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Investigation of metal-enhanced photoluminescence of zinc oxide films induced by platinum nanoparticles of different sizes

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Abstract. This study examines the influence of platinum nanoparticles on plasmon-enhanced photoluminescence in films prepared from semiconductor zinc oxide nanocrystals. Metal nanoparticles with different average sizes from 48 to 82 nm were synthesized by a gas discharge method with additional in-flow heat treatment at 985 °C and deposited by dry aerosol printing on quartz glass followed by ZnO film fabrication. The relationship between the size of nanoparticles processed in the tube furnace and the working gas flow rate as well as the correlation between the enhancement factor of ZnO ultraviolet photoluminescence and the size of the Pt nanoparticles were established. A relationship between the photoluminescence enhancement factor and layers' configuration in nanostructures was also found. Theoretical calculations were also performed to determine the effects of plasmonic enhancement of ZnO photoluminescence.

Keywords: platinum nanoparticles, spark discharge, tube furnace, plasmonic nanostructures, ultraviolet metal-enhanced photoluminescence

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Исследование усиленной металлом фотолюминесценции пленок оксида цинка в присутствии наночастиц платины разного размера

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Аннотация. Данное исследование посвящено изучению влияния наночастиц платины на плазмон-усиленную фотолюминесценцию в пленках, приготовленных из полупроводниковых нанокристаллов оксида цинка. Металлические наночастицы со средними размерами от 48 до 82 нм были синтезированы методом газового разряда с дополнительной термической обработкой в потоке газа при 985 °C и нанесены методом сухой аэрозольной печати на кварцевое стекло с последующим формированием пленки ZnO. Были установлены зависимость между размером наночастиц, обработанных в трубчатой печи, и скоростью потока рабочего газа, а также корреляция между коэффициентом усиления ультрафиолетовой фотолюминесценции ZnO и размером наночастиц Pt. Также была обнаружена зависимость между коэффициентом усиления фотолюминесценции и конфигурацией слоев в наноструктурах. Кроме того, были проведены теоретические расчеты для определения эффектов плазмонного усиления фотолюминесценции ZnO.

Ключевые слова: наночастицы платины, газовый разряд, трубчатая печь, плазмонные наноструктуры, ультрафиолетовая металло-усиленная фотолюминесценция

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Introduction

Modern nanotechnology offers diverse fabrication methods for plasmonic nanostructures, with applications in photonics, electronics, biomedicine, and microscopy [1–3]. Pt nanoparticles exhibit plasmonic resonance in the ultraviolet region and attract scientists for the development of various biological, optoelectronic and catalytic devises [4, 5]. Designing of plasmonic structures capable of amplifying electromagnetic fields within targeted spectral regions is employed in a variety of custom devices such as solar cells [6, 7], bio and chemical sensors. Therefore, it is important to study their dimensional and optical properties. To study the enhancement of photoluminescence (PL) near plasmonic structures based on noble metal nanoparticles, zinc oxide nanoparticles are commonly used as an ultraviolet phosphor, owing to their widespread applications in pharmaceutical, cosmetic and electrical industries [8]. Therefore, it is of considerable interest to study the interaction of Pt nanoparticles (NPs) with zinc oxide NPs in order to evaluate the possibility of using plasmon enhancement of photoluminescence in the ultraviolet range. The purpose of this work is to study the dependence of photoluminescence enhancement of ZnO films in the presence of Pt nanostructures with varying sizes and configurations formed by dry aerosol printing from nanoparticles, synthesized by a gas discharge method with additional heat treatment at 985 °C. The role of layer sequence in nanostructure design to optimize the amplification properties is also investigated. The novelty of this work is the use of a gas discharge setup combined with a tubular furnace to change the size of Pt NPs by precisely regulating the gas flow and to show application of obtained Pt NPs for plasmon-enhanced luminescence.

