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Ultraviolet photoluminescence enhancement of zinc oxide nanocrystals in colloidal mixtures with spark discharge aluminum nanoparticles

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Abstract. Currently, nanoplasmonics is considered one of the most appealing areas of nanophotonics for researchers especially in studies on aluminum as one of the most attractive metal for pushing plasmonics into ultraviolet (UV) devices. Aluminum plasmonics has been shown to be effective for several applications including ultraviolet enhanced fluorescence, optoelectronics, photocatalysis, imaging and biosensing. This work investigated ultraviolet photoluminescence enhancement in mixture colloids of zinc oxide with aluminum nanoparticles. Where aluminum nanoparticles, synthesized by spark discharge method, were with an average size 22.3 ± 7.7 nm and five aluminum colloids with various concentrations of metal from 0.001 to 0.015 g/L were obtained in isopropyl alcohol solution. At the same time, zinc oxide colloids were with two concentrations 0.022 and 0.22 g/L with an average size of the nanocrystals 26.6 ± 7.4 nm. In our research, we have achieved photoluminescence enhancement up to 2.4-fold of zinc oxide emission at wavelength 377 nm in mixture colloids of zinc oxide with aluminum nanoparticles at excitation wavelengths of 300 nm and 325 nm.

Keywords: Photoluminescence (PL), ultraviolet (UV), colloidal mixture, spark discharge method, aluminum nanoparticles (Al NPs), zinc oxide nanoparticles (ZnO NPs)

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Материалы конференции
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Ультрафиолетовое усиление фотолюминесценции нанокристаллов оксида цинка в коллоидных смесях с наночастицами алюминия, синтезированных в газовом разряде

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Аннотация. В данной работе исследовано усиление ультрафиолетовой фотолюминесценции в смеси коллоидных растворов нанокристаллов оксида цинка с наночастицами алюминия. Наночастицы алюминия, синтезированные методом газового разряда, имели средний размер 22,3 ± 7,7 нм. Из них были получены пять коллоидов алюминия с концентрацией наночастиц металла от 0,001 до 0,015 г/л в растворе изопропилового спирта, а коллоиды оксида цинка средним размером кристаллов 26,6 ± 7,4 нм использовались с двумя концентрациями 0,022 и 0,22 г/л. В нашем исследовании, мы добились усиления фотолюминесценции до 2,4 раза эмиссии оксида цинка на длине волны 377 нм в смеси коллоидов оксида цинка с наночастицами алюминия при длинах волн возбуждения 300 нм и 325 нм.

Ключевые слова: Фотолюминесценция (ФЛ), ультрафиолет (УФ), коллоидная смесь, метод газового разряда, наночастицы алюминия, наночастицы оксида цинка

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Introduction

Nowadays, interest in the synthesis of aluminum nanoparticles and structures has especially increased after the theoretical substantiation of the use of aluminum as a cheap and promising material with surface plasmon resonance in ultraviolet region which makes it possible to enhance the photoluminescence of organic dyes and semiconductor structures by several times. This phenomenon actively can be used in various fields of science and technology such as in medicine, solar cells, fluorescent lamps and microelectronics [1–3].

Spark discharge synthesis, it is considered to be a simple and potential method to produce plasmonic aluminum nanoparticles in the UV region [4]. Additionally, stabilization suspensions of Al nanoparticles is a challenging process for researchers to obtain nano-inks, study their morphological, physicochemical and optical properties [5–8] that can be used for the nanostructures' and film fabrication [9].

In this research, we obtained colloids of plasmonic Al NPs, synthesized by spark discharge method, and their mixtures with an ultraviolet phosphor, namely, ZnO NPs and we studied the effect of plasmonic Al NPs to enhance the photoluminescence in liquid dispersions in the UV region of the spectrum.

Materials and Methods

ZnO NPs colloids were prepared by the method which is described in [8, 9] by dilution using chromatographically pure isopropyl alcohol (Scharlau) to get concentrations 0.022 and 0.22 g/L.

Aerosol aluminum nanoparticles were synthesized using the spark discharge generator [4], that used in atmosphere of argon of purity 6.0 at pressure 1.2 atm with Al electrodes (solid cathode 8 mm in diameter, anode with the hole 3.5 mm), discharge voltage 1.5 kV, discharge period 2 ms, gas flow 600 mL/min and one hour for passivation with argon 4.8.

For Al NPs colloids, citric acid in chromatographically isopropyl alcohol (0.01 g/L) (buffer solution) was used as surface active agents to form stable Al dispersions with the desired dimensional parameters. Then, ultrasonic treatment of dispersion (0.4 g/L) of Al NPs was carried out for 30 minutes to crush agglomerated particles.

