorption of semiconductors, because they have large absorption/scattering cross-sections and can strongly focus light close to their surface, due to localized surface plasmon resonance (LSPR) [21, 22]. The optical properties of the nanostructures presented in Fig. 2 are obtained by UV-Vis transmission spectroscopy. These spectra show the characteristic surface plasmon resonance band of AgNPs centered at about 355 nm, for samples before and after the laser annealing.

The UV-Vis spectrum of Pd/ZnO demonstrates that the characteristic absorption edge of ZnO after the annealing is red-shifted leading to a loss of transmission in the blue and violet regions and lower absorption of the UV light is observed. This transition is presented on Fig. 2 (curves 1 - before and 5 - after the annealing of Pd/

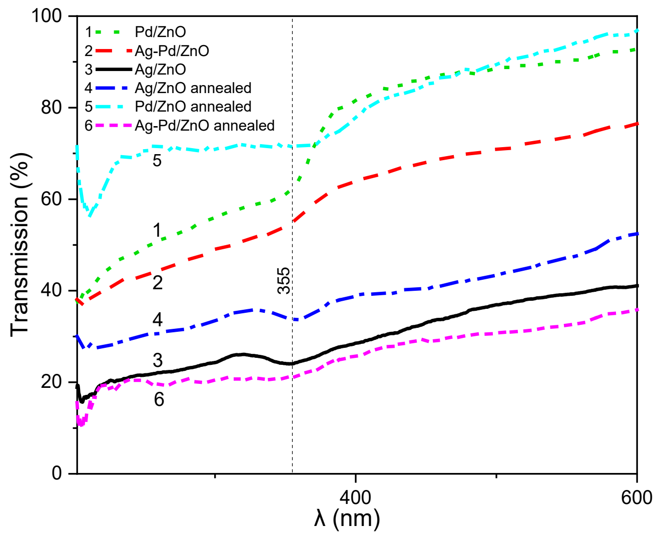

Fig. 2. Transmission spectra of ps-laser grown ZnO/noble metal nanostructures before and after the ns-laser annealing.

ZnO). The red shift in the optical absorption edge, which means the band gap decreases, allowing the material to absorb visible light more effectively. This happens because after the annealing the dopant introduces new energy levels within the band gap, shifting the absorption threshold to lower energies (longer wavelengths). These processes are accompanied by appearance of a narrow absorption band at about 212 nm, which can be associated with Pd nanoparticles. The small spherical PdNPs exhibit SPR between 200 nm and 300 nm [17, 23]. A weakly pronounced absorption edge of ZnO is observed in the deposited sample of Ag-Pd/ZnO. Here, the presence of monometallic Ag or Pd nanoparticles is not confirmed. The presence of Pd in the alloy NPs suppresses the SPR band of Ag before the annealing and the spectra of the Ag-Pd/ZnO could be considered as confirming that the nanostructures and NPs are composed of Ag-Pd alloy formations in ZnO matrix. The absence of even a shoulder at the absorption for the silver plasmon band rules out a preferential reduction of silver. The appearance of a shoulder and minima in the range of 200 - 360 nm is observed after the annealing of this sample and this is associated with nanoparticles formation of the noble metals, where the absorption is more pronounced for Pd.

The PL measurements are carried out and are presented on Fig. 3. A peak around 380 nm is observed, which is due to the band gap transition of ZnO. The peaks in the wavelength region of 450–600 nm are assigned to exitonic PL emission, resulting from surface defects or vacancies. All samples showed amplification of the UV PL signal after the annealing, which is associated with the direct transition of electrons from the conduction band to the valence band. An intense PL emission in the visible region is observed for both monometallic noble metal/ZnO samples. The intense visible PL emission of Ag/ZnO and Pd/ZnO before the annealing is associated with defects, like oxygen vacancies or zinc interstitials. These defects can trap photogenerated charge carriers (electrons and holes) and then release the trapped energy as light in the visible spectrum. The laser annealing impacts the defect density. The laser modification tends to enhance UV near band-edge emission and reduce the deep level emission, thanks to improved crystallinity and defect passivation. A quite different behaviour is observed for bimetallic NPs (Ag-Pd) in the ZnO nanostructure. The Vis peak intensity is