Methods and materials

Pt nanoparticles were synthesized in a pulsed-periodic gas discharge using electric erosion of Pt electrodes in the form of cylinders with outer and inner diameters of 8 mm and 7 mm, respectively, containing pure material (99.9999%) in an argon atmosphere with a chemical purity of 6.0 at an excess pressure of 0.6 atm. To achieve this, a voltage of 1.5 kV was applied between the electrodes, with a current of 30 mA, a generation frequency of 500 Hz, and a capacitor capacity of 40 nF. The obtained primary nanoparticles were transported along the gas path and then subjected to modification in a tube furnace heated to 985 °C. The synthesis was carried out at various gas flow rates (50, 100 and 300 ml/min) using Pt electrodes. The sintered nanoparticles were subsequently focused through a nozzle and deposited on quartz glass substrates by means of dry aerosol printing. The formation of Pt films took place at a constant distance from the nozzle to the substrate of 2.5 mm and a constant step between the lines of 150 micrometers. The velocity of the substrate relative to the nozzle varied from 1000 to 6000 micrometers/s.

Three different film configurations were created for Pt nanoparticles prepared at 100 ml/min flow rate: Pt+ZnO+Pt, ZnO+Pt and Pt+ZnO. To create a Pt+ZnO+Pt design, Pt nanoparticles were first deposited to quartz glass via dry aerosol printing. Subsequently, a layer of ZnO nanocrystals from liquid suspension was applied over the surface of the obtained Pt films by micro-plotter printing using a commercial SonoPlot GIX Microplotter II in a semi-contact printing mode. Finally, an additional Pt nanoparticle layer was applied to complete the structure. The ZnO+Pt configuration was fabricated by initial deposition of ZnO nanocrystals on quartz substrate, followed by dry aerosol printing of Pt nanoparticles. To create a Pt+ZnO design, Pt nanoparticles were applied to quartz glass by dry aerosol printing. Subsequently, a ZnO nanocrystal layer was fabricated atop the Pt film via microplotter printing. Ultraviolet-emitting reference films were prepared by microplotter deposition of pure 27 nm in size ZnO nanoparticles dispersed in isopropanol, demonstrating photoluminescence peak at 377 nm. Their emission intensity provided a baseline for quantitative comparison with designed Pt+ZnO nanostructures of different design (Pt+ZnO, ZnO+Pt, Pt+ZnO+Pt). To do this, the corresponding Pt+Pt PL spectrum was subtracted from the Pt+ZnO+Pt spectrum, and the corresponding Pt spectrum was subtracted from the ZnO+Pt and Pt+ZnO spectra. Pt+ZnO design were used to evaluate the influence of metal nanoparticles size on the amplification of ZnO photoluminescence. The morphology of the nanoparticles was examined using a transmission electron microscope (TEM) Jeol JEM 2100 (200 kV). The absorption spectra of film plasmon nanostructures were analyzed using a JASCO V—770 spectrophotometer. The photoluminescence spectra of the obtained films were measured on a Jasco 8300 fluorimeter with an excitation wavelength (Ex) of 325 nm (the power of the exciting radiation is 3.8 eV).

To study the luminescence enhancement of semiconductor zinc oxide nanocrystals in the presence of platinum nanoparticles, luminescence spectra were compared for films of various configurations with platinum nanoparticles and films with suspensions of semiconductor zinc oxide nanocrystals.

Results and Discussion

It follows from the TEM images (Fig. 1, *a*—*c*) that the Pt powder was composed of nearly spherical particles. The selected area electron diffraction (SAED) pattern presented in the inset of Figure 1d consists of rings corresponding to interplanar spacings of 2.26, 1.96, 1.39 and 1.17 E. These values are in good agreement with those characteristics of (111), (200), (220), and (311) planes of face-centered cubic crystal system of Fm3m platinum. According to the data from the TEM image analysis, the nanoparticles synthesized at a flow rate of 50 ml/min have an average size of 82 ± 24 nm (Fig. 1, *a*), at a flow of 100 ml/min — 75 ± 25 nm (Fig. 1, *b*), NP produced at a flow of 300 ml/min characterized by the average size 48 ± 21 nm (Fig. 1, *c*). The size-distribution of nanoparticles follows a log-normal function. (Fig. 1, *e*). It was found that the nanoparticles size decreases linearly with increasing flow rate (Fig. 1, *f*).