Five suspensions of Al NPs were prepared with different concentrations 0.001, 0.003, 0.005, 0.010 and 0.015 g/L by dilution with buffer solution.

At room temperature, to study photoluminescence enhancement at excitation wavelengths of 300 nm and 325 nm, mixtures of ZnO NPs with Al NPs (v:v) (1:1) were prepared and compared with mixture of ZnO NPs with pure isopropanol (1:1).

The size and crystal structure of primary NPs were received by transmission electron microscope (TEM) Jeol JEM 2100 (200 kV) and energy dispersive X-ray (EDX) spectrometer X-MAXN OXFORD Instruments. UV-vis-NIR spectra and luminescence emission were obtained using JASCO V-770 and JASCO FP-8300 spectrometers, correspondingly.

The photoluminescence inner filter correction of the colloidal mixture and pure ZnO NPs colloids according to the approach described in our previous work [8] was used.

Results and Discussion

According to TEM and electron diffraction images, spherical shape and core-shell structure with metal crystal core and oxide shell for aluminum nanoparticles were observed.

The average primary particle size of Al nanoparticles, which formed large agglomerates, was 22.3 ± 7.7 nm including the shell thickness (about 3 nm), while 26.6 ± 7.4 nm for ZnO nanocrystals.

EDX maps of several agglomerates confirmed the formation of Al-ZnO complexes presented in (Fig. 1). Elemental line profile (Fig. 1,*c*) of the agglomerate confirms the presence of separate ZnO (yellow peaks) and metal Al nanoparticles (red peaks).

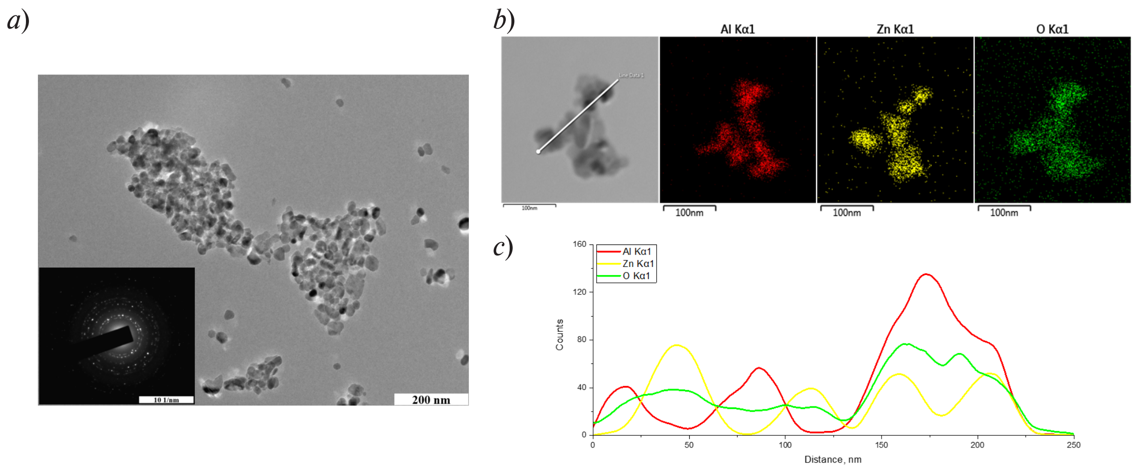

Fig. 1. Typical TEM image with corresponding SAED pattern (on the insert) for an Al-ZnO complex found in the colloidal mixture of Al 0.003 g/L with ZnO 0.22 g/L (*a*); STEM image of an Al-ZnO agglomerate found in the colloidal mixture of Al 0.015 g/L with ZnO 0.022 g/L and corresponding EDX elemental maps (*b*); EDX line profile (*c*)

The photoluminescence spectra of ZnO NPs colloids (0.022 and 0.22 g/L) and their mixtures with Al NPs colloids of different concentrations were obtained at excitation wavelengths of 300 nm and 325 nm (Fig. 2,*a*).

Fig. 2,*b* showed the increase of the luminescent enhancement factor from 1.21 to 2.4 for the colloidal mixtures of ZnO and Al NPs when the concentration of metal nanoparticles grows up regardless of the mass fraction of semiconductor nanocrystals. The enhancement factor was calculated by dividing the corrected intensity of the PL peak at 377 nm for a solution mixture of ZnO and Al NPs by the corrected PL intensity of a ZnO NPs colloid with the same fluorophore concentration using inner filter effect correction [10].