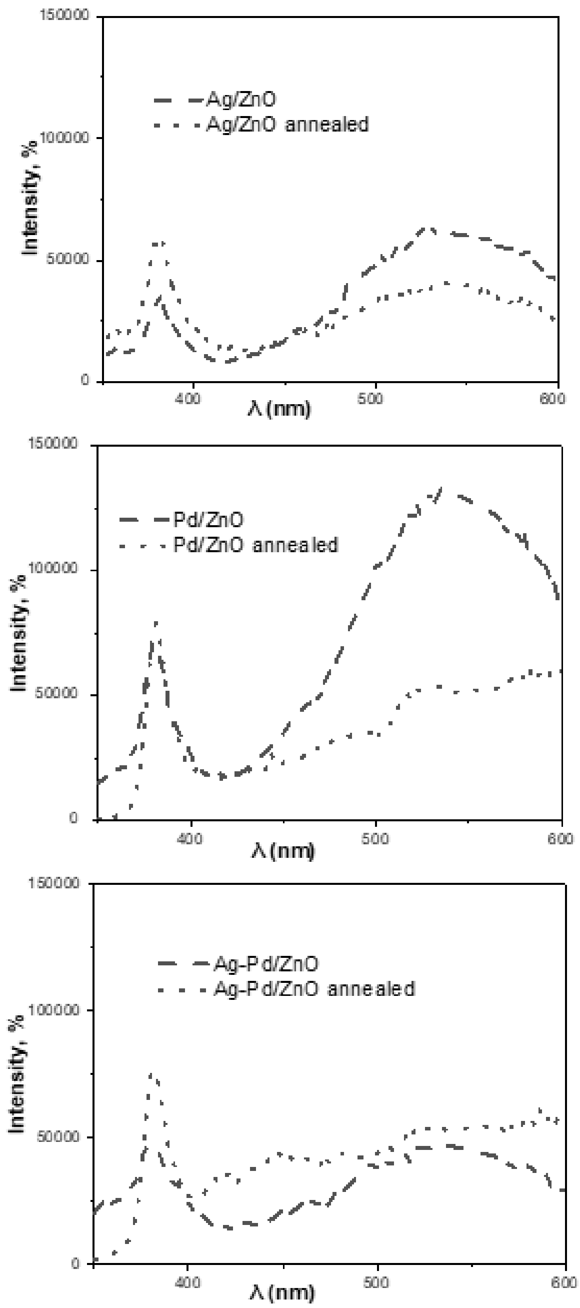

Fig. 3. Photoluminescence spectra of composite noble metal/ ZnOnanostructures grown by ps-PLD before and after the ns-laser annealing.

considerably lower for the laser grown nanostructures before the annealing. A lower intensity of visible photoluminescence emission, especially compared to the UV emission, indicates that the defects act as non-radiative recombination centers, reducing the efficiency of light emission in the visible range. The presence of smaller nanoparticles tends to exhibit strong surface-to-volume ratio, which can boost both defect concentration and non-radiative surface trap recombination. Yet at small sizes, the non-radiative pathways are dominant, thus lowering PL efficiency. The trapped charge carriers can lose their energy through pathways that don't involve light emission, thus reducing the overall intensity of the visible PL.

The laser modification has an impact on the UV signal amplification of the Ag-Pd/ZnO sample. The effective applications of ZnO-supported bimetallic nanoparticles (NPs), particularly those composed of Ag-Pd, benefit significantly from synergetic effects that arise due to the combination of their distinct properties, inclusive the noble metal plasmon resonance and palladium's ability to trap electrons [24].

CONCLUSIONS

In this study, the ZnO-based nanostructures incorporating mono-(Ag, Pd) and bimetallic (Ag-Pd) nanoparticles are successfully fabricated by laser methods. The synergistic behaviour of the bimetallic nanostructures before and after annealing is shown in relation to the monometallic nanostructures. The combination of ps-laser deposition and ns-laser annealing provides an efficient route to control the morphology, optical response, and defect structure produced nanocomposites. The spherical nanoparticles and nanonetworks, are obtained for all deposited samples. The well-defined individual NPs are observed for Ag/ZnO with clear surface plasmon resonance (SPR) band, that does not change significantly after annealing. The Ag-Pd/ZnO sample exhibited the smallest and most uniform nanoparticles compared to the monometallic systems, with reduced agglomeration and preserved porosity. The distinct optical behaviour depending on the incorporated noble metals are observed. The laser annealing led to the emergence or enhancement of surface plasmon resonance absorption bands, mainly for Pd containing samples. The red shift of ZnO optical absorption edge after annealing of Pd/ZnO indicates a decrease in the band gap, caused by dopant-induced energy levels within the gap. This shift allows the material to absorb lower-energy visible light more effectively, enhancing its optical response. The LSPR of PdNPs occurred at deep UV region after the annealing in the samples with and without silver. The presence of spectral shoulders for the bimetallic Ag-Pd/ZnO system after the annealing indicated alloy nanoparticle formation, demonstrating strong electronic coupling between Ag and Pd components. The relative PL intensity ratio between the UV emission and deep-level emission is investigated. The Ag/ZnO and Pd/ZnO samples demonstrate enhanced UV near-band-edge emission and reduced visible deep-level emission after the laser annealing, indicating improved crystallinity and defect passivation. The bimetallic Ag-Pd/ZnO nanostructure exhibited distinct PL behaviour with minimal DLE emission even before annealing, due to dominant non-radiative recombination in small nanoparticles. The post-annealing treatment significantly increases the photoluminescence UV emission of this sample, highlighting the synergistic interaction between Ag and Pd, where Ag contributes plasmonic enhancement and Pd facilitates electron trapping. The investigated noble metal/ZnO systems demonstrate structural homogeneity and tailored optical properties, making them promising candidates for applications in photocatalysis, optoelectronics and plasmon-enhanced sensing.