The obtained Pt metal nanoparticles exhibited the resonance absorbance in the ultraviolet range from 270 to 300 nm [9], which were deposited on the quartz substrate and covered by the homogeneous layer of ZnO nanocrystals.

Fig. 2, *a* demonstrates the significant impact of nanostructural design, specifically the layer order and arrangement of Pt metal nanoparticles with an average size of 75 ± 25 nm relative to the phosphor ZnO crystals, on the observed photoluminescence enhancement. All fabricated structures maintained a consistent average thickness for the pure Pt metal layers at a wavelength of 325 nm. The optimal photoluminescence enhancement was achieved in the Pt+ZnO configuration, where the zinc oxide phosphor layer was deposited atop the platinum nanoparticle array, yielding a maximum gain factor of 40% relative to the pure ZnO reference.

The second goal of the work was to obtain the influence of Pt nanoparticle size on the enhancement of ZnO films in multilayer Pt+ZnO nanostructures. Fig. 2, *b* presents a comprehensive analysis of plasmon-enhanced luminescence in Pt+ZnO multilayer nanostructures, namely, the dependence of the enhancement factor and intensity of ZnO PL (insert) in the presence of Pt nanostructures with an optical density from 0.15 (measured at a wavelength of 325 nm) with various metal NPs sizes. A non-linear dependence was obtained, which showed growth of PL with

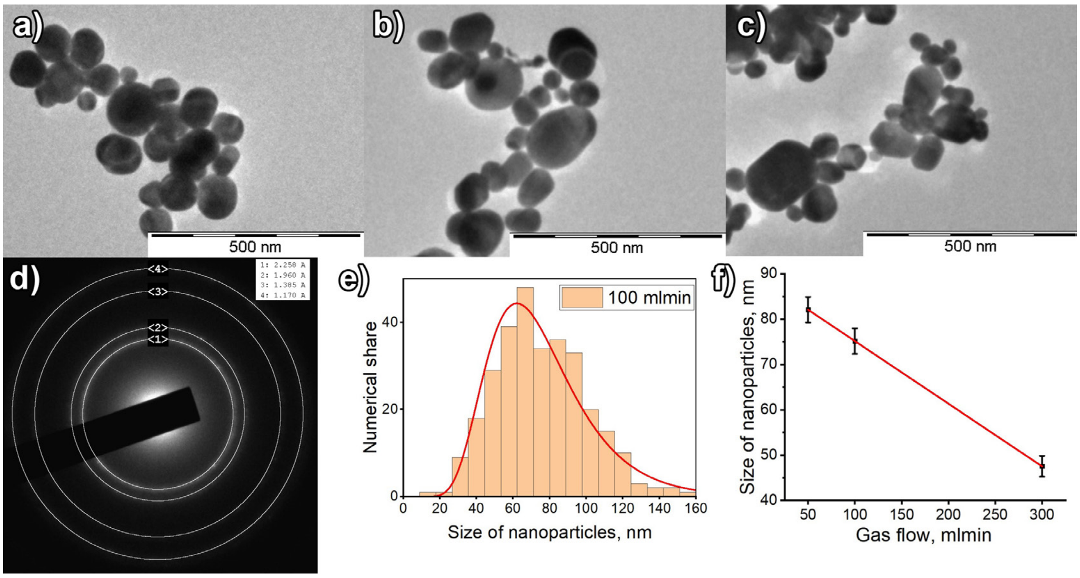

Fig. 1. Dimensional properties of produced Pt nanoparticles by spark discharge with additional in-flow thermal treatment at 985 °C: TEM image of Pt nanoparticles, synthesized in a gas flow rate of: 50 ml/min (*a*); 100 ml/min (*b*); 300 ml/min (*c*), the typical SAED pattern of the Pt nanoparticles (*d*), histogram of the size distribution of nanoparticles obtained at a flow of 100 ml/min with log-normal approximation (*e*), the dependence of the average size of Pt NPs via the gas flow rate (*f*)

increasing size of metal NPs. The maximum luminescence enhancement was achieved for the largest Pt nanoparticles, with an average diameter of 82 nm, and compiled a maximum enhancement factor of 43% relative to the pure ZnO reference. In contrast, systems with smaller NPs average size (48–75 nm) exhibited quenching up to ~73–80 % compared to pure ZnO film PL.