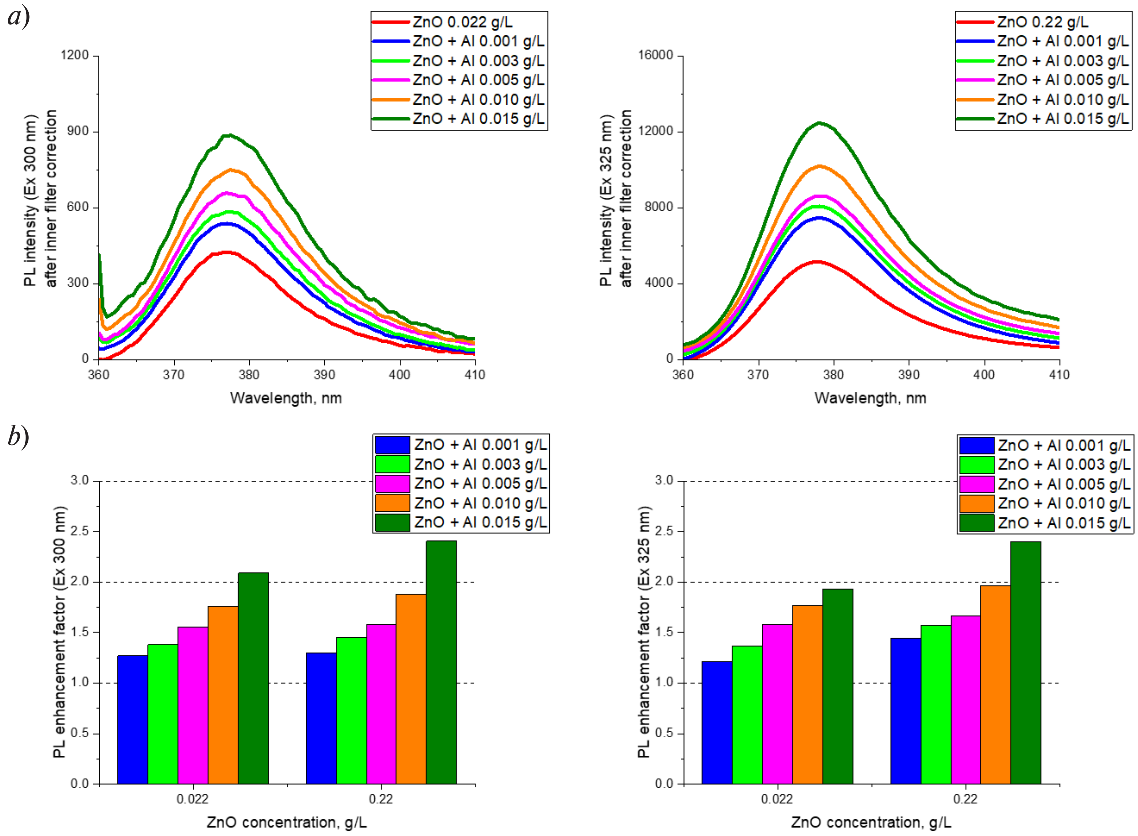

Fig. 2. Photoluminescence emission spectra of pure ZnO NPs colloids (red line) and their mixtures with Al NPs colloids of various concentrations (from 0.001 to 0.015 g/L) (*a*); PL enhancement factor for mixtures with different concentrations of ZnO and Al NPs (*b*); at excitation wavelengths of 300 nm (left) and 325 nm (right)

It was found that an increase in photoluminescence intensity of ZnO nanoparticles up to 240% at an emission wavelength 377 nm was observed with an increase in the concentration of Al nanoparticles from 0.001 to 0.015 g/L with an average size 22.3 ± 7.7 nm. In our previous study using other aluminum nanoparticles [8], we achieved PL enhancement up to 2.9- and 3.0-fold at excitation wavelengths of 300 nm and 325 nm, correspondingly. That was in colloidal mixtures using Al nanopowder, produced by electrical explosion of wires with an average size 54.6 ± 25.1 nm. Where concentrations of Al NPs colloids were from 0.00285 to 0.057 g/L while ZnO nanoparticles colloids with concentrations from 0.022 to 0.44 g/L. The best achieved enhancement up to 7 times in solutions was shown by Staruknin et al. in colloids of silver nanoparticles and phthalocyanines metallocomplexes [11]. On the other side, A. Muravitskaya et al. [12] presented in 2020 the maximum possible enhancement of ZnO nanocrystals (9.7-fold) on the array of oval Al nanoparticles.

Based on the obtained results, we have observed the effect of particle size and concentration on the PL enhancement factor related to the formation of Al-ZnO complexes in mixture colloids.

Conclusion

We demonstrated that photoluminescence enhancement of ZnO NPs in presence of plasmonic metal Al NPs, synthesized by spark discharge method, at excitation wavelengths of 300 nm and 325 nm was achieved up to 2.4-fold in UV region at an emission wavelength 377 nm in colloid solutions. So, these promising colloids can be used as nano-inks to fabricate biomedical and opto-electronic sensors in ultraviolet region of the spectrum based on Al nanostructures.

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