Acknowledgments

The authors acknowledge the financial support of the bilateral project IC-CZ/03/2025-2026 between the Bulgarian Academy of Sciences and the Czech Academy of Sciences.

Authors' contributions

Conceptualization, M.K.; methodology, M.K., A.D., and N.N.; investigation, M.K. and T.G.; writing original draft preparation, M.K. All authors have read and agreed to the published version of the manuscript.

REFERENCES

1. R. Zahoor, A. Jalil, S.Z. Ilyas, S. Ahmed, A. Hassan, Optoelectronic and solar cell applications of ZnO nanostructures, Results in Surfaces and Interfaces, 2, 2021, 100003. https://doi.org/10.1016/j.rsurfi.2021.100003
2. M. Koleva, N. Nedyalkov, N. Fukata, W. Jevasuwan,

S. Amoruso, T. Koutzarova, G. Avdeev, B. Georgieva, D. Karashanova, Laser assisted approach for synthesis of plasmonic Ag/ZnO nanostructures, Superlattices and Microstructures, 109, 2017, 886-896. https://doi.org/10.1016/j.spmi.2017.06.007
3. T. Yang, B. Lu, Y. Zuo, J. Huang, Configuration Engineering of Plasmonic-Metal/Semiconductor Nanohybrids for Solar Fuel Production Chemistry of Materials, 37, 5, 2025, 1685-1715. https://doi.org/10.1021/acs.chemmater.4c031704
4. M. Nycz, K. Arkusz, From Nano- to Microsilver: Morphology Control and Shape Evolution of Facile One-Step Electrochemical Synthesis of Silver Particles on TiO_2 Nanotubes, Langmuir, 41, 25, 2025, 15963-15973. https://doi.org/10.1021/acs.langmuir.5c01022
5. C. Charton, M. Fahland, Optical properties of thin Ag films deposited by magnetron sputtering, Surf. Coat. Technol., 174-175, 2003, 181-186. https://doi.org/10.1016/S0257-8972(03)00700-X
6. M. Rodrigues, J. Borges, C. Lopes, R. Pereira, M. Vasilevskiy, F. Vaz, Gas sensors based on localized surface plasmon resonances: synthesis of oxide films with embedded metal nanoparticles, theory and simulation, and sensitivity enhancement strategies. Appl. Sci. 11, 2021, 5388. https://doi.org/10.3390/app11125388
7. D. Ntemogiannis, M. Tsarmpopoulou, A. Stamatelatos, S. Grammatikopoulos,V. Karoutsos, D. Anyfantis, A. Barnasas, V. Alexopoulos, K. Giantzelidis, E. Ndoj, M. Sigalas, P. Poulopoulos, ZnO matrices as a platform for tunable localized surface plasmon resonances of silver nanoparticles, Coatings 14, 2024, 69. https://doi.org/10.3390/coatings14010069
8. D. Gan, Zh. Wang, X. Li, J. Zhou, B. Dai, L. Yang, S. Xia, Green synthesis of bimetallic PdAg alloy nanoparticles supported on polydopamine-functionalized kaolin for catalytic reduction of 4-nitrophenol and organic dyes, Applied Clay Science, 244, 2023, 107091. https://doi.org/10.1016/j.clay.2023.107091
9. S. Kunwar, P. Pandey, S. Pandit, M. Sui, J. Lee, Improved Morphological and Localized Surface Plasmon Resonance (LSPR) Properties of Fully Alloyed Bimetallic AgPt and Monometallic Pt NPs Via the One-Step Solid-State Dewetting (SSD) of the Ag/Pt Bilayers, Nanoscale Res. Lett., 14, 2019, 332. https://doi.org/10.1186/s11671-019-3170-0
10. E. Elemike, D.C. Onwudiwe, L. Wei, L. Chaogang, Zh. Zhiwei, Noble metal - semiconductor nanocomposites for optical, energy and electronics applications, Solar Energy Materials and Solar Cells, 201, 2019, 110106. https://doi.org/10.1016/j.solmat.2019.110106
11. M.E. Koleva, A.Og. Dikovska, N.N. Nedyalkov, P.A., Atanasov, I.A. Bliznakova, Enhancement of ZnO, photoluminescence by laser nanostructuring of Ag, underlayer, Applied Surface Science, 258, 23, 2012, 9181-9185. https://doi.org/10.1016/j.apsusc.2012.01.052
12. M. Koleva, N. Nedyalkov, R. Nikov, R. Nikov, G. Atanasova, D. Karashanova, V. Nuzhdin, V. Valeev, A. Stepanov, A. Rogov, Fabrication of Ag/ZnO nanostructures for SERS applications, Applied Surface Science, 508, 2020, 145227. https://doi.org/10.1016/j.apsusc.2019.145227
13. M. Koleva, A. Dikovska, N. Nedyalkov, T. Genova, G. Atanasova, Laser synthesis and processing of composite nanostructures, J. Chem. Technol. Metall., 59, 4, 2024, 831-839. https://doi.org/10.59957/jctm.v59.i4.2024.11
14. R. Radičić, D. Maletić, D. Blažeka, J. Car, N. Krstulović, Synthesis of Silver, Gold, and Platinum Doped Zinc Oxide Nanoparticles by Pulsed Laser Ablation in Water, Nanomaterials, 12, 2022, 3484. https://doi.org/10.3390/nano12193484
15. M. Włodarski, M. P. Nowak, M. Putkonen, P. Nyga, M. Norek, Surface Modification of ZnO Nanotubes by Ag and Au Coatings of Variable Thickness: Systematic Analysis of the Factors Leading to UV Light Emission Enhancement, ACS Omega, 9, 1, 2023, 1670-1682. https://doi.org/10.1021/acsomega.3c08253
16. X. Wang, Q. Ye, LH. Bai, X. Su, T.-T. Wang, T.-W. Peng, X.-Q. Zhai, Y. Huo, H. Wu, C. Liu, Y.-Y. Bu, X.-H. Ma, Y. Hao, J.-P. Ao, Enhanced UV Emission from ZnO on Silver Nanoparticle Arrays by the Surface Plasmon Resonance Effect, Nanoscale Res. Lett., 16, 2021, 8. https://doi.org/10.1186/s11671-020-03470-2
17. X.S. Shen, G.Z. Wang, X. Hong, W. Zhu, Shape-Controlled Synthesis of Palladium Nanoparticles and Their SPR/SERS Properties, Chin. J. Chem. Phys., 22, 4, 2009, 440-446. https://doi.org/10.1088/1674-