To probe plasmonic luminescence enhancement in Pt nanoparticles, we calculated the enhancement factor using Mie theory, incorporating influence of quantum yield of emitter (non-radiative energy transfer) [10]. Simulations were performed for the sample with polydisperse lognormal size distribution of Pt NPs and an average size of 75 ± 25 nm. Fluorescence intensity map was calculated in the ultraviolet region from 200 to 600 nm for phosphor with intrinsic quantum yield $Q_0 = 0.13$ and emission wavelength at 380 nm similar to the case of the employed ZnO nanoparticles via the distance between the surface of a metal nanoparticles and an emitter and presented

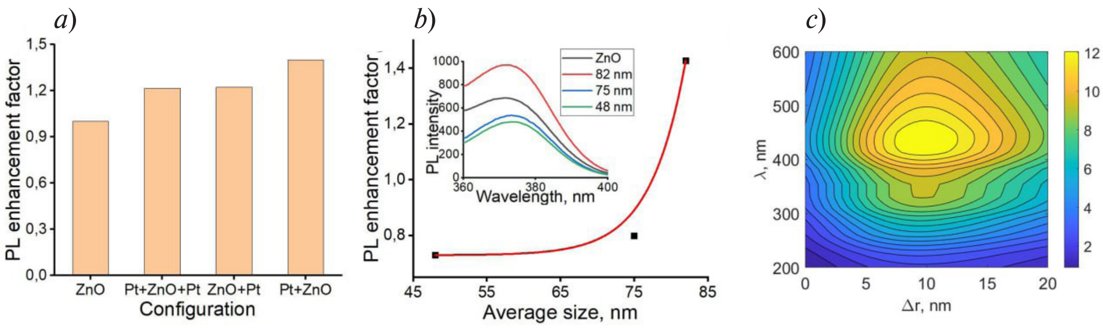

Fig. 2. PL properties of obtained nanostructures: the luminescence enhancement factor of ZnO film via the order of layers' configuration with Pt NPs (*a*), relationship between the PL enhancement factor and the average size of Pt nanoparticles in Pt+ZnO design (*b*) and PL spectra of the obtained multilayer Pt+ZnO nanostructures (*b*: insert), calculated photoluminescence intensity enhancement factor map versus Ex wavelength and metal-emitter spacing for polydisperse Pt nanoparticles with mean diameter of 75 nm (*c*)

in a Fig 2, *c*. Fig. 2, *c* results in the growth of the enhancement factor from 2 to 8 times at the Ex wavelength of 325 nm depending on distance between the metal NP and emitter.

A study was conducted [11], which showed a 7-fold increase in photoluminescence for platinum nanoparticles of 80 nm in size at an excitation wavelength of 325 nm, which is consistent with our theoretical studies. Also, in comparison with the articles [12], our method allows us to control the size of platinum nanoparticles and considers the interaction of platinum nanoparticles with ZnO crystals, rather than with a continuous film. According to the study [10] of zinc oxide films in the presence of Al nanoparticles, the worst enhancement is for the Al+ZnO+Al structure, and the best gain is for the Al+ZnO structure, which is consistent with the data obtained for Pt+ZnO films. For aluminum nanoparticles, it was also found that photoluminescence increases by 50 percent with an increase in particle size from 10 to 55 nm [13]. The same correlation is true for platinum particles, on which photoluminescence increases by 67 percent with an increase in particle size from 48 to 82 nm.

The discrepancy between theoretical and experimental data can be caused by several factors. Our method does not allow us to adjust the distance between platinum particles and ZnO crystals, which may affect the maximum possible enhancement (Fig. 2, *c*). The model also considers the amplification in the presence of a single ZnO particle, whereas the experiment involves the interaction of several ZnO particles with a platinum particle and plasmon coupling between metal NPs.