0068/22/04/440-446
18. B. Kaufmann, T. Billovits, P. Supancic, Observation of an electrical breakdown at ZnO Schottky contacts in varistors, Journal of the European Ceramic Society, 41, 3, 2021, 1969-1974. https://doi.org/10.1016/j.jeurceramsoc.2020.10.052
19. H. Basri, , R. Talib, R. Sukor, S. Othman and H. Ariffin, Effect of synthesis temperature on the size of zno nanoparticles derived from pineapple peel extract and antibacterial activity of ZnO - starch nanocomposite films, Nanomaterials 10, 2020, 1061. https://doi.org/10.3390/nano10061061
20. S. Raha, Md. Ahmaruzzaman, ZnO nanostructured materials and their potential applications: progress, challenges and perspectives, Nanoscale Adv., 4, 2022, 1868-1925, https://doi.org/10.1039/D1NA00880C
21. R.B. Jiang, B.X. Li, C.H. Fang, J.F. Wang, Metal/Semiconductor Hybrid Nanostructures for Plasmon-Enhanced Applications, Adv. Mater., 26, 2014, 5274-5309. https://doi.org/10.1002/adma.201400203
22. P. Sudhagar, A. Devadoss, T. Song, P. Lakshmipathiraj, H. Han, V.V. Lysak, C. Terashima, K. Nakata, A. Fujishima, U. Paik, Y.S. Kang, Enhanced photocatalytic performance at a Au/N-TiO_2 hollow nanowire array by a combination of light scattering and reduced recombination, Phys. Chem. Chem. Phys., 16, 2014, 17748-17755. http://dx.doi.org/10.1039/C4CP02009J
23. Y. Xiong, J. Chen, B. Wiley, Y. Xia, Y. Yin, Z.Y. Li, Size-Dependence of Surface Plasmon Resonance and Oxidation for Pd Nanocubes Synthesized via a Seed Etching Process, Nano Lett. 5, 7, 2005, 1237-1242. https://doi.org/10.1021/nl0508826
24. S.J. Lee, H.J. Jung, R. Koutavarapu, S.H. Lee, M. Arumugam, J.H. Kim, M.Y. Choi, ZnO supported Au/Pd bimetallic nanocomposites for plasmon improved photocatalytic activity for methylene blue degradation under visible light irradiation, Appl. Surf. Sci., 496, 2019, 143665. https://doi.org/10.1016/j.apsusc.2019.143665