Conclusion

Thus, we reported size- and configuration-dependent plasmonic enhancement of ZnO luminescence in the presence of Pt nanoparticles. We have demonstrated the possibility of production of platinum particles of different sizes in a gas discharge using additional in-flow sintering in a tubular furnace and get Pt NPs with average sizes of 82 ± 24, 75 ± 25 and 48 ± 21 nm were at flow rates of 50, 100 and 300 ml/min, respectively. It was found that the best configuration for creating multilayer nanostructures is Pt+ZnO, where ZnO nanocrystal layer was fabricated atop the Pt film deposited on quartz by dry aerosol printing. It was found that Pt nanoparticles revealed the average size 82 nm are optimal ones to achieve the maximum plasmon-enhancement factor of ZnO the photoluminescence up to 1.43 times in ultraviolet region. Theoretical calculations established the growth of the enhancement factor from 2 to 8 times via the increase of particle-emitter spacing from 1 to 10 nm.

REFERENCES

1. **Kruis F.E., Fissan H., Peled A.,** Synthesis of nanoparticles in the gas phase for electronic, optical and magnetic applications—a review, Journal of Aerosol Science. 29 (5–6) (1998) 511–535.

2. **Sokovnin S.Yu., Il'Ves V.G.,** Production of Nanopowders Using Pulsed Electron Beam. Ferroelectrics, 436 (1) (2012) 101–107.

3. **Dhand C., Dwivedi N., Loh X.J., et al.,** Methods and strategies for the synthesis of diverse nanoparticles and their applications: a comprehensive overview, RSC Advances. 5(127) (2015) 105003–105037.

4. **Bauch M., Toma K., Toma M., et al.,** Plasmon-Enhanced Fluorescence Biosensors: a Review, Plasmonics. 9 (4) (2014) 781–799.

5. **Thrithamarassery Gangadharan D., Xu Z., Liu Y., et al.,** Recent advancements in plasmon-enhanced promising third-generation solar cells, Nanophotonics. 6 (1) (2017) 153–175.

6. **Wang Y., Zhang J., Liang W.,** Rational Design of Plasmonic Metal Nanostructures for Solar Energy Conversion, CCS Chemistry. 4 (4) (2022) 1153–1168.

7. **Yu P., Yao Y., Wu J.,** Effects of Plasmonic Metal Core -Dielectric Shell Nanoparticles on the Broadband Light Absorption Enhancement in Thin Film Solar Cells, Scientific Reports. 7 (1) (2017) 7696.

8. **Kołodziejczak-Radzimska A., Jesionowski T.,** Zinc Oxide—From Synthesis to Application: A Review. Materials. 7(4) (2014) 2833–2881.

9. **Lizunova A.A., Novosyolov A.K., Khramov E.S., et al.,** Absorbance Variation of Plasmon Al and Pt Nanostructures Formed by Dry Aerosol Printing for Label-Free Detection of BSA Luminescence, Bulletin of the Russian Academy of Sciences: Physics. 88 (S2) (2024) S211–S216.

10. **Lizunova A.A., Malo D., Guzatov D.V., et al.,** Plasmon-Enhanced Ultraviolet Luminescence in Colloid Solutions and Nanostructures Based on Aluminum and ZnO Nanoparticles, Nanomaterials. 12 (22) (2022) 4051.

11. **Ma K., Zhou X., Kan C., et al.,** Pt nanoparticles utilized as efficient ultraviolet plasmons for enhancing whispering gallery mode lasing of a ZnO microwire via Ga-incorporation, Physical Chemistry Chemical Physics. 23 (11) (2021) 6438–6447.

12. **Chen S., Pan X., He H., et al.,** 60-fold photoluminescence enhancement in Pt nanoparticle-coated ZnO films: role of surface plasmon coupling and conversion of non-radiative recombination, Optics Letters. 40 (12) (2015) 2782.

13. **Malo D.,** Investigation of plasmon-enhanced ultraviolet luminescence of zinc oxide semiconductor nanocrystals in the presence of aluminum nanoparticles synthesized by gas-phase methods: dis. (2024).